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Sorption and diffusion of aromatic penetrants into natural rubber blends

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Sorption and diffusion of aromatic hydrocarbon penetrants through different NR blends such as NR/BIIR, NR/CIIR, NR/neoprene, NR/EPDM, NR/polybutadiene and NR/SBR have been studied. The diffusion coefficient (*D*) of aromatic penetrants range from 6.8 to 84.3 $\times 10^{-8}$ cm^2/s at a temperature range of 25–60°C. Transport data are affected by the nature of the interacting solvent molecule rather than its size and also by the structural variations of the elastomers blended with NR. Chlorobenzene and bromobenzene have shown higher transport data compared to nitrobenzene penetrant. The temperature dependence of the transport coefficient has been used to estimate the activation parameters from the Arrhenius plots. The activation parameters for the diffusion of aromatic penetrants range from 4.16 to 30.48 kJ/mol. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: sorption; NR blends; diffusion)

INTRODUCTION

The sorption and diffusion of aromatic liquids into crosslinked rubbery network elastomer systems have been studied by several authors[1–7]. In all these studies, it has been pointed out that the rate of solvent transport within a polymer matrix depends upon the nature of the functional group and its interaction with the polymer chain segments. Structural characteristics, chain flexibility and segment packing density of the polymer are also important factors which affect the mass transfer. The Fickian trend of diffusion mechanism was observed and the kinetics of sorption was of first order. The principal objective of this study was to determine the sorption (*S*), diffusion (*D*) and permeability (*P*) coefficients of aromatic penetrants over the temperature range of 25–60°C. Such data have enough relevant applications in a variety of areas such as controlled release systems (drugs and pesticides)[1] and hazardous waste water treatments[2]. Ethylene propylene diene terpolymer (EPDM), styrene butadiene rubber (SBR), chloro-butyl rubber (CIIR), bromo-butyl rubber (BIIR), neoprene (CR) and natural rubber (NR) are well known elastomers which are used in engineering and technology. In all these application areas, it is likely that these elastomers may come in contact with the organics (liquids or vapours) which may affect the performance of the materials.

A survey of the literature reveals that, the elastomeric blends have not been studied thoroughly. This research article reports the experimental sorption and diffusion results of nitrobenzene, bromobenzene and chlorobenzene for the NR blends with BIIR, CIIR, neoprene, EPDM, polybutadiene and SBR. The sorption experiments were performed at 25, 40 and 60°C and these results are used to estimate the Arrhenius parameters. The results are discussed in terms of the nature of polymer–solvent interaction. In addition to the effects noted in our earlier work[7,8], the present study highlights the discussion on the correlation of the thermodynamic quality of the solvent and its structure with the molecular transport properties of liquid–polymer systems.

EXPERIMENTAL

Reagents and specimen preparation

The double distilled, AR grade solvents, namely nitrobenzene, bromobenzene and chlorobenzene are used. The formulations for these blends are given in *Table 1*. The elastomers and ingredients are mixed in the same order as given in the table. A 16 × 13-inch laboratory mill was used to mix the compound. These compounded blends were moulded into sheets of dimensions 14 × 12 × 0.2 cm using a hydraulic press at about 160 kg/cm^2 pressure. The curing time and temperatures followed in this experiments are shown in *Table 1*.

These cured NR blends were cut into uniform circular pieces (diameter 1.5 cm) using a sharp edged die. The initial thicknesses of the specimens were measured at several points and ranged from 0.200 to 0.260 cm (precision ±0.001 cm). The cut specimens were dried in a dessicator before being used. Dry weights of the cut samples were taken before immersion into the air tight, metal capped test bottles containing the liquid. After immersion into the respective liquids, the bottles were placed in a thermostatically controlled oven (±0.5°C).

The representative engineering properties, such as tensile strength, percent elongation, surface hardness, etc., were measured as per ASTM specification and are given in *Table 2*.

Diffusion experiments

The thicknesses and initial weights of the specimens were measured, then each specimen was submerged in its respective penetrant in air tight bottles. Experiments were carried out at 25, 40 and 60°C in triplicate.

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Table 1 Recipe for different natural rubber blends and curing conditions

Ingredients	NR/BIIR	NR/CIIR	NR/neoprene	NR/EPDM	NR/poly butadiene	NR/SBR
ZnO	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0
PBN	1.0	1.0	1.0	1.0	1.0	1.0
CBS	0.6	0.6	0.6	0.6	0.6	0.6
MBTS	0.1	0.1	0.1	0.1	0.1	0.1
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5
Curing temp. (°C)	160	160	160	160	160	160
Curing time (min)	8	9	13	6	5	9

All the above blends contained about 75 phr of natural rubber and 25 phr of blending rubber

Table 2 Properties of different natural rubber blends

NR blends	Hardness (Shore A)	Tensile stress ($N/m^2 \times 10^{-4}$)	Stress at 300% elongation ($N/m^2 \times 10^{-4}$)	Elongation at break (%)
NR/BIIR	29	59.32	4.68	1032
NR/CIIR	33	87.31	5.70	963
NR/neoprene	29	67.16	8.95	892
NR/EPDM	32	102.11	12.29	857
NR/polybutadiene	37	96.06	13.11	830
NR/SBR	35	60.00	11.80	705

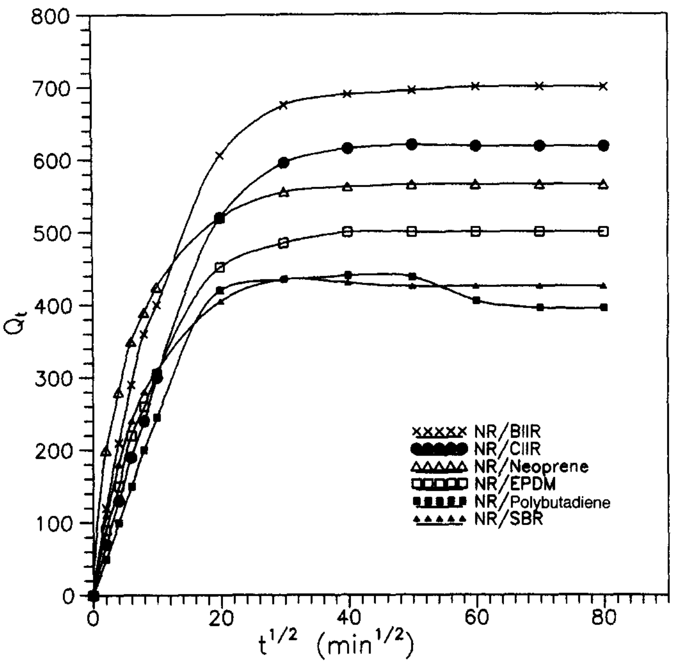

Figure 1 Percentage mass uptake *versus* square root of time for different NR blends with chlorobenzene penetrant at 40°C

The liquid uptake was monitored gravimetrically by weighing the specimens at regular intervals. When the samples were removed from the bottles, they were carefully blotted to remove excess liquid on the surface. The percentage mass uptake of liquid was determined until equilibrium state was reached.

RESULTS AND DISCUSSION

Sorption results were interpreted in terms of mass increase in concentration per 100 g of the NR blends *versus* square root of time, $t^{1/2}$. Some typical plots of all the blends in chlorobenzene at 40°C are presented in *Figure 1*. It is observed that the sorption of chlorobenzene is greater with NR/BIIR, NR/CIIR and NR/neoprene. This may be due to the presence of polar groups such as bromide and chloride in BIIR, CIIR and neoprene. The sorption plots of NR/BIIR in nitrobenzene at different temperatures are shown in *Figure 2* to show the effect of temperature. It was found that for all blends, the sorption increases with a rise in temperature. This effect follows the conventional theory that at higher temperatures, an increase in free volume occurs due to an increased movement of the chain segments of the elastomers. The sorption (*S*) i.e. maximum mass uptake (obtained from the plateau region of the sorption plots), of all blends in chlorobenzene and bromobenzene follow the order NR/BIIR>NR/CIIR>NR/neoprene>NR/EPDM>NR/polybutadiene>NR/SBR. During initial sorption stages, i.e. up to 50% of the completion of the sorption, penetrant uptake increased linearly with $t^{1/2}$ values. At later stages of the sorption experiments, due to the saturation

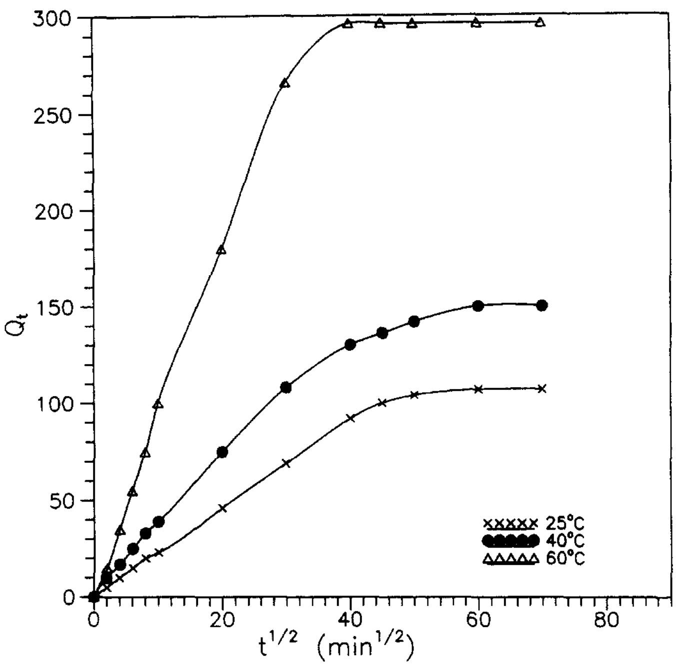

Figure 2 Percentage mass uptake *versus* square root of time for NR/BIIR blend with nitrobenzene penetrant at different temperatures

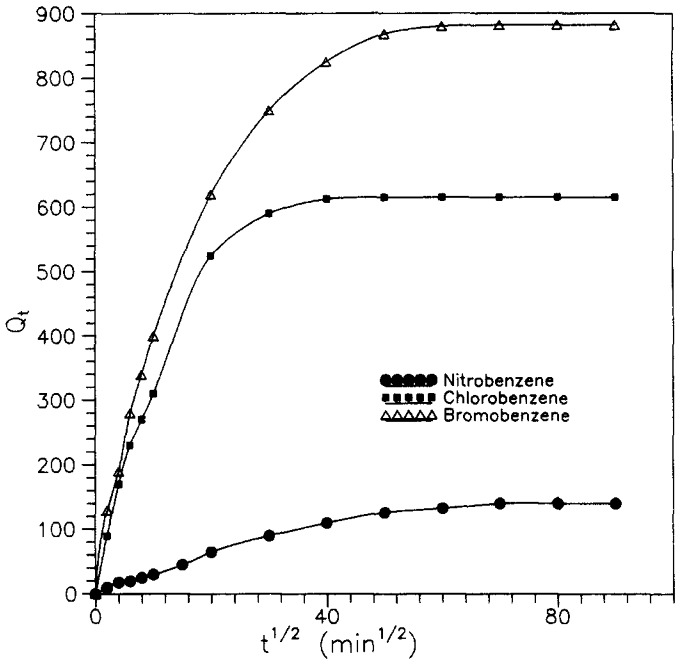

Figure 3 Percentage mass uptake *versus* square root of time for NR/CIIR blend with different penetrants at 40°C

equilibrium, the sorption curves for all penetrants and at all temperatures attained plateau regions.

The sorption plots of the NR/CIIR blend in all the three penetrants at 40°C are presented in *Figure 3*. Other blends also show similar trends. The S-values of nitrobenzene in the NR/EPDM blend show lower values (about 150 × 10^{-2} g/g at 60°C) compared to other blends. The chloro- and bromobenzene penetrants also show relatively lower values for the NR/EPDM blend. Such small values of sorption for EPDM are attributed to its tightly packed structure of EPDM thereby exhibiting both the toughness of the plastic and the elasticity of the gum elastomer phase. This intrinsic property of EPDM might restrict the free movement of penetrant molecules thus causing the lower values of sorption. This behaviour was also seen earlier for EPDM with several solvents, as published elsewhere[9–13]. Another striking feature of the sorption data for EPDM elastomer is that with an increase in the size or solubilty of the penetrant molecules, there is an increase in equilibrium sorption. However, this is not true of other elastomers. In order to investigate the type of diffusion mechanism, attempts were made to estimate the values of n and k from the following relation[3,4];

$$\log M_t/M_\infty = \log K + n \log t \qquad (1)$$

where k and n are system parameters, M_t and M_∞ are the uptake values at time t and at equilibrium.

In order to determine k and n, plots of $\log(M_t/M_\infty)$ *versus*

Table 3 Sorption data n- and k-values of natural rubber blends in aromatic penetrants at different temperatures

NR blends	Temperature (°C)	Nitrobenzene		Chlorobenzene		Bromobenzene	
		$n \pm$ 0.01	$k \times 10^2$ (g/g min^n)	$n \pm$ 0.01	$k \times 10^2$ (g/g min^n)	$n \pm$ 0.01	$k \times 10^2$ (g/g min^n)
NR/BIIR	25	0.54	1.44	0.50	6.27	0.52	3.69
	40	0.50	2.47	0.50	9.07	0.50	8.89
	60	0.50	2.68	0.50	9.63	0.50	11.30
NR/CIIR	25	0.52	2.22	0.50	5.05	0.58	1.94
	40	0.51	2.60	0.50	5.84	0.50	5.29
	60	0.50	2.90	0.50	8.05	0.50	9.63
NR/neoprene	25	0.56	2.28	0.55	4.33	0.51	10.86
	40	0.50	2.27	0.50	10.03	0.52	2.73
	60	0.50	4.50	0.51	7.02	0.52	10.03
NR/EPDM	25	0.50	3.14	0.51	7.01	0.52	4.98
	40	0.50	4.08	0.50	10.03	0.51	10.65
	60	0.50	4.60	0.51	10.65	0.52	13.08
NR/polybutadiene	25	0.50	3.33	0.50	10.03	0.50	7.50
	40	0.50	3.84	0.51	10.44	0.50	6.08
	60	0.50	4.16	0.51	11.08	0.50	10.03
NR/SBR	25	0.53	2.38	0.51	12.05	0.50	6.08
	40	0.50	3.34	0.51	14.09	0.50	9.88
	60	0.50	4.16	0.50	15.01	0.50	11.08

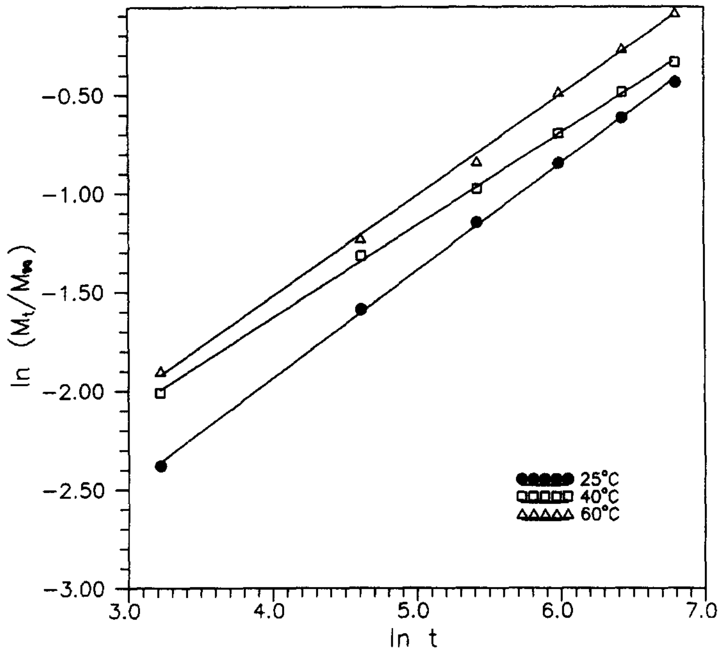

Figure 4 $\ln M_t/M_\infty$ *versus* $\ln t$ for NR/BIIR blend with nitrobenzene penetrant at different temperatures

log t were constructed. Values for the parameters n and k are given in *Table 3*, and *Figure 4* represents a typical plot for NR/BIIR in nitrobenzene. The average uncertainty in the estimation of n is around ± 0.01. A general variation of n from a minimum value of 0.50–0.58 was observed indicating the process to be nearly Fickian type.

The values of n are not indicating any systematic variation with temperature. But the k-value increases with increase in temperature for all the blend–penetrant systems[5,6].

By assuming a negligible concentration dependance of diffusivity over the concentration intervals studied in a sorption experiment (i.e. before attainment of 50% equilibrium saturation); a value of the mutual diffusion coefficient, D, can be calculated from the initial slope of the sorption curve as[9–13]:

$$D = \pi[h\theta/4M_\infty]^2 \qquad (2)$$

where M_∞ is the maximum mass uptake of solvent by 100 g of the polymer sample, h is the initial thickness of the specimen and θ is the initial slope of the sorption curve. The computed values of D are accurate to ± 0.01 units.

The calculated D-values for all blend–penetrant systems are given in *Table 4*. The variation in the diffusion coefficient also depends on the nature of the penetrant molecule in addition to the structural characteristics of the elastomers. The diffusion coefficient of liquids in NR blends

Table 4 Diffusion (*D*), sorption (*S*) and Permeation (*P*) coefficient values of natural rubber blends in aromatic penetrants at different temperatures

NR blends	Temperature (°C)	Nitrobenzene			Chlorobenzene			Bromobenzene		
		$D \times 10^7$ (cm^2/s)	$S \times 10^2$ (g/g)	$P \times 10^7$ (cm^2/s)	$D \times 10^7$ (cm^2/s)	$S \times 10^2$ (g/g)	$P \times 10^7$ (cm^2/s)	$D \times 10^7$ (cm^2/s)	$S \times 10^2$ (g/g)	$P \times 10^7$ (cm^2/s)
NR/BIIR	25	0.68	108	0.743	2.30	740	17.02	2.91	920	26.77
	40	0.91	150	1.365	3.40	700	23.08	4.00	855	34.00
	60	1.35	286	3.861	5.69	980	55.76	4.40	1040	45.07
NR/CIIR	25	0.97	86	0.834	3.10	650	20.15	1.30	810	10.05
	40	0.87	138	1.435	3.20	615	19.68	2.40	835	20.00
	60	1.04	270	2.808	4.50	875	39.32	4.80	880	42.02
NR/neoprene	25	0.83	172	1.431	2.19	620	13.52	1.30	850	11.00
	40	1.07	220	2.354	4.39	565	24.80	3.00	875	26.02
	60	1.45	460	6.067	4.62	815	37.65	3.66	895	42.02
NR/EPDM	25	0.98	82	0.803	3.00	530	15.09	2.40	670	16.00
	40	1.09	116	1.264	4.42	500	22.01	3.40	655	22.02
	60	1.25	150	0.875	5.03	655	32.95	3.60	705	25.03
NR/polybutadiene	25	0.89	108	0.961	6.75	485	32.73	4.20	645	27.00
	40	1.27	150	1.905	7.80	400	31.02	4.22	610	25.07
	60	1.13	242	2.735	8.43	420	35.40	4.80	625	30.00
NR/SBR	25	0.96	126	1.209	4.07	485	19.73	3.50	620	21.00
	40	1.35	158	2.133	5.82	425	24.73	4.50	645	29.00
	60	2.06	222	4.057	6.90	452	31.18	5.00	620	31.00

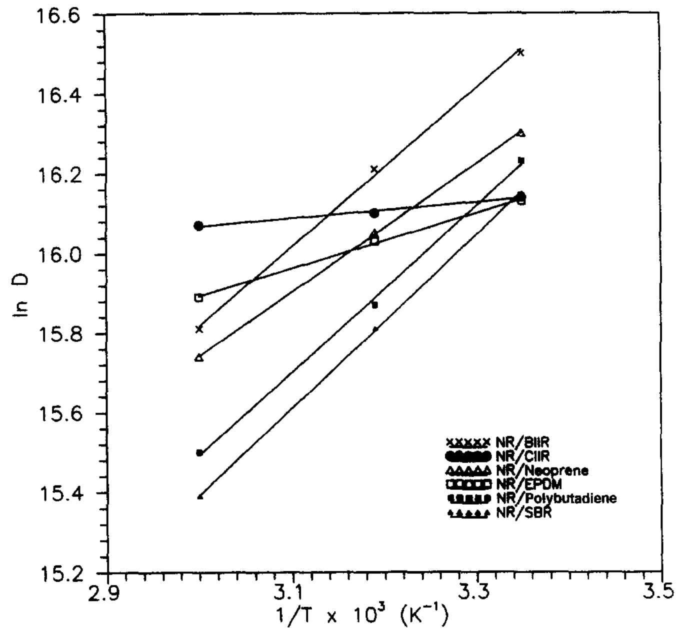

Figure 5 Arrhenius plots of diffusivity for blends in nitrobenzene

follows the Einstein[14] and Eyring theories[15]. All the blends, except NR/BIIR, show the *D*-values in increasing order of nitrobenzene < bromobenzene < chlorobenzene whose viscosities are in the reverse order. Thus, the *D*-values increase with a decrease in penetrant viscosity. But no systematic dependance of sorption (*S*) values was observed with the size of the penetrant molecules. The calculated molecular volumes of nitrobenzene, bromobenzene and chlorobenzene are 170, 173.6 and 169 $Å^3$, respectively. The chlorobenzene and bromobenzene have shown higher *S*-values compared to nitrobenzene. The *D*-values of nitrobenzene range from 0.68 to 2.06×10^{-7} cm^2/s whereas aryl halides range from 1.30 to 8.43×10^{-7}. It is also observed that no systematic dependence of *D*-values exists with molecular size of the penetrants. However, the *D*-values calculated using equation (2) are more reliable[16].

The permeability coefficient *P* is calculated from the simple relation;

$$P = DS \tag{3}$$

The *P*-values of penetrants are tabulated in *Table 4*. The *P*-values neither follow the order of *D* nor *S*.

The diffusion data at different temperatures have been used to estimate the activation energy E_D for the process of diffusion from the Arrhenius plots.

The Arrhenius plots namely $\log D$ *versus* $1/T$ are presented in *Figure 5*. The activation energy E_D has been calculated from the slope of this plot and tabulated in *Table 5*. The activation energy E_D does not show any

Table 5 Activation parameters E_D (kJ/mol); ΔH (kJ/mol) ± 4; ΔS (J/mol/K) ± 1 of natural rubber blends in aromatic penetrants

NR blends	Activation parameters	Nitrobenzene	Chlorobenzene	Bromobenzene
NR/BIIR	E_D	16.62	22.86	16.62
	ΔH	25.52	6.38	6.38
	$-\Delta S$	30.00	4.78	2.87
NR/CIIR	E_D	5.54	7.10	30.88
	ΔH	12.76	6.38	3.19
	$-\Delta S$	13.00	2.80	8.61
NR/neoprene	E_D	27.79	19.95	16.62
	ΔH	19.14	19.14	6.38
	$-\Delta S$	32.00	8.60	4.78
NR/EPDM	E_D	4.16	17.81	22.17
	ΔH	19.14	6.38	3.19
	$-\Delta S$	5.74	1.90	12.44
NR/polybutadiene	E_D	30.48	6.67	2.33
	ΔH	19.14	9.57	9.57
	$-\Delta S$	13.00	1.90	56.48
NR/SBR	E_D	20.78	13.06	8.31
	ΔH	19.14	9.57	5.74
	$-\Delta S$	19.00	9.50	9.57

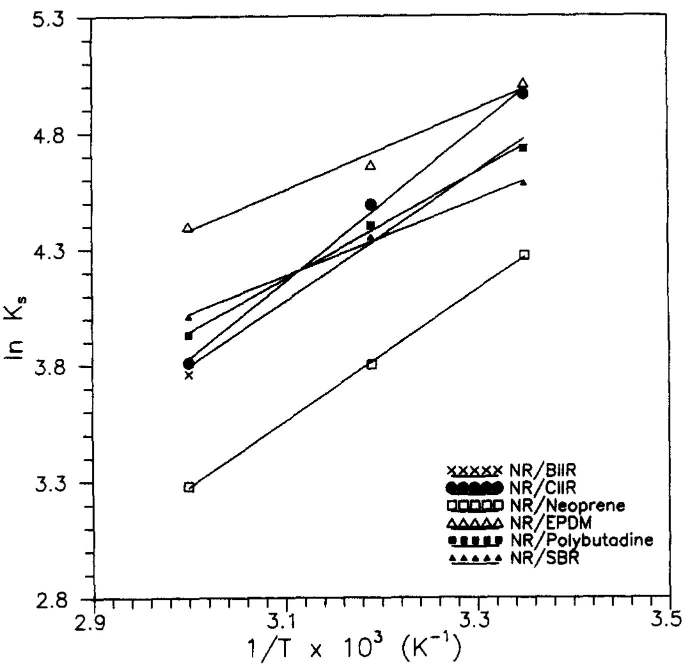

Figure 6 van't Hoff plots of log k_s *versus* $1/T$ for NR blends in nitrobenzene

systematic trend with the size of the penetrants. E_D values of aromatic penetrants lie in the range of 4.16–30.48 kJ/mol. These values are within the range expected for rubbery polymers, well above their glass transition temperatures[9–13]. The enthalpy ΔH and entropy ΔS of sorption values are also estimated from van't Hoff's relation using temperature dependent equilibrium sorption constant K_S. van't Hoff's plots, namely log K_S *versus* $1/T$, are presented in *Figure 6*.

ΔH and ΔS have been calculated from the slope and intercepts, respectively. The average estimated error in ΔH is about ± 4 J/mol whereas, for ΔS, it is about ± 1 J/mol/K; see *Figure 6*. It is noticed from *Table 5* that, in the majority of cases, the ΔH-values are positive and those for ΔS are negative for all blends. This suggests that the structure of the solvent molecules is retained even in the sorbed state.

CONCLUSIONS

The work described in this article summarizes the results of sorption and transport of aromatic solvents such as nitro-, chloro-, and bromobenzene into structurally different NR blends. The Fickian model has been used to estimate the diffusion coefficient and trasport data. It is observed that factors such as solvent type and nature of the elastomeric blend seem to exert tremendous influence on the transport characteristics. The diffusion-coefficient for all the blends except NR/BIIR vary in the sequence: nitrobenzene < bromobenzene < chlorobenzene. The D-values of these penetrants range from 0.68 to 8.63×10^{-7} cm²/s in the temperature range of 25–60°C. The temperature dependence of transport coefficients have been used to compute the activation parameters from the Arrhenius plots. Activation energy for diffusion (E_D) of

NR blend–penetrant systems lies in the range of 4.16–30.48 kJ/mol.

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