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Diffusion in Ethylene Polymers. III. Effects of Temperature and Pressure

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The concentration-dependent diffusion of some organic liquids, mostly hydrocarbons, has been examined in polyethylene as a function of temperature, pressure and the concentration and structure of the diffusing substances. The studies primarily involved branched polyethylene, though some studies of permeability and solubility were carried out on linear polyethylene. The dependence on concentration and temperature was examined by a desorption method and a "time lag" method. The pressure dependence of diffusion was studied by a new dielectric method. Activation energies were found to be about 15 kcal./mole for these liquids. This independence of the identity of the solvent suggests that this value describes hindrances to motions of the polymer molecules. In terms of the theory of absolute reaction rates, an entropy of activation is obtained and is interpreted on the basis of postulated constraints to chain motion. Volumes of activation are compared for the solvents and are examined in the light of Eyring's "hole" theory for liquids. A simple model is offered which relates the measured volumes of activation in diffusion to the structures of the diffusing molecules.

I. Introduction

In order to obtain an understanding of complex polymer systems on a molecular scale, it is essential to employ a multiple approach, using a variety of techniques and conditions, and seeking an interpretation consistent with all the experimental findings. In this series of studies we attempt to acquire a picture of molecular motion in ethylene polymers by means of diffusion measurements,[1] complementing studies made by nuclear magnetic resonance spectroscopy[2] and by dielectric absorption.

Studies of molecular motion usually can be described in terms of τ_c, the *correlation time* for the motion involved. For example, a maximum in dielectric loss implies the existence of dipole rotation, with the correlation time representing the characteristic time that a molecular dipole spends in a potential minimum. Similarly, in the diffusion experiment, if one views the process as a random walk between potential minima, there is again a correlation time which represents the average time a molecule spends in a given potential well. By the same token, nuclear magnetic resonance line width experiments may be analyzed, as a function of temperature, to yield yet another τ_c. Other processes, such as mechanical relaxation, may be treated similarly.

The correlation times obtained from the various experiments are not to be compared directly in most systems, for although the processes must ultimately be governed by the same intermolecular forces, still the relationships are complex. On the other hand, in the case of polyethylene, it appears that the molecular processes involved in diffusion, dielectric relaxation and nuclear resonance line narrowing are closely related. The evidence for this conclusion comes from similarities among the activation energies and correlation times found among the various kinds of measurement. However, the measurement of these quantities is not precise, and the assignment of the model is uncertain. Therefore, it is of considerable interest to enlarge the number of variables which may be independently controlled.

It is almost universally observed that the various τ_c's vary exponentially with temperature

$$\tau_c = A\exp(E/RT) \qquad (1)$$

where E is termed the activation energy. In terms of the theory of absolute reaction rates,[3] E is related to the free energy of activation, $\Delta F^{\ddagger}$, according to

$$\Delta F^{\ddagger} = E + RT - T\Delta S^{\ddagger} \qquad (2)$$

The correlation time is then given, in analogy to (1), by the relation

$$\tau_c = A'\exp(\Delta F^{\ddagger}/RT) \qquad (3)$$

Regardless of the details of the theoretical model, it seems reasonable that a relation such as equation 3 is valid. If this is assumed and if the proportionality constant A' is insensitive to pressure variations, it follows that

$$(\partial \ln \tau_c/\partial p)_T = \Delta V^{\ddagger}/RT \qquad (4)$$

where $\Delta V^{\ddagger}$ is the volume of activation of the process under consideration.

According to the theory of absolute reaction rates,[3] $\Delta V^{\ddagger}$ is the difference in volume between the activated and normal states. This definition is vague even when specialized to specific systems and processes. $\Delta V^{\ddagger}$ should be valuable, however, in identifying the motional processes. For example, if dielectric measurements are attributed to the same molecular process as dynamic mechanical measurements, a test of the correctness of the assignment may be made by determining and comparing $\Delta V^{\ddagger}$ for the two experimental methods. Though not conclusive, such a comparison should be helpful. Moreover, an empirical study of $\Delta V^{\ddagger}$ should be rewarding in its own right, since the quantity is very likely related, in some way, to molecular motions.

The present paper deals with the concentration-dependent diffusion of some low molecular weight organic compounds in polyethylene. The study had the particular aim of improving the understanding of molecular motion in polyethylene. The diffusion coefficient was studied as a function of temperature, pressure and the concentration and structure of the diffusing substance. The dependence upon temperature and concentration was studied by a desorption method and also by a "time lag" method. However, the variables of tem-

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[1] D. W. McCall, *J. Polymer Sci.*, **26**, 151 (1957).

[2] D. W. McCall and W. P. Slichter, *ibid.*, **26**, 171 (1957).

[3] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941.

perature and concentration have not been studied independently of one another. The pressure dependence of diffusion has been studied by a new technique involving dielectric measurements. To our knowledge these data are the first to describe the pressure behavior of diffusion in polymers. Although the studies were made chiefly on low-density (branched) polyethylene, some information has been obtained on high-density (linear) polyethylene.

II. Experimental

A. Desorption.—The technique used in the desorption experiments has been described elsewhere.[1] Briefly, the weight of thin slab of polymer, initially saturated with liquid, is measured as a function of time. The results are then compared with desorption curves computed numerically on the basis of an assumed functional form for the concentration dependence of the diffusion coefficient. It has been found that the function

$$D = D_0 \exp(\delta c) \tag{5}$$

yields close agreement with the data. δ is a parameter for which various constant values are chosen, a calculation being carried out for each. The units for c are conveniently chosen such that $c = c_0 = 1$ at saturation.

The experiments have been implemented by an automatic analytical balance which records weight changes continuously[4]; this device not only saves labor but also produces data superior to those obtainable from weighings made manually. An oven was placed directly beneath the balance, and for desorption experiments above room temperature the sample was suspended inside the oven by means of a string attached to the balance arm.

Volume swelling was measured as follows. Rectangular sheets of polyethylene were soaked in the liquids until saturated. Then, with the samples still immersed in the liquids, linear dimensions were measured with vernier calipers (length and breadth) and a micrometer (thickness). The specimens were then allowed to dry thoroughly in the air. The linear dimensions were again measured. The linear swelling is defined as $\delta l_1/l_1$, where δl_1 is the change in the linear dimension l_1, the latter referring to the dry polymer. The volume swelling, S, is given by $S = 100[(\delta l_1/l_1) + (\delta l_2/l_2) + (\delta l_3/l_3)]$, expressed in per cent. (1,2 and 3 refer to the three dimensions.) It should be mentioned that the individual $\delta l_1/l_1$'s are not equal in all cases. Presumably this is an indication of stresses remaining in these molded sheets. The measurements of S are reproducible to ±1%.

A comment is in order regarding a method we have used to determine the diffusion coefficient at zero concentration, D_0. In a desorption experiment in which D is *not* a function of concentration, a graph of the natural logarithm of the quantity within the slab *versus* time becomes linear[5] (after a short induction period) with slope $\pi^2 D/l^2$, for a slab of thickness l. With a diffusion coefficient varying as in equation 5, $D(c) \rightarrow D_0$ a constant, as $c \rightarrow 0$. Whether or not D depends upon c, the same concentration profile is approached (*i.e.*, zero across the slab), and thus the slope of a desorption curve for an exponentially variable diffusion coefficient should approach $\pi^2 D/l^2$ when the time is long enough. In the cases met here, "long enough" means that $100Q < c_0 l$, where Q is the quantity of liquid remaining in the slab at the time t and c_0 is the saturation concentration. Under these circumstances $c(t)$ has become very small, and D varies by only a few per cent. across the slab and changes slowly with time.

B. Time Lag.—If one measures the rate of flow of a vapor through a film of material in which the vapor dissolves, there is an interval from the moment the gas contacts the film until it emerges at a constant rate at the other side. When the concentrations of vapor at each gas-film interface are kept constant, the quantity of vapor transmitted as a function of the time assumes the form shown in Fig. 1. The steady-state portion of the curve, extrapolated back to the time axis, makes an intercept (L) which can be related at once[5] to the diffusion coefficient, provided the coefficient does not depend upon the concentration. In the case of concentration-dependent diffusion, the curve has the same superficial form but because of the non-linearity of the diffusion equation, one may no longer determine D directly from the time lag, L. However, Frisch[6] has shown that by assuming the functional form of the concentration-dependent diffusion coefficient, one may relate the diffusion coefficient to the time lag, without an explicit solution of the diffusion equation. The approach is treated more fully below.

The time-lag experiments were done in two ways. In some of them the permeation cell consisted of an aluminum dish, filled with the solvent, and covered with a sheet of the polymer which was clamped in place. In most of the time-lag experiments, the cell consisted of a screw-cap bottle made of the polymer. Prior to beginning the experiment, the bottle and the liquid were each brought to the temperature of the oven, whereupon the liquid was introduced and the weight measurements were begun, using the automatic analytical balance.

C. *Dielectric* Measurement of Sorption Kinetics.—Polyethylene is known to contain a small amount of oxygen, probably incorporated into the chains as carbonyl groups.[7-9] A broad maximum in dielectric loss is observed near 10^8 cycles/second at room temperature. Owing to the large dipole moment of the carbonyl group[10] and the mobility of the chains in the amorphous regions, this maximum is attributed to the amorphous portions. When the polymer is oxidized further (as by milling in air at high temperatures), this loss peak is found to increase in intensity. It is not appreciably shifted in frequency, however, until the concentration of carbonyl groups becomes so great that dipole–dipole interactions become important. A second loss peak is observed near 10^2 cycles/second and is attributed to the carbonyl activity in the crystalline regions.

When relatively small, non-polar molecules are sorbed by the polymer, the violence of chain motion is increased, as evidenced by the fact that the loss peak near 10^8 cycles/second shifts to higher frequencies. On the other hand, the loss peak near 10^2 cycles/second is sharpened by the presence of the solute. This means that some of the dipoles responsible for the loss in the region 10^3–10^6 cycles/second in the dry polymer are more firmly bound in the swollen polymer. These two results lead to the following situation. If one measures the dielectric loss as a function of the amount of liquid sorbed, at a constant frequency, say 10^4 cycles/second, the dielectric loss is observed to decrease with increasing concentration. A typical loss spectrum is shown in Fig. 2.

Let us now consider the experiment performed in the present study. A thin slab of slightly oxidized polyethylene is placed between the plates of a parallel plate capacitor. The slab thickness is such that a loose fit is obtained. At time $t = 0$ the chosen liquid is added to the capacitor, filling all the space not occupied by the polymer. Since the liquids are non-polar, their loss is negligible, and the measured loss of the capacitor is due entirely to the polyethylene. The dielectric loss is measured as a function of time, all measurements being made at constant frequency, in the present study 10^4 cycles/second.

The dielectric loss, tan δ, is related to the sorption kinetics through the following assumption: it is supposed that the total quantity of liquid sorbed per unit area at time t, $Q(t)$, is proportional to the change observed in tan δ. Consequently

$$Q(t)/c_0 l = \frac{\tan \delta(_{t=0} - \tan \delta)_{t=t}}{\tan \delta(_{t=0} - \tan \delta)_{t=\infty}} \tag{6}$$

where again c_0 is the saturation concentration and l is the slab thickness. This assumption has been justified at atmospheric pressure by comparison of the dielectric result with independent (weight loss) data. However the accuracy of measurement for tan δ is low.

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(4) P. D. Garn, *Anal. Chem.*, **29**, 839 (1957).

(5) R. M. Barrer, "Diffusion in and through Solids," The University Press, Cambridge, England, 1951.

(6) H. L. Frisch, *J. Phys. Chem.*, **61**, 93 (1957).

(7) W. Jackson and J. S. A. Forsythe, *J. Inst. Elec. Engrs.*, **92**, 23 (1945).

(8) W. Oakes and D. W. Robinson, *J. Polymer Sci.*, **14**, 505 (1954).

(9) G. P. Mikhailov, S. P. Kabin and B. I. Sazhin, *Zhur. Tek. Fiz. SSSR*, **25**, 590 (1955).

(10) C. P. Smyth, "Dielectric Constant and Structure," McGraw-Hill Book Co., New York, N. Y., 1956.

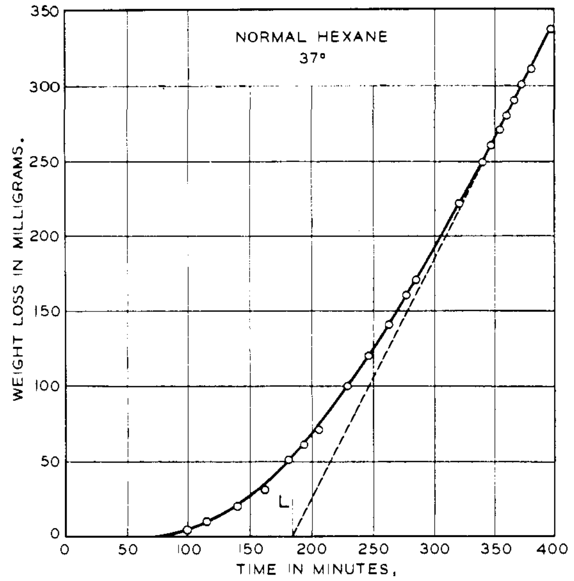

Fig. 1.—Typical time lag curve: normal hexane in branched polyethylene, at 37°.

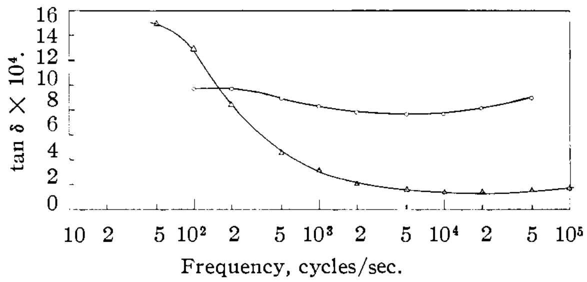

Fig. 2.—Dielectric loss as a function of frequency, in dry polyethylene (O) and in polyethylene saturated with *n*-hexane (Δ) at 23°.

It has been shown previously[1] that $Q(t)/c_0l$ can be used to obtain the diffusion coefficient for the small molecule in the polymer. However, owing to the low accuracy of the measurement of tan δ, we prefer to use an average diffusion coefficient[1]

$$D = 0.0492l^2/t_{1/2} \qquad (7)$$

where $t_{1/2}$ is the time at which $Q/c_0l = 1/2$. Since we are only interested in obtaining pressure coefficients by this method, the average value of D is all that is necessary. Although the precise nature of the average is not known, it is the same at each pressure, and hence the pressure coefficient should be unaffected.

The dielectric loss was measured with a General Radio type 716-C capacitor bridge. The capacitor and pressure system have been described previously.[11] The pressures ranged up to 8000 p.s.i. for most of the solvents.

D. Materials.—The experiments on desorption and dielectric loss were performed on a high-pressure, branched polyethylene, made by the Bakelite Division, Union Carbide and Carbon Corporation, and designated DYNK by the manufacturer. The material was milled in air for 3 hr. at 170° to bring the dielectric loss up to a conveniently measured value. It has been shown[1] that such oxidation has little or no effect on the diffusion process. The polymer was used in the form of compression-molded sheets about 0.05″ thick. The liquids employed were as follows: *n*-hexane, hexene-2 (Phillips Petroleum Co., 95 mole % purity); *n*-octane, *n*-decane, 3-methylpentane, neohexane, cyclohexane (Phillips Petroleum Co., 99 mole %); benzene (Merck and Co., Inc., reagent grade); carbon tetrachloride (Allied Chemical and Dye Corp., General Chemical Division, reagent grade); *p*-dioxane (Eastman Kodak Co., Distillation Products Division). All were used without further purification.

III. Results

A. Solubility and Swelling.—The solubilities were determined from the desorption curves, using the weight of the swollen sample at $t = 0$, found by extrapolation of the curve to the initial time, and the weight of the fully desorbed polymer. Because the weight loss in the initial stages of desorption occurs quite rapidly, especially at the higher temperatures, this method of finding solubilities is somewhat less satisfactory than would be the analogous experiment done by absorption. Figure 3 shows the dependence of solubility upon vapor pressure[12] for a number of the solvents in the branched polyethylene; the solubility is expressed in moles per mole of methylene groups in the polymer. Note that the temperature is an implicit variable, since it affects both vapor pressure and solubility. The data take no account of the fact that the solvent is lodged only in the amorphous portions but are in terms of the gross sample. As has been observed elsewhere,[13] the solubilities of the *n*-alkanes vary inversely with molecular weight. The differences between *n*-hexane and its two isomers, which differ progressively in branching, are noteworthy.

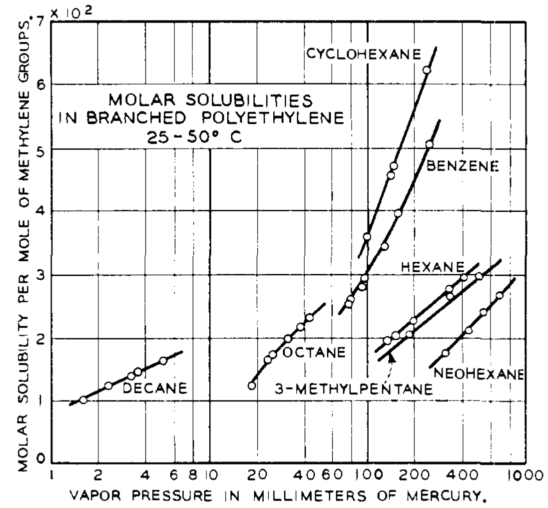

Fig. 3.—Molar solubilities of solvents per mole of methylene groups, as a function of the vapor pressure of the solvent, 25–50°.

It is instructive to compare the solubilities on the basis of the *atom* fraction, x_a, of solvent occurring in the amorphous regions, since such a figure is a measure of compatibility between solvent molecules and polymer segments which evades the effect of molecular size. This quantity is computed from the expression

$$x_a = c_0/[c_0 + (1 - \epsilon)(M_L/14m)] \qquad (8)$$

where ϵ is the degree of crystallinity, M_L is the molecular weight of the liquid and m is the number of atoms in a molecule of the liquid (excluding hy-

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[11] D. W. McCall, *Rev. Sci. Instr.*, **28**, 345 (1957).

[12] "Selected Values of Properties of Hydrocarbons," The American Petroleum Institute, 1949.

[13] R. B. Richards, *Trans. Faraday Soc.*, **42**, 10 (1946).

drogen). The degree of crystallinity was taken to be 0.7. The number 14 is the molecular weight of a polymer chain segment. It would doubtless be interesting to extend these results into a study involving comparisons of cohesive energy densities, as has been done by Richards[13] for some other organic liquids in polyethylene.

The figures for x_a, and also the solubilities and swelling factors, are given in Table I. It is interesting to note that the paraffin hydrocarbons all have nearly the same value of x_a.

TABLE I

SOLUBILITY, ATOM FRACTION AND SWELLING FACTOR IN BRANCHED POLYETHYLENE AT 25°

Liquid	Solubility, c_0 (wt. %)	Atom fraction, x_a (%)	Swelling factor, S (%)
n-Hexane	12.6[a]	29	14
n-Octane	11.7	28	15
n-Decane	11.2	27	11
3-Methylpentane	13.8	30	11
Neohexane	10.6	26	9
Cyclohexane	22.8	43	22
Benzene	17.2	38	16
Hexene-2	13.3	31	12
Carbon tetrachloride	52.5	45	26
p-Dioxane	4.7	14	7

[a] The solubility of *n*-hexane was previously reported[1] incorrectly. The ratio of solubilities reported for DYNK and Marlex 50 polyethylenes is in error by the same factor.

B. Desorption.—The desorption curves were analyzed in the manner used previously.[1] Figure 4 shows a typical desorption plot for cyclohexane. The time axis is given in units of integration steps. The computed curve is fitted to the data at $Q/c_0l = 1/2$. Figure 4 is a composite plot of four separate experiments, in which the thickness was varied by a factor of two. The excellent agreement is typical of all the liquids studied. The invariance with respect to thickness, and hence with respect to the time scale of the experiment, shows that there are no time effects apart from the diffusion itself and that there are no important effects stemming from differences in molding.

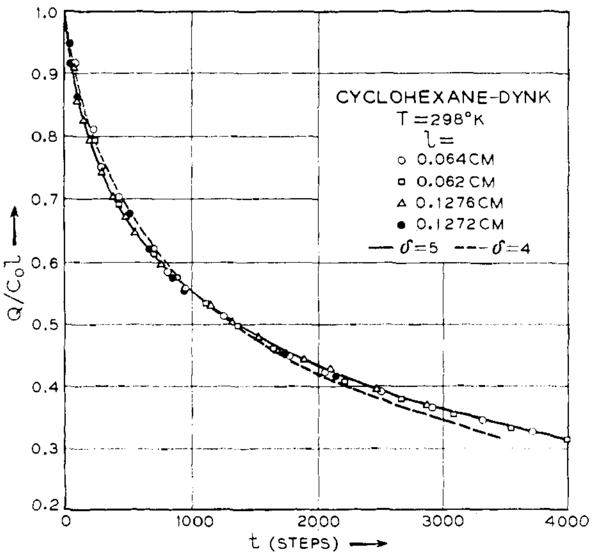

Fig. 4.—Quantity of solvent remaining in polymer, in reduced units, as a function of elapsed time, in integration steps (ref. 1).

The solid curve in Fig. 4 is a theoretical curve computed for $\delta = 5.0$; the agreement with the data indicates this to be the room-temperature value for cyclohexane. The sensitivity to a variation in δ may be judged from the dashed curve, which is a plot for $\delta = 4.0$. It is seen that this curve does not deviate greatly from the measured points. Hence the curve fitting does not offer a very critical measurement of δ. Probably the accuracy is about ± 0.5 δ units. The magnitude of δ decreases with increasing temperature. With cyclohexane, for example, δ ranges from 5 to 3 as the temperature is increased from 25 to 50°.

Having assigned a δ-value, one may use the methods of reference 1 to find D_0. Since these methods are quite inaccurate, we prefer the limiting slope method for D_0 (see above). Table II lists values of D_0 and δ for 25°. From the temperature dependence of D_0, one may calculate an activation energy (E_0) in the customary way. Values of E_0 are given in Table II and are discussed in Section IV (below).

TABLE II

VALUES OF D_0 AND δ AT 25° AND VALUES OF ACTIVATION ENERGY

Liquid	$10^9 D_0$, cm.²/sec.	δ	E_0, kcal./mole
n-Hexane	6.4	5.0	15.6
n-Octane	4.4	4.0	14.7
n-Decane	4.8	4.0	15.9
3-Methylpentane	4.9	4.5	14.8
Neohexane	3.4	5.0	15.5
Cyclohexane	4.8	5.0	14.6
Benzene	11.8	4.0	15.4
Hexene-2	8.3	4.0	13
Carbon tetrachloride	3.7	4.5	19.8
p-Dioxane	5.1	3.0	18.0

C. Time Lag.—Frisch[6] has shown that the asymptote to the curve describing weight loss as a function of time, in the "time lag" experiment, is

$$W_a(t) = \left[\frac{1}{l}\int_0^{c_0} D(c)\,\mathrm{d}c\right](t - L) \qquad (9)$$

where L, the time lag, is given by

$$L = \frac{l^2 \int_0^{c_0} wD(w) \int_w^{c_0} D(u)\,\mathrm{d}u\,\mathrm{d}w}{\left[\int_0^{c_0} D(u)\,\mathrm{d}u\right]} \qquad (10)$$

If one substitutes the functional form used in the desorption studies, equation 5, it may be shown that

$$W_a(t) = \frac{D_0(e^{\delta} - 1)(t - L)}{\delta l} \qquad (11)$$

and

$$L = \frac{l^2[e^{2\delta}(2\delta - 3) + 4e^{\delta} - 1]}{4D_0(e^{\delta} - 1)^3} \qquad (12)$$

(recalling that $c_0 = 1$ in our δ-units). The time-lag graphs yield two pieces of data, the time lag, L, and the slope of the steady-state asymptote, $s = D_0\,(e^\delta - 1)/\delta l$. One may show[14] that

$$Ls/\delta c_0 = \frac{(2\delta - 3)e^{2\delta} + 4e^\delta - 1}{4\delta(e^\delta - 1)^2} \qquad (13)$$

The relation between δ and the measured quantities is shown graphically in Fig. 5.

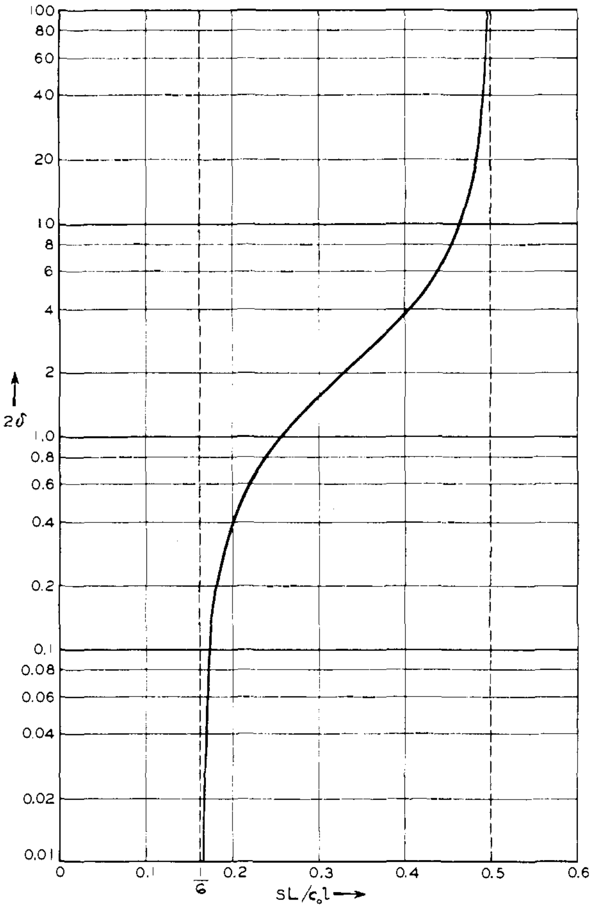

Fig. 5.—Theoretical variation of δ with the ratio Ls/lc_0, for a diffusion coefficient of the form $D = D_0 \exp(\delta c)$.

Figure 1 shows a typical time lag curve, in this case for *n*-hexane in branched polyethylene. Table III lists the values obtained for δ, D_0 and E_0 in the time lag experiments. Upon comparison with Table II, it is seen that only moderate agreement exists between the desorption experiments and the time lag studies. The difficulties which attend the determination of δ or D_0 by the time lag method are evident from Fig. 5, for a modest uncertainty in any of the four measured quantities clearly entails a sizable inaccuracy in δ, and likewise in D_0. The difficulties are compounded when one seeks to find E_0, the activation energy at zero concentration, from the values of D_0; the figures for E_0 in Table III seem entirely too high.

TABLE III

TIME LAG EXPERIMENTS: VALUES OF D_0 AND δ AT 25° AND VALUES OF ACTIVATION ENERGY

Liquid	$10^9\ D_0$, cm.²/sec.	δ	E_0, kcal./mole
n-Hexane	6	5	19
n-Octane	11	7	17
n-Decane	8	7	19
3-Methylpentane	12	3	19
Neohexane	2	9	23
Cyclohexane	10	6	18
Benzene	12	5	18
Hexene-2	9	5	16

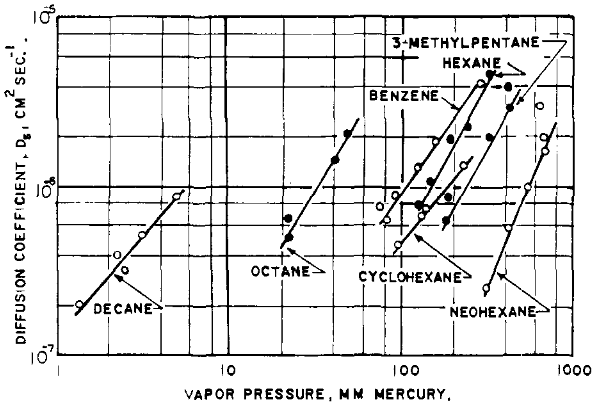

Fig. 6.—Diffusion coefficient at saturation, D_s, as a function of vapor pressure, 25–50°.

Although the time lag method does not seem well suited to a detailed study of the functional form of the concentration-dependent diffusion coefficient, the experimental method is valuable for finding the diffusion coefficient at saturation, D_s. Figure 6 shows D_s as a function of the vapor pressure[12] of the liquid, the values for D_s being the quotient of the steady-state permeability and the saturation concentration. It should be recalled that the vapor pressure in these studies is implicitly fixed by the temperature. Since all of the solvents were studied over the same temperature range, 25 to 47°, one may infer from Fig. 6 the effect of temperature under the conditions of equal numbers of molecules in the gas phase. It is interesting to note that D_s for the three isomers of hexane decreases with increasing extent of branching, even though the vapor pressure at a given temperature increases with increasing branching. (The molar solubilities of the three isomers are nearly the same at a given temperature, as may be judged from Fig. 3.) The values of D_s for the three normal paraffins vary inversely with molecular weight, as one would expect. One must be cautious about seeking to extend the results in Fig. 6 to still higher vapor pressures (temperatures), for undoubtedly there is some decrease in crystallinity over the small temperature range used here, owing to heat and solvent action. From the solubility studies by Richards,[13] for some other solvents in polyethylene, one would expect D_s to increase more rapidly with vapor pressure at higher temperatures.

D. High Density Polyethylene.—Measurements on high density (linear) polyethylene have been confined to saturation values of solubility and diffusion coefficient; solubility was found from desorp-

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(14) H. L. Frisch, private communication.

tion experiments and permeability was found from steady-state values in a time lag experiment. Table IV lists the room temperature values of the diffusion coefficient at saturation, D_s, and compares the molar solubilities, for both the high-density and the low-density polymers. As before, these solubilities are based on the gross sample, even though the solvent is lodged in the amorphous regions. The ratio of solubilities also is given. Except for the cyclic molecules, the ratio is about 2.5, a figure which approximates the ratio of the amorphous contents of these two classes of polymers.[15] The ratio is substantially higher for the cyclic solvents, both of which have markedly higher solubilities in the branched polyethylene than do the other solvents, very likely reflecting a sizable dissolution of crystallites. As would be expected, the swelling of the linear polymer is minor, amounting to no more than a few per cent. at room temperature.

TABLE IV

DIFFUSION COEFFICIENTS, D_s, AND MOLAR SOLUBILITIES, AT 25°

	D_s, cm.²/sec., × 10^7		Solubility[a] × 10^2		Solubility ratio
Liquid	Branched	Linear	Branched	Linear	
n-Hexane	11	4.4	2.00	0.72	2.8
n-Octane	4.2	1.8	1.44	.60	2.4
n-Decane	1.9	0.69	1.10	.51	2.2
3-Methylpentane	5.8	2.4	2.24	.90	2.5
Neohexane	2.6	0.71	1.72	.63	2.7
Cyclohexane	4.4	2.3	3.80	.68	5.6
Benzene	8.4	4.9	3.08	.86	3.6
Hexene-2	13	4.5	2.22	.87	2.6

[a] In moles of solvent per mole of methylene groups in the sample.

The diffusion coefficient is the ratio of the permeability to the solubility, and as obtained here it represents the gross sample, not explicitly the amorphous regions, in which the diffusion must occur. The differences between the linear and the branched polymer may stem in part from the morphological differences: the path for diffusion is less continuous in the highly crystalline material than in the branched polymer. But presumably the differences in D_s for the two kinds of polymer also come from dissimilarities in the amorphous regions themselves. From studies by nuclear magnetic resonance[2] and X-ray diffraction,[16] it is evident that the high degree of crystallinity leads to constraints in both separations and motions of chain segments.

E. Dielectric Measurement of Sorption Kinetics.—The dielectric technique was used only to allow the measurement of the effect of hydrostatic pressure. Recalling equation 4, and the relation[5] $D = \lambda^2/2\tau_c$, where λ is the length of a jump in the diffusion process, it follows that

$$\Delta V^{\ddagger} = -RT\,(\partial \ln D/\partial p)_T \qquad (14)$$

provided that λ does not vary strongly with pressure. Since an average diffusion coefficient is given by (7), $\Delta V^{\ddagger}$ may be determined from the slope of a plot of ln $(t_{1/2}/l^2)$ *versus* p. Figure 7 shows a typical plot of this sort. The large scatter makes it desirable to use a least squares fit to the points. The result of such a fit is shown as the solid line in Fig. 7. The experimental values for $\Delta V^{\ddagger}$ are shown in Table V, together with standard deviations calculated in the usual way.

TABLE V

VOLUME OF ACTIVATION

Liquid	$\Delta V^{\ddagger}$ (cm.³)	Stand. dev.[17]
n-Hexane	47	9
n-Octane	54	7
n-Decane	47	11
3-Methylpentane	64	2
Neohexane	70	7
Cyclohexane	116	1
Benzene	84	7
Hexene-2	79	17

Discussion

It seems clear that the diffusion coefficient depends exponentially on the concentration, but it does not seem possible to distinguish between

$$D = D_0 \exp(\delta c) \qquad (5)$$

and a relation proposed by Long and his coworkers.[18,19]

$$D = D_0(1 + \alpha c)\exp(\alpha c) \qquad (15)$$

at least on the basis of our experiments. Indeed, it would involve a very precise determination of the concentration dependence to make this choice, with the values of the exponent met with the present solvents. The ambiguity is illustrated in Fig. 8, which is a plot of these two functional forms of D, matched at $c = 0$ and $c = 1$.

As indicated in Section I, this discussion will be based upon the absolute reaction rate theory.[3] In that theory the diffusion coefficient is given by[20]

$$D = (e\lambda^2\, kT/h)\exp(\Delta S^{\ddagger}/R)\exp(-E/RT) \qquad (16)$$

where the symbols have their usual meanings. From the exponential dependence of D upon c we infer

$$E = E_0 - \delta cRT \qquad (17)$$

where E_0 is a constant. Thus, in equation 5

$$D_0 = (e\lambda^2 kT/h)\exp(\Delta S^{\ddagger}/R)\exp(-E_0/RT) \qquad (18)$$

Let us now turn to the molecular interpretations of E_0 and δ. One of the most obvious properties of E_0 as measured here is its indifference to the molecular structure of the diffusing species. It is about 15 kcal./mole for all the liquids (except *p*-dioxane). This result suggests that E_0 describes hindrances to motions of the polymer molecules. Thus the E_0 measured by diffusion should be comparable to activation energies found from nuclear magnetic resonance, dielectric relaxation and dynamic mechanical relaxation, at least if the processes are comparable. Most of the activation energies obtained from these other methods are lower than 15 kcal./mole, falling in the range 8–12 kcal./mole.[2,8,9] Evidently the diffusion process requires more en-

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(15) The degree of crystallinity was not measured in this study, but with comparable materials it has widely been found that the degree of crystallinity is 65–75% in branched polyethylene and about 90% in linear polyethylene.

(16) W. P. Slichter, *J. Polymer Sci.*, **21**, 141 (1956).

(17) W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N.Y., 1951, p. 42.

(18) S. Prager and F. A. Long, THIS JOURNAL, **73**, 4072 (1951).

(19) R. J. Kokes, F. A. Long and J. L. Hoard, *J. Chem. Phys.*, **20**, 1711 (1952).

(20) Ref. 3, p. 524.

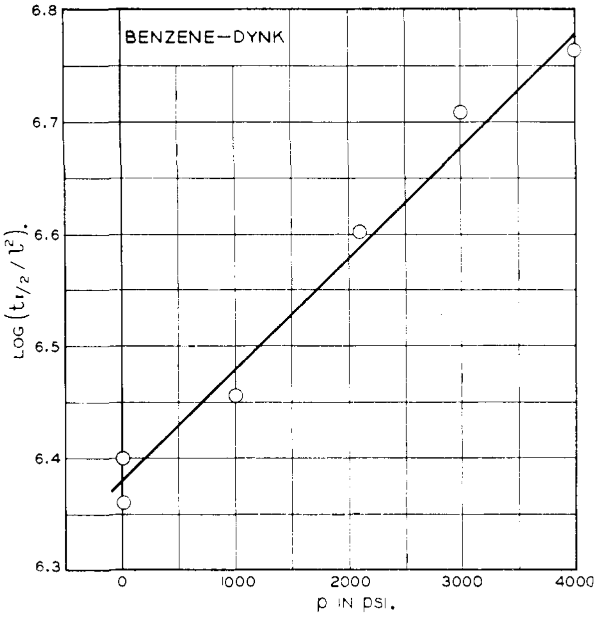

Fig. 7.—Typical plot of ln ($t_{1/2}/l^2$) *versus* pressure: benzene in branched polyethylene (DYNK).

ergy, and very likely is more complex, than the processes associated with the other experiments. We do not offer an explanation of this result other than to remark that a careful examination of the interpretations of the activation energies determined by various means is needed. This is particularly true in cases, such as in polyethylene, where the distribution of relaxation times is spread over many decades of frequency.

We must remark in passing on conclusions drawn previously[1] concerning the activation energy. It was suggested then that

$$\delta = (E_0 - E_l)/RT \qquad (19)$$

over the entire concentration range (*i.e.*, to the pure liquid), where E_l is the activation energy for diffusion in the pure liquid. Equation 19 was used to determine E_0, on the basis of an estimate of the proportionality between c_0 and the molecular concentration in the pure liquid. The resulting values of E_0 for benzene and hexane, about 9 kcal., were too low, in the light of the present experiments. Three sources of disparity are evident. In the first place, it is clear from Table I that x_a, the atom fraction, is about 0.3; hence the concentration corresponding to the pure liquid ought to be about $3c_0$, instead of $2c_0$, as assumed previously. Secondly, it is evidently now that δ varies rather widely with temperature for most of the solvents studied here, so that equation 19 is a fair approximation over only a limited temperature range. Finally, there is a factor involving the entropy of activation which must be reckoned with (see below).

Our interpretation of δ is implied by equation 17. That is, δcRT is the amount by which the activation energy for diffusion is reduced by the sorption of liquid. In principle, then, δ is a measure of plasticizer action of the liquid. Although it is not possible at this juncture to measure δ with sufficient accuracy for a detailed study of the criteria of plasticizing power, one may anticipate a relation to the cohesive energy parameters discussed by Richards.[13]

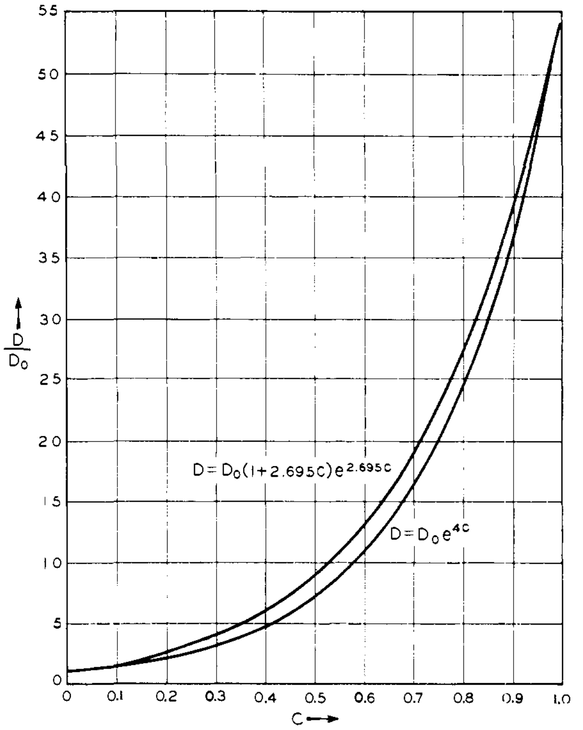

Fig. 8.—Comparison of diffusion coefficients described by two exponential forms of concentration dependence.

Having embraced the theory of absolute reaction rates in the preceding discussion, we must look into its consequences. In particular, we must consider $\Delta S^{\ddagger}$, which in a normal non-polar liquid is approximately zero. Taking $E_0 \cong 15$ kcal./mole, $D_0 \cong 10^{-8}$ cm.^{2}/sec., and $\lambda \cong 10^{-7}$ cm., it is found that $\Delta S^{\ddagger} \cong 20$ e.u. The large, positive entropy of activation indicates that the activated state is considerably less ordered than the initial state. This result might have been anticipated, for the chain segments in the amorphous regions are not endowed with the translational freedom characteristic of true liquids, but suffer from constraints imposed by the crystallites; this is particularly so in the neighborhood of the crystallites (and will be more obvious in linear polyethylene than in branched polyethylene.)[16] This constraint is disrupted by the formation of the activated state, and $\Delta S^{\ddagger}$ should be comparable to the entropy of fusion. The value $\Delta S^{\ddagger} = 20$ e.u. suggests, on this basis, that some 10–11 chain segments are involved in the activation process, for ΔS_f in polyethylene has been shown to be 1.90 e.u. per chain segment.[21] The near constancy of $\Delta S^{\ddagger}$ throughout the liquids in the present study is added evidence that the activation process is one which is primarily concerned with the motion of the polymer molecules.[22]

Let us now turn to the pressure dependence of the diffusion coefficients and the interpretation of

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(21) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, New York, 1953, p. 573.

(22) It is obvious that the largeness of $\Delta S^{\ddagger}$ here does not arise because of the implicit assumption that the transmission coefficient[8] is unity. Any deviation of the transmission coefficient from unity would make $\Delta S^{\ddagger}$ still larger.

the volumes of activation. Empirically, the pressure dependence is adequately described by equation 14, where $\Delta V^{\ddagger}$ is constant. This result implies the existence of a $p\Delta V^{\ddagger}$ term in the free energy of activation.

Eyring and his co-workers have discussed the volume of activation associated with the viscosity of simple liquids.[23-26] They were able to relate (empirically) the energy of activation for viscosity to the heat of vaporization, for some *n*-alkanes: $E_{\text{vap}}/E_{\text{vis}} = 4$. Volumes of activation were related to the molar volume by $V_M/\Delta V^{\ddagger}_{\text{vis}} = 8$, this conclusion being based on very limited experimental data. From these considerations they concluded that the volume of activation is the extra volume required to form the activated state and that the energy of activation is the energy required to form a hole of this size.

Our results for diffusion in polyethylene do not seem to fit the interpretations of the Eyring model, for we find that the activation energy is independent of the volume of activation. It would be interesting to investigate the volumes of activation for diffusion in pure liquid *n*-alkanes to ascertain whether the finding in the present case is a consequence of the diffusion process (*versus* that involved in viscosity) or of the fact that we are concerned here with polymers. For the present we prefer to retain the Eyring interpretation of the activation energy and simply supplement it with the assumption that above a certain volume the energy of hole formation is independent of hole size.

In any case, some conclusions regarding the details of the diffusion process can be drawn from the volumes of activation. In the series *n*-hexane, *n*-octane, *n*-decane, $\Delta V^{\ddagger}$ is essentially constant, = 50 cm.^{3}. In the initial state the chains of polymer and solvent are presumed to lie parallel to one another. Thus a volume of about two chain segments is swept out when a molecule moves parallel to its chain axis from one site to the next. This model accounts for the magnitude of $\Delta V^{\ddagger}$ and offers a simple explanation for the fact that $\Delta V^{\ddagger}$ in the *n*-alkanes studied does not depend upon chain length. Furthermore, the addition of side groups would be expected to increase $\Delta V^{\ddagger}$ as is observed for 3-methylpentane and neohexane. The magnitude of the increment in $\Delta V^{\ddagger}$ does not equal the volume of a methyl group: the observed increment is about 10 cm.^{3} per methyl group, whereas the molar volume of a methyl group is about 25 cm.^{3}. Probably the disparity for the branched solvents has to do with the fact that there is unoccupied space even when the molecule resides in a site. It is interesting to note that benzene requires a volume of activation equal to the molar volume of the solvent, which reflects the lack of conformity of benzene with the polymer chains.

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(23) J. O. Hirschfelder, D. Stevenson and H. Eyring, *J. Chem. Phys.*, **5**, 896 (1937).

(24) D. Frisch, H. Eyring and J. F. Kincaid, *J. Appl. Phys.*, **11**, 75 (1940).

(25) J. F. Kincaid, H. Eyring and A. E. Stearn, *Chem. Revs.*, **28**, 301 (1941).

(26) R. E. Powell, W. E. Roseveare and H. Eyring, *Ind. Eng. Chem.*, **33**, 430 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

The Reaction of O-Methylhydroxylamine and its N-Methyl Derivatives with Diborane

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The borane adducts of O-methyl-, O,N-dimethyl- and O,N,N-trimethylhydroxylamine have been prepared. Their thermal decomposition and hydrolysis have been studied. An internal oxidation-reduction reaction involving shift of a methoxy group from nitrogen to boron and of hydrogen from boron to nitrogen is described and discussed.

Many of the reactions of the boron hydrides are assumed to occur through the addition of a Lewis base to the borane group followed by decomposition of the adduct.[1] A study of the decomposition of the borane adducts of the methylhydroxylamines has provided interesting possibilities for processes of this type and has been of further interest because of the possibility of obtaining ring and chain structures with the –B–N–O– linkage.

The O-methyl- or methoxyamines (CH_3ONR_2, R = H or CH_3) differ appreciably from the hydroxylamines ($HONR_2$) in their reactions with diborane as well as in their other physical and chemical properties.[2] Since the reactions between diborane and the O-methylhydroxylamines are somewhat easier to interpret than the corresponding reactions involving the hydroxylamines, the preparation, properties and chemistry of the O-methylhydroxylamine-boranes are considered herein.

O-Methylhydroxylamine–Borane, $(CH_3O)NH_2\text{-}BH_3$. **a. Preparation and Characterization.**—In the presence of diethyl ether pure O-methylhydroxylamine and pure diborane react at −112° to produce O-methylhydroxylamine–borane.[3]

The pure white solid addition compound melts sharply at 55°, with rapid evolution of hydrogen gas (see Table I). Its solubility in ether is appreciable at room temperature but falls off as the tem-

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[1] H. G. Weiss and S. Shapiro, THIS JOURNAL, **75**, 1221 (1953).

[2] T. C. Bissot, R. W. Parry and D. H. Campbell, *ibid.*, **79**, 796 (1957).

[3] Because of the relatively low stability of dimethyl ether–borane and the relatively high stability of the amine–boranes, coördination through nitrogen rather than oxygen is assumed.