Molecular Transport of Benzene and Methyl-Substituted Benzenes into Filled Natural Rubber Sheets

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SYNOPSIS

Sorption and diffusion of benzene and methyl-substituted benzenes were investigated through natural rubber reinforced with four types of carbon black: superabrasion furnace, intermediate superabrasion furnace, high-abrasion furnace, and semireinforcing furnace. The rubber loaded with superabrasion furnace took the lowest amount of solvents among all the samples. It was observed that the mechanism of transport deviates from the normal Fickian trend with a decrease in particle size of the fillers. The diffusion coefficients were determined considering the changes in thickness as well as the diameter of the natural rubber samples. From the temperature dependence of diffusivity, the activation energy for the diffusion process was computed. The sorption data were used to estimate the rubber–solvent interaction parameter, enthalpy, and entropy of the sorption process. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The sorption and transport of organic liquids through elastomers have been investigated extensively by several researchers.[1-4] It is generally accepted that the transport process through rubbers is controlled by factors such as the nature of rubber,[5] its crosslink density,[6] penetrant size,[7] temperature,[8] etc. Another important factor is the nature of filler incorporated into the rubber matrix. Several outstanding studies regarding the influence of fillers on the swelling of elastomers exist.[9-14] Boonstra and Dannenberg[15] studied the sorption and diffusion through natural rubber (NR) and a number of synthetic membranes. They observed that the fillers like carbon black caused a reduction in swelling of the membranes, which is commensurate with the volume loading of filler. Porter[16] examined the degree to which high-abrasion furnace (HAF) black resists the swelling of conventionally vulcanized NR in n-decane. In that work, the HAF black was found to cause an increase of up to 25% in the yield of polymer to polymer crosslinks. Candia et al.[17] studied the

transport properties of networks filled with carbon black to obtain information about the rubber–filler interaction. Lawandy and Wassef[18] followed the penetration of oils into polychloroprene rubber loaded with different types of carbon black. They pointed out that the penetration rate increased with an increase in particle size and a decrease of aggregate structure of carbon black. Although many other major contributions can also be cited from the literature, the influence of reinforcing fillers on the transport process through elastomers still needs additional information.

The goal of the present work was to study the influence of four different types of carbon black on the sorption and diffusion of four aromatic hydrocarbons, benzene, toluene, p-xylene, and mesitylene, through crosslinked NR. Stress was given to follow the influence of particle size of carbon black on the mechanism of transport, diffusion coefficient, activation energy, rubber–penetrant interaction parameter, enthalpy, and entropy of sorption.

EXPERIMENTAL

Materials

The NR used was of ISNR-5 grade. The fillers used were superabrasion furnace (SAF), intermediate su-

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perabrasion furnace (ISAF), HAF, and semirein-
forcing furnace (SRF) with particle size 20, 23, 29,
and 60 nm, respectively. The solvents benzene, tol-
uene, p-xylene, and mesitylene were of reagent grade
and were double distilled before use. All other
chemicals were of reagent grade.

Preparation of Samples

The NR samples were vulcanized by conventional
technique, using accelerated sulfur, to their optimum
cure time (t_{90}). The t_{90} represents the time to attain
90% of the maximum rheometric torque. For all
practical purposes rubber products are cured to t_{90}
to obtain the best balance of physical properties.
For hundred parts of rubber, the basic formulation
involves stearic acid (1.5), zinc oxide (5.0), morpho-
line benzothiazyl sulfenamide (0.6), and sulfur (2).
In addition, each mix contains 30 phr (parts per
hundred rubber) of one of the four black fillers. The
mixing was done on a two roll mixing mill (6 × 12
in.) with a friction ratio 1 : 1.4. The vulcanization
behavior of the samples was followed by a Monsanto
Rheometer-R100. The vulcanization was carried out
on a hydraulic press at 160°C under a pressure of
30 tonnes.

Sorption Experiments

Circular samples were punched out from the vul-
canized sheets using a sharp edged steel die of 2-cm
diameter. The thicknesses of the samples were mea-
sured at several points with an accuracy of ±0.001
cm by using a micrometer screw gauge. An average
of several values was taken as the initial sample
thickness. The samples were soaked in liquids taken
in sorption bottles kept at constant temperatures in
an air oven. At regular intervals, they were taken
out and weighed in an electronic balance (Shimadzu,
Libror AEU-210, Japan) that measured reproducibly
within ±0.0001 g. The samples were then placed into
the test bottles containing liquids. The process was
continued until the samples attained equilibrium
swelling. The experiments were conducted at 28, 50,
and 70°C. A possible chance of error in this method
arises during the weighing operation where the
sample has to be removed from the bottle. However,
because the weighing was done within 30–40 s, this
error can be neglected.

RESULTS AND DISCUSSION

The results of the sorption experiments are pre-
sented as the mol % uptake Q_t of the liquid by 100

g of the rubber as a function of square root of time.
The standard deviations in Q_t values are in the range
0.02–0.08.

The diffusion curves of NR samples reinforced
with the four types of fillers, SAF, ISAF, HAF, and
SRF, are shown in Figures 1 and 2. The samples
were cured to t_{90}. The solvents used were benzene
and toluene. The experiments were done at 28°C.
The figures clearly show that NR loaded with SAF
absorbs the lowest amount of liquid and that with
SRF takes up the highest. The samples loaded with
ISAF and HAF take intermediate positions. The
reason for this trend can be attributed to the dif-
ference in the particle size of fillers reinforced into
the rubber matrix. As the particle size increases the
degree of filler reinforcement in the rubber network
decreases. The SRF black, having highest particle
size, and hence having the lowest degree of rein-
forcement, does not offer much resistance to the
rubber chain flexibility during sorption and diffu-
sion. The SAF black, which has the lowest particle
size, gets reinforced in the matrix in such a way that
the possibility for the rubber chain rearrangement
is quite low. Another factor to be mentioned here is
the role of bound rubber[19] in carbon black loaded
rubbers. The bound rubber formation increases with
increase in surface area of the black particles and
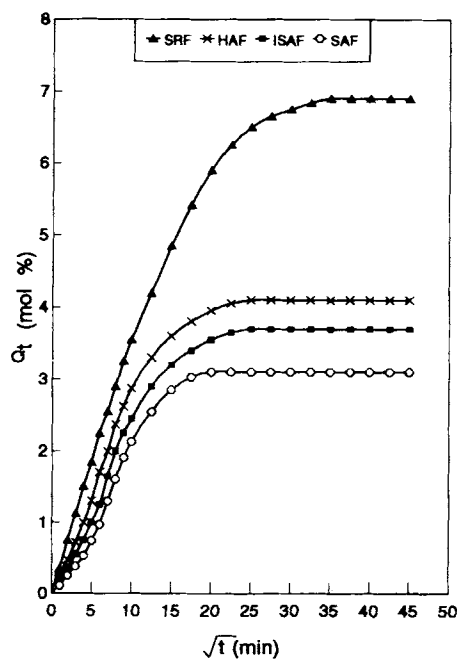enhances the bonding between individual polymeric

Figure 1   Mol % benzene uptake of natural rubber with
different fillers at 28°C. The samples were cured to the
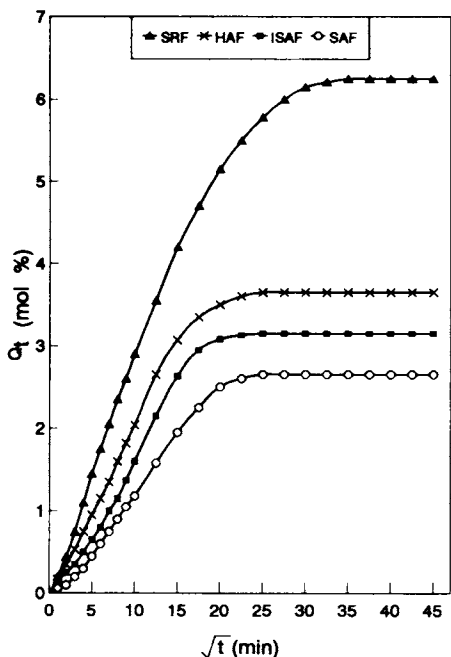optimum cure time.

Figure 2 Mol % toluene uptake of natural rubber with different fillers at 28°C. The samples were cured to the optimum cure time.
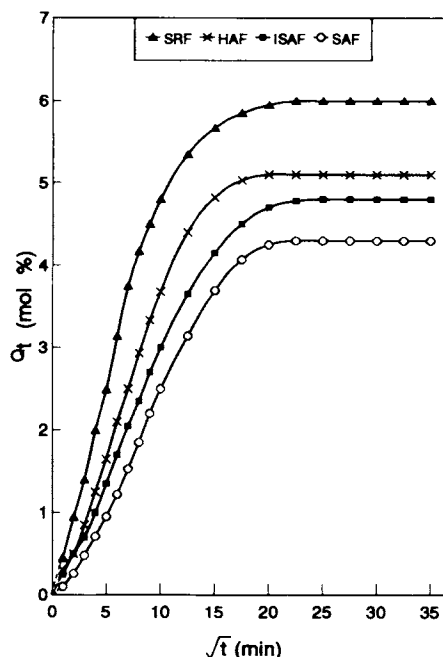
chains. This in turn causes the rubber samples to exhibit low sorption behavior. The SAF loaded rubber samples, with lowest particle size and thus highest surface area of fillers in them, probably have the highest bound rubber content and the SRF filled ones have the lowest. Therefore, the restriction to rubber chain mobility is maximum in SAF loaded

Figure 3 Rheographs showing the curing of NR samples to the same torque; (a) SAF, (b) ISAF, (c) HAF, (d) SRF.

Figure 4 Mol % benzene uptake of natural rubber with different fillers, cured to the same torque.

samples and minimum in SRF loaded ones. This also accounts for the observed solvent uptake behavior of different samples.

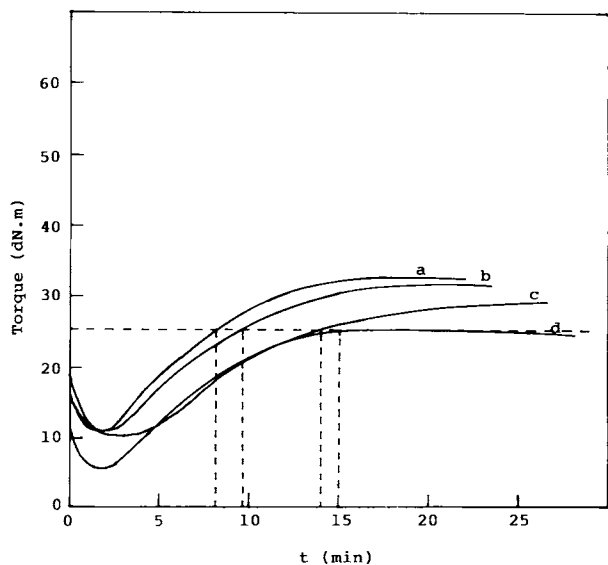The reinforcing effect of the different fillers on the sorption process can be followed by considering
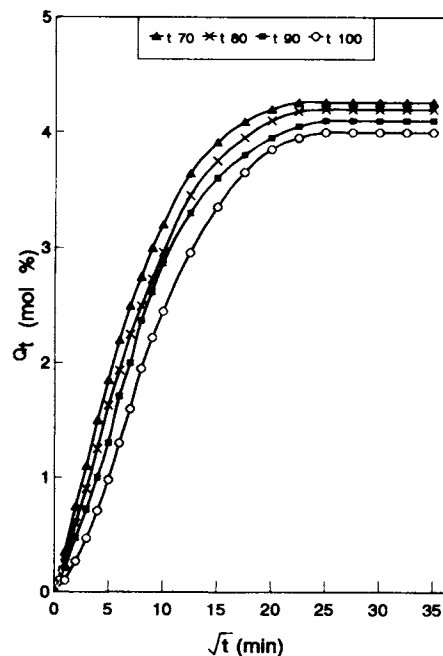

Figure 5 Mol % benzene uptake of HAF filled natural rubber samples with different cure time.

the volume fraction of rubber (ϕ) in different swollen samples calculated using the equation,[20]

$$\phi = \frac{(d - fw)\rho_r^{-1}}{(d - fw)\rho_r^{-1} + A_o\rho_s^{-1}} \quad (1)$$

where d is the weight after drying out the sample, w is the initial weight of the sample, A_o is the weight of the absorbed solvent, f is the fraction of insoluble components, and ρ_r and ρ_s are the densities of rubber and solvent, respectively. The volume fraction of rubber in SAF, ISAF, HAF, and SRF loaded samples swollen in benzene were 0.2127, 0.1901, 0.1711, and 0.0971, respectively. Because ϕ values and crosslink density are directly related, the differences in the liquid uptake behavior of different filler loaded samples is definitely associated with their different crosslink density values.

To see whether the same trend exists under other conditions too, we cured all the samples to the same rheometric torque (Fig. 3). Because torque is proportional to crosslink density, it is reasonable to think that all the samples cured to the same torque have approximately the same crosslink density. Figure 4 explains the sorption behavior of NR samples having different fillers cured to the same rheometric torque in benzene. It is seen that these samples also exhibit the trend just like that of the samples cured to t_{90}. Because these samples have approximately the same crosslink density, the flexibility of crosslinks in the rubber network accounts for the differences in the behavior of the rubber samples in the solvents. The NR samples vulcanized by the conventional technique introduces flexible polysulfidic linkages ($\sim$C$-$S$_x$$-C\sim$) between rubber chains. The flexibility of the polysulfidic linkages is effectively reduced by the highly reinforcing SAF particles and eventually this lowers the overall flexibility of the rubber chains in such samples, which then can accommodate only quite low amount of solvents. The reinforcing effect of fillers decreases with increase in particle size, and thus from SAF to SRF loaded samples, the flexibility of the rubber chains regularly increases. This explains the exhibited sorption behavior of different samples.

We cured the NR samples to different cure times, that is, t_{70}, t_{80}, t_{90}, and t_{100}, to follow the effect of cure time on the sorption process. It may be noted that t_{70} represents the time to which a sample was cured to 70% of the maximum rheometric torque. Similarly t_{80}, t_{90}, and t_{100} represent the time for curing the samples to 80, 90, and 100% of the maximum torque. The effect of cure time on the diffusion process of benzene in the HAF loaded sample is pre-

sented in Figure 5. The rate and maximum mol % liquid uptake decrease with an increase in cure time. Because cure time and crosslink density are directly related, the observed trend is due to the increase in crosslink density with cure time.

There is a systematic trend in the behavior of solvents of different molecular size. There occurs a decrease in the value of Q_t with an increase in the molecular size of the solvents. Figure 6 represents the linear relationship between the maximum sorption value Q_∞, and the molecular weight of the penetrants for NR samples loaded with the four types of carbon black.

The mechanism of diffusion in the filler loaded NR samples under investigation was followed from the equation[21,22]

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

where Q_t and Q_∞ are the mol % sorbed concentration at time t and at equilibrium saturation. The values of n suggest the mechanism of transport. For the normal Fickian mode of transport, where the rate of polymer chain relaxation is higher compared to the diffusion rate of the penetrant, the value of n is 0.5. When $n = 1$, the transport approaches non-Fickian behavior where chain relaxation is slower than the liquid diffusion. If the value of n is in be-
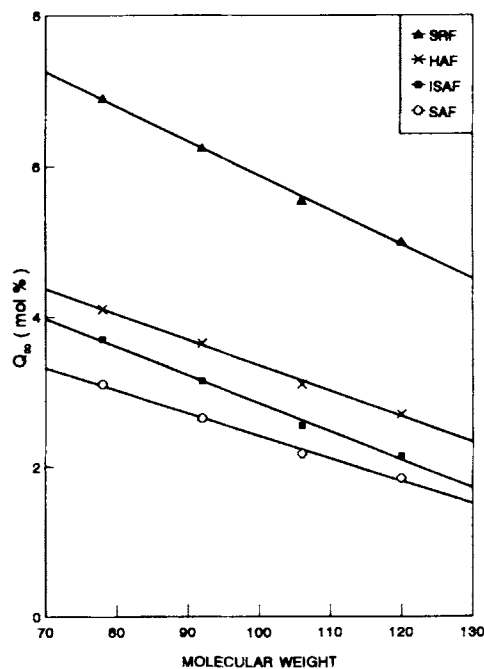

Figure 6 Dependence of Q_∞ on the molecular weight of the solvents.

Table I Values of n (NR Samples Cured to t_{90})

Solvent	Temperature (°C)	SAF	ISAF	HAF	SRF
Benzene	28	0.80	0.77	0.73	0.70
	50	0.77	0.75	0.69	0.68
	70	0.76	0.72	0.67	0.66
Toluene	28	0.77	0.75	0.72	0.68
	50	0.76	0.73	0.70	0.67
	70	0.74	0.72	0.68	0.65
p-Xylene	28	0.75	0.73	0.71	0.67
	50	0.74	0.72	0.69	0.66
	70	0.72	0.70	0.68	0.64
Mesitylene	28	0.74	0.71	0.69	0.65
	50	0.72	0.69	0.68	0.64
	70	0.71	0.67	0.66	0.64

tween 0.5 and 1, the mode of transport is classified as anomalous. k is a constant depending on the interaction between the rubber and solvent. The estimated values of n for different systems in this work are given in Table I. It can be seen that for all filler loaded samples, the values of n vary from 0.64 to 0.80, and thus the diffusion process can be classified as anomalous. It is interesting to see that the n values increase with a decrease in the particle size of the fillers loaded in NR, for a given penetrant. As the degree of reinforcement increases, the rate of polymer chain relaxation decreases compared to the concurrent penetrant diffusion rate and the mechanism regularly deviates from the normal Fickian trend. It is also interesting to see that the n values decrease with a rise in temperature. This indicates that the mode of transport tends to approach the regular Fickian mode at higher temperatures.

It is basically accepted that for thick rubber sections, the initial stage of swelling is restricted to the thickness direction until sufficient solvent has reached the central region of the sample.[23] Therefore, we calculated the diffusion coefficient in the Z direction D_z using the equation[24]

$$D_z = \pi \left[\frac{hY}{4Q_\infty} \right]^2 \qquad (3)$$

where h is the sample thickness, Y the slope of the initial part of the sorption curve, and Q_∞ has the same meaning as in eq. (2). The estimated values of D_z are given in Table II. Because significant swelling of NR samples was observed during sorption experiments in all solvents, corrections to diffusion coefficients under swollen conditions are essential. Hence, by considering the changes in thickness as well as diameter of the samples the modified diffusion coefficient $\bar{D}$, was calculated using the relation[25]

$$\bar{D} = D_z \left[1 + \frac{\bar{h}}{\bar{r}} \left[\frac{D_r}{D_z} \right]^{1/2} + \frac{\bar{h}}{2\pi\bar{r}} \left[\frac{D_\theta}{D_z} \right]^{1/2} \right]^2 \qquad (4)$$

where $\bar{h}$ and $\bar{r}$ are the average thickness and diameter of the samples before and after swelling and D_r and D_θ are the diffusion coefficient along the radial and angular directions of the disk shaped samples.[26] For isotropic diffusion, $D_r = D_\theta = D_z$ and eq. (4) reduces to

$$\bar{D} = D_z \left[1 + \frac{\bar{h}}{\bar{r}} + \frac{\bar{h}}{2\pi\bar{r}} \right]^2. \qquad (5)$$

The determined values of $\bar{D}$ are also given in Table II. It follows from the table that the diffusivity values increase from the SAF filled samples to SRF loaded ones in a given solvent. The variation of $\bar{D}$ with the particle size of the fillers is presented in Figure 7. The diffusion coefficient values decrease with an increase in the molecular weight of the penetrant for a given sample.

The temperature dependence of diffusion in the systems under study was followed by carrying out the sorption experiments at 50 and 70°C. From the values of the modified diffusion coefficient at 28, 50,

Table II Values of Diffusion Coefficient (NR Samples Cured to t_{90})

Solvent	$D_z \times 10^7$ (cm²/s) System				$\bar{D} \times 10^7$ (cm²/s) System			
	SAF	ISAF	HAF	SRF	SAF	ISAF	HAF	SRF
Benzene	4.80	5.13	6.20	8.56	7.61	8.17	9.97	13.78
Toluene	3.92	4.71	5.64	8.01	6.09	7.38	8.91	12.65
p-Xylene	3.10	3.99	4.89	7.10	4.71	6.07	7.57	10.93
Mesitylene	2.80	3.22	4.01	6.59	4.12	4.67	6.01	9.89

Figure 7 Dependence of modified diffusion coefficient on the particle size of fillers.

Figure 8 Arrhenius plots of log $\bar{D}$ vs. $1/T$ for filled natural rubber samples + benzene.

and 70°C, the activation energy, E_D, was calculated using the equation[25]

$$\bar{D} = \bar{D}_o e^{-(E_D/RT)} \qquad (6)$$

where $\bar{D}_o$ is the preexponential factor, R the universal gas constant, and T the temperature on the absolute scale. The determined values of activation energy are given in Table III. The Arrhenius plots showing the temperature dependence of the diffusion coefficient for different samples in benzene are presented in Figure 8. To reduce the number of figures, the plots for other solvents are not incorporated. But they also show the same trend. The E_D values increase regularly from SAF filled samples to SRF loaded ones for a given solvent. This readily suggests
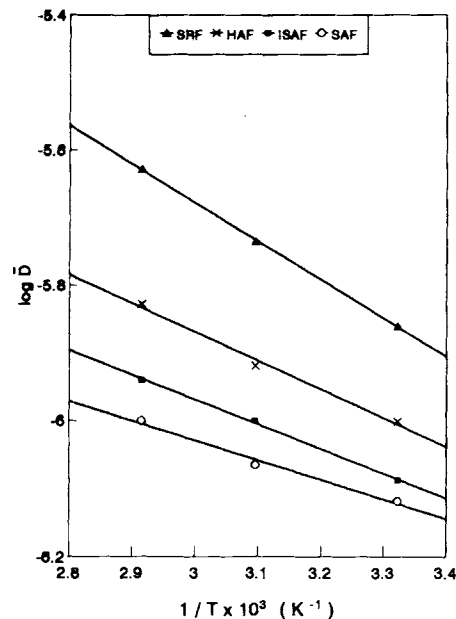
the increase in temperature susceptibility of NR samples with an increase in particle size of the filler reinforcement.

We calculated the rubber–solvent interaction parameter χ using the equation[27]

$$\chi = \frac{(d\phi/dT)\{[\phi/(1-\phi)] + N\ln(1-\phi) + N\phi\}}{\{2\phi(d\phi/dT) - \phi^2 N(d\phi/dT) - \phi^2/T\}} \qquad (7)$$

where ϕ is the volume fraction of rubber in the solvent swollen sample and N is calculated from ϕ using the equation

$$N = \frac{\phi^{2/3}/3 - 2/3}{\phi^{1/3} - 2\phi/3} . \qquad (8)$$

Table III Values of Activation Energy and Interaction Parameter (NR Samples Cured to t_{90})

Solvent	E_D (kJ/mol)				χ			
	System				System			
	SAF	ISAF	HAF	SRF	SAF	ISAF	HAF	SRF
Benzene	6.63	8.75	8.72	10.92	0.64	0.61	0.59	0.57
Toluene	7.51	8.98	9.76	11.97	0.58	0.54	0.53	0.51
p-Xylene	9.01	9.73	9.95	13.03	0.51	0.45	0.44	0.42
Mesitylene	9.28	9.95	9.98	14.01	0.49	0.44	0.43	0.41

Table IV Thermodynamic Functions ΔH and ΔS (NR Samples Cured to t_{90})

Solvent	$-\Delta H$ (kJ/mol) System				ΔS (J/mol/k) System			
	SAF	ISAF	HAF	SRF	SAF	ISAF	HAF	SRF
Benzene	0.43	0.62	0.96	1.68	16.43	18.73	21.55	25.20
Toluene	0.39	0.51	0.82	1.32	14.64	16.91	19.24	22.31
p-Xylene	0.31	0.42	0.63	1.14	11.81	13.41	16.91	19.40
Mesitylene	0.26	0.34	0.56	1.01	9.32	11.60	13.82	16.48

The computed values of X are given in Table III for different systems. The interaction parameter values decrease with an increase in particle size of the fillers for a given solvent. This clearly suggests the higher degree of interaction of SRF loaded NR samples with the liquids compared to the other samples. The decrease in the values of the interaction parameter with an increase in molecular weight of the penetrant, for a given sample, is due to the differences in the values of the solubility parameter. Such findings were reported in earlier literature.[3] Detailed investigation regarding the interaction parameter values of filled systems in different solvents is in progress.

The enthalpy and entropy of the sorption process in the samples under study were calculated from the maximum mol % uptake of the solvent expressed as sorption constant, K_s, using the Van't Hoff's relation,

$$\log K_s = \frac{\Delta S}{2.303R} - \frac{\Delta H_s}{2.303RT}. \qquad (9)$$

The obtained values of ΔH_s are negative in all cases, which become more negative from SAF to SRF samples in a given solvent (Table IV). These values also exhibit a regular increase from benzene to mesitylene for a given sample. These trends suggest an increased exothermicity of the sorption process as one moves from the SAF to SRF and a decreased exothermicity with an increase in molecular size of the penetrant for a given sample. The ΔS values also show a regular trend; that is, an increase from SAF to SRF samples for a given penetrant.

CONCLUSION

The results of this work demonstrated the systematic transport behavior of benzene and methyl-substituted benzenes through black filled NR vulcani-zates based on the penetrant size as well as the size of the carbon black particles. The solvent uptake follows the trend SRF > HAF > ISAF > SAF loaded NR samples. The reason for this trend was attributed to the increased restriction to the overall chain mobility and flexibility of polysulfidic linkages with a decrease in the size of carbon black particles. The bound rubber content in the rubber samples also plays a considerable role. The mechanism of diffusion was observed to deviate from the regular Fickian trend with an increase in the degree of reinforcement of the filler particles. The diffusion coefficient values, determined by considering isotropic swelling in the samples, decrease with a decrease in the size of the reinforcement. The activation energy values are found to be highest for SRF loaded rubber samples, which indicate their highest temperature susceptibility. The interaction parameter values decrease regularly from SAF to SRF loaded vulcanizates, in a given penetrant, which clearly suggests the higher degree of interaction between SRF filled samples and solvents. The computed values of enthalpy show the increase in exothermicity of the sorption process with an increase in the particle size of fillers in the rubber network.

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