

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

OSMAN T. ABOUL-NASR* and ROBERT Y. M. HUANG, *Chemical Engineering Department, University of Waterloo, Waterloo, Ontario, Canada*

Synopsis

A dynamic absorption technique was employed to determine the solubility of benzene, hexane, and heptane in modified polyethylene films. Films were modified by solvent annealing, crosslinking, and combinations thereof. Solvent annealing was found to increase the solubility while crosslinking led to its diminution. The effect of combined treatment on the solubility was found to be dependent on the sequence of treatment, the swelling power of the conditioning agent, and the irradiation dose. A slight effect of the solvent-diffusant pair was also observed. The solubility of the various vapors in crosslinked films was found to vary linearly with temperature. Solubility of some vapors in some of the conditioned films showed maxima with respect to temperature. The changes in solubility were explained in terms of the relative changes in the molecular volume of the diffusant and of the segmental mobility of the network chains with the various experimental conditions.

INTRODUCTION

The study of transport properties of small molecules in polymer films is of both academic and practical importance. First, it may help elucidate some of the complexities of the network structure. Second, it may lead to the appropriate design or choice of a certain membrane to suit a specific permselective process. Most of the studies in this field have been carried out on gas-polymer systems. On the other hand, less work has been done on vapors and liquids, where interactions between the diffusant and the membrane material lead to concentration dependence. Most of this work was concerned with binary permeant mixtures. In such systems, the complexities arising from the interaction between the individual diffusants and the membrane material is overshadowed by the effect of one component of the mixture on the transport properties of the other. It is therefore imperative to study the permeation of a single component as a preliminary step in elucidating both the characteristics of binary permeation processes and the design and choice of a membrane for a permselective duty. Furthermore, since permeability is a function of the solubility and the diffusivity, a study in which the separate determination of those properties is possible would help throw more light on the transport process than a classic permeation study. An unsteady-state absorption technique, featuring this characteristic was reported in an earlier work.¹

Modification of polymer films for vapor and liquid permeation processes has been done by several workers. Michaels et al.^{2,3} observed an increase in both the solubility and selectivity of various liquids in polyethylene conditioned in

* Present address: Department of Chemistry, University of Western Ontario, London, Ontario, Canada.

different solvents. They attributed this increase to either the formation of pockets in the amorphous regions during conditioning,² or the reduction in the effective crosslinking imposed on the amorphous regions by the crystallites.³ Such modifications were not permanent.³ Similar results were reported by Pasternak et al.⁴ Bent⁵ found that the solubility and permeability of small penetrants in polyethylene decreased with irradiation; while those of larger penetrants increased. Siegel and Coughlin⁶ found that irradiation of polyethylene in the fully swollen state leads to a permanent increase in its permeability toward benzene and toluene. It was reported⁷ that irradiation of high-pressure polyethylene with a dose of 30 Mrads leads to the inversion of the sorption isotherm of hexane, becoming concave downward instead of upward. Huang and Kanitz⁸ found that for the same total dose, air irradiation of polyethylene leads to a smaller crosslink density than vacuum irradiation. Fels and Huang⁹ found that grafting of polystyrene onto polyethylene leads to a marked increase in the solubility of benzene and, to a lesser extent, of hexane. These changes were attributed to the change in the solubility parameter of the network and the partial destruction of crystallites on grafting, respectively. Modification of polymer films by methods, other than those mentioned above, are beyond the scope of this work, therefore, they will not be discussed here.

It is the purpose of this study to employ the technique described in an earlier work¹ in investigating the effect of γ ray-induced crosslinking, solvent conditioning, and combinations thereof on the solubility of some hydrocarbons in polyethylene. Attempts will be made to relate the changes in solubility to the changes in free volume and the segmental mobility of the polymer network.

EXPERIMENTAL

The solubilities of the vapors in modified polyethylene films have been determined by measuring the equilibrium weight increase of films suspended in a stream of vapors. A Cahn electrobalance was used to determine the weight gain. Details of the experimental apparatus are reported elsewhere.¹ The accuracy of the balance was within ± 0.001 mg, representing less than $\pm 0.1\%$ of the total weight gain. Results were reproducible to within $\pm 2\%$ of the average results reported here. Usually the variation was less than $\pm 1\%$.

Benzene, *n*-hexane, and *n*-heptane were used both as vapors and as conditioning solvents. These were obtained from Fischer Scientific Co. and were reagent grade and spectroscopically pure. They were used without further purification. Polyethylene was supplied by the Plastic Film Division of the Canadian Industries Ltd., Toronto, Ontario. It contained no plasticizer or antiblock agents. Its density was 0.9157 g/cc, its melt index 7 g/10 min, and its thickness 10 mil.

The membranes were conditioned in either of the three solvents and/or subjected to γ irradiation at a dose rate of 0.6 Mrad/hr. Details of the modification procedures are reported in detail elsewhere.⁶ The membranes were designated according to the nature and to the sequence of treatment. Irradiation was designated by the symbol I(*n*), where *n* stands for the irradiation period in hours. B, P, and X stands for conditioning in benzene, heptane, and hexane, respectively, with U standing for unconditioned films. The sequence in which the symbols appear represents the sequence of modification. For example, XI25

stands for a membrane that was conditioned in hexane then irradiated for 25 hr, while I06U is a membrane irradiated for 6 hr without any solvent conditioning; and I50B is a membrane irradiated for 50 hrs and then conditioned in benzene.

Solubilities were measured at 25°, 30°, and 35° ± 0.1°C and under a pressure of 50 ± 3 mm Hg.

RESULTS AND DISCUSSION

Tables I–III show the results for all the films tested. Also shown are the percentage changes in the solubility due to various modifications relative to the untreated films.

It was noticed that the solubilities were little affected by temperature. This indicates a low heat of solution. For the thermodynamically stable films, the ones that were not modified by solvent conditioning, no general trend could be detected.

It was also noticed that heptane showed the highest solubility in all the membranes and hexane, the lowest. This can be discussed in terms of both the condensibility and the molecular size of the vapors. Condensibility can be defined as the tendency of the vapor to exist in the liquid state at a given temperature. Either the vapor pressure or the ratio of the experimental temperature to the critical temperature of the compound can be taken as an indicator for condensibility. The higher these values are, the lower the condensibility is. Ordering the three vapors in an increasing order of condensibility would give benzene, heptane, then hexane. The expected increasing order of solubility,

TABLE I
Solubility Results of Heptane (wt/wt × 100)

Film no.	Film	25°C		30°C		35°C	
		Solu-bility	Percent Change	Solu-bility	Percent Change	Solu-bility	Percent Change
1	I00U	4.046	0.00	3.993	0.00	3.910	0.00
2	I00P	5.035	24.44	6.233	56.10	5.219	33.48
3	I00B	4.662	15.22	5.278	32.18	5.163	32.05
4	I00X	4.919	21.58	5.840	46.26	5.321	36.09
5	I06U	3.902	-3.56	3.886	-2.68	3.760	-3.84
6	I15U	3.759	-7.09	3.650	-8.59	3.608	-7.72
7	I25U	3.745	-7.44	3.630	-9.09	3.512	-10.18
8	I50U	3.741	-7.54	3.538	-11.39	3.430	-12.28
9	I25P	6.066	49.93	6.257	56.70	5.963	52.51
10	PI25	5.668	40.09	5.645	41.37	5.224	33.61
11	I25B	5.796	43.25	6.002	50.31	5.938	51.87
12	BI25	5.000	23.58	5.382	34.79	5.027	28.57
13	I25X	5.700	40.88	5.967	49.44	5.492	40.46
14	XI25	5.183	28.10	5.663	41.82	5.430	38.87
15	I50P	6.135	51.63	6.220	55.77	6.002	53.50
16	PI50	5.046	24.72	4.875	22.09	4.999	27.85
17	I50B	5.943	46.89	6.036	51.16	5.683	45.35
18	BI50	4.864	20.22	5.805	45.38	4.421	13.07
19	I50X	6.102	50.82	6.261	56.80	5.852	49.67
20	XI50	5.024	24.17	4.952	24.02	4.816	23.17

TABLE II
Solubility Results of Hexane (w/w × 100)

Film no.	Film	25°C		30°C		35°C	
		Solubility	Percent Change	Solubility	Percent Change	Solubility	Percent Change
1	I00U	1.904	0.00	1.992	0.00	2.089	0.00
2	I00P	2.644	38.87	2.842	42.67	3.603	72.47
3	I00B	1.990	4.52	2.579	29.47	3.329	59.36
4	I00X	2.357	23.79	2.867	43.93	3.552	70.03
5	I06U	1.801	-5.41	1.882	-5.52	1.900	-9.05
6	I15U	1.622	-14.81	1.709	-14.21	1.825	-12.64
7	I25U	1.544	-18.91	1.623	-18.52	1.711	-18.09
8	I50U	1.502	-21.11	1.597	-19.83	1.635	-21.73
9	I25P	2.682	40.86	2.951	48.14	3.122	49.45
10	PI25	2.285	20.01	2.985	49.85	2.833	35.62
11	I25B	2.761	45.01	3.021	41.66	2.631	25.95
12	BI25	2.078	9.14	2.375	19.23	3.357	60.70
13	I25X	2.788	46.43	3.126	56.93	3.237	54.95
14	XI25	2.168	13.87	2.353	18.12	3.118	49.26
15	I50P	2.550	33.93	2.809	41.01	2.876	37.67
16	PI50	2.465	29.46	2.595	30.27	2.326	11.35
17	I50B	2.547	33.77	2.853	43.22	2.665	27.57
18	BI50	2.004	5.25	2.316	16.27	2.015	-3.54
19	I50X	2.686	41.07	2.824	41.77	3.582	71.47
20	XI50	2.551	33.98	2.798	40.46	2.665	27.57

based solely on condensibility considerations, would be the same. On the other hand, molar volume increases from benzene (140 cc/g-mole) to hexane (162 a/g-mole) to heptane (187 a/g-mole). The solubilities, based solely on molecular size considerations, should be ordered the same way. Because of the difference in geometric shape as well as in chemical nature between benzene and polyethylene, the order should be rearranged to account for this factor. Consideration of the solubility parameter difference should also be taken into account. Polyethylene has a solubility parameter of 7.7 to 8.4, while the values for benzene, hexane and heptane are 9.2, 7.3, and 7.4, respectively. Since the absolute value of the difference between the vapor and the polymer solubility parameters is a measure of likely interaction, the ordering would be heptane, then hexane, then benzene, in decreasing order. From this discussion, it can be concluded that any one approach cannot be satisfactorily employed in explaining the behavior of systems where interactions may occur.

Untreated Films

Figure 1 shows the variation of the solubility of the different vapors in the untreated films with temperature. Benzene and hexane show an increase in solubility with temperature, while heptane shows a decrease. This may be explained in terms of the relative changes in segmental mobility, molar volume, and condensibility as follows: an increase in temperature would lead to an increase in the segmental mobility and a decrease in condensibility. The increase in the segmental mobility would allow more vapor molecules to enter the polymer

TABLE III
 Solubility Results of Benzene (w/w × 100)

Film no.	Film	25°C		30°C		35°C	
		Solubility	Percent Change	Solubility	Percent Change	Solubility	Percent Change
1	I00U	3.293	0.00	3.362	0.00	3.405	0.00
2	I00P	3.520	6.89	4.462	32.72	3.937	15.62
3	I00B	3.569	8.38	3.730	10.95	4.222	23.99
4	I00X	3.415	3.70	4.022	19.63	3.987	17.09
5	I06U	3.244	-1.49	3.319	-1.28	3.393	-0.35
6	I15U	3.210	-2.52	3.290	-2.14	3.375	-0.88
7	I25U	3.108	-5.62	3.014	-10.35	2.928	-14.01
8	I50U	3.023	-8.20	2.994	-10.95	2.866	-15.83
9	I25P	3.702	12.42	4.218	25.46	4.374	28.46
10	PI25	3.662	11.21	3.880	15.41	3.613	6.11
11	I25B	3.908	18.68	3.614	7.50	3.699	8.63
12	BI25	3.826	16.19	3.591	6.81	3.592	5.49
13	I25X	4.711	43.06	4.213	25.31	4.465	31.13
14	XI25	3.526	7.08	3.402	1.19	3.523	3.47
15	I50P	3.997	21.38	4.210	25.22	4.322	26.93
16	PI50	3.731	13.30	3.387	0.74	3.316	-2.61
17	I50B	3.910	18.74	3.940	17.19	3.946	15.89
18	BI50	3.495	6.13	3.289	-2.17	3.113	-8.58
19	I50X	3.984	20.98	3.996	18.86	3.891	14.27
20	XI50	3.610	9.63	3.299	-1.87	3.267	-4.05

network. Decrease of condensibility leads to the opposite. Depending on which of these two effects occur to a larger extent, the solubility shows a slight increase with temperature, indicating that the increase in segmental mobility overcompensates the decrease in condensibility. For heptane, the opposite seems to be true.

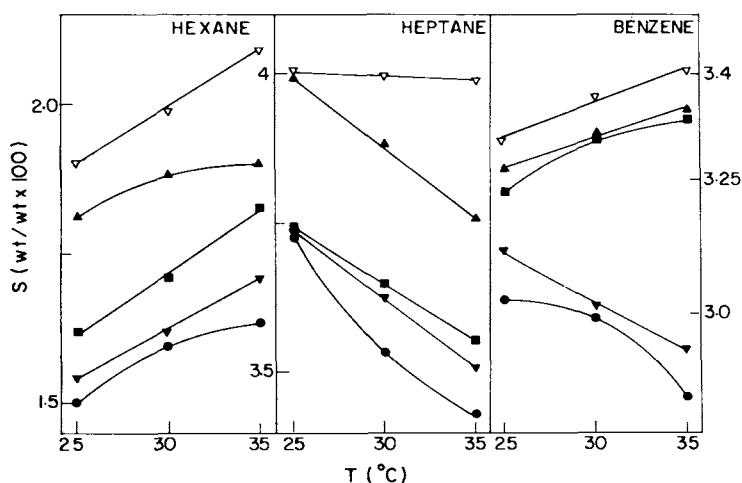


Fig. 1. Effect of temperature on the solubility of hexane, heptane, and benzene in unconditioned irradiated films: (∇) I00U; (\blacktriangle) I06U; (\blacksquare) I15U; (\blacktriangledown) I25U; (\bullet) I50U.

Irradiated Films

Figure 2 shows that the solubilities of the three vapors in irradiated films decrease with increasing irradiation dose. For all vapors at all temperatures, the solubility decreased sharply with low irradiation doses. The rate of decrease of solubility with irradiation dose decreased with increased irradiation. A saturation value was almost reached between 15 and 30 Mrads. Since irradiation of polyethylene leads to crosslinking, branching, and unsaturation,⁷ the behavior of solubility may be discussed in terms of these changes. The crosslink density is directly proportional to the irradiation dose irrespective of the dose rate.¹¹ It is possible to compare the decrease in solubility on irradiation to the increase in insoluble, i.e., highly crosslinked matter obtained on irradiation. Table IV shows these values.

The reduction in solubility is proportional to the increase in the percent insoluble matter for all cases except the first (dose 3.6 Mrad). This may be due to the fact that below 4 to 5 Mrads, only slight crosslinking occurs.¹²

The solubility of benzene was found to be the least affected by irradiation. Contrary to expectation, hexane experienced a greater change in solubility than did heptane. This is possibly because of the slight but nevertheless greater swelling action of heptane. Also, due to the low condensibility, the solubility of hexane is affected more significantly by the changes in the network conditions. Irradiation leads to an increase in the matrix rigidity which is unfavorable for

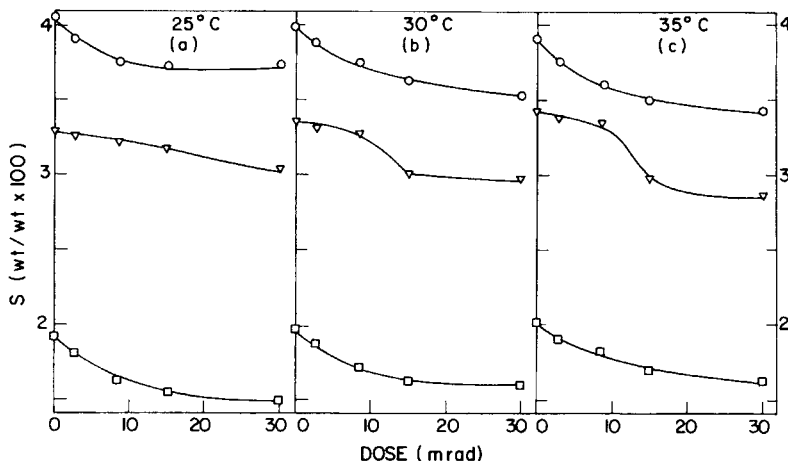


Fig. 2. Effect of irradiation dose on the solubility of hexane, heptane, and benzene in unconditioned films: (□) hexane; (○) heptane; (▽) benzene.

TABLE IV
Effect of γ Irradiation on the Amount of Insoluble Matter

Dose, Mrads	Percent insoluble matter	
	Charlesby et al. ¹¹	Atchison ¹²
3.6	33	29
9.0	59	63
15.0	69	73
25.0	74	78 ^a

^a Extrapolated value.

the dissolution of hexane. The effect of temperature on the mobility of the chains with the consequent effect on the solubility is exemplified here. Figure 1 shows these results. For benzene and heptane, the solubility in films subjected to low doses of 3.6 and 9 Mrads showed a slight increase with temperature. On the other hand, solubilities of these two vapors in the other films, subjected to 15 and 30 Mrads, decreased with temperature. In the latter two cases, the polymer network is too rigid to be affected by the slight increase in temperature, and hence the solubility decreases. On the other hand, the solubility of hexane showed a steady increase with increase in temperature in all films. For this case the increase in segmental mobility with temperature rise exceeds the decrease in condensibility, thereby leading to a more favorable condition for dissolution.

Conditioned Films

As shown in Figure 3, heptane conditioning leads to the largest increase in solubility of the three vapors, while benzene conditioning leads to the smallest effect. This may be explained in terms of the different processes that take place during conditioning. Conditioning, or solvent annealing, leads to a partial recrystallization of the polymer network. On the other hand, this treatment does not affect the crystallinity level,³ but the crystallites assume a more uniform, smaller size. The larger the swelling effect, the smaller the crystallite size. An increase in the treatment temperature leads to the same effect. This is also accompanied by a more important phenomenon by which "pockets" are formed during this process.³ These pockets conform in shape with the molecular shape of the conditioning solvent at that temperature. The solubility parameter difference may be taken as a measure of the compatibility between the solvent and the polymer. From this point, heptane would swell polyethylene more than hexane, while benzene would have the lowest swelling effect.

The manner in which the solubility changes with temperature is interesting. It is also dependent upon the vapor-conditioner pair. Heptane shows a mono-

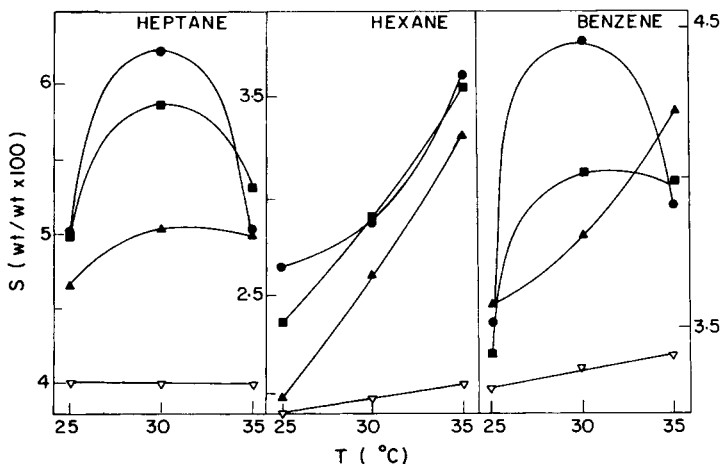


Fig. 3. Effect of temperature on the solubility of heptane, hexane, and benzene in conditioned films: (▽) I00U; (●) I00P; (■) I00X; (▲) I00B.

tonic increase in solubility with a sharp rise in the interval 30°–35°C. Benzene shows a maximum in solubility in hexane- and heptane-conditioned film and a steady increase in benzene-conditioned ones. This may be explained in terms of some of the phenomena accompanying this process. An increase in temperature would lead to an increase in segmental mobility. This might lead to the destruction, or at least the distortion, of some of the pockets formed during the conditioning process. The presence of some of the vapor, which acts as a swelling agent at the same time, would enhance this effect. The increase in segmental mobilities leads also to an increase in the ability of the polymer network to accommodate more vapor molecules. On the other hand, the molar volume of the vapor increases with temperature. If the latter effect does not exceed the former ones, solubility continues to increase with temperature. In some cases a maximum in solubility with respect to temperature was observed. This might be attributed to the decrease in the average number of vapor molecules that can be accommodated in the pockets already present, due to the combined effects mentioned.

The effect of the vapor-conditioner pair is shown clearly in the results of benzene which show that the rate of change of solubility in a particular conditioned film, relative to the untreated film, is highest for the benzene-conditioned films. Heptane and hexane conditioning led to looser networks that are most affected by temperature. It may also be attributed to the difference in geometric shape of the pockets formed during conditioning. This effect is important in the case of benzene due to the difference in molecular shape between benzene on one hand and heptane on the other. It is not effective in hexane and heptane due to the relatively small difference between their swelling powers as well as their molecular volume and shape.

Tables I–III show that the solubility of benzene is the least affected by conditioning, followed by heptane. This is due to its small molecular size and, more important, the difference in chemical nature between the network and benzene, which acts as a limit on its solubility. Hexane, being the least condensible and yet quite compatible with the network as judged from the solubility parameter difference, shows an increase in solubility with temperature whenever the conditions are favorable, and hence it is affected the most.

Combined Treatment

A combination of irradiation and solvent conditioning treatments were carried out in different sequences. Due to the complexity of the effect of the conditioning process, the additivity of both effects should not necessarily be expected. The sequence in which these two treatments were carried out affected the results both qualitatively and quantitatively. Irrespective of the sequence, the solubilities of the diffusants in these films were all higher than those in films which were only subjected to simple radiation treatment.

Figure 4 shows typical plots of the solubilities of the various vapors in the postirradiation conditioned films versus the irradiation dose showing the difference between the effect of the three conditioning solvents. Conditioning in heptane or hexane led to an increase in the solubility that was high at low irradiation dose and almost reaching a saturation value of the higher doses. This may be explained as follows: the crosslinked network is more rigid than the

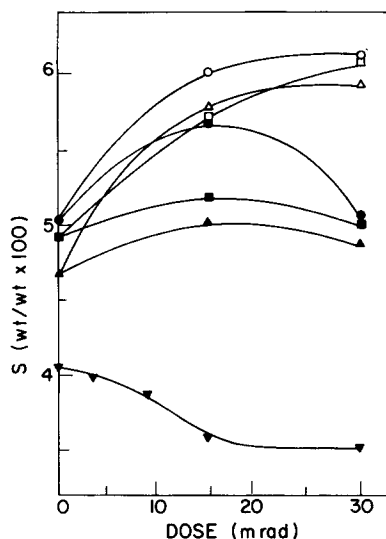


Fig. 4. Effect of irradiation dose on the solubility of heptane in conditioned, irradiated films at 25°C: (▼) I(n); (○) I(n)P; (□) I(n)X; (△) I(n)B; (●) PI(n); (■) XI(n); (▲) BI(n).

uncrosslinked one, thus the effect of conditioning may be more preserved in a crosslinked network than it would be in an uncrosslinked one. On the other hand, the increase in the rigidity of the network tends to reduce the extent to which this conditioning effect takes place. The shapes of the various curves indicate that the swelling and recrystallization actions of heptane and hexane conditioning overcome the effect of the chain rigidity. The swelling effect of benzene, being the lowest amongst the three, does not overcome this rigidity. This is indicated by a decrease of the solubility of the various diffusants relative to that of the unirradiated film.

It was found that the solubilities of the three vapors was higher in postirradiation conditioned films than those in films which were conditioned first and then irradiated. The distinction becomes clearer with higher irradiation doses. This is shown by inspecting Figure 5, for example. This might be attributed to the larger extent of distortion, destruction, or both occurring at higher doses.

The effect of temperature on the solubility follows the general trend stated earlier. The existence of a minimum with respect to temperature indicates that a maximum occurs at a somewhat lower temperature.

A consideration of the conditioning solvent-vapor pairs leads to some interesting results. Heptane conditioning, with either post- or preirradiation, leads to the largest increase in solubilities of both benzene and heptane. This may be attributed to its stronger swelling action. However, heptane being only a slightly stronger swelling agent than hexane leads to some "selectivity" as far as solubilities of hexane are concerned. Postirradiation conditioning shows an increase in the solubility of hexane in hexane-conditioned films relative to those conditioned in heptane before irradiation. Thus, the difference in the solubility between hexane and heptane in hexane-conditioned films decreases. This is shown in Figure 6.

On the other hand, conditioning of irradiated films in heptane leads to an increase in the solubility of the three vapors. The relative increase was highest

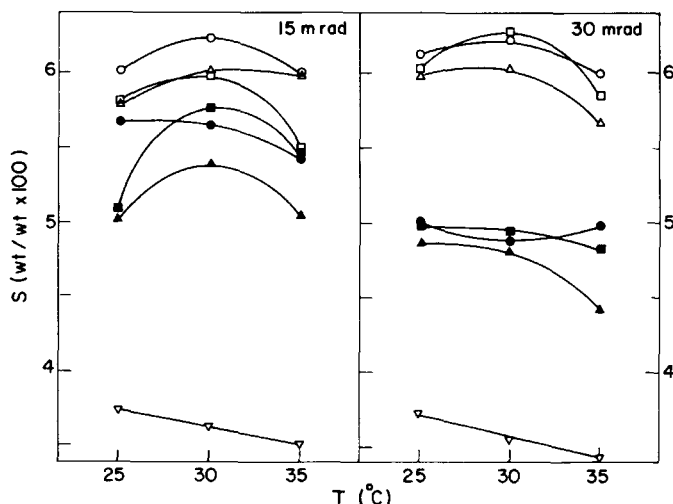


Fig. 5. Effect of temperature on the solubility of heptane in irradiated, conditioned films: (∇) I(n)U; (O) I(n)P; (\square) I(n)X; (Δ) I(n)B; (\bullet) PI(n); (\blacksquare) XI(n), (\blacktriangle) BI(n).

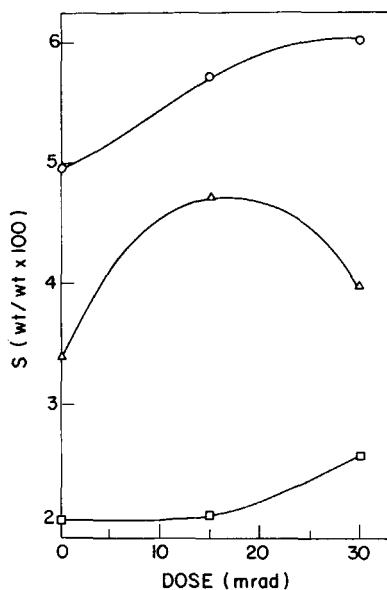


Fig. 6. Effect of irradiation dose on solubility of heptane, benzene, and hexane in I(n)X at 25°C: (\bullet) heptane; (\blacktriangle) benzene; (\blacksquare) hexane.

for heptane. Figure 7 shows that the difference in solubility between heptane and benzene increased by about 50% relative to that of unirradiated films. The same result may be observed in the difference between the solubilities of heptane and hexane. This result may be useful in the separation process, where the film is actually swollen by the permeants and the separation depends to a large extent on the solubility of both permeants in the film. Since the permeability is a product of the solubility and the diffusivity, this change in the relative extent of solubility means that in a binary mixture the relative rate of permeation may

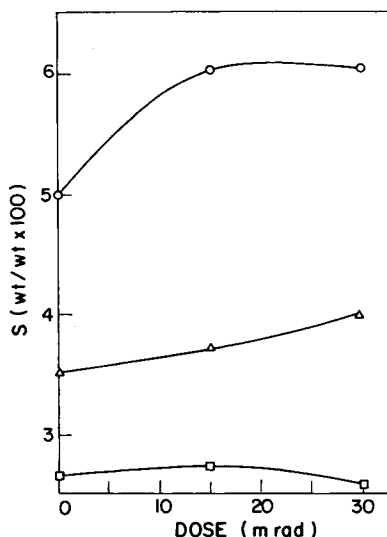


Fig. 7. Effect of irradiation dose on the solubility of heptane, benzene, and hexane in I(n)P at 25°C: (O) heptane; (Δ) benzene; (□) hexane.

be increased, provided the diffusivities of both the components remains unchanged. In fact, it has been found that the diffusivities change in a favorable way, that is, in the direction of increasing the differential permeation rates. These results are reported elsewhere.¹⁰

CONCLUSIONS

The solubility of heptane, hexane, and benzene in modified polyethylene films was investigated. It was found that irradiation leads to a decrease in the solubility of the three vapors. The threshold dose was found to decrease with increase in molecular volume, after which a marked decrease in solubility and a saturation value were observed. Solvent conditioning was found to lead to an increase in the solubility of the three diffusants over that in the untreated films, the extent of which was proportional to the swelling power of the conditioning solvent. Some maxima in the solubilities in the conditioned films with respect to temperature were observed. These maxima were explained in terms of the relative change in the segmental mobility of the swollen network both with temperature and in the presence of the diffusant, which acts as a swellant itself, as well as the number of diffusant molecules that can be accommodated in a single "hole" or "pocket" formed during the conditioning process.

When the films were both irradiated and conditioned, irrespective of the sequence, the solubility of the various vapors showed an increase over that of the untreated films or films undergoing simple irradiation or simple conditioning. This was attributed to the fact that crosslinking would fix the effect of the conditioning process. However, with increased crosslink density, the network would become more and more rigid, with a subsequent drop in the solubility. The solubility in the postirradiation conditioned films was always higher than those in the preirradiation conditioned films. This was attributed to the distortion or destruction of the pockets, formed during conditioning, by irradiation in the

latter case, while in the former case, the pockets are formed in a more rigid network, thus are less susceptible to change. This difference was found to increase with increase in dose rate.

This research program was supported by the National Research Council of Canada and the Defence Research Board, Ottawa, Canada.

References

1. O. T. Aboul-Nasr and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **23**, 1819 (1979).
2. R. F. Baddour, A. S. Michaels, H. J. Bixler, R. P. DeFillipi, and J. A. Barrie, *J. Appl. Polym. Sci.*, **8**, 897 (1964).
3. A. S. Michaels, R. F. Baddour, H. J. Bixler, and C. Y. Choo, *Ind. Eng. Chem., Proc. Des. Dev.*, **1**, 14 (1962).
4. R. A. Pasternak, T. F. Schimscheimer, and J. Heller, *J. Polym. Sci. A2*, **8**, 467 (1970).
5. H. A. Bent, *J. Polym. Sci.*, **24**, 387 (1957).
6. R. D. Siegel and R. W. Coughlin, *J. Appl. Polym. Sci.*, **14**, 2431 (1970).
7. A. Chapiro, *Radiation Chemistry of Polymers*, Wiley, New York, 1963.
8. P. J. F. Kanitz and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **14**, 2739 (1970).
9. M. Fels and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **14**, 537 (1970).
10. O. T. Aboul-Nasr and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **23**, 1833 (1979).
11. C. A. Charlesby and L. Callaghan, *J. Phys. Chem. Solids*, **4**, 306 (1958).
12. G. J. Atchison, *J. Polym. Sci.*, **35**, 557 (1957).

Received August 12, 1977

Revised April 7, 1978