

Diffusion and Sorption of Organic Liquids through Polymer Membranes. VI. Polyurethane, Neoprene, Natural Rubber, Nitrile Butadiene Rubber, Styrene Butadiene Rubber, and Ethylene Propylene Diene Terpolymer versus Organic Esters

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SYNOPSIS

Sorption and diffusion of eight esters into six commercial polymer membranes have been studied by immersion/weight gain experiments to determine how the transport behavior is affected by the choice of the solvent molecules and the chemical structures of the polymer membranes. The temperature dependence of transport parameters was found to follow the Arrhenius activation theory. It has been proved that the kinetics of equilibrium concentration can be described by the first-order kinetic rate equation. Furthermore, the results of transport parameters have been discussed in terms of the size, shape, and chemical nature of the diffusant molecules.

INTRODUCTION

Over the past several years, polymer membranes have been preferred over conventional materials in a variety of engineering and membrane science applications. Because these applications invariably entail contact with liquids, their membrane properties under such conditions must be of prime consideration. These materials may undergo chemical degradation, change their dimensions significantly, or change their mechanical properties by loss of strength and rigidity.

The interactions between polymer membranes and organic liquids have been widely investigated over the past 30 years. The most significant findings in this area have been recently reviewed by Aminabhavi and co-workers.¹⁻³ Despite the broadness of the subject and numerous possible variations, most of these studies have been classified into two conceptual approaches. The first one focuses on the mechanism of liquid penetration, where emphasis

is given to questions related to the transport kinetics and diffusion mechanism.⁴⁻⁶ The second approach concerns polymer-solvent interactions and their results, such as chemical degradation, polymer leaching, crazing, and cracking.⁷⁻⁹

The present investigation is a part of our continuing program¹⁰⁻¹⁸ concerning the diffusion and sorption of esters through commercially important polymer membranes such as polyurethane (PU), ethylene propylene diene terpolymer (EPDM), neoprene (CR), natural rubber (NR), nitrile butadiene rubber (NBR), and styrene butadiene rubber (SBR). In polymer industries, esters have been frequently used as plasticizing agents. The barrier properties of polymers may be seriously impaired in the presence of such esters which might penetrate and thereby plasticize the polymer. It would, therefore, be useful to forecast conditions and penetrants which might cause such plasticization and to predict the consequences on the transport behavior.

In this paper, diffusion and sorption results of esters like methyl acetate, ethyl acetate, *n*-propyl acetate, *n*-butyl acetate, *iso*-amyl acetate, methyl acetoacetate, ethyl acetoacetate, and methyl salicylate into the above-mentioned commercial polymer membranes have been studied over the temperature

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interval of 25–60°C. Activation parameters for the transport processes have been calculated and attempts were made to relate the transport properties to the molecular dimensions and interactions between the polymer and solvent molecules. These correlations seem to provide a basis for at least qualitatively useful predictions of sorption equilibria and diffusion kinetics.

EXPERIMENTAL

Reagents and Materials

The esters used were all of reagent grade which were doubly distilled before use. The observed boiling points and molar volumes of the solvents used are listed in Table I. The polyurethane membrane was the same used earlier.^{13–15} The other membranes, namely, EPDM, CR, NR, NBR, and SBR, were obtained from UTEX, Weimer, Texas. The rubber compositions and their representative engineering properties were given in our earlier papers.^{10–12,17}

Sorption Experiments

Sorption experiments were performed on circularly cut (diameter = 1.94 cm) polymer membranes of uniform thickness by placing them in screw-tight test bottles containing about 25–30 cm³ of the liquid. These were then placed in an electric precision oven (Memmert, Germany) maintained at the desired constant temperature within $\pm 0.5^\circ\text{C}$. The experiments were carried out at 25, 44, and 60°C. At specified time intervals, the samples were removed from the test bottles and surface adhered-liquid drops were blotted with Kimwipes. These were then weighed to the nearest 0.05 mg under closed environments and placed back immediately into the test bottles and then transferred to the oven. Experi-

ments were continued until attainment of the equilibrium at which no further weight gains of the samples occurred.

RESULTS AND DISCUSSION

Kinetics of Solvent Transport

The equilibrium mole percent sorption Q_∞ expressed as mol solvent sorbed by 100 g polymer material are given in Table II. The sorption plots displaying the dependence of sorption Q_t on the square root of time, $t^{1/2}$, for some typical polymer–solvent systems are presented in Figures 1 and 2. It is observed that in all cases, most generally, sorption increases initially in a linear fashion up to about 50% attainment of equilibrium and later levels off, showing complete equilibration. The sorption coefficients S or Q_∞ were obtained from the plateau regions of these plots. The equilibrium values and the time taken to reach equilibrium saturations are different for different polymer–solvent systems. The solvent sorption within a polymer generally depends on the polymer structure and on the nature of solvent molecules. Sorption, being a time-dependent phenomenon, makes the movement of solvent molecules easier because it helps to expand the spaces between segments of the polymeric material by filling them with the mobile solvent molecules. In the absence of no significant interactions between solvent molecules and polymeric chain segments, sorption follows the Fickian mechanism. Deviations from the Fickian mode of sorption are attributed to variations in the response of the polymer chain segments to a swelling stress induced by the presence of solvents. Thus, for some polymer–solvent systems, the initial portions of Q_t versus $t^{1/2}$ curves are slightly sigmoidal, indicating a slight departure from the regular Fickian mode of transport.

Table I Some Physical Properties of Solvents

Solvent	Formula	B.P. (°C)	Molar Volume at 25°C (cm ³ /mol)
Methyl acetate	CH ₃ COOCH ₃	59.9	79.8
Ethyl acetate	CH ₃ CH ₂ COOCH ₃	77.1	98.5
<i>n</i> -Propyl acetate	CH ₃ (CH ₂) ₂ COOCH ₃	101.5	115.7
<i>n</i> -Butyl acetate	CH ₃ (CH ₂) ₃ COOCH ₃	126.1	132.6
<i>iso</i> -Amyl acetate	(CH ₃) ₂ CH(CH ₂) ₂ COOCH ₃	142.0	150.4
Methyl acetoacetate	CH ₃ COCH ₂ COOCH ₃	171.1	108.3
Ethyl acetoacetate	CH ₃ CH ₂ COCH ₂ COOCH ₃	180.8	127.4
Methyl salicylate	<i>o</i> -HOC ₆ H ₄ COOCH ₃	233.3	129.1

Table II Mol Percent Equilibrium Sorption (Q_{∞}) Data for Polymer-Solvent Systems at Various Temperatures

Solvent	Temp (°C)	mol Solvent/100 g Polymer					
		EPDM	CR	NR	NBR	SBR	PU
Methyl acetate	25	0.087	0.304	0.224	1.129	0.328	0.779
	40	0.106	0.327	0.263	1.121	0.380	0.834
	50	0.120	0.342	0.292	1.108	0.409	0.879
Ethyl acetate	25	0.130	0.460	0.462	0.885	0.622	0.587
	44	0.174	0.462	0.538	0.847	0.676	0.597
	60	0.200	0.464	0.586	0.814	0.691	0.600
<i>n</i> -Propylacetate	25	0.183	0.500	0.612	0.717	0.762	0.537
	44	0.230	0.490	0.678	0.681	0.794	0.514
	60	0.266	0.480	0.719	0.658	0.804	0.514
<i>n</i> -Butyl acetate	25	0.224	0.481	0.666	0.544	0.790	0.428
	44	0.267	0.470	0.730	0.518	0.800	0.432
	60	0.304	0.467	0.862	0.506	0.793	0.429
<i>iso</i> -Amyl acetate	25	0.230	0.417	0.610	0.364	0.670	0.332
	44	0.264	0.406	0.644	0.353	0.679	0.323
	60	0.304	0.391	0.778	0.343	0.692	0.332
Methyl acetoacetate	25	0.010	—	0.017	0.777	0.032	0.205
	44	0.014	0.237	0.027	0.848	0.047	0.239
	60	0.018	0.176	0.032	0.876	0.044	0.269
Ethyl acetoacetate	25	0.017	0.279	0.039	0.805	0.065	0.248
	44	0.022	0.263	0.050	0.819	0.081	0.279
	60	0.026	0.241	0.060	0.830	0.097	0.301
Methyl salicylate	25	0.128	0.659	0.531	1.078	0.839	0.541
	44	0.172	0.629	0.671	1.057	0.918	0.564
	60	0.212	0.665	0.842	1.062	0.953	0.595

EPDM, which is known for its high resistivity toward water and aqueous salt solutions,¹⁹ also exhibits a minimum sorption for esters used in this work. This may be attributed to the possible mild interactions between alkane type chains of the EPDM membrane and the solvent molecules. In general, there is a systematic increase of sorption with temperature; also, a linear relation exists between the sorption values and the size of the penetrant molecules from methyl acetate to *n*-butyl acetate. The results of Q_{∞} for *n*-butyl acetate and *iso*-amyl acetate are identical, although the molar volume of the latter is greater than that of the former. Similarly, the sorption of methyl salicylate (an aromatic ester) and ethyl acetate are identical, though they differ considerably in their sizes. However, methyl acetoacetate and ethyl acetoacetate exhibit extremely low values of sorption; the latter showed higher sorption than the former.

Natural rubber behaves almost identical to that of EPDM membrane and the sorption of NR is nearly two to three times higher than EPDM. The maximum sorption increases systematically from

methyl acetate to *n*-butyl acetate; the sorption of *iso*-amyl acetate is similar to that of *n*-propyl acetate. Methyl salicylate shows an intermediate behavior between those of *n*-propyl acetate and *n*-butyl acetate. Methyl acetoacetate also shows lower Q_{∞} values than for ethyl acetoacetate, a similar observation was also found earlier for the EPDM membrane.

Styrene butadiene rubber which generally shows higher sorption for all the esters, other than EPDM and NR, also exhibits a similar sorption pattern to those of EPDM and NR from methyl acetate to *n*-butyl acetate. However, with SBR, we could not observe any significant increase in Q_{∞} values from 25 to 60°C and, also, *n*-propyl acetate and *n*-butyl acetate exhibit almost identical sorption data. Similarly, we find that *iso*-amyl acetate exhibits almost similar Q_{∞} results to that of ethyl acetate. The higher sorption values of methyl salicylate exhibited by SBR is attributed to the π - π interactions between aromatic moieties of the SBR and of the methyl salicylate molecule.

For neoprene, the sorption increases from methyl

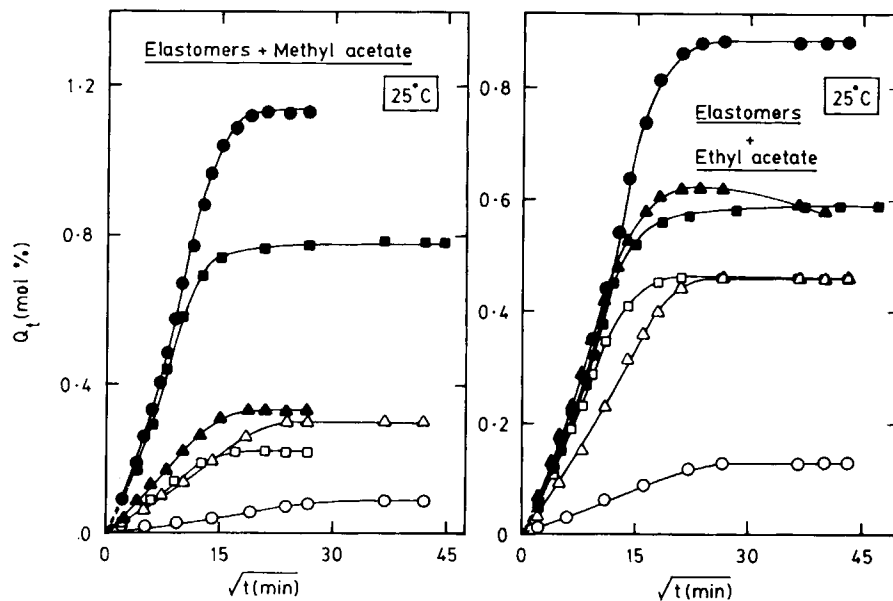


Figure 1 Dependence of mole percent sorption on square root of time for all membranes with methyl acetate and ethyl acetate at 25°C. Symbols for membranes are: (○) EPDM; (△) CR; (□) NR; (●) NBR; (▲) SBR; (■) PU.

acetate to *n*-propyl acetate via ethyl acetate; for *n*-butyl acetate, the Q_{∞} data are lower than that of *n*-propyl acetate, but identical to ethyl acetate. Interestingly, with neoprene for all the esters except

methyl and ethyl acetates, a decrease in sorption is observed with an increase in temperature. However, this effect is not systematic with methyl salicylate. This may be the result of induced crystallinity at

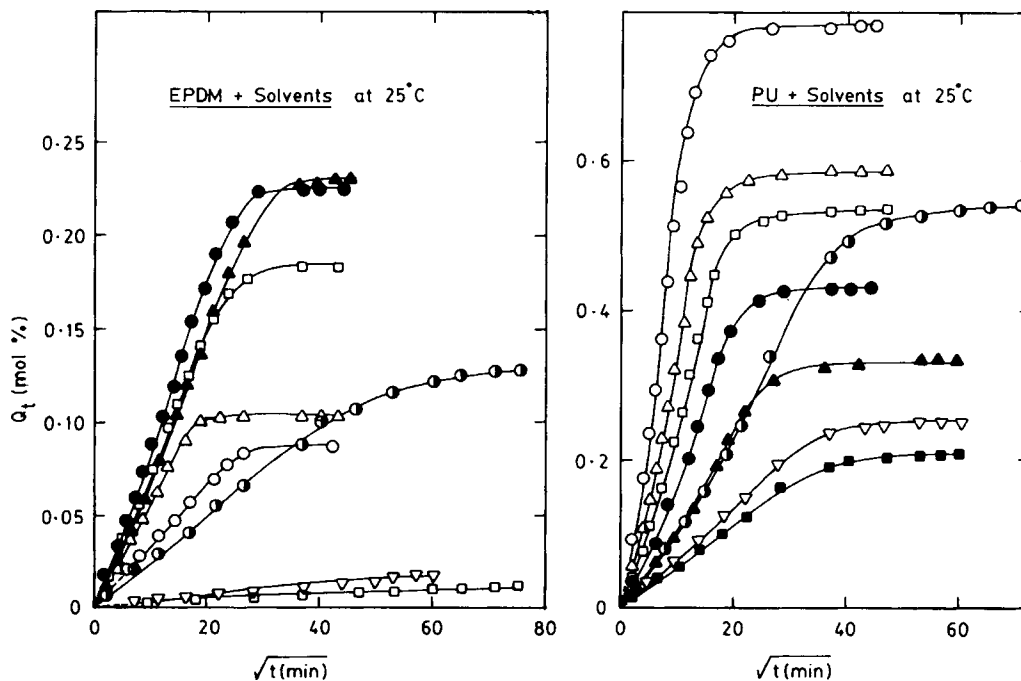


Figure 2 Dependence of mole percent sorption on square root of time for all solvents with EPDM and PU membranes at 25°C. Symbols for solvents are: (○) methyl acetate; (△) ethyl acetate; (□) *n*-propyl acetate; (●) *n*-butyl acetate; (▲) *iso*-amyl acetate; (■) methyl acetoacetate; (▽) ethyl acetoacetate; (◐) methyl salicylate.

higher temperatures in the presence of solvent molecules. Induced crystallinity reduces the free energy of mixing, thereby decreasing the solvent uptake.²⁰ Methyl acetoacetate did not reach equilibrium at 25°C even after about 30 days of continuous solvent immersion.

Sorption results of NBR and polyurethane are somewhat identical, i.e., in these systems, the equilibrium values of sorption decrease systematically from methyl acetate to *iso*-amyl acetate. Also, for NBR a continuous decrease in Q_∞ is observed with increase in temperature; but, for methyl and ethyl acetoacetates with NBR, the Q_∞ values increase with a rise in temperature. With methyl salicylate, no systematic behavior is seen for NBR over the temperature interval studied. However, methyl aceto-

acetate shows higher sorption for NBR (except at 25°C, for which it is reversed) than ethyl acetoacetate. The sorption of PU increases systematically with a rise in temperature for methyl-, ethyl-, and *n*-propyl acetates.

In order to investigate the mechanism of solvent transport in the polymer matrix, the sorption results before completion of 50% equilibrium have been analyzed for slab geometry of the polymer material by using¹⁴⁻²¹

$$Q_t/Q_\infty = kt^n \quad (1)$$

where k is a constant which indicates the structural characteristics of the polymer network. The value of the exponent n indicates the type of the transport

Table III Analysis of Penetrant Transport Using Eq. (1) at Various Temperatures

Solvent	Parameter	Temp (°C)	EPDM	CR	NR	NBR	SBR	PU
Methyl acetate	$k \times 10^2$ ^a	25	3.92	3.83	5.97	3.07	5.23	4.45
		40	5.20	4.77	7.20	4.09	6.72	5.31
		50	6.07	5.28	7.57	4.48	7.12	6.04
Ethyl acetate	$k \times 10^2$ ^a	25	3.79	3.09	5.05	2.59	4.23	3.78
		44	5.69	3.85	5.52	3.43	5.24	5.40
		60	7.14	4.63	6.39	4.22	5.88	5.77
<i>n</i> -Propyl acetate	$k \times 10^2$ ^a	25	3.62	2.48	3.69	2.07	3.50	3.03
		44	4.86	3.17	4.45	2.78	3.92	4.25
		60	5.74	4.03	4.91	3.37	4.65	5.23
<i>n</i> -Butyl acetate	$k \times 10^2$ ^a	25	3.33	2.19	3.17	1.77	2.88	3.11
		44	4.16	2.73	4.48	2.38	3.73	3.99
		60	5.06	3.51	4.50	2.82	4.10	4.45
<i>iso</i> -Amyl acetate	$k \times 10^2$ ^a	25	2.42	1.64	2.62	1.24	2.48	2.10
		44	3.46	2.53	3.27	1.91	3.11	2.94
		60	4.63	3.11	3.76	2.33	3.68	3.99
Methyl acetoacetate	$k \times 10^2$ ^a	25	6.95	—	4.75	1.64	6.48	2.71
		44	2.09	0.67	5.12	2.00	3.02	3.29
		60	3.09	1.61	6.32	2.72	4.43	4.43
Ethyl acetoacetate	$k \times 10^2$ ^a	25	2.99	0.54	4.00	1.27	2.79	2.18
		44	1.40	1.11	5.58	1.81	3.59	3.10
		60	3.54	1.85	6.27	2.33	4.85	4.11
Methyl salicylate	$k \times 10^2$ ^a	25	2.29	1.15	2.07	0.79	1.22	1.36
		44	3.53	1.80	2.58	1.28	2.10	2.54
		60	3.52	2.19	2.67	1.64	2.53	2.92
	\bar{n} ^b	25-60	0.50	0.56	0.55	0.59	0.60	0.57

^a k is expressed in the units of g/g minⁿ.

^b The average value of the exponent, n of eq. (1) is considered.

mechanism. A value of n of 0.50 implies the Fickian transport, a value of n of 1.00 implies the Case-II transport, and for values of n of $0.50 < n < 1.00$, the anomalous transport is observed.¹⁴ The above relation is valid for $Q_t/Q_\infty < 0.5$. For Fickian transport, the rate of diffusion is smaller than polymer relaxation due to mechanical and structural modes of polymers. For Case-II transport, diffusion would be rapid as compared to the simultaneous relaxation process, and, hence, sorption may be complicated by swelling of the membranes. This leads one to assume that, for the anomalous transport, both diffusion and relaxation rates are comparable and that diffusivities are not highly concentration-dependent.

The least-squares estimations of k and n of eq. (1) at 95% confidence level are listed in Table III. Typical plots of $\log(Q_t/Q_\infty)$ versus $\log t$ for SBR and PU membranes with all the esters considered are given in Figure 3. Only the average values, \bar{n} , of the exponent value of n taken over the interval of 25–60°C are included in Table III because there are not considerable variations in the values of n over the investigated range of temperature. For all the polymer-solvent systems, the values of \bar{n} are found to vary between 0.50 and 0.60, suggesting the transport mechanism to be of anomalous type, and it deviates slightly from the Fickian mode. This fact is also obvious from the observation of some of the typical sorption plots given in Figures 1 and 2. Such aspects have also been discussed earlier in the literature for a variety of many polymer-solvent systems.²²⁻²⁴ The values of the parameter k show a systematic trend with the size of esters and the experimental temperature. For instance, k decreases with an increase in molar volume from methyl acetate to *iso*-amyl acetate. However, most generally, with a rise in temperature the values of k also increase.

Kinetic Rate Constants

Sorption and desorption of a solvent by a polymer membrane is attributed to the possible structural changes which accompany the solvent transport. These changes require a rearrangement of polymer segments that can dominate the kinetic behavior, and these in turn are considered to be affected by the total free volume and its distribution within the polymer matrix.²⁵ If sorption is controlled by the rate of polymer expansion, then a more reasonable suggestion is that sorption rate will be proportional to the difference in osmotic pressure inside and outside the polymer film. As a first approximation, we can relate this to simple vapor pressure, and if, up

to the equilibrium point, vapor pressure of a liquid in the film is proportional to its concentration, then the following first-order kinetic equation may be used²⁶:

$$dQ/dt = k'[Q_\infty - Q_t] \quad (2)$$

where k' is the first-order rate constant. Integration of eq. (2) gives

$$k't = 2.303 \log[Q_\infty/(Q_\infty - Q_t)] \quad (3)$$

Here, Q_t and Q_∞ represent, respectively, the concentrations at time t and at infinite time (i.e., equilibrium sorption). These results are given in Table IV and a typical kinetic plot of $\log(Q_\infty - Q_t)$ versus t is shown in Figure 4 for the NBR + ethyl acetoacetate system.

Results given in Table IV suggest a systematic decrease in kinetic rate constants for methyl acetate to *iso*-amyl acetate for NBR over the investigated range of temperature. A slight increase in k' values for NBR + methyl acetoacetate followed by decreasing values of k' for ethyl acetoacetate and methyl salicylate is observed. However, with NR, SBR, and PU membranes, k' decreases systematically from methyl acetate to methyl salicylate. On the other hand, no systematic trend in k' values are observed for EPDM and CR membranes with n -

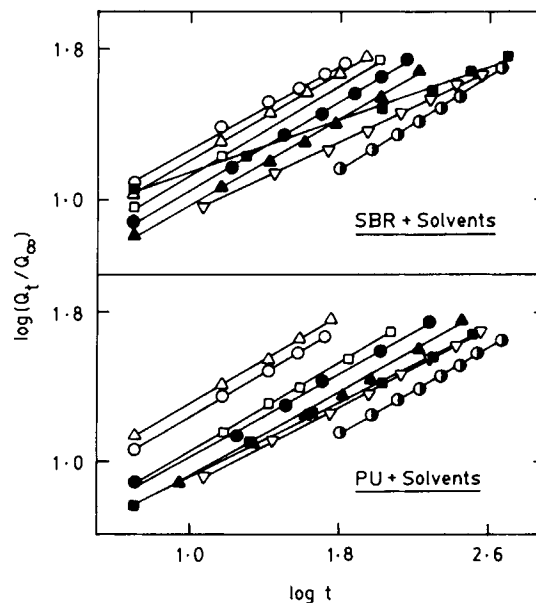


Figure 3 Dependence of $\log(Q_t/Q_\infty)$ on $\log t$ for SBR and PU membranes with solvents at 25°C. All symbols for solvents have the same meaning as in Figure 2.

Table IV Kinetic Rate Constants ($k' \times 10^3, \text{min}^{-1}$) for Polymer-Solvent Systems at Various Temperatures

Solvent	Temp (°C)	EPDM	CR	NR	NBR	SBR	PU
Methyl acetate	25	3.46	4.80	10.78	7.50	9.49	10.39
	40	9.19	8.89	16.87	11.02	13.12	15.88
	50	9.57	9.22	20.27	14.18	15.34	17.88
Ethyl acetate	25	4.98	5.12	9.70	5.34	8.76	7.72
	44	9.34	7.12	13.81	8.00	13.23	13.75
	60	14.33	10.56	17.94	10.09	16.63	18.60
<i>n</i> -Propyl acetate	25	3.85	3.55	7.08	3.14	6.75	5.07
	44	7.42	6.27	12.02	5.57	9.67	9.63
	60	10.90	9.38	13.56	7.70	12.72	13.37
<i>n</i> -Butyl acetate	25	3.58	2.64	5.97	1.86	5.02	3.87
	44	7.00	5.61	12.24	3.82	8.90	7.38
	60	9.96	7.33	11.79	5.29	10.06	11.03
<i>iso</i> -Amyl acetate	25	2.44	1.62	4.32	0.97	3.45	2.71
	44	4.80	3.40	6.56	1.96	5.52	4.86
	60	6.93	4.76	9.46	3.16	9.05	7.70
Methyl acetoacetate	25	0.78	—	2.38	1.50	1.61	1.78
	44	1.81	3.62	6.37	2.94	2.93	4.07
	60	3.68	9.60	12.22	4.90	5.30	7.23
Ethyl acetoacetate	25	0.79	0.20	2.03	1.40	1.31	1.66
	44	1.94	0.77	5.53	2.67	3.51	3.79
	60	5.01	1.63	8.55	4.32	5.83	6.37
Methyl salicylate	25	0.91	0.71	1.62	0.60	1.23	1.09
	44	2.92	1.99	2.94	1.57	3.01	3.21
	60	3.88	3.02	4.11	2.75	4.53	5.23

alkane chain containing esters. For instance, with EPDM and CR membranes, k' values are smaller for methyl acetate than ethyl acetate; however, from ethyl acetate to *iso*-amyl acetate, k' values decrease systematically.

Diffusion and Permeation Coefficients

If the interaction between a polymer and solvent does not affect the morphology of the polymer, then the diffusion coefficient D will be independent of

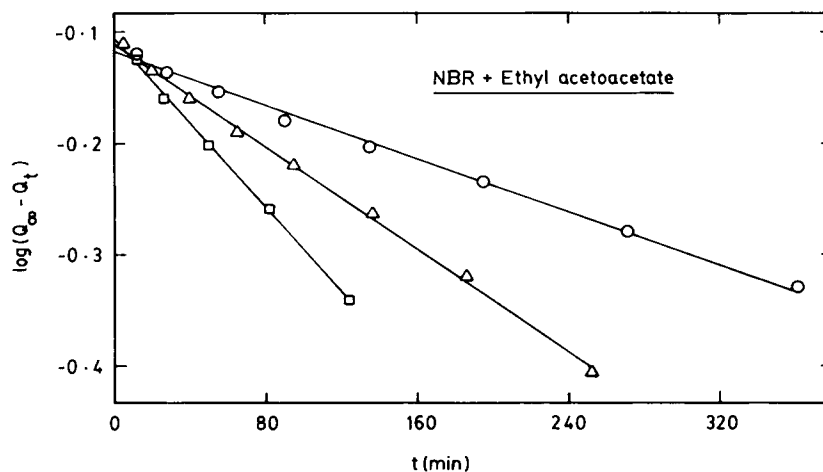


Figure 4 Dependence of $\log(Q_\infty - Q_t)$ on t for NBR + ethyl acetoacetate system at (○) 25°C; (△) 44°C; (□) 60°C.

penetrant concentration. Therefore, the flux of the penetrant at constant temperature is given by Fick's first law with constant diffusion coefficient as

$$D = \pi[h\theta/4Q_{\infty}]^2 \quad (4)$$

where θ is the slope of the initial linear part of the sorption curves. This observation is made easier by the fact that, for a constant D , the sorption curve is linear, within the normal limits of experimental error for sorption up to about 50%. Thus, eq. (4) is applicable if the thickness h of the membrane remains unchanged (preswollen condition). In the rubbery state, where the temperature is above the glass transition of the polymer, sorption follows Henry's law and diffusion follows the Ficks first law with a concentration-independent D .^{27,28} Since, no significant swelling is observed in the present polymer-solvent systems, the values of D have been calculated from eq. (4). The estimated diffusion coefficients are given in Table V.

Typically, when a solvent diffuses into a polymer membrane, its rate depends on the penetration ability of the solvent in addition to its molecular size. In the absence of any chemical reaction between

polymer and solvents, the diffusion coefficients should decrease with increasing molar volume of the penetrants. This is indeed the case from methyl acetate to *iso*-amyl acetate for all the present membranes except EPDM and CR. For the latter, with methyl acetate values of D are smaller than ethyl acetate; however, from ethyl acetate to *iso*-amyl acetate, D decreases further with the size of esters. The same dependency is also observed for the kinetic rate constants given in Table IV. For methyl acetoacetate, ethyl acetoacetate, and methyl salicylate, the values of D are quite smaller than for the remaining esters. For methyl acetoacetate, due to nonavailability of equilibrium data at 25°C diffusivity, data are not determined for this system.

The diffusion results can be explained in terms of size of solvent molecules and availability of free volume in the polymer matrix. If the chain separations are larger than the molecular diameter of solvent molecules, an activated diffusion takes place due to the successive jumps of solvent molecules from one site to the other. As the size of the solvent molecules increases, the displacements of the molecules depends upon rotation of the chain segments and the availability of voids larger than the size of

Table V Diffusion Coefficients ($D \times 10^7$, cm²/s) for Polymer-Solvent Systems at Various Temperatures

Solvent	Temp (°C)	EPDM	CR	NR	NBR	SBR	PU
Methyl acetate	25	2.02	4.12	6.84	5.43	6.33	3.38
	40	6.05	6.84	12.10	7.82	8.93	5.58
	50	6.72	8.20	15.08	10.32	11.14	5.96
Ethyl acetate	25	3.41	4.19	6.20	3.45	5.91	2.65
	44	6.42	7.00	9.92	5.54	9.39	4.62
	60	9.65	9.29	13.42	7.66	12.27	6.87
<i>n</i> -Propyl acetate	25	2.32	2.93	5.14	1.93	4.58	1.59
	44	5.01	5.38	8.21	3.51	6.87	3.32
	60	7.62	7.46	9.64	5.28	9.27	4.60
<i>n</i> -Butyl acetate	25	2.16	2.38	4.20	1.18	3.63	1.14
	44	4.68	4.58	6.40	2.49	6.04	2.30
	60	6.71	5.72	7.64	3.64	8.35	3.63
<i>iso</i> -Amyl acetate	25	1.39	1.27	2.72	0.49	2.21	0.80
	44	3.04	2.83	5.13	1.27	3.88	1.55
	60	4.64	4.25	6.19	2.10	6.00	2.42
Methyl acetoacetate	25	0.39	—	1.09	0.74	0.83	0.49
	44	1.34	0.27	3.37	1.98	2.19	1.35
	60	2.81	0.82	8.03	3.00	3.65	2.26
Ethyl acetoacetate	25	0.40	0.14	1.13	0.84	0.75	0.50
	44	1.53	0.61	3.14	1.80	2.07	1.22
	60	3.42	1.29	5.39	2.76	3.59	2.03
Methyl salicylate	25	0.55	0.49	0.82	0.28	0.86	0.36
	44	1.70	1.53	1.84	0.92	1.82	0.95
	60	2.97	2.53	2.48	1.90	2.98	1.70

the solvent molecules. In such cases, a small change in penetrant size might result in a substantial change in D . As the temperature increases, the amplitude of the segmental motion increases the size of the voids, thereby increasing the solvent diffusion rates. It has been well established²⁹⁻³¹ that the diffusion coefficient decreases with increasing penetrant size and the dependence of diffusion coefficient on the penetrant size diminishes as the free volume of the polymer increases.³² Diffusion studies of a number of homologous paraffin hydrocarbons have been made,^{33,34} wherein it was found that, for the branched hydrocarbons, the diffusivities are smaller than the straight chain analogues. This is in agreement with the present systems.

The slight sigmoidal shapes of the sorption curves as observed in case of polymer-solvent systems except that of EPDM (see Figs. 1 and 2) are attributed to the departure from the Fickian transport. In order to determine whether this anomalous behavior is due to swelling induced breakup of an agglomerate filler structure, we have repeated the sorption experiments of the already desorbed samples to see if subsequent sorption showed the same anomalous character or not. To our surprise, the same type of anomalous diffusive pattern was observed and thus, the diffusion coefficients obtained from eq. (4) remained the same even after successive cycles of sorption and desorption, a fact that was also observed earlier.¹⁷ The sorption curves observed for polymer-solvent systems were analyzed by using the Joshi-Astarita procedure.³⁵ The model parameters were varied incrementally over a prescribed range, and a fit to the experimental data was subjected to the least-squares test to select the best set of values. The resulting diffusion coefficients are plotted versus concentration (wt %) at 25°C for methyl acetate + polymer systems in Figure 5. No considerable swelling was observed in case of EPDM, and, thus, D does not seem to depend strongly on concentration for this system. However, for NBR and PU membranes, we could observe sharp maxima. Similar observations were found earlier³⁶ for diffusion of toluene in natural rubber.

The permeability coefficient P is a product of maximum sorption Q_∞ and diffusivity D . However, the equilibrium sorption Q_∞ or S may be regarded as the equilibrium sorption constant designated by the symbol K_s . The simple relationship $P = D \cdot S$ holds for the permeation process when D obeys Fick's law and S obeys Henry's law. It is not certain to what degree with the polymer-solvent systems used in this study one or both the laws are actually obeyed. Thus, P values presented in Table VI are

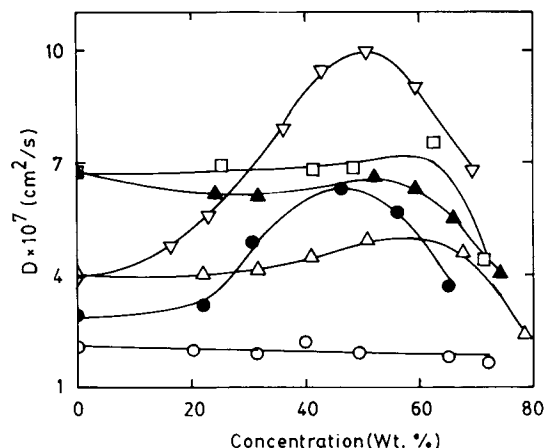


Figure 5 Dependence of diffusion coefficients D on penetrant concentration for methyl acetate with all membranes at 25°C. Symbols: (○) EPDM; (△) CR; (□) NR; (▽) NBR; (▲) SBR; (●) PU.

to be considered as estimates of the permeability coefficients expressed in the same units as those of diffusivities. We could not observe any systematic variation of permeability data with the penetrant size. For EPDM and NR membranes, P values increase with solvent size (from methyl acetate to *n*-butyl acetate; see Table VI); however, with NBR and PU membranes, P values decrease from methyl acetate to *iso*-amyl acetate.

Arrhenius Activation Parameters

The diffusion coefficient has been observed to follow an Arrhenius relationship characteristic of an activated process:

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

Here E_D is the activation energy required to produce an opening between polymer chains large enough to allow the penetrant molecule to diffuse. The activation energy is a function of the intra- and inter-chain forces that must be overcome in order to create the space for a unit diffusional jump of the penetrant molecule. E_D will be greater the larger the penetrant molecule, the stronger the polymer cohesive energy, and the more rigid the chains. The preexponential factor D_0 is considered as a measure of the density and size of free volume.

Similarly, over a reasonable temperature range, the apparent solubility coefficient S can be expressed in terms of the van 't Hoff relationship and a preexponential factor S_0 :

$$S = S_0 \exp(-\Delta H_S/RT) \quad (6)$$

Table VI Permeability Coefficients ($P \times 10^7$, cm²/s) for Polymer-Solvent Systems at Various Temperatures

Solvent	Temp (°C)	EPDM	CR	NR	NBR	SBR	PU
Methyl acetate	25	0.131	0.927	1.135	4.540	1.537	1.949
	40	0.513	1.657	2.354	6.497	2.513	3.459
	50	0.599	2.076	3.258	8.467	3.370	3.877
Ethyl acetate	25	0.391	1.697	2.525	2.687	3.240	1.368
	44	0.984	2.849	4.702	4.133	5.593	2.429
	60	1.700	3.797	6.927	5.492	7.470	3.633
<i>n</i> -Propyl acetate	25	0.435	1.495	3.212	1.411	3.569	0.873
	44	1.175	2.694	5.684	2.441	5.569	1.741
	60	2.067	3.659	7.077	3.546	7.616	2.417
<i>n</i> -Butyl acetate	25	0.563	1.329	3.251	0.747	3.333	0.567
	44	1.452	2.502	5.424	1.497	5.619	1.152
	60	2.366	3.099	7.645	2.136	7.687	1.804
<i>iso</i> -Amyl acetate	25	0.415	0.688	2.165	0.234	1.929	0.346
	44	1.045	1.498	4.298	0.582	3.431	0.652
	60	1.836	2.163	6.270	0.936	5.405	1.046
Methyl acetoacetate	25	0.005	—	0.022	0.668	0.031	0.116
	44	0.022	0.074	0.107	1.950	0.119	0.374
	60	0.057	0.168	0.295	3.051	0.187	0.706
Ethyl acetoacetate	25	0.009	0.052	0.057	0.881	0.064	0.162
	44	0.044	0.179	0.205	1.919	0.218	0.442
	60	0.114	0.405	0.419	2.979	0.452	0.797
Methyl salicylate	25	0.106	0.494	0.663	0.454	1.103	0.295
	44	0.446	1.464	1.877	1.478	2.537	0.816
	60	0.957	2.560	3.175	3.063	4.322	1.539

Here the heat of sorption, ΔH_S , is a composite parameter involving both Langmuir and Henry's sorption mechanisms. It may be realized¹⁴ that S has the same meaning as Q_∞ or K_S . Henry's law mode requires both the formation of a site and the dissolution of the species into that site. The formation of a site generally involves an endothermic contribution to this process. In the case of Langmuir mode, the site already exists within the polymer matrix, and, hence, sorption by hole filling produces more exothermic heats of sorption. By substituting eqs. (5) and (6) into $P = D \cdot S$ and expressing permeability in terms of Arrhenius relationship, we get

$$P = P_0 \exp(-E_P/RT) \quad (7)$$

where

$$E_P = E_D + \Delta H_S \quad (8)$$

The least-squares estimations of E_D , ΔH_S , and the calculated values of E_P are given in Table VII.

From a knowledge of the structures of esters used (Table I), activation energies (E_P and E_D), and the heats of sorption (ΔH_S), one can tentatively interpret the sorption results. NBR, CR, and PU membranes possess segments with polar sites where interaction might occur possibly with polar ester molecules. However, polymers like EPDM, NR, and SBR with no significant sorption contain no polar groups. A suggested mechanism for ester interactions with these membranes is not possible from the present experimental data. However, it is tempting to conjecture that the interaction might occur probably through the dipole or van der Waals forces. Furthermore, the negative ΔH_S values for NBR + several solvents are suggestive of the presence of a Langmuir mode of sorption. For a majority of polymer-solvent systems, ΔH_S is positive, suggesting Henry's mode of sorption, and the activation parameters (E_D , E_P , and E_A) do not seem to bear any relationship with the size of the ester molecules. In general, the molecular shape and the flexibility of ester molecule influence directly the transport data than the size, i.e., the molar volume.³⁷

Table VII Activation Parameters and Thermodynamic Functions for Polymer-Solvent Systems

Solvent	Parameter (kJ/mol)	EPDM	CR	NR	NBR	SBR	PU
Methyl acetate	E_D	40.20	22.39	25.67	20.39	18.06	18.91
	E_A	34.29	21.96	20.49	21.20	15.52	17.82
	E_P	50.72	26.19	34.10	19.79	25.13	22.73
	ΔH_S	10.52	3.80	8.43	-0.60	7.07	3.82
Ethyl acetate	E_D	24.64	18.95	18.28	18.19	17.35	22.59
	E_A	25.00	16.94	14.54	17.16	15.14	20.94
	E_P	34.90	19.15	23.94	16.94	19.89	23.11
	ΔH_S	10.26	0.20	5.66	-1.25	-2.21	0.52
<i>n</i> -Propyl acetate	E_D	28.24	22.28	15.09	23.89	16.64	25.37
	E_A	24.71	23.00	15.71	21.35	14.98	23.10
	E_P	37.04	21.32	18.93	21.82	17.93	24.29
	ΔH_S	8.80	-0.96	3.84	-2.07	1.29	-1.08
<i>n</i> -Butyl acetate	E_D	27.04	21.06	14.92	26.78	19.75	27.42
	E_A	25.95	24.51	16.81	24.98	17.99	24.88
	E_P	34.19	20.33	20.25	25.03	19.84	27.44
	ΔH_S	7.15	-0.73	5.33	-1.75	0.09	0.02
<i>iso</i> -Amyl acetate	E_D	28.74	28.81	19.77	34.40	23.57	26.21
	E_A	24.81	25.68	18.45	27.94	22.58	24.61
	E_P	35.29	27.33	25.29	33.03	24.31	26.13
	ΔH_S	6.55	-1.48	5.52	-1.37	0.74	-0.08
Methyl acetoacetate	E_D	46.62	—	47.25	33.53	35.21	36.62
	E_A	36.48	—	38.75	28.02	28.03	33.12
	E_P	59.25	—	62.11	36.41	43.27	43.05
	ΔH_S	12.63	—	14.86	2.88	8.06	6.43
Ethyl acetoacetate	E_D	50.66	52.63	37.29	28.23	37.18	33.17
	E_A	43.37	50.36	34.42	26.60	35.53	31.90
	E_P	61.22	48.63	47.52	28.95	46.58	37.77
	ΔH_S	10.56	-4.00	10.28	0.72	9.40	4.60
Methyl salicylate	E_D	40.43	39.08	26.51	45.66	29.33	36.93
	E_A	34.95	34.75	22.13	36.40	31.17	37.56
	E_P	52.37	39.19	37.32	45.29	32.37	39.18
	ΔH_S	11.94	0.11	10.81	-0.37	3.04	2.25

CONCLUSIONS

The solvent transport parameters have been estimated for a variety of polymer-solvent systems from the immersion/weight-gain method, and these data are discussed in terms of the size, shape, and chemical nature of the ester molecules. The temperature and concentration dependencies of the transport parameters are also studied. The result of this study indicate that several factors can adversely affect the polymer membrane: time, temperature, and mechanical stress. Although the last two are usually considered when designing a piece of hardware, the first one is not always taken into account. Part of the reason for disregarding time is the lack of reliable aging information. In order to evaluate a materials

lifetime expectancy in a short laboratory test, the temperature is increased, and a time-temperature relationship is sought for some property of the material; of course, there is a limit as to how high the temperature can be (e.g., 80–90°C for most elastomers) without inducing extraneous and unrealistic chemical reactions. A temperature interval of 25–60°C appears to be a reasonable range for the investigation in such systems, and no chemical degradative reactions appear to take place in this interval of temperature.

Typically, the present approach seems to be effective for screening the available polymer materials for a particular application, but not optimum for providing guidelines to improve membrane performance by scientific alteration of the polymer

structure. As an adjunct to this typical approach, correlations of penetrant diffusion coefficients and solubilities with the chemical and physical characteristics of the polymers and penetrants have been discussed with a hope of rationalizing the influence of the size and shape of the penetrant molecules on the transport parameters.

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