Diffusion coefficients and activation energies of diffusion of low molecular weight migrants in poly(ethylene terephthalate) bottles

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Introduction

Poly(ethylene terephthalate) (PET) is nowadays the packaging material of choice for mineral water and soft drinks. Reasons for this are its resistance to breaking as well as the clarity of the PET material and its good barrier towards moisture and oxygen. In addition, post-consumer PET packaging can be remanufactured into new soft drink and water bottles. The good barrier properties and the recyclability are due to the very inert character of PET packaging materials. The high inertness leads to low interactions of the packaging material with the packed foodstuff. As a consequence, the overall migration as well as the specific migration of the monomers ethylene glycol, diethylene glycol and terephthalic acid is extremely low so that it is most unlikely that the current legal migration limits are exceeded under normal conditions of use[1]. In addition, the specific migration limits for the catalyst antimony trioxide or its reaction products with ethylene glycol are far below the migration limit, even for storage times of several years[2].
Increasing knowledge of the mass transport parameters controlling migration from PET as well as its high use level for food packaging material makes this polymer a good candidate for the application of non-experimental migration evaluation i.e. for mathematical migration modelling. However, the use of migration modelling instead of experimental migration tests needs proper determination of relevant parameters of the polymer. Therefore, knowledge of the diffusion coefficients at a particular temperature as well as the temperature dependency of the diffusion coefficients is necessary for the selection of the basic parameter set for the prediction of the migration of organic compounds from PET into contact media.

Current Migration Model

The current migration model is described in detail in Lit[3]. For the prediction of the diffusion coefficients, so-called A_P' and τ values are defined. The dimensionless A_P' parameter can be considered as the conductance of the polymer. Higher values of A_P' lead to increased diffusion coefficients D_P of the migrants in the polymer. The polymer specific term τ represents a portion of the activation energy of diffusion of a migrant in the polymer and has the formal dimension of temperature (K). According to the current migration model, τ is set for different polymers either to τ = 0 K (activation energy E_A = 87 kJ mol^{-1}) or to τ = 1577 K (E_A = 100 kJ mol^{-1}). The actual generally recognized A_P' values for PET are 6.4 at temperatures above the glass transition temperature T_g and A_P' =3.1 below T_g. Both values are used in combination with τ = 1577 K[3].

Results and Discussion

The use of certain τ value is a major simplification of the current migration model and had been done because experimental data for activation energies are very rare in the scientific literature. On the other hand, these τ values were selected conservatively to ensure a general over-estimation of the migration behaviour of any substance from PET, which means that the use of the actual A_P' values lead to worst case migration scenarios for packaging materials.
Figure 1 shows a correlation between the molecular weight of a molecule and their diffusion coefficients at 40 °C (literature data from Lit[4]). As expected, the diffusion coefficients decrease with increasing molecular weight. A clear and precise correlation cannot be derived from the literature data. However, the proposed correlation (dotted line in Figure 1) provides an acceptable fit over the specified range of molecule when considering the potential "inhomogeneity" with respect to PET types of the data sources. The predicted diffusion coefficients with A_P' = 3.1 and τ = 1577 K are also given in Figure 1. It turns out that the predicted values for molecules below and above 60 g mol^{-1} are higher or lower, respectively, than the diffusion coefficients derived from experimental studies.
From the results of this study it is evident and reaffirmed that the current migration model (which was designed conservative on purpose) with the default modelling parameters (A_P' = 3.1, τ = 1577 K) cannot realistically describe the diffusion coefficients.

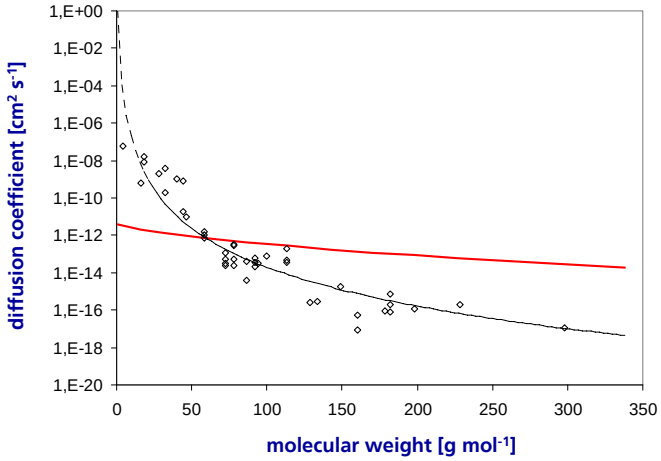

Figure 1: Correlation between the molecular weight and the diffusion coefficients at 40 C (literature data from Lit[4], — predicted according to the current migration model with A_P' = 3.1, τ = 1577 K)

It appears that, along with the underestimation of migration of very small molecules, higher molecular weight compounds with activation energies above 100 kJ mol^{-1} will be overestimated by the current migration model. From a food law compliance point of view such an overestimation will not be critical because the predicted migration will be higher than found in experimental migration tests. As long as predicted migration values are still below the legal specific migration limits for migrants of interest, compliance of the PET bottle is given. The safety margin or the degree of overestimation is, however, not exactly known.
For more realistic migration calculations, as for instance needed for the purpose of the prediction of the cleaning efficiencies of PET recycling processes, such an overestimation is not desirable and, therefore, more accurate modelling parameters should be available and used. As an important result and conclusion of this study the key parameter for more realistic migration modelling is the activation energy of diffusion of a migrant in the PET polymer. Therefore, more attention should be paid in future work to derive these activation energies of diffusions for a set of potential migrants (or model compounds) and to apply these parameters appropriately, either directly through the activation energy approach or through recalculation into more suitable τ values and using more refined A_P' values for modelling migration from PET.

References

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