

Diffusion of Hydrocarbons in Rubber, Measured by the Pulsed Gradient NMR Method

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Synopsis

The pulsed field gradient spin echo method was used to measure the diffusion of ten paraffin hydrocarbons in several uncrosslinked rubbers at 51°C. We obtain various free volume parameters from the concentration dependences, establish the approximate proportionality of the translational friction coefficient to paraffin molecular weight, and confirm the equal intrinsic efficiency of the diffusion mechanism of decane and hexadecane in rubbers.

INTRODUCTION

The diffusion of liquid or gaseous diluents in rubbery polymers has been studied in considerable detail¹⁻⁶ using a variety of techniques, with the purpose of characterizing the local chain mobility of the rubber, and the influence on it of thermodynamic variables and the presence of the diluents, including antioxidants and extender oils in commercial rubbers. The free volume theory, as applied to diffusion,⁷ has been fruitfully employed in the analysis of much of this work.

Among the various techniques for measuring diffusion, the pulsed field gradient NMR method^{8,9} is relatively convenient when it is desired to study specimens at finite diluent equilibrium concentrations, permitting explicit concentration dependences of the diffusion to be studied; it also facilitates the measurement of temperature dependences since a single sample may be indefinitely reused. These advantages have been applied in studying diluent diffusion in polymers and polymer self-diffusion¹⁰ as well as the diffusion of the extender oil in a commercial rubber.¹¹

Beyond the most basic application of the free volume model, much may be learned from the correlation of the results using series of rubber types or diluents. For example, the internal friction coefficient of several paraffin hydrocarbons has been found to be approximately proportional to their molecular weights in several rubbers.⁶ Also, a comparison of the diffusion coefficients of two diluents in various polymers may shed light on differences in diffusion mechanism between the diluents.^{3,6}

The present work was undertaken with the primary aim of extending the range and detail of diffusion measurements of linear paraffin hydrocarbons in various rubbery polymers, with emphasis on the application of the free volume model to the concentration dependence, leading to reliable extrapolations to zero diluent concentration, and yielding free volume fractions of the hydrocarbons. This permits the dependence of diffusion on diluent molecular weight and on rubber type to be explored along the lines alluded to. We find significant differences

in the systematics of hydrocarbon diffusion in *cis*-polyisoprene and SBR, most of which yield to analysis by aspects of the free volume theory.

A preliminary report of this work has been given.¹²

EXPERIMENTAL

Sample Materials

Specimens of several types of uncrosslinked rubber were obtained through L. J. Fetters and A. N. Gent at the Institute of Polymer Science of The University of Akron. They contain no extender oils and only trace amounts of antioxidants and accelerators. In some cases these additives could be weakly detected on the basis of their proton spin echo at temperatures near 80°C. Our most sensitive criterion for the presence of fluid additives was the diffusional attenuation of their spin echo by field gradient pulses (see below) when the sample was swelled with CCl₄. All specimens in which (diffusing) additives were observed were cleaned by dissolving in tetrahydrofuran, reprecipitating with methanol, and drying in vacuo for 24 hr or more. In no case could any diffusing species be detected after this treatment. A list of the rubber samples used is given in Table I.

Ten paraffin hydrocarbons, in the range from *n*-octane to *n*-hexatriacontane, were obtained from K & K Labs (ICN Pharmaceuticals Co.). Solutions were prepared by mixing requisite amounts (by weight) of rubber and diluent directly in 7-mm O.D. NMR sample tubes. Homogeneity was attained by moderate heating (near 80°C) and occasional mechanical agitation. For low-molecular-weight diluent samples, the temperature was kept near 60°C, for times no longer than 24 hr, to minimize the escape of evaporating diluent through the temporary seal (final concentrations were derived after correction for loss of diluent weight). In preparations containing high-molecular-weight diluents, any gross concentration inhomogeneities could easily be detected at temperatures well above the melting point of the diluent, through the presence of a wide distribution of the

TABLE I
Characteristics of Undiluted Polymers Used in This Study

Polymer	Source ^a	Code	ρ (25°C)	Details
PI- <i>cis</i>	GTR	Natsyn 2200	0.91	—
SBR	BFG	Ameripol 1513	0.963	40 wt. % styrene; C:T:V = 11:69:20
NR	—	SMR 5	0.91	—
PB- <i>cis</i>	FTR	45 NF	0.89	high <i>cis</i>
EPT	Enjay	3509	0.86	ethylene-propylene terpolymer
PIB	PCL	Polysar Butyl 100	0.92	0.6–1.0 mole % unsaturation
SBS	S	Kraton 1102	0.94	23% styrene-butadiene- styrene triblock
SIS	Univ. Akron	(expt.)	0.98	styrene-isoprene-styrene triblock

^a BFG: B. F. Goodrich Co.; Enjay: Enjay Chemical Co., Div. of Humble Oil Corp.; FTR: Firestone Tire & Rubber Co.; GTR: Goodyear Tire & Rubber Co.; PCL: Polymer Corp. Ltd. (Canada); S: Shell Oil Corporation.

measured diffusion coefficients. Samples were therefore annealed for times up to three weeks, several times as long as needed to remove any detectable inhomogeneity. Because of the enhanced sensitivity of the spin echo methods to trace amounts of rapidly diffusing diluents, it seemed advisable to avoid accelerating the homogenization by introducing (and later evacuating) a light swelling agent.³

Experiments were conducted at 51°C, the lowest temperature at which a diluent spin echo for hexatriacontane-containing samples could be measured to the needed precision, consistent with an echo delay long enough for the necessary gradient pulses. This temperature is below the melting points of the pure hydrocarbons with molecular weights of tetracosane or greater; no effects observed in our experiments could be attributed to this fact.

Diffusion Measurements

The theory and practice of pulsed field gradient spin echo diffusion measurements have been described^{8,9} as have our equipment and methods.¹¹ Briefly, the (proton) NMR spin echo following a 90° - τ - 180° rf pulse sequence is attenuated from amplitude A_0 to A through the application of a small constant field gradient G_0 and two field gradient pulses of magnitude G and duration $\delta < \tau$, each starting at time t_1 after an rf pulse. If a very slowly diffusing or nondiffusing species is also present and accounts for a fraction h of the echo height, then⁹

$$A/A_0 = h + (1 - h) \exp(-\gamma^2 D x) \quad (1)$$

where γ is the nuclear gyromagnetic ratio,

$$x = \delta^2 \left(\tau - \frac{1}{3} \delta \right) G^2 - \delta \left[(t_1^2 + t_2^2) + \delta(t_1 + t_2) + \frac{2}{3} \delta^2 - 2\tau^2 \right] G G_0 + \frac{2}{3} \tau^3 G_0^2$$

and

$$t_2 = \tau - t_1 - \delta$$

In our experiment, $G_0 \approx 1$ gauss/cm, and G varied from 50 to 300 gauss/cm. The unattenuatable echo fraction h arises from the host polymer, particularly at high temperatures or diluent concentrations, when segmental mobility is increased without giving rise to diffusion.

We have developed a batch computer program which accepts our data ($A \pm \Delta A$ at various δ) and performs a least-squares fit of eq. (1) in logarithmic form, yielding h and the diffusion constant D together with their uncertainties.¹³ The intercept of a plot of $\ln(A/A_0)$ versus x should be zero, but was always initially left free to adjust together with h and D to provide a check of the applicability of eq. (1). With samples prepared to exhibit two or more distinct nonzero diffusion constants, a finite intercept is produced even when the quality of the fit is otherwise still satisfactory. In this work, no significant intercept was ever generated; the final values of D and h in all cases are derived by the program from a two-parameter fit without adjustable intercept. The use of our eq. (1) represents a refinement of the usual method of interpretation, which often ignores terms in G_0 (i.e., the last two terms in x) for ratios G/G_0 not even as large as ours.

In this two-parameter fit, D and h are uniquely determined within their

uncertainties; they characterize a single sample at its equilibrium diluent concentration and temperature and are reproducible in similar samples at equal temperatures. This type of experiment measures diffusion in the laboratory reference frame (here equivalent to the polymer-fixed frame, since no polymer diffusion takes place, see below) and along one axis (whose orientation is variable but unimportant here). During one set of measurements of A versus δ , the characteristic diffusion time, $\tau - (\delta/3)$, does not change appreciably since typically $\tau = 25$ msec and $\delta < 10$ msec. As in earlier work,¹¹ we found no variation of D in explicit tests of its dependence on diffusion time and thus confirmed the absence of significant barriers to diffusion with spacings below at least $8 \mu\text{m}$.

The unattenuatable fraction h of the spin echo falls in the expected way with increasing diluent content, but also depends on the T_2 relaxation times of both host rubber and diluent in a complex way and is not useful in our analysis. There was in no case any distortion of our results by diffusion of polymer host molecules even at our highest diluent concentrations (≤ 50 vol. %). The initially adjustable intercept in fitting eq. (1) to the data was designed to detect this; our earlier experience with oil-extended *cis*-polyisoprene¹¹ shows that polymer diffusion tends to be unobservable below about 100°C . Moreover, any significant polymer diffusion would have become obvious during the search for diffusing additives remaining in the highly CCl_4 -swelled rubbers after cleaning (see above).

Much of the present work was performed under adverse signal-to-noise conditions of the spin echo signal. To increase the speed and precision of the data taking, a microcomputer was attached to the spectrometer to provide signal averaging of those echoes which were deemed (by a programmed set of criteria) to satisfy certain stability and reliability requirements.⁹ Because of the strong dependence of the echo height as well as the diffusion rate on temperature, the computer also monitors sample temperature and rejects data during temperature excursions, typically after a series of large, long gradient pulses. The computerization of this experiment is described elsewhere.¹³

RESULTS AND DISCUSSION

General Considerations

In order to obtain a complete and self-consistent free volume interpretation of diluent diffusion, temperature as well as diluent concentration dependences should be measured. The former is described by the expression of Williams, Landel, and Ferry,¹⁴ which for diffusion takes the form

$$\ln \frac{D}{D_s} = \frac{c_1(T - T_s)}{c_2 + (T - T_s)} \quad (2)$$

where s refers to a reference temperature T_s to be chosen. The temperature dependence of D_{dil} for a particular diluent concentration in a rubber is then interpreted by fitting it with eq. (2), where c_1 , c_2 , and D_s must generally all be adjusted. Of particular interest is c_1 , identified with B_d/F_0 , the ratio of minimum relative vacancy size to fractional free volume of the sample at T_s . Determination of c_1 for at least two diluents, at several diluent concentrations, can then be combined with complementary information from the concentration dependences to yield fractional free volumes for the rubber and each of the diluents as well as B_d .

We have studied several such temperature dependences between 20° (or higher if the spin echo signal strength was not sufficient) and about 100°C (or less, to prevent possible sample degradation) and find that each set of data is described by eq. (2). However, simultaneous optimization of three parameters, particularly the combination c_1 and c_2 , makes high demands on experimental precision, since c_2 is entirely determined by the very small curvature in a plot of $\ln D$ versus T^{-1} . Since all three parameters affect the intercept, they are inextricably coupled, leading to a propagation of the large c_2 uncertainties to c_1 and D_s . In the case of hexadecane diffusion in SBR, we find that c_1 and c_2 can be determined only to within $\pm 50\%$ and $\pm 40\%$, respectively, unless additional assumptions or estimates for free volume parameters are introduced (this dilemma is also described in our previous work¹¹). The need for extraneous estimates sharply reduces the usefulness of the temperature dependence, since these can be introduced into the more useful concentration dependences directly. This consideration, together with the diminishing applicability¹⁴ of eq. (2) so far above the glass transition temperatures of some of our rubbers, led us to abandon the temperature studies and thus the attempt at a completely autonomous free volume characterization of our systems. It will be seen, however, that the introduction of reliable literature values for the fractional free volumes of two rubbers (of uncertainty no larger than 2% each) into the interpretation of the concentration dependences permits us to estimate free volume fractions for each paraffin. Instead of the temperature dependence, we then use the comparison of paraffin diffusion in the two rubbers to assess B_d , but are only able to obtain the ratio of B_d in the two rubbers. Thus, our final paraffin free volumes must utilize an extraneous scaling of B_d , chosen consistent with published values for both rubbers containing similar hydrocarbons.

The results of our interpretation are at first given with only the uncertainties propagated from our measurements, ignoring any contributions from uncertainties in the parameters from the literature. Reasonable upper limits on these are then included in the final values for the diluent free volumes.

Concentration Dependence

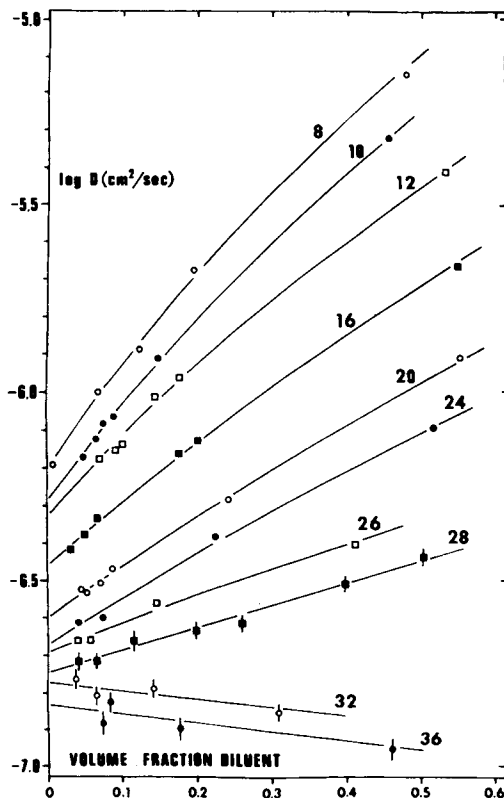
Two rubbers, synthetic *cis*-polyisoprene (Goodyear Natsyn 2200) and 40% styrene SBR (Goodrich Ameripol 1513) were selected for a study of the concentration dependence of hydrocarbon diffusion. Between four and eight samples of each rubber-diluent combination were prepared; their diluent volume fractions v_1 were computed given the weights and densities and assuming volume additivity. The region of interest was to be $v_1 \leq 0.5$. The results of the measurements are shown in Figures 1(a) and 1(b), respectively.

The free volume model may be applied to each rubber-diluent combination. The Fujita-Doolittle expression⁷ may be written in the form

$$\log D = \log D_0(T) + \frac{1}{2.303} \left(\frac{B_d s v_1}{1 + s f_0(T) v_1} \right) \quad (3)$$

where

$$s = \frac{\gamma(T) - f_0(T)}{f_0^2(T)}$$



(a)

Fig. 1. Concentration dependence of the diffusion of ten linear hydrocarbons in (a) cleaned Natsyn 2200 (*cis*-polyisoprene) and (b) cleaned Ameripol 1513 SBR at 51°C. Each symbol represents an average of several measurements. Numbers refer to hydrocarbon length: 8 = octane, etc. Solid lines represent fits of Fujita-Doolittle expression, eq. (2) in text, to data; results are given in Table II.

D_0 is the diffusion coefficient at zero diluent content and will depend on both polymer and diluent as well as temperature. The free volume fraction of the undiluted polymer is f_0 , which depends on temperature but not on the diluent species, and γ is the free volume fraction of the diluent, which should be independent of the polymer species being diluted. B_d relates the size of the diffusing molecule to the minimum vacancy size permitting a displacement and is generally assumed to be unity⁷ in the absence of an independent measurement.

An inspection of eq. (3) shows that $B_d s / 2.303$ is the slope of a plot of $\log D$ versus v_1 for low values of v_1 . Since both f_0 and γ are less than about 0.2 (see below), this approximation is a good guide for a first examination of Figure 1 over the entire range. We believe ours to be the first direct observation of a concentration dependence with a negative s value, indicating that dotriacontane and hexatriacontane (and probably octacosane in SBR) have smaller free volumes than their polymer hosts at this temperature.

In order to determine the free volume parameters, a nonlinear least-squares curve-fitting program¹⁵ was used to fit eq. (3) in its exact form to each concen-

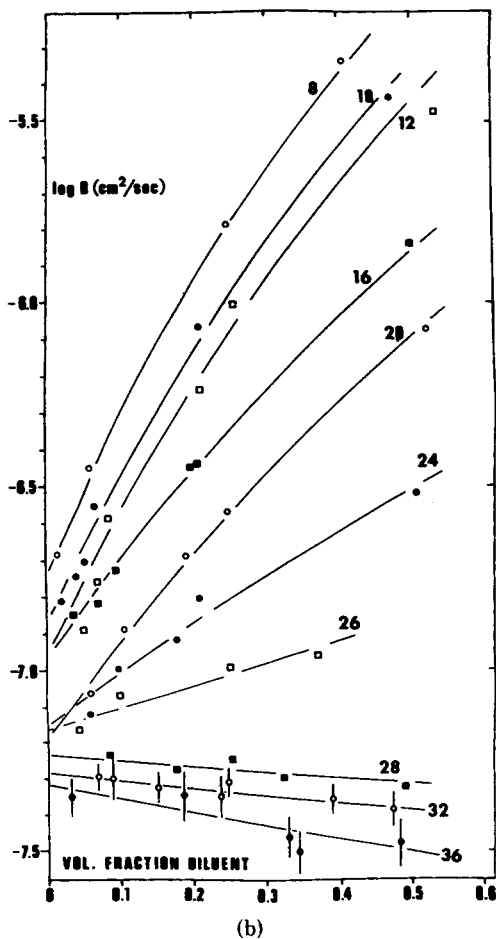


Fig. 1. (Continued from previous page.)

tration dependence separately, setting $B_d = 1$ and requiring that f_0 be identical among all series for a given rubber. By operating directly on the $\log D$ -versus- v_1 data, this fitting procedure eliminates the usual data transformations such as replotting $1/\log(D/D_0)$ versus $1/v_1$ with different D_0 until a linear plot is obtained^{7,10} and is superior to it in that the uncertainties in the diffusion data, including unequal uncertainties, are properly accounted for, and that the optimal values of the adjustable parameters (here $\log D_0$, s , and f_0) are determined by the program together with their uncertainties. Also, the statistical goodness of the fit is evaluated during its final stage.

The fits obtained are satisfactory but are rather insensitive to the exact values of f_0 . We obtain $f_0(51^\circ\text{C}) = 0.12 \pm 0.05$ for isoprene and 0.13 ± 0.06 for SBR, creating large corresponding uncertainties in γ after substitution into s (which is determined quite precisely). This difficulty was also found in earlier work by us¹¹ and stems from the fact that f_0 is determined entirely by the curvature in the data in Figure 1, this being either essentially absent or nearly obscured by the scatter in much of the data. Therefore, useful determinations of γ must rely on the availability of independent estimates for f_0 . Using measured or in-

terpolated free volumes,⁴ glass transition temperatures,^{16,17} and expansivities,^{16,18} we estimate⁷ $f_0(51^\circ\text{C}) = 0.085$ for Natsyn 2200 and 0.089 for Ameripol 1513. With these values, two-parameter fits for $\log D_0$ and s (and hence γ) were performed and are satisfactory in their chi-square measure of goodness. The fitted curves are shown in Figure 1, and the optimal values of $\log D_0$ and γ are listed in Table II, still assuming $B_d = 1$.

Because measurements below $v_1 = 0.05$ were generally performed, the zero-concentration extrapolations D_0 are derived with high precision, even where f_0 (and B_d) are separately ill defined: the fit reproduces the intercept, slope, and curvature of the data, but the coupling of s , f_0 (and B_d) in eq. (3) prevents their unambiguous separation—this is reflected in the resulting large uncertainties. The insensitivity of D_0 to the exact values of these other parameters was later exploited in work with other rubbers (see section on variation with host rubber), where only rough estimates of f_0 were available to be used in obtaining D_0 with a similar fitting procedure.

In comparing the results for $\gamma(51^\circ)$ in *cis*-polyisoprene and SBR, close agreement is observed for tetracosane to hexatriacontane, but increasingly significant disagreement exists for the lower molecular weight diluents. There is no combination of f_0 values for the two rubbers which produces agreement in γ values over the entire range. Since the fit quality with the estimated f_0 is superior to that of the trials with less plausible f_0 combinations, we accept the former as definitive. Given the perfect mutual solubility of our systems, no compatibility-related free volume enhancements can be invoked as explanation of the differences between columns 3 and 5 in Table II.

The principal remaining source of disturbance is our assumption that $B_d = 1$ in all cases. It may be safely assumed merely⁶ that in a given rubber, B_d is identical for a series of chemically similar diluents, as here. The limitations of our data once again did not permit separate B_d values for each rubber to be determined. However, we find that good agreement between the two sets of γ values is obtained if B_d in SBR is postulated to be larger than in our *cis*-poly-

TABLE II
Diffusion Parameters of Hydrocarbon Diluents in Two Rubbers at 51°C

No. of C atoms in diluent molecule	M_{dil}	<i>cis</i> -Polyisoprene ^a (51°C)		40% styrene-butadiene ^b (51°C)	
		γ_{dil}	$\log D_0$	γ_{dil}	$\log D_0$
8 ^c	114.2	0.132 ± 0.002	-6.20 ± 0.01	0.162 ± 0.003	-6.73 ± 0.02
10	142.3	0.128	-6.28	0.158	-6.88
12	170.3	0.119	-6.32	0.157	-6.96
16	226.5	0.115	-6.47	0.132	-6.97
20	282.6	0.109	-6.59	0.132	-7.19 ± 0.03
24	338.7	0.106	-6.67	0.109	-7.14
26	366.7	0.097 ± 0.003	-6.70	0.095 ± 0.004	-7.16
28	394.8	0.096	-6.75 ± 0.015	0.083	-7.23
32	450.9	0.082 ± 0.004	-6.77 ± 0.02	0.082	-7.28 ± 0.04
36	507.0	0.081	-6.83 ± 0.04	0.079 ± 0.005	-7.32 ± 0.05

^a Goodyear Natsyn 2200; undiluted free volume fraction estimated $f_0(51^\circ\text{C}) = 0.085$, $B_d = 1$ assumed.

^b B. F. Goodrich Ameripol 1513; estimated $f_0(51^\circ\text{C}) = 0.089$, $B_d = 1$ assumed.

^c *n*-Octane, for example.

isoprene by a factor

$$\frac{B_d(\text{paraffins in SBR})}{B_d(\text{paraffins in PI})} = 1.5 \pm 0.1 \quad (4)$$

In other words, assuming $B_d(\text{PI}) = 0.67$ instead of 1.0 changes column 3 in Table II so as to reproduce column 5 within the combined experimental errors, provided $B_d(\text{SBR})$ is still assumed to be unity; absolute magnitudes of the B_d , and hence the γ , could not be determined. Inclusion of $B_d \neq 1$ in the fitted eq. (3) produces no discernible differences in the appearance or quality of the fits, the principal effect being a tradeoff between s and B_d in the numerator of eq. (3).

If γ for hexadecane is as large as 0.22, reported¹ for 40°C, the value of $B_d(\text{PI})$ must be an unreasonably small 0.3 to obtain agreement with our data. However, our value for the B_d ratio is in good agreement with the suggestion of Chen and Ferry² that B_d for 23% styrene-butadiene rubber is approximately unity, whereas for natural rubber, close in its properties to Natsyn 2200, B_d is abnormally small, near 0.64. We therefore propose that $B_d(\text{paraffins in Ameripol 1513}) = 1$, $B_d(\text{paraffins in Natsyn 2200}) = 0.67 \pm 0.05$ is the appropriate combination for the interpretation of our data. To obtain the best values for the diluent free volume fractions, the PI and SBR fit results using these B_d values were averaged for each diluent. The free volume v_f per mole of diluent is given by $v_f = \gamma M / \rho$, ρ being the diluent (liquid) density at 51°C. Table III gives a list of these results. As expected, v_f initially rises linearly as a function of the number of carbon atoms per molecule but reaches a plateau after about 20 carbons, in accord with other deductions of the nature of segmental mobility.¹⁹ An extrapolation of the initial linear region suggests that about 7 cm³ free volume per mole is associated with each diluent chain end in addition to about 1.5 cm³ free volume per mole for each carbon below about 24.

In an effort to describe the additional uncertainties in the paraffin free volumes of Table III arising from errors in the literature values used in the analysis, reasonable upper limits on these errors were estimated as follows: $f_0(\text{PI}) = 0.085 \pm 0.002$, $f_0(\text{SBR}) = 0.089 \pm 0.002$, $B_d(\text{SBR}) = 1.0 \pm 0.1$ [and hence $B_d(\text{PI}) = 0.67 \pm 0.2$]. Given the complexity of our analysis, it proved convenient to repeat the fitting procedure several times, with parameters randomly incremented or decremented by their assigned error limits. The spread in the paraffin free

TABLE III
Free Volumes in Hydrocarbons at 51°C

No. of C atoms per paraffin molecule	Molar free volume, cm ³ /mole
8 (<i>n</i> -octane)	25.7 ± 0.5 ^a
10	29.4 ± 0.6
12	31.8 ± 0.7
16	38.4 ± 0.9
20	44.7 ± 1.1
24	49.1 ± 1.3
26	47.2 ± 1.4
28	47.6 ± 2.0
32	45.3 ± 2.3
36	50.1 ± 3.2

^a Uncertainties reflect only our experimental error. About ±6 cm³/mole should be added to include effects of probable imprecision in $f_0(\text{PI})$, $f_0(\text{SBR})$, and B_d scaling factor.

volumes obtained in this way was roughly independent of molecular weight and suggests an addition of about $6 \text{ cm}^3/\text{mole}$ to the purely internal uncertainties of column 3. From the standpoint of inner consistency, these additional errors are systematic and do not obscure the trends of the results, but the larger total uncertainties apply to any comparison with results of other work; we are unaware of directly comparable measurements.

Molecular Weight Dependence

The friction coefficients for internal translational motion $\zeta_1 = kT/D$ for three paraffin hydrocarbons in several types of rubber have been found to be approximately proportional to the molecular weight of the hydrocarbons.⁶ The interpretation is simplified if the diluent concentration is kept very small; in our case, the zero-concentration extrapolations D_0 can be used; $\zeta_0 \equiv \zeta_1(v_1 \rightarrow 0) = kT/D_0$. To test this proportionality, the data of the previous section is therefore plotted in the form $\log \zeta_0$ versus $\log M_{\text{dil}}$, and shown in Figure 2. We have also measured diffusion of biphenyl in the same hosts and determined D_0 as described above; it is seen that in both rubbers biphenyl diffusion proceeds somewhat more slowly than for paraffins of comparable molecular weight, a familiar effect³ expected on the basis of the less favorable geometric aspect ratio of the biphenyl molecule.

In the *cis*-polyisoprene, a least-squares fit of a straight line to the paraffin data is successful, yielding a slope of 1.02 ± 0.02 , consistent with a proportionality of ζ_0 to M_{dil} . In the SBR, where the data have higher uncertainties, a similarly good fit shows that diffusion proceeds more slowly by a factor of approximately 3 and displays a slightly less pronounced molecular weight dependence, $\zeta_0 \propto M^{0.85 \pm 0.08}$. To the extent that this deviation from proportionality is significant,

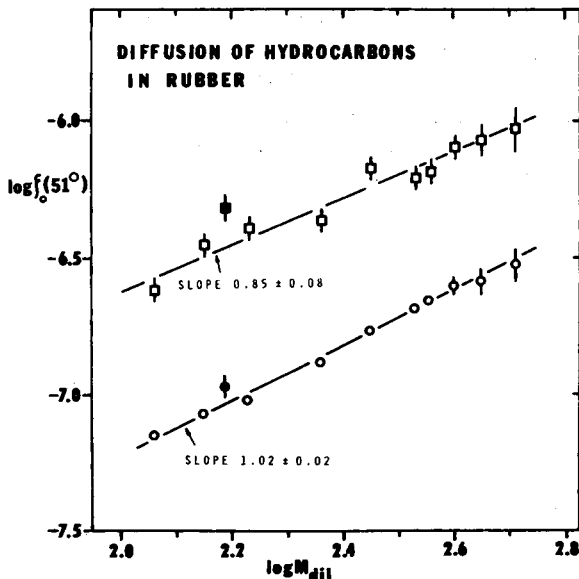


Fig. 2. Internal translational friction coefficients at infinite dilution of hydrocarbons in two rubbers. Lines are least-squares fits of straight lines to data. Solid symbols represent biphenyl diffusion and are not included in the fit: (\square) Ameripol 1513 SBR; (\circ) Natsyn 2200 PI.

it implies that some small chemical or geometrical incentive may exist for the diffusion of the heavier paraffins in SBR, in addition to effects captured explicitly by free volume parameters in eq. (3). It might be pointed out that this deviation from strict proportionality arises from data trends much more subtle than those producing the disagreement between columns 3 and 5 in Table II, so that these effects cannot be simply different aspects of the same systematic measurement or analysis error.

To examine the difference in diffusion coefficients of given penetrants in various rubbers, the use of the relation⁷

$$\log D = \log A_d - B_d/2.303F_0 \quad (5)$$

has been proposed²; A_d may be assumed to be relatively independent of the nature of the polymer. We may eliminate A_d by subtracting two such equations, one for each rubber, and taking the limit of zero diluent concentration. Thus,

$$2.303 [\log D_0(\text{PI}) - \log D_0(\text{SBR})] = \left(\frac{B_d}{f_0}\right)_{\text{SBR}} - \left(\frac{B_d}{f_0}\right)_{\text{PI}} \quad (5a)$$

The left side varies between 1.30 and 1.11 across the series of diluents. If we take note of the relative closeness of our estimated f_0 values, it is clear that B_d in SBR must be somewhat higher than in PI. We obtain agreement with our results in the previous section and with the results of Chen and Ferry²: Using our f_0 estimates and keeping $B_d(\text{SBR}) = 1$, we solve for $B_d(\text{PI}) = 0.8 \pm 0.1$, ignoring possible systematic errors.

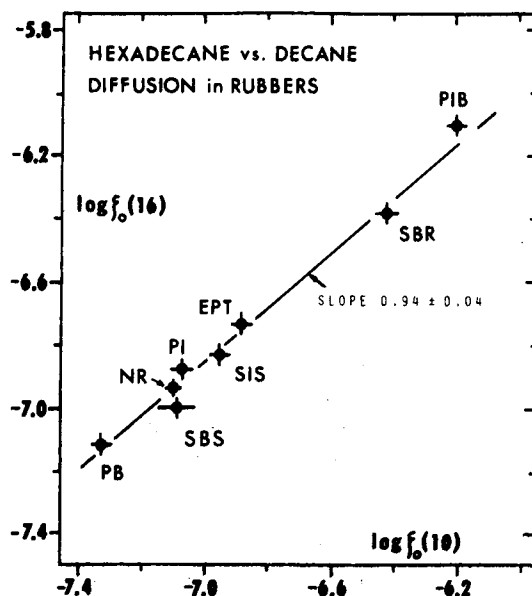


Fig. 3. Comparison of translational internal friction coefficients of hexadecane and decane in several rubbers. Abbreviations identify the rubbers in Table I.

Variation with Host Rubber

The free volume treatment of Fujita⁷ permits inferences about the relative efficiency of the diffusion mechanisms of two diluents by comparing their internal friction coefficients in different rubbers at equal temperatures.^{3,6} It was shown³ that

$$\log \zeta_1^\beta = (B_\alpha^\beta/B_\alpha^\alpha) \log \zeta_1^\alpha + K(\alpha, \beta) \quad (6)$$

where α and β refer to the diluents and K is independent of the polymers being diluted.

We prepared several concentrations of decane and hexadecane in each of eight rubbers described in Table I, measured the diluent diffusion coefficients at 51°C, and extrapolated these to zero diluent concentration as described earlier. Figure 3 shows this comparison. The scatter in the data and the relatively small range of friction coefficients encountered combine to limit the precision of the slope determination but yield a slope, i.e., the ratio of B_d for the diluents, consistent with unity, as expected for very similar diluents. Hexadecane diffuses more slowly than decane in these rubbers by a factor of 1.42 ± 0.16 , roughly the square of the factor determined at 25°C in comparing dodecane and hexadecane diffusion.³ The identity of B_d within the paraffin series, assumed in the section on concentration dependence, seems to be well established now.^{3,6}

It may be noted that while a plot like Figure 3 cannot give information about the magnitudes of B_d through its slope, the relative position along the line, combined with independent knowledge of f_0 , provides correlations. For example, both PI and natural rubber are found among polymers whose f_0 are generally estimated well above 0.12 at 51°C, pointing again to a relatively low B_d for *cis*-polyisoprene.

CONCLUDING REMARKS

The free volume model has been successful in explaining all major features of our data, although not all of its parameters could be independently determined by this experiment. It is now evident that concentration dependences of diluent diffusion can in practice only yield reliable f_0 values when γ and f_0 values differ by amounts greater than they do here in most cases.^{10,11} Moreover, inspection of eq. (3) shows that independent determinations of f_0 and B_d using a single concentration dependence are impossible in principle since s , f_0 , and B_d are not linearly independent of each other in eq. (3). These limitations are, of course, not confined to pulsed gradient NMR diffusion measurements.

Application of the pulsed gradient method posed some practical difficulties here, mainly related to the low signal-to-noise ratio with high molecular weight diluents. For practical reasons associated with the width of the unnarrowed echo we were not able to approach our previous lowest value¹¹ $D_{\min} \approx 3 \times 10^{-9}$ cm²/sec in spite of a substantially lowered minimum acceptable signal-to-noise ratio per echo.¹³

Our determination of the free volume parameters has a satisfying consistency, particularly evidenced by the deduction of the abnormally low B_d for *cis*-polyisoprene by two unconnected sets of evidence found by comparison with SBR: the inconsistencies of diluent γ values when B_d is assumed the same and the large differences in D_0 values with equal diluents. The possibility of either an increase

or a diminution of total free volume by adding diluents to polymers is predicted by the theory. We have observed a continuous transition between these two regimes, governed by the diluent molecular weight. The measured γ depend on M_{dil} in the expected way with respect to chain-end contribution and effective segment length.

A most basic assumption of the free volume theory is the additivity of free volume in multicomponent systems. This assumption is subject to a sensitive experimental test by diffusion measurements in, for example, a polymer diluted with a mixture of two penetrants, provided the free volumes of the components are known. Such a study is presently being undertaken. Explorations of the effects of crosslinking, partial crystallinity, and an approaching glass transition are in progress using similar techniques.

The authors wish to thank Professor L. J. Fetters and Professor A. N. Gent for supplying the rubber specimens, and the latter for several enlightening discussions and his critical reading of the manuscript. Professor C. W. Wilson III contributed several valuable suggestions. R. D. Burgan was instrumental in developing hardware and some software in the computerization of this experiment. The support of the Faculty Research Committee of the University of Akron under Grant No. RG 559 is gratefully acknowledged.

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Received August 4, 1978

Revised October 13, 1978