Pulsed-Field Gradient NMR Measurements of Diffusion of Oil in Rubber

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Synopsis

The pulsed-gradient NMR method of Stejskal and Tanner was used to measure the diffusion of oil in synthetic *cis*-polyisoprene. The diffusion encounters no barriers with spacings at least up to several μm and generally displays free-volume behavior, obeying the WLF temperature dependence between $-10°$ and $+130°$C, and the Fujita-Doolittle concentration dependence between 10 and 90 vol-% oil.

INTRODUCTION

Studies of the microscopic distribution and diffusion kinetics of diluents in polymers[1-7] have been largely confined to model systems and low (or single) molecular weight liquids; commercially important oil-extended rubbers may have seemed forbidding because of their complexities or the low diffusion constants encountered. This study was undertaken to approach this subject more closely; a simple synthetic *cis*-polyisoprene similar to natural rubber and a low- to medium-viscosity oil used in a commercial oil-extended rubber were selected. Of particular interest are the temperature and concentration dependences of the diffusion constant of the oil in rubber, so as to test the applicability of free-volume theories of diffusion. Also, systematic spatial barriers to diffusion, if detected, could give clues to possible aggregation of oil in preferred locations.

An early use of nuclear magnetic resonance (NMR) spectroscopy to study diffusion of liquids in rubber was that of Woessner,[7] who used a constant magnetic-field gradient to study benzene diffusion in several rubbers. This method is limited to diffusion constants above about 10^{-7} cm^2/sec; Stejskal and Tanner[8] and Tanner[9] have described a pulsed-field gradient method which has since been used to study diffusion of diluents in polymers.[10] This method extends the lower limit of measurable values of diffusion constants D to about 10^{-9} cm^2/sec, a limit approached in this study. The precision and range of this method make it possible to cover considerable temperature and concentration ranges in the present system; this was necessary to apply the expression of Williams, Landel, and Ferry (WLF)[11] to the temperature dependence of D, and that of Doolittle[12] and Fujita[13] to the concentration dependence of D of oil in the rubber.

Stejskal and Tanner's method in its simpler form calls for the application of a $90°-\tau-180°$ rf pulse sequence, the echo of amplitude A_0 occurring at time 2τ. At all times, a constant magnetic-field gradient G_0 is permitted, but a pulsed-field gradient G $(G > G_0)$ of duration δ is added at $t = t_1$ after each rf pulse. With $G\delta > 0$, the echo amplitude at 2τ falls to A in a manner given by the following equation,[8,9] which holds for systems in which the resonant nuclei (here protons), of gyromagnetic ratio γ, encounter no barriers to their diffusion:

$$\ln \frac{A(2\tau)}{A_0} = -\gamma^2 D(B + x) \tag{1}$$

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where

$$B = \frac{2}{3}\,\tau^3 G_0^2$$

$$x = \delta^2 \left(\tau - \frac{1}{3}\delta\right)G^2 - \delta\left((t_1^2 + t_2^2) + \delta(t_1 + t_2) + \frac{2}{3}\delta^2 - 2\tau^2\right)GG_0\cos\theta$$

and

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

The angle θ between the directions of G and G_0 will be zero if both arise from a common source, i.e., a set of gradient coils. For convenience, the full form for x was used to reduce all data, even when $G_0 \ll G$.

EXPERIMENTAL

Samples

Starting materials were Natsyn 400 (Goodyear Corporation), an uncured synthetic cispolyisoprene (specific gravity 0.906 ± 0.007) containing approximately 2 wt-% additives such as antioxidants, and a light hydrocarbon oil of average molecular weight near 395, specific gravity 0.823 ± 0.005, and viscosity at 26°C of 2.0 ± 0.15 poises. These are used in the manufacture of Natsyn 450 (Goodyear Corporation), an approximately 30% oil extension of Natsyn 400, and itself a principal subject of this study. Additionally, ten other dilution ratios were prepared by intimately mixing Natsyn 400 and oil. The concentrations of oil in these samples were determined from the weights of rubber and oil before mixing and corrected for losses and for the presence of impurities, mainly antioxidants. For the effect of these impurities on the observed oil diffusion, see results section below. The corrected oil concentration in Natsyn 450 was (29 ± 3)% by volume. All samples, including pure oil, were sealed in 7 mm O.D. Pyrex NMR sample tubes and heated to 125°C for 20 hr.

To test for possible degradation, pulsed NMR spectra and diffusional echo attenuation before and after heat treatment were compared in each sample. In the few instances where differences were noticed, the sample was rejected. During diffusion measurements thereafter, samples were never exposed to temperatures above 100°C, except for oil and Natsyn 450. In these, up to five exposures to temperatures between 120° and 130°C during diffusion measurements produced no changes in any NMR or diffusion-related parameter; NMR and other evidence of degradation was not generally encountered until 145°C and above.

Equipment

A Spin-Lock, Ltd., Model CPS-2 33-MHz NMR pulse spectrometer was used to observe the spin echo after a 90°–τ–180° rf sequence. A Bruker Model BE 40Z 11 hd gradient compensator, mounted on the poles of the Varian 11-in. magnet, ensured the absence of unwanted static field-gradient components. The echo signal was stored in a Biomation Model 805 transient recorder whose output, after variable analog filtering, was displayed on an oscilloscope; the echo heights

A_0 and A (2τ) for events satisfying certain stability criteria[9] were directly.

Magnetic field gradient pulses were applied after a delay t_1 after each rf pulse for a duration δ which was digitally constant except for an additive correction applied to either pulse to offset the effects of power supply surge or drain on G. The field gradient attachment design by the "Institut Jošef Stefan" was adapted and modified to operate with from one to seven parallel stages of a transistor switch whose internal resistance governed the current through the gradient coils. The coils were wound on the cylindrical surface of the NMR probe's rf shield in the manner described by Zupančič and Pirš.[14] In addition to an adjustable constant gradient G_0, typically near 1 G/cm, these coils produced pulsed gradients G between ca. 76 and 320 G/cm for periods up to 15 msec. Values of G were calibrated in each of three ways: from first principles with corrections for induced magnetic image[14] and eddy current effects, through the use of substances with known D values, and finally through a mapping of the spin echo time duration[15] as function of G_0 extrapolated to the coil current during the G pulses. Because of the prevalence of eddy current gradient pulse distortions at the shortest pulse widths, and the relative scarcity of substances of well-documented values of $D \simeq 10^{-7}$ cm^2/sec, of interest here, the third method was accepted as definitive, yielding uncertainties of 2% in G and 0.5% in G_0. Values of G were corrected for the temperature-dependent variation in coil resistance.

The gradient coil/rf probe assembly was mounted in a temperature-controlled (Varian V4540) air flow which also served to carry off the heat created by the gradient pulses. Sample temperature was monitored continuously with a calibrated thermistor installed near the rf coil, 8 mm from the center of the sample. Pulse sequence repetition rate was limited by gradient pulse-induced temperature drift rather than spin-lattice relaxation time. Below room temperature, the air flow was cooled and dehumidified by direct contact with solid CO_2.

Experiments

Two main types of experiment were performed. To test for barriers to diffusion, echo attenuation ratios were measured as function of the diffusion time $\tau - (\delta/3)$, varying τ. The majority of measurements involved determination of diffusion constants and their distribution, performed as function of gradient pulse length δ. A computer program was written to give least-squares fits of B and D in eq. (1) to requisite data. For cases where a second, essentially non-diffusing species was present, the program performed a fit of B, D, and f in the modified equation

$$\ln \frac{A(2\tau)}{A_0} = \ln \{(1 - f) \exp [-\gamma^2 D (B + x)] + f\} \qquad (2)$$

where f represents the fraction of echo height which cannot be attenuated with the magnitudes of $G\delta$ used in studying the fast-diffusing species. This fitting procedure proved to be much superior to the determination of D from the initial slope[9] of a plot of echo attenuation versus x. Least-squares fits of all other equations to data in this work were performed using a nonlinear metric minimization routine.[16]

The temperature range covered in this work, between $-10°$ and $130°$C, spans the entire useful range, being limited below by the shortness of the oil spin–spin

relaxation times T_2 combined with decreasing D values[9] and instability in the induced echo attenuation, and above, by possible sample degradation (see above under "Samples.").

RESULTS AND DISCUSSION

Natsyn 400

At a pulse separation $\tau = 25$ msec, a small liquid-related spin echo was observed, which was found to be at all temperatures of strength $(8 \pm 2)\%$ of the oil echo in a similar sample of Natsyn 450. This spurious echo also showed diffusional attenuation; its D was found to be within 20% of that of the oil in Natsyn 450 at all temperatures. It was suspected that this echo is due to the antioxidants, known to be similar to the oil in molecular weight. A specimen of Natsyn 400, cleaned twice by dissolving in benzene followed by reprecipitation in methanol, showed an impurity spin echo less than 4% of that before cleaning, confirming the hypothesis. The relative smallness of the impurity echo before cleaning, and the similarity of its attenuation to that of the oil in Natsyn 450, obviate a separate analysis or correction for it in the extended rubbers.

When CCl_4 was used to swell the cleaned rubber sample, a strong echo was observed, particularly at high temperatures, but it could not be attenuated conveniently. Swelling thus increases the segmental mobility, and hence T_2, of the rubber itself, an effect which should occur and was observed in Natsyn 450 as well, leaving a fraction of its total echo amplitude unattenuated.

Oil

The diffusional echo attenuation in this oil is well characterized at all temperatures by a single diffusion coefficient; Figure 1 includes typical data.

The temperature dependence of D, as shown in Figure 2, implies an average activation energy of self-diffusion $E_a \simeq 9.6$ kcal/mole but demonstrates a curvature characteristic of liquids above a glass transition temperature T_g. The expression of Williams, Landel, and Ferry[11] was fitted to the data:
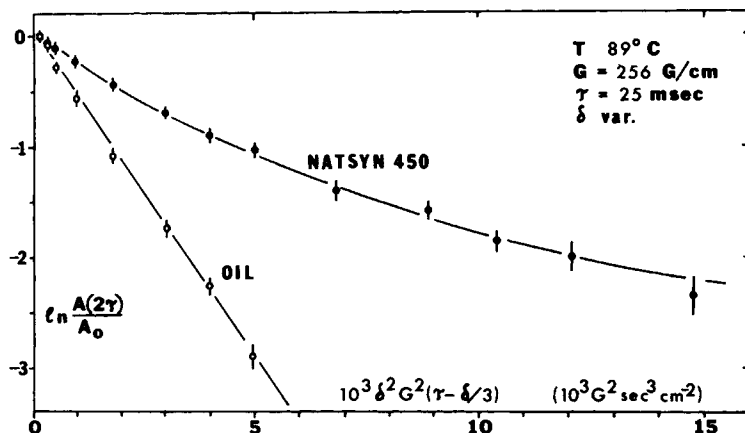

Fig. 1. NMR spin echo attenuation at increasing gradient pulse length δ. Data for oil is fitted (solid line) to eq. (1), and for Natsyn 450, to eq. (2) to isolate the oil diffusion. Abscissa closely approximates x in eqs. (1) and (2). $T = 89°C$; $G = 256$ G/cm; $\tau = 25$ msec; δ var.
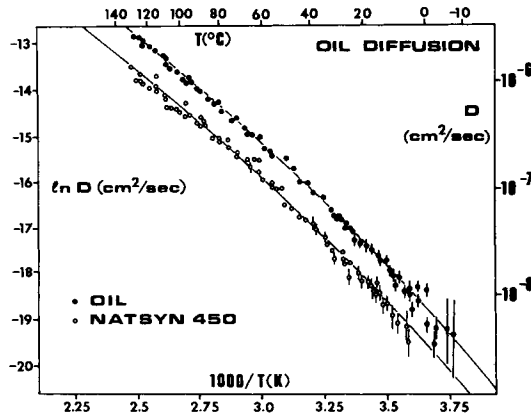
Fig. 2. Temperature dependence of oil diffusion in oil and rubber. Error bars are shown where they substantially exceed the size of the symbols. Lines represent fits of eq. (3) to data: (●) oil; (○) Natsyn 450.

$$\ln \frac{D}{D_g} = \frac{C_1(T - T_g)}{C_2 + (T - T_g)} \tag{3}$$

The four-parameter fit was satisfactory and yielded $T_g = (168.1 \pm 1)°$K and C_2 = $(51 \pm 4)°$K. However, adjustments in C_1 and $\ln D_g$ far above T_g have a very similar effect on the shape of the plot of $\ln D$ versus T^{-1} (Fig. 2), so that the values of C_1 and D_g are strongly correlated and could not be unambiguously separated in fitting our data. With a standard estimate[17] $C_1 = 40$, we obtain $D_g = (1.72 \pm 0.05) \times 10^{-20}$ cm^2/sec. (Taken separately, we could only determine $C_1 = 45 \pm 15$, with a large corresponding spread in D_g values.) The distant extrapolation to T_g and the decreasing reliability of the WLF equation above $T + 120°$ limit these parameter values, and similar ones found for Natsyn 450, to a semiquantitative significance.

Natsyn 450

At temperatures below about 56°C, the echo attenuation data follow eq. (1) closely, showing no distribution of oil diffusion coefficients. Explicit tests for restricted diffusion were made. Tanner[9] has shown that an adherence of echo attenuation versus x [in our eq. (1)] to a single exponential decrease for various τ values implies that the diffusion encounters no barriers with spacings comparable to the diffusion distance

$$R_{rms} = \{2D[\tau - (\delta/3)]\}^{1/2} \tag{4}$$

Given the data in Figure 3, with the appropriate $D = 1.0 \times 10^{-7}$ cm^2/sec at 56.5°C and the range of τ and δ shown, we conclude that any significant barriers, if present, must have spacings large compared with 0.8 μm. A similar experiment at 98°C extends this value to beyond 2 μm.

Above about 56°C the unattenuable fraction f of the echo height arising from the (nondiffusing) rubber became noticeable. All data above 50°C were therefore fit to eq. (2); f was found to rise gradually from 0 at 55°C to about 0.3 at 125°C. Figure 2 shows the temperature dependence of D attributed to the oil; rubber diffusion was not observed. Again, the departure from the Arrhenius relation is evident; a fit of eq. (3) to the data was satisfactory and gives $T_g = (173.9 \pm 1)°$K,
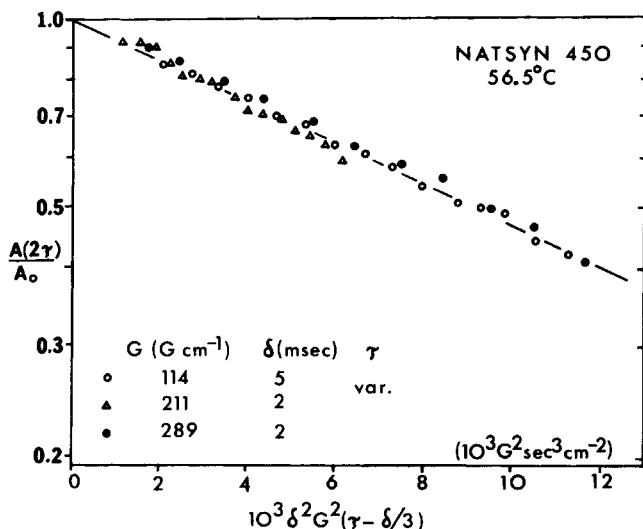
Fig. 3. Echo attenuation in Natsyn 450 as function of diffusion time $\tau - (\delta/3)$, for various gradients and pulse durations. Adherence to a single exponential decrease is evidence of absence of restricted diffusion. As in Figure 1, abscissa closely approximates x in eqs. (1) and (2).

$C_2 = (55 \pm 6)°K$. Again, C_1 and $\ln D_g$ are nearly degenerate fit variables. With the best available estimate, $C_1 = 38.7$ (hevea rubber), we obtain $D_g = (3.1 \pm 0.2) \times 10^{-20}$ cm^2/sec; we note that our C_2 value is also consistent with those found in hevea and similar rubbers[18].

With the standard $T_g = 200°K$ for cis-polyisoprene, the T_g for the oil as found above and estimates of certain free-volume parameters as determined below, a value of T_g for the extended rubber was calculated[17] some 10° above the value inferred from measurement. This disagreement may be due to the unreliability of the temperature extrapolations in obtaining T_g for both the oil and the solution, suggesting that their difference is actually larger than found here.

Concentration Dependence

The diffusion constants of oil in ten samples of oil-mixed Natsyn 400 are shown in Figure 4 at three temperatures as function of v_1, the volume fraction of oil; values for pure oil are also shown. In a similar study of benzene diffusion in polyisobutylene,[10] the theory of Fujita and Doolittle[12,13] was found to apply. In the notation of Fujita,[13]

$$\ln \frac{D}{D_0} = B_d \left\{ f(0,T) \left(1 + \frac{f(0,T)}{(\gamma(T) - f(0,T))v_1} \right)^{-1} \right\} \qquad (5)$$

where D_0 represents D in the limit of zero diluent concentration, B_d relates to the limiting vacancy size for diffusion, and $f(0,T)$ and $\gamma(T)$ are the free-volume fractions in the pure polymer and the diluent, respectively.

Equation (5), in its full nonlinear form, was first fitted[16] to all data in Figure 4, but deviations from the best-fit curves were statistically detected above $v_1 = 0.9$, particularly at 28°C. Similar, larger divergences were noted in polyisobutylene-benzene[10] and attributed to the existence of microscopic concentration inhomogeneities at high v_1, causing D to be dominated by small oil-rich regions. (It should be pointed out that no distribution of D values was observed in any
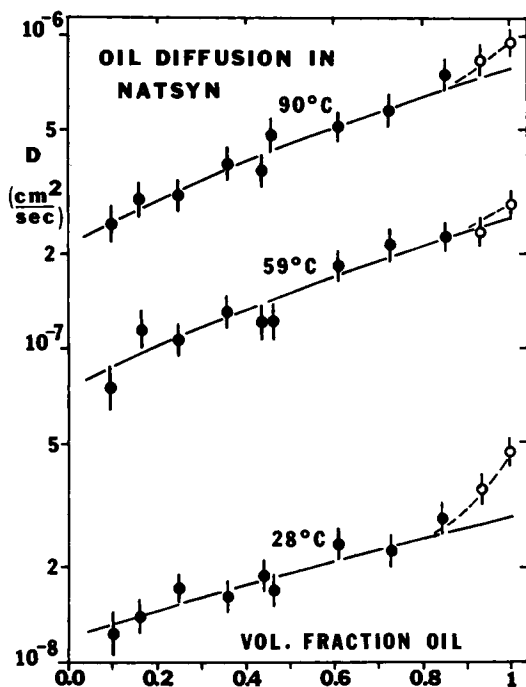
Fig. 4. Concentration dependence of oil diffusion in oil–Natsyn 400 solution. Solid lines represent fits of eq. (5) to data below $v_1 = 0.9$ (solid symbols). Dashed lines suggest deviations from free-volume behavior.

of our samples, eliminating the possibility of macroscopic inhomogeneity.) Since the causes and concentration domain of this deviation should not differ greatly in the present system, the data were refitted omitting points above $v_1 = 0.9$. The resulting best fits now have satisfactory chi-square measures of goodness; these curves are shown in Figure 4 together with suggested upward deviations above $v_1 = 0.9$.

In these fits, B_d was assumed[10,13] to have the value unity, the values of D_0, $f(0,T)$ and $\gamma(T)$ being adjusted. However, the uncertainties in the determination of the last two quantities were found to be large. This difficulty was traced to the smallness of the curvatures of the best-fit lines in Figure 4, as compared to the experimental uncertainties in D: analysis of eq. (5) shows that a separate determination of $f(0,T)$ and $\gamma(T)$ depends on these nearly obscured downward concavities below $v_1 = 0.9$, whereas the quantity $[\gamma(T) - f(0,T)]/[f(0,T)]^2$, approximating the slope of $\ln D$ versus v_1, can, of course, be much more precisely determined. These values, as well as those of $\ln D_0$, are shown in Table I. The only useful separate determination of both free-volume fractions was possible at 90°C: $f(0, 90°C) = 0.16 \pm 0.06$, yielding $\gamma(90°C) = 0.20 \pm 0.09$, but with $\gamma > f(0)$ (as in other systems[1,2,10]), as dictated by the positive slope. These values are easily reproduced within their large uncertainties by a free-volume-based calculation[13] using our measurements, or estimates, for T_g and thermal expansivities for oil and rubber separately. Furthermore, at all three temperatures, the "slope" parameter (column 3 in Table I) is closely approximated using the free volumes calculated in this way.

TABLE I
Diffusion and Free-Volume Parameters[a] for Oil in Natsyn 400

T, °C	$\ln D_0$	$\dfrac{\gamma(T) - f(0,T)}{[f(0,T)]^2}$	$f(0,T)$
28	-18.22 ± 0.01	0.96 ± 0.03	[b]
59	-16.40 ± 0.01	1.53 ± 0.02	[b]
90	-15.35 ± 0.01	1.67 ± 0.01	0.16 ± 0.06

[a] B_d was assigned a value of 1.0.
[b] No meaningful determination was possible.

CONCLUSIONS

To our knowledge, the molecular weight of our diluent is higher and its diffusion constant an order of magnitude lower than for any other pulsed-gradient investigation of a polymer–diluent system. The similarity of the temperature dependences of the oil diffusion in rubber with its self-diffusion is striking. Our system is relatively simple in that no distribution of D values or barriers to diffusion were observed.

Our temperature range is well above T_g or the temperature ($\simeq T_g + 20°C$) where according to WLF[11] some effects of a glass transition will be evident on the time scale of our experiment (~25 msec). From the temperature dependence of D we tentatively infer a T_g for oil about 30°C lower than the reference value for our rubber; the T_g value measured in the mixture is only marginally higher—there is some doubt about its quantitative reliability. By far the most significant difference in the kinetics of oil motion between oil and Natsyn 450 is the decrease in D at equal temperatures by a factor of 2.17 ± 0.05 over the 140°C range measured. Figure 4 suggests that this factor would be even smaller if there were no deviations from free-volume behavior at high v_1.

In contrast with the results of other work[1,2] (by other methods) far above T_g in analogous solutions, the present system displays a comparatively weak concentration dependence of the diffusional activation energy: when computed between the 28° and 90°C data, the activation energy rises from 7.6 ± 0.5 kcal/mole at $v_1 = 0.1$ to 10.8 ± 0.4 kcal/mole at $v_1 = 0.8$, decreasing slightly to 9.8 ± 0.4 kcal/mole at $v_1 = 1$ (oil self-diffusion). Slight evidence for diffusion of the host polymer chain segments was found only above 120°C ($\simeq T_g + 220°C$).

The magnitude of the diffusion constant at 25°C ($\log D \simeq -7.92$, extrapolated to infinite dilution of the oil, number-average molecular weight 395) is somewhat lower than that ($\log D \simeq -7.48$) in the comparable case of n-dotriacontane (molecular weight 448) diffusing in uncrosslinked natural rubber.[6] This negates a simple confirmation of the observed proportionality[2,3,6] of the translational friction coefficient to molecular size among similar diluents in a given type of rubber. Rather than reflecting significant differences in diluent–rubber compatibility or diluent molecular flexibility, this disagreement may be mainly due to the preferential weighting of our measured D values by the larger molecules in our wide-cut oil.

Some of the questions raised by this investigation are being explored further through measurements of the NMR relaxation times T_1, $T_{1\rho}$, and T_2. Explorations of the effects of a nearby glass transition, crystallinity, and crosslinking on diluent diffusion using the pulsed-gradient method are in progress.

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18. J. D. Ferry, *Viscoelastic Properties of Polymers,* 2nd ed., Wiley, New York, 1970, p. 316. Note that the use of natural logarithms in our eq. (3) necessitates multiplying the cited C_1 value by 2.303.