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Self-Diffusion Anisotropy of Small Penetrant Molecules in Deformed Elastomers

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ABSTRACT: The self-diffusion anisotropy of *n*-hexane, *n*-heptane, *n*-octane, and *n*-decane in uniaxially compressed natural rubber samples with different cross-link densities was detected by pulsed-gradient stimulated spin−echo NMR. The effective diffusion coefficients and the displacement probabilities of alkane penetrant molecules were measured along and perpendicular to the direction of the compression force. For all solvents, the diffusion anisotropy increases with increasing compression. The microscopic theory of diffusion on the basis of the free volume is adapted to predict the dependence of the diffusion anisotropy on the deformation ratio. The theoretical dependence is in good agreement with the measurements on toluene and *n*-hexane swollen in cross-linked natural rubber samples. The anisotropy of diffusion of small penetrant molecules in elastomers could be used for NMR investigation of the deformation of polymer networks by the changes in the shape of the free volume.

Introduction

Investigations of molecular self-diffusion provide important information on molecular organization and interactions with the environment in many systems.[1−4] The diffusion of small atoms and molecules through a polymeric solid especially in the rubbery state, i.e., at temperatures above the glass transition temperature T_g, has long been a subject of theoretical and experimental research.[5,6] Much of the theoretical work in this field falls into two categories: free-volume models that focus on the statistical distribution of holes in the lattice, and molecular models that are more dynamical in character and include the nature of the interactions between penetrant molecules and a polymer network.[7−19] Moreover, the extensive development in recent years of techniques for the computer simulation of polymeric systems provides a new approach to gain insight into the nature of diffusion.

A well-known consequence of the theory of rubber elasticity is segment orientation.[20] Deformation of an elastomer induces anisotropy of the backbone segments of the polymer coil. In recent NMR studies of rubber elasticity, the mechanism of deformation and the orientation of network chains has received increasing attention. One- and two-dimensional NMR spectroscopy of ^{1}H and ^{2}H has been used intensively in the past decade to measure the dipolar correlation effect, homonuclear and heteronuclear residual dipolar couplings, and corresponding dynamic order parameters.[21,22] Another potential method for this purpose is self-diffusion of small molecules that are soluble within the polymer network. As these molecules diffuse within the deformed network, they occasionally collide with the polymer segments and suffer anisotropic steric hindrance. The diffusing molecules "inherit" the orientational order of the host network, albeit significantly reduced by a numerical factor whose magnitude depends on the subtle details of the averaging of the molecule−segmental interaction. Nevertheless, a study of diffusion of penetrant molecules in highly stretched *cis*-polyisoprene has reported that the self-diffusion coefficients (D) are essentially isotropic and elongation independent.[23] Recently, the anisotropy of self-diffusion of toluene in uniaxially compressed natural rubber samples with different cross-link densities was detected using the pulsed-gradient stimulated spin−echo NMR method.[24] The effective diffusion coefficients and the displacement probabilities of toluene were measured along and perpendicular to the direction of the compression force. The diffusion anisotropy increases with increasing compression and cross-link density.

The effect of the shape and flexibility of diffusant molecules has been investigated in the past.[25−27] Significantly, anisometric molecules of plasticizers in rubbery poly(vinyl chloride) were found to diffuse more rapidly than expected on the basis of their molecular volume. The diffusion of these molecules in a glassy host is itself anisotropic, i.e., more rapid along the long axis of the diffusant molecules.

The main goal of this work is to discuss a theoretical model for the existence of diffusion anisotropy of small penetrant molecules in a deformed polymer network. The prediction of this model is tested by the diffusion anisotropy of toluene and normal alkane molecules (C_nH_{2n+2} with $n = 6$, 7, 8, and 10) incorporated in cross-linked natural rubber by swelling.

Theory

Free-Volume Treatment of Diffusion. The free-volume theory[1,5−7] in the formulation and parameters of Vrentas *et al.*[8−17] has been applied to evaluate the self-diffusion coefficients of small penetrant molecules in glassy and rubbery polymers. The concept central to the free-volume theory is that movement through the available free volume governs diffusion of small penetrants in polymeric matrixes. Thus, the diffusion

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coefficients predicted by the theory are strongly dependent on the "space filling" properties of both penetrant and polymer matrix.

The basic formulation used by Vrentas *at al.*[11−17] for the prediction of the diffusion coefficient in an isotropic rubbery polymer−solvent system is based on the expression:

$$\ln D_1 = \ln D_0 - \frac{E^*}{RT} - \left\{\frac{(1-w_\mathrm{p})\hat{V}_1^* + \xi w_\mathrm{p}\hat{V}_2^*}{\hat{V}_\mathrm{FH}/\gamma}\right\} \tag{1}$$

where D_1 is the diffusion coefficient of the penetrant (hereafter species 1), and the polymer is component 2. D_0 is an effectively constant preexponential factor and E^* is the effective energy per mole that a molecule needs to overcome attractive forces, R is the universal gas constant, T is the absolute temperature, and w_p is the polymer weight fraction. The specific hole free volumes required for a jump of penetrant and polymer are denoted by $\hat{V}_1^*$ and $\hat{V}_2^*$, respectively. It is primarily through the "size parameter" ξ, that solvent size influences the diffusion process. The value of ξ is estimated as follows[14]

$$\xi = \frac{\xi_L}{1 + \xi_L\left(1 - \dfrac{\bar{A}}{\bar{B}}\right)} \tag{2}$$

where $\xi_L = \tilde{V}_1^0(0)/\tilde{V}_2^*$ and $\tilde{V}_1^0(0)$ is the molar volume of the equilibrium liquid solvent (penetrant) at $T = 0\ K$. The aspect ratio of the solvent molecule is $\bar{A}/\bar{B}$ and $\tilde{V}_2^*$ is the critical free volume per mole of jumping units required for a jump.

The average hole free volume per unit mass of mixture is denoted by $\hat{V}_\mathrm{FH}$, and γ is an average overlap value in the mixture. The quantity $\hat{V}_\mathrm{FH}$ is related to the number of jumping units of components 1 and 2 and the average hole free volume per mole of jumping units of these components. For rubbery systems, $\hat{V}_\mathrm{FH}/\gamma$ can be calculated as follows[15]

$$\frac{\hat{V}_\mathrm{FH}}{\gamma} = (1-w_\mathrm{p})\frac{K_{11}}{\gamma_1}(K_{21} + T - T_\mathrm{g1}) + \frac{w_\mathrm{p}\hat{V}_\mathrm{FH2}}{\gamma_2} \tag{3}$$

where K_{11} and K_{21} are free-volume parameters for the solvent, γ_1 represents the overlap factor for the free volume of pure component 1, and T_g1 is the glass transition temperature of this component. The quantity $\hat{V}_\mathrm{FH2}/\gamma$ depends on whether the system is above or below the glass transition temperature of the polymer matrix T_g2. The quantity γ is an overlap factor that is introduced because the same free volume is available to more than one molecule. For the rubbery state, i.e., for $T > T_\mathrm{g2}$, we can write[15]

$$\hat{V}_\mathrm{FH2} = \hat{V}_2{}^0(T_\mathrm{g2})[f_\mathrm{H2}^\mathrm{G} + \alpha_2(T - T_\mathrm{g2})] \tag{4}$$

where $\hat{V}_2{}^0(T_\mathrm{g2})$ is the specific volume of the polymer at T_g2, f_H2^G is the fractional hole volume of the polymer at T_g2, and α_2 represents the thermal expansion coefficient for the equilibrium liquid−polymer. The parameters f_H2^G and γ_2 are given by

$$f_\mathrm{H2}^\mathrm{G} = \alpha_2 K_{22} \tag{5}$$

and

$$\gamma_2 = \frac{\tilde{V}_2^0(T_\mathrm{g2})\alpha_2}{K_{12}/\gamma_2} \tag{6}$$

where K_{22} is one of the polymer free-volume constants, and K_{12}/γ_2 is a polymer free-volume parameter. The free-volume parameters K_{22} and K_{12}/γ_2 are stated to be calculated by the expressions[15]

$$K_{22} = (C_2^\mathrm{g})_2 \tag{7}$$

and

$$\frac{K_{12}}{\gamma_2} = \frac{\hat{V}_2^0(0)}{2.303(C_1^\mathrm{g})_2(C_2^\mathrm{g})_2} \tag{8}$$

where $(C_1^\mathrm{g})_2$ and $(C_2^\mathrm{g})_2$ are the WLF constants of the polymer.

Diffusion Anisotropy. To evaluate the diffusion coefficients of the small penetrant molecules in a deformed polymer network, it is necessary to establish a model for the deformation. We will consider the simplest model of affine volume changes of deformed elastomer gels. In the case of uniaxial deformation, the network is either stretched or compressed in a single direction (hereafter the z-direction). For affine volume deformations, the other two dimensions of the network in the x- and y-directions adjust so that the sample volume remains constant. For a volume-conservative uniaxial deformation with a deformation ratio $\lambda = L_z/L_{z0}$, where L_{z0}, and L_z are the initial and final dimensions along the z-direction, the deformation tensor in the deformation principal axis frame is given by

$$\overleftrightarrow{\lambda} = \begin{pmatrix} \lambda^{-/2} & 0 & 0 \\ 0 & \lambda^{-1/2} & 0 \\ 0 & 0 & \lambda \end{pmatrix} \tag{9}$$

The deformed vector that characterizes the deformed network can be written as

$$\vec{L} = \overleftrightarrow{\lambda}\vec{L}_0 \tag{10}$$

In the following, we will make the assumption that the network deformation will affect the diffusion coefficients only via the size parameter ξ given by eq 2. The diffusion tensor of small penetrant molecules in a uniaxially deformed polymer network can be written from eqs 1 and 2 as

$$\ln \overleftrightarrow{D}_1 = \left[\ln D_0 - \frac{E^*}{RT} - \frac{(1-w_\mathrm{p})\hat{V}_1^*}{\hat{V}_\mathrm{FH}/\gamma}\right]\overleftrightarrow{1} - \frac{w_\mathrm{p}\hat{V}_2^*}{\hat{V}_\mathrm{FH}/\gamma}\overleftrightarrow{\xi} \tag{11}$$

where the unit tensor is denoted by and the size parameter tensor is given by

$$\overleftrightarrow{\xi} = \begin{pmatrix} \xi_x & 0 & 0 \\ 0 & \xi_y & 0 \\ 0 & 0 & \xi_z \end{pmatrix} \tag{12}$$

For a uniaxial deformation $\xi_x = \xi_y$.

For a quasispherical molecule, the aspect ratio is $\bar{A}/\bar{B} \approx 1$, and from eq 2 we get $\overleftrightarrow{\xi} \approx \overleftrightarrow{\xi}_L$. As a further assumption, we request that only $\tilde{V}_2^*$, i.e., the critical free volume per mole of jumping units required for a jump, is a function of deformation ratio λ. Finally we

Table 1. Properties of the Series of Cross-Linked Natural Rubber (NR) Samples

sample	sulfur−accelerator content (phr)	shear modulus[a] G (dNm)	equilibrium toluene concentration[b] c_s (%)
NR1	1−1	5.2	0.652
NR4	4−4	13.2	0.692
NR7	7−7	16.2	0.800

[a] The uncertainties are less than 10%. [b] The uncertainties are less than 1%.

can write

$$\vec{\xi}_L = \frac{\tilde{V}_1^{(0)}(0)}{\tilde{V}_2^*(\lambda = 1)}\begin{pmatrix} \lambda^{1/2} & 0 & 0 \\ 0 & \lambda^{1/2} & 0 \\ 0 & 0 & \lambda^{-1} \end{pmatrix} \tag{13}$$

The degree of anisotropy of the diffusion process can be evaluated in an uniaxially deformed polymer network by combining eqs 11−13. Finally, we get

$$\ln\left(\frac{D_1^{xx}}{D_1^{zz}}\right) = \frac{w_{\mathrm{p}}\hat{V}_2^*}{\hat{V}_{\mathrm{FH}}/\gamma}\cdot\frac{\tilde{V}_1^{(0)}(0)}{\tilde{V}_2^*(\lambda = 1)}\cdot\frac{1 - \lambda^{3/2}}{\lambda} \tag{14}$$

The dependence of $\ln(D_1^{xx}/D_1^{zz})$ on the deformation ratio λ can be separated from the other network parameters by taking the natural logarithm of both sides of eq 14, i.e.,

$$\ln\left(\left|\ln\left(\frac{D_1^{xx}}{D_1^{zz}}\right)\right|\right) = \ln\left(\frac{w_{\mathrm{p}}\hat{V}_2^*}{\hat{V}_{\mathrm{FH}}/\gamma}\cdot\frac{\tilde{V}_1^{(0)}(0)}{\hat{V}_2^*(\lambda = 1)}\right) + \ln\left(\frac{|1 - \lambda^{3/2}|}{\lambda}\right) \tag{15}$$

The above equation describes the cases of polymer network compression ($\lambda < 1$) as well as elongation ($\lambda > 1$).

It is noted again that the main assumption that leads to eq 15 is that none of the quantities involved in eqs 3−8 are essentially affected by the network deformation. This will be justified below by the agreement of our experiments with the above assumption and theory.

Experimental Section

Materials. A series of differently cross-linked samples from commercially available natural rubber (NR) SMR10 (Malaysia) was investigated. The additives were 3 *p*arts-per-*h*undred-*r*ubber (phr) ZnO and 2 phr stearic acid. These cross-link natural rubber samples NR1, NR4, and NR7 were prepared with the sulfur and accelerator contents given in Table 1. The accelerator is of the standard sulfenamide type (benzothiazyl-2-*tert*-butyl-sulfenamide, TBBS). After mixing the compounds in a laboratory mixer at 50 °C, the samples were vulcanized at 160 °C in a Monsanto MDR-2000-E vulcameter. The degree of cross-linking was measured by the low-frequency shear modulus (G) or torque at a temperature of 160 °C in the vulcameter directly after vulcanization.

Alkane solvents such as *n*-hexane, *n*-heptane, *n*-octane, and *n*-decane were obtained from Sigma-Aldrich. These solvents and toluene were incorporated into the cross-linked natural rubber samples NR1, NR4, and NR7 by swelling at room temperatures. Circular samples were cut from the vulcanized sheets and were dried overnight in a vacuum desiccator. The samples were then immersed in the test solvents. At regular intervals, the test samples were removed from the solvent and damp dried for 5−10 s between filter papers to remove the excess solvent on their surface. To establish the sorption kinetics, they were than weighed immediately with an electronic balance. Because weighting was done within 30−40 s, the error owing to evaporation of other than surface-absorbed liquid is considered insignificant. The results of sorption experiments are expressed as moles of liquid Q_{w} sorbed by 100 g of NR.[28] The quantity Q_{w} measured in mole % was determined as

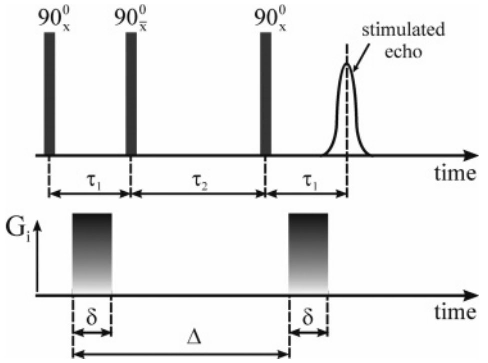

Figure 1. Pulse gradient stimulated echo (PGSE) scheme for measuring self-diffusion coefficients. The magnetic field gradients (G_i) are applied along the direction of the static magnetic field ($i = z$) and perpendicular to this field ($i = x$ or y). These pulsed gradients have the duration δ and are separated by the diffusion time Δ.

$$Q_{\mathrm{w}} = \frac{(\textit{Weight of sorbedsolvent})/(\textit{Molecular weight of solvent})}{\textit{Initial weight of rubber}} \cdot 100\%$$

The disk-shape samples of natural rubber were exposed to toluene and alkane solvents for several hours until the equilibrium value was reached (see Figure 2 below). Beside the direct mixing, swelling in alkane vapors was also tested. In the limit of experimental errors, the diffusivities do not change as a function of the swelling protocol.

NMR Measurements. The NMR experiments were performed at a ^{1}H frequency of 299.870 MHz on a Bruker DMX-300 spectrometer. The diffusivity of toluene and alkane solvents in the NR samples was measured with the pulse gradient stimulated echo (PGSE) method at a temperature of 293 K.[2−4] The radio frequency pulse sequence and pulsed magnetic field gradients separated by the diffusion time Δ are shown in Figure 1. The stimulated-echo attenuation factor by ordinary diffusion is given by[2−4]

$$\frac{E(q)}{E(0)} = \exp\left\{-Dq^2\left(\Delta - \frac{\delta}{3}\right)\right\} \tag{16}$$

where $q = \gamma G\delta/2\pi$ is the reciprocal space vector, γ is the magnetogyric ratio, G is the gradient strength, and δ is the duration of the pulsed gradient. An effective diffusivity D is measured by the fit of the experimental data with eq 1. The effective diffusivity is due to the heterogeneities of the samples. Moreover, the diffusion coefficient D depends on the diffusion time Δ.[24] This anomalous diffusion can be described by the relationship $D \propto \Delta^{k-1}$. It was shown that in compressed NR the diffusion coefficient becomes anisotropic but the dependence on the diffusion time is mainly isotropic.[24]

The parameters of the pulse sequence shown in Figure 1 were: 13.5 μs 90° pulse length, 1 s recycle delays, 0.474 T/m maximum strength and 1 ms duration of the gradient pulses. The gradient strength was changed in 64 equidistant steps. The diffusivities of the organic molecules were measured for two gradient orientations parallel (z-direction) and perpendicular (x-direction) to the static magnetic field. The proton signal of the elastomer gives a constant contribution to the amplitude of the stimulated echo that was taken into account in the data processing. The uniaxial compression was applied parallel to the z-direction. A home-built device was built for

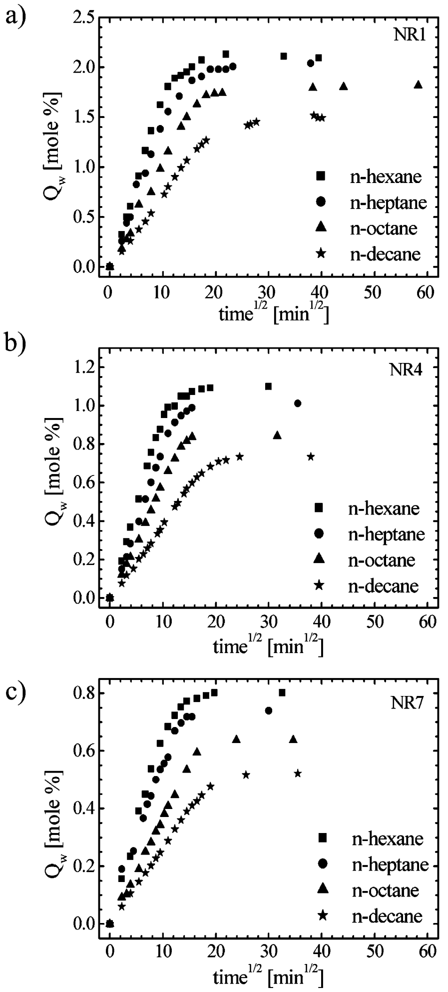

Figure 2. Mole percent Q_w of alkane solvent uptake of cross-linked rubber samples NR1 (a), NR4 (b), and NR7 (c) at 20 °C.

applying compression forces along the direction of the static magnetic field.

Results and Discussion

The measurements of the anisotropy of the diffusion coefficients were done on toluene swollen at equilibrium in NR4 and a series of alkane solvents on NR1, NR4, and NR7. For the last case, the mole percent values Q_w were plotted against the total immersion time in Figure 2. In every case, the kinetics of solvent sorption deviates from the regular Fickian trend in agreement with previous measurements made on other samples of natural rubber and reported in ref 25. These measurements show that after about 2 h the equilibrium concentrations of the solvent were reached for each NR sample. In all the diffusivity measurements, the natural rubber samples were investigated at the equilibrium concentrations of toluene, *n*-hexane, *n*-heptane, *n*-octane, and *n*-decane.

The measured normalized amplitudes $E(q)/E(0)$ (cf. eq 16) of the stimulated echoes can be fitted for all samples and solvents by a single-exponential decay function that depends on the square of the reciprocal space vector q^2. Two examples of these decays are shown in Figure 3 for *n*-hexane and *n*-decane swollen at equilibrium in uniaxially compressed NR1 (cf. Table 1) for a compression ratio $\lambda \approx 0.5$, a diffusion time $\Delta = 1$s, and two orthogonal orientations of the magnetic field gradient. A week diffusion anisotropy is observed for all the solvents. For the alkane solvents as well as toluene, the stimulated echo decays for the *x*- and *z*-gradient orientations depend on the NR cross-link density.[24]

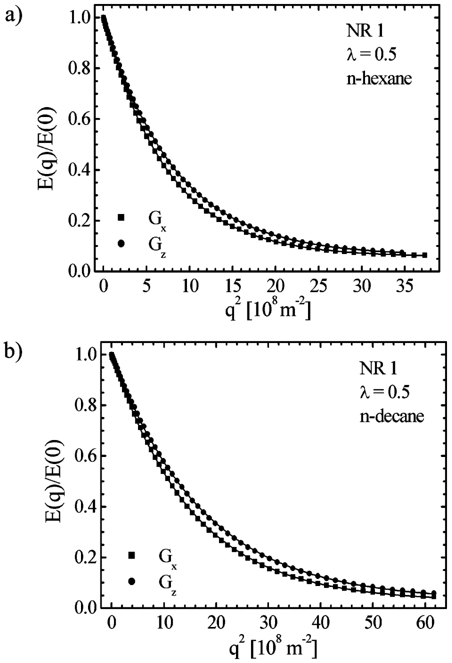

Figure 3. Normalized stimulated echo decays of the natural rubber sample NR1 (see Table 1) for a diffusion time of $\Delta = 1$ s, and uniaxial compression along the *z*-direction with compression ratio of $\lambda \approx 0.5$. The decays are depicted for the equilibrium swelling in *n*-hexane and *n*-decane in (b) and (c), respectively. The data were fitted with an exponential decay (continuous lines).

The effective diffusion tensor components D_{ii} ($i = x, z$) in the laboratory reference frame, e.g., can be obtained from an exponential fit of the stimulated echo data in q^2 (Figure 3). The dependence of the diffusivities D_{xx} and D_{zz} on the equilibrium mole percent Q_w of alkane solvents in NR1 and NR7 are shown in Figure 4a and c, respectively. It is evident from these graphs that the difference $D_{xx} - D_{zz}$ does not change much with the change in the molar mass of the solvent. This can be explained by the fact that, in the investigated range of molecular mass of solvents, the molecules explore approximately the same free volume, and the microscopic parameters of diffusion do not essentially change from solvent to solvent. Furthermore, the average differences in the diffusivity measured along the deformation direction and perpendicular to this direction does not essentially change from NR1 to NR7 (see Figure 4a and c). This behavior was also reported for toluene swollen in a series of the cross-linked natural rubber samples NR1−NR7.[24]

For all solvents, the anisotropy of the effective diffusivity defined by $a_D = (D_{xx} - D_{zz})/D_{\text{iso}}$, where the isotropic value is $D_{\text{iso}} = (2D_{xx} + D_{zz})/3$, increases with the cross-link density (cf. Figures 4b and 4d) and the molar mass of the alkane solvents. This behavior was also detected for toluene in NR1−NR7.[24] This effect is mainly due to the changes in the values of D_{iso} for different solvents and cross-link densities.

The displacement probabilities or propagators[1−4] of *n*-hexane and *n*-decane molecules diffusing in the uniaxially compressed sample NR1 were obtained for $\Delta = 1$ s and $\lambda \approx 0.5$ after Fourier transformation of the

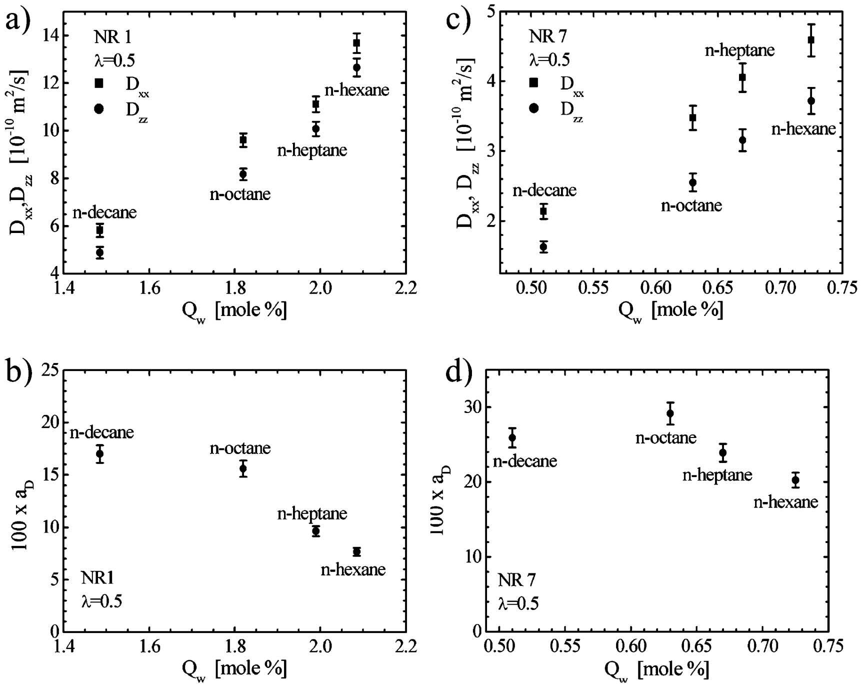

Figure 4. Effective diffusivities D_{xx} and D_{zz} of alkane solvents for NR1 (a) and NR7 (c) for a compression ratio of $\lambda = 0.5$ and a diffusion time of $\Delta = 1$ s as a function of the equilibrium mole percent parameter Q_w. The diffusion tensor anisotropy a_D versus Q_w for NR1 (b) and NR7 (d) for different alkane solvents.

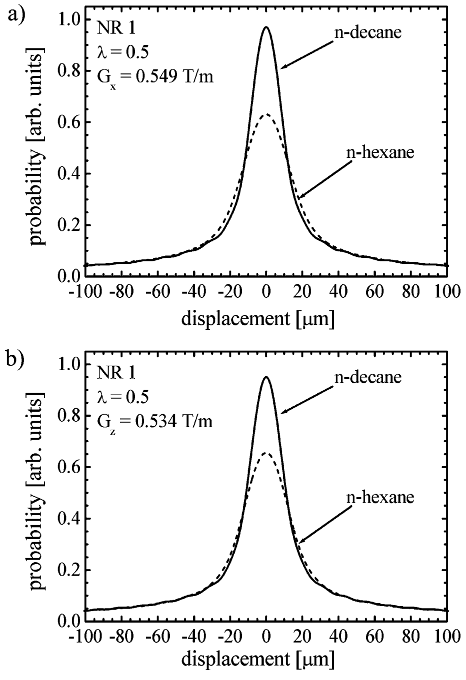

Figure 5. Displacement probabilities of n-hexane and n-decane measured in NR1 under uniaxial compression for $\lambda \approx 0.5$ in the x (a) and z (b) directions orthogonal and parallel to the direction of compression.

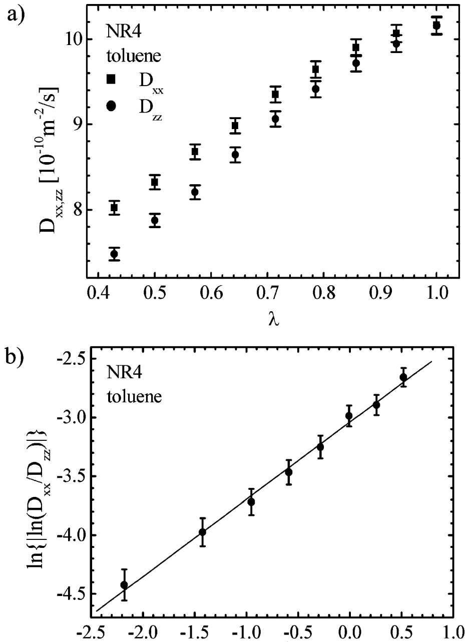

Figure 6. (a) Diffusivities D_{xx} and D_{zz} of toluene as a function of the compression ratio λ measured for NR4. (b) The correlated dependence of $\ln\{|\ln(D_{xx}/D_{zz})|\}$ and $\ln\{|1 - \lambda^{-3/2}|/\lambda\}$ for the data shown in (a). The solid line is the best fit to this dependence according to eq 15.

stimulated echo decays. These propagators are shown in Figure 5 for two gradient field orientations relative to the compression direction. Similar to the case of toluene swollen in NR4, which has been reported previously,[24] the shape of the propagators is given by Gaussian functions for all the alkane solvents investigated. This is consistent with other cases of self-diffusion.[1] The width of the propagators is related to the average molecule displacement that is correlated with the diffusivity. Therefore, as expected, Figure 5 shows that the diffusivity of n-decane is slightly smaller than the diffusivity of n-hexane in both directions. Moreover, the diffusivity along the x-direction is larger than that along the z-direction (cf. Figures 5a and b).

The dependence of the diffusion coefficients D_{xx} and D_{zz} of toluene on the compression ratio λ is shown in Figure 6a for the sample NR4. For about the same range of compression ratios, the changes in the n-hexane diffusivities for sample NR1 are shown in Figure 7a. To test the validity of the assumptions invoked in the derivation of eq 15, the quantity $\ln\{|\ln(D_{xx}/D_{zz})|\}$ is

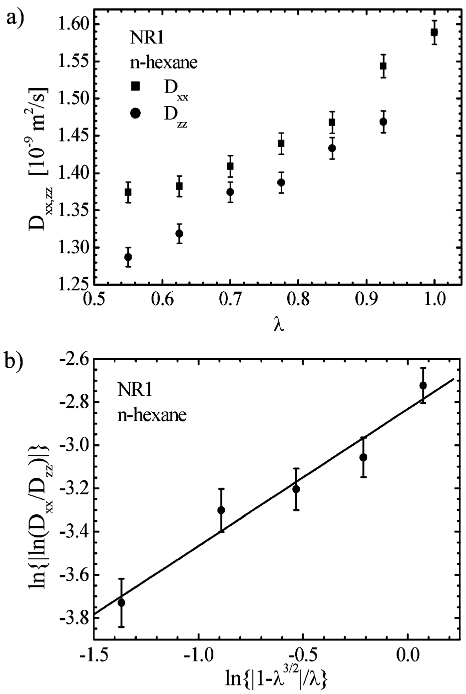

Figure 7. (a) Diffusivities D_{xx} and D_{zz} of *n*-hexane as a function of the compression ratio λ measured for NR1. (b) The correlated dependence of $\ln\{|\ln(D_{xx}/D_{zz})|\}$ and $\ln\{|1 - \lambda^{-3/2}|/\lambda\}$ for the data shown in (a). The solid line is the best fit to this dependence according to eq 15.

represented as a function of $\ln\{|1 - \lambda^{-3/2}|/\lambda\}$. These dependences are shown in Figures 6b and 7b. For both samples, NR1 and NR4, and two solvents, toluene and *n*-hexane, the above dependence can be well-fitted by a straight line. As predicted by eq 15, the slopes of these lines are close to unity, being independent of the sample/solvent properties. The above facts show that eq 15 derived in the approximation of penetrant molecules with the size parameter $\xi \approx \xi_L$ describes the dependence of diffusivity anisotropy measured by the ratio D_{xx}/D_{zz} on the deformation ratio λ in a good approximation. We note that the relationship (eq 15) is also valid for natural rubber with different cross-link densities.

The toluene and *n*-hexane molecules have different aspect ratios. The values for $\bar{A}/\bar{B}$ were evaluated in ref 14 using the ADAPT software.[29] The reported values are: for toluene solvent in poly(vinyl acetate) (PVAC) $\bar{A}/\bar{B} \approx 0.805$, and for *n*-hexane in the same polymer $\bar{A}/\bar{B} \approx 0.454$.[14] Therefore, on the basis of eq 2, the size parameter of the toluene molecules fulfilled the condition $\xi \approx \xi_L$. If the assumptions made for derivation of the dependence of ξ_L on the deformation ratio λ are justified, the dependence described by eq 15 will be in a good agreement with the experimental data. This is indeed the case, as shown in Figure 6b. Indirectly, that shows that the aspect ratio of toluene in cross-linked natural rubber is also close to unity as in the PVAC case.[14] The behavior of *n*-hexane is expected to be different because the aspect ratio is about half of that of toluene in PVAC. Nevertheless, the correlation of the size parameter and aspect ratio on the basis of the results reported in ref 14 leads to $\xi_{\text{toluene}} \approx \xi_{n-\text{hexane}}$. Because for *n*-hexane in PVAC the product $\xi_L(1 - \bar{A}/\bar{B})$ is smaller than unity, we finally get $\xi \approx \xi_L$.[14] This can explain why also for *n*-hexane, eq 15 describes the dependence of the diffusion anisotropy on the network deformation in a good approximation (cf. Figure 7b). Moreover, for *n*-hexane, it is plausible to assume a wide range of conformations as their dihedral angle potentials are relatively flat and the molecule average shape in the polymer matrix is close to that of toluene.

For the alkane molecules with larger molar mass such as heptane and octane that have smaller values of the aspect ratio $\bar{A}/\bar{B}$ (see ref 14), the general eq 2 has to be used. This is likely to lead to a different dependence of the diffusion anisotropy measured in terms of D_{xx}/D_{zz} on deformation ratio λ. This is a topic of further investigation.

Conclusions

A small diffusion anisotropy on the order of 10% was detected for several alkane molecules swollen at equilibrium in cross-linked natural rubber samples. This mainly reflects the deformation of the free volume under compression. The anisotropy increases with the cross-link density and the compression ratio. The difference between the diffusion coefficients along and perpendicular on the direction of uniaxial compression is not very sensitive to the molar masses of the alkane solvents used. The diffusion anisotropy is difficult to detect for a solvent concentration lower than the equilibrium value.

The functional dependence of the diffusion anisotropy of the penetrant molecules in elastomers on the deformation ratio was derived on the basis of the following assumptions: (i) The diffusion process can be described by the microscopic theory of Vrentas et al.[8−17] In this theory, it is assumed that most penetrants of interest jump as single units. Large, asymmetric molecules can jump as single units because their shape enhances the availability of hole free volume. (ii) Only the quantity $\tilde{V}_2^*$, i.e., the critical free volume per mole of jumping units required for a jump is supposed to be a function of the deformation ratio. (iii) The aspect ratio is close to unity, i.e., the size parameter ξ is not a function of $\bar{A}/\bar{B}$. (iv) The change of the free volume follows the uniaxial deformation polymer network and can be approximated by an affine transformation. (v) The diffusion anisotropy is described and measured along and perpendicular to the direction of the uniaxial deformation.

The results presented in this study show that the solvent size influences the anisotropy of the diffusion process through the size parameter ξ. Hence, information on the effect of solvent size, shape, and flexibility on the diffusion process can be refined by measuring the size parameter anisotropy for a wide variety of solvents diffusing in different polymers.

The anisotropy of diffusion can be used for NMR investigations of the theories of polymer networks deformation in the presence of penetrant solvents.

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