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Fraunhofer Institute for Process Engineering and Packaging IVV

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Analysis of NIAS in PET and evaluation of migration by use of an activation energy based diffusion modelling approach

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Agenda

1. Virgin PET versus recycled PET
   - How to ensure the safety and quality of "virgin" PET
   - Why does the concept for virgin PET not work for recycled PET
2. Evaluation of recycled PET
   - Potential migrants in PET packaging materials
   - Analytical strategies for NIAS in recycled PET
3. Realistic modelling of diffusion in PET
   - How to get "realisitic" diffusion coefficients and activation energies for PET
   - Activation energy based prediction of diffusion coefficients
   - Validation data
   - Back calculation migration to corresponding bottle wall concentration
4. Methods of analysis
   - Methods used for NIAS analysis in recycled PETConclusions for analysis and evaluation of NIAS in recycled PET
   - Conclusions from modelling for analysis and evaluation of NIAS
5. Conclusions

Analysis of NIAS in PET and evaluation of migration by modelling

01

Virgin PET versus recycled PET

How to ensure safety and quality for "virgin" PET

- Monomers or additives for food packaging must be listed in Annex I of EU Regulation 10/2011
- Specific migration limits are given in Annex I of EU Regulation 10/2011
- Specific migration testing of listed substances at conditions according 10/2011 (end of shelf life or forced migration conditions like 10 d at 60 °C)
- Non-intentionally added substances (NIAS) mainly known
  - NIAS typically found in virgin PET
  - NIAS from additives
- Compliance of the packaging materials can be shown based on experimental migration tests or on diffusion modelling and analysis of content in the material
- Test at regular intervals is sufficient for compliance testing

Why does this concept not work for recycled PET

- Target substances in recycled PET basically unknown:
  - Post-consumer substances from all kind of fillings
  - Cross-contamination during recollection (from other fillings including technical products e.g. motor oil, household cleaners, solvents, …)
  - Degradation products of additives and polymers generated during recycling
  - Substances from "misuse" of PET bottles for storage of non-food liquids (e.g. solvents, household and garden chemicals, …)
- Concentrations of contaminants in recycled material depend on:
  - Re-collection system (curbside collection, green-dot systems, deposit, …)
  - Frequency of contamination (flavours, contamination by misuse of bottles)
  - Cleaning efficiency of the washing process (conventional recycling technology) and the deep-cleansing process (super-clean recycling technology)

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02

Evaluation of recycled PET

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Potential migrants in PET packaging materials

Migrants

IAS
intentionally added substances

- Polymer additives
- Monomers
- Catalysts
- …

- Specific migration testing
- Quantification in polymer
- Migration modelling
- Specific Migration Limits (SML)

NIAS
non-intentionally added substances

- Degradation products of polymers and additives
- Impurities of polymers and additives
  Polymerisation side-products
  contaminants
- Post-consumer substances
- …

- Identification and risk assessment on each individual substance

Typical NIAS in virgin PET bottles (examples)

Origin of NIAS	Examples of Substance(s)
Degradation products from PET	
	Acetaldehyde
	2-Methyl-1,3-dioxolane
Impurities from additives and masterbatches	
	Aminobenzonitrile
	Toluene
	Cyclopentanone
Polymerisation side products	
	Linear and cyclic oligomers
Sporadic contamination from masterbatches	
	Chlorobenzene
	Tetrahydrofuran

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Typical additional NIAS in recycled PET samples (examples)

Origin of NIAS	Examples of substance(s)
Flavour substances	
	Limonene
Degradation products during recycling	
	Benzene
Substances from cross contamination	
	Bisphenol A
	Phthalate and adipate esters
Other contaminants	
	…

Analytical strategies for NIAS in recycled PET

NIAS

migration testing
(non target methods)

- Time consuming (10 d at 60 °C)
- Sensitive methods required (detection limits <10 µg/l in food or food simulants)
- Accelerated testing (10 d at 60 °C) in many cases overestimating

- Concentration in food (simulant) is directly available

polymer testing
(non-target methods)

- Fast testing (no storage time) Detection limits of 1 mg/kg in PET usually sufficient (for SML 10 µg/kg in food)
- Routine test methods available at the recycler or packaging manufacturer

- Diffusion modelling needed for migration evaluation

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03

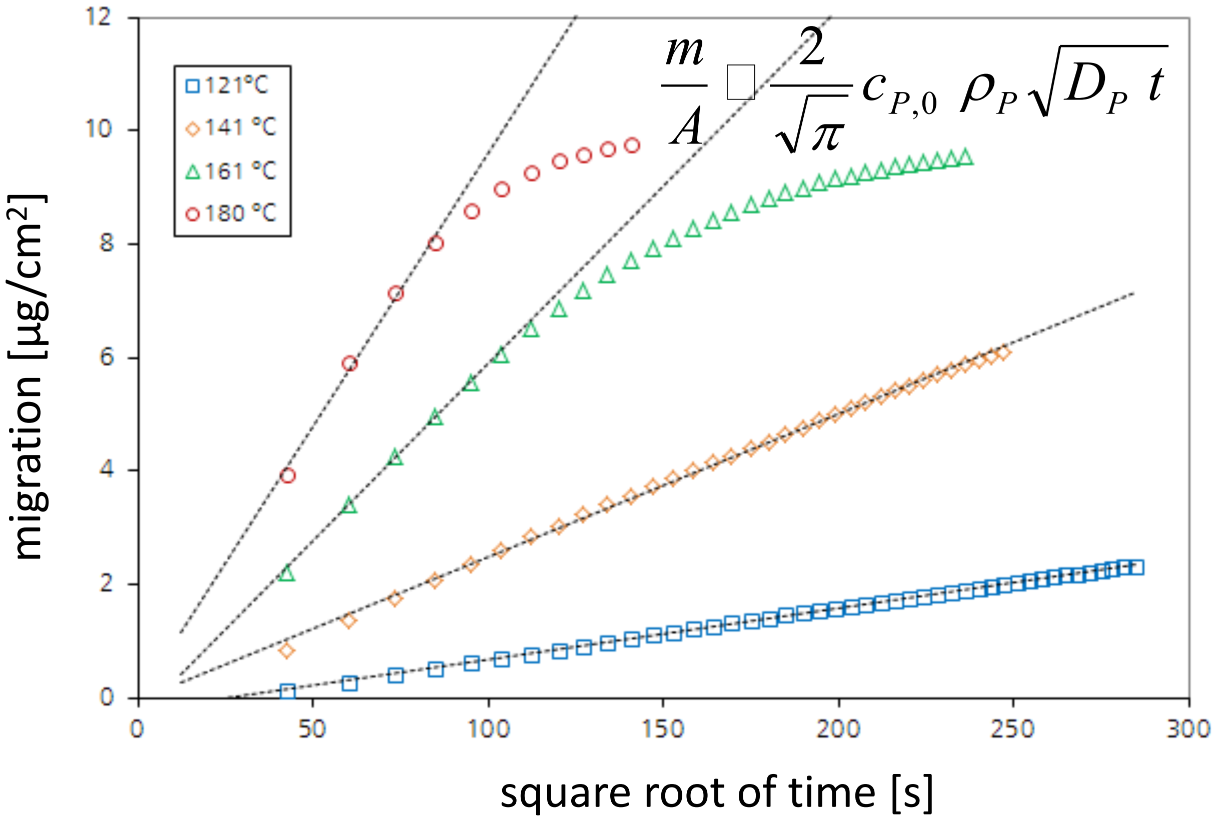
Realistic modelling of diffusion in PET

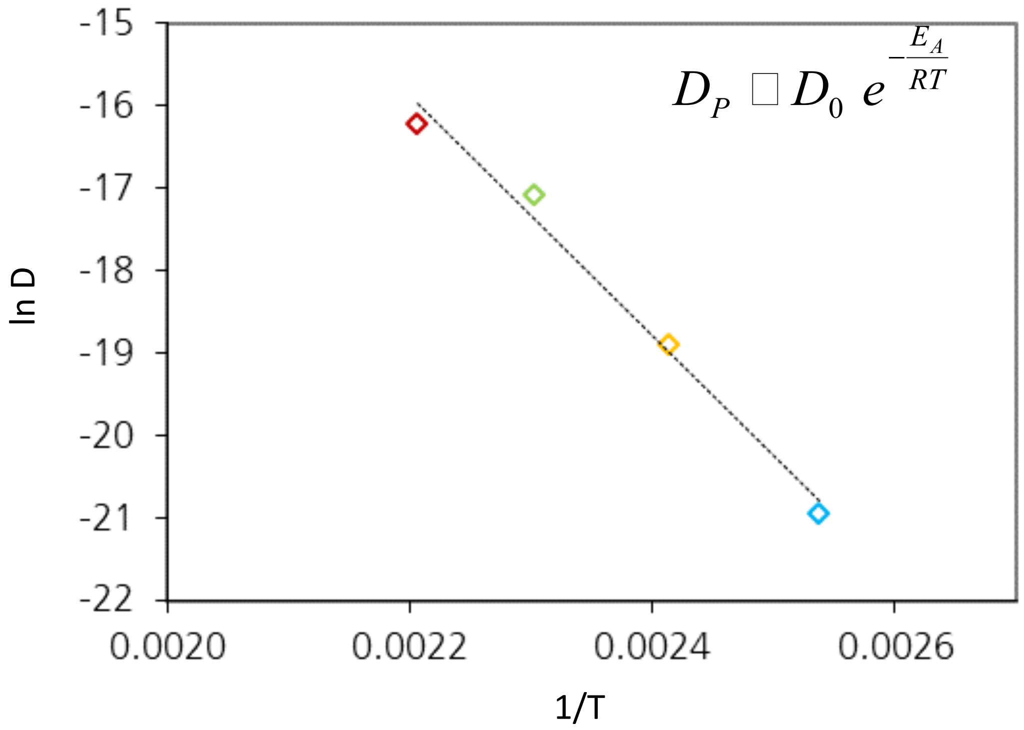
How to get "realisitic" diffusion coefficients and activation energies for PET

- Diffusion coefficients of potential migrants in PET are rare in the scientific literature
- Food simulants like 50% or 95% ethanol are swelling PET especially at high temperatures
  - Swelling of the polymer increases the diffusivity
  - leads to unrealistically high diffusion coefficients
  - Leads to unrealistically migration values
- Our approach to generate diffusion coefficients:
  artificially spiked PET materials (similar to a Challenge Test)
  - Spiking during PET bottle (or sheet) manufacturing with spiking levels of up to 1000 mg/kg
  - Diffusion coefficients were derived from migration kinetics
  - Activation energies were derived from kinetics at different temperatures (in minimum four temperatures!)
  - Only migration kinetics into non-swelling simulants or into the gas phase were considered

Determination of Diffusion coefficients and Activation Energies of Diffusion

- Desorption into gas phase from spiked sheets
- Example: Toluene





Activation energy from Arrhenius Equation:

E_A = 121.4 kJ/mol

D_0 = 3.5 10^6 cm^2/s

Lit: J. Ewender, F. Welle, Determination of the activation energies of diffusion of organic molecules in poly(ethylene terephthalate), Journal of Applied Polymer Science, 2013, 128(6), 3885-3892

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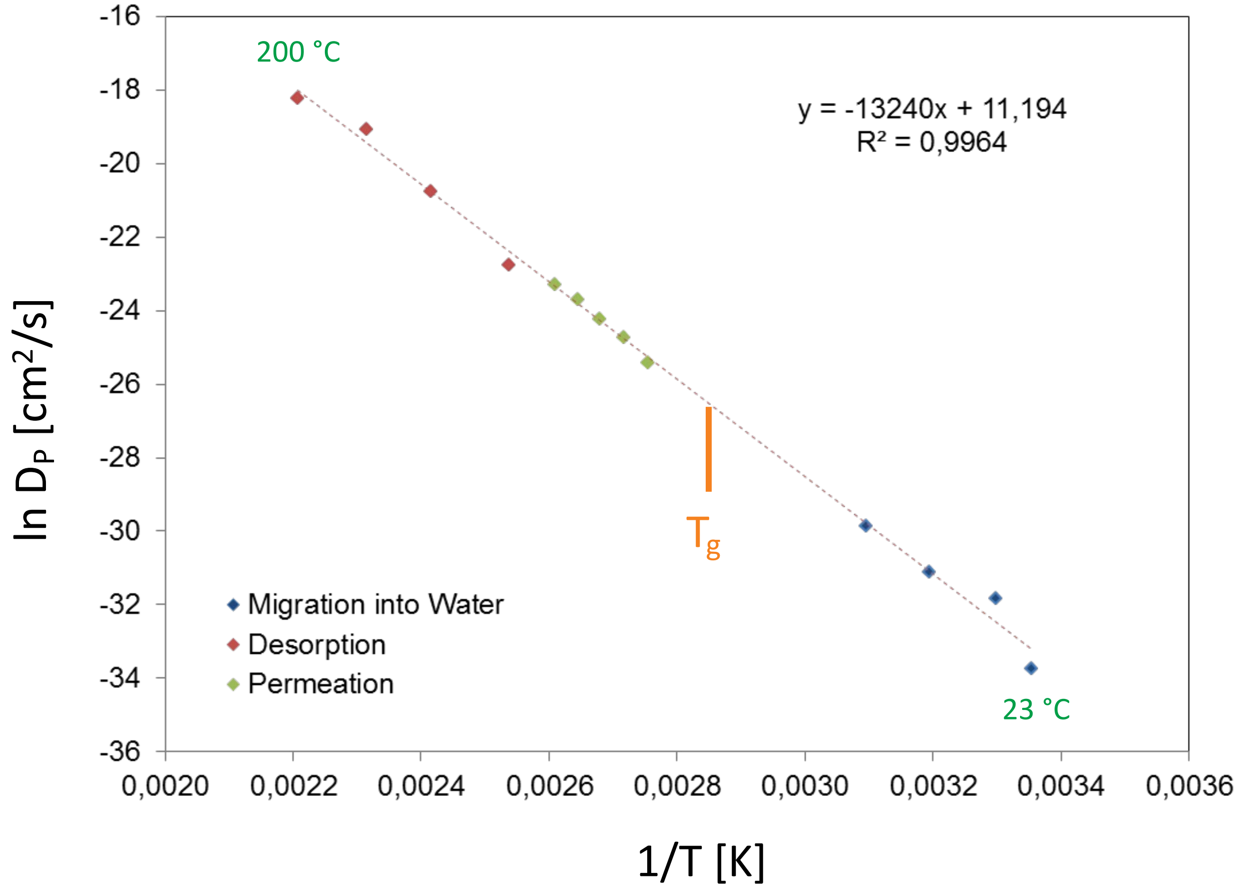
Determination of Activation Energies of Diffusion

Comparison of different methods for determination of diffusion coefficients

Example: Tetrahydrofuran THF



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

Migration into Water
E_A = 112.3 kJ/mol

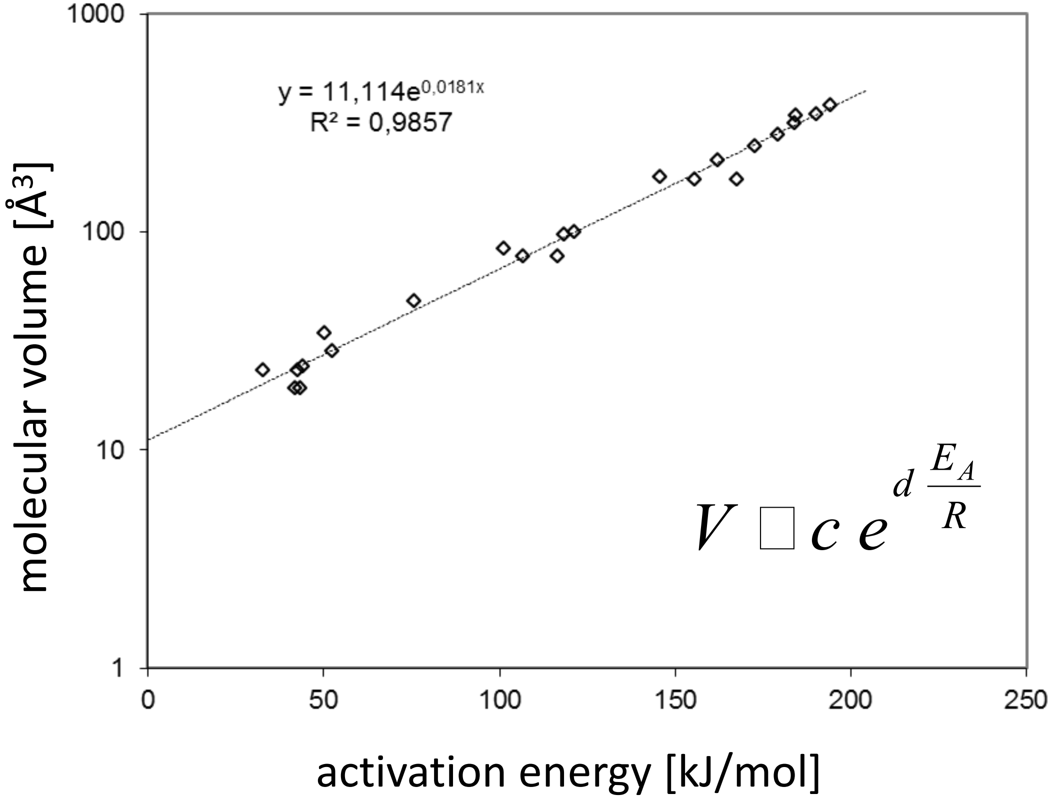
Permeation through thin films
E_A = 121.5 kJ/mol

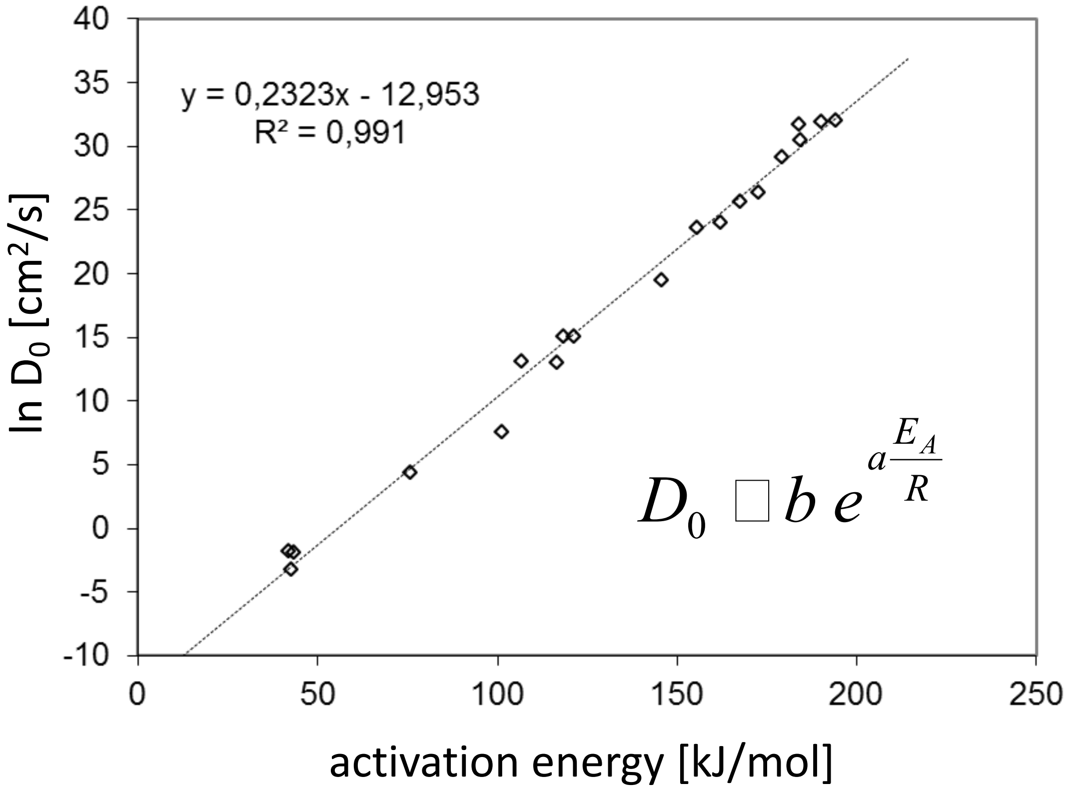
Desorption from spiked films
E_A = 116.4 kJ/mol

Ewender, J. and F. Welle (2022). "A new method for the prediction of diffusion coefficients in poly(ethylene terephthalate)—Validation data." Packaging Technology and Science plus additional data.

Correlation E_A versus Molecular Volume and Pre-exponential factor D_0

- Activation energies of diffusion
  - 16 activation energies for organic molecules, 8 activation energies for permanent gases and water from literature





Lit: F. Welle, A new method for the prediction of diffusion coefficients in poly(ethylene terephthalate), Journal of Applied Polymer Science, 2013, 129(4), 1845-1851

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Prediction of D_P from Molecular Volume

Arrhenius Equation: $$D_P = D_0 \, e^{-\frac{E_A}{RT}}$$

Two correlations: $$D_0 = b \, e^{a \frac{E_A}{R}}$$

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

$$E_A = \frac{R}{d}\left(\ln \frac{V}{c}\right)$$

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

	Activation Energy based Modelling Parameters for PET
a	$1.93 \, 10^{-3}$ 1/K
b	$2.37 \, 10^{-6}$ cm^2/s
c	11.1 $Å^3$
d	$1.50 \, 10^{-4}$ 1/K
V	molecular volume in $Å^3$
T	Temperature in K

- Parameters a to d: Slopes and intercepts of correlations V versus E_A and D_0 versus E_A
- The parameters have a physical background
- Prediction possible when substance is not clearly identified but if molecular volume can be estimated
- Estimation V from molecular weight MW: V [$Å^3$] ≈ MW [g/mol] * 1.13 [$Å^3$*mol/g]

Lit: F. Welle, A new method for the prediction of diffusion coefficients in poly(ethylene terephthalate), Journal of Applied Polymer Science, 2013, 129(4), 1845-1851

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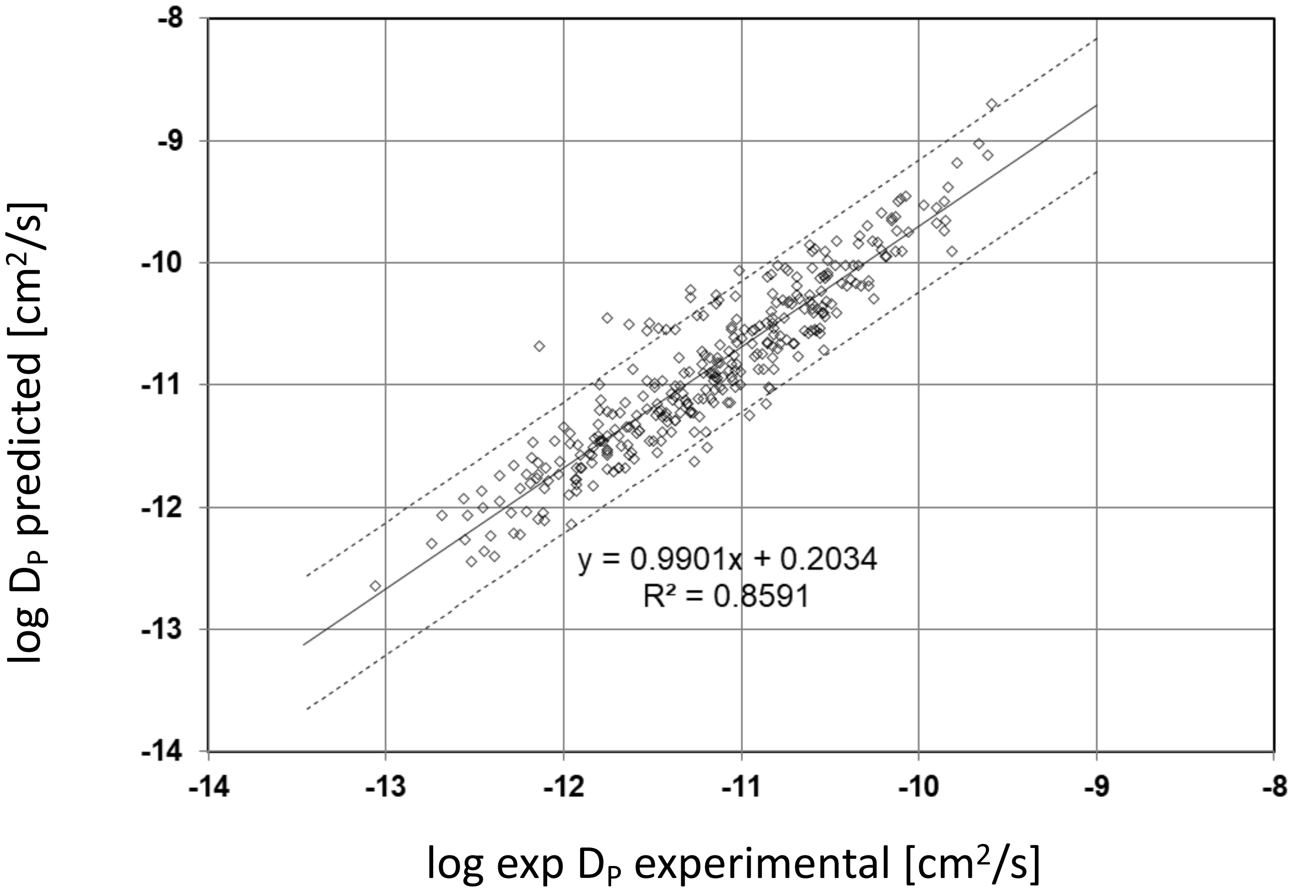
Validation data

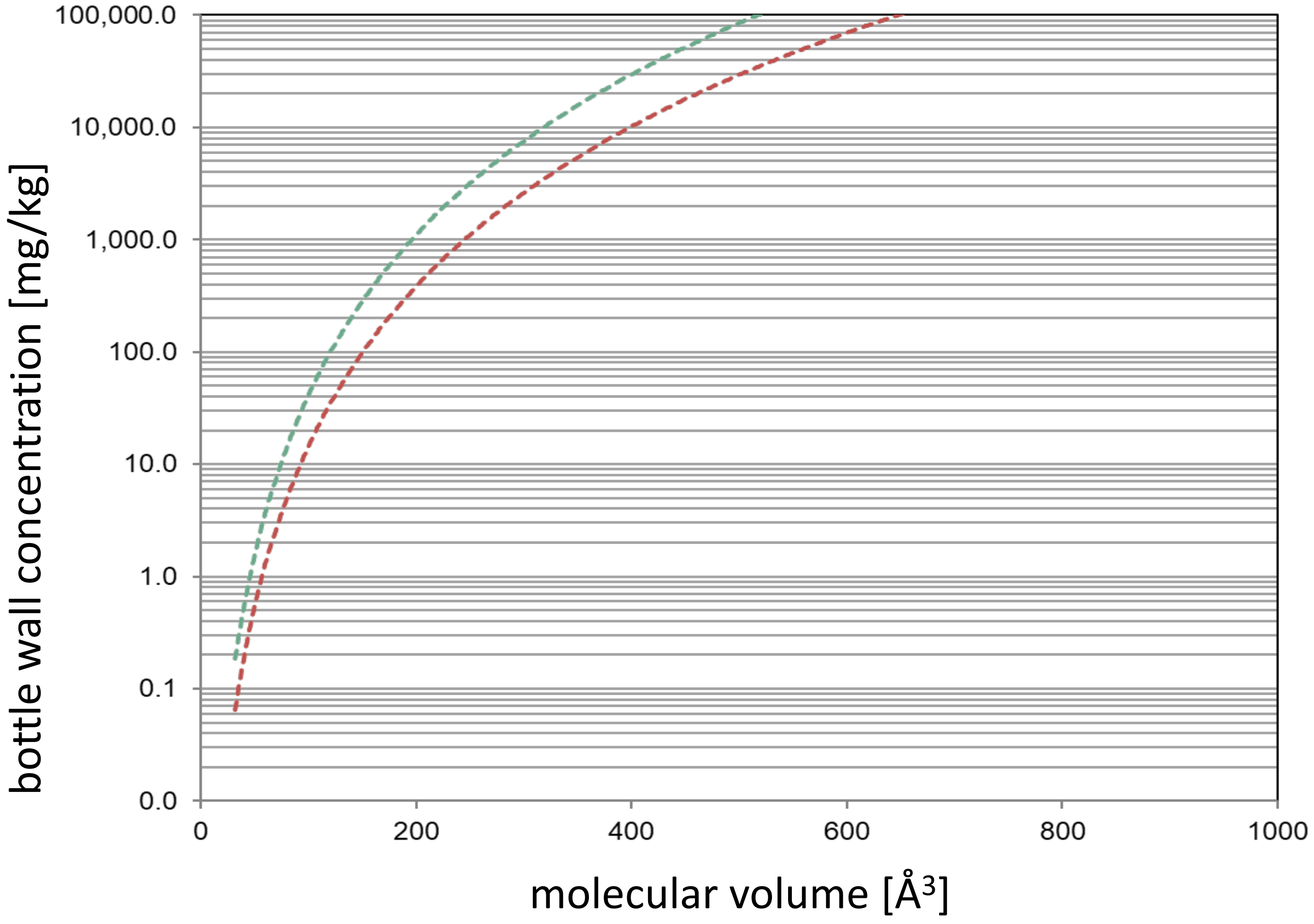
263 diffusion coefficients from 66 different substances determined at temperatures between 40 °C and 120 °C



- The prediction model slightly over-estimates the real migration by a factor of 1.3 in average.
- Reduction of the molecular volume of 20% results in an average over-estimation of 3 of the migration in average.
- With 20% reduction of molecule size the predicted diffusion coefficients are in any case higher as the experimental diffusion coefficients.

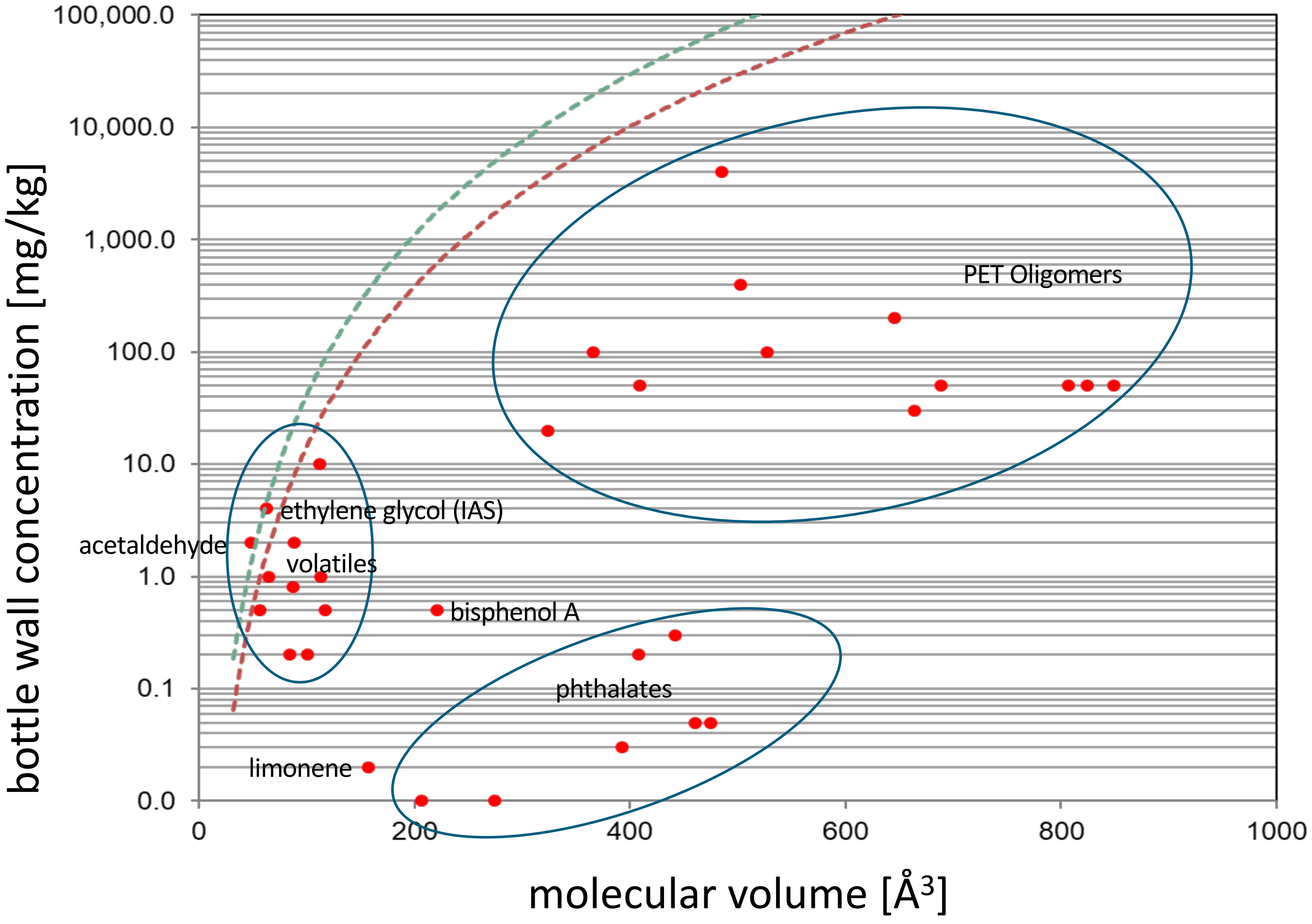
Ewender, J. and F. Welle (2022). "A new method for the prediction of diffusion coefficients in poly(ethylene terephthalate)—Validation data." Packaging Technology and Science **35**(5): 405-413.

Back-calculation migration → corresponding bottle wall concentration Calculated PET bottle wall concentrations corresponding to 10 µg/l



- Prediction of the maximum concentration correlating with a migration limit of 10 µg/l
- 10 µg/l migration after storage for 365 d at 25 °C (6 dm^2, 1 kg food)
  green line
- Reduction of the molecular volume of 20% as worst case
  red line
- Realistic but still over-estimative migration modell based on activation energies of diffusion

Calculated PET bottle wall concentrations corresponding to 10 µg/l and typical concentrations of components



green line: predicted with molecular volume

red line: predicted with molecular volume -20% (worst case, but still realistic)

red points: Experimentally determined concentrations of NIAS in "super-clean" recycled PET

storage conditions 365 d at 25 °C (6 dm^2, 1 kg food)

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Methods of analysis

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Methods used for NIAS analysis in recycled PET

- Non-target screening for volatile NIAS
  - Headspace gas chromatography (FID, MS, …)
  - Thermodesorption coupled with gas chromatography (FID, MS, …)
- Non-target screening for medium-volatile NIAS
  - Extraction of polymer followed by gas chromatography (FID, MS, …)
- Non-target screening for non-volatile NIAS
  - Extraction of polymer followed by HPLC MS
- Target analysis on specific substances
  - Benzene
  - Bisphenol A
  - Phthalate and adipate esters
  - PET linear and cyclic oligomers
  - Additive degradation products?

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Conclusions from modelling for analysis and evaluation of NIAS

- Most of the NIAS typically found in recycled PET are far below the concentrations in PET corresponding with a migration of 10 µg/l
- The most critical substances are small and volatile NIAS
- Headspace gas chromatography is therefore the most important method to determine NIAS in post-consumer PET recyclates
- Substances of which a genotoxic potential cannot be excluded need a lower migration limit (in absence of specific limits, 0.15 µg/l according TTC concept).
  - Migration and concentration in bottle wall are proportional
  - Calculation of maximum limit in bottle wall by division with factor 67 (10 µg/l → 0.15 µg/l)
- In this case and in order to cover polar small substances also medium volatile NIAS are relevant → extraction & liquid injection GC
- Non-volatiles have a very low migration potential, migration not expected
  - Non-target screening by LC-MS at actual state of knowledge not necessary

Application Note for the Applied Headspace Method

APPLICATION NOTE

Gas Chromatography

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Determination of Benzene, Acetaldehyde and Limonene in Polyethylene Terephthalate by Headspace GC

Introduction

Polymers play an ever-expanding role in our everyday lives. Some are easy to identify, such as food packaging, but many others are hidden in the everyday things all around us, from automotive parts to electronic circuit boards, and the insulation of houses and buildings. The road to our current polymer-infused world began taking shape in the mid-1900s. In 1950, global polymer production was about two million tons[1]. In the early 1970s, a trend of increasing polymer production began to emerge[2]. By the year 2018, global polymer production was at about 360 million tons, with revenue of more than 700 billion USD, and packaging was long established as the front runner in polymer use[3].

- Free available in the internet
- All details of the headspace method are given
- Details for calibration of benzene, acetaldehyde and limonene are given
- Method is suitable for companies or recyclers (100% control)
- In Europe lots of PET recyclers have established this headspace method in their quality control lab

https://perkinelmer.cl/wp-content/uploads/2021/09/Determination-of-Benzene-Acetaldehyde-and-Limonene-in-Polyethylene-Terephthalate-by-Headspace-GC.pdf

Conclusions: How to evaluate NIAS in recycled PET?

- Non-target screening tests on PET (e.g. Headspace GC, extraction followed by GC, HPLC for special target substances like oligomers and phthalates)
- Low molecular weight substances are the most critical NIAS
- Identification of NIAS (or estimation of molecular weight/volume if identification is not possible)
- Quantification or semi-quantification of substances found in recycled PET
- Prediction of diffusion coefficient from molecular volume or molecular weight based on a "realistic" activation energy based prediction model (for critical compounds: Experimental determination of diffusion coefficients)
- Calculation of the migration from the concentration in recycled PET and the predicted diffusion coefficient (molecular volume -20% as worst-case, but still realistic)
- For production control: Correlation between concentration in preforms/bottles and a migration limit of 10 µg/l at the end of product shelf life
- If the analytical method is installed at the recycler company a 100% control of each batch can be achieved

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Thank you for your attention

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