

# Additive Diffusion from LDPE Slabs into Contacting Solvents as a Function of Solvent Absorption

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**ABSTRACT:** This article describes the simultaneous diffusion of a migrant and a solvent in low density polyethylene (LDPE). The migrant (Irganox 1076) moves out of the slab, while the solvent (isooctane, *n*-heptane or cyclohexane) moves inwards. Solvent absorption was measured separately by following the increase of the mass of the slab in time. It can be described by the Fick diffusion equation with a diffusivity depending on the solvent concentration, and an interface concentration depending on time. The final absorptions were 12% for isooctane, 14% for *n*-heptane, and 29% for cyclohexane. Additive concentrations in the slab were determined at different positions by microtoming. Experiments

were done for several contacting times. The concentration profiles were strongly affected by the solvent. A larger local solvent concentration increases the diffusivity of the migrant. The Fick equation with a migrant diffusivity depending on the solvent concentration gives a good description for the results with isooctane and *n*-heptane. The description is less good for the measurements with cyclohexane (when the polymer swells strongly). © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1609–1617, 2003

**Key words:** diffusion; polyethylene; additives; swelling

## INTRODUCTION

There are many applications of polymers that require an understanding of diffusion of small molecules through the polymer. Such applications include, for example, polymers in controlled release of pharmaceuticals, in active packaging, and in packaging of food in polymers. An important problem affecting the diffusion rate occurs when the diffusion of the small molecules takes place simultaneously with absorption of solvent into the polymer. This process of simultaneous diffusion has not been studied adequately.

Diffusion of a nonvolatile compound from a polymer into a contacting solvent depends on polymer properties, such as physical state and degree of crystallinity, and on compound properties, such as size and shape. However, it also depends on solvent properties, in particular on the solubility of the solvent in the polymer and the solubility of the diffusing compound in the solvent. When the solvent hardly dissolves in the polymer, diffusion of the compound from the polymer into the solvent can be described by the Fick diffusion equation with a constant diffusivity.<sup>1</sup> However, as the solubility increases a considerable

amount of solvent is absorbed and deviations from this model arise. Due to swelling of the polymer, the diffusion rates of both the solvent and the compound will increase.<sup>1,2</sup> This type of diffusion is often described by an empirical equation, in which the diffusivity is an exponential function of solvent concentration<sup>3–5</sup> (see THEORY section, below). The equation has been shown to give a good description of the absorption and desorption of solvents in different polymers.<sup>6,7</sup> However, not much is known about the applicability of the equation to describe the diffusion of compounds with low molar mass present in the swelling polymer.<sup>8–10</sup>

The purpose of this article is to study how solvent absorption affects the diffusion of antioxidant Irganox 1076 in low density polyethylene (LDPE). We are interested to find out whether the simple equation for concentration dependent diffusivity can be used to describe additive diffusion using knowledge on solvent sorption parameters and the additive diffusion coefficient in the nonswollen polymer. Three solvents with different solubility in LDPE were selected: isooctane (2,2,4-trimethylpentane), *n*-heptane, and cyclohexane. In all three solvents the antioxidant has a good solubility and they are all liquid at the experimental temperature of 40°C. Additive diffusion was determined by measuring concentration profiles in the polymer after different contact times. This is different

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from the commonly applied method of measuring additive concentrations in the solvent, since additive concentration is obtained as a function of both space and time. The applied method was evaluated and described earlier for diffusion in a nonswelling polymer.<sup>11</sup>

## THEORY

### Free-volume concept

Different empirical equations have been suggested for calculating concentration dependent diffusion coefficients in polymers.<sup>3,6-10,12-13</sup> The most common form is

$$D = D_0 \exp(\gamma c) \quad (1)$$

where  $D_0$  ( $\text{m}^2 \text{s}^{-1}$ ) is the diffusion rate at infinite diffusant dilution (at  $c = 0$ ),  $\gamma$  (-) is an adjustable parameter and  $c = C/C_{\text{max}}$  (-), in which  $C$  is the solvent concentration ( $\text{kg m}^{-3}$ ) and  $C_{\text{max}}$  the solubility of the pure solvent in equilibrium with the polymer ( $\text{kg m}^{-3}$ ).

Equation (1) is considered to originate from the work of Doolittle,<sup>14</sup> who described the fluidity of simple hydrocarbon liquids using an exponential dependency between fluidity and available volume. Cohen and Turnbull<sup>15</sup> gave this relation a theoretical basis using the free-volume concept. According to this concept, there is a continuous redistribution of the free-volume holes between the molecules in a liquid, in other words, the space that is not occupied by the liquid molecules. Molecular transport occurs if a sufficiently large hole is formed next to a molecule, allowing a displacement of that molecule, and the original hole of the diffusing molecule is filled by another molecule. The diffusion coefficient is thus related to the probability of a molecule finding a free-volume hole of a specific size.<sup>16</sup> The free-volume concept was extended to diffusion in polymers by Fujita<sup>17</sup> and Vrentas and Duda.<sup>18</sup> Their equations, as well as eq. (1), were derived in analogy with the Doolittle equation. In this study, eq. (1) was used due to its practical applicability and few model parameters.

### Solvent diffusion

Solvent absorption by the polymer was described by the diffusion equation of Fick for diffusion in one dimension given by

$$\frac{\partial c^s}{\partial t} = \frac{\partial}{\partial x} \left( D^s(c^s) \frac{\partial c^s}{\partial x} \right) \quad (2)$$

where  $c^s$  (-) is the solvent concentration,  $x$  (m) the position along the thickness of the polymer slab,  $t$  (s) the time, and  $D^s$  ( $\text{m}^2 \text{s}^{-1}$ ) the diffusion coefficient depending on solvent concentration. Equation (2) was discretized as

$$c_{i+1,j}^s = c_{i,j}^s + \frac{\Delta t}{\Delta x^2} \times [D_{i,j-0.5}^s(c_{i,j-1}^s - c_{i,j}^s) - D_{i,j+0.5}^s(c_{i,j}^s - c_{i,j+1}^s)] \quad (3)$$

with  $i$  steps in time and  $j$  steps through the thickness of the slab. Concentration dependent diffusion coefficients were calculated by eq. (1) that was discretized as

$$D_{i,j\pm 0.5}^s = D_0^s \exp\left(\gamma^s \frac{c_{i,j}^s + c_{i,j\pm 1}^s}{2}\right) \quad (4)$$

Since the diffusion processes from the two opposite surface sides of the slab were considered to be symmetrical, only half of the slab thickness ( $L$ ) was considered for estimation of the solvent absorption parameters. The center of the slab ( $x = 0$ ) was assumed to be an isolated point with

$$\left[ \frac{\partial c^s}{\partial x} \right]_{x=0} = 0 \quad (5)$$

which was discretized as

$$c_{i,-1}^s = c_{i,l}^s \quad (6)$$

At the interface between polymer and solvent ( $x = L$ ), the solvent concentration was assumed to attain its maximum value immediately, or a time dependent surface concentration was introduced given by<sup>6</sup>

$$\left[ \tau \frac{\partial c^s}{\partial t} \right]_{x=L} = [c_\infty^s - c_t^s]_{x=L} \quad (7)$$

where  $\tau$ (s) is a first-order constant,  $c_t^s$  the surface solvent concentration at time  $t$ , and  $c_\infty^s$  the maximum surface solvent concentration (equal to 1 for calculations with dimensionless concentrations). Equation (7) was discretized as

$$c_{i+1,J}^s = c_{i,J}^s + \frac{\Delta t}{\tau} (c_\infty^s - c_{i-1,J}^s) \quad (8)$$

with step number  $J$  at  $x = L$ . At  $t = 0$ , the solvent concentration in the polymer was taken to be zero.

### Additive diffusion

Similar to solvent absorption, additive diffusion from the polymer was described by

$$\frac{\partial c^a}{\partial t} = \frac{\partial}{\partial x} \left( D^a(c^s) \frac{\partial c^a}{\partial x} \right) \quad (9)$$

with  $c^a$  (–) the additive concentration and  $D^a$  ( $\text{m}^2 \text{s}^{-1}$ ) the additive diffusion coefficient depending on solvent concentration. Equation (9) was discretized similarly to eq. (3) and additive diffusion coefficients were calculated by

$$D_{i,j\pm 0.5}^a = D_0^a \exp \left( \gamma^a \frac{c_{ij}^s + c_{i,j\pm 1}^s}{2} \right) \quad (10)$$

with  $D_0^a$  ( $\text{m}^2 \text{s}^{-1}$ ) the additive diffusion coefficient at zero solvent concentration. Since additive concentration profiles were measured throughout the polymer slab, the total slab thickness was considered for additive concentration calculations. Solvent concentrations required for the additive concentration calculations were also carried out in this case for the total slab thickness, using eq. (7) as boundary condition at both surface sides.

At the interface between polymer and solvent, the additive was assumed not to be influenced by any contact resistance since it was well soluble in all solvents. Under this assumption, the additive concentrations at the interface remain constant and the ratio of concentration differences between boundary and bulk will be proportional to the square root of the diffusion coefficients in polymer and solvent according to<sup>4</sup>

$$\frac{c_0^a - c^{a*}}{c_{\text{sol}}^{a*}} = \sqrt{\frac{D_{\text{sol}}^a}{D^a}} \quad (11)$$

where  $c_0^a$  (–) is the initial additive concentration in the polymer,  $c^{a*}$  (–) is the additive concentration at the polymer side of the interface,  $c_{\text{sol}}^{a*}$  (–) is the additive concentration at the solvent side of the interface and  $D_{\text{sol}}^a$  is the diffusion rate of additive in the solvent. Since the solvent volume was much larger than the polymer volume, the additive bulk concentration in the solvent was approximately equal to zero during the entire experiment. Equation (11) is valid as long as the additive concentration in the center remains constant, in other words, the slab can be considered as a semi-infinite medium. When the additive concentration in the center decreases, the assumption is no longer valid and the boundary concentrations will decrease.

Model parameters were estimated by minimizing the sum of squared errors between experimental and predicted values.<sup>19</sup>

## EXPERIMENTAL

### Materials

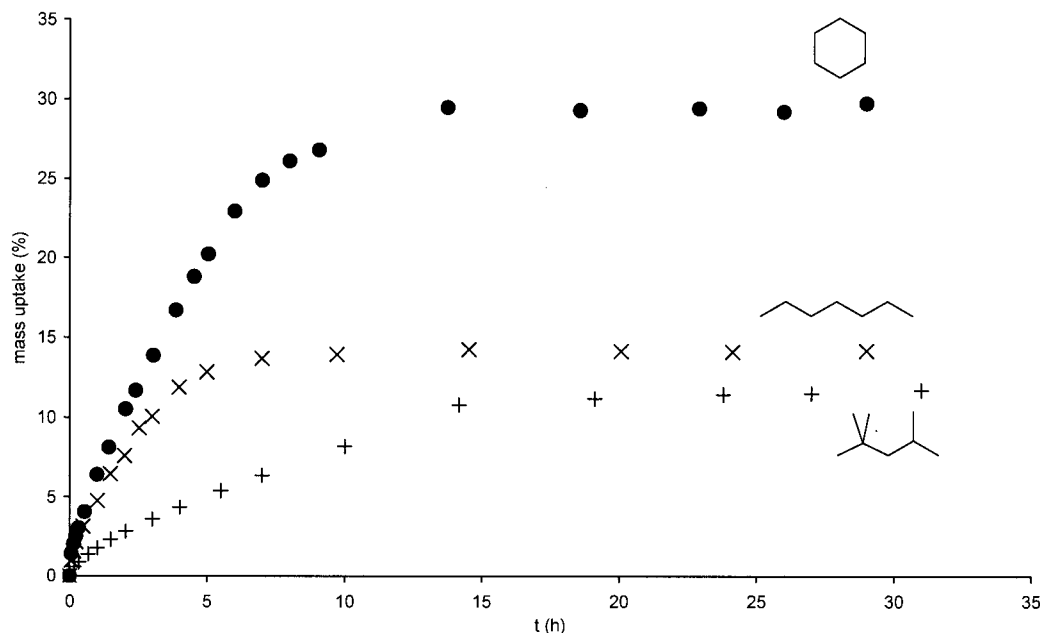
Compression molded slabs of LDPE with a density of  $0.922 \text{ kg dm}^{-3}$  and a nominal thickness of 1.61 mm were kindly provided by DSM Research (Geleen, the Netherlands). Slabs with and without Irganox 1076 (octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate), at a concentration of  $3300 \text{ mg kg}^{-1}$ , were specially produced for this study.

### Solvent absorption

Solvent absorption was measured by the mass uptake method.<sup>3</sup> Polymer slabs of  $6 \text{ cm} \times 8 \text{ cm}$  without additives were submerged in an excess of the solvent at  $40^\circ\text{C}$ . At predefined time intervals, the slabs were removed from the solvent, quickly surface dried, and weighed on an analytical balance (Mettler Toledo,  $d = 0.001\text{g}$ ), after which they were immediately placed back into the solvent. Measurements continued until no further mass increase could be detected. The mass change was assumed to be caused by solvent absorption only, since the maximum loss of low-molecular polymer parts into isooctane, *n*-heptane or cyclohexane was determined to be less than 0.7%.

### Additive concentration profiles

Additive concentration profiles inside the polymer were determined by using the slicing method described in a previous article.<sup>11</sup> In that article, validation of the method and accuracy tests were carried out with LDPE and the nonswelling solvent ethanol. Polymer slab pieces of  $2 \text{ cm} \times 2 \text{ cm}$  were immersed in the test solvent at  $40^\circ\text{C}$  during a predefined time period, after which the pieces were cooled to  $-20^\circ\text{C}$  to stop the diffusion process. A circle with an area of  $1.33 \text{ cm}^2$  was punched from the center of the polymer slab and sliced perpendicularly to the main surface sides. Slices of approximately  $20 \mu\text{m}$  thickness were collected three by three in preweighed vials, the absorbed solvent was allowed to evaporate for at least 1 h, after which the vials were weighed and the slices were extracted with isooctane. Additive concentration was determined by analyzing the extracts with gas chromatography with a flame ionization detector (GC-FID) (for details see Helmroth et al.<sup>11</sup>). Concentrations were calculated per mass of polymer and normalized to the initial additive concentration in the polymer. For the diffusion process the actual concentration in the swol-



**Figure 1** Mass uptake curves of cyclohexane (●), *n*-heptane (×), and isooctane (+) by LDPE slabs with thickness 1.6 mm at 40°C. Points are average data of at least two measurements. The molecular structure of each solvent is illustrated next to the corresponding curve.

len polymer matrix determines the transport rate. By using the concentration per mass of polymer the additive concentration is therefore overestimated to some extent. However, a correction of this overestimation using information on solvent absorption would introduce even more uncertainty, since the local amount of solvent in each slice would have to be obtained from simulations based on the experimental mass-time curve. The overestimation in additive concentration is therefore neglected in this article.

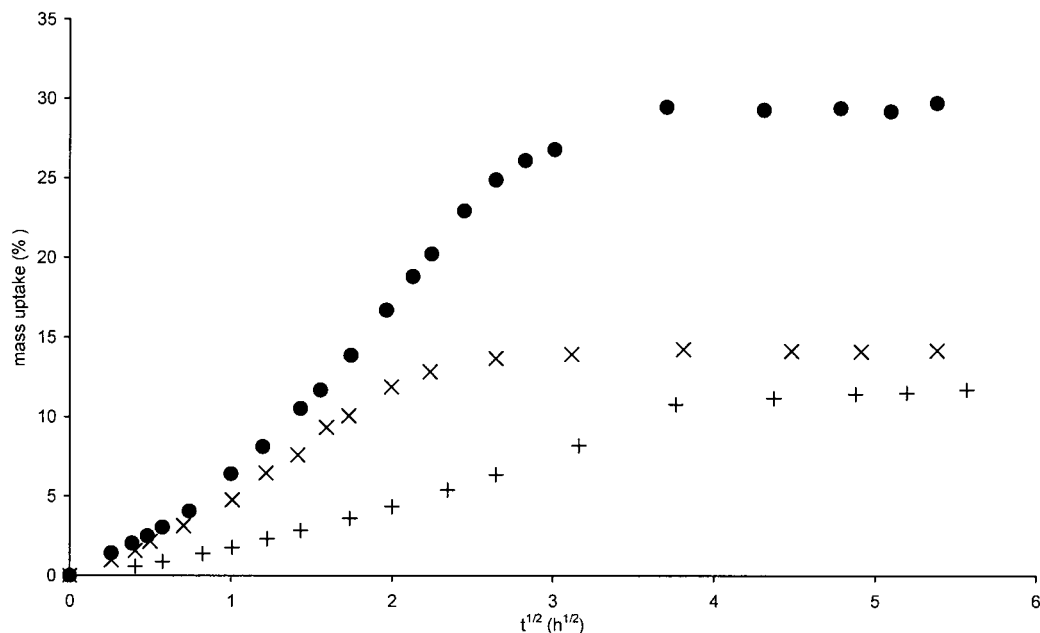
The position along the thickness of the slab was calculated by relating the mass of the slices in each vial (after evaporation of the absorbed solvent) to the total mass of all slices. These values were converted to positions by using the measured final thickness of the polymer slab piece. Because of local variation in the uptake of solvent (more on the edge and less in the center) this conversion leads to an underestimation of the step size at the edge and an overestimation of the step size in the center of the polymer slab. Since the thickness increase of the polymer for the solvents and exposure times used is estimated to be lower than 10%, this will result in a maximum of 10% larger actual step size than is used for converting the experimental data. This means that the actual concentration gradient is less than 10% smaller than the calculated one and this difference is here considered to be negligible. The influence of this and previously mentioned assumptions on the results will be discussed in the next section.

## RESULTS AND DISCUSSION

Mass uptake curves of isooctane, *n*-heptane, and cyclohexane by the LDPE slabs at 40°C are shown in Figure 1. Equilibrium was reached within 10 h with *n*-heptane, 15 h with cyclohexane, and 25 h with isooctane. The maximum mass uptake of the three solvents was 29% (w/w) for cyclohexane, 14% (w/w) for *n*-heptane, and 12% (w/w) for isooctane. The solubility of molecules in polymers generally decreases with increasing molar mass.<sup>20</sup> The molar mass of cyclohexane, *n*-heptane, and isooctane are 84 g mol<sup>-1</sup>, 100 g mol<sup>-1</sup>, and 114 g mol<sup>-1</sup>, which confirms this general trend.

Remarkably, cyclohexane is absorbed twice as much as *n*-heptane. This shows that solubility is also affected by molecular shape. This may be explained as follows. For the linear *n*-heptane molecules, it is entropically more favorable to be in solution than between the polymer chains since in the latter case their freedom of rotation is restricted. For the cyclic cyclohexane molecules, the difference in number of degrees of freedom between being in solution or within the polymer is less. So diffusion into the polymer will therefore be entropically more favorable for cyclohexane than for *n*-heptane.

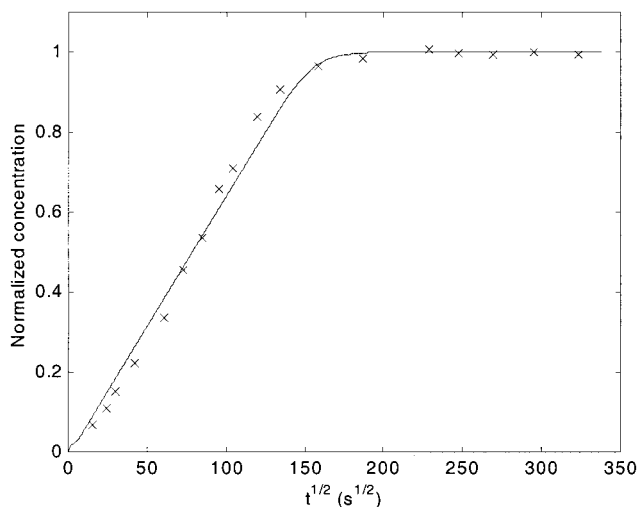
The s-shaped curve of the mass uptake as a function of the square root of time (Fig. 2) shows that the sorption of these solvents cannot be described as Fickian diffusion with constant diffusivity, which would



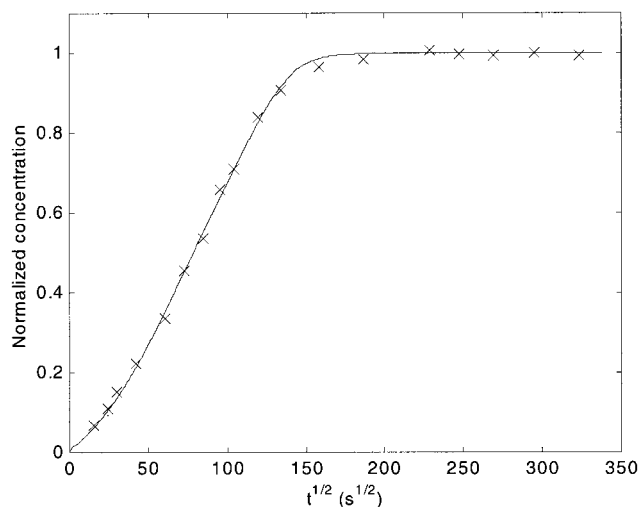
**Figure 2** Mass uptake curves as a function of the square root of time of cyclohexane (●), *n*-heptane (×), and isooctane (+) by LDPE slabs with thickness 1.6 mm at 40°C. Points are average data of at least two measurements.

have given a straight initial line. In rubbery polymers, it is generally assumed that chain relaxation of the polymer molecules is rapid compared with sorption, which implies that diffusivity is only a function of concentration as described by eq. (1).<sup>3</sup> Figure 3 shows the fit of eqs. (1) to (6) to the sorption data of heptane with  $D_0^s = 6 \times 10^{-13} \text{ m}^2\text{s}^{-1}$  and  $\gamma^s = 4.8$ . The model gives a reasonable, though not perfect, description of the experimental data. This result is in accordance with that for the sorption of hexane in LDPE and natural rubber obtained by Hedenqvist and Gedde,<sup>6</sup>

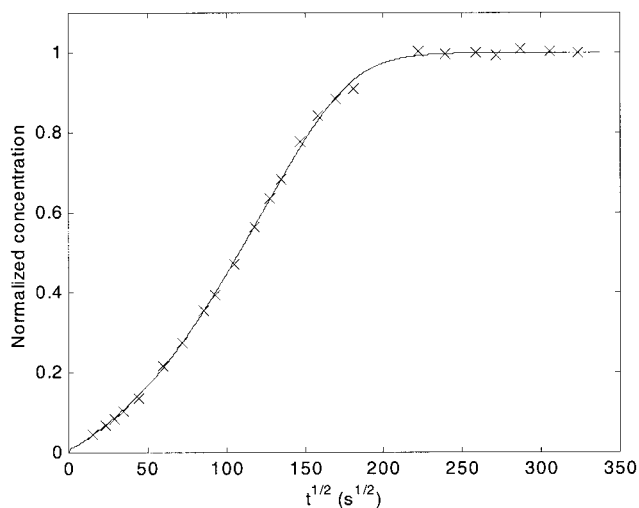
who showed that a model only using a concentration dependent diffusivity does not lead to an s-shaped curve and that the concentration in the polymer at the interface must depend on time. Hedenqvist and Gedde therefore suggested to include the boundary condition in eq. (7). The reason for this time dependency is considered to be that the swollen surface is subjected to compressive stresses caused by the non-swollen parts within the polymer.<sup>3,6</sup> At the polymer surface, the maximum solvent concentration is not instantly reached, but only after a certain time-lag.



**Figure 3** Fit of eqs. (1)–(6) to the sorption data of *n*-heptane in LDPE with  $D_0^s = 6 \times 10^{-13} \text{ m}^2\text{s}^{-1}$  and  $\gamma^s = 4.8$ . Experimental data shown by 'x' and predicted data by a solid line.



**Figure 4** Fit of eqs. (1)–(8) to the sorption data of *n*-heptane in LDPE with the parameters given in Table I. Experimental data shown by 'x' and predicted data by a solid line.

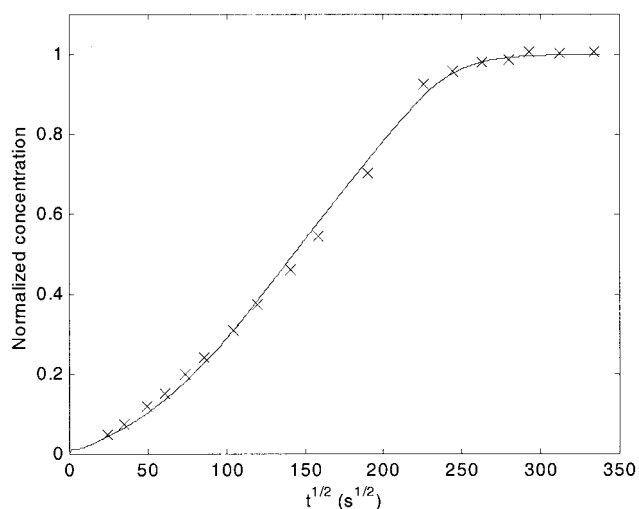


**Figure 5** Fit of eqs. (1)–(8) to the sorption data of cyclohexane in LDPE with the parameters given in Table I. Experimental data shown by 'x' and predicted data by a solid line.

Recently, Hedenqvist et al.<sup>21</sup> verified this time dependency of the solvent surface concentration experimentally by IR measurements.

Two model parameters are introduced, namely an initial surface concentration  $c_0^s$  and a first-order constant  $\tau$ . Figures 4–6 show that indeed good fits to the three experimental sorption curves were obtained by including a time dependent surface concentration. Estimated model parameters are given in Table I.

The concentration profiles of Irganox 1076 diffusing from the LDPE slabs into the three test solvents are shown in Figures 7–9. Also shown in these figures are the fits of eqs. (9) to (11) to the experimental concentration profiles, taking into account the solvent con-



**Figure 6** Fit of eqs. (1)–(8) to the sorption data of isooctane in LDPE with the parameters given in Table I. Experimental data shown by 'x' and predicted data by a solid line.

centrations simulated by eqs. (1) to (4), (7), and (8) with the parameters given in Table I.  $D_0^s$  in eq. (10) is the value of the diffusion coefficient for zero solvent concentration (the nonswollen polymer). This value of  $1.1 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$  was obtained from the diffusion of Irganox 1076 from the LDPE slab into ethanol<sup>10</sup>; ethanol is hardly absorbed by LDPE.

The additive concentration at the interface between polymer and solvent, according to eq. (11), was determined by extrapolation from the experimental additive concentrations. Estimated values of  $\gamma^a$  are given in Table II.

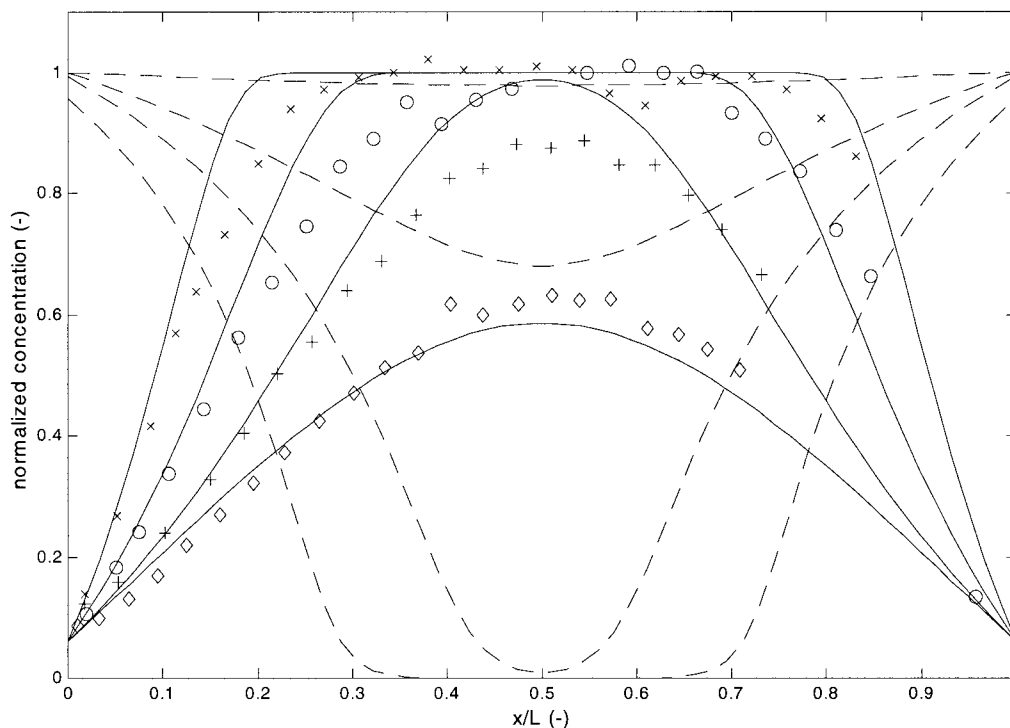
The experimental data clearly show that additive diffusion is affected by solvent absorption. The decrease of the additive concentrations within the LDPE slab as a function of time is the quickest for cyclohexane and slowest for isooctane. This result was expected since cyclohexane has the highest solubility in LDPE and thus adds most free-volume to the polymer, resulting in a higher diffusion rate of the additive.

The model curves give a reasonable prediction of the additive diffusion as a function of time. However, systematic deviations between experimental and predicted concentrations are observed. The predicted concentration gradient is generally steeper than the experimental one. Consequently, predicted concentrations are slightly lower than experimental values near the edge and higher near the center, particularly for cyclohexane. The deviations could be due to either the model description or the experimental set-up. Some considerations concerning the calculation of the  $x$ -positions of each slice and the additive concentration in each slice due to solvent absorption were discussed in the EXPERIMENTAL section. As shown in Table III, the assumption of a maximum increase of thickness of 10% at the different contacting times is indeed acceptable. Some of the deviation may be due the use of concentrations based on polymer mass (converted to volume) instead of the total mass of polymer and solvent.

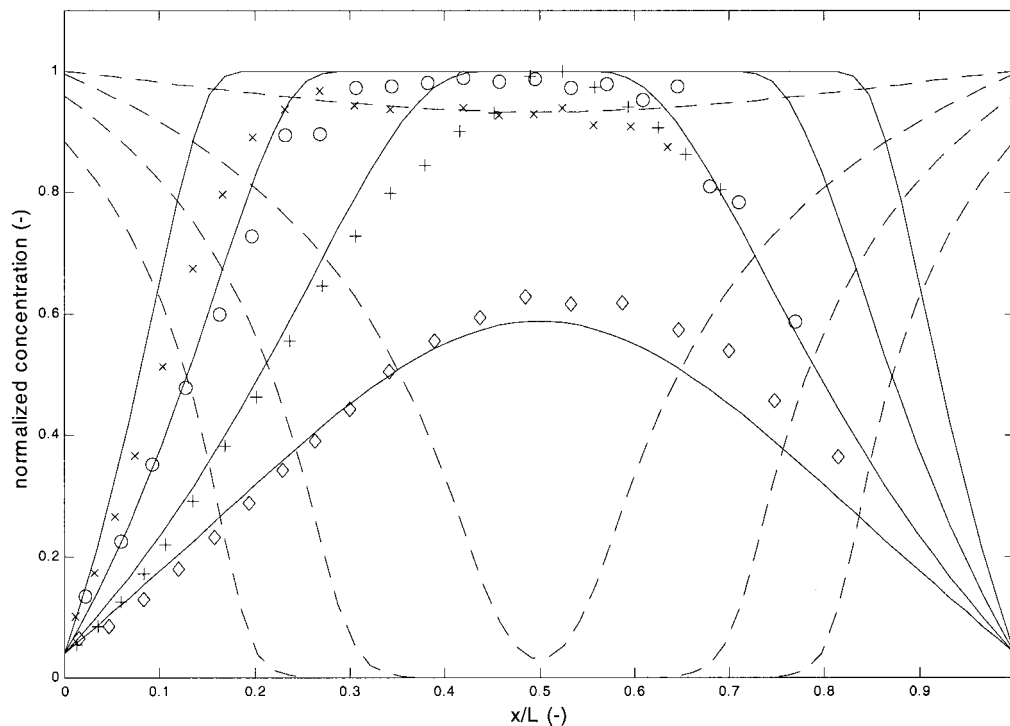
In contrast with the results for ethanol,<sup>11</sup> the additive concentrations at the interface between polymer and solvent were not zero for the solvents used in this study. This may be explained by looking at eq. (11), which shows that the ratio of concentration differences between boundary and bulk are proportional to

**TABLE I**  
Estimated Parameters for the Absorption of the Test Solvents into LDPE Slabs at 40°C

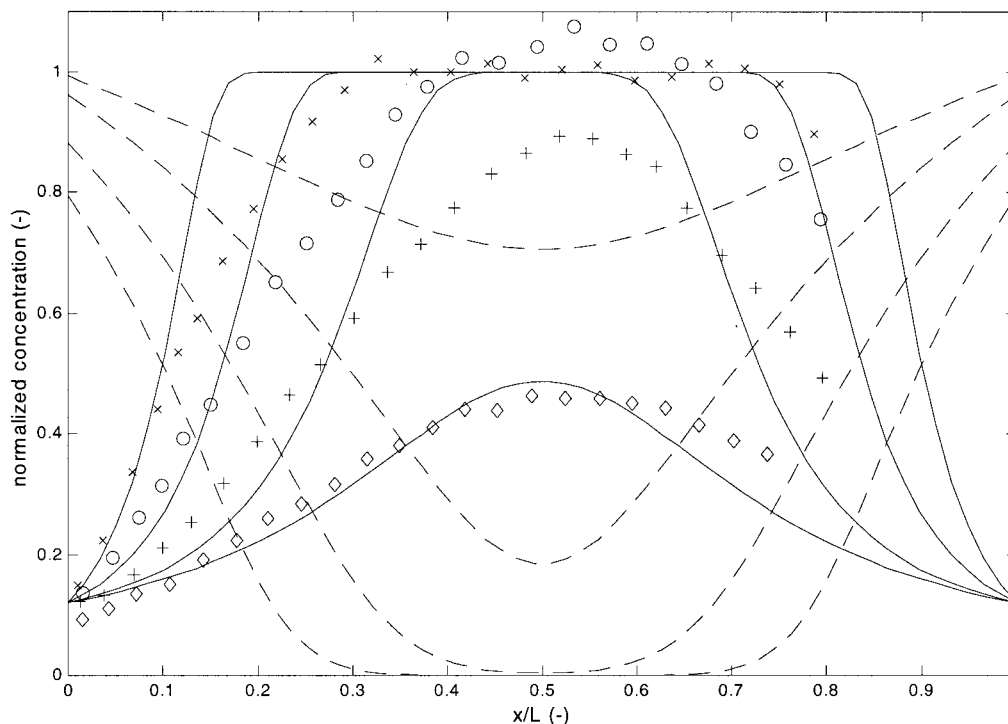
	Isooctane	<i>n</i> -Heptane	Cyclohexane
$D_0^s$ ( $\text{m}^2 \text{ s}^{-1}$ )	$5.2 \times 10^{-13}$	$2.4 \times 10^{-12}$	$3.4 \times 10^{-12}$
$\gamma^s$ (-)	4.0	3.4	2.4
$\tau$ (h)	1.9	0.56	1.8
$c_0^s$ (-)	0.67	0.75	0.64



**Figure 7** Fit of eqs. (1)–(4) and (7)–(13) to the experimental concentration profiles of Irganox 1076 diffusing from the LDPE slab into *n*-heptane after 1 ('x'), 2 ('O'), 4 ('+'), and 7 ('◆') h using the parameters given in Tables I and II. Predicted additive concentrations are shown by a solid line and predicted solvent concentrations by a dashed line (notice that the solvent is being absorbed by the slab while the additive is diffusing out from the slab).



**Figure 8** Fit of eqs. (1)–(4) and (7)–(13) to the experimental concentration profiles of Irganox 1076 diffusing from LDPE slabs into isooctane after 2 ('x'), 4 ('O'), 8 ('+'), and 17 ('◆') h with the parameters given in Tables I and II. Predicted additive concentrations are shown by a solid line and predicted solvent concentrations by a dashed line (notice that the solvent is being absorbed by the slab while the additive is diffusing out from the slab).



**Figure 9** Fit of eqs. (1)–(4) and (7)–(13) to the experimental concentration profiles of Irganox 1076 diffusing from LDPE slabs into cyclohexane after 1 ('x'), 2 ('o'), 4 ('+'), and 7 ('♦') h with the parameters given in Tables I and II. Predicted additive concentrations are shown by a solid line and predicted solvent concentrations by a dashed line (notice that the solvent is being absorbed by the slab while the additive is diffusing out from the slab).

the square root of the relative diffusion rates in the polymer and solvent. When solvent is absorbed by the polymer, the additive diffusion coefficient in the polymer increases and the difference between the initial additive concentration and the concentration at the boundary on the polymer side at time  $t$  will decrease. The higher the absorption, the closer the diffusivity will be to that in the solvent (approximately  $10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) and the higher the boundary concentration will be. This theory is confirmed by the result that the boundary concentration was the highest for cyclohexane and the lowest for isooctane.

Even when experimental uncertainties are taken into account, it seems that eq. (1) is not fully adequate to describe the additive diffusion as a function of time. Especially for high solvent absorption, the constraint of using the diffusion coefficient in the nonswollen polymer has to be compensated for by an extremely

steep concentration gradient. This results in a large value of  $\gamma^t$  for diffusion into cyclohexane. It should be noted that this result can only be observed by measuring additive concentration profiles in the polymer. Measurements in the contacting solvent as a function of time give only the integrated amount of additive that has diffused into the solvent and provide no information on the distribution.

## CONCLUSIONS

The empirical equation relating diffusion coefficients of compounds in a polymer to concentration according to the free-volume theory has been used to describe the complex process of additive diffusion from an LDPE slab into a contacting solvent taking place

**TABLE II**  
Estimated Parameters for the Diffusion of Irganox 1076 from LDPE Slabs into the Test Solvents at 40°C

	$\gamma^t$ (-)
Isooctane	4.2
<i>n</i> -Heptane	4.9
Cyclohexane	6.9

**TABLE III**  
Thickness Increase of Polymer Slab in the Test Solvents After Different Contact Times

Cyclohexane		<i>n</i> -Heptane		Isooctane	
$t$ (h)	(%)	$t$ (h)	(%)	$t$ (h)	(%)
1	7.1	1	4.1	2	2.8
2	8.5	2	4.9	4	3.5
4	9.8	4	6.7	8	4.5
7	12.0	7	6.8	17	5.5



simultaneously with solvent absorption. For a solvent absorption of less than 15% (w/w), concentration profiles were fairly well predicted. For a higher solvent absorption, 29% (w/w), the equation was not able to describe the diffusion process adequately.

The importance of measuring concentrations of the diffusants in the polymer as a function of both time and place is emphasized by the results obtained in this study. The measurement method used here, microtoming of the polymer slab, is straightforward and gives good results. However, it still needs to be improved at some points that have been discussed. Sophisticated imaging techniques, such as microscopy FTIR or Raman, may be good alternatives to microtoming, especially for measuring both solvent and additive concentrations inside the polymer. The challenge will be to convert obtained signals to real concentrations.

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