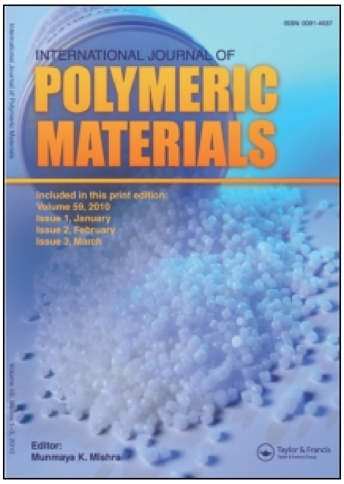

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Diffusion of n-Hexane in Polyethylenes

B. Kogarkoa[a]; M. Markelov[b]
[a] Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia [b] ACS Labs., Chesterland, OH, USA

To cite this Article Kogarkoa, B. and Markelov, M.(1998) 'Diffusion of n-Hexane in Polyethylenes', International Journal of Polymeric Materials, 41: 3, 249 — 262

To link to this Article: DOI: 10.1080/00914039808041049

URL: http://dx.doi.org/10.1080/00914039808041049

Intern. J. Polymeric Mater., 1998, Vol. 41, pp. 249-262
Reprints available directly from the publisher
Photocopying permitted by license only

Diffusion of *n*-Hexane in Polyethylenes

B. KOGARKO[a,]* and M. MARKELOV[b]

[a] *Institute of Chemical Physics, Russian Academy of Sciences,*
4, Kosygin St., Moscow, 11734, Russia;
[b] *ACS Labs., Chesterland, OH, 44026, USA*

(Received 20 September 1997)

The diffusion coefficients of *n*-Hexane in two compositions of Polyethylene were estimated as function of temperature, concentration and film thickness.

Keywords: Hexane; diffusion coefficient; polyethylene

INTRODUCTION

The problem of diffusion coefficient estimation of low molecular weight chemical in polymers is classic one. Many investigators solved this problem for different cases. Our objective was to measure diffusion coefficient of Hexane (n-C_6) in two compositions of polyethylene as function of temperature, concentration and film thickness because of the technological importance of this problem.

EXPERIMENTAL

The system consists of four major parts: 1. Test and Sweep gases flow control blocks; 2. Thermostated chamber that houses two permeation cells; 3. Heated valving system capable of automated cell switching and timed sampling and injection of sweep gas aliquots (1 ml); 4. Gas chromatograph equipped with a Flame Ionization Detector and a

---

*Corresponding author.

column capable of fast separation of Hexane. The output of the detector was connected to HP 3393 integrator equipped with Basic programming capabilities and Disk drive interface.

Gases

Two Al tanks with 0.5% and 2.0% of Hexane (C_6) in N_2 were ordered from Matheson Gas Co. Both gases and additional He lines were connected to 3-port valves that were used to clean the cells and films before tests.

Flows

The optimal sweep gas flow (He) was estimated and set up based on the expected values of diffusion and solubility coefficients and varied with the film thickness and temperature of a particular test. The test gas flows were changed during tests. They were fast (200 ml/min) in the initial stages of experiment (2–3 min) to fill cell quickly and then were adjusted to about 10 ml/min for the duration of the test.

Valving System

Two 6-port gas sampling valves were equipped with matched 1 ml sample loops and electrical actuators. These valves were connected to analytical chambers of both cells and to the inlet of the GC column. The valves and loops were housed in an oven Thermostated at 130°C. The valves were plumbed in a such way that when the sweep gas of one cell was flowing through the sample loop of one valve, the sample loop of the other valve was purget by a carrier gas into GC. The position of the valves was controlled by an automatic timing device that also was used to initiate a GC run on the integrator during valves switching.

Permeation Cells

The PTFE coated Al cells are depicted. The film area exposed to the test gas was 126.6 cm^2 and volume of each gas chamber was 76.6 cm^3.

GC Conditions

Chromatographic conditions were set up as follows: GC column – 6′× 1/8′ SS packed with 10% SP 1200 on 80 – 100 mesh of Chromosorb AW. Temperature – 60°C isothermal. Carrier flow – 50 ml/min (25 ml/min through each valve). Injector – 150°C. Detector (FID) – 200°C.

Calibration

One ml of 0.5% and 2.0% of C_6 in N_2 were manually injected into the GC column at the conditions above. The results were used to build a calibration table. The stability of the calibration was checked before and after of every test by injecting 1 ml of 0.5% C_6 test gas. The calibration is not necessary for determination of diffusivity but was used for permeability and solubility calculations.

Data Acquisition

The test begins when an operator calls Permeation Test Program (Copyright ACS Labs. Sept. 1994). The program asks the operator for the values of sample thickness, temperature of experiment, sweep gas flow rates, test gas concentrations, and the names of the files where to be placed the data in. The program waits for the operator to switch 3-way valve from He to test gas flow and to activate the timing device. This is the point "O" from which the timing begins. The chromatograms from both cells are recorded on the integrator with the frequency controlled by the preset timers. Odd run numbers correspond to one cell and even ones to an other. The values of C_6 reported were extracted by a specially written basic program into two files as functions of time. Each file contained data only from one cell. The program also calculated and printed running values of diffusion, permeability and solubility coefficients after each GC run as if it was the steady state region. The test was finished (steady state) when no substantial change of these coefficients was observed for several GC runs.

Data Management

The program also prints a summary report after each test. This summary report contained the values of concentration of C_6, total quantity of C_6, diffusion, permeability, and solubility coefficients as function of running time of experiment. This report is stored as a file on the floppy disk. The program also permits to conduct a statistical evaluation of data in any time region of the steady state portion of the recorded kinetics.

The final data for diffusion and where possible, for permeability and solubility were placed into spread sheets (Excel) for further evaluation.

Samples

Films of various thickness and compositions were received from Occidental Chemicals Co. as 1 ft^2 square pieces. An area of a piece of the sample was cut and weighed for determination of an average film thickness taking density into account. The surface of the film was cleaned with methanol and wiped dry before testing. The film was then placed into the cell and sealed with PTFE O-rings. The cells were connected to gaseous lines and placed into a Thermostated chamber under streams of He. They were heated at the test temperature and purged with He for at least 10 hours before test.

RESULTS AND DISCUSSION

Theoretical Background of Permeation

The process of permeation of a gas under constant partial pressure "P" through a membrane with thickness "L" as a function of time into a fixed volume chamber can be represented by Figure 1, where P is the pressure measured on the other side of the membrane. The evaluation of permeation kinetic curves in terms of diffusion, permeability, and solubility coefficients was originally described in [1].

The coefficients of permeability (P), diffusion (D), and solubility (K) are related through Eq. (1).

$$P = D \times K \tag{1}$$

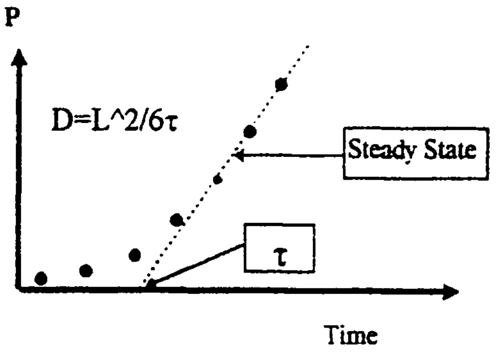

FIGURE 1 Typical permeation curve. Accumulation of test gas on analytical side of membrane.

General approach for determination of D, P and K involves calculation of P from the steady state region of kinetic curve in Figure 1 and calculation of D from the intercept to steady state line with Time-axes. The solubility constant K is calculated as a ratio of P and D (Eq. 1).

This experimental technique has however, one sensus drawback, The concentration of a diffusant on the analytical side of the film is changing with time and, therefore changes the driving force of the permanent process.

We prefered differential version of the experiment that was described in detail in the experimental section of this paper.

The technique depicted in Figure 2 gave us the control over the concentration of the diffusant on the analytical side of the films *via* adjustments of flow rates of the sweep gas (He). Moreover, this setup maintains constant gradient of concentrations across the membrane. It also permits statistical evaluation of the steady state region. Indeed, in contrast with the "integral approach" (Fig. 2), this method alows us to verify steady state conditions without any concerns about build up levels of the diffusant on the analytical side of the cell.

The experiments were set up in a such way that the steady state concentration (C_s) was less then 10% of the concentration on the test gas side of the membrane (C_o). Therefore, the gradient of concentration across the film was essentially equal to C_o. Eq. (2) shows the methodology of permeation coefficient determination:

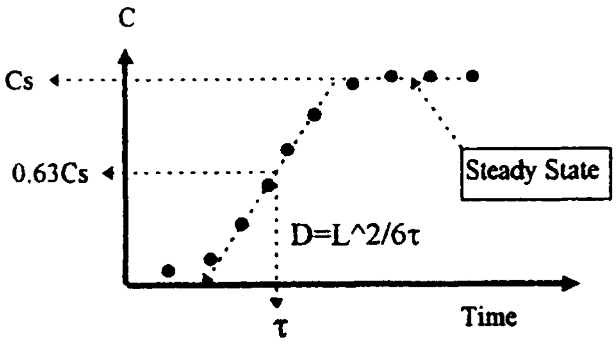

FIGURE 2 Typical permeation curve. Sweeping of test gas from analytical side of membrane.

$$P = (C_s \times F \times L)/(A \times C_o) \qquad (2)$$

where F is the flow rate of the sweep gas and A is the area of one side of the film.

Diffusion coefficients were calculated as shown in figure *via* Eq. (3):

$$D = L^2/6 \qquad (3)$$

Solubility coefficient (K) was calculated *via* Eq. (1).

Theoretical Background of Desorption

Diffusion coefficient of desorption can be determined from the plot shown in Figure 3 [2]. Y-Axes of the plot represent the natural logarithm of the rate of decreasing concentration of C_6 in the vapor phase over the membrane. Diffusion coefficient is determined from the slope of the linear portion of the curve (Fig. 3) using Eq. (5).

$$D = L^2 \times \text{Slope}/^2 \qquad (5)$$

This treatment of the desorption data is valid only when the following conditions are satisfied:

a. The diffusant is uniformly distributed in the polymer matrix at time zero.
b. The linearity of the plot in figure takes place when (D^*t) (0.1^*L^2).

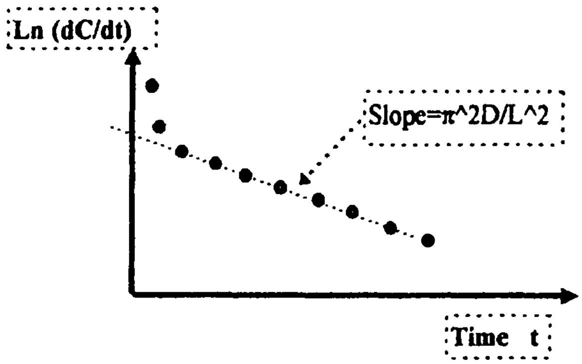

FIGURE 3 Typical desorption curve.

Results

1. The experimental setup used in this work permits measurements of diffusion, permeability, and solubility coefficients of low molecular weight chemicals in polymers.
2. The results of all measurements at 40, 60, 70, 80 and 90 deg.C with concentrations of *n*-C_6 in the range of 0.5–2.0% v/v and film thickness varied from 0.5 mm to 1.4 mm are compilted in Table I.
3. The statistical evaluation of diffusion measurements at 93 deg.C for PE with density 0.950 (10 data points from Tab. I) showed the following:
    a. Average diffusion coefficient calculated over the range of concentrations and thickness was $2.62 \times 10^{-7} cm^2/$ sec with RSD = 4.6%. This indicates satisfactory precision of the measurements and independence of diffusion on concentration of *n*-C_6 and thickness of PE files.
    b. It also indicates statistical equality of diffusion coefficients obtained in permeation and desorption experiments (D desorption = 2.58×10^{-7}. See Tab. I).
    c. The diffusion coefficient in PE with density 0.950 is statistically different from diffusion coefficient in PE with density 0.953 ($D = 2.17 \times 10^{-7}$. See Tab. I).
4. The dependence of diffusion coefficients ($D\,cm^2/sec$) on temperature (T–deg.K) in the range of temperatures from 40 to 93 deg.C can be

expressed by the following equations:

- For PE (L5005) with Density = 0.95: LnD = 6.8008 – 8040.7/T
- For PE (M5370) with Density = 0.953: LnD = 4.5332 – 7275.9/T

5. The dependence of solubility coefficients (*K* – Conc. in polymer/Conc. in gas) on temperature can be expressed by the following equations:

   - For PE (L5005) with Density = 0.950: LnK = 2898/T – 5.8653
   - For PE (M5370) with Density = 0.953: LnK = 2928/T – 6.1893

6. The dependence of permeability coefficients (P cm^2/sec) on temperature can be expressed by the following equations:

   - For PE (L5005) with Density = 0.950: LnP = –5206.1/T – 1.1267
   - For PE (M5370) with Density = 0.953: LnP = –4301.9/T – 1.7338

Discussion of the Experimental Results

Typical permeation plot is depicted in Figure 4. The integration of these data produces accumulation plot presented in Figure 5. We already mention the dangers associated with experiments where actual accumulation of diffusant on the analytical side takes place. The differential experiment plotted in Figure 4 shows that the steady is achieved at the concentration of about 30 ppm on the analytical side.

Figure 5 shows that if the diffusant would be allowed to accumulate in the analytical chamber, its concentration there would reach more than 3.000 pp. It may create the partitioning restriction of the diffusion. Indeed, this situation was observed in our initial experiments. The data from these experiments are marked with "*" in the summary Table I. These data showed unreasonably low diffusion coefficients when the concentration on the analytical side was in the excess of 3% of the test gas (5000 ppm).

Figure 6 is the typical plot of the desorption data. It shows that the linear portion begins only in 50 min from the beginning of desorption. This satisfies the theoretical condition "*b*" for this particular test. One has to be careful of apparent linearity of the data in the logarithmic scale.

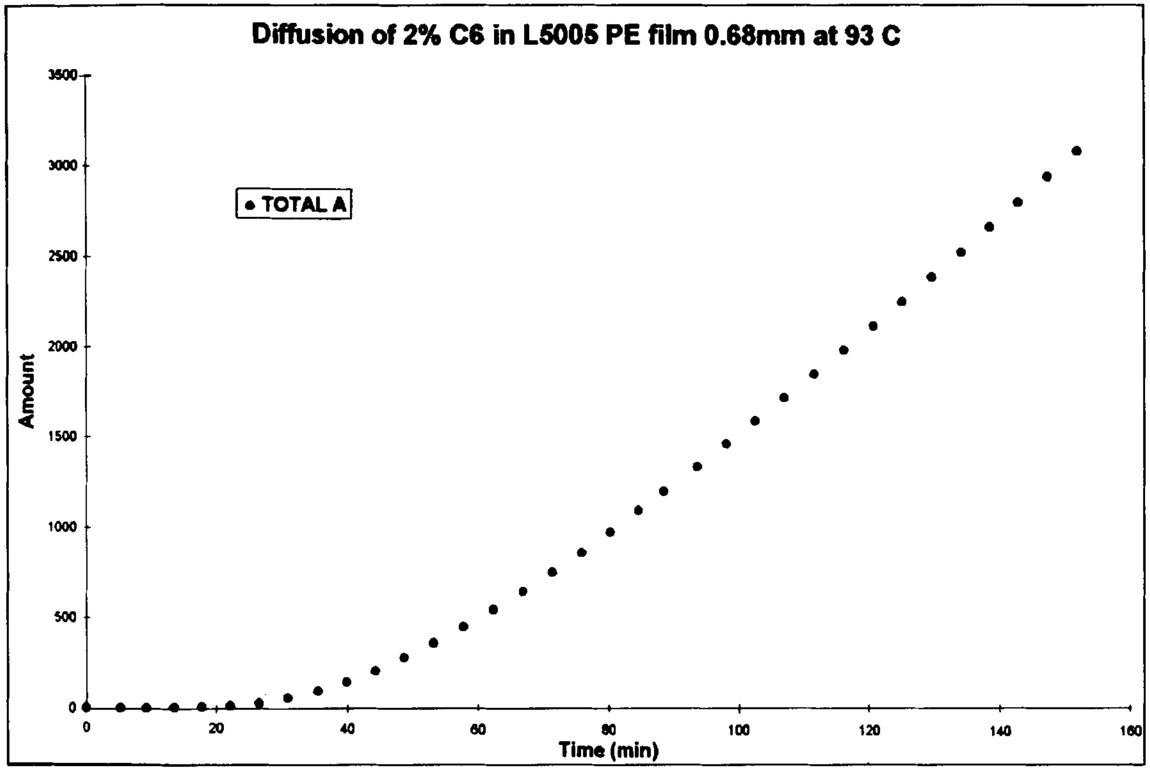

FIGURE 4 Diffusion of 2% C_6 in L5005 PE film 0,68 mm at 93°C.

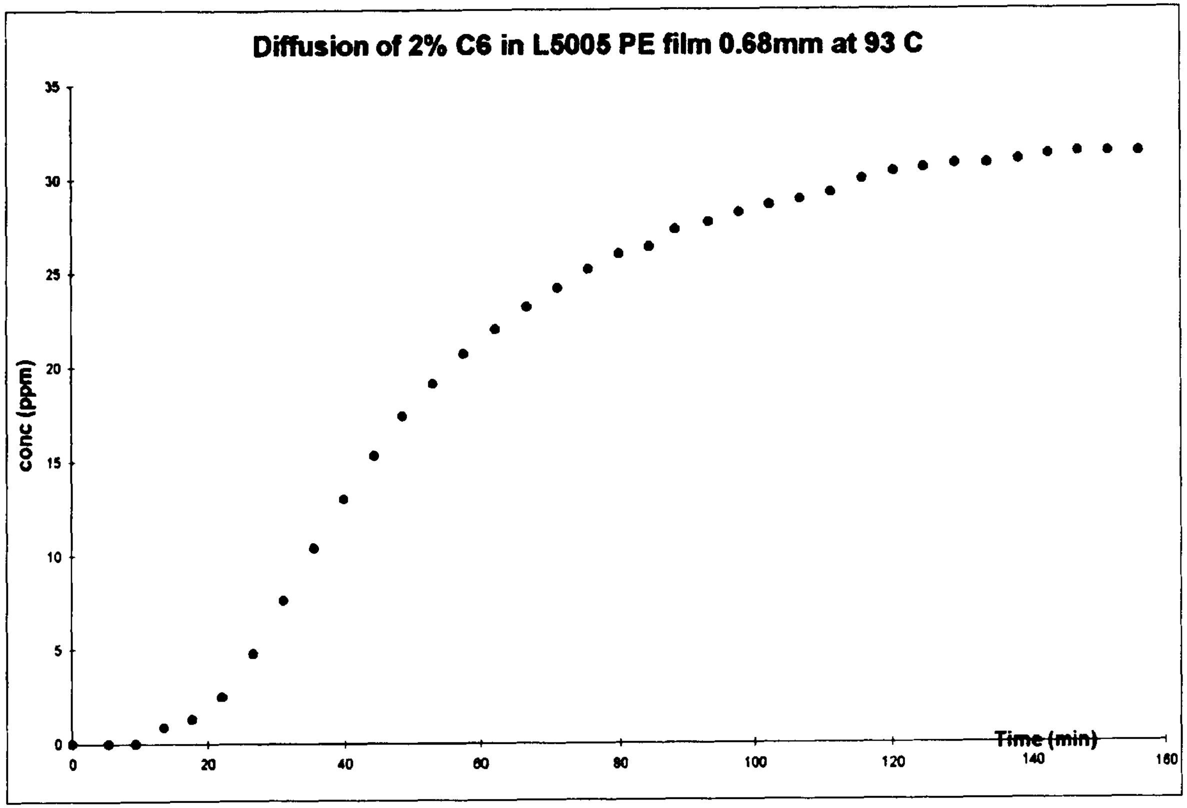

FIGURE 5 Diffusion of 2% C_6 in L5005 PE film 0,68 mm at 93°C.

TABLE I Summary of results diffusion, permeation, and solubility results for *n*-Hexane in polyethylene

T	*C* = 5000 *ppm*				*C* = 20000 *ppm*			
deg C	*L mm*	D^*E7	P^*E7	*K*	*L mm*	$D''E7$	$P''E7$	*K*
93	0.54*	1.9	18.58	9.8	0.89	2.89	21.84	7.5
93	0.77*	2.2	19.56	8.9	0.91	2.51	20.61	8.2
93	0.89	2.48	22.12	8.9	1.19ˆ	2.59	19.35	7.5
93	0.89	2.68	22.07	8.4	0.91	2.55	20.80	8.1
93	1.02	2.6	21.13	8.1	1.27	2.75	21.47	7.7
93	1.32	2.6	21.46	8.5	1.27	2.5	20.64	8.2
M5370 93 C	1.08	2.18	12.95	6.0	1.10	2.15	13.59	6.3
80	0.58	1.24	11.02	8.9	0.58	1.20	12.19	10.1
80					1.14	1.16	11.78	10.1
80	1.42	1.36	11.57	8.5				
M5370 80 C					1.09	1.05	8.42	8.0
70	0.55	0.55	7.40	13.5	0.57	0.56	7.82	14.0
70	0.87	0.60			0.90	0.72		
M5370 70 C					1.09	0.57	6.07	10.6
60	0.89	0.28	4.33	15.2	0.91	0.31	4.95	16.0
40	0.56	0.060	1.87	31.0	0.58	0.063	2.13	33.9
93 D	0.58	2.55						
93 D	0.56	2.60						
80 D	0.56	1.23						
80 D	0.58	1.14						

*Concentration on the analytical side was < than 10% of the test gas. This may result in partition restriction of diffusion.

ˆThis is not a single film. Two films 0.57 and 0.62 mm were put on top of each other and placed in the cell. This was an attempt to observe surface effects if any.

D: This is the result of the desorption experiments on the film saturated in the contact with 0.5% C_6 in N_2.

Effect of Thickness

The results summarized in Table I showed that there was not any functionally between the thickness of the membrane and diffusion coefficients measured. This indicates that the surface mass-transport properties are similar to that of the bulk. To confirm this observation, a special "sandwich" experiment was conducted. Two thin films (0.57 and 0.63 mm) were put on top of each other and placed in the cell. The results ($D = 2.59 * 10^{-7}$) showed that this "sandwich" behaved similar

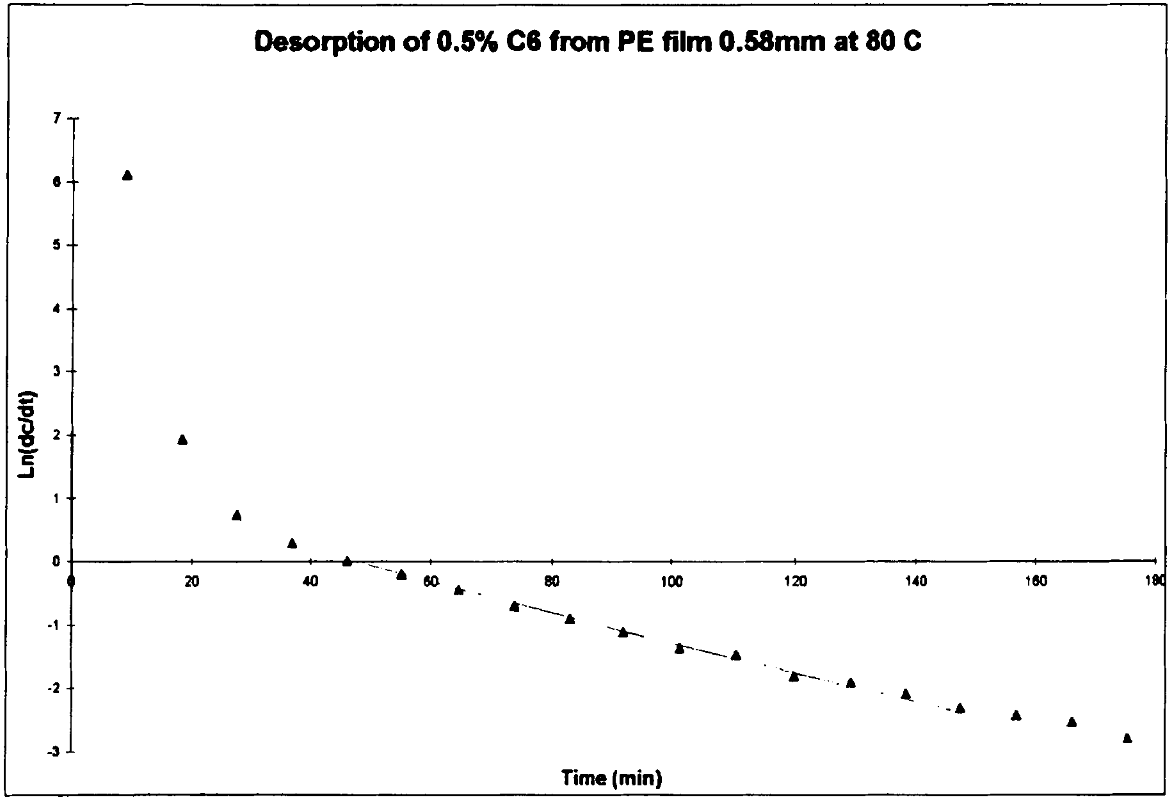

FIGURE 6 Desorption of 0,5% C_6 from PE film 0,58 mm at 80° C.

to other films tested (Dav = $2.6 * 10^{-7}$) where the percentage of surface structure material was twice less. Moreover, no correlation between solubility coefficients and film thickness was observed.

Effect of Diffusant Concentration

Polymer-organic solvent systems often exhibit concentration dependence of diffusion coefficients. It was not the case for our system in the range of concentrations studied. The data in Table I showed no statistically significant variation of diffusion or solubility coefficient with concentration of the test gas used at various temperatures. In other words, the polymeric matrix did not undergo any structural changes under exposure to the vapors of *n*-Hexane.

Effect of Temperature

Effect of temperature on diffusion, permeability, and solubility coefficients can be described by the equations submitted in the "Results" section of this work. The slopes of these curves exhibit convincing linearity. This indicated that the mechanisms of mass-transport and thermodynamics are not changing with temperature and apparent energies of diffusion and enthalpies of solubility can be calculated. They are completed in the Table II below.

The apparent activation energy of desorption was estimated using only 4 data points obtained at 93 and 80 deg.C for PE with 0.950 density. Its value was 15.2 Kcal/mol.

The table above indicates that two polymers investigated have similar properties in the respect of mass-transport and solubility.

TABLE II Apparent activation energies

	Kcal/mol		
Density	*D*	*P*	*K*
0.950	15.9	10.3	−5.7
0.953	14.4	8.5	−5.8

CONCLUSION

The system PE/*n*-Hexane exhibited classical behavior. It showed no presence of any specific interactions between components or any nonhomogeneity between the surface and the bulk of the polymer or any change in mechanisms of transport with temperature.

References

[1] Ameronger, G. I. (1964). *van Rubb. Rev.*, **37**(5), 1065.
[2] Crank, J. and Park, G. S. (1966). Diffusion in Polymers, L.-N.Y., Acad. Press.