

# Hybrid Model for the Diffusion of Simple and Complex Penetrants in Polymers

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**ABSTRACT:** A hybrid model, which combines the characteristic features of the Pace–Datyner molecular model with those of the Kulkarni–Stern free-volume model, was developed to assess the effect of temperature, penetrant concentration, and polymer crystallinity on penetrant diffusivity. The predictive capabilities of the proposed model were tested by a direct comparison with experimental data. The diffusivity of ethylene and propylene vapors in semicrystalline polyethylene and isotactic polypropylene was experimentally measured using a magnetic suspension microbalance.

Sorption kinetic measurements were carried out at temperatures up to 80°C and pressures up to 80 atm. The diffusivity was found to increase with temperature and penetrant concentration. Apparently, there was a very good agreement between the theoretical values predicted by the new hybrid diffusion model and the experimentally determined diffusivities. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2877–2885, 2007

**Key words:** diffusivity; molecular model; free-volume model

## INTRODUCTION

In many industrial applications (e.g., polymer membranes drying, coating of substrates with polymers, catalytic polymerization, as well as polymer industries product designing, including food packaging materials and separation membranes), the interpretation of kinetic data, modeling of the processes, as well as the design of new catalytic systems and processes require the knowledge of gas sorption kinetics within the polymer matrix. The mass-transfer mechanism of gaseous small molecules through the polymer phase follows two stages: (i) solution of the gas (vapor) on the polymer surface and (ii) diffusion through the polymer phase. Solution of the gas (vapor) on the polymer surface is considered to be an instantaneous process,<sup>1</sup> with the concentration reaching immediately the solubility value. On the other hand, diffusion through the polymer phase is a slow process and considered to be the controlling stage of the mass transport process, from the outer bulk phase within and through the polymer matrix. Experimental determination of the diffusion coefficient is crucial, but modeling of the diffusion coefficient dependence on temperature, crystallinity, and penetrant concentration, simultaneously, through a unique numerical model becomes of profound importance when it comes to product design or process design and optimization.

It is now well established that the diffusion of simple penetrants through polymers both below and above the glass transition temperature,  $T_g$ , is Fickian.<sup>2</sup> Moreover, the diffusion coefficient in any given penetrant–polymer system is a function of temperature, polymer crystallinity, and penetrant concentration.<sup>2–25</sup> A great number of predictive models dealing with the diffusivity of gases and vapors in polymer materials have been reported in the open literature.<sup>3,4</sup> These predictive models can be grouped in two different types: the molecular and the free-volume models. The former<sup>2,5–12</sup> are based on the relative motions of penetrant molecules and polymer chains during the diffusion process, and take into account the pertinent intermolecular forces, while the later<sup>13–21,24,25</sup> do not describe in detail the penetrant–polymer system but, on the basis of statistical mechanical considerations, they relate the diffusivity to the free volume ("empty" volume) of the system.

In 1946, Brandt<sup>5,6</sup> expressed the activation energy for the diffusion of small molecules in polymers, based on the molecular structure of the polymer. In 1963, DiBenedetto proposed a molecular model,<sup>7</sup> based on the polymer cell theory he had developed,<sup>8</sup> assuming that the activation energy is a result of the destruction of the Van der Waals bonds during the polymer chain separation, which allows the penetrant molecules movement through the polymer matrix. Finally, in 1979, Pace and Datyner proposed a new correlation between the diffusion activation energy and the physical parameters that describe a penetrant–polymer system.<sup>2,9,10</sup> A new expression for the calculation of the diffusion coefficient was derived, based on DiBenedetto's polymer cell approximation,<sup>7</sup>

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using only one adjustable parameter. This new expression is capable to predict the dependence of the diffusion coefficient on penetrant concentration in certain cases.<sup>11,12</sup>

On the other hand, in 1957, Wilkens and Long proposed a free-volume model based on the free-volume fluctuations occurring around the activated region of the penetrant–polymer system.<sup>13</sup> In 1960, Vasenin<sup>14,15</sup> assumed that the diffusion rate of a molecule in the polymer matrix is proportional to the probability that a cavity formation with a size similar to the penetrant molecule will occur. This cavity acts as a distortion, traveling the penetrant molecule through the polymer matrix. In 1961, Fujita expressed the diffusivity in terms of the penetrant–polymer system's free volume, taking into account the effect of temperature and penetrant concentration on the free volume.<sup>16,17</sup> In his theory, Fujita assumes that the diffusion of a penetrant is a result of the free-volume redistribution within the polymer matrix.<sup>18</sup> In 1976, Vrentas and Duda,<sup>19–21</sup> following the theories of Beuche<sup>22</sup> and Cohen and Turnbull,<sup>23</sup> calculated the overall diffusion coefficient as an expression of the penetrant and the polymer molecules self-diffusion coefficients. Finally, in 1981, Kreituss and Frisch<sup>24</sup> proposed a variation of the Fujita model, to express the diffusivity of small molecules in semicrystalline polymers. The parameters of the modified model were experimentally calculated by Kulkarni and Stern,<sup>25</sup> in 1983.

The predictive capabilities of the diffusion models reported in the literature<sup>2–26</sup> were found in good agreement with experimental data in a limited range of temperature or penetrant concentration, as free-volume models have the advantage of expressing the dependence of the diffusion coefficient on the penetrant concentration and polymer crystallinity, but fail to describe its dependence on the temperature due to their phenomenological nature; while molecular models provide a detailed description of the diffusivity dependence on the temperature and crystallinity, through the diffusion activation energy, disregarding the penetrant concentration within the polymer matrix, as they take into account the interactions between the penetrant molecules and the neighboring polymer chains but ignore the possibility of the presence of a neighboring penetrant molecule. Thus, in 1992, Doong and Ho<sup>26</sup> suggested that a hybrid model, taking into account both the molecular and the free-volume approximations, could exhibit better prediction capability over a wide range of pressures and temperatures. Therefore, they combined the models proposed by Pace–Datyner and Vrentas–Duda to express the effective diffusion coefficient in terms of temperature and penetrant concentration. The hybrid diffusion model includes three adjustable parameters that have to be experimentally evaluated for each penetrant–polymer system.

Finally, in 2001, Dimos<sup>3,4</sup> proposed a new hybrid diffusion model, taking into account the key features of Pace and Datyner's molecular model and Fujita's free-volume model, including the modifications proposed by Frisch and Kreituss<sup>24</sup> and Kulkarni and Stern,<sup>25</sup> to express the effective diffusivity dependence on temperature  $T$ , penetrant concentration  $\phi_1$ , and polymer degree of crystallinity  $\phi_c$ .

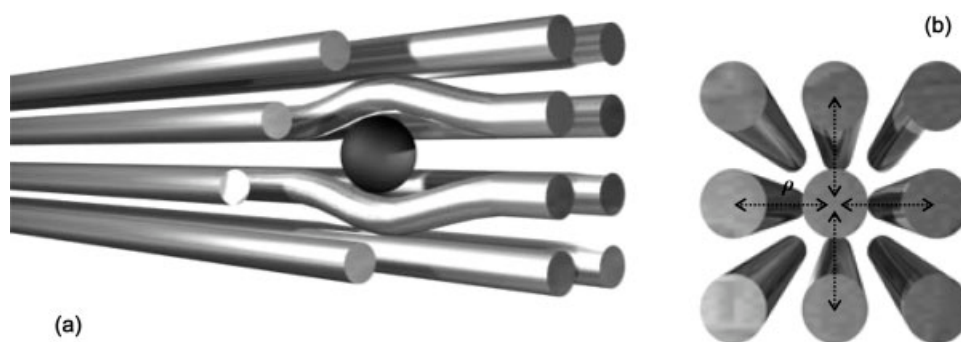
In the present study, modifications of the previously proposed hybrid diffusion predictive model<sup>3,4</sup> are presented, to provide a descriptive but simple numerical model, depended the less possible in experimental data, which can be used in industrial product design or process description. Furthermore, three well-studied penetrant–polymer systems (ethylene–high-density polyethylene, ethylene–isotactic polypropylene, and propylene–high density polyethylene) were chosen to validate the operation of a newly installed Rubotherm<sup>®</sup> magnetic suspension microbalance. The diffusivity values obtained from the experimental data were compared with the theoretical diffusivity predictions, to prove the validity of the proposed modifications and determine the model's "adjustable parameters," namely the mean diffusion jump length,  $\bar{L}$ , and the concentration coefficient factor,  $K$ , to provide a functional descriptive tool, at least within the studied temperature range, although the physical meaning and the correlations derived for the "adjustable parameters" indicate the predictive capability of the model beyond the studied range.

## CALCULATION OF THE EFFECTIVE DIFFUSION COEFFICIENT

To describe the effective diffusion coefficient,  $D_{\text{eff}}$ , of gaseous molecules in semicrystalline polymers one should carefully take into account the local interactions between the polymer chains and the penetrant molecules, the swelling of the polymer matrix, induced by the sorbed molecules, and the extent of polymer crystallinity. In general,  $D_{\text{eff}}$  will be a function of temperature  $T$ , penetrant concentration  $\phi_1$ , degree of polymer crystallinity  $\phi_c$ , as well as other molecular characteristics of the penetrant–polymer system. The proposed hybrid model expresses the diffusivity as a product of three terms:

$$D_{\text{eff}}(d, T, \phi_1, \phi_c) = D_d(d, T, \phi_c) \times f(\phi_1, \phi_c) \times g(\phi_1) \quad (1)$$

where  $D_d(d, T, \phi_c)$  is the thermodynamic diffusion coefficient at zero penetrant concentration,  $f(\phi_1, \phi_c)$  is a factor expressing the swelling effect, due to the sorbed mass, and  $g(\phi_1)$  is a correction factor accounting for the net bulk flow of the penetrant–polymer system.<sup>4,27</sup>



**Figure 1** Amorphous polymer cell with locally parallel chains and a coordination number of 4. (a) A spherical molecule sorbed within the polymer matrix; (b) polymer cell equanimity chain separation distance ( $\rho$ ).

### Thermodynamic diffusion coefficient

In the present study, the thermodynamic diffusion coefficient,  $D_d(d, T, \varphi_c)$ , is calculated using the key features of the Pace and Datyner's molecular model.<sup>2</sup> Based on DiBenedetto's theory, an approximately semicrystalline order in the amorphous polymer region can be assumed, considering locally parallel chain bundles along distances of several nanometers. A coordination number of 4 is assumed for the loose-packed noncrystalline regions (Fig. 1), rather than 6 which represents crystalline microstructure closest packing. A penetrant molecule can move through the amorphous polymer phase (Fig. 2) either (a) freely along the axis of a tube formed by four adjacent parallel chains, or (b) perpendicular to this axis, requiring sufficient separation of the polymer chains to permit passage of the penetrant molecule to an adjoining tube. The later move requires activation energy equal to that necessary to produce the minimum chain separation that will accommodate the molecule, thus minimum chain-separation distance equals the diameter of the diffusing molecule.

While no penetrant molecule is present, or when a penetrant molecule is moving along the axis of a tube, the polymer chains remain at the "equilibrium" separation distance which characterizes the amorphous phase of the polymer and the coordination number of 4, assumed earlier, when no intramolecular force is exerted on the chains, with respect to the ones between them as well as those of adjoining chains [equanimity chain separation distance  $\rho$ , Fig. 1(b)].



**Figure 2** A spherical molecule moving within the polymer matrix and approaching an entanglement: (a) free movement along the axis of a tube; (b) perpendicular movement, requiring sufficient separation of the polymer chains to permit passage of the penetrant molecule to an adjoining tube.

Based on these assumptions,  $D_d$  of a penetrant molecule, with an effective diameter of  $d$ , may be calculated as a function of  $T$ , taking also into account the polymer degree of crystallinity, using the following relations:

$$D_d(d, T, \varphi_c) = 9.10 \times 10^{-4} \frac{\bar{L}^2}{\lambda^2} \left( \frac{\varepsilon^*}{\rho^*} \right)^{5/4} \left( \frac{\sqrt{\beta}}{m^*} \right)^{1/2} \times \frac{d'}{\partial \Delta E / \partial d} e^{-\Delta E / RT} \quad (2)$$

where

$$\Delta E = 5.23 \left( \frac{\beta}{d'} \right)^{1/4} \left( \frac{\varepsilon^* \rho^*}{\lambda^2} \right)^{3/4} \times \left\{ 0.077 \left[ \left( \frac{\rho^*}{\rho} \right)^{11} (\rho - 10d) - \rho^* \left( \frac{\rho^*}{\rho^* + d} \right)^{10} \right] - 0.58 \left[ \left( \frac{\rho^*}{\rho} \right)^5 (\rho - 4d) - \rho^* \left( \frac{\rho^*}{\rho^* + d} \right)^4 \right] \right\} \quad (3)$$

and

$$d' = d + \rho^* - \rho \quad (4)$$

where  $\varepsilon^*$  and  $\rho^*$  are the average Lennard-Jones energy and distance parameters of backbone element, respectively,  $\lambda$  is the mean backbone element separation measured along the chain axis,  $\beta$  is the average effective single-chain bending modulus per unit length (which is a function of chain geometry),  $d'$  is the equivalent diameter of the penetrant molecule,  $\rho$  is the equa-

nimity chain separation distance [the distance of the chain centers at equilibrium, Fig. 1(b)],  $m^*$  is the molecular weight per polymer backbone element,  $\Delta E$  is the diffusion activation energy, namely the minimum energy required for an effective separation of polymer chains equal to the penetrant diameter, and  $\bar{L}$  is the mean diffusion jump length, being the distance traveled by the diffusing molecule within a polymer cell tube until a barrier such as an entanglement, a crosslink, or a crystallite is reached (Fig. 2). Although  $\bar{L}$  cannot be generally predicted, Pace and Datyner<sup>10</sup> suggested that it is a function of  $\Delta E$  and  $\varphi_c$  and presented a graphical correlation of experimental data that helps estimate the value of the mean diffusion jump length. Thus  $\bar{L}$  is assumed the first adjustable parameter, depended on  $\Delta E$  and  $\varphi_c$ . Numerical values of the  $\varepsilon^*$ ,  $\rho^*$ ,  $\lambda$ ,  $\beta$ , and  $d$  parameters can be found in the literature.<sup>9,12</sup>

The equanimity chain separation distance  $\rho$  increases with temperature, depicting the reduction of the polymer density, as the polymer chains move away from one another. In the present study,  $\rho$  is expressed as a function of temperature  $T$ :

$$\rho(T) = \rho_{\text{ref}} + \frac{\alpha}{2} \rho^*(T - T_{\text{ref}}) \quad (5)$$

where  $\alpha$  is the polymer free-volume thermal expansion coefficient and  $\rho_{\text{ref}}$  is the equanimity chain separation distance at  $T_{\text{ref}}$ . Equation (5) is deduced from the Cohen and TurnBull theory,<sup>23</sup> from which it is clear that the equanimity chain distance increases linearly with temperature. Values for  $(\rho^*/\rho)_{\text{ref}}$  ratio, at  $T_{\text{ref}}$ , can be found in the literature,<sup>9</sup> allowing the calculation of the value of  $\rho_{\text{ref}}$ .

### Swelling effect due to the sorbed mass

Having determined  $D_d$ , the swelling effect factor can be extracted from the Fujita model, taking into account the modifications that have been proposed by Kreituss and Frisch<sup>24</sup> and Kulkarni and Stern.<sup>25</sup> Assuming that the exponential factor of the Fujita's free-volume model accounts for the effect of the swelling on the diffusion coefficient, thus the effect of penetrant concentration on diffusivity, the following expression can be deduced:

$$f(\varphi_1, \varphi_c) = \exp\left(\frac{BG\varphi_1}{1 + G\varphi_1}\right) \quad (6)$$

where

$$B = \frac{B_d}{v_f^*(T)(1 - \varphi_c)} \quad (7)$$

and

$$G = \frac{\gamma}{v_f^*(T)} \quad (8)$$

where  $\varphi_1$  is the penetrant volume fraction in the amorphous polymer phase,  $B_d$  a free-volume characteristic

parameter,  $\gamma$  the concentration coefficient, and  $v_f^*(T)$  is the pure polymer free-volume fraction. An equation proposed by Kulkarni and Stern<sup>25</sup> expresses the pure polymer free-volume fraction as a function of temperature:

$$v_f^*(T) = v_{fg} + \kappa(T - T_g) = 0.025 + \kappa(T - T_g) \quad (9)$$

where  $v_{fg}$  is the pure polymer's free-volume fraction at the glass transition temperature, having a value of 0.025 for all polymers,<sup>25</sup> and  $\kappa$  is a "universal" expansion constant having the value of  $4.8 \times 10^{-4} (\text{°C})^{-1}$ , as suggested by Williams et al.<sup>28</sup> However, eq. (9) is only valid for temperatures within the range of  $[T_g, T_g + 100\text{°C}]$ . In the present study, the expansion constant  $\kappa$  is replaced by the polymer free-volume thermal expansion coefficient  $\alpha$ , since most of the industrial processes are carried out at temperatures exceeding that range:

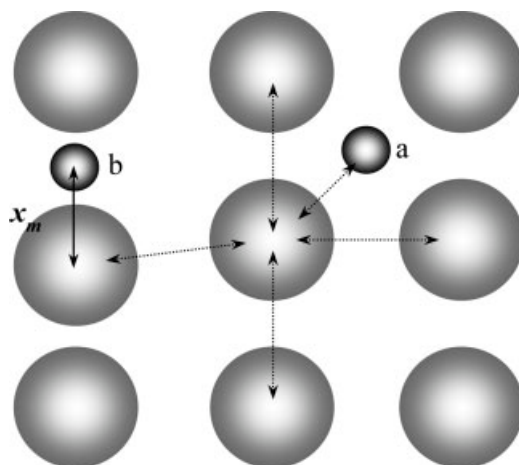
$$v_f^*(T) = 0.025 + \alpha(T - T_g) \quad (10)$$

The polymer free-volume thermal expansion coefficient can be taken equal to the polymer thermal expansion coefficient, with the assumption that the polymer thermal expansion is a direct result of the free-volume thermal expansion.  $B_d$  expresses the relative size of the penetrant molecule and the polymer chain segments that move due to the swelling induced by the penetrant to a polymer cell. To determine its value,  $D_{\text{eff}}$  is experimentally determined at the limit of zero penetrant concentration for each studied system, and a linear transformation of the Fujita equation<sup>24,25</sup> is used:

$$\ln \frac{D_{\text{eff}}}{RT} = \ln A_d - \frac{B_d}{v_f^*(T)(1 - \varphi_c)} \quad (11)$$

where  $D_{\text{eff}}$  is the effective diffusion coefficient and  $R$  the universal gas constant. At the limit of zero penetrant concentration, the diffusion coefficient is not affected by the penetrant concentration (swelling is negligible), so one may assume that the effective diffusion coefficient becomes equal to the thermodynamic diffusion coefficient. Taking into account this assumption, a theoretical calculation of  $D_{\text{eff}}$  is proposed in the present study, thus eqs. (2)–(4) and (9) are employed to calculate the values of  $D_d$  and  $v_f(T)$  at a range of temperatures around the studied, against the described experimental approximation, leading to the accurate calculation of  $B_d$  by a graphical representation of  $\ln D_d/RT$  with respect to  $1/v_f^*(T)(1 - \varphi_c)$  [eq. (11)]. Furthermore Kulkarni and Stern<sup>25</sup> suggest that the concentration coefficient  $\gamma$  is proportional to the fractional volume expansion of the polymeric cell due to the penetrant molecules:

$$\gamma = \frac{K}{A} \left[ \left( \frac{x_m}{\rho} \right)^2 - 0.5 \right] \quad (12)$$



**Figure 3** (a) Penetrant molecule traveling across a tube, (b) penetrant molecule jumping across two separated polymer chains,  $x_m$  the minimum proximity of a penetrant molecule to a polymer chain center.

where  $K$  is the proportional constant,  $A$  the penetrant liquid molar volume divided by  $22,414cc_{STP} \text{ mol}^{-1}$ ,  $\rho$  the equanimity chain separation distance, and  $x_m$  is the minimum distance between a penetrant molecule and the nearest polymer chain center (Fig. 3). Determination of  $x_m$  can be achieved using the potential energy function<sup>25</sup> to calculate the distance from a polymer chain center at which the penetrant molecule possesses the minimum potential energy.

Although Kulkarni and Stern suggest that  $K$  has the same value for all the penetrant–polymer systems at any given temperature, experimental data presented in Figure 11 of their publication<sup>25</sup> suggest that  $K$  remains constant at the range of temperature, but has a unique value for each penetrant–polymer system, indicating the free-volume expansion effect of the polymer on the concentration coefficient. It is apparent (same figure<sup>25</sup>) that  $\gamma A$  follows a linear relationship with the quantity  $[(x_m/\rho)^2 - 0.5]$ . Thus,  $K$  is assumed

to be the second adjustable parameter of the proposed model, depending on the penetrant–polymer system.

#### Net bulk flow correction factor

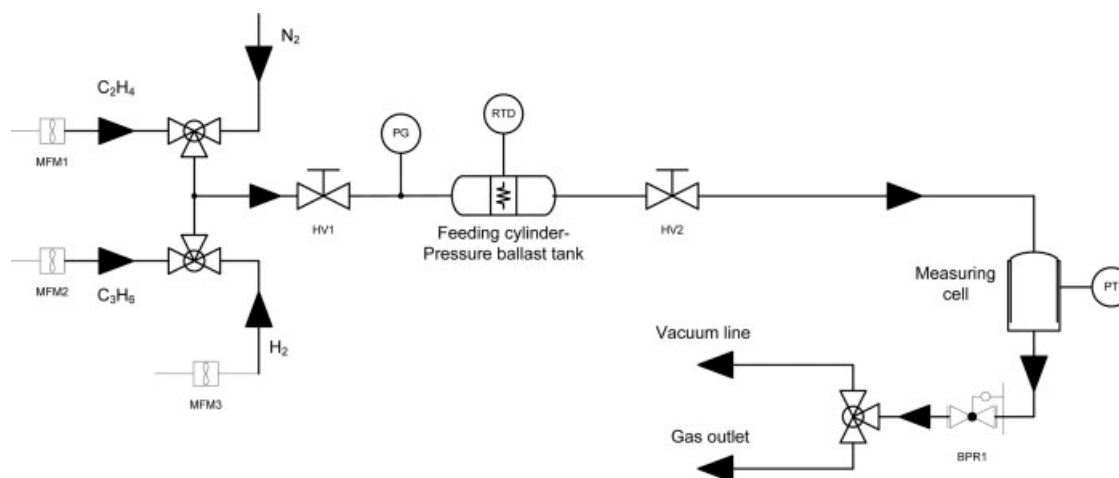
Finally, the correction factor  $g(\phi_1)$  which accounts for the net bulk flow of the polymer–penetrant system is expressed as follows:<sup>27</sup>

$$g(\phi_1) = (1 - \phi_1)^3 \quad (13)$$

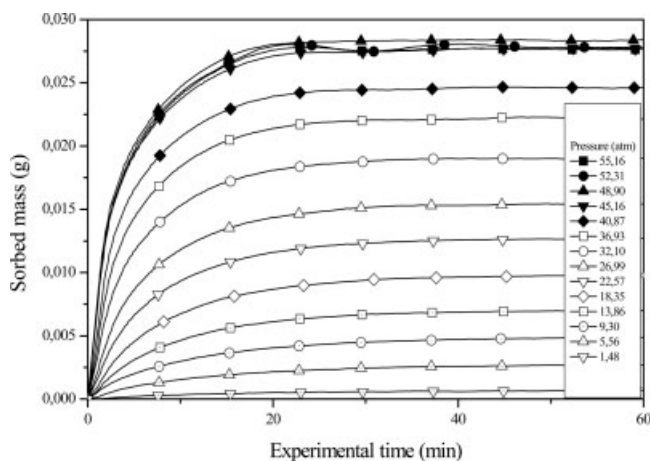
The suggested predictive model [eq. (1)] depends only on two “adjustable” parameters, while the rest of the parameters are either presented in the literature, or can be theoretically calculated using the procedures described here. The mean diffusion jump length  $\bar{L}$ , and the concentration coefficient  $K$  can both be determined from experimental data, for any given penetrant polymer system (see Result and Discussion).

#### EXPERIMENTAL SORPTION MEASUREMENTS

The mass uptake of ethylene and propylene vapors by semicrystalline polyethylene ( $\omega_c = 74\%$ ) and isotactic polypropylene films ( $\omega_c = 55\%$ ) was measured using a Rubotherm two-position magnetic suspension balance. A schematic representation of the apparatus is illustrated in Figure 4. Four gas lines allow the feed of the system with pure gases, or mixtures of them. Mixture concentration can be controlled through the mass flow meter controllers installed in each feed line. The gas mixture (or pure gas, as is the case in the present study) can be stored in the feeding cylinder to conduct “static” sorption experiments (where there is no gas flow through the system, but the sample is immersed in a constant pressure gas atmosphere), or can be continuously fed to the microbalance sample cell to conduct “continuous flow” experiments. In the later case, the pressure of the sample cell is kept constant using



**Figure 4** Apparatus flowchart.



**Figure 5** Experimental ethylene sorption in polyethylene kinetic curves, at 50°C, at various pressures.

the back pressure regulator valve installed in the outlet line.

Polyethylene (No. 18190-0;  $M_w = 125,000$  and  $d = 0.95$ , melting point determined at 131°C; Aldrich) and isotactic polypropylene (No. 42811-6;  $M_w = 12,000$  and  $d = 0.902$ , melting point determined at 152°C; Aldrich) films of 0.4 mm thickness were prepared with the aid of a hot-press apparatus by heating and pressing polymer grains at a temperature of about 120 and 140°C, respectively, for 20 min. The mass fraction crystallinity of each film,  $\omega_c$ , was measured with a differential scanning calorimeter. The volume fraction crystallinity was calculated by:

$$\varphi_c = \frac{\omega_c}{(d_{pc}/d_p)} \quad (14)$$

where  $d_{pc}$  and  $d_p$  are 100% crystalline polymer density and the sample polymer density, respectively. Sorption kinetics was recorded under isothermal and isobaric conditions through "static" integral sorption experiments.

During the sorption measurements, the studied polymer samples, located in the sample basket, were placed in the measuring cell, which was degassed for a period of 2 h, to ensure that no gas was sorbed in the sample at the beginning of each experiment. Subsequently, both the measuring cell and gas-feeding tank (ballast tank) were heated to the desired temperature, while the pressure in the feeding tank was set to a predetermined value. When the specified conditions (e.g., feeding tank pressure and system temperature) were reached, the measuring cell was connected to the feeding tank and the online recording of the sorbed gas mass by the polymer sample films was automatically initiated. During the experiments, the temperature and pressure of the measuring cell were controlled, to ensure the satisfaction of the specified isothermal and isobaric conditions. After equilibrium had been

reached, the measuring cell was isolated from the ballast tank and degassed till the complete desorption of the sorbed gas from the polymer sample. Typical obtained sorption kinetic curves are presented in Figure 5.

Apparently (Fig. 5), the rate of sorption increases with the penetrant gas pressure. Furthermore, at pressures exceeding the critical pressure of the penetrant gas, the rate of sorption remains constant and independent of the gas pressure. The same applies to the total penetrant mass uptake.<sup>3,4</sup> The time ( $t_{1/2}$ ) at which the sorbed mass becomes equal to the half of its equilibrium value was obtained using the reduced sorption isotherms ("half-time" method).<sup>29</sup> The effective diffusion coefficient for each studied case was calculated by the following equation:

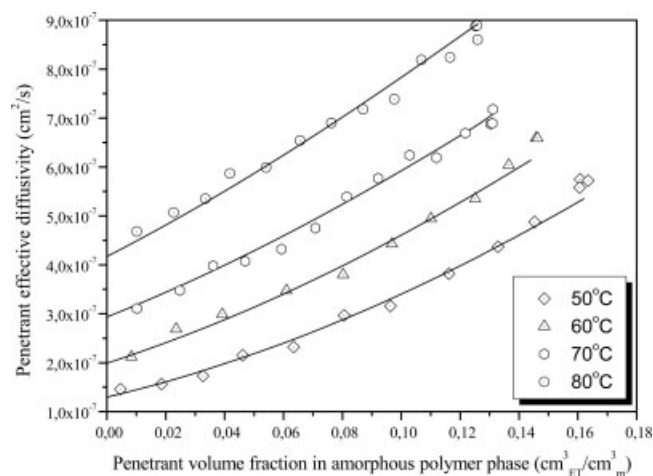
$$D_{\text{eff}} = \frac{0.049}{(t_{1/2}/l^2)} \quad (15)$$

where  $l$  is the thickness of the corresponding polymer sample film.

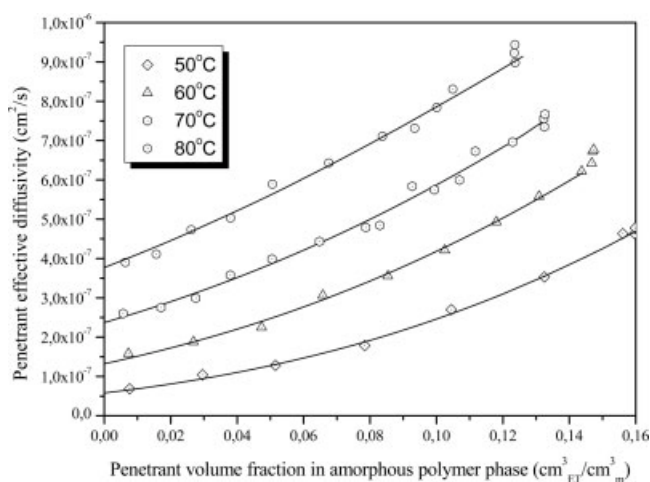
## RESULTS AND DISCUSSION

A number of sorption experiments were carried out to determine the diffusivity of ethylene in semicrystalline polyethylene and isotactic polypropylene, as well as the diffusivity of propylene vapors in semicrystalline polyethylene. For each case, the sorption kinetics was recorded at four different temperatures (e.g., 50, 60, 70, and 80°C). For all temperatures studied, ethylene experiments were carried out at pressures up to 80 atm, while propylene experiments up to the corresponding dew point.

In Figures 6–8, experimentally determined values of penetrant effective diffusivity (shown by the discrete points) are plotted with respect to the penetrant



**Figure 6** Ethylene diffusivity in semicrystalline polyethylene at various temperatures.

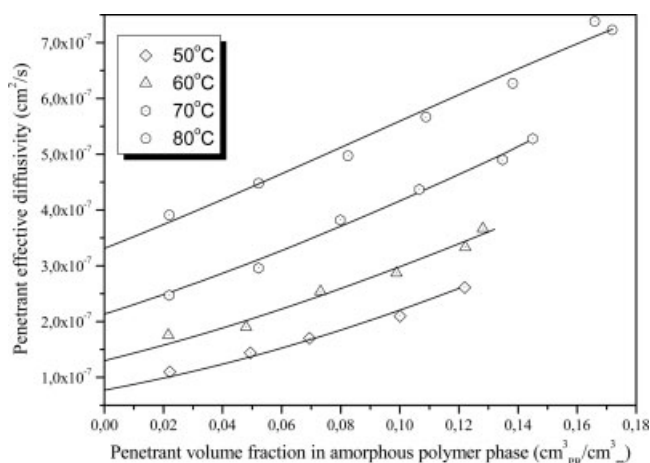


**Figure 7** Ethylene diffusivity in semicrystalline isotactic polypropylene at various temperatures.

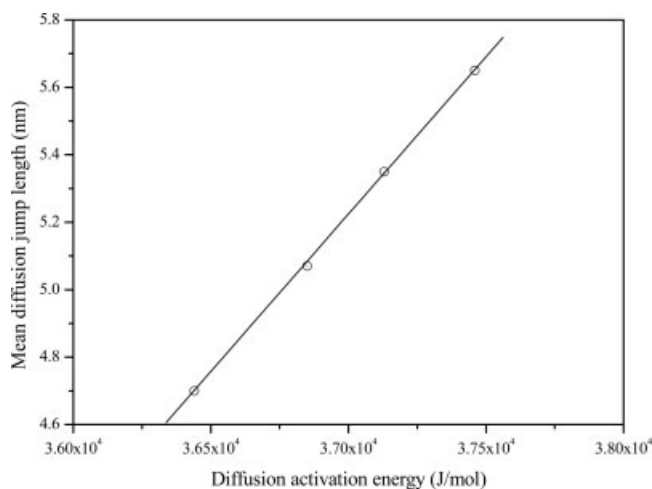
volume fraction in the amorphous polymer phase, at various temperatures. Continuous lines represent the values of diffusivity predicted by the proposed diffusion model [eqs. (1)–(13)]. It is apparent that penetrant diffusivity increases with temperature and penetrant concentration. However, for each temperature, the diffusivity reaches a maximum value at the critical pressure of the penetrant gas. For higher pressures, diffusivity remains constant and equal to its maximum value.

### Fitting procedure

The model described earlier was employed to calculate the dependence of effective diffusivity  $D_{\text{eff}}$ , on temperature  $T$ , and penetrant concentration in the amorphous polymer phase,  $\phi_1$ , for the given polymer crystallinity,  $\phi_c$ . The parameters needed (except for the two adjustable parameters) were extracted from the literature<sup>9,12</sup> or were calculated theoretically as mentioned earlier. The values of the adjustable parameters (namely  $\bar{L}$  and



**Figure 8** Propylene vapors diffusivity in semicrystalline polyethylene at various temperatures.



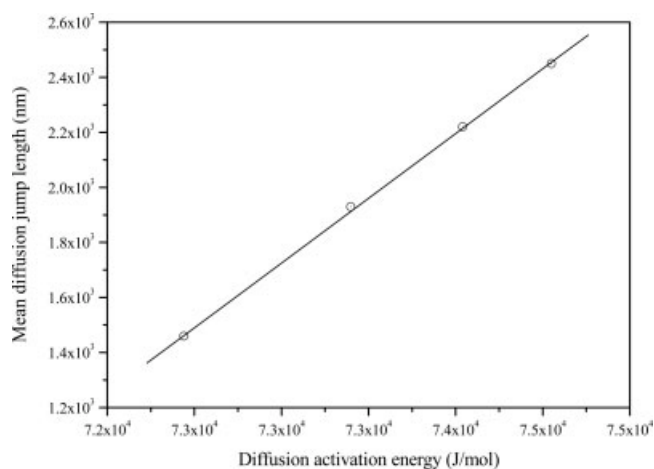
**Figure 9** Mean diffusion jump length of ethylene in semicrystalline polyethylene.

$K$ ) were defined through comparison with the experimental data, although a first approximation of them was taken from the literature.<sup>10,25</sup> As  $\bar{L}$  is used in the model to determine the diffusivity at zero penetrant concentration, certain values were assumed to fit correctly the low-concentration experimentally determined diffusivity values. Furthermore, the value of  $\bar{L}$  is expected to rise with the activation energy, as the higher diffusion activation energy reflects the difficulty of a molecule to jump to an adjoining tube of the polymer matrix, as more energy is needed to separate the chains to the minimum chain separation distance, thus the molecule will travel farther distances, back and forth, within a certain tube before a chain separation that allows jumping to an adjoining tube occurs. Taking into account that concept, the value of  $\bar{L}$  was lowered for higher temperatures, and a plot of  $\bar{L}$  versus  $\Delta E$  surprisingly exhibits a linear relationship between them (Figs. 9–11). Thus, during fitting, the values of  $\bar{L}$  were determined to fit the experimental diffusivity data at the low concentration end and to follow linear relationship with the diffusion activation energy calculated through eq. (3).

The value of  $K$ , used for the simulations, was determined afterwards to fit correctly the experimentally determined diffusivity values at the high concentration end, as it reflects the swelling effect, induced by the penetrant molecules to the polymer matrix, on the diffusivity of the penetrant. As stated earlier,  $K$  is expected to depend only on the penetrant–polymer system, thus its value was kept constant for each studied system and was determined as the one that produces the best fitting results for all the diffusivity curves of each system.

### Application of the hybrid model—Results

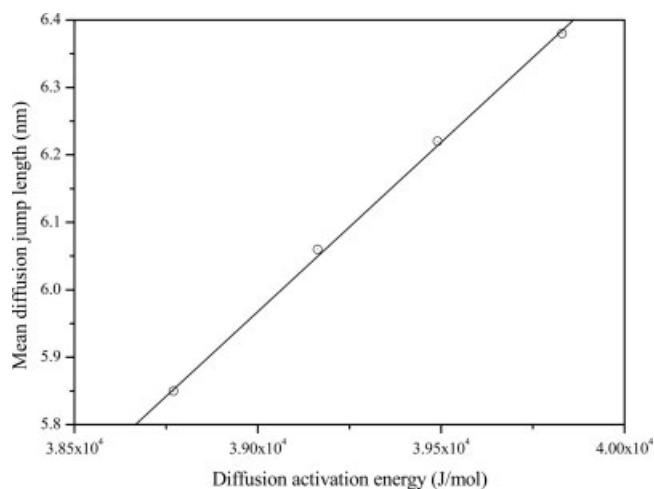
Model predictions of ethylene diffusivity in semicrystalline polyethylene ( $\omega_c = 74\%$ ) indicate that the value



**Figure 10** Mean diffusion jump length of ethylene in semicrystalline isotactic polypropylene.

of the adjustable parameter  $K$  remains constant in the range of temperature and penetrant concentration, and equal to 2.311. On the other hand, the mean diffusion jump length (Fig. 9) remains independent of penetrant concentration but shows a linear correlation with the diffusion activation energy. That is because as the minimum energy,  $\Delta E$ , required for the effective separation of polymer chains decreases with temperature, the probability of a penetrant molecule jump to an adjoining tube increases. Predictions of ethylene diffusivity in isotactic PP ( $\omega_c = 55\%$ ) also indicate that the value of  $K$  remains constant and equal to 2.95, while  $\bar{L}$  is a linear function of the diffusion activation energy,  $\Delta E$  (Fig. 10).

In Figure 8, the diffusivity of propylene vapors in PE ( $\omega_c = 74\%$ ) is presented. For low temperatures (e.g., 50, 60, and 70°C),  $K$  has a numerical value of 1.322. As the temperature approaches propylene critical point, the value of  $K$  slightly increases ( $K = 1.436$  at  $T =$



**Figure 11** Mean diffusion jump length of propylene vapors in semicrystalline polyethylene.

80°C), reflecting the smooth transition of the penetrant–polymer system reported by many investigators.<sup>30</sup> Figure 11 shows the linear correlation followed between the mean diffusion jump length and the diffusion activation energy.

## CONCLUSIONS

Sorption kinetic measurements of ethylene and propylene vapors in semicrystalline polyethylene and isotactic polypropylene have shown that diffusivity increases with temperature and penetrant concentration. For any given temperature, diffusivity reaches a maximum value at the penetrant's critical pressure. A hybrid diffusion model combining the main features of the Pace–Datyner molecular model and those of the Fujita free-volume model was developed to assess the effect of temperature, penetrant concentration, and polymer crystallinity on the penetrant diffusivity. The proposed diffusion model employs physical parameters of the penetrant–polymer system as well as two adjustable parameters, the mean diffusion jump length,  $\bar{L}$ , and the concentration coefficient factor  $K$ . Both  $\bar{L}$  and  $K$  have physical meaning. Thus,  $\bar{L}$  exhibits a linear dependence of the diffusion activation energy, and decreases as  $\Delta E$  increases. On the other hand,  $K$  depends on the fractional volume expansion of the polymer cell and has a characteristic value for each penetrant–polymer system. Deviations of  $K$  value occur when approaching the penetrant critical point. The predictive capabilities of the proposed model were tested by a direct comparison of model predictions with experimental measurements. The results have shown that predictions and experimental data are in very good agreement. Therefore, the proposed correlations for the calculation of the equanimity chain separation distance, the pure polymer's free-volume fraction, and the free-volume characteristic parameter  $B_d$ , using the theoretical calculated diffusivity at zero penetrant concentration, have significantly improved model prediction capabilities.

Furthermore, the numerical value of  $K$ , as well as a correlation of  $\bar{L}$  versus  $\Delta E$ , can be established by experimental investigation of any given penetrant–polymer system, making the theoretical calculation of diffusivity possible for the said system, and thus providing a useful tool for product designing and process optimization. Investigation of the effect of polymer crystallinity on  $\bar{L}$  would also provide useful information for the proposed model.

## NOMENCLATURE

### Definitions

- $A$  Reduced liquid molar volume
- $B_d$  Free-volume characteristic parameter



$d$	Spherical molecule diameter (cm)
$d_p$	Polymer density ( $\text{g cm}^{-3}$ )
$D_d$	Thermodynamic diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ )
$D_{\text{eff}}$	Effective diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ )
$K$	Concentration coefficient factor
$\bar{L}$	Mean diffusion jump length (nm)
$l$	Film thickness (cm)
$R$	Universal gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$T$	Temperature (K)
$T_g$	Glass-transition temperature (K)
$v_f^*(T)$	Pure polymer's free-volume fraction
$x_m$	Minimum proximity distance (cm)

### Symbols

$\alpha$	polymer free-volume thermal expansion coefficient
$\gamma$	Concentration coefficient
$\rho$	Equanimity chain-separation distance (cm)
$\phi_1$	Volume fraction of penetrant in amorphous polymer
$\phi_c$	Volume-fraction crystallinity
$\omega_c$	Mass-fraction crystallinity

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