

# Sorption and Diffusion of Acrylonitrile Monomer Through Crosslinked Nitrile Rubber

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**ABSTRACT:** As the first step for the preparation of interpenetrating polymer networks from nitrile rubber and polyacrylonitrile, the sorption and diffusion of acrylonitrile monomer through nitrile rubber crosslinked by three different vulcanization systems—conventional (CV), dicumyl peroxide (DCP), and a mixture consisting of sulfur and peroxide (mixed)—were studied in the temperature interval of 30–70°C. Kinetic curves have been generated for these systems to compute diffusion and sorption coefficients. The equilibrium sorption is found to be maximum for the CV system. The molar mass between crosslinks ( $M_c$ ) has estimated and compared with affine and phantom models. It was found that the  $M_c$  values follow the affine model. The diffusion coefficient values are highest for DCP and lowest for CV. It was observed that the kinetics of liquid sorption followed an anomalous behavior. The temperature dependence of the transport parameters was followed by an Arrhenius relationship, from which the activation energy for diffusion, permeation, and sorption were calculated. It is found that temperature activates diffusion in all cases. The polymer–solvent interaction parameter was determined. The amount of polysulfidic linkages in the rubber network was also estimated. The experimental results were compared with theoretical predictions. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 941–952, 2000

**Key words:** nitrile rubber; acrylonitrile; transport; interpenetrating networks

## INTRODUCTION

The study of transport of organic liquids through polymers is important for a variety of engineering applications. The transport of liquids causes polymers to swell and the extent of swelling depends on temperature, chemical nature, and degree of crosslinking of the polymer in addition to the molar mass of the polymer and of liquid molecules. Applications include controlled release of drugs and pesticides<sup>1</sup>; encapsulation of electronic

devices<sup>2</sup> and cable materials; making packing material for food and vegetables<sup>3,4</sup>; and as selective barriers for the separation of gaseous and liquid mixtures.<sup>5–7</sup> They are also useful in the preparation of IPN (interpenetrating polymer networks).

In order to discover the suitability of a membrane material for a specific application it is essential to know about the molecular interaction of liquids with polymeric membranes. In all membrane-related applications, mass transfer is considered to occur by a sorption diffusion mechanism.

The diffusion in polymer membranes is classified into three types. In the first case, the rate of diffusion can be much smaller than that of poly-

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**Table I** Details of Materials Used

Materials	Characteristics	Values	Source
Nitrile rubber— (Aparene N553NA)	Volatile matter (%)	0.130	Gujarat Apar Polymers Ltd., Mumbai
	Antioxidant (%)	1.400	
	Organic acid (%)	0.250	
	Soap (%)	0.004	
	Mooney viscosity (ML <sub>1+4</sub> 100°C)	40.000	CDH Lab Reagents
	Bound acrylonitrile (%)	34.000	
	Intrinsic viscosity (dL/g)	1.527	
Acrylonitrile	Molecular weight	53.06	CDH Lab Reagents
	Minimum assay (GLC)	99%	
	Wt/mL at 20°C	0.805 g	
	Refractive index ( $n_D^{20}$ )	1.391–1.392	

mer relaxation due to physical changes in the polymer–solvent system. Such types of systems are said to be Fickian or Case I. In Case II or non-Fickian type of diffusion, the rate of diffusion is much greater than that of polymer relaxation. In the anomalous type of diffusion, both the diffusion rate and the relaxation rate are nearly the same.

In noncrystalline polymers, it is generally accepted that the diffusion coefficient decreases linearly with crosslink density.<sup>8</sup> The crosslinks are introduced between rubber chains by vulcanization. Depending on the sulfur/accelerator ratio, the accelerated vulcanizing system has been classified into conventional and efficient techniques. A high concentration of sulfur relative to accelerator is used in conventional vulcanization, which introduces polysulfide linkages (C—S<sub>x</sub>—C) between rubber chains.<sup>9</sup> In efficient vulcanization, a high concentration of accelerator to sulfur is used. It produces mono or disulfidic linkages between rubber chains (C—S—C) or (C—S<sub>2</sub>—C). These crosslinks are shorter than those formed during conventional vulcanization, but they have better thermal stability than the polysulfidic linkages.<sup>10</sup> Another method of crosslinking is the free-radical initiation process by peroxides where C—C bonds are formed between rubber chains. Yet another method of crosslinking is the use of a mixed system consisting of sulfur and peroxide, which produces polysulfidic as well as C—C links between rubber chains. It is well known that polymer structure, crosslink density, nature of crosslinks, presence of fillers, penetrant size, and temperature<sup>11–13</sup> affect the transport of solvents through rubbery polymers.

The swelling and sorption of NBR samples in the presence of monomers like acrylonitrile is of

great interest, since it constitutes the preliminary step in the preparation of IPN.<sup>4,14</sup> A clear knowledge about the swelling rate of the polymers in the monomer helps in controlling the composition, morphology, and properties of the resulting IPN. The present study has been aimed at a comparative study of the nature of crosslinks on the diffusion and transport of acrylonitrile solvent through nitrile rubber membranes. NBR was vulcanized by three vulcanizing systems: CV, DCP, and mixed. The samples were subjected to swelling in acrylonitrile under four different temperature conditions: 30, 50, 60, and 70°C. The polysulfidic linkages of the three systems were estimated by propane-thiol treatment. The molecular weight between crosslinks ( $M_c$ ) was compared with the affine and phantom models. This is the primary step in our program for the development of IPN based on NBR/polyacrylonitrile (PAN) with various morphological features.

## EXPERIMENTAL

### Material

NBR (Aparene N553 NS), with a 34% bound acrylonitrile content, was supplied by Gujarat Apart Polymers Ltd. Mumbai, India. Distilled acrylonitrile (supplied by CDH, Mumbai, India) was used as the monomer. The basic characteristics of NBR and acrylonitrile are given in Table I. Compounding ingredients like dicumyl peroxide (DCP), stearic acid, zinc oxide, sulfur, and *N*-cyclohexyl 2-benzothiazyl sulfenamide (CBS) etc. were of laboratory reagent grade.

### Preparation of Vulcanizates

The mixes were prepared on a laboratory-size two-roll mixing mill (30 × 50 cm) at a friction

**Table II** Recipe for Mixing

Conventional (CV)	DCP	Mixed
NBR, 100 g	NBR, 100 g	NBR, 100 g
ZnO, 5 g	DCP, 4 g	ZnO, 5 g
Stearic acid, 1 g		Stearic acid, 1 g
S, 1.5 g		DCP, 4 g
CBS, 1 g		S, 1.5 g
		CBS, 1 g

ratio 1 : 1 : 25 according to ASTM D 3085-88. The formulations of the mixes are given in Table II. The cure time of the mixes was determined on a Monsanto Rheometer R-100 at 160°C according to ASTM D 2084-88. The rheographs of the mixes are given in Figure 1. The DCP curing that proceeds by free-radical mechanism occurs rapidly. The curing of CV and mixed system involves an intermediate formulation, which leads to an induction period before the onset of cure.

The cure time obtained for the mixes are (a) CV, 1224; (b) DCP, 1008 s; and (c) mixed, 1062 s. The samples are then cured at 160°C. The schematic representation of the three types of crosslinks in CV, DCP, and mixed systems is given in Figure 2.

### Sorption Experiments

Circular disc-shaped polymer samples (diameter, 1.9 cm; thickness, 0.2 cm) were cut from large polymer sheets using a sharp-edged carbon steel die and the cut samples were dried overnight in a vacuum desiccator before use. The dried samples were soaked in screw-tight test bottles containing about 15–20 ml of acrylonitrile maintained at desired temperatures ( $\pm 1$  K) in a hot air oven. The solvent immersion experiments were conducted at 30, 50, 60, and 70°C. Polymer samples were removed periodically, and the surface-adhered solvent drops were wiped off carefully by pressing them between filter paper wraps. The mass of the sorbed sample was determined immediately on a digital sartorius balance with an accuracy of  $\pm 0.01$  mg. As the weighing was done within 30–40 s, the error due to evaporation of other than surface absorbed liquid is considered insignificant.<sup>15</sup>

## RESULTS AND DISCUSSION

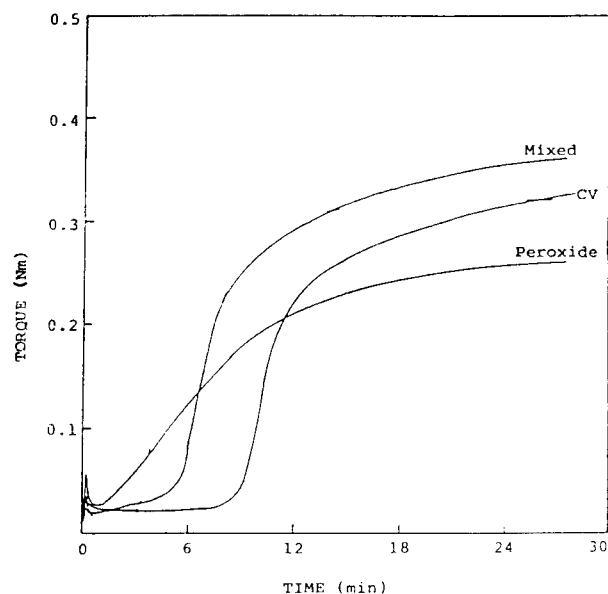
The mole percent uptake of the monomer acrylonitrile by the NBR samples ( $Q_t$ ) is calculated from

the diffusion data. The  $Q_t$  values were determined as

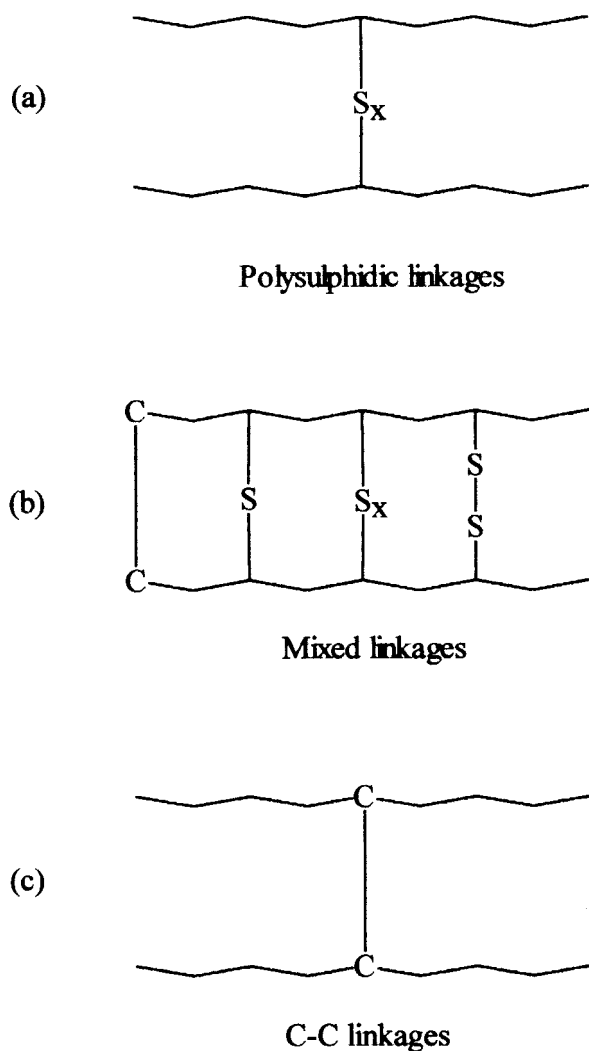
$$Q_t = \left( \frac{\text{Wt of the solvent sorbed at a given time}}{\text{Mol wt of the solvent}} \right) \frac{1}{\text{Initial wt of the rubber specimen}} \times 100 \quad (1)$$

At equilibrium sorption,  $Q_t$  becomes  $Q_\infty$ . The values for equilibrium sorption at different temperatures are given in Table III.

It is seen that the  $Q_\infty$  values are maximum for conventional samples and minimum for the DCP system, whereas the mixed system comes in between. This trend can be explained by the nature of crosslinks formed during vulcanization. In the CV system polysulfidic linkages are present that are highly flexible and labile, which results in easy monomer uptake. Figures 3, 4, 5, and 6 show the plot of  $Q_t$  versus  $\sqrt{\text{time}}$  (or,  $t^{1/2}$  in min) at 30, 40, 50, 60, and 70°C, respectively. Here also the uptake is in the order CV > mixed > DCP. This figure directly shows the effect of the nature of crosslinks on the diffusion of acrylonitrile through NBR. In a CV system polysulfidic linkages are present. They make the network more flexible. In a DCP system C—C linkages are present. They are highly rigid and so the flexibility of the hydrocarbon chain is least. In a mixed system mono, di, and polysulfidic linkages, along

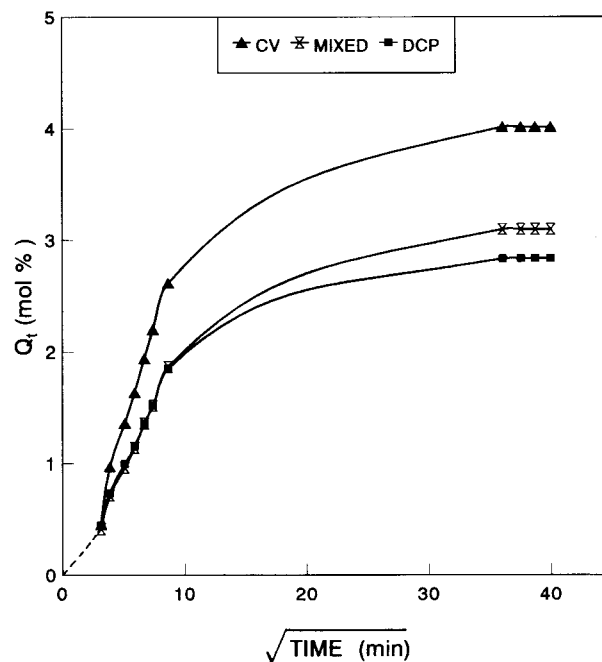


**Figure 1** Rheograph of the mixes cured at 160°C.



**Figure 2** Structure of the various crosslinks formed during vulcanization: (a) CV system, (b) mixed system, and (c) DCP system.

with C—C linkages, are present. The flexibility of the hydrocarbon chain comes in between that of DCP and CV systems. Hence, due to the chain



**Figure 3** Sorption curve showing the mol % acrylonitrile uptake of CV, mixed, and DCP samples at 30°C.

flexibility, the  $Q_{\infty}$  values are in the order CV > mixed > DCP.

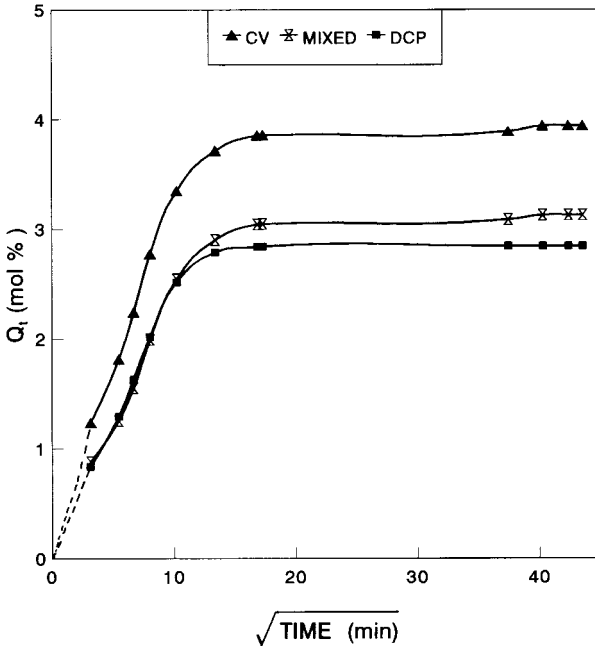
The mechanism of diffusion was investigated using the equation,

$$\log Q_t/Q_{\infty} = \log k + n \log t \quad (2)$$

The value of  $k$  depends on the structural features of polymer, whereas the value of  $n$  determines diffusion mechanism. For the Fickian mode, the value of  $n$  is 0.5 and it occurs when the rate of diffusion of penetrant molecules is much less than the relaxation rate of the polymer chains. For Case II or non-Fickian transport, where the  $n$ -value is 1, the diffusion is rapid when compared with the simultaneous relaxation process. How-

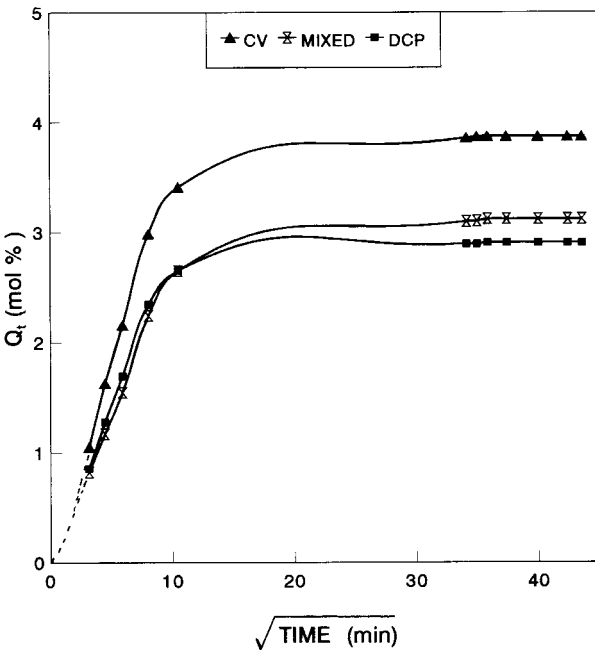
**Table III** Values of  $Q_{\infty}$  (mol %) at Different Temperatures

Sample	System	Temperature (°C)			
		30	50	60	70
NBR	Conventional	4.015	3.942	3.870	3.602
	Peroxide	2.837	2.845	2.905	3.043
	Mixed	3.098	3.128	3.121	3.169

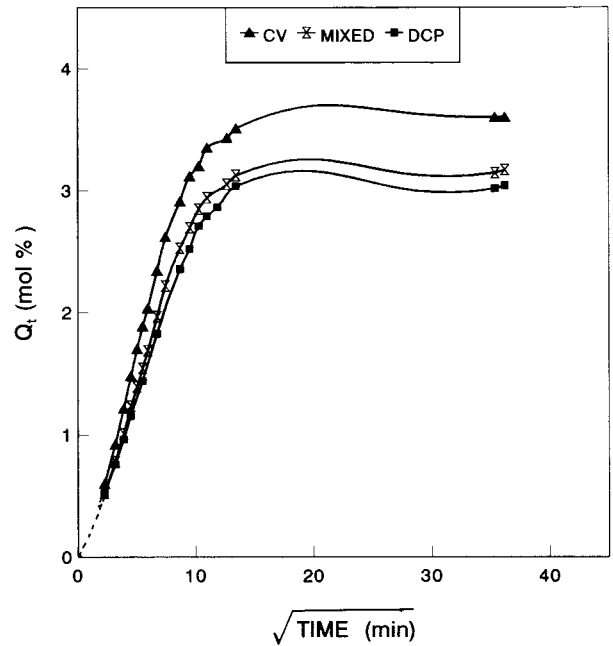


**Figure 4** Sorption curve showing the mol % acrylonitrile uptake of CV, mixed, and DCP samples at 50°C.

ever, in the case of anomalous transport, both solvent diffusion and polymer relaxation rates are comparable. The values of  $n$  and  $k$  are given in



**Figure 5** Sorption curve showing the mol % acrylonitrile uptake of CV, mixed, and DCP samples at 60°C.



**Figure 6** Sorption curve showing the mol % acrylonitrile uptake of CV, mixed, and DCP samples at 70°C.

Table IV. In the present investigation,  $n$  varies between 0.5 and 1 and, hence, the transport mechanism may be an anomalous type.<sup>15,18-21</sup>

The polymer swelling is also affected by solvent transport and nature of the polymer matrix. As swelling increases, free volume increases due to increased chain mobility, which facilitates transport process. The diffusion coefficient can be determined using the relation<sup>15,22</sup>

$$\frac{Q_t}{Q_\infty} = 1 - \sum_{n=0}^{\infty} \left[ \left( \frac{8}{(2n+1)^2\pi^2} \right) e^{-(2n+1)^2\pi^2(Dt/h^2)} \right] \quad (3)$$

where  $t$  is the time and  $h$  is the initial thickness of the polymer sheet. Although this equation can be solved readily, it is instructive to examine the short time-limiting expression as well.

$$\frac{Q_t}{Q_\infty} = \left( \frac{4}{\pi^{1/2}} \right) \left( \frac{Dt}{h^2} \right)^{1/2} \quad (4)$$

A single master curve is obtained from a plot of  $Q_t$  versus  $t^{1/2}$ , which is initially linear. Thus  $D$  can be calculated from a rearrangement of eq. (4) as

$$D = \pi \left( \frac{h\theta}{4Q_\infty} \right)^2 \quad (5)$$

**Table IV** Values of  $n$  and  $k$  at 30, 50, 60, and 70°C

Sample	System	Temperature (°C)			
		30	50	60	70
$n$ -values	CV	0.9744	0.4221	0.5537	0.6523
	Peroxide	0.7333	0.4647	0.5366	0.5736
	Mixed	0.7798	0.4215	0.6330	0.6160
$k \times 10^2$ (g/g min <sup>n</sup> )	CV	0.0138	0.1157	0.4775	0.0578
	Peroxide	0.0315	0.0985	0.0866	0.0673
	Mixed	0.0242	0.1028	0.0763	0.0606

where  $\theta$  is the slope of the linear portion of the sorption curve  $Q_t$  versus  $t^{1/2}$ . From the  $D$  values, the intrinsic coefficient values  $D^*$  were calculated using the equation,

$$D^* = \frac{D}{\phi^{7/3}} \quad (6)$$

The values of  $D^*$  are given in Table V. The  $D^*$  values vary in the order CV > mixed > DCP. The variation  $D^*$  depends on the solvent uptake, which is maximum for the CV system. The permeation of a solvent into a polymer membrane will also depend on the sorptivity of the penetrant in the membrane. Hence, sorption coefficients ( $S$ ) has been calculated using the relation<sup>21</sup>

$$S = M_s/M_p \quad (7)$$

where  $M_s$  is the mass of the solvent at equilibrium swelling and  $M_p$  is the mass of the polymer sample. The values of  $S$  are also given in Table V. It is found that the sorption coefficient is maximum for the CV system and minimum for the DCP system, whereas mixed system comes in between. This may be due to the availability of

space for solvent molecules in the highly flexible networks.

Since the permeability depends on both diffusivity and sorptivity, the permeation coefficient has been determined using the relation<sup>21-23</sup>

$$P^* = D^* \times S \quad (8)$$

The values obtained for  $P^*$  are given in Table V. It can be seen that  $D^*$  and  $P^*$  follow the same trend. So it can be concluded that in the permeation of the system, diffusion of the solvent predominates over sorption. The permeability coefficient shows the net effect of sorption and diffusion process.

As diffusion is influenced by polymer morphology, we have estimated the molar mass between crosslinks ( $M_c$ ) from the sorption data. The rubber solvent interaction parameter  $\chi$ , which is needed for the estimation of  $M_c$ , has been calculated using the equation<sup>24-26</sup>

$$\chi = \beta + \frac{V_s}{RT}(\delta_s - \delta_p)^2 \quad (9)$$

where  $V_s$  is the molar volume of the solvent;  $\delta_s$  and  $\delta_p$  are solubility parameters of solvents and

**Table V** Values of Intrinsic Diffusion Coefficient ( $D^*$ ), Sorption Coefficient ( $S$ ), and Permeation Coefficient ( $P$ )

Temperature (°C)	$D \times 10^{-7}$ (cm <sup>2</sup> /sec)			$S$ (g/g)			$P \times 10^{-7}$ (cm <sup>2</sup> /sec)		
	CV	Mixed	DCP	CV	Mixed	DCP	CV	Mixed	DCP
30	195.55	129.83	146.03	2.15	1.66	1.52	420.43	215.50	221.98
50	101.79	89.55	92.91	2.11	1.68	1.53	214.81	150.26	141.69
60	214.73	65.63	113.20	2.08	1.67	1.86	445.50	115.40	207.00
70	231.06	187.49	169.28	1.91	1.68	1.62	442.04	310.65	273.30



**Table VI** Values of the Volume Fraction of the Polymer ( $\phi$ )

System	Temperature (°C)			
	30	50	60	70
CV	0.2467	0.2804	0.2841	0.3006
Mixed	0.3315	0.3293	0.3298	0.3287
DCP	0.3513	0.3506	0.3459	0.3372

polymer, respectively, taken from Polymer Hand Book;  $R$  is the gas constant and  $T$  the absolute temperature;  $\beta$  is the lattice constant and is taken as 0.34 in this calculation. The values of  $\chi$  calculated at 30, 50, 60, and 70°C are 0.7653, 0.7132, 0.6918, and 0.6716, respectively. It is seen that the  $\chi$  value decreases with temperature.

Using  $\chi$  values, the molar mass between crosslinks ( $M_c$ ) of the network polymer was estimated from the Flory–Rehner theory.<sup>27,28</sup>

$$M_c = \frac{-\rho_p V \phi^{1/3}}{[\ln(1 - \phi) + \phi + \chi \phi^2]} \quad (10)$$

where  $\rho_p$  is the density of the polymer;  $\phi$ , the volume fraction of swollen polymer;  $V$ , the molar volume of the solvent; and  $\chi$ , the interaction parameter. The volume fraction of polymer  $\phi$  is calculated using the equation<sup>25,29</sup>

$$\phi = \frac{M_p/\rho_p}{M_p/\rho_p + M_s/\rho_s} \quad (11)$$

where  $M_p$  and  $\rho_p$  are weight and density of the polymer;  $M_s$  and  $\rho_s$  are the weight and density of the solvent. The estimated values of  $\phi$  are given in Table VI. It is observed that  $\phi$  values increase in the order CV < mixed < DCP. This shows that the uptake is maximum for the CV system and lowest for the DCP system; the mixed system comes in between. In most cases,  $\phi$  values decrease with temperature for a given system. This indicates that as temperature increases uptake also increases, that is, temperature activates the diffusion process.

The estimated values of  $M_c$  are given in Table VII. Using the  $M_c$  values, the crosslink density ( $\nu$ ) can be calculated using the equation.

$$\nu = 1/2M_c \quad (12)$$

Flory and Rehner<sup>30</sup> relations were developed for a network deforming affinely. In accordance with the affine model, the components of each chain vector transform linearly with macroscopic deformation and the junction points are assumed to be embedded in the network without fluctuations. In the phantom network model proposed by James and Guth,<sup>31</sup> chains may move freely through one another. The junction points fluctuate over time around their mean position without being hindered by the presence of the neighboring chains and are independent of deformation. The molecular weight between crosslinks calculated ( $M_c$ ) were compared with the affine and phantom models using eqs. (12) and (13).

$$M_c(\text{affine}) = \frac{-\rho_p V_s \nu_{2c}^{2/3} \nu_{2m}^{1/3} \left(1 - \frac{\mu}{\nu} \nu_{2m}^{1/3}\right)}{[\ln(1 - \nu_{2m}) + \nu_{2m} + \chi \nu_{2m}^2]} \quad (13)$$

where  $\mu$  and  $\nu$  are called the number of effective chains and junctions;  $\nu_{2m}$  is the polymer volume fraction at swelling equilibrium;  $\nu_{2c}$  is the polymer volume fraction during crosslinking; and  $\rho_p$ ,  $\chi$ , and  $V_s$  have the same meaning as explained earlier.

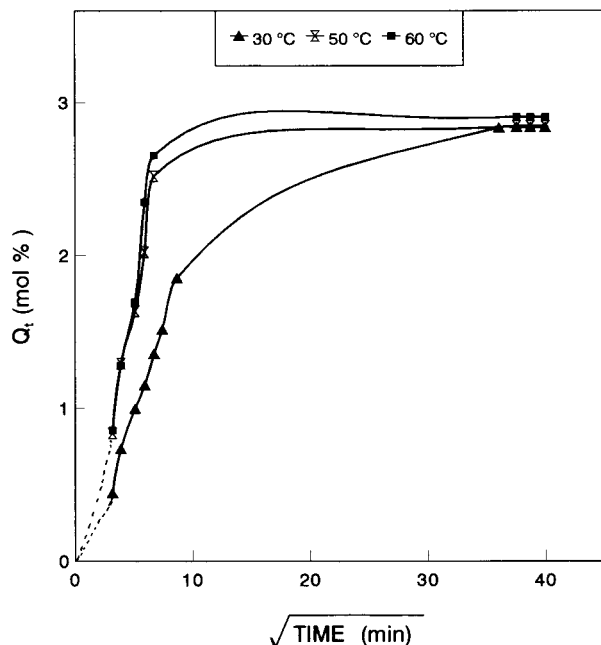
$$M_c(\text{ph}) = \frac{-\left(1 - \frac{2}{\phi}\right) \rho_p V_s \nu_{2c}^{2/3} \nu_{2m}^{1/3}}{[\ln(1 - \nu_{2m}) + \nu_{2m} + \chi \nu_{2m}^2]} \quad (14)$$

where  $\phi$  is the junction functionality.  $M_c(\text{aff})$  and  $M_c(\text{ph})$  were compared with  $M_c(\text{chem})$  and are given in Table VII. It is seen that  $M_c(\text{chem})$  values are close to  $M_c(\text{aff})$ .

The values of  $\nu$  are also given in Table VII. As  $\nu$  value increases, the uptake of solvent decreases. It is observed that in the CV system the  $\nu$  is the least and in the CV system only polysulfidic linkages are present. They are more flexible than mono- and disulfidic linkages. This results in maximum solvent uptake for the CV system. In

**Table VII** Values of  $M_c$  and  $\nu$ 

System	$M_c$ (chem)	$M_c$ (aff)	$M_c$ (ph)	$\nu$
CV	3730	3532	1178	$1.34 \times 10^{-4}$
Mixed	3470	3203	1068	$1.44 \times 10^{-4}$
DCP	3503	3412	1138	$1.43 \times 10^{-4}$



**Figure 7** Sorption curve showing the diffusion of acrylonitrile through NBR in DCP system at 30, 50, 60, and 70°C.

the mixed and DCP system,  $\nu$  values are high; correspondingly, uptake is also less in these two systems.

It was found that the amount of polysulfidic linkages was greater in the CV system and none in the DCP-cured system. Amounts of polysulfidic linkages in CV and mixed systems are  $0.17 \times 10^{-4}$  and  $0.11 \times 10^{-4}$ , respectively. This is in accordance with the fact that in the CV system, the crosslinks are mainly polysulfidic, whereas in mixed system, mono-, di-, and polysulfidic linkages along with the C—C linkages are present. In fact, the concentration of polysulfidic crosslinks was estimated from the change in crosslink density of the vulcanizates before and after treatment with propane-2-thiol and piperidine, which cleaves the polysulfidic crosslinks in the network.<sup>32-34</sup>

The temperature dependence of the diffusion process of the three vulcanizing systems was determined by conducting the experiments at 30, 50, 60, and 70°C. The influence of temperature in the diffusion of acrylonitrile through a DCP-initiated NBR matrix is shown in Figure 7. The temperature dependence of CV, peroxide, and mixed system is clear from Table III, where the  $Q_{\infty}$  values of the system at different temperature are

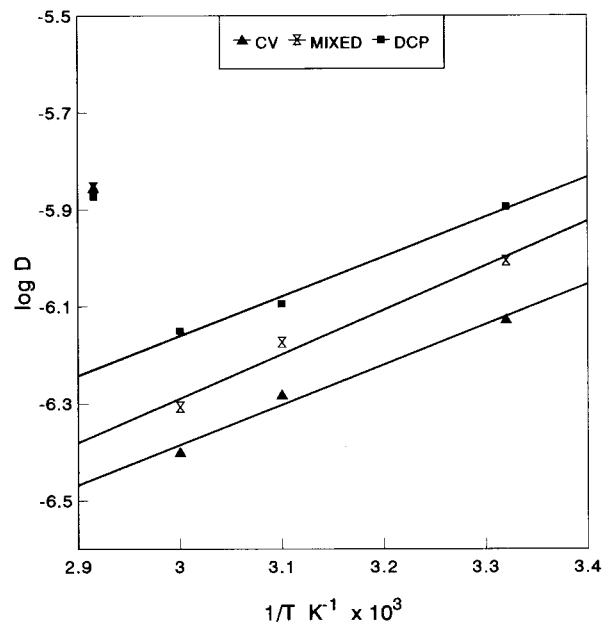
given. In CV desorption occurs at high temperature (due to chain mobility). The peroxide linkages are less flexible and temperature susceptible and the sorption values increase gradually. In the mixed system, the combination of monosulfidic, disulfidic, and C—C linkages provides moderate flexibility and the  $Q_{\infty}$  value rises.

The initial rate of diffusion increases with an increase in temperature and  $Q_{\infty}$  values increase with an increase in temperature. Generally, as temperature increases,  $D$  increases. This is because as temperature increases the chain flexibility increases and therefore the penetration of the solvent also increases.

The energy of activation for the diffusion, permeation, and sorption process is calculated using the Arrhenius relationship<sup>23</sup>

$$X = X_0 \exp(E_x/RT) \quad (15)$$

where  $X$  is  $P$ ,  $D$ , or  $S$  and  $X_0$  denotes  $P_0$ ,  $D_0$ , or  $S_0$  which is a constant.  $E_x$  is the activation energy,  $R$  is the universal gas constant, and  $T$  is temperature on absolute scale. Typical Arrhenius plots of  $\log D$  versus  $1/T$  are given in Figure 8. The calculated values of  $E_P$ ,  $E_D$ , and  $E_S$  are given in Table VIII. The heat of sorption was estimated from the differences between  $E_P$  and  $E_D$ . The Arrhenius plots of  $\log P$ ,  $\log S$ , and  $\log K_s$  versus



**Figure 8** Arrhenius plots of  $\log D$  versus  $1/T$  for crosslinked NBR in acrylonitrile.



**Table VIII** Values of  $E_P$ ,  $E_D$ , and  $\Delta H$  and  $\Delta S$ 

System	$E_P$ (J/mol)	$E_D$ (J/mol)	$E_s$ (J/mol)	$\Delta H$ (J/mol)	$\Delta S$ (J/mol)
CV	-12081.82	126.39	2169.1	-2971.64	-36.34
Mixed	-7210.79	126.46	-235.78	413.52	-27.54
Peroxide	-1020.27	133.48	-2422.18	1336.09	-25.31

$1/T$  are given in Figures 9, 10, and 11, respectively.

The values of  $E_P$  and  $E_D$  are in the order CV < mixed < DCP. The values are higher for the DCP system. This is due to the nature of the crosslinks. In the DCP system, the crosslinks are more rigid and tight. So the activation energy required for diffusion and permeation is higher for DCP than for mixed and CV systems.

The molar equilibrium coefficient ( $K_s$ ) is defined as<sup>35</sup>

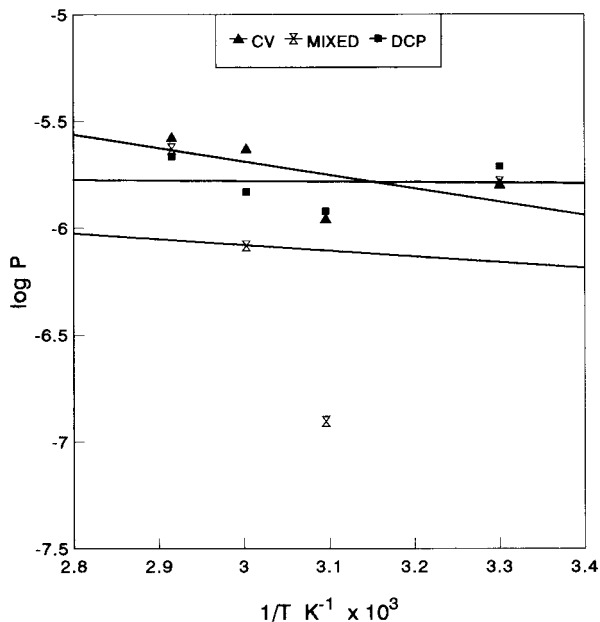
$$K_s = \frac{\text{No. of moles of solvent sorbed at equilibrium}}{\text{Mass of the polymer}} \quad (16)$$

The values of  $K_s$  are estimated and are given in Table IX. They are in the order CV > mixed

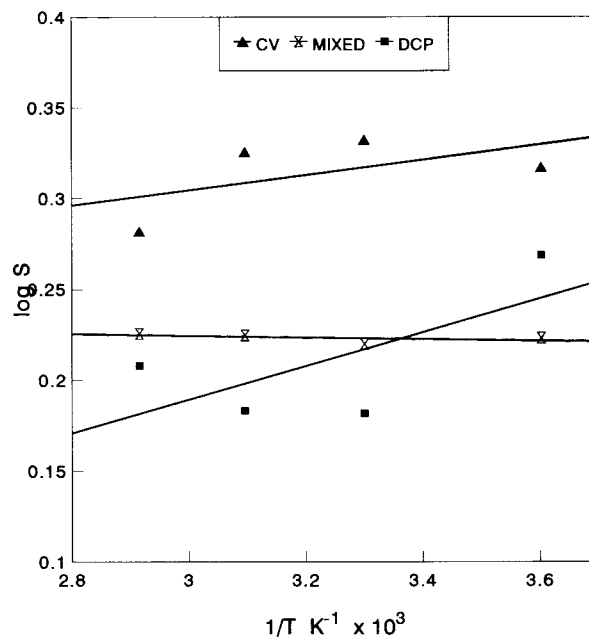
> DCP for a given temperature. It is found that the  $K_s$  values decrease with temperature for CV, slightly increase for DCP and relatively insensitive for mixed system. This may be due to the decrease in crosslink density observed for DCP and an increase in crosslink density observed for CV after the sorption in acrylonitrile. The temperature insensitivity of the mixed samples is also clear from Table X. From the values of  $K_s$ , the entropy ( $\Delta S$ ) and enthalpy ( $\Delta H$ ) of sorption are determined using the van't Hoff equation,

$$\log K_s = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (17)$$

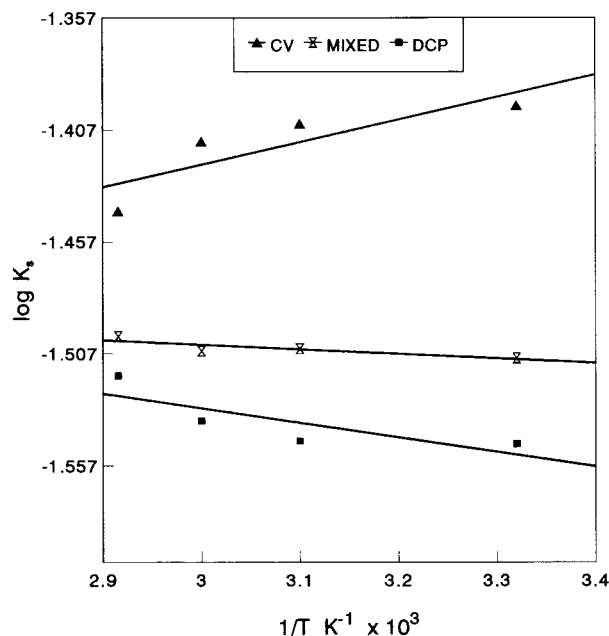
The values  $\Delta S$  and  $\Delta H$  are given in Table VIII. The  $\Delta H$  values decrease regularly from the DCP to CV system. The  $\Delta S$  values are negative in all cases, suggesting the retainment of liquid state



**Figure 9** Arrhenius plots of  $\log P$  versus  $1/T$  for crosslinked NBR in acrylonitrile.



**Figure 10** Arrhenius plots of  $\log S$  versus  $1/T$  for crosslinked NBR in acrylonitrile.



**Figure 11** Arrhenius plots of  $\log K_s$  versus  $1/T$  for crosslinked NBR in acrylonitrile.

structure of solvent molecules even in the sorbed state. The values of  $\Delta S$  are in the order  $CV > \text{mixed} > DCP$ .

In order to justify the anomalous transport in the present system, we have attempted to calculate the theoretical sorption curves and compared them with experimental curves for the CV, mixed, and DCP systems in Figures 12, 13, and 14, respectively. The theoretical curves are drawn according to the following equation:

$$\frac{Q_t}{Q_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp[-D(2n+1)^2 \pi^2 t / h^2] \quad (18)$$

**Table IX** Molar Sorption Constants ( $K_s \times 10^{-2}$ )  $\text{mol g}^{-1}$  at Different Temperatures

Temperature ( $^{\circ}\text{C}$ )	Vulcanization Systems		
	CV	Mixed	DCP
30	4.01	3.09	2.83
50	3.94	3.13	2.84
60	3.87	3.12	2.91
70	3.60	3.16	3.04

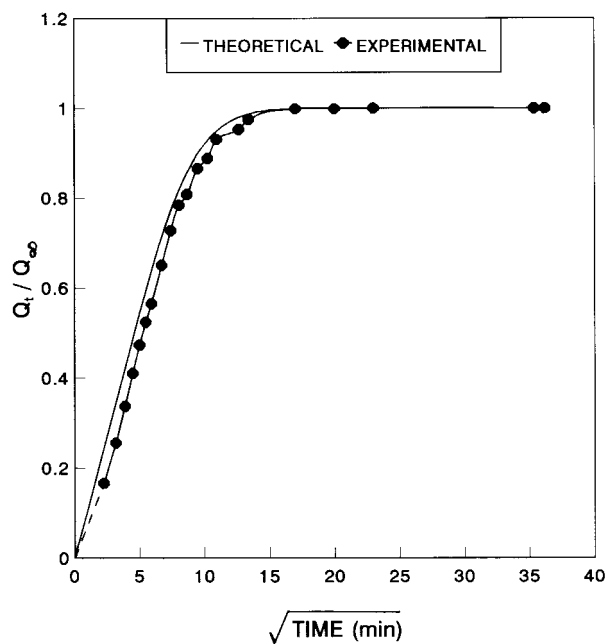
**Table X** Chemical Crosslink Density after Sorption in Acrylonitrile ( $\nu \times 10^{-4}$ )

Temperature ( $^{\circ}\text{C}$ )	Vulcanization Systems		
	CV	Mixed	DCP
30	1.35	1.45	1.44
50	1.37	1.44	1.43
60	1.39	1.44	1.42
70	1.40	1.43	1.41

where  $Q_t$ ,  $Q_\infty$ ,  $h$ ,  $t$ ,  $D$ , and other variables have the same meaning as given earlier. It is observed that the curve deviates from the normal Fickian mode. This supports the anomalous sorption mechanism shown by the present system. A similar trend was shown by other systems.

## CONCLUSIONS

The work presented here describes the influence of the nature of crosslinks on diffusion of acrylonitrile monomer in NBR. The effect of temperature on swelling properties was studied. The NBR samples swell readily in acrylonitrile. In NBR,



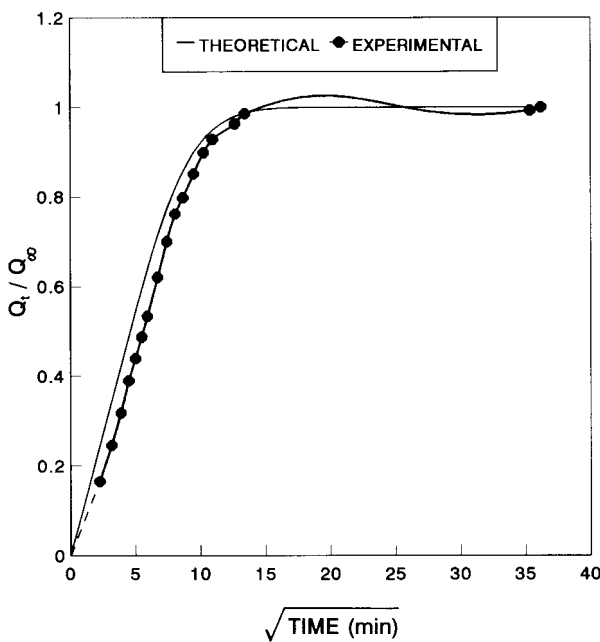
**Figure 12** Comparison between experimental and theoretical sorption curves of CV system in acrylonitrile at  $70^{\circ}\text{C}$ .

the equilibrium sorption is maximum for conventionally vulcanized samples and minimum for peroxide samples, whereas the mixed system shows intermediate uptake. This has been explained in terms of the difference in the types of crosslinks formed between rubber chains during different vulcanization techniques and also by difference in crosslink densities. The polysulfidic linkages present in these systems were calculated. The CV system showed the maximum amount of polysulfidic linkages.

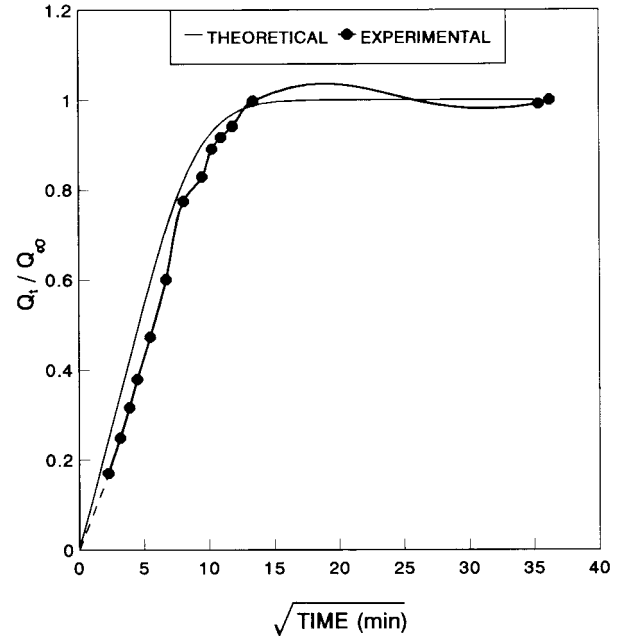
The molecular weight between crosslinks ( $M_c$ ) was calculated and compared with the affine and phantom models. It was found that the  $M_c(\text{chem})$  values satisfy the affine model, indicating that the components of each chain vector transform linearly with macroscopic deformation.

The diffusion coefficient value is highest for the DCP system with lowest uptake and lowest for the CV system with highest uptake. The permeation coefficient follows the same trend as diffusion coefficient.

The swelling was studied in the temperature range of 30–70°C. It was found that temperature activates diffusion in all cases. The theoretical curves drawn deviate from the normal Fickian mode. This supports the anomalous sorption mechanism. Finally, it is important to add that



**Figure 13** Comparison between experimental and theoretical sorption curves of mixed system in acrylonitrile at 70°C.



**Figure 14** Comparison between experimental and theoretical sorption curves of DCP system in acrylonitrile at 70°C.

the present investigation has been conducted as a preliminary step for the preparation of interpenetrating polymer network from this laboratory. A detailed knowledge about the swelling of NBR in the monomer is essential in controlling the composition and thereby the morphology and properties of the IPNs to be developed.

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