Sorption and Diffusion of Aldehydes and Ketones into Natural Rubber Blends

SIDDARAMAIAH,[1] S. ROOPA,[1] U. PREMAKUMAR,[1] A. VARADARAJULU[2]

[1] Department of Polymer Science & Technology, S.J. College of Engineering, Mysore—570 006, India

[2] S.K. University, Anantapur—515 003, India

ABSTRACT: Sorption and diffusion of aldehydes and ketones through different NR blends of bromobutyl (BIIR), chlorobutyl (CIIR), neoprene, EPDM, polybutadine, and SBR were studied at 25, 40, and 60°C. From the data, the Arrhenius activation parameter for diffusion, E_D, was determined. From the temperature dependence of the sorption constant, the enthalpy of sorption, ΔH, and entropy of sorption, ΔS, were also determined. The activation parameters are found to follow the conventional trend. Transport properties are affected by the nature of the interaction of solvent molecule, by its size, and also by the structural variation of the elastomers. For all the solvents, the polymer blends remained intact but the blends in the presence of benzaldehyde showed degradative reactions at higher temperature. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 101–112, 1998

INTRODUCTION

The sorption and diffusion of organic liquids into crosslinked rubber network systems were studied by several authors.[1–8] In all these studies, it was pointed out that the rate of solvent transport within a polymer material depends upon the nature of the functional groups in the solvents and their interaction with the polymer chain segments. It has also been observed that the diffusion mechanism follows the Fickian trend and the kinetics of sorption is of first order. The primary goal of these studies has been to estimate the sorption [S], diffusion [D], and permeation [P] coefficients besides system parameters n and k and to study their temperature dependence. These data have relevance in areas like controlled-release systems[1] (drugs and pesticides), hazardous waste treatments,[2] reverse osmosis,[3] and pervaporation.[4] In the present study, some aldehydes and ketones are used as penetrants. These occur widely in nature and play an important role in living organisms—both contain the carbonyl group. Their transport characteristics with respect to polymer membranes is important.

A survey of the literature reveals that the elastomeric blends have not been studied thoroughly. This article reports the experimental sorption and diffusion results of aldehydes and ketones for the natural rubber (NR) blends of bromobutyl (BIIR), chlorobutyl (CIIR), neoprene, EPDM, polybutadiene, and SBR. The sorption experiments are performed at 25, 40, and 60°C and these results are used to estimate the Arrhenius parameters.

EXPERIMENTAL

Reagents and Specimen Preparation

A 6 × 13 inch laboratory mill was used to mix the rubber compound for molding sheets of dimensions 14 × 12 × 0.2 cm in a hydraulic press. The

---

Table I   Recipe for Different NR Blends and Curing Conditions

Ingredients	NR/BIIR	NR/CIIR	NR/Neoprene	NR/EPDM	NR/Polybutadiene	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
Sulfur	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 NR and 25 phr of a blending rubber.

compounded blends were cured at 160°C and the curing time is different for different formulations, which are shown in Table I.

AR-grade solvents, namely, acetaldehyde, benzaldehyde, furfural, acetone, acetophenone, and cyclohexanone, were distilled twice before use. The polymer samples were cut circularly (diameter 1.5 cm) using a sharp-edged steel die. The thickness of the specimen lies in the range of 0.2–0.26 cm.

Sorption Experiment

Sorption and diffusion of aldehydes and ketones was studied using an immersion/weight gain method at different temperatures of 25, 40, and 60°C. The samples were immersed in an air-tight glass bottle containing the respective solvents maintained at the desired temperature. At an interval of 3–4 h, the specimen was removed and wiped off by filter paper and weighed.

RESULTS AND DISCUSSION

Sorption results are interpreted in terms of a mass increase in concentration per 100 g of the NR blend vs. the square root of time $t^{1/2}$. Some typical plots of the variation of % mass uptake with $t^{1/2}$ for the NR/CIIR blend in ketones at 40°C are presented in Figures 1 and 2, respectively. The plots of all NR blends in furfural at 40°C and in cyclohexanone at 25°C are given in Figures 3 and 4, respectively. The NR/SBR blend shows the attainment of equilibrium more quickly than any other blend in furfural (Fig. 3). In ketones, except NR/BIIR in cyclohexanone, all blends have reached equilibrium almost at the same time. However, with all the blends in the aldehyde se-

ries, the percentage mass uptake and the time required to attain equilibrium saturation are found to be inversely proportional to the size of the solvent molecules. However, an interesting observation of a sudden overshoot followed by an equilibrium and subsequent decrease in the sorption of furfural in the case of NR/neoprene (Fig. 1) was made. The molecular transport of organic liquids through elastomers is well known but is not completely understood. Alfery et al.[5] classified the transport phenomena as case I or Fickian when the solvent concentration is low and swelling is not important. At higher concentrations, however, swelling to relieve the mechanical stresses becomes important so that transport is case II or non-Fickian. Here, the solvent front is sharp and moves at a constant velocity when transport dominates the process. If, on the other hand, both mechanisms are operative, the time exponent varies between 1/2 and 1 according to the relation

$$M_t/M_\infty = kt_n \qquad (1)$$

where k and n are system parameters, and M_t and M_∞ are the mass uptake values at time t and at equilibrium, respectively. From a least-square analysis of the log M_t/M_∞ vs. log t, the values of k and n were obtained for aldehydes and ketones and these are included in Tables II and III, respectively (Fig. 7). It is found that the values of n of all NR blends vary between 0.50 and 0.63, suggesting that their transport behavior is expected to be of near-Fickian type. However, it is observed that there is no systematic dependence of n on temperature but k increases systematically with temperature due to an increase in segmental motion with the increase in temperature.[6,7]

The sorption plots presented in Figures 1–6
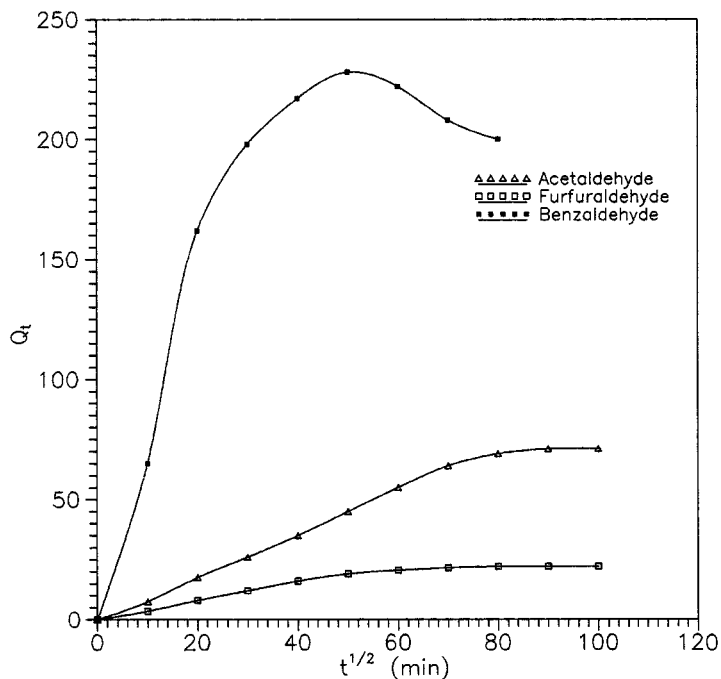
Figure 1 Percentage mass uptake Q_t vs. square root of time for NR/neoprene blend with different aldehyde penetrants.

appear to show linear relations in the beginning, suggesting the transport mechanism to be of a Fickian type. However, more complex effects seem to be operative at the root of the non-Fickian responses that manifest themselves as sigmoidal deviations from the linearity in the plots. An ex-
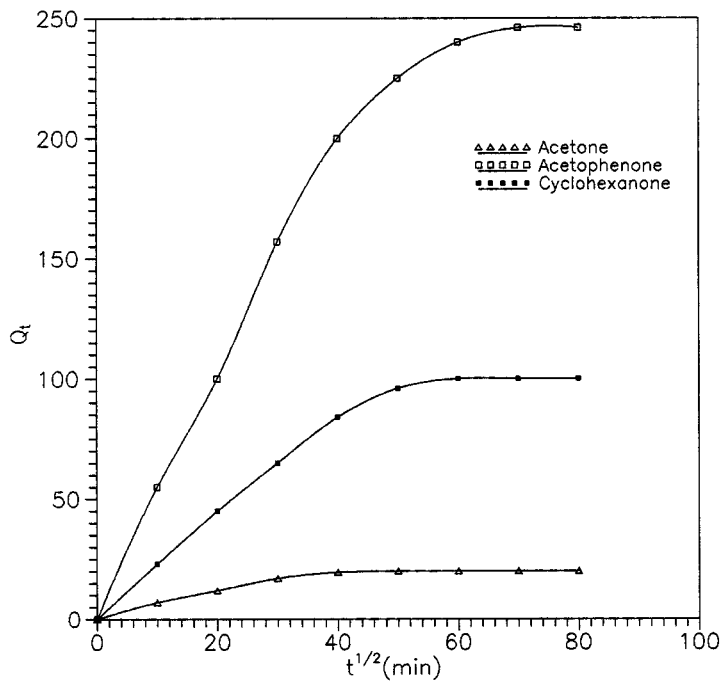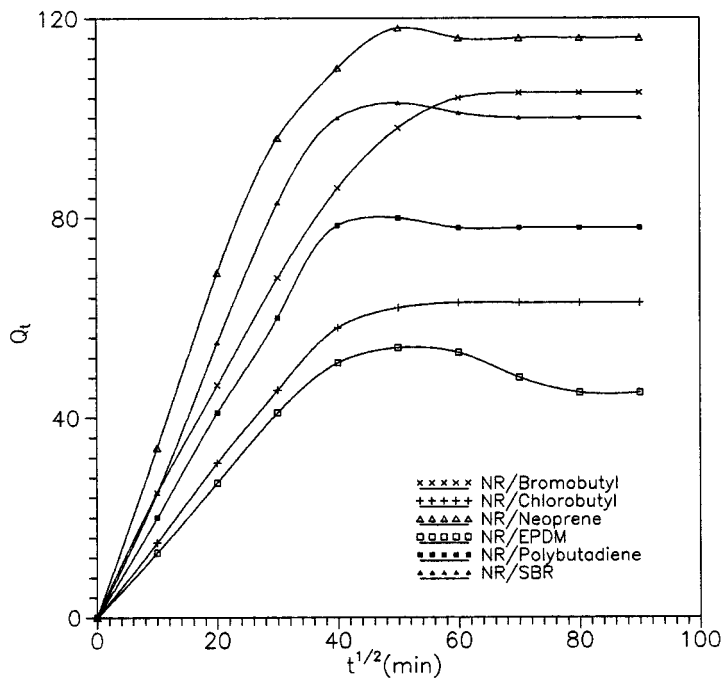
Figure 2 Percentage mass uptake Q_t vs. square root of time for NR/CIIR blend with different ketone penetrants at 40°C.
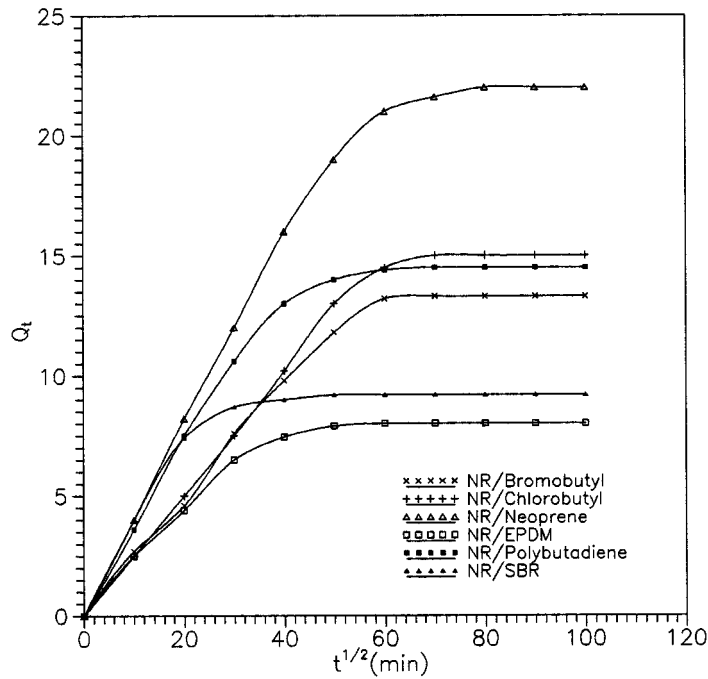
Figure 3   Percentage mass uptake Q_t vs. square root of time for different NR blends with furfuraldehyde penetrant at 40°C.

ample of such a non-Fickian response is shown in Figure 2 for NR/CIIR in furfural. When the solvent concentration is low and swelling is not important, the transport is found to be Fickian.[5] But at higher concentrations, however, swelling to relieve the mechanical stresses becomes important[5]
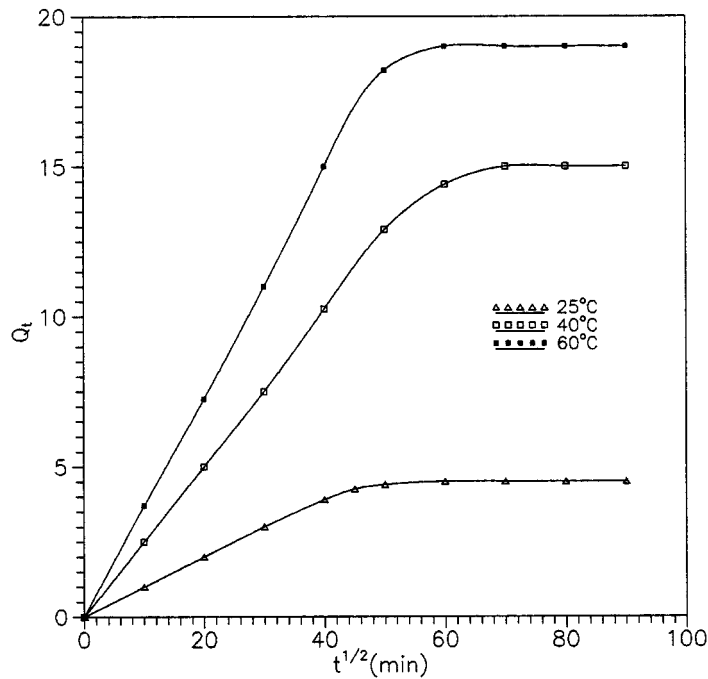
Figure 4   Percentage mass uptake Q_t vs. square root of time for different NR blends with cyclohexanone penetrant at 25°C.

Table II   Sorption Data n and k Values of NR Blends in Aldehydes at Different Temperatures

NR Blends	Temp (°C)	Benzaldehyde		Furfural		Acetaldehyde	
		n	$k \times 10^2$ (g/g min^n)	n	$k \times 10^2$ (g/g min^n)	n	$k \times 10^2$ (g/g min^n)
NR/BIIR	25	0.50	3.08	0.54	1.28	0.50	1.47
	40	0.50	3.88	0.54	1.59	0.50	3.14
	60	—	—	0.50	2.80	0.50	3.21
NR/CIIR	25	0.50	3.02	0.53	3.27	0.52	1.18
	40	0.50	3.24	0.50	1.23	0.50	1.62
	60	—	—	0.51	1.90	0.51	3.21
NR/neoprene	25	0.63	1.36	0.60	0.87	0.50	1.18
	40	0.50	7.20	0.50	1.80	0.50	1.62
	60	—	—	0.50	2.20	0.50	1.69
NR/EPDM	25	0.57	1.30	0.55	1.91	0.50	1.13
	40	0.50	3.84	0.50	3.69	0.50	1.51
	60	—	—	0.50	5.29	0.50	2.68
NR/polybutadiene	25	0.57	2.47	0.50	2.47	0.50	2.02
	40	0.55	3.34	0.50	3.02	0.50	2.38
	60	—	—	0.50	3.92	0.50	2.52
NR/SBR	25	0.52	2.11	0.50	3.02	0.50	4.60
	40	0.53	3.76	0.50	4.00	0.51	5.00
	60	—	—	0.50	4.50	0.50	5.20

Table III   Sorption Data n and k Values of NR Blends in Ketones at Different Temperatures

| NR Blends	Temp (°C)	Acetone		Cyclohexanone		Acetophenone	
		n	$k \times 10^2$ (g/g min^n)	n	$k \times 10^2$ (g/g min^n)	n	$k \times 10^2$ (g/g min^n)
NR/BIIR	25	0.52	6.39	0.52	2.03	0.50	1.83
	40	0.50	10.97	0.53	1.83	0.52	1.94
	60	0.50	12.00	0.50	3.21	0.54	2.52
NR/CIIR	25	0.50	6.08	0.51	2.07	0.54	1.09
	40	0.50	6.40	0.52	1.72	0.52	1.98
	60	0.50	6.65	0.54	1.86	0.50	3.27
NR/neoprene	25	0.50	3.34	0.50	3.50	0.51	1.56
	40	0.50	6.02	0.50	2.80	0.51	2.38
	60	0.51	2.73	0.51	4.40	0.52	3.84
NR/EPDM	25	0.53	3.69	0.52	2.42	0.58	1.33
	40	0.50	5.30	0.55	2.76	0.56	1.74
	60	0.53	5.30	0.50	2.84	0.50	2.02
NR/polybutadiene	25	0.54	2.60	0.50	2.65	0.52	1.83
	40	0.52	2.87	0.50	2.79	0.51	2.07
	60	0.50	9.07	0.50	3.24	0.51	2.13
NR/SBR	25	0.53	6.86	0.50	3.08	0.50	1.83
	40	0.53	3.60	0.50	3.02	0.50	2.45
	60	0.50	10.23	0.50	3.18	0.51	2.82

Figure 5 Percentage mass uptake Q_t vs. square root of time for NR/CIIR blend with furfuraldehyde penetrant at different temperatures.

so that the transport becomes non-Fickian. Here, the solvent front is sharp and moves at a constant velocity characteristic of the interplay between the establishment of the local swelling stress and the relaxation response of the elastomers to the stress. This phenomenon results in an initial linear uptake for a time sufficiently small to maintain a negligible concentration gradient in the swollen region behind the advancing front.[8-10]

As shown in Figures 2 and 4, NR/EPDM be-
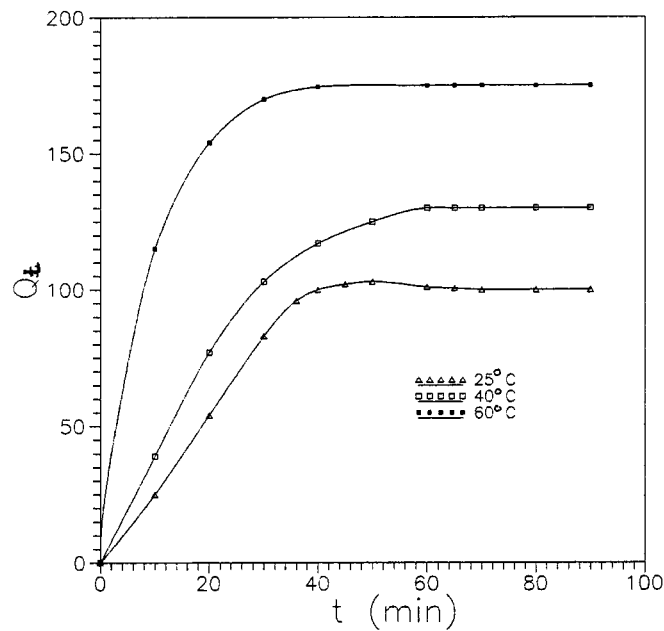
Figure 6 Percentage mass uptake Q_t vs. square root of time for NR/SBR with cyclohexanone penetrant at different temperatures.
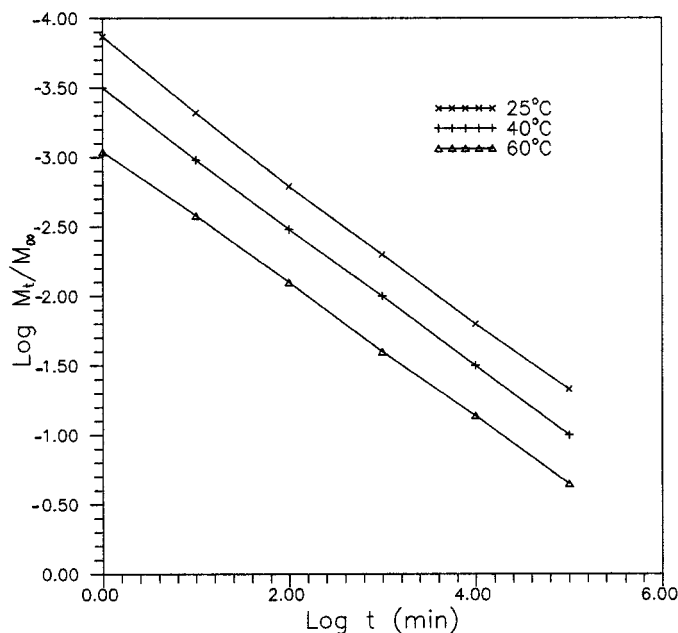
Table IV   Diffusion Coefficient [D], Sorption [S], and Permeation [P] Coefficient Values of NR Blends in Aldehydes at Different Temperatures

NR Blends	Temp (°C)	Benzaldehyde			Acetaldehyde			Furfural		
		$D \times 10^7$ (cm²/s)	$S \times 10^2$ (g/g)	$P \times 10^7$ (cm²/s)	$D \times 10^7$ (cm²/s)	$S \times 10^2$ (g/g)	$P \times 10^7$ (cm²/s)	$D \times 10^7$ (cm²/s)	$S \times 10^2$ (g/g)	$P \times 10^7$ (cm²/s)
NR/BIIR	25	0.86	93	0.799	0.34	20	0.069	0.49	12.2	0.060
	40	1.32	73	0.963	0.36	73	0.262	0.50	13.4	0.674
	60	—	—	—	0.45	105	0.472	0.52	24.0	0.125
NR/CIIR	25	1.22	93	1.134	0.54	14	0.075	0.68	4.5	0.030
	40	1.53	110	1.683	0.72	29	0.208	0.68	15.2	0.104
	60	—	—	—	0.84	65	0.054	0.75	18.8	0.014
NR/neoprene	25	1.14	176	2.000	0.27	14	0.037	0.39	15.2	0.074
	40	1.55	200	3.001	0.35	70	0.024	0.47	22.0	0.085
	60	—	—	—	0.43	171	0.735	0.96	34.0	0.326
NR/EPDM	25	0.42	98	0.411	0.24	11	0.026	0.84	4.6	0.038
	40	0.75	125	0.937	0.25	52	0.129	1.20	7.4	0.088
	60	—	—	—	0.28	116	0.224	2.18	11.5	0.250
NR/polybutadiene	25	1.02	112	1.142	0.29	16	0.046	0.28	64.5	0.012
	40	1.52	140	2.128	0.42	44	0.186	1.27	7.6	0.096
	60	—	—	—	0.51	94	0.481	1.63	20.0	0.032
NR/SBR	25	0.97	126	1.222	0.23	10	0.002	0.89	6.8	0.060
	40	2.02	112	2.026	2.52	18	0.093	2.38	9.1	0.216
	60	—	—	—	0.93	82	0.762	3.20	14.4	0.460

Table V Diffusion Coefficient [D], Sorption [S], and Permeation [P] Coefficient Values of NR Blends in Ketones at Different Temperatures

NR Blends	Temp (°C)	Acetone			Acetophenone			Cyclohexanone		
		$D \times 10^7$ (cm²/s)	$S \times 10^2$ (g/g)	$P \times 10^7$ (cm²/s)	$D \times 10^7$ (cm²/s)	$S \times 10^2$ (g/g)	$P \times 10^7$ (cm²/s)	$D \times 10^7$ (cm²/s)	$S \times 10^2$ (g/g)	$P \times 10^7$ (cm²/s)
NR/BIIR	25	2.88	8.3	0.239	0.58	265	1.325	0.65	48	0.032
	40	4.01	12.8	0.513	0.64	325	2.080	0.86	102	0.885
	60	5.42	25.0	1.355	1.51	600	9.060	0.97	223	2.174
NR/CIIR	25	3.76	10.0	0.376	0.40	210	0.855	0.82	63	0.513
	40	4.82	19.1	0.920	0.69	244	1.680	0.94	100	0.094
	60	5.55	100.0	5.550	1.03	375	3.862	2.70	116	4.320
NR/neoprene	25	0.98	20.0	0.196	0.43	330	1.419	1.12	110	1.232
	40	1.10	25.2	0.272	0.97	335	3.249	1.20	154	1.848
	60	2.60	135.0	3.510	0.43	510	7.293	2.37	256	5.931
NR/EPDM	25	2.79	9.0	0.251	0.46	150	0.750	0.76	45	0.342
	40	2.98	34.2	1.019	0.50	198	0.910	0.96	86	0.826
	60	3.40	80.0	2.072	0.79	405	3.199	0.97	120	1.164
NR/polybutadiene	25	1.18	15.5	0.182	0.26	186	0.489	0.84	78	0.655
	40	2.04	65.0	0.326	0.58	237	1.388	0.84	119	0.990
	60	9.62	32.5	3.126	0.26	550	5.180	1.19	170	2.020
NR/SBR	25	2.09	13.0	0.272	0.45	218	0.981	1.14	100	1.140
	40	3.20	97.5	3.120	0.85	240	2.040	1.24	130	1.612
	60	4.20	87.0	3.654	1.03	550	5.665	1.84	175	3.220

Figure 7 Log M_t/M_∞ vs. Log t for NR/SBR with cyclohexanone penetrant at different temperatures.

haves distinctly different, in that its swelling tendencies are slightly low when compared to other blends. The diffusion coefficient (D) and sorption (S); i.e., the maximum mass uptake obtained from plateau regions of the sorption curves for aldehydes and ketones, are given in Tables IV and V, respectively. From these tables, it is evident that the S values of aldehydes vary in the range 4.5–200 of the dry sample weight, whereas for ketones, they vary from 8.3 to 600 of the dry sample weight. Such relatively small values of S for NR/EPDM are attributed to a relatively tightly packed structure of EPDM, thereby exhibiting the toughness of the plastic and the elasticity of the gum elastomeric phase. This intrinsic property of EPDM may restrict the free movement of penetrant molecules and thus cause the low values of sorption. This distinguishing behavior has also been observed by others for EPDM with several solvents.[11,12] Another striking feature of the sorption data for all NR blends is that sorption increases with increase in the size of the ketones. Further, there is an increase in sorption values. However, this is not true in aldehydes. It is observed from Figures 2 and 4 that aldehydes with NR/BIIR and NR/neoprene blends show higher S values. Similarly, ketones with NR/BIIR, NR/CIIR, and NR/neoprene blends (Table V) also show higher values. This clearly suggests that for NR/BIIR, NR/CIIR, and NR/neoprene blends the

polar groups such as bromine and chlorine can interact with the carbonyl group of aldehydes or ketones, thereby increasing the sorption values.

The higher S values of 200×10^{-2} g/g for NR/neoprene in benzaldehyde at 40°C may be due to the presence of the chloride group on the neoprene chain segments which may increase its ability to sorb a polar molecule such as benzaldehyde. Similarly, higher values of 550×10^{-2} g/g for NR/SBR in acetophenone at 60°C may be due to the fact that actophenone, being an aromatic, is attracted by aromatic styrene of the SBR chain according to the principle "like absorbs like."

Regarding the effect of temperature on sorption, it is found that the sorption increases with an increase in temperature for all blends except NR/SBR in acetone. The dependence of the percentage mass uptake of NR/CIIR in furfural and NR/SBR in cyclohexanone on the square root of time at different temperatures are shown in Figures 5 and 6, respectively (see also Fig. 7). This effect follows the conventional wisdom that at higher temperatures an increase in the free volume occurs. The diffusion coefficient D can be calculated[13–18] as

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

where θ is the slope of the linear portion of the sorption curve (Figs. 1–6); h, the thickness of

Table VI   Activation Parameters (E_D [kJ/mol]; ΔH [kJ/mol]; ΔS [J/mol/K]) of NR Blends in Aldehydes and Ketones

NR Blends	Activation Parameters	Furfural	Acetaldehyde	Acetone	Cyclohexanone	Acetophenone
NR/BIIR	E_D	2.33	7.56	15.24	18.29	19.95
	H	19.14	38.29	24.20	32.00	20.00
	S	11.48	90.95	28.72	67.97	35.42
NR/CIIR	E_D	2.30	12.79	18.29	12.17	27.78
	H	35.10	35.74	35.00	23.00	20.00
	S	62.22	11.80	45.96	37.34	26.33
NR/neoprene	E_D	29.09	13.36	22.86	23.75	44.02
	H	25.52	46.00	22.00	22.00	20.00
	S	32.55	134.00	9.57	33.50	13.40
NR/EPDM	E_D	16.62	5.12	6.49	11.78	15.87
	H	25.52	54.00	42.00	27.00	25.00
	S	18.18	124.00	89.00	43.08	41.12
NR/polybutadiene	E_D	8.31	14.89	27.00	14.25	43.98
	H	−31.91	40.42	24.80	20.00	23.00
	S	−140.73	93.00	30.06	21.06	37.34
NR/SBR	E_D	8.31	19.00	19.40	15.87	22.56
	H	19.14	54.71	31.70	16.00	21.00
	S	5.74	86.17	59.36	11.48	31.59

the sample; and M_∞, the maximum mass uptake which has been estimated by the least-square procedure. However, an approximation was made here by considering the slight sigmoidal shape as a linear one.

The variation of the diffusion coefficient depends on the nature of the penetrant molecules besides the structural characteristics of the elastomers. The calculated values of the molecular volumes of the benzaldehyde, furfural, and acetaldehyde are found to be 168.8, 137.6, and 92.8 A^3, respectively. From Table IV, it is observed that the diffusion coefficients increased with the molecular volumes of the penetrants. However, no correlation could be established for S values.

The molecular volumes of the penetrants, acetone, cyclohexanone, and acetophenone are calculated to be 121.9, 172.1, and 193.7 A^3, respectively. From Table V, it is observed that the D values decreased, whereas the S values increased with increase in the molecular volumes of the penetrants.

The permeability coefficient, P, is calculated from the simple relation

$$P = DS \qquad (3)$$

The obtained P values of aldehydes and ketones are tabulated in Tables IV and V, respectively.

An interesting observation was made from the sorption curves in Figure 1 for the NR/neoprene blend with the benzaldehyde penetrant. A sudden overshoot is observed in the uptake values initially, followed by a decrease in sorption, and, finally, near attainment of equilibrium sorption. However, this effect is not prevalent in the case of furfural and acetaldehyde. A similar observation was made by Aminabhavi and Munnolli[19] in the case of elastomers with acetone. This effect was attributed by them as due to the molecular relaxations in the rubbery elastomer system when in contact with polar solvents. A similar observation was also made for NR/neoprene, NR/SBR, NR/
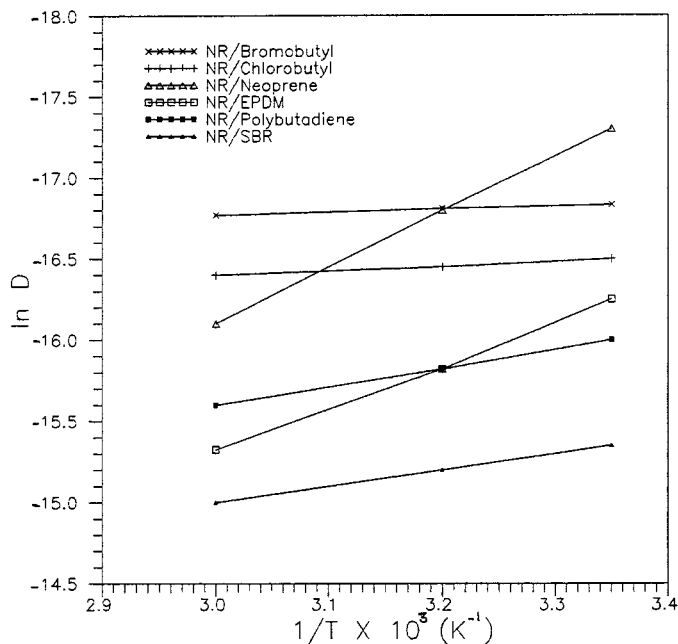
Figure 8 Arrhenius plots for diffusivity for NR blends in furfuraldehyde.

polybutadiene, and NR/EPDM with the cyclohexanone penetrant (Fig. 4).

Activation Parameters

The activation energy, E_D, for the process of diffusion is estimated from the Arrhenius relation:

$$D = D_0 \exp(-E_D/RT) \qquad (4)$$

where D_0 is the preexponential factor; R, the molar gas constant; and T, the absolute temperature. Similarly, the temperature-dependent equilibrium sorption constant, K_s, values may be fitted to the van't Hoff relation to estimate the enthalpy
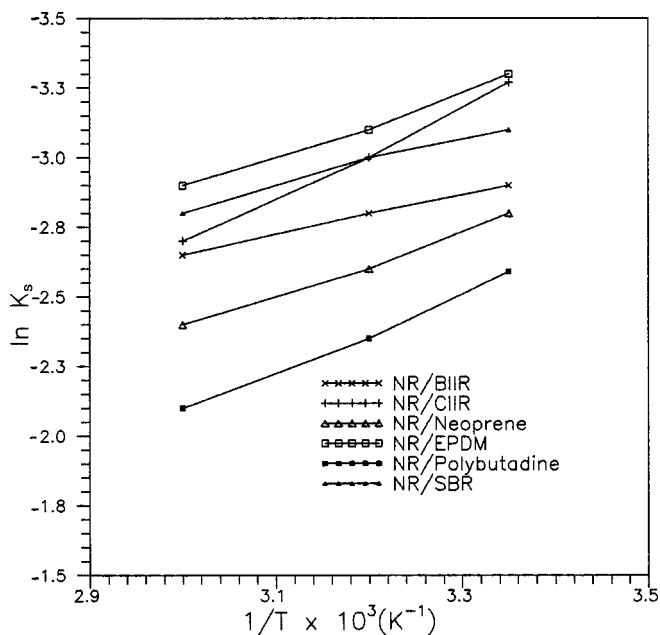

Figure 9 Van't Hoff plots of log K_s vs. $1/T$ for NR blends in furfuraldehyde.

ΔH and entropy ΔS of sorption. These values are summarized in Table VI and some Arrhenius and van't Hoff plots are given in Figures 8 and 9, respectively. The E_D values vary from about 2.33 to 44.02 kJ/mol for the penetrants under study. There is a systematic increase in the E_D value for both aldehydes and ketones. In aldehydes, E_D decreases in the order of acetaldehyde > furfural, and in ketones, acetophenone > cyclohexanone > acetone except in NR/polybutadiene. These results could be explained on the basis of Eyring's hole theory[20] according to which the energy required "to open a hole" in the polymer matrix to accommodate a diffusing molecule bears a direct relationship with E_D. Thus, the larger molecules in a related series will have larger E_D. In the majority of cases, the ΔH data are positive except for NR/polybutadiene in furfural which has shown a negative value. The ΔH values are negative for all the systems (except NR/polybutadiene with furfural), which suggests that the structure of the solvent molecules is retained even in the sorbed state.

CONCLUSIONS

The work described here summarizes the results of the sorption and transport of aldehydes and ketones into structurally different NR blends. The Fickian model was used to estimate the diffusion coefficients and transport data. It is observed that factors such as the solvent type and chemical nature of the elastomers seem to exert tremendous influence on the transport characteristics. The NR/EPDM blend exhibits high restrictivity toward aldehydes and ketones as evidenced by its low values of sorption and diffusion. All NR blends with acetone have shown higher diffusion coefficient values ranging from 2.60 to 9.62 $\times$ 10^{-7} cm^2/s. All NR blends showed a degradative reaction with benzaldehyde at higher temperatures. However, the other blends remain intact in the presence of all the penetrant molecules. From the temperature dependence of the transport coefficients, the

activation parameters were calculated and the values fall in the range of 2.33–44.02 kJ/mol.

REFERENCES

1. N. E. Cooke, *J. Polym. Sci. Part B Polym. Phys.,* **29,** 1633 (1991).
2. R. S. Khinnavar, T. M. Aminabhavi, R. H. Balundgi, S. S. Shukla, and A. Kutsac, *J. Hazard Mater.,* **28,** 281 (1991).
3. S. Sourirajan, *Ind. Eng. Chem. PDD,* **6,** 154 (1967).
4. B. K. Dutta and S. K. Sikdar, *AlChem. J.,* **37,** 581 (1991).
5. T. Alfrey, E. F. Gurnce, and W. J. Lloyd, *J. Polym. Sci. C-12,* 249 (1996).
6. U. S. Aithal and T. M. Aminabhavi, *J. Chem. Ed.,* **67,** 82 (1990).
7. U. S. Aithal, T. M. Aminabhavi, and P. E. Cassidy, *Polym. Prepr.,* **307**(1), 17 (1989).
8. W. J. Koros and M. W. Hellums, Eds., *Encyclopedia of Polymer Science and Engineering, 2nd ed.,* Wiley, New York, 1989, Suppl. Vol., p. 798.
9. M. Moadded and W. J. Koros, *Polym. Prepr.,* **32**(2), 287 (1991).
10. C. B. Lin, K. S. Lice, and S. Lee, *J. Polym. Sci. Part B Polym. Phys.,* **29,** 1457 (1991).
11. S. B. Harogoppad and T. M. Aminabhavi, *Indian J. Chem. A,* **30,** 209 (1991).
12. S. B. Harogoppad, T. M. Aminabhavi, and R. H. Balundgi, *Indian J. Chem. A,* **31,** 328 (1992).
13. S. B. Harogoppad and T. M. Aminabhavi, *Polym. Commun.,* **32,** 120 (1991).
14. S. B. Harogoppad and T. M. Aminabhavi, *J. Appl. Polym. Sci.,* **42**(8), 2329 (1991).
15. S. B. Harogoppad and T. M. Aminabhavi, *Macromolecules,* **24,** 2598 (1991).
16. S. B. Harogoppad and T. M. Aminabhavi, *Polymer,* **32,** 870 (1991).
17. S. B. Harogoppad, R. S. Khinnavar, and T. M. Aminabhavi, in *Polymer Science, Contemporary Themes,* S. Sivaram, Ed., Tata McGraw-Hill, New Delhi, 1991, Vol. II, p. 646.
18. T. M. Aminabhavi, S. B. Harogoppad, and R. S. Khinnavar, *Polym. Plast. Technol. Eng.,* **30**(5,6), 529 (1991).
19. T. M. Aminabhavi and R. S. Munnolli, *Polym. Int.,* **32,** 61 (1993).
20. B. J. Ewalinski, H. Eyring, and C. E. Reese, *J. Phys. Colloid Chem.,* **53,** 1426 (1949).