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Diffusion of toluene and n-heptane in polyethylenes of different crystallinity

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Abstract

Diffusivity and solubility data for toluene and n-heptane in semi-crystalline polyethylene were obtained by gravimetric sorption experiments conducted in two different laboratories. The effects of temperature, concentration and degree of crystallinity on the diffusion and solubility behaviour were investigated at 70°C. The diffusivity data were correlated using a modification of the Vrentas–Duda free-volume theory. All the parameters in the free-volume model were estimated from pure component data except the size of the jumping units, the tortuosity, and the free-volume characteristics of the polymers. These results indicate that both the diffusivity and penetrant solubility in the polymer amorphous phase decrease with increasing crystallinity. Further, the tortuosity or the length of the diffusion path around the crystals increases with the degree of crystallinity. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Gravimetric sorption; Polyethylenes; Vrentas–Duda free-volume theory

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Nomenclature

D	polymer–solvent binary mutual-diffusion coefficient (cm^2 s^{-1})
D_{01}	constant pre-exponential factor (cm^2 s^{-1})
f_a	free-volume of the amorphous phase without the presence of crystals (cm^3 g^{-1})
f_b	correlation factor for crystallinity influence on the free-volume (cm^3 g^{-1})
$\hat{V}_1^*$	solvent specific critical hole free-volume (cm^3 g^{-1})
$\hat{V}_2^*$	polymer specific critical hole free-volume (cm^3 g^{-1})
$\hat{V}_{FH_a}$	hole free-volume in the amorphous phase (cm^3 g^{-1})
$\tilde{V}_{2j}$	polymer jumping unit (cm^3 mol^{-1})
$\hat{V}_{FH_{1a}}$	hole free-volume of the solvent (cm^3 g^{-1})
$\hat{V}_{FH_{2a}}$	hole free-volume of the amorphous polymer (cm^3 g^{-1})

Greek Letters

γ	overlap factor accounting for shared free-volume
ξ	ratio of solvent and polymer jumping unit
ϕ_{ia}	volume fraction of component i in the amorphous phase
ω_{ia}	weight fraction of component i in the amorphous phase
τ	tortuosity factor
τ_a	correlation factor for influence of crystallinity on the tortuosity
χ	Flory–Huggins interaction parameter

1. Introduction

In the production of most polymers, residual low molecular weight species, such as monomers or solvents remain in the finished polymer product. In order to meet quality, safety, health, and environmental standards, these low molecular weight species must be removed by devolatilization steps. Detailed information concerning the solubility and diffusion of solvents in the polymer are required to design and optimize devolatilization processes. In most cases, devolatilization occurs at temperatures above the glass transition temperature of the polymer where the diffusion coefficient for the polymer–solvent system can be a strong function of temperature and solvent concentration. Theories based on free-volume concepts provide excellent correlations and, in some cases, predictions of the concentration and temperature dependence of small molecules within amorphous polymers under devolatilization conditions [1]. The devolatilization of semi-crystalline polymers such as polyethylene, however, can be conducted at conditions where amorphous and crystalline phases coexist and standard free-volume theories are not applicable. Studies of diffusion of small penetrant molecules in semi-crystalline polyethylene clearly reveal that the diffusion process is

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greatly complicated by the presence of the two phases [2,3].

Although various models were conceived to correlate diffusivity data for semi-crystalline polyethylene–solvent systems, several assumptions are common to all. Solvents are generally considered to be insoluble in the crystallite regions of the polymer and mass transfer or diffusion occurs only in the continuous amorphous phase existing between the crystallites. Barrer [2] states that twisting crystalline lamellae are thought to grow out from several centres, producing spherulitic structures in polyethylene. Michaels et al. [3] consider the lamellae to be the inpenetrable domains and not the spherulites. The lamellae are thought to be in close proximity thereby restricting the routes for diffusion and rendering very tortuous pathways. The amorphous content between the spherulites never fully disappears [4], rather the amorphous region is envisioned to supply the growing spherulites with polymer, resulting in a permanent entanglement in the spherulites. The mobility of the polymer chains decreases as a result of this entanglement and ultimately the crystal growth stops. Correspondingly, the mobility of solvents in the amorphous region are also presumed to be retarded by these entanglements which cause a tightening or loss of free-volume in the amorphous phase.

The presence of the solvent is generally assumed not to influence the number of crystallites or their morphology. There are certain systems where this assumption is invalid since the presence of solvents can either promote the formation of crystals [5,6], or destroy them [7]. In the former, the solvent plasticizes the polymer and facilitates its approach to thermodynamic equilibrium. In constrast, when crystals are dissolved by the solvent, the thermodynamic equilibrium state is altered. In this study, diffusivity data for toluene and n-heptane in several polyethylene samples of varying crystallinity were measured by gravimetic sorption and correlated by a free-volume theory of diffusion that was modified to incorporate the complexities of diffusion in semi-crystalline polymers.

2. Theory

The most successful models for describing diffusion of low molecular weight penetrants or solvents in amorphous polymers above the glass transition are based on free-volume concepts in which the components of the system are envisioned to migrate by jumping into free-volume holes formed by natural thermal fluctuations. These basic free-volume concepts were first proposed by Cohen and Turnbull [8], modified by Fujita [9] for the case of diffusion in amorphous, rubbery polymers and refined by Vrentas and Duda [10] for both self and mutual diffusion in polymer–solvent systems.

The critical difference between the Fujita and Vrentas–Duda theories is the utilization of the free-volume per unit volume of solution by the Fujita theory [11] and the average free-volume per jumping unit by the Vrentas–Duda theory. It was shown that the Fujita theory is a restricted form of the Vrentas–Duda theory [12]. Both theories can correlate diffusivity data equally well. The strength of the Vrentas–Duda theory, however, is its semi-predictive capability, for example, when a few diffusivity data points for one solvent are available to determine key parameters, the model can be applied to predict diffusional behaviour for that solvent or others over a broad spectrum of temperature and concentration. Consequently, the results of the correlation presented in this study can be used to predict molecular diffusion of other solvents in polyethylene.

The free-volume theory can be modified to describe mutual binary diffusion in a semi-crystalline polymer by considering the hole free-volume of the amorphous phase and the effect of crystallite size on the tortuosity:

$$D=\left[D_{01}\exp\left(-\frac{(\omega_{1a}\hat{V}_1^*+\omega_{2a}\hat{V}_2^*\xi)}{\hat{V}_{\mathrm{FH_a}}/\gamma}\right)\right]\times\left[(1-2\chi\varphi_{1a})(1-\varphi_{1a})^2\right]\left[\frac{1}{\tau}\right] \quad (1)$$

In Eq. (1), the mutual binary diffusion coefficient, *D*, is constructed of the product of three terms. The first term is an approximation for the self-diffusion coefficient of the solvent in the polymer based on the free-volume concepts [10]. The second term is a thermodynamic term which relates the mutual binary diffusion coefficient to the self-diffusion coefficient based on the Flory–Huggins thermodynamics model [13]. This model has the adjustable parameter χ which indicates the strength of the interaction between the polymer and solvent. Although the crystallites serve to impede swelling similar to cross-links, the concentration range examined in this study is sufficiently low so that the effect of cross-links can be neglected. For higher solvent concentrations use of the Flory–Rehner [14] thermodynamic model may be more appropriate. The third term in Eq. (1) is a tortuosity, τ, which accounts for the longer pathway a penetrant must follow to circumvent the crystalline regions. In this formulation, subscript 1 refers to solvent, subscript 2 refers to the polymer, and subscript "a" refers to the amorphous phase. The definition and physical significance of all the parameters in the first two terms are available in several references [15]. The specific volume of the polymer–solvent solution in the amorphous phase that facilitates molecular diffusion, $\hat{V}_{\mathrm{FH_a}}$, is referred to as the hole free-volume and can be determined from the hole free-volumes of the individual species in the amorphous phase:

$$\hat{V}_{\mathrm{FH_a}}/\gamma=\omega_{1a}\hat{V}_{\mathrm{FH_1}}/\gamma+\omega_{2a}\hat{V}_{\mathrm{FH_{2a}}}/\gamma \quad (2)$$

where γ reflects the amount of free-volume shared between molecules. Although this model has numerous parameters, they all have specific physical significance and several of them can be estimated from pure component data [1,16]. The critical volumes, $\hat{V}_1^*$ and $\hat{V}_2^*$ can be estimated from group contribution correlations [17,18]. The pre-exponential term, D_{01} and the free-volume associated with the solvent,$\hat{V}_{\mathrm{FH}_1}$, can be estimated from the temperature dependence of the solvent viscosity and density along with the solvent critical properties. For most polymers, the free-volume associated with the polymer, $\hat{V}_{\mathrm{FH}_2}/\gamma$, can be determined from a free-volume correlation of the viscosity of the polymer as a function of temperature. In the case of a semi-crystalline polymer, however, it is difficult to determine the free-volume characteristics of the amorphous phase of the polymer. Further, the free-volume of the amorphous phase may be influenced by the presence of the crystallites. Consequently, the free-volume of the amorphous phase was determined from a correlation of the diffusivity data. As a first approximation the amount of free-volume in the amorphous polymer was assumed to be a linear function of the volume fraction of the crystals, ϕ_c:

$$\hat{V}_{\mathrm{FH}_{2a}}/\gamma = f_a - f_b\phi_c \tag{3}$$

where f_a is the free-volume of the amorphous phase without the presence of the crystals and f_b is a parameter which correlates the influence of crystallinity on the amorphous phase. Similarly, as a first approximation, the tortuosity is assumed to be a linear function of the degree of crystallinity:

$$\tau = 1 + \phi_c\tau_a \tag{4}$$

One of the key parameters in the Vrentas–Duda theory is ξ, which represents the ratio of the volumes of the diffusive jumping units of the solvent to the polymer. Although correlations were presented to estimate this parameter [16], the theory was most successful when this parameter is determined from the correlation of diffusivity data.

For the thermodynamic function in Eq. (1) the solvent volume fraction in the amorphous phase, ϕ_{1a}, can be related to the weight fraction of the solvent in the amorphous phase, ω_{1a}, by the density of the two components. The Flory–Huggins interaction parameter, χ, can be determined from solubility data or estimated by various thermodynamic models.

In the application of the Vrentas–Duda free-volume model for completely amorphous polymers the polymer free-volume is obtained from viscosity or relaxation data. For the case of a semi-crystalline polymer, however, the complexities associated with the presence of the crystals dictate that diffusivity data be correlated using four adjustable parameters: f_a, f_b, τ_a and ξ. Fortunately, such a correlation is not completely empirical since three of these parameters, f_a, f_b and τ_a are fixed by the characteristics of the polymer and are independent of the solvent. Further, reasonable values for the ratio of the jumping units, ξ, are constrained to a range consistent with the size of the solvent molecules relative to segments of the polymer chain.

In this study, the free-volume model modified for semi-crystalline polymers (Eqs. (1)–(4)) was evaluated using diffusivity measurements for toluene and n-heptane in three polyethylene samples possessing different degrees of crystallinity. The interaction parameter, χ, was obtained for each solvent–polymer pair from equilibrium sorption measurements that were obtained as an integral part of the diffusion experiment. The solvent specific parameters, D_{01}, and $\hat{V}_{\mathrm{FH}_1}$, were determined from literature values which are based on pure component solvent data. Finally, the data sets for both solvents were correlated to determine five parameters: f_a, f_b, τ_a, ξ (toluene) and ξ(n-heptane).

3. Experimental

The gravimetric sorption experiment is a common experiment for studying diffusion in solvent–polymer systems, and details concerning the experimental technique and data analysis are available in the literature [19]. In this study, a thin film (approximately 1.5 mm thick) of the polyethylene was exposed to a constant vapour pressure of the solvent, and the weight gained by the polymer film was measured as a function of time at isothermal conditions. The equilibrium solubility of the solvent in the polymer at a particular solvent vapour pressure and temperature were determined by the final equilibrium weight gained by the polymer sample. The mutual binary diffusion coefficient was determined from the measured relationship between the weight gain and the time of exposure to the solvent. The diffusivity dependence on concentration was determined from the initial slope technique using a correlation for the influence of concentration on the diffusivity [20].

Independent measurements from two different laboratories are presented as a check on both the equilibrium and diffusivity data. Although both experiments were based on gravimetric sorption, the equipment employed were significantly different. The gravimetric sorption balance in the Centre for the Study of Polymer–Solvent Systems exposes a polymer sample to a pure solvent vapour and relies on the extension of a quartz spring, from which the polymer is suspended, to determine the solvent weight gain. In the DSM Research Laboratory, the polymer sample was exposed to a flowing gas stream composed of the solvent and an inert gas, the solvent weight gain was determined by an electronic balance. The characteristics of the three types of polyethylene employed in this study are presented in Table 1. Reagent-grade toluene and normal heptane were used as supplied.

The vapour pressure of the solvent was controlled by a second constant temperature bath. Diffusivity data were obtained as a function of solvent concentration by conducting a series of sorption experiments consisting of step changes in the vapour pressure of the solvents.

4. Results and discussion

4.1. Thermodynamic data and analysis

Gravimetric sorption experiments were conducted with three different polyethylenes at 70°C over a broad range

Table 1
Polymer characteristics

Sample	Crystal volume fraction, ϕ_c	Density at 70°C, ρ_2 (g cm^{-3})
LDPE, low density polyethylene	0.35	0.8907
LLDPE, linear low density polyethylene	0.45	0.9097
HDPE, high density polyethylene	0.70	0.9477

of concentration. Fig. 1 shows a correlation of the equilibrium sorption data for toluene in the three polyethylene samples where the volume fraction of the toluene based on the total volume of the polymer, ϕ_1, is presented as a function of the toluene activity. The solvent activity is defined as the ratio of the vapour pressure of the solvent to which the polymer sample is exposed relative to the vapour pressure of the pure solvent at 70°C. The data shown as open symbols in this figure and all subsequent figures are from the Centre for the Study of Polymer–Solvent Systems (CSPSS) while the data shown as closed symbols represent measurements taken at DSM Research (DSM). The Flory–Huggins correlations of the solubility data are presented in Fig. 1 along with regressed values of the interaction parameters. Generally good agreement was obtained between the correlations and the solubility data.

Since conventional wisdom suggests that a solvent will only absorb in the amorphous phase of a semi-crystalline polymer, a more reasonable solubility correlation should be based on the volume fraction of solvent in the amorphous polymer phase. This correlation is shown in Fig. 2 for toluene. In this correlation, the data for the LDPE and the LLDPE merge so that a single value of χ correlates all the data, including the highest solubility data measurements. The equivalent solubilities suggest that the amorphous phases in the LDPE and the LLDPE are similar, whereas the amorphous phase of the HDPE is somehow different since the solubility in this phase is significantly less. This could be interpreted to mean that less free-volume exists in the amorphous phase of the HDPE than in LDPE and LLDPE. This characteristic, however, should also be reflected in the diffusivity measurements.

Figs 1 and 2 also reveal that the solubility data from the DSM Research Laboratory are consistently lower than those determined in the CSPSS laboratory. These differences may be caused by subtle changes in the amorphous phase of the high density polyethylene resulting from differences in the history or pretreatment of the polymer sample. The temperature–time history of the sample influences the polymer morphology through crystal size and shape. Such structural changes can influence the characteristics of the amorphous polymer between the crystals. These effects are expected to be most prominent in the high density polyethylene since it is the most crystalline and only a small amount of amorphous phase is distributed between the crystalline phases.

Similar correlations for the n-heptane solubility data are presented in Fig. 3. As before, analyzing the volume fraction of the solvent in the amorphous polymer phase does a better job of correlating the data for the LDPE and the LLDPE. As in the case of toluene, the data for the n-heptane clearly show that the solubility is lower in the amorphous regions of the HDPE than in LDPE and LLDPE.

4.2. Diffusivity data and analysis

The analysis of the diffusivity data is based, as the solubility correlations, on the concentration of the solvents

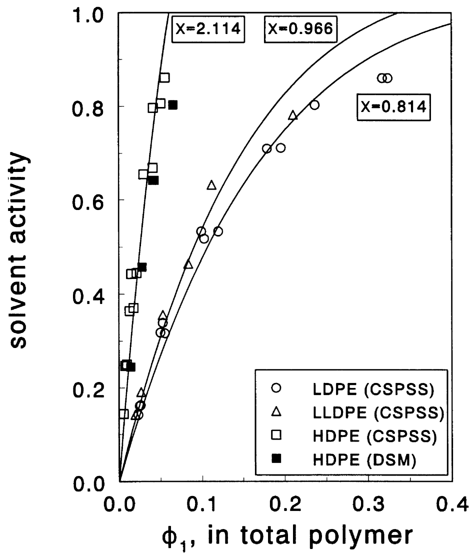

Fig. 1. Correlation of toluene solubility in semi-crystalline polyethylene at 70°C (343 K) utilizing Flory–Huggins model with solubility based on volume fraction of solvent in the total polymer including amorphous and crystalline phases.

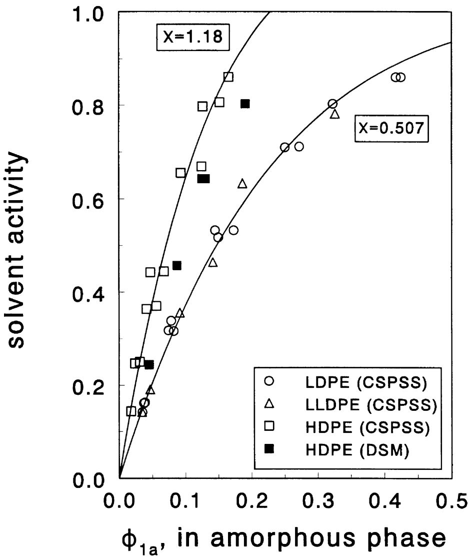

Fig. 2. Correlation of toluene solubility in semi-crystalline polyethylene at 70°C (343 K) utilizing Flory–Huggins model with solubility based on volume fraction of solvent in the amorphous phase of the polymer.

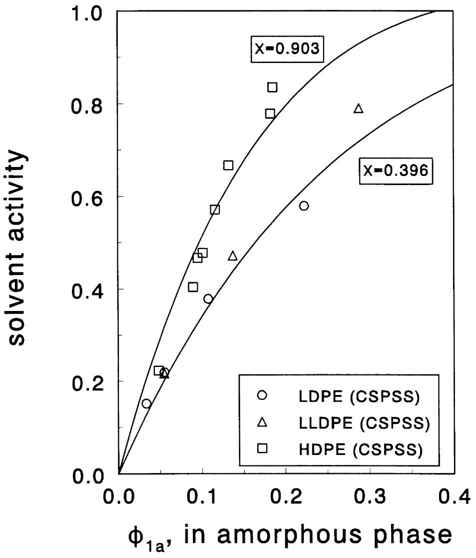

Fig. 3. Correlation of *n*-heptane solubility in semi-crystalline polyethylene at 70°C (343 K) utilizing Flory–Huggins model with solubility based on volume fraction of solvent in the amorphous phase of the polymer.

in the amorphous polymer phases. The solvent parameters in the free-volume model of diffusion in semi-crystalline polymers as represented by Eqs. (1)–(4) and can be estimated from solvent physical property data available in the literature. These parameters for toluene and normal heptane are presented in Table 2. As discussed earlier, three parameters in the model, f_a, f_b, and τ_a, are specific for polyethylene, and the ratio of the species jumping units, ξ, is the only parameter related to the characteristics of both the polymer and the specific solvent. The specific occupied volume of the polymer, $\hat{V}_2^*$, can be estimated by group contribution techniques [16]. For polyethylene, this value is 1.005 $cm^3\ g^{-1}$.

Employing the solvent parameters given in Table 1, the estimate of $\hat{V}_2^*$, the interaction parameters indicated in Figs 2 and 3, and all the diffusion data for the two solvents in the three polyethylene samples, Eqs. (1)–(4) were used to determine the following five parameters: f_a, f_b, τ_a, ξ (toluene) and ξ (n-heptane) (See Tables 2 and 3).

The experimental diffusivity data and the resulting free-volume correlation (shown as solid lines) are depicted in Figs 4 and 5. The effective diffusivity values are significantly different in the three polyethylene samples.

Table 2
Free-volume parameters for solvents

	Toluene	n-Heptane
$\hat{V}_1^*$ ($cm^3\ g^{-1}$)[a]	0.917	1.115
D_{01} ($cm^2\ s^{-1}$)[a]	1.87×10^{-4}	3.43×10^{4}
$\hat{V}_{FH_1}/\gamma$(70°C) ($cm^3\ g^{-1}$)[b]	0.5307	0.5265
ξ[c]	0.615	0.750

[a] Determined from group contribution techniques [17,18].

[b] Determined from solvent viscosity and critical properties [16].

[c] Correlated from solvent-polyethylene experimental data.

Table 3
Polyethylene characteristics based on correlating parameters: $f_a = 0.164$, $f_b = 8.49 \times 10^{-2}$ and $\tau_a = 7.57$

Sample	ϕ_c	τ	$\hat{V}_{FH_{2a}}/\gamma$
LDPE	0.35	3.65	0.134
LLDPE	0.45	4.40	0.125
HDPE	0.70	6.30	0.104

The measured effective diffusion coefficients decrease, as expected, with an increase in the volume fraction of the crystalline phase. Overall, the free-volume correlation represents the diffusion data well, although some deviation is clearly evident for the LLDPE data. For both toluene and n-heptane in LLDPE, the curvature of the diffusivity versus the weight fraction of the solvent relationship is well represented while the absolute values of the diffusion coefficients are somewhat over-predicted. This suggests that the polymer free-volume correlation is accurate for LLDPE while the tortuosity factor is low. This result could arise from the fact that a linear dependence of tortuosity on the volume fraction of the crystal phase (Eq. (4)) was imposed. At this time, however, a more detailed dependence of tortuosity on crystallinity is unavailable.

Previous studies [16] have shown that the thermodynamic factor of Eq. (1) dominates at high solvent concentrations, so that the diffusivity reaches a maximum and then decreases as solvent concentration increases. Predictions based on the free-volume theory indicate that this maximum occurs at the lowest concentration for the high-density polyethylene. Resulting from the low solubility of both toluene and n-heptane in the HDPE, experimental data could not be obtained at the concentration sufficiently high to verify the predicted maximum in the diffusivity. Maxima in diffusion data are common in non-crystalline polymer systems and indicate a strong coupling between the solvent mobility and

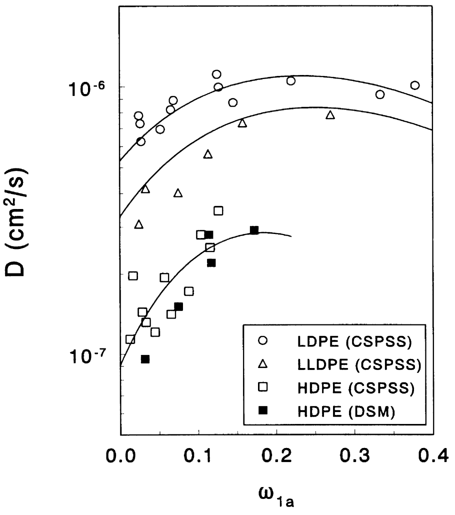

Fig. 4. Free-volume model correlation of toluene diffusion in semi-crystalline polyethylene.

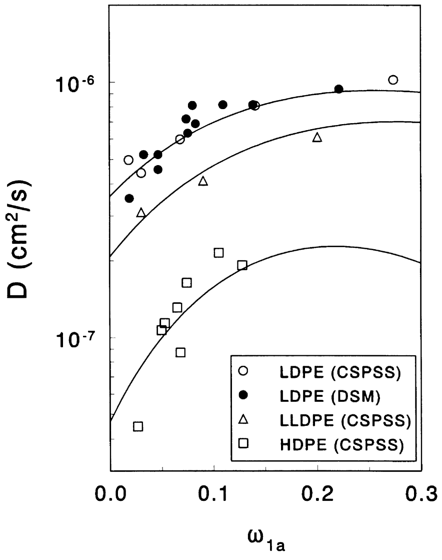

Fig. 5. Free-volume model correlation of n-heptane diffusion in semi-crystalline polyethylene.

the thermodynamic factor in determining the overall mutual binary diffusion coefficient.

This study is consistent with the study of Fleischer [21] in which pulsed field gradient n.m.r. was used to examine the self-diffusion of alkanes in polyethylene. Fleischer correlated his experimental results with Fujita's free-volume theory. His estimates of the fractional free-volume in the amorphous polymer volume are in good agreement with the results of this study. N.m.r. self-diffusion measurements provide a more direct means of establishing the influence of crystals on the free-volume characteristics of the amorphous phase than mutual binary diffusion measurements. Most previous investigators measured mutual binary diffusion coefficients and incorporated tortuosity factors but did not include the influence of the crystal phase on the overall mobility characteristics of the amorphous polymer phase. Hedenqvist et al. [22] show, in agreement with this study, that the free-volume of the non-crystalline component of the polymer strongly decreases with increasing crystallinity, particularly at crystallinity levels below 60%. These results are based on the sorption and permeation measurements to determine the mutual binary diffusivity and solubility of n-hexane and oxygen in a wide range of linear and branched polyethylenes with crystallinities ranging from 40% to 97%.

The estimates of the amorphous phase free-volume of polyethylene by Hedenqvist et al. [22] are in good agreement with those of Fleischer [21] and the results presented here in Table 3. These estimates of the amorphous phase free-volume do not agree with the free-volume characteristics determined by Dekmezian et al. [23] using n.m.r. T_1 relaxation measurements. The Dekmezian investigation indicates that $\hat{V}_{FH_{2a}} = 0.208\ \mathrm{cm}^3\ \mathrm{g}^{-1}$ at 70°C, which is significantly higher than the correlating values presented in Table 3. No information is provided regarding the crystallinity or physical properties of the polyethylene used in the Dekmezian n.m.r. study. We expect, however, that the discrepancy arises from omitting the relaxation time at the reference temperature in their evaluation of the free-volume parameters.

The influence of crystallinity on the free-volume of the amorphous phase determined in this and previous studies is consistent with the dynamic n.m.r. study of the non-crystalline phase by Chen et al. [24] Their study revealed that the motion of the CH_2 carbons in the amorphous region are more constrained in the polyethylene with high crystallinity.

5. Conclusions

In this study, diffusivity and solubility data were presented for toluene and n-heptane in three different semi-crystalline polyethylenes. These data were obtained at 70°C over a broad range of concentration. This study reveals that a correlation exists between the free-volume within the amorphous parts of the polyethylene and the crystallinity. The trends and magnitudes of the resulting tortuosities and free-volumes of the amorphous phases seem reasonable (see Table 3).

The results are in good agreement with most previous investigations and the general concept that crystallinity increases will decrease solvent mobility in the amorphous polymer phases and increase tortuosities. The functional relationships between free-volume, tortuosity, and the degree of crystallinity do not necessarily follow the simple linear relationships employed in this study. For example, Eby [25] as well as Sha and Harrison [26] have shown that the orientation of the lamellar crystals in polyethylene can influence molecular diffusion. At present, however, insufficient data exist to justify use of more complex relationships. To a first approximation the effective diffusivity of any solvent in polyethylene can be determined by the model represented by Eqs. (1)–(4) if the free-volume characteristics of the solvent are known. Further, since toluene is expected to jump as a single unit, the results of this study suggest that a polyethylene jumping unit volume of $\tilde{V}_{2j} = 138.3\ \mathrm{cm}^3\ \mathrm{mole}^{-1}$ can be used to estimate the parameter ξ for other polyethylene-solvent systems.

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