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Transport of aromatic hydrocarbons through poly(ethylene-co-vinyl acetate) membranes

S. Anil Kumar and Sabu Thomas*
School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills PO, Kottayam-686 560, Kerala, India

and M. G. Kumaran
Rubber Research Institute of India, Kottayam-686 009, Kerala, India
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Solvent transport of aromatic hydrocarbons through both crosslinked and uncrosslinked poly(ethylene-co-vinyl acetate) (EVA) membranes has been studied using sorption gravimetric analysis. EVA was crosslinked by using dicumyl peroxide (DCP). Diffusion through membranes containing different loading of DCP was also carried out to follow the effect of crosslinking density on diffusion. It was found that as the extent of crosslinking increases the equilibrium uptake decreases. The dependence of transport process on the size of the penetrant and temperature was also investigated. Arrhenius activation parameters for the process of diffusion, sorption and permeation have been estimated. Also, thermodynamic quantities like enthalpy, entropy, and free energy change have been calculated. The molecular mass between crosslinks of the network polymer were calculated using Flory Rehner theory. Both first order and second order kinetics models were used to investigate the transport kinetics. A correlation between theoretical predictions and experimental results was also done. The transport phenomenon was found to follow the anomalous mode at 28°C and it approaches non-Fickian at higher temperatures.

(Keywords: ethylene-co-vinyl acetate; diffusion; transport; swelling)

INTRODUCTION

The wide range applications of polymers as barrier materials have created a great interest in the molecular transport of liquids through polymers. The use of polymer as barrier layers, cable coatings, food packagings, encapsulation of electronic circuits[1], etc. is extremely widespread. Nowadays selective permeable polymer materials are extensively used in the field of reverse osmosis[2,3], pervaporation separation[4], etc. Successful application of polymers in these fields depends very much on their response to liquids. The diffusion process is also important because the permeating molecule can be used as a molecular probe to determine the polymer morphology.

The polymer–solvent interaction has been extensively studied and reviewed by many researchers[5–10]. Molecular transport in rubbery polymers can be generally explained by Fick's law of diffusion. However deviations from the Fickian behaviour are also reported[11]. Rate of diffusion through a polymer depends on the polymer structure, type of crosslinking, crosslinking density, size of the penetrants, temperature, etc. Recently Harogoppad and Aminabhavi[12] investigated the transport of organic liquids through a series of polymeric membranes and found that swelling depends on the polymer structure. Barrer and coworkers[13] followed the effect of crosslinking density on diffusion. The effect of penetrant size on diffusion was studied by different researchers[14] and it was found that equilibrium sorption of the sorbents decreases with the increasing penetrant molecular size. Aminabhavi *et al.*[15] examined the molecular transport properties of santoprene rubber in the presence of aliphatic hydrocarbons. According to them, for all liquids, equilibrium uptake was influenced by penetrant size, shape, polymer morphology and temperature. Previous research findings from our research group[16–19] include the study of transport and sorption of various organic liquids through a variety of polymers which include natural rubber, styrene–butadiene rubber, epoxidized natural rubber and nitrile rubber.

EVA is a random copolymer of ethylene and vinyl acetate which finds many applications. A wide range of physical properties can be obtained by adjusting the copolymer composition. The polymer is extensively used in many engineering and industrial areas because of its toughness, chemical resistance, intrinsic flexibility, excellent processability, etc. The copolymer has been used in many biomedical applications due to its chemical stability, biocompatibility and biological inertness. Earlier Thomas and coworkers[20] have shown that the EVA membranes can be successfully used for pervaporation separation of liquid mixtures. The solubility of EVA in aromatic hydrocarbons is minimal at room temperature.

The principal objective of the present study is to investigate the effect of peroxide vulcanization on the sorption and the transport of aromatic hydrocarbons

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* To whom correspondence should be addressed

through EVA. Diffusion experiments were monitored by the weight gain analysis of the polymer samples. The transport characteristics of the crosslinked EVA was studied in the temperature interval of 28–70°C. However, for the uncrosslinked samples the studies were carried out only at room temperature. Transport through EVA membranes with different loading of DCP was also carried out to study the effect of crosslinking density. The sorption, diffusion, permeation coefficients and the temperature dependence of diffusion have been estimated. Both first order and second order kinetics have been used to analyse the transport process. Finally, experimental results of diffusion were compared with theoretical predictions.

Table 1 Details of the material used

Material	Properties		Source
Poly(ethylene-co-vinyl acetate) Pilene 1802	Melt flow index (g/10 min)	2.000	PIL, Madras
	Density (g cc^{-1})	0.937	
	Vicat softening point (°C)	59.000	
	Vinyl acetate (wt%)	18.000	
	Intrinsic viscosity (dl g^{-1})	0.170	

Table 2 Composition of the mixes

Amount of polymer (g)	Amount of DCP (g)	No. of moles of DCP	Representation of samples
100	0	0	D_0
100	1	0.0015	D_1
100	2	0.0030	D_2
100	4	0.0060	D_4
100	6	0.0090	D_6
100	8	0.0120	D_8

EXPERIMENTAL

Materials

Poly(ethylene-co-vinyl acetate), EVA (Pilene, 1802), used was supplied by Polyolefin Industries Limited, Madras, India. The basic characteristics of the copolymer are given in *Table 1*. The crosslinking agent used was dicumyl peroxide (DCP) (40% activated). The solvents benzene, toluene and xylene were of reagent grade (99% pure) and were distilled three times before use to ensure purity. All other chemicals were of reagent grade.

Sample preparation

Crosslinked and uncrosslinked poly(ethylene-co-vinyl acetate) membranes were prepared. To prepare uncrosslinked samples, the EVA granules were sheeted out in a two roll mixing mill having a friction ratio 1/1.4. The sheeted out stock was compression moulded in a hydraulic press at 170°C and at a pressure of 25 tonnes to obtain uncrosslinked membrane samples.

EVA was vulcanized by peroxide technique using dicumyl peroxide. The formulation of the mixes are given in *Table 2*. The DCP modified samples are represented as *D*. Samples with different loading of DCP was prepared. The mixing was done in a two roll mixing mill as before. The cure characteristics of the samples were studied in a Goettfert rheometer. The rheographs of the mixes are given in *Figure 1*. The samples containing DCP were cured up to their optimum cure times (t_{90}) at 170°C in a hydraulic press under a pressure of 25 tonnes.

Diffusion experiments

The EVA samples were cut circularly (diameter 1.96 cm) by means of a sharp-edged steel die. The thicknesses of the samples were measured at several points using a micrometer screw gauge having an accuracy of 0.001 cm and average value was taken as

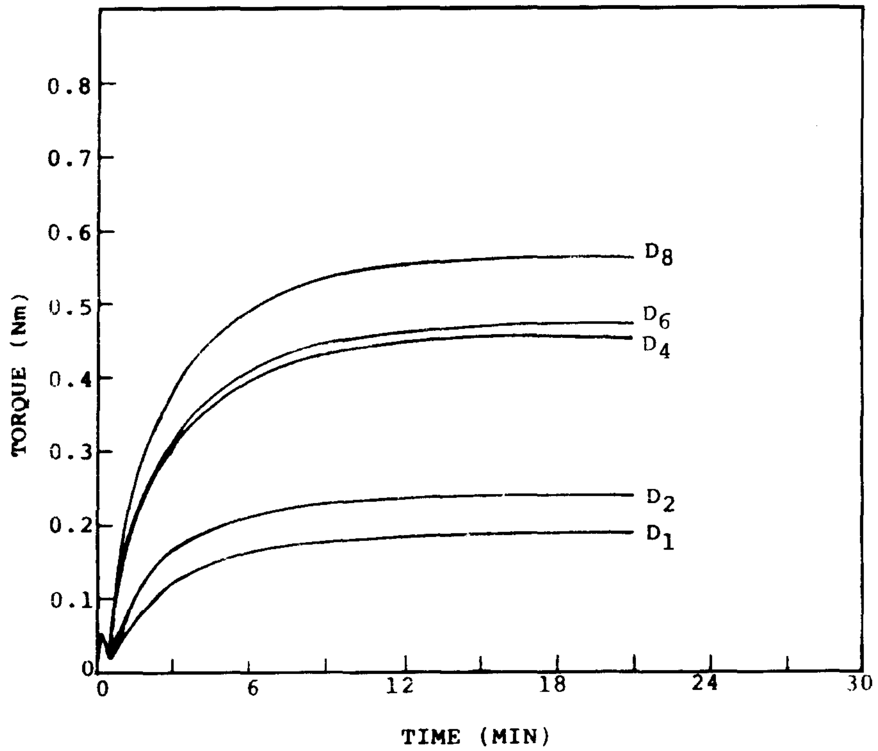

Figure 1 Rheographs of the mixes

the thickness. The circularly cut samples were soaked in about 20 ml of the solvent taken in test bottles which were kept at constant temperature in a thermostatically controlled oven. The samples were removed at regular intervals and then weighed after wiping the adhering solvent with a tissue paper. The samples were immediately replaced into the test bottles. Since removal of samples from the test bottles may generate error, time for each weighting was kept to a minimum of 30 s in order to minimize the error[16]. The process of weighing was continued until equilibrium swelling was attained.

The amount of solvent taken by the polymer was expressed as moles of solvent sorbed by 100 g of the polymer.

RESULTS AND DISCUSSION

Effect of crosslinks on diffusion

The diffusion curves of uncrosslinked poly(ethylene-co-vinyl acetate) (EVA) and DCP crosslinked EVA (D) expressed as mol% uptake, Q_t, of the liquid vs. square root of time, $t^{1/2}$, were plotted and given in *Figure 2*. The solvent used was benzene and the experiment was conducted at 28°C. The uncrosslinked EVA shows a lower solvent uptake (Q_t, mol%) whereas for D_1 samples the mol% uptake is higher. Similar trends are also observed with the other two solvents.

The low solvent uptake for the uncrosslinked poly(ethylene-co-vinyl acetate) is due to the crystalline nature of the polymer. The long range order generates a compact structure and hence a lower porosity. The porosity is increased by the presence of moderate amounts of DCP because these molecules introduce some disorder by forming C–C networks. This is illustrated schematically in *Figure 3*. X-ray diffraction studies of the uncrosslinked and crosslinked EVA support the above data and are given in *Figure 4*. Crystallinity is substantially reduced in the crosslinked sample.

For the crosslinked samples the solvent uptake behaviour varies in the order $D_1 > D_2 > D_4 > D_6 > D_8$. The Q_∞ values are given in *Table 3*. When the amount of DCP used for crosslinking is increased the extent of crosslinking also goes up. When the amount of DCP becomes too large, the polymer chains become very rigid due to crosslinking and this prevents the diffusion of the solvent molecules into the network. In fact, the decrease in crystallinity is offset by the increase in the crosslink density.

Effect of the penetrant size

There is a systematic trend on the sorption behaviour of liquids of different molecular size. With an increasing size of solvent molecule there is a decrease in the solvent uptake. The sorption curves of D_1 sample in three different aromatic hydrocarbons are presented in *Figure 5*. It is observed that among the solvents used, benzene uptake is maximum while xylene uptake is minimum and toluene uptake is intermediate. The decrease in Q_t mol% uptake with increase in penetrant size might be due to the greater activation energy required for activating the sorption process. The values of Q_∞ decrease with increase in molecular weight of the solvents. Similar trends were also observed for other systems. The Q_∞ values are given in *Table 3*.

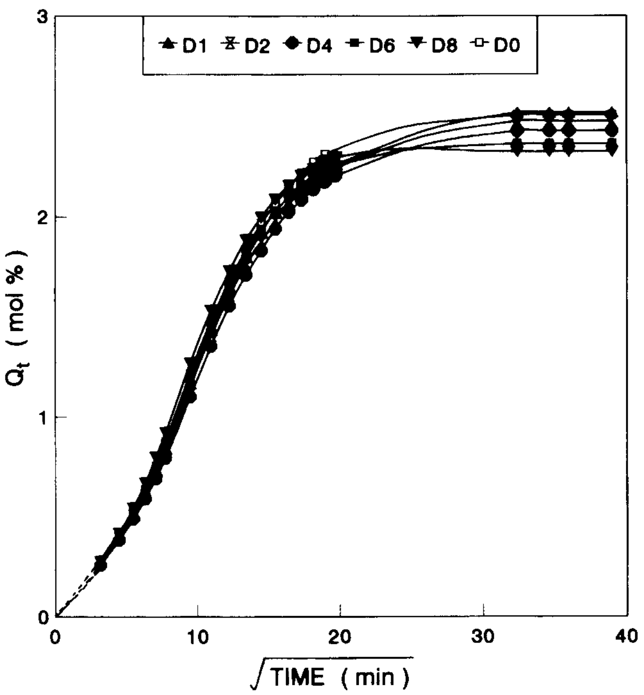

Figure 2 Mole per cent benzene uptake of uncrosslinked and crosslinked EVA samples at 28°C

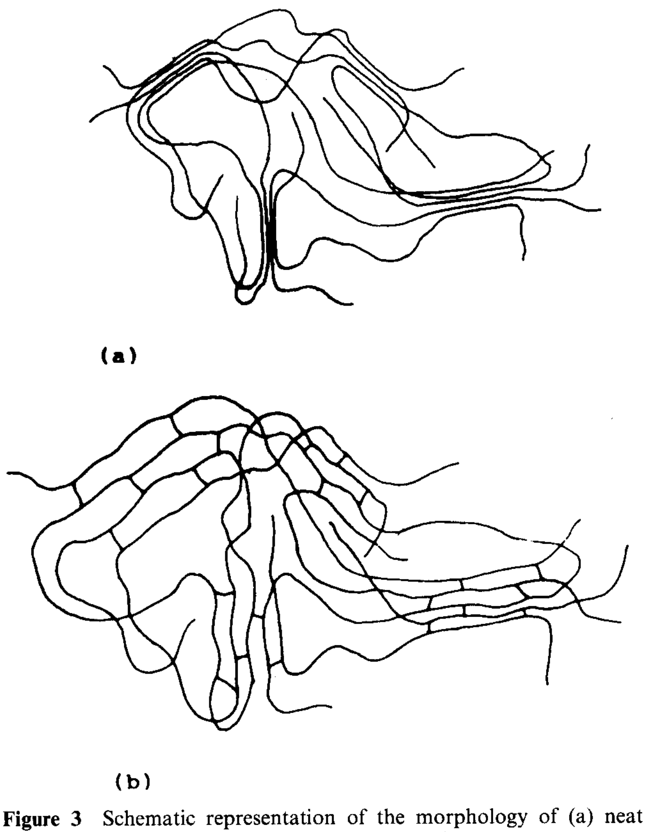

Figure 3 Schematic representation of the morphology of (a) neat (unmodified) and (b) crosslinked (modified) EVA

Sorption behaviour

The mechanism of the penetrant transport into a polymer has been analysed in terms of the empirical relation[12,21,22]

$$\log Q_t/Q_\infty = \log k + n \log t \tag{1}$$

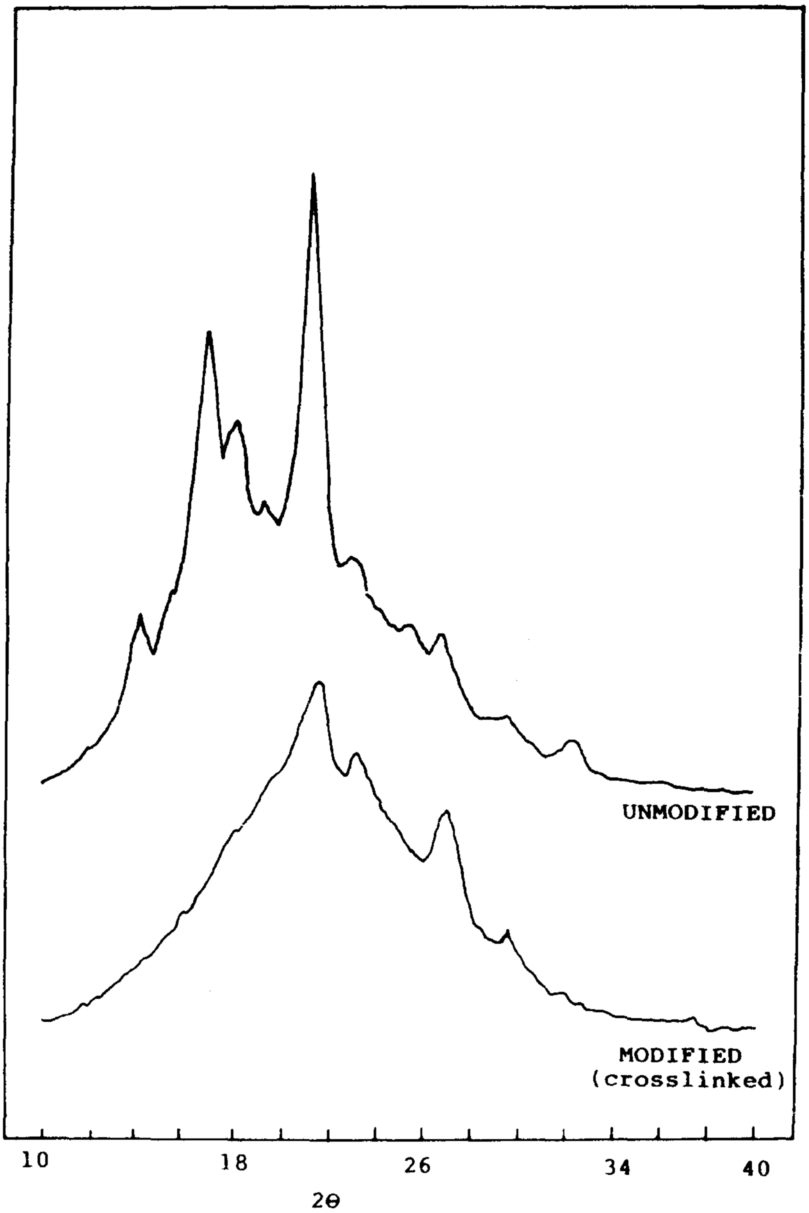

Figure 4 X-ray diffraction patterns of neat (unmodified) and crosslinked (modified) membranes

Table 3 Values of equilibrium sorption (Q_∞)

Solvent	Temp. (°C)	Uncrosslinked (D_0)	D_1	D_2	D_4	D_6	D_8
Benzene	28	2.508	2.520	2.477	2.423	2.364	2.325
	50		13.855	7.979	5.381	4.250	3.572
	70		14.088	8.211	5.426	4.346	3.673
Tolune	28	2.409	2.449	2.409	2.330	2.321	2.305
	50		11.762	7.099	4.920	3.992	2.998
	70		12.228	7.455	5.013	3.999	3.271
Xylene	28	1.996	2.012	1.990	1.965	1.946	1.919
	50		9.616	5.989	4.369	3.429	2.901
	70		10.499	6.726	4.422	3.476	3.002

where Q_t is the mol% solvent uptake at a time t and Q_∞ is the equilibrium mol% solvent uptake. The factor, k, is a constant and it depends on the structural characteristics of the polymer and also on the polymer–solvent interaction. The value of n determines the mode of sorption mechanism. For the Fickian mode, the value of n is 0.5 and it occurs when the rate of diffusion of the permeant molecules is much less than the relaxation rates of the polymer chains. If the value of n is 1, the mode of diffusion is non-Fickian and it arises when the rate of diffusion of permeant molecules is much faster than the polymer relaxation process. When the value of 'n' lies between 0.5 and 1, the mode of diffusion is anomalous. This occurs when the rates of permeant mobility and polymer relaxation process are similar. Plots of $\log(Q_t/Q_\infty)$ vs. $\log t$ were constructed and the data up to 50% sorption from the sorption curves were used to compute the value of n and k. A linear regression analysis is used to get the values of n and k, and the estimated values are compiled in *Table 4*. For the crosslinked samples at 28°C, the values of 'n' range between 0.57 and 0.66, indicating an anomalous mode of diffusion. But at higher temperatures, there is a tendency to approach the non-Fickian behaviour in all the solvents. This occurs when the diffusion of the penetrant molecules is faster than the polymer relaxation process. For the uncrosslinked EVA samples, the mechanism of the transport is Fickian as the value of n is close to 0.5 in all three solvents (*Table 4*). For all crosslinked samples, the values of k are found to decrease systematically with an increase in the molecular size of the aromatic hydrocarbons suggesting a decreased polymer–solvent interaction. But for the uncrosslinked sample a reverse trend was observed.

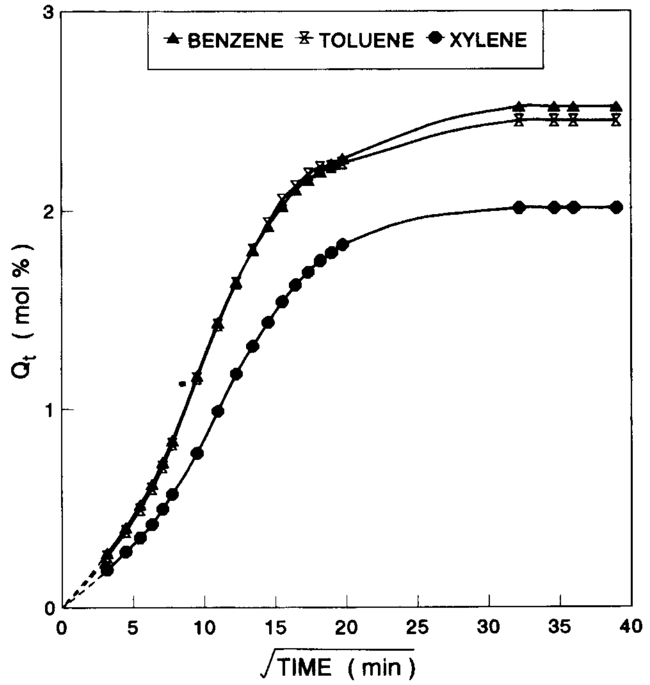

Figure 5 Mol% solvent uptake of D_1 sample at 28°C

Diffusion, sorption and permeation coefficients

From the data of the swelling experiments the diffusion coefficient D was calculated using the equation[12,23,24]:

$$D = \pi\left[\frac{h\Theta}{4Q_\infty}\right]^2 \tag{2}$$

where Θ is the slope of the linear portion of the sorption curve, h is the initial thickness of the polymer sample and Q_∞ is the equilibrium mol% uptake. The calculated values of diffusion coefficients are given in *Table 5*. The uncrosslinked EVA samples possess low values for diffusion coefficients. Also, it can be seen from the table that the D_8 sample with the lowest Q_∞ value, shows the highest value for D and the D_1 sample with higher Q_∞ values shows the lowest D value. It was found that as the extent of crosslinking increases (when the amount of DCP increases), the diffusion coefficient values increase.

According to the free volume theory[14,25] for the diffusion process, the rate of diffusion depends on the size of the permeant molecules. As the permeant molecular size increases, diffusion coefficients decrease. However, in our case, such systematic trends are only observed for D_6 and D_8 samples.

Sorption describes the initial penetration and dispersal of permeant molecules into the polymer matrix. Sorption coefficient is a thermodynamic factor which depends on the strength of polymer–solvent interactions and is calculated using the equation[24]

$$S = \frac{M_\infty}{M_0} \tag{3}$$

where M_∞ is the mass of the penetrant at equilibrium swelling and M_0 is the initial mass of the polymer.

The permeability of solvent molecules into the polymer membrane depends on both diffusion and sorption. Therefore permeation coefficient, P, can be calculated as the product of the diffusion coefficient and

Table 4 Analysis of sorption data of aromatic hydrocarbons in EVA at different temperatures

		n						$k \times 10^{-2}$ (g g^{-1} min^n)					
Solvent	Temp. (°C)	Uncrosslinked	D_1	D_2	D_4	D_6	D_8	Uncrosslinked	D_1	D_2	D_4	D_6	D_8
Benzene	28	0.564	0.593	0.593	0.595	0.642	0.635	3.122	2.740	2.729	2.792	2.538	2.727
	50		1.057	0.959	0.895	0.930	0.853		0.331	0.614	1.153	1.132	1.483
	70		1.056	0.977	0.931	0.889	0.907		0.505	0.854	1.221	1.463	1.583
Tolune	28	0.539	0.608	0.663	0.627	0.642	0.637	3.516	2.563	2.649	2.733	2.244	2.093
	50		1.053	0.974	0.913	0.827	0.819		0.317	0.593	0.968	1.359	1.746
	70		0.984	1.015	0.902	0.898	0.864		0.654	0.773	1.444	1.624	1.996
Xylene	28	0.418	0.575	0.581	0.599	0.565	0.596	4.747	2.485	2.368	2.435	2.322	2.175
	50		1.060	0.964	0.901	0.848	0.804		0.261	0.509	0.803	1.088	1.402
	70		0.951	0.974	0.981	0.923	0.948		0.634	0.821	0.968	1.190	1.190

Table 5 Values of $D \times 10^{-7}$ ($cm^2 s^{-1}$) at different temperatures for EVA samples

Solvent	Temp. (°C)	Uncrosslinked (D_0)	D_1	D_2	D_4	D_6	D_8
Benzene	28	2.799	3.005	3.049	3.367	3.750	4.324
	50		3.865	3.817	7.526	10.223	11.209
	70		4.785	8.619	12.644	14.976	18.079
Tolune	28	2.644	3.109	3.965	3.697	3.739	3.214
	50		3.523	3.902	6.627	7.058	11.222
	70		5.244	9.804	13.627	19.151	20.172
Xylene	28	1.299	1.914	1.941	2.222	2.029	2.248
	50		2.112	2.864	4.189	5.443	6.263
	70		3.719	7.227	11.155	13.063	15.106

Table 6 Values of sorption coefficients (S) and permeation coefficients ($P = DS$)

		S ($g g^{-1}$)						$P \times 10^{-7} cm^2 s^{-1}$					
Solvent	Temp. (°C)	Uncrosslinked (D_0)	D_1	D_2	D_4	D_6	D_8	Uncrosslinked (D_0)	D_1	D_2	D_4	D_6	D_8
Benzene	28	1.959	1.968	1.935	1.827	1.823	1.816	5.483	5.916	5.902	6.152	6.838	7.854
	50		10.822	6.233	4.203	3.320	2.791		40.690	23.789	31.634	33.937	31.283
	70		11.004	6.414	4.239	3.395	2.869		52.651	55.289	53.595	50.844	51.877
Tolune	28	2.221	2.257	2.221	2.147	2.139	2.124	5.772	7.019	8.803	7.937	7.998	6.828
	50		10.838	6.542	4.533	3.679	2.762		38.149	25.524	30.042	25.963	31.000
	70		11.267	6.870	4.620	3.685	3.014		59.088	67.350	62.946	70.573	60.806
Xylene	28	2.120	2.137	2.113	2.086	2.067	2.038	2.755	4.092	4.101	4.635	4.194	4.582
	50		10.209	6.360	4.637	3.641	3.081		22.561	18.211	19.427	19.816	19.294
	70		11.147	7.141	4.696	3.691	3.188		41.453	51.611	52.381	48.211	48.155

the solubility of the liquid in the membrane[23,24], i.e.

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

Table 6 gives the values of S and P. It is found that sorption coefficient is maximum for D_1 samples in all solvents and minimum for D_8 samples. The maximum value for the D_1 samples indicates better accommodation of solvent molecules in the highly flexible polymer chains. The lowest value for the D_8 system shows the least capability to accommodate solvent molecules. As the amount of DCP increases, extent of crosslinking increases and therefore polymer chains become rigid and their sorption decreases. The low sorption of the uncrosslinked system is due to the crystallinity of the polymer. For all crosslinked systems, the sorption coefficients are found to increase with increasing temperature in all solvents. Therefore sorption is activated by temperature. Permeability of the solvent molecules is maximum for the D_8 system and least for the uncrosslinked system. The diffusion coefficient shows the ability of solvent molecules to diffuse through the polymer matrix. The sorption coefficient is related to the maximum uptake of solvent molecules. A high 'S' value indicates the tendency of the solvent molecule to dissolve into the polymer. The permeability coefficient shows the net effect of sorption and diffusion. Temperature activates permeation also. It can be seen from *Table 6* that permeation coefficients increase with rise in temperature.

Temperature effects and activation parameters

The temperature dependence of diffusion through the crosslinked EVA systems was followed by conducting the experiments at 50 and 70°C in addition to 28°C. In *Figure 6*, Q_t mol% uptake is plotted as a function of time at various temperatures for the D_1 system. The solvent used is benzene. It has been observed that Q_∞ values increase with increasing temperature. The same trend is shown by other systems and in all solvents also. The increase in solvent uptake at high temperature is due to the increase in free volume. The Q_∞ values at high temperatures are given in *Table 3*. With the uncrosslinked systems, the high temperature diffusion experiments were not possible because the samples are found to be dissolved by the solvent at high temperatures.

The values of diffusion coefficients at high temperatures are given in *Table 5*. For all systems, the diffusion coefficient increases with rise in temperature indicating that temperature activates the diffusion process.

The diffusion, sorption and permeation process are considered to be activated by temperature and therefore the energy of activation for diffusion, E_D, and that for permeation, E_P, can be obtained by using Arrhenius equations[23]. For diffusion process,

$$D = D_0 \exp(-E_D/RT) \qquad (5)$$

where D is the diffusion coefficient, D_0 is the pre-exponential factor, E_D is the activation energy for diffusion, R is the gas constant and T is the temperature in absolute scale.

For permeation process,

$$P = P_0 \exp(-E_P/R_T) \qquad (6)$$

where P is the permeation coefficient, P_0 is the pre-exponential factor and E_P is the activation energy for permeation. Arrhenius plots of $\log D$ or $\log P$ vs. $1/T$ were constructed and from the slopes of the curves, the values of E_D and E_P are estimated by linear regression analysis. The values of E_D and E_P obtained are given in *Table 7*. It can be seen that the E_D values increased from D_1 to D_8 system. It is obvious that when the amount of DCP increases, the extent of crosslinking is higher and hence penetrant molecules require more activation energy to diffuse through the rigid polymer chains. The value of E_D increases with the increasing size of the penetrant molecules. Larger penetrant molecules do not fit into the sites or free space already available in the polymer matrix. They therefore require more energy to create additional space within the polymer matrix.

The activation energy for permeation E_P was found to be higher than E_D. There is no systematic variation for E_P for the different crosslinking system. The variation of E_P with the penetrant size is not uniform for D_1, D_2 and D_4 systems. But a systematic trend was observed for D_6 and D_8, i.e. activation energy for permeation increases with increase in penetrant size.

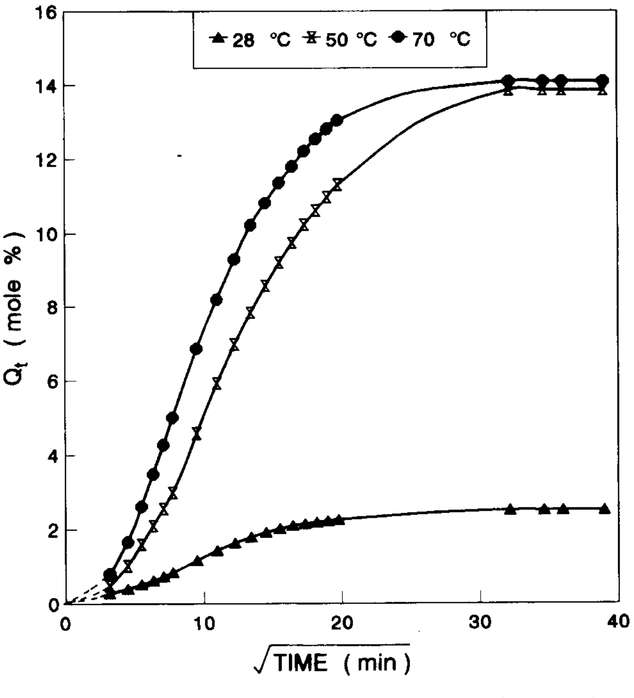

Figure 6 Temperature dependence of mol% uptake of D_1 sample

The heat of sorption ΔH_s, was calculated using the equation[23]

$$\Delta H_s = E_P - E_D \qquad (7)$$

The value of ΔH_s gives additional information about the molecular transport through the polymer matrix. ΔH_s is a composite parameter involving contributions from Henry's law and Langmuir-type sorption. *Table 7* gives the values of ΔH_s. All the values are found to be positive suggesting that sorption is mainly dominated by Henry's law, i.e. the formation of sites and the filling of these sites by penetrant molecules. Hence the process of sorption is endothermic. The heat of sorption is highest for D_1 system and least for D_8 system in all solvents.

The molar equilibrium sorption constant (K_s) is defined by Hung[26]

$$K_s = \frac{\text{No. of moles of solvent sorbed at equilibrium}}{\text{Mass of the polymer sample}} \qquad (8)$$

Thermodynamic sorption constant is a measure of the solvent uptake by the polymer. The values of K_s are compiled in *Table 8*. For crosslinked system, the highest values are obtained for the D_1 system and least for D_8 system. This again supports the fact that as the extent of crosslinking increases, the polymer chains become rigid and thus solvent uptake decreases. For the uncrosslinked samples the K_s values are smaller than that of D_1 samples. This is due to the close packing of polymer chains in the uncrosslinked system. As the size of the penetrant increases the sorption constant decreases for all the systems. It was also found that sorption constants increase with increasing temperature.

The values of K_s can be used to calculate the standard entropy (ΔS^0) for the crosslinked EVA by using Van't Hoff's equation[23]

$$\log K_s = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \qquad (9)$$

The standard free energy change (ΔG^0) for the process of diffusion was determined by using the equation

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (10)$$

The values of ΔG^0 and ΔS^0 are given in *Table 9*. ΔS^0 values are found to be positive in most cases and thus entropy factor favours the spontaneity of the process. Entropy change is highest for the D_1 system and least for the D_8 system. Thus entropy change decreases when the degree of crosslinking becomes higher. A systematic trend for the entropy change was not observed with the increasing size of the penetrants. For all systems the entropy change is minimum in toluene and maximum in benzene.

The free energy change values are found to be positive in all solvents. Since ΔG^0 is positive, the sorption process

Table 7 Activation parameters of diffusion

	E_D, kJ mol^{-1}					E_P, kJ mol^{-1}					ΔH_s, kJ mol^{-1}				
Solvent	D_1	D_2	D_4	D_6	D_8	D_1	D_2	D_4	D_6	D_8	D_1	D_2	D_4	D_6	D_8
Benzene	3.7598	9.1702	11.9898	12.6442	13.0127	19.7415	20.2969	19.8103	18.4058	17.2526	15.9817	11.1267	7.8205	5.7616	4.2399
Toluene	4.2726	7.8659	11.6954	14.5876	16.7242	19.1937	18.3382	18.8045	19.6406	19.9224	14.9211	10.4723	7.1091	5.0530	3.1982
Xylene	5.6126	11.6664	14.4127	16.7876	17.1825	20.9201	22.9212	21.9367	22.1776	21.3247	15.3075	11.2548	7.5260	5.3900	4.1422

Table 8 Thermodynamic sorption constants ($K_s \times 10^{-2}$ mol g^{-1})

Solvent	Temp. (°C)	Uncrosslinked (D_0)	D_1	D_2	D_4	D_6	D_8
Benzene	28	2.508	2.520	2.477	2.339	2.334	2.325
	50		13.855	7.978	5.381	4.250	3.573
	70		14.088	8.212	5.427	4.347	3.674
Tolune	28	2.410	2.450	2.409	2.330	2.321	2.306
	50		11.763	7.100	4.920	3.993	2.998
	70		12.228	7.456	5.013	3.999	3.272
Xylene	28	1.997	2.013	1.990	1.965	1.947	1.920
	50		9.616	5.990	4.368	3.429	2.902
	70		10.499	6.726	4.423	3.476	3.003

Table 9 Thermodynamic parameters, standard free energy ΔG^0 (kJ mol^{-1}) and standard entropy ΔS^0 (J mol^{-1})

	ΔG^0					ΔS^0				
Solvent	D_1	D_2	D_4	D_6	D_8	D_1	D_2	D_4	D_6	D_8
Benzene	8.671	8.892	9.135	9.222	9.288	93.529	55.577	29.475	13.483	1.543
Toluene	8.795	8.998	9.176	9.245	9.389	84.911	50.204	23.919	7.979	3.198
Xylene	9.312	9.498	1.092	9.690	9.776	86.196	54.537	—	9.231	—

is non-spontaneous in poly(ethylene-co-vinyl acetate). Free energy change is maximum for the D_8 system and least for the D_1 system. Therefore it can be concluded that the sorption process is more spontaneous in the D_1 system and less feasible in the D_8 system. Standard free energy change increases with increasing penetrant size. Thus the sorption process is more spontaneous in benzene.

Sorption kinetics

Earlier it was shown that transport of liquids through polymer membrane is considered as a rate controlled kinetic process which can be followed by first order kinetics[27]. During diffusion and sorption of liquids through polymer membranes a structural rearrangement occurs in the polymer matrix and this will induce kinetic behaviour. Kinetics mainly depends on the segmental mobility and availability of free volume within the matrix. We have calculated first order rate constant k_1 using the equation

$$\frac{d_c}{d_t} = k_1(C_\infty - C_t) \qquad (11)$$

which on integration gives

$$k_1 t = 2.303 \log \frac{C_\infty}{C_\infty - C_t} \qquad (12)$$

where k_1 is the first order rate constant (mm^{-1}). C_t and C_∞ represent concentration at a time t and at equilibrium. Plot of $\log(C_\infty - C_t)$ vs. time is shown in *Figure 7*. The slope of the graph gives the value of K_1 and are given in *Table 10*. The kinetic rate constant is a measure of the speed with which the solvent molecules migrate within the polymer matrix.

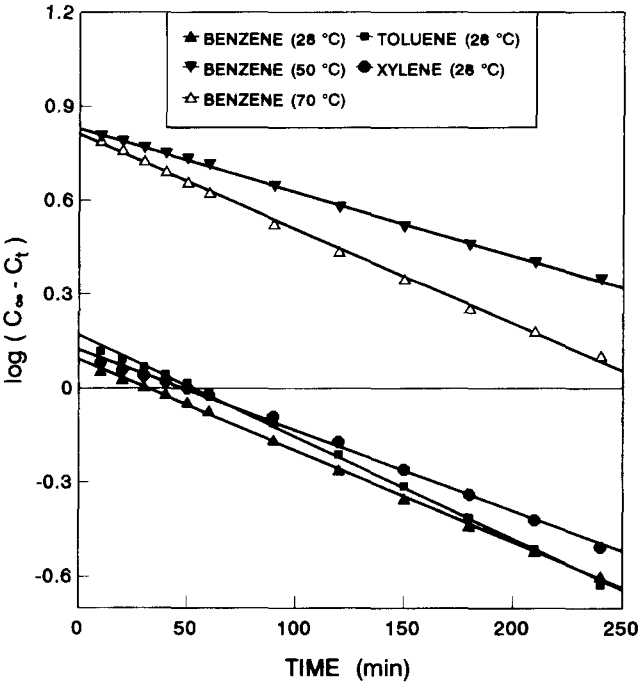

Figure 7 First-order kinetics plot for the D_1 sample in three solvents and at different temperatures

The k_1 values follow a regular trend of increasing with temperature except for D_1 system. The increase in k_1 values indicate the increase in the rate of diffusion with temperature. For D_1 system, the value of rate constant at 50°C is less than that at 28°C, but at 70°C the rate constant is higher. Even though solvent uptake is higher for D_1 system, the value of rate constant is low. This fact is also supported from the low D values for the D_1 system (*Table 5*). The plot of first order kinetics for D_1 system in benzene at three different temperatures are given in *Figure 7*. For D_4, D_6 and D_8, the values of rate constant increase with rise in temperature but for D_1 and D_2

Table 10 Sorption data for uncrosslinked and crosslinked poly(ethylene-co-vinyl acetate)

Solvent	Temp. (°C)	Uncrosslinked (D_0)	First order kinetics, $k_1 \times 10^{-3}$ min^{-1}				
			D_1	D_2	D_4	D_6	D_8
Benzene	28	6.936	6.617	6.607	6.768	8.060	8.691
	50		4.729	6.809	11.659	12.970	12.812
	70		7.168	9.211	12.271	12.372	15.635
Toluene	28	7.847	6.917	10.16	8.140	6.782	5.652
	50		5.719	8.291	12.094	10.133	16.472
	70		7.307	10.06	12.308	14.757	16.571
Xylene	28	6.197	5.194	4.867	6.094	3.929	4.515
	50		4.431	6.236	7.772	8.103	8.509
	70		6.655	13.19	12.406	12.963	14.081

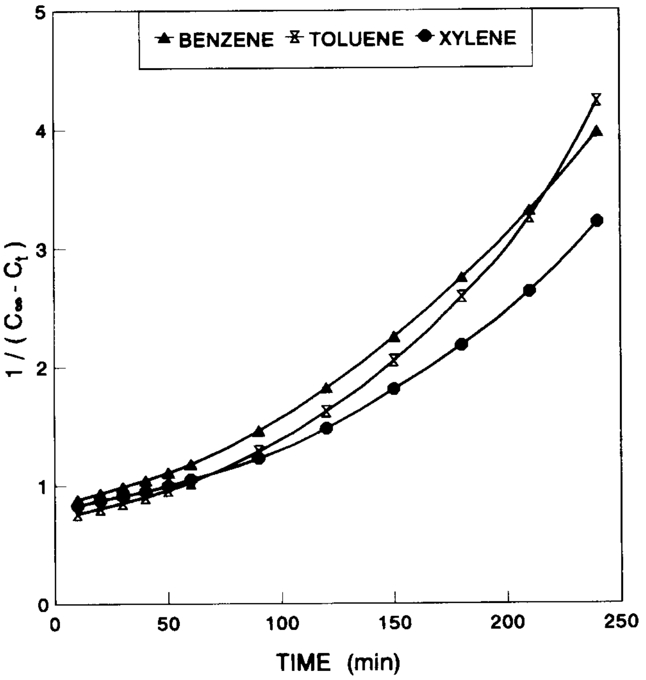

Figure 8 Second-order plots for the D_1 sample at 28°C

samples the values of rate constant at 50°C are less than that at 28°C.

Schott[28] explained the use of second order kinetics for swelling experiments. The equation for second order swelling is

$$\frac{d_c}{d_t} = k_2(C_\infty - C_t)^2 \qquad (13)$$

where k_2 is the second order rate constant. The integrated form of the equation is

$$k_2 t = \frac{1}{C_\infty - C_t} - \frac{1}{C_\infty} \qquad (14)$$

The typical second order kinetics plot of aromatic hydrocarbons at 25°C for the D_1 system is given in *Figure 8*. The slope of the curves gives the value of k_2 and are compiled in *Table 11*. However the plot is slightly curved at the middle. At 28°C k_2 values are higher than k_1 values. Since a straight line graph is obtained for first order kinetics, it seems to be more appropriate than second order kinetics for the transport of aromatic hydrocarbons through EVA.

Swelling parameters

The swelling coefficient (∞) is determined by the equation[29]

$$\infty = \frac{M^1_\infty - M_0}{M_0} \times \frac{1}{\rho_s} \qquad (15)$$

M^1_∞ is the mass of the solvent swollen rubber and M_0 is the initial mass of the polymer, ρ_s is the density of the solvent. The values of swelling coefficients are placed in *Table 12*. D_1 system possesses the highest value for ∞

Table 11 Sorption data for uncrosslinked and crosslinked poly(ethylene-co-vinyl acetate)

Solvent	Temp. (°C)	Uncrosslinked (D_0)	Second order kinetics, $k_2 \times 10^{-3}$ min^{-1}				
			D_1	D_2	D_4	D_6	D_8
Benzene	28	9.506	8.496	8.438	9.031	12.566	14.287
	50		0.968	2.584	9.611	14.289	14.774
	70		1.859	4.074	9.897	11.698	22.953
Toluene	28	10.309	7.799	16.950	11.067	7.626	5.455
	50		1.239	3.396	8.962	7.724	24.978
	70		1.650	4.324	9.453	15.865	25.377
Xylene	28	8.288	5.803	5.166	7.603	3.574	4.487
	50		0.902	2.209	4.125	5.369	6.907
	70		1.442	6.709	9.345	11.417	16.082

and D_8 system shows the least value for swelling coefficients. The low swelling values again indicate that the degree of crosslinking is higher in D_8 system. For uncrosslinked system ∞ values are less than D_1 samples. For all systems swelling coefficient is found to be highest in toluene.

Table 13 shows the values of volume fraction of solvent swollen polymer. The volume fraction (ϕ) of the polymer is calculated using the equation[30]

$$\phi = \frac{w_1/\rho_1}{\dfrac{w_1}{\rho_1}+\dfrac{w_2}{\rho_2}} \tag{16}$$

where w_1 and ρ_1 are the weight and density of the polymer sample respectively and w_2 and ρ_2 are the weight and density of the solvent. The ϕ values are given in *Table 13*. The value of volume fraction is a measure of the degree of crosslinking. It is clearly evident that when the amount of DCP used for crosslinking was increased the degree of crosslinking was also increased. The highest value of volume fraction for D_8 system indicates that degree of crosslinking is maximum in D_8 system. Values of volume fraction decreased when temperature was increased. This trend was also observed for all systems in all solvents.

The molecular mass between the crosslinks (M_c) of the network polymer was estimated using the equation developed from Flory–Rehner theory[31]

$$M_c = \frac{-\rho_p V \phi^{1/3}}{\ln(1-\phi)+\phi+\chi\phi^2} \tag{17}$$

where ρ_p is the density of the polymer, V is the molar volume of solvent, χ is the polymer–solvent interaction parameter estimated as reported earlier[16] and ϕ is the volume fraction polymer. We have calculated the values of M_c for D_6 and D_8 samples and they are given in *Table 14*. As the value of M_c increases, the spacing between crosslinks increases, thereby decreasing the number of crosslinks between polymer chains. Hence more solvent molecules can be accommodated easily between the crosslinks. The D_8 samples have low M_c values and this supports the low solvent uptake for D_8 samples.

Comparison with theory

The experimental diffusion coefficients were compared with theoretical predictions. The theoretical sorption curves were generated using the equation[29]

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

where M_t and M_∞ are the mass of solvent uptake at time t and at equilibrium, and h is the thickness of the polymer sample. This equation describes a Fickian mode of diffusion. Experimentally obtained values of diffusion coefficients are substituted in the above equation and the resulting curves obtained are shown in *Figures 9* and *10*.

Figure 9 gives a comparison of the experimental and theoretical diffusion curves of D_1 sample at 28°C in toluene. Both theoretical and experimental results were not in good agreement. The experimental curve deviates from the theoretical curve which is fully a Fickian mode of diffusion. The deviation is also evident from the value of n (*Table 4*). *Figure 10* gives the comparison of experimental and theoretical diffusion curves of D_1 sample at 50°C in toluene. A large deviation from the theoretical prediction was observed. This is due to the fact that at high temperatures (50°C) the mechanism of diffusion approaches non-Fickian mode. This fact is also supported by the value of n (*Table 4*). *Figure 11* gives the comparison of experimental and theoretical curves of D_8 sample at 28°C. Here also large variation could be seen.

Table 14 Values of molecular weight between the crosslinks

	Molecular weight between the crosslinks M_c	
Solvents	D_6	D_8
Benzene	34 726.19	12 416.63
Toluene	23 136.82	10 163.32
Xylene	16 411.46	11 469.91

Table 12 Values of swelling coefficients, ∞

Solvent	Uncrosslinked (D_0)	D_1	D_2	D_4	D_6	D_8
Benzene	2.239	2.249	2.216	2.088	2.084	2.076
Toluene	2.588	2.630	2.588	2.502	2.493	2.476
Xylene	2.494	2.514	2.485	2.455	2.431	2.398

Table 13 Volume fraction (ϕ) of swollen polymer

Solvent	Temp. (°C)	Uncrosslinked (D_0)	D_1	D_2	D_4	D_6	D_8
Benzene	28	0.32280	0.32176	0.32549	0.33822	0.33869	0.33956
	50		0.07943	0.13030	0.18178	0.21954	0.25071
	70		0.07822	0.12708	0.18054	0.21572	0.24553
Toluene	28	0.29197	0.28858	0.29197	0.29898	0.29978	0.30121
	50		0.7791	0.12279	0.16805	0.19930	0.24895
	70		0.07516	0.11762	0.16544	0.19903	0.23300
Xylene	28	0.29968	0.29798	0.30038	0.30303	0.30504	0.30799
	50		0.08160	0.12484	0.16362	0.19946	0.22747
	70		0.07526	0.11271	0.16191	0.19730	0.22153

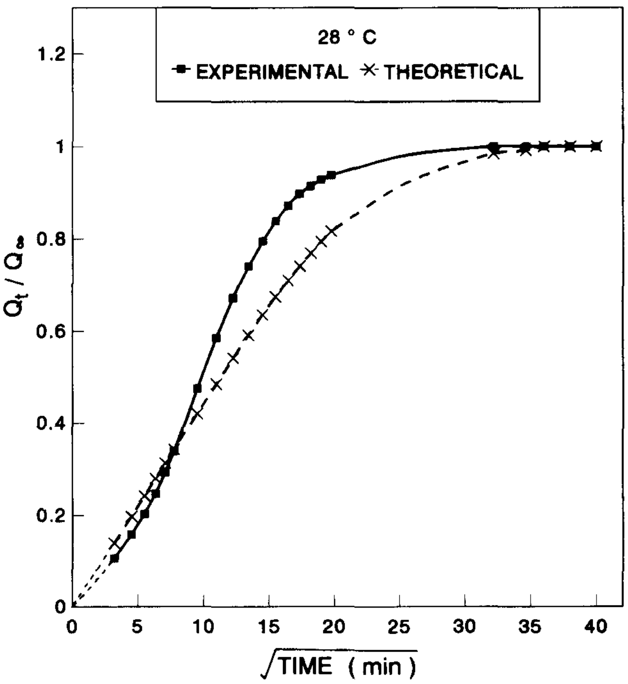

Figure 9 Comparison between experimental and theoretical sorption curves of D_1 at 28°C

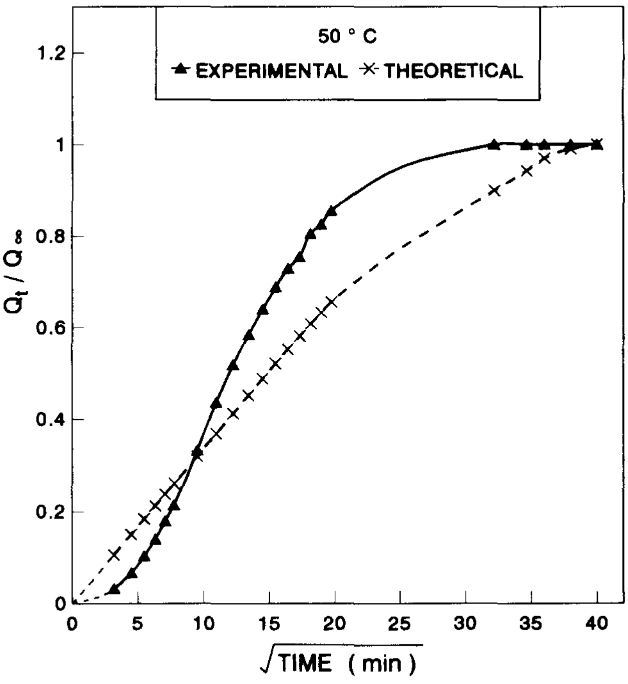

Figure 10 Comparison between experimental and theoretical sorption curves of D_1 at 50°C

CONCLUSIONS

The transport of aromatic hydrocarbons through poly(ethylene-co-vinyl acetate) has been studied by the use of sorption gravimetric analysis. The results of these studies on polymer–solvent interaction is important in the successful application of these materials in pervaporation experiments and barrier packagings. It is found that the introduction of crosslinks in EVA has profound influence on the transport process. For the uncrosslinked sample, solvent uptake is low due to the crystalline nature of the polymer. For the crosslinked samples solvent uptake decreases in the order $D_1 > D_2 > D_4 > D_6 > D_8$. This is mainly due to the increase in the extent of crosslinking. Thus D_1 samples exhibit higher solvent uptake because of their lowest crosslinking density. As the penetrant size increases the maximum solvent uptake decreases. The mechanism of diffusion deviates from the normal Fickian behaviour and the mechanism is anomalous at 28°C. At higher temperature diffusion approaches to non-Fickian mode. It is found that the temperature activates the diffusion process which is supported by the higher D values. At higher temperatures, equilibrium penetrant uptake is high due to the increase in the polymer free volume. Arrhenius parameters were estimated for the transport process. Van't Hoff's equation is used to obtain entropy and enthalpy of sorption. Gibb's free energy for sorption is found to be positive.

Transport kinetics has been studied in terms of the first and second order kinetics model. However, first order kinetics seem to be more appropriate for the systems studied. The polymer network structure has been analysed by estimating the molecular mass between the crosslinks. The experimental diffusion results are found to deviate from the theoretical predictions.

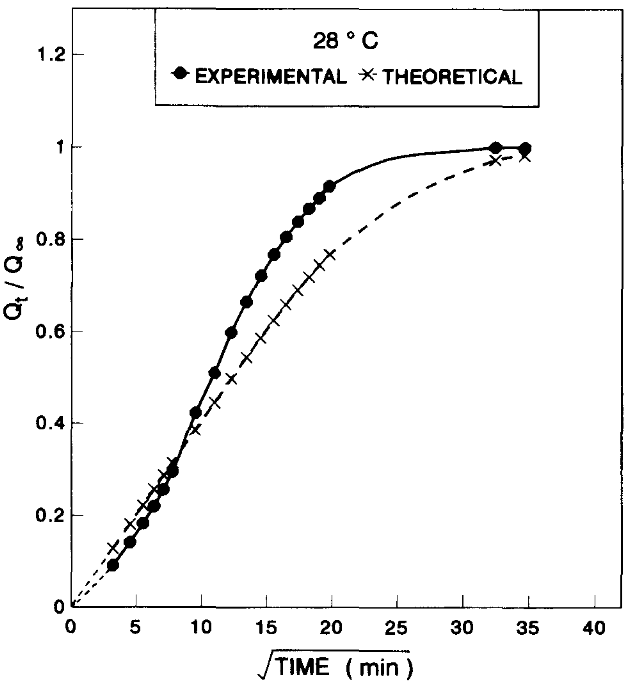

Figure 11 Comparison between experimental and theoretical sorption curves of D_8 at 28°C

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