[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Diffusion of Hydrocarbons in Polyisobutylene[1]

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The diffusion coefficients of six hydrocarbons (propane, *n*-butane, isobutane, *n*-pentane, isopentane and neopentane) in polyisobutylene have been calculated from sorption data at 35°. They all increase exponentially with increasing concentration of the hydrocarbon in the polymer. An increase in both the degree of branching and the size of the diffusing molecules lowers the diffusion coefficient, although the former effect is much more pronounced than the latter. These results are accounted for on the basis of Eyring's hole theory of diffusion.

While many studies of diffusion in polymeric systems have been made, systematic surveys of a series of closely related systems are still rather rare in the literature. Some examples of the latter are the studies of Barrer[2] and of Doty, Aiken and Mark[3,4] on the permeation of inert gases and water vapor, respectively, through polymer membranes.

Even more rarely is the concentration dependence of the diffusion coefficient taken into account; either the concentration of diffusing material is kept so low that the diffusion coefficient can justly be considered constant (as in the work referred to above), or the experimental results are left in terms of half-times or permeabilities. Consideration of the concentration dependence is particularly important when activation energies of diffusion are to be determined. If, as is to be expected, the activation energy varies with concentration, neglect of this variation will produce some kind of average activation energy with no very profound physical significance.

Concentration dependent diffusion coefficients have been studied by Rouse[5] for the diffusion of water in polythene and nylon, and by Crank and Park[6] for the diffusion of chloroform in polystyrene. Park[7] has recently published data on the concentration dependence of the diffusion coefficients for a series of halomethane–polystyrene systems at several temperatures.

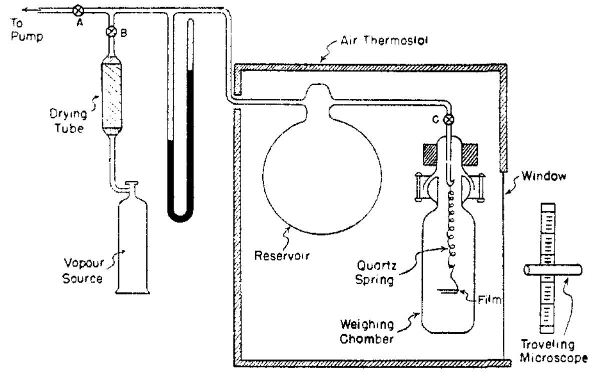

Fig. 1.—Apparatus for following the sorption of vapors by polymer films.

In this paper we present an investigation of the diffusion in polyisobutylene of six hydrocarbons (propane, *n*- and isobutane, and *n*-, iso- and neopentane). This particularly simple series was chosen in order to obtain information on the effect of the size and shape as well as of the concentration of the diffusing molecules on their diffusion coefficients. The above systems are as free as possible from phenomena which might compete with and obscure the effects to be studied. Both the small molecule and the polymer components are non-polar; the former constitute a homologous series, and the latter is non-crystalline and well above its second order transition temperature, so that orientation and strain relaxation will not complicate the diffusion process.

A secondary reason for carrying out diffusion measurements on such simple systems is to determine whether Fick's laws with the usual boundary conditions can be applied to polymeric systems. This question arose in connection with data obtained on the diffusion of methylene chloride and acetone in cellulose acetate[8] and nitrate. For these systems it was found that when the amount of penetrant absorbed by a film of the polymer was plotted as a function of the time, the resulting curves were inflected. It can be shown that such results cannot be accounted for even by a concentration dependent diffusion coefficient if the concentration at the film surfaces is assumed to remain constant.

Experimental

The diffusion coefficients were calculated from sorption and desorption data obtained with the apparatus shown in Fig. 1. A film of polyisobutylene is suspended from a sensitive quartz spring in an evacuated weighing chamber. Vapor of the hydrocarbon in question is then admitted into the chamber at a pressure p. The increase in weight of the film due to absorption of the vapor is then measured as a function of time by observing the extension of the spring through a cathetometer. After the film has come to equilibrium with the surrounding vapor the chamber is evacuated again and the resulting desorption process observed as before. This entire procedure is then repeated at several different values of p.

The polyisobutylene was Vistanex B-100 furnished by the Enjay Co. of Elizabeth, N. J.; it had a viscosity average molecular weight of about 10^6. In order to remove any low molecular weight components of the polymer, we reprecipitated it with acetone from benzene solution, recovering about 80% of the original material. The resulting material was dissolved in cyclohexane, and the films were cast from this solution by pouring it into a glass ring floating on mercury. After casting, the solution was allowed to stand for a day in a desiccator in order to permit trapped air bubbles to escape. The solvent was then removed by slowly drawing air through the desiccator for a day, after which the ring with the film attached was lifted off the mercury and placed in a leaching bath of methanol. This latter part of the procedure was suggested by the effectiveness of water leaching

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[1] Presented in part before the Division of High Polymer Chemistry at the 118th Meeting of the American Chemical Society, Chicago, Ill., September, 1950.

[2] R. M. Barrer, *Trans. Faraday Soc.*, **35**, 628 (1939).

[3] P. M. Doty, W. H. Aiken and H. Mark, *Ind. Eng. Chem., Anal. Ed.*, **16**, 686 (1944).

[4] P. M. Doty, W. H. Aiken and H. Mark, *Ind. Eng. Chem.*, **38**, 788 (1946).

[5] P. E. Rouse, THIS JOURNAL, **69**, 1068 (1947).

[6] J. Crank and G. S. Park, *Trans. Faraday Soc.*, **45**, 240 (1949).

[7] G. S. Park, *ibid.*, **46**, 624 (1950).

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

in the drying of cellulose acetate films cast from acetone solutions; methanol was used instead of water because the latter is immiscible with cyclohexane. It is doubtful whether leaching in methanol has a particularly beneficial effect on the solvent removal; however, once started, this procedure was carried out with all films for the sake of consistency. Finally, after a day's leaching the film was dried in a vacuum oven at 45° for a day. For actual use in sorption experiments a piece was cut out of the film prepared as above with a circular steel punch 2.00 cm. in diameter. Because of the rubbery, sticky nature of the polymer at room temperature the cutting was performed on a block of dry ice; it was found that further handling of the film could be carried out satisfactorily under methanol. The film thickness was calculated from the known weight and area of the films, using 0.91 g./cc. for the density of polyisobutylene.

Calculations

Our results consist of the weight of vapor sorbed (Q_s) and desorbed (Q_d) determined as functions of the time for each system at several vapor pressures. We also have at each of these pressures the equilibrium weight of vapor taken up (Q_e); this can be readily converted to the equilibrium concentration (C_p) of vapor, which we express as weight of vapor per unit weight of polymer.

If the diffusion processes involved in sorption and desorption obey Fick's law

$$\frac{\partial C}{\partial t} = \frac{\partial^2}{\partial x^2}(\overline{D}(C)C) \tag{1}$$[9]

with boundary conditions corresponding to instantaneous equilibration at the surfaces of the film

$$\begin{aligned} C(0,t) = C(l,t) &= \begin{cases} C_p \text{ (sorption)} \\ 0 \text{ (desorpion)} \end{cases} \\ C(x,0) &= \begin{cases} 0 \text{ (sorption)} \\ C_p \text{ (desorption)} \end{cases} \end{aligned} \tag{2}$$

then it can be shown[10] that, until the concentration in the center of the film changes appreciably from its initial value

$$Q_s/Q_e = K_s\sqrt{t}/l \qquad Q_d/Q_e = K_d\sqrt{t}/l \tag{3}$$

In the above three equations $C(x, t)$ is the concentration of vapor expressed as a function of distance (x) into the film and time (t), $\overline{D}$ is the integral diffusion coefficient of the vapor in the polymer, l is the film thickness, and K_s and K_d are constants depending only on C_p and not on film thickness or area.

K_s and K_d can be readily found by taking the initial slopes of plots of Q_s/Q_e and Q_d/Q_e, respectively, *vs.* $\sqrt{t}/l$. According to Crank and his associates[6,11] the integral diffusion coefficient corresponding to C_p is then given to a good approximation by

$$\overline{D}(C_p) = (\pi/32)(K_s^2 + K_d^2) \tag{4}$$

Equation (4) has been checked[6,11] by computing sorption and desorption curves for a number of hypothetical forms of $D(C)$. The greatest discrepancy found between the calculated and the actual $\overline{D}$ was 3% for a $D(C)$ which in the concentration range covered increased linearly to eleven times its initial value. We ourselves have calculated $\overline{D}$ for the isobutane–polyisobutylene system using a method involving the approximation of $D(C)$ by a step-function,[12] and have found satisfactory agreement with the results obtained from equation (4). In view of these checks we have felt justified in using (4) to calculate $\overline{D}$.

Results

A typical pair of Q/Q_e *vs.* $\sqrt{t}/l$ plots for sorption and desorption are shown in Fig. 2; it will be seen that they are indeed linear up to the half-time and beyond, thus showing that equations (1) and (2) satisfactorily describe the diffusion processes involved. The fact that the diffusion of hydrocarbon vapors into polyisobutylene obeys Fick's law is in marked contrast to the conclusions reached for diffusion into cellulosic polymers.[8]

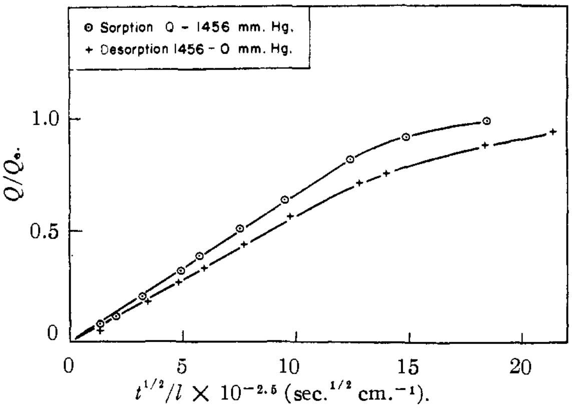

Fig. 2.—Typical sorption–desorption curves for polyisobutylene–hydrocarbon systems (propane at 35°).

The results of our measurements and calculations are summarized in Table I, which gives values of l, p, C_p and $\overline{D}$; Fig. 3 shows $\overline{D}$ as a function of C_p for the six hydrocarbons studied. Reproducibility from film to film was good for propane, *n*- and isobutane, and neopentane, not quite so good for *n*- and isopentane. The diffusion coefficients increase rapidly with concentration, and in Fig. 4 we have plotted log $\overline{D}$ *vs.* C. From the linearity of these plots we see that we may fit the $\overline{D}$ *vs.* C curves by equations of the form

$$\overline{D} = \overline{D}_0\, e^{AC} \tag{5}$$

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[9] We prefer to write Fick's law in terms of the integral diffusion coefficient instead of the more familiar differential diffusion coefficient because we believe the former to be more closely related to a quantity of fundamental interest, namely, the frequency with which a diffusing molecule jumps from its current site to a neighboring one. Equation (1) can be derived in a straightforward fashion by considering that the diffusing molecules are characterized by a jump frequency (ν) and are arranged in planes which are normal to the direction of diffusion and separated by the average length (a) of a jump. When ν is concentration dependent, the net rate (P) of permeation of diffusing material through a cross-section of unit area is

$$P = -\frac{\partial}{\partial x}(\overline{D}(C)C)$$

from which equation (1) can easily be deduced. If a is assumed constant, $\overline{D}(C)$ is given in terms of $\nu(C)$ by

$$\overline{D}(C) = 1/6a^2\nu(C)$$

If ν is constant, then the integral and differential diffusion coefficients are equal. This is no longer the case when ν varies with C; the differential diffusion coefficient is then given by

$$D = 1/6a^2\left\{\nu + C\frac{d\nu}{dC}\right\}$$

If ν depends on x explicitly (as in the case of an inhomogeneous film) the distinction between the two ways of writing Fick's law becomes particularly important, for they are then no longer equivalent.

[10] L. Boltzmann, *Wied. Ann.*, **53**, 959 (1894).

[11] J. Crank and M. G. Henry, *Trans. Faraday Soc.*, **45**, 636 (1949).

[12] S. Prager, *J. Chem. Phys.*, **19**, 537 (1951).

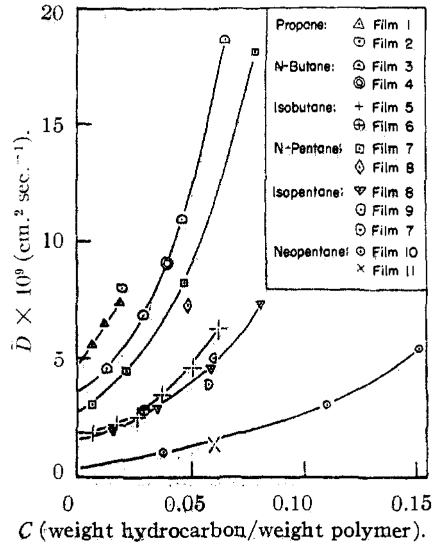

Fig. 3.—Integral diffusion coefficients for polyisobutylene-hydrocarbon systems at 35°.

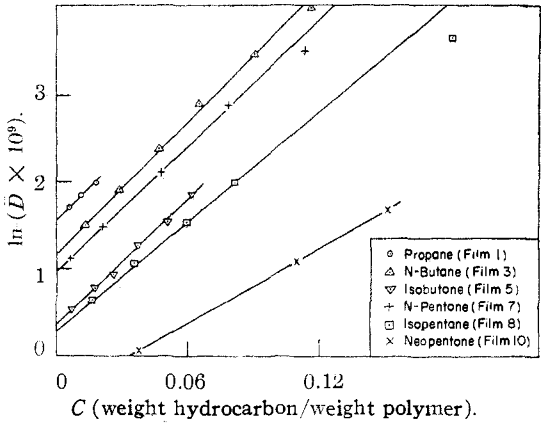

Fig. 4.—ln ($\bar{D} \times 10^9$) *vs.* C for polyisobutylene-hydrocarbon systems at 35°.

The constants $\bar{D}_0$ and A have been presented in Table II.

For comparison with other diffusion data, the differential diffusion coefficient may be evaluated from $\bar{D}$ by the relation

$$D = \frac{d}{dC}(C\bar{D}) = (1 + AC)\bar{D} \qquad (6)$$

Thus D has the same initial value as $\bar{D}$, but increases much more rapidly with the hydrocarbon concentration.

So far as diffusion into polyisobutylene is concerned the hydrocarbons studied fall into three groups: the straight chain hydrocarbons (propane, *n*-butane, *n*-pentane), which have the highest diffusion coefficients, the singly branched hydrocarbons (isobutane, isopentane) with intermediate diffusion coefficients, and the doubly branched hydrocarbon neopentane with the lowest diffusion coefficient of the series. Within each group the diffusion coefficient decreases with increasing molecular size.

Discussion

From the data of Figs. 3 and 4 we see that branching has a much greater effect on the diffusion coefficient than does molecular size. This result may be explained on the basis of Eyring's "hole" theory of diffusion.[13] According to this theory there are in any liquid or solid a number of holes, arising from thermal fluctuations; diffusion takes place by a molecule leaving its current position and jumping into one of these holes. Usually the hole is not the size of the entire molecule, and sev-

TABLE I

$\bar{D}$ AS A FUNCTION OF CONCENTRATION FOR SIX POLYISOBUTYLENE–HYDROCARBON SYSTEMS AT 35°

Hydrocarbon	p, mm.	Film no.	l (cm.)	C_p	$\bar{D} \times 10^9$ (cm.² sec.⁻¹)
Propane	496	1	0.0234	0.0061	5.6
Propane	941	1	.0234	.0116	6.4
Propane	1446	2	.0272	.0185	8.0
Propane	1452	1	.0234	.0183	7.4
n-Butane	242	3	.0309	.0126	4.5
n-Butane	503	3	.0309	.0288	6.8
n-Butane	662	4	.0355	.0392	9.1
n-Butane	763	3	.0309	.0466	10.9
n-Butane	994	3	.0309	.0653	18.6
n-Butane	1243	3	.0309	.0905	33.0
n-Butane	1448	3	.0309	.1162	56.8
Isobutane	210	5	.0218	.0069	1.7
Isobutane	488	5	.0218	.0171	2.2
Isobutane	712	5	.0218	.0260	2.5
Isobutane	767	6	.0254	.0281	2.8
Isobutane	980	5	.0218	.0373	3.6
Isobutane	1246	5	.0218	.0509	4.7
Isobutane	1460	5	.0218	.0622	6.4
n-Pentane	32	7	.0269	.0061	3.1
n-Pentane	104	7	.0269	.0213	4.4
n-Pentane	207	7	.0269	.0474	8.2
n-Pentane	212	8	.0244	.0478	7.3
n-Pentane	306	7	.0269	.0787	18.1
n-Pentane	388	7	.0269	.1132	33.7
Isopentane	106	8	.0244	.0156	1.9
Isopentane	222	8	.0244	.0353	2.9
Isopentane	324	7	.0269	.0570	3.9
Isopentane	333	8	.0244	.0587	4.7
Isopentane	333	9	.0271	.0596	5.1
Isopentane	422	8	.0244	.0808	7.3
Isopentane	666	8	.0244	.1795	39.0
Neopentane	489	10	.0082	.0373	1.1
Neopentane	703	11	.0309	.0595	1.4
Neopentane	1052	10	.0082	.1104	3.0
Neopentane	1240	10	.0082	.1515	5.4

TABLE II

VALUES OF THE PARAMETERS $\bar{D}_0$ AND A IN THE EQUATION $\bar{D} = \bar{D}_0e^{AC}$

Hydrocarbon	$\bar{D}_0 \times 10^9$ (cm.² sec.⁻¹)	A
Propane	4.81	24.6
n-Butane	3.24	25.5
Isobutane	1.45	24.1
n-Pentane	2.64	24.3
Isopentane	1.32	21.1
Neopentane	0.62	14.4

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(13) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., Chap. IX.

eral jumps must occur in the same direction before the molecule has been displaced by an amount equal to its length. In order to form a hole a certain number of van der Waals "bonds" must be broken, giving rise to a site of higher energy; the amount of energy required increases with the size of the hole. Thus according to Boltzmann's law the concentration of holes decreases exponentially with their size.

The first consequence of this picture is that an elongated molecule will diffuse almost solely along its long axis, since the hole size required for diffusion in this direction is so much smaller than that for diffusion normal to the long axis. We may visualize, then, a hydrocarbon as a chain diffusing segment by segment through the polymer; if the hydrocarbon is branched, one of the segments is larger than the others, its size depending on the extent of the branching. The hole size required for diffusion depends, of course, on the size of these segments: it should be the same for all straight chain hydrocarbons, somewhat larger for the singly branched ones, and larger still for doubly branched molecules. Since the concentration of holes decreases exponentially with their size, the observed effects of branching and molecular size on the diffusion coefficient are accounted for.

For unbranched molecules it is reasonable to suppose that at a given concentration and temperature the friction factor f in Einstein's equation

$$\bar{D} = RT/f \qquad (7)$$

will be roughly proportional to the chain length, so that $\bar{D}$ would be inversely proportional to the chain length. This is approximately borne out at low concentrations by the data (Table III). For branched molecules the diffusion of the group with the side chain is the rate-controlling step, so that molecules (except straight chain molecules) with the same degree of branching should have practically identical diffusion coefficients provided that they do not differ too greatly in length. This also is verified by Fig. 3 for isobutane and isopentane.

TABLE III

RELATIONSHIP BETWEEN $\bar{D}_0$ AND CHAIN LENGTH FOR THE STRAIGHT CHAIN HYDROCARBONS

Hydrocarbon	($\bar{D}_0$ × no. of carbon atoms in molecule) × 10^9
Propane	14.4
n-Butane	13.0
n-Pentane	13.2

The "bonds" which must be broken in order to form a hole may be between two polymer segments, a polymer segment and a molecule of the diffusing hydrocarbon, or between two molecules of the hydrocarbon, although the last case is rare when the hydrocarbon concentration is low. The fraction of these bonds which are polymer to hydrocarbon should, at low values of the hydrocarbon concentration, be proportional to C. If we assume that polymer–hydrocarbon bonds are weaker than polymer–polymer bonds, the energy required to form a hole of a certain size decreases linearly with increasing hydrocarbon concentration. Consequently the number of holes big enough to permit diffusion should increase exponentially with increasing hydrocarbon concentration. Since $\bar{D}$ is approximately proportional to the number of these holes per unit volume,[14] its concentration dependence should therefore be given by equation (5), which has already been discovered empirically.

It is of course also possible to account for the observed concentration dependence of $\bar{D}$ by postulating a "loosening" of the polymer structure due to the penetration of the hydrocarbon molecules. While this will certainly lead to a $\bar{D}$ which increases with C, the nature of this increase is somewhat difficult to predict.

It should be mentioned here that by tacitly assuming in our calculation of $\bar{D}$ that the polymer film does not swell during sorption, we have actually calculated a diffusion coefficient with respect to a plane which always has the same mass of polymer on either side, rather than one with respect to a plane which is fixed in space; furthermore, we have neglected the effect of mass flow. These complications are discussed by Crank and Hartley[15] in a recent article. In view of the low values of C used by us, we have felt justified in not correcting for them.

We are at present extending the diffusion data on hydrocarbon–polyisobutylene systems to other temperatures. The sorption isotherms obtained in conjunction with the kinetic data will be discussed in a separate paper when equilibrium results at other temperatures are available.

We wish to express our gratitude to Army Ordnance, under whose auspices this work was carried out.

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(14) This assumes that the variation in $\bar{D}$ is due entirely to the variation of the jump frequency ν. Actually the average length (a) of a jump is probably also dependent on the concentration of diffusing material. It is quite unlikely, however, that a would rise exponentially with increasing concentration, as does $\bar{D}$, and we feel justified therefore in attributing the majority of the concentration dependence of $\bar{D}$ to ν.

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