Interaction of *n*-Alkanes with Crosslinked *cis*-1,4-Polybutadiene

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ABSTRACT: Permeation of n-alkanes through *cis*-1,4-polybutadine crosslinked using conventional, efficient, and peroxide vulcanizing systems was studied by a gravimetric method. Four alkanes from n-hexane to *n*-nonane were used. In *n*-octane, the studies were conducted in the temperature range of 27–70°C. The sorption data was used to estimate the diffusion and permeability coefficients, the activation energy for diffusion and permeation, the entropy and enthalpy of sorption, polymer–solvent interaction parameter, and the degree of crosslinking. The various parameters estimated indicate that permeability of the membranes depends more on the degree of crosslinking than on the nature of crosslinks. Increase in permeant chain length was found to lower permeability. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 2404–2413, 2001

Key words: transport; permeability; diffusion; solvent; interaction; polybutadene

INTRODUCTION

The wide-range application of polymers as barrier materials has stimulated great interest in the transport of small molecules through polymers. Understanding of penetrant transport is crucial for optimization of polymerization rates, and has great significance in polymer processing. Impermeable polymers are required for anticorrosion coatings,[1,2] food packaging,[3,4] encapsulation of electronic goods, etc. Selectively permeable polymers are used in separation processes,[6,7] in a number of bio-medical applications, certain food packaging, etc.

The development in the field of barrier polymers could not have taken place without a proper understanding of the factors, which influence the permeation properties of the polymers involved. Polymer–solvent interaction has been extensively studied and reviewed by many authors.[10–15]

The diffusion of liquids through a polymer is governed by the relative rates of penetrant diffusion and the segmental mobility of polymer chains. A general expression that can describe the transport kinetics can be written as,[16,17]

$$Q_t/Q_\infty = kt^n \tag{1}$$

where Q_t is the mol % uptake after time t, and Q_∞ is the equilibrium mol % uptake. Here, k is a constant that depends on the structural characteristics of the polymer and its interaction with the solvent. n, the diffusional exponent, tells us the mode of diffusion. When $n = 1/2$, diffusion obeys Fick's law and is said to be Fickian. This occurs when the segmental mobility of the poly-

mer chains is faster than the rate of diffusion of permeant Molecules. This happens in the case of diffusion into polymers, which are above their glass transition temperature up to about 50% of the equilibrium penetrant uptake.

When $n = 1$, the diffusion process exhibit a case II behavior. This occurs when the permeant diffusion rates are much faster than polymer relaxation process. When $1/2 < n < 1$, the diffusion is said to be anomalous. This is the case when permeant mobility and polymer segmental relaxation rates are almost equal.

The effects of nature of polymer and penetrant size on diffusion of organic solvents through various elastomers have been extensively studied,[18-20] but detailed data on solvent transport properties of polybutadiene is nonexistent in literature. In the present contribution we have investigated the mode of diffusion and the extent of interaction for the transport of *n*-alkanes through crosslinked *cis*-1,4-polybutadiene using a sorption gravimetric method. The effect of nature of crosslinking on diffusion has been studied by preparing compounds with different vulcanizing systems, viz, conventional, efficient and peroxide. To study the effect of temperature on diffusion and permeation, entropy and heat of sorption have been evaluated. To compare the solvent interaction of the three vulcanizing systems, the polymer–solvent interaction parameters were calculated using a modified form of Flory-Rehner equation. The effect of increase in solvent chain length has been studied using four normal hydrocarbons from *n*-hexane to *n*-nonane.

EXPERIMENTAL

cis-1,4-Polybutadiene, having 96% *cis* content synthesized by Indian Petrochemicals Corporation

Table I   Composition of the Mixes (in phr)

Ingredients	CV	EV	DCP
Cisamer G. P	100	100	100
Stearic acid	2	2	—
Zinc oxide	5	5	—
MOR	2	2.5	—
Sulfur	2	0.3	—
TMTD	—	1.5	—
DCP	—	—	0.5

Phr: parts per hundred rubber.
MOR: 4-morpholinyl-2-benzothiazole disulfide.
TMTD: Tetramethyl-thiuram disulfide.
DCP: Dicumyl peroxide.

Table II   Cure Characteristics of Mixes at 150°C

Cure Properties	CV	EV	DCP
Minimum torque (dNm)	12	11	12.5
Maximum torque (dNm)	81.2	81	82.8
Cure time (min) for torque of 73 (dNm)	57	23.5	40
Optimum cure time (min)	57	23.5	43

Limited, Vadodara, was used. Compounding was done with three formulations for the three different vulcanizing systems viz., conventional (CV), efficient (EV), and dicumyl peroxide (DCP). The formulations of the mixes are given in Table I.

The first part of the mixing was done in a Francis Shaw Intermix for four minutes at a rotor speed of 60 rpm with an initial temperature of 65°C and final temperature of 106°C. After this, the mixes were run through a laboratory two-roll mill. The curing properties of the mixes, determined by a Monsanto rheometer R-100, are given in Table II.

Reagent-grade *n*-hexane, *n*-heptane, *n*-octane, and *n*-nonane, having 99% initial purity, was doubly distilled before use to ensure purity. Their density at 25°C agreed well with the literature values.[21]

Crosslinked polybutadiene samples of thickness 2 mm were cut circularly (diameter 1.6 cm) by means of a sharp-edged steel die from dried vulcanized sheets. Thickness measurements were made at several points with an accuracy of ±0.001 cm using a micrometer screw gauge.

The cut polymer samples were weighed, and sorption experiments were performed by immersing them in solvents contained in test bottles having air-tight stoppers, maintained at the desired temperature in an air oven. The samples were periodically removed from the solvent and weighed quickly on an electronic balance to an accuracy of 0.1 mg. The procedure was repeated until equilibrium was attained. The final weighings were done after 48 h.

RESULTS AND DISCUSSION

Effect of Nature of Crosslinks

The sorption curves expressed as mol % uptake of the liquid vs. square root of time $t^{1/2}$ for the three
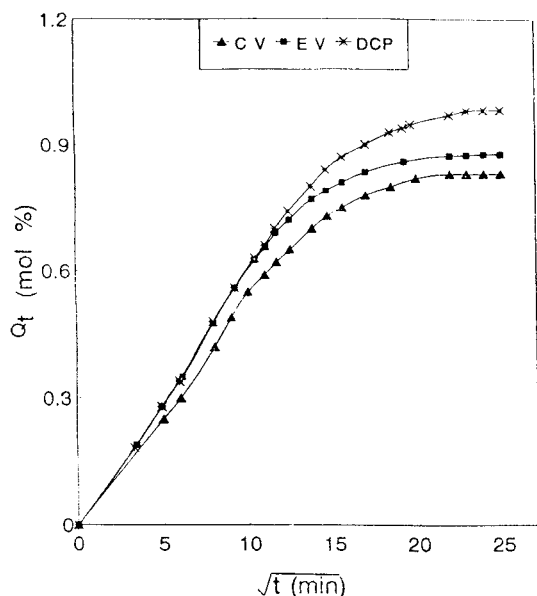
Figure 1 Sportion curves for the three vulcanizing systems CV, EV, and DCP.

vulcanizing systems CV, EV, and DCP in n-octane, are shown in Figure 1. Similar curves have been obtained for normal hexane, heptane, and nonane. For samples of all the three vulcanizing systems sorption increases linearly up to about 50% of equilibrium sorption and later levels off indicating the attainment of complete equilibrium. The curves indicate that in all the four solvents, polybutadiene crosslinked with DCP takes up the highest amount of solvent, and that crosslinked with CV has the lowest solvent uptake. EV system has intermediate values. This can be easily understood from the values of equilibrium mole percent solvent uptake, Q_∞, given in Table III.

The nature of the crosslinks formed by the three vulcanizing systems are shown in Figure 2(a), (b), and (c). The conventionally vulcanized

Table III   Values of Q_∞ in Various Solvents for the Three Vulcanizing Systems

Solvent	System		
	CV	EV	DCP
n-Hexane	0.9285	0.9909	1.0426
n-Heptane	1.1117	1.1468	1.1894
n-Octane	0.8304	0.8760	0.9821
n-Nonane	0.7395	0.7683	0.8208
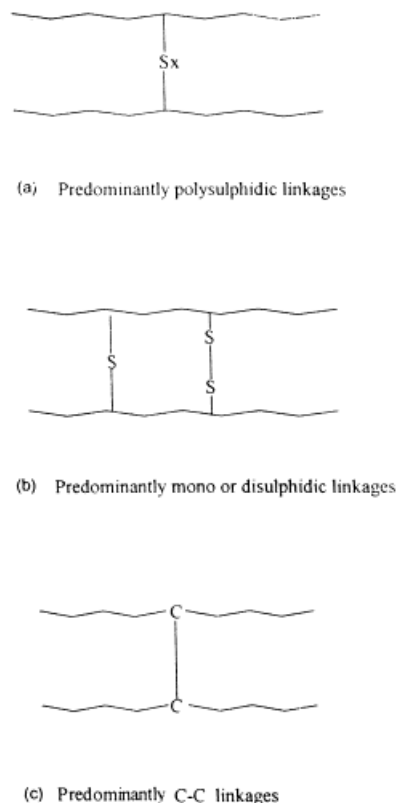
Figure 2 (a–c) Nature of crosslinks formed by the three vulcanizing systems.

samples contain polysulfidic crosslinks, the efficiently vulcanized samples contain mostly mon-o and disulfidic crosslinks, and the samples vulcanized using peroxide have C—C crosslinks between polymer chains.[18] Our expectation was that the lowest solvent uptake will be for samples of the peroxide vulcanizing systems that has the most rigid crosslinks, and that the highest solvent uptake will be for samples of the CV system that has the most flexible crosslinks. But the results obtained were contradictory to our expectation. However, this behavior has been explained based on the crosslinked density of the samples, which would be discussed later. To further analyze the comparative uptake of n-alkanes by the three vulcanizing systems, a few more parameters were calculated. The sorption data were fitted with eq. (1). The least-squares estimation of n and k in eq. (1) are given in Table IV.

The values of n are close to 0.5 ± 0.05 in all the studies done, indicating a Fickian mode of transport. In most of the studies k was found to be highest for the DCP system and lowest for the CV system. This indicates that solvent–polybuta-

Table IV   Values of *n* and *k* in Various Solvents

Solvents	*n*			$k \times 10^2$ min^{-n}		
	CV	EV	DCP	CV	EV	DCP
n-Hexane	0.49	0.54	0.60	6.08	7.42	9.92
n-Heptane	0.56	0.55	0.54	5.84	6.69	6.68
n-Octane	0.53	0.56	0.54	4.51	6.78	6.20
n-Nonane	0.53	0.54	0.53	4.07	5.08	5.18

diene interaction is maximum for the DCP system and minimum for the CV system.

Transport Coefficients

From the slope θ, of the initial linear portion of the sorption curves of Q_t vs. $t^{1/2}$, diffusion cofficient D, has been calculated using eq. (2):[22,23]

$$D = \frac{\pi}{16} \left[\frac{h\theta}{Q_\infty} \right]^2 \tag{2}$$

where h is the initial sample thickness. The values of D in the four *n*-alkanes for the three systems are shown in Table V. Comparison of the diffusion coefficient of the three vulcanizing systems does not show any systematic trend. The permeability of a small molecule into a polymer membrane is dependent on the diffusivity as well as the sorption or solubility of the liquid in the membranes. Therefore, sorption coefficient, S, was calculated using the formula:[24]

$$S = \frac{M_\infty}{M_p} \tag{3}$$

where M_∞ is the mass of the solvent taken up at equilibrium swelling, and M_p is the mass of the polymer sample. The values of S are given Table V. S is found to be maximum for the DCP system

and minimum for the CV system in all the solvents. Thus, sorption coefficients, unlike the diffusion coefficient, are showing a regular trend in all the solvents. The maximum sorption coefficient for the DCP system indicates that the absorbed solvent molecules are better accommodated by the DCP crosslinked polymer matrix than by the EV system, and samples with CV system crosslinking shows least capability to accommodate the solvent molecules.

The solution-diffusion model[25,26] for permeability can be mathematically expressed as

$$P = DS \tag{4}$$

where P is the permeability coefficient. The estimated values of P are given in Table V. Permeability coefficients are found to be maximum for the DCP system and minimum for the CV system in all the four *n*-alkanes.

The diffusion coefficient characterizes the average ability of the penetrant to move among the polymer segments. The sorption coefficient is thermodynamic in nature, and is related to the equilibrium sorption of the penetrant. Permeability coefficient reflects the net effect of sorption and diffusion. From Table V it can be seen that diffusion coefficients do not show any regular trend, whereas sorption coefficients and permeability coefficients show exactly the same trend in

Table V   Values of *D*, *S*, and *P* for the Three Systems in *n*-Alkanes

Solvent	$D \times 10^7$ (cm^2 s^{-1})			S (g/g)			$P \times 10^7$ (cm^2 s^{-1})		
	CV	EV	DCP	CV	EV	DCP	CV	EV	DCP
n-Hexane	10.81	10.5	11.86	0.79	0.85	0.89	8.63	8.94	10.64
n-Heptane	8.48	9.07	9.02	1.11	1.17	1.19	9.44	10.65	10.73
n-Octane	7.57	8.01	8.02	0.94	0.99	1.11	7.17	7.99	8.78
n-Nonane	0.05	6.12	5.84	0.94	0.98	1.05	5.72	6.01	6.13
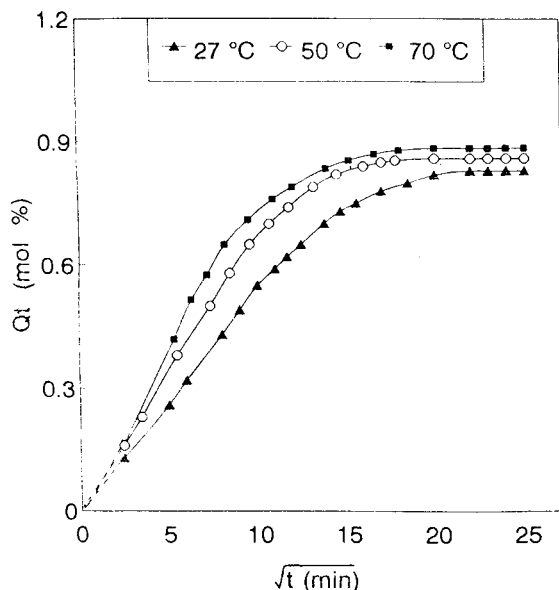
Figure 3 Plot of Q_t vs. $t_{1/2}$ for the CV system in *n*-octane at three temperatures.

all the solvents. So one can conclude that for the permeation process of the systems under study sorption predominates diffusion. The results in Table V clearly indicate that samples crosslinked with DCP system are most permeable and those with CV system are least permeable.

Thermodynamic Analysis

To further probe the variation of interaction of *n*-alkanes with the three vulcanizing systems, studies in *n*-octane were made at two more temperatures (50 and 70°C) in addition to the studies at 27°C. The plots of Q_t vs. $t_{1/2}$ for the CV system in *n*-octane at the three temperatures are shown in Figure 3. Similar plots were obtained for the EV and DCP systems. For samples of all the three crosslinking systems at all the three temperatures studied, sorption increases linearly up to about 50% equilibrium swelling and later levels off. Even at 70°C the shape of the curves remains

the same as that at 27°C for all the systems studied. This indicates that the solvent transport process occurs by the same mechanism in the temperature range studied. The values Q_∞ at the three temperatures are given in Table VI.

The slope of the curves and the Q_∞ values increase with temperature, indicating that temperature activates solvent uptake. The values of the constant k and the exponent n in eq. (1) for the three vulcanizing systems at the three temperatures are obtained by power regression analysis of the respective (Q_t/Q_∞) values up to about 50% of equilibrium solvent uptake against time in minutes. These are also given in Table VI. The values of n show no significant deviation from 0.5. This indicates that Fickian mode of solvent transport occurred even at higher temperatures. The value of k is found to increase with temperature, suggesting increased interaction between polymer membrane and solvent molecules.

A modification of the Flory-Rehner theory[24,27] to interpret equilibrium swelling is used to calculate the solvent–polymer interaction parameter and M_c, the molecular weight between crosslinks. The treatment was suggested and used earlier by Aithal et al.[24]

In this approach the Flory-Rehner equation is expressed as a derivative of volume fraction of the polymer, ϕ, in the completely swollen state with respect to temperature T on the Kelvin scale, so that

$$\chi = \frac{d\phi}{dT} \frac{[\phi/(1-\phi) + N \ln(1-\phi) + N\phi]}{[2\phi(d\phi/dT) - \phi^2 N(d\phi/dT) - \phi^2/T]} \quad (5)$$

where the volume fraction of the swollen polymer is calculated as

$$\phi = \frac{M_p/\rho_p}{M_p/\rho_p + M_\infty/\rho_s} \quad (7)$$

M_p is the mass of the polymer before swelling, M_∞ the mass of the solvent taken up at equilib-

Table VI   Analysis of *n*-Octane Transport at Various Temperatures

	CV			EV			DCP		
	27°C	50°C	70°C	27°C	50°C	70°C	27°C	50°C	70°C
Q_∞ mol %	0.83	0.86	0.88	0.88	0.90	0.93	0.96	0.99	1.01
N	0.53	0.52	0.48	0.56	0.50	0.52	0.53	0.50	0.50
$k \times 10^2$ min^{-n}	4.51	6.99	8.21	6.08	7.51	9.07	6.20	6.86	8.63

Table VII   Fraction of the Polymer ϕ at Various Temperatures for Polybutadiene in *n*-Octane

Temperature °C	CV	EV	DCP
27	0.423	0.410	0.388
50	0.415	0.403	0.381
70	0.408	0.396	0.377

Table VIII   Results from Flory-Rehner Theory for Polybutadiene Samples in *n*-Octane

	CV	EV	DCP
χ	0.31	0.92	0.27
M_c	1741	1796	1915
$\nu \times 10^4$ (mol/cc)	2.92	2.78	2.16

rium swelling, ρ_p the density of the polymer, and ρ_s the density of the solvent.

The ϕ values are plotted against T to find out $d\phi/dT$ for the three vulcanizing systems in *n*-octane. The ϕ values are given in Table VII), and the plots of ϕ vs. temperature are shown in Figure 4.
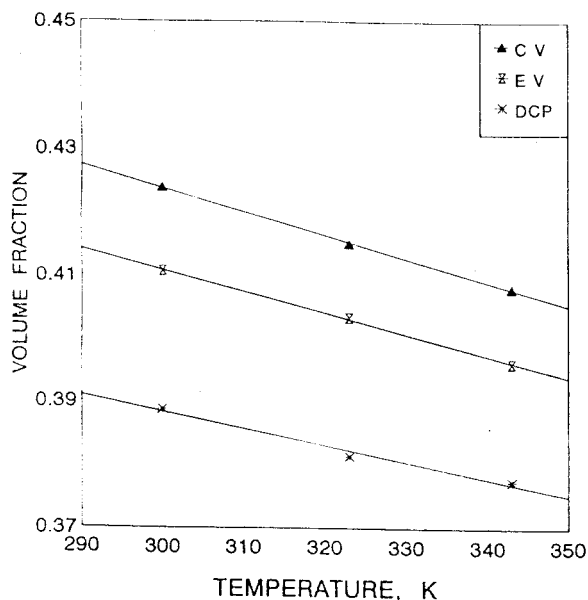
The molecular weight between crosslinks M_c of the polybutadiene samples were estimated using the Flory-Rehner relation[24]

$$M_c = \frac{-\rho_s V(\phi)^{1/3}}{[\ln(1 - \phi) + \phi + \chi\phi^2]} \qquad (8)$$

where V is the molar volume of the solvent. The value of the degree of crosslinking is determined using the relationship[28]

$$\nu = \tfrac{1}{2} M_c \qquad (9)$$

The values of χ, M_c, and ν are given in Table VIII.

Figure 4   Plots of ϕ vs. temperature.

As χ increases, solvent interaction with the polymer decreases. Samples of the CV system have the highest value of χ, i.e., 0.31. This indicates that CV system has least interaction with *n*-octane. The lowest χ value is for the samples of the DCP systems, indicating that this system has the highest solvent interaction. Thus, χ and Q_∞ values indicate the same trend of solvent uptake. From Table VIII, it can be seen that the samples vulcanized with DCP have the highest value for M_c, the molecular weight between crosslinks. This indicates that the crosslinks are farthest in the DCP samples. Therefore, the free volume available for solvent molecules to permeate is maximum for the DCP samples. Table VIII indicates that degree of crosslinking, ugr;, is the lowest for the samples of the DCP system and highest for the samples having the CV formulation. This explains the highest solvent uptake observed for the samples with the peroxide vulcanization composition and the lowest solvent uptake by CV samples.

Over a limited range of temperatures the following Arrhenius relationship can be used for the calculations of energy of activation for diffusion E_D and for permeation E_P[26]

$$\ln D = \ln D_0 - \frac{E_D}{RT} \qquad (10)$$

where D_o is a constant.
   Similarly,

$$\ln P = \ln P_0 - Ep/RT \qquad (11)$$

where P_0 is a constant.

The values of the diffusion coefficient D and the permeation coefficient P, for the transport of *n*-octane through polybutadiene samples at the three temperatures are given in Table IX.

Plots of $-\ln D$ vs. $1/T$ and $-\ln P$ vs. $1/T$ are shown in Figures 5 and 6, respectively. The slope of above linear plots are obtained by least-square

Table IX   Solvent Transport Data at Various Temperatures for Polybutadiene in *n*-Octane

	CV			EV			DCP		
	27°C	50°C	70°C	27°C	50°C	70°C	27°C	50°C	70°C
$D \times 10^7$ cm^2 s^{-1}	7.39	10.32	11.96	8.01	11.49	12.78	8.02	11.22	12.41
S g/g	0.95	0.98	1.01	0.99	1.03	1.06	1.09	1.13	1.15
$P \times 10^7$ cm^2 sec^{-1}	6.99	10.12	12.06	7.99	11.83	13.56	8.78	12.68	14.24
K_s millimol g^{-1}	8.3	8.6	8.8	8.76	9.03	9.31	9.6	9.91	10.07

analysis. The values of E_D and E_P were calculated from the slopes of the respective plots. The results are shown in Table X. Both E_D and E_P are maximum for samples of the CV system and minimum for samples of the DCP system. This indicates greater diffusion of *n*-octane through samples of polybutadiene crosslinked using the peroxide vulcanization system. The higher activation energy of the CV system compared to EV and DCP systems indicates greater energy requirements for the transport of penetrant into the samples of the CV system, and explains lower equilibrium uptake of penetrants by these samples. The heat of sorption was calculated using the relationship

$$\Delta H_s = E_P - E_D \qquad (12)$$

The values are included in Table XI.

All the ΔH_S values are found to be positive and the highest value is for the conventionally vulca-

nized samples. These values also indicate the lower permeability of the conventionally vulcanized samples.

The molar equilibrium sorption coefficient K_s is considered as a thermodynamic sorption constant.[24] K_s is defined by the equation:

$$K_s \approx \frac{\begin{array}{c}\text{No. of mol of the penetrant} \\ \text{sorbed at equilibrium}\end{array}}{\text{Mass of the polymer sample}} \qquad (13)$$

K_s for the samples of the three types of vulcanizing systems at 27, 50, and 70°C are given in Table IX. The values of K_s are substituted in the following Van't Hoff equation to obtain the values of $\Delta S°$ and $\Delta H°$

$$\ln K_s = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (14)$$
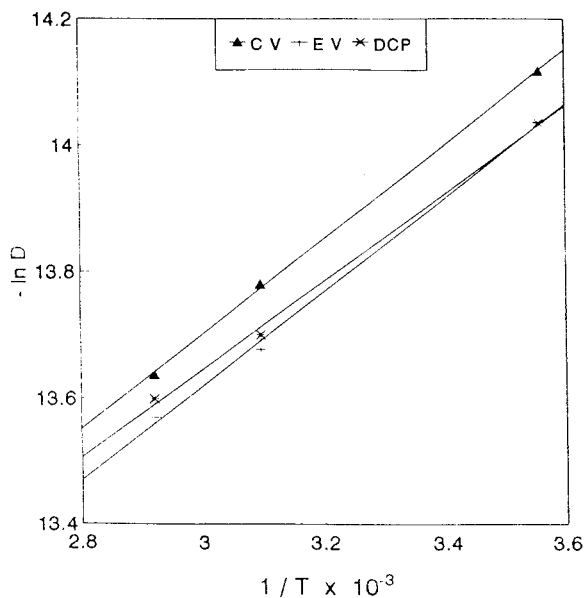
Figure 5   Plots of $-\ln D$ vs. $1/T$.
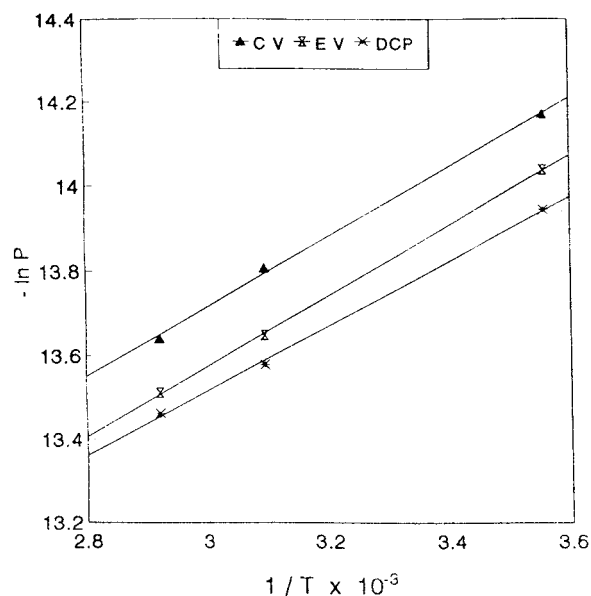
Figure 6   Plots of $-\ln P$ vs. $1/T$.

Table X   Activation Parameters for Polybutadiene Samples in *n*-Octane

| Type of Vulcanization	CV	EV	DCP
E_D kJ mol^{-1}	10.8	9.10	7.90
E_P kJ mol^{-1}	12.15	10.29	9.07
H_S kJ mol^{-1} ($E_P - E_D$)	1.35	1.19	1.16

In this equation $\Delta S°$ is the standard entropy of sorption, and $\Delta H°$ is the standard heat of sorption. The plots of ln K_s vs. $1/T$ shown in Figure 7 are linear. From the intercept of linear plot on the X-axis $\Delta S°$ is calculated and $\Delta H°$ is calculated from the slope. The estimated values are given in Table XI. The $\Delta H°$ values are in reasonable agreement with the values obtained from E_P–E_D, which are given in Table X.

The $\Delta S°$ values are all found to be negative, indicating that vaporization of solvent molecules inside the polymer matrix has not taken place, and disordered movement of the liquid molecules is restricted within the polymer matrix. The $\Delta S°$ values are found to be most negative in the case of the CV system, and least negative in the case of the DCP system. This indicates that there is greater restriction for the solvent molecules to move about within the matrix of the sample crossliked with the conventional vulcanization system. This again points to the higher crosslink density in the samples of the CV system.

Thus, for samples of polybutadiene crosslinked using the three vulcanizing systems viz, CV, EV, and DCP, even at the same rheometric torque the crosslink density is found to be different. The various parameters analyzed indicate that the solvent transport process and equilibrium swelling of polybutadiene in *n*-alkanes depends mostly on the crosslink density rather than on the nature of the crosslinks. So even though the C—C crosslinks present in the samples vulcanized using DCP are more flexible than the sulfidic crosslinks formed in the EV and CV systems, DCP samples show the highest solvent transport

Table XI   Thermodynamic Functions for Polybutadiene in *n*-Octane

| Type of Vulcanization	CV	EV	DCP
$H°$ kJ mol^{-1}	1.3	1.25	1.04
$S°$ J mol^{-1}	39.21	38.78	38.16
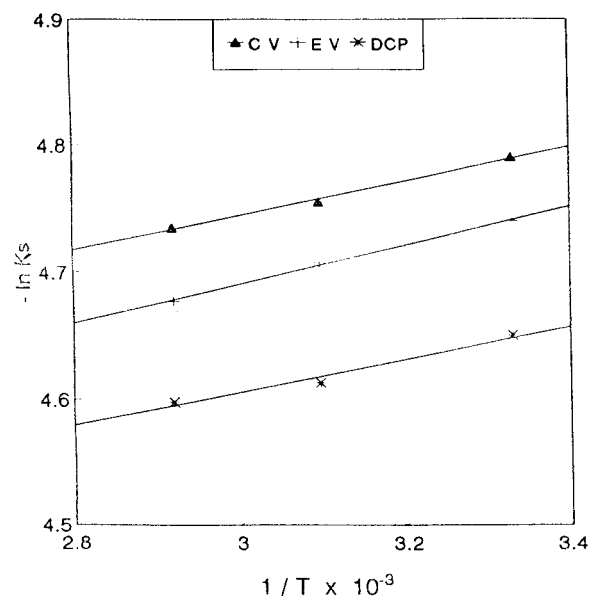
Figure 7   Plots of ln K_s vs. $1/T$.

properties owing to the lowest crosslink density. Similarly, even though the polysulfidic crosslinks in the CV system are the weakest and the most flexible, samples of this system show the lowest solvent transport properties as a result of the highest crosslink density present in these samples.

Effect of Size of the Permeant

The sorption curves for the transport of *n*-hexane, *n*-octane, and *n*-nonane through polybutadiene crosslinked by the CV formulation is shown in Figure 8. Exactly similar plots were obtained for the samples of the EV and DCP systems. In the normal trend as the size of the permeant molecule increases in homologous series, diffusivity decreases. The Q_∞ values of the four solvents are given in Table III. In the case of *n*-hexane, even though as expected the initial uptake by the polymer is faster than that of the other solvent studies, the equilibrium uptake is much lower than that of heptane. Such results were reported earlier.[29–31]

The least-squares estimation of k in eq. (1) is given in Table IV. The k values show a regular decrease from *n*-hexane to *n*-nonane, indicating lesser polymer solvent interaction with increase in the size of the solvent molecules. The diffusion coefficient D, given in Table V, shows a regular decrease with increase in molecular size of the permeant. But permeability coefficients increase
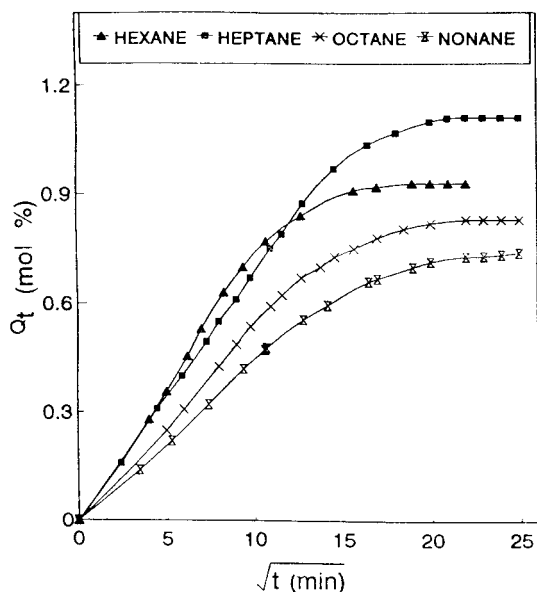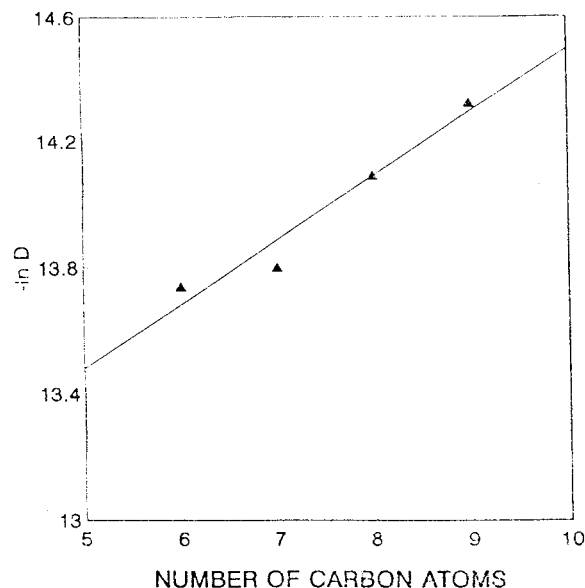
Figure 8 Sorption curves for the transport of n-hexane, n-octane, and n-nonane.

Figure 9 Plots of $-\ln D$ vs. number of carbon atoms for the CV system.

from hexane to heptane, and then show regular decrease from heptane to octane and from octane to nonane. This can be explained based on the fact that permeability is the net effect of diffusion and sorption. The diffusivity decreases as the size of the penetrant increases. This is due to the higher energy of activation for diffusion to occur as the size of the penetrant increases. But the sorption coefficients, which are shown Table V, increase from hexane to heptane and then decreases. Increase in permeant size tends to increase the solubility of the solvent in the polymer matrix.[32,33] This is due to the easier condensability and increase in the heat of sorption, which leads to enhanced plasticization of the polymer chains. The opposing trends of diffusivity decrease and solubility increase with increasing permeant size usually leads to lowering of permeability with increase of permeant size. But from hexane to heptane it seems that the increase in solubility with the size of the permeant predominates over the decrease in diffusivity with size increase.

Variation of diffusion coefficient for the sample of the CV systems with the number of carbon atoms of the solvent are given as plot of $-\ln D$ vs. number of carbon atoms in Figure 9. The variation of $-\ln P$ with the number of carbon atoms is given in Figure 10. The plot of $-\ln D$ shows nearly linear trend from hexane to nonane for the CV system. The plot of $-\ln P$ shows a nearly linear trend from heptane to nonane.

CONCLUSION

Using a simple mass-uptake technique, the detailed analyses of sorption and diffusion of normal alkanes through polybutadiene membrane crosslinked using conventional, efficient, and peroxide vulcanizing compositions were carried out over the temperature range of 27–70°C. It is found that the diffusion
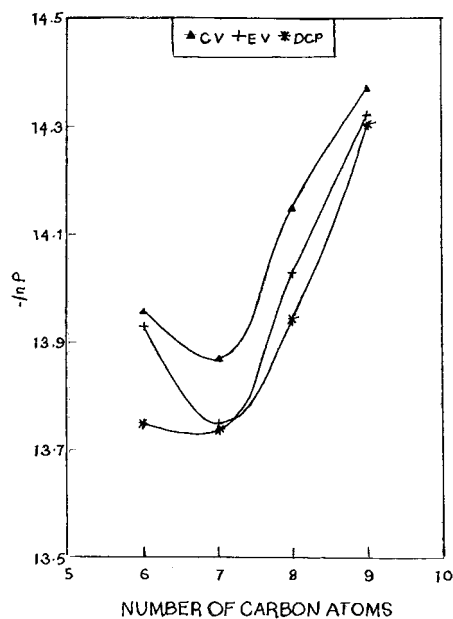
Figure 10 Plots of $-\ln P$ vs. number of carbon atoms for the three cure systems.

follows Fickian trend up to more than 50% equilibrium solvent uptake. Equilibrium solvent uptake and permeability are highest for samples of the DCP system, which has the lowest crosslink density even though the C—C crosslinks in these samples are more rigid than the sulfidic crosslinks. Similarly, even though the polysulfidic crosslinks in the CV system are the weakest of the three systems studied, samples of the CV system have the lowest solvent transport properties owing to the highest crosslink density. So solvent uptake in these samples depends more on the crosslink density than on the nature of the crosslinks.

The solvent interaction parameter is found to be highest for the CV system and lowest for the DCP system. This is in agreement with the earliest observation of lowest permeability for the CV system and highest permeability for the DCP system.

The variation of diffusion coefficient and permeability coefficient with temperature was found to obey the standard Arrhenius relationship in the temperature range studied. The energy of activation for diffusion and permeation, estimated from this, were found to be highest for the CV system and lowest for the DCP system. The variation of equilibrium sorption coefficient with temperature was fitted with the van't Hoff equation, and the enthalpy of sorption and entropy of sorption were estimated for the three vulcanizing systems. These values also support the earlier observation in permeability from the CV to EV to DCP systems.

It was observed that the diffusion coefficients decrease regularly from *n*-hexane to *n*-nonane. But the permeability coefficient increased from *n*-hexane to *n*-heptane and then decreased from *n*-heptane to *n*-nonane. This is attributed to higher solubility coefficient of *n*-heptane in the systems under study. The general trend observed is that as the solvent molecular size increases, solvent uptake decreases.

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