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# A New Method for the Prediction of Diffusion Coefficients in Poly(ethylene terephthalate)

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**ABSTRACT:** Poly(ethylene terephthalate) (PET) is used in several packaging applications, especially for beverages. Due to the low concentration of potential chemical compounds like polymer additives or monomers leached out of the polymers and found in food or beverages, the compliance of a PET packaging material is shown often by use of migration modeling. Diffusion coefficients for migrants, however, are rare in the scientific literature. The aim of the study was to develop an equation for the prediction of diffusion coefficients in PET on the basis of activation energies of diffusion for possible migrants in PET. As a result, a correlation between experimentally determined activation energies of diffusion $E_A$ and the volume of the migrant $V$ was established for PET. In addition, a correlation of the pre-exponential factor $D_0$ with the activation energy $E_A$ was found. Combining both correlations lead to an equation where the diffusion coefficients $D_P$ are predictable from the molecular volume $V$ of the migrant. The equation might be useful for migration prediction and consumer exposure estimations. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 1845–1851, 2013

**KEYWORDS:** packaging; polyesters; kinetics; properties and characterization

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## INTRODUCTION

Poly(ethylene terephthalate) (PET) is used in several packaging applications. In the last decade, the amount of PET in packaging applications increased significantly, and nowadays PET is the main packaging material for beverages. On the other hand, PET is used increasingly for packaging films as well as for trays. PET is a very inert polymer, which means that the interactions between the packaging material and the foodstuff are low. As a consequence, the specific migration of organic compounds like additives, residual monomers, or impurities is—under normal conditions of use—far below the specific migration limits.[1] The low migration of PET is one of the major advantages in comparison to other packaging materials. However, from a food law point of view, the compliance of the PET bottles has to be shown even if the migration of chemical compounds from the polymer like additives or monomers into the foodstuff is negligible. Due to the low concentration of potential migrants in food or beverages, the compliance of a PET packaging material is shown often by use of migration modeling.

An overview of migration modeling is given in a recently published review.[2] In general, the migration of chemical compounds from a polymer can be calculated at a certain temperature according to eq. (1).[3] The parameter $m/A$ is the area related mass transfer from the polymer into the foodstuff. The concentration of the migrant in the polymer before the migration experiment is $c_{P,0}$. The diffusion coefficient of the migrant in the polymer is $D_P$ and $t$ is the storage time. $\rho_P$ is the density of the polymer and the thickness of the packaging material is $d_P$. The factor $\alpha$ [eq. (2)] contains the partition coefficients $K_{P,F}$ and the volumes of the packaging and foodstuff ($V_P$ and $V_F$).

$$\frac{m}{A} = c_{P,0}\ \rho_P\ d_P \left(\frac{\alpha}{1+\alpha}\right)\left[1 - \sum_{n=1}^{\infty} \frac{2\alpha\ (1+\alpha)}{1+\alpha+\alpha^2 q_n^2} e^{\left(-D_P\ t\ \frac{q_n^2}{d_P^2}\right)}\right] \quad (1)$$

$$\alpha = \frac{1}{K_{P,F}}\ \frac{V_F}{V_P} \quad (2)$$

For a given polymer or packaging material, parameters like polymer density, film or bottle wall thickness, and volume of the foodstuff are easily available. Therefore, most of the parameters in eq. (1) are well known. In addition, the concentration of the migrant in the packaging material ($c_{P,0}$) can be determined experimentally by extraction of the packaging material. Only the diffusion coefficient $D_P$ and the partition coefficient $K_{P,F}$ are typically not directly available. The partition coefficient plays a minor role for low diffusive polymers like PET, because the equilibrium between packaging and food—which is represented by the partition coefficient $K_{P,F}$—can hardly be reached under

**Table I.** Equations for the Prediction of the Diffusion Coefficients

| Equation | Parameters | Comment | Ref. |
|---|---|---|---|
| $D = 10^4 \, e^{A_P - \alpha M_W - \frac{b}{T}}$ | $D$: diffusion coefficient ($cm^2\ s^{-1}$)<br>$A_P$: polymer specific constant (dimensionless)<br>$M_W$: molecular weight of migrant (Da)<br>$T$: temperature (K)<br>$\tau$: correlation constant<br>$b$: correlation constant | For PET: $A_P$ is −3; $\tau$ and $b$ are 0.01 and 10,454 | 5 |
| $D = D'_0 e^{\left(\alpha\sqrt{M_W} - K\sqrt[3]{\frac{M_W}{T}}\right)}$ | $D$: diffusion coefficient ($cm^2\ s^{-1}$)<br>$D'_0$: diffusion coefficient at infinite temperature ($cm^2\ s^{-1}$)<br>$\alpha$: polymer parameter (dimensionless)<br>$K$: polymer parameter (dimensionless)<br>$T$: temperature (K)<br>$M_W$: molecular weight of migrant ($g\ mol^{-1}$) | Validated only for polyolefins | 6 |
| $D = 10^4 e^{A_P - 0.1351M^{2/3} + 0.003M - \frac{10454}{T}}$ with $A_P = A'_P - \frac{\tau}{T}$ | $D$: diffusion coefficient ($cm^2\ s^{-1}$)<br>$M$: molecular weight of migrant (Da)<br>$T$: temperature (K)<br>$A_P$: polymer specific parameter (dimensionless)<br>$A'_P$: athermal term of $A_P$<br>$\tau$: parameter associated with the activation energy (K) | For PET $A'_P$ is 3.1$\tau$ is 1577 K for $T$ <175 °C, which is related to an activation energy of 100 $kJ\ mol^{-1}$ for any migrant | 7,8 |
| $D_{P,i} = D_u e^{\left(w_{i,e} - w_{p,e} \cdot 0.14 w_l^{2/3} (14j+2)^{2/3} - w w_{i,e}^{2/3} \frac{T_g R}{RT}\right)}$<br>with $w_{i,e} = \left(\frac{1+2\pi}{i}\right)^{i/e}$ $w_{p,e} = \left(\frac{1+2\pi}{p}\right)^{p/e}$ $w = 2^{2\pi/e}$<br>$w_1 = \sqrt{1+2\pi i} = \frac{M_{r,i}-2}{14} j = \left(\frac{M_{r,i}-2}{14}\right)^{1/3} p = \left(\frac{M_{r,p}}{14}\right)^{1/3}$ | $M_{r,i}$: molecular weight of migrant (Da)<br>$M_{r,p}$: molecular weight of polymer (Da)<br>$T$: temperature (K)<br>$T_g$: glass transition temperature (K) | For PET below the glass transition temperature. Similar equations are available from temperatures above the glass transition temperature | 9 |

normal storage conditions of packed foodstuffs.[4] As a consequence, the most important factor influencing the migration from the PET packaging into the foodstuff is the diffusion coefficient $D_P$.

Diffusion coefficients for every possible migrant cannot be determined by use of experimental tests, because it is a too time consuming and laborious process. Therefore, several approaches have been published to predict the diffusion coefficients of migrants. Examples for such equations for the predictions of diffusion coefficients from the literature are given in Table I. All these approaches are using empirical equations, which fit experimental available diffusion coefficients in a worst-case scenario. Therefore, the diffusion coefficients predicted by use of these equations are in any case higher than the diffusion coefficients found for the same migrant in experimental tests. Such a worst-case prediction of the diffusion coefficients is useful for compliance testing, because the migration will be overestimated. If the calculated migration is below the current specific migration limits, experimental tests are not necessary.

In the case of PET, another point gets obvious. Most of the published migration data are using high ethanolic solutions as food simulants. It is known that food simulants like 50% or 95% ethanol swell the polymer matrix and increase the transfer of migrants into the simulant (for a discussion see, for example, Ref. 4). The swelling conditions increase the diffusion coefficient which directly increases the migration. As a consequence, for swelling food simulants, the diffusion coefficient $D_P$ of a migrant in the polymer is not constant over time. From a food law compliance point of view, such an overestimation of the migration is again favorable because under real migration conditions swelling of the PET polymer did not normally occur. Therefore, migration testing into 50% or 95% ethanolic simulants can be considered as the worst case for nearly all kinds of foodstuffs. On the other hand, if such diffusion coefficients determined under swelling conditions are used for the parameterization of the empirical equations given in Table I, the prediction of the diffusion coefficients is overestimative.

The currently general accepted equation for the prediction of the diffusion coefficients in packaging polymers is the so-called Piringer Equation (entry 3 in Table I).[10] The polymer specific parameter $A'_P$ is set for PET to 3.1 for temperatures below the glass transition temperature and 6.4 for temperatures above. The activation energy of diffusion of a migrant in the polymer is represented in this model by the factor $\tau$. The current $\tau$ value

for PET is 1577 K, which represents an activation energy of diffusion $E_A$ of 100 kJ mol$^{-1}$.[10] This activation energy was set as a conservative default parameter for compliance evaluation purposes and applied for all kinds of migrants. This fixed activation energy is another reason for the overestimation of the diffusion coefficients, because high-molecular-weight compounds had significantly higher activations energies of diffusion in comparison to low-molecular-weight molecules.[11]

In conclusion, the equations for the prediction of the diffusion coefficients in PET (or in polymers in general) given in Table I are developed for food law compliance evaluation. Overestimation of the diffusion coefficients is part of this concept. However, the degree of overestimation is typically not known. For other purposes, for example, consumer exposure evaluation, an overestimation of the diffusion is not purposeful. A more precise prediction of the diffusion coefficients of migrants in PET is necessary for such purposes.

The aim of the study was therefore the development of a new equation for the prediction of the diffusion coefficients in PET. The basis of the new equation is experimentally determined, variable activation energies of diffusion determined under nonswelling testing conditions for migrants in PET.

## EXPERIMENTAL

### Calculation of the Molecular Volume of the Migrants

The molecular volume $V$ of the molecules was calculated for any migrant by use of molecular modeling approaches. Within this study, the free internet program *molinspiration* was used.[12] This program calculates the van der Waals volume of organic molecules. The method for calculation of molecule volume (in Å$^3$) developed is based on group contributions. These have been obtained by fitting sum of fragment contributions to "real" volume for a training set of about 12,000 molecules. The molecular geometries for a training set were fully optimized by the semiempirical AM1 method.

### Activation Energies of Diffusion

Activation energies of diffusion of permanent gases and organic molecules in PET are found in the scientific literature. Because the diffusion coefficients for PET (as well as the activation energies) are significantly influenced by swelling effects, only literature data that are determined under nonswelling conditions were taken into account. Swelling of the polymer results in significantly higher diffusion coefficients and therefore lower activation energies of diffusion. For PET, nonswelling migration conditions are established if the diffusion coefficients are determined from the migration kinetics into water, 3% acetic acid, 10% ethanol, isooctane, and the gas phase.

The activation energies of diffusion are typically derived from the correlation between the logarithm of the experimentally determined diffusion coefficient and the reciprocal temperature (in K) according to eq. (3) (Arrhenius approach). To get a reliable Arrhenius correlation, only literature data of activation energies were considered in this study which used a minimum of four diffusion coefficients for the Arrhenius correlation. In these cases, the linear behavior 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 a higher temperature range is applied, the slope of the Arrhenius correlation is better defined and therefore the activation energies can be determined more precisely.

## RESULTS

Diffusion of migrants in polymers is an activated process. The diffusion coefficient of a migrant in polymer can be described at a certain temperature by the activation energies of diffusion according to the Arrhenius approach [eq. (3)]. In this equation, $E_A$ is the activation energy of diffusion and $D_0$ is the pre-exponential factor. The constant $R$ (8.314 J K mol$^{-1}$) is the gas constant and $T$ is the temperature (in K).

$$D_P = D_0\, e^{-\frac{E_A}{RT}} \tag{3}$$

Using eq. (3) as the basis of the new approach, the diffusion coefficients $D_P$ of a potential migrant can be calculated if activation energy of diffusion $E_A$ and the pre-exponential factor $D_0$ are available. Experimental data for activation energies of diffusion are rare in the scientific literature. Therefore, the approach in this study was to establish a correlation between available activation energy data in the scientific literature with suitable molecule properties like the molecular weight or molecular volumes of the migrants. If such a correlation can be established, the activation energy of diffusion can be predicted from this correlation for any migrant.

Typically, the molecular weights of the migrants are used for the prediction of the diffusion coefficients. Within this study, the molecular volume was preferred because the molecular weight of the molecule gives no indication about the shape of the migrant. Therefore, it is expected that the use of the molecular volume instead of the molecular weight results in a (slightly) better correlation with the activation energy. On the other hand, the molecular weight of a migrant is easily available if the chemical structure of the migrant is known. In addition, the molecular weight can be estimated also for "unknown" compounds from experimental data, e.g., the retention time in the gas chromatograms is predicted from mass spectrometry data. Therefore, a correlation between the volume of the migrant and the molecular weight of organic molecules (alkanes, aromatics, hetero aromatics, alcohols, ketones, carbonic acids, esters, typical polymer additives, etc.) was established. For this purpose, the volume of 216 different organic molecules was calculated. The correlation between the molecular volumes $V$ of the migrants (in Å$^3$) and their molecular weight $M_W$ (in g mol$^{-1}$) is shown in Figure 1. The best fit of this correlation is given in eq. (4). The deviation from the linear correlation given in eq. (4) is about 20% in both directions (green and red line in Figure 1). It should be noted here that the factor 1.13 Å$^3$ mol g$^{-1}$ is only valid for the above-mentioned groups of organic molecules. The molecular volume of other chemical species (e.g., chlorinated, brominated, or metal organic compounds like catalysts) might deviate from this correlation and should be calculated using the above-mentioned (or similar) program.

$$V = 1.13\, M \tag{4}$$

One major goal of the present study was the correlation of the activation energies of diffusion of migrants in PET with the

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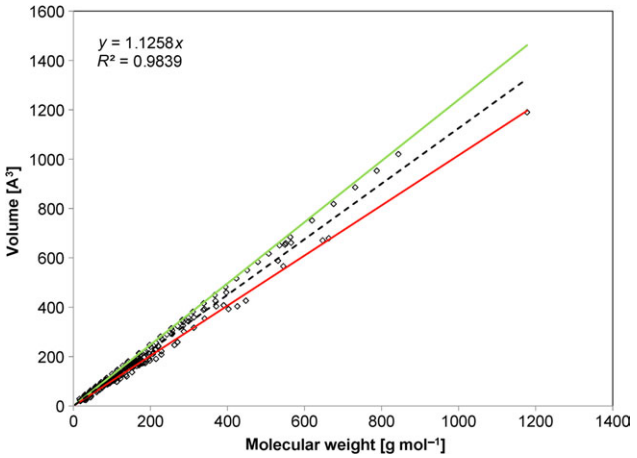


**Figure 1.** Correlation of the molecular weight of the migrants with the volume of the migrants ($n = 216$), red and green lines: variance of 20% on the molecular volume $V$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

molecular weight or the molecular volume of the migrant. For this purpose, literature data of the activation energies of diffusion in PET are compiled, which are determined under nonswelling conditions and from Arrhenius plots with four kinetic points from a minimum temperature range of 25°C. By using such strict criteria, some of the literature data for the activation energies of diffusion could not be taken into account. For example, Begley et al.[8] compiled the activation energies of diffusion of 17 substances. Unfortunately, analytical details and the simulants are not given within this study. Therefore, it is not clear if the diffusion coefficients are determined under swelling or nonswelling conditions. In addition, the activation energies were calculated only from two diffusion coefficients at different temperatures. Another set of diffusion coefficients for 13 compounds in PET is given by Pennarun et al.[13] These diffusion coefficients were determined under nonswelling conditions, but only two diffusion coefficients per substance were determined. So, it is unclear if the Arrhenius equation results in a linear correlation or not.

The compilation of the activation energies and the pre-exponential factors, which are in compliance with the above mentioned strict evaluation criteria, are given in Table II. Figure 2 shows the correlation between the experimentally determined activation energies of diffusion $E_A$ and the molecular weights of the migrants. As expected, a slightly better correlation was established using the molecular volume $V$ instead of the molecular weight $M$ (Figure 3). From this correlation, it can be concluded that the molecular volume is an exponential function of the activation energy $E_A$ (in J mol$^{-1}$) according to eq. (5). From the experimental data, the factors $c$ and $d$ were determined as 11.1 Å$^3$ and 1.50 $\times$ 10$^{-4}$ K$^{-1}$, respectively. The red and green lines in Figure 3 represent a deviation of 20% found in Figure 1.

$$V = c\, e^{d \frac{E_A}{R}} \tag{5}$$

The Arrhenius equation [eq. (3)] has three variables, the activation energy $E_A$, the pre-exponential factor $D_0$, and the temperature $T$. The activation energy of diffusion $E_A$ is available from eq. (5). The molecular volume can be calculated and the factors $c$ and $d$ for PET are available from the correlation shown in Figure 3. For the prediction of the migration, the pre-exponential factor $D_0$ is also important and needs to be known. Several authors mentioned that the pre-exponential factor $D_0$ is also a function of the activation energy (see, for example, Refs. 19, 21–25). This means that the pre-exponential factor $D_0$ and the activation energy $E_A$ correlate with each other. Most of these authors proposed an expression given in eq. (6) for this correlation. The experimental data used in this study show indeed such a correlation between the natural logarithm of the pre-exponential factor $D_0$ and the activation energy of diffusion $E_A$ (Figure 4, data from Table II). From the experimental data, the factors $a$ and $b$ were determined as 1.93 $\times$ 10$^{-3}$ K$^{-1}$ and 2.37 $\times$ 10$^{-6}$ cm$^2$ s$^{-1}$, respectively.

$$D_0 = b\, e^{a \frac{E_A}{R}} \tag{6}$$

As shown in Figure 4, the pre-exponential factor $D_0$ also correlates with the activation energy $E_A$. Combining the Arrhenius equation [eq. (3)] with eq. (6) leads to an equation where the diffusion coefficient $D_P$ is only a function of the activation energy $E_A$ and the temperature $T$ [eq. (7)]. The activation energy is available from the correlation established within this study [eq. (5)]. Furthermore, combining eq. (7) with eq. (5), the diffusion coefficient $D_P$ is only a function of the molecular volume $V$ and the temperature $T$ [eq. (8)]. This equation can be further reduced to the simplified eq. (9). Following this approach, the diffusion coefficients $D_P$ are predictable from the molecular volume $V$ [or the molecular weight $M_W$ if eq. (4) is taken into account].

$$D_P = b\, e^{a \frac{E_A}{R}}\, e^{-\frac{E_A}{RT}} \tag{7}$$

$$D_P = b\, e^{a \frac{\frac{R}{d}\left(\ln \frac{V}{c}\right)}{R}}\, e^{-\frac{\frac{R}{d}\left(\ln \frac{V}{c}\right)}{RT}} \tag{8}$$

$$D_P = b \left(\frac{V}{c}\right)^{\frac{a - \frac{1}{T}}{d}} \tag{9}$$

## DISCUSSION

Within the study, a correlation between experimentally determined activation energies of diffusion $E_A$ and the volume of the migrant $V$ was established for PET [eq. (5)]. Based on this correlation, an equation for the prediction of the diffusion coefficient of a migrant was established [eq. (9)]. This equation can be considered as equivalent to the approaches compiled in Table I. Due to experimental uncertainties and different PET materials used for the determination of the activation energies of diffusion, the correlation shows a slight variance. However, if a variance of ±20% on the calculated molecular volume was taken into account, the diffusion coefficients $D_P$ can be predicted as a best-case (green line in Figure 3) or as worst-case diffusion coefficients (red line in Figure 3). The prediction of the diffusion coefficients $D_P$ from the molecular volume $V$ is not overestimating, because experimentally determined activation energies of diffusions are used for the parameterization of eq. (9) and

**Table II.** Activation Energies of Diffusion for the Investigated Model Compounds and Some Literature Data in PET

| Compound (molecular weight) | Testing conditions | Temperature range (°C) | Activation energy [kJ mol$^{-1}$] | Pre-exponential factor $D_0$ [cm$^2$ s$^{-1}$] | Ref. |
|---|---|---|---|---|---|
| Helium (4) | Permeation | 25°C–135°C | 20.1 | Not given | 14 |
| Methane (16) | Permeation | 50°C–135°C | 52.3 | Not given | 14 |
| Water (18) | Permeation | 20°C–60°C | 41.9 | 0.167 | 15 |
| Water (18) | Permeation | 25°C–55°C | 43.5 | 0.153 | 16 |
| Nitrogen (28) | Permeation | 25°C–135°C | 44.0 | Not given | 14 |
| Oxygen (32) | Permeation | 25°C–55°C | 42.8 | 0.041 | 16 |
| Oxygen (32) | Permeation | 5°C–55°C | 32.8 | Not given | 17 |
| Carbon dioxide (44) | Permeation | 35°C–135°C | 50.2 | Not given | 14 |
| Acetaldehyde (44) | Migration into mineral water | 23°C–50°C | 75.7 | 81 | 18 |
| Tetrahydrofuran (72) | Migration into distilled water | 23°C–50°C | 106.8 | $4.8 \times 10^5$ | 18 |
| Tetrahydrofuran (72) | Migration into gas phase | 120°C–180°C | 116.5 | $4.4 \times 10^5$ | 11 |
| Benzene (78) | Migration into mineral water | 23°C–50°C | 101.4 | $1.9 \times 10^3$ | 18 |
| Toluene (92) | Migration into gas phase | 121°C–180°C | 121.4 | $3.5 \times 10^6$ | 11 |
| Chlorobenzene (113) | Migration into gas phase | 121°C–180°C | 118.4 | $3.4 \times 10^6$ | 11 |
| Decane (142) | Migration into gas phase | 120°C–179°C | 145.7 | $2.8 \times 10^8$ | 11 |
| Phenyl cyclohexane (162) | Migration into gas phase | 121°C–180°C | 167.5 | $1.4 \times 10^{11}$ | 11 |
| Dodecane (170) | Migration into gas phase | 120°C–179°C | 162.2 | $2.6 \times 10^{10}$ | 11 |
| Benzophenone (182) | Migration into gas phase | 121°C–180°C | 155.4 | $1.8 \times 10^{10}$ | 11 |
| Tetradecane (198) | Migration into gas phase | 120°C–179°C | 172.8 | $2.8 \times 10^{11}$ | 11 |
| Hexadecane (226) | Migration into gas phase | 120°C–179°C | 179.2 | $4.5 \times 10^{12}$ | 11 |
| Octadecane (254) | Migration into gas phase | 120°C–179°C | 184.1 | $5.9 \times 10^{13}$ | 11 |
| Eicosane (282) | Migration into gas phase | 120°C–179°C | 190.0 | $7.5 \times 10^{13}$ | 11 |
| Methyl stearate (298) | Migration into gas phase | 121°C–180°C | 184.3 | $1.8 \times 10^{13}$ | 11 |
| Docosane (310) | Migration into gas phase | 120°C–179°C | 194.3 | $7.8 \times 10^{13}$ | 11 |
| Antimony oxide[a] | Migration into 3% acetic acid | 90°C–150°C | 190.0 | $5.0 \times 10^{13}$ | 20 |

[a]Molecular mass of migrating substances not clear.

because swelling conditions for the PET are excluded. For parameterization of eq. (9), the four PET specific parameters *a* to *d* are necessary, which are determined experimentally from the correlations in this study. The parameters for PET are compiled in Table III.

From the data used in this study, an exponential relation was found between the activation energy of diffusion and the molecular volume (or molecular weight). Some literature studies proposed a linear correlation for the molecular diameter (which is also correlating with the molecular weight) and the activation energy (e.g., Refs. 19, 22–25). So the findings of this study seem to be in contrast to previous studies. The reason might be that previous studies found a linear correlation in most cases, e.g., permanent gases or small molecules with very low molecular weight range. Therefore, a linear or exponential behavior (or all other functions) cannot be clearly distinguished. An important point gets evident here: the molecular weight (or volume or molecular diameter) range for the correlation should be as broad as possible. If higher molecular weight compounds (e.g., molecular weight compounds up to about 300 g mol$^{-1}$) were introduced into the correlation, the function of the correlation gets much clearer and it gets evident that an exponential function gives a much better correlation than a linear one.

Literature data of diffusion coefficients in PET, which were experimentally determined at 40°C and 35°C, are compiled in a previous study (Table 3 in Ref. 18). These data can be used for verification of eq. (9). The correlation of these diffusion coefficients versus the calculated molecular volume is given in Figure 5. This figure also contains the predicted diffusion coefficients from eq. (9) (filled line in Figure 5) together with a variance of ±20% in the calculated volume (dotted lines in Figure 5). As a result, the diffusion coefficients at 40°C are following exactly the correlation, and the data are in good agreement with the predictions from eq. (9).

Another point needs to be stressed here: for the derivation of eq. (9) activation energies of diffusion were also used for the correlation, which were calculated from diffusion coefficients above the glass transition temperature $T_g$. These activation energies fit into the correlation of the molecular weight versus the

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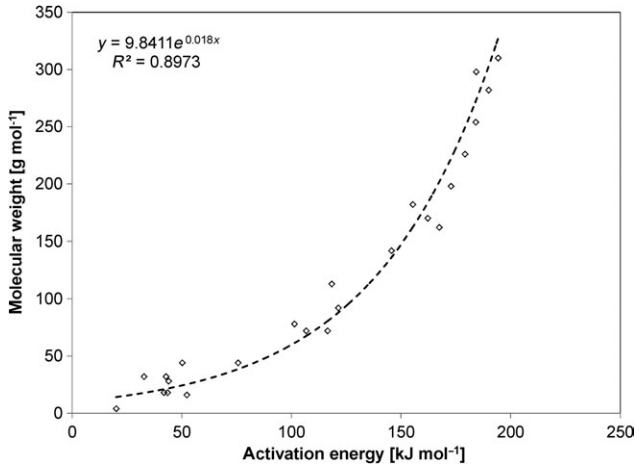


**Figure 2.** Correlation of the experimentally determined activation energy of diffusion $E_A$ with the molecular weight of the migrants.

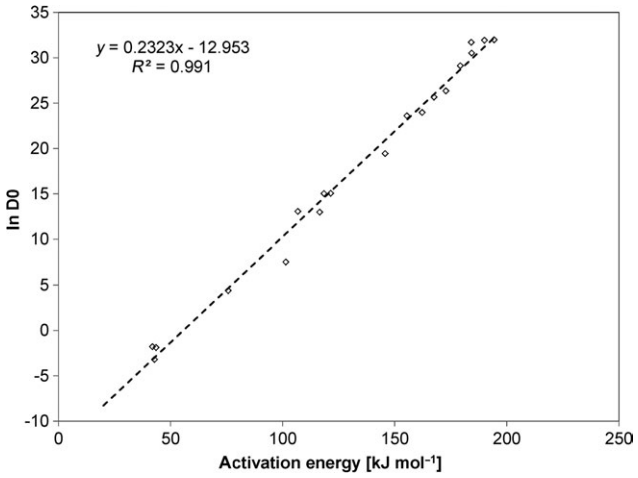


**Figure 4.** Correlation of the activation energy of diffusion $E_A$ with the natural logarithm of $D_0$ (both experimentally determined).

molecular volume together with activation energies determined below the glass transition temperature. Therefore, it can be concluded that the activation energies of diffusions are not significantly influenced if the diffusion coefficients are measured above or below the glass transition temperature of PET and are within the variance of ±20% assumed in this study. For tetrahydrofuran (THF), it was experimentally verified that the activation energies determined from Arrhenius plots above and below the glass transition temperature are very similar.[11]

The role of the correlation between the pre-exponential factor $D_0$ and the activation energy [eq. (6)] is discussed in the literature as a so-called "compensation effect" or "Meyer–Neldel rule" (e.g., Refs. 25 and 26). According to this compensation effect, the activation energy of diffusion $E_A$ correlates with the pre-exponential factor $D_0$ in the Arrhenius approach. As a consequence, all linear correlations in the Arrhenius plot have an intersection at a certain temperature. At this isokinetic temperature $T_{iso}$, the diffusion coefficients $D_P$ for all molecules are equal. From the results of this study, this isokinetic temperature is the reciprocal factor $a$ ($T_{iso}$ (PET) = 245°C), which is approximately the melting point of PET. At this isokinetic temperature, the diffusion coefficient for all molecules is the factor $b$.

**Table III.** Experimentally Determined Coefficients for the Prediction of the Diffusion Coefficients in PET According to eq. (9)

| | Value |
|---|---|
| $a$ | $1.93 \times 10^{-3}$ K$^{-1}$ |
| $b$ | $2.37 \times 10^{-6}$ cm$^2$ s$^{-1}$ |
| $c$ | 11.1 Å$^3$ |
| $d$ | $1.50 \times 10^{-4}$ K$^{-1}$ |

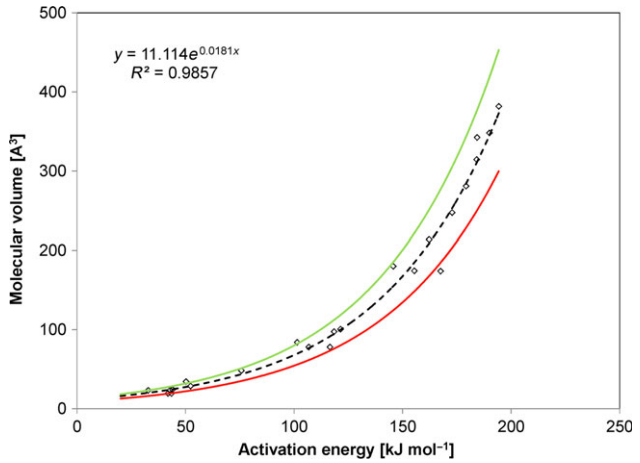


**Figure 3.** Correlation of the experimentally determined activation energy of diffusion $E_A$ with the calculated volume of the migrants, red and green lines: variance of 20% on the molecular volume $V$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

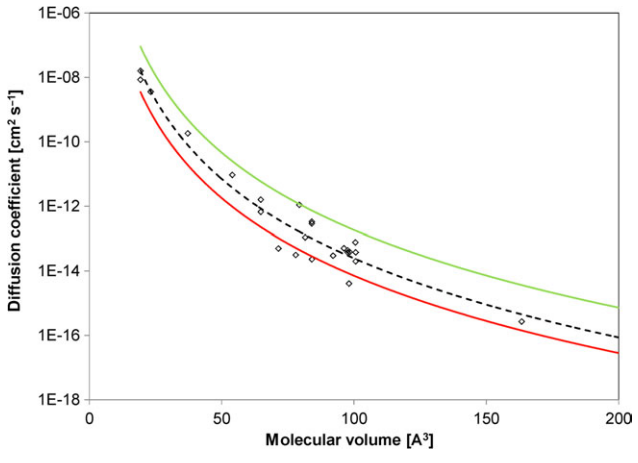


**Figure 5.** Correlation of literature of the diffusion coefficients in PET at 35°C and 40°C (Table 3 in Ref. 18) with the calculated molecular volume, black line: predicted diffusion coefficients from eq. (9), green and red line: variance of ±20% of the molecular volume $V$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

## CONCLUSIONS

Within this study, a new equation for the prediction of the diffusion coefficient $D_P$ of a migrant in PET based on experimental determined activation energies of diffusion was established. In comparison to previous overestimative approaches, eq. (9) results in a more realistic prediction of the diffusion coefficients. Such a realistic prediction of the migration is desirable, e.g., for exposure estimations or high temperature applications of PET like microwave trays or cooking facilities. The determination of the activation energies of diffusion for higher molecular weight compounds plays an important role within this approach. The recently published method[11] for the determination of diffusion coefficients from migration experiments into the gas phase might give an important contribution to the determination of the activation energies of diffusion for high-molecular-weight molecules. In principle, the correlation for PET found in eq. (9) might also be valid for other polymers. The factors *a* to *d* are polymer-specific constants, which should be typical for each individual polymer and might be predicted from polymer-specific parameters like the glass transition temperature or melting temperature. For a clear prediction of the factors *a* to *d*, more data for the activation energies of diffusion for different kinds of molecules should be available for other polymers.

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