

Diffusion of Saturated Hydrocarbons in Low Density Polyethylene (LDPE) Films

ABDUL-FATTAH A. ASFOUR,* M. SALEEM, and D. DE KEE,
*Chemical Engineering Department, University of Windsor, Windsor,
Ontario, Canada N9B 3P4* and B. H. HARRISON, *Department of
National Defence, Defence Research Establishment Ottawa,
Ottawa, Ontario, Canada K1A 0Z4*

Synopsis

The diffusion coefficients at zero penetrant concentration, D_0 , of *n*-hexane, *n*-heptane, *n*-octane, *n*-decane, and 2,2,4-trimethylpentane (TMP) in LDPE were obtained in the range of 25–50°C, using the desorption method. The dependence of D_0 on the size and shape of the penetrant is reported. It was found that D_0 decreases with increasing penetrant molecule size. The activation energies of diffusion in the temperature range of 25–50°C increase with increasing penetrant molecule size and are independent of temperature. The results are interpreted in terms of the free volume theory and semiquantitative estimates of the free volume parameters are reported.

INTRODUCTION

In an earlier communication,¹ the influence of the size and shape of the penetrant molecules on the diffusion coefficients of several penetrants in LDPE was reported. It was established that:

- the diffusion coefficient decreases with increasing penetrant size
- a linear relationship exists between $\log D_0$ and the molar volume of the penetrant

However, these findings were limited to penetrants of relatively small size and to a single temperature.

There are suggestions^{2,3} that the dependence of diffusion coefficient on the size of the diffusing molecule diminishes as the free volume of the system increases. Also, the activation energy of diffusion increases with the size of the penetrant molecule until it reaches a constant value which is equal to the activation energy of viscous flow.⁴ This can be checked by studying the penetrant size effect on the diffusion coefficient at various temperatures.

Diffusion of a number of homologous paraffin hydrocarbons has also been studied.^{5,6} It was found that the side methyl groups in the diffusant lowered

*Author to whom correspondence should be addressed. Currently on leave, with Qatar University, P.O. Box 2713, Doha, Qatar.

the diffusivities more than in the case of the corresponding linear molecules. But these investigations pertained to diffusants of up to five carbon atoms and thus to a low molar volume range. Moisan⁷ in a study involving commercial stabilizers in polyethylene pointed out the importance of the deformations of diffusing molecules as well as of the polymer chains. Small molecules (additives of low molecular weight) diffuse as gases, whereas larger molecules behave like polymer chains in self-diffusion. His experiments consisted of pressing several layers of polymer film between plates containing the chosen additive. The pressure employed is about 5 kg/cm². Diffusion kinetics are determined via analytical techniques such as liquid chromatography and spectroscopy (IR or UV). Relations between diffusion, molecular structure, and temperature are interpreted via Klein's⁸⁻¹⁰ entanglement ideas.

For LDPE we decided to choose members of the same series with 6 to 10 carbon atoms. We intend to correlate the size effect without the interference of shape contributions by the penetrant, for the latter effect can be observed during the diffusion of an additional branched penetrant, TMP, which formed part of this work.

Earlier data on the diffusion of paraffins in rubbers,^{5,6} as well as for the first four members of *n*-alkyl acetate esters in poly(methyl acrylate)¹¹ suggests that, though the temperature dependence of D_0 was fitted by an Arrhenius type relationship, the activation energy of diffusion, E_d , was identical for each series. This gave support to the view that, for a series of homologous organic compounds in a given polymer, the activation energy is practically independent of the size of the diffusing molecule provided that it is comparable with the size of the monomer unit of the polymer. Later, work on polybutadienes¹² and plasticized poly(vinyl chloride)³ showed an increase in activation energy with the increasing size of the penetrant. The difference in these two sets of findings lies in the different natures of the polymers, as well as those of the penetrants. In this work, the polymer and the diffusants have the same basic chemical structures; nevertheless, the penetrant sizes are considerably larger than the basic monomer unit of the polymer. Moisan¹³ reported on the diffusion kinetics of ester compounds with increasing aliphatic chain lengths. He showed an increase in activation energy up to a value related to the energy of relaxation in polyethylene. Moisan¹⁴ also reported on the effect of structural changes of LDPE on diffusion of commercial additives. He found the diffusion coefficient normal to the direction of stretching to be higher than the diffusion coefficient parallel to the deformation direction, with a maximum between 100 and 200% deformation. The polymer samples were obtained by blow molding.

Diffusion in semicrystalline polymers is much more complicated than in amorphous polymers. The difficulty arises from the inhomogeneity of the polymer matrix, consisting of a continuous amorphous phase with enclosed impermeable microcrystalline islands. Furthermore, the degree of crystallinity may change on cooling, heating, annealing, or swelling of the polymer. This will consequently accompany a change in diffusion and solubility properties. Moisan¹⁵ studied the relation between entanglement density and crystallinity. He pointed out that solubility is very sensitive to the polymer molecular weight. Polyethylene also falls under this category of polymers and recently its transport properties have been investigated by a number of researchers.¹⁶⁻²³

Michaels and Parker²⁴ suggested that diffusion in semicrystalline polyethylene can be described by

$$D = D_a/\tau\beta \quad (1)$$

where D_a is a diffusion coefficient in a completely amorphous polymer, τ is a geometric impedance factor, and β represents a chain immobilization factor depending on the polymer morphology. The factor τ is assumed to be independent of molecular size, whereas β is a size-dependent parameter which reflects the reduction in amorphous chain segment mobility caused by the proximity of crystallites.

A reduction in free volume on drawing the LDPE has been reported^{16,23} and a drop in diffusivity was demonstrated. Similar investigations on the transport properties of LDPE¹⁷ suggest that these properties can be used as an extremely sensitive probe for detecting small variations in the micromorphology and in the structure of the amorphous phase.

The dependence of the diffusion coefficient at zero concentration, D_0 , on temperature, concentration, and the size of the penetrant molecule can reasonably be interpreted in terms of the free volume theory.

Fujita et al.¹¹ presented the following equation:

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

where A and B are constants which depend on the molecular size of the penetrant and on the polymer. B increases with increasing penetrant size and thus leads to a decrease in the diffusion coefficient. If D_0 and the fractional free volume f_0 of the polymer are known, then the values of A and B can be obtained. Consequently, a correlation can be made between diffusant size and D_0 . The fact that the fractional free volume has no clear-cut definition, is a drawback, but for the purpose of "semiquantitative" estimates can be considered proportional to the fractional free volume of the amorphous polymer, f_a , in the Williams, Landel, and Ferry (WLF) expression,²⁵ which is given by

$$f_a = f_g + \alpha(T - T_g) \quad (3)$$

where T_g is the glass transition temperature of the polymer, f_g is the fractional free volume of the polymer at T_g , and α is the difference between the thermal expansion coefficient above and below T_g . This may hold true for an amorphous polymer but further complications arise for a semicrystalline polymer with amorphous as well as crystalline components. Assuming that the densities of the crystalline and amorphous phase can be added, as reported previously,¹⁹ leads to the following equation for the fractional free volume of the semicrystalline polymer, f_0 :

$$f_0 = f_a(1 - \phi_c) \quad (4)$$

where f_a is the fractional free volume of the completely amorphous polymer and ϕ_c is the volume fraction crystallinity.

Substitution of eq. (3) into eq. (4) for semicrystalline polymers yields

$$f_0 = [f_g + \alpha(T - T_g)](1 - \phi_c) \quad (5)$$

Despite extensive work on LDPE, it appears that no valid correlation between crystallinity and fractional free volume of the solvent-free polymer has been established. Therefore, under the circumstances, we will test eq. (5) on the data obtained in this work.

EXPERIMENTAL

A CIL-produced low density polyethylene sheet (grade 503) was used in this work. It had a thickness of 0.15 mm and a density of 918.0 kg/m³.

Gold label grade *n*-hexane, *n*-heptane, *n*-octane, *n*-decane, and 2,2,4-trimethylpentane (TMP) were obtained from Aldrich Chemical Co., and were used without further purification.

A Cahn 2000 electrorecording balance was used to monitor the desorption kinetics. Details of the procedure have already been described elsewhere.¹ Instead of using a chart recorder, the weight changes in the polymer sample were monitored by a microcomputer, which enabled us to achieve further accuracy for very small weight changes. Temperature fluctuations in the balance's hangdown tube containing the polymer sample were kept within $\pm 0.02^\circ\text{C}$.

RESULTS AND DISCUSSION

As described previously,¹ the diffusion coefficient at zero penetrant concentration, D_0 , can be obtained from the final stages of a sorption experiment, using the following expression:

$$\frac{d}{dt} [\ln(M_t - M_\infty)] = -\pi^2 D_0 / l^2 \quad (6)$$

where M_t and M_∞ denote the weights of the dry film and the liquid contained in the film per unit area at times 0, t , and ∞ , respectively.¹ The thickness of the polymer film is denoted by l .

The D_0 values thus obtained at various temperatures for the five penetrants are reported in Table I.

Dependence of Diffusion Coefficient on the Size of the Penetrant

Figure 1 shows the dependence of the diffusion coefficient on the size of the penetrant molecule. There is a decrease in D_0 as the penetrant molecule size increases. As shown in Figure 1, the relationship between $\log D_0$ and the molar volume of this series of *n*-alkane penetrants is linear. This is consistent with our previous findings,¹ where the same relationship was found for the diffusion of substituted benzenes and chlorinated solvents in LDPE. The ratio between $\log D_0$ and the molar volume obeys the following order:

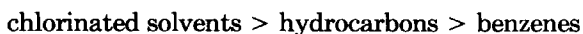


TABLE I
Diffusion Coefficients D_0 and Activation Energy E_d for Diffusion
of Saturated Hydrocarbons in LDPE

Penetrant	Molar volume of penetrant ($\times 10^6$ m ³ /mol) at 25°C	$D_0 \times 10^{12}$ m ² /s					Activation energy (kJ/mol)	$A \times 10^{10}$ (m ² mol/J s)	B
		Temperature (°C)							
		25	35	40	45	50			
<i>n</i> -Hexane	130.7	1.26	3.06	4.66	6.50	10.89	67.7	8.83	0.525
<i>n</i> -Heptane	146.5	0.97	3.34	4.48	6.74	9.02	70.9	16.33	0.553
<i>n</i> -Octane	162.5	0.86	2.61	4.32	7.80	9.95	80.7	113.08	0.631
<i>n</i> -Decane	194.9	0.43	1.86	3.27	5.45	8.88	96.8	211.76	0.761
TMP	165.1	0.32	0.73	1.43	2.39	4.27	83.5	64.63	0.652

This suggests that if the hydrocarbons are investigated in a narrow size range like that of chlorinated solvents, one may not observe any size effect. Therefore, in order to evaluate the penetrant size effect on diffusion in polymers, penetrants of similar chemical nature provide more meaningful information than molecules of increasing size, but of diverse chemical structures.

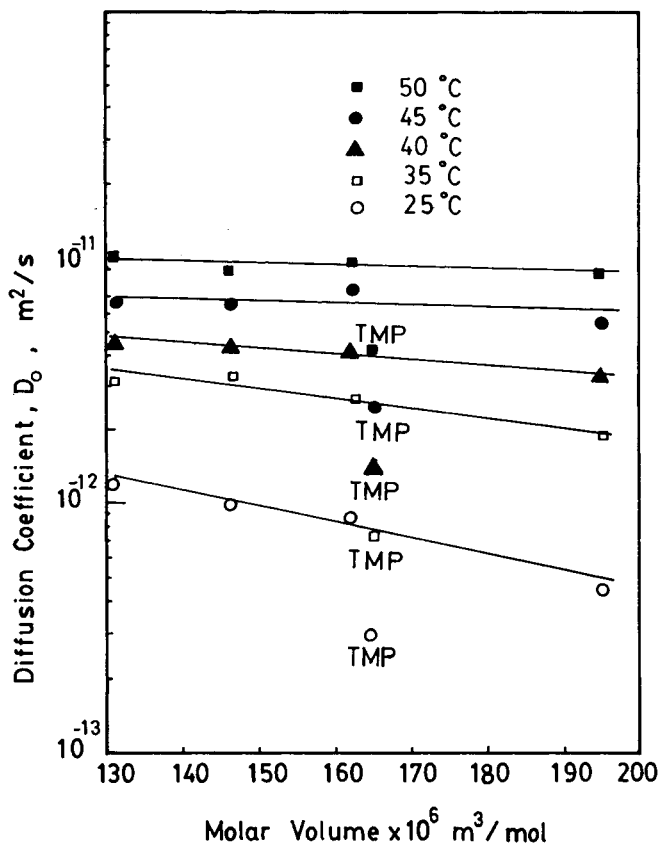


Fig. 1. Variation of the diffusion coefficient D_0 with the molar volume of penetrants at different temperatures.

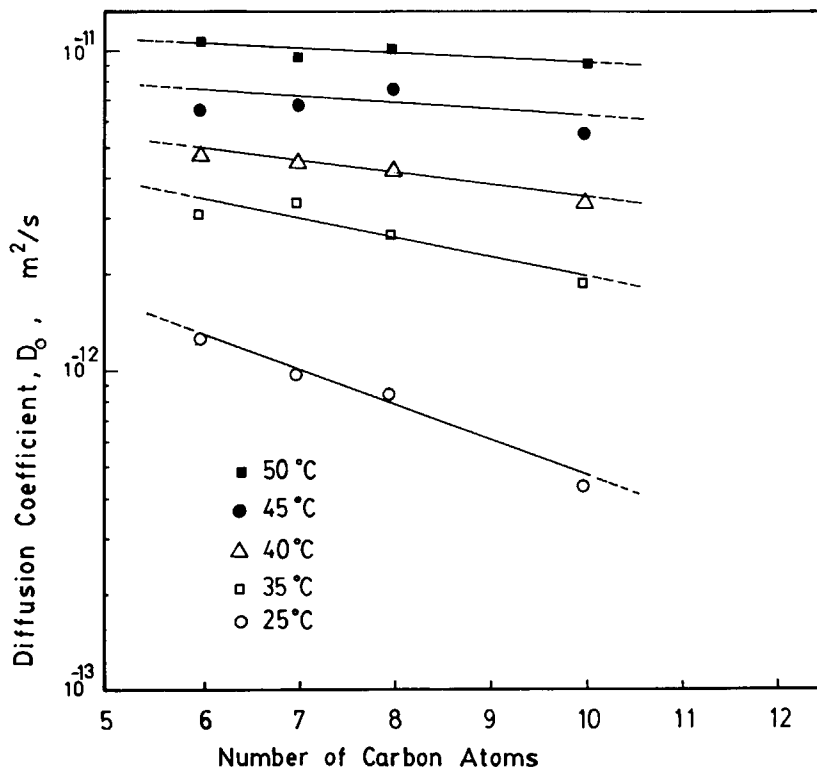


Fig. 2. Variation of the diffusion coefficient D_0 with the number of carbon atoms in saturated hydrocarbons.

It is apparent that the dependence of D_0 on the penetrant size decreases with increasing temperature and almost becomes insignificant at 50°C. This was expected, since an increase in temperature will accompany an increase in the free volume of the polymer. As pointed out earlier,^{2,3} when this happens the dependence of D_0 on the penetrant size diminishes.

Figure 2 provides a plot of $\log D_0$ against the number of carbon atoms in $\text{CH}_3-(\text{CH})_{2n}-\text{CH}_3$. Again, a decrease is apparent. The findings for the alkyl acetate series in polymethylacrylate [11] were replotted by Brown and Park² and their plot of $\log D_0$ versus the number of carbon atoms in the ester shows a tenfold decrease in D_0 for four carbon atoms, whereas in our case there is about a 1.5 decrease in this range. This is understandable considering the nature of these two different systems.

Dependence on the Shape of the Penetrant Molecule

It has been established^{1,2,3,6,12} that the shape of the penetrant molecule has a profound effect on the diffusion in polymers. A linear and flexible molecule should be expected to diffuse more quickly than a rigid and unsymmetrical molecule. The rigidity of TMP has already been compared with the long and linear *n*-hexadecane molecule diffusing in polybutadienes, by using two different techniques.¹² Therefore, in this work we observed the shape effect of

isomeric paraffin hydrocarbons of comparable size. It was found that at all the temperatures studied the values of D_0 for TMP are considerably lower than the expected values of a linear molecule of the same size.

If we denote the diffusion coefficient of TMP, expected just on size consideration, by D_e and its actually observed diffusion coefficient by D_0 , then the ratio D_e/D_0 at 35°C is about 3.3. This ratio for TMP drops to 2.2 at 50°C, but a difference still persists. The effect of the length of the corresponding linear molecules tends to disappear at higher temperatures. This variation for TMP must be due to its larger diameter. This would then suggest that the effect of the length of the molecule is less than the effect of the diameter of the diffusant. The pendant methyl groups in TMP with its larger diameter still cannot locate an appropriate "hole size." It appears that this effect for the TMP molecule will be observed until a temperature is reached at which enough free volume becomes available to allow its complete mobility.

Conversely, when penetrant molecules are of comparable diameter but of varying length, the effect of the length of the molecule will play a dominant role. This was the case for the flexible and long molecule of *n*-hexadecane,³ whose measured diffusion coefficient in plasticized PVC is much lower than would have been expected on the basis of its diameter.

Dependence on Temperature

The activation energy of diffusion, E_d , can be obtained from the plots of $\log D_0$ against $1/T$ using the following Arrhenius type relationship:

$$D_0 = A \exp(-E_d/RT) \quad (7)$$

For many polymer/penetrant systems these plots are linear over a small temperature range. Curved plots are observed when larger temperature ranges are investigated.²⁶ In this work, a temperature range of 25–50°C is covered. Figure 3 indicates that the plot of $\log D_0$ vs. $1/T$ is linear which confirms that E_d is independent of temperature in the covered range. For *n*-hexane, *n*-heptane, and *n*-octane these plots tend to overlap each other around a temperature of 40°C, indicating the possibility that if the experiments are conducted above 50°C, one may not observe any distinction between the activation energies of these penetrants. The larger molecule of *n*-decane and relatively rigid molecule of TMP do not demonstrate such an effect in this region. In spite of repeated experiments the D_0 of TMP at 25°C lies above the Arrhenius plot and is probably associated with the error which is encountered during the longer desorption time required for this penetrant at 25°C.

The activation energies for all five penetrants are calculated from the best fitted straight lines. The results are given in Table I. These results indicate that there is an increase in E_d with increasing size of the penetrant molecule. On previous occasions it was noticed that there was no increase in activation energy for diffusion of lower series of paraffin hydrocarbons in polyisobutylene and natural rubber.^{5,6} This difference in previous findings should be attributed to the nature of the polymer and the size of the penetrant under consideration.

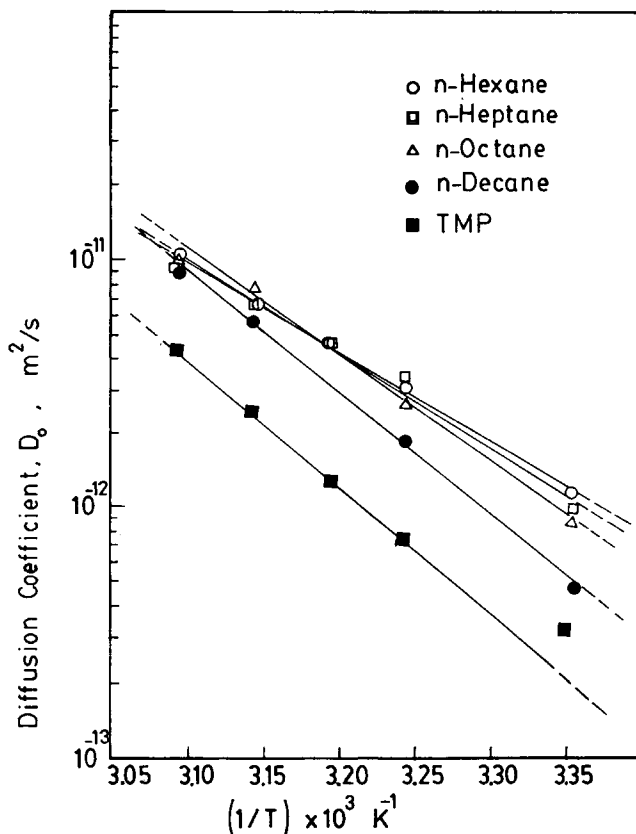


Fig. 3. Temperature dependence of the diffusion coefficient D_0 of various penetrants in LDPE.

It has been suggested⁴ that the activation energy of diffusion shows an increase with penetrant molecule size until a value approximately equal to the activation energy of viscous flow, E_v , is reached. This is true for an amorphous polymer with large fractional free volume, which is the case for soft polymers like rubber where no activation energy change is expected for small penetrants like *n*-butane, *n*-pentane, and their isomers. Similarly, there was no difference between the activation energies for benzene and *n*-hexadecane in highly plasticized poly(vinyl chloride). The activation energy for the diffusion of *n*-hexadecane is greater than that of benzene in poly(vinyl chloride) with low plasticizer content. In LDPE the partial crystallinity will reduce the available free volume and, consequently, the relatively larger penetrant molecules, under study, will require more activation energy. Figure 4 also shows an increase in the activation energy with an increasing number of (CH_2) groups in the series. There is no evidence of activation energy reaching the value of viscous flow. For each additional CH_2 group, there is an increase of about 7.5 kJ/mol in the activation energy.

The TMP molecule has three pendant methyl groups which contribute to its larger diameter and consequently it requires a larger "hole size." Therefore, it has a higher activation energy than its isomer *n*-octane of a similar size.

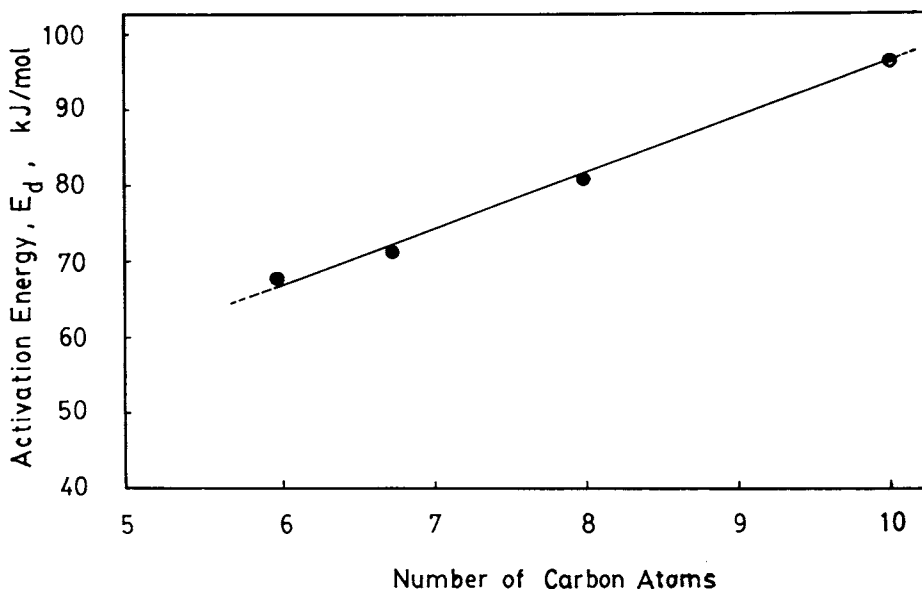


Fig. 4. Variation of the activation energy of diffusion, E_d , with the number of carbon atoms in $\text{CH}_3(\text{CH}_2)_n\text{CH}_3$ hydrocarbon molecule.

Application of the Free Volume Theory

The dependence of the diffusion coefficient on concentration, temperature, and penetrant size can be explained by the free volume theory. In this theory, however, free volume is not clearly defined. It is therefore difficult to provide quantitative predictions. Nevertheless, "semiquantitative" estimates of the free volume parameters A and B in eq. (2) can be made, provided that the fractional free volume f_0 is known.

The fractional free volume can be evaluated from the WLF expression in eq. (3), where the universal values of $f_g = 0.025$ and $\alpha = 4.8 \times 10^{-4}$ can be used. Amorphous polyethylene is reported to have a glass transition temperature of -75°C .²⁷ No attempt was made to determine the crystallinity of the LDPE under study. It has the same density (918 kg/m^3) as that reported by Kreitus and Frisch,¹⁹ where its fractional crystallinity ϕ_c is reported to be 0.5. Therefore, this value can be safely used in our calculations of the fractional free volume f_0 . This obviously involves the following assumptions:

- i. WLF free volume is considered to be equal to the free volume f_0 in eq. (2)
- ii. The crystalline fraction of the polymer is assumed to be impermeable and does not contribute to the free volume of the polymer
- iii. Previous swelling of the polymer has no effect on the polymer morphology

In any case the contribution of the crystalline portion to the free volume, if any, will be very small and can be easily ignored. Also, the D_0 values were obtained at very low concentrations; theoretically, zero concentration. Thus, the net effect of the solvent will be negligible.

TABLE II
Free Volume Estimates for LDPE at Various Temperatures

Temperature (°C)	Fractional free volume f_0
25	0.0365
35	0.0389
40	0.0401
45	0.0413
50	0.0425

In this way the free volume, f_0 , values were obtained through eq. (5) and are reported in Table II for LDPE at all the temperatures studied.

Where D_0 and f_0 are known, the values of the parameters A and B can be obtained through eq. (2). A plot of $1/f_0$ against $\ln(D_0/RT)$ gives a straight line with a slope equal to B and an intercept equal to $\log A$. The f_0 values, given in Table II, are used to construct these plots. An example of this is given in Figure 5. The B and A values obtained for various penetrants are given in Table I. It can be seen that B increases with increasing size of the penetrant

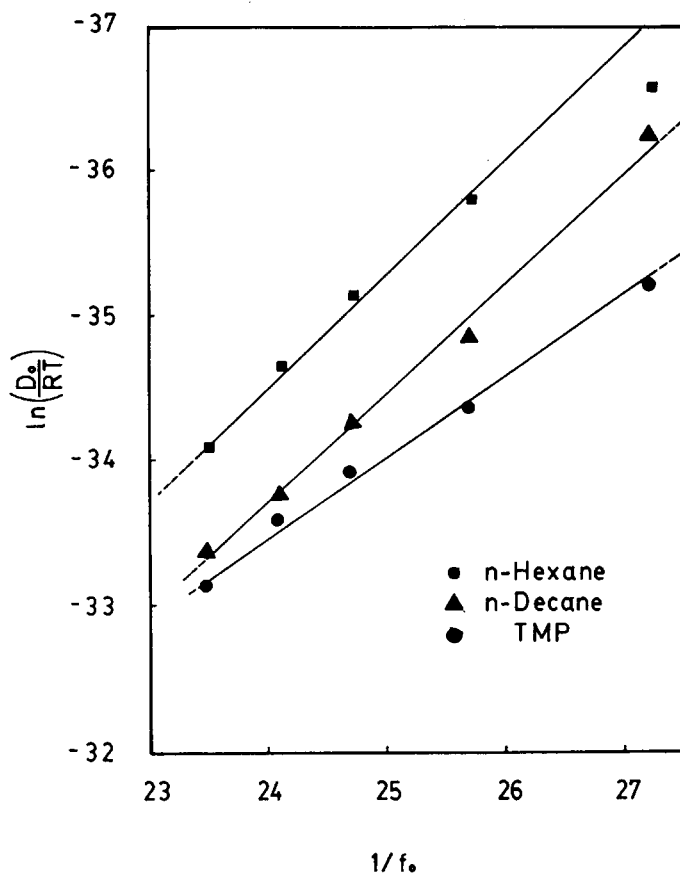


Fig. 5. Variation of $\ln(D_0/RT)$ with $1/f_0$.

molecule, which is consistent with the free volume theory. Generally, a decrease is expected in A but in this case, A also increases with increasing penetrant size. This is rather surprising, but similar results were reported for polymers below their glass transition temperatures³ and perhaps the same applies to partially crystalline polymers. This also suggests that both A and B largely depend on the penetrant size.

Our fractional free volume estimate for LDPE is lower than the reported value of 0.066 by Fleischer,²² but is almost in agreement with the value of 0.038 obtained at 25°C through the sorption method by Fels and Li.²⁸ If the crystalline fraction is not taken into account, our results match those reported by Fleischer.²² The value of B for heptane was found to be 0.221,¹⁹ which is much lower than our estimated value of 0.551, but Fels and Li found this value by an extrapolation technique which, according to those authors, is subject to errors of considerable magnitudes.

Estimates of viscous energy of flow, E_v , can also be made from the knowledge of the activation energy and parameter B . The zero shear melt viscosity of the polymer, η_0 , is given by¹¹

$$\eta_0 = A \exp(1/f_0) \quad (8)$$

Comparing this equation with eq. (2), Fujita et al.¹¹ obtained the following relationship for the energy of viscous flow:

$$E_v = (E_d - RT)/B \quad (9)$$

substituting the E_d and B values from Table I into eq. (9) yields a value of 125 kJ/mol for the energy of viscous flow of normal paraffin hydrocarbons, which corresponds to E_d of a linear hydrocarbon molecule with 14 carbon atoms. Until that limit of molecular size is reached, there is a possibility of increase in activation energy with increasing penetrant molecule size diffusing in LDPE.

CONCLUSIONS

- i. The diffusion coefficient D_0 was found to decrease linearly with increasing the size of the penetrant for the n -alkanes investigated in this study. It was also found that the dependence of D_0 on penetrant size decreases with increasing the temperature.
- ii. The diffusivity values D_0 for TMP at all temperature levels investigated in this study were considerably lower than the corresponding values for a linear molecule of a similar size, viz., n -octane. This can be attributed to the rigidity of the TMP molecule.
- iii. An increase in the activation energy was observed as the number of the (CH_2) groups in n -alkane series increases. The TMP molecule seems to require a higher activation energy for diffusion than its isomer n -octane which has a similar size.

The authors acknowledge with thanks Contract No. 20ST.97714-4-2701 from the Defence Research Establishment Ottawa. One of the authors (A.A.A.) acknowledges with thanks an operating research grant from the Natural Sciences and Engineering Research Council of Canada (NSERC).

References

1. M. Saleem, Abdul-Fattah A. Asfour, D. De Kee and B. Harrison, *J. Appl. Polym. Sci.*, **37**, 617 (1989).
2. W. R. Brown and G. S. Park, *J. Paint Technol.*, **42**, 16 (1970).
3. M. Saleem, Ph.D. thesis, University of Wales, 1977.
4. R. J. Kokes and F. A. Long, *J. Am. Chem. Soc.*, **75**, 6142 (1953).
5. A. Aitken and R. M. Barrer, *Trans. Faraday Soc.*, **51**, 116 (1955).
6. S. Prager and F. A. Long, *J. Am. Chem. Soc.*, **73**, 4072 (1951).
7. J. Y. Moisan, *Eur. Polym. J.*, **16**, 979 (1980).
8. J. Klein, *J. Sci. Phys.*, **15**, 2057 (1977).
9. J. Klein and B. J. Briscoe, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 2065 (1977).
10. J. Klein and B. J. Briscoe, *Proc. R. Soc. Lond. A*, **365**, 53 (1979).
11. H. Fujita, A. Kishimoto and K. Matsumoto, *Trans. Faraday Soc.*, **56**, 424 (1960).
12. W. R. Brown, R. B. Jenkins, and G. S. Park, *J. Polym. Sci., Polym. Symp.*, **41**, 45 (1973).
13. J. Y. Moisan, *Eur. Polym. J.*, **17**, 857 (1981).
14. J. Y. Moisan, *Eur. Polym. J.*, **16**, 997 (1980).
15. J. Y. Moisan, *Eur. Polym. J.*, **16**, 989 (1980).
16. L. Araimo, F. DeCandia, V. Vittoria and A. Peterlin, *J. Polym. Sci.*, **16**, 2087 (1978).
17. F. DeCandia, R. Russo, V. Vittoria, and A. Peterlin, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 2083 (1980).
18. F. DeCandia, R. Russo, V. Vittoria and A. Peterlin, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 269 (1982).
19. A. Kreitus and H. L. Frisch, *J. Polym. Sci.*, **19**, 889 (1981).
20. M. Bischoff and P. Eyerer, *J. Membr. Sci.*, **21**, 333 (1984).
21. D. W. McCall, D. C. Douglas, H. E. Bair, G. E. Johnson, L. L. Blyler, and L. W. Jelinski, *Macromolecules*, **17**, 1644 (1984).
22. G. Fleischer, *Polym. Commun.*, **26**, 20 (1985).
23. H. C. Ng, W. P. Leung, and C. L. Choy, *J. Polym. Sci., Polym. Phys. Ed.*, **23**, 973 (1985).
24. A. S. Michaels and R. B. Parker, *J. Polym. Sci.*, **41**, 53 (1959).
25. M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).
26. G. J. van Amerongen, *J. Polym. Sci.*, **5**, 307 (1950).
27. P. Manaresi and V. Giannella, *J. Appl. Polym. Sci.*, **4**, 251 (1960).
28. M. Fels and N. N. Li, in *Permeability of Plastic Films and Coatings*, H. P. Hoffenberg, Ed., Plenum, New York, 1974, p. 357.

Received January 11, 1988

Accepted August 23, 1988