A convenient method for the determination of partition coefficients $K_{P/F}$ for migrants between polymer and foods

Annika Seiler[1], Catherine Simoneau[2], Malcolm Driffield[3], Perfecto Paseiro Losada[4], Peter Mercea[5], Valer Tosa[6], Roland Franz[1]

[1]Fraunhofer Institute for Process Engineering and Packaging (IVV), Giggenhauser Straße 35, 85354 Freising, Germany, [2]European Commission JRC Unit Chemical Assesment and Testing, Via D Fermi 1, 21020 Ispra (Varese), Italy, [3]Food and Environment Research Agency (Fera), Sand Hutton, YO41 1LZ York, United Kingdom, [4]Universidade de Santiago de Compostela, Dpt. Química Analítica, Nutrición E Bromatoloxia, Santiago de Compostela, Spain, [5]Fabes Forschungs-GmbH, Schragenhofstraße 35, 80992 München, Germany, [6]INCDTIM, str. Donath, no. 65-103 400293, Cluj-Napoca, Romania

Introduction

It is well established that mass transfer of migrants from plastics food contact materials obeys in most cases Fick's law of diffusion and is therefore predictable[1]. This can be achieved by migration modeling which, in principle, is based on two essential parameters:

- The diffusions coefficient in polymer DP and
- The partition coefficient $K_{P,F}$ between food contact polymer and food.

Diffusion coefficients which are known or can be calculated, for instance using the PIRINGER equation, are easily accessible.
The partition coefficients are in most cases assumed by default values $K_{P,F}$ = 1000 for low solubility and $K_{P,F}$ = 1 for high solubility in food simulant[2]. In the EU project FOODMIGROSURE it turned out that migration into foodstuffs is largely controlled by the partition coefficient $K_{P,F}$ which, depending on the nature of the foodstuffs, spans a spectrum of $K_{P,F}$ values between and far beyond these two default values[3]. Therefore, for more realistic into-food migration modeling in support of exposure estimation a convenient method for determination of partition coefficients between LDPE polymer and large variety of foods was developed.
It is well known that the analysis of migrants in foods is cost and time intensive. Therefore a simplified approach i.e. measurement of the time dependent decrease in polymer was taken: Measuring the decrease of the concentration of the migrant in the polymer over migration time (Figure 1). This approach is equivalent to the increase of the migrant in the food when mass balance is assured. As a verification experiment, both the time dependent decrease of three model migrants in the polymer as well as the increase of these migrants in orange juice and in 95% ethanol was determined and the mass balance was calculated. The recovery of the mass balance was in all cases above 85% which was considered as satisfactory.

Methods

A LDPE film was spiked with benzophenone (Bz), trans,trans-1,4-diphenyl-1,3-butadiene (DiBP) and 2,5-bis(5-tert-butyl-2-benzoxazolyl)thiophene (trade name: e.g. Uvitex OB). For the determination of the spiked LDPE film was fortified with an internal standard and extracted with dichloromethane for 24 h at 40 °C. Another part of the spiked film was immersed (e.g. in orange juice) and incubated at different time-temperature conditions. After migration contact an internal standard was added and the film was extracted as well.
The concentration of the model substances in the dichloromethane extract of the film and of the orange juice and in the ethanolic solution, respectively, were analysed by GC/FID. Duplicate samples were produced in each case. In addition the recovery of the model migrants in orange juice was determined using the standard addition procedure.

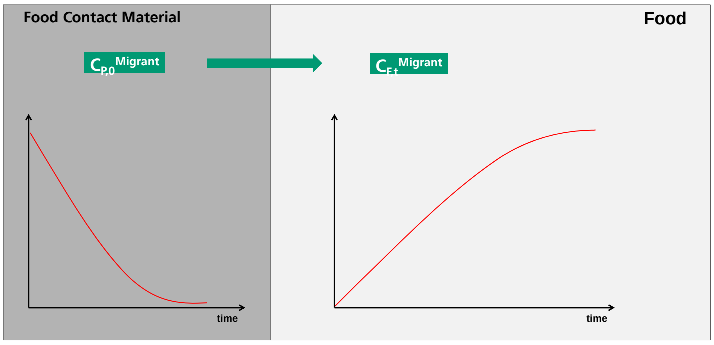

Figure 1: Decrease of the model migrant in the polymer (left) vs. increase of the model migrant in the food (right)

Results

The partition coefficient $K_{P,F}$ is defined as the ratio of the concentration of a migrant in the polymer and in the food at equilibrium (equation 1). Assuming mass balance, the partition coefficient can be calculated without knowing the concentration of the model migrant in the food using equation 2.

Eq 1: $$K_{P/F} = \frac{c_{P\infty}}{c_{F\infty}} \text{ with } c_{F\infty} = \frac{(c_{P0} - c_{P\infty}) \cdot m_P}{m_F}$$

Eq 2: $$K_{P/F} = \frac{c_{P\infty} \cdot m_P}{(c_{P0} - c_{P\infty}) \cdot m_F}$$

where $c_{p,0}$ is the initial concentration and c_∞ is the concentration at equilibrium in mg kg^{-1}.

With this method approx. 600 partition coefficients between LDPE and 37 foodstuffs for 17 model migrants at temperatures between 5 °C and 60 °C were determined. From evaluation of these results the solubility characteristics of foods for migrants which influences their migration behavior can be roughly classified into three groups:

(1) Little or almost no migration into food ($K_{P/F}$ > and >> 500)
(2) Considerable migration into food (500 > $K_{P/F}$ > 20)
(3) High or almost exhaustive migration into food ($K_{P/F}$ < 20)

Typical examples for these categories are highly aqueous foods such as red wine (1), cloudy drinks such as orange juice (2) and fatty foods such as cheese or edible oils (3).

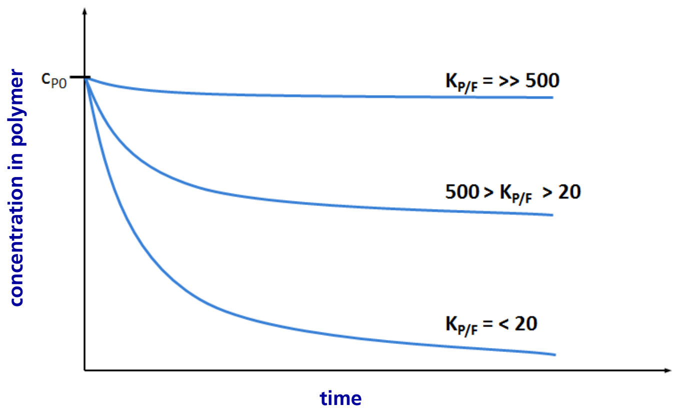

Figure 2: Classification of partition coefficients

References

[1] Prininger, O-G, Baner, AL (editors), Plastic packaging materials for food – barrier function, mass transport, quality assurance and legislation. Weilheim, Wiley-VCH 2000.
[2] Brandsch, J. et al. Migration modeling as a tool for quality assurance of food packaging, Food Addit Contam. 2002;19 Suppl:29-41
[3] FOODMIGROSURE project, contract number QLK-CT2002-2390

Poster presentation at the 5th international Symposium on Food Packaging, 14-16 November 2012, Berlin