

Determination of partition coefficients of migrants between layers used in multi-layer multi-material structures intended for food contact

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Introduction

Migration modelling has made enormous progress during the last two decades. It can be used either as a conservative screening test in the sense of the EU Regulation No 10/2011 based on generally recognized diffusion models or in support of exposure estimations with the demand to provide rather more realistic than overly migration concentrations in food [1]. In both cases, there is a lack of availability of experimental data for the partition coefficient between the different layer materials present in a multi-layer structure [2].

Aim of this study was to develop a method for the determination of partition coefficients of organic compounds between polymers of different polarity and thus being representative of other polymers with similar polarity. Paper & board which represents another important multi-layer material should also be included.

Materials and Methods

The envisaged methodology was to bring a surrogate spiked donor material with an unspiked acceptor material under appropriate t , T -conditions in contact so that a partitioning equilibrium will be achieved which can be measured by analysis of both materials.

Materials used in the study were LDPE ($d = 500 \mu\text{m}$) acting as donor and PET ($d = 13 \mu\text{m}$), PA ($d = 16 \mu\text{m}$) as well as paperboard ($d = 480 \mu\text{m}$) all acting as acceptor. The LDPE donor film was prepared by soaking in a surrogate spiked solution at 60°C for 2 days. For this an ethanol solution containing seven organic substances (surrogates, see Table 2) at defined levels between 2000-5000 $\mu\text{g}/\text{ml}$ was used.

Procedure: two stripes of $4 \times 5 \text{ cm}^2$ spiking film were sandwiched with a similar size of acceptor film in the middle position (Figure 1). In case of paper & board, one stripe of donor was sandwiched with one piece of paper & board. The sandwiched films wrapped with aluminium foil were placed into a hermetically closed stainless steel migration cell and stored at a defined temperature for sufficient long times (for instance up to maximum 15 days at 80°C) with enough sample set-ups to measure the transfer time dependently. At defined time points, sample set-ups were removed and the migrants were then extracted from the materials using dichloromethane (2 days at 40°C) and quantitatively analysed by GC-FID.

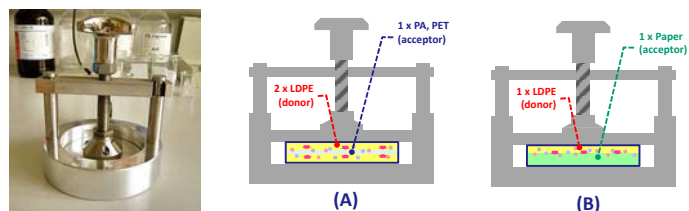


Figure 1: Stainless steel migration cell and cross-section of sandwiched films, LDPE/PA/LDPE (A), LDPE/PET/LDPE (A) and LDPE/Paper (B)

The mean concentration ratio between acceptor to donor was considered as partition coefficient where the equilibrium was reached. The partition coefficient between material 1 and 2, $K_{1/2}$ is defined as:

$$K_{1/2} = (M_1/V_1) / (M_2/V_2)$$

Where M_1 and M_2 is the respective mass (μg) of the compound in acceptor and donor and V_1 and V_2 is the respective volume (cm^3) of acceptor and donor.

Results and Discussion

Some results for partition coefficients of the surrogate substances at 80°C are shown in Table 1. The trends of partition coefficient of substances in 3 different multi-layer materials were significantly related to the $\text{Log } P_{o/w}$. The hydrophilic substances (low $\text{Log } P_{o/w}$) prefer to migrate into polar (PA) and medium-polar polymer (PET) rather than to stay in non-polar one (LDPE). On the other hand, as a result of little amounts of hydrophobic migrants (high $\text{Log } P_{o/w}$) found at equilibrium in the paper & board acceptor layer paper & board can be also considered as a polar material when compared to LDPE. For further evaluation of the measured data, the internet based SPARC program was used. This program uses computational algorithms based on fundamental chemical structure theory to estimate a wide variety of reactivity parameters strictly from molecular structure [3]. By replacing usual solvents in this program with molecules of similar polarity as the polymer of interest a thermodynamic simulant of the polymer can be designed and used to calculate partition coefficients for organic substances between two different polymers.

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Table 1: Surrogates used and experimental $K_{1/2}$ values

Substances	Molecular weight	Vapour pressure (Pa @ 25°C)	Log $P_{o/w}$	$K_{1/2}$ (mass/volume) at 80°C		
				PA/LDPE	PET/LDPE	Paper/LDPE
Benzophenone	182.2	2.57E-1	3.18	2.03	4.11	6.71
Lauro lactam	197.3	4.94E-4	2.92	25.7	1.93	1.07
DPB	206.3	8.94E-4	5.29	1.36	2.28	0.31
DIPN	212.3	6.67E-2	6.08	0.42	0.47	0.06
Triacetin	218.2	3.31E-1	0.25	10.1	13.1	2.79
DEHA	370.6	1.13E-4	8.12	0.06	0.04	0.03
DINCH	424.7	1.28E-4	9.82	0.82	1.34	0.04

*The vapour pressure and Log $P_{o/w}$ data are obtained from EPIWEB v.4.0.

Figure 2 illustrates a comparison between measured $\text{log } K_{PA/LDPE}$ values and SPARC calculations. Hexacontane ($\text{C}_{60}\text{H}_{122}$) was used as a thermodynamic simulant for LDPE assuming similar polarity and thus solubility properties for organic substances. For PA three different molecules, caprolactam, a Nylon oligomer and 6-aminocaproic acid, were selected as PA simulants. The correlation between $\text{log } P_{o/w}$ and $\text{log } K_{PA/LDPE}$ shows that the slope of the regression line from the experimental values is very similar to all three PA polymer simulants, but fits best with Caprolactam. In conclusion, the methodology of SPARC calculator in combination with an appropriate choice for a polymer simulant can be a powerful tool for estimation of partition coefficients for any migrant between two different polymers.

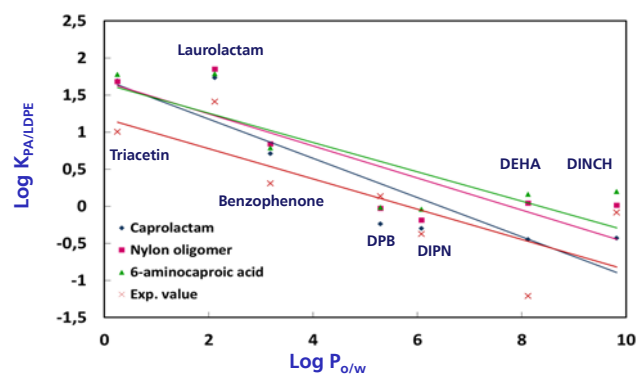


Figure 2: Correlation between $\text{Log } P_{o/w}$ and $\text{Log } K_{PA/LDPE}$ at 80°C

With this developed experimental method numerous partition coefficients between the materials used in this study were determined at temperatures between 20 and 80°C and used for establishing migration modelling parameters within the framework of the FACET project.

Acknowledgements

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References

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