STUDY OF THE DIFFUSION AND SOLUBILITY FOR A POLYETHYLENE-CYCLOHEXANE SYSTEM USING GRAVIMETRIC SORPTION ANALYSIS

A Thesis in
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by

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Abstract

Crystallinity is an important factor in the diffusivity and solubility of a polymer-solvent system. The melt temperature acts as the transition point between a semi-crystalline and completely amorphous polymer. The purpose of this work was to examine the diffusivity and solubility of cyclohexane in high density polyethylene across a range of temperatures that cover both the semi-crystalline state of the polymer and the completely amorphous state reached above the melt temperature. At each of these temperatures, a range of concentrations was analyzed.

Gravimetric sorption analysis was used to evaluate the HDPE-cyclohexane system using Crank’s model for diffusion calculations. Experiments are conducted at temperatures of 90, 100, and 105°C below the melt using polymer pellets as well as 140, 150, and 160°C above the melt using polymer sheets. The transition to sheets is necessary because of flow that occurs above the melt.

The Vrentas-Duda Free-Volume Theory was used as a predictive method of estimating the diffusion coefficients. Since this theory does not account for crystallinity effects on diffusion, a model that accurately calculates the completely amorphous behavior above the melt provides valuable insight to whether crystallinity is affecting diffusion in the system. Analysis using the free-volume model appears to indicate that tortuosity has little effect on the diffusivity.
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1. Introduction

From common household items such as plastic bags and bottles that are used to hold everyday products like food or shampoo to bullet proof vests that are being used to save lives, polyethylene production is one of the most important polymer industries in the world. Whether on its own or mixed as part of a copolymer, the uses for polyethylene are seemingly endless. Because of the regular use of this polymer, the demand for polyethylene is great, and in turn, the demand for research and information about its properties is just as great [1].

Polyethylene is produced in many different forms and is characterized based upon both its branching and density. Three of the more common classifications of polyethylene are low density polyethylene (LDPE), linear low density polyethylene (LLDPE), and high density polyethylene (HDPE). LDPE is polyethylene that has a density in the range of 0.920 to 0.940 g/cm$^3$ and has a large amount of branching with both short and long chains [2, 3]. LLDPE is a more specific term that is used to describe polyethylene that contains only short chain branches and is considered an intermediate between LDPE and HDPE [3, 4]. It has a density of 0.920 g/cm$^3$ [5]. In contrast, HDPE has very little branching which allows for the molecules to pack more tightly. This classification is used for any polyethylene product that has a density value from 0.940 to 0.970 g/cm$^3$ [2, 3].

During manufacturing of polymers, many chemicals are in close proximity to the finished product. Whether it is some remaining monomer, an additional side product, or another chemical needed during the process, interactions with the polymer are inevitable. Polymer-
solvent systems become extremely important in many aspects of polymer production including synthesis and devolatilization. Therefore, it is important to look into the behavior of polymer-solvent systems. Two properties that are often examined when considering these types of systems are diffusivity and solubility. Many factors such as temperature, concentration, and crystallinity can affect these two properties [6, 7]. This creates an issue because most of the time literature values do not exist for the exact system of interest. Approximations must be made to get as close as possible to the desired polymer-solvent system. For polyethylene, this is where the classification becomes important. Often times, full tables of literature values are not available for the exact composition of the relevant polyethylene so comparison is often based upon a general value for LDPE, LLPDE, or HDPE that, hopefully, will give a close approximation.

As stated previously, temperature is a major factor for both diffusion and solubility. Since literature values are not always in the desired range for a given system, there is a need to look at temperature’s influence. The purpose of this work was to measure the diffusivity and solubility of a high density polyethylene-cyclohexane system for various solvent concentrations over a range of temperature. One area of potential complication is what occurs as a polymer approaches and surpasses its melt temperature. The physical properties transition as crystallinity breaks down and the solid polymer turns into a melt. This work examined what happens once polyethylene is heated above its melting point. One objective of this work is to find the impact that higher temperatures have on the polymer-solvent system in question. Temperatures both above and below the melting point were looked at to determine whether
working with the polymer as a melt causes any noticeable changes with respect to diffusivity and solubility.
2. Diffusion

2.1 Background

Diffusion is the term used to describe the random motions of molecules that causes a material to move through a system. Each molecule undergoes a random walk motion where the direction of the movement is unpredictable, but the mean-square distance travelled can be found. During diffusion, molecules will have a tendency to move from a position of higher concentration to a region where concentration is lower until the concentration throughout the system is constant [8]. Although this process of reaching equilibrium may seem to contradict the random walk theory in that the molecules seem to follow a desired path, it can actually be explained by random movement. Some molecules near the higher concentration will by random motion move to the area of lower concentration. At the same time, molecules will be moving from the lower concentration to the higher one. However, with more molecules in the higher concentration region compared to the lower region, there are a greater number of molecules that will be randomly moving towards the lower concentration. Since there are more molecules that have the opportunity to move out of the high concentration area, an equilibrium concentration will eventually be reached from random motion [9]. The mathematical model for diffusion in a particular area based on the random walk derived by Fick in 1855 is displayed in Equation 2.1 [10].

\[ J = -D \frac{\partial C}{\partial x} \]  

(2.1)
In this equation, \( J \) is the flux of diffusion with \( x \) being the direction normal to that area through which the flux refers. The concentration of the diffusing solvent is \( C \), and \( D \) is known as the diffusivity or diffusion coefficient and is usually reported in units of \( m^2/s \) or \( cm^2/s \). For the purpose of this paper, all diffusion coefficients will be listed in units of \( cm^2/s \). For polymers, the diffusion coefficient is dependent on the solvent concentration in the system. This equation also assumes that the material through which diffusion is taking place is isotropic.

Considering a three dimensional volume, the summation of the concentration change with respect to time, \( t \), and the changes of the transfer rates in each of the three dimensions should be equal to zero:

\[
\frac{\partial C}{\partial t} + \frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z} = 0
\]  

(2.2)

A relationship for each of the three transfer rates can be found using Equation 2.1. Each of these terms can be placed into Equation 2.2 to form the fundamental differential diffusion equation through an isotropic material. Assuming that the diffusion coefficient is dependent on the concentration, it cannot be taken out of the differential, and the equation becomes:

\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left( D \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left( D \frac{\partial C}{\partial z} \right)
\]  

(2.3)
2.2 Crank Model

2.2.1. Spherical Model

Because the fundamental differential equation for diffusion depends upon the geometry of the system, the coordinate system must be changed when a spherical sample is used. Spherical coordinates were particularly important in the current work because the polymer samples were received in pellet form. These pellets are most closely represented by a spherical shape. The following equations are used to make the change from Cartesian to spherical coordinates:

\[ x = r \sin \theta \cos \phi \]  \hspace{1cm} (2.4)

\[ y = r \sin \theta \sin \phi \]  \hspace{1cm} (2.5)

\[ z = r \cos \theta \]  \hspace{1cm} (2.6)

Combining these three equations with the fundamental equation for diffusion given by Equation 2.3, a new differential equation for diffusion in spherical coordinates is formed in Equation 2.7.

\[ \frac{\partial C}{\partial t} = \frac{1}{r^2} \left[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial C}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( D \sin \theta \frac{\partial C}{\partial \theta} \right) + \frac{D}{\sin^2 \theta} \frac{\partial^2 C}{\partial \phi^2} \right] \]  \hspace{1cm} (2.7)

Assuming spherical symmetry, the diffusion equation simplifies to its strictly radial form seen in Equation 2.8.
\[
\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial r^2} + 2 \frac{\partial C}{r \partial r} \right)
\]  

(2.8)

With this equation as the basis, a formula that characterizes the diffusion through a sphere was derived by Crank [9] and is given by Equation 2.9.

\[
\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^\infty \frac{1}{n^2} \exp \left( - \frac{Dn^2 \pi^2 t}{R^2} \right)
\]  

(2.9)

Here, \(M_t/M_\infty\) is the fraction mass uptake with \(M_t\) being the mass uptake at time, \(t\), and \(M_\infty\) being the equilibrium uptake at infinite time. The radius of the sphere is given as \(R\). A solution for this equation is:

\[
\frac{M_t}{M_\infty} = 6 \left( \frac{Dt}{R^2} \right)^{\frac{1}{2}} \left( \frac{1}{\pi^2} + \sum_{n=1}^\infty \text{erfc} \left( \frac{nR}{\sqrt{Dt}} \right) \right) - 3 \frac{Dt}{R^2}
\]  

(2.10)

Working from this equation, the integral complementary error function makes solving for the diffusion coefficient from experimental results very difficult. Calculations were made using reasonable assumptions for the diffusivity and radius of the sphere that determined that the summation term is negligible compared to the other terms in the equation for any fractional uptake below 50%. Therefore, the equation for small uptake was simplified to:

\[
\frac{M_t}{M_\infty} = \frac{6}{\pi^2} \left( \frac{Dt}{R^2} \right)^{\frac{1}{2}} - 3 \frac{Dt}{R^2}
\]  

(2.11)

A few assumptions are made when this equation is used to model the diffusion through a sphere. It is assumed that the diffusion coefficient remains constant throughout the sphere.
The sphere must be completely uniform in size and composition. It also suggests that diffusion is completely radial with no angular movement. The diffusing material is traveling directly into the sphere along the radial lines of the sphere so that the pathway of diffusion is just the radius of the sphere seen in Figure 2.1.

![Spherical Diffusion](image)

Figure 2.1: Schematic of Diffusion through a Sphere

### 2.2.2. Flat Sheet Model

An equation for diffusion through a flat sheet has also been derived by Crank [9]. The fundamental differential equation for diffusion in Cartesian coordinates in Equation 2.3 was used as the basis. This equation was simplified to a one-dimensional equation using only the x direction defined as the direction of the thickness of the sheet.

\[
\frac{\partial C}{\partial t} = D \frac{\partial^3 C}{\partial x^2}
\]  

(2.12)
From there, the model seen in Equation 2.13 was designed for diffusion through a flat sheet.

\[
\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{D(2n+1)^2}{{4L}^2}t\right)
\]  

(2.13)

The similarities to the spherical model can be seen where the thickness, \( L \), replaces the radius as the pathway of diffusion. As with the spherical geometry, this equation has a simplified solution.

\[
\frac{M_t}{M_\infty} = 2 \left(\frac{Dt}{L^2}\right)^{\frac{1}{2}} \left(\frac{1}{\pi^2} + 2 \sum_{n=1}^{\infty} (-1)^n \text{erfc} \frac{nL}{\sqrt{Dt}}\right)
\]  

(2.14)

Again, it is concluded that the integral complementary error function is negligible compared to the first term below a mass uptake of 50% so that the summation term drops out of the equation giving Equation 2.15.

\[
\frac{M_t}{M_\infty} = \frac{2}{\pi^2} \left(\frac{Dt}{L^2}\right)^{\frac{1}{2}}
\]  

(2.15)

This equation is only valid under certain assumptions. The first is that diffusion takes place only in the dimension of the thickness. The other dimensions must be large enough with respect to the thickness so that they are comparably infinite in size. Therefore diffusion in those directions has a small enough effect to be considered negligible. The composition and thickness of the material must both be uniform. Finally, the diffusion pathway is assumed to follow direct paths along the thickness of material.
Diffusion through a flat sheet may be either one- or two-sided. If the diffusing material enters and moves through the polymer from only one surface of the sample it is considered one-sided. On the other hand, if the diffusing material comes in contact with the polymer on both sides of the sheet, the diffusion is considered two-sided. The model for diffusion through a flat sheet given in Equation 2.15 is for one-sided diffusion. If two-sided diffusion is occurring, the equation must be corrected by replacing each $L$ term with an $L/2$ because the diffusion pathway would be half of the total thickness of the sample in this case. This is an important aspect to take into account when polymer samples must be prepared in the flat sheet geometry because the thickness is usually taken into consideration during the preparation step. The thickness dictates the amount of time that it will take the solvent to diffuse into the polymer so
the sample sheet is usually prepared so that experiments are neither too short nor too long. It is necessary to determine whether one-sided or two-side diffusion will be used so that the appropriate calculation of the thickness can be made.
3. Crystallinity

3.1. Melt Temperature

When talking about a polymer, the melt temperature is an important term. When a polymer is heated above its melt temperature it does not make a transition from a solid to a liquid. Instead, at this temperature, the crystalline structure within the polymer breaks down and the material becomes completely amorphous. This definition for a polymer’s melt temperature is much different than a normal material’s transition from solid to liquid[11]. For the high density polyethylene the melt temperature is in the range of 130°C to 135°C [12]. For the HDPE used during this research the melt temperature has been determined to be 131.5°C by the manufacture.

The melt temperature should not be confused with the glass transition temperature which is the transition point in an amorphous solid. At the glass transition temperature, the amorphous solid will change from a glassy to a softened, rubbery state upon heating. Below the glass transition temperature, the amorphous solid is hardened with no distinct order which differs from the crystalline structure growth which occurs at the melting temperature. The glass transition temperature is lower than the melt temperature [13].

The melt temperature of a polymer is only relevant for thermoplastics like polyethylene that can be melted and remolded [14]. These polymers can reach their melt temperature before degradation occurs unlike thermosetting polymers that would degrade far before they
reached a temperature at which they could melt [15]. Once a thermoplastic reaches its melt temperatures, crystals within the structure will cease to exist, and the polymer will be a completely amorphous solid. As the polymer is heated further past its melt temperature, it will begin to take on more of the properties of a liquid as the polymer itself begins to soften. This will continue until the polymer will be able to flow slowly as a viscous liquid [14]. If the thermoplastic is heated too far above its melt temperature, degradation will take place, which permanently changes the properties of the polymer [16]. In the case of polyethylene and other polymers used in previous experiments, evidence of degradation comes in the form of a color change from the typical white or transparent color of the polymer to a dark brown or black [17].

3.2. Definition

Crystallinity is the term used to describe long range order at the atomic level within a polymer. A polymer can be completely amorphous having no long range order and no crystallinity or have some degree of crystallinity. The degree of crystallinity in a polymer is the percentage of the polymer’s volume that is crystalline. Theoretically the degree of crystallinity can range from 0 to 100% in a polymer. However higher values of crystallinity are not obtainable in a real polymer [18]. Typically for HDPE, the highest obtainable degree of crystallinity is reported around 80% [19].

The degree of crystallinity varies with temperature. When a polymer is heated, its crystalline structure begins to break down as it turns more amorphous. As stated previously,
the crystalline structure or the long range order of atoms will slowly disappear until the melt temperature is reached at which point the polymer becomes completely amorphous in composition [20].

For the experiments in this work, crystallinity became an issue because the polyethylene pellets that have been received for analysis have a very high degree of crystallinity compared to other polymers. The room temperature degree of crystallinity for the HDPE pellets used in these experiments is 83.7% which is one of the highest obtainable values in a real polymer sample. Such a high degree of crystallinity must be considered when looking at the final results. Additionally, since the experiments above the melt temperature will be completely amorphous, any comparison between the two values must take into consideration only the amorphous phase values.

The importance of crystallinity is that it can affect both diffusivity and solubility. The crystalline structures within a polymer are essentially impenetrable. Therefore, the solvent is only capable of diffusion through the amorphous regions. Also, because of the inability to move into the crystalline regions, the solubility is limited to the amorphous regions. This means that the solubility will depend on the degree of crystallinity with the higher solubilities (on a total weight basis) occurring in polymers that are completely amorphous [21].

This inability of the solvent to travel into the crystals affects the diffusion models that were created by Crank. Looking specifically at the spherical model, an assumption that diffusion occurs strictly along the radius lines of each sphere is used. The crystalline portions hinder diffusion blocking these pathways, and therefore, diffusion cannot be strictly radial within the sphere. Instead, the solvent will have to wind through the amorphous sections of the polymer
along tortuous pathways until equilibrium is reached, and the amorphous sections are completely saturated.

The property of the winding pathways is known as the polymer’s tortuosity. In the polymer, the exact positioning of the crystalline structures is unknown. Therefore, within a polymer, the tortuosity is not exactly known. This presents a problem because the exact effects on the diffusion pathways are unknown, and therefore, calculating the diffusion of the polymer becomes complicated. For the initial analysis, this work used the assumption that the pathways of diffusion do not vary much due to tortuosity and that the radius is a viable prediction of the pathway. From there, an exploration into the exact effect of tortuosity was conducted using the Vrentas-Duda free-volume theory. Since the theory does not account specifically for tortuosity, any effects that it may have on the diffusion were observed when the calculated diffusion results were compared against the free-volume theory predictions for those values. If the melt temperature has a noticeable effect on the experiments, it will most likely be noticed because of crystallinity and tortuosity.

3.3. Differential Scanning Calorimetry

Differential scanning calorimetry is an analytical tool used to monitor heat uptake or release with respect to temperature. In this process, a sample is subjected to a constant rate of temperature change over time. Differential scanning calorimetry records the changes in the required heat as a function of temperature. The results are then used to create a curve that corresponds to the heat flux with respect to time [22].
This curve becomes a valuable technique because the area underneath it can be used to calculate the heat of fusion. This is particularly important when working with a polymer sample. The heat of fusion for a polymer can be compared against a reference value that has been determined for 100% crystallinity (a theoretical value that cannot be obtained with a real polymer). The ratio of these two terms provides the percentage of crystalline material within the polymer [23].

Most times, for crystallinity calculations, three sets of heat flux curves are created. To start the polymer is heated well above its melting temperature to ensure that the crystalline structure completely breaks down into a fully amorphous state. From there, the sample is then cooled at a rate that is linear with time to below room temperature. Finally, a second heating step is carried out which again takes the polymer at a constant rate from this value below room temperature to a temperature at which it will be completely amorphous again. This second heating curve is generally used for the crystallinity calculations and is considered more accurate than the first heating curve.

3.4. Determination of Crystallinity

The polymer manufacturer has provided a differential scanning calorimetry curve that shows that the crystalline structure begins to break down at room temperature for the high density polyethylene used in these experiments. From this curve, the percentage of crystalline material was determined to be 83.7%. This value, however, accounts for a curve that starts at room temperature and therefore corresponds to the room temperature crystallinity for the
sample. Since the curve shows that the degree of crystallinity begins to decrease starting right at room temperature, this value will not be accurate for the experiments that have been conducted for this paper. In a semi-crystalline there are three types of chains within the amorphous phase: (1) those completely free from a crystalline region, (2) those with one end tied to a crystal region, and (3) those with both ends tied to a crystal region. The latter two types of chains could be the reason that crystal breakdown is observed before the melt temperature [24].

The experiments conducted in this work below the melt ranged from 90 to 105°C. It is believed that crystallinity should not change much within this small temperature range. Thus, the crystallinity was assumed to be constant, and the value estimated at 100°C was used. To find this value, the area under the differential scanning calorimetry curve was calculated starting at 100°C and continuing until the polymer was completely amorphous. Comparing the heat of fusion for this portion of the curve to the literature value for 100% crystallinity, a value of 77.6% was determined for the crystallinity at 100°C.

This value of crystallinity is only a best estimate. This method used assumes that the crystallinity reaches equilibrium at each temperature as the temperature increases or decreases. The rate of crystallization is relatively slow, and if the sample was held at 100°C for an extended period of time, further changes in the crystalline structure are possible. Since the manufacturer of the polymer has not run differential scanning calorimetry starting from the desired temperature, this is the only method currently available for calculating the crystallinity. The value of 77.6% was used for the calculations in this paper. It is, however, known that 77.6% is the highest possible value. This has been determined from the knowledge that the
differential scanning calorimetry curve will not double back on itself because the polymer sample cannot regain crystallinity once those regions have become amorphous without cooling taking place first.
4. Vrentas-Duda Free-Volume Theory

4.1. Prediction

The basis for this theory is that the molecular transport through a material is controlled by the idea of free volume. For this concept, the total volume of the material is broken down into two types of volume, occupied volume and free volume. The occupied volume is the portion of the volume that is actually taken up by the molecules. The free volume, on the other hand, is the volume of the unoccupied portion that lies between the molecules. This volume is essentially the open spaces caused by the fact that the molecules cannot fit together without gaps. The occupied volume is a constant value that is not affected by temperature changes whereas the free volume is a temperature dependent quantity [25].

The Vrentas-Duda free-volume theory separates the free volume into two parts, an interstitial free volume that takes too much energy to redistribute itself and the hole free volume which can redistribute very easily. The hole free volume is used to defines molecular diffusion as the molecules moving from their current position into the holes. For a molecule to jump into a new position, three conditions are required. The first is that the molecule must have a hole in one of its adjacent positions so that there is somewhere for it to jump. Secondly, the adjacent hole must be of significant size for the molecule to be able to fit into it with no hindrance from the surrounding molecules. Finally, the molecule that is jumping into the hole must have the necessary amount of energy for the jump to occur. Joining the first two requirements into one, the diffusivity can be characterized as a combination of the probabilities
that the molecule will have an adjacent hole with sufficient size to jump into and that the jumping molecule possesses the necessary amount of energy to move into the hole \cite{26, 27}.

Cohen and Turnbull \cite{28} were the first group to look into using free-volume theory as a way to describe molecular diffusion. Building off of their work, Macedo and Litovitz \cite{29} came up with an equation for the self diffusion coefficient, $D_1$, using the requirements necessary for molecule jumping.

$$D_1 = D_0 \exp\left(-\frac{\gamma V_1^*}{\bar{V}_{FH}}\right) \exp\left(-\frac{E^*}{kT}\right)$$

\text{(4.1)}

In this equation and further free-volume equations, the subscript 1 refers to the solvent. In future free-volume equations, the subscript 2 will be used for the polymer. The first exponential term provides the probability that a sufficient hole size is adjacent. The variable $D_0$ is a pre-exponential factor that is considered constant. The critical volume for the hole size that is large enough for a jump to occur is $V_1^*$ and $\gamma$ is an overlap factor. This term is necessary because the same free volume hole is available for all of the surrounding molecules. The average free volume of a hole is $\bar{V}_{FH}$. It is possible for diffusion to occur even if the average volume value is smaller than the critical volume value because some of the individual holes’ volumes can still be equal to or greater than the critical volume. The second exponential term corresponds to the probability that the molecule contains enough energy for the jump to occur where $E^*$ is the critical energy that is necessary. In this equation $k$ is the Boltzmann constant and $T$ is the temperature.

The desire is to use the free-volume theory as a predictive model for diffusion.

Unfortunately, the critical energy value is unattainable without using experimental diffusion.
data to calculate it. The only way to predict a value for this term is to assume that it is negligible which Vrentas [30] suggested. This is a reasonable approximation because the variations in the free-volume probability have a stronger effect on diffusion than the energy probability and because it is the only estimation available without using the diffusion data. Using this assumption, Equation 4.1 simplifies to:

\[ D_1 = D_0 \exp \left( -\gamma \frac{\hat{V}_1^*}{\hat{V}_{FH}} \right) \quad (4.2) \]

As stated previously, this equation is only valid for self-diffusion of the solvent which is a one component system. Vrentas and Duda [26, 27] started with this concept to build a more general equation that can be used for a two component polymer-solvent system.

\[ D_1 = D_0 \exp \left( -\gamma \left( \omega_1 \hat{V}_1^* + \omega_2 \hat{V}_2^* \xi \right) \right) \quad (4.3) \]

The specific critical hole volumes for the solvent and polymer required for diffusion are \( \hat{V}_1^* \) and \( \hat{V}_2^* \) respectively. These values can be approximated using the molar volumes at absolute zero [31]. The specific average hole free volume is \( \hat{V}_{FH} \). The terms \( \omega_1 \) and \( \omega_2 \) correspond to the weight fractions of the solvent and polymer respectively, and \( \xi \) is the ratio of the molar volume of the solvent jumping units, \( \hat{V}_{1j} \), to the molar volume of the polymer jumping units, \( \hat{V}_{2j} \). It is defined in Equation 4.4 as [26, 27]:

\[ \xi = \frac{\hat{V}_{1j}}{\hat{V}_{2j}} \quad (4.4) \]
The ratio term becomes another difficult value to predict and one that is a topic of controversy. Zielinski and Duda [31] provide an estimation that assumes that each solvent molecule jumps as a whole for small molecules. Therefore, the molar volume of the solvent jumping units can be simplified to the molar hole free volume of the solvent. This assumption is reasonable because the solvent used in this paper is cyclohexane which is a small tightly bonded molecule. However, the polymer does not jump as a whole molecule. Instead, a segment of the polymer becomes the jumping unit. The length of this segment determines the stiffness of the molecules with longer segments being stiff and short segments being more flexible. Because previous work had been done that shows that the stiffness of a polymer chain depends on the glass transition temperature \( T_{g2} \) [32], Zielinski and Duda [31] were able to determine the following correlation:

\[
\bar{V}_{2j} = 0.6224 T_{g2}(K) - 86.95
\]  

(4.5)

Using this correlation, Equation 4.4 becomes:

\[
\bar{\xi} = \frac{M_1 \hat{V}_1}{0.6224 T_{g2}(K) - 86.95}
\]  

(4.6)

Equation 4.6 provides a way to estimate \( \bar{\xi} \) without using diffusion data. The molecular weight of the solvent, \( M_1 \), and the specific critical hole free volume of the solvent are used to calculate the molar volume of the solvent jumping units. However, this equation is not exact and, according to Zielinski and Duda [31] will fail at lower values of the glass transition temperature because the predicted jump volume is zero at 140K. Therefore, it must be used with caution.

Going back to the work that Vrentas and Duda did to build a free-volume theory for diffusion in a two component polymer-solvent system [26, 27], Equation 4.3 is only valid for the
self-diffusion part of the total mutual diffusion. A separate equation for the polymer self-diffusion coefficient, $D_2$, was also created.

$$D_2 = -\frac{A_0}{N^*M_2} \exp \left( -\gamma \left( \omega_1 \hat{V}_1^* + \omega_2 \hat{V}_2^* \xi \right) \right)$$

(4.7)

Similar to the solvent equation, there is a pre-exponential factor, $A_0$, in the diffusion equation. The term $N^*$ is the effective number of segments that each polymer chain is broken into, and $N$ is the number of these segments that are freely orientated. The molecular weight of the polymer is $M_2$.

The two self diffusion equations can be used to describe the mutual diffusion coefficient, $D$, of the polymer-solvents system.

$$D = \frac{D_1 x_2 + D_2 x_1}{RT} \left( \frac{\partial \mu_1}{\partial \ln x_1} \right)_{T,P}$$

(4.8)

In this equation, $x_1$ and $x_2$ are the molar fractions of the solvent and polymer. The gas constant, $R$, is used and the chemical potential of the solvent, $\mu_1$, is needed. A good assumption is that the polymer diffusivity is negligible compared to the solvent diffusivity in most systems. Thus,

$$D = \frac{D_1 x_2}{RT} \left( \frac{\partial \mu_1}{\partial \ln x_1} \right)_{T,P}$$

(4.9)

Vrentas and Duda [26, 27] used Flory’s work [33] to express the solvent chemical potential. They used the relationship found in Equation 4.10 that is valid for small solvents.

$$\mu_1 = RT \left( \ln [1 - \phi_2] + \phi_2 + \chi \phi_2^2 \right)$$

(4.10)
The volume fraction of the polymer is $\phi_2$ and the Flory Huggins interaction parameter is $\chi$. The interaction parameter changes very little with temperature and was assumed to be constant in this paper. An expression that can be used to calculate this interaction parameter is given by Bristow and Watson's [34] semi-empirical equation:

$$\chi = 0.35 + \frac{V_1}{RT} (\delta_1 - \delta_2)^2$$  \hspace{1cm} (4.11)

For this expression, $V_1$ is the solvent molar volume and $\delta_1$ and $\delta_2$ are the solubility parameters for the solvent and polymer respectively. For this paper the Hildebrand solubility parameters were used [35]. Other approximations for the interaction parameter are possible but solubility data are necessary, and the desire is for a completely predictive method. Variation in the interaction parameter has been determined to have very little effect on the diffusion coefficient so any error in the calculation of this value will have little effect on the free-volume model [31].

With this knowledge of diffusion, a combination of Equation 4.9 with Equation 4.10 provides a useful equation for the mutual diffusion coefficient in a binary polymer-solvent system.

$$D = D_1 (1 - 2\chi\phi_1)(1 - \phi_1)^2$$  \hspace{1cm} (4.12)

Further substitution of the equation for self-diffusion of the solvent transforms this equation into:

$$D = D_0 \exp \left( -\frac{\gamma (\omega_1 V_1^{*} + \omega_2 V_2^{*} \xi)}{V_{FH}} \right) (1 - 2\chi\phi_1)(1 - \phi_1)^2$$  \hspace{1cm} (4.13)
The specific average hole free volume is a term that must be evaluated. The full derivation for this term will not be covered here but is carried out in detail in the work in Vrentas and Duda [26, 27].

\[
\hat{V}_{FH} = \omega_1 K_{11}(K_{21} - T_{g1} + T) + \omega_2 K_{12}(K_{22} - T_{g2} + T)
\]

(4.14)

The K terms in this equation are all free-volume parameters that depend on the components in the system. Substituting Equation 4.14 in to Equation 4.13 gives the final equation for diffusion.

\[
D = D_0 \exp \left( - \frac{\left( \omega_1 \hat{V}_{1}^* + \omega_2 \hat{V}_{2}^* \right)}{\omega_1 K_{11}(K_{21} - T_{g1} + T) + \omega_2 K_{12}(K_{22} - T_{g2} + T)} \right) (1 - 2\chi \phi_1)(1 - \phi_1)^2 \exp \left( \frac{E^*}{kT} \right)
\]

(4.15)

The parameters \(D_0\), \(\xi\), and \(\chi\) are all mixture dependent parameters. They vary with both the solvent and polymer in the system. All of the other parameters in this equation are pure component parameters. A list of the values for these parameters has been compiled. The solubility parameters were taken from Barton [35]. The free-volume parameters for cyclohexane were obtained Hong [36] and the parameters for HDPE were from Lützow [7] and Becker [37]. All three of these papers used the Williams-Landel-Ferry coefficients to calculate the K parameter. The glass transition temperature for HDPE was taken from Barnetson [38]. The relevant values are given in Appendix B, Table B.1.

Expressions for two of the mixture dependent parameters, \(\xi\) and \(\chi\), have already been discussed previously. These equations are reasonable estimations that do not depend on the use of diffusion data and can therefore be used for prediction. The pre-exponential factor
becomes a difficult value to determine. The most reasonable way to calculate this term would involve using diffusion data. However, a completely predictive method is desired. Using work from Dullien [39] and Vrentas and Duda [26, 27], a predictive method was developed by Zielinski and Duda [31] that relies on the temperature dependence of both the solvent’s viscosity, \( \eta_1 \), and its specific volume, \( \hat{V}_1 \).

\[
\ln \left( \frac{0.124 \times 10^{-16} \bar{V}_{c1}^{2/3} RT}{\eta_1 M_1 \hat{V}_1} \right) = \ln (D_0) - \frac{\gamma \hat{V}_1^*}{K_{11}} - \frac{E}{RT} \left( \frac{1}{K_{21} - T_{g1} + T} \right) \tag{4.16}
\]

In this equation, \( \bar{V}_{c1} \) is the solvent’s critical molar volume. Taking into account the assumption from earlier that the activation energy is negligible, this equation reduces to:

\[
\ln \left( \frac{0.124 \times 10^{-16} \bar{V}_{c1}^{2/3} RT}{\eta_1 M_1 \hat{V}_1} \right) = \ln (D_0) - \frac{\gamma \hat{V}_1^*}{K_{11}} \left( \frac{1}{K_{21} - T_{g1} + T} \right) \tag{4.17}
\]

From this equation \( D_0 \) can be calculated using regression techniques. The values for the solvent’s viscosity and specific volume with respect to temperature have been calculated and used in this equation. There are some questions to the validity of this equation because most temperature dependent models for viscosity are only valid in small temperature ranges. This equation also suggests that the pre-exponential factor is strictly a solvent parameter and that the polymer has no significant effect which is untrue. The equation was used in the paper because it provides the desired predictive method for analyzing diffusion whereas other methods of determining this value require diffusion data for calculation. The value that this equation gives for \( D_0 \) along with the calculated values for \( \xi \) and \( \chi \) can be found in Table B.2.
4.2. Regression

$D_0$ and $\xi$ values are the most controversial terms in the prediction. Typically, these parameters cannot accurately be predicted because of their dependence on the both components of the system. The validity of any completely predictive free-volume model can be questioned. Therefore, a regression for $D_0$ and $\xi$ with the diffusion data obtained in this work was also used to model the diffusion behavior.

The regression was done using a program designed for free-volume analysis. The parameters collected in Appendix B, Table B.1 were inputted along with the experimental diffusivities to regress the values of $D_0$ and $\xi$. The values obtained during this regression are given in Appendix B, Table B.3.

4.3. Tortuosity

A second regression was done using only the experiments above the melt temperature. These parameters are given in Appendix B, Table B.4. This regression provides a completely amorphous model that was then corrected with a tortuosity factor. From Wong, Altinkaya, and Mallapragada [40], a tortuosity factor, $\tau$, can be added to the free-volume theory.

$$D_{corr} = \frac{D}{\tau} \quad (4.18)$$

Here, $D_{corr}$ is the corrected diffusivity that would be expected if the tortuosity has an effect on diffusion, and $D$ is the diffusivity of an amorphous value of the diffusion from the free-volume
theory. The tortuosity factor is dependent on the morphology of the polymer. The tortuosity in a polymer is unknown because the positioning of the crystals within the polymer is unknown. According to Lützow et al. [41], the tortuosity factor can be approximated as a linear function of the degree of crystallinity, $\phi_c$.

$$\tau = 1 + \phi_c \tau_a$$  \hspace{1cm} (4.19)

Here, $\tau_a$ is a correlation factor that is polymer specific and has a value of 7.57 for polyethylene. Using 77.6% as the degree of crystallinity for the high density polyethylene in this work, the tortuosity factor is equal to 6.9.
5. Experimental

5.1. Gravimetric Sorption Column

For all of the research performed in this paper, a gravimetric sorption column was used. This column contains an inner sample chamber which is a long cylindrical glass column that has a rod positioned across the top end of it. Both a quartz spring and a mercury thermometer hang from this rod. The polymer sample for the experiment hangs from this spring. The purpose of the thermometer is twofold in that it serves both as a way to monitor the temperature within the column and as a convenient backdrop to provide better viewing of the spring because otherwise the spring blends in with the background of the box. It is therefore important to ensure that the spring properly hangs in front of the thermometer with a reasonable portion of the thermometer below the spring to allow for stretching. The top of the glass column is removable to allow for loading and unloading of the sample into the chamber.

The column itself is contained within a large insulated wooden box that serves as the heating chamber. The purpose of this box is to keep heat from fluctuating within the column during the experiment. A PDI controller in an external control box is used to control the column’s temperature and to insure that it remains constant at the desired value for the experiment. The PDI controller works with a thermocouple and heater system to accomplish this task.
At the bottom of the glass chamber, an inlet line is connected to an insulated boiler. The desired solvent is contained in the boiler, and Valve A is opened to admit solvent into the...
column when necessary. A PDI controller setup similar to that of the column is used to bring the boiler to the desired temperature. A magnetic stirring rod inside the boiler mixes the liquid to ensure that heating is consistent and no hot spots occur.

Towards the top of the column is a second inlet/outlet line connected to a vacuum pump through Valve B. The vacuum is also used in the desorption process to remove the solvent from the polymer once an experiment has ended. A pressure transducer is attached to this line with a display that is present in the external control box to monitor the pressure within the chamber. When the vacuum pump is turned off, this upper inlet/outlet can also be exposed to the room’s air supply to bring the column to atmospheric pressure. This is an important feature for loading and unloading of the sample as well as for any maintenance done on the column.

Both of the lines that run from the column will contain solvent vapor throughout the course of the experiment. Therefore, it is important to monitor the temperatures of these lines so that condensation cannot occur inside of them. This is accomplished by having thermocouples at varies spots along them that are attached to a multi-terminal switch and a display screen in the external control box. The inlet/outlet lines are wrapped with heating tapes and then with insulation. These heaters correspond to control dials that are used to adjust the temperatures of the inlet/outlet lines.

Additionally, inside of the insulated box, there are auxiliary heaters that are used along with a circulation fan that is attached to external fan motors outside of the box so that no hot or cold spots can exist. Other thermocouples are used with both the controller and internal
mercury thermometer to show that there is not a temperature gradient along the length of the
glass column. The wooden box itself contains a removable lid that is the only access point into
column as well as glass viewing window on the front of the box. The thermometer and the
sample hanging inside the chamber are visible through this window. A cathetometer is used to
get a better view of the spring as it stretches during the course of the experiment. This provides
an easy way to track the exact elongation of the spring. Additional information on the column is
provided in Appendix A.

5.2. Sample Preparation

All of the experiments discussed in this paper used high density polyethylene as the
sample. The polymer was received in pellet form. These pellets had a reported percent
crystallinity of 83.7% and a density of 0.9586 g/cm$^3$ at room temperature. The preferred
method was to use these pellets in initial form. Therefore in the lower temperature range of 90,
100, and 105°C, the pellets were used as received. A total of 10 pellets were used in these
experiments. It was determined that each pellet had a spherical radius of approximately 0.19
cm to start from the mass and density. These pellets were placed in an aluminum basket and
hung at the end of the quartz spring for the experiment.

An issue occurred, however, in the higher temperature range of 140, 150, and 160°C.
These temperatures were chosen because they are above the melt temperature of the polymer
and the desired comparison was the difference between these two ranges. Once the melt
temperature is exceeded, the polymer slowly begins to lose its shape and starts to flow. At first, the polymer pellets were placed in a basket and placed into an oven at a temperature of 160°C. The pellets deformed from their original shape so the spherical assumption could no longer be used. However they did not melt enough to form a single sheet within the aluminum basket so a flat sheet model could not be used either.

Since the geometry of the melted pellets did not fit into one of the classifications for a desired geometry needed to analyze the experiments, a sample had to be prepared that would have a defined diffusion length. The solution to the problem was to create a flat sheet from the polymer pellets that would fit into the aluminum basket which was used to hold the sample during the experiment. To do so, polymer pellets were placed into a press with weights on top of the press for added force. The press was held under vacuum and heated in an oven to a temperature of 160°C. The sample was kept at this constant temperature over the course of three days. This time length was used to ensure that the polymer had adequate time to completely melt while in the press so the final result would be a flat circular sheet of uniform thickness.

The press was then taken out and allowed to slowly cool to room temperature with the weights still on the top of the press. Once the polymer had completely cooled, it was taken out of the press and cut into a circular shape so that it would have the exact diameter necessary to fit snugly into the basket without any gaps between it and the basket itself. The final polymer disk had a weight of 94.25 mg and a thickness of 0.41 mm.
5.3. Procedure

5.3.1. Setup

The first step in setting up an experiment was to ensure that any residue from previous polymer-solvent systems is no longer present. The column was evacuated for several hours using the vacuum pump. Before the desired solvent could be introduced into the system, the boiler, o-rings, and all of the connections had to be thoroughly cleaned so that no solvent other than cyclohexane was contained within the apparatus. Once this was done, the boiler was filled with the solvent and reattached to the column.

A polymer-filled aluminum basket was then hooked to the end of the quartz spring and slowly lowered into the glass chamber. During this process, it was important to ensure that the sample was carefully lowered down to the rod that it rested on because the spring is very fragile. Contact with the glass walls should be minimal to avoid damage or breakage. Extra care had to be taken to ensure that the basket remained level for the runs above the melt temperature because at these temperatures, the polymer will flow. An uneven basket in this temperature range would cause an uneven sheet. The diffusion analysis requires a uniform flat sheet with a defined diffusion length in order to obtain reliable results.

After the sample was in place, the top of the column was sealed, and vacuum was applied to completely evacuate any air. Pressure tests were run before each experiment using
the pressure transducer to determine if any leaks were present in the system. If a leak was found, all of the connections were taken apart, cleaned, and then reattached.

Once the column was leak-free, the temperatures of both the column and boiler were set using the PDI controllers. The column temperatures were 90, 100, 105, 140, 150, and 160°C. Each run was designed to reach a certain activity, \( a_1 \), which in turn, determined what the boiler temperature had to be. The activity is the ratio of the fugacity, \( f_1 \), to a reference state fugacity, \( f_{1}^{0} \).

\[
a_1 \approx \frac{f_1}{f_{1}^{0}} \quad (5.1)
\]

For a gas, the fugacity is:

\[
f_1 = x_1 \gamma_1 P \quad (5.2)
\]

The molar fraction, \( x_1 \), is one because the solvent vapor is the only gas present in the gravimetric sorption column. The fugacity coefficient is \( \gamma_1 \), and the pressure is \( P \). For a low pressure environment, the fugacity coefficient and the reference fugacity coefficient are approximately equal. The reference pressure is set as the saturated vapor pressure, \( P_{1}^{\text{sat}} \), so that equation 5.1 simplifies to:

\[
a_1 \approx \frac{P}{P_{1}^{\text{sat}}} \quad (5.3)
\]

The boiler temperature was dependent on both the solvent activity and the column temperature. Before the experiment, the solvent temperature was set a bit higher than the
experiment’s actual temperature because the pressure change when opening the valve between the boiler and evacuated column caused the temperature to drop slightly at the start of each experiment due to evaporative cooling.

After both temperatures reached their desired values, the boiler was degassed. This process was conducted to ensure that there was no air in the boiler. Degassing consisted of closing the vacuum valve and then opening the column to the boiler. Once a steady pressure was reached, the column was evacuated. This procedure was repeated until a consistent pressure change was seen each time the solvent was introduced into the glass chamber. This pressure change should correspond to the solvent's vapor pressure at the temperature of the boiler. Degassing had to be done the day before the experiment was run so that there was adequate time before the experiment to ensure that all of the solvent vapor was completely evacuated from the column, and any of the solvent that may have diffused into the polymer during the process had properly desorbed. Any unaccounted for mass uptake into the polymer before the experiment would invalidate the results.

5.3.2. Experimental Run

To begin each experimental run, the initial starting position of the polymer basket must be noted. Looking through the cathetometer, a reference point was chosen on the spring. This point can be anything from the tip of the hook at the end of the spring to a glue spot on the spring. The exact choice was not important as long as the point was easily recognizable and
found quickly. The entire cathetometer was moved up or down the pole to which it was attached so that this point was towards the top of the length scale. Once the cathetometer’s position was set, it was recorded along with the evacuated chamber pressure as the zero time point for the experiment.

Now that a reference point was set for the experiment, the valve to the vacuum pump was closed. From there, the boiler valve was opened slowly, and a timer was started simultaneously. It was important to open the valve as slowly as possible to try to avoid a powerful vapor stream rushing into the column. If this happened, the spring would have large oscillations and recording points at the beginning of the experiment would be extremely difficult. As soon as the valve was opened, the controller for the boiler temperature was readjusted to the desired temperature because it was originally offset to counteract the temperature drop that occurred with the expansion of the solvent into the column.

The spring gradually extended as the mass uptake into the polymer increased due to sorption. Starting at roughly minute intervals the reference point on the spring was found while looking through the cathetometer. The time, spring position, and column pressure were quickly recorded for each point. As the uptake began to slow the time between each data point was spread out. The pressure initially had a large change at the beginning of the experiment that corresponded to the vapor pressure of the solvent under the experimental conditions and then leveled off to a constant value within a few minutes. After a period of 45 minutes to an hour, however, the valve to the boiler was closed to prevent the possibility of any leak into the boiler affecting the experiment. This time frame was chosen because by then a substantial amount of
vapor entered the column, and closing the valve to the boiler no longer affected the results of the experiment.

The process of taking points continued until the experiment reached equilibrium. Equilibrium occurs when the spring no longer stretched any further. Depending on the diffusion rate and the thickness of the polymer sample, this could take anywhere from 30 minutes to 10 hours. After equilibrium was reached, a series of four or five more data points were obtained to ensure that the experiment truly ended. Once this happened, the experiment progressed in one of two ways. In some cases, a new experiment was started at a higher activity step. A new boiler temperature was set as soon as the valve to the boiler was closed during the first experiment. After equilibrium, the timer was reset. The equilibrium conditions were taken as zero point values for the new experiment. The boiler valve was opened and the timer restarted. Then the same experimental procedure was carried out. This process can be used as many times as necessary to obtain a desired number of activity steps. The other option was to evacuate the column over night to completely desorb the solvent from the polymer. This was done when no more sequential steps were desired.

5.3.3. Spring Calibration

In addition to all of the experimental steps that were run, the quartz spring had to be calibrated either before or after the experiment. For this, three weights within the springs capacity limit were needed. These weights were usually aluminum sheets with known masses.
A calibration weight was attached to the spring and lowered into the column. From there, the column was evacuated, and the weight’s position was recorded at three different column temperatures. The temperatures should have been in close proximity to the temperature range of the desired experiments because the spring constant was temperature dependent. Positions were taken for each of the three weights at each of the three temperatures.

Once the nine data points were taken, plots of mass versus displacement were created for each of the three temperatures. The plots should be linear according to Hooke’s Law.

\[ F = -kx \]  \hspace{0.5cm} (5.4)

Here, \( F \) is the force, \( x \) the displacement, and \( k \) the spring constant. Therefore, the slopes of these lines corresponded to the spring constants at each temperature. Mass was being used instead of force, but the two only differ by acceleration due to gravity. The gravity term was grouped into the spring constant and accounted for in this way throughout all later calculations. The three spring constants should be very close if the temperatures were close so that these three values were averaged to give a spring constant that was used in later calculations. For the experiments below the melt temperature, the spring that was used had a constant of 0.0327 g/cm. A different spring was used above the melt temperature with a constant of 0.0412 g/cm. A sample spring calibration plot is displayed in Figure 5.2. There is not an intercept term in Hooke’s Law. The plots created during the spring calibration process, however, did not run through the origin of the graph. This discrepancy was caused by the zero point of the length
scale not being the same as the zero point of spring extension that would correspond to no mass. This did not affect the calibration because the slope remained unchanged by this length scale shift.

Figure 5.2: Spring Calibration for S1 Spring at 140°C

5.4. Complications/Adjustments

5.4.1. Problems with the Polymer Sample

Throughout the experimental work for this paper many complications arose. The first of these complications had to do with the polymer pellets themselves. For the lower temperature range, the pellets were used as they were received because that was the desired morphology. Any heat applied or solvent added would have changed the crystalline structure of the polymer.
Although the pellets were generally quite similar, they were not all exactly the same size and shape. Therefore, pellets of similar size were picked for use. A second problem was that the pellets were created using an extrusion process so that they were not completely spherical in shape. There was not a simple model available for this type of shape so an assumption had to be made in order to analyze the results for these runs. Through previous work done by Russell [42], it had been determined that a spherical model was the best approximation for this type of polymer pellets. The spherical model most accurately replicated the shape of the experimental data in a comparison that also used the infinite flat sheet and infinite cylinder models. In Russell’s study, the spherical model was the only one to consistently predict the results. The assumption was that diffusion through the pellet was similar enough to that through a sphere of the same weight and density so that any differences were negligible.

Figure 5.3: Diagram of the Actual Pellet Shape Compared to the Assumed Shape

Geometric issues were not limited to pellet experiments. At the higher temperatures, there were also some concerns with geometry. Although the pressed polymer sheet fit tightly into the basket at room temperature, its shape had a tendency to deform as it transitioned through the melt temperature. At the higher temperatures, the polymer pulled itself away from the side of the basket. This tendency was unavoidable, but it was believed that the change in
surface area and thickness of the pellet was small enough to be negligible in the calculations. Furthermore, it was assumed that the thickness was small enough compared to the radius to model the disk as an infinite flat sheet instead of a short cylinder.

![Diagram of the Top View for the Actual Polymer Sheet Compared to the Assumed Shape](image)

Figure 5.4: Diagram of the Top View for the Actual Polymer Sheet Compared to the Assumed Shape

Beyond the geometric constraints while modeling the system, other problems were encountered. The pellets started as a highly crystalline material. However, the polymer began to lose its crystallinity starting from around room temperature as it was heated. Once the polymer reached the melt phase, it became completely amorphous so for the higher temperature range crystallinity could be assumed to be zero for that set of experiments. The experiments at 90, 100, and 105°C were still semi-crystalline though. A direct comparison of the two temperature ranges is only viable with similar crystallinities. This was impossible to do experimentally since the crystallinity was temperature dependent.

Therefore, calculations must be on an amorphous phase basis. For the higher temperature range, this was simply the total mass, but for the pellets, it was the percentage of the material that was not crystalline. Although the crystallinity was known at room temperature, it slowly decreased until it neared the melt temperature where the crystalline
structure broke apart much more easily. Since this process was slow until very close to the melt temperature of 131.5°C, the crystallinity could be assumed to be constant in the range of 90 to 105°C, and the value at 100°C was chosen. The best approximation for the crystallinity came from the differential scanning calorimetry curve that the polymer manufacturer initially used to find the room temperature crystallinity. Starting at 100°C and finding the heat of fusion, a percent crystallinity of 77.6% was found by comparing that calculated heat of fusion to the literature value for 100% crystalline HDPE.

Further studies into the polymer crystallinity were carried out using differential scanning calorimetry. Three polymer samples were heated and then cooled to determine how the morphology of the polymer changed with temperature. The first sample was heated to 90°C, the second sample to 90°C and then 160°C, and the third to 90, 160°C and then cooled back to 90°C. After the samples cooled to room temperature, each was analyzed using differential scanning calorimetry. A fourth scan was taken using the polymer as it was received from the manufacturer. The sample taken only to 90°C had a lower crystallinity than original polymer whereas the other two had crystallinities comparable to it. These results did not provide much insight into the morphology because no distinct trend was present.

There were concerns with the effects of swelling and heating caused by the sorption process. It had been determined that if small activities steps were used that these effects would be limited [43]. Additionally, swelling was accounted for in the polymer sample by considering the amount of solvent uptake from the previous step and recalculating a new radius or
thickness depending on the geometry of the sample. These changes in the diffusion pathway were very small from one experiment to the next.

A final concern about the polymer came in the higher temperature range. When a polymer was heated quickly or remained at high temperature for an extended period of time degradation could occur. The polymer would discolor from its white or clear color to a much darker brown color. Care was taken to observe the polymer throughout the experiments so that any change in color could be identified immediately. If degradation had occurred, the polymer would have been replaced and the experiment would be restarted. However, this was not necessary during the experiments conducted for this work because no discoloration or other signs of degradation were seen.

5.4.2. Problems with the Equipment

In addition to issues with HDPE, the equipment provided further complications to the experiments. The column itself was designed to run at low pressures and cannot hold a constant environment at a pressure above atmospheric. Once a pressure that high is reached one of the seals for the column will give way, and a leak out of the system will occur. In previous experiments, this typically was not an issue. However, cyclohexane has a relatively high vapor pressure. Coupled with the desire to run at higher than normal temperature, the column pressure became a concern in these experiments. Because of the atmospheric pressure constraint on the system, measurements were restricted to low activity steps. This inability to reach high activities was most noticeable at the higher temperatures above the melt.
The column pressure was not the only problem that the high temperatures presented. The entire column has a maximum temperature limit of 160°C which was one of the temperatures where results were desired. Extra precaution had to be taken while heating to this temperature. The extent of damage that overheating the column would cause is unknown, but many precautions were taken to avoid it. Even though the column was never taken above its temperature limit, the effects of being close to it were still seen. The circulation fan motor wore out and had to be replaced. The new motor was working too close to its temperature limit and continually overheated. The fan has a shutoff safety feature which allowed for a cool down period once it had overheated. Unfortunately, the fan must be running continuously to keep circulation within the heating chamber so that a temperature gradient did not occur. Therefore, an additional cooling fan had to be added to the system with the sole purpose of making sure that the circulation fan did not overheat.

The weight of the aluminum baskets used to hold the polymer presented a problem while running the experiments. The weight of each basket was significantly greater than the amount of polymer contained within it. Springs with higher maximum loads were needed to hold the extra weight that the baskets added to the sample. Since the springs had a high maximum load, the small amounts of mass that diffused into the polymer stretched the spring very little. With the position changes being very small, any small changes in the angle at which the reference point was viewed through the cathetometer from point to point could significantly affect the results of the experiment. Typically, the distance changes are much greater during experiments so that changes in eye level have little effect and are attributed to
experimental error. In the case of these experiments, a conscious effort was taken so that the data points were consistently taken at the same eye level.

Another problem with the baskets was that the upper loops or handles of the baskets were not rigid. They were made of aluminum wire that was strung through holes on either side of the basket. Therefore the basket had the ability to swing back and forth on this axis instead of remaining stationary. For the lower temperatures this was not a problem, but once the polymer was taken above its melt temperature, the possibility of flow became a concern. Since the polymer had to be a flat sheet with uniform thickness for Crank’s model to be valid, the basket could not be allowed to hang unevenly as this could result in a non-uniform geometry. Soldering was considered at each of the potential pivot points to make the basket completely rigid. However, at an experimental temperature of 160°C, most of the common soldering materials would melt. Instead, the wire was pinched at both of its connection points with the basket. Although this was not a perfect solution, it limited the movement of the basket. During the hanging process for the experiments in the higher temperature range, the basket was lowered carefully and repositioned if it was not hanging level.

The assumption that the basket sufficiently sealed the bottom surface of the sample was made. Since the solvent vapor could not freely move into a position where it was in contact with the bottom face of the sheet, diffusion was considered to be one-sided. The flat sheet model for diffusion was used as presented in Section 2.2.2 of this work, and the diffusion pathway term remained the total thickness instead of half of the thickness which would have been used if the diffusing material could have enter from both sides.
5.5. Data Analysis

Once all of the data had been collected, an effective way of analysis was necessary. During previous experiments, a useful EXCEL spreadsheet was created that inputs the time and distance of each data point as well as various information about the polymer and solvent such as density and molecular weight. Using Hooke’s Law and the spring calibration information the total mass uptake was calculated from the equilibrium spring extension. This solvent weight was corrected with a buoyancy factor to account for the space that the spring, basket, and polymer sample take up within the glass chamber. Typically, this correction accounts for anywhere from 1 to 10% of the mass uptake.

The next calculation needed involved finding the distance through which the solvent diffused into the polymer. For the spherical pellets the radius was calculated from the known mass of the polymer, its density, and the spherical volume equation. The direction of diffusion for the flat sheet was through its thickness which was calculated similarly.

The spreadsheet was setup to create plots of the mass uptake ratio versus the square root of time. From there, the plot was compared to the simplified form of either the spherical or flat Crank models discussed in Chapter 2. Both models were only valid for small amounts of uptake, and therefore only data up to 50% uptake were used to ensure that the models’ assumptions were still valid. The spherical model was nonlinear so a curve fitting program had to be used to calculate a constant value for $D/R^2$ through nonlinear regression (Equation 2.11). Slidewrite was used for this nonlinear regression. Since the $D/R^2$ parameter was the only
parameter that was unknown and had to be fit using this method, reaching a convergent value did not become a problem as it would have been if more parameters were desired. The flat sheet data were linear at small amounts of uptake with respect to the square root of time. The initial slope corresponded to a group of constants in Crank’s model using linear regression (Equation 2.15). The diffusivity of the system was calculated using the slope because all of the other parameters in the equation were known.

\[ Const = \frac{D}{R^2} \quad \text{(Spherical)} \tag{5.5} \]

\[ Slope = \frac{2}{\pi^{1/2} L} D^{1/2} \quad \text{(Flat Sheet)} \tag{5.6} \]
6. Results

6.1. Below the Melt Temperature

6.1.1. Solubility

Below the melt temperature, three activity steps were run at each of three temperatures. The solubility of each of these nine steps was desired. The solubility is directly related to the equilibrium weight fraction, \( X \), of the solvent vapor which is defined in Equation 6.1 as the mass uptake of the solvent vapor \( (m_{\text{sol}}) \) compared to the summation of this mass with the polymer mass \( (m_{\text{poly}}) \):

\[
X = \frac{m_{\text{sol}}}{m_{\text{sol}} + m_{\text{poly}}} \quad (6.1)
\]

A mass balance was used to weigh the polymer before the experiments were started. For the runs at 90, 100, and 105°C, the polymer mass was 0.276 g. However, this was the total mass of the polymer, and for comparison against the higher temperature data, only the amorphous phase was desired. The amorphous fraction of the mass was the percentage that was not occupied by the crystalline material. Since the crystalline portion was 77.6% of the polymer, 22.4% of the mass or 0.0618 g was amorphous.

Once the equilibrium weight fraction was calculated, it was plotted against both the solvent activity and the solvent vapor pressure. At 90°C, a solvent activity of 0.6 was reached within the restrictions of the column’s pressure threshold. For 100°C and 105°C, 0.4 was the
highest obtainable activity. The expected trend was that solubility increased as solvent activity increased (Figure 6.1). Since the solvent pressure is directly proportional to the activity this trend also followed in that plot (Figure 6.2). Through these graphs, it can be noted that solubility increased with temperature at a given activity. The solvent pressure graph provided little theoretical insight but is of practical interest.
Figure 6.1: Solubility of Cyclohexane in High Density Polyethylene at Temperatures below the Melt
Figure 6.2: Solubility of Cyclohexane in High Density Polyethylene as a Function of Pressure at Temperatures below the Melt
6.1.2. Diffusivity

Once the solubility had been determined, the next step was to calculate the diffusivity. To do so, a ratio of the mass uptake at a given time compared to the total equilibrium uptake known as the normalized uptake was necessary. Since the spring constant was constant for both terms, it was factored out so that this equation simplifies to a ratio of length changes at a given time versus equilibrium.

\[
\text{Normalized Uptake} = \frac{x_0 - x(t)}{x_0 - x_{\text{equil}}} \tag{6.2}
\]

Here \(x_0\) was the initial height, \(x(t)\) was the height at time \(t\), and \(x_{\text{equil}}\) was the final height of the experiment that corresponded to the equilibrium value. A plot versus time similar to the one in Figure 6.3 was used. This figure was one of the nine plots created and corresponded to the 0 to 0.45 activity step at 90°C.

![Figure 6.3: Uptake Curve for Cyclohexane in HDPE at 90°C, 0 to 0.45 Activity](image)

Figure 6.3: Uptake Curve for Cyclohexane in HDPE at 90°C, 0 to 0.45 Activity
In the figure, a large gap in the data appears. This was because the experiments below the melt temperature ran very slowly due to the diffusion rate and the distance through which the diffusion occurred. The system reached equilibrium somewhere between 8 to 10 hours after the start of the experiment. The gap in the data represented a period of time overnight at which no data points were taken. Although this accounted for a large period of time without any data for the run, the experiment had reached a stage where additional data points were not needed. The overall desired shape of the curve was present and the initial data used to calculate diffusion were intact along with the final data that was used for solubility analysis.

The initial data up to around 50% of the uptake were considered for analysis of the diffusion. The uptake had to be corrected to account for the data shift caused by the buoyancy and the time lag at the beginning of each experiment. This was be accomplished by subtracting the y-intercept of the initial data from both the mass uptake at a given time and the equilibrium uptake in the normalized uptake. This correction shifted the starting point of the data to the origin. Software was used to perform a nonlinear regression to find $D/R^2$. From there, the diffusion coefficient was found because the radius of the pellets was known. As a check, a dimensionless square root of time curve was created by dividing out the diffusivity and radius terms. The curve was made dimensionless in this manner to make all plots uniform so that one universal, spherical model curve could be used for comparison. A sample plot at 90°C is shown in Figure 6.4. As expected, the data followed very closely to the predicted spherical model for all of the experiments.
A plot of the diffusion coefficient versus weight percent of the solvent cannot use the same equilibrium percentage that was used in the solubility graphs because diffusion is a function of weight fraction. Therefore, a corrected weight fraction must be found because the weight fraction changed throughout the course of the experiment. As shown by Vrentas, Duda, and Ni [44], the preferred corrected concentration is 70% of the total uptake. This correction assumed that the diffusion coefficients calculated corresponded to a weight fraction 70% of the way between the initial and final weight fractions. For an experiment that started with a completely evacuated column, this correction was simply calculated by taking 70% of the equilibrium weight fraction. However if a multistep experiment was run, where some solvent uptake had already occurred, the 70% correction was used only for the new uptake, and the entire uptake from the previous experiment was added. As in the solubility calculations, only
the amorphous phase of the polymer was considered so that the results could later be compared to the data obtained from the experiments above the melt temperature.

Similar to the solubility graphs, certain trends were expected for the diffusion plot (Figure 6.5). Diffusion increased slightly with the corrected weight fraction. The diffusivity also increased as temperature increased. This plot shows that there are two properties that affected the diffusivity. Temperature and concentration both played a role in determining the diffusion coefficient.
Figure 6.5: Diffusivity of Cyclohexane in High Density Polyethylene at Temperatures below the Melt
6.2. Above the Melt Temperature

6.2.1. Solubility

The solubility above the melt temperature was calculated in the same way as below the melt with one major difference. Since the polymer was complete amorphous at this point, the entire 0.09425 g of polymer were used for analysis. The highest obtainable activity was 0.20 for 140°C, 0.16 for 150°C, and 0.14 for 160°C. At these higher temperatures, the activity steps were very low compared to the usual values used in gravimetric experiments typically run in the past. These activity maximums were chosen with the knowledge that the column cannot operate above atmospheric pressure (760 mmHg). Typically, the pressure in the system rises slightly during experiments. Therefore, only a pressure of 700 mmHg was approached to allow for this pressure increase. Furthermore, the lowest pressure obtainable under vacuum conditions was 20 mmHg which was also accounted for because it contributed to the total pressure inside the column. With these two adjustments, a maximum solvent pressure of 680 mmHg was used. This value corresponded to the maximum activities of 0.20, 0.16, and 0.14 at their respective temperatures.

As before, the solvent activity and solvent pressure were both plotted against the equilibrium weight fraction for each set of temperatures. Both graphs followed the desired trend of solubility increasing with both solvent activity and pressure. The solubility again increased with temperature at a constant solvent activity.
Figure 6.6: Solubility of Cyclohexane in High Density Polyethylene at Temperatures above the Melt
Figure 6.7: Solubility of Cyclohexane in High Density Polyethylene as a Function of Pressure at Temperatures above the Melt
6.2.2. Diffusivity

Like the lower temperature experiments, the first step in calculating the diffusion coefficients above the melt was to find the normalized uptake using Equation 6.2. From there plots were made again versus the square root of time. The plot for the solvent activity step of 0 to 0.10 at 140°C is provided in Figure 6.8 for comparison to the lower temperature example seen in Figure 6.3.

![Uptake Curve for Cyclohexane in HDPE at 140°C, 0 to 0.10 Activity](image)

Figure 6.8: Uptake Curve for Cyclohexane in HDPE at 140°C, 0 to 0.10 Activity

Unlike the experiments below the melt using the spherical pellets, diffusion through the flat sheets was very rapid. Equilibrium was reached around the 30 minute mark of each of these experiments. This set of experiments was very fast compared to the typical experiments run during gravimetric sorption analysis. The time it takes to reach equilibrium is a function of both the thickness of the sheet and the temperature.
These experiments presented another problem while running these experiments. The data useful for diffusion calculation are those up to approximately 50% of the uptake. With the short experimental time and the diffusion rate, the majority of the uptake was reached within five to ten minutes of each experiment. Even if the spring oscillations at the start of each experiment were held to a minimum, very few data points could be taken before more than the 50% limit on the uptake was reached. Data points were, therefore, taken as quickly as possible at the start of the experiment, and only a relatively few number of data points could be used to calculated the slope from the corrected uptake.

The corrected uptake was calculated in the same manner as previously, and again, buoyancy and time lag were accounted for at the beginning of the experiment. The corrected uptake was plotted against the dimensionless square root of time. This time the dimensionless square root of time term was calculated by dividing out the diffusion coefficient and thickness terms since the geometry was a flat sheet instead of a spherical pellet. A universal flat sheet model was added to the plot for comparison.
As before, the weight fraction for diffusion was corrected to the 70% value that corresponds to the diffusion range. Unlike the spherical data, the initial data were linear allowing for a simple linear regression. The slope of this portion of the graph was found. From there, the diffusion coefficient was calculated for each step. The corrected weight fractions were calculated the same way as before. This time the amorphous weight fraction that was found was equal to the entire weight fraction for the experiment. The diffusivity was plotted against the corrected weight fraction. The desired trends were seen again with the diffusion coefficient increasing with weight fraction and temperature.
Figure 6.10: Diffusivity of Cyclohexane in High Density Polyethylene at Temperatures above the Melt
7. Comparison

7.1. Above the Melt vs. Below the Melt

One desire of this work was to determine whether or not the melt temperature had a significant effect on the solubility and diffusivity of a solvent into a polymer. To do so, the nine experiments below the melt were compared to the nine above it for cyclohexane in high density polyethylene. As discussed in earlier sections, the difficulty with this was that the two temperature ranges had much different crystallinities which made a comparison between the total weight fractions useless. Differing crystalline structures affected the mass uptake so steps had to be taken to ensure that all of the weight fractions corresponded strictly to the amorphous phase so that a direct comparison could be made.

The first noticeable difference between the two sets of experiments was the time frame for each experiment. The experiments at 90, 100, and 105°C were extremely slow, taking between 8 to 10 hours to reach equilibrium, compared to the experiments at 140, 150, and 160°C which were at equilibrium after only 30 minutes. At first look, this discrepancy would suggest that there was a significant difference in the diffusivities of the two temperature ranges. For experiments of the same polymer-solvent system, these time scales would suggest that there were orders of magnitude differences in the diffusion coefficients and that exceeding the melt temperature had a significant effect on the diffusion. However, the results for each experiment that are displayed in Appendix B, Table B.5 did not show the expected gap in these values.
Looking at the diffusivities, there was only about half an order of magnitude difference when going from below the melt temperature to above it. This gap could be attributed to the facts that diffusivity increases with temperature and there is a large temperature change between the two sets of experiments. The time scale discrepancy must be attributed to the change in the length of the diffusion pathway between the two experiments. The geometric differences affected the rate of the experiment time frames because the diffusivity depends upon both the shape and primary pathway of diffusion. Therefore, looking at the changes in the time scales did not provide much insight into whether there was a significant change in the diffusion process once the polymer was taken above its melt temperature and further investigation was necessary.

A deeper look into the data was necessary. The next step was to look at the trends of both the higher and lower temperature ranges to try to see if there was a noticeable temperature trend. An effective way to do this was to use graphs for comparison. Therefore, all of the collected data was combined so that all eighteen data points were plotted on the same sets of graphs that were used previously. There were two important types of graphs used for analysis. One of these graphs was used to look at the solubility of the solvent into the polymer. This graph was of the solvent activity and plotted against the equilibrium weight fraction. (Figure 7.1).
Figure 7.1: Solubility of Cyclohexane in High Density Polyethylene
Looking at the solvent activity plot, the desire was to find any noticeable difference between the data above compared to below the melt point that was significant enough to suggest that the melting the polymer had a significant effect on the solubility. Particular attention was paid to the temperature range between 105 and 140°C. Examining the results for solvent activity, no significant changes occurred from the trends of the lower temperature data to the higher temperatures. Furthermore, all of the data points fell close together in line and no large gap was present in the 105°C to 140°C range. There was nothing in this graph to suggest that the melt temperature had any effect on solubility. The slope of the 140°C data was slightly different than the other temperatures, but the overall trend of the data remained constant. This was not surprising since only the amorphous phase was accounted for in these calculations.

The second graph used for analysis, came from the diffusion data at the beginning of the experiment. The diffusion coefficient was plotted versus the corrected weight fraction. Again, all eight results were plotted together to look for significant evidence that the melting point had an effect on the solvent-polymer system. The graph in Figure 7.2 was a combination of the data above and below the melt temperature for the diffusion of cyclohexane into HDPE.
Figure 7.2: Diffusivity of Cyclohexane in High Density Polyethylene
Looking at the diffusion plot, the inability to reach higher solvent activities due to the equipment’s maximum experimental pressure constraint was much more noticeable than with the solubility plots. Only a very low range of weight fractions were obtainable. At higher weight fractions, the value of the diffusion coefficient levels off more and becomes more constant. It became difficult to compare the two temperature ranges because of this. Ideally, values at higher weight fractions would have been obtained so that the flatter portions of the curve would be present and the temperatures could be better compared.

Even with the lack of data at higher weight fractions for the 140, 150, and 160°C temperatures, the data above the melt temperature appeared to behave differently than the experiments below the melt. The slopes of the diffusivities were steeper at higher temperatures. The concentration of the solvent seemed to have a greater affect above the melt temperature. At lower temperatures, the amount of solvent had almost no effect on the diffusion coefficient, while temperature had a significant effect. As temperature increased, the effect of the concentration also increased so at the high temperatures, both the temperature and concentration had a significant effect on the diffusion.

### 7.2. Free-Volume Theory Comparison

Using the free-volume theory given by Duda and Vrentas in Equation 4.15, the diffusion coefficients were predicted for each temperature. These predictions are plotted with respect to weight fraction of the solvent and are displayed in Figure 7.3. The prediction model performed
well at the high temperature range, but was not as accurate for experiments below the melt temperature of the polymer.

Additionally, the full experimental data were regressed to give another fit to the free-volume model. All of the data were used together for this fit (Figure 7.4). In this case, all of the data are correlated relatively well.

Another regression using only the amorphous phase data (140-160°C) was done. In addition, adjusted values using the estimated tortuosity factor were calculated for the semi-crystalline data (90-105°C) only as shown in Figure 7.5. The regression using only the amorphous data fit the semi-crystalline region better than the prediction but not as well as the full regression. Use of the tortuosity factor did not fit the data at all.

These free-volume predictions and correlations suggest that diffusion was not hindered by the semi-crystalline portion of the polymer, and that the polymer behaved as if no tortuosity factor was needed. There are two possible explanations for this unexpected behavior. The first is that the data could not be fully interpreted because of the inability to calculate the exact crystallinity for the experimental temperature range. The crystallinity decreased as the temperature increased, but the exact temperature dependence was unknown. The crystallinity could also be affected by the concentration of the solvent. A polymer’s morphology can be changed with the introduction of a solvent, and the crystals could at least partially dissolve. No experiments were conducted to determine the effect of cyclohexane on the crystallinity of HDPE, but dissolved crystals could explain the observations. If the crystals did not dissolve, the other explanation for the observed behavior is that the polymerization process for this specific
polymer created an unusual morphology where the crystals aligned so that the diffusion pathway was uninhibited.
Figure 7.3: Free-Volume Theory Prediction of Diffusivity of Cyclohexane in High Density Polyethylene
Figure 7.4: Free-Volume Theory Regression of Diffusivity of Cyclohexane in High Density Polyethylene
Figure 7.5: Free-Volume Theory Amorphous Regression of Diffusivity of Cyclohexane in High Density Polyethylene
7.3. Literature Comparison

The only literature results that could be found for a polyethylene-cyclohexane system came from Becker’s thesis work [38]. His values corresponded to infinite dilution values for linear low density polyethylene. Since LLDPE is an intermediate between LDPE and HDPE, its structure and density are reasonably close enough to HDPE for these literature values to be relevant. No literature was found that used cyclohexane as a solvent with HDPE.

Table 7.1: Infinite Dilution Diffusion Coefficients for PE-Cyclohexane System from Becker

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Inf. Dil. D (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40°C</td>
<td>1.69E-09</td>
</tr>
<tr>
<td>60°C</td>
<td>7.66E-09</td>
</tr>
<tr>
<td>80°C</td>
<td>2.51E-08</td>
</tr>
</tbody>
</table>

The free-volume predictions at infinite dilution were used as an approximation since those values were not available from the experiments discussed in this work. Becker’s results were plotted in Figure 7.4 with the free-volume prediction and regression. The free-volume theory predicted Becker’s results reasonably well, but regression was further off. Through discussions with the manufacturer, the experimental values found in this paper correlated well with the numbers the manufacturer had calculated from their own work.

The free-volume prediction came closer to Becker’s data than the regression. Depending on which model is more accurate for the true behavior of the system, the experimental results either match Becker’s work well or are approximately an order of magnitude larger. However,
both models are only approximations using the free-volume theory, and no actual data were obtained at infinite dilution for a direct comparison. If the regression is more accurate, Becker’s results seem to exhibit the tortuosity constraint that was not observed with the results from this work. If this is true, the reason for the varying behavior from Becker’s work to the current experiments is unknown.
Figure 7.6: Infinite Dilution Behavior for Diffusion in a Cyclohexane in Polyethylene
8. Conclusions and Recommendations

From the work done in this paper, new data were obtained for the diffusion and solubility of cyclohexane in high density polyethylene using gravimetric sorption analysis. The experiments provided insight into the systems behavior in the temperature ranges of 90 to 105 and 140 to 160°C and a solvent weight fraction range of 0.015 to 0.15. The lower temperature range was below the melt temperature, and the polymer was therefore semi-crystalline. The polymer was above the melt temperature in the 140 to 160°C range making it completely amorphous. The solubility showed a dependence on both the temperature and concentration.

Diffusivity showed a dependence on both the temperature and concentration. Comparing the two temperature ranges, the melt temperature seemed to have an effect on the diffusion behavior of the HDPE-cyclohexane system analyzed in that the dependence of the diffusivity on concentration changed after exceeding the melting temperature of 131.5°C. The diffusivity increased more rapidly with concentration when the melt temperature was exceeded.

Comparison using the free-volume theory in a purely predictive mode showed better agreement above the melt than in the semi-crystalline region. The free-volume theory when regressed with all of the data corresponded reasonably well in both temperature ranges, whereas the regression of only the amorphous data did not fit the semi-crystalline behavior as well. When a tortuosity factor was added for correction, the free-volume theory failed. This suggested that diffusion through a semi-crystalline polymer was not greatly affected by
hindered pathways. The degree of crystallinity could have changed because of heating or the introduction of solvent which would decrease the effect of tortuosity. If the crystallinity did not change, then the polymer had an unusual morphology that did not block the pathways along the radial lines.

If future studies are to be carried out on this polymer-solvent solvent system, it would be recommended to look more into the behavior below the melt. Running experiments with the same geometry would eliminate some additional factors so that no variations in the calculation of the diffusion coefficients would affect the comparison. The recommendation would be to use flat sheet samples and conduct experiments at temperatures closer to the melt temperature. An experiment at the melt temperature could provide valuable insight into the behavior of the transition.

A study of the temperature and solvent affects on crystallinity would be useful. If a method is available to calculate the crystalline fraction of the polymer, an investigation using various temperatures and exposures to the solvent would provide valuable insight to the data obtained in this work below the melt.
References


42. Private Conversations with Marc Russell.


Appendix A. Column Maintenance

A.1. Changing of the Solvent

In order to obtain good gravimetric sorption data, a number of maintenance procedures may be necessary. To change the solvent, the following steps should be followed. The solvent boiler remains outside of the chamber and is completely removable from the system. Once the column is at atmospheric pressure, the clips holding the ball and socket joint together can be removed, and the connection can be broken. The two heating tapes for this line must be unplugged along with the plug for the boiler heater. The thermocouple must also be removed from this inlet line. The insulations jacket should be taken from around the outside of the boiler. After all of these steps are taken the boiler can be removed.

From here, the boiler can be moved into the ventilation hood. Once this is done, the valve can be opened to pressurize the boiler so that the clamp can be removed, and the lid can be taken off. The boiler can then be cleansed and the solvent changed, or the boiler can be cleaned. It is essential to clean the boiler regularly. The o-ring and its groove are most important because an improper seal at this connection could cause a leak into the boiler. Other notable areas that should be cleaned are the inside of the lid and the heating rod because residue builds up in these areas. With the cleaning or filling procedures done, the boiler should be closed again and can be returned to its functional position. Everything should be reconnected, and care should be taken to ensure that the boiler is positioned on the stirrer so
that the stirring rod moves freely without getting stuck against the sides. It is necessary for the stirrer to work probably so that the solvent will be heated evenly.

A.2. Leaks

Leaks tend to occur at one of three locations within the experimental setup. When a leak is noticed on the pressure readout, care should be taken to ensure that the three locations (the boiler lid, ball and socket joint, and the lid for the glass chamber) are all connected properly. These areas should be cleaned with an appropriate solvent and reconnected. If it has been determined that the solvent contained within the boiler will not react with vacuum grease, a very thin coating should be placed on the o-rings at the boiler and column lids. The ball and socket joint should also be properly greased.

A.3. Vacuum Oil

If a sufficient vacuum cannot be reached, the vacuum oil must be changed. To do so, the vacuum valve should be closed, and the pump should be turned off. The column should be exposed to the room so that atmospheric pressure is reached by first opening the room valve and then the pump valve. From here, the drain at the bottom of the pump should be opened with a drip tray positioned under it so all of the dirty oil flows into the tray. Once the pump is completely drained, the pump should be sealed again at the bottom, and the inlet line should
be taken off of the top of it. Oil is funneled into the top until the oil level falls within the proper operating limits. After the inlet line is returned, the valves to the room and pump are closed and the pump is turned on. After the pump valve is opened again, the pressure readout is checked to determine if the pump is working properly. If the vacuum pressure is not adequate or if a lot of residue comes out in the dirty oil, the process of draining and refilling with clean oil should be repeated until a satisfactory vacuum has been reached.
Appendix B. Tables

Table B.1: Free-Volume Parameters for Pure Cyclohexane and HDPE [7, 32-35]

<table>
<thead>
<tr>
<th>Parameter</th>
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</thead>
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<tr>
<td>$V_1^*$ (cm$^3$/g)</td>
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</tr>
<tr>
<td>$V_2^*$ (cm$^3$/g)</td>
<td>1.006</td>
</tr>
<tr>
<td>$\frac{K_{11}}{\gamma}$ (cm$^3$/g*K)</td>
<td>3.02E-03</td>
</tr>
<tr>
<td>$\frac{K_{12}}{\gamma}$ (cm$^3$/g*K)</td>
<td>1.02E-03</td>
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<td>$\delta_1$ (cal/cm$^3$)$^{1/2}$</td>
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<tr>
<td>$\delta_2$ (cal/cm$^3$)$^{1/2}$</td>
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Table B.2: Predicted Free-Volume Parameters for Cyclohexane-HDPE Mixture

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<th>Parameter</th>
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<td>1.172</td>
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<tr>
<td>$D_0$ (cm$^2$/s)</td>
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</table>
Table B.3: Regressed Free-Volume Parameters for Cyclohexane-HDPE Mixture

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cyclohexane/HDPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>ξ</td>
<td>0.6471</td>
</tr>
<tr>
<td>$D_0 \text{ (cm}^2/\text{s})$</td>
<td>4.24E-05</td>
</tr>
</tbody>
</table>

Table B.4: Regressed Free-Volume Parameters for Cyclohexane- Amorphous HDPE Mixture

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cyclohexane/HDPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>ξ</td>
<td>0.9173</td>
</tr>
<tr>
<td>$D_0 \text{ (cm}^2/\text{s})$</td>
<td>1.51E-04</td>
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</tbody>
</table>
Table B.5: Amorphous Solubility and Diffusivity of Cyclohexane in High Density Polyethylene

<table>
<thead>
<tr>
<th>Temp</th>
<th>Sample</th>
<th>Final Activity</th>
<th>Pressure (mmHg)</th>
<th>Eq Weight Fraction</th>
<th>Corr Weight Fraction</th>
<th>Diffusivity (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90C</td>
<td>Beads</td>
<td>0.299</td>
<td>297.5</td>
<td>0.059</td>
<td>0.041</td>
<td>5.008E-07</td>
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<tr>
<td></td>
<td></td>
<td>0.451</td>
<td>448.3</td>
<td>0.109</td>
<td>0.076</td>
<td>5.781E-07</td>
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<tr>
<td></td>
<td></td>
<td>0.601</td>
<td>597.6</td>
<td>0.149</td>
<td>0.121</td>
<td>6.482E-07</td>
</tr>
<tr>
<td>100C</td>
<td>Beads</td>
<td>0.200</td>
<td>262.4</td>
<td>0.047</td>
<td>0.033</td>
<td>7.485E-07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.300</td>
<td>392.5</td>
<td>0.076</td>
<td>0.053</td>
<td>7.975E-07</td>
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<tr>
<td></td>
<td></td>
<td>0.400</td>
<td>523.8</td>
<td>0.103</td>
<td>0.072</td>
<td>8.365E-07</td>
</tr>
<tr>
<td>105C</td>
<td>Beads</td>
<td>0.200</td>
<td>298.6</td>
<td>0.052</td>
<td>0.037</td>
<td>7.869E-07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.300</td>
<td>448.3</td>
<td>0.079</td>
<td>0.055</td>
<td>8.697E-07</td>
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<tr>
<td></td>
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<td>0.399</td>
<td>595.7</td>
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<td>0.089</td>
<td>8.725E-07</td>
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<td>0.016</td>
<td>1.445E-06</td>
</tr>
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<td>0.150</td>
<td>507.0</td>
<td>0.045</td>
<td>0.032</td>
<td>1.667E-06</td>
</tr>
<tr>
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<td>0.200</td>
<td>675.2</td>
<td>0.068</td>
<td>0.054</td>
<td>2.002E-06</td>
</tr>
<tr>
<td>150C</td>
<td>Sheet</td>
<td>0.080</td>
<td>331.6</td>
<td>0.022</td>
<td>0.015</td>
<td>1.499E-06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.120</td>
<td>497.1</td>
<td>0.038</td>
<td>0.026</td>
<td>1.773E-06</td>
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<tr>
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<td>0.160</td>
<td>662.8</td>
<td>0.050</td>
<td>0.035</td>
<td>2.150E-06</td>
</tr>
<tr>
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<td>353.5</td>
<td>0.024</td>
<td>0.017</td>
<td>1.658E-06</td>
</tr>
<tr>
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<td></td>
<td>0.110</td>
<td>555.3</td>
<td>0.039</td>
<td>0.028</td>
<td>2.169E-06</td>
</tr>
<tr>
<td></td>
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<td>0.142</td>
<td>717.9</td>
<td>0.049</td>
<td>0.035</td>
<td>2.554E-06</td>
</tr>
</tbody>
</table>
Appendix C. Control Box

Figure C.1: Control Box
1. Solvent Temperature PDI Controller

2. Column Temperature PDI Controller

3. Thermocouple Readout

4. Multi-terminal Switch
   a. Thermocouple 2 (Vacuum Line) [Terminal 2]
   b. Thermocouple 3 (Boiler Line) [Terminal 3]
   c. Thermocouple 4 (Boiler Entrance to Insulated Box) [Terminal 4]
   d. Thermocouple 6 (Inside Insulated Box) [Terminal 5]

5. Pressure Readout

6. Power Switch

7. Duct Heater

8. Window Heater

9. Left Top Heater in the Insulated Box

10. Heater 1 (Vacuum Line)

11. Heater 2 (Boiler Line)

12. Heater 3 (Boiler Line)

13. Heater 4 (Boiler Entrance to Insulated Box)