

Sorption and Diffusion of Aldehydes and Ketones Through Castor Oil-Based Interpenetrating Polymer Networks of PU–PS

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ABSTRACT: Sorption and diffusion of some aldehydes and ketones into interpenetrating polymer networks (IPNs) of polyurethane–polystyrene (PU–PS) have been investigated in the temperature interval of 25–60°C. Transport data were found to be affected by the nature of the interacting solvent molecule rather than its size. The diffusion coefficient of ketones range from 9.2×10^{-8} to 645×10^{-8} cm²/s and for aldehyde from 11.5×10^{-8} to 154.5×10^{-8} cm²/s. For all solvents, the polymer remained intact. From the temperature dependence of sorption data, the Arrhenius activation parameter and the thermodynamic parameter, such as entropy and enthalpy for the process of equilibrium sorption, have been estimated. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 2047–2055, 1998

Key words: interpenetrating polymer network; sorption; diffusion; aldehydes; ketones; PULPS membrane

INTRODUCTION

The sorption and diffusion of organic liquids into crosslinked rubbery network elastomer systems have been studied by several authors.^{1–4} 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. Extensive literature exists on a wide variety of polymer–solvent systems, which leads to an increased understanding about the molecular transport phenomenon into elastomeric systems. In this article, sorption and diffusion of some aldehydes and ketones into polyurethane–polystyrene (PU–PS) IPNs is discussed. Polyurethane (PU) and its IPNs are known to exhibit unique mechanical properties, primarily as a result of

two-phase morphology.¹ In view of the importance of PU as barrier materials in several engineering areas,^{2,3} it is important to know its transport characteristics with respect to common organic solvents.

This article reports the experimental sorption and diffusion of aldehydes and ketones for the IPNs of PU–PS. The sorption experiments are performed at 25, 40, and 60°C, and these results are used to estimate the Arrhenius parameter for the transport processes concerned. The results discussed in terms of the nature of polymer–solvent interactions. The present study highlights the discussion on the correlation of the thermodynamics quality of the solvent and its structure with the molecular transport properties of the liquid–polymer IPN system.

EXPERIMENTAL

Materials

Castor oil was obtained from local market (OH values –170; \bar{M}_w –930; and purity-98%); and meth-

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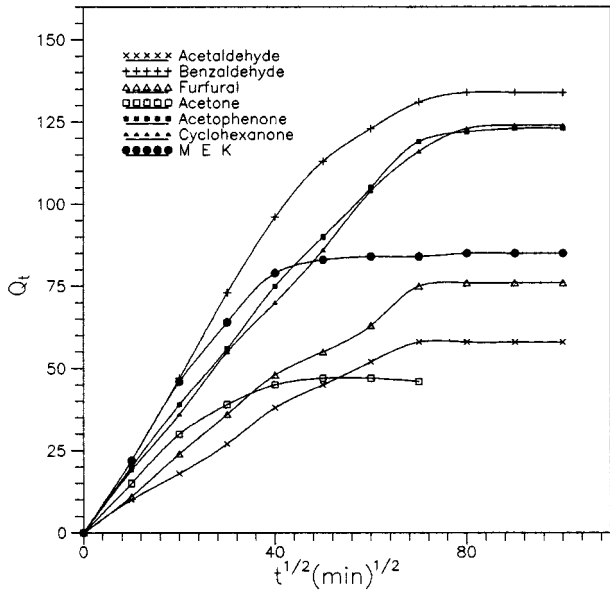


Figure 1 Percentage mass uptake Q_t versus square root of time for 60/40 IPNs with different aldehydes and ketones at 40°C.

ylene di-isocyanate (Fluka, Switzerland), benzoyl peroxide (Aldrich, USA), and styrene (Merck, Germany) were used to prepare IPNs. The AR-grade penetrants, such as acetaldehyde, benzaldehyde, furfural, cyclohexanone, acetone, acetophenone, and methyl ethyl ketone (MEK) were used after distillation. The IPNs of different molar ratios

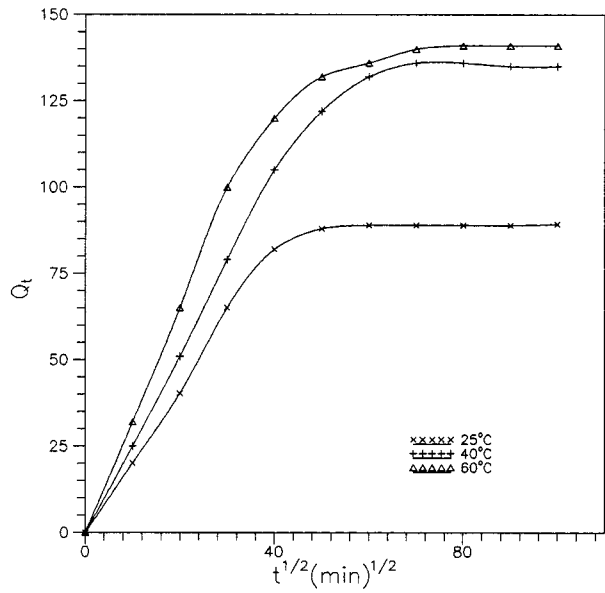


Figure 3 Percentage mass uptake Q_t versus the square root of time for 75/25 IPNs with benzaldehyde at different temperatures.

were prepared according to the reported procedure.^{5,6} The IPN sheets were cut into uniform size circular pieces (1.76 cm diameter) using a sharp edged steel die. The initial thickness of the specimens were made at several points and ranged from 0.694 to 0.800 cm (precision ± 0.001 cm). The cut IPN specimens were dried in a desiccator, in a con-

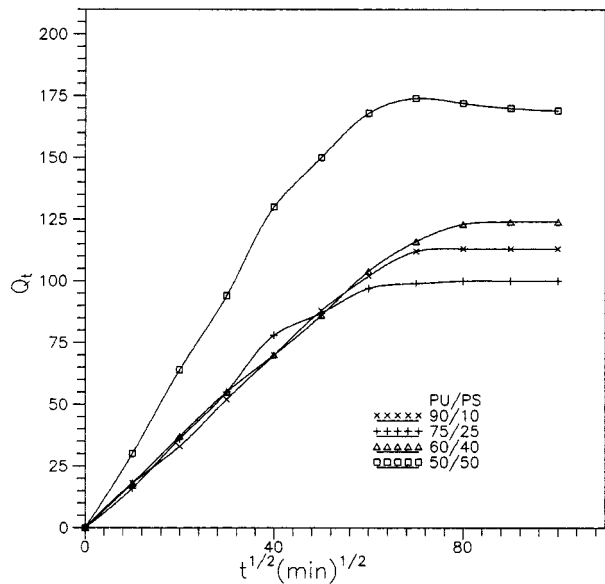


Figure 2 Percentage mass uptake Q_t versus the square root of time for all IPNs with acetophenone at 40°C.

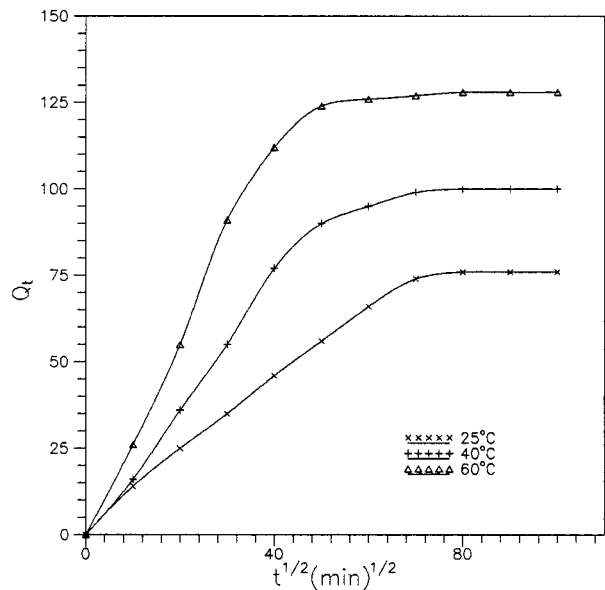


Figure 4 Percentage mass uptake Q_t versus the square root of time for 75/25 IPNs with acetophenone at different temperatures.

Table I Analysis of Sorption Data for IPN–Solvent Systems

Penetrants	Temperature (°C)	$n \pm 0.007$				$k \times 10^2 \pm 0.004$ (g/g min ⁿ)			
		90/10	75/25	60/40	50/50	90/10	75/25	60/40	50/50
Acetone	25	0.850	0.906	—	—	14.95	12.24	—	—
	40	0.500	0.538	—	—	13.53	22.76	—	—
	60	—	—	—	—	—	—	—	—
MEK	25	0.588	0.500	0.528	0.545	27.25	30.10	10.02	33.87
	40	0.500	—	0.502	0.550	28.64	—	20.18	28.93
	60	0.533	—	0.500	0.685	30.11	—	22.31	19.20
Cyclohexanone	25	0.500	0.532	0.501	0.602	18.26	16.50	14.59	13.80
	40	0.551	0.611	0.634	0.532	10.02	9.35	7.42	13.26
	60	0.521	0.601	0.500	0.500	13.53	12.49	21.87	38.60
Acetophenone	25	0.620	0.500	0.503	0.503	9.07	21.90	19.20	27.25
	40	0.585	0.750	0.512	0.601	11.08	8.98	11.64	13.53
	60	0.540	1.300	0.500	0.500	18.26	2.24	22.65	33.87
Acetaldehyde	25	0.509	0.583	0.720	0.525	12.31	15.72	7.50	14.37
	40	0.503	0.504	0.640	0.533	14.66	13.53	8.20	15.72
	60	0.506	0.500	0.500	0.500	17.90	27.80	18.26	25.92
Furfural	25	0.514	0.500	0.572	0.520	22.30	16.86	21.87	21.22
	40	0.501	0.501	0.512	0.503	39.85	15.10	12.24	9.25
	60	0.504	0.502	0.501	0.500	16.86	13.40	13.53	30.42
Benzaldehyde	25	0.566	0.517	0.900	—	14.23	14.95	9.53	53.25
	40	0.512	0.558	0.800	0.720	16.53	15.25	8.63	9.25
	60	0.501	0.504	0.500	—	19.80	14.08	26.18	44.90

trolled humidity atmosphere, for two days before sorption experiments. Dry weights of the cut samples were taken before immersion into the airtight, metal-capped test bottles containing the liquid. After immersion into the respective liquids, the bottles were placed in a thermostatically controlled oven ($\pm 0.5^\circ\text{C}$).

Sorption Experiments

The sorption and diffusion experiment was done by the immersion–weight gain method. The circularly cut specimens were immersed in airtight glass bottle containing respective penetrants and maintained at the desired temperature. Each specimen was removed, wiped off by filter paper, and weighed at regular intervals of time until a constant weight was obtained.

RESULTS AND DISCUSSION

Sorption results are interpreted in terms of the percent penetrant uptake, Q_t , versus the square root of time $t^{1/2}$. Some typical plots at 40°C for

60/40 PU–PS IPN are presented in Figure 1. With 60/40 IPN in acetone and MEK, the attainment of equilibrium was quicker than other pene-

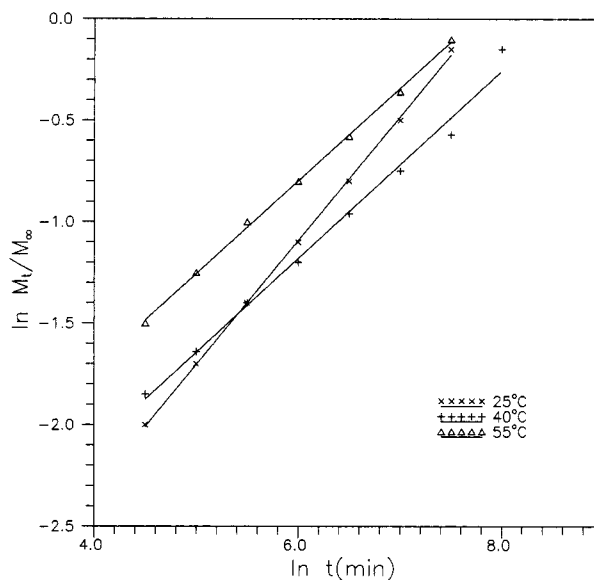


Figure 5 $\ln M_t/M_\infty$ versus $\ln t$ for 90/10 IPNs with acetophenone at different temperatures.

Table II Sorption (S) and Diffusion (D) Coefficients of PU/PS IPN–Solvent Systems

Penetrants	Temperature (°C)	S (mol %)				$D \times 10^7 \pm 0.004$ (cm ² /s)			
		90/10	75/25	60/40	50/50	90/10	75/25	60/40	50/50
Acetone	25	0.560	0.660	0.620	0.750	6.17	19.23	64.50	4.84
	40	0.510	0.500	0.460	0.600	8.05	14.43	19.75	8.84
	60	—	—	—	—	—	—	—	—
MEK	25	0.770	0.740	0.850	0.850	8.93	17.30	13.41	10.24
	40	0.720	0.880	1.230	0.980	7.51	20.10	15.25	10.74
	60	1.530	0.630	1.540	1.140	10.96	27.69	15.45	14.62
Cyclohexanone	25	1.130	0.750	1.400	0.980	1.05	3.14	8.06	2.06
	40	1.150	1.000	1.220	1.740	1.19	4.80	3.22	0.92
	60	1.080	1.250	1.580	2.060	1.79	7.25	12.90	4.70
Acetophenone	25	1.160	1.470	1.400	1.420	1.50	8.78	9.99	1.93
	40	1.150	0.840	1.220	2.040	1.58	6.21	4.16	1.30
	60	1.200	0.860	1.580	2.180	2.55	7.21	13.94	4.47
Acetaldehyde	25	0.410	0.250	0.600	0.940	2.25	8.28	8.33	0.90
	40	0.610	0.640	0.580	0.960	1.52	1.84	4.56	1.15
	60	0.120	0.350	0.220	0.230	1.45	11.96	6.86	3.76
Furfural	25	0.560	0.610	0.800	0.960	2.09	4.64	11.01	1.26
	40	1.410	0.830	0.750	1.460	7.12	4.78	4.26	1.22
	60	0.820	0.850	0.910	0.820	2.35	3.70	4.79	1.68
Benzaldehyde	25	1.120	0.890	1.550	1.240	2.20	7.74	10.31	2.15
	40	1.240	1.350	1.340	1.900	1.38	4.84	5.69	1.98
	60	1.210	1.400	1.600	2.040	3.09	7.36	15.45	6.90

trants. This may be due to the lower molecular volume of the respective penetrants. Sorption plots of IPNs of all the composition are presented in Figure 2. They have reached equilibrium almost at the same time.

The sorption plots of 75/25 IPNs of PU–PS system with benzaldehyde and acetophenone were shown in Figures 3 and 4, respectively, at different temperatures. These plots shows the linearity in the beginning, suggesting the transport mechanism is to be of the Fickian type. However, more complex effects seem to be operative at the root non-Fickian responses that manifest themselves as sigmoidal deviations from the linearity in the plots. Molecular transport of organic compounds into elastomers are not completely understood. Several theories⁴ have been advanced; yet, in the majority of studies, the results have been satisfactorily discussed through phenomenological approaches. In order to investigate the type of diffusion mechanism, the sorption data of all the penetrant polymer system have been fitted to the following relation:

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

where M_t and M_∞ represents their mass uptake at time t and equilibrium, respectively, and n and k are system parameters in which n tells some-

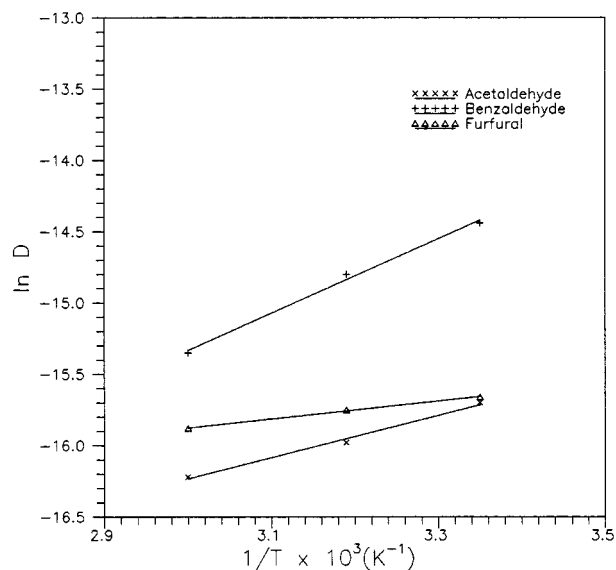


Figure 6 Arrhenius plots ($\ln D$ versus $1/T \times 10^3$) of diffusivity for 50/50 IPN with aldehydes.

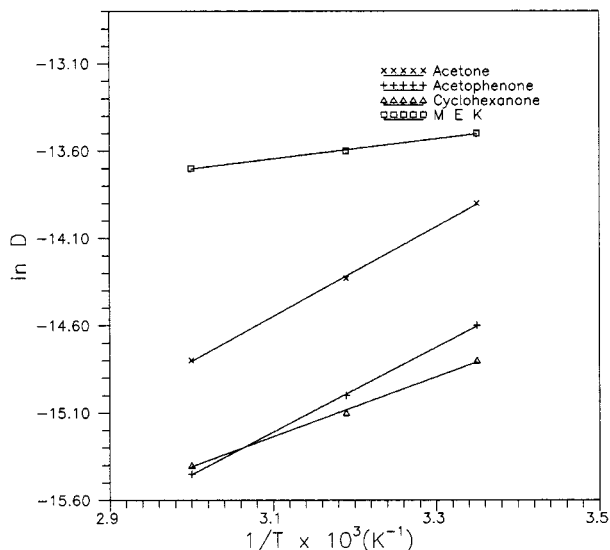


Figure 7 Arrhenius plots ($\ln D$ versus $1/T \times 10^3$) of diffusivity for 50/50 IPN with ketones.

thing about type of transport mechanism. A value of $n = 0.5$ represents the Fickian mechanism, and $n = 1$ indicates the non-Fickian transport. The

constant k depends on the structural characteristics of the polymer network in addition to its interactions with the solvent. From the least-square analysis of the $\log M_t/M_\infty$ data versus $\log t$, the values of n and k have been obtained, and these are included in the Table I. Typical plots for 90/10 IPN in acetophenone are presented in Figure 5. The average uncertainty in the estimation of n is around ± 0.007 . It was found that for 75/25 and 60/40 IPNs, and for penetrants, expect for acetone and benzaldehyde, the n values varied from 0.50 to 0.72, suggesting their transport behaviour to be that expected of the near-Fickian type. However, the same IPNs in acetone and benzaldehyde exhibit n values between 0.50 and 0.906, a process nearing the non-Fickian mechanism but deviating somewhat from the Fickian process. The n values do not show any systematic variation with temperature but, in the majority of cases, the k value increases (Table I) with temperature, suggesting an increase in segmental motion with the raise in temperature. An interesting observation can be made from the sorption curves given in Figures 3 and 4 with 75/25 IPNs with benzaldehyde and

Table III Equilibrium Sorption Constant (K_s) and Permeation Coefficient (P) of PU/PS IPN-Solvent Systems

Penetrants	Temperature (°C)	$K \pm 0.01$ (m mol/g)				$P \times 10^7$ (cm ² /s)			
		90/10	75/25	60/40	50/50	90/10	75/25	60/40	50/50
Acetone	25	9.63	11.36	10.60	12.91	3.46	12.69	39.98	3.63
	40	8.78	8.60	7.91	10.33	4.11	7.22	9.07	5.31
	60	—	—	—	—	—	—	—	—
MEK	25	10.68	10.26	20.40	11.78	6.87	12.8	19.72	8.70
	40	10.01	12.20	11.65	13.60	5.41	17.69	12.8	10.53
	60	22.11	8.74	11.92	15.81	16.76	17.44	13.11	16.60
Cyclohexanone	25	11.51	7.64	8.66	10.00	1.18	2.35	6.85	2.03
	40	11.71	10.18	12.53	17.70	1.37	4.8	3.96	1.61
	60	11.00	12.73	15.70	20.98	1.93	9.06	19.86	9.68
Acetophenone	25	9.65	14.40	11.65	11.81	1.74	15.19	14.00	2.74
	40	9.57	10.65	10.15	16.98	1.82	7.95	5.07	2.65
	60	9.99	12.73	13.15	18.14	3.06	7.28	22.02	9.78
Acetaldehyde	25	9.30	19.3	13.6	21.36	0.92	2.07	4.99	0.85
	40	13.8	14.54	13.18	21.81	0.92	1.17	2.65	1.11
	60	2.70	7.95	5.00	5.23	0.17	4.18	1.51	0.86
Furfural	25	5.82	6.34	8.84	9.67	1.17	2.83	8.81	1.17
	40	14.68	8.64	7.80	10.92	10.04	3.97	3.20	1.28
	60	8.53	8.85	9.47	12.28	1.93	3.14	4.36	1.98
Benzaldehyde	25	10.55	8.38	14.6	11.68	2.46	6.89	15.98	2.67
	40	11.68	12.72	12.63	17.90	2.85	6.53	7.62	3.76
	60	11.40	13.20	15.06	19.22	3.74	3.14	24.72	14.07

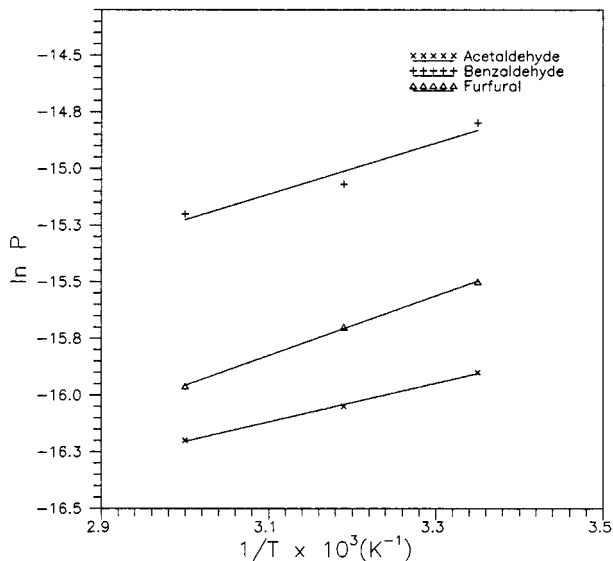


Figure 8 $\ln P$ versus $1/T$ of permeability for 90/10 IPN with aldehydes.

acetophenone penetrants: a sudden overshoot is observed in the uptake values, followed by a decrease in sorption, and, finally, the attainment of equilibrium. However, this effect is not prevalent in the case of acetone and MEK for 60/40 and 50/50 IPNs. This effect may be due to the molecular relaxation in the rubbery phase of IPNs system when they are in contact with polar solvents.

A striking feature that can be observed from Table II is the sorption (S) values for both aldehydes and ketones increases with an increase in molecular volume in their respective series. The molecular volume of different penetrants are calculated using the following relation:

$$\text{Molecular volume} = \frac{\text{Molecular weight}}{\text{density}} \times \text{Avagadro number} \quad (2)$$

Thus, the sorption data are found to vary in according to the sequence of acetophenone > cyclohexanone > MEK > acetone in the ketone series and benzaldehyde > furfural > acetaldehyde in the aldehyde series. The 50/50 IPN in benzaldehyde has the highest sorption among the system studied in this work and it varies from 1.24 to 2.04 g/g in the range of temperature investigated.

Before 50% completion of equilibrium sorption, the diffusion coefficient can be calculated as follows:⁷⁻¹⁵

$$D = \pi [h\theta/4M_\infty]^2 \quad (3)$$

where θ and h are initial slopes and thickness of the specimen, and M_∞ is the mass uptake at equilibrium. The D values for each IPN–penetrant system are included in Table II. A triplicate evaluation of D from sorption curves gave us D values with an error of ± 0.003 units at 25°C, ± 0.004 units at 40°C, and ± 0.005 units at 60°C for all IPN–penetrant systems. The variation of D depends on the nature of the penetrant molecules in addition to the composition of the PU–PS and morphology of IPNs to some extent. The variation in D values are shown in Figures 6 and 7. The D values do not show any systematic trend with the size of penetrants. These values range from 9.2×10^{-8} to 645×10^{-8} cm²/s for ketones and 11.5×10^{-8} to 154.5×10^{-8} cm²/s for aldehydes.

The permeability coefficients P are calculated by the following relation:⁷

$$P = D \times S \quad (4)$$

The P values are reported in Table III. Variation of P values with respect to temperature for different penetrants are shown in Figures 8 and 9. An interesting observation has been made from sorption curves in Figure 1 for 60/40 PU–PS IPN with penetrant benzaldehyde. 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 acetal-

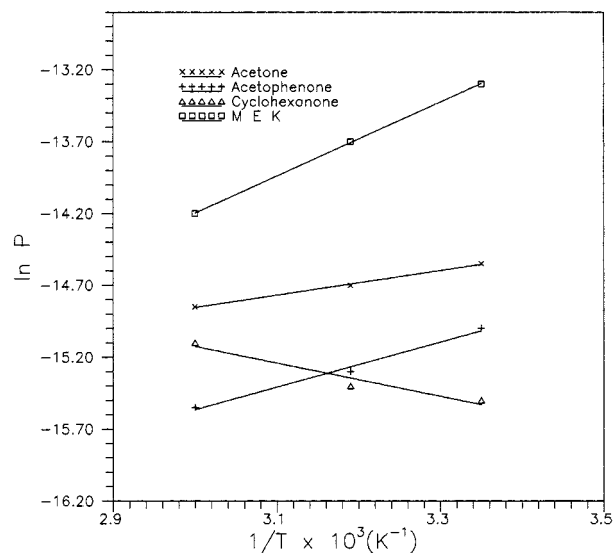


Figure 9 $\ln P$ versus $1/T$ of permeability for 90/10 IPN with ketones.

Table IV Activation Energy for Diffusion (E_D kJ/mol), Permeation (E_P kJ/mol), Enthalpy of Sorption (ΔH kJ/mol \pm 4 J/mol), and Entropy of Sorption (ΔS J/mol K \pm 1) for PU/PS IPN–Ketone Solvent Systems

Penetrant	Parameter	PU–PS IPN Compositions			
		90/10	75/25	60/40	50/50
Acetone	E_D	16.63	16.60	27.60	22.17
	E_P	11.08	24.94	—	9.50
	ΔS	–6.90	–9.98	–11.22	–10.14
	ΔH	5.00	6.17	16.07	12.19
MEK	E_D	16.62	9.50	10.70	15.44
	E_P	21.38	9.53	21.40	15.44
	ΔS	–3.82	–5.82	–2.50	2.00
	ΔH	3.88	3.80	12.35	17.13
Cyclohexanone	E_D	10.71	32.06	36.02	23.75
	E_P	10.70	30.90	23.75	4.76
	ΔS	—	3.16	5.74	6.81
	ΔH	2.38	12.11	14.25	7.48
Acetophenone	E_D	11.87	17.82	8.32	26.13
	E_P	14.25	19.00	10.69	30.00
	ΔS	1.49	–1.08	1.16	7.48
	ΔH	0.71	12.82	1.66	9.98

dehyde.¹⁶ This effect is due to the molecular relaxation in the rubbery elastomer system. When in contact with polar solvent, a similar observation has been made for other IPNs with cyclohexanone and acetophenone penetrants.

Thermodynamic and Activation Parameters

The activation energy for diffusion (E_D) and permeation (E_P) are estimated from the Arrhenius

relation. Attempts have also been made to calculate the thermodynamic equilibrium constant K_s (Table IV) by considering that the equilibrium process is occurring in the liquid phase at constant temperature and pressure⁵ thus,

$$K_s = \frac{\text{the number of moles of penetrant sorbed}}{\text{polymer unit mass}} \quad (4)$$

The temperature dependence of K_s values are

Table V Activation Energy for Diffusion (E_D kJ/mol), Permeation (E_P kJ/mol), Enthalpy of Sorption (ΔH kJ/mol), and Entropy of Sorption (ΔS J/mol K) for PU/PS IPN–Aldehyde Solvent Systems

Penetrant	Parameter	PU/PS IPN Compositions			
		90/10	75/25	60/40	50/50
Acetaldehyde	E_D	11.89	7.13	28.50	3.56
	E_P	38.00	16.63	28.50	3.56
	ΔS	2.80	–7.48	–4.90	–1.54
	ΔH	21.06	0.95	0.24	2.14
Furfural	E_D	7.13	2.38	16.62	11.87
	E_P	13.06	19.40	15.45	11.88
	ΔS	–6.65	–4.98	–3.24	11.91
	ΔH	7.60	8.07	3.20	5.46
Benzaldehyde	E_D	10.69	16.63	41.57	16.62
	E_P	9.50	9.50	7.13	39.20
	ΔS	–2.48	3.24	2.50	6.40
	ΔH	7.60	5.22	7.76	11.88

used to calculate enthalpy (ΔH) and entropy (ΔS) of sorption from van't Hoff's relation. The calculated values of these data are given in Tables IV and V. The average estimated error in ΔH is about ± 4 J mol, whereas for ΔS , it is about ± 1 J mol $^{-1}$ K $^{-1}$. Some representative Arrhenius and van't Hoff's plots are presented in Figures 10 and 11.

For different composition of PU-PS IPNs, ΔS vary from -7.48 to 11.91 J mol $^{-1}$ K $^{-1}$, increasing progressively with increasing PS content. ΔH_0 for benzaldehyde is slightly higher than acetaldehyde and furfural. Whereas in the case of ketones, ΔS_0 for acetophenone is higher than the remaining in the 50/50 IPN. More or less, almost the same trend was observed, except in one or two penetrants or other IPNs. The ΔH_0 values are positive, but no systematic variation of these values was observed correspondingly with different penetrants with different IPNs.

CONCLUSIONS

The work described here summarizes the results of sorption and transport of aldehyde and ketone into different composition of IPNs. It was observed that for factors such as the solvent type and morphology, the chemical nature of the IPNs seems to exert tremendous influence on the transport characteristics. 60/40 IPN exhibits a high

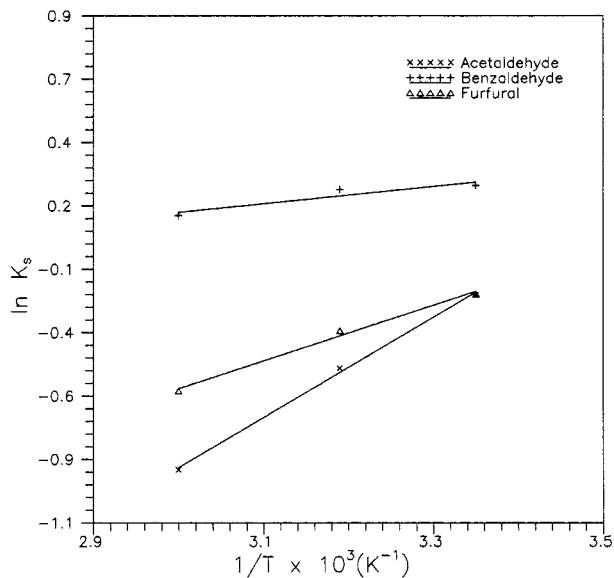


Figure 10 van't Hoff plots of $\ln K_s$ versus $1/T$ for 90/10 IPN with aldehydes.

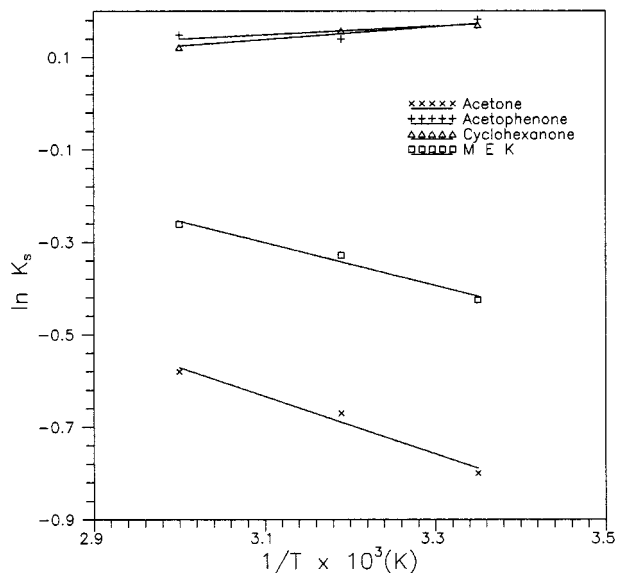


Figure 11 van't Hoff plots of $\ln K_s$ versus $1/T$ for 90/10 IPN with ketones.

resistivity towards aldehydes and ketone as evidenced by its low values of sorption, diffusion, and permeation. In all these studies, it has been pointed out that the rate of solvent transport within polymer materials depends upon the nature of the functional groups. Structural characteristics, chain flexibility, and segment packing density of the polymer are also important factors that affect the rate of mass transfer, and it was also observed that the diffusion mechanism followed the Fickian trend and that the kinetics of sorption was of the first order.

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