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Swelling and Transport in Polyisoprene Networks Exposed to Benzene−Cyclohexane Mixtures: A Case Study in Multicomponent Diffusion

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ABSTRACT: Equilibrium uptake data for cross-linked polyisoprene networks exposed to benzene−cyclohexane mixtures are presented: the data show that the equilibrium swelling ratio is increased by the presence of the second solvent and display virtually no evidence of selective uptake from the mixture. Both features agree qualitatively with a Flory−Rehner description of swelling generalized to a binary mixture. Pulsed-field-gradient spin-echo NMR results for the self-diffusion coefficients of benzene and cyclohexane within the swollen networks are also obtained: they indicate that the self-diffusion coefficient of cyclohexane is significantly enhanced by the presence of benzene. These results are correlated with the results of simple sorption (weight uptake) experiments for cross-linked polyisoprene spheres exposed to the same solvents. In particular, the mutual diffusion coefficients that can be extracted from the sorption data reflect the trends found in the self-diffusion coefficients results.

I. Introduction

Multicomponent solvent transport in polymeric materials and elastomeric swelling in the presence of a multicomponent solvent are topics of considerable technological importance. A working understanding of these areas is required for the design of a diverse array of devices ranging from medical drug delivery implants to fluid containment systems in the automotive and aerospace industry. However, thus far most of the research effort concerning diffusion and swelling in polymers and elastomers has been devoted to situations involving a single diffusant.

From a technological standpoint the most effective way to treat the process of diffusion in a polymeric material is to employ a macroscopic description.[1] This should be capable of predicting, from the values of a few phenomenological quantities (such as diffusion coefficients and equilibrium uptakes), how the concentration profiles of the diffusants within the polymer evolve as a function of time. A correct macroscopic description is also required in order to properly interpret and situate experimental data as well as information that might be obtained from microscopic approaches such as computer simulations.

Recently, significant progress has been made toward a correct macroscopic description for situations involving a single diffusant. Equations capable of accounting for the movement (swelling) of the polymer as solvent moves into it have been given,[2,3] and their validity has been verified for solvent diffusing into loosely cross-linked elastomers.[4] The role of elastic deformations and of plasticization induced by a diffusant in a glassy polymer has been clarified, and long-standing confusion in the interpretation of the sorption curves for these systems has been dispelled.[5−7]

Diffusion processes involving multicomponent solvents present significant additional challenges compared to the case of a single diffusant. The different components in the mixture may interact in nontrivial ways; therefore, dealing with the solvent mixture as if it were a single "effective" solvent can only be regarded as a rough approximation. The equilibrium thermodynamics problem of predicting the final swelling ratio for a network exposed to a binary mixture was considered long ago by Krigbaum and Carpenter and by Shultz and Flory.[8] Their approach consists of extending to a solvent mixture the Flory−Rehner treament of equilibrium swelling in the presence of a single solvent.[9] The formalism developed by these authors also provides an expression for the separate equilibrium uptake of each solvent in terms of the Flory−Huggins interaction parameters and of the density of cross-links within the network. Qualitative experimental confirmation of the predictions of this treatment has been reported.[10] By contrast, the kinetics of multicomponent uptake seems to have received little theoretical attention, although recently a simple computer model that seeks to capture at least some defining features of this problem has been described.[11]

From an experimental standpoint, a number of techniques are available to study multicomponent diffusion. Self-diffusion coefficients (or "tracer diffusion coefficients") associated with the motion of a labeled component can, in principle, be measured by the same techniques employed in the case of a single solvent. In recent years pulsed-field-gradient spin-echo (PFGSE) NMR[12] has emerged as the preferred method in this context because of its accuracy and availability; it has been applied to a few multicomponent systems.[13−16]

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Experimental methods are also becoming available to measure transport diffusion for each separate component within the system. For methanol−toluene mixtures diffusing into ethylene−vinyl alcohol copolymers (EVOH), separate toluene and methanol sorption curves have been obtained using FTIR spectroscopy.[17] The time evolution of the concentration profile of paramagnetic diffusants within a swollen network has been determined using electron spin resonance (ESR) imaging.[18] NMR imaging has been used to follow the separate uptake of acetone and methanol in polycarbonate exposed to mixtures of the two solvents.[19,20] In principle, it should be possible to obtain the separate concentration profiles using these techniques.[21] It should also be possible, for appropriate solvents, to obtain high-resolution concentration profiles using ion beam techniques such as Rutherford backscattering spectrometry[22] and forward recoil electron spectrometry.[23]

In this paper we focus on the problem of binary solvent mixtures of benzene (B) and cyclohexane (C) being taken up by an elastomeric material, polyisoprene cross-linked to different degrees. This is a particularly simple model system: both benzene and cyclohexane are good solvents for polyisoprene, and the values of the two Flory−Huggins interaction parameters are close.[24] Since the separate behaviors of the two solvents in polyisoprene are very similar, the system is especially suited to highlight effects due to the two-component nature of the solvent. A complementary investigation of the diffusion of mixtures of one good solvent (cyclohexane) and one poor solvent (isopropanol) in cross-linked polyisoprene is currently under way. This line of research was motivated by the common technological problem of having to predict the flux and composition of multicomponent fluids permeating through a rubber seal. In particular, the objective of this study was to shed light on the physical processes that are relevant to this problem. In the corresponding situation involving a single diffusant, both information regarding the final equilibrium state and information regarding the kinetics of the process (diffusion coefficients) are required to attack the problem. We expect this to also be the case for a multicomponent solvent.

In order to probe the equilibrium properties of our system, we measured for a number of different mixtures both the final equilibrium swelling ratio and the equilibrium uptake of each solvent at different cross-linking levels. The qualitative features of these results agree with the predictions of the model of ref 8. In order to probe the kinetic properties of the system, we performed two different kinds of experiments. The self-diffusion coefficients of the two solvents within the swollen networks were measured by PFGSE NMR. These data display nontrivial behavior, including a sizable increase in the diffusion coefficient of cyclohexane in samples swollen by the mixtures. The self-diffusion coefficients obtained in this way describe the rate of random molecular motion (molecular mobility) under conditions of macroscopic equilibrium. On the other hand, in situations involving macroscopic transport of solvent, for example, in the problem of a mixture permeating across a seal, the relevant kinetic parameters are the mutual (or transport) diffusion coefficients. In order to obtain information on these quantities, we performed a number of simple weight uptake experiments for cross-linked polyisoprene specimens exposed to different mixtures. We did not attempt to obtain separate sorption curves for the two solvents; nevertheless, by analyzing the weight uptake data with the methods of refs 2 and 3, we were able to obtain estimates for the ("effective") mutual diffusion coefficients. We find that these results correlate well with the data for the self-diffusion coefficient obtained by PFGSE NMR.

This paper is organized as follows. In the next (experimental) section we describe the polymer preparation, the swelling experiments, and the NMR technique used to obtain the self-diffusion coefficients of benzene and cyclohexane. In the third section we present our equilibrium swelling data including the swelling ratios for networks cross-linked to different extents and the data for the composition of the solvent within the swollen network; we also report our data for the self-diffusion coefficients D_B (of benzene) and D_C (of cyclohexane), both within the swollen networks and within the binary mixtures to which the networks were exposed. Furthermore, we describe our procedure to obtain estimates of the mutual diffusion coefficients D_M from the sorption data and report the results obtained in this way. In the fourth section we include an analysis of the equilibrium swelling results based on the model of ref 8 and a comparison of the self-diffusion coefficients with the mutual diffusion coefficients estimated from the sorption experiments. A brief summary and conclusions are presented in the final section.

II. Experimental Section

Polymer Preparation. Cross-linked polyisoprene (cPI) samples were prepared by mixing commercial *cis*-1,4-polyisoprene (Natsyn 2200 supplied by Goodyear) with 1−10 phr (parts per hundred rubber, by weight) of dicumyl peroxide (Varox DCP−R supplied by R. T. Vanderbilt, Inc.) on a small two-roll mill at ambient temperature, as described previously.[4] The mixture was used to fill spherical (1.25−6 mm in diameter) or cylindrical (1.25−7.5 mm in diameter) steel molds and press cured at 150 °C for 90 min. Hereafter, we shall use for these samples the notation cPI*n*, where *n* is phr of dicumyl peroxide.

Equilibrium Swelling and Sorption Experiments. Cross-linked samples were swollen at room temperature by immersion in neat solvents or solvent mixtures whose volume was always much larger than that of the samples. The solvents, benzene (>99.9%) and cyclohexane (>99.9%), were HPLC grade from Sigma and used as received. Both spherical and cylindrical polymer samples were used, and the size of the samples was such that equilibrium swelling was achieved within 2 or 3 days. During this time the swelling samples and the solvents were held in glass containers sealed with Teflon-lined caps to ensure that no changes in mixture composition or loss of solvent occurred. The equilibrium swelling ratio was determined for cPI*n* samples with $n = 1$, 3, 5, and 10 in pure benzene (B), in pure cyclohexane (C), and in mixtures with B/C = 1/3, 1/1, and 3/1 by volume, by weighing the swollen samples after having quickly blotted their surface dry. Sorption data (solvent weight uptake vs time) for swelling spherical samples were collected in the same way. In the sorption experiments the sample was returned to the solvent after each weighing; no correction for the relatively short time (less than 2 min) that a sample spent out of the solvent during each measurement was applied to the sorption data.

The composition of the solvent within networks swollen by immersion in mixtures of benzene and cyclohexane of different compositions was determined as follows. The swollen samples were taken out of the mixture and, after their surface had quickly been dried with blotting paper, were transferred to containers filled with pure methanol. The volume of methanol in these containers was much larger (at least 60 times) than the volume of the swollen samples. This procedure induced almost complete[25] deswelling of the rubber samples, as the

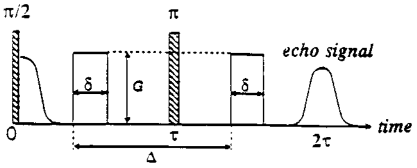


Figure 1. Pulse-field-gradient spin-echo sequence for measurement of the self-diffusion coefficient *D*.

benzene and cyclohexane within the rubber diffused into the methanol.

Once deswelling equilibrium had been reached, samples of the benzene–cyclohexane–methanol mixture obtained in this way were analyzed for composition by direct liquid injection via an autosampler into a Hewlett-Packard 5890(II) gas chromatograph (GC) fitted with a Hewlett Packard 5972 mass spectrometer (MS). The separation column in the GC was a 30-m Restek Stablewax column with a diameter of 0.25 mm and an internal coating of 0.25-μm thickness. The MS was operated in SIM mode, which enhances analytical sensitivity. The standard against which these samples were analyzed was prepared by serial dilution in methanol of a 50/50 (by weight) mixture of benzene and cyclohexane. Four standards were prepared to produce a linear standard curve. For each cross-linking ratio and each mixture composition, two rubber specimens were swollen and deswollen in this way, and for each specimen, two samples of the methanol–benzene–cyclohexane mixture were analyzed by mass spectrometry.

Diffusion Measurements. The solvent-swollen cPI*n* samples were placed in 5-mm-o.d. NMR tubes to a height of 8 mm and sealed with a glass plug or with Teflon tape. The temperature was kept constant within ±1 K. The solvent mixture in the NMR experiments contained equal parts by volume of protiated and deuteriated solvents, for the deuterium lock.[26] The deuteriated solvents, benzene-d_6 (from MSD Isotopes) and cyclohexane-d_{12} (from Matheson Isotec Inc), contained >99.6 atom % deuterium and were used as received.

The self-diffusion coefficients of benzene and cyclohexane in the neat solvents, the solvent mixtures, and the swollen cPI*n* samples were measured at 300 K with a JEOL GSX spectrometer operating at 270 MHz for protons. The spin-echo sequence ($\pi/2$, τ, π), and the two field gradient pulses of width δ and intensity G are shown in Figure 1. The decay of the echo intensity due to the gradient pulses is given by

$$\ln\frac{A(\delta)}{A(0)} = -\frac{2\tau}{T_2} - \gamma^2 G^2 D \delta^2\left(\Delta - \frac{\delta}{3}\right) \qquad (1)$$

where $A(\delta)$ and $A(0)$ are the echo intensities at 2τ with and without the gradient pulse, respectively, T_2 is the spin–spin relaxation time of the protons, τ is the pulse interval, γ is the gyromagnetic ratio of the proton, and D is the self-diffusion coefficient. The duration of the $\pi/2$ pulse was ≈6 μs, the τ and Δ values were 30 ms, and δ varied in the range 0.001–0.32 ms. All experiments were performed using a probe with a maximum field gradient of 588 G/cm. The spectral width was 4 kHz, the number of points was 4K, and typically 16–32 scans were needed for a reasonable signal-to-noise ratio. The echo intensity was measured as a function of δ, and D was measured from the slope of a plot of $\ln(A(\delta)/A(0))$ vs $\gamma^2 G^2 D \delta^2(\Delta - \delta/3)$. For each system 9–12 spectra were measured in a range of δ values. The measured values of D were corrected, based on the D value of 2.5×10^{-5} cm^2/s for water at 303 K as the calibration. We estimate a total error margin of 10% in the values of D.

III. Results

Equilibrium Swelling Results. Equilibrium solvent uptakes at 300 K by cPI*n* are given in Table 1. For each solvent (or solvent mixture) at each cross-linking level, the table reports the final swelling ratio, *e.g.*, the ratio (final swollen volume)/(initial dry polymer volume).

Table 1. Solvent Uptake at Room Temperature[a]

solvent	cPI1	cPI3	cPI5	cPI10
benzene	5.77 (4.67)	3.99 (2.90)	3.04 (1.95)	2.31 (1.24)
B/C = 3/1	6.33 (5.07)	4.15 (2.97)	3.41 (2.24)	2.32 (1.22)
B/C = 1	6.63 (5.20)	4.26 (2.98)	3.42 (2.19)	2.54 (1.38)
B/C = 1/3	6.60 (5.02)	4.21 (2.85)	3.40 (2.10)	2.35 (1.17)
cyclohexane	6.05 (4.39)	4.07 (2.65)	3.25 (1.91)	2.32 (1.11)

[a] For each solvent or solvent mixture (first column) and each cross-linking level (first row), the table reports the swelling ratio, e.g., the ratio (final swollen volume)/(initial dry polymer volume), and in parentheses the original gravimetric measurement (g of solvent/g of polymer). The following values for the densities (in g/cm^3) were used to calculate the swelling ratios: $\rho(C_6H_6) = 0.8765$, $\rho(C_6H_{12}) = 0.7785$, ρ(cPI1) = 0.896, ρ(cPI3) = 0.904, ρ(cPI5) = 0.916, and ρ(cPI10) = 0.925.

Table 2. Solvent Composition within the Swollen Networks[a]

mixtures	0.339	0.534	0.770
cPI1	0.333	0.532	0.745
cPI3	0.357	0.535	0.756
cPI5	0.352	0.535	0.748
cPI10	0.360	0.535	0.768

[a] The first row gives the volume fraction of cyclohexane in the mixtures used to swell the rubber specimens. The remaining four rows (one for each cross-linking level) give the volume fractions of cyclohexane within the solvent extracted from the specimens swollen in each mixture.

The swelling ratios were deduced from the original gravimetric measurements (g of solvent/g of polymer) reported in parentheses. To this end, it was assumed that no volume change occurred upon mixing. Furthermore, to obtain the swelling ratios for the mixtures, it was assumed that the relative amount of benzene and cyclohexane within the swollen samples is the same as that in the mixtures: this assumption is justified in view of the results for the composition of solvent within the swollen samples presented below (see Table 2). Typical error margins for these data are on the order of a few percent. At the same level of cross-linking, the swelling ratios are somewhat larger in the case of cyclohexane than in the case of benzene and are greater in the mixtures than in the pure solvents. This effect is particularly evident at the lowest cross-linking level.

Our results for the composition of solvent found in the equilibrium swollen samples are collected in Table 2. The volume fraction of cyclohexane in the three mixtures used to swell the samples is reported in the first row. The volume fractions of cyclohexane in the solvent extracted from the swollen specimens are given in the successive four rows, each for a different cross-linking level. For each mixture and each cross-linking level, the value reported for the volume fraction of cyclohexane is obtained by averaging data from four samples of solvent: these were extracted from two different swollen rubber specimens (two solvent samples for each rubber specimen). In all cases the cyclohexane volume fraction in the individual solvent samples is within ±2% of the reported value. The data in Table 2 show that the composition of the extracted solvent is always very close to that of the mixture in which the rubber specimens were swollen: e.g., there is almost no evidence for selective uptake. The only apparent trend is a very slight increase in the relative amount of cyclohexane as the cross-linking level increases.

NMR Results. The variation of the amplitude of the benzene (at ≈7.2 ppm) and cyclohexane (≈1.4 ppm) signals as a function of the field-gradient pulse duration

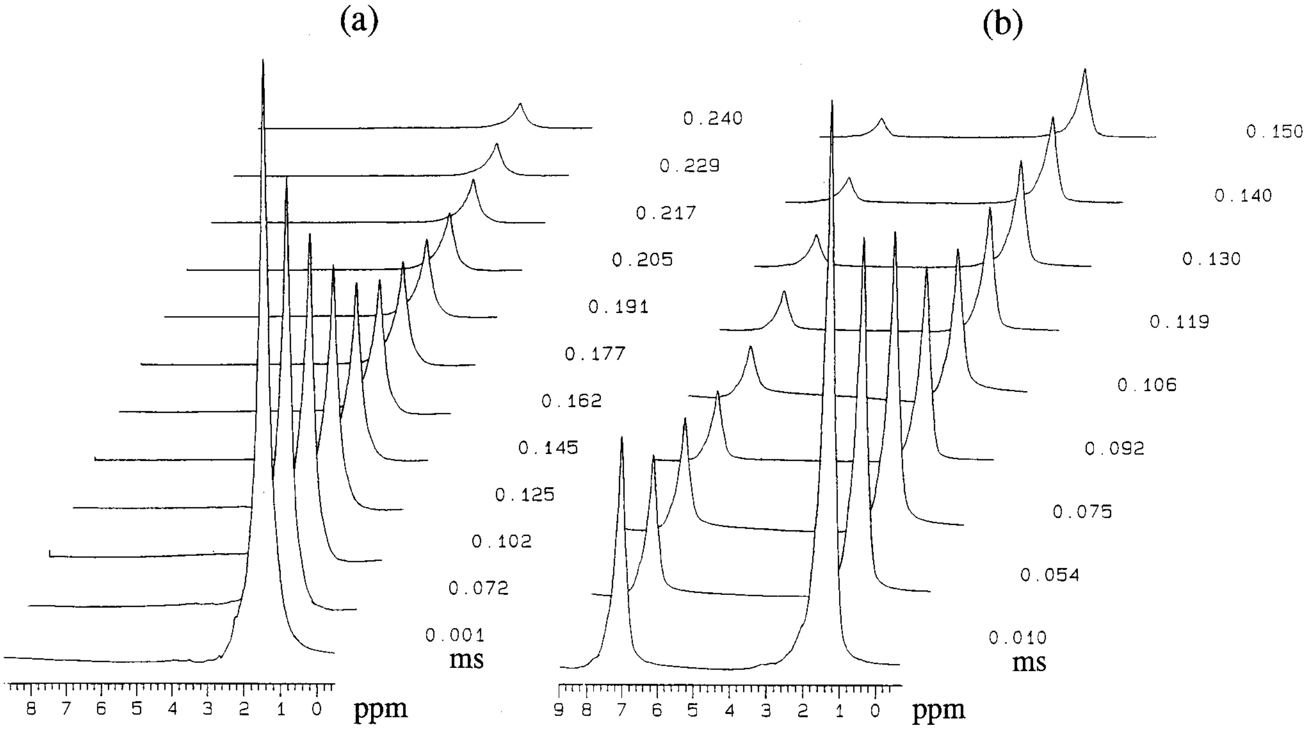


Figure 2. Spin-echo ^{1}H NMR spectra as a function of field gradient pulse duration δ: (a) cyclohexane in cPI3 swollen by neat C and (b) benzene and cyclohexane in cPI3 swollen by the B/C = 1/1 mixture.

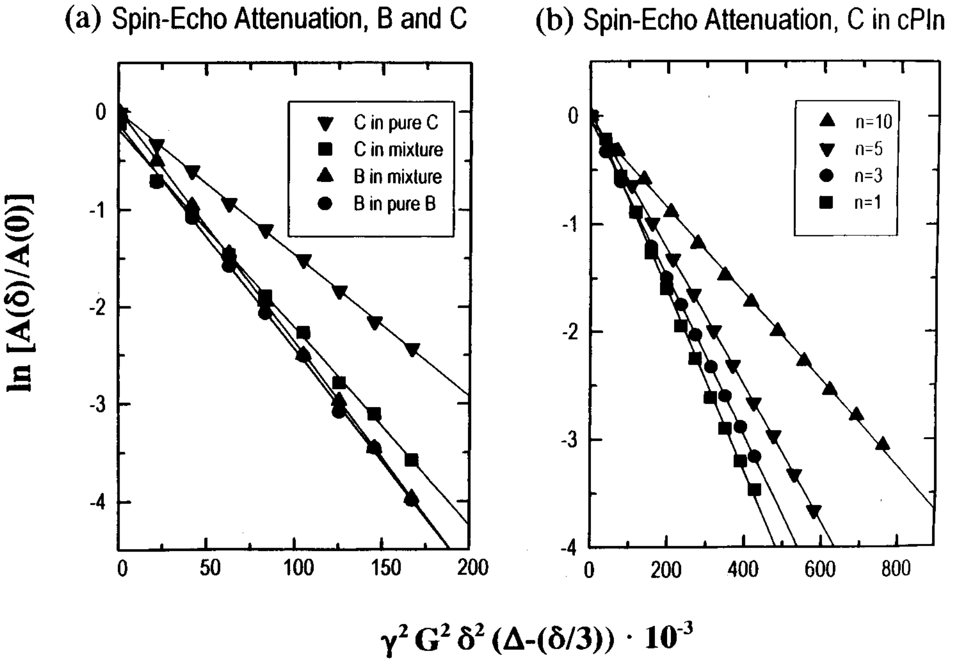


Figure 3. (a) Attenuation of the spin-echo intensity due to the diffusion of benzene in neat B (●), benzene in the B/C = 1/1 mixture (▲), cyclohexane in the B/C = 1/1 mixture (■), and cyclohexane in neat C (▼). (b) Attenuation of the spin-echo intensity as a function of the degree of cross-linking due to the diffusion of cyclohexane in cPI*n* swollen by neat C. Notation: $n = 1$ (■), $n = 3$ (●), $n = 5$ (▼), and $n = 10$ (▲).

δ served as a basis for the determination of the corresponding self-diffusion coefficients. Typical spin-echo ^{1}H NMR spectra at 300 K are shown in parts a (for cPI3 swollen by cyclohexane, cPI3/C) and b (for cPI3 swollen by the solvent mixture with B/C = 1/1) of Figure 2.

The attenuation of the spin-echo intensity in a PFGSE experiment due to diffusion is shown in Figure 3a, for neat B, for neat C, and for each solvent in the B/C = 1/1 mixture. Figure 3b shows the attenuation for C in networks swollen with neat C as a function of the degree of cross-linking. The self-diffusion coefficients for B and C in the various systems are collected in Table 3.

Sorption Results. Estimate of the Mutual Diffusion Coefficients. An example of our sorption data obtained from a spherical specimen is shown in Figure 4: the increase in sample volume (in units of the original volume) is plotted as a function of $\sqrt{t}$. In this particular case the specimen was a cPI1 sample swollen in a B/C = 1/1 (by volume) mixture. Since the sorption data were obtained gravimetrically, the volume increase

Table 3. Self-Diffusion Coefficients from PFGSE NMR[a]

	D_B (10^{-5} cm^2/s)	D_C (10^{-5} cm^2/s)
B	2.32	
C		1.43
B/C = 1/1	2.32	2.03
cPI1 in B	1.38	
cPI3 in B	1.18	
cPI5 in B	1.05	
cPI10 in B	0.91	
cPI1 in C		0.75
cPI3 in C		0.68
cPI5 in C		0.58
cPI10 in C		0.37
cPI1 in B/C = 1/1	1.66	1.25
cPI3 in B/C = 1/1	1.30	1.12
cPI5 in B/C = 1/1	1.09	1.00
cPI10 in B/C = 1/1	0.57	0.44
cPI3 in B/C = 1/3	1.33	1.05
cPI3 in B/C = 3/1	1.51	1.23

[a] The table reports our experimental data for the self-diffusion coefficients D_B and D_C of benzene (B) and cyclohexane (C) in neat benzene, in neat cyclohexane, in a B/C = 1/1 mixture, and in a number of swollen CPI*n* samples. All data are in units of 10^{-5} cm^2/s. Each solvent contained equal parts by volume of the corresponding protiated and deuteriated compounds.

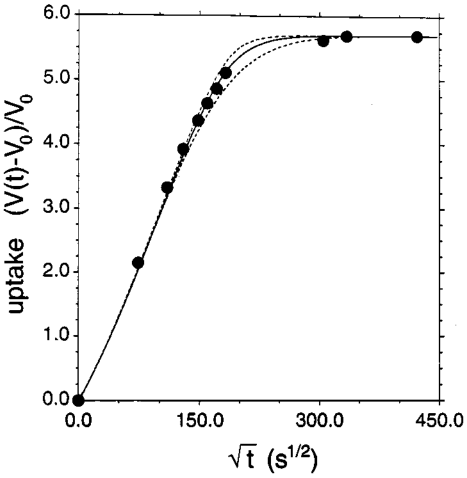


Figure 4. This figure shows an example of our sorption data (●). It gives the increase $(V(t) - V_0)/V_0$ in the volume of the sample, in units of the original volume, as a function of $\sqrt{t}$: here $V(t)$ is the volume of the sample at time t (measured in seconds), and V_0 is the original volume. The data were obtained by swelling a CPI1 sphere of diameter 0.62 cm in a B/C = 1/1 mixture. The three curves shown in the figure are calculated by solving the equations for the kinetics of swelling as described in the text and using for the mutual diffusion coefficient the expression of eq 2 with $\alpha = 0$ (lower broken curve), $\alpha = 3$ (continuous curve), and $\alpha = 6$ (upper broken curve).

Table 4. Mutual Diffusion Coefficient Obtained from the Sorption Data[a]

	D_M (10^{-6} cm^2/s)
cPI1 in B	2.8 ± 0.5
cPI3 in B	2.7 ± 0.7
cPI1 in C	1.6 ± 0.4
cPI3 in C	1.5 ± 0.3
cPI1 in B/C = 1/1	2.8 ± 0.5
cPI3 in B/C = 1/1	3.2 ± 0.7
cPI1 in B/C = 1/3	2.4 ± 0.4
cPI3 in B/C = 1/3	2.3 ± 0.4
cPI1 in B/C = 3/1	2.9 ± 0.5
cPI3 in B/C = 3/1	2.8 ± 1.3

[a] The table reports our estimates for the values of the mutual diffusion coefficient D_M at the swelling equilibrium concentration for the systems listed in the first column. These estimates were obtained by assuming for the dependence of D_M on polymer concentration the form given in eq 2 with $\alpha = 3$. It must be stressed that for mixed solvents D_M should be regarded as an effective mutual diffusion coefficient, representing a weighted average of the separate transport properties of benzene and cyclohexane. All data are in units of 10^{-6}cm^2/s.

was deduced as in the case of the equilibrium swelling ratios. In particular, in order to obtain the volume increase for specimens swelling in a mixture, we had to assume that throughout the swelling process the composition of solvent within the rubber was the same as that in the mixture. This assumption implies that our volume increase results are only approximate:[27] however, we believe that the error associated to this approximation is small and does not significantly affect the main qualitative trends that we are trying to recognize.

We estimated the mutual diffusion coefficient of the solvent in the swelling rubber specimen as follows. Each set of experimental sorption data (such as that presented in Figure 4) was fitted to the solutions of the equation describing the kinetics of swelling of a spherical network introduced in refs 2 and 3. This equation is based on Fick's law and accounts for the fact that polymer is displaced as solvent moves into the swelling network. It has been shown[3,4] that the equation can correctly account for such observed qualitative features as the presence of an inflection point in the sorption curve and desorption being faster than sorption. However, the equation makes no attempt to account for the elastic stresses that may arise and are eventually released during the swelling process:[1,3,4] for this reason we expect it to become increasingly inadequate as the cross-linking level (and thus the elastic modulus of the network) increases.

We solved the equation describing the kinetics of swelling using the same procedure that was employed in ref 4 to fit sorption data for toluene in cross-linked polyisoprene. The boundary condition required to solve the equation was deduced from the final equilibrium swelling ratio for the specimen under consideration. We chose for the mutual diffusion coefficient the following dependence on the local volume fraction of rubber ϕ_R:

$$D_M(\phi_R) = D_0 e^{\alpha(1-\phi_R)} \tag{2}$$

Here D_0 and α are constants to be determined from the fitting procedure, the only fitting parameters in the entire procedure.

The continuous and broken curves in Figure 4 show three different solutions of the equation describing the kinetics of swelling for the specific sample to which the data refer. The three curves were obtained using α = 0, 3, and 6 and choosing in each case the value of D_0 that produced the best fit to the data. Once α and D_0 for a given solvent and a given specimen are estimated, it is possible from eq 2 to find the value $D_M(\phi_R = \phi_R^{(eq)})$ of the mutual diffusion coefficient at a concentration corresponding to swelling equilibrium. The self-diffusion coefficients reported in Table 3 were obtained after the rubber specimen had been swollen to equilibrium, and therefore they also refer to a volume fraction of rubber $\phi_R = \phi_R^{(eq)}$. Table 4 reports the values of $D_M(\phi_R = \phi_R^{(eq)})$ obtained by applying the fitting procedure to both neat solvents and solvent mixtures at each cross-linking level. In the case of swelling in a solvent mixture, our procedure treats the mixture as a single effective solvent and produces a single effective mutual diffusion coefficient, namely, a weighted average of the separate mutual diffusion coefficients for benzene and cyclohexane.[28] The estimates for $D_M(\phi_R=\phi_R^{(eq)})$ listed in Table 4 were obtained using $\alpha = 3$: this value produces the most satisfactory visual fit to the data. In practice, it should be clear from the three curves in Figure 4 that it is not easy to discriminate between different values of α from this fitting procedure.[3,4] However, we have verified that if different values of α were used in the fit, the results for $D_M(\phi_R=\phi_R^{(eq)})$ would still follow the trends displayed in Table 4.

IV. Discussion

Equilibrium Swelling Results. The experimental equilibrium swelling results presented in the previous section can be rationalized using the description initiated by Flory and Rehner[9,29] and its generalization to a binary solvent mixture.[8,30] Indeed, almost 40 years ago, Bristow[10] used this approach to interpret swelling data for cross-linked natural rubber swollen in benzene-cyclohexane mixtures. Here we briefly discuss how, even in its simplest form, the Flory−Rehner approach can account for the main qualitative features of our equilibrium swelling data, specifically for the increased degree of swelling in the mixtures compared to that in the pure solvents, and for the near absence of selective solvent uptake.

In the case of a network swollen by a single solvent, the equilibrium volume fraction of polymer v can be obtained by equating the chemical potential of the pure solvent to that of the solvent in the polymer-occupied region. Under the simplifying assumptions that the molar volume of the solvent is equal to that of the monomer and that all of the chains in the network are elastically active, the volume fraction v of polymer in the swollen equilibrium state is obtained from[29]

$$\ln(1-v) + \chi v^2 + v\left(1-\frac{1}{x}\right) + \frac{1}{x}\left(v^{1/3}-\frac{v}{2}\right) = 0 \qquad (3)$$

Here x is the number of monomers between cross-links and χ is the Flory−Huggins parameter describing polymer−solvent interactions. Estimates of χ for benzene and cyclohexane in natural rubber can be found in ref 24. We use $\chi = 0.42$ for benzene and $\chi = 0.40$ for cyclohexane: these values imply that cyclohexane is a slightly better solvent than benzene in accord with the experimental swelling ratio results. Using these values for the χ's and the swelling ratio values reported in Table 1 for neat solvents, we can estimate x. We find $x \approx 67$ for cPI1, $x \approx 22$ for cPI3, $x \approx 10$ for cPI5, and $x \approx 2$ for cPI10. In view of the low values of x corresponding to the higher cross-linking levels, the simplifying assumptions leading to eq 3 are likely to be inadequate: in particular, for cPI5 and cPI10 changes in the values of the χ's due to the high number of cross-links[31] are likely to be significant. However, we do not attempt a more detailed treatment since accounting for these effects entails introducing additional phenomenological constants.

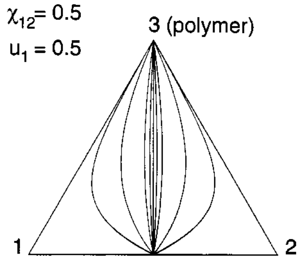


Figure 5. Curves displaying the relation between v_1, v_2, and v_3 when $u_1 = 0.5$ and $\chi_{12} = 0.5$. From left to right the nine curves refer to $\chi_{13} - \chi_{23} = -5, -2, -0.5, -0.2, 0.0, 0.2, 0.5, 2,$ and 5, respectively.

For the case of a binary solvent mixture,[8,30] the chemical potential of each solvent within the mixture is equal to the solvent chemical potential within the equilibrium swollen sample. Benzene−cyclohexane mixtures in the 20−50 °C range are known to be described well[32] by an excess Gibbs free energy of mixing per mole having the simple form $g^E \propto x_1x_2$: here x_1 and $x_2 = 1 - x_1$ are the mole fractions of the solvents in the mixture. Therefore, it is not unreasonable to use as a first approximation for the heat of mixing between the solvents the usual Flory−Huggins expression $\chi_{12}u_1u_2$, where u_1 and $u_2 = 1 - u_1$ are the volume fractions of the solvents in the mixture. Then, denoting with v_1, v_2, and v_3 the volume fractions of cyclohexane, benzene, and polyisoprene, respectively, in the polymer-occupied region, we find under the same assumptions used to obtain eq 3

$$\ln v_1 + v_3\left(1-\frac{1}{x}\right) + (1-v_1)(\chi_{12}v_2 + \chi_{13}v_3) - \chi_{23}v_2v_3 + \frac{v_3^{1/3}}{x} = \ln u_1 + \chi_{12}(1-u_1)^2 \qquad (4a)$$

$$\ln v_2 + v_3\left(1-\frac{1}{x}\right) + (1-v_2)(\chi_{12}v_1 + \chi_{23}v_3) - \chi_{13}v_1v_3 + \frac{v_3^{1/3}}{x} = \ln(1-u_1) + \chi_{12}u_1^2 \qquad (4b)$$

where χ_{12}, χ_{13}, and χ_{23} are three pair interaction parameters describing respectively the cyclohexane−benzene, cyclohexane−polyisoprene, and benzene−polyisoprene pair interactions. Parts a and b of eq 4 together with the relation

$$v_1 + v_2 + v_3 = 1 \qquad (4c)$$

provides a set of three coupled equations that can be solved numerically to obtain the volume fractions v_1, v_2, and v_3 as functions of the composition of the binary mixture (e.g., of u_1), of the number of monomers x between crosslinks, and of the three interaction parameters χ_{12}, χ_{13}, and χ_{23}.

Subtracting eq 4b from 4a, we obtain

$$\ln\frac{v_1}{v_2} + \chi_{12}(v_2 - v_1) + (1 - v_1 - v_2)(\chi_{13} - \chi_{23}) = \ln\frac{u_1}{1-u_1} + \chi_{12}(1-2u_1) \qquad (5)$$

For a fixed u_1 this equation defines both v_2 and $v_3 = (1 - v_2 - v_1)$ if v_1 is given. In other words, it defines a curve on the composition diagram for the ternary mixture. Figure 5 shows a family of such curves obtained by solving numerically eq 5: each curve in the figure corresponds to a different value of the quantity

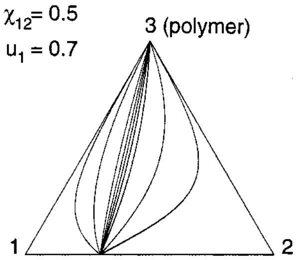


Figure 6. The curves display the relation between v_1, v_2, and v_3 when $u_1 = 0.7$ and when $\chi_{12} = 0.5$. From left to right the nine curves refer to $\chi_{13} - \chi_{23} = -5, -2, -0.5, -0.2, 0.0, 0.2, 0.5, 2,$ and 5, respectively.

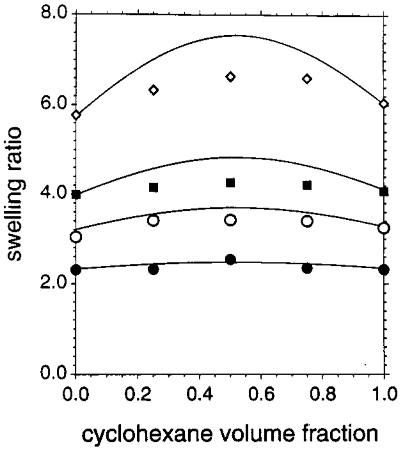


Figure 7. Curves showing the swelling ratios vs cyclohexane volume fraction calculated by solving numerically eqs 4 with interaction parameters $\chi_{12} = 0.5$ (cyclohexane–benzene), $\chi_{13} = 0.4$ (cyclohexane–polyisoprene), and $\chi_{23} = 0.42$ (benzene–polyisoprene). The four curves correspond to $x = 67$, $x = 22$, $x = 10$, and $x = 2$ (from top to bottom). These values of x were chosen because they match the experimental swelling ratios for the pure solvents. The symbols show the swelling ratios reported in Table 1. Notation: cPI1 (◇), cPI3 (■), cPI5 (○), and cPI10 (●).

$(\chi_{13} - \chi_{23})$. All of the curves refer to $u_1 = 0.5$ and $\chi_{12} = 0.5$: the latter value seems reasonable on the basis of the available literature data.[32] Figure 6 shows the family of curves corresponding to $u_1 = 0.7$ and to the same values of χ_{12} and of $\chi_{13} - \chi_{23}$ (note that information for $u_1 = 0.3$ can also be read off this figure by changing v_1 into v_2 and vice versa). As usual, if a particular point within the ternary diagram is chosen, the distance between this point and the side opposite to the ith vertex gives v_i (with $i = 1, 2, 3$). These curves predict significant preferential absorption only when $|\chi_{13} - \chi_{23}|$ is sizable. Since in our system $\chi_{13} \approx 0.40$ and $\chi_{23} \approx 0.42$, it is not surprising that the results of Table 2 show hardly any evidence for selective uptake. It should be stressed that, in spite of the fact that the number x of monomers between crosslinks does not appear explicitly in eq 5, x controls the value of v_3. In other words, moving along one of the curves in Figures 5 and 6 corresponds to changing the cross-linking level.[33]

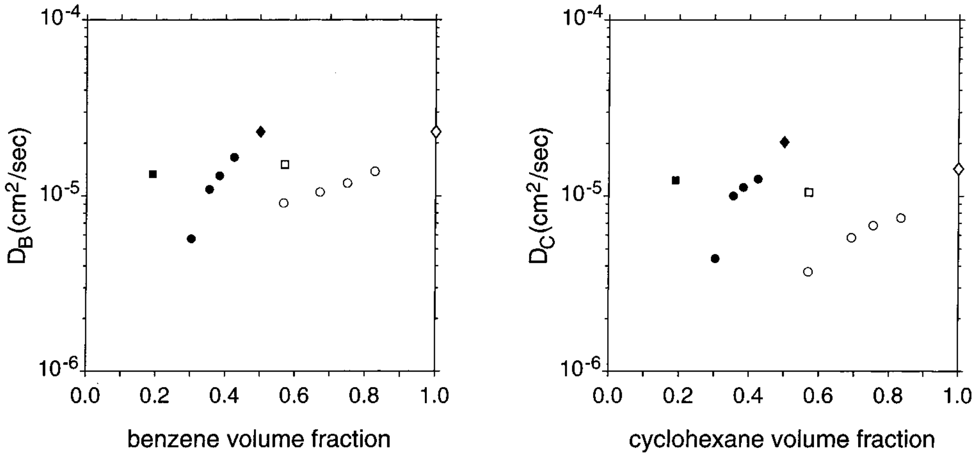
The curves in Figure 7 show the value of the swelling ratio ($1/v_3$) as a function of u_1 (the cyclohexane volume fraction in the mixture) obtained by solving numerically eq 4. We used $\chi_{12} = 0.50$, $\chi_{13} = 0.40$, and $\chi_{23} = 0.42$. The four curves correspond to the four different values of x obtained for cPI1, cPI3, cPI5, and cPI10 by matching the swelling data of Table 1 in neat solvents. According to these curves, swelling in the mixtures should be larger than that in the pure solvent, and this effect should become less pronounced as the level of cross-linking increases. Since in this case χ_{13} and χ_{23} are close, the curves predict that maximum swelling will occur when the volume fraction u_1 of cyclohexane is just above 0.5. All of these results are in qualitative agreement with the experimental results of Table 1, which are shown by the symbols in the figure. However, it is clear that our simplified calculation overestimates considerably the increase in swelling occurring in the mixtures.

Self-Diffusion Coefficients in Neat Solvents and Solvent Mixtures. The data of Table 3 indicate that, while the self-diffusion coefficient D_B of benzene is essentially the same in neat benzene and in the mixture with B/C = 1/1 (by volume), the self-diffusion coefficient of cyclohexane increases significantly (from 1.43×10^{-5} cm^2/s to 2.03×10^{-5} cm^2/s) in going from the neat solvent to the mixture. The dependence of the self-diffusion coefficients D_B and D_C on mixture composition has been discussed in the literature, but existing data are not in complete agreement. An early compilation of data[34] suggests that both D_B and D_C will exhibit maxima when plotted against x_C, the mole fraction of cyclohexane, with $D_B(\max) \approx 2.4 \times 10^{-5}$ cm^2/s at $x_C \approx 0.4$ and $D_C(\max) \approx 2.2 \times 10^{-5}$ cm^2/s at $x_C \approx 0.2$. Our data are, within experimental error, in agreement with the values reported in ref 34. On the other hand, measurements of self-diffusion coefficients using radioactive tracers (benzene and cylohexane enriched with ^{14}C and ^{3}H) have produced a minimum in the plot of D_C vs x_C and a maximum in the plot of D_B vs x_C.[35] While the data for the pure solvents reported in ref 35 are in agreement with our results, the data for the mixture are not. It seems worth noting that none of the experimental data on benzene–cyclohexane mixtures cited in the literature are based on PFGSE NMR measurements of the diffusion coefficients.

Reference 36 presents a molecular dynamics calculation of the self-diffusion coefficients in benzene–cyclohexane mixtures: the benzene–cyclohexane interactions are modeled by six-centers Lennard-Jones potential. The results of this calculation appear to agree with the data of ref 34 (and with our data) if some guessing is made on their presentation.[36] In particular, the results for D_C vary in the range $(1.4-2.1) \times 10^{-5}$ cm^2/s depending on mixture composition; the results for D_B fall in the $(2.0-2.4) \times 10^{-5}$ cm^2/s range. These particular values are produced in the computer simulation of ref 36 as a result of the specific solvent–solvent interaction: there does not seem to be any simple physical explanation capable of accounting for the calculated behavior.

Self-Diffusion Coefficient in the Swollen Networks. A few general trends are identifiable from the data of Table 3. First of all, it is clear that for a given solvent the value of the self-diffusion coefficient increases with solvent concentration. The more loosely cross-linked is the network, the greater is the equilibrium solvent concentration (or swelling ratio): i.e., lower amounts of cross-linker result in higher self-diffusion coefficients at equilibrium.

The second general trend in Table 3 is that the self-diffusion coefficients within the networks swollen by mixtures are higher than the corresponding quantities within networks swollen by a single solvent. It is reasonable to conjecture that there are two separate processes causing this behavior. The first is that the



(a)

(b)

Figure 8. (a) Benzene self-diffusion coefficients reported in Table 3 plotted against the benzene volume fractions. The symbols refer to (○) polyisoprene swollen by pure benzene, (●) polyisoprene swollen by B/C = 1/1 mixtures, (■) polyisoprene swollen by B/C = 1/3 mixtures, (□) polyisoprene swollen by B/C = 3/1 mixtures, (◇) pure benzene, and (◆) B/C = 1/1 mixture. (b) Cyclohexane self-diffusion coefficients reported in Table 3 plotted against the cyclohexane volume fractions. The symbols refer to (○) polyisoprene swollen by pure cyclohexane, (●) polyisoprene swollen by B/C = 1/1 mixtures, (■) polyisoprene swollen by B/C = 3/1 mixtures, (□) polyisoprene swollen by B/C = 1/3 mixtures, (◇) pure cyclohexane, and (◆) B/C = 1/1 mixture.

equilibrium solvent concentration within the swollen networks is higher for the mixtures than for the neat solvents. Since the diffusion coefficients are expected to increase with solvent concentration, part of the observed increase is probably due to the higher swelling ratios. However, both the large size of the increases (especially in D_C) and our results for the B/C = 1/1 mixture in the absence of polymer suggest that also within the swelling network specific solvent–solvent interactions are at work and that these may be the main cause of the increase in D_C. It should be noted in this respect that, for the more loosely cross-linked networks, the volume fraction of solvent in the polymer-occupied region at equilibrium is in the 0.8–0.85 range; therefore, it is reasonable to expect that in this situation solvent–solvent interactions play a greater role than the interaction between the solvent and the polymer.

In ref 15 PFGSE NMR data were reported for the separate diffusion coefficients of benzene and cyclohexane in low-density polyethylene (LDPE) swollen by benzene–cyclohexane mixtures. The range of swelling ratios (<1.5) to which the data of ref 15 refer is quite different from the equilibrium swelling ratios in our specimens (see Table 1). As a result, the solvent volume fractions in amorphous LDPE are much lower (always less than 0.3) than those considered here. In ref 15 the self-diffusion coefficient data were plotted against the volume fractions of the separate solvents. Similar plots are shown in Figure 8 for the data reported in Table 3: these plots highlight the increase in the self-diffusion coefficient due to the presence of the second solvent. In the limit of zero solvent volume fraction the curves for different mixture compositions should converge to the same point. The low-volume fraction data of ref 15 display this behavior clearly; by contrast, for our data the solvent volume fractions are too large to permit reliable extrapolation.

Correlation between the Self-Diffusion Coefficients and the Mutual Diffusion Coefficients. In view of our self-diffusion coefficient data, it is natural to ask how the microscopic (molecular) behavior represented by the self-diffusion coefficients is reflected at the macroscopic (transport) level: e.g., in the mutual diffusion coefficients. This is especially important from a practical standpoint since the same mutual diffusion coefficients control both the kinetics of swelling and transport through an elastomeric seal separating a multicomponent solvent from the outside.

It is interesting in this context to note that the estimates for the mutual coefficient at the equilibrium swelling concentration reported in Table 4 display the same trends that were found in the self-diffusion measurements. The mutual diffusion coefficients for the polyisoprene–benzene systems are 70–80% larger than those for the polyisoprene–cyclohexane systems: the same approximate relation is displayed by the corresponding self-diffusion coefficients.

In the case of the mixtures, we cannot separately estimate the benzene and cyclohexane mutual diffusion coefficients from the sorption results. Instead, as noted in the previous section, the values for D_M reported in Table 4 should be regarded as an effective mutual diffusion coefficient, representing a weighted average of the separate benzene and cyclohexane mutual diffusion coefficients.[28] Nevertheless, it is clear that once again the data given in Table 3 for the self-diffusion coefficients are closely mirrored by the results of Table 4: the largest values for D_M are found in the B/C = 1/1 and in the B/C = 3/1 mixtures; the value for D_M estimated for the B/C = 1/3 mixture is intermediate between these and D_M for cyclohexane. Weighted averages of the corresponding self-diffusion coefficients of Table 3 exhibit the same behavior.

The relation between self-diffusion and mutual diffusion coefficients has been considered extensively in the literature,[37] and various expressions relating the two sets of quantities have been proposed. In particular, for a binary system in the limit of vanishing concentration of one of the components, a simple proportionality relation between self-diffusion and mutual diffusion coefficients holds.[38] However, at higher concentrations this relationship breaks down: the self-diffusion coefficient depends only on the autocorrelation of individual molecule velocities, while the mutual diffusion coefficient depends on the correlation between the velocities of different molecules.[39,40] It is, therefore, remarkable that, even at the very high solvent concentrations typical of our system, the two sets of quantities exhibit the same general trends.

V. Conclusions

We have investigated the uptake of a number of benzene–cyclohexane mixtures in polyisoprene networks cross-linked to different extents. This system was chosen as a simple model problem to shed light on the phenomenon of multicomponent transport through elastomeric materials. Both benzene and cyclohexane are good solvents for polyisoprene, and the Flory–Huggins polymer–solvent interaction parameters are comparable. Therefore, features specifically due to the two-component nature of the solvent should be conspicuous in this system. Indeed, a number of such features were identified: both the equilibrium thermodynamics and the kinetics of the problem are affected by the two-component nature of the diffusant.

We confirmed the results of much earlier work[10] indicating that the equilibrium swelling ratio in the mixed solvent is higher than that found for each solvent separately. This seems to be a general phenomenon which is predicted by a simple extension of the Flory–Rehner approach to ternary systems. For both the equilibrium uptake and the composition of solvents within the swollen networks, the predictions are in qualitative agreement with our experimental results.

The fact that two solvents are present has a dramatic effect on the kinetics: the self-diffusion coefficient of cyclohexane within the networks swollen by a mixture is increased by as much as 60–70% compared to the networks swollen by pure cyclohexane. While the equilibrium solvent uptake is higher in the networks swollen by the mixtures, it is clear that this factor alone cannot account for the drastic increase. In fact, a similar increase in the cyclohexane self-diffusion coefficient is observed in the absence of the polymer. For the pure mixture this behavior has also been found by a recent molecular dynamics computer simulation[36] and appears to be the result of the specific solvent–solvent interactions; however, there does not seem to be any simple physical explanation for this behavior.

The increase in the self-diffusion coefficient of cyclohexane for networks swollen by a mixture (rather than by pure cyclohexane) is mirrored in the values of the mutual diffusion coefficient controlling solvent transport within the networks. For example, for the B/C = 1/1 mixture our estimate of the effective mutual diffusion coefficients controlling the kinetics of swelling in the mixture is significantly higher than the average between the mutual diffusion coefficients of benzene and cyclohexane controlling swelling in the neat solvents.

On the basis of these results, it can be expected that transport of a mixture of good solvents through an elastomeric seal will differ in several respects from transport through a seal confining a single solvent. Increases in the swelling ratio imply a higher concentration of solvent within the seal surface in immediate contact with the mixture; since diffusion coefficients can be expected to increase with solvent concentration, the diffusion coefficients themselves will be somewhat higher because of this effect. In addition to this increase, significant changes in the diffusion coefficients may occur because of specific solvent–solvent interactions. Our cyclohexane results are an example of this behavior. The direction of the changes (increase or decrease) will depend, in general, on the specific mixture composition and on the concentration of polymer. For example, in the case of a polyisoprene seal exposed to a B/C = 1/1 (by volume) mixture, each one of the mechanisms listed above induces an increase of the total flux through the seal.

This paper highlights some of the phenomena that may be expected to play a role in the process of diffusion within a polymeric material exposed to a multicomponent mixture. Although the system that we examined is one of the simplest, we uncovered evidence of nontrivial transport behavior. We hope that this work may prove to be a useful step toward a better understanding of an area that has received comparatively little attention, in spite of its obvious technological importance.

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(27) The assumption is strictly correct only if the separate mutual diffusion coefficients for benzene and cyclohexane transport within the network are the same throughout the swelling process and if the equilibrium solvent composition in the swollen specimens is the same as the composition of the mixtures.

(28) A nonequilibrium thermodynamics description of the (isothermal) diffusion process is based on writing the flux F_i of the ith component as a linear combination of the concentration gradients of all of the components: $F_i = \sum_j D_{ij} \nabla \phi_j$. Thus, for our system four separate mutual diffusion coefficients (e.g., four proportionality constants D_{ij}) have to be introduced. The effective mutual diffusion coefficient obtained from the sorption data reflects the separate values of these four quantities.

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