Research Article

Diffusion Coefficients of $n$-Alkanes and 1-Alcohols in Polyethylene Naphthalate (PEN)

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Polyethylene naphthalate (PEN) is a polyester polymer with well-known good barrier properties. Compared to the commodity sister polymer polyethylene terephthalate (PET), the barrier properties towards permanent gases like oxygen are significantly higher [1–3]. PEN has also good mechanical properties such as strength, heat resistance, dimensional stability, and higher capability of absorbing UV radiation [4]. Due to its favourable properties, PEN had been used in the food packaging area, e.g., as material for refillable bottles for soft drinks, juices, and beer [5]. As another advantage, the higher glass transition temperature of PEN (124°C) compared to PET (70°C) allows higher temperatures in the washing process of the refillable bottles as well as being hot-filled. However, due to the high price of PEN compared to PET or other packaging polymers, PEN was substituted as packaging material. To our knowledge, PEN refillable bottles are no longer on the market [5]. PEN is now mainly used in technical applications. The improved thermal and barrier properties such as resistance to oxidation make PEN an interesting polymer for technical applications, e.g., for data storage tapes and organic light-emitting diode (OLED) applications. It is also used in electronic components such as capacitors, electric insulation, and solar cell protection and for optical purposes. It has also been used for barrier films for medical applications. For all these applications, knowledge about the diffusion behaviour is necessary. The diffusion process is dominating the migration of residual monomers and additives as well as the permeation of gases through the PEN membranes. For permanent gases like carbon dioxide, oxygen, and water vapor, the barrier efficiency of PEN is known [1–3] and the gas barrier of PEN is approximately five times higher than that of PET [6]. Whereas the permeation properties of permanent gases in PEN had been investigated in several publications, studies on the diffusion behaviour of organic molecules in PEN are rarely published in the scientific literature. To our knowledge, only one publication mentioned the diffusion coefficients $D_p$ of a couple of organic compounds in PEN [7]. The aim of the study was the determination of the diffusion coefficients of organic molecules in PEN. For this purpose, the permeation rates of

1. Introduction

Polyethylene naphthalate (PEN) is a polyester polymer with well-known good barrier properties. Compared to the commodity sister polymer polyethylene terephthalate (PET), the barrier properties towards permanent gases like oxygen are significantly higher [1–3]. PEN has also good mechanical properties such as strength, heat resistance, dimensional stability, and higher capability of absorbing UV radiation [4]. Due to its favourable properties, PEN had been used in the food packaging area, e.g., as material for refillable bottles for soft drinks, juices, and beer [5]. As another advantage, the higher glass transition temperature of PEN (124°C) compared to PET (70°C) allows higher temperatures in the washing process of the refillable bottles as well as being hot-filled. However, due to the high price of PEN compared to PET or other packaging polymers, PEN was substituted as packaging material. To our knowledge, PEN refillable bottles are no longer on the market [5]. PEN is now mainly used in technical applications. The improved thermal and barrier properties such as resistance to oxidation make PEN an interesting polymer for technical applications, e.g., for data storage tapes and organic light-emitting diode (OLED) applications. It is also used in electronic components such as capacitors, electric insulation, and solar cell protection and for optical purposes. It has also been used for barrier films for medical applications. For all these applications, knowledge about the diffusion behaviour is necessary. The diffusion process is dominating the migration of residual monomers and additives as well as the permeation of gases through the PEN membranes. For permanent gases like carbon dioxide, oxygen, and water vapor, the barrier efficiency of PEN is known [1–3] and the gas barrier of PEN is approximately five times higher than that of PET [6]. Whereas the permeation properties of permanent gases in PEN had been investigated in several publications, studies on the diffusion behaviour of organic molecules in PEN are rarely published in the scientific literature. To our knowledge, only one publication mentioned the diffusion coefficients $D_p$ of a couple of organic compounds in PEN [7]. The aim of the study was the determination of the diffusion coefficients of organic molecules in PEN. For this purpose, the permeation rates of
homologous rows of nonpolar \( n \)-alkanes and polar 1-alcohols through a commercial 12\( \mu \)m biaxial-oriented PEN film were determined.

2. Materials and Methods

2.1. Sample Materials and Model Compounds for Permeation Testing. Permeation of \( n \)-alkanes and 1-alcohols was determined through a biaxial-oriented PEN film of 11.6 ± 0.2 \( \mu \)m thickness (trade name Teonex® Q51). The glass transition temperature of the investigated PEN film was determined to be 124°C by use of Differential Scanning Calorimetry (DSC). The permeation rates were determined for \( n \)-alkanes from methane to \( n \)-tetradecane as well as for 1-alcohols from 1-propanol to 1-octanol. The homologous rows of substances with different polarities were chosen in order to establish correlations between the diffusion coefficients \( D_p \) and the molecular volume \( V \) which might be useful to predict the diffusion behaviour of other nontested substances.

The permeants were applied in two sets. Set 1 was a mixture of the \( n \)-alkanes from \( n \)-pentane to \( n \)-tetradecane. Set 2 was a mixture of the 1-alcohols from 1-propanol to 1-octanol. In addition, permanent gases methane to \( n \)-butane were tested in a separate set-up. The starting concentrations \( c_{\text{gas,phase}} \) of the permeants and their molecular weights and volumes [8] are given in Table 1.

2.2. Permeation Measurements of Liquid Permeants. The 12\( \mu \)m PEN film was clamped in a permeation steel cell between two sealant rings. The surface area of the tested films was 191 cm\(^2\). The permeation cell with the film was placed in a climate chamber. The cell has a lower and an upper space separated by the film. The lower space of the permeation cell had a volume of 7667 cm\(^3\). The permeants are injected as a liquid mixture (set 1 and set 2) into the lower space of the permeation cell through a septum by use of a syringe. After injection, the liquid mixture of permeants evaporated immediately at the high temperatures (100°C to 140°C) applied in the permeation tests. The graph phase concentrations in the lower space are given in Table 1. The upper space of the permeation cell was permanently rinsed with a pure stream of nitrogen (20 ml/min) which moved the permeated substances out of the cell. The nitrogen stream went through a connected enrichment unit, and the permeants were trapped on this unit over a period of 20 min. The enrichment unit was connected to a gas chromatograph with flame ionisation detection (GC/FID). The permeants were directly desorbed into the gas chromatograph, and the amount of permeants was determined quantitatively. During the GC run, the next sample was trapped on the enrichment unit and subsequently injected into the GC. By use of this method, one kinetic point was measured every 45 min. Gas chromatographic conditions: column: Rxi 624, length: 60 m, internal diameter: 0.32 mm, film thickness: 1.8 \( \mu \)m, and carrier gas: 120 kPa helium. Temperature program: 40°C (2 min), rate 20°C/min to 280°C hold for 7 min. Pretrap: substances collected on 20 mm length by 5 mm diameter of Carbopack B, desorbed at 350°C. Main trap: substances focused at -46°C on 30 mm length by 1.4 mm diameter of Carbopack B, desorbed at 320°C. Calibration was performed with injections of known amounts of the applied permeants.

2.3. Permeation Measurements on Permanent Gases. The permanent gases methane, ethane, \( n \)-propane, and \( n \)-butane were tested with the permeation cell as described for the liquid permeants. However, for the permanent gases, a slight different set-up has been used. A mixture of the four gaseous alkanes was flushed through the lower space of the permeation cell with a constant gas flow. The gas phase concentrations are given in Table 1. Gas chromatographic conditions: column: PoraPLOT Q, length: 30 m, internal diameter: 0.53 mm, film thickness: 20 \( \mu \)m, and carrier gas: 120 kPa helium. Temperature program: 70°C (0.5 min), rate 30°C/min to 150°C hold for 5 min. Pretrap: substances collected on 20 mm length by 5 mm diameter of Carbopack B, desorbed at 350°C. Main trap: substances focused at -46°C on 30 mm length by 1.4 mm diameter of active charcoal 140-280 \( \mu \)m, desorbed at 320°C. Calibration was performed with injections of known amounts of the applied permeants.

2.4. Calculation of the Diffusion and Partition Coefficients. From the experimental data, the permeation rates as well as the lag times of the applied permeants are available. The diffusion coefficient \( D_p \) of the applied permeants in PEN was calculated from the lag time and the film thickness \( t \) according to equation (1) [9]. The lag time is determined as the intercept of the asymptote to the permeation curve on the time axis [9]. The partition coefficient \( K_{g/b} \) is defined as the quotient between the gas phase concentration \( c_{\text{gas,phase}} \) and the concentration in the PEN film in the equilibrium (equation (2)). The partition coefficient \( K_{g/b} \) can be calculated from the slope of the permeation curve, the area of the film, the diffusion coefficient \( D_p \), and the thickness of the film \( l \) according to equation (3) [10]. The activation energies of diffusion \( E_A \) and the preexponential factors \( D_p \) were calculated from the temperature dependency of the diffusion coefficients \( D_p \) by use of the Arrhenius equation (equation (4)).

\[
D_p = \frac{A}{6 \lambda^2},
\]

\[
K_{g/b} = \frac{c_{\text{gas,phase}}}{c_{\text{polymer},co}},
\]

\[
K_{g/b} = \frac{A c_{\text{gas,phase}} D_p}{l \text{ slope}},
\]

\[
D_p = D_0 e^{-(E_A/RT)}.
\]

2.5. Calculation of Molecular Volumes. The molecular volume \( V \) of the molecules was calculated with the free internet program Molinspiration [8]. This program calculates the van der Waals volume of organic molecules. The method for the calculation of the molecular volume developed is based on group contributions.
3. Results and Discussion

3.1. Diffusion Coefficients. The permeation curves of 14 \(n\)-alkanes and six \(1\)-alcohols through a commercial 12 \(\mu\)m biaxial-oriented PEN film were determined within this study. The lag times and diffusion coefficients were determined at temperatures between 100\(^\circ\)C and 140\(^\circ\)C, in intervals of 5\(^\circ\)C. At lower temperatures, the permeation rates for the applied \(n\)-alkanes as well as the \(1\)-alcohols were too low and therefore below the analytical detection limits of the applied method. Higher gas phase concentrations might increase the permeation rates. However, higher concentrations of the permeants in the gas phase might also lead to interactions between the chemicals in the applied mixtures which might influence also the diffusion coefficients. Therefore, we choose the concentrations as low as possible in order to minimize these interactions. The spiked starting concentrations of the permeation on the lower cell (Table 1) were chosen that they are a factor of approx. 200 below the saturated vapor pressure at each temperature. This avoids condensation of the permeants on the surface of the polymer membrane, and swelling of the polymer can be excluded. Swelling of the polymer increases the diffusivity of the polymer and leads to a faster diffusion of the permeants in the polymer.

Examples for the experimental permeation curves for \(n\)-pentane to \(n\)-decane at 130\(^\circ\)C are given in Figure 1. The permeation curves of the other substances measured within this study follow a similar behaviour.

The diffusion coefficients \(D_P\) were calculated from the experimentally determined lag times for each permeant according to equation (1). The diffusion coefficients \(D_P\) for the applied permeants are summarized in Table 2. A correlation between the diffusion coefficients \(D_P\) and the molecular volume \(V\) of the permeants is given in Figure 2. The calculation of the molecular volume is based on the group

| Table 1: Substances used for permeation testing, their molecular weights and volumes, and the upstream concentrations used in permeation testing. |
|-------------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| Substance        | Molecular weight (g/mol) | Molecular volume \([\text{Å}^3]\) | Upstream concentration \(c_{\text{gas phase}}\) (mg/l) |
|------------------|--------------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| Methane         | 16.0                      | 28.6              | 35.5             | 35.5             | 35.5             | 35.5             | 35.5             | 35.5             | 35.5             |
| Ethane          | 30.1                      | 45.8              | 32.6             | 32.6             | 32.6             | 32.6             | 32.6             | 32.6             | 32.6             |
| Propane         | 44.1                      | 62.6              | 19.3             | 19.3             | 19.3             | 19.3             | 19.3             | 19.3             | 19.3             |
| \(n\)-Butane    | 58.1                      | 79.4              | 12.9             | 12.9             | 12.9             | 12.9             | 12.9             | 12.9             | 12.9             |
| \(n\)-Pentane   | 72.2                      | 96.2              | 262              | 226              | 194              | 161              | 137              | 137              | 137              |
| \(n\)-Hexane    | 86.2                      | 113               | 138              | 119              | 102              | 85.1             | 72.3             | 72.3             | 72.3             |
| \(n\)-Heptane   | 100                       | 130               | 71.6             | 61.7             | 52.8             | 44.0             | 37.4             | 37.4             | 37.4             |
| \(n\)-Octane    | 114                       | 147               | 36.8             | 31.7             | 27.1             | 22.6             | 19.2             | 19.2             | 19.2             |
| \(n\)-Nonane    | 128                       | 163               | 22.5             | 19.4             | 16.6             | 13.9             | 11.8             | 11.8             | 11.8             |
| \(n\)-Decane    | 142                       | 180               | 11.5             | 9.87             | 8.46             | 7.05             | 6.00             | 6.00             | 6.00             |
| \(n\)-Undecane  | 156                       | 197               | 6.20             | 5.34             | 4.58             | 3.81             | 3.24             | 3.24             | 3.24             |
| \(n\)-Dodecane  | 170                       | 214               | 3.14             | 2.70             | 2.32             | 1.93             | 1.64             | 1.64             | 1.64             |
| \(n\)-Tridecane | 184                       | 231               | 1.58             | 1.36             | 1.17             | 0.974            | 0.828            | 0.828            | 0.828            |
| \(n\)-Tetradecane | 198                     | 247               | 0.800            | 0.688            | 0.590            | 0.491            | 0.418            | 0.418            | 0.418            |
| \(1\)-Propanol  | 60.1                      | 70.8              | 118              | 101              | 84.1             | 70.0             | 56.0             | 56.0             | 56.0             |
| \(1\)-Butanol   | 74.1                      | 87.6              | 59.3             | 50.8             | 42.4             | 35.3             | 28.25            | 28.25            | 28.25            |
| \(1\)-Pentanol  | 88.2                      | 104               | 23.9             | 20.4             | 17.0             | 14.2             | 11.4             | 11.4             | 11.4             |
| \(1\)-Hexanol   | 102                       | 121               | 11.9             | 10.2             | 8.51             | 7.09             | 5.68             | 5.68             | 5.68             |
| \(1\)-Heptanol  | 116                       | 138               | 6.00             | 5.14             | 4.28             | 3.57             | 2.86             | 2.86             | 2.86             |
| \(1\)-Octanol   | 130                       | 155               | 2.43             | 2.08             | 1.74             | 1.45             | 1.16             | 1.16             | 1.16             |

Figure 1: Experimental permeation curves for \(n\)-pentane to \(n\)-decane at 130\(^\circ\)C (lag time for \(n\)-heptane and \(n\)-octane: intercept of the red line on the time axis).
contribution of the van der Waals volume. As expected, the diffusion coefficients show a strong dependency on the molecular volume as well as on temperature. The diffusion coefficients of large molecules are significantly lower as for small molecules. Lower temperatures result also in lower diffusion coefficients for each individual permeant. Within this study, nonpolar n-alkanes as well as polar 1-alcohols had been tested. It is interesting to note that the polarity of the permeants plays a minor role on the diffusion coefficients.

The homologous row of polar 1-alcohols follows a similar correlation as for the nonpolar n-alkanes (Figure 2). The diffusion coefficient for a substance at a certain temperature is therefore mainly a function of its molecular volume \( V \).

This is in good agreement with previous studies on films of the same thickness on oriented PA6 [11] and PET [10, 12]. The dashed lines in Figure 2 are correlations for both n-alkanes and 1-alcohols.

### 3.2. Partition Coefficients

The thermodynamic part of the permeation process is represented by the partition coefficient \( K_{gb} \) between the gas phase and the PEN film. The partition coefficient was calculated from the slope of the

| Substance   | 140°C | 135°C | 130°C | 125°C | 120°C | 110°C | 100°C |
|-------------|-------|-------|-------|-------|-------|-------|-------|
| Methane     | \( 7.3 \times 10^{-10} \) | \( 7.3 \times 10^{-10} \) | \( 6.7 \times 10^{-10} \) | \( 6.1 \times 10^{-10} \) |
| Ethane      | \( 5.4 \times 10^{-10} \) | \( 3.6 \times 10^{-10} \) | \( 2.3 \times 10^{-10} \) | \( 1.3 \times 10^{-10} \) |
| n-Propane   | \( 1.3 \times 10^{-10} \) | \( 5.7 \times 10^{-11} \) | \( 2.4 \times 10^{-11} \) | \( 1.1 \times 10^{-11} \) |
| n-Butane    | \( 4.5 \times 10^{-11} \) | \( 1.7 \times 10^{-11} \) | \( 6.3 \times 10^{-12} \) | \( 2.5 \times 10^{-12} \) |
| n-Pentane   | \( 4.0 \times 10^{-11} \) | \( 2.9 \times 10^{-11} \) | \( 1.7 \times 10^{-11} \) | \( 1.1 \times 10^{-11} \) | \( 6.7 \times 10^{-12} \) |
| n-Hexane    | \( 2.8 \times 10^{-11} \) | \( 1.8 \times 10^{-11} \) | \( 9.3 \times 10^{-12} \) | \( 5.0 \times 10^{-12} \) | \( 3.3 \times 10^{-12} \) |
| n-Heptane   | \( 1.9 \times 10^{-11} \) | \( 9.8 \times 10^{-12} \) | \( 5.6 \times 10^{-12} \) | \( 2.6 \times 10^{-12} \) | \( 1.4 \times 10^{-12} \) |
| n-Octane    | \( 1.3 \times 10^{-11} \) | \( 5.8 \times 10^{-12} \) | \( 3.3 \times 10^{-12} \) | \( 1.3 \times 10^{-12} \) |
| n-Nonane    | \( 9.3 \times 10^{-12} \) | \( 3.7 \times 10^{-12} \) | \( 1.9 \times 10^{-12} \) |
| n-Decane    | \( 5.9 \times 10^{-12} \) | \( 2.0 \times 10^{-12} \) | \( 1.1 \times 10^{-12} \) |
| n-Undecane  | \( 4.0 \times 10^{-12} \) | \( 1.3 \times 10^{-12} \) | \( 8.9 \times 10^{-13} \) |
| n-Dodecane  | \( 3.8 \times 10^{-12} \) |
| 1-Propanol  | \( 7.7 \times 10^{-11} \) | \( 5.5 \times 10^{-11} \) | \( 3.8 \times 10^{-11} \) | \( 3.0 \times 10^{-11} \) | \( 1.8 \times 10^{-11} \) |
| 1-Butanol   | \( 4.6 \times 10^{-11} \) | \( 3.1 \times 10^{-11} \) | \( 2.1 \times 10^{-11} \) | \( 1.4 \times 10^{-11} \) |
| 1-Pentanol  | \( 2.9 \times 10^{-11} \) | \( 1.8 \times 10^{-11} \) | \( 1.1 \times 10^{-11} \) | \( 7.5 \times 10^{-12} \) |
| 1-Hexanol   | \( 2.0 \times 10^{-11} \) | \( 1.2 \times 10^{-11} \) | \( 6.0 \times 10^{-12} \) | \( 3.6 \times 10^{-12} \) |
| 1-Heptanol  | \( 1.3 \times 10^{-11} \) | \( 7.2 \times 10^{-12} \) | \( 3.4 \times 10^{-12} \) | \( 1.4 \times 10^{-12} \) |
| 1-Octanol   | \( 9.0 \times 10^{-12} \) | \( 5.1 \times 10^{-12} \) | \( 1.9 \times 10^{-12} \) |

**Table 2: Experimentally determined diffusion coefficients \( D_p \).**
asymptote according to equation (3) \[10\]. After reaching steady state conditions, which is indicated by a constant permeation rate over time, equilibrium between the gas phase and the polymer is established and the partition coefficients can be calculated from the slope of the lag time curve. Another side condition is a linear sorption isotherm indicated by a linear relationship between the gas phase concentration and the corresponding equilibrium concentration \[9\]. Due to the low gas phase concentrations applied in this study, it can be assumed that the sorption isotherm is linear even if it was not shown experimentally within this study.

The results of the partition coefficients between the gas phase and the barrier film $K_{gb}$ are given in Table 3. The correlation between the molecular volume $V$ of the permeants and their partition coefficients is given in Figure 3. From the data, it gets obvious that the temperature plays only a minor effect on the partition coefficients. The ratio of partition coefficients of permeant pairs of similar molecular volume like pentane and 1-butanol, hexane and 1-pentanol, heptane and 1-hexanol, and octane and 1-heptanol is a factor of approx. 23. This means that the permeation rate of 1-alcohols is a factor of approx. 23 higher than the permeation rate of $n$-alkanes of similar molecular volume $V$ due to the higher partition coefficient. Similar effects had been found on polyamide 6 (see Figure 1 in Ref. 11). The partition coefficients between the gas phase and PEN determined for the $n$-alkanes are similar to the partition coefficients determined for PET \[10\].

### 3.3. Activation Energies of Diffusion

The Arrhenius plots, which are the correlation between reciprocal temperature (in K) versus diffusion coefficients $D_p$, are given in Figure 4 ($n$-alkanes) and Figure 5 (1-alcohols), respectively. In all cases, the Arrhenius plots show good linearity for the investigated permeants. This indicates that the diffusion process follows the Fickian laws of diffusion, and the swelling of the polymer of the permeants can be excluded under the experimental conditions applied within this study. From the slopes and the intercepts, the activation energies of diffusion $E_A$ as well as the preexponential factors $D_0$ were derived. The activation energies are only calculated when in minimum four kinetic points are available and when the Arrhenius plot shows good linearity ($r^2 > 0.99$). The results are summarized in Table 4.

The activation energies were derived from diffusion coefficients determined between 100°C and 140°C. The glass transition temperature $T_g$ of PEN (124°C) is in between

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| Substance          | 140°C | 135°C | 130°C | 125°C | 120°C | 110°C | 100°C |
|--------------------|-------|-------|-------|-------|-------|-------|-------|
| Methane            | 9.0 $10^{-1}$ | 1.4 | 2.1 | 2.9 |
| Ethane             | 2.5 | 3.1 | 3.2 | 2.8 |
| $n$-Propane        | 3.5 | 3.2 | 2.6 | 1.9 |
| $n$-Butane         | 2.7 | 2.2 | 1.7 | 1.2 |
| $n$-Pentane        | 1.2 | 1.5 | 1.6 | 1.2 |
| $n$-Hexane         | 9.6 $10^{-1}$ | 1.2 | 9.4 $10^{-1}$ | 1.0 | 9.2 $10^{-1}$ |
| $n$-Heptane        | 6.9 $10^{-1}$ | 7.5 $10^{-1}$ | 7.1 $10^{-1}$ | 7.6 $10^{-1}$ | 4.8 $10^{-1}$ |
| $n$-Octane         | 5.5 $10^{-1}$ | 5.2 $10^{-1}$ | 5.2 $10^{-1}$ | 5.4 $10^{-1}$ |
| $n$-Nonane         | 4.1 $10^{-1}$ | 3.6 $10^{-1}$ | 3.1 $10^{-1}$ |
| $n$-Decane         | 2.4 $10^{-1}$ | 1.9 $10^{-1}$ | 1.9 $10^{-1}$ |
| $n$-Undecane       | 1.5 $10^{-1}$ | 1.3 $10^{-1}$ | 2.4 $10^{-1}$ |
| $n$-Dodecane       | 2.0 $10^{-1}$ |
| 1-Propanol         | 6.9 $10^{-2}$ | 6.8 $10^{-2}$ | 6.7 $10^{-2}$ | 6.9 $10^{-2}$ | 6.8 $10^{-2}$ |
| 1-Butanol          | 6.4 $10^{-2}$ | 6.0 $10^{-2}$ | 6.8 $10^{-2}$ | 6.0 $10^{-2}$ |
| 1-Pentanol         | 5.0 $10^{-2}$ | 4.5 $10^{-2}$ | 5.0 $10^{-2}$ | 4.9 $10^{-2}$ |
| 1-Hexanol          | 3.7 $10^{-2}$ | 3.5 $10^{-2}$ | 3.5 $10^{-2}$ | 3.2 $10^{-2}$ |
| 1-Heptanol         | 2.6 $10^{-2}$ | 2.5 $10^{-2}$ | 2.8 $10^{-2}$ | 1.4 $10^{-2}$ |
| 1-Octanol          | 1.7 $10^{-2}$ | 2.5 $10^{-2}$ | 3.2 $10^{-2}$ |

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![Figure 3: Correlation between the molecular volume of the permeants and the partition coefficients $K_{gb}$ (black dots: $n$-alkanes; red dots: 1-alcohols).](image-url)
the applied temperature interval. The slopes of the Arrhenius plots seem to be not significantly changed at the glass transition temperature. This indicates that the diffusion behaviour of PEN below and above the glass transition temperature is similar and the activation energies of diffusion can be derived over the whole temperature interval. A reason might be that the PEN film is partly crystalline due to the biaxial orientation process. However, it should be noted that the temperature interval of the permeation tests was very narrow. The permanent gases methane to butane were measured between 100°C and 130°C. The other compounds were measured at 120°C to 140°C. We tried to expand this temperature interval but without success. At higher temperatures, the permeation was too fast and the diffusion coefficient could not be determined properly from the very short lag times. At lower temperatures, the permeation rates were too low so that the permeants were not detectable. Increasing the spiked concentration might increase the permeation rates but pose the risk of interactions between the applied permeants. On the other hand, the behaviour of PEN at the glass transition temperature is in agreement with a previous study on the activation energies of diffusion of PET, where also no significant change of the diffusion behaviour has been determined at the glass transition temperature [12].

In addition, activation energies of tetrahydrofuran are available in the scientific literature. The activation energies were determined below and above the glass transition temperature. Migration kinetics into distilled water between 23°C and 50°C result in an activation energy of 106.8 kJ/mol ($D_0 = 4.8 \times 10^5 \text{cm}^2/\text{s}$) [12, 13]. Desorption kinetics into the gas phase above the glass transition temperature of PET between 120°C and 180°C result in an activation energy of diffusion of 116.5 kJ/mol (4.4 $\times 10^5 \text{cm}^2/\text{s}$) [12, 14], which is in good agreement with the value from the migration kinetics into distilled water below the glass transition temperature. Very similar results were found for benzene (migration kinetics into mineral water at 23°C and 50°C).
and toluene (gas phase kinetics between 121°C and 180°C) with 101.4 kJ/mol \((D_0 = 1.9 \times 10^3 \text{ cm}^2/\text{s})\) [12, 13] and 121.4 kJ/mol \((3.5 \times 10^3 \text{ cm}^2/\text{s})\) [12, 14], respectively.

### 3.4. Comparison to Literature Data

Within this chapter, the diffusion coefficients determined from organic substances in PEN are compared to literature data on PET. In addition, activation energies of diffusion \(E_A\) were compared between PEN and PET. Activation energies of diffusion \(E_A\) are given in the scientific literature for PEN [7] and PET [7, 10, 13–15]. However, in some cases, the methods on how the diffusion coefficients were determined are not described or the amount of kinetic points are low [7, 15]. Therefore, in this study, only literature data of activation energies were considered which used diffusion coefficients from a minimum temperature range of 25°C. If lower temperature ranges are applied, the slope of the Arrhenius correlation might not be correctly defined due to the experimental uncertainties of the diffusion coefficients, and therefore, the activation energies cannot be determined precisely. To our knowledge, only one scientific publication has published diffusion coefficients and activation energies \(E_A\) of organic molecules in PEN [7]. Unfortunately, within this paper, neither the method nor the experimental details of the determination of the diffusion coefficients were given. In addition, the activation energies are determined from diffusion coefficients from only two temperatures. As mentioned above, such activation energies based on only two diffusion coefficients are very weak. On the other hand, the diffusion coefficients and activation energy data from Ref. [7] are in good agreement with the results of this study. This can be concluded from the correlation between the activation energies \(E_A\) for acetaldehyde, toluene, limonene, ethyl butyrate, chloroform, ethylene glycol, methanol, ethanol, benzaldehyde, and methyl dioxyolane and their molecular volume of the diffusants and the data determined in this study with \(n\)-alkanes and 1-alcohols. The correlation between the activation energies of diffusion \(E_A\) and the corresponding molecular volume \(V\) of the applied permeants is shown in Figure 6. Another correlation between the activation energies of diffusion \(E_A\) and the corresponding preexponential factor \(D_0\) is given in Figure 7. Both correlations are compared to published data on PET [10, 13]. For both polymers, the activation energies of diffusion are very similar for small molecules up to a molecular volume of approx. 100 Å³ and for activation energies of about 150 kJ/mol. For bigger molecules, the activation energies for PEN increase to a significant higher amount as found for PET. The preexponential factors \(D_0\) for both polymers follow a strong linear correlation of over approximately 20 orders of magnitude. The slope of both correlations, however, are slightly different. In the cases of small activation energies determined for small molecules, the preexponential factor \(D_0\) is significantly lower as for PET. Going to larger molecules with higher activations of diffusion \(E_A\), the preexponential factors \(D_0\) for PEN and PET are getting more and more similar.

The role of the correlation between the preexponential factor \(D_0\) and the activation energy has been discussed in the literature as a so-called “compensation effect” or “Meyer-Neldel rule” [16, 17]. As a consequence of this effect, the activation energy and the preexponential factor are not independent from each other. According to this compensation effect, the activation energy of diffusion \(E_A\) correlates with the preexponential factor \(D_0\) in the Arrhenius plot which has been found also in this study.

### 4. Conclusions

Within the study, the diffusion coefficients \(D_0\) as well the partition coefficients \(K_{gb}\) for \(n\)-alkanes (methane up to \(n\)-tetradecane) and 1-alcohols (1-propanol to 1-octanol) at temperatures between 100°C and 140°C for a commercial

![Figure 6: Correlation between the activation energy of diffusion \(E_A\) and the molecular volume \(V\) for PEN (this study, blue dots) and PET (nonsolid red dots from Ref. [10]; solid red dots from Ref. [12]).](image-url)

### Table 4: Activation energies of diffusion \(E_A\) and the preexponential factor \(D_0\) derived from diffusion coefficients from Table 2.

| Substance      | Temperature range (°C) | Activation energy (kJ/mol) | Preexponential factor (cm²/s) |
|----------------|------------------------|----------------------------|-------------------------------|
| Methane        | 100-130                | 7.9                        | 7.8 \times 10⁻⁶                |
| Ethane         | 100-130                | 59.1                       | 2.5 \times 10²                 |
| \(n\)-Propane  | 100-130                | 103.4                      | 3.2 \times 10⁵                 |
| \(n\)-Butane   | 100-130                | 120.8                      | 1.9 \times 10⁵                 |
| \(n\)-Pentane  | 120-140                | 123.5                      | 1.7 \times 10⁵                 |
| \(n\)-Hexane   | 120-140                | 149.0                      | 1.9 \times 10⁸                 |
| \(n\)-Heptane  | 125-140                | 177.1                      | 4.7 \times 10¹¹                |
| \(n\)-Octane   | 125-140                | 207.5                      | 2.2 \times 10¹⁵                |
| 1-Propanol     | 120-140                | 94.5                       | 8.9 \times 10¹                  |
| 1-Butanol      | 125-140                | 106.3                      | 1.3 \times 10³                 |
| 1-Pentanol     | 125-140                | 125.0                      | 1.8 \times 10⁵                 |
| 1-Hexanol      | 125-140                | 157.1                      | 1.4 \times 10⁹                 |
| 1-Heptanol     | 125-140                | 206.3                      | 1.7 \times 10¹⁵                |
birefringent PEN film were determined. From the diffusion coefficients at several temperatures, the activation energies of diffusion $E_A$ and the preexponential factor $D_0$ were available. According to the diffusion theory, the diffusion coefficients $D_p$ as well as partition coefficients $K_{g/b}$ are material constants of PEN for a permeant/temperature combination [18]. By use of the activation energies $E_A$ and the preexponential factors $D_0$, the diffusion coefficients $D_p$ can be predicted for other temperatures by use of the Arrhenius equation (equation (4)). The activation energies of diffusion $E_A$ follow a correlation with the molecular volume $V$ of the molecules (Figure 6). Assuming that other molecules are also following such correlations, the diffusion coefficients can be predicted from the molecular volume of the molecules of interest. In addition, the preexponential factor $D_0$ also follows a correlation with the activation energy of diffusion $E_A$ (Figure 7). From this correlation, the preexponential factor $D_0$ is available for other molecules of interest. Therefore, from the results of this study, the permeation of organic molecules through PEN barriers can be predicted. The mathematical description for the diffusion of a permeant through a polymer membrane has been published by Crank [9]. According to Crank, the diffusion coefficient $D_p$ as well as the partition coefficient $K_{g/b}$ described the permeation process of a permeant through a polymer membrane. The correlations between the diffusion coefficients $D_p$ and the molecular volume $V$ at the temperatures applied in this study are given in Figure 2. As expected, the diffusion coefficients are influenced by the applied temperature and the molecular volume. The glass transition temperature ($T_g$) of the investigated PEN at 124°C is passed in the experimental tests. In principle, at the glass transition temperature, the diffusion behaviour of a polymer might be changed. The experimental data for PEN, however, show no significant change of the diffusion behaviour at the glass transition temperature of PEN.

The correlations between the partition coefficients and the molecular volume of the permeants are given in Figure 3. As expected, the polarity of the investigated permeants is influencing the partition coefficients significantly. The partition coefficients $K$ for the $n$-alkanes are a factor of approx. 23 higher than determined for 1-alcohols of similar molecular volume. The prediction of the partition coefficients for other nontested organic molecules is much harder, because the influence of the polarity of other functional groups is not known. More homologous rows of molecules need to be tested in order to predict this influence of the polarity on the partition coefficients. It is interesting to note that the partition coefficients of the $n$-alkanes show a good linear correlation with the molecular volume $V$, which is nearly independent from the temperature.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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