

Research Article

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

Johann Ewender and Frank Welle 

Fraunhofer Institute for Process Engineering and Packaging, IVV, Giggenhauser Strasse 35, 85354 Freising, Germany

Correspondence should be addressed to Frank Welle; frank.welle@ivv.fraunhofer.de

Received 25 July 2018; Revised 14 December 2018; Accepted 17 January 2019; Published 14 February 2019

Academic Editor: Antonio Facchetti

Copyright © 2019 Johann Ewender and Frank Welle. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Polyethylene naphthalate (PEN) is a polyester polymer with well-known good barrier properties. PEN had been used in the food packaging area till 2012 especially as refillable bottles for soft drinks, juices, and beer. Now, PEN is mainly used in technical applications, e.g., for data storage tapes and organic light-emitting diode (OLED) applications. The aim of the study was the determination of the diffusion coefficients of organic molecules (*n*-alkanes, 1-alcohols) in PEN. Diffusion and partition coefficients were determined from the lag times of the permeation process of the permeants through a commercial 12 μm biaxial-oriented PEN film. In addition, activation energies of diffusion E_A were calculated according to the Arrhenius approach. The activation energy of diffusion E_A follows a correlation with the molecular volume V of the investigated permeants. In addition, the preexponential factor D_0 follows a correlation with the activation energy of diffusion E_A . The results of this study for PEN (e.g., E_A , D_p) were compared to literature data on PET.

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 μm 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 $11.6 \pm 0.2 \mu\text{m}$ 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 μm 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 gas 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 μm , 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 Carboxen B, desorbed at 350°C. Main trap: substances focused at -46°C on 30 mm length by

1.4 mm diameter of Carboxen 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 μm , 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 Carboxen 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 μm , 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 l according to equation (1) [9]. The lag time is defined 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_0 were calculated from the temperature dependency of the diffusion coefficients D_p by use of the Arrhenius equation (equation (4)).

$$D_p = \frac{l^2}{6 \text{ lag time}}, \quad (1)$$

$$K_{g/b} = \frac{c_{\text{gas phase,co}}}{c_{\text{polymer,co}}}, \quad (2)$$

$$K_{g/b} = \frac{A c_{\text{gas phase}} D_p}{l \text{ slope}}, \quad (3)$$

$$D_p = D_0 e^{-(E_A/RT)}. \quad (4)$$

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.

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 [8] (\AA^3)	Upstream concentration $c_{\text{gas phase}}$ (mg/l)						
			140°C	135°C	130°C	125°C	120°C	110°C	100°C
Methane	16.0	28.6			35.5		35.5	35.5	35.5
Ethane	30.1	45.8			32.6		32.6	32.6	32.6
Propane	44.1	62.6			19.3		19.3	19.3	19.3
<i>n</i> -Butane	58.1	79.4			12.9		12.9	12.9	12.9
<i>n</i> -Pentane	72.2	96.2	262	226	194	161	137		
<i>n</i> -Hexane	86.2	113	138	119	102	85.1	72.3		
<i>n</i> -Heptane	100	130	71.6	61.7	52.8	44.0	37.4		
<i>n</i> -Octane	114	147	36.8	31.7	27.1	22.6	19.2		
<i>n</i> -Nonane	128	163	22.5	19.4	16.6	13.9	11.8		
<i>n</i> -Decane	142	180	11.5	9.87	8.46	7.05	6.00		
<i>n</i> -Undecane	156	197	6.20	5.34	4.58	3.81	3.24		
<i>n</i> -Dodecane	170	214	3.14	2.70	2.32	1.93	1.64		
<i>n</i> -Tridecane	184	231	1.58	1.36	1.17	0.974	0.828		
<i>n</i> -Tetradecane	198	247	0.800	0.688	0.590	0.491	0.418		
1-Propanol	60.1	70.8	118	101	84.1	70.0	56.0		
1-Butanol	74.1	87.6	59.3	50.8	42.4	35.3	28.25		
1-Pentanol	88.2	104	23.9	20.4	17.0	14.2	11.4		
1-Hexanol	102	121	11.9	10.2	8.51	7.09	5.68		
1-Heptanol	116	138	6.00	5.14	4.28	3.57	2.86		
1-Octanol	130	155	2.43	2.08	1.74	1.45	1.16		

3. Results and Discussion

3.1. Diffusion Coefficients. The permeation curves of 14 *n*-alkanes and six 1-alcohols through a commercial $12\ \mu\text{m}$ biaxial-oriented PEN film were determined within this study. The lag times and diffusion coefficients were determined at temperatures between 100°C and 140°C, in intervals of 5°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°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

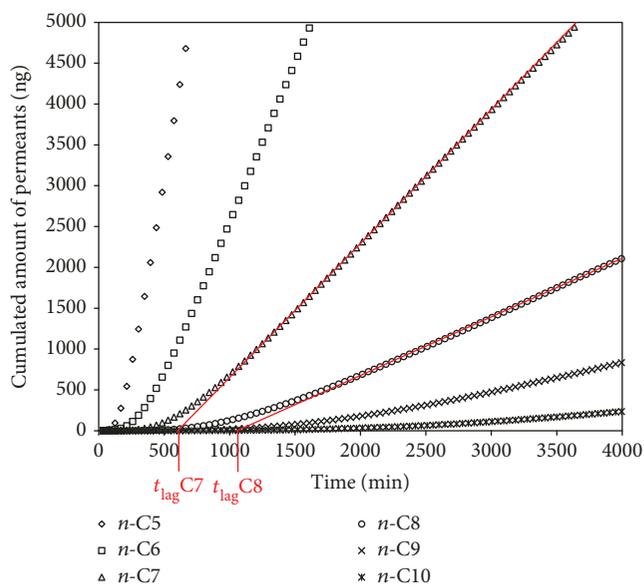
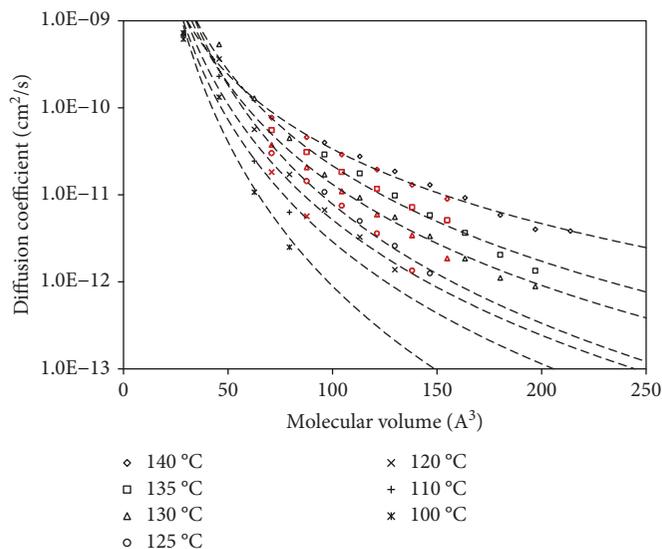


FIGURE 1: Experimental permeation curves for *n*-pentane to *n*-decane at 130°C (lag time for *n*-heptane and *n*-octane: intercept of the red line on the time axis).

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 2: Experimentally determined diffusion coefficients D_p .

Substance	Diffusion coefficient D_p (cm ² /s)						
	140°C	135°C	130°C	125°C	120°C	110°C	100°C
Methane			$7.3 \cdot 10^{-10}$		$7.3 \cdot 10^{-10}$	$6.7 \cdot 10^{-10}$	$6.1 \cdot 10^{-10}$
Ethane			$5.4 \cdot 10^{-10}$		$3.6 \cdot 10^{-10}$	$2.3 \cdot 10^{-10}$	$1.3 \cdot 10^{-10}$
<i>n</i> -Propane			$1.3 \cdot 10^{-10}$		$5.7 \cdot 10^{-11}$	$2.4 \cdot 10^{-11}$	$1.1 \cdot 10^{-11}$
<i>n</i> -Butane			$4.5 \cdot 10^{-11}$		$1.7 \cdot 10^{-11}$	$6.3 \cdot 10^{-12}$	$2.5 \cdot 10^{-12}$
<i>n</i> -Pentane	$4.0 \cdot 10^{-11}$	$2.9 \cdot 10^{-11}$	$1.7 \cdot 10^{-11}$	$1.1 \cdot 10^{-11}$	$6.7 \cdot 10^{-12}$		
<i>n</i> -Hexane	$2.8 \cdot 10^{-11}$	$1.8 \cdot 10^{-11}$	$9.3 \cdot 10^{-12}$	$5.0 \cdot 10^{-12}$	$3.3 \cdot 10^{-12}$		
<i>n</i> -Heptane	$1.9 \cdot 10^{-11}$	$9.8 \cdot 10^{-12}$	$5.6 \cdot 10^{-12}$	$2.6 \cdot 10^{-12}$	$1.4 \cdot 10^{-12}$		
<i>n</i> -Octane	$1.3 \cdot 10^{-11}$	$5.8 \cdot 10^{-12}$	$3.3 \cdot 10^{-12}$	$1.3 \cdot 10^{-12}$			
<i>n</i> -Nonane	$9.3 \cdot 10^{-12}$	$3.7 \cdot 10^{-12}$	$1.9 \cdot 10^{-12}$				
<i>n</i> -Decane	$5.9 \cdot 10^{-12}$	$2.0 \cdot 10^{-12}$	$1.1 \cdot 10^{-12}$				
<i>n</i> -Undecane	$4.0 \cdot 10^{-12}$	$1.3 \cdot 10^{-12}$	$8.9 \cdot 10^{-13}$				
<i>n</i> -Dodecane	$3.8 \cdot 10^{-12}$						
1-Propanol	$7.7 \cdot 10^{-11}$	$5.5 \cdot 10^{-11}$	$3.8 \cdot 10^{-11}$	$3.0 \cdot 10^{-11}$	$1.8 \cdot 10^{-11}$		
1-Butanol	$4.6 \cdot 10^{-11}$	$3.1 \cdot 10^{-11}$	$2.1 \cdot 10^{-11}$	$1.4 \cdot 10^{-11}$			
1-Pentanol	$2.9 \cdot 10^{-11}$	$1.8 \cdot 10^{-11}$	$1.1 \cdot 10^{-11}$	$7.5 \cdot 10^{-12}$			
1-Hexanol	$2.0 \cdot 10^{-11}$	$1.2 \cdot 10^{-11}$	$6.0 \cdot 10^{-12}$	$3.6 \cdot 10^{-12}$			
1-Heptanol	$1.3 \cdot 10^{-11}$	$7.2 \cdot 10^{-12}$	$3.4 \cdot 10^{-12}$	$1.4 \cdot 10^{-12}$			
1-Octanol	$9.0 \cdot 10^{-12}$	$5.1 \cdot 10^{-12}$	$1.9 \cdot 10^{-12}$				

FIGURE 2: Correlation between the molecular volume V of the permeants and their diffusion coefficients D_p (black dots: *n*-alkanes; red dots: 1-alcohols; dashed lines: correlations for *n*-alkanes and 1-alcohols).

contributions 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 at the given temperature.

3.2. Partition Coefficients. The thermodynamic part of the permeation process is represented by the partition coefficient $K_{g/b}$ between the gas phase and the PEN film. The partition coefficient was calculated from the slope of the

TABLE 3: Experimentally determined partition coefficients $K_{g/b}$.

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

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 $K_{g/b}$ 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.

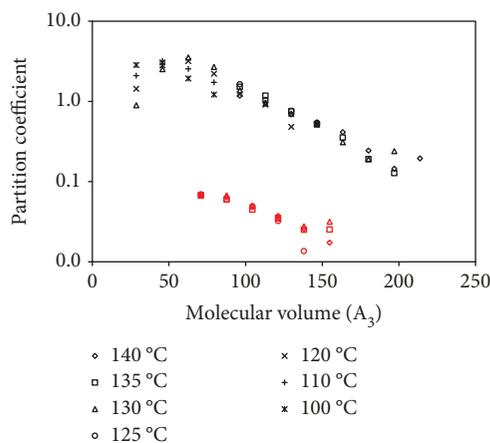


FIGURE 3: Correlation between the molecular volume of the permeants and the partition coefficients $K_{g/b}$ (black dots: *n*-alkanes; red dots: 1-alcohols).

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

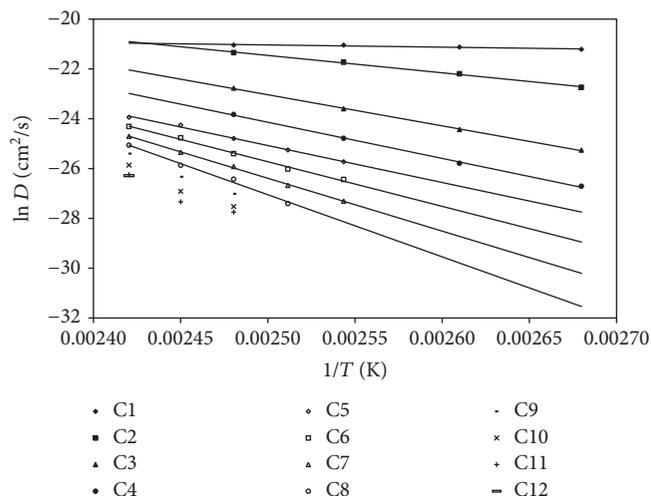


FIGURE 4: Correlation between the reciprocal temperature and the logarithm of the diffusion coefficient D_p (Arrhenius plot) for the investigated n -alkanes.

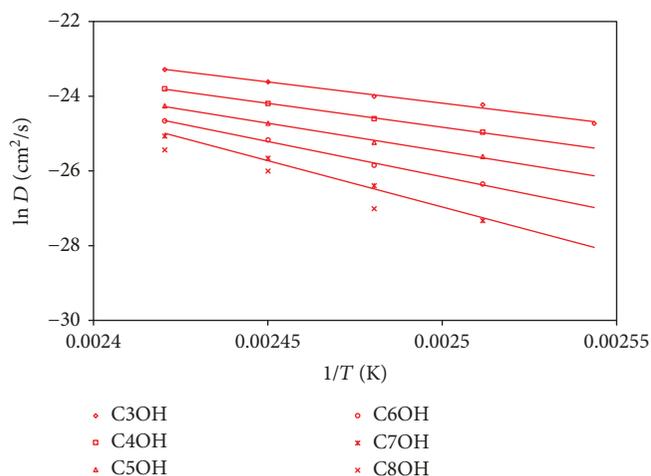


FIGURE 5: Correlation between the reciprocal temperature and the logarithm of the diffusion coefficient D_p (Arrhenius plot) for the investigated 1-alcohols.

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 ($D_0 = 4.8 \cdot 10^5 \text{ cm}^2/\text{s}$) [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 ($4.4 \cdot 10^5 \text{ cm}^2/\text{s}$) [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)

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 (cm ² /s)
Methane	100-130	7.9	$7.8 \cdot 10^{-9}$
Ethane	100-130	59.1	$2.5 \cdot 10^{-2}$
<i>n</i> -Propane	100-130	103.4	$3.2 \cdot 10^3$
<i>n</i> -Butane	100-130	120.8	$1.9 \cdot 10^5$
<i>n</i> -Pentane	120-140	123.5	$1.7 \cdot 10^5$
<i>n</i> -Hexane	120-140	149.0	$1.9 \cdot 10^8$
<i>n</i> -Heptane	125-140	177.1	$4.7 \cdot 10^{11}$
<i>n</i> -Octane	125-140	207.5	$2.2 \cdot 10^{15}$
1-Propanol	120-140	94.5	$8.9 \cdot 10^1$
1-Butanol	125-140	106.3	$1.3 \cdot 10^3$
1-Pentanol	125-140	125.0	$1.8 \cdot 10^5$
1-Hexanol	125-140	157.1	$1.4 \cdot 10^9$
1-Heptanol	125-140	206.3	$1.7 \cdot 10^{15}$

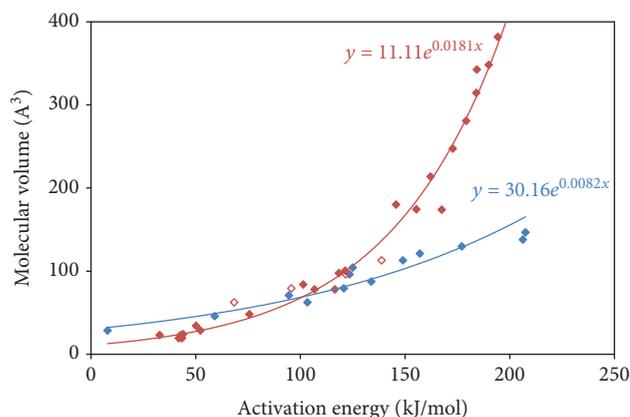


FIGURE 6: Correlation between the activation energy of diffusion E_A and the molecular volume V for PEN (this study, blue dots) and PET (nonsolid red dots from Ref. [10]; solid red dots from Ref. [12]).

and toluene (gas phase kinetics between 121°C and 180°C) with 101.4 kJ/mol ($D_0 = 1.9 \cdot 10^3$ cm²/s) [12, 13] and 121.4 kJ/mol ($3.5 \cdot 10^6$ cm²/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 a minimum of four diffusion coefficients for the Arrhenius correlation. In these cases, the linear behaviour of the Arrhenius correlation is indicated. In addition, only 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 dioxolane 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_p as well the partition coefficients $K_{g/b}$ 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

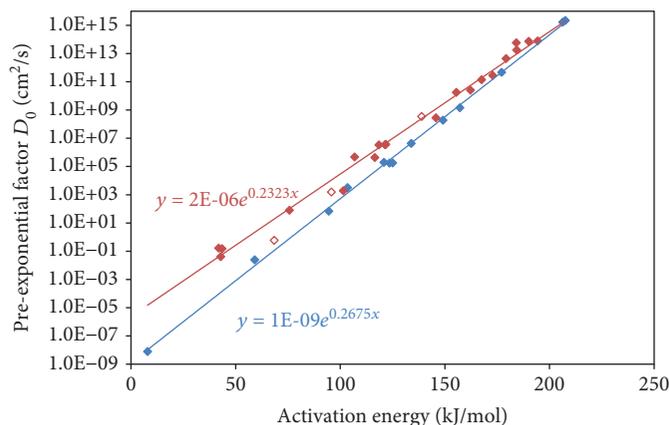


FIGURE 7: Correlation between the activation energy of diffusion E_A and the preexponential factor D_0 for PEN (this study, blue dots) and PET (nonsolid red dots from Ref. [10]; solid red dots from Ref. [12]).

biaxial-oriented 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.

References

- [1] M. A. Hernandez-Rivera, G. G. de la Mora, D. Likhatchev et al., "Oxygen and carbon dioxide transport through high barrier polyester blends," *Polymer Engineering and Science*, vol. 49, no. 8, pp. 1635–1641, 2009.
- [2] J. B. Brolly, D. I. Bower, and I. M. Ward, "Diffusion and sorption of CO₂ in poly(ethylene terephthalate) and poly(ethylene naphthalate)," *Journal of Polymer Science Part B: Polymer Physics*, vol. 34, no. 4, pp. 769–780, 1996.
- [3] R. R. Light and R. W. Seymour, "Effect of sub- T_g relaxations on the gas transport properties of polyesters," *Polymer Engineering and Science*, vol. 22, no. 14, pp. 857–864, 1982.
- [4] P.-S. R. Cheung, C. W. Roberts, and K. B. Wagener, "Synthesis, photodegradation, and energy transfer in a series of poly(ethylene terephthalate-co-2,6-naphthalenedicarboxylate) copolymers," *Journal of Applied Polymer Science*, vol. 24, no. 8, pp. 1809–1830, 1979.

- [5] S. Pacitti, "Polyethylene naphthalate," *Plastics in Packaging*, vol. 2, pp. 26-27, 2018.
- [6] J. Newton, "Film, oriented polyester," in *The Wiley Encyclopedia of Packaging Technology*, A. L. Brody and K. S. Marsh, Eds., pp. 408-415, Wiley, New York, NY, USA, 2nd edition, 1997.
- [7] T. Begley, L. Castle, A. Feigenbaum et al., "Evaluation of migration models that might be used in support of regulations for food-contact plastics," *Food Additives and Contaminants*, vol. 22, no. 1, pp. 73-90, 2005.
- [8] "The molecular volumes were calculated from the free internet program "Molinspiration"," 2018, <http://www.molinspiration.com>.
- [9] J. Crank, *The Mathematics of Diffusion*, Oxford University Press, 1975.
- [10] J. Ewender and F. Welle, "Determination and prediction of the lag times of hydrocarbons through a polyethylene terephthalate film," *Packaging Technology and Science*, vol. 27, no. 12, pp. 963-974, 2014.
- [11] J. Ewender and F. Welle, "Functional barrier performance of a polyamide-6 membrane towards n-alkanes and 1-alcohols," *Packaging Technology and Science*, vol. 29, no. 6, pp. 277-287, 2016.
- [12] F. Welle, "A new method for the prediction of diffusion coefficients in poly(ethylene terephthalate)," *Journal of Applied Polymer Science*, vol. 129, no. 4, pp. 1845-1851, 2013.
- [13] F. Welle and R. Franz, "Diffusion coefficients and activation energies of diffusion of low molecular weight migrants in poly(ethylene terephthalate) bottles," *Polymer Testing*, vol. 31, no. 1, pp. 93-101, 2012.
- [14] J. Ewender and F. Welle, "Determination of the activation energies of diffusion of organic molecules in poly(ethylene terephthalate)," *Journal of Applied Polymer Science*, vol. 128, no. 6, pp. 3885-3892, 2013.
- [15] P. Y. Pennarun, P. Dole, and A. Feigenbaum, "Functional barriers in PET recycled bottles. Part I. Determination of diffusion coefficients in bioriented PET with and without contact with food simulants," *Journal of Applied Polymer Science*, vol. 92, no. 5, pp. 2845-2858, 2004.
- [16] A. R. Overington, M. Wong, J. A. Harrison, and L. B. Ferreira, "Estimation of mass transfer rates through hydrophobic pervaporation membranes," *Separation Science and Technology*, vol. 44, no. 4, pp. 787-816, 2009.
- [17] W. Meyer and H. Neldel, "Über die Beziehung zwischen der Energiekonstanten ϵ und der Mengenkosten a in der Leitwerts-Temperatureformel bei oxydischen Halbleitern," *Zeitschrift für Technische Physik*, vol. 12, pp. 588-593, 1937.
- [18] H. Diehl and F. Welle, "How to determine functional barrier performance towards mineral oil contaminants from recycled cardboard," *Food Packaging and Shelf Life*, vol. 5, pp. 41-49, 2015.

