

Diffusivity and Solubility of Organic Vapors in Modified Polyethylene Films. II. Diffusivity Studies

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Synopsis

The diffusion coefficient at zero concentration and the free volume parameters in Fujita's free volume theory were measured for benzene, hexane, and heptane in modified polyethylene films using an unsteady-state absorption technique. Films were modified by gamma irradiation, solvent conditioning, and post- and preirradiation conditioning. $D_{c=0}$ was found to drop with irradiation, the drop being larger the larger the molecular size of the diffusing molecule. A relationship for the dependence of $D_{c=0}$ on the crosslink density is proposed. Solvent conditioning led to an increase in $D_{c=0}$ directly proportional to the swelling power of the conditioning agent and to the molecular size of the diffusant molecule. In most cases, combined treatment resulted in an increase in $D_{c=0}$, the extent of which was dependent upon the relative effect of the swellant and the irradiation dose. In all cases, postirradiation conditioning led to values of $D_{c=0}$ higher than those obtained by preirradiation conditioning. The fractional free volume of the polymer was found to decrease with irradiation, showing a marked drop at low doses when reaching a state where the dose was of small effect. Changes in $f(0, T)$ with conditioning and with combined treatment followed the same general pattern as $D_{c=0}$. $\beta(T)$ was unaffected by any kind of treatment studied. B_d changed in practically the same manner as $f(0, T)$ but in the opposite direction. A method is proposed for the optimum choice of a membrane modification procedure based on solubility and diffusivity results.

INTRODUCTION

The study of transport of small molecules in polymer membranes has attracted much attention in recent years. Most of the work done was carried out in the field of gas permeation, where the studies are morphological and rather academic in nature. In the area of liquid and vapor transport, more attention has been directed toward the phenomenological aspects in binary separation than to the basic principles involved in permeation of a single species. Whereas the former approach is more applied in nature, the study of transport properties of pure components in polymeric films furnishes the basic knowledge required for the design and choice of a membrane for a binary separation process.

Determination of the diffusion coefficient has mostly been carried out through permeability measurements.¹⁻⁴ The concentration dependence of the diffusion coefficient necessitates the introduction of some simplifying assumptions such as a certain concentration profile within the membrane, the use of data of the early stages where enough accuracy is not guaranteed, or through time lag measurements. Experimental evidence, backed by theoretical justifications, indicates that sorption techniques are more fit for such jobs than permeation techniques. Fels and Huang⁵ proposed a desorption technique for diffusion

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coefficient measurement. However, absorption techniques prove to be superior to desorption techniques, both from the experimental point as well as in simplicity of analysis of the data.⁶ Many models for the concentration dependence of the diffusion coefficient of vapors and liquids have been proposed. Fujita's basic model for the free volume of polymer-diluent systems⁷ and its extension to diffusion processes¹ will be adopted in this paper.

Polymeric films can be modified by relatively simple means. Michaels et al.^{8,9} found that by annealing polyethylene films in several solvents, their permeation and separation characteristics could be largely enhanced. However, these results were only temporary. Similar results were obtained by Pasternak et al.³ Siegel and Coughlin¹⁰ found that irradiation of the fully swollen membrane leads to a more permanent effect. However, the permanence took place at the expense of reduced selectivity. Crosslinking of polyethylene led to an increase in its permeability toward many hydrocarbons.¹¹ Furthermore, Kanitz and Huang¹² found that the atmosphere of irradiation plays an important role in the final properties of the irradiated films. They also found that the destruction of crystallites may occur at high irradiation doses.

It is the purpose of this paper to study the effect of gamma irradiation-induced crosslinking, solvent conditioning, and combinations of these treatments on the diffusion coefficient and the free volume parameters for some organic vapors in polyethylene, using the absorption technique described earlier.⁶

EXPERIMENTAL

The apparatus, experimental procedure, and analysis of results are described elsewhere.⁶ In essence, a sample of the polymer film is subjected to a steady stream of the vapor at constant temperature and pressure. The weight of the sample is continuously measured using a Cahn electrobalance. From the equilibrium weight increase of the sample, the solubility can be determined. Samples used were 7×1.5 cm each, weighing about 150 mg.

Materials. The polyethylene film was supplied by the Plastic Film Division of Canadian Industries Limited, Toronto, Ontario. It contained no plasticizer or antiblock agents. Its density was 0.9157 g/ml; its melt index, 7 g/10 min; and its, thickness 10 mil.

Benzene, *n*-hexane, and *n*-heptane used were obtained from Fisher Scientific Co. and were spectroscopically pure, reagent-grade chemicals. They were used without further purification.

Modification of Films. The films were modified by simple γ irradiation, simple solvent conditioning, preirradiation conditioning, or postirradiation conditioning. Solvents used in the conditioning of the films were benzene, hexane, and heptane, which were used as diffusants as well.

Solvent Conditioning. The films, cut to the proper dimensions, were fully immersed in the solvent in a vapor-tight glass container. This was immersed in a water bath regulated at $60^\circ \pm 0.1^\circ\text{C}$ for 24 hr. Directly after the treatment, the films were vacuum dried for 24 hr to remove most of the solvent without weight recording. Then they were vacuum dried to constant weight. Experiments on conditioned samples were conducted within four days of this procedure, while γ irradiation was performed directly after it.

Gamma Irradiation. The films, cut to the proper dimensions, were placed

in a vacuum ampoule and evacuated for 24 hr. The ampoule was then sealed and subjected to gamma ray irradiation at a dose rate of 0.6 ± 0.007 Mrad/hr at 33–35°C. The source employed was a Co-60 Gamma-Cell 220 irradiation unit located at the Chemical Engineering Department, University of Waterloo. The cell was manufactured by the Commercial Products Division, Atomic Energy of Canada Ltd. Samples were subjected to total doses of 3.6, 9, 15, and 30 Mrad, corresponding to 6, 15, 25, and 50 hr, respectively, of irradiation. In combined treatment, samples were subjected to the second stage of modification right after the first stage.

Nomenclature. The membranes were designated so as to distinguish the nature and the sequence of treatment. Conditioning in benzene, hexane, and heptane was designated by the symbols B, X, and P, respectively. Unconditioned membranes were designated by the symbol U. Irradiation was designated by $I(n)$, where n is the number of hours the membranes were subjected to γ irradiation at a dose rate of 0.6 Mrad/hr. Combined treatment was designated by a combination of symbols arranged in the order of treatment. For example: PI50 designates a membrane conditioned in heptane prior to irradiation for 50 hr, I50X indicates a membrane irradiated for 50 hr and then conditioned in hexane, while I00U stands for the unirradiated unconditioned film, and I00P is a film modified by conditioning in heptane without any pre- or postconditioning irradiation.

RESULTS AND DISCUSSION

According to Fujita's free volume theory,⁶⁻⁸ the diffusion coefficient D is related to molar mobility m by

$$D = RTm \quad (1)$$

where m is defined by

$$m = A_d \exp \left\{ \frac{-B_d}{f(V_p, T)} \right\} \quad (2)$$

and

$$f(V_p, T) = f(0, T) + \beta(T)V_p \quad (3)$$

where A_d is a quantity dependent upon the size and shape of the diffusant molecule; B_d is a measure of the volume which must be cleared, or the minimum hole required, in order that a successful diffusion step may occur; $f(V_p, T)$ is the fractional free volume of a polymer-diffusant mixture at temperature T , in which the volume fraction of the diffusant is V_p ; $f(0, T)$ is the fractional free volume of the pure polymer; $\beta(T)$ is a proportionality constant describing the change in the fractional free volume of the system with diffusant concentration and is temperature dependent.

From these basic postulates Huang et al.^{5,6} arrived at the following expression for the diffusion coefficient:

$$D = D_{c=0}(1 - V_p)^3 \exp \left\{ \frac{V_p}{a + bV_p} \right\} \quad (4)$$

where

$$a = \frac{[f(0, T)]^2}{B_d \beta(T)}, \quad b = \frac{f(0, T)}{B_d}$$

and $D_{c=0}$ is the diffusion coefficient at zero concentration.

Determination of the four parameters in eq. (4) was carried out according to the method described in detail earlier.⁶ Briefly, this is a method of finding the set of parameters that would give the same weight increase-time relationship as obtained experimentally.

Diffusion Coefficient at Zero Concentration, $D_{c=0}$

Values of $D_{c=0}$ obtained for each run were within $\pm 1\%$ of the average value reported here. Individual experiments gave results with an average of $\pm 2\%$ deviation from the final average value. These values are listed in Tables I-IV, together with the difference relative to the values of the untreated film at the same temperature.

Table IV typifies the reproducibility of the method. Results of duplicate runs on the absorption of heptane at 35°C in membranes treated by solvent annealing in hexane are shown. The values of $D_{c=0}$ and the free volume parameters are also shown as they were calculated at 20% intervals of the experimental time. The difference between the calculated and observed amount absorbed is also shown.

The expression for the diffusion coefficient contains separate terms for the effect of the diffusant, and the effect of its concentration on the segmental mobility and the free volume of the polymer. Such distinction leads to a deeper understanding of the phenomena occurring during the diffusion process. While the free volume parameters determine the overall available free volume within the polymer network, $D_{c=0}$ may be useful in determining its distribution. It may be possible to treat $D_{c=0}$ in a manner analogous to the diffusion coefficient of simple gases in polymer films.

TABLE I
 $D_{c=0}$ Values of Heptane, in $(\text{cm}^2/\text{sec}) \times 10^9$

Film no.	Film	25°C		30°C		35°C		$\Delta E_{D,c=0}$
		$D_{c=0}$	% Change	$D_{c=0}$	% Change	$D_{c=0}$	% Change	
1	I00U	1.22	0.00	1.63	0.00	2.19	0.00	-10.68
2	I00P	1.44	18.03	1.93	18.40	2.55	16.44	-10.43
3	I00B	1.37	12.30	1.87	14.12	2.48	13.24	-10.83
4	I00X	1.41	15.57	1.91	17.18	2.51	14.61	-10.52
5	I06U	1.00	-18.44	1.37	-15.95	1.86	-15.07	-11.42
6	I15U	0.96	-20.90	1.33	-18.40	0.73	-21.00	-10.65
7	I25U	0.93	-24.18	1.25	-23.31	1.61	026.48	-10.11
8	I50U	0.88	-28.20	1.14	-30.06	1.44	-34.24	-9.07
9	I25P	1.58	29.51	2.10	28.83	2.80	27.85	-10.45
10	PI25	1.53	25.41	2.03	24.54	2.70	23.29	-10.37
11	I25B	1.39	13.93	1.81	11.04	2.56	16.90	-11.17
12	BI25	1.30	6.56	1.71	4.91	2.43	10.96	-11.44
13	I25X	1.48	21.31	1.99	22.09	2.61	19.18	-10.35
14	XI25	1.34	9.84	1.81	11.04	2.50	14.16	-11.39
15	I50P	1.51	23.77	2.04	25.15	2.76	26.03	-11.01
16	PI50	1.41	15.57	1.92	17.79	2.57	17.35	-10.96
17	I50B	1.19	-2.46	1.58	-3.06	2.13	-2.74	-10.63
18	BI50	1.13	-7.38	1.45	-11.04	2.01	-8.22	-10.53
19	I50X	1.31	7.38	1.66	1.84	2.43	10.96	-11.31
20	XI50	1.25	2.46	1.63	0.00	2.25	2.74	-10.74

TABLE II
 $D_{c=0}$ Values of Hexane, in (cm²/sec) $\times 10^9$

Film no.	Film	25°C		30°C		35°C		$\Delta E_{D_{c=0}}$
		$D_{c=0}$	% Change	$D_{c=0}$	% Change	$D_{c=0}$	% Change	
1	I00U	1.35	0.00	1.84	0.00	2.45	0.00	-10.88
2	I00P	1.51	11.85	2.03	10.33	2.75	12.24	-10.95
3	I00B	1.42	5.19	1.94	5.43	2.65	8.16	-11.39
4	I00X	1.47	8.89	1.99	8.15	2.71	10.61	-11.17
5	I06U	1.11	-17.78	1.51	-17.93	2.02	-17.55	-10.93
6	I15U	1.09	-19.26	1.46	-20.65	1.96	-20.00	-10.71
7	I25U	1.05	-22.22	1.33	-27.72	1.74	-28.98	-9.23
8	I50U	0.92	-32.22	1.29	-29.89	1.61	-34.29	-10.29
9	I25P	1.66	22.96	2.17	17.93	3.00	22.45	-10.82
10	PI25	1.59	17.78	2.11	14.67	2.81	14.69	-10.40
11	I25B	1.44	6.67	2.02	9.78	2.63	7.35	-10.98
12	BI25	1.36	0.74	1.76	-4.35	2.43	-0.82	-10.61
13	I25X	1.51	11.85	2.05	11.41	2.74	11.84	-10.88
14	XI25	1.44	6.67	1.97	7.07	2.67	8.98	-11.27
15	I50P	1.79	32.59	2.42	31.52	3.22	31.43	-10.72
16	PI50	1.60	18.52	2.27	23.37	3.01	22.86	-11.53
17	I50B	1.25	-7.41	1.73	-5.98	2.28	-6.94	-10.97
18	BI50	1.21	-10.37	1.65	-10.33	2.18	-11.02	-10.74
19	I50X	1.64	21.48	1.99	8.15	2.52	2.86	-7.85
20	XI50	1.54	14.07	1.92	4.35	2.40	-2.04	-8.10

 TABLE III
 $D_{c=0}$ Values of Benzene, in (cm²/sec) $\times 10^9$

Film no.	Film	25°C		30°C		35°C		$\Delta E_{D_{c=0}}$
		$D_{c=0}$	% Change	$D_{c=0}$	% Change	$D_{c=0}$	% Change	
1	I00U	1.43	0.00	2.21	0.00	3.37	0.00	-15.65
2	I00P	1.62	13.29	2.52	14.03	3.84	13.95	-15.76
3	I00B	1.48	3.50	2.31	4.52	3.55	5.34	-15.97
4	I00X	1.52	6.29	2.35	6.33	3.60	6.82	-15.74
5	I06U	1.33	-6.99	2.10	-4.98	3.17	-5.93	-15.85
6	I15U	1.29	-9.79	2.02	-8.60	3.14	-6.82	-16.24
7	I25U	1.25	-12.59	1.89	-14.48	2.85	-15.43	-15.05
8	I50U	1.19	-16.78	1.74	-21.27	2.51	-25.52	-13.63
9	I25P	1.72	20.28	2.63	19.00	3.98	18.10	-15.32
10	PI25	1.66	16.08	2.59	17.19	3.95	17.21	-15.83
11	I25B	1.54	7.69	2.46	11.31	3.88	15.13	-16.87
12	BI25	1.53	6.99	2.41	9.05	3.77	11.87	-16.47
13	I25X	1.61	12.59	2.59	17.19	3.94	16.91	-16.33
14	XI25	1.57	9.79	2.51	13.57	3.91	16.02	-16.66
15	I50P	2.11	47.55	2.93	32.58	4.01	18.99	-11.72
16	PI50	1.95	36.36	2.75	24.43	3.97	17.80	-12.99
17	I50B	1.77	23.78	2.51	13.57	3.66	8.61	-13.27
18	BI50	1.57	9.79	2.35	6.33	3.40	0.89	-14.10
19	I50X	2.00	39.86	2.86	29.41	3.91	16.02	-12.23
20	XI50	1.71	19.58	2.59	17.19	3.85	14.24	-14.82

An increase in temperature was found to lead to an increase in the value of $D_{c=0}$ for all diffusant-film pairs. An Arrhenius-type plot was plotted for each pair and an energy factor was calculated. An example of these plots is shown in

TABLE IV
Comparison of Two Duplicate Runs for the Absorption of Heptane in 100X at 35°C

	Run 1	Run 2
Dry weight, mg	171.24	157.28
Amount absorbed, mg	8.83	8.13
Solubility, % wt/wt	5.16	5.18
Time, sec	1680	1790
After 20%		
$D_{c=0}$, (cm ² /sec) × 10 ⁹	2.57	2.51
$f(0,T)$	0.0358	0.037
$\beta(T)$	0.36	0.35
Difference in weight, mg (calcd - observed)	+0.0059	-0.0072
After 40%		
$D_{c=0}$	2.59	2.53
$f(0,T)$	0.038	0.0385
$\beta(T)$	0.347	0.35
Difference in weight	+0.072	-0.000
After 60%		
$D_{c=0}$	2.56	2.53
$f(0,T)$	0.037	0.037
$\beta(T)$	0.37	0.36
Difference in weight	-0.005	+0.011
After 80%		
$D_{c=0}$	2.59	2.57
$f(0,T)$	0.039	0.040
$\beta(T)$	0.39	0.36
Difference in weight	+0.080	+0.102
After 100%		
$D_{c=0}$	2.58	2.58
$f(0,T)$	0.037	0.036
$\beta(T)$	0.35	0.36
Difference in weight	+0.102	+0.137

Figure 1. The values of these factors are reported in Tables I-III. Due to the practical limitations on the attainable temperatures these values should be considered approximate and will be used to show the general trend without attaching emphasis on their numerical values. The diffusion coefficient contains other temperature-dependent terms, therefore this energy factor should not be confused with the conventional activation energy of diffusion. For clarity this term will be called "the activation energy for diffusion at zero concentration, $\Delta E_{D,c=0}$."

It was found that $\Delta E_{D,c=0}$ was highest for benzene and lowest for heptane and increased slightly with conditioning. Irradiation leads to a decrease in its value, the effect being more marked at higher doses. Post- or preirradiation conditioning of films in benzene leads to almost the same value of $\Delta E_{D,c=0}$ irrespective of the treatment sequence. This is due to the low swelling power of benzene with a limited effect on the segmental mobility. The same was observed for heptane conditioning, yet it stems from another source, namely, the strong effect of heptane-conditioning on the segmental mobility which curtails the impedance introduced by radiation-induced crosslinking. Postirradiation conditioning in hexane leads to higher values of $\Delta E_{D,c=0}$ for hexane and lower values for benzene and heptane than those in films conditioned in hexane before irradiation. The difference between heptane and hexane as diffusants may be attributed to

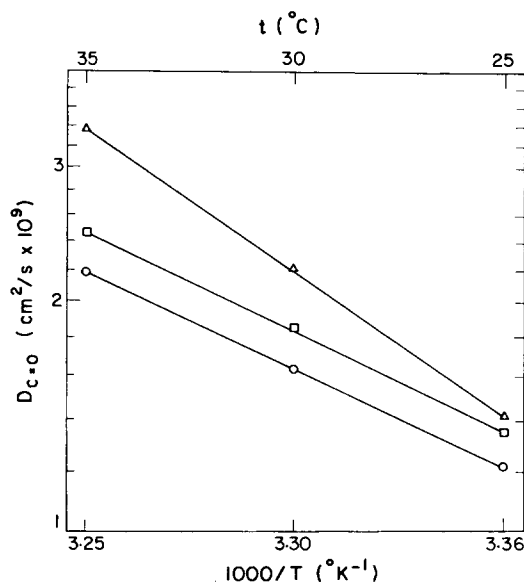


Fig. 1. Effect of temperature on $D_{c=0}$ for benzene, hexane, and heptane in unmodified films: (Δ) benzene; (\square) hexane; (\circ) heptane.

the smaller swelling action of hexane as well as its smaller molecular size. Distinction between hexane and benzene, as diffusants, results from the difference in their chemical nature and molecular shape.

It was also found the $D_{c=0}$ values were highest for benzene and lowest for heptane in all films. This is in agreement with the order of their molecular size.

Another way of looking at the effect of temperature on the diffusion process is by evaluating the activation energy of the diffusion process. In general, the temperature dependence of the diffusion coefficient is given by

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

from which we can define ΔE as

$$\Delta E = RT^2 \left[\left(\frac{\partial D}{\partial T} \right) / D \right] \quad (6)$$

From eq. (4), it follows that for the particular model considered,

$$\Delta E = -(V_p RT^2) \{ f'(0, T) B_d \beta(T) [2 + V_p \beta(T)] - f(0, T) B_d' \beta(T) [1 + V_p \beta(T)] - f(0, T) [B_d' \beta(T) + \beta'(T) B_d] \} / [f(V_p, T)]^2 \quad (7)$$

where the prime indicates the derivative with respect to temperature.

This expression is different from the expression given by Pattle and Smith,¹⁴ since they did not consider the volume change due to the presence of the diffusant, and from the expression given by Moore and Ferry,¹⁵ since they assumed B_d to be a constant and equal to unity. Implicit in the derivation of eq. (7) is that χ , the Flory-Huggins interaction parameter, is independent of temperature. The validity of this assumption stems from the fact that $\partial \chi / \partial T$ is inversely proportional to T^2 .¹⁶ No attempt was made to calculate ΔE from eq. (7). Firstly, most of the films were conditioned and hence are not in a state of ther-

modynamic equilibrium. Secondly, the free volume parameters are not precise enough. (As will be shown later, accuracy of determination of the free volume parameters was $\pm 5\%$, which may lead to an error in ΔE of more than $\pm 10\%$.)

Untreated Films

Figure 1 shows an Arrhenius type plot for the three diffusants. Benzene has the highest values for $D_{c=0}$ and was the most affected by temperature, while heptane showed the lowest $D_{c=0}$ values. The slopes of the curves for hexane and heptane indicate a small difference in $\Delta E_{D,c=0}$. The high value of $\Delta E_{D,c=0}$ for benzene may be attributed to the chemical dissimilarity between benzene and polyethylene, and the difference in molecular shape between heptane and hexane on one hand and benzene on the other.

Conditioned Films

For all cases the diffusion coefficient increased with conditioning. The most effective conditioning solvent was heptane and the least effective was benzene. This is a result of their strength as network swelling agents as judged from their solubility parameters. Since benzene already possesses the highest $D_{c=0}$ values it was the least affected by this treatment. On the other hand, $D_{c=0}$ values of heptane were the most strongly affected. Changes in $\Delta E_{D,c=0}$ were almost the same for hexane and heptane, with hexane conditioning introducing a slightly higher change. The effect of benzene conditioning leads to the largest change

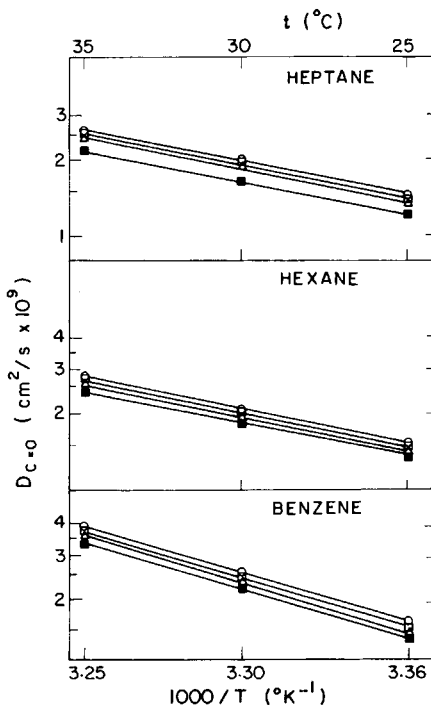


Fig. 2. Effect of temperature on the $D_{c=0}$ of heptane, hexane, and benzene in conditioned unirradiated films: (■) I0U; (○) I0P; (□) I0X; (△) I0B.

in $\Delta E_{D,c=0}$, as indicated by the slopes in Figure 2. This shows that the change in $\Delta E_{D,c=0}$ is inversely proportional to the swelling power. Combining this with the fact that changes in $D_{c=0}$ are directly proportional to the swelling power, an interesting fact emerges. At or around a certain higher temperature, the values of $D_{c=0}$ for conditioned and unconditioned films will be the same, irrespective of the swelling power of the conditioning solvent. This may be viewed in the following way: with the temperature rise the segmental mobility increases and some of the pockets forming during conditioning are destroyed. At the same time, the segmental mobility of untreated films increases to such an extent that the changes in segmental mobility induced by conditioning are inconsequential. At high temperatures the segmental mobility will be only slightly affected by conditioning, consequently $D_{c=0}$ will follow the same trend.

Irradiated Films

Irradiation leads to a decrease in all $D_{c=0}$ values relative to unirradiated films. The change was highest for heptane and lowest for benzene. This can be attributed to their molecular volume. The decrease was marked even at the lowest radiation dose and increased rapidly with the dose. These results are shown in Figure 3. The change, relative to untreated films, also increased with temperature. This change at "higher" doses, 15 and 30 Mrads, increased with temperatures at higher rates than did the change at "lower" doses, 3.6 and 9 Mrads. The limit between the higher and the lower doses changed with the diffusant. For benzene and hexane this limit was between 9 and 15 Mrads, while for heptane it was between 3.6 and 9 Mrads. Again this is a result of the difference in molecular size which can also be observed from values of $\Delta E_{D,c=0}$. These observations indicate that at a certain lower temperature, where the segmental mobility is too low to be affected by further crosslinking, $D_{c=0}$ should be independent of the crosslink density.

A semilogarithmic plot of $\log D_{c=0}$ versus the radiation dose (which is proportional to the crosslink density) gave a straight line for almost all cases (Fig.

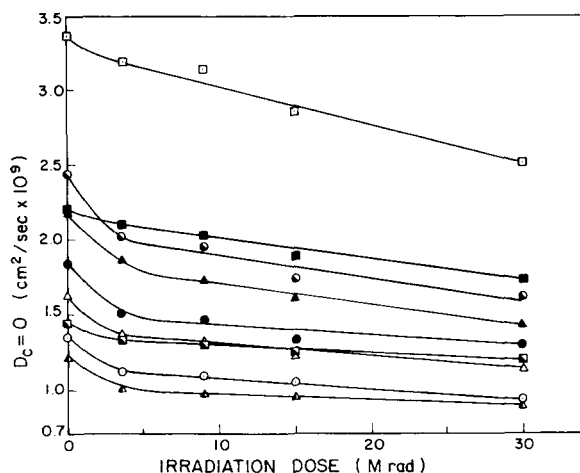


Fig. 3. Effect of irradiation on $D_{c=0}$ for unconditioned films. Benzene: (□) 25°C; (■) 30°C; (□) 35°C. Hexane: (○) 25°C; (●) 30°C; (●) 35°C. Heptane: (▲) 25°C; (▲) 30°C; (▲) 35°C.

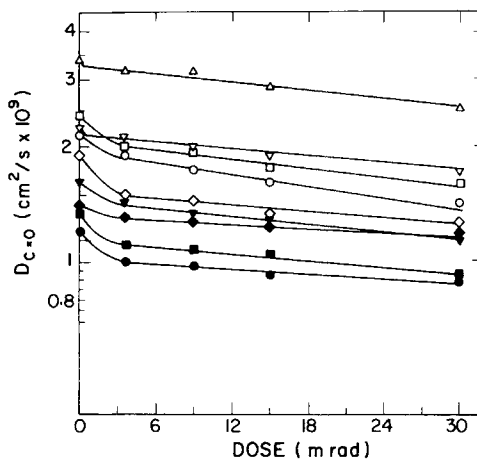


Fig. 4. Effect of irradiation dose $D_{c=0}$ of heptane, hexane, and benzene in unconditioned films. Heptane: (●) 25°C; (◆) 30°C; (○) 35°C. Hexane: (■) 25°C; (◇) 30°C; (□) 35°C. Benzene: (▼) 25°C; (▽) 30°C; (△) 35°C.

4). The values for the untreated films were always higher than the values obtained by extrapolating the straight line portion of the curve to zero irradiation dose. The following relationship is proposed to describe the dependence of $D_{c=0}$ on crosslink density:

$$D_{c=0,x} = D'_{c=0,0} \exp\{-f(M,T)x\} \quad (8)$$

where $D_{c=0,x}$ is the value of $D_{c=0}$ for a diffusant in a film in which the crosslink density is x , $D'_{c=0,0}$ is the value of $D_{c=0}$ obtained by extrapolating this line to zero crosslink density, $f(M,T)$ is a function of the diffusant-film pair and temperature, and x is the crosslink density.

The value of $D'_{c=0,0}$ has limiting values equals to $D_{c=0}$ for the uncrosslinked film at the melting point of the polymer and its T_g . The value of the function $f(M,T)$ should be positive and should be increasing monotonically with either the temperature or the molecular size of the diffusant. The data available in this work are too limited to suggest an appropriate form for this function. Values of $D'_{c=0,0}$ and $f(M,T)$ are shown in Table V.

Combined Treatment

The values of $D_{c=0}$ and their change with treatment depended mainly on the diffusant and to a large extent on the sequence of the treatment. The order of $D_{c=0}$ values of the three diffusants remained the same. Conditioning followed by irradiation leads to higher $D_{c=0}$ values than those obtained from postirradiation.

TABLE V
 $D'_{c=0,0}$ and $f(M,T)$ Values for Irradiated Polyethylene Films

Diffusant	25°C		30°C		35°C	
	$D'_{c=0,0}$	$f(M,T)$	$D'_{c=0,0}$	$f(M,T)$	$D'_{c=0,0}$	$f(M,T)$
Heptane	1.05	0.57	1.3	0.53	1.95	1.70
Hexane	1.2	0.93	1.55	0.87	2.1	1.63
Benzene	1.46	0.90	2.20	1.53	3.35	2.80

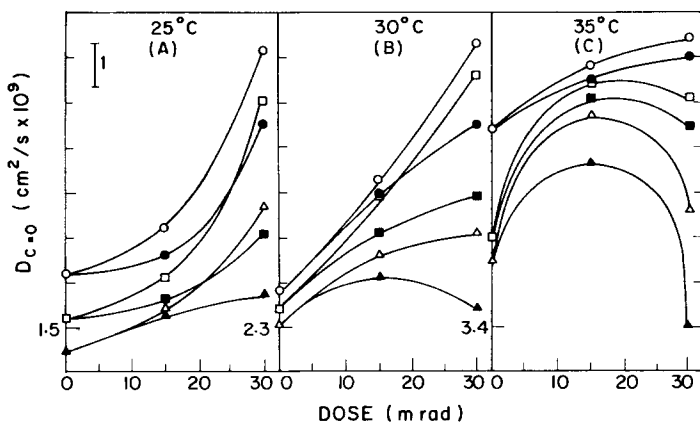


Fig. 5. Effect of irradiation dose on $D_{c=0}$ of benzene in conditioned films: (O) I(n)P; (●) PI(n); (□) I(n)X; (■) XI(n); (△) I(n)B; (▲) BI(n).

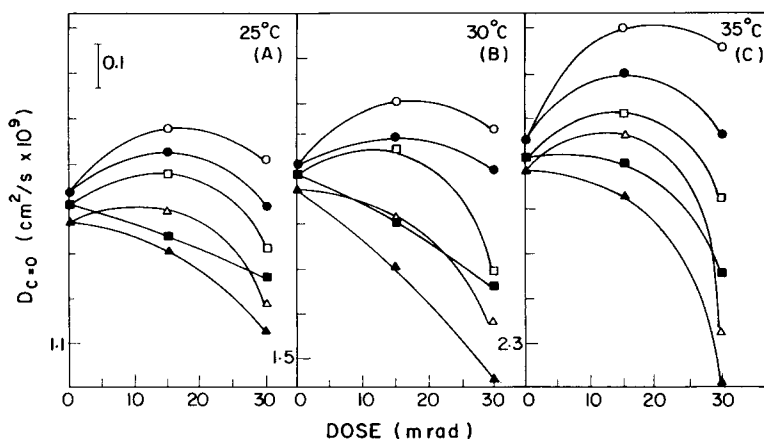


Fig. 6. Effect of irradiation dose on $D_{c=0}$ of heptane in conditioned films: (O) I(n)P; (●) PI(n); (□) I(n)X; (■) XI(n); (△) I(n)B; (▲) BI(n).

ation conditioning. This may be due to the destruction and/or distortion of pockets formed during conditioning.

For benzene at 25 and 30°C, $D_{c=0}$ values were higher even than those of unirradiated conditioned films. However, examination of Figures 5–7 shows a fundamental change. Although at 25°C, Figure 5(a), the values of $D_{c=0}$ seem to be increasing indefinitely with dose for all films, at 30°C, Figure 5(b), the rate with which they are increasing drops significantly. In two cases [I(n)B, XI(n)], they seem to be approaching a maximum. Films BI(n) already exhibit such a maximum with total dose. At 35°C, Figure 5(c), all films other than PI(n) and I(n)P exhibit such a maximum, with these two leveling off. The explanation for this difference in behavior is a relatively simple one. A diffusion step occurs as a result of the cooperative movement of several chain segments. It may be postulated that irradiation of conditioned films preserved the pockets formed during conditioning, since it is carried out only a short time after conditioning. Irradiation may also lead to destruction or distortion of these pockets. Conditioning of irradiated samples leads to the formation of such pockets in a relatively

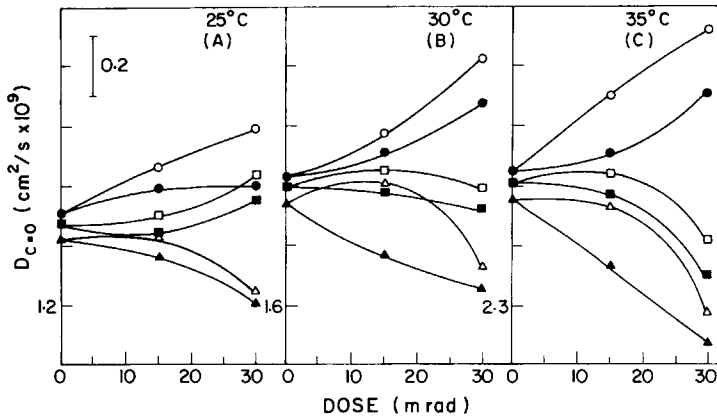


Fig. 7. Effect of irradiation dose on $D_{c=0}$ of hexane in conditioned films: (○) I(n)P; (●) PI(n); (□) I(n)X, (■) XI(n); (△) I(n)B; (▲) BI(n).

stable and rigid network. The extent to which these pockets are formed depends on the conditioning agent. Stronger swelling agents form more and larger pockets, since the solubility parameter difference decreases and solubility increases with increased molecular weight. The extent to which these pockets are preserved, as well as the rigidity of the network depends on the irradiation dose. All factors depend on the sequence of treatment. Preirradiation conditioning of the films leads to a more flexible network as compared to postconditioning of irradiated films. An increase in temperature leads to an increase in segmental mobility and hence the number of sites available for a successful diffusion step. Also the temperature rise leads to an increase in the molecular volume of the diffusant. Taking all these facts in consideration gives the required explanation.

The increase in the molecular volume of the diffusant with temperature is larger than the increase in the segmental mobility with temperature. At 25°C, the difference in segmental mobility between post- and preconditioned irradiated films is relatively small. The pockets are still well preserved. The degree to which these pockets are preserved increases with irradiation for the range studied. It follows, therefore, that $D_{c=0}$ increases with total dose. At 30°C, the increase in the segmental mobility for films BI(n), the one with the least number of pockets and the highest rigidity, is surpassed by the increase in the molecular volume of benzene. A maximum with respect to total dose is therefore attained. Slightly less rigid networks [I(n)B, XI(n)] approach a maximum. More flexible networks continue to increase. At 35°C, the more rigid networks, BI(n), I(n)B, XI(n), and I(n)X, exhibit a maximum. The drop, after reaching this maximum, is directly proportional to the network rigidity. On the other hand, the more flexible networks, PI(n) and I(n)P, level off.

This discussion leads to a very important point. A given value of $D_{c=0}$ for any diffusant may be obtained by the proper choice of the irradiation dose, the conditioning solvent, and the treatment sequence. However, the dose required to attain a certain value of $D_{c=0}$ is directly proportional to the swelling power of the conditioning solvent.

Equation (9) represents the free volume of the pure liquid. Implicit in this solution is the assumption that the free volumes of the polymer and the liquid are additive. This is not far from the real situation.⁵⁻⁸

Determination of these parameters was subject to some inaccuracies: they were very sensitive to changes in a and b , eqs. (4a) and (4b), while the concentration profile was not very sensitive to change in the latter quantities.⁵ a and b converged to within $\pm 3\%$ at each integration level. There was a slight though systematic increase in these values with progress of integration, i.e., with concentration, but the changes were still within $\pm 3\%$. This might be a result of the nonisothermal nature of the process. These errors resulted in Figures 1 and 2. Inspection of these figures, together with Tables I–III, shows that the difference between $D_{c=0}$ values for both modes of treatments decreased with temperature. These values drop, in certain cases, below the values for untreated films. These two observations, together with the fact that the effect of conditioning on $D_{c=0}$ decreases with temperature, leads to the fact that $D_{c=0}$ value approach a certain limit with increasing temperature. This limit might well be the value of $D_{c=0}$ of unconditioned films subjected to the same total dose.

The Free Volume Parameters

The free volume parameters $f(0, T)$, $\beta(T)$, and B_d were obtained from the solution of the expressions for a and b as given by eq. (4) simultaneously with

$$f(1, T_1) = f(1, T_2) + \alpha_l(T_1 - T_2) \quad (9)$$

where α_l is the thermal expansion of the diffusant.

Qualitatively, similar arguments hold for the cases of hexane, (Fig. 6) and heptane (Fig. 7). The quantitative difference, i.e., the point at which the curve reaches a maximum, depends on the molecular size of the diffusant, with the result that $D_{c=0}$ might drop below its value in the untreated film. The maximum shifted toward lower doses with increase in molecular size of the diffusant and with decrease in swelling power of the solvent.

As mentioned earlier, postconditioning irradiation results in a more rigid network relative to preconditioning irradiation. As a result $D_{c=0}$ values were always lower in the former case than they were in the latter. This is shown in Figures 5–7.

Examples of the effect of temperature of $D_{c=0}$ are shown in an average accuracy of determination of $f(0, T)$ and B_d of $\pm 6\%$; the error in $f(0, T)$ being inversely proportional to the total amount sorbed. $\beta(T)$, being not too sensitive to variations in a and b , can be taken as accurate to within $\pm 3\%$.

It was observed that $\beta(T)$ was hardly affected by any type of modification; changes being within $\pm 2\%$ in all systems studied, which is within the experimental and computational errors. $\beta(T)$ values were 0.34, 0.35, and 0.36 for heptane; 0.33, 0.34, and 0.35 for hexane, and 0.38, 0.39 and 0.41 for benzene at 25°, 30°, and 35°C, respectively. Although these values are very close, the trend of increase in $\beta(T)$ with temperature was obvious for all the films. These results indicate a slight increase with $\beta(T)$ with increase in chain length, as may be deduced from swelling power using the solubility parameter difference as a measure (solubility parameter δ for heptane 7.4, for hexane 7.3, and for polyethylene 7.7–8.4). From the small changes in $\beta(T)$ with modification, it may be concluded that $\beta(T)$ is a function of the diffusant and the chemical nature of the polymer chain.

Although B_d was the most sensitive to changes in a and b , the way in which it varied may lead to some interesting conclusions. The theory predicts that

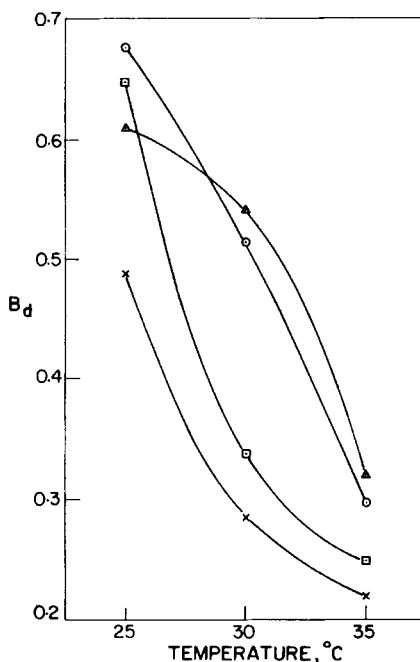


Fig. 8. Effect of temperature on B_d of benzene in unirradiated films: (x) unconditional; (O) conditioned in heptane; (□) conditioned in hexane; (Δ) conditioned in benzene.

B_d is independent of temperature. However, examination of eq. (1) shows that the increase in molecular mobility m must be accompanied by a decrease in B_d and/or increase in $f(V_p, T)$. It was observed that B_d values for hexane and heptane remained fairly constant in the temperature range considered, even though they showed a slight tendency to decrease with temperature. On the other hand, B_d values for benzene showed a marked decrease with temperature as exemplified by Figure 8. Such a difference in behavior may be attributed mainly to the difference in geometrical shape between benzene on one hand and hexane and heptane on the other. Hexane and heptane, being aliphatic as polyethylene, may, during diffusion, align themselves parallel to the chains thus requiring an extra volume, and hence the number of chains required to move so that a diffusion step may occur is small. Thus, the value of B_d and the number of degrees of freedom, in the sense of Barrer's theory,¹⁷ is slightly affected by temperature. In the case of benzene, although its molecular size is smaller, its shape is different from the network. Thus, for a benzene molecule to diffuse, it requires the movement of a larger number of chain segments. With increase in temperature, the mobility of the segments increases and the additional volume required to accommodate a diffusing benzene molecule decreases.

The third free volume parameter determined in this study is the fractional free volume of the pure polymer, $f(0, T)$. The values are listed in Tables VI–VIII. In most cases, the values obtained from heptane and benzene measurements agreed within experimental and computational error. Values obtained from hexane measurements were lower, due to the larger error expected in their determination. It was observed that $f(0, T)$ and $f(V_p, T)$, as calculated from eq. (3), changed in the same manner as the solubility.¹⁸ For the thermodynamically

TABLE VI
 $f(0,T)$ Values for Heptane

Film no.	Film	25°C		30°C		35°C	
		$f(0,T)$	% Change	$f(0,T)$	% Change	$f(0,T)$	% Change
1	I00U	0.0334	0.00	0.0317	0.00	0.0310	0.00
2	I00P	0.0409	22.37	0.0451	42.03	0.0345	11.23
3	I00B	0.0352	5.14	0.0366	15.43	0.0383	23.32
4	I00X	0.0439	31.36	0.0449	41.62	0.0358	15.45
5	I06U	0.0329	-1.78	0.0315	-0.58	0.0306	-1.21
6	I15U	0.0328	-2.07	0.0308	-2.99	0.0309	-0.34
7	I25U	0.0321	-3.92	0.0312	-1.71	0.0305	-1.67
8	I50U	0.0323	-3.43	0.0311	-1.90	0.0305	-1.76
9	I25P	0.0481	43.73	0.0470	48.27	0.0432	39.18
10	PI25	0.0354	5.84	0.0365	14.99	0.0317	2.06
11	I25B	0.0410	22.52	0.0424	33.76	0.0411	32.60
12	BI25	0.0356	6.43	0.0367	15.76	0.0358	15.52
13	I25X	0.0430	28.50	0.0448	41.23	0.0389	25.51
14	XI25	0.0396	18.33	0.0398	25.35	0.0423	36.51
15	I50P	0.0481	43.67	0.0447	40.86	0.0397	28.00
16	PI50	0.0379	13.38	0.0408	28.46	0.0379	22.18
17	I50B	0.0492	47.20	0.0463	45.99	0.0405	30.41
18	BI50	0.0379	13.41	0.0387	21.91	0.0316	1.96
19	I50X	0.0475	42.03	0.0473	49.20	0.0457	47.29
20	XI50	0.0407	21.68	0.0382	20.51	0.0377	21.42

 TABLE VII
 $f(0,T)$ Values for Hexane

Film no.	Film	25°C		30°C		35°C	
		$f(0,T)$	% Change	$f(0,T)$	% Change	$f(0,T)$	% Change
1	I00U	0.0136	0.00	0.0124	0.00	0.0114	0.00
2	I00P	0.0184	35.96	0.0152	22.74	0.0141	23.49
3	I00B	0.0141	4.16	0.0139	12.38	0.0137	19.29
4	I00X	0.0151	11.40	0.0142	14.33	0.0175	53.15
5	I06U	0.0124	-8.49	0.0123	-0.79	0.0114	-0.74
6	I15U	0.0123	-9.17	0.0114	-7.79	0.0112	-1.94
7	I25U	0.0121	-10.62	0.0115	-7.07	0.0104	-9.11
8	I50U	0.0121	-10.48	0.0111	-10.51	0.0100	-12.91
9	I25P	0.0143	5.67	0.0154	24.24	0.0154	34.65
10	PI25	0.0140	3.24	0.0226	82.31	0.0191	67.19
11	I25B	0.0182	34.02	0.0170	36.84	0.0115	0.56
12	BI25	0.0134	-1.24	0.0154	23.99	0.0167	45.80
13	I25X	0.0177	30.92	0.0185	49.06	0.0164	43.17
14	XI25	0.0114	-16.07	0.0147	18.38	0.0128	12.23
15	I50P	0.0164	21.00	0.0143	15.59	0.0146	27.17
16	PI50	0.0193	42.53	0.0172	38.47	0.0172	49.91
17	I50B	0.0177	30.47	0.0169	36.00	0.0119	3.67
18	BI50	0.0136	0.32	0.0127	2.33	0.0115	0.39
19	I50X	0.0215	58.76	0.0205	64.91	0.0219	91.23
20	XI50	0.0145	7.21	0.0141	13.58	0.0137	19.96

stable networks, i.e., the untreated and the simply irradiated, the effect of temperature was too small to be determined.

TABLE VIII
 $f(0, T)$ Values for Benzene

Film no.	Film	25°C		30°C		35°C	
		$f(0, T)$	% Change	$f(0, T)$	% Change	$f(0, T)$	% Change
1	I00U	0.0282	0.00	0.0207	0.00	0.0178	0.00
2	I00P	0.0351	24.41	0.0322	55.69	0.0251	40.96
3	I00B	0.0336	19.13	0.0241	16.84	0.0208	16.68
4	I00X	0.0322	14.19	0.0325	57.27	0.0250	40.36
5	I06U	0.0255	-9.62	0.0204	-1.53	0.0175	-1.72
6	I15U	0.0246	-12.99	0.0200	-3.44	0.0175	-1.80
7	I25U	0.0244	-13.53	0.0200	-3.40	0.0171	-4.36
8	I50U	0.0239	-15.39	0.0189	-8.70	0.0156	-12.44
9	I25P	0.0322	14.00	0.0273	32.22	0.0265	48.82
10	PI25	0.0362	28.29	0.0221	7.09	0.0203	13.89
11	I25B	0.0360	27.42	0.0242	16.98	0.0197	10.27
12	BI25	0.0327	15.82	0.0220	6.39	0.0203	14.09
13	I25X	0.0450	59.46	0.0259	25.40	0.0240	34.52
14	XI25	0.0303	7.37	0.0304	47.12	0.0247	38.54
15	I50P	0.0346	22.65	0.0290	40.28	0.0196	10.10
16	PI50	0.0349	23.42	0.0257	24.36	0.0232	30.13
17	I50B	0.0353	25.13	0.0226	9.11	0.0234	31.41
18	BI50	0.0302	6.92	0.0245	18.51	0.0214	19.74
19	I50X	0.0328	16.25	0.0253	22.58	0.0231	29.32
20	XI50	0.0314	11.32	0.0235	13.78	0.0207	16.12

Practical Applications

From the discussion of the effect of the combined irradiation conditioning treatment on the solubility¹⁸ and $D_{c=0}$, it was found that the relative change in these properties occur in a way dependent on the diffusant-conditioning pair, irradiation dose, and temperature. Furthermore, a given value of $D_{c=0}$ for the same diffusant may be obtained at two irradiation doses. From these results, a theoretical method may be developed for the optimum choice of a membrane for a binary separation process. Using the treatment and temperature conditions giving the maximum difference in $D_{c=0}$ and solubility, and putting their corresponding values together with the respective free volume parameters in the theoretical relationship for binary permeation developed by Huang and Fels,⁹ the choice may be made. This method eliminates the need for exploratory permeation runs. However, two difficulties underlie this approach. First, no accurate theoretical relationships have been developed for any of the above-mentioned properties. In the absence of such relationships, an experimental sorption study must be performed beforehand. Second, the free volume parameters cannot be determined accurately enough to predict the permeation behavior.

Since steady-state permeation occurs through practically fully swollen membranes, the combination of the solubility and diffusion coefficient results reported here for postirradiation conditioned films, give an explanation for the high permeabilities of irradiated films observed elsewhere.^{10,11}

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