

A new method for the prediction of diffusion coefficients in poly(ethylene terephthalate)

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Introduction

Poly(ethylene terephthalate) (PET) is used in several packaging applications especially for beverages. 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 modelling. Diffusion coefficients for possible migrants, however, are rare in the scientific literature. Therefore, several approaches have been published to predict the diffusion coefficients of migrants.

The currently general accepted equation for the prediction of the diffusion coefficients D_p in packaging polymers is the so-called Piringer Equation. The polymer specific parameter A_p' is set 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 by the factor τ . The current τ value for PET is 1577 K, which represents an activation energy of diffusion E_A of 100 kJ mol⁻¹. This activation energy was set as a conservative default parameter for compliance evaluation purposes and applied for all kind of migrants. This fixed activation energy leads to an over-estimation of the diffusion coefficients, because high molecular weight compounds have significantly higher activation energies of diffusion in comparison to low molecular weight molecules.

In conclusion, the equations for the prediction of the diffusion coefficients in PET (or in polymers in general) are developed for compliance testing. Over-estimation of the diffusion coefficients are part of this concept. However, the degree of over-estimation is not known. For other purposes, e.g. consumer exposure evaluation or the prediction of the cleaning efficiencies of PET recycling processes, an over-estimation of the diffusion is not purposeful. A more precise prediction of the diffusion coefficients of migrants in PET is necessary for such applications.

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 for possible migrants in PET. By using such data the predicted diffusion coefficients D_p of possible migrants should be realistic and not over-estimative.

Development of the New Model

Diffusion of migrants in polymers is an activated process, which follows the Arrhenius equation (Equation 1). 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 much rarer than for the diffusion coefficients. Therefore, the approach in this study was to establish the correlation between available activation energy data in the scientific literature with suitable molecule properties like the molecular volumes V of the migrants.

Due to the fact, that the diffusion coefficients for PET (as well as the activation energies) are significantly influenced by swelling effects only literature data, which were determined under non-swelling conditions, were taken into account. Swelling of the polymer will result in significantly higher diffusion coefficients or significantly lower activation energies of diffusion. For PET, non-swelling conditions can be considered, if the diffusion coefficients were determined from the migration kinetics for example into water, 3% acetic acid, 10% ethanol, *iso*-octane, Tenax® and into the gas phase.

Within this study it was found, that also the pre-exponential factor D_0 correlates with the activation energy according to equation 2. So combining Equation 1 and 2 results in an Arrhenius-like equation, where the diffusion coefficient is only a function of the activation energy E_A and the temperature T (Equation 3). The correlation of the activation energies and the molecular volume V is given in Figure 1 and Equation 4.

Furthermore, combining Equation 3 with Equation 4, the diffusion coefficient D_p is only a function of the molecular volume V and the temperature T (Equation 5). Following this approach, the diffusion coefficients D_p are predictable from the molecular volume V and the PET specific factors a to d given in Table 1. The prediction of the diffusion coefficients D_p from the molecular volume V , however, is not over-estimating, because experimentally determined activation energies of diffusions are used for the parameterisation of Equation 5 and because of the fact swelling conditions for the PET are excluded. The realistic (and not over-estimating approach) has the disadvantage, that the experimental data spread around the exponential correlation. However, if a variance of $\pm 20\%$ on the calculated molecular volume V was taken into account, the diffusion coefficients D_p can be predicted as a best case (green line in Figure 1) or a worst case (red line in Figure 1).

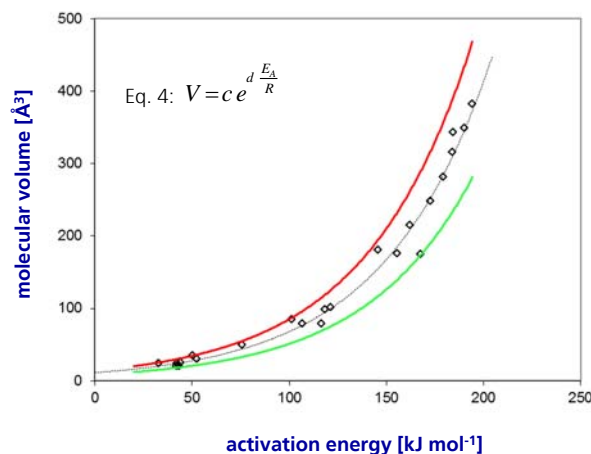


Figure 1: Correlation of the experimentally determined activation energy of diffusion E_A with the calculated volume of the migrants, red and green lines: variance of 20% on the molecular volume V

$$\text{Eq. 1: } D_p = D_0 e^{-\frac{E_A}{RT}}$$

$$\text{Eq. 2: } D_0 = b e^{\frac{E_A}{R}}$$

$$\text{Eq. 3: } D_p = b e^{\frac{E_A}{R}} e^{-\frac{E_A}{RT}}$$

$$\text{Eq. 5: } D_p = b \left(\frac{V}{c} \right)^{\frac{a-T}{d}}$$

Table 1: Experimentally determined coefficients for the prediction of the diffusion coefficients in PET according to Equation 5

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

Conclusions

A correlation between experimentally determined activation energies of diffusion E_A and the volume of the migrant V was established for PET. In addition, the pre-exponential factor D_0 correlate also with the activation energy E_A . Combining both correlations, an equation was established where the diffusion coefficients D_p are predictable from the molecular volume V of the migrant. Such a realistic prediction of the migration is desirable e.g. for exposure estimations or high temperature applications of PET. The realistic approach for organic migrants has a side-effect, that also permanent gases like oxygen and carbon dioxide follow the correlation of the activation energies and the volume of the molecule. Therefore for the first time, a general equation for the prediction of the diffusion coefficients all kinds of molecules has been established.

In principle, the Equation 5 might be also valid for other polymers. The factors a to d are polymer specific constants, which should be typical for each individual polymer. Some of the factors might be valid for all kinds of polymers and some of the factors might be predicted from polymer specific parameters like the glass transition 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.

Reference

[1] F. Welle, A new method for the prediction of diffusion coefficients in poly(ethylene terephthalate), *Journal of Applied Polymer Science*, submitted.