Correlation of partition coefficients $K_{Polymer/Food}$ and $K_{Octanol/Water}$ for potential migrants in food contact polymers

Asako Ozaki[1,2], Anita Gruner[2], Angela Störmer[2], Rainer Brandsch[3], Roland Franz[2]

[1]Osaka City Institute of Public Health and Environmental Sciences, 8-34 Tojo-cho, Tennouji-ku, Osaka 543-0026, Japan,
[2]Fraunhofer Institute for Process Engineering and Packaging (IVV), Giggenhauser Straße 35, 85354 Freising, Germany,
email: stoermer@ivv.fraunhofer.de, phone: ++49 8161 491 720
[3]Macrodynamic Chemical Technologies Limited (MDCTec Ltd.), Untere Läng 8c, 82205 Gilching, Germany

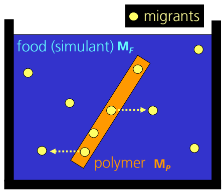
Introduction

Polymers used in food packaging applications contain a wide variety of additives and residual monomers that may migrate into food. Numerous specific migration limits are set on these compounds in the EU positive list to regulate their migration levels into food. As a consequence however, there is a need to carry out a large number of migration tests. The aim of this work is to establish a new methodology to reduce time and cost expenditures for such testing.
Log P_{OW}, logarithmic value of octanol-water partition coefficient, is one important physico-chemical parameter of chemical compounds. It is widely used in environmental, pharmaceutical, biochemical and toxicological sciences to describe the lipophilicity of various compounds. Migration largely depends on the partitioning of migrants between polymer (P) and food/food simulant (F). An investigation was undertaken to determine the correlation between the partition coefficient $K_{P,F}$ and log P_{OW} of migrants in LDPE (low density polyethylene) and PA6 (polyamide 6) as representatives for non-polar and polar food contact polymers, respectively.

Partitioning process:

$$K_{P,F} = C_{P,\infty} / C_{F,\infty} = (M_P / V_P) / (M_F / V_F)$$

M_P: mass of the migrants in polymer film [µg]
M_F: mass of the migrants in food (simulant) [µg]
V_P: volume of polymer film [ml]
V_F: volume of food simulant [ml]



Materials and Methods

Polymer	Food simulant	Migrant's* log P_{OW} (number of migrants)
LDPE (thickness: 0.5µm, density: 0.92)	10, 50, 95% ethanol Olive oil	0.36-18.08 (15)
PA6 (thickness: 0.15µm, density: 1.13)	10, 50, 95% ethanol	0.36-9.52 (14)

*Migrant: styrene, 1-octene, limonene, benzophenone, 2,6-di-*tert*-butyl-4-methylphenol, diphenylphthalate, dinonylphthalate, dimethylphthalate, bis(2-ethylhexyl)adipate, 1,4-diphenyl-1,3-butadiene, triacetine, acetyl tributyl citrate, Irganox 1076, Chimassorb 81, Irgafos 168, caprolactam

Preparation of spiked polymer film: Volatile compounds (styrene, 1-octene and limonene) were introduced by sandwiching the film with the filter paper soaked with 1 ml of 3000 µg/ml solution in ethanol. Sandwiched films were wrapped with aluminum foil and then put into the stainless steel ring cell. After closing tightly, it was exposured at 40 °C for 5 days. Other compounds were introduced by soaking the film in a 2000 - 15000 µg/ml solution in ethanol at 40 °C for 5 days.

Results

Migration kinetics of compounds into 95% ethanol at 40 ℃ are shown in Figure 1. It can be seen that migration of smaller molecules such as styrene reached the equilibrium after 1 day whereas bigger molecules required longer time (bis(2-ethylhexyl) adipate: 2 days, Irganox 1076 and Irgafos 168: 7 days).

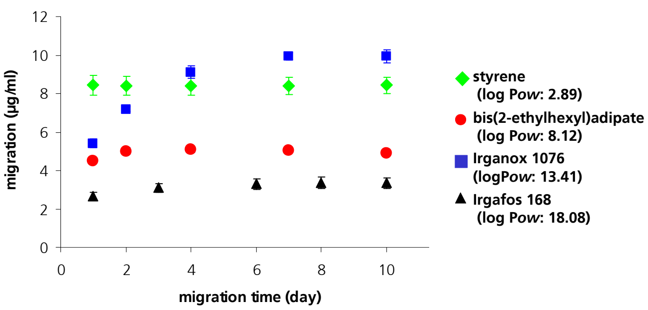


Figure 1: Migration kinetics of model compounds from LDPE into 95% ethanol (10 days at 40 ℃)

Figure 2 shows the results for all tested simulants and compounds: $K_{P,F}$ values increased with increasing log P_{OW} values. A priori, PA6 was expected to show a totally different behavior compared to LDPE because of its opposite polarity compared to LDPE. However it was found that only the slopes of the correlation lines were smaller compared to LDPE (slopes, 10% ethanol: LDPE 1.07 vs PA6 0.66, 50% ethanol: 0.39 vs 0.14, 95% ethanol: 0.051 vs 0.034). Migration test with a food (Leberkäse: German boiled sausage) was conducted with PA6 film for 2 h at 100 °C. In Directive 85/572/EEC, simulant A (distilled water) or simulant D (olive oil) with reduction factor 4 are referenced as food simulant for "processed meat products (ham, salami, bacon and other)". However, migration to Leberkäse was most precisely simulated with 95% ethanol.

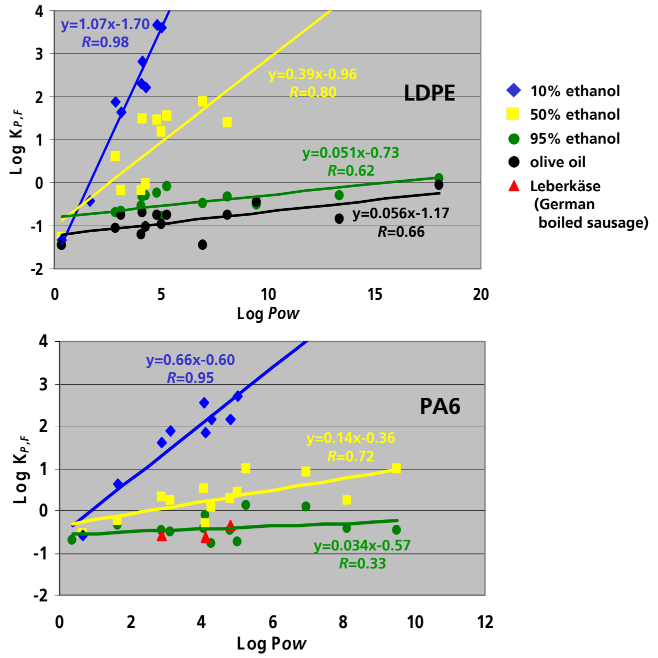


Figure 2: Correlation between log P_{OW} and log $K_{P,F}$ in LDPE and PA6

Conclusion

It was shown that in all tested simulants and for both test films (LDPE and PA6) that $K_{P,F}$ values increased with increasing log P_{OW} values of the migrants. Using linear regression lines, $K_{P,F}$ values could be predicted from the log P_{OW} values of the migrants. Consequently migration can be estimated more precisely by migration modeling when the additives/monomer concentration in the polymer are known. This model could reduce much time to carry out an enormous number of specific migration test.

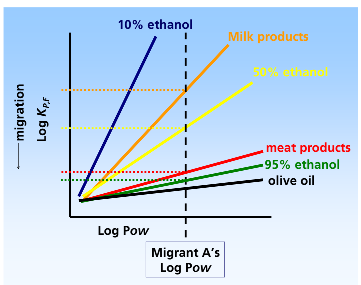


Figure 3: Illustrative relationship between log P_{OW} and log $K_{P,F}$ of migrants

Moreover, migration testing with a meat product (Leberkäse) showed that 95% ethanol is more suitable than the assigned simulants in EU Directive. Figure 3 illustrates the potential of this new approach. The best simulation for a food group would be the closest line which exhibits equal or higher partitioning compared to the food (e.g. 50% ethanol for milk, 95% ethanol for meat product). To make this approach more universal, studies will be extended to other foods and polymers within the FACET project. This will allow in the future to select the most appropriate food simulant for a particular foodstuff.

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