

Pressure Effects on Diffusion of Linear Aliphatic Esters Through Polyethylene

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Diffusion of linear aliphatic mono- and diesters having 13–68 main-chain atoms (carbons plus one or two oxygens) through bulk medium density polyethylene (MDPE) was studied at 90°C under hydrostatic pressures of up to 2500 bar. Three triglycerides (laurin, myristin and stearin) and phenyl stearate were also used for comparison. Diffusion coefficient, D , was determined from concentration distribution of the diffusants through stacked MDPE films, which was known from the optical absorbance by each component film due to C=O stretching vibration mode of the diffusant. With respect to the linear hydrocarbon esters studied, a relationship $D \propto N^\alpha$ was found to hold at constant pressure, N being the number of main-chain atoms. Under the atmospheric pressure, α became -2.10 in accordance with de Gennes's proposal, $D \propto N^{-2}$, introduced in 1971 on the basis of the reptation model, as well as with the earlier experimental results reported by Klein and Briscoe (1979) for N larger than 30. D 's for the glycerides were found to deviate from the relationship found for the linear esters toward smaller values by comparison at the same N . The exponent α is pressure-dependent. It decreased with increasing pressure according to $\alpha = -2.10 - 0.000942P$ where P is measured in bar and became -4.44 at 2500 bar. Plots of $\ln D$ vs. P for all the diffusants showed linear relationships with negative slope, from which activation volume for diffusion, ΔV^\ddagger , was calculated. ΔV^\ddagger increased slowly with increasing V_{Ki} , the intrinsic molecular volume of the diffusant, from 39.3 cm³/mol for ethyl caprate ($V_{Ki} = 136$ cm³/mol) to 76.8 cm³/mol for behenyl behenate ($V_{Ki} = 466$ cm³/mol). Influence on ΔV^\ddagger by terminal phenyl group or by chain-branching was found not significant. An attempt to measure the length taken along the wrinkle defect of the chain molecular diffusant in connection with reptation was unsuccessful because of uncertainty of the contribution from the free volume inherently distributed in the polymer matrix before activation.

KEY WORDS: Diffusion/ Linear aliphatic esters/ Polyethylene/ Reptation model/ Hydrostatic pressure/ Activation volume/

INTRODUCTION

In the previous investigations¹⁻³⁾, a "multiple-sheets" method was applied to the study of diffusion of aromatic compounds through polymers under hydrostatic high pressures of up to 5000 bar. A stacked-polymer sheets sample was placed in the solution of the diffusant under given pressure and temperature. After an interval of diffusion, a concentration distribution of the diffusant arised across the sheets, which could be determined, under the atmospheric pressure, from the optical absorbance by each component sheet. By analysing the diffusion profile so obtained, the diffusion coefficient, D , was calculated and its pressure dependence lead to the activation volume for the diffusion, ΔV^\ddagger , according to^{4,5,6)}

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$$\Delta V^{\ddagger} = -RT \left(\frac{\partial \ln D}{\partial P} \right)_T \quad (1)$$

where P , T and R are the pressure, the temperature and the gas constant, respectively.

In the present paper, pressure effects on the diffusion of linear aliphatic esters, R_1 -O-CO- R_2 and R_1 -O-CO- R_2 -CO-O- R_1 , through polyethylene was described, where R_1 and R_2 represent linear alkyl groups. Branched esters written as R_1 -CO-O-CH₂-CH(O-CO- R_1)-CH₂-O-CO- R_1 were also used for comparison.

It was demonstrated by Klein and Briscoe⁷⁾ that the diffusion behavior of the above flexible long chain molecule in molten polyethylene could be explained by the theory of reptile diffusion introduced by de Gennes⁸⁾. They indicated that the reptation motion persists down to the diffusant size of $N=30$, where N is the number of the carbon atoms plus the ester oxygens in the main chain. Rennie and Tabor⁹⁾ extended the diffusion experiments by Klein and Briscoe under high hydrostatic pressures. For the diffusion of linear aliphatic esters ranging in N from 18 to 260 in molten polyethylene, they estimated ΔV^{\ddagger} has a value lying between 26 and 52 cm³/mol which corresponds to the occupied volume of only two to five CH₂ units.

The objects of the present paper are, firstly, to apply the multiple stacked sheets method¹⁰⁾, a simple way to know diffusion coefficient, to the study of the diffusion of linear aliphatic esters through solid polyethylene under high hydrostatic pressures, and, secondly, to examine the pressure effects on the diffusion in a more systematic way as a function of P and N , while our previous studies on the diffusion of such rigid molecules as aromatic compounds will give typical references. The temperature will be hold constant at 90°C, for the time being.

EXPERIMENTAL

Materials

Medium density polyethylene (MDPE) was used which was supplied in a form of sheet by courtesy of Dr. Toshio Taka of Showa Denko Co. The sheet was 50 μm thick and its molecular weight and linearity characteristics are $M_w=130000$, $M_n=26700$, $M_w/M_n=4.9$ and $\text{CH}_3\text{CH}_2/1000\text{C}=1.04$ (IR)-1.5 (NMR). The sheet was washed in *n*-decane at 100°C for 4 h, extracted with boiling *n*-pentane in a Soxhlet extractor for 1 h and dried at 60°C in vacuum. In the course of this pretreatment, the sheet showed a weight-loss of ca. 2.2 %. The density of the dried sheet was 0.952 g/cm³ (30°C) and the degree of crystallinity evaluated from the density was 0.68 by volume. The DSC peak melting point was 131°C.

The esters used in the present study were listed in Table 1. All the esters, otherwise stated, were commercial materials having minimum purities 96-99% on the manufacturer's catalogue (Sigma Chemical Co. and Tokyo Chemicals Ltd.) and were used without further purification. Purified crystals of C₁₈H₃₇-O-CO-C₁₈H₃₆-CO-O-C₁₈H₃₇ (obs. m.p. 76.8°C) and C₂₂H₄₅-O-CO-C₂₀H₄₀-CO-O-C₂₂H₄₅ (obs. m.p. 82.8°C) were both supplied by courtesy of Dr. Yoshihiro Ogawa of Kumamoto University. Lauryl stearate (Tokyo Chemicals Ltd., minimum purity 65%) was recrystallized several

times from ether/ethyl alcohol mixed solvents solution; obs. m.p. 41.8°C (lit. 42.0°C¹¹).

Principles and Method

When a substance of diffusant, that was initially ($t=0$) constrained and dispersed uniformly in a very thin flat layer, was allowed to diffuse into host matrices joined with on both sides, the diffusant concentration, $c(x, t)$, at time t and distance x normal to the central thin layer will be given¹²⁾ by

$$c(x, t) = \frac{\lambda}{2\sqrt{(\pi Dt)}} \exp\left(-\frac{x^2}{4Dt}\right), \quad (2)$$

where D is the diffusion coefficient of the diffusant and λ its total amount. In eq. (2) the diffusion is assumed to proceed in Fickian manner, with D being independent of concentration. From eq.(2) the relationship between $\ln c(x, t)$ and $x^2/4t$ becomes linear, the slope and the intercept at $x^2/4t=0$ giving $-1/D$ and $\ln(\lambda/(2\pi Dt))$, respectively.

The thin layer initially containing a uniform dispersion of the diffusant was obtained by casting a film from xylene solution in which MDPE sheet and ester (diffusant) were dissolved so that the final content of ester in the cast film became about 8–20% by weight. Results of D were found not affected by this ester content as will be described later.

The above cast film, 10–20 μm in thickness, was sandwiched between two host MDPE matrices, each consisted from 15 MDPE sheets. These were pressed, using a special tool, in a molding press at 100°C under a nominal pressure of 50 kg/cm² for 30 s to form a transparent cake of the sheets, 1 cm \times 3 cm \times 0.15 cm (thickness) in size. A small amount of contamination of the diffusant from the central cast sheet into the two directly neighbored sheets was confirmed to be safely negligible. Such multiple sheets sample was placed between two flat stainless steel plates and fixed tightly in a heat-shrinkable Teflon tube with two open ends. The whole sample was then inserted in a high-pressure cylinder³⁾ which had been preliminarily heated to the temperature of diffusion, 90°C. Hot water (90°C) as the pressure transmitting medium was then poured into the cylinder through a small hole by using a syringe. The whole assembly was quickly transferred into a heating polyethyleneglycol bath thermostatted at 90 \pm 0.1°C and pressurized to a given pressure within 30 s. In this course, the pressure transmitting water in the cylinder was separated, with a Teflon plug, from the pressure transmitting low viscosity silicone oil supplied from the pressure pump. The pressure of the silicone oil was measured by a 16" Bourdon tube gauge (Heise Co., Conn., U.S.A.) and could be maintained within $\pm 1\%$ variation. Pressure drop due to friction of the Teflon plug was neglected. After passage of time t , the pressure was released to the atmospheric pressure, the diffusion cell was quickly removed from the cylinder and cooled with tapwater.

Each component sheet constituting the multiple sheets sample could be peeled off¹³⁾ and was numbered, from the inner to the outer side, $i=1, 2, 3, \dots$ and $i=-1, -2, -3, \dots$. For the central cast sheet $i=0$. The concentration distribution of the diffusant, which had been discontinuously constrained within the central sheet at $t=0$, was

now broadened by diffusion. The broadened concentration distribution was measured as follows⁷. The absorbance A_i of the i -th component sheet due to the C=O stretching vibration mode was determined by the base-line method at $\nu=1740 \text{ cm}^{-1}$ on the diagram chart scanned by a Nihon Bunko IR spectrophotometer type A-202. The thickness of each individual sheet, d_i , was measured with a micrometer which could be read to $0.1 \mu\text{m}$ (Mitsutoyo type MHF-2.5 V). The mean concentration c_i (by an arbitrary unit), the distance x_i and the reduced distance η_i for the i -th sheet, were given by eq.(3)–(4) and used in the next section to construct the concentration profile of c_i vs. x_i or c_i vs. η_i relationship.

$$c_i = \frac{A_i}{d_i} \quad (3)$$

$$x_i = \frac{1}{2}(d_0 - d_i) + \sum_{\substack{j=1 \\ (j=-1)}}^i d_j \quad (4)$$

$$\eta_i = x_i / (2\sqrt{t}) \quad (5)$$

It is worth noting that the actual concentration of the diffusant after broadening in each component sheet was found to vary between 0.03 and 0.3 wt. %.

RESULTS

Diffusion Profiles

Figure 1 shows an example of c_i vs. η_i relationship obtained for stearin at $P=1000$ bar, $T=363 \text{ K}$ and $t=2775$ min. Figure 2 is the corresponding $\ln c_i(x_i, t)$ vs. $x_i^2/4t$ plots. It is found that the points in Figure 2 gives a linear relationship within the experimental error in accordance with eq.(2). By the least squares fit, D and λ were determined when two points (triangle marks) were neglected because of deviations over a predetermined range of error. With these D and λ , the theoretical concentration distribution according to eq. (2) was drawn in Figure 1 where observed points are seen to

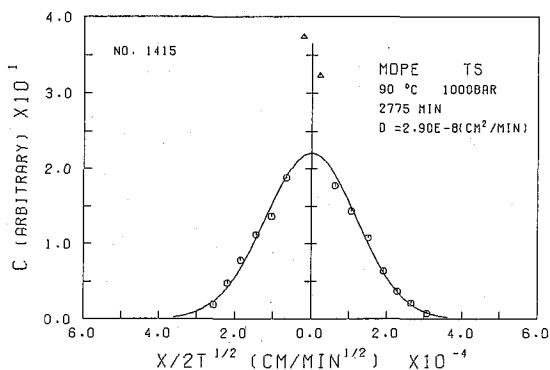


Fig. 1. Diffusion profile (c_i vs. η_i plots) for the diffusion of stearin in MDPE at 90°C , 1000 bar and $t=2775$ min (46 h and 15 min). With respect to the theoretical curve and two triangle marks, see text.

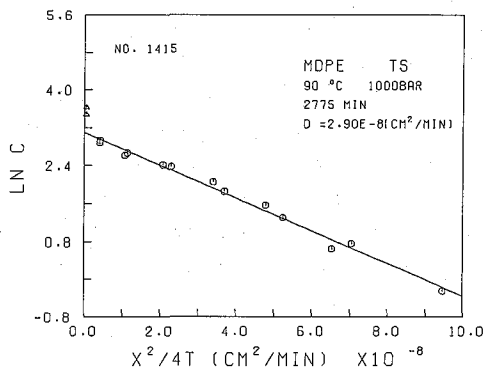


Fig. 2. Plot of $\ln c$ vs. $x^2/4t$ from the data shown in Figure 1, leading to D and λ (see eq. (2) in the text).

scatter within the experimental error. It was often unsuccessful to peel off and separate the central "diffusant-source" sheet from the two directly neighbored sheets because of adhesion. In the case of Figure 1, the three sheets were peeled off into two parts which gave the two deviating points in Figures 1 and 2 (triangle marks).

It may be argued that the interfaces between individual sheets existing in the multiple sheets may affect the D -value because of the discontinuity of the matrix material. In order to examine such interface effect, the thickness of the component sheet was varied in Figure 3 as 25, 50 and 100 μms for the diffusion of lauryl stearate (C_{31}) at 90°C under the atmospheric pressure. The above three sheet samples were prepared by Showa Denko Co. from the same source of MDPE where the only difference was the thickness. The D -values in Figure 3 are seen to be essentially independent of the thickness of the component sheet, indicating little interface effects. The next problem to be examined is whether the morphology of the diffusant dispersed in the cast "diffusant-source" sheet before diffusion will influence the D -value, although the diffusion temperature (90°C) was higher than the melting points at atmospheric pressure of all the diffusants listed in Table 1. In Figure 4, for the purpose of varying the morphology, the concentration of the ester (C_{45}) in the cast film was varied between

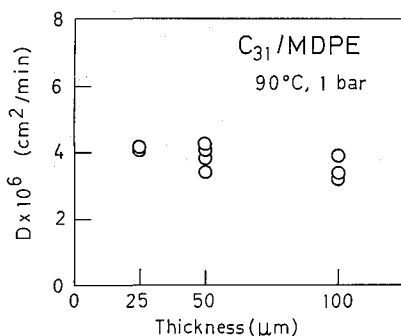


Fig. 3. Influence of the thickness of the component film constituting stacked "multiple film" sample on diffusion coefficient.

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Table 1. Molecular weight (MW), intrinsic molecular volume (V_{Ki}) and chemical structure for a series of linear and branched aliphatic esters.

C_N	Diffusant	MW	V_{Ki} (cm^3/mol)	Structure
C_{13}	Ethyl Caprate	200	136	$\text{CH}_3(\text{CH}_2)_8\text{-CO-O-CH}_2\text{CH}_3$
C_{17}	n-Butyl Laurate	256	178	$\text{CH}_3(\text{CH}_2)_{10}\text{-CO-O-(CH}_2)_3\text{CH}_3$
C_{21}	Capryl Caprate	313	219	$\text{CH}_3(\text{CH}_2)_8\text{-CO-O-(CH}_2)_9\text{CH}_3$
C_{21}	Ethyl Stearate	313	219	$\text{CH}_3(\text{CH}_2)_{16}\text{-CO-O-CH}_2\text{CH}_3$
C_{23}	n-Butyl Stearate	341	239	$\text{CH}_3(\text{CH}_2)_{16}\text{-CO-O-(CH}_2)_3\text{CH}_3$
C_{25}	Lauryl Laurate	369	260	$\text{CH}_3(\text{CH}_2)_{10}\text{-CO-O-(CH}_2)_{11}\text{CH}_3$
C_{31}	Lauryl Stearate	453	322	$\text{CH}_3(\text{CH}_2)_{16}\text{-CO-O-(CH}_2)_{11}\text{CH}_3$
C_{37}	Stearyl Stearate	537	384	$\text{CH}_3(\text{CH}_2)_{16}\text{-CO-O-(CH}_2)_{17}\text{CH}_3$
C_{45}	Behenyl Behenate	649	466	$\text{CH}_3(\text{CH}_2)_{20}\text{-CO-O-(CH}_2)_{21}\text{CH}_3$
C_{19}	Phenyl Stearate	361	244	$\text{CH}_3(\text{CH}_2)_{16}\text{-CO-O-C}_6\text{H}_5$
C_{58}	Diocadecyl Octadecanedioate	847	596	$\text{CH}_3(\text{CH}_2)_{17}\text{-O-CO-(CH}_2)_{18}\text{-CO-O-(CH}_2)_{17}\text{CH}_3$
C_{68}	Didocosyl Eicosanedioate	988	699	$\text{CH}_3(\text{CH}_2)_{21}\text{-O-CO-(CH}_2)_{20}\text{-CO-O-(CH}_2)_{21}\text{CH}_3$
$C_3(C_{13})_3$	Laurin	639	428	$\text{C}_3\text{H}_5\text{[-O-CO-(CH}_2)_{10}\text{CH}_3]_3$
$C_3(C_{15})_3$	Myristin	723	490	$\text{C}_3\text{H}_5\text{[-O-CO-(CH}_2)_{12}\text{CH}_3]_3$
$C_3(C_{19})_3$	Stearin	891	613	$\text{C}_3\text{H}_5\text{[-O-CO-(CH}_2)_{16}\text{CH}_3]_3$

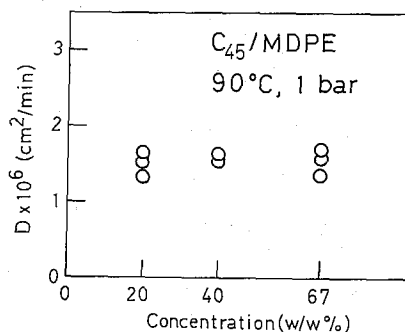


Fig. 4. Influence of the concentration of the diffusant in the central film before diffusion on diffusion coefficient.

20 and 67%, from which the morphology suspected above to influence the diffusion (coefficient) is argued not significant.

Diffusion Coefficient as a Function of Pressure

All the diffusion experiments were carried out at 90°C and are summarized in Table 2, in which D -values for the diffusants with increasing N are listed as a function of pressure from atmospheric pressure up to 2500 bar with 500 bar interval. D -value obtained at atmospheric pressure will be denoted by D_0 . With respect to each diffusant, molecular weight and molar occupied volume, V_{Ki} (cm^3/mol)^{14,15}, which was

Table 2. List of data of D at 90°C as a function of pressure and the corresponding ΔV^* . CC and ES denote capryl caprate and ethyl stearate, respectively, both having the same N , 21.

C_N	Diffusant	MW	V_{Ki} (cm^3/mol)	$D \times 10^7$ (cm^2/min)					ΔV^* (cm^3/mol)	
				pressure (bar)						
				1	500	1000	1500	2000	2500	
C_{13}		200	136	224	106	42.0	26.9	13.1	8.29	39.3
C_{17}		256	178	129	51.1	22.3	11.4	5.96	4.31	40.5
C_{21}	(CC)	313	219	58.3	26.0	10.3	4.67	1.51	0.633	55.1
C_{21}	(ES)	313	219	48.0	27.7	8.38	4.03	1.26	0.712	53.4
C_{23}		341	239	45.3	17.7	6.82	2.55	1.19	0.461	55.2
C_{25}		369	260	49.8	16.9	6.50	3.27	1.28	0.864	49.4
C_{31}		453	322	34.6	9.99	2.95	1.06	0.395	0.229	63.2
C_{37}		537	384	22.5	7.28	1.67	0.791	0.256	0.103	64.5
C_{45}		649	466	16.5	3.95	0.990	0.260	0.0951	0.0269	76.8
$C_{19}C_6H_5$		361	244	45.7	15.4	6.50	2.56	0.929	0.540	55.1
C_{58}		847	596	7.35						
C_{68}		988	699	6.13						
$C_3(C_{13})_3$		639	428	6.82	1.74	0.551	0.197	0.0708		68.3
$C_3(C_{15})_3$		723	490	4.34	1.20	0.410	0.0921	0.0447		70.7
$C_3(C_{19})_3$		891	613	3.68	0.876	0.273	0.108			71.6

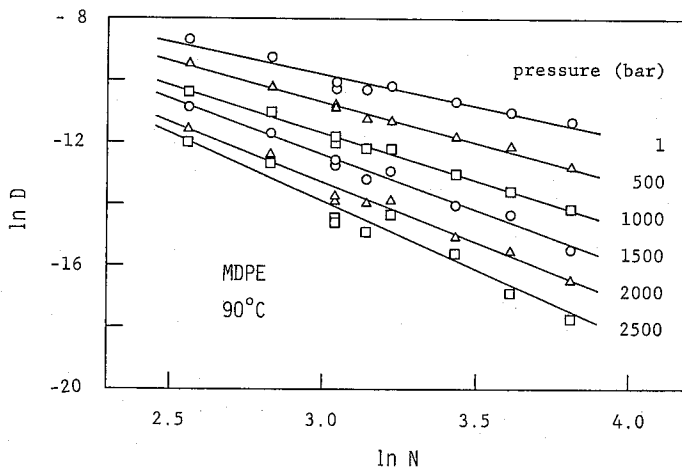


Fig. 5. Plot of $\ln D$ vs. N at respective pressures.

calculated by Kitaigorodskii's method, were also given.

In Figure 5, $\ln D$ was plotted against $\ln N$ under respective pressures where it is seen, under constant pressures, an approximately linear relationship exists between $\ln D$ and $\ln N$, with some scatter of plots seen at 2000 and 2500 bar.

Accepting linear relationships, it was found D can be expressed as a function of N according to eq. (6). The coefficients B_1 and B_2 ,

$$D = e^{B_1} N^{B_2} \tag{6}$$

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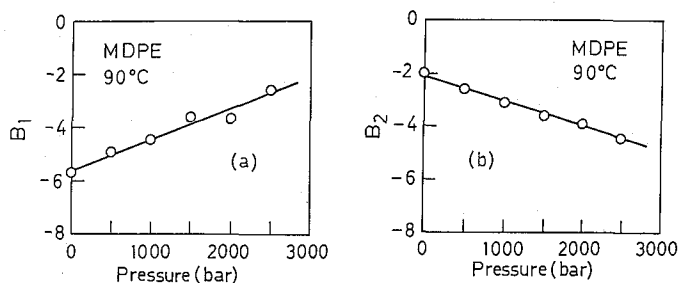


Fig. 6. Variation of the exponents B_1 and B_2 with pressure.

calculated by the least squares fit, were plotted against pressure in Figure 6 where it is found B_1 increases while B_2 decreases, both linearly, with increasing pressure, leading to eqs. (7) and (8) where P is measured in bar.

$$B_1 = -5.61 + 0.00117P \quad (7)$$

$$B_2 = -2.10 - 0.000942P \quad (8)$$

Under the atmospheric pressure ($P=1$), eq.(9) results,

$$D_0 \propto N^{-2.10} \quad (9)$$

which, within the experimental error, is in accordance with de Genne's proposal by his reptation model⁸⁾,

$$D \propto N^{-2}. \quad (10)$$

Next, in order to deduce ΔV^\ddagger on the basis of eq.(1), $\ln D$ was plotted against P in Figures 7 and 8. It is found that $\ln D$ decreases with increasing P in a linear manner for all the diffusants, the slope increasing with increasing N . Such linear relationship with negative slope between $\ln D$ and P was also reported in our previous

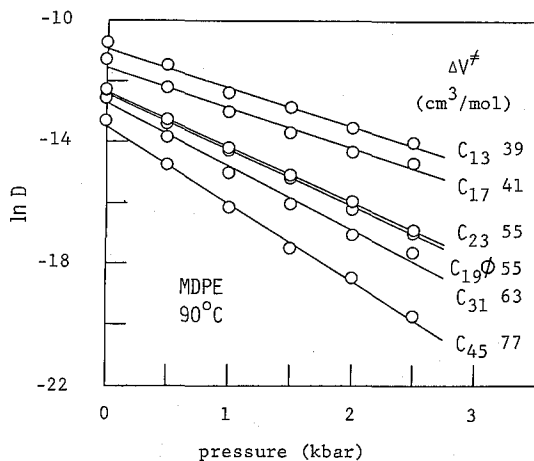


Fig. 7. Plot of $\ln D$ vs. pressure for the diffusion of six aliphatic esters listed in Table 1 in MDPE at 90°C.

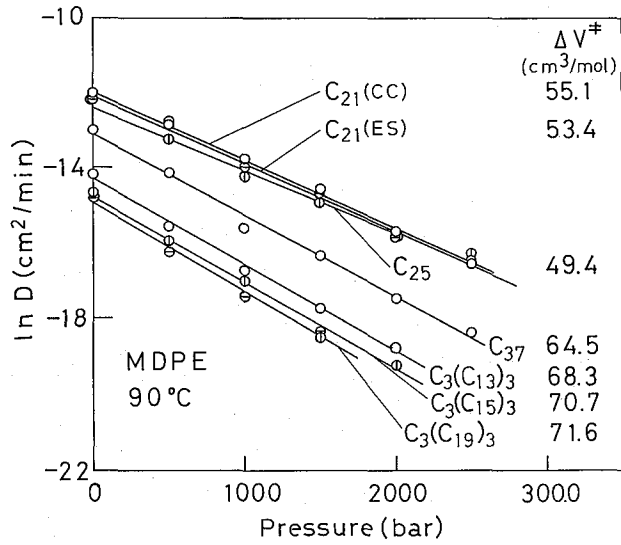


Fig. 8. Plot of $\ln D$ vs. pressure for the diffusion of seven aliphatic esters including three glycerides.

investigations¹⁻³) as well as in the studies by other authors^{5,6,9}). Because the slope is negative and constant, ΔV^\ddagger is positive and independent of pressure. The ΔV^\ddagger 's at 90°C obtained by the least squares fit were listed in the last column in Table 2.

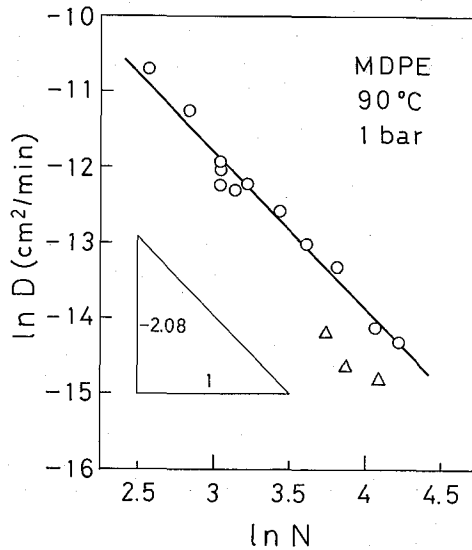


Fig. 9. Relationship between $\ln D_0$ and $\ln N$ for the diffusion of aliphatic esters through bulk MDPE at 90°C. Three triangle marks denote glycerides.

DISCUSSION

From the results obtained in Table 2, $\ln D_0$ was replotted against $\ln N$ in Figure 9 for all the diffusants (excepting phenyl stearate because of uncertainty on counting N). Again, Eq.(9), calculated before based on Figure 5, is confirmed. Eq. (9) is consistent with the results obtained by Klein and Briscoe⁷⁾ for molten polyethylene and similar long chain hydrocarbons with N ranging from 30 to 1400. The above authors discarded data for $N=14, 16, 18$ and 25 because of a systematic deviation from Eq. (9). Since reptation model for the diffusion of chain molecule can be argued as well with respect to a solid polymer matrix with high protrusion of tie molecules¹⁶⁾ as in the present case of MDPE sheet, Figure 9 reveals de Genne's reptation model apparently holds for the diffusion of linear aliphatic esters with N down to as low as 13, much lower than 30 as described by Klein and Briscoe. Presently, the results found in Figure 9 and represented by eq.(9) should be regarded as empirical because our diffusants suffer a theoretical drawback of having lengths too short to be treated by the random coil statistics.

In Figure 9, results by branched diffusants, denoted by triangle marks, deviate down toward smaller values from the linear relationship for the linear diffusants. This is reasonable because long branches on a chain molecule will interfere with diffusion by reptation mode and increase friction by entanglements. It is seen $\ln D_0$ for these branched diffusants decreases likewise with increasing $\ln N$ but the variation range of N for the branched diffusants was so narrow that any formulation will be unreliable.

It is remarkable, as was shown in Figure 5, that de Genne's rule: $D \propto N^{-2}$ can only be valid under the atmospheric pressure. The exponent α in $D \propto N^\alpha$ is strongly pressure-dependent and decreases from a value of -2.03 at the atmospheric pressure to a value of -4.44 at a pressure of 2500 bar, at 90°C .

In order to give a theoretical explanation for the pressure dependence of α found above, it seems necessary, based on the tube model explanation¹⁷⁾, to predict how the chain statistics of the diffusant and the friction coefficient of the diffusant depend on pressure, which is presently beyond the scope of this paper focusing mainly on description of the experimental evidence. However, here it is worth quoting the study on the chain length- and the temperature-dependence of self-diffusion coefficient in polystyrene reported recently by Antonietti, Coutandin and Sillescu¹⁸⁾ where α is dependent on temperature under the atmospheric pressure decreasing from a value of -2.02 at 208°C to a value of -2.45 at temperatures between 167 and 153°C . The above authors were unsuccessful to give explanation for the temperature dependence of α found above.

The activation volume for diffusion, ΔV^\ddagger , will now be discussed below. It is, by definition, the excess in partial molar volume of the diffusant in the activated (\bar{V}^\ddagger) over the initial (\bar{V}_R) state,

$$\Delta V^\ddagger = \bar{V}^\ddagger - \bar{V}_R \quad (11)$$

In general, ΔV^\ddagger is understood as the local volume change associated with motion⁴⁾ and arises, in our case, from the sum of three main contributions:³⁾ the intrinsic

volume term (ΔV_W^\ddagger)¹⁹⁾, the interaction (solvation) term (ΔV_i^\ddagger)¹⁹⁾ and the "Eyring hole" term (ΔV_{EH}^\ddagger)³⁾, written as

$$\Delta V^\ddagger = \Delta V_W^\ddagger + \Delta V_i^\ddagger + \Delta V_{EH}^\ddagger. \quad (12)$$

ΔV_W^\ddagger represents the volume change which results, in forming the activated state, from the change of the intrinsic volume of the diffusant molecule, and ΔV_i^\ddagger those induced by the intermolecular interactions between the diffusant and the surrounding polymer matrix. ΔV_{EH}^\ddagger corresponds to the part contributed by the Eyring hole which must be opened up for accommodation in the direct neighborhood of the activated diffusant²⁰⁾. The hole is formed by the thermal segmental motion of the polymer molecule, accompanied by a local free volume expansion. Of the three factors on the right hand side of eq.(12), only the last term prevails, because our diffusion is accompanied neither by chemical reaction nor by ionization, but only by weak intermolecular interactions between aliphatic molecules. Consequently, ΔV^\ddagger may be put equal to ΔV_{EH}^\ddagger .

$$\Delta V^\ddagger = \Delta V_{EH}^\ddagger. \quad (13)$$

In contrast to the diffusion of rigid aromatic molecules as previously studied in which the whole molecule was considered to jump at a time for diffusion, diffusion of chain molecule must proceed, on the reptation model⁸⁾, by a mechanism in which some wrinkle of the flexible chain moves along it and is released at the chain end. According to this mechanism, as a first approximation based on the Boltzmann distribution, ΔV_{EH}^\ddagger is equal to the occupied volume of the part of the wrinkle measured along its "stored length (SL)"⁸⁾, V_{SL} , as given by

$$\Delta V_{EH}^\ddagger = V_{SL}. \quad (14)$$

Since a contribution from the free volume which existed in the initial state must have been involved in ΔV_{EH}^\ddagger and if this contribution is denoted by $V_{f, local}$, then, from eqs.(13) and (14), $V_{f, local}$ plus the activation volume is equal to V_{SL} , as,

$$V_{f, local} + \Delta V^\ddagger = V_{SL}. \quad (15)$$

From eq.(15),

$$\Delta V^\ddagger = V_{SL} \quad \text{when} \quad V_{f, local} = 0 \quad (16)$$

and

$$\Delta V^\ddagger = 0 \quad \text{when} \quad V_{f, local} \geq V_{SL}. \quad (17)$$

ΔV^\ddagger listed in Table 2 was plotted against N in Figure 10. As shown in Figure 10, it is found ΔV^\ddagger increases slightly with increasing N , in contrast to the results obtained by Rennie and Tabor⁹⁾ for the diffusion of stearamide (C_{18}), behenyl behenate (C_{45}) and 260-carbon deuterated polyethylene in molten linear polyethylene at 150°C (three triangle marks in Figure 10) where ΔV^\ddagger remains almost constant, with respect to the region of N concerned with us, at 26–30 cm³/mol.

In order to approach on the basis of eqs.(13) through (17), it is much better to plot

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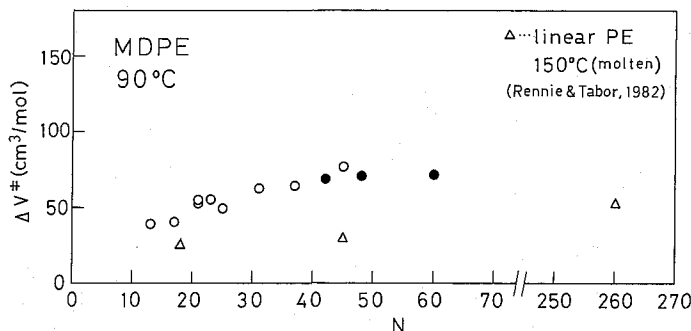


Fig. 10. Variation of activation volume for the diffusion, ΔV^\ddagger , as a function of the number of the main-chain atoms.

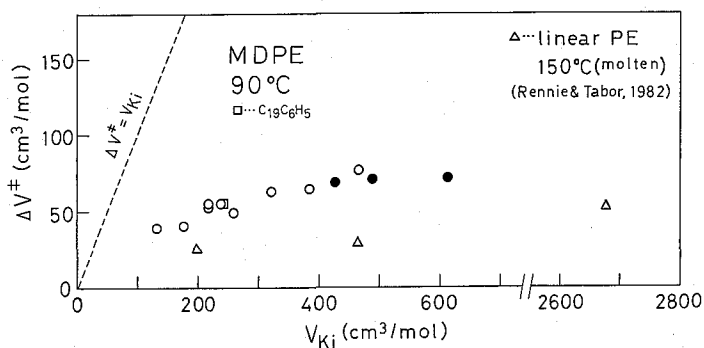


Fig. 11. Variation of ΔV^\ddagger with intrinsic occupied volume of the diffusants, V_{Ki} . Square mark denotes phenyl stearate.

ΔV^\ddagger against V_{Ki} of the diffusant instead of N , although V_{Ki} is approximately proportional to N for the aliphatic chain diffusants presently used. This is shown in Figure 11 in which the limiting condition, $\Delta V^\ddagger = V_{Ki}$, on the assumption that $V_{f, local}$ is zero and, moreover, the activated diffusant moves at a time to a wholly new position, was shown by broken line. In Figure 11 where V_{Ki} is used as variable, the result obtained for phenyl stearate is now introduced. As seen from Figure 11, ΔV^\ddagger increases slightly from 39.3 cm^3 for C_{13} ($V_{Ki}=136 \text{ cm}^3$) to 76.8 cm^3 for C_{45} ($V_{Ki}=466 \text{ cm}^3$) with a slope of nearly 10 cm^3 per increase in V_{Ki} of 100 cm^3 . With respect to C_{13} , ΔV^\ddagger is 29% of V_{Ki} and corresponds to a SL of 3.8 CH_2 units, while, for C_{45} , they are 16% and 7.5. In molten state at 150°C , ΔV^\ddagger varies from 26 cm^3 for stearamide to 52 cm^3 for deuterated polyethylene with 260 carbons. These correspond to a SL having 2.5 to 5.0 CH_2 units which are roughly half as low as the results obtained in the present paper for the solid state MDPE matrix at 90°C . It is interesting to note that the behavior of phenyl stearate is very normal whose plot (square mark) is found on the same line as for the other diffusants, indicating little influence of terminal phenyl group on ΔV^\ddagger .

More remarkable is that the slight slope shown in Figure 11 makes another contrast when compared with the results obtained in the previous studies on the diffusion of

rigid aromatic molecules³⁾ where ΔV^\ddagger was demonstrated to increase linearly with increasing V_{Ki} with steeper, more definite slopes which were even resolvable between the azo and the anthraquinone derivatives³⁾. Moreover, for the diffusion in polyethylene terephthalate, the linear relationships between ΔV^\ddagger and V_{Ki} came near to the broken line, $\Delta V^\ddagger = V_W^{3)}$, V_W corresponding to V_{Ki} in the present study.

On the reptation model, it is expected SL will not be dependent on N as N becomes large. This means ΔV^\ddagger will be independent of N . If the model is described by the tube model¹⁷⁾, SL is to correspond to be twice the diameter of the tube. Such characteristics of the reptile diffusion model seems to be reflected on the results shown in Figures 10 and 11 by Rennie and Tabor⁹⁾ at 150°C. Our results obtained at 90°C in the MDPE solid matrices are seen to locate between the two extremes, $\Delta V^\ddagger = V_{Ki}$ and the reptile diffusion stated above. The difference in ΔV^\ddagger amounting to two times between our results and Rennie and Tabor's should principally be ascribed to the difference in $V_{f, local}$ because this increases with increasing temperature and, according to eq. (15), ΔV^\ddagger must decrease if V_{SL} is assumed to be independent of temperature.

Much interests, of course, tend to be focused on questioning how long a SL is accompanied when chain-molecular diffusant moves by reptation mode. However, because we have presently no means to evaluate $V_{f, local}$ quantitatively, our aim to measure SL by dividing V_{SL} , which will be deduced from the observed ΔV^\ddagger by using eq. (15), by the volume increment of one CH_2 unit, $10.3 \text{ cm}^3/\text{mol}$, is strongly hampered. Thus, the SL lengths measured in CH_2 units as described before, 3.8 to 7.5 at 90°C and 2.5 to 5.0 at 150°C, should be regarded as the lower limit value.

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