

# Theoretical Estimations of Diffusion Coefficients

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## Synopsis

A model calculating the diffusion coefficients of liquids in polymeric membranes from the diffusion coefficients at zero concentration was developed. This model is based on Fujita's volume theory and considers crystallinity in the polymer and is tested by using available data in the literature, i.e., *n*-hexane-polyethylene and benzene-polyethylene systems. The calculated diffusion coefficients were simulated by calculating the pure liquid permeabilities in a pervaporation system. When comparing the predicted pure liquid permeabilities with the experimental values, these calculated values were found to be in fairly good agreement.

## INTRODUCTION

In order to predict the separation factors and permeabilities in pervaporation systems, the diffusion coefficients of liquids through the membranes should be known. Since the diffusion coefficients are concentration dependent, diffusion coefficients for the case where the membrane is in contact with the liquid mixture (or pure liquid) in the membrane cell are needed to calculate separation factors and permeabilities in pervaporation systems. Once the diffusivity of the solvents at various relative pressures by means of proper methods, such as the sorption-desorption method etc., the parameters in Fujita's volume theory can be determined. From these parameters and solubility data obtained through swelling equilibrium measurements, the diffusion coefficients of liquids can be obtained.

Crank<sup>1</sup> describes several ways to obtain the diffusion coefficient of organic vapors. Kreituss and Frisch<sup>2</sup> discussed the more detailed transport phenomena of small molecules in semicrystalline polymers considering that the  $B_d$  parameter is not constant but varies linearly with the volume fraction of diffusing species and that there is a simple additivity relationship for the densities of the amorphous and partially crystalline polymer. A unified approach based on Fujita's theory was attempted to interpret the transport phenomena in polymeric media, such as diffusion studies in polymeric solutions, gels, semicrystalline polymers, crosslinked polymers, filled polymers, block and graft copolymers, and polymer blends.<sup>3,4</sup> Similarly the transport of small molecules in incompatible polymer blends, semicrystalline polymers, and filled polymer systems were studied in terms of transient sorption and permeation experiments.<sup>5</sup> Liu and Neogi<sup>6</sup> obtained diffusion coefficients from differential sorption data and then calculated them at zero concentration and also the parameters in Fujita's free volume theory from the experimentally measured diffusion coefficients for *n*-hexane

and benzene in polyethylene films. Fels and Huang<sup>7</sup> had developed a numerical procedure to analyze desorption data, i.e., optimizing Fujita's free volume parameters in the concentration-dependent equation by comparing the numerically integrated amount of liquid in the membrane with the experimentally determined quantity of liquid. Diffusivity of organic vapors was obtained from the absorption method following the Fels and Huang calculation procedure by Aboul-Nasr and Huang.<sup>8,9</sup> Kulkarni and Stern<sup>10</sup> developed semiempirical correlations for the parameters  $A_d$ ,  $B_d$ , and  $\gamma$  (concentration coefficient,  $\partial v_f / \partial v$  in terms of physicochemical properties of the penetrants and of the penetrant-polymer systems), which can be used to predict permeation rates of various pure gases and gas mixtures through polyethylene films as a function of both temperature and applied penetrant pressure.

Most of the diffusion models can be considered in terms of "molecular" or "free-volume" mechanisms. The molecular model interprets the diffusion process in terms of specific postulated motions of penetrant molecules and polymer chains.<sup>11-13</sup> The latter model is based on an oversimplified view of molecular processes, i.e., do not take account of the detailed molecular structure of the polymer-penetrant system but relate the diffusion coefficient to the free volume ("hole") of the system on the basis of the fluctuation analysis.<sup>14,15</sup> The free-volume model proposed by Fujita<sup>16</sup> has been found to satisfactorily describe the diffusion of a number of organic liquids and vapors in polymers. However, the original diffusion equation of Fujita is strictly applicable only to amorphous polymers. Kreituss and Frisch<sup>2</sup> extended Fujita's free-volume model by considering the effect of polymer crystallinity.

The purpose of the present study is to develop a calculation method to obtain the diffusion coefficient of liquids through the membrane and its concentration dependence when the diffusion coefficients at zero concentration from desorption data are known. The calculations have been done for *n*-hexane and benzene in polyethylene films. The diffusion coefficient data at zero concentration were taken from ref. 17.

## THEORY

Fujita<sup>16</sup> extended the free-volume theory of diffusion to account for the dependence of the diffusion coefficient on the concentration of the diffusing molecules in polymeric films. In Fujita's study, the free volume was defined as the volume within the cage of a molecule minus the volume of the molecule itself. Thus the free volume is analogous to the hole that is opened up by thermal fluctuations of the polymer chains. The mobility of a diffusing species in the polymer film is assumed to be given by

$$m_d = A_d \exp \frac{-B_d}{f(1 - \phi_c)} \quad (1)$$

where  $m_d$  is the mobility of a diffusing species in the membrane, the parameters  $A_d$  and  $B_d$  are proportionality factors whose values are dependent on the size and shape of the diffusing molecule. In this case,  $B_d$  is taken to be the ratio

between the size of the diffusing species and the size of the polymer chain segments,<sup>6</sup>  $f$  is the fractional free volume of the system, and  $\phi_c$  is the degree of the crystallization. The mobility of a diffusing species is defined as

$$D_T = RTm_d \quad (2)$$

where  $D_T$  is the thermodynamic diffusion coefficient that considers the resistance of the diffusing species in the polymer network. Combining eq. (1) with eq. (2), we have

$$D_T = RTA_d \exp \frac{-B_d}{f(1 - \phi_c)} \quad (3)$$

In eq. (3),  $f$ , which is the fractional free volume of the system at temperature  $T$  and now expressed as  $f(v_i, T)$ , is assumed to be given by

$$f(v_i, T) = f(0, T) + \beta(T)v_i \quad (4)$$

where  $f(0, T)$  is the fractional volume of the polymer itself,  $\beta(T)$  is a proportionality constant representing the ability of the penetrant to increase the volume, and both of  $f(0, T)$  and  $\beta(T)$  are functions of temperature, and  $v_i$  is the volume fraction of liquid component  $i$  ( $i = 1$  or  $2$ ) in the membrane. When  $v_i = 1$ ,  $f(1, T)$  is the free volume of the pure substance, and for  $v_i = 0$ , the diffusion coefficient  $D_{c=0}$  is expressed as

$$D_{c=0} = RTA_d \exp \left[ \frac{-B_d}{f(0, T)(1 - \phi_c)} \right] \quad (5)$$

Dividing eq. (5) into eq. (3) and taking the logarithm of both sides,

$$\left( \ln \frac{D_{c=0}}{D_T} \right)^{-1} = \frac{f(0, T)(1 - \phi_c)}{B_d} + \frac{(1 - \phi_c)[f(0, T)]^2}{B_d \beta v_i} \quad (6)$$

As a result, the diffusion coefficient resulting from  $D_{c=0}$  of a partially crystalline polymer reflects effects due to the presence of the crystalline component on the transport properties of the amorphous phase; thus, the polymer sample is now treated as a medium composed of two phases.

Further, the thermodynamic diffusion coefficient can be related to  $D_{i3}$  by

$$(D_T)_i = \frac{D_{i3}}{(1 - v_i)} \frac{\partial \ln v_i}{\partial \ln a_i} \quad (7)$$

where  $a_i$  is the activity of the penetrant  $i$  in the membrane and  $D_{i3}$  is the diffusion coefficient of penetrant  $i$  in the membrane. If the diffusion coefficient  $D_{c=0}$  and the parameter  $f(0, T)$  are known, the parameters  $A_d$  and  $B_d$  can be determined from eq. (5), and the thermodynamic diffusion coefficient  $D_T$  and

the diffusion coefficient in polymer might be determined from eq. (3) and eq. (7), respectively. We will discuss this in more detail later.

### Determination of Free-Volume Fraction

It was reported that the free volume in a liquid can be considered to be that volume seemingly arising from the total thermal expansion of the liquid without phase change.<sup>18</sup> Furthermore, the smallest, most compact volume of a liquid, i.e., no free volume in a liquid, is the volume at 0 K. Therefore, the free-volume fraction  $f(1, T)$  can be defined as

$$f(1, T) = \frac{v_f - v_0}{v_f} \quad (8)$$

where  $v_f$  is the volume per gram of liquid at any temperature, and  $v_0$  is the volume of a gram of liquid extrapolated to absolute zero without change of phase. Further it was considered<sup>18</sup> that the most obvious method of extrapolating densities to absolute zero would be to set up a density function in the form of a Taylor expansion. The known density function with the form of a Taylor expansion<sup>19</sup> was extrapolated to  $T = 0$  to obtain  $v_0$  in eq. (7) for benzene. For *n*-hexane,  $v_0$  was obtained from interpolation of the known  $v_0$  values of alkane liquid groups.<sup>18</sup>

The  $\beta(T)$  parameter can be calculated from the following definition [in eq. (4), when  $v_i = 1$ ]

$$f(1, T) = f(0, T) + \beta(T) \quad (9)$$

For the free-volume fraction of polyethylene, the following correlation, which is often used and widely accepted,<sup>6,7</sup> is given by

$$f(0, T) = 0.025 + 7 \times 10^{-4}(T - T_g) \quad (10)$$

where the glass transition temperature,  $T_g$ , for polyethylene is  $-75^\circ\text{C}$ . From this correlation, the free-volume fraction of polymer can be determined.

### Determination of Binary Interaction Parameter

There are various theories that concern the volume fraction of the diffusing species with the activity. The activity of a component in the membrane can be obtained from Flory-Huggins thermodynamics.<sup>20</sup> For binary systems, i.e., pure liquid (component 1 or 2) and membrane (component 3), the term  $\partial \ln v_i / \partial \ln a_i$  in eq. (7) for pure liquid can be expressed as

$$\frac{\partial \ln a_i}{\partial \ln v_i} = 1 - \left(1 - \frac{V_i}{V_3}\right)v_i - 2\chi_{i3}v_iv_3 \quad (11)$$

where  $a_i$  is the activity of component  $i$ ,  $\chi_{i3}$  is the Flory-Huggins interaction parameter between pure liquid and the polymer, and  $V_i$ ,  $V_3$  are the molar volume

of penetrant and polymer, respectively. It was reported that two methods, equilibrium swelling measurements and inverse chromatography, are available for the evaluation  $\chi_{13}$  and  $\chi_{23}$  parameters.<sup>21</sup> The former method is recommended because of the disadvantage of the latter method. According to Flory-Rehner,<sup>20,21</sup> the free energy change  $\Delta G$  is equal to the sum of the free energy change of mixing,  $\Delta G_m$ , and the elastic free energy,  $\Delta G_{el}$ :

$$\Delta G = \Delta G_m + \Delta G_{el} \quad (12)$$

At swelling equilibrium,  $\Delta G = 0$ , thus,

$$\ln(1 - v_p) + v_p + \chi v_p^2 + \frac{V_1}{M_c v_p} \left( v_p^{1/3} - \frac{1}{2} v_p \right) = 0 \quad (13)$$

where  $V$  is the molar volume,  $v_p$  is the specific volume of the polymer,  $v_p$  is the volume fraction of the polymer, and  $M_c$  is the average molecular weight between two crosslinks. It was reported that the volume of the final term in eq. (13) does not significantly affect the results of the present study for the polyethylene-hexane-benzene system and has been dealt with in a previous publication by Fels and Huang.<sup>7</sup> Therefore, with the omission of the last term, eq. (13) can be reduced to a simpler form as follows:

$$\chi = - \frac{[\ln(1 - v_p) + v_p]}{v_p^2} \quad (14)$$

### Calculation of Pure Liquid Permeabilities by Pervaporation

Unfortunately, no data that can be compared with the calculated diffusion coefficients are available in the literature. The ideal to strive for is the calculation of pure liquid permeabilities from Fick's law of diffusion. At steady state,  $\partial c / \partial t = 0$ , and with integration of membrane thickness,  $L$ , the resulting equation can be expressed as (see ref. 7)

$$\int_0^{C_i} \frac{D_i}{1 - v_i} dC_i = N_i L \quad (15)$$

where  $C_i$  is the concentration of pure liquid in the membrane,  $D_i$  is the diffusion coefficient of each liquid, and  $N_i L$  is known as the permeability ( $P_i$ ).

## RESULTS AND DISCUSSION

Using literature data from ref. 17, the diffusion coefficient at zero concentration was obtained for low-density polyethylene (PE) film with a crystallinity of 43.5% and calculated by

TABLE I  
Solubilities and Binary Interaction Parameters of *n*-Hexane and Benzene in Polyethylene

System	Temp. (°C)	Solubility <sup>a</sup>	$\chi_{13}$
Hexane(1)-PE(3)	25	0.1611	1.4022
	30	0.1766	1.3393
	35	0.1927	1.2878
	40	0.2116	1.2302
	45	0.2284	1.1842
Benzene(2)-PE(3)	25	0.1483	1.4569
	30	0.1751	1.3483
	35	0.1991	1.2675
	40	0.2225	1.1999
	45	0.2343	1.1692

<sup>a</sup> Solubility: liquid cm<sup>3</sup>/(liquid cm<sup>3</sup> + polymer cm<sup>3</sup>).

$$\phi_c = \frac{V_c}{V} = \frac{\rho - \rho_a}{\rho_c - \rho_a} \quad (16)$$

where  $V = V_a + V_c$  is the total volume of the membrane sample;  $V_a$  and  $V_c$  are volumes of amorphous and crystalline components, respectively; and  $\rho_a$  and  $\rho_c$  are densities of amorphous and crystalline components, respectively.

The solubility data taken from ref. 17 and the Flory-Huggins binary interaction parameters between *n*-hexane and polyethylene, benzene-polyethylene, at various temperatures, calculated from solubility data by using eq. (14), are given in Table 1 and Fig. 1. As expected, the interaction parameters decrease with increasing temperatures for both cases, i.e., with increasing affinity of the solvent with a membrane. Generally, in polymer solution  $\chi$  values are less than

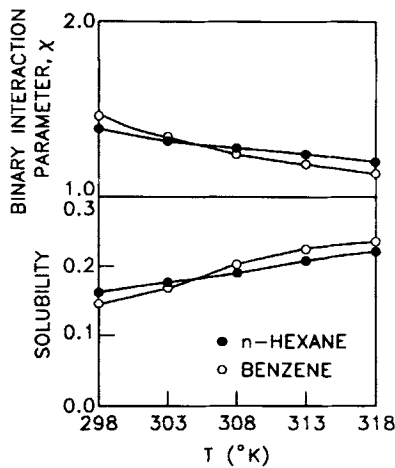


Fig. 1. Solubilities and binary interaction parameters of *n*-hexane and benzene in PE films as a function of temperature: solubility = liquid cm<sup>3</sup>/(liquid cm<sup>3</sup> + polymer cm<sup>3</sup>).

0.5, whereas in swollen polymers  $\chi$  is usually greater than 0.5. As can be seen in Fig. 1, the solubilities of benzene are higher than the values of *n*-hexane from 35°C while the binary interaction parameters show lower values.

The diffusion coefficient  $D_{c=0}$  values, which were obtained directly from the desorption curves, are used in this study.<sup>17</sup> Briefly, from the typical desorption plot of  $\ln[Q(t)/Q(0)]$  against time at long times, the slope is equal to  $-D_{c=0}\pi^2/4l^2$ . From this principle, the diffusion coefficient  $D_{c=0}$  can be determined.

Figure 2 shows the Arrhenius-type plots of experimentally obtained  $\log D_{c=0}$  against  $T^{-1}$  for hexane-polyethylene and benzene-polyethylene systems, respectively. Figure 3 shows the linear relationship between the logarithm of the diffusion coefficient against the reciprocal of free-volume fraction of the polymer [see eq. (5)]. In the case of benzene, it shows quite good agreement, however, the data of *n*-hexane deviates slightly from the linear relationship. From the slopes and intercepts in Fig. 3,  $A_d$  and  $B_d$  values can be determined. These two parameters are independent of temperatures and have an important role in the determination of the diffusion coefficient. The calculated  $A_d$  and  $B_d$  values from the least-square method are shown in Table II. Kulkarni and Stern<sup>10</sup> estimated that the values of  $A_d$  and  $B_d$  for benzene and *n*-hexane are  $4.704 \times 10^{-6}$  and 0.63,  $2.39 \times 10^{-7}$  and 0.46, respectively. Their values are consistent with our results except for the  $A_d$  value for benzene. This difference may exist because they calculated these parameters only at the midpoint of the temperature range studied. Liu and Neogi<sup>6</sup> showed that  $A_d$  and  $B_d$  parameters are independent of the temperatures in the range 25–60°C as demanded by the original Fujita

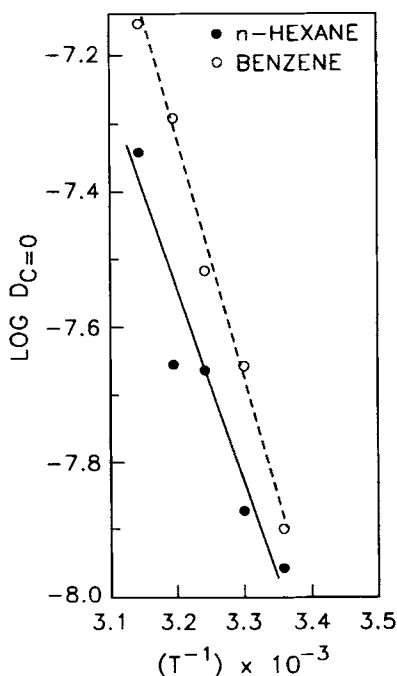


Fig. 2. Arrhenius plots of  $\log D_{c=0}$  (experimentally obtained) against  $T^{-1}$  for *n*-hexane-PE and benzene-PE systems.

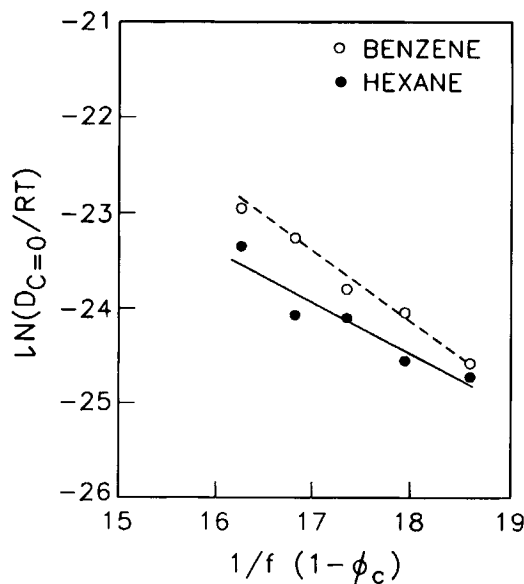


Fig. 3. Diffusion coefficient at zero concentration plotted against free volume.

volume theory. As mentioned earlier,  $B_d$  is taken to be the ratio of the sizes of the diffusing species and the polymer chain segments that have to move cooperatively to allow the formation of a hole in the membrane to accommodate a diffusing molecule. It is reported that the  $B_d$  value is, in general, less than one and can be correlated with the size of the diffusing species.<sup>2</sup>

In order to calculate  $f(1, T)$  values, the densities at 0 K of liquids are needed as mentioned earlier. From eqs. (8) and (10), the volume fraction of liquid and polymer at the temperatures in question can be determined because the free-volume fraction of a polymer is a unique property and should be independent of the nature of the penetrant. Consequently, the  $\beta(T)$  parameter, which represents the ability of the diffusing species to increase the free volume, can be

TABLE II  
Free-Volume Parameters for Diffusion of *n*-Hexane and Benzene in Polyethylene Films

System	Temp. (°C)	$A_d$	$B_d$	$f(0, T)$	$\beta(T)$	$f(1, T)$
<i>n</i> -Hexane-PE	25	$2.83 \times 10^{-7}$	0.5216	0.0950	0.1681	0.2631
	30	—	—	0.0985	0.1697	0.2682
	35	—	—	0.1020	0.1714	0.2734
	40	—	—	0.1055	0.1731	0.2786
	45	—	—	0.1090	0.1749	0.2839
Benzene-PE	25	$7.66 \times 10^{-6}$	0.6863	0.0950	0.1964	0.2914
	30	—	—	0.0985	0.1973	0.2958
	35	—	—	0.1020	0.1981	0.3001
	40	—	—	0.1055	0.1990	0.3045
	45	—	—	0.1090	0.2000	0.3089



calculated from eq. (9). The calculated free-volume parameters at each temperature are given in Table II and Fig. 4. As expected,  $\beta(T)$  and  $f(1, T)$  are functions of the temperature and increases with increasing temperature and show the same trend in as Fels and Huang,<sup>7,17</sup> and it shows that chemically similar *n*-hexane is seen to have higher values of  $\beta$  than benzene.

Fels and Huang<sup>7,17</sup> estimated the preceding free-volume parameters solving the diffusion equation by a numerical method. The reported values for *n*-hexane and benzene are considerably lower than the results of the present study. One of the reasons for this difference is due to the parameter estimation of  $f(0, T)$  by a different procedure;  $f(0, T)$  values obtained by these investigations are lower than those of the present study; they used  $4.8 \times 10^{-4}$  instead of  $7 \times 10^{-4}$  in eq. (10). In the case of using the value of  $4.8 \times 10^{-4}$ , the calculated permeability for *n*-hexane-PE system at 25°C shows lower value of 0.013 g cm/cm<sup>2</sup> s than the experimental permeability as expected because of lower thermal expansion coefficient. In addition, they used the same Flory-Huggins interaction parameter, 0.5, for the entire range of temperature, while this value is much lower than the values calculated in the present study. They reported that changes of 0.5 in the Flory-Huggins interaction parameter resulted in 10% change in the thermodynamic diffusion coefficient. This could be another reason for the large difference between the free-volume parameters of the previous Fels and Huang investigation and the present study. The thermodynamic diffusion coefficients and diffusion coefficients of pure liquids in polyethylene films can be determined from eqs. (3) and (7). The activity of a component in

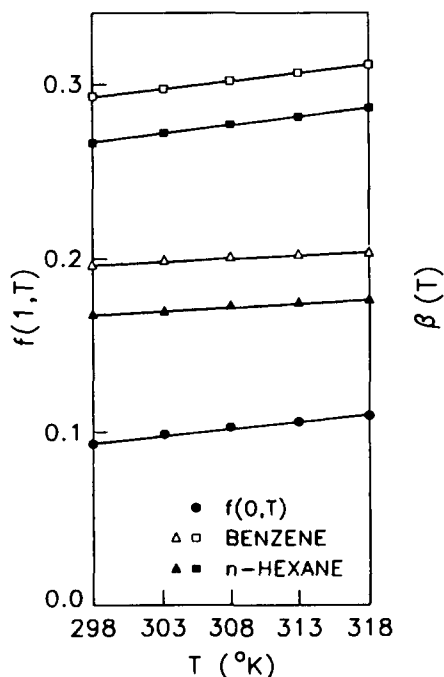


Fig. 4. Free-volume parameters of pure *n*-hexane and benzene in PE films at various temperatures.

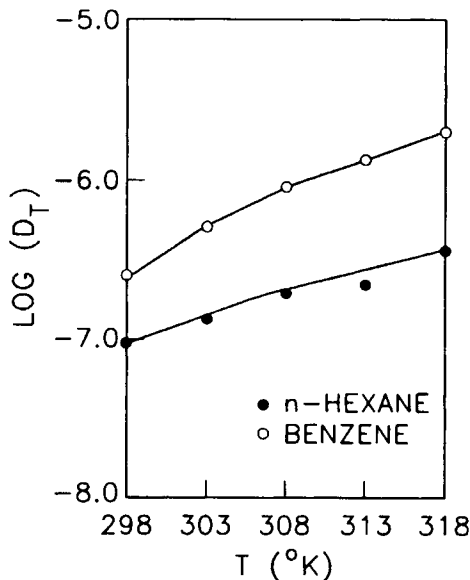


Fig. 5. Calculated thermodynamic diffusion coefficients of *n*-hexane and benzene in PE films.

the polymer film and Flory-Huggins binary interaction parameter were obtained from eqs. (11) and (14). These diffusion coefficients are also plotted in Figs. 5 and 6.

In order to check whether the calculated diffusion coefficients are correct, the permeabilities of pure liquids were calculated by using eq. (15). Table III shows the comparison between the calculated and experimental permeabilities in polyethylene membranes at various temperature. As can be seen, the permeabilities of *n*-hexane show fairly close values, and those of benzene show

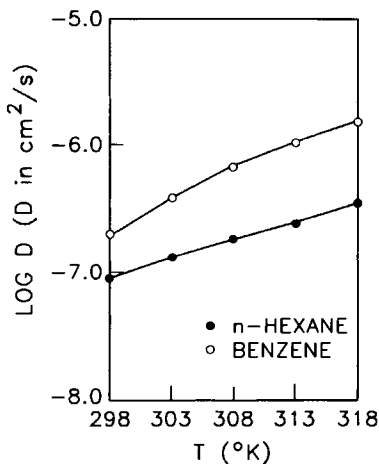


Fig. 6. Calculated diffusion coefficients of *n*-hexane and benzene in PE films.

TABLE III  
Comparison of Calculated and Experimental Permeabilities of *n*-Hexane  
and Benzene in Polyethylene Films

	Temp. (°C)	Calculated (g cm/cm <sup>2</sup> h × 10 <sup>4</sup> )	Experimental (g cm/cm <sup>2</sup> h × 10 <sup>4</sup> )	Ratio <sup>a</sup>	Ratio <sup>b</sup>
<i>n</i> -Hexane	25	0.48	0.64	0.74	1.84
	30	0.78	1.00	0.78	1.82
	35	1.31	1.57	0.83	1.86
	40	2.20	2.38	0.92	1.98
	45	3.46	3.54	0.98	2.02
Benzene	25	1.28	1.13	1.13	2.71
	30	3.11	1.74	1.79	3.30
	35	6.67	2.71	2.46	3.68
	40	13.00	4.22	3.08	4.12
	45	19.74	6.41	3.08	3.15

<sup>a</sup> Ratio = calculated permeability/experimental permeability.

<sup>b</sup> Ratio taken from ref. 17.

more deviations when compared with the experimental results. However, our results are close to the experimental permeabilities when compared to those calculated from the previous Fels and Huang study for, at least, the systems in question (last column in Table III).

## CONCLUSION

Even if the present study is sensitive to the accuracy of the diffusion coefficients at zero concentration, i.e., there is some uncertainty for the determination of  $A_d$  and  $B_d$  from plots  $\ln(D_{c=0}/RT)$  vs.  $1/f(1 - \phi_c)$ , it can be said that the calculated diffusion coefficients of pure liquids show good agreement when comparing the predicted pure liquid permeabilities with the experimental values. The present model cannot be applied to the case where only one diffusion coefficient at zero concentration is known, i.e., this model needs at least two diffusion coefficients at zero concentration at two different temperatures. However, once the  $A_d$  and  $B_d$  parameters are known, the diffusion coefficient can be determined at any other temperature. Also the present model is more convenient and easier to use to determine the diffusion coefficients.

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