Solvent Self-Diffusion in Crosslinked Polymers

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SYNOPSIS

A theory is developed for predicting the solvent self-diffusion coefficient in a crosslinked, amorphous polymer. The theory is based on a modification of the free-volume theory of transport for the presence of crosslinks in the polymer. The general predictions of the theory for the variations of the self-diffusion coefficient with temperature, concentration, degree of crosslinking, and solvent size are compared with general experimental trends.

INTRODUCTION

The free-volume theory of transport can be used to provide satisfactory descriptions of the temperature and concentration variations of solvent self-diffusion cofficients and of mutual diffusion coefficients in concentrated solutions of amorphous polymers.[1-6] It seems reasonable to expect that this theory can be extended to describe the self-diffusion process in amorphous, crosslinked polymers. A few studies have considered a theoretical description of the effect of crosslinks on the diffusion process,[7-9] but the proposed models do not provide a predictive method for taking into account the presence of the crosslinks in the polymer. In one of the proposed theories, the functional form of the dependence of the diffusion coefficient on the mesh size is not known,[7,8] whereas another theory provides only a correlative basis for examining the diffusion process.[9]

The purpose of this paper is to propose an alternative approach that leads to a predictive theory for the solvent self-diffusion process for crosslinked, amorphous polymers. The theory is developed in the second section of the paper, and general predictions of the theory are presented in the third section. Comparisons of the predictions of the theory with general experimental observations are presented in the fourth section of the paper.

FORMULATION OF THEORY

In the free-volume theory of transport, the solvent self-diffusion coefficient, D_1, for a polymer–penetrant mixture can be determined using the following equations[3,4]:

$$D_1 = D_0 \exp\left[-\frac{E}{RT}\right]$$

$$\times \exp\left[-\frac{\gamma(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)}{\hat{V}_{FH}}\right] \quad (1)$$

$$\xi = \frac{\hat{V}_1^* M_{j1}}{\hat{V}_2^* M_{j2}} \quad (2)$$

$$\hat{V}_{FH} = \omega_1 \hat{V}_{FH1} + \omega_2 \hat{V}_{FH2}. \quad (3)$$

Here, ω_I is the mass fraction of component I, $\hat{V}_I^*$ is the specific critical hole free volume of component I required for a jump, ξ is the ratio of the critical molar volume of the solvent jumping unit to the critical molar volume of the polymer jumping unit, and M_{jI} is the molecular weight of a jumping unit of component I. Also, D_0 is a constant preexponential factor, E is the energy per mole that a molecule needs to overcome attractive forces that hold it to its neighbors, T is the temperature, $\hat{V}_{FH}$ is the average hole free volume per gram of mixture, $\hat{V}_{FHI}$ is the specific hole free volume of pure component I at T, and γ is an overlap factor introduced because the same free volume is available to more than one molecule.

The above equations have been used[3-6] to describe the solvent self-diffusion process in amorphous, uncrosslinked polymers, and it is now of interest to see what modifications must be made to extend the theory to crosslinked materials. We consider here amorphous polymers that are not too tightly crosslinked. Roughly speaking, the discussion is limited to polymer chains that have in the order of 50 or more chain carbon atoms between crosslinks. For such materials, it seems reasonable to expect the following assumptions will lead to a satisfactory characterization of the transport and volumetric behavior of the system:

1. The energetics of solvent migration and the jump distance for the solvent molecule are independent of the degree X of crosslinking. Here, X is some measure of the amount of crosslinking in the polymer, and $X = 0$ denotes the uncrosslinked material. This assumption means that D_0 and E are independent of X.
2. The solvent properties $\hat{V}_1^*$, M_{j1}, and $\hat{V}_{FH1}$ are independent of X.
3. The free-volume configuration in the polymer and the size of its jumping unit are independent of X. Hence, γ and M_{j2} are assumed to be independent of the crosslink density. Clearly, $\xi \hat{V}_2^*$ is also independent of X.
4. The thermal expansion coefficient for the total specific volume of the polymer and the thermal expansion coefficient for the sum of the specific occupied volume and the specific interstitial free volume[10] are assumed to be independent of the crosslink density. Some justification for this type of assumption is provided in Table I using specific volume data for natural rubber crosslinked with sulfur.[11] The thermal expansion coefficient for the

rubber–sulfur vulcanizate is essentially independent of the crosslink density up to a sulfur content of about 10%.

The above assumptions should be valid for many materials over a range of crosslink densities near $X = 0$. The exact extent of this range will, of course, depend on the nature of the crosslinking in the polymeric material.

It is clear from the above discussion and the imposed assumptions that the introduction of crosslinking into the polymer will affect D_1 only through the quantity $\hat{V}_{FH2}$, the specific hole free volume of the pure polymer at a particular temperature T. Consequently, the above equation set will be modified by allowing for a dependence of $\hat{V}_{FH2}(T, X)$ both on temperature and the degree of crosslinking. It can be easily shown, using assumption (4) above, that the following volumetric relationships are valid:

$$\frac{\hat{V}_{FH2}(T, X)}{\hat{V}_{FH2}(T, 0)} = \frac{\hat{V}_2^0(0, X)}{\hat{V}_2^0(0, 0)} = \frac{\hat{V}_2^0(T, X)}{\hat{V}_2^0(T, 0)} = \delta. \quad (4)$$

Here, $\hat{V}_2^0(T, X)$ is the specific volume of the pure polymer at a particular temperature T and a prescribed degree of crosslinking as denoted by X. Consequently, the effect of the crosslinking on the free volume of the polymer is characterized by a single parameter δ, and this quantity can be determined directly using volumetric data on the crosslinked and uncrosslinked polymer. Furthermore, volumetric behavior of the crosslinked and uncrosslinked materials at two temperatures T_1 and T_2 is described by the following result:

$$\frac{\hat{V}_2^0(T_1, X)}{\hat{V}_2^0(T_1, 0)} = \frac{\hat{V}_2^0(T_2, X)}{\hat{V}_2^0(T_2, 0)}. \quad (5)$$

Table I   Dependence of Thermal Expansion Coefficient for Natural Rubber on Crosslink Density

Sulfur Content (%)	Specific Volume (cm³/g)	Thermal Expansion Coefficient (°C⁻¹)
0	1.095	7.08×10^{-4}
2.0	1.078	7.07
3.9	1.060	7.06
6.1	1.040	6.99
7.3	1.025	6.71
9.1	1.010	7.01

Data taken from ref. 11.

Equation (5) can be used to provide a further test of assumption (4). Volumetric data for the natural rubber–sulfur system[11] at two temperatures are used to provide a test of the validity of eq. (5). From results presented in Table II, it seems reasonable to again conclude that the thermal expansion coefficient for the system is essentially independent of X, as proposed in assumption (4).

With the proposed modification for the presence of crosslinks in the polymer, the expression for D_1 now takes the form

$$D_1 = D_0 \exp\left[-\frac{E}{RT}\right]$$

$$\times \exp\left[-\frac{(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)}{\left(\omega_1 \dfrac{\hat{V}_{FH1}}{\gamma} + \omega_2 f_2 \delta\right)}\right] \quad (6)$$

$$f_2 = \frac{\hat{V}_{FH2}(T, 0)}{\gamma}, \quad (7)$$

where f_2 simply refers to the free-volume properties of the uncrosslinked polymer. Clearly, eq. (6) reduces to the result for solvent self-diffusion in an uncrosslinked polymer when $\delta = 1$, and the extension of the free-volume theory of transport from uncrosslinked to crosslinked materials involves the introduction of only one additional parameter δ. Furthermore, as noted above, this quantity can be determined directly from density data. Clearly, if self-diffusion coefficients can be predicted for the uncrosslinked material, then it is possible to make predictions for the crosslinked polymer also using appropriate density data. It is important to note here that the precise nature of the crosslinking in the polymer is not required for this theory. Only the effect of the crosslinking on the volumetric properties of the material is needed in the formulation

Table II Effect of Crosslinking on Volumetric Behavior for Natural Rubber

Sulfur Content (%)	$\dfrac{\hat{V}_2^0(323, X)}{\hat{V}_2^0(323, 0)}$	$\dfrac{\hat{V}_2^0(273, X)}{\hat{V}_2^0(273, 0)}$
2.0	0.984	0.986
3.9	0.967	0.969
6.1	0.951	0.953
7.3	0.933	0.935
9.1	0.919	0.920

Temperature is indicated in °K for $\hat{V}_2^0(T, X)$.
Data taken from ref. 11.

of a volume-based theory of transport, such as the free-volume theory of diffusion. General predictions, based on eq. (6), for the variations of D_1 with temperature, concentration, crosslinking, and solvent size are considered in the next section.

GENERAL PREDICTIONS OF THEORY

Since the solvent self-diffusion coefficient D_1 and the mutual diffusion coefficient D are related as follows

$$D(\omega_1 = 0) = D_1(\omega_1 = 0), \quad (8)$$

it is possible to use eq. (6) to predict not only D_1 but also the mutual diffusion coefficient in the limit of zero solvent mass fraction. One convenient method of assessing the effect of crosslinking on $D_1(\omega_1, T, X)$ is to study the diffusion process in the limit $\omega_1 = 0$ and determine the change of D_1 or D with increasing crosslink density. It is easy to show from eq. (6) that the ratio r_1

$$r_1 = \frac{D_1(0, T, X)}{D_1(0, T, 0)} \quad (9)$$

is given by the expression

$$r_1 = \exp\left[-\frac{\xi \hat{V}_2^*}{f_2} \frac{(1 - \delta)}{\delta}\right]. \quad (10)$$

Clearly, r_1 gives the ratio of the solvent self-diffusion coefficient or the mutual diffusion coefficient at $\omega_1 = 0$ in a crosslinked polymer to the diffusivity in the uncrosslinked material. In general, crosslinking decreases the specific volume of the polymer, so, from eq. (4), it is evident that $\delta \leq 1$. Consequently, it follows from eq. (10) that crosslinking decreases the diffusion coefficient in the polymer:

$$D_1(0, T, X) < D_1(0, T, 0). \quad (11)$$

There is a monotonic decrease of D_1 with increasing degree of crosslinking. Furthermore, it is possible to assess the effect of solvent size on the diffusion process in crosslinked polymers by considering the quantity q:

$$q = \ln\left[\frac{D_1(0, T, X_1)}{D_1(0, T, X_2)}\right]. \quad (12)$$

From eq. (6), it is easy to show that, for diffusion of two solvents A and B,

$$\frac{q \,(\text{solvent } A)}{q \,(\text{solvent } B)} = \frac{\check{V}_1^* \,(\text{solvent } A)}{\check{V}_1^* \,(\text{solvent } B)}, \qquad (13)$$

where $\check{V}_1^*$ is the molar volume of the jumping unit of the solvent. Equation (13) is an indication of how the change of D_1 with crosslink density depends on solvent size. Clearly, the effect of crosslinking on $D_1(0, T, X)$ is more pronounced for the larger solvents. The prediction of eq. (13) can, of course, be checked by measuring diffusion coefficients for different solvents in polymer samples with different crosslink densities.

The temperature dependence of the diffusion process can be determined by evaluating an activation energy E_D at $\omega_1 = 0$ for fixed crosslink density:

$$E_D = RT^2 \left(\frac{\partial \ln D_1}{\partial T} \right)_{\omega_1 = 0}. \qquad (14)$$

If it is assumed that the energy of attraction E is small enough to be ignored when compared to temperature effects caused by free-volume changes (the diffusion process is dominated by free-volume rather than energy effects), then it follows from eqs. (6) and (14) that E_D is given by the following expression:

$$E_D = \frac{RT^2 \dfrac{df_2}{dT} \xi \hat{V}_2^*}{f_2^2 \delta}. \qquad (15)$$

Consequently, it is evident that the change of the activation energy with crosslink density can be represented by the expression:

$$\frac{E_D(T, X)}{E_D(T, 0)} = \frac{1}{\delta}. \qquad (16)$$

Since $\delta \leqq 1$, it follows that E_D increases with increasing crosslink density

$$E_D(T, X) > E_D(T, 0). \qquad (17)$$

There is a monotonic increase of E_D with increasing degree of crosslinking. In addition, it is evident from eq. (15) that the effect of the solvent size on the activation energy can be represented by the following expression for two solvents A and B diffusing in a particular polymer at a prescribed crosslink density:

$$\frac{[E_D(T, X)]_A}{[E_D(T, X)]_B} = \frac{\check{V}_1^* \,(\text{solvent } A)}{\check{V}_1^* \,(\text{solvent } B)}. \qquad (18)$$

Sometimes,[12] the diffusion process in a crosslinked polymer is described by the following expression at $\omega_1 = 0$:

$$D_1 = \tilde{D}_0 e^{-E_D/RT} \qquad (19)$$

From eqs. (6) and (15), it can be shown that

$$\tilde{D}_0 = D_0 \exp \left[\frac{\xi \hat{V}_2^* \left(T \dfrac{df_2}{dT} - f_2 \right)}{\delta f_2^2} \right] \qquad (20)$$

so that $\tilde{D}_0$ depends on the crosslink density. Since, in general,

$$T \frac{df_2}{dT} - f_2 > 0 \qquad (21)$$

it follows from eq. (20) that $\tilde{D}_0$ increases with increasing crosslink density.

Finally, we consider the concentration dependence of D_1 in a crosslinked polymer at a fixed temperature. This is done by considering the effect of crosslinking on the slope of the $\ln D_1$ vs. ω_1 curve at $\omega_1 = 0$. It can be easily shown that this concentration dependence is described by the following equation:

$$\left(\frac{\partial \ln D_1}{\partial \omega_1} \right)_{\omega_1 = 0, X = X} = \frac{\left(\dfrac{\partial \ln D_1}{\partial \omega_1} \right)_{\omega_1 = 0, X = 0}}{\delta^2} + \frac{(1 - \delta) \hat{V}_1^*}{f_2 \delta^2}. \qquad (22)$$

For most polymer–solvent systems, D_1 increases as ω_1 increases. Thus, since $\delta \leqq 1$, it is clear from eq. (22) that the ratio r_2

$$r_2 = \frac{\left(\dfrac{\partial \ln D_1}{\partial \omega_1} \right)_{\omega_1 = 0, X = X}}{\left(\dfrac{\partial \ln D_1}{\partial \omega_1} \right)_{\omega_1 = 0, X = 0}} \qquad (23)$$

is greater than unity, and thus the initial slope of the $\ln D_1$ vs. ω_1 curve increases monotonically as the crosslink density increases. This result is de-

pendent on the fact that the above expression for $D_1(\omega_1, T, X)$ cannot be written as the product of a concentration effect and a crosslink effect. When D_1 can be written in such a factored form, there is no effect of the crosslink density on the concentration dependence of $\ln D_1$.

COMPARISON WITH EXPERIMENTAL TRENDS

The predictions of the above theory for self-diffusion in crosslinked polymers can be checked if appropriate self-diffusion and density data are available for a particular crosslinked polymer–penetrant system. Unfortunately, it does not appear that a comprehensive data set of this type is available, and, hence, no direct data-theory comparison for the effect of crosslinking on the self-diffusion process is possible at this time. However, it is still possible to see if the theory is capable of predicting the general trends that are observed experimentally. Consequently, interest is focused here on comparing the predicted variations of D_1 with temperature, concentration, crosslinking, and solvent size with several sets of data available in the literature. Data on the effect of crosslinking, temperature, and solvent type on D at $\omega_1 = 0$ have been reported by Aitken and Barrer[13] for crosslinked rubbers, and Chen and Ferry[14] have presented data for the diffusion of trace amounts of cetane in crosslinked rubber samples. Hayes and Park[15] reported data on the effect of crosslinking and solvent concentration on D for the benzene–rubber system. Barrer and Skirrow[12] presented diffusion data for the effect of crosslinking, temperature, and solvent type on the mutual diffusion process for crosslinked rubbers, but the concentration levels at which the diffusivities were obtained were not reported. We shall assume here that

the reported diffusion coefficients for the two smallest penetrants they used, nitrogen and methane, are reasonably good approximations for D and, hence, D_1 at $\omega_1 = 0$. The concentration levels for these two penetrants should be relatively low.

The experimental results for the above investigations can be summarized as follows:

1. Data from all four investigations[12-15] show that there can be a significant decrease in the diffusion coefficient at $\omega_1 = 0$ with increasing crosslink density.
2. The activation energy data of Barrer and Skirrow[12] show that E_D increases with increasing degree of crosslinking. Data illustrating this point are presented in Table III. For the data reported by Aitken and Barrier,[13] the changes in E_D are in general too small to allow any definitive conclusion about the effect of crosslinking on E_D.
3. The data of Barrer and Skirrow and the data of Aitken and Barrer show that the effect of crosslinking on $D_1(0, T, X)$ is more pronounced for the larger penetrants. Specific data illustrating this point are presented in Tables IV and V.
4. The data of Barrer and Skirrow indicate that the activation energy for diffusion in a polymer with a particular crosslink density increases with increasing solvent size. Data illustrating this point are presented in Table III.
5. The data of Barrer and Skirrow show that $\tilde{D}_0$ increases with increasing crosslink density.
6. The data of Hayes and Park[15] appear to indicate (see the comments of Fujita[16]) that the slopes at $\phi_1 = 0$ of $\log \bar{D}$ vs. ϕ_1 curves are greater for crosslinked rubbers than for a

Table III **Dependence of Activation Energy on Crosslink Density and Solvent Size for Diffusion of Nitrogen and Methane in Natural Rubber at 60°C**

% Sulfur	E_D (nitrogen) (kcal/gmol)	E_D (methane) (kcal/gmol)	$\dfrac{E_D \text{ (methane)}}{E_D \text{ (nitrogen)}}$
1.7	8.00	8.25	1.03
2.9	8.50	8.52	1.00
7.15	9.70	10.6	1.09
11.3	11.0	12.3	1.12

Predicted E_D (methane)/E_D (nitrogen) = 1.16.
Data taken from ref. 12.

Table IV   Solvent Effects on Diffusion Coefficients for Diffusion of Nitrogen and Methane in Natural Rubber at 60°C

% Sulfur	q (Nitrogen)	q (Methane)	$\dfrac{q \text{ (Methane)}}{q \text{ (Nitrogen)}}$
2.9	0.203	0.302	1.49
7.15	1.07	1.21	1.13
11.3	1.72	1.87	1.09

$q = \ln[D_1(0, 333, 1.7)/D_1(0, 333, X)]$, where temperature is indicated in °K and X is indicated in % sulfur for $D_1(\omega_1, T, X)$.
Predicted q (methane)/q (nitrogen) = 1.16.
Data taken from ref. 12.

material free of crosslinks. Here, ϕ_1 is the volume fraction of the solvent and

$$\bar{D} = \frac{D}{(1 - \phi_1)^3}. \qquad (24)$$

It is easy to show that this means that the slopes at $\omega_1 = 0$ of log D vs. ω_1 curves increase with increasing crosslink density. Furthermore, since D_1 is close to D near $\omega_1 = 0$, the above result suggests that the slopes at $\omega_1 = 0$ of log D_1 vs. ω_1 curves increase as the degree of crosslinking increases.

The predictions of the proposed theory are now compared to the six experimental observations listed above. The prediction of the theory for the effect of the crosslink density on the self-diffusion coefficient at $\omega_1 = 0$ is given by eq. (11). Clearly, this equation is in agreement with the first experimental observation listed above. The effect of crosslinking on the activation energy for the diffusion process is given by eq. (17), and the prediction of this equation is in agreement with the second experimental observation. From eq. (13), it is evident that the effect of crosslinking on D_1 is more pronounced for the larger penetrants, and this prediction of the theory

is consistent with the third experimental observation presented above. Furthermore, from Tables IV and V, it is evident that the predicted ratio of q values [see eq. (13)] is in reasonable agreement with the experimentally determined q ratio. The RHS of eq. (13) was evaluated by estimating $\tilde{V}_1^*$ using the volumetric properties of the equilibrium liquid at 0°K. Volumes at 0°K were calculated using procedures discussed by Haward.[17] For all four of the solvents considered (nitrogen, methane, isobutane, and neopentane), it was assumed that the entire molecule performs a jump. For the other hydrocarbons used by Aitken and Barrer,[13] this may not be the case.

From eq. (18), it is evident that the theory predicts that the activation energy for diffusion in a particular polymer with a prescribed crosslink density increases with increasing solvent size, and this prediction is consistent with the fourth experimental observation listed above. Furthermore, it is evident from Table III that the predictions of eq. (18) are in fair agreement with the experimental results. Also, from eqs. (20) and (21), it follows that $\bar{D}_0$ increases as the degree of crosslinking increases, and this prediction is consistent with the fifth experimental observation. Finally, it is evident from eq.

Table V   Solvent Effects on Diffusion Coefficients for Diffusion of Isobutane and Neopentane in Rubber at 40 and 50°C

Molecular Weight between Crosslinks	T (°C)	q (isobutane)	q (neopentane)	$\dfrac{q \text{ (neopentane)}}{q \text{ (isobutane)}}$
5,070	40	0.161	0.187	1.16
3,780	40	0.219	0.267	1.22
5,070	50	0.128	0.161	1.26
3,780	50	0.153	0.223	1.46

$q = \ln[D_1(0, T, 4.6 \times 10^{-5})/D_1(0, T, X)]$, where X is indicated in terms of the reciprocal of the molecular weight between crosslinks.
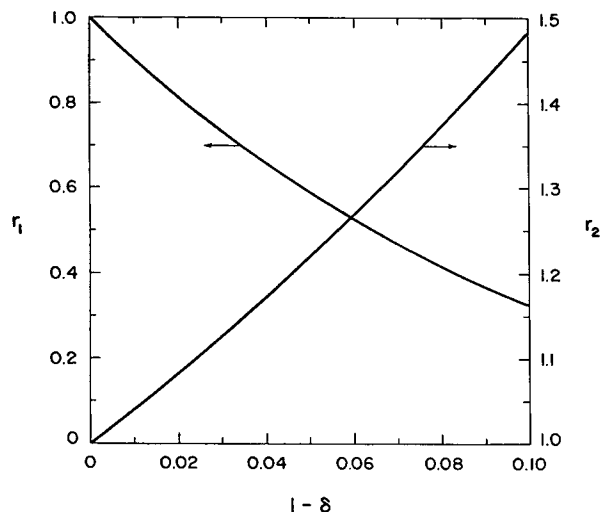Predicted q (neopentane)/q (isobutane) = 1.20.
Data taken from ref. 13.

Figure 1 Dependence of r_1 and r_2 on the degree of crosslinking for a typical polymer–solvent system. For this figure, $\xi = 1$, $\hat{V}_1^* = 1 \text{ cm}^3/\text{g}$, $\hat{V}_2^* = 1 \text{ cm}^3/\text{g}$, $\hat{V}_{FH1}/\gamma = 0.15$ cm^3/g, and $f_2 = 0.1 \text{ cm}^3/\text{g}$.

(22) that the slope of $\ln D_1$ vs. ω_1 at $\omega_1 = 0$ increases as the crosslink density increases, and this prediction is in agreement with the sixth experimental observation. Thus, the predictions of the proposed theory are consistent with all six experimental observations, and the theory represents one interesting possibility for analyzing the self-diffusion process in crosslinked polymers and in swollen networks. Appropriate density and self-diffusion data are needed to provide a direct evaluation of how well the proposed theory describes the self-diffusion process in crosslinked materials. Finally, an example of how r_1 and r_2 change with crosslink density is presented in Figure 1 for a polymer–solvent system with typical free-volume properties. This figure gives some idea of the type of changes that can be expected for the diffusion process as crosslinks are introduced into an amorphous polymeric material.

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