Reexamination of the Molecular Size Dependence of Diffusivities of Hydrocarbons in Natural Rubber†

Mitsuyasu KAWAKAMI, Hideaki IWANAGA, and Shuichi KAGAWA*

Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Nagasaki 852

(Received May 24, 1980)

Diffusion coefficients at zero concentration, D_0, for hydrocarbon vapors in natural rubber have been determined, and their dependence on the size and shape (or length) of the penetrants has been reexamined. For normal hydrocarbons, D_0 decreased gradually with increasing the number of carbon atoms up to 5 and then leveled off. For branched hydrocarbons, such as iso- and neo-paraffins, D_0 was considerably lower than that for the corresponding normal ones. The dependence of D_0 on the size and shape of penetrants could be explained by assuming that the principal resistance to diffusion is defined by the cross-sectional area at the most bulky portion of the major axis and also that an additional resistance due to the molecular length contributes for relatively lower hydrocarbons. The latter resistance was practically negligible for hydrocarbons with more than 4 carbon atoms in the major chain. The effective cross-sectional dimension could be estimated successfully in terms of the group dimension of Pauling.

Extensive studies of gas or vapor diffusion in polymers have been made for elucidating the mechanisms of diffusion and the microstructure of polymers. The free volume theory seems to succeed in interpreting diffusion phenomena in polymer substances (see, for example, Refs. 1—3). However, estimation of the critical size of a hole required for diffusion to take place has not been achieved.

Natural rubber is one of the materials studied from the earliest period because of its high permeability. For common gases, the general dependence of diffusion properties in natural rubber on the size of diffusant molecule seems to be fairly well established and predictable. For organic vapors, on the other hand, the phenomena are more complicated. The diffusion coefficient varies, in general, with the concentration of the vapor in the rubber. Therefore, the diffusion coefficient at zero concentration, D_0, has often been employed to estimate the diffusivity; it is found to be a function not only of the size but also of the shape of a given penetrant molecule.

According to information published earlier (see, for example, Refs. 4 and 5), the characteristic behavior of D_0 for hydrocarbons in rubber can be summarized as follows. (1) D_0 for normal hydrocarbons decreases with an increase in the number of carbon atoms up to 4 and then levels off, (2) D_0 for branched hydrocarbons such as iso- or neo-paraffins are remarkably lower than the values for the corresponding normal ones.

The effect of length or branching of a penetrant molecule on diffusivity has been studied, but few attempts have been made to explain all these effects together. It is the purpose of this work to reexamine the dependence of D_0 for hydrocarbons in rubber on the size and shape of penetrants, and to discuss how a penetrant molecule moves through rubber.

Experimental

The average permeability coefficient, $\bar{P}$ was determined by means of a conventional permeation apparatus.[6] That is, the pressure increase at the low pressure compartment due to vapor transport through a rubber film was measured as a function of time with a Pirani gauge which was calibrated previously through a McLeod gauge.[7] $\bar{P}$ was calculated, then, from the steady state permeation rate, $\Delta p/\Delta t$, using the expression

$$\bar{P} = \frac{273.2}{76T}\frac{V_c}{p_h}\frac{l}{A}\frac{\Delta p}{\Delta t}, \quad (1)$$

where V_c and T are the volume and temperature, respectively, of the measuring chamber, p_h is the applied pressure of the penetrant, and A and l are the effective area and the thickness of the membrane. The change of l due to swelling was not taken into account in the calculation of $\bar{P}$ from Eq. 1. However, the resulting effect on the diffusion coefficient will be compensated for when the average diffusion coefficient is extrapolated to zero concentration.

The solubility coefficient, S, is defined as

$$S = \frac{c}{p}, \quad (2)$$

where c is the equilibrium concentration of a penetrant in the film and p is the partial pressure at sorption equilibrium. When Henry's law is obeyed, S is a constant. Sorption isotherms were measured by a volumetric method. The apparatus used in this experiment was essentially the same as that of Aitken and Barrer.[8]

The average diffusion coefficient, $\bar{D}$, was calculated from $\bar{P}$ and the solubility coefficient, S_h at the high pressure side of the membrane using the relation

$$\bar{D} = \frac{\bar{P}}{S_h}, \quad (3)$$

where the sorption equilibrium is assumed to be established at the both surfaces of the film. A series of $\bar{D}$ was measured as a function of $c_h(=p_h S_h)$, and the diffusion coefficient at zero concentration, D_0, was obtained by extrapolating $\bar{D}$ to $c_h=0$.

The rubber film was prepared by casting a benzene solution of smoked sheet on a glass plate. This was first air dried, followed by vacuum drying at room temperature for at least 2 days. The average thickness of a film used in the measurements was determined from the density and the weight per unit area of the film. Six kinds of lower hydrocarbons of 99.0% minimum purities (Seitetsu Kagaku Co.) and four kinds of liquid ones of commercial reagent grade (Tokyo Kasei Kogyo Co.) were employed. They

† A preliminary report of this work was presented at the 40th National Meeting of the Chemical Society of Japan, Fukuoka, October 1979.

TABLE 1. DIFFUSIVITY AND SOLUBILITY DATA AT 298 K FOR HYDROCARBONS IN NATURAL RUBBER

Hydrocarbon	Symbol	$10^7 D_0$ / $cm^2 s^{-1}$		β[a]	S_0 / cm^3 (STP) cm^{-3} MPa^{-1}	α[a]
Methane	C_1	6.8	(8.9)[b]		3.35	
Ethane	C_2	4.7			6.78	
Propane	C_3	2.1	(2.1)[b]		52.9	
Butane	C_4	1.5		1.8	159	2.1
Pentane	C_5	1.3		7.3	640	2.3
Hexane	C_6	1.3		7.7	1520	3.0
Isobutane	iso-C_4	0.91		4.8	101	2.4
Isopentane	iso-C_5	0.70		7.5	362	2.9
Neopentane	neo-C_5	0.47		5.5	164	2.5
Neohexane	neo-C_6	0.43		4.3	701	3.1

a) These parameters have the unit of cm^3(rubber)cm^{-3}(penetrant as liquid). b) The values in parentheses represent the data of Michaels and Bixler.[13]

were subjected to repeated freeze-thaw cycles to remove dissolved gases before being introduced into the apparatus.

Results and Discussion

For lighter hydrocarbons such as methane, ethane, and propane, P did not show any pressure dependence in the applied pressure range (up to about 50 kPa for lighter hydrocarbons) and Henry's law was obeyed. In this case, the diffusion coefficient, D, is essentially independent of c and may be also determined directly from the time lag observed in the permeation measurement. Actually, the values of D obtained by the time lag method and those from Eq. 3 were in excellent agreement.

For heavier hydrocarbons, on the other hand, the concentration dependence of solubility coefficients was observed. Thus, Henry's law was no longer obeyed. In the range of measurements (the range was limited by the vapor pressure at room temperature for liquid hydrocarbons), the sorption isotherms could be well represented by the equation

$$S = S_0 \exp(\alpha c), \tag{4}$$

where S_0 is the solubility coefficient at zero concentration and α is a constant. Equation 4 can be derived from a simplified form of the Flory-Huggins equation

$$\ln a = \ln v + (1-v) + \chi(1-v)^2, \tag{5}$$

where a and v are the activity and the volume fraction of the penetrant, and χ is the interaction parameter. That is, assuming $a=p/p_0$ (where p_0 is the vapor pressure of the penetrant at the measuring temperature), making the substitutions and neglecting higher terms, we obtain the expression

$$S = S_0 \exp[2(1+\chi)c]. \tag{6}$$

Therefore, it is clear that the parameter α in Eq. 4 is approximately equal to $2(1+\chi)$.[9-12] The solubility coefficient, S_h required to calculate $\bar{D}$ from Eq. 3 was estimated from Eq. 4.

Average permeabilities, and therefore, average diffusion coefficients varied with the applied pressure for C_4 and higher hydrocarbons. The concentration dependence of $\bar{D}$ could be expressed fairly well by the equation

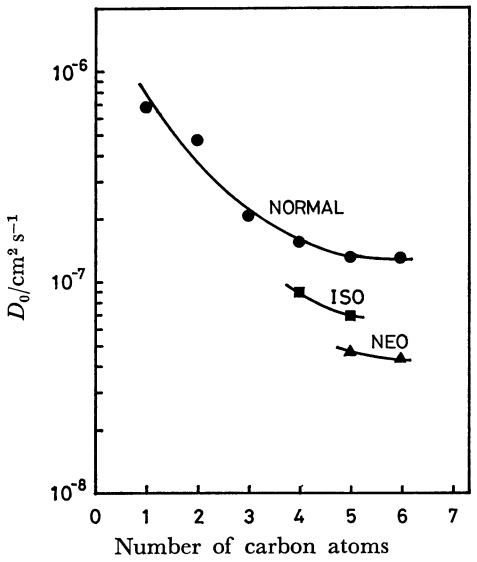

Fig. 1. Dependence of D_0 for hydrocarbons in natural rubber at 298 K on the number of carbon atoms.

$$\bar{D} = D_0 \exp(\beta c_h), \tag{7}$$

where β is a constant (see, for example, Refs. 9—12). Then, D_0 was determined readily by extrapolation of the ln $\bar{D}$ *vs.* c_h plot. The results are shown in Table 1. The vslues of D_0 for methane and propane are in fair agreement with those obtained by Michaels and Bixler.[13]

The values of S_0 satisfy the relation between S_0 and the boiling or critical temperature which has been reported earlier.[14] The parameter α can be taken as being roughly constant for the seven hydrocarbons examined. This means that the Flory-Huggins interaction parameters are also the same for the systems of these hydrocarbons and natural rubber. According to the free volume theory,[1-3] the concentration dependence parameter of D is a function of the critical size of the hole required for diffusion to take place. In the present work, however, the parameter β only represents the extent of the concentration dependence of $\bar{D}$ and has a complicated meaning. Moreover, these values can not be compared as such, be-

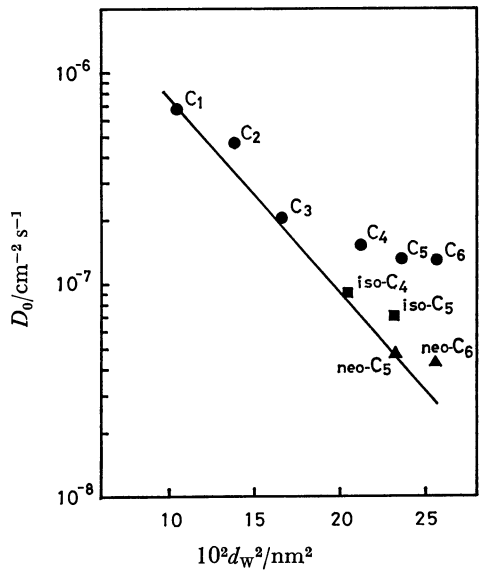

Fig. 2. Correlation of D_0 with d_W^2. Symbols refer to hydrocarbons given in Table 1.

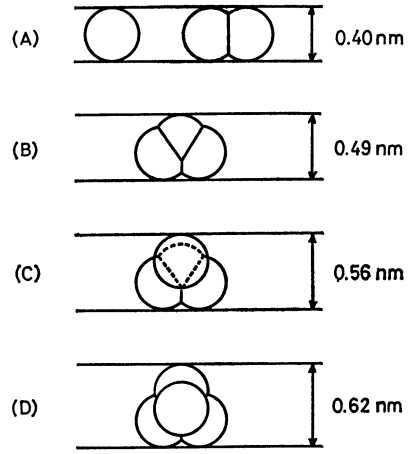

Fig. 3. Schematic drawing of the effective cross-sectional dimension, d_P. (A) Methane and Ethane, (B) Normal hydrocarbons above Propane, (C) Branched hydrocarbons with a single methyl group, (D) Branched hydrocarbons with two methyl groups on the same carbon atom.

cause the concentration ranges measured are appreciably different. The dependence of D_0 on the size of a penetrant molecule will now be discussed.

In Fig. 1, D_0 values are plotted against the number of carbon atoms. Obviously, D_0 for normal paraffins decreases with the chain length from C_1 to C_5, to reach a constant value at C_5 and higher homologues. Note also that the branching of a penetrant molecule increases somewhat its effective dimension and hence yields a lower value of D_0.

For diffusion in polymers it is generally accepted that the hole formation in a given polymer-diffusant system as a result of thermal fluctuations of the diffusant molecule and/or the polymeric jumping unit is responsible for the diffusivity. According to Fujita's free volume theory,[2,5] the diffusivity is proportional to the probability of finding a hole exceeding a critical volume, and can be described as

$$D = A_d \exp\left(-\frac{B_d}{f}\right), \tag{8}$$

where B_d is a parameter corresponding to the minimum hole required for diffusion, f is the average fractional free volume of the system, and A_d is a proportionality factor which is considered to be dependent primarily on the size and shape of the diffusant molecule. Some attempts have been made to correlate the diffusivities with the size and shape of diffusant vapors.

As one idea, the "diffusive cross-section" difined as the ratio of the molar volume $\bar{V}$ and the maximum molecular length $\bar{L}$ of the penetrant has been proposed for the diffusivities of organic vapors (see, for example, Refs. 15—17). This parameter, however, could not be applied to the present systems, as shown in Fig. 1. The value of D_0 decreases with the number of carbon atoms from C_3 to C_6 normal hydrocarbons, while that of $\bar{V}/\bar{L}$ is almost constant for them. This measure tends to overestimate the effective size, especially for lighter hydrocarbons.

In Fig. 2, D_0 is plotted against the square of the van der Waals diameter, d_W^2, instead of the number of carbon atoms. This dimension can be considered to represent the size of molecule regarded as spheres. In the figure, the points of methane (C_1) and neopentane (neo-C_5), whose the shapes are practically spherical, are connected by a solid line for convenience. It can be noted that all the points for other non-spherical hydrocarbons studied here are above this line. This means these hydrocarbons have more preferable shape for diffusion than a spherical molecule. The effective size of such penetrants, therefore, must be smaller than d_W^2.

As previously described, D_0 for normal paraffins decreases gradually with an increase in the number of carbon atoms and finally levels off for homologues higher than C_4. This implies a mode of diffusion in which the diffusant molecule moves through rubber with its major axis aligned with the diffusion direction. Under such circumstances the resistance to diffusion may be a function of the cross-sectional area normal to the main axis and the length of a given penetrant. When the cross-sectional dimension is not uniform along the axis, that at the most bulky part must become the predominant factor. Thus, for estimating such a dimension, an alternative measure, d_P, was proposed. Speculations on these dimensions in terms of the group dimension of Pauling[18] are illustrated in Fig. 3, where the diameters of methylene and methyne group have been both assumed to be 0.4 nm, which is the methyl group diameter.

The relationship between D_0 and d_P^2 is shown in Fig. 4, in which a line joining the points of C_1 and neo-C_5 is also drawn for convenience. This line can be considered to reflect the effective size of the spherical penetrant. For isomeric butanes and pentanes in cross-linked natural rubber, Aitken and Barrer[8] have demonstrated that D_0 decreased linearly with the size expressed as the product of the minimum dimension, l_1 and the next smallest dimension, l_2 of the molecule. Such a dimension $l_1 l_2$ may be a useful measure of

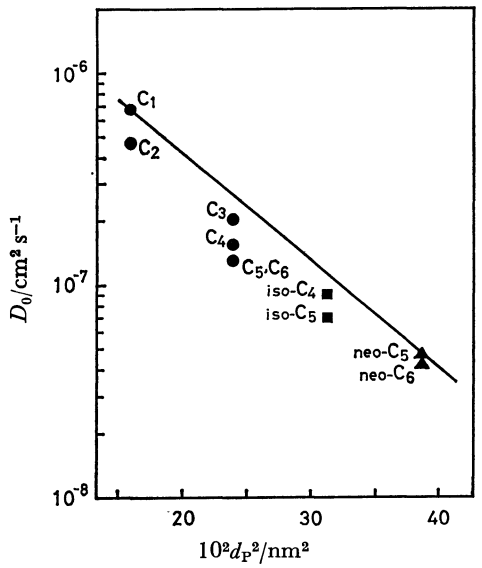

Fig. 4. Correlation of D_0 with d_P^2. Symbols refer to hydrocarbons given in Table 1.

the cross-section when the diffusant is not spherical. They have suggested that the maximum dimension has little significance, but did not explain further. We have also confirmed that a reasonably linear relationship holds between D_0 and $l_1 l_2$ for isomeric butanes, pentanes, and hexanes. The data for C_1 and C_2, however, deviated considerably from the rectilinear relationship. In addition, the appreciable difference between D_0 for C_1 and C_2 implies that the maximum length of the molecule has some significance. In Fig. 4, the distance along the ordinate between a certain point and the line may suggest the effect of the molecular length. It is inferred that the extent of this effect is more significant at the first increase in the number of carbon atoms in major axis, and then gradually diminishes with a subsequent increase in length. Thus, Fig. 4 is a convenient illustration for understanding the effects of both the size and shape (or length) of hydrocarbon penetrants on their diffusivities.

From above discussion, we obtain the following conclusions. A hydrocarbon molecule moves through rubber matrix with its major axis aligned in the diffusion direction. The largest resistance to diffusion is thus determined by the cross-sectional area at the most bulky part of the axis. An additional effect is caused by the length of major chain, but this effect practically diminishes for more than 4 carbon atoms. The effective cross-sectional area at the most bulky part can be estimated successfully using the group dimension concepts of Pauling.

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