

MDC Tec Systems GmbH

Provinostrasse 52
86153 Augsburg
Germany

ANNEX 8.5
Estimation of polymer diffusion properties to be used for migration modeling in support of exposure and material safety assessment.

Dr. Rainer Brandsch, MDC Tec Systems GmbH, Augsburg, Germany

Theoretical considerations
Estimation procedures for diffusion coefficients

Estimation procedures for diffusion coefficients rely on a number of physico-chemical parameters. Most of them need to be determined experimentally with more or less efforts. From a feasibility/economic point of view experimental determination of the required parameters in most of the published estimation procedures is of limited applicability, reason for which simple empirical estimation procedures as presented in [Fehler! Textmarke nicht definiert.] were developed. The estimation procedure uses an Arrhenius type relationship to consider the dependence of diffusion coefficients from temperature (see equation 1). Rationales for the empirical estimation procedure can be found in [i].

Equation 1
$$D_P = 10^4 \cdot \exp \left[A_P - 0.1351 \cdot M_r^{2/3} + 0.003 \cdot M_r - \frac{10454}{T} \right] \left(\frac{\text{cm}^2}{\text{s}} \right)$$

- | | |
|-----------------------|---|
| D_P | - Diffusion coefficient ($D_0 = 10^4 \text{ cm}^2/\text{s}$) |
| $A_P = A_P' - \tau/T$ | - polymer specific constant (τ – activation energy increment) |
| M_r | - relative molecular mass of migrant in Dalton |
| T | - temperature in K |
| E_A | - reference activation energy (= $R \cdot 10454 = 86,9 \text{ kJ}$, $R = 8,314 \text{ J/K} \cdot \text{mol}$) |

The dimensionless polymer (matrix) specific constant (A_P), the relative molecular weight of the migrant ($-0.1351 \cdot M_r^{2/3} + 0.003 \cdot M_r$) and the reference activation energy (constant $10454 \cdot R$) are the three parameters which build up the Arrhenius equation for estimation of diffusion coefficients of organic molecules solved in polymers.

The A_P -value itself is temperature dependent according to the relationship $A_P = A_P' - \tau/T$ built from two parameters A_P' which is temperature independent and τ the temperature increment serving as an adjustment parameter to the reference activation energy for individual polymers.

The parameter A_P' and the relative molecular weight dependence build up the temperature independent pre-exponential factor of the Arrhenius equation (D_0). The original empiric relationship published in 1994 [ii] by Piringer missed the term $0.003 \cdot M_r$ which was introduced later [iii] by the author to adjust for dependency of diffusion coefficients of organic molecules solved in polymers from molecular weight to experimental findings published in scientific literature. According to the author the

applicability of the estimation procedure in its final form [Fehler! Textmarke nicht definiert.] is limited to a molecular weight range of 20 to 2.000 g/mol (or Dalton).

The constant $10454 \cdot R$ is a fixed value for all polymers resulting from theoretical considerations of the author. It can be understood as the reference activation energy for the diffusion process of hydrocarbons in an amorphous polyethylene matrix. The parameter "tau" is introduced by the author to expand the applicability of the estimation procedure from polyethylene to other polymers. The sum of the constant 10454 with the temperature equivalent tau multiplied by the gas constant R give the activation energy (E_A) of the diffusion process for organic molecules dissolved in polymers.

Diffusion modeling was introduced in food contact materials legislation in 2001 with the sixth amendment to Directive 90/128/EEC [iv] after finishing the EU project dedicated to the validation of the estimation procedure for diffusion coefficients of molecules dissolved in polymers based on A_P -values [v]. The estimation procedure for diffusion coefficients based on polymer specific constants as defined in [Fehler! Textmarke nicht definiert.] became part of the Practical Guide supporting the Plastics Directive. The Chapter in the Practical Guide dedicated to Diffusion Modeling was replaced in 2010 by the Scientific and Technical Report "Applicability of generally recognized diffusion models for the estimation of specific migration in support of EU Directive 2002/72/EC" on Migration Modeling [vi] and updated in 2015 by the JRC Technical Report "Practical guidelines on the application of migration modelling for the estimation of specific migration - In support of Regulation (EU) No 10/2011 on plastic food contact materials." [vii] of the European Commission Joint Research Centre - Institute for Health and Consumer Protection (JRC-IHCP).

For drinking water contact materials, a dedicated Modeling Guideline in support of safety assessment of plastics in contact with drinking water was set up by the German Umweltbundesamt [viii].

The authors of the A_P -value based estimation procedure for diffusion coefficients never gave a reliable phenomenological interpretation of the parameters used in their estimation procedure. In the following paragraphs an attempt will be made to give a phenomenological interpretation of the parameters used in the A_P -value based estimation procedure for diffusion coefficients of organic molecules dissolved in polymers.

Relative molecular weight: It is generally recognized and well documented in the literature that in a first approximation diffusion of organic molecules in polymers depends on the size of the molecule, i.e. small molecules exhibit high and big molecules exhibit low diffusion coefficients in a given polymeric matrix. The molecular weight of the molecule may be used in a first approximation as a measure for its size. This attempt is reasonable for molecules predominantly build from carbon atoms but becomes less reliable for molecules containing heteroatoms like, chlorine, bromine, silicon, etc. A more precise measure for the molecule size might be its volume, but less available in practice.

Polymer specific constant: From a phenomenological point of view the polymer (matrix) specific A_P -value can be interpreted as a measure for the intrinsic mobility and free volume of the polymer matrix at molecular level. Polymers with high intrinsic mobility and free volume show high A_P -values and polymers with low intrinsic mobility and free volume show low A_P -values. Diffusion of organic molecules in polymers requires cooperative movement of the molecule and the polymer under the influence of a difference in the chemical potential between the two adjacent media.

Intrinsic mobility and free volume of polymers is related to polymers in the amorphous state. In the crystalline state the mobility of the polymer segments is inhibited and no free volume is available reason for which diffusion rates of organic molecules become extremely low. At room temperature crystalline regions in a polymer can be considered impermeable for organic molecules. In addition, thermodynamic constraints contribute to exclusion of organic molecules from the crystalline phase of the polymer towards the amorphous phase. The temperature influence on the polymer and migrant mobility is accounted for by the activation energy of the diffusion process.

Activation Energy: The A_P -value based estimation procedure works with fixed activation energy for all polymers and molecules - the reference activation energy - and ignores the fact that the activation energy of the diffusion process depends on the nature of the polymer and the nature of the diffusing molecule. The author himself gives in Appendix I to [i] an overview of literature data for diffusion

related activation energies. The attempt to estimate diffusion coefficients of organic molecules dissolved in polymers with an Arrhenius like relationship based on a fixed activation energy given by the constant $10454 \cdot R$ for all polymers is a significant deficiency of the A_P -value related estimation procedure. The constant 10454 multiplied by the gas constant $R = 8.3145 \text{ (J/mol/K)}$ gives the reference activation energy of $E_A = 86.92 \text{ (kJ/mol)}$. Compared to literature data this value for the activation energy is at the lower end of activation energies for diffusion processes of organic molecules in polymers.

Due to the use of the low end activation energy at a low temperature, e.g. room temperature (20-25°C), diffusion coefficients estimated for small molecules (low molecular weight) are quite accurate, but for big molecules (high molecular weight) high overestimates result which in addition are dependent from the nature of the polymer under investigation.

Tau-value: According to the authors, they decided to keep Equation 1 functional by working only with a minimum number of specific variables. Therefore, in a first approximation they arbitrarily gave tau two values, i.e. 0 and 1577. Because tau is a temperature increment it adds to the reference activation energy and the corresponding activation energies of $E_A = 87 \text{ kJ/mol}$ ($\tau = 0$) and 100 kJ/mol ($\tau = 1577$) result.

From phenomenological point of view the value $\tau = 0$ can be attributed to polymers which are completely amorphous and the value $\tau = 1577$ to polymers exhibiting a significant percentage of crystallinity. Influence of crystallinity on the diffusion behavior is caused by the volume fraction of the crystalline phase in the polymer matrix which (i) reduces mobility of the amorphous regions in its vicinity and (ii) is itself impermeable for a migrant. Decreased mobility and free volume of the matrix will cause an increase in diffusion activation energy.

According to the A_P -values published by the author in [**Fehler! Textmarke nicht definiert.**] the value $\tau = 1577$ was attributed to the polymers high density polyethylene (HDPE), isotactic polypropylene (iPP) and polyethyleneterephthalate (PET) all of which exhibit significant crystallinity and the value $\tau = 0$ was attributed to the amorphous polymers low density polyethylene (LDPE) and polystyrene (PS). $\tau = 0$ was attributed to polyamide 6,6 (PA66) too, despite of the fact that this polymer exhibits significant crystallinity. This is reasonable under worst case considerations and due to the fact that a very limited data set namely only a few migration data for a few migrants were available, which did not allow a more detailed interpretation.

"Upper limit" and "mean" polymer specific constants and related diffusion coefficients

Polymer specific constants are calculated from diffusion coefficients determined experimentally by means of Equation 1. From a set of diffusion coefficients related to a specific polymer a set of A_P -values results. A_P -values for a polymer scatter due to various reasons like: the fixed activation energy assumed in Equation 1, scattering in the experimental data or scattering in polymer morphology of the investigated sample. For a set of A_P -values characterizing a polymer a mean value and an upper limit value defined as the upper bound 95% confidence interval can be calculated.

The "upper limit" polymer specific constant (A_P^*) (upper limit value indicated by "***") is of legal interest when assessing compliance of materials with substance specific restrictions by use of diffusion modeling. Diffusion coefficients estimated with Equation 1 by use of upper limit A_P^* -values will result in upper limit diffusion coefficients (D_P^*) and the diffusion model will generate overestimated migration or emission values.

The "mean" polymer specific constant (A_P) is of interest if a realistic migration or emission value is expected. The diffusion model will generate realistic migration values based on "mean" polymer specific constants respectively realistic diffusion coefficients which can be expected to be close to the corresponding experimental result. However, a risk of underestimation exists.

Correlation of polymer specific constants with the glass transition temperature of polymers

Plotting "mean" and "upper limit" polymer specific constants for well-defined polymers (no reactor blends like HIPS) as published by [Fehler! Textmarke nicht definiert.] against the glass transition temperature of the polymers [ix] a linear correlation with a correlation coefficient of $R^2 = 0.9582$ respectively $R^2 = 0.9773$ is observed:

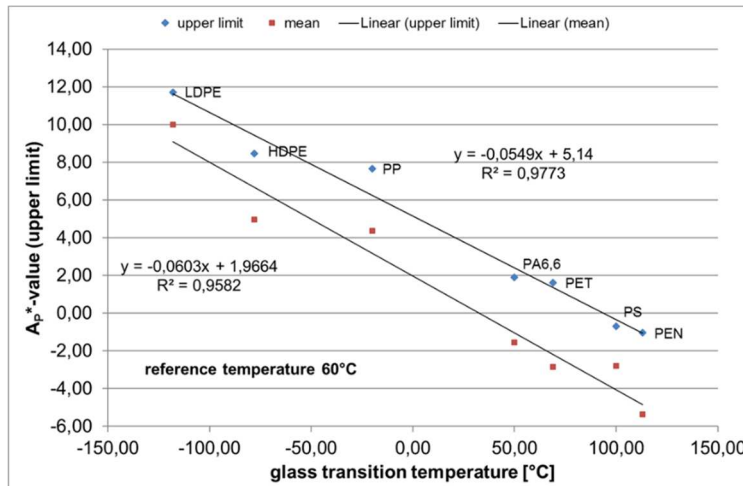


Figure 1 Correlation of mean polymer specific constants A_p (lower line) and upper limit polymer specific constants A_p^* (upper line) with glass transition temperature of polymers T_g at a reference temperature of $T = 60^\circ\text{C}$

Polymer specific constant published later as outcome of the EU-Project "Certified Reference Materials" [xii] were considered in the Scientific and Technical Report on "Applicability of generally recognized diffusion models for the estimation of specific migration in support of EU Directive 2002/72/EC" [v] and support the original finding, i.e. linear correlation of the polymer specific constants with the glass transition temperature of the polymer.

Plotting "upper limit" polymer specific constants for well-defined polymers (no reactor blends like HIPS and PP-rubber or block-copolymers like SBS) against the glass transition temperature of the polymers [ix] a linear correlation with a correlation coefficient of $R^2=0.9331$ is observed (see Figure 2):

Equation 2 $y = -0,0668 \cdot x + 4,7417$

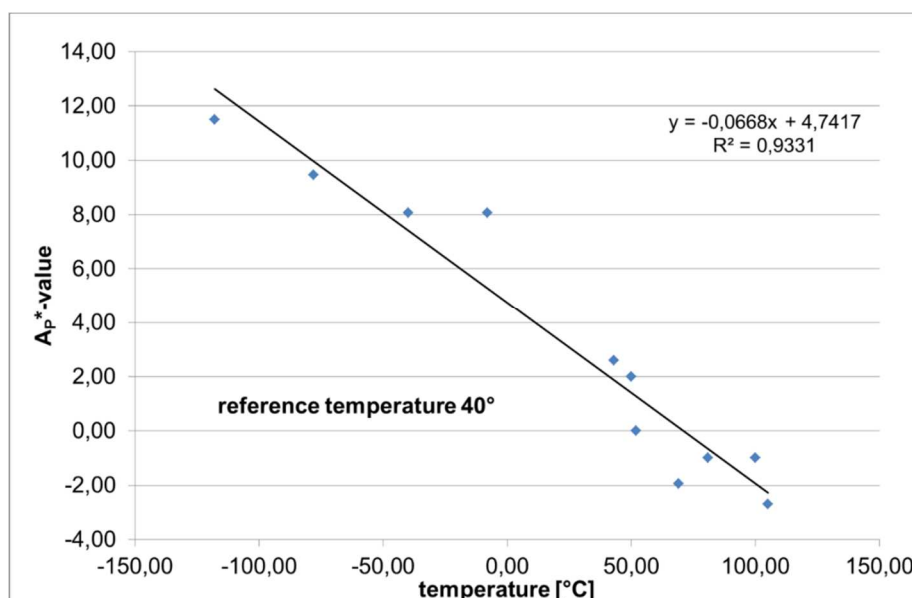


Figure 2 Correlation of mean polymer specific constants A_P with glass transition temperature of polymers T_g at a reference temperature of $T = 60^\circ\text{C}$

Table 1 Upper limit polymer specific constants ($A_P^* = A_P^* - \tau/T$) at $T = 40^\circ\text{C}$ from $[\eta]$ and glass transition temperatures for polymers from [Fehler! Textmarke nicht definiert.]

Polymer	T_g [°C]	Crystallinity	A_P^* -value	τ	A_P^* -value [at 40°C]
LDPE	-118		11.50	0	11.50
HDPE	-78	expected	14.50	1577	9.46
PP, isotaktic	-8	expected	13.10	1577	8.06
PP, random	-40	expected	13.10	1577	8.06
PET	69	expected	3.10	1577	-1.94
PVC, rigid	81		-1.00	0	-1.00
PS	100		-1.00	0	-1.00
PA6	52	expected	0.00	0	0.00
PA66	50	expected	2.00	0	2.00
PA12	43	expected	2.60	0	2.60
PMMA	105		-2.70	0	-2.70

Glass transition temperatures reported for polymers scatter due to the fact that the determined values depend on the method of determination as well as from the history of the sample investigated. However, this scattering does not alter the general finding that a linear dependence of polymer specific constants from glass transition temperature of polymers exists. Similar a linear relationship between mean A_P -values and glass transition temperature of polymers exists.

Based on the above linear correlation it is possible to identify the upper limit A_P^* -value of a polymer from its T_g by interpolation. Knowing the upper limit A_P^* -value of a polymer means knowing the diffusion properties of a polymer and hence prediction of upper limit diffusion coefficients of organic molecules dissolved in the polymer is possible.

The highest deviation from the linear correlation is observed for polypropylene (PP) where the A_P^* -value is above the correlation line and for polyethyleneterephthalate (PET) where the A_P^* -value is below the correlation line. The higher A_P^* -value for PP is caused by allocation of all PP types whether pure isotactic or with ethylene co-monomer content in one and the same category. The ethylene co-monomer content has a significant impact on the glass transition temperature of the PP and hence on its diffusion properties. The lower A_P^* -value for PET is observed, because the dataset was used, which describes the diffusion properties of PET below its glass transition temperature. Furthermore, both polymers exhibit significant crystallinity which has as well an impact on their diffusion behavior which in practice cause more pronounced scattering of the experimental data.

Based on the polymer specific constants (A_P -values) of a polymer and the molecular weight of the migrant the diffusion coefficient of the migrant in the polymer can be estimated by the Arrhenius type dependence from temperature without any experimental work. For validation purpose of the linear correlation between polymer specific constants and glass transition temperature a polymer with unknown diffusion properties was selected and investigated experimentally with respect to its diffusion behavior.

Migration modeling under repeated use conditions

Discussion and outlook

Polymer diffusion properties are well known for high volume polymers on the market but are missing for most specialty polymers used in consumer products and packaging. Understanding the migration and emission behavior of materials which are strongly influenced by the diffusion properties of polymers makes related consumer exposure and safety assessment of materials possible. Diffusion rates of components in materials are in most of the cases the rate determining step in migration or emission processes contributing to the overall mass transfer.

An extended estimation procedure for polymer diffusion properties by interpolation of diffusion properties of well characterized polymers expressed as polymer specific constants (A_P -values) is considered based on the observation that the polymer specific constants exhibit a linear correlation with the glass transition temperature (T_g) of the polymers. The linear correlation between A_P -value and T_g extends the applicability of diffusion modeling to nearly any homogeneous polymer based on organic material including multilayer structures for which the glass transition is available or can be determined.

Based on the polymer specific constants (A_P -values) of a polymer and the molecular weight of the migrant the diffusion coefficient of the migrant in the polymer can be estimated by the Arrhenius type dependence from temperature without any experimental work.

The simplifying assumptions and inbuilt limitations of the A_P -value based estimation procedure for diffusion coefficients of organic molecules in polymers bear implications with respect to usability of the approach.

As a consequence future work needs to focus on improved estimation procedures for diffusion coefficients which consider more precisely the dependence of diffusion coefficients from size of the molecule in the various polymer based materials on the market. The size of the migrant needs to be considered as contribution to the activation energy of the diffusion process, to overcome the inbuilt deficiency of the A_P -value based estimation procedure for diffusion coefficients of organic molecules solved in polymers.

Annex

Impact of polymer chain mobility and free volume on the polymer specific constants (A_p -value)

Addition of plasticisers will change the mobility and free volume of the polymer. This effect is best described for PVC where the polymer specific constant (A_p -value) changes when adding plasticisers to rigid PVC. An upper limit A_p^{**} -value of -1 is observed for rigid PVC and an upper limit A_p^{**} -value of 14.5 is observed for PVC plasticized with 30% of typical plasticizers like Diethylhexylphthalate (DEHP), Diethylhexyladipate (DEHA), Diisononylphthalate (DINP) and Acetyltributylcitrate (ATBC). A linear dependence of the A_p -value from the plasticizer percentage is observed [x].

Table 2 Plasticizer content in [%] of PVC samples investigated (DEHP - diethylhexyl phthalate; DEHA - diethylhexyladipate; DINP - diisononyl phthalate; ATBC - acetyltributylcitrate)

Sample No.	SP1	SP2	SP3	SP4	
DEHP [%]	0,5	8,9	16,4	28,2	
Sample No.	SP5	SP6	SP7	SP8	SP9
DEHA [%]		28,2		16,6	
DINP [%]	28,2		16,6		
ATBC [%]					16,6

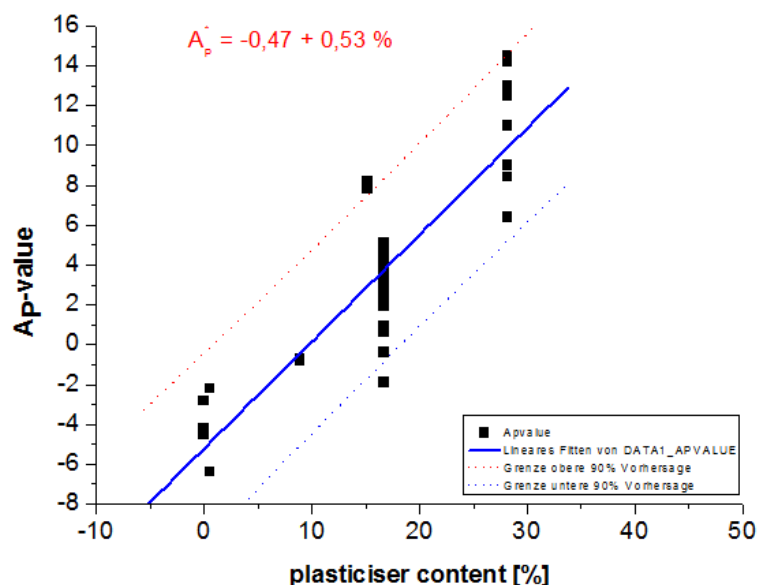


Figure 3 Correlation of polymer specific constants A_p with percentage of plasticizer in PVC

In the same time the glass transition temperature of PVC will change according to figure 3 of [xi] from 350 K to 270 K. The dependence of glass transition temperature from the mass fraction of DEHP is fairly linear.

Another example from practice is the diffusion behavior of polyamide 6 (PA6), which depends strongly on humidity. When a monolayer PA6 film is brought into contact with aqueous media (e.g. food simulants like water, acetic acid 3% or ethanol 10%) completely different diffusion properties are

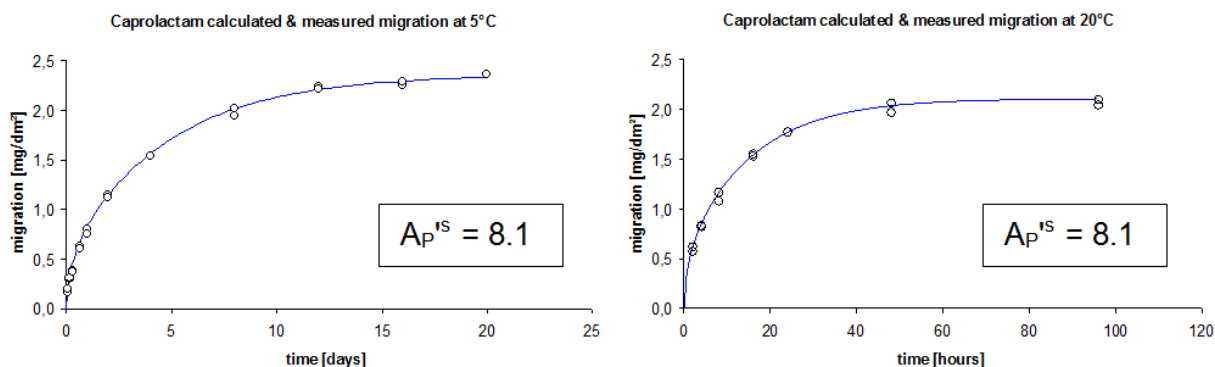
observed compared to a polyamide 6 film under ambient conditions (approximate 23°C and 50% relative humidity) because water acts as plasticizer for polyamide 6. The water content of PA6 will be approximate 8.5% when in direct contact with water and approximate 3.0% under ambient conditions.

Kinetic migration investigations of caprolactam from a PA6 film with the aqueous food simulants water, ethanol 10% and acetic acid 3% were performed to establish a systematic view on the diffusion properties of polyamide in support of migration modelling.

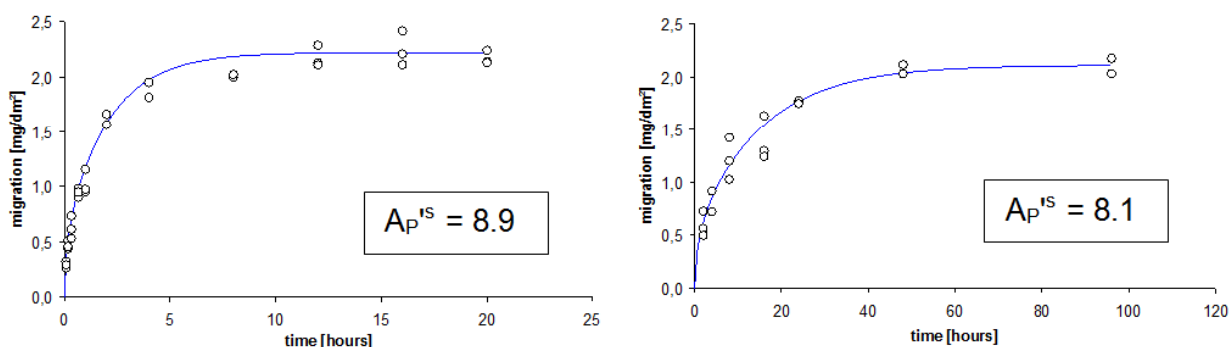
In the kinetic experiments an overlap of two the following two processes will be observed (a) diffusion controlled sorption of water in the PA6 and (b) diffusion controlled release of caprolactam from the PA6 plasticized by water.

Because water is a small molecule it will diffuse faster into the plastic than the bigger caprolactam will diffuse out of the plastic. As a consequence, overall a diffusion like release of the caprolactam from the PA6 under plasticized conditions will be observed. In terms of polymer specific constants, the A_P -value for the polyamide and the A_P -value of the polyamide plasticized by water will differ significantly.

Migration into water at 5°C to 20°C:



Migration into acetic acid 3% at 5°C and 20°C:



Migration into ethanol 10% at 20°C:

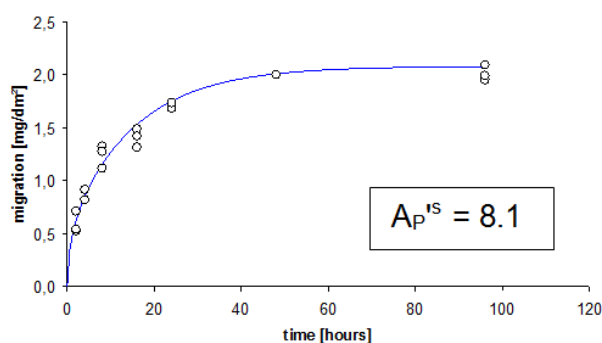


Figure 4 Migration kinetics of caprolactam from polyamide 6 into food simulants (water, acetic acid 3%, ethanol 10%) at 5°C and 20°C and polymer specific constants A_P derived therefrom

In the EU-Project "Certified Reference Materials" ^[xii] the diffusion properties of polyamide 6 (PA6) under ambient conditions (approximate 23°C and 50% relative humidity) were investigated. Migration kinetics from PA6 into iso-octane were performed for caprolactam and polymer specific constant of $A_P' = 1.3$ at 40°C, $A_P' = 1.1$ at 60°C and $A_P' = 0.8$ at 80°C derived therefrom.

Comparing the A_P -value at 40°C for PA6 at ambient conditions and PA6 in direct contact with aqueous media an increase of up to 8 units (from $A_P' = 1$ to $A_P' = 8.9$) is observed.

References

- ⁱ Piringer O.-G. and, Baner A.L. Ed. Plastic Packaging Materials for Food. Barrier Function, Mass Transport, Quality Assurance and Legislation- interactions with food and pharmaceuticals. 2nd ed., WILEY-VCH, Weinheim, New York **2008**
- ⁱⁱ Piringer O., Evaluation of plastics for food packaging. Food Additives and Contaminants (**1994**), 11, 221-230
- ⁱⁱⁱ Brandsch, J.; Mercea, P.; Rüter, M.; Tosa, V.; Piringer, O.; Food Additives and Contaminants **2002**, 19(Suppl.):29-41
- ^{iv} EU Directive 2001/62/EC, 6th amendment to EU Directive 90/128/EEC
- ^v Final Report of the EU-project contract SMT-CT98-7513, "Evaluation of Migration Models in Support of Directive 90/128/EEC"; EUR 20604 EN; European Commission, Brussels **2002**
- ^{vi} C. Simoneau, ed., "Application of generally recognise diffusion models for the estimation of specific migration in support of EU Directive 2002/72/EC", JRC Scientific and Technical Reports, **2010**
- ^{vii} E. Hoekstra, ed.; "Practical guidelines on the application of migration modelling for the estimation of specific migration - In support of Regulation (EU) No 10/2011 on plastic food contact materials."; JRC Technical Reports; **2015**; EUR 27529 EN
- ^{viii} Guideline for the Mathematical Estimate of the Migration of Individual Substances from Organic Material in Drinking Water (Modelling Guideline); German Federal Environment Agency (UBA); October **2008**
- ^{ix} Brandrup J., Immergut E.H., Grulke E.A., Polymer Handbook 4th ed., Wiley & Sons Inc. **1999**
- ^x Experimental Data submitted to the Modelling Task Force of the EU Commission hosted by the EU Joint Research Centre for inclusion in the Migration Modelling Guideline. Main contribution from a research project sponsored by PlasticsEurope Deutschland e.V.; 2003.
- ^{xi} Todd M. Martin, Douglas M. Young; Polymer, Volume 44, Issue 16, July 2003, Pages 4747-4754, ISSN 0032-3861, 10.1016/S0032-3861(03)00446-4.
- ^{xii} Stoffers, N. H.; Brandsch, R.; Bradley, E.; Cooper, J.; Dekker, M.; Störmer, A.; Franz, R.; Food Additives. and Contaminants **2005**, 22 (2), 173-184