Diffusion of Radioactively Tagged Penetrants Through Rubbery Polymers. I. Penetrants with Very Low Solubility

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Synopsis

The diffusion of radioactively tagged n-hexadecane, 1,7-heptanediol, and ethylene glycol has been studied in one polar and six nonpolar rubbery polymers. The penetrant–polymer pairs included some in which the two components were miscible in all proportions and some in which they were nearly incompatible (solubility of penetrant in polymer of the order of 1%). The theory for the thin smear method for measuring the diffusion coefficient was evaluated for incompatible pairs with two cases: case 2, when the rate-limiting step is diffusion through the polymer; and case 3, when the rate-limiting step is entry into the polymer across the penetrant–polymer interface. They are easily distinguished experimentally from each other and from case 1, which refers to completely miscible pairs. In examples of case 3, e.g., ethylene glycol with butadiene or styrene–butadiene rubbers, the half-time for saturating the polymer surface in contact with the penetrant was found to be several days at 25°C. The diffusion coefficients, when compared in four hydrocarbon rubbers, of n-hexadecane and 1,7-heptanediol were similar in magnitude even though in each rubber the hexadecane was soluble in all proportions and the diol only very slightly. The diffusion coefficient of ethylene glycol, despite its extreme thermodynamic incompatibility, appeared to be somewhat larger than those of the other penetrants.

INTRODUCTION

In previous studies of the diffusion of radioactively tagged penetrants through rubbery polymers,[1–4] the penetrants have been hydrocarbons (mostly n-hexadecane), completely compatible with the rubbers. In the thin smear method for measuring diffusion coefficients,[1] a thin smear of the penetrant dissolves immediately and completely into the polymer upon contact with the lower surface of a disc-shaped sample of the latter. As the concentration at the upper surface increases (and is measured by radioactivity counts), the concentration at the lower surface decreases, the total amount of dissolved penetrant remaining constant (case 1 in the theory discussed below).

The present study was undertaken to throw some light on the behavior of a penetrant which is almost insoluble in the rubber, the one being polar and the other nonpolar. In this situation, the boundary conditions are different. A reservoir of undissolved penetrant remains in contact with the lower surface throughout the experiment. Two cases may be distinguished. If the penetrant crosses the interface rapidly in comparison with the subsequent diffusion, the concentration at the lower surface remains constant at the saturation value and

the concentration elsewhere increases, approaching the saturation value at equilibrium (case 2). If the crossing of the interface is slow, the concentration at the lower surface approaches the saturation value gradually (case 3). Examples of both cases 2 and 3 are found experimentally.

EXPERIMENTAL

Materials

As an example of a polar rubbery polymer containing hydroxyl groups, in which the hydrocarbon penetrant n-hexadecane would have a low solubility, an epichlorohydrin–ethylene oxide copolymer with weight ratios of 65:35 of the respective components (Hydrin 200) was kindly furnished by G. Mann of the B. F. Goodrich Company. The weight-average molecular weight (M_w) was 1.5×10^6, and the density (ρ) was 1.27 g/cc at 25°C.

The following nonpolar polymers, in which the polar penetrants ethylene glycol and 1,7-heptanediol have low solubilities, were kindly provided by Dr. N. Tokita of Uniroyal, Inc.: S-SBR, a solution-polymerized styrene–butadiene rubber with 21% by weight of styrene, $\rho = 0.932$ g/cc; Diene 35, a polybutadiene with cis:trans:vinyl = 36:53:11, $M_w = 2.6 \times 10^5$, $\rho = 0.894$; NR-SS, a natural rubber from smoked sheet; and NR-SMR, a natural rubber from standard Malaysian rubber.

As a final example of limited solubility due to high crosslinking rather than cohesive energy density mismatch, a sample of highly crosslinked 1,2-polybutadiene was used with n-hexadecane as penetrant. The polybutadiene was kindly furnished by Dr. G. Kraus of Phillips Petroleum Company; cis:trans:vinyl = 4.7:6.9:88.4 and $M_w = 2.9 \times 10^5$. It was crosslinked with 1% dicumyl peroxide for 10 min at 155°C. The modulus was obviously leathery rather than rubbery, and the swelling in n-hexadecane was very slight (3.0 weight per cent). From the latter figure, the average molecular weight between crosslinks was estimated by the Flory equation to be about 60. Although the equation is not applicable, it gives an indication of the very high crosslink density.

Except for the last mentioned, all the polymers were uncrosslinked. They were molded into sheets 1 to 2 mm thick, usually by pressing at 85°C for 3 hr at 5000 psi, followed by gradual cooling to room temperature. The disk-shaped samples used for diffusion measurements, of 1-in. diameter, were cut from the sheets by an electric punch.

The dilution and use of n-hexadecane tagged with ^{14}C has been described previously.[2,3] Ethylene glycol and 1,7-heptanediol, tagged with ^{14}C, were purchased from International Chemical Nuclear Corporation, in methanol and aqueous solution, respectively. The ethylene glycol solution was diluted first with nonradioactive ethylene glycol (Phillips Petroleum Company, 99% purity), and the methanol was removed by passing nitrogen gas over the mixture; the activity of the final product was 0.43 μCi/mg. (An earlier attempt to evaporate the methanol before adding more ethylene glycol resulted in loss of most of the radioactive glycol because of its perceptible vapor pressure.) The water was removed from the 1,7-heptanediol in the same manner, after adding nonradioactive heptanediol (Aldrich, purity 95%); the final activity was 0.73 μCi/mg.

Methods

Diffusion measurements were made by the thin smear method as described previously.[2-6] For a nonpolar penetrant (n-hexadecane) in nonpolar polymer, the amount of penetrant was less than 1 mg as always used previously; for such a small proportion of penetrant, the polymer is not significantly diluted and the experiment corresponds closely to one of self-diffusion of isolated penetrant molecules in a polymer matrix. For a polar penetrant and a nonpolar polymer, or vice versa, at least 10 mg penetrant was used to ensure an excess over the solubility capacity of the polymer sample. It was found necessary to absorb the penetrant in a circle of thin lens paper to prevent the excess from climbing the edge of the polymer. Examination at the end of each experiment confirmed that a reservoir of undissolved penetrant remained. The solubility was sufficiently small so that the correspondence to self-diffusion of isolated molecules still holds. All measurements were made at 25.00°C.

By the use of two Geiger–Müller tubes and two scalers, two experiments could be run simultaneously. Data acquisition was made automatic by connecting the scalers to a digital timer with clock (Newport Laboratories Model 6700-2) and a digital printer (Systron–Donner Model 5103). Details of the method are given elsewhere.[6]

Solubilities were measured by immersing weighed thin samples of polymer in the respective nonradioactive liquids and blotting and weighing to determine the amounts of absorbed liquid. Weighings were repeated until equilibrium was reached, of the order of two months, at room temperature.

THEORY

Three cases with different boundary conditions can be distinguished as mentioned above.

Case 1: Penetrant Completely Soluble in Polymer

This applies to all work previously reported. The activity in counts per minute detected at the top surface, N at time t, is given by the equation[2]

$$N/N_e = 1 + 2 \sum_{n=1}^{\infty} (-1)^n e^{-n^2\pi^2\theta/(1+n^2 b)} \tag{1}$$

where N_e is the final activity when the penetrant is uniformly distributed through the polymer sample; $\theta = Dt/h^2$; $b = (\pi/\mu h)^2$; D is the diffusion coefficient; h is the sample thickness; and μ is the absorption coefficient of the β particles in the rubber, taken as 326 cm^{-1} for our calculations. In practice, the term $n^2 b$ is a small correction which is negligible when the Geiger tubes detect the penetrant concentration at the surface only. Data for log $N(t)$ against log t are matched to a doubly logarithmic plot of $N(t)/N_e$ against θ for the appropriate value of b, to determine D.

Case 2: Solubility of Penetrant Very Small, Entry into Polymer Relatively Rapid

Here, the concentration of penetrant at the lower surface of the polymer is maintained constant at the saturation value throughout the duration of the ex-
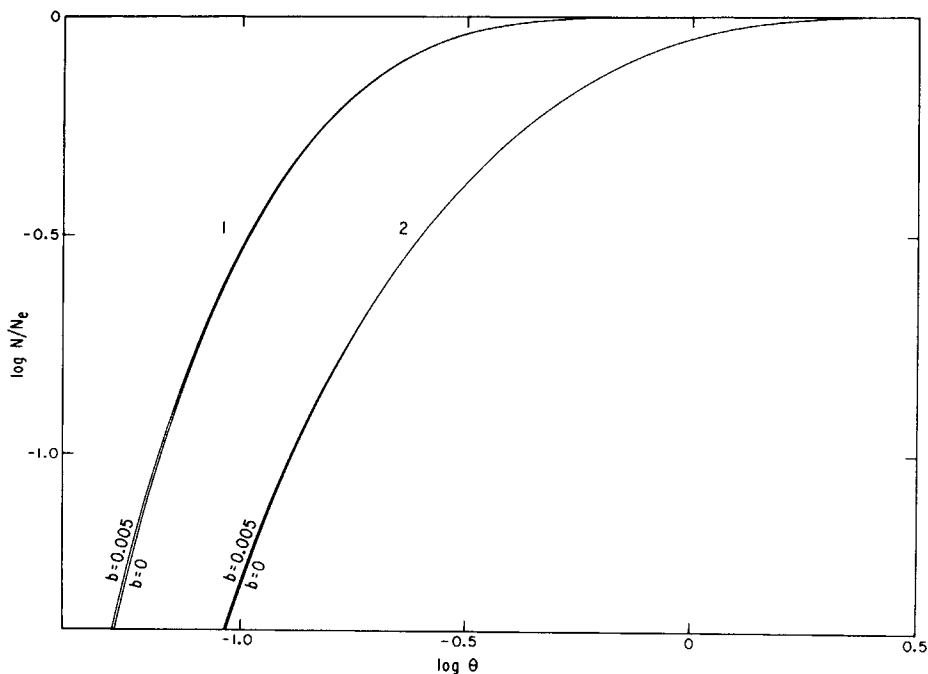
Fig. 1. Theoretical curves for activity measured at top of sample relative to final equilibrium value plotted logarithmically against θ for case 1 and case 2, with two values of b as indicated for each.

periment. Solution of the diffusion equations for the appropriate boundary conditions[6] results in the relation

$$N/N_e = 1 - \frac{4}{\pi(1 - e^{-\pi/\sqrt{b}})}\left[\sum_{n=0}^{\infty}\frac{(-1)^n e^{-(2n+1)^2\pi^2\theta/4}}{(2n+1)\{1 + (2n+1)^2 b/4\}}\right.$$
$$\left. + \sum_{n=0}^{\infty}\frac{e^{-\pi/\sqrt{b}}(\sqrt{b})e^{-(2n+1)^2\pi^2\theta/4}}{2\{1 + (2n+1)^2 b/4\}}\right] \quad (2)$$

This was evaluated numerically for several values of b by a Univac 1108 computer. In Figure 1, $\log N/N_e$ is plotted against $\log\theta$ for $b = 0$ and $b = 0.005$, to compare case 1 and case 2. For the same value of θ, the penetrant reaches the top surface more slowly in case 2 and the shape of the curve is quite different. The shapes are compared more clearly in Figure 2, where the reduced time scales have been shifted. It is thus easy to distinguish between the two cases experimentally.

Case 3: Solubility of Penetrant Very Small, Entry into Polymer Relatively Slow

When it was found that certain data, especially for ethylene glycol as penetrant, could not be fitted by either case 1 or case 2, the influence of a slow crossing of the penetrant-polymer interface was examined. This is treated by Crank[7] with the assumption that the concentration at the (lower) surface rises proportionally to $1 - e^{-\beta t}$ subsequent to contact between the two phases. (The same form of time dependence has been found for the saturation of a surface during adsorption
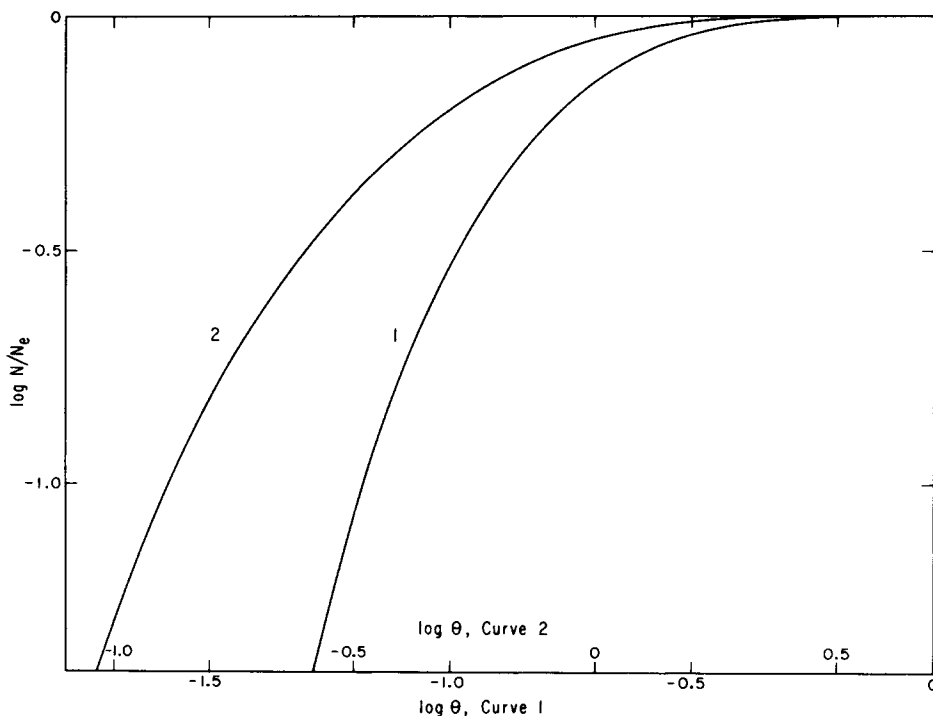
Fig. 2. Theoretical curves from Fig. 1 for $b = 0$ with abscissa scales shifted for comparison of shapes.

of acids on silica gel or charcoal[8] and adsorption of polymers on charcoal.[9]) Calculation of the observed activity at the upper surface in our experiment requires some rather complicated manipulations[6] which provide the relation

$$N/N_e = 1 - \frac{1}{(1 - e^{-\pi/\sqrt{b}})}\left[\frac{e^{-C^2\theta}\{1 - e^{-\pi/\sqrt{b}}(\cos C + C\sqrt{b}\sin C/\pi)\}}{\cos C(1 + bC^2/\pi^2)}\right.$$
$$\left. + \frac{16}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n e^{-(2n+1)^2\pi^2\theta/4}\{1 + (-1)^n(2n+1)\sqrt{b}\,e^{-\pi/\sqrt{b}/2}\}}{(2n+1)\{4 - \pi^2(2n+1)^2/C^2\}\{1 + (2n+1)^2 b/4\}}\right] \quad (3)$$

where $C = (\beta h^2/D)^{1/2}$; C is a measure of the relative rates of crossing the interface and reaching the opposite surface by the diffusion process. This was evaluated numerically for various values of b and C. In Figure 3, log N/N_e is plotted against log θ for $b = 0.005$ and several values of C. The shape is again quite different and easily distinguishable; for small values of C, the plot is nearly linear in the early stages and has a much lower slope than those for cases 1 and 2. For values of C larger than 2, the curves become very similar to those of case 2.

RESULTS AND DISCUSSION

Examples of fits of experimental data to theoretical curves for cases 2 and 3 are shown in Figures 4 and 5, respectively. It may be noted that experiments with penetrants of low solubility required much longer times (by a factor of the
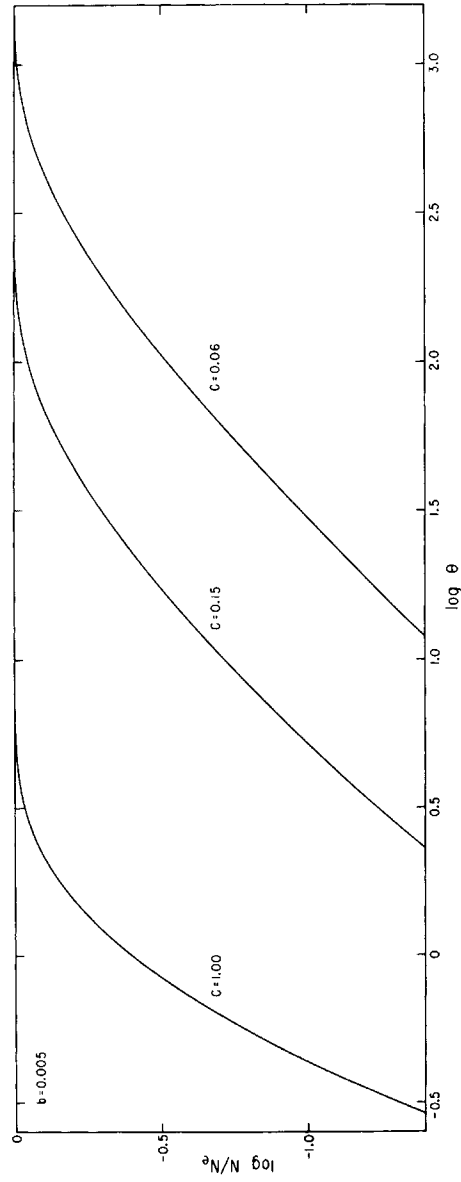
Fig. 3. Theoretical curves plotted as in Fig. 1 for case 3 with three values of C as indicated.
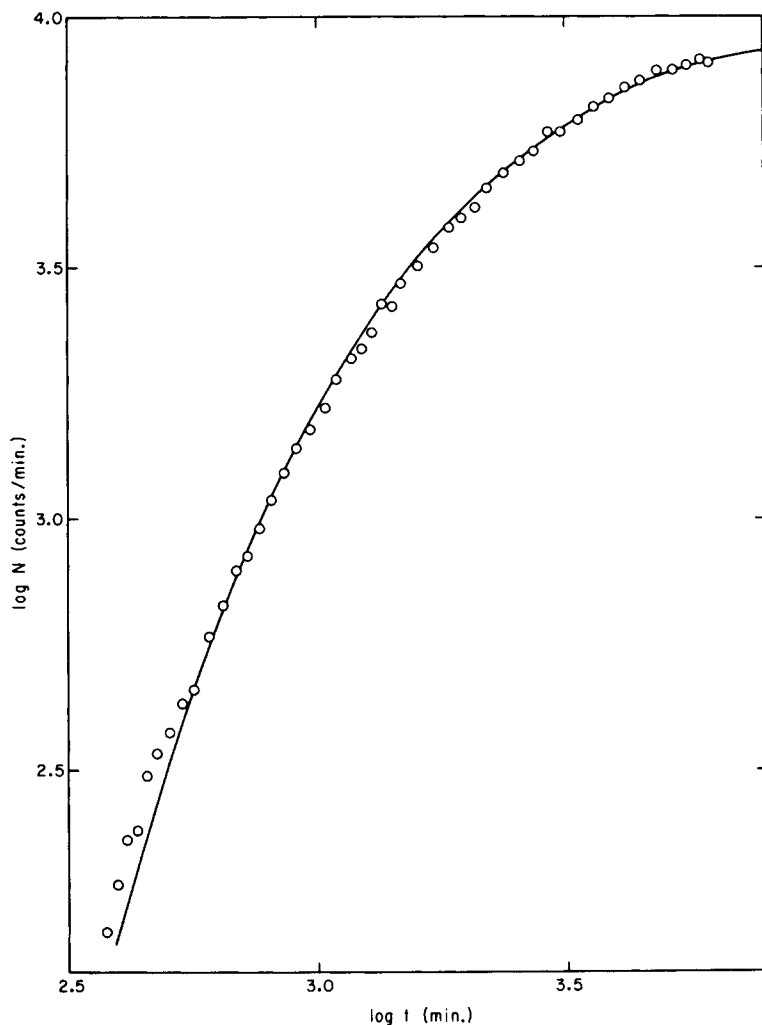
Fig. 4. Activity in counts per minute plotted logarithmically against time in minutes, for n-hexadecane in Hydrin 200. Curve is case 2, with $b = 0.009$.

order of 30) than those with completely miscible penetrants, even when the calculated D values were similar in magnitude. From these and similar plots, values of D (and, for case 3 plots, also values of C and β) were determined for various combinations of polymers and penetrants, and are summarized in Table I together with data for solubility.

It is evident that all the systems for which the polymer and pentrant are completely compatible (miscible in all proportions) conform to the case 1 theory, as they have in many earlier investigations. The correlation between solubility and the distinction between cases 2 and 3 is not so clear. Ethylene glycol in hydrocarbon polymers follows case 3; 1,7-heptanediol can be either case 2 or 3 depending on the polymer. The hydrocarbon penetrant n-hexadecane in the polar polymer Hydrin 200 follows case 2; in highly crosslinked 1,2-polybutadiene,
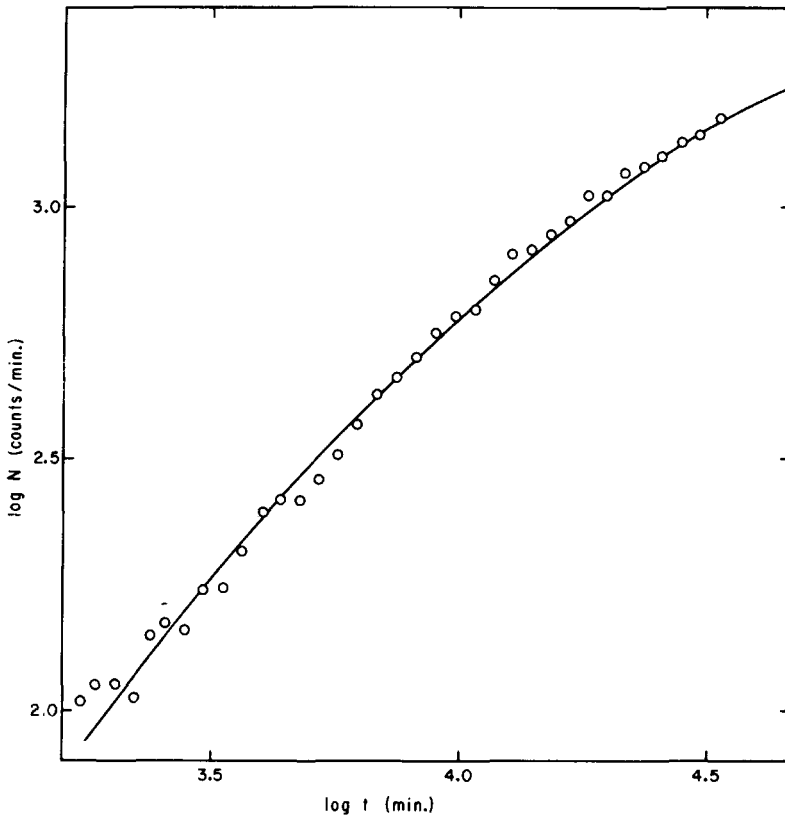
Fig. 5. Activity in counts per minute plotted logarithmically against time in minutes, for ethylene glycol in styrene–butadiene rubber. Curve is case 3, with $b = 0.004$, $C = 0.20$.

where the low swelling is associated with dense crosslinking rather than thermodynamic incompatibility, it follows case 3.

The coefficient β, which is a measure of the rate of entry across the penetrant–polymer interface, is, for the case 3 examples, of the order of 10^{-6} to 10^{-5} sec^{-1}; i.e., the half-time for saturation at the surface is about from one to several days. Even in case 2 examples, the saturation may require a matter of hours, since the diffusion is so slow that it would still be the limiting step of the process for such a slow crossing of the interface.

The most important conclusion is that the diffusion coefficients of penetrants of high and low solubility, similar in size, in the same polymer are similar in magnitude. For this purpose, n-hexadecane may be compared with 1,7-heptanediol in four hydrocarbon polymers. If molecular size were the only determinant, the diol should have a slightly larger diffusion coefficient. It is found to be either larger or smaller, but the ratio for diol to hexadecane ranges only from 0.51 to 1.38. Thus, the mechanism for diffusion for the two penetrants may be presumed to be the same even though their compatibilities and thermodynamic interactions with the polymers are enormously different.

The diffusion coefficients for ethylene glycol are somewhat surprisingly higher than those for the diol. This effect appeared even more strikingly for some data

TABLE I
Diffusion Coefficients and Related Data

Polymer	Penetrant[a]	Solu-bility, wt %	Case no.	b	C	$\log \beta,$ sec^{-1}	$\log D,$ cm^2 sec^{-1}
S-SBR	n-HXD	(∞)	1	0.006			−7.12
	EG[b]	0.7	3	0.004	0.2	−6.25	−6.43
				0.009	0.15	−6.43	−6.40
	1,7-HD	0.4	2	0.006			−7.13
Diene 35	n-HXD	(∞)	1	0.005			−6.67
	EG	1.1[c]	3	0.004	0.15	−5.17	−5.11
	1,7-HD	0.9[c]	2	0.004			−6.53
NR-SS	n-HXD	(∞)	1	0.007			−7.15
	1,7-HD		3	0.003	0.8	−6.06	−7.33
NR-SMR	n-HXD	(∞)	1	0.005			−7.13
	1,7-HD		3	0.003	0.7	−6.22	−7.42
Hydrin 200	n-HXD	0.3	2	0.006			−7.75
1,2-PB-XX[e]	n-HXD	3.0	3	0.017	1.5	−5.30	−8.52
1,2-PB	n-HXD	(∞)	1				−8.97[d]

[a] n-HXD = n-Hexadecane; EG = ethylene glycol; 1,7-HD = 1,7-heptanediol.

[b] The two entries refer to polymer discs of different thicknesses.

[c] These solubilities actually refer to another polybutadiene with higher cis content.

[d] Data of Chen[2] corrected for small difference in microstructure by use of eqs. (1) and (2) of ref. 4.

[e] Highly crosslinked.

for diffusion in polyisobutylene, which are not reported because of uncertainty in fitting to the case 3 theory.   Of course, ethylene glycol is a smaller molecule, but this can hardly explain the factor of 27 observed for the two low-compatibility penetrants in Diene 35.   It may be suggested that the extreme mismatch of cohesive energy density with ethylene glycol is associated with a positive volume change of mixing which produces extra free volume in the immediate vicinity of the penetrant molecules, and that this facilitates the diffusion process.   This is, however, very speculative.

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