Determination of the activation energies of diffusion of organic molecules in poly(ethylene terephthalate)

Johann Ewender, Frank Welle

Fraunhofer Institute for Process Engineering and Packaging (IVV), Giggenhauser Straße 35, 85354 Freising, Germany,
email: welle@ivv.fraunhofer.de, phone: ++49 8161 491 724

Introduction

From all plastic packaging materials used for beverages, poly(ethylene terephthalate) (PET) is one of the most inert materials with low interactions between the packaging materials and the foodstuffs. The high inertness leads to low diffusion coefficients. As a consequence, experimental studies on the experimental determination of the migration of polymer impurities or additives failed because the necessarily very low detection limits cannot be reached. Therefore, migration models are often used as an alternative for the confirmation of the food law compliance of PET[1]. In general, one of the key factors of migration modelling is the diffusion coefficient of the migrants in PET. However, the determination of the migration kinetics is very time consuming, labour intensive and expensive.

Aim of this study was therefore the development of a fast and precise method for the determination of the diffusion coefficients and activation energies of diffusion of organic compounds in PET up to temperatures of about 200 °C. The high temperatures are necessary for the fast and precise determination of the migration kinetics of higher molecular weight compounds in PET. From the temperature dependency of the diffusion coefficients the activation energies of diffusion should be calculated using the Arrhenius approach.

Materials and Methods

The applied method for the determination of the diffusion into the gas phase has been published by Vandenburg and Gramshow[2]. We used the same principle, but further developed the method to an automated system. The modified method was able to determine a gas chromatogram every 30 min. Stripes of 1.0 cm x 3.5 cm were given into a cylindric migration cell (14 mm, length: 150 mm). The migration cell was heated and the compounds migrating from the PET bottle wall stripes were purged out of the extraction cell by a helium stream of 20 ml min^{-1}. The migrants were trapped at a temperature of -50 °C. Every 30 min the loaded trap was completely desorbed by heating up to 350 °C within 10 s directly onto the gas chromatograph, where the migrants were separated and quantified. Calibration was achieved by injection of neat standard solutions of the migrants into the migration cell. As the only real contaminant in PET the solvent tetrahydrofurane was used at a concentration of 8.7 ppm.

Results and Discussion

The results of the migration kinetics of tetrahydrofurane (THF) is shown in Figure 1. As a result, the migration of THF follows Fickian laws of diffusion resulting in a linear correlation of the square root of time and the migration. The following diffusion coefficients were determined from the slopes of the linear regression: 1.4 10^{-10} cm^2 s^{-1} (121 °C), 1.1 10^{-9} cm^2 s^{-1} (141 °C), 5.6 10^{-9} cm^2 s^{-1} (159 °C), and 1.3 10^{-8} cm^2 s^{-1} (180 °C). The correlation between the logarithm of the diffusion coefficients of THF in PET and the reciprocal temperature (Arrhenius plot) is shown in Figure 2. From this linear correlation, the activation energy of the diffusion of THF in the investigated PET bottle was determined to 116.5 kJ mol^{-1} (D_0 = 4.8 10^5 cm^2 s^{-1}).

The activation energy determined in this study is in good agreement with literature data measured between 23 °C and 50 °C into water (106.8 kJ mol^{-1}, D_0 = 2.2 10^4 cm^2 s^{-1})[3].
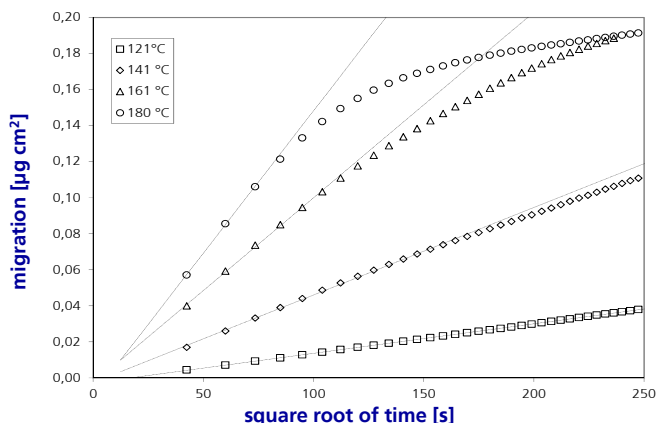

Figure 1: Migration kinetics of tetrahydrofurane from PET (concentration 8.7   1.0 ppm) into the gas phase

Conclusions

Within the study a fast and automated method for the determination of the activation energies of diffusion in PET (or in low diffusive polymers in general) was developed. The method is suitable for the fast and precise determination of diffusion coefficients of migrants in PET at different temperatures. The gas phase migration will provide realistic diffusion coefficients without swelling effects.

For tetrahydrofurane it could be shown, that the diffusion coefficients below the glass transition temperature of about 80 °C follow more or less the same slope in the Arrhenius as found for the diffusion coefficients above the glass transition temperature. It is interesting to note, that the Arrhenius equation obeys over approximately 16 orders of magnitude. This indicates, that for PET bottles the change in the migration behaviour below and above the glass transition temperature seems to be not significant. However, more experimental data for other migrants are necessary to confirm these findings. The developed method is a good tool to establish realistic activation energies of diffusion e.g. for exposure evaluations[4].
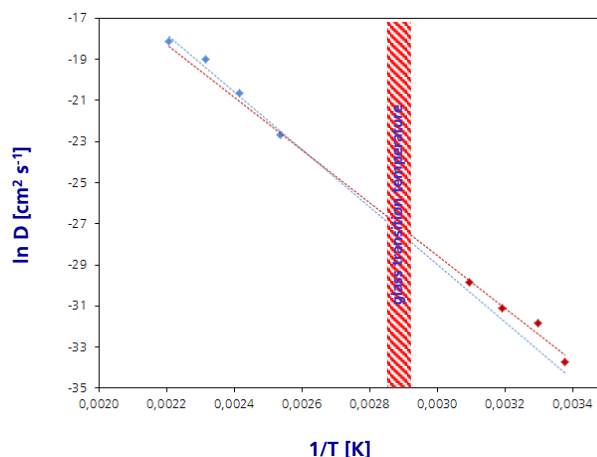

Figure 2: Correlation between the logarithm of the diffusion coefficients of tetrahydrofuran in PET and the reciprocal temperature (Arrhenius plot, blue dots: this study, kinetic into gas phase; red dots: literature data, migration into water[3])

References

[1] C. Simoneau (editor), Applicability of generally recognised diffusion models for the estimation of specific migration in support of EU Directive 2002/72/EC, EU report 24514 EN, **2010**, ISBN 978-92-79-16586-3.

[2] H. J. Vandenburg, J. W. Gramshaw, A rapid method for the determination of diffusion coefficients of migrants and prediction of migration from thermoset polyesters using a dynamic headspace gas chromatography technique, Deutsche Lebensmittel-Rundschau, **1997**, 93(2), 52-56.

[3] F. Welle, R. Franz, Diffusion coefficients and activation energies of diffusion of low molecular weight migrants in poly(ethylene terephthalate) bottles, Polymer Testing, **2012**, 31(1), 93-101.

[4] J. Ewender, F. Welle, Determination of the activation energies of diffusion of small molecules in poly(ethylene terephthalate), Journal of Applied Polymer Science, in press, DOI: 10.1002/APP.38623.