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Removal of polycyclic aromatic hydrocarbons from water by migration into polyethylene

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Abstract

Water was spiked with three polycyclic aromatic hydrocarbons (PAHs) and filled into a steel diffusion chamber. Low-density polyethylene sheet combined of five polyethylene foils was used as a partition in the chamber. Depth of PAHs migration into the sheet was followed for 143 h, using high performance liquid chromatography with selective fluorimetric detection after extraction of PAHs from the foils peeled off. On the basis of the results obtained, the process of PAHs migration into PE was characterised as a one-dimensional diffusion into polyethylene bulk. The diffusion coefficients were calculated for individual compounds using the second Fick law. It was concluded that PAHs are primarily adsorbed on the polyethylene surface with subsequent migration into bulk polymer. Transportation of PAHs through the bulk can be described satisfactorily by Fickian laws of diffusion and is consistent with the theory of the depth adsorption of PAHs in polyethylene. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In recent years, research focus on plastic packaging/food interactions has been mainly aimed at migration processes of various compounds from plastics (e.g. plasticizers, antioxidants, monomers, and oligomers) into food products during storage or microwave cooking, (Lickly, Bell, & Lehr, 1990; Benfenati, Natangelo, Davoli, & Faneli, 1991; Begley & Hollifield, 1990). Till, Reid, Schwartz, Sidman, Valentine, and Whelan (1982) proposed a simple predictive equation for the migration of additives into food, and the same equation has been used for calculation of diffusion coefficients of di-(2-ethylhexyl)adipate plasticizer for a migration rate from PVC film into Cheddar cheese (Mercer, Castle, Comyn, & Gilbert, 1990). Kondyli, Demertzis, and Kontominas (1992) found that the rate-determining step in the migration process of plasticizers from PVC into ground meat is the diffusion from the bulk of the PVC film to its surface.

Ten years ago, initial studies on the sorption of compounds by plastic materials were published. All these studies deal with a selective sorption of sensory active compounds from fruit juices packed aseptically into polyethylene. Shimoda, Ikegami, and Yutaka (1988), in model studies, and Linssen, Verheul, Roozen, and Posthumus (1991), in artificially flavoured commercial drink yoghurts, showed that sorption of flavour components increased with increasing carbon chain length. Charara, Williams, Schmidt, and Marshall (1992) observed that a low-density polyethylene sorbed flavour compounds more intensively than high density polyethylene packaging materials. To depress the sorption ability, Matsui, Mizumoto, Kotani, Imakura, Shimoda, and Osajima (1990) treated ethylene-vinyl acetate copolymer foils with electron beam irradiation. Fukamachi, Matsui, Shimoda, Nakashima, and Osajima (1993) depressed the sorption of hydrocarbons, ethyl octanoate and decanal into ethylene–vinyl acetate copolymer by surface hydrolysis using a methanolic solution of NaOH. All these mentioned papers were aimed at a study of formation as well as prevention of 'off flavour' phenomena that arise in foods packed into plastic polymers, mainly low-density polyethylene.

On the other hand, the high ability of plastics to sorb some compounds is very interesting, because this could be a very effective way for eliminating some contaminants from foods. In this way, a concentration of polycyclic aromatic hydrocarbons (PAHs) in a liquid

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smoke flavour was lowered by two orders during 14 days (Šimko & Bruncková, 1993). The same principles were used for removal of polychlorinated biphenyl congeners from water and peanut oil (Pascall, Zabik, Zabik, & Hernandez, 1997). It was found (Šimko, Šimon, Khunová, Bruncková, & Drdák, 1994) that the rate-limiting step of the PAHs sorption from liquid smoke flavours onto polyethylene packaging material is the diffusion in liquid media.

The sorption of nonelectrolytes at the solid-solution interface may be viewed in terms of two somewhat different physical pictures. The first one is that adsorption is essentially confined to a monolayer next to the solid surface, with the implication that succeeding layers are virtually normal bulk solution. The other is that of an interfacial layer or region, multimolecular in depth, over which a more slowly decaying interaction potential with the solid is present. From this point of view, adsorption from solution corresponds to a partition between a bulk and an interfacial phase (Adamson, 1990).

On the basis of these facts, the aim of this study was to elucidate the processes in the solid phase, i.e. the mechanism of PAHs behaviour on polyethylene surfaces after leaving the liquid medium.

2. Materials and methods

2.1. Materials

2.1.1. Polyethylene

Polyethylene sheets used in the experiment were made of a low-density polyethylene (LDPE), type Bralen RA2-19, with a density of 922 kg m^{-3} (Slovnaft, Bratislava, Slovak Republic). As a liquid medium, water twice-distilled in a glass apparatus was used.

2.1.2. PAHs

Three compounds with different numbers of condensed benzene nuclei in a molecule were used in the experiment: fluoranthene (Fl), pyrene (Py), and benzo(a)pyrene (BaP). All compounds were of analytical grade, purchased from Supelco (Gland, Switzerland), and Fluka (Buchs, Switzerland).

2.1.3. Solvents

All organic solvents (acetonitrile was HPLC grade purchased from Fluka, Buchs, Switzerland, hexane and methanol of analytical grade purchased from Lachema Brno, Czech Republic) were rectified before use in a distillation apparatus.

2.2. PE sheets

PE sheet (thickness 1 mm), composed of five layers (thickness 200 μm), was prepared from LDPE using a hydraulic press under the following conditions: preheating period 5 min, pressing temperature 200°C, period of pressing 4 min, and period of cooling 10 min. Cooled PE foil (thickness 2 mm) was then pressed again to obtain a foil with the thickness of 200 μm under these conditions: preheating period 3 min, period of pressing 3 min, temperature of pressing 200°C. Finally, after cooling, five pieces of this foil were pressed together using a preheating period 1.25 min, period of pressing 0.75 min, temperature of pressing 102°C. PE sheets prepared in this way were free of air bubbles and compact, but it was easily possible to peel off the

Table 1
Decrease of PAHs concentration (μg kg^{-1}) in water at various time intervals

Time (h)	Fl	Py	BaP
0.00	1350	537	191
0.75	1348	536	190
1.50	1344	534	190
2.50	1337	531	189
3.00	1324	525	188
69.0	1153	455	169
143.0	1054	417	165

Fl, Fluoranthene; Py, Pyrene; BaP, Benzo(a)pyrene.

Table 2
Concentration of PAHs (μg kg^{-1}) in individual layers of PE sheet at various time intervals

Time (h)	Compound	Layer no.				
		1	2	3	4	5
0.00	Fl	ND	ND	ND	ND	ND
	Py	ND	ND	ND	ND	ND
	BaP	ND	ND	ND	ND	ND
0.75	Fl	523	ND	ND	ND	ND
	Py	244	ND	ND	ND	ND
	BaP	86	ND	ND	ND	ND
1.50	Fl	647	43	ND	ND	ND
	Py	268	25	ND	ND	ND
	BaP	98	11	ND	ND	ND
2.50	Fl	894	57	39	ND	ND
	Py	395	26	15	ND	ND
	BaP	146	6	3	ND	ND
3.00	Fl	1087	101	77	62	ND
	Py	458	42	22	14	ND
	BaP	193	16	10	7	ND
69.00	Fl	6614	1861	319	86	57
	Py	2275	632	122	31	22
	BaP	1242	129	27	17	5
143.00	Fl	7709	2154	1493	459	182
	Py	4009	1060	626	142	79
	BaP	2083	376	109	42	27

ND, not detectable.

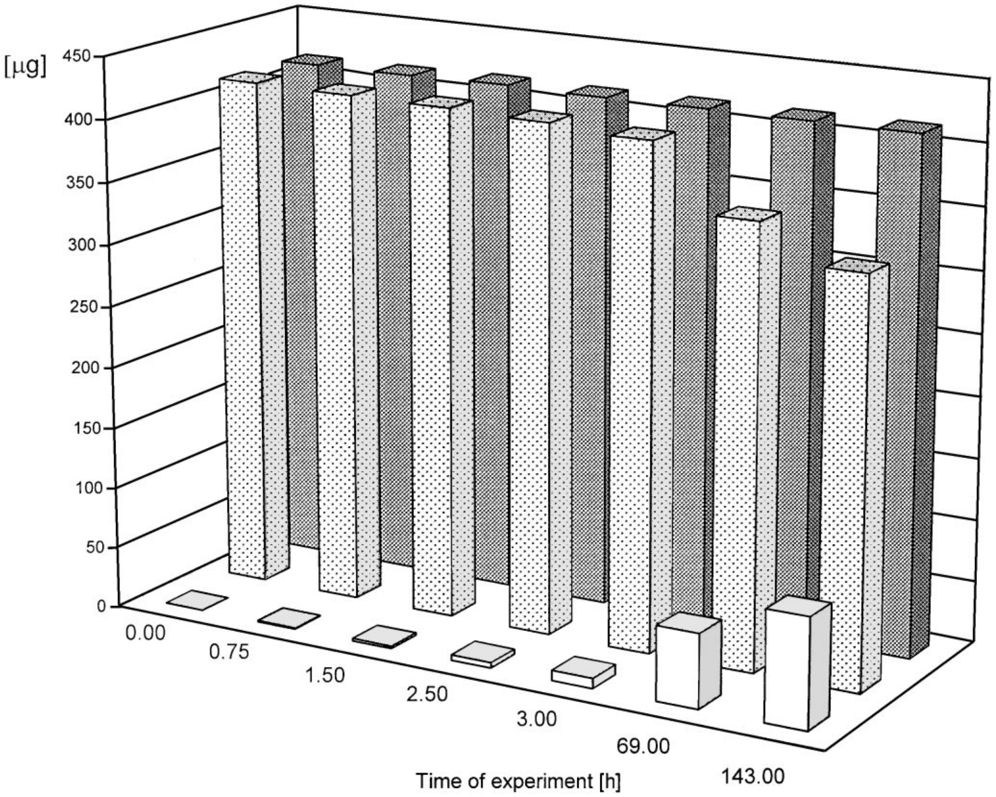

Fig. 1. Amounts of PAHs in: ▩ water before the experiment, □ PE during the experiment, ⬚ water during the experiment.

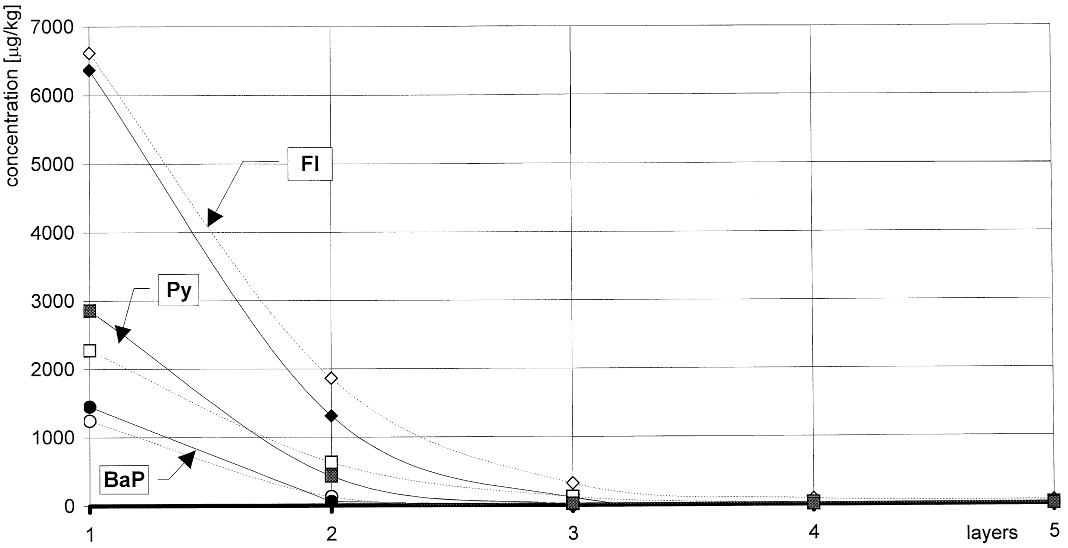

Fig. 2. Dependence of PAHs concentration on the depth of migration in time 69 h: ... measured values; — calculated values. Fl, fluoranthene; Py, pyrene; BaP, Benzo(a)pyrene.

individual foils from the sheets after finishing the experiment.

2.3. Experimental

First, all organic solvents, water, and PE sheet were analysed for the presence of PAHs in order to eliminate the effect of accidental contamination on the measured values. Then, water was spiked with a methanolic solution of PAHs at a level of total concentration 2077 µg kg^{-1}, and 200 g of this water was filled into the diffusion chamber constructed of stainless steel according to Moisan, 1985 and Malík, Hrivík, and Tuan (1993). The chamber was divided into two parts that were separated

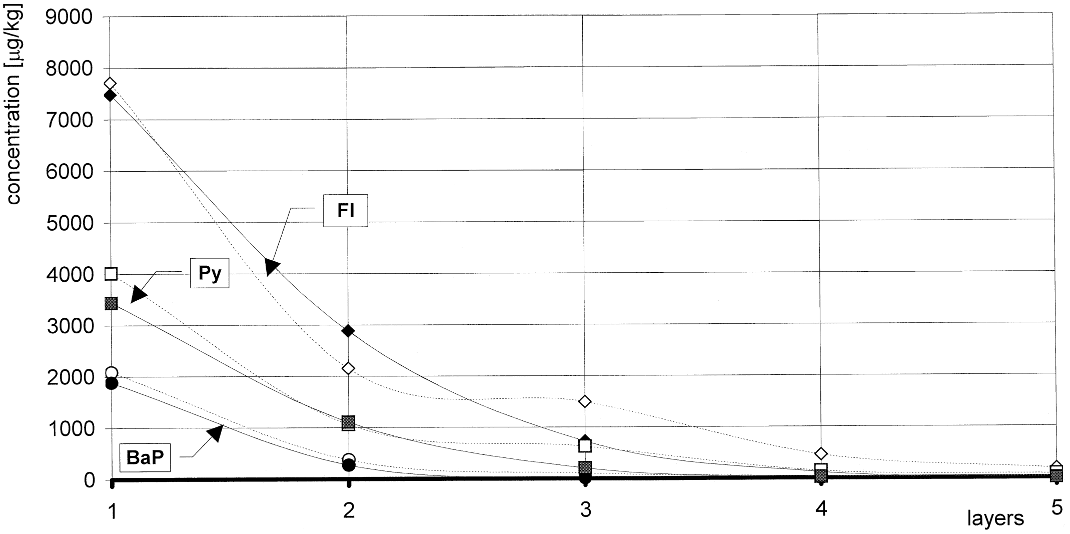

Fig. 3. Dependence of PAHs concentration on the depth of migration in time 143 h: … measured values; — calculated values. Fl, fluoranthene; Py, pyrene; BaP, Benzo(a)pyrene.

Table 3
Solubilities and diffusion coefficients of individual PAHs in LDPE

Compound	S (µg kg^{-1})	D × 10^{10} (cm^2 s^{-1})
Fl	10 430	7.05
Py	5030	5.47
BaP	3360	2.53

Fl, fluoranthene; Py, pyrene; BaP, Benzo(a)pyrene.

by PE sheet. The size of the sheet was 8×4 cm. After water-tight connection, 200 g of contaminated water was filled into one part of the cell, and the interaction of PAHs with PE sheets was monitored at 0.75, 1.5, 2.5, 3.0, 69.0 and 143.0 h. At each time interval, the water was poured out, the chamber dissassembled, and individual PE foils peeled off immediately and put into Erlenmeyer flasks. During the experiment, temperature of the chamber was kept at 24°C.

2.4. Sample preparation

2.4.1. Polyethylene foils

To obtain PAHs from PE foils, 100 ml of hexane was added into each Erlenmeyer flask and the flasks were placed into a shaker for 1 h, then sonicated for 5 min. After filtering, the PE foils were extracted again twice with 50 ml of hexane; combined hexane layers were evaporated to near dryness using a vacuum rotary evaporator, and the residue dissolved in 1 ml of methanol.

2.4.2. Water

One hundred g of water were extracted three times with 50 ml of hexane. Combined hexane layers were dried with anhydrous Na_2SO_4, evaporated to near dryness and dissolved in 1 ml of methanol.

2.4.3. HPLC analysis

HPLC analyses were carried out as described earlier (Šimko et al., 1994). All determinations in both, water and PE, were performed in triplicate.

3. Results and discussion

Before the main part of the work, a 'blank' experiment was carried out substituting PE sheet with an aluminium foil in order to detect eventual sorption onto cell walls. Analysing the PAHs concentration in the water, no statistically significant differences were found in the PAHs concentrations before and after 168 h of the experiment.

As can be seen from Table 1, the PAHs concentrations in water started to decrease immediately after beginning the experiment. Table 2 shows that the presence of PAHs in the first layer of PE sheet was possible to determine as early as after 0.75 h. With the extension of experimental time, the presence of PAHs was determined also in further layers and, after 69 h, PAHs were determined in all layers of PE sheet. In all these cases, the standard deviation σ of parallel determinations did not exceed the value of 2.6. The total amounts of PAHs in water before the experiment, as well as water and PE during the experiment, can be seen in Fig. 1.

The solution of the second Fick law for the diffusion of PAHs in polymer in the diffusion cell (Crank, 1975; Moisan, 1985) gives the equation

$$c = S\,erfc\left(\frac{x}{2\sqrt{Dt}}\right) \qquad (1)$$

where c is the concentration of PAHs in the polymer at time t and at the distance x, D is the diffusion coefficient and S is the solubility of PAHs in the polymer. From Eq. (1) it can be simply derived that the amount of diffusant in the region $x-h$ to x is given by formula (2)

$$Q = A\rho \int_{x-h}^{x} c(x,t)\mathrm{d}x \tag{2}$$

where A is the area, ρ is the density of polyethylene and h is the thickness of the polymer layer. It can be derived from Eqs. (1) and (2) that the amount of PAHs in the nth polymer layer expressed as a weight of PAHs per a weight of polymer, w, is

$$w = S \int_{n-1}^{n} erfc\left(\frac{hn}{2\sqrt{Dt}}\right)\mathrm{d}n \tag{3}$$

where n is the number of the layer.

The experimental data have been treated using Eq. (3). The solubilities of individual PAHs in LDPE and the related diffusion coefficients have been obtained from a comparison of the theoretical values given by Eq. (3) and the experimental values listed in Table 2 using the nonlinear least-squares method. The minimisation of the sum of squares between theoretical and experimental values has been done by the simplex method. Integration in Eq. (3) has been performed using the Simpson formula. For example, the courses of experimentally obtained and calculated values are shown in Figs. 2 and 3 for 69, or 143 h of experiment, respectively. The relationships between measured and calculated values are fairly good. The solubilities and diffusion coefficients decrease in the order Fl > Py > BaP (Table 3), which is obviously a consequence of increasing the molar mass and size of the compounds. These calculated values of diffusion coefficients are more precise than similar values only estimated for the same material in previous work (Šimko, Khunová, Šimon, & Hrubá, 1995).

On the basis of the results obtained, it can be concluded that, after leaving the liquid media, PAHs are primarily adsorbed on the polyethylene surface, with subsequent migration into bulk polymer. Transport of PAHs through the bulk can be described satisfactorily by the Fickian laws of diffusion this and this also complies with the theory about depth of adsorption of solid phase from solution mentioned by Adamson.

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