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<td>Kawakami, Mitsuyasu; Kagawa, Shuichi</td>
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Sorption and Diffusion of Normal Hydrocarbons in Natural Rubber

by

Mitsuyasu KAWAKAMI* and Shuichi KAGAWA**

Solubility and diffusion coefficients of normal C_2-C_6 hydrocarbons in unvulcanized natural rubber have been determined. Data on concentration dependence of the solubility constant could be correlated by $S = S_0 \exp (ac)$ and the parameter $a$ are related to the Flory-Huggins interaction parameter $\chi$ approximately by $a = 2\chi + 1$. The concentration dependence of diffusion coefficients are fitted by the expression $D = D_0 (1 - ac) \exp (\beta c)$ derived from a first-approximation free volume theory. The diffusion coefficient, $D_0$, extrapolated to zero concentration and its activation energy decrease with increasing molecular size up to C_3 and reach a constant value for C_4 and higher hydrocarbons. The parameter $\beta$ is almost constant for C_4-C_6 hydrocarbons. It is demonstrated that these hydrocarbons would move through polymeric media like a needle in concert with the thermal motion of polymer segments and only the free volumes larger than the effective cross-sectional diameter of the diffusant molecule is available for diffusion.

INTRODUCTION

Vapor transport through polymer films is of technical interest from the view point of barrier properties as, for example, in packaging materials, and more recently, in permeable media for separation of gas or vapor mixtures. From a scientific standpoint, the diffusion of organic vapors in polymeric solids has been studied as a probe for elucidating segment motions of the polymer.

In diffusing, a penetrant molecule exchanges its position with a part of polymer molecule to move through polymer substances. When the diffusant is relatively large, this exchange requires a cooperative movement of several successive bonds, i.e., the so-called polymer segment. This segment motion characteristic of polymers becomes a dominant factor on diffusion as the size of penetrant molecule is at least, close to that of the monomer unit of the polymer. For inorganic gases, it has been generally accepted that the diffusion coefficient decreases almost monotonously with increasing the size of penetrant. For organic vapors, it is necessary to take into account another important factor. These substance are easily condensable and of relatively large solubility for organic polymers. This leads to the swelling or plasticizing of polymer molecules and therefore, concentration dependence of diffusivity and/or solubility of a penetrant in the polymer. In such a case, the diffusion coefficient $D_0$ extrapolated to zero concentration has mainly been discussed.

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*Department of Industrial Chemistry.
**To whom correspondence should be sent.
Values of $D_o$ for normal hydrocarbons have been found to decrease with the number of carbon atoms up to 4 and then level off in either vulcanized natural rubber\textsuperscript{31, 41} or polyisobutylene\textsuperscript{42, 43}. Further, $D_o$ for pentane isomers in these polymers have been reported to decrease in the order, $n >$ iso $> \text{neo}$- isomer.\textsuperscript{41, 42} These works suggest that $D_o$ depends not only on molecular size but also on shape of the diffusant molecule. Little is known, however, about shape dependence of diffusion coefficient.

The concentration dependence of diffusion coefficient has been also an attractive subject. With respect to this phenomenon theoretical interpretations have been advanced in terms of free volume concept (see, for example, Refs. 7–13). A number of experimental works have been hitherto performed for various systems (see, for example, Refs. 1–8, 11–15). In most of these investigations, however, the measurement was limited over the range of concentration obeying the Henry law.

In the present study the solubility and diffusion coefficients of normal C$_2$–C$_6$ hydrocarbons (here, the subscript denotes the number of carbon atoms) in unvulcanized natural rubber were determined in a relatively wide concentration range. The concentration dependence of these properties together with the effects of size and shape of penetrant on diffusion were discussed.

**EXPERIMENTAL**

Permeation rate was measured manometrically using a permeation cell. That is, one side of a rubber film was exposed to a penetrant gas or vapor and the other side was evacuated continuously by a rotary vacuum pump. The average permeability coefficient $P$ was calculated from a slight decrease in pressure at high pressure side using the equation,

$$P = \frac{\nu_m V \ell}{p_A R T} \frac{d p_s}{d t} = \frac{\nu_m V \ell}{p_A R T} \frac{d \ln p_s}{d t},$$

where $A$ and $\ell$ are the effective area and thickness of film, $p_s$ and $V$ are the pressure and volume of the high pressure compartment, respectively, $\nu_m$ is the liquid molar volume of the penetrant at the temperature $T$, $R$ is the gas constant, and $d p_s/d t$ is the rate of decrease in pressure. The value of $d \ln p_s/d t$ can be obtained from the slope of a tangent of the plot for $d \ln p_s$ vs. time $t$. The plot, however, could be regarded as rectilinear in the narrow region of the pressure change.

As usual, by assuming that a sorption equilibrium holds on the surface of a film and the diffusion through a film is the rate-determining step, the average diffusion coefficient $\bar{D}$ can be calculated from $P$ and the solubility coefficient $S_s$ at the surface of high pressure side by the equation,

$$\bar{D} = \frac{P}{S_s}.$$  \hspace{1cm} (2)

Here, $\bar{D}$ is related to the mutual diffusion coefficient $D$ by the formula,

$$\bar{D} = \frac{1}{c_n} \int_{c_n}^{c_{\infty}} D dc,$$  \hspace{1cm} (3)

where, $c$ is the concentration of penetrant component in the film and $c_n$ is that at the surface of high pressure side, which is assumed to be in equilibrium with $p_s$. In the present work $c$ was expressed as the liquid volume dissolved per 1 cm$^3$ of rubber. The value of $D$ as a function of $c$ can be obtained in principle by differentiating $c_n \bar{D}$ with $c_n$. When $D$ is independent of the concentration, $\bar{D}$ is equal to $D$.

On the other hand, the solubility coefficient $S$ is defined as

$$S = c/p,$$ \hspace{1cm} (4)

where $p$ is the equilibrium pressure in the system attaining to a sorption equilibrium. The unit of $S$ turns out to be cm$^3$(liq.) cm$^{-3}$(rubber) atm$^{-1}$ provided that of $c$ was taken as described above. Sorption isotherms were measured by a volumetric method with an apparatus similar to that employed by Barrer and co-workers.\textsuperscript{16}

A rubber film was prepared by casting a benzene solution of smoked sheet on a glass plate and air-drying, followed by vacuum drying at a room temperature for about 2 days. Ten kinds of normal hydrocarbons of the number of carbon atoms from 2 to 6 were employed. They are all commercial origin and used without further purification. The measurements of both permeability and solubility were carried out in the pressure range up to 400
mmHg for gaseous hydrocarbons and to the vapor pressure at a room temperature for liquid ones.

RESULTS and DISCUSSION

Solubility Coefficient

The concentration dependence of solubility coefficient was found for C_{4}-C_{6} hydrocarbons in the pressure range measured. The results are shown in Fig. 1, suggesting that this dependence may be represented by the formula,

\[ S = S_0 \exp(a + c) \]  

(5)

\[ \ln S = \ln S_0 + ac \]  

(6)

where \( S_0 \) corresponds to \( S \) extrapolated to zero concentration and \( a \) is a constant. The values of \( S_0 \) and \( a \) are given in Table 1. In conformity with the previous work\(^1\), \( S_0 \) for a given vapor can be correlated with its boiling or critical temperature. The parameter \( a \) seems to be practically constant for six hydrocarbons examined.

The activity \( a \) of solvent component in a concentrated polymer solution can be represented by the well-known Flory-Huggins equation,

\[ \ln a = \ln \phi + (1 - \phi) \chi (1 - \phi)^2 \]  

(6)

where \( \phi \) is the volume fraction of solvent and \( \chi \) is the interaction parameter. Using the relation of \( \phi = c/(1 + c) \) and the approximation of \( a = \phi/\phi' \), the values of \( \chi \) were calculated from solubility data. Here \( \phi' \) denotes the vapor pressure of pure hydrocarbon and its value was quoted from literatures, otherwise estimated by the Antoine equation. Consequently \( \chi \) did not vary with concentration for any hydrocarbons, while some scattering. This is consistent with the result of Prager, et al.\(^2\) for polyisobutylene-hydrocarbon system. The mean values of \( \chi \) obtained are presented in Table 1. These values seem to be almost constant regardless of the kinds of hydrocarbons examined. The value of \( \chi \) for pentane is somewhat smaller than that for the polyisobutylene-pentane system, 0.68.\(^2\)

Introducing the approximation of \( \phi = c \) and neglecting the term of \( c^2 \), a relation

\[ \ln \frac{S}{p} = \ln S = -\ln \phi' - 1 + (1 + 2\chi)c \]  

(7)

may be derived from Eq. (6). At the limit of \( c = 0 \) it becomes \( \ln S_0 = -\ln \phi' - 1 - \chi \) and thus it can be written ultimately as

\[ S = S_0 \exp [(1 + 2\chi)c] \]  

(8)

Comparison between Eqs. (5) and (8) yields the
relation $a = 1 + 2x$. From Table 1 this correlation may be found to hold roughly. The independence of $a$, viz. $x$, on the kinds of hydrocarbons suggests that the strength of interactions between respective hydrocarbon and rubber are about the same.

**Heat of Solution**

From an Arrhenius-type expression of temperature dependence of $S_0$, the heat of solution $\Delta H_s$ was calculated. Measurements of $S$ were made at 25, 35, and 45°C. When $S$ varied with the concentration, $S_0$ was used. Furthermore, as the solution process can be divided into condensation and mixing, the partial molar heat of mixing at infinite dilution $\Delta H_m$ was obtained from the relation of $\Delta H_m = \Delta H_s - \Delta H_c$, where $\Delta H_c$ is the heat of condensation and was estimated from vapor pressure data by using the Clausius-Clapeyron equation. The results are illustrated in Fig. 2. The abscissa indicates the van der Waals diameter and thus this figure demonstrates that $\Delta H_s$ increases negatively with the size of penetrant molecule, while $\Delta H_m$ is almost constant irrespective of the size. Clearly the contribution of $\Delta H_m$ is small and practically $\Delta H_c$ is predominant to $\Delta H_s$.

The change in chemical potential $\Delta \mu$ resulted from mixing is written as

$$\Delta \mu = RT \ln a = RT \left[ \ln v + (1-v) + x(1-v)^2 \right]$$

and then $\Delta H_m$ can be given by

$$\Delta H_m = RT x (1-v)^2.$$  \hspace{1cm} (9)

At the limit of $v = 0$, the relation $\Delta H_m = RT x$ is valid. Therefore it can be said that the constancy of $\Delta H_m$ for a series of hydrocarbons used is attributed to the constancy of $x$. The mean value of $\Delta H_m$ for seven hydrocarbons examined is about 1.4 kJ mol$^{-1}$ and then $x$ turns out to be 0.55. This value is in fair agreement with those presented in Table 1.

**Diffusion Coefficient**

The average diffusion coefficients for C$_2$ and C$_3$ hydrocarbons, such as ethylene, ethane, propylene, and propane did not show pressure dependence in the range of 100–400 mmHg. On the other hand, those for normal C$_4$–C$_6$ hydrocarbons, in which 1-butene, 2-butene isomers, 1-pentene, pentane, and hexane were contained, increased with concentration in rubber. In a range of sufficiently low concentration a plot for ln $\tilde{D}$ vs. $c_h$ gave an approximately straight line, from which $D_0$ was determined. The results are given in Table 1.

In the system in which the diffusivity depends on concentration, it is necessary to derive $D$ from $D_0$ as a function of $c$. Usually, as can be seen from Eq. (3), it is achieved by numerical or graphical differentiation of a plot for $\tilde{D} c_h$ vs. $c_h$. This method, however, accompanies appreciable errors and requires a large number of data to obtain reliable $D$. In the present work, the concentration dependence of $D$ was theoretically discussed at first and then determined with the data of $\tilde{D}$ by a curve fitting method.

According to the theory based on the free volume model, the diffusivity of a small molecule in a given polymer is governed by the amount of free volume present in the system, which is primarily determined by the micro-Brownian motion of the polymer segment. Thus a following relation between the thermodynamic diffusion coefficient $D_T$ and the average fractional free volume $f$ holds,
where $C$ and $B$ are constants characteristic of the system and assumed to be independent of concentration and temperature. Specifically, $B$ is a parameter representing the size of minimum hole required for diffusion to take place. For the concentration dependence of $f$, Fujita, et al. introduced an assumption that the increase in free volume due to an addition of diffusant species can be given by the equation,

$$f = f_0 + \gamma \nu$$  \hspace{1cm} (11)

where $f_0$ corresponds to $f$ at zero concentration, that is, represents the average fractional free volume in the pure polymer and $\gamma$ is a proportionality constant. Thus the limiting expression of Eq. (10) at volume fraction of diffusant $\nu \rightarrow 0$ can be written as

$$D_{T, \nu \rightarrow 0} = D_0 = CRT \exp (- B f_0).$$  \hspace{1cm} (12)

Substitution of Eqs. (11) and (12) into Eq. (10) gives

$$D_T = D_0 \exp \left( B \frac{\nu}{f_0} + \gamma \nu \right).$$  \hspace{1cm} (13)

The thermodynamic diffusion coefficient can be correlated to the mutual diffusion coefficient $D$ by the equation,

$$D_T = D \left( \frac{\ln c}{\ln a} \right).$$  \hspace{1cm} (14)

Further, if the solubility coefficient is expressed by Eq. (5), a following relation can be derived from Eqs. (4), (5), and the approximation of $a = p/p'$,

$$\frac{\ln a}{\ln c} = 1 - ac.$$  \hspace{1cm} (15)

Substituting Eqs. (14) and (13) into Eq. (15), introducing the approximation of $v = c$, and then regarding $\gamma \nu$ as negligible in comparison with $f_0$, one obtains,

$$D = D_0 (1 - ac) \exp (\beta c),$$  \hspace{1cm} (16)

where $\beta = B f_0$. Then, substituting into Eq. (3), it follows that,

$$D = \frac{D_0}{c_a} \int_0^{c_a} (1 - ac) \exp (\beta c) dc.$$  \hspace{1cm} (17)

If $D_0$, $a$, $\beta$, and $c_a$ are given, $D$ can be calculated by numerical integration of Eq. (17). Thus, for $D_0$ and $a$ known system the value of $\beta$ can be determined by fitting a computed curve of $D$ vs. $c_a$ to experimental results. In the present study the calculation was performed on a FACOM 270-20 computer.

The results for hexane is shown in Fig. 3. The curve in this figure refers to that calculated with $\beta = 10$. The data indicated by open circles fall satisfactorily on the curve. The value of $\beta$ so obtained is presented together with those for other hydrocarbons in Table 1. The parameter $\beta$ can be also regarded as constant for six kinds of hydrocarbons while they show some scatter.

When the concentration of diffusant is so low that the approximation $\exp (\beta c) = 1 + \beta c$ holds, Eq (16) leads to $D = D_0 [1 + (\beta - a) c - a \beta c^2]$. Then, neglecting the $c^2$ term yields $D = D_0 [1 + (\beta - a) c]$. An empirical formula $D = D_0 (1 + bc)$, on the other hand, was obtained independently by Prager, et al. and Barrer, et al. for the systems of polyisobutyl-hydrocarbon (C₃-C₅) and cross-linked natural rubber-hydrocarbon (C₅-C₅), respectively. These measurements were limited to such a low concentration range as the Henry law held. As the value of parameter $b$ for pentane at 35°C, they had obtained 32.8 and 27.8 (the unit of concentration was converted into cm³(liq.) cm⁻³(rubber) atm⁻¹ by the authors), respectively. The present discussion demonstrates that $b$ is identical with $\beta - a$, and yields $b = 7.7$ from $\beta = 10$ and $a = 2.3$ for the unvulcanized natural rubber-pentane system at 25°C. By taking into account $\beta = B f_0$, it can be supposed that a larger value of $f_0$ of unvulcanized rubber leads to a smaller $\beta$, consequently a smaller $b$.

The result that the diffusion coefficients for C₅...
and C₅ hydrocarbons did not show appreciable concentration dependence in the pressure range examined may be due to their poor solubility in rubber, that is, their concentration is low enough under the present conditions.

Effects of Molecular Size and Shape of Diffusant

Being related to \( B \), which represents the size of minimum hole required for diffusion in polymers, by Eq. (12), \( D_0 \) is expected to depend not only on size but also on shape of a diffusant molecule. The relation between \( D_0 \) and the van der Waals diameter regarded as sphere is illustrated in Fig. 4.

![Fig. 4 Plots for \( D_0 \) vs. van der Waals diameter \( d \). Numbers refer to hydrocarbons given in Table 1.](image)

It is clear that \( D_0 \) decreases with the molecular size of diffusants for up to C₄ hydrocarbons and then remains approximately constant for larger homologs. This trend agrees with those observed by Prager, et al.²¹,²² and Barrer, et al.³¹,³² independently for the systems described before. These facts suggest a diffusion mode of normal hydrocarbons.

In view of the steric interactions it may be reasonable to consider that a given normal hydrocarbon penetrates the rubber like a needle in concert with the thermal motion of polymer segments. Under such a circumstance the effective diameter of a diffusant may be determined by the cross-sectional dimension.* According to the group dimension of Pauling,²¹ its value is about 4.0 Å for propane and higher homologs, respectively.²² In addition, the dimension for propylene is about 4.7 Å, somewhat smaller than that for propane, if the group dimension of methylene could be taken similarly to methyl or methylene as 2 Å. For ethylene and monoolefins higher than C₄, the dimension may be the same as that for corresponding paraffin homologs. The relative magnitude of these dimensions accounts for satisfactorily the molecular size dependence of \( D_0 \). Double bond may not have an appreciable effect on the diffusion motion of a penetrant as compared with molecular size.

It is of interest that the values of \( \beta \) for C₄ and higher hydrocarbons are independent of the kinds of penetrant. Since B can be regarded as taking a same value among these penetrants, the relation of \( \beta = B\gamma/\delta \) suggest that the values of \( \gamma \) are also constant. This quantity \( \gamma \) may be related to the interaction parameter \( \chi \).

Activation Energy for Diffusion

The temperature dependence of \( D_0 \) followed an Arrhenius-type equation very closely over the experimental conditions. The activation energy for diffusion \( E_d \) determined with the data at 25, 35, and 45 C are given in Table 1. \( E_d \) seems to be almost constant at about 34–51 kJ mol⁻¹ regardless of the kinds of diffusant components. To be more exact, this may hold for C₄ and higher hydrocarbons. According to Auerbach, et al.,²³ \( E_d \) for octadecane in pale crepe is 33–36 kJ mol⁻¹ (40–80°C), which is comparable to those observed for the present system. This is particularly surprising in view of the number of carbon atoms of 18. Further, according to Saunders, et al.,²⁴ the activation energy for viscous flow of unvulcanized natural rubber over the range of 60–140°C is about 33.9 kJ mol⁻¹, very close to \( E_d \) values obtained for

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* It may be equivalent to the minimum effective cross-sectional area of a hole allowing the passage of hydrocarbon molecule at the molecular sieving in such as zeolite.
SORPTION AND DIFFUSION OF NORMAL HYDROCARBONS IN NATURAL RUBBER

hydrocarbons higher than C₄.

The activation energy is primarily predominated by B and the temperature dependence of the partition function of fractional free volume in a pure polymer. Thus, if B is the same for C₄ and higher hydrocarbons Eₐ should be also constant for them. The result seems to demonstrate the validity of the hypothesis on diffusion mode proposed in the preceding section.

References