



# Modelling migration of substances from polymers into drinking water. Part 1 - Diffusion coefficient estimations

P.V. Mercea<sup>a,\*</sup>, A. Kalisch<sup>a</sup>, M. Ulrich<sup>a</sup>, H. Benz<sup>a</sup>, O.G. Piringer<sup>a</sup>, V. Toşa<sup>b</sup>, R. Schuster<sup>c</sup>, S. Aranyi<sup>d</sup>,  
P. Sejersen<sup>d</sup>

<sup>a</sup> FABES GmbH, Schragenhofstr. 35, 80992 Munich, Germany

<sup>b</sup> National Institute R&D Isotopic & Molecular Technologies, Str. Donath 65-103, 400239 Cluj-Napoca, Romania

<sup>c</sup> Federal Environment Agency (UBA), Heinrich-Heine-Straße 12, 08645 Bad Elster, Germany

<sup>d</sup> The European Plastic Pipes & Fittings Association (TEPPFA), Avenue de Cortenbergh 71B, 1000 Brussels, Belgium

## ARTICLE INFO

### Keywords:

Diffusion  
Migration  
Permeation  
Migration modelling  
Polyolefins  
Drinking water

## ABSTRACT

In a first part of this work the permeation through and diffusion/migration from high density polyethylene, polybutylene, polypropylene and cross linked polyethylene films was investigated experimentally with three different methods to determine diffusion coefficients in these polyolefins for a series of additives, their degradation products and other organic substances in the 20–60 °C temperature range. The experimental methods used were dynamic permeation through additive free the polymer films, kinetic desorption from additivated films into water and kinetic migration from additivated into additive free polymer films. It was found that in general the temperature dependence of the obtained diffusion coefficients was well represented by the Arrhenius law. Some of these results also suggested that the contact of the polyolefins with water had an influence on the magnitude of the diffusion coefficients and on their apparent activation energy of diffusion.

In the second part of this work the obtained pools of diffusion coefficients for each of the investigated polymers were used to develop an approach to estimate theoretically and without any further experimentation “conservative” diffusion coefficients for any organic substance, with molecular mass ranging from 50 to 1250 g/mol, diffusing in these polymers at temperatures between 15 and 85 °C. The possibility to estimate such conservative diffusion coefficients is very important when it comes to use efficiently migration modelling as an alternative method to test the compliance of polymeric articles with the existing national and/or European standards for drinking water. The use of polymer specific diffusion coefficients in migration modelling is required in the framework of the “Migration modelling guideline” recommendation of the German Environment Agency.

## 1. Introduction

In most nations worldwide before drinking water, (DW), is consumed by the population it comes in contact with articles made of polymers. These might be pipes, tanks, parts of pumping devices and valves, coatings, etc. used in the plants which process raw water to DW. Then in the supply network DW often comes in contact with tanks, pipes, coatings and other appliances made of polymeric materials. Finally the population often consumes and/or stores DW from appliances/containers made of polymers. It is known that, depending on their final application, all polymeric articles from the market contain not only the polymer resin but also one or a series of substances added because of technical reasons; antioxidants, heat and/or ultra-violet stabilizers, plasticizers, pigments, fillers, catalysts, flame retardants,

smoke suppressors, blowing agents, solvents, lubricants or processing aids. Most of these substances are not firmly bound to or trapped in the matrix of the host polymer exhibiting therefore a mobility (diffusivity) in the network of the polymer's macromolecules. Once such a polymer comes into contact with DW these added substance/s may leach/migrate from the polymer into DW. A high diffusion rate of the substance in the matrix of the polymer and a good solubility in DW favors this process.

Worldwide in many countries there are strict regulations for the quality of DW. But the limits of many of the contaminants of DW are not typical substances of DW contact materials. For the time being the European drinking water directive [1] has only basic requirements for the materials and products in contact with drinking water. Only for metallic products the limits of the directive are helpful. In Germany the

\* Corresponding author.

E-mail address: [petermercea@gmail.com](mailto:petermercea@gmail.com) (P.V. Mercea).

limitations on DW contamination originating from several types of organic materials (plastics, organic coatings, elastomers, and lubricants) are laid down in the Federal Environment Agency, (Umwelt Bundesamt-(UBA)), guidelines [2]. In the framework of the amended German Drinking Water Ordinance (GDWO) [3] UBA has been commissioned since December 2012 to stipulate mandatory evaluation criteria for materials and substances that come into contact with DW. For the time being the guidelines published by UBA are not legally binding. However it is planned to implement the UBA mandatory evaluation criteria into the GDWO in the next future. After that the mandatory evaluation criteria for organic materials in contact with DW will be legally binding.

In Germany the requirements to be fulfilled by plastics in contact with DW are laid down in the “Organic materials in contact with drinking water” guideline, (KTW-guideline), [4]. To specify specific migration limits (SML's) from plastics into DW the KTW-guideline used as reference the SML's stipulated in the framework of the EU-Regulation 10/2011 for “Plastic materials and articles intended to come into contact with food” [5]. The SML's stipulated in Annex A of this later document for several hundreds of substances were transferred into the KTW-guideline but reduced/divided by the factor 20. For all substances which are not listed in the DW positive list the compliance threshold for migration in DW was set at 0.1 µg/L.

For the European Union (EU) the methods for testing experimentally the compliance of products in contact with drinking water are stipulated in the European standards EN 12873-Parts 1 and 2 [6,7]. In agreement with these standards in the KTW-guideline the relevant migration conditions and duration of migration periods are specified for the testing procedures [4]. A central part of these tests is the chemical analysis of the water brought into contact with the plastic articles during some of the test's migration periods. However practice shows that it is often difficult, time consuming and expensive to develop analytical methods with sufficient sensitivity to detect migration at or even below the very low levels stipulated for DW. Especially, but not only, in such cases the theoretical estimation/modelling of migration of substances from plastic articles into DW might be considered as an additional tool for a quick and less expensive compliance testing of polymeric materials. In practice to estimate the migration of a substance from a polymer into DW specific mass transport equations must be solved by using appropriate input data and taking into account the initial and boundary conditions of the migration process. One of the important input data in such calculations is the diffusion coefficient,  $D_p$ , of the migrating substance in the matrix of the plastic article. The aim of this work was to develop a method to estimate easily and without any further experimentation such  $D_p$ 's for additives and/or other organic substances migrating from a series of polymers into water. The polymers chosen in this respect were four types of polyolefins which are often used to manufacture appliances for the drinking water production/distribution sector. Because of that these polymers have often a marked influence on the quality of the drinking water consumed by the population.

## 2. Materials and methods

### 2.1. Materials used

The four polyolefin polymers investigated were High Density Polyethylene (HDPE), Polybutylene (PB), cross-linked Polyethylene (PEX) and respectively Polypropylene (PP). The PP was a homo polymer while the PEX samples were silane cross-linked (PEX-B type). Using these raw materials Basell Polyolefine GmbH from Frankfurt a.M./Germany custom produced for the intended investigations two lots of thin films. A first lot, (L1), included practically additive free films which were calendered to get a target thickness of  $d_p = 200 \mu\text{m}$ . In the second lot, (L2), the HDPE, PB, and PP films were additivated with one out of three combinations of three organic substances. Half of these samples were calendered to get the same target thickness of

$d_p = 200 \mu\text{m}$  the other half a  $d_p = 480 \mu\text{m}$ . Measurements in different parts of the film rolls obtained from Basell showed that the thickness of the films varied slightly around the intended target values. Each of the additivated films from L2 contained one out of three well known antioxidants (AO's) plus two specific degradation products (DP's) of that AO. The gravimetric amounts of AO's and DP's added to the polymer resins of L2 were chosen to get in each film target initial concentrations of about 2000 mg/kg for the AO's and a combined total of about 1500 mg/kg of DP's. As result the samples of L2 contained nine different types of polyolefin films labeled, HDPE-1, HDPE-2, HDPE-3, PB-1, PB-2, PB-3, PP-1, PP-2 and respectively PP-3. Additivated PEX films were not produced. For the theoretical modelling of diffusion/migration process from the films of L2 the knowledge of the actual initial additive concentrations,  $C_{p0}$ 's, in the finished films is an important information. Because of that these  $C_{p0}$ 's were determined analytically. For this 0.2 g from each type of polymer from L2 was cut into small snippets which were then immersed in ethanol 95%. The HDPE-1, HDPE-2, PB-1, PB-2, PP-1 and PP-2 snippets were extracted in separate vials and repeatedly for 24 h @60 °C while for the snippets from the HDPE-3, PB-3 and PP-3 films the same procedure was followed for 12 h at 70 °C. These procedures were repeated until no more AO and DP's were extracted from the samples. For each extraction the combined solutions were analyzed by HPLC/UV and the quantification was done specifically using external calibration curves. Knowing the amounts of AO and DP's in the extraction solutions the actual  $C_{p0}$ 's summarized in Table 1 were calculated.

The  $C_{p0}$ 's listed in Table 1 differ in many cases from the intended target values. In this respect two opposite trends could be observed. First, with a single exception Irganox®1010 in sample PP-2, the actual  $C_{p0}$ 's of the AO's in the samples was found to be somewhat lower than the intended target one. This might have been due to a partial degradation and/or loss of the AO's during the preparation and/or storage of the samples before being analyzed. The second trend refers to the sum of the measured initial concentrations,  $\Sigma C_{p0}$ 's, of the DP's in each polymer type. These  $\Sigma C_{p0}$  were in all cases, excepting for HDPE-3, above the intended target level of 1500 mg/kg. The source of this result might have been too the partial degradation of the AO's during the preparation and/or storage of the samples. Interesting too was the fact that in all film samples of L2 the AO's Irganox®1076 and Irganox®1010 were detected. But Irganox®1076 was deliberately additivated only to the samples HDPE-2, PB-2 and PP-2 while Irganox®1010 only to the samples HDPE-1, PB-1 and PP-1. The presence of these AO's in the other samples might be the result of an original contamination of the HDPE, PB and PP granules used in the manufacturing of the films with small amounts of Irganox®1076 and Irganox®1010.

### 2.2. Experiments for the determination of diffusion coefficients

To determine the diffusion coefficients,  $D_p$ , of the organic substances listed in Table 1 and Annex A in the matrix of our four polyolefins three different experimental methods were used.

#### 2.2.1. Permeation experiments

The first method, (EM-1), were permeation experiments. The PB, HPDE, PEX and PP samples used in these experiments were additive free films from L1. In a permeation experiment the investigated polymer film separated inside a glass permeation cell an “upstream” chamber (CH-1) from a “downstream” one (CH-2). The later chamber, of volume  $V_2 = 25 \text{ cm}^3$ , was filled with in house produced high purity deionized water (DIW). The permeation experiment was started by filling CH-1, of volume  $V_1 = 150 \text{ cm}^3$ , with a solution containing a cocktail of 2, 3 or even 4 out of 32 specifically selected organic substances (see Annex A) solved in DIW. All the substances solved in these solutions were of analytical purity and used as purchased from the suppliers. A number of eleven such solutions were prepared. The nature and number of the substances solved in each solution were carefully

Download English Version:

<https://daneshyari.com/en/article/7825411>

Download Persian Version:

<https://daneshyari.com/article/7825411>

[Daneshyari.com](https://daneshyari.com)