[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Diffusion of Organic Vapors into Polyvinyl Acetate[1]

BY R. J. KOKES AND F. A. LONG

RECEIVED SEPTEMBER 8, 1953

The diffusion at 40° of vapors of propyl chloride, allyl chloride, propylamine, isopropylamine and carbon tetrachloride into films of polyvinyl acetate has been studied as a function of concentration. Two other vapors, 1-propanol and benzene, have been studied at three temperatures, 30, 40 and 50°. The diffusion is Fickian and for low concentrations of penetrant the data all follow the equation $\bar{D} = \bar{D}_0 \exp(\alpha v_1)$ where v_1 is volume fraction of penetrant in the polymer. The values of $\bar{D}_0$, the diffusion coefficient for the pure polymer, vary with size and shape of the diffusing molecule but do not appear to depend strongly on the chemical nature of the penetrant. However, the slope, α, of $\ln \bar{D}$ *vs.* v_1 increases with the value of the Flory–Huggins interaction parameter, χ_1, for the penetrant–polymer mixture. For the penetrants acetone, propanol and benzene the energies of activation for $\bar{D}_0$ are all 40 kcal. per mole within experimental error. The temperature coefficient of the melt viscosity of polyvinyl acetate has been measured and at a temperature of 45° the energy of activation for viscous flow is about 45 kcal., which suggests that the activation processes for viscous flow and for diffusion of the larger organic vapors are similar.

Introduction

Data on the rate of diffusion of organic vapors into polymers are now available for several systems. When the polymer–penetrant mixtures are above their second-order transition, Fick's law applies with, however, a diffusion coefficient which increases with concentration.[2–4] For other systems Fick's law is not obeyed and the diffusion is termed non-Fickian or anomalous.[4–7] The influence of size and shape of the penetrant molecule has been studied in some detail for two polymers, polyisobutylene[2] and polystyrene.[3] Both of these are non-polar polymers and with polystyrene the interpretation is complicated by the fact that the diffusion is anomalous, at least for low concentrations of penetrant.[7]

In this paper we report studies on the influence of penetrant molecule on the rate of diffusion into the polar polymer, polyvinyl acetate. This polymer is non-crystalline and can be conveniently studied at temperatures above that for the second-order transition of the pure polymer, 30°. Previous studies with acetone and polyvinyl acetate have shown that at temperatures of 30° or higher the diffusion obeys Fick's law.[4] Most of the studies reported here are at 40°, but for two of the systems temperature coefficient studies have been made. Finally we have made studies of the temperature coefficient of the melt viscosity of polyvinyl acetate to see how the energy of activation for viscous flow compares to that for small molecule diffusion.

Experimental

Diffusion coefficients were determined from rates of sorption and desorption of vapors in polymer films, using the apparatus described earlier.[2] Carefully dried films of known area were suspended from a quartz spiral balance in an evacuated chamber. At zero time the organic vapor was admitted and the rate of sorption was determined by following the weight increase of the film as a function of time. After sorption equilibrium was reached, the chamber was rapidly evacuated and the rate of desorption was measured. Measurements were made for several vapor pressures of each diffusing species.

Descriptions of the polyvinyl acetate used and of the method of film preparation are given in a previous publication.[4] All of the organic liquids were redistilled and dried prior to use.

The melt viscosity of polyvinyl acetate was measured with capillary viscometers similar to those described by Fox and Flory.[8] Bubble-free samples of the polymer were prepared by heating to 217° in a nitrogen atmosphere. During sample preparation a slight discoloration occurred; however, since different samples gave similar results, this slight reaction apparently has little or no effect on the viscosity. The experimental conditions were always such that the viscosity, η, was independent of the rate of shear; hence the flow was Newtonian. Values of η were calculated from the dimensions of the viscometer and the pressure using Poiseuille's equation. Except for the highest values, η was precise to 10% and in no case was the error greater than 20%.

Calculations

Diffusion coefficients were calculated from the measurements of sorption and desorption using essentially the method described previously.[2,4] The relevant form of Fick's law is

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}x}\left(D\,\frac{\mathrm{d}c}{\mathrm{d}x}\right) \qquad (1)$$

where t is time, D is the diffusion coefficient, and c is concentration, in grams solvent per gram polymer, at a distance x from the film surface. The usual boundary condition of instantaneous equilibration at the surface of the film is assumed. From the Boltzmann solution of Fick's law for the case of an "infinite solid" it follows that during the initial stages of sorption and desorption, *i.e.*, before the concentration at the film center changes appreciably

$$\frac{Q}{Q_e} = K(c_i, c_f)\,\frac{\sqrt{t}}{l} \qquad (2)$$

where Q is weight of vapor sorbed or desorbed at time t, Q_e is the equilibrium weight sorbed or desorbed, l is film thickness and $K(c_i, c_f)$ is a function only of the initial and final equilibrium concentrations. When both sorption and desorption data are available for a concentration interval $0 \rightarrow c_f$, then a good approximation for the integral diffusion coefficient at the concentration c_f is given by[2,4]

$$\bar{D} \equiv \frac{1}{c_f}\int_0^{c_f} D\,\mathrm{d}c = \frac{\pi}{32}\left[\overline{K_s(0,c_f)}^2 + \overline{K_d(c_f,0)}^2\right] \qquad (3)$$

where $K_s(0, c_f)$ and $K_d(c_f, 0)$ are the initial slopes (from eq. 2) for sorption and desorption, respectively. From measurements at varying values of c_i and c_f, $\bar{D}$ can be obtained as a function of concentration. Values of D, the ordinary diffusion coefficient, can if desired be calculated from the relation

$$D = \mathrm{d}(c\bar{D})/\mathrm{d}c \qquad (4)$$

For a more precise evaluation of D, account should be taken of the change in film thickness with diffusion into the film.[9] This correction is small for low concentrations of

---

[1] Work supported by a grant from Office of Ordnance Research, U. S. Army.

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

[3] G. S. Park, *Trans. Faraday Soc.*, **46**, 684 (1950); **48**, 11 (1952).

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

[5] Leo Mandelkern and F. A. Long, *J. Polymer Sci.*, **6**, 457 (1951).

[6] J. Crank and G. S. Park, *Trans. Faraday Soc.*, **47**, 1072 (1952).

[7] F. A. Long and R. J. Kokes, THIS JOURNAL, **75**, 2232 (1953).

[8] T. G Fox and P. J. Flory, *ibid.*, **20**, 2384 (1948).

[9] G. S. Hartley and J. Crank, *Trans. Faraday Soc.*, **45**, 801 (1949).

penetrant and hence has not been made for the data reported here.

All values of diffusion coefficients are reported for the units cm.^{2} per sec.

Results and Discussion

Sorption–desorption experiments at 40° have been carried out with polyvinyl acetate and the following organic vapors: 1-propanol, propyl chloride, propylamine, isopropylamine, allyl chloride, benzene and carbon tetrachloride. Figure 1 shows typical plots of Q/Q_e *vs.* $\sqrt{t}/l$ for sorption and desorption experiments, in this case for the system benzene–polyvinyl acetate. All plots are initially linear indicating that the diffusion is Fickian in the sense that eq. 2 is obeyed. The fact that for both concentration intervals the slope for sorption is greater than for desorption and also the fact that the slopes of both sorption and desorption are larger for the higher concentration show that the diffusion coefficient increases with concentration. Except in the case of allyl chloride, all the sorption–desorption plots are similar in form to those in Fig. 1. With allyl chloride the sorption plots show a slight curvature at the very start although the corresponding desorption plots are initially linear. The reason for this behavior is not known. In the calculation of $\bar{D}$ for this system this initial lack of linearity was ignored and the slope of the linear portion of the sorption curve was employed.

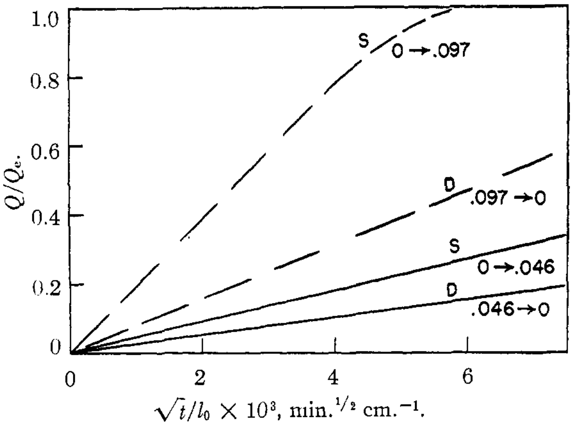

Fig. 1.—Sorption (S) and desorption (D) of benzene by polyvinyl acetate at 40°. Along with each curve are the initial and final concentrations of benzene in grams per gram polymer.

For all of the penetrants the integral diffusion coefficient, $\bar{D}$, was evaluated as a function of concentration from the slopes of sorption–desorption plots using eq. 3. The results of these calculations for experiments at 40° are shown in Figs. 2 and 3 as plots of log $\bar{D}$ *vs.* *c*. It may be seen that $\bar{D}$ is a strong function of concentration varying as much as a thousand-fold in the concentration range studied. Furthermore, each of the plots of log $\bar{D}$ *vs.* *c* is linear at low solvent concentrations. This logarithmic relation between $\bar{D}$ and *c* appears to be quite general and has been found to hold for most polymer–small molecule systems for which diffusion is Fickian.[2–4] If this relationship is expressed as

$$\bar{D} = \bar{D}_0 e^{\beta c} \qquad (5)$$

the data for the lower concentrations of Figs. 2 and 3 can be summarized in terms of the two parameters $\bar{D}_0$ and β. Values of $\bar{D}_0$ and β are shown in columns 3 and 4 of Table I for the sorption–desorption data on polyvinyl acetate. For diffusion of carbon tetrachloride only the one point of Fig. 3 is available; the listed $\bar{D}_0$ value of Table I was obtained by assuming a value of 70 for the parameter β. For completeness, data are also given for diffusion of acetone[3] and methanol[10] into polyvinyl acetate.

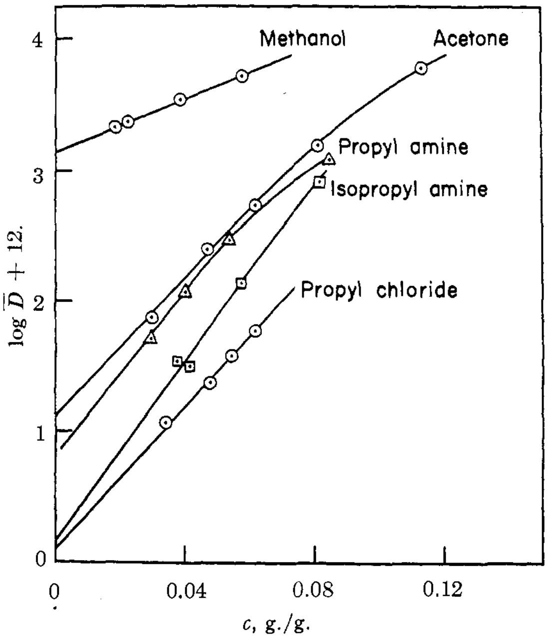

Fig. 2.—Concentration dependence of $\bar{D}$ for polyvinyl acetate, 40°.

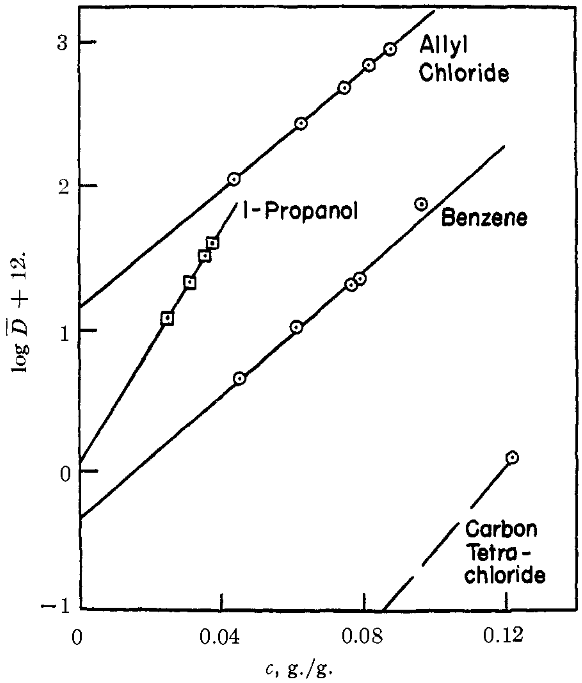

Fig. 3.—Concentration dependence of $\bar{D}$ for polyvinyl acetate, 40°.

---

(10) J. Wilkens and F. A. Long, unpublished data.

An alternative expression to eq. 5 is one where the concentration is given in terms of volume fraction of penetrant

$$\bar{D} = \bar{D}_0 e^{\alpha v_1} \qquad (6)$$

Park[3] has pointed out that this formulation may have more physical significance than eq. 5. For the narrow concentration ranges studied here there is little choice between the two equations. Equation 5 is perhaps slightly preferable simply because it utilizes directly determined experimental quantities, *i.e.*, for the calculation of v_1 of eq. 6 it is usually necessary to assume additivity of volumes of penetrant and polymer. However, for convenience in later discussion we have included in Table I calculated values of the parameter α for all penetrants except methyl alcohol, where the assumption of volume additivity seems particularly dubious, and carbon tetrachloride, where too few data are available.

TABLE I

DIFFUSION COEFFICIENTS INTO POLYVINYL ACETATE, 40°

Penetrant	$\bar{V}_0$, cc./mole	$10^{12}\bar{D}_0$, cm.²/sec.	β	α	χ_1
Carbon tetrachloride	98.6	(3×10^{-4})	(70)	..	..
Benzene	91	0.48	53	46	0.36
Propyl chloride	90	1.3	64.5	63	.75
Isopropylamine	88.4	1.7	78	55	.67
Propylamine	84.6	5.1	80	49	.58
Allyl chloride	83.5	13	48	44	.28
Propyl alcohol	76	1.1	96	78	1.10
Acetone	75.5	13	61	45	0.35
Methyl alcohol	41.3	1.4×10^3	24	..	..

Table I also gives values of $\bar{V}_0$, the molar volume for the liquid penetrant at 40° and of χ_1, the interaction parameter for equilibrium between the penetrant and polyvinyl acetate. Values of χ_1 were calculated from equilibrium sorption data,[11] under the assumption that the volumes of penetrant and polymer were additive, using the well-known equation[12,13]

$$\ln (p/p_0) = \ln v_1 + v_2 + \chi_1 v_2^2 \qquad (7)$$

where v_1 and v_2 are volume fractions of diluent and polymer, respectively, and χ_1 is the interaction parameter.

All of the organic penetrants of Table I are solvents for polyvinyl acetate except for propanol which is only a limited swelling agent. It is noteworthy that propanol gives by far the largest value of χ_1, 1.10. For the solvents, the χ_1 values range from 0.28 to 0.75.

The penetrants of Table I involve still other variations beyond this difference in solvent power. There are variations in size, in shape and in functional group. This last seems to have little if any effect on the diffusion coefficient For the several propyl compounds of Table I the $\bar{D}_0$ values vary only about 10-fold and most of the variations can be more easily explained in terms of changes in either molar volume or shape, than by changes in functional group.

There is a definite effect of molecular shape of the penetrant on the rate of diffusion. Diffusion of isopropylamine is slower than that of the normal propylamine and diffusion of carbon tetrachloride is much slower than would be expected from its molar volume. The influences of size and molar volume are shown more completely in Fig. 4 which is a plot of log $\bar{D}_0$ *vs.* molar volume. The straight line in this plot is drawn in primarily for convenience in discussion. It is evident, at least for the straight chain compounds, that there is an approximately linear relation between log D_0 and molar volume. Propyl alcohol falls somewhat off the curve as do allyl chloride and benzene. However, the striking departure is for carbon tetrachloride. Even though the $\bar{D}_0$ value for this compound is only crudely estimated it is evident from Fig. 3 also that this spherical molecule diffuses much more slowly compared to the straight chain compounds than would be expected from its molar volume alone. This result is consistent with previous studies. Prager and Long[2] noted that for diffusion of hydrocarbons into polyisobutylene branching was a more important variable than molar volume; Park,[3] in his extensive study with polystyrene, noted this same effect. The results from all these studies lead to the same conclusion: that both the size and shape of the penetrant molecules markedly influence the magnitude of the rate of diffusion into polymers.

The physical significance of the parameters β and α of eq. 5 and 6 is less clear than that of $\bar{D}_0$. Prager and Long[2] suggested that the generally observed increase of $\bar{D}$ with concentration may be due to the fact that polymer–penetrant "bonds" are weaker than those between polymer segments. This implies a relation between the extent of polymer–penetrant interaction and the value of the slope α(or β). A useful measure of solvent–polymer interaction is the Flory–Huggins parameter χ_1 of eq. 7 which has large values for poor solvents and small or negative values for good solvents. Table I gives values of χ_1 at 40° for several of the penetrants studied. Figure 5 gives a plot of χ_1 *vs.* the parameter α, which is simply the slope of a plot of ln $\bar{D}$ *vs.* volume fraction of penetrant. It is apparent from Fig. 5 that there is a good correlation between χ_1 and α in the sense that for large values of χ_1 the slope of the ln $\bar{D}$ *vs.* v_1 curve is large. In other words diffusion increases more rapidly with concentration for a poor solvent than for a good solvent.

The question of correlation between solvent type and rate of diffusion was discussed recently by Boyer[14] for the case of plasticizer molecules. Although pointing to some data in which high χ_1 values are associated with large diffusion rates of plasticizer, Boyer also pointed to cases of the opposite sort, *i.e.*, where plasticizers with very low χ_1 values diffused more rapidly. According to the results of the present study, to predict diffusion rates one must actually consider not only the solvent ability of a penetrant molecule but also its size and shape. The value of $\bar{D}_0$ probably does not depend greatly on solvent ability but more on the size and shape of

---

[11] R. J. Kokes, A. R. Di Pietro and F. A. Long, THIS JOURNAL, **75**, in press (1953).

[12] P. J. Flory, *J. Chem. Phys.*, **10** 51 (1942).

[13] M. L. Huggins, *ibid.*, **9**, 440 (1941).

[14] R. F. Boyer, *J. Appl. Phy.*, **20**, 540 (1949).

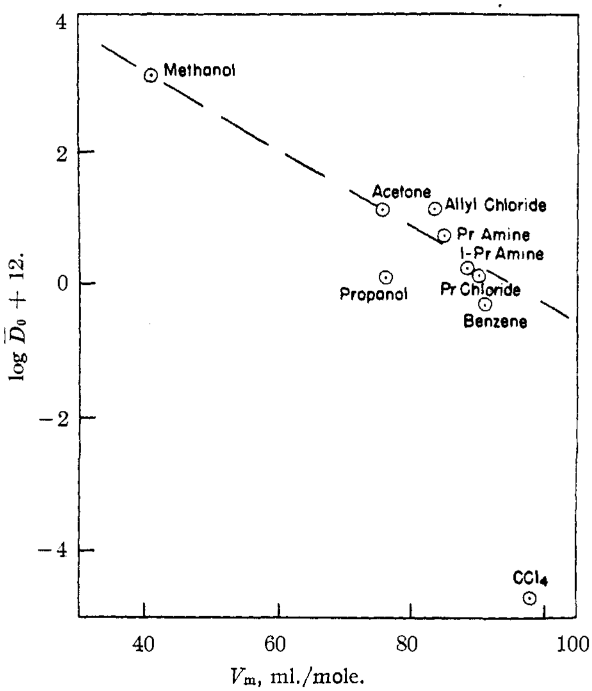

Fig. 4.—log $\bar{D}_0$ *vs.* molar volume of penetrants, 40°.

the penetrant molecule. In contrast, the dependence of the diffusion coefficients on concentration will vary with solvent power. However, the relations between diffusion rate and properties of the penetrant molecules are clearly complex so that more data will be needed to substantiate these conclusions.

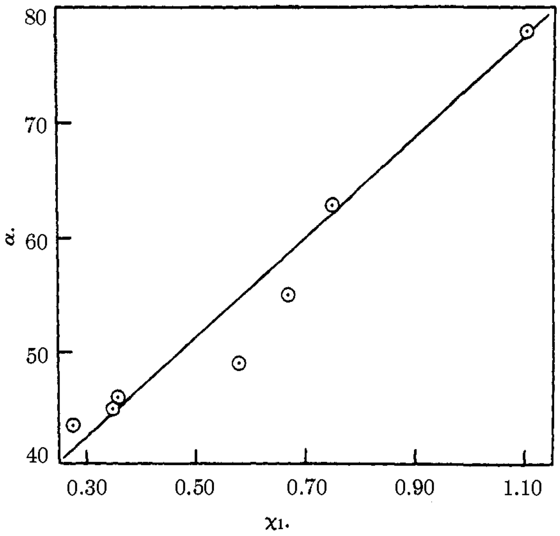

Fig. 5.—Slope, α, of log $\bar{D}$ *vs.* v_1 plotted against the polymer-diluent interaction parameter, χ_1.

It is implicit in the hole theory of diffusion that diffusion is an activated process and previous studies[4,15] have shown that the temperature dependence of $\bar{D}_0$ (and also of $\bar{D}$ generally) follows the Arrhenius equation

$$\bar{D}_0 = Be^{-E_d/RT} \qquad (8)$$

where E_d is presumably the energy needed for hole formation in the polymer. One would thus expect a dependence of E_d on the size and shape of the penetrant molecule and also on its concentration. Studies with acetone and polyvinyl acetate led to a value of E_d of 39 kcal. per mole for $\bar{D}_0$ and also showed a gradual decrease of E_d with concentration of acetone, down to a value of 26 kcal. at an acetone concentration of 0.1 g. per g. of polymer. We have now made studies of the temperature coefficient of diffusion into polyvinyl acetate of two other penetrants, benzene and 1-propanol. Figure 6 gives plots of log $\bar{D}$ *vs.* c for these penetrants at temperatures of 30, 40 and 50°. In all cases the plots are linear within experimental error.

It may be seen in Fig. 6 that for both penetrants the slopes of log $\bar{D}$ *vs.* c are parallel for the three temperatures, suggesting that E_d is independent of concentration. This is in contrast to the results with acetone–polyvinyl acetate where E_d drops considerably with concentration. Actually this contrast is probably more apparent than real. For the present systems the diffusion has not been studied over such large concentration ranges as was done for acetone, and over these comparatively narrow ranges the experimental errors make it difficult to detect any change of E_d with concentration.

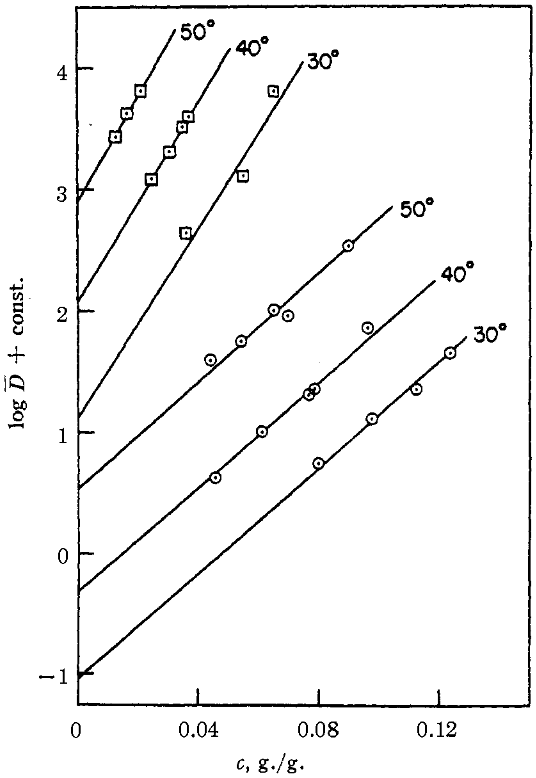

Fig. 6.—Log $\bar{D}$ + 12 *vs.* c for benzene–polyvinyl acetate, —⊙—; log $\bar{D}$ + 14 *vs.* c for propanol–polyvinyl acetate, —⊡—.

The data of Fig. 6 are fairly well represented by the Arrhenius equation and Table II gives the Arrhenius parameters for these penetrants along with the parameters for acetone, methanol[10] and water.[16] The values of E_d are accompanied by

---

[15] S. Prager, E. Bagley and F. A. Long, THIS JOURNAL, **75**, 1255 (1953).

[16] L. J. Thompson and F. A. Long, unpublished data.

limits of error which have been estimated from the precision and completeness of the data.

TABLE II

ARRHENIUS PARAMETERS FOR DIFFUSION IN POLYVINYL ACETATE

Penetrant	$\overline{V}^{0}$, ml./mole	$10^{12}\overline{D}_0$, 40°. cm.²/sec.	log B	E_d, kcal.
Water	18	1.2×10^5	3.6	15 ± 1
Methanol	41	1.5×10^3	5.8	21 ± 2
Acetone	76	13	16.3	39 ± 3
1-Propanol	76	1.1	16.7	41 ± 4
Benzene	91	0.48	13.5	37 ± 4

For the three penetrants of comparable molar volume, acetone, benzene and propanol, the energies of activation are the same within experimental error. The frequency factors are also similar. For the smaller penetrants, methanol and water, the energies of activation are considerably smaller. It is of interest that for methanol and water the frequency factors are also considerably smaller, *i.e.*, although the diffusion of methanol and water is faster than for the larger penetrants, it is not as fast as would be predicted by the low values of E_d alone.

The decided drop in E_d for the smaller molecules, methanol and water, would be expected from the hole theory of diffusion, since the energy to make a hole should increase with size of penetrant molecule. However, the lack of increase of E_d from the two molecules of similar size, acetone and propanol, to the distinctly larger molecule, benzene, is unexpected and suggests that as the molecular size of the penetrant increases the value of E may be asymptotically approaching a limiting value of roughly 40 kcal. This is not an unreasonable suggestion since it is quite possible that as the size of the penetrant molecule increases the limiting situation is movement of similar sized polymer segments, *i.e.*, for large penetrant molecules the activation step is "self-diffusion" of polymer segments around the penetrant molecule. This implies a limiting value of E_d roughly the same as the energy of activation for self-diffusion of the polymer. Since the activation energies of self-diffusion and viscous flow of a polymer are equal,[17] one might thus expect to find similar values for E_d(max), the limiting energy of activation for diffusion of large penetrant molecules, and E_η, the activation energy for viscous flow.

To test this possibility we have measured the melt viscosities of polyvinyl acetate as a function of temperature. The data are given in Table III. A plot of log η *vs.* $1/T$ is decidedly curved indicating that, as with other polymers,[8,18] E_η varies with temperature. From the log η *vs.* $1/T$ plot one can obtain approximate E_η values at various temperatures and the last column of Table III gives the values so obtained for polyvinyl acetate. The estimated error for these is ±4 kcal. per mole. The values given in Table III at 30 and 40° are obtained from slopes of an extrapolation of the log η *vs.* $1/T$ curve to these temperatures.

TABLE III

MELT VISCOSITY (POISES) OF POLYVINYL ACETATE (VISCOSITY AV. MOL. WT. OF 170,000)

Temp., °C.	$\log_{10} \eta$	E_ϵ,* kcal.
200	4.1	15
150	5.1	23
100	7.3	37
80	8.5	39
60	10.0	42
40	..	(44)
30	..	(45)

It is evident from the data of Tables II and III that E_d for the larger penetrant molecules and E_η are of similar size which lends support to the suggestion of a similar activation process. Further support is given by a comparison of diffusion and melt viscosity data for polyisobutylene. Fox and Flory[8] report an energy of activation of viscous flow for this polymer of about 16 kcal. at 35°. Prager, Bagley and Long[15] found that for diffusion of hydrocarbons with molar volumes of from 100 to 120 ml./mole the energy of activation at 35° varied from 16 to 18 kcal., values which are again very similar to that for viscous flow. From these results for two polymers it seems likely that the energy of activation for diffusion of vapors does actually reach a limiting value close to that for viscous flow of the polymer. However, it is clearly necessary to test this further by studying still larger penetrants than employed so far.

This correlation of diffusion and viscous flow has several consequences. Since E_η is a function of temperature one might expect E_d to be also. (The available studies of diffusion are over too narrow a temperature range to show such a dependence.) The comparatively slow decrease in E_d with concentration might be expected to also be observed for E_η. Finally, since the concentration dependence of $\overline{D}$ appears to be a function of the polymer-diluent interaction a similar dependence of melt viscosity on concentration and type of diluent may exist.

ITHACA, N. Y.

---

[17] F. Bueche, W. M. Cashin and P. Debye, *J. Chem. Phys.*, **20**, 1956 (1952).

[18] R. S. Spencer and R. E. Dillon, *J. Colloid Sci.*, **3**, 163 (1948); **4**, 241 (1949).