

Stabilization of Aroma Compounds through Sorption–Release by Packaging Polymers

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Plastic packaging materials are often associated to aroma losses and to a decrease of the organoleptic quality of foods. This work defines situations where, on the contrary, plastics play a regulating role on the concentration of reactive aroma compounds in foods. These systems can be described by a two step mechanism; first, aroma is sorbed in the polymer, while the fraction in solution degrades quickly; in a second step, as the concentration is close to zero in the solution, the polymer liberates progressively the sorbed aroma back to the food. A simple numerical model is proposed, describing competitive processes of aroma degradation in solution and sorption by a polymer in contact with a homogeneous aqueous food. The classical limonene/low density polyethylene (LDPE) system is studied experimentally for the validation of the model: in an acidic medium, limonene both degrades quickly and is sorbed quickly, with a large solubility in LDPE. To define which aroma packaging systems could also display this interesting behavior, all types of possible interactions, using thermodynamic and kinetic parameters describing most practical situations, are simulated. For that purpose, 35 values of reference diffusion coefficients and 35 partition coefficients of usual aroma compounds between polymers and water have been measured and combined with the few available data from literature. The situations where polymers regulate the aroma concentration in food correspond to large partition coefficients (above 10), large diffusion coefficients ($> 10^{-9} \text{ cm}^2 \times \text{s}^{-1}$), and large degradation constants.

KEYWORDS: Aroma; degradation; polymer; packaging; diffusion; sorption

INTRODUCTION

Losses of aroma compounds in foodstuffs packaged with plastics may be due to different phenomena which are reported in abundant literature: losses by sorption and permeation through the packaging, by oxidation due to oxygen permeating through the packaging and by intrinsic degradation of aroma in given pH/temperature conditions.

The complexity of the whole phenomena has led to a specialization of related literature. One can distinguish the following:

(i) A literature specialized on the relationship between *sensory evaluation* and analytical approaches. In model studies, authors look for drastic concentration changes (e.g., limonene solution in contact with a polyolefin, which quickly sorbs large percentages of hydrophobic aroma compounds). Some authors identify a clear relationship (1, 2), while other authors find no sensible changes by sensory evaluation (3) on very close systems. The complexity of sensory evolution has been underlined, as it is not only connected to aroma losses but also to the formation of off odors (4, 5).

(ii) Other papers, dedicated to the physicochemical mechanisms of matter exchanges, are based on simple systems, where the experimental conditions inhibit the degradation of aroma compounds. Mass transfers are mainly monitored by permeation experiments. Classical description by diffusion coefficients and solubility/or partition coefficients are used (6–8).

(iii) Another literature focuses on *degradation mechanisms* of aroma compounds in inert (glass) containers, which is a complex issue (9), even without any relation with sensory. The degradation of citrus juice is thus associated to a long list of possible degradation products, which are themselves further degraded, leading to a second list of degradation products (10–12). These complex mechanisms can fortunately be described by apparent first-order degradation kinetics (13).

(iv) A few papers deal with the competition between aroma degradation and sorption. They give a mass balance of the phenomena at given times. Generally, a dominant mechanism is identified: either sorption or degradation depending on aroma/packaging system. However, two papers suggested a two step mechanism (14, 15): (i) in the first period of contact, the polymer sorbs aroma compounds, and (ii) when their concentration in food becomes low (both through degradation and through sorption effects), packaging liberates back aroma compounds into the solution. It has been proposed that the packaging film

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could contribute positively to the quality of packaged foods, by regulating the concentration of reactive aroma compounds in foods. However, since no modeling has been done on these case studies, it is not yet possible to predict whether this behavior may be general and when it could become important.

Our first aim is to study experimentally this limonene/polyolefine system and to propose a model taking into account both degradation and mass transport.

The second aim is to characterize the aroma/material systems which may display a similar behavior. To study all types of possible interactions, thermodynamic and kinetic parameters of 35 aroma (aqueous solutions)/polymer couples are measured. These parameters will be used to simulate all types of realistic polymer/aroma contact situations.

EXPERIMENTAL PROCEDURES

Materials. Polymer films are supplied by ATOFINA; low-density polyethylene (LDPE) 95 μm thick (LACQTENE 1008FE24), polypropylene (PP) 20 μm thick (PPH3050), oriented polypropylene (OPP) 25 μm thick (PPH4050), ethylene vinyl acetate copolymer (EVA) 21 μm thick (EVATANE 1003VN4, 13% vinyl acetate).

Thin PET films are obtained by thermoforming. The objective of this operation is to obtain a *very thin* (8.5 μm) material easy to test by permeation (to reduce the duration of the tests), and whose physical structure (orientation and crystallinity) is as close as possible to that of bottles. Films are processed by thermoforming amorphous PET sheets (200 μm thick) with an ILLIG SB53c apparatus. PET sheets are heated for 7 s under infrared lamps. After removing the lamps, the sheet is blown to the bottom of a cylindrical mould by quick application of vacuum.

Aromas are supplied by Aldrich France: ethyl butyrate (BE), limonene, γ -terpinene, octanal, nonanal, linalol, citral, α -terpineol, perillaldehyde, DMDS (dimethyl disulfide), hexanal, butanol, heptanone, nonanone.

GC Analysis. *Analysis of Solutions in Diethyl Ether.* Analyses of liquid solutions concern (i) the determination of aroma concentrations in polymer films by ether extraction and (ii) the determination of aroma concentration in diethyl ether solutions extracts of aqueous solutions (1:10 vol/vol).

Conditions of Analysis. On-column injection: Column, DBWAX 0.32 mm \times 30 m, 0.5 μm , J&W. He: 2 mL/min. Temperature program: 40 $^{\circ}\text{C}$ for 4 min, 6 $^{\circ}\text{C}/\text{min}$ until 220 $^{\circ}\text{C}$. FID Detection.

Internal standard is ethyl octanoate, 200 ppm in diethyl ether. A 100- μL aliquot of this solution is added to 1 mL of tested sample before injection. Calibration curves are run in the 0–500 ppm range. The limit of quantification of all aroma compounds studied is close to 1 ppm.

Gas-Phase Analysis. Apparatus: Chrompack GC FID CP 9002, purge and trap injector PTI Chrompack CP 4010.

The following protocol was used for permeation tests (determination of diffusion coefficient) conditions of analysis: PTI (-100°C , purge 4 min, 15 mL/min.); column, CP–Porabond Q Fused Silica 25 m \times 0.32 mm (Chrompack); Carrier gas, N_2 40 kPa; oven, isotherm at 250 $^{\circ}\text{C}$; FID detection.

Partition Coefficients. Partition coefficients are measured at 23 $^{\circ}\text{C}$. Polymer films are put in contact with aroma solutions at different concentrations: 5, 20, 70, 100, 200, 300 mg/L.

A 50 000 ppm aroma solution in deoxygenated ethanol (prepared by nitrogen bubbling) is diluted with deoxygenated water, up to the target concentration; three 4- \times -4-cm film samples are then immersed in 10 mL aqueous solution for 15 days at 23 $^{\circ}\text{C}$. Films are then quickly (2 s) rinsed in cold ethanol (0 $^{\circ}\text{C}$) and extracted for 24 h in diethyl ether (complete extraction, as checked by a second extraction). The concentration is determined by GC after addition of 100 μL internal standard solution.

Determination of D by Permeation. An 8-cm diameter film is used to separate the two compartments of a Pyrex permeation cell, fitted with a Teflon-coated seal. The upstream compartment (100 mL) of the permeation cell is totally filled with water. The downstream compartment is connected to the PTI injector. Injection cycles are

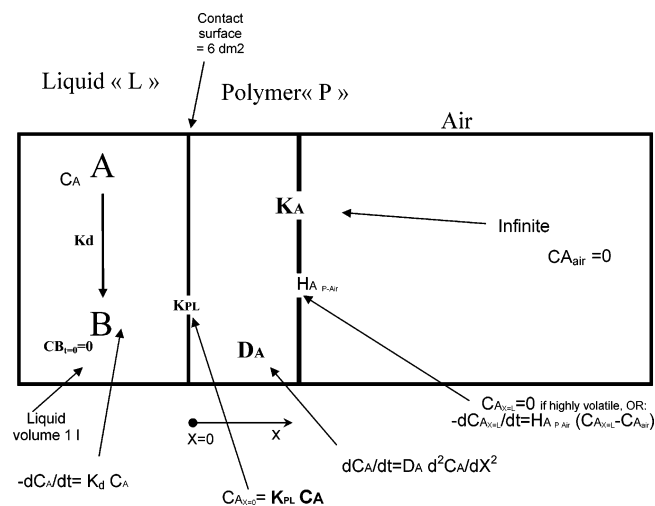


Figure 1. Basic equations and assumptions used in the numerical model.

repeated every 10 min until complete elimination of parasite peaks on the chromatogram. At $t = 0$, a solution of the compounds (500 ppm in ethanol) is added (2/1000 volume/volume) in the upstream compartment. The downstream compartment is purged for 1 min with nitrogen (500 mL/min), just before injection. The last operation is repeated regularly (1–12 h interval times depending on tested polymer), until a constant permeation flux. The diffusion coefficient is calculated from the permeation lag time. The following panel was tested: ethanol, butanol, butanedione, butyric acid, dimethyl disulfide, hexanal, isovaleric acid, heptanone, ethyl butyrate, octanal, limonene, γ -terpinene, nonanal, nonanone, perillaldehyde, citral, α -terpineol, and linalool.

Measure of Parameters for Model Validation. Limonene degradation: A limonene solution (50 000 mg/L) in deoxygenated ethanol (nitrogen bubbling) is diluted (2/1000) in citric acid (1.5 g/L). The solution is stored at 23 $^{\circ}\text{C}$. Direct injections in CPG are of diethyl ether extract (1/10 vol/vol).

Diffusion in Polymer. A limonene solution of 50 000 mg/L in deoxygenated ethanol (nitrogen bubbling) is diluted 500 times with deoxygenated water. The solution (8 mL) is put in contact with a stack of 60 (4- \times -4-cm, 95- μm thick) films (16, 17). The area of contact is 4 cm^2 . The experiment is stored at 23 $^{\circ}\text{C}$ in the dark. After contact, each film of the stack is extracted separately for 1 day with diethyl ether (1 mL) at room temperature. Three times of contact were tested. Limonene concentration is determined by GC after addition of 100 μL internal standard solution.

“Real” Contact. A limonene solution (50 000 mg/L) in deoxygenated ethanol (nitrogen bubbling) is diluted 500 times with a citric acid aqueous solution (1.5 g/L). The solution (8 mL) is put in contact with a stack of 60 (4- \times -4-cm films) (16). The area of contact is 4 cm^2 . The experiment is stored at 23 $^{\circ}\text{C}$. After contact, each film of the stack is extracted and analyzed as above. Six times of contact were tested.

Modeling. The software elaborated in this study is freely available on the INRA web site (<http://www.inra.fr/Internet/Produits/securite-emballage/pagefr.html>). It allows simulation of the contact of up to three aroma compounds with a polymer. Several options offered by the program are not detailed below, as they are not used in this paper, such as the variation of diffusion coefficients with the concentration of plasticizing species (e.g., food constituents penetrating into the polymer matrix), or the secondary degradation of a primary degradation product. In the current study, only the case of a *single* aroma compound submitted to a competition between its degradation and its sorption by (or its permeation through) the polymer in contact is envisaged.

The system, basic equations, and assumptions are schematized on Figure 1.

Initial State. A single aroma is homogeneously dispersed in a liquid at a given concentration. It is ideally soluble in the liquid. This solution (finite volume) is in contact with a virgin plane sheet (finite thickness), which on the other side is in contact with surrounding atmosphere (air, infinite volume).

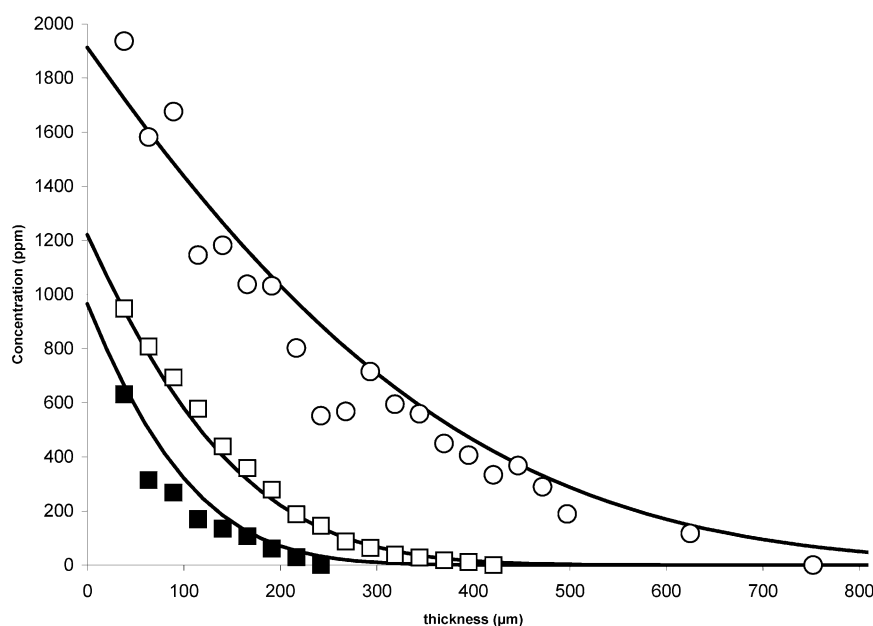


Figure 2. Limonene concentration profile in the thickness of LDPE stack—Initial concentration of limonene in the *stabilized* solution is 80 ppm—experimental data: ■, $t = 2.88 \cdot 10^4$ s, □, $t = 5.37 \cdot 10^4$ s, ○, $t = 2.59 \cdot 10^5$ s. Black curve is the best fit with the following parameters $DA = 3 \cdot 10^{-9}$ cm²/s, $H = 1.3 \cdot 10^{-7}$ cm/s, $KPL = 38.2$.

187 *Degradation.* In the liquid solution, the aroma is submitted to
188 degradation reactions. These reactions are considered to be governed
189 only by apparent first-order kinetics (first-order constant K_d). In the
190 polymer and in air, it is assumed that no degradation occurs.

191 *Diffusion.* The diffusion is considered instantaneous in air and in
192 the liquid. In the polymer, diffusion is described by a Fick law, with
193 a constant diffusion coefficient DA .

194 *Interfaces.* The equilibrium at the liquid/polymer interface is
195 described by a partition coefficient K_{LP} . This equilibrium is assumed
196 to be instantaneous (no effect of mass transfer). At the polymer/
197 atmosphere interface, the equilibrium concentration is zero, as the
198 volume of atmosphere is considered infinite. This equilibrium is
199 either not instantaneous (desorption into air being controlled by mass
200 transfer), or instantaneous (concentration at polymer surface equal to
201 zero).

202 A numerical resolution is used to calculate at each time loop the
203 local concentrations in the thickness of the polymer (spatial discreti-
204 sation by 100 ΔX elements) and the concentration in the solution (18,
205 19). The validity of numerical calculations is controlled by comparing
206 the numerical data to common resolutions in extreme cases: no
207 diffusion, only degradation kinetics; and no degradation, only Fickian
208 sorption.

209 Results of the calculations are expressed in **Table 1** as a function of
210 L (thickness of the polymer in μm), DA (in cm²/s), K_{LP} partition
211 coefficient, and K_d (in s⁻¹). The results are given only for systems
212 leading to the most important losses: $CA_{t=100} < 70\%$ of the initial
213 concentration.

214 Results are Expressed in 2 Columns. The column “losses by
215 permeation” gives the amount having permeated at $t = 100$ days
216 ($Q_{\text{perm},100}$) as a fraction of the total initial aroma quantity Q_{max} :
217 (++) , $Q_{\text{perm},100}$ is between Q_{max} and $0.1 Q_{\text{max}}$; (+), $Q_{\text{perm},100}$
218 is between 0.001 and $0.1 Q_{\text{max}}$; (-), $Q_{\text{perm},100}$ is less than 0.001
219 Q_{max}

220 The column “ratio” evaluates the polymer effect on aroma loss
221 kinetics: it is expressed by the ratio ($CA_{t=100}$, calculated in given
222 conditions (for a set of parameters L - DA - K_{LP} - K_d))/($CA_{t=100}$, calcu-
223 lated from simple degradation (K_d) without polymer contact). The
224 following notations are used: (++++), $1000 < \text{Ratio} < 10\,000$;
225 (+++), $100 < \text{Ratio} < 1000$; (++) , $10 < \text{Ratio} < 100$; (+), $1 <$
226 $\text{Ratio} < 10$; (1), $\text{Ratio} \approx 1$; (-), $0.1 < \text{Ratio} < 1$; (- -), $0.01 < \text{Ratio}$
227 < 0.1 ; (- - -), $\text{Ratio} < 0.01$.

RESULTS AND DISCUSSION

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The complete description of a whole food/package system
involves many parameters and/or experimental determinations.
The approach followed here consists of the determination of a
wide range of aroma/package partition coefficients and of
diffusion constants. Typical and extreme values are thus
obtained. The influence of changes between the extreme values
is then investigated using the numerical model.

**Experimental Evaluation of the Limonene/Low-Density
Polyethylene System.** The limonene/low-density polyethylene
system has been often studied, either for sorption or for
reactivity. In the presence of acids, limonene is degraded within
a few days. Limonene sorption in LDPE is very fast, and the
apolar character of both this aroma compound and the polymer
induces a high partition coefficient. This system is interesting
to have a complete overview of sorption/reactivity competition,
since sorption and degradation kinetics are of the same order
of magnitude (no preponderant mechanism)

In **Figure 2** are given the experimental sorption profiles of
limonene in a LDPE stack of films. In these experiments, the
limonene solution is stabilized, and no degradation occurs. Only
the sorption mechanism has to be taken into account for the fit
of concentration profiles, measured at different contact times.
It can be observed in **Figure 2** that the profiles do not intercept
at time 0, which indicates that the surface concentration is time
dependent and that the equilibrium concentration is not reached
instantaneously at the surface (in contradiction with the simple
assumption of **Figure 1**). Modeling using a constant (equilib-
rium) concentration at the surface failed. This indicates that
sorption is governed not only by diffusion in the bulk but also
by mass transfer at the interface, which is time dependent. H is
the mass transfer coefficient introduced to take into account
non instantaneous solution/polymer equilibrium (18, 19). The
best fit of experimental sorption profiles led to the following
values: $K_{PL} = 38.2$, $H = 1.3 \cdot 10^{-7}$ cm/s, $DA = 3 \cdot 10^{-9}$
cm²/s.

As expected, the values of DA and KP/L are quite high, since
LDPE is sorbed quickly and strongly by limonene.

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Table 1. Predicted Interactions of Aroma Compounds with Food Contact Materials of Different Thicknesses in Different Conditions of Contact^a

μm	DA cm^2/s	K_{PL}	Kd s^{-1}	losses by permeation	ratio	μm	DA cm^2/s	K_{PL}	Kd s^{-1}	losses by permeation	ratio
300	1.00E-08	1	1.00E-14	++	-	50	1E-12	0.02	2.7E-06	-	+
300	1.00E-10	50	1.00E-14	++	-	50	1E-11	0.02	2.7E-06	-	o
300	1.00E-09	50	1.00E-14	++	--	50	1E-10	0.02	2.7E-06	-	o
300	1.00E-08	50	1.00E-14	++	---	50	1E-09	0.02	2.7E-06	-	o
300	1.00E-09	1	2.7E-08	+	o	50	1E-08	0.02	2.7E-06	+	o
300	1.00E-08	1	2.7E-08	++	-	50	1E-13	1	2.7E-06	-	++
300	1.00E-11	50	2.7E-08	+	o	50	1E-12	1	2.7E-06	-	+++
300	1.00E-10	50	2.7E-08	++	-	50	1E-11	1	2.7E-06	-	o
300	1.00E-09	50	2.7E-08	++	--	50	1E-10	1	2.7E-06	+	o
300	1.00E-08	50	2.7E-08	++	---	50	1E-09	1	2.7E-06	+	-
300	1.00E-13	0.02	2.7E-06			50	1E-08	1	2.7E-06	++	--
300	1.00E-12	0.02	2.7E-06		+	50	1E-13	50	2.7E-06	-	++++
300	1.00E-11	0.02	2.7E-06	-	++	50	1E-12	50	2.7E-06	+	++++
300	1.00E-10	0.02	2.7E-06	-	++	50	1E-11	50	2.7E-06	+	+
300	1.00E-09	0.02	2.7E-06	-	o	50	1E-10	50	2.7E-06	+	-
300	1.00E-08	0.02	2.7E-06	-	o	50	1E-09	50	2.7E-06	++	---
300	1.00E-13	1	2.7E-06		++	50	1E-08	50	2.7E-06	++	---
300	1.00E-12	1	2.7E-06	-	+++	50	1E-13	0.02	2.7E-07		o
300	1.00E-11	1	2.7E-06	-	+++	50	1E-12	0.02	2.7E-07	-	o
300	1.00E-10	1	2.7E-06	+	+++	50	1E-11	0.02	2.7E-07	-	o
300	1.00E-09	1	2.7E-06	+	o	50	1E-10	0.02	2.7E-07	-	o
300	1.00E-08	1	2.7E-06		-	50	1E-09	0.02	2.7E-07	+	o
300	1.00E-13	50	2.7E-06		++++	50	1E-08	0.02	2.7E-07	+	o
300	1.00E-12	50	2.7E-06		++++	50	1E-13	1	2.7E-07	-	o
300	1.00E-11	50	2.7E-06	-	++++	50	1E-12	1	2.7E-07	-	o
300	1.00E-10	50	2.7E-06	+	++++	50	1E-11	1	2.7E-07	+	o
300	1.00E-09	50	2.7E-06	++	o	50	1E-10	1	2.7E-07	+	o
300	1.00E-08	50	2.7E-06	++	---	50	1E-09	1	2.7E-07	++	-
2000	1.00E-10	50	1.00E-14	-	-	50	1E-08	1	2.7E-07	++	--
2000	1.00E-09	50	1.00E-14	++	-	50	1E-13	50	2.7E-07	-	o
2000	1.00E-08	50	1.00E-14	++	---	50	1E-12	50	2.7E-07	+	o
2000	1E-08	1	2.7E-08	++	-	50	1E-11	50	2.7E-07	+	o
2000	1E-13	50	2.7E-08	-	o	50	1E-10	50	2.7E-07	++	-
2000	1E-12	50	2.7E-08	-	o	50	1E-09	50	2.7E-07	++	---
2000	1E-11	50	2.7E-08	-	-	50	1E-08	50	2.7E-07	++	---
2000	1E-10	50	2.7E-08	-	-	300	1E-13	0.02	2.7E-07		o
2000	1E-09	50	2.7E-08	+	--	300	1E-12	0.02	2.7E-07		o
2000	1E-08	50	2.7E-08	++	---	300	1E-11	0.02	2.7E-07	-	o
2000	1E-13	0.02	2.7E-06	-	o	300	1E-10	0.02	2.7E-07	-	o
2000	1E-12	0.02	2.7E-06	-	+	300	1E-09	0.02	2.7E-07	+	o
2000	1E-11	0.02	2.7E-06	-	++	300	1E-08	0.02	2.7E-07	+	o
2000	1E-10	0.02	2.7E-06	-	++	300	1E-13	1	2.7E-07		o
2000	1E-09	0.02	2.7E-06	-	+++	300	1E-12	1	2.7E-07		o
2000	1E-08	0.02	2.7E-06	-	o	300	1E-11	1	2.7E-07	-	o
2000	1E-13	1	2.7E-06	-	++	300	1E-10	1	2.7E-07	+	o
2000	1E-12	1	2.7E-06	-	++	300	1E-09	1	2.7E-07	+	o
2000	1E-11	1	2.7E-06	-	+++	300	1E-08	1	2.7E-07	++	-
2000	1E-10	1	2.7E-06	-	++++	300	1E-13	50	2.7E-07		o
2000	1E-09	1	2.7E-06	-	++++	300	1E-12	50	2.7E-07		o
2000	1E-08	1	2.7E-06	+	++	300	1E-11	50	2.7E-07	-	o
50	1E-13	50	2.7E-06	-	++++	300	1E-10	50	2.7E-07	++	o
50	1E-12	50	2.7E-06	-	++++	300	1E-09	50	2.7E-07	++	--
50	1E-11	50	2.7E-06	-	++++	300	1E-08	50	2.7E-07	++	---
50	1E-10	50	2.7E-06	-	++++	2000	1E-13	0.02	2.7E-07	-	o
50	1E-09	50	2.7E-06	-	++++	2000	1E-12	0.02	2.7E-07	-	o
50	1E-08	50	2.7E-06	++	++++	2000	1E-11	0.02	2.7E-07	-	o
50	1E-09	1	1.00E-14	++	-	2000	1E-10	0.02	2.7E-07	-	o
50	1E-08	1	1.00E-14	++	--	2000	1E-09	0.02	2.7E-07	-	o
50	1E-11	50	1.00E-14	++	o	2000	1E-08	0.02	2.7E-07	+	o
50	1E-10	50	1.00E-14	++	-	2000	1E-13	1	2.7E-07	-	o
50	1E-09	50	1.00E-14	++	---	2000	1E-12	1	2.7E-07	-	o
50	1E-08	50	1.00E-14	++	---	2000	1E-11	1	2.7E-07	-	o
50	1E-08	0.02	2.7E-08	+	o	2000	1E-10	1	2.7E-07	-	o
50	1E-09	1	2.7E-08	++	-	2000	1E-09	1	2.7E-07	+	o
50	1E-08	1	2.7E-08	++	--	2000	1E-08	1	2.7E-07	+	o
50	1E-12	50	2.7E-08	+	+	2000	1E-13	50	2.7E-07	-	o
50	1E-11	50	2.7E-08	++	o	2000	1E-12	50	2.7E-07	-	o
50	1E-10	50	2.7E-08	++	-	2000	1E-11	50	2.7E-07	-	o
50	1E-09	50	2.7E-08	++	---	2000	1E-10	50	2.7E-07	-	o
50	1E-08	50	2.7E-08	++	---	2000	1E-09	50	2.7E-07	+	-
50	1E-13	0.02	2.7E-06			2000	1E-08	50	2.7E-07	++	--

^a The polymer aroma–food–polymer system is represented by a diffusion coefficient DA (cm^2/s), by the partition coefficient K_{PL} and by the aroma degradation constant Kd s^{-1} . Losses by permeation are the percentage of aroma permeated at $t = 100$ days: (++) , between 1 and 0.1; (+), between 0.001 and 0.1; (-), less than 0.001. The Ratio is the ratio of aroma compound with and without polymer contact at $t = 100$ days: (++++), $1000 < \text{ratio} < 10000$; (+++), $100 < \text{ratio} < 1000$; (++) , $10 < \text{ratio} < 100$; (+), $1 < \text{ratio} < 10$; (1), ratio ≈ 1 ; (-), $0.1 < \text{ratio} < 1$; (---), $0.01 < \text{ratio} < 0.1$, (----), ratio < 0.01 .

Stabilization of Aroma Compounds

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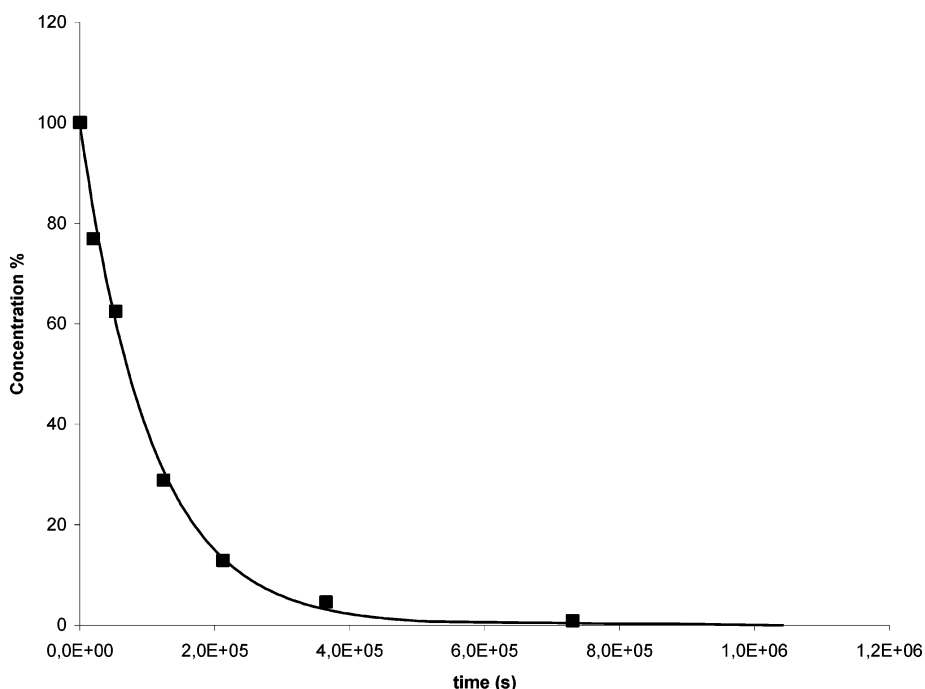


Figure 3. Limonene degradation kinetics in unstabilized conditions; initial concentration is 80 ppm. Black curve is the best fit, assuming first-order degradation: $K_d = 9.5 \cdot 10^{-6} \text{ s}^{-1}$.

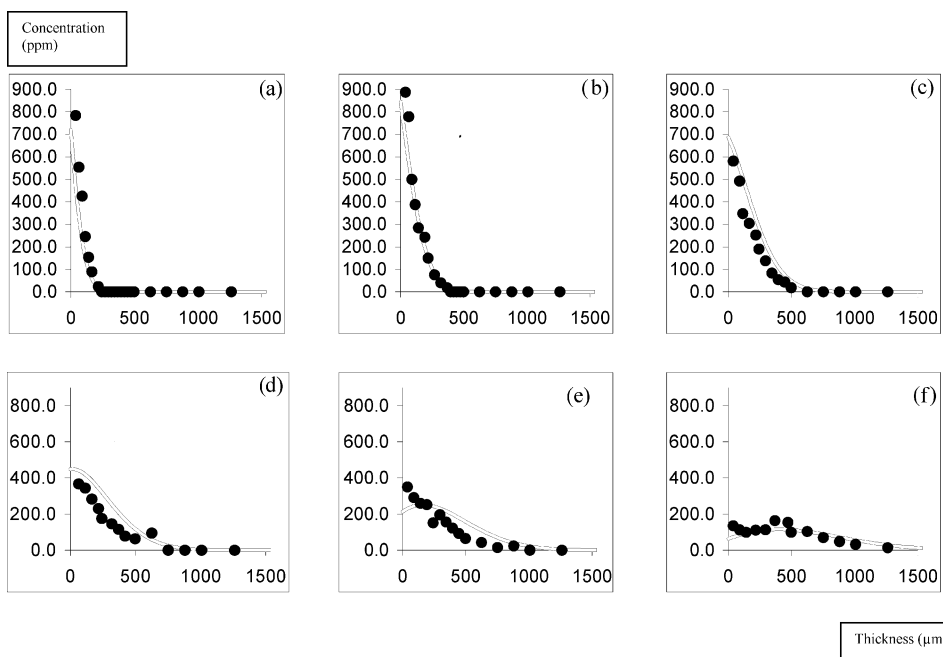


Figure 4. Limonene concentration profiles in the thickness of LDPE stack. Initial concentration of limonene in the *UNstabilized* solution is 80 ppm. (a) $t = 5.58 \text{ h}$, (b) $t = 14.75 \text{ h}$, (c) $t = 34.58 \text{ h}$, (d) $t = 58.92 \text{ h}$, (e) $t = 101.42 \text{ h}$, (f) $t = 202.92 \text{ h}$. Continuous curves are calculated from constants determined in Figures 2 and 3.

266 **Figure 3** shows the degradation kinetics of limonene in a
 267 glass vial. In this experiment, no polymer is in contact, no
 268 sorption takes place, only degradation may occur. The fit of
 269 experimental data, assuming apparent first-order kinetics, leads
 270 to the following first-order rate constant

$$K_d = 9.5 \times 10^{-6} \text{ s}^{-1}$$

271 The degradation is quasi complete after 1 day storage. As
 272 expected, both phenomena are in the same order of magnitude
 273 and are in competition.

274 The parameters obtained previously can be used to simulate
 275 (with the numerical model) a contact of limonene in an acidic

medium (degradation) with LDPE (sorption). The theoretical
 data are shown in **Figure 4**, together with experimental diffusion
 profiles in the thickness of LDPE, measured at different contact
 times of an acidic solution of limonene in contact with a stack
 of films. Experimental data are correctly simulated by the
 parameters obtained from the different model tests. Our simpli-
 fied description of the aroma degradation/sorption mechanism
 describes adequately the real mechanisms of aroma losses.

Moreover, the evolution of the sorption profile is in good
 agreement with the sorption desorption two step mechanism
 proposed by Lebossé (14): during the first 24 h of contact, the
 concentration of the reactive aroma compound in the solution

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288 is high, and an apparent sorption mechanism is observed. The
 289 limonene that remains in the solution is quickly degraded. When
 290 its concentration in the solution becomes very low, desorption
 291 from the film into the solution occurs. The desorption can be
 292 evaluated in two ways: (i) from the decrease of the surface
 293 under the concentration profiles, which corresponds to the
 294 quantity of the aroma sorbed (Figure 4), and (ii) from the change
 295 in the shape of the profiles shape, showing that the concentration
 296 of limonene decreases near the interface with the liquid.

297 The overall result of this mechanism is an apparent attenuation
 298 of the degradation in the solution, the polymer thus playing a
 299 regulating function. The stack of films plays the same role as a
 300 thick material, which has a strong regulating effect.

301 **Partition Coefficient: Experimental Determination of**
 302 **Typical Values.** The aim of this part of the work is to determine
 303 the range covered typically by partition coefficients of aroma
 304 compounds between water and the polymers used currently in
 305 packaging applications. There are several difficulties to directly
 306 using the values proposed in the literature:

307 (i) There are few general studies for aqueous systems (20).
 308 Most papers are focused on a specific polymer/aroma system
 309 (14, 21), on a method of characterization (22), or on nonaqueous
 310 solutions (23)

311 (ii) The possibility to use a constant (not concentration
 312 dependent) partition coefficient has to be clarified: generally
 313 aroma sorption by vapor permeation methods displays non linear
 314 isotherms (24), which is in contradiction with the use of a
 315 constant partition coefficient in works on polymers in direct
 316 contact with liquids.

317 We therefore chose to experimentally determine partition
 318 coefficients on a large panel of aroma compounds (Table 1)
 319 and polymer couples at different concentrations. Typical sorption
 320 curves are given in Figure 5. In most of the cases, isotherms
 321 are linear (Figure 5a), which justifies the use of a constant K_{PL} ,
 322 partition coefficient between polymer and liquid.

323 Deviations of linearity, due to plasticization effects, are
 324 observed for systems with large partition coefficients, where
 325 concentrations of aroma compounds in polymers exceed 3000
 326 ppm (Figure 5b). Aroma compounds at such concentrations
 327 behave as plasticizers of the packaging polymers. We can
 328 remark that this concentration level is seldom reached with real
 329 systems (juices) in contact with polymers.

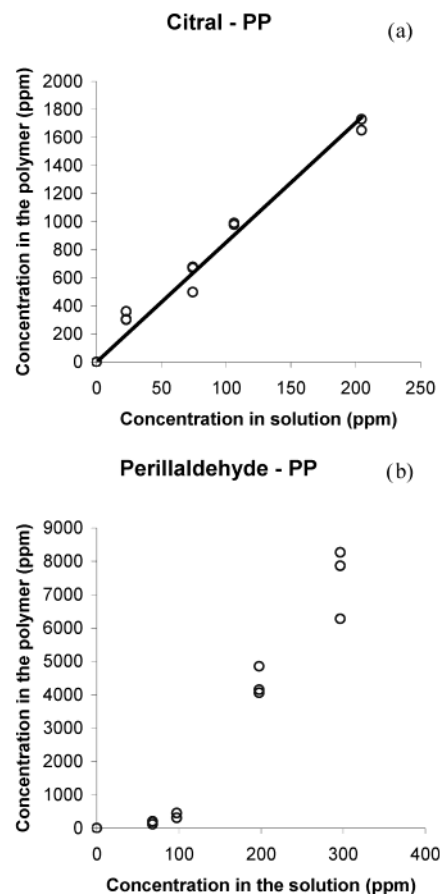
330 Partition coefficients measured in PP, LDPE, EVA, and OPP,
 331 are given in Figures 6 and 7. Experimental values range from
 332 0.3 to 50. In most cases, KPL is larger than 1 (i.e., the affinity
 333 is obviously higher to the polymer than to water). The polarity
 334 tends to decrease the KPL value (e.g., limonene compared to
 335 linalool), but molecular weight effects cannot be excluded (ethyl
 336 butyrate shows the lowest KPL).

337 With the polymers studied here, there is little effect of
 338 polymer polarity. However, Nielsen (20) determined partition
 339 coefficients for a broader range of polymer polarity: when their
 340 polarity increases, KPL tends to 1.

341 In conclusion of this section, the partition coefficient can be
 342 considered as a constant for a given polymer/aroma system (not
 343 concentration dependent in the range 0–3000 ppm). It mainly
 344 ranges from 0.3 to 50.

345 **Experimental Determination of the Ranges Covered by**
 346 **the Diffusion Coefficient.** The diffusion coefficient of organic
 347 species in polymers is mainly a function of molecular weight
 348 and polymer type (25, 26). Piringer (27) has proposed a general
 349 linear relation between $[\log D]$ and the molecular weight of the
 350 diffusants

$$\text{Log } D = A - BM - C/T,$$



351 **Figure 5.** Determination of partition coefficients. Examples of the two
 352 types of behavior observed. The case (a) (linear relation, constant partition
 353 coefficient) is the more common case. Case (b) (non linear) was observed
 354 for perillaldehyde in PP, EVA and LDPE

355 where A , B , and C are constants depending on the polymer, T
 356 is the temperature (K), and M is the molecular weight (g/mol).

357 Because the range of molecular weight covered by aroma
 358 compounds is usually not very large (they are all low molecular
 359 weight compounds), their diffusion coefficient should be mainly
 360 a function of polymer type. Our results confirm these assumptions.
 361

362 **Figure 8** shows the values of diffusion coefficients of aromas
 363 determined in LDPE, PP, and OPP. The variation of D in each
 364 matrix covers less than 1 order of magnitude. Only two alcohols,
 365 α -terpineol and linalool, have lower values than other aromas.
 366 In apolar matrixes, alcohols may interact with themselves and
 367 diffuse as dimers, with an apparent 2 M molecular weight (17).
 368

369 For a given polymer, ethyl butyrate (highest limit) and
 370 nonanal (lowest limit) can be chosen as references to define
 371 the ranges covered by diffusion coefficients of aromas. **Figure**
 372 **9** shows the diffusion coefficient of these two reference
 373 compounds in different polymers. The effect of matrix type is
 374 clearly illustrated: the effect of molecular weight leads to a
 375 variation of less than 1 order of magnitude, while matrix changes
 376 lead to variations of D up to 4 orders of magnitude.
 377

378 Diffusion coefficients in PET could not be measured; despite
 379 the use of thin films (12 μm) and long contact times (3 weeks),
 380 the permeation lag time was not reached even for ethyl butyrate.
 381 From the value measured for PET in contact with ethanol, it
 382 can be expected that the diffusion coefficient of ethyl butyrate
 383 is lower than 10^{-13} cm^2/s . This is consistent with values we
 384 have obtained in a previous work (28, 29), for the diffusion in

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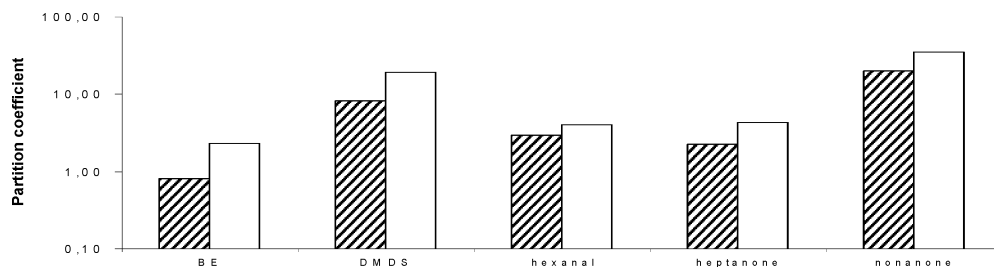


Figure 6. Partition coefficients (KPL) in LDPE (lined bar), and OPP (white bar).

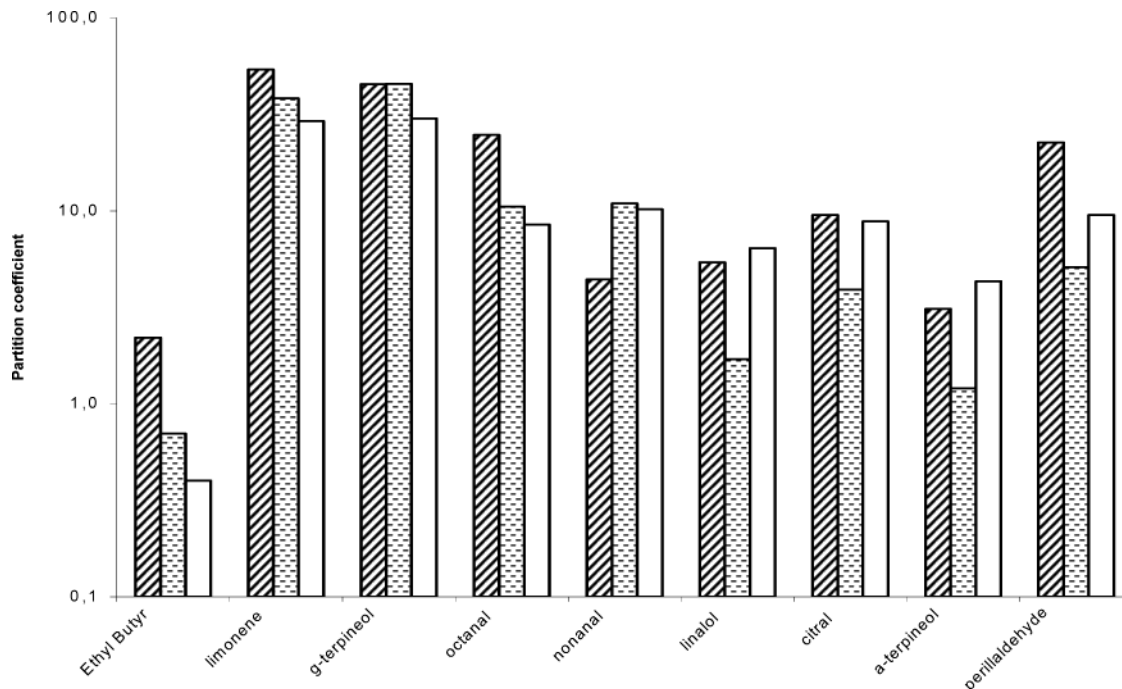


Figure 7. Partition coefficients (KPL) in PP (lined bar), LDPE (hatched bar), and EVA (white bar).

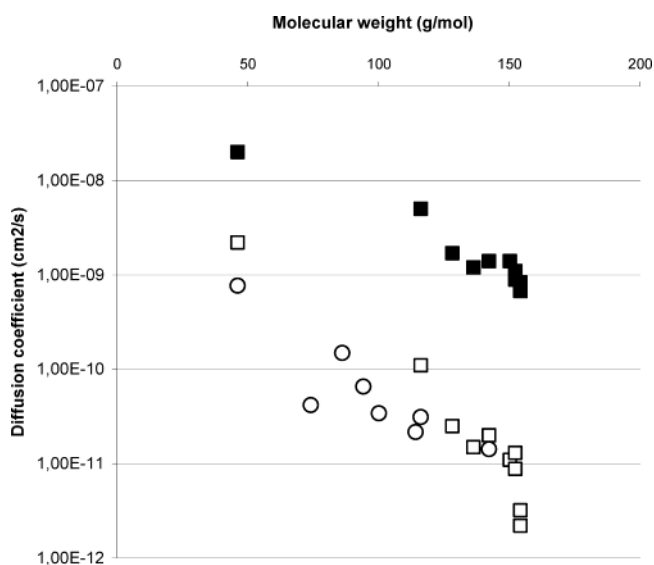


Figure 8. Diffusion coefficients at 23 °C in LDPE ■, PP □, and OPP ○.

379 PET of model contaminants, in the same range of molecular
 380 weight as aroma: values extrapolated at 25 °C are lower than
 381 10^{-13} cm²/s.

382 **Numerical Experiments.** Numerical experiments have been
 383 carried out using the largest range of variables observed in
 384 bibliography and obtained in this study.

385 **Diffusion Coefficients Vary between 10^{-8} and 10^{-14} cm²/**
 386 **s.** Schematically, the aroma diffusion coefficient is between 10^{-8}

and 10^{-11} cm²/s for rubbery polymers and between 10^{-11} and
 10^{-14} cm²/s for glassy polymers. Lower values can even be
 obtained for glassy polymers, but at this (low) level of mobility,
 it can be considered that there is no exchange between polymer
 and solution.

Degradation Rate Constants Vary between 10^{-6} and 10^{-8}
s⁻¹. We did not study this parameter experimentally, as we must
 envisage very unstable compounds, as well as totally stable
 compounds. We preferred to use limit values of Kd: the range
 chosen corresponds to a 90% degradation in 1 day (like
 limonene in acidic medium) to 90% degradation in 1000 days.
 Of course, even higher degradation rates exist (very unstable
 compounds), but for real systems, they would have no interest.
 On the opposite, the case of totally stable compounds (Kd =
 0) can be taken as a reference for degradation constants below
 10^{-8} cm²/s. The range explored is also very large, but it
 corresponds to real cases of food packaging, from fresh products
 to long storage times.

In principle, partition coefficients may vary from zero to
 infinite. Our values range between 0.3 and 50. Generally, most
 values are above 1, as their affinity to the polymer is higher
 than that for water. Therefore, our simulations using values
 ranging from 1/50 to 50 should cover most practical situations.

There is a little knowledge on typical values of mass transfer
 coefficients of organic solutes from polymers to liquids (H).
 Mass transfer is considered as instantaneous in all the polymer
 aroma literature. This assumption has also been made in our
 numerical simulations, despite the fact that we have experi-

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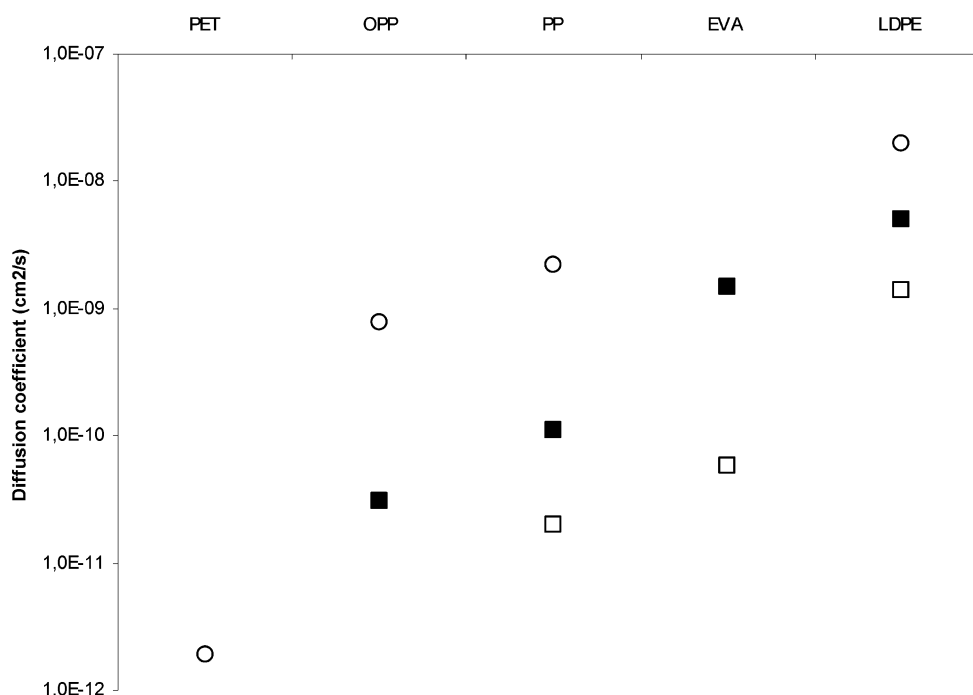


Figure 9. Diffusion coefficients at 23 °C of ethanol ○, ethyl butyrate ■, and nonanal □.

415 mentally observed a rate limiting mass transfer (see the section
 416 on model validation). In fact, regarding the competition between
 417 aroma degradation and their interaction with a polymer, diffusion
 418 and mass transfer play the same role (increase of DA or H leads
 419 to faster sorption); looking only at a variation of DA will provide
 420 a FIRST qualitative approach of this competition. If real systems
 421 are to be investigated in more detail, it will be important to
 422 include a mass transfer contribution.

423 The kinetics of aroma evaporation in air (from polymer to
 424 air HA_{P-Air}) is well studied for liquid/air systems, but polymer/
 425 air systems are not well-known. Vergnaud (30) gives the
 426 following equation:

$$-D\left(\frac{\partial C}{\partial x}\right)_{\text{surface}} = HA_{P-Air}(C_{\text{surface}} - C_{\text{ext}})$$

427 where HA_{P-Air} is the rate of evaporation when diffusion is not
 428 rate limiting and C_{ext} is the external concentration (zero in our
 429 case, infinite external medium).

430 Typical HA_{P-Air} values are not available, but HA_{P-Air} is
 431 connected to the enthalpy of vaporization, and we can remark
 432 that in the aroma molecular weight range, the rate of evaporation
 433 can vary largely: from instantaneous desorption (low molecular
 434 weight aroma compounds), to negligible desorption (aroma
 435 compounds between 150 and 200 g/mol). In the simulations
 436 carried out, we considered only high rates of evaporation to
 437 limit the number of calculations. Simulations with limiting
 438 evaporation have been, however, done in specific cases.

439 The thickness range of the materials has been chosen
 440 considering typical types of packaging: films, 50 μm ; thermo-
 441 formed trays, 300 μm ; thick containers, 2 mm. The other
 442 parameters are chosen to correspond to classical conditions of
 443 packaging food contact: maximum time of contact, 100 days;
 444 packaging surface/food volume ratio, 6 dm^2/L .

445 A total 216 simulations have been carried out. Of the total,
 446 142 simulations show aroma losses lower than 30% of the initial
 447 quantity. These situations correspond to low degradation
 448 constants, coupled with low losses by sorption and perme-
 449 ation: low D , thick polymer, and low partition coefficients.

450 The following discussion is centered on the other systems,
 451 characterized by large aroma losses. The results are displayed
 452 in Table 1 (only systems showing aroma losses higher than 30%
 453 of the initial quantity are displayed). As discussed in the
 454 Introduction, the polymer in contact can behave with a positive
 455 or with a negative effect: positive when it plays a regulating
 456 role, as observed for the thick LDPE/limonene system; negative
 457 when the polymer, in the considered period of contact, leads
 458 mainly to losses by sorption and permeation. To directly evaluate
 459 the polymer effect, we expressed in **Table 1** the ratio between
 460 the concentration in the solution and the concentration which
 461 could be obtained in the same conditions (same K_d) but without
 462 polymer contact. The ratio is given at $t = 100$ days. If the ratio
 463 is close to 1, the polymer can be considered as inert; if it is
 464 much larger than 1, the polymer plays mainly a regulating role;
 465 if it is much lower than 1, losses by sorption and permeation
 466 are more important than by degradation.

467 *Ratio Close to 1.* These systems are generally good barrier
 468 polymers ($DA < 10^{-11}$ cm^2/s), with a large degradation constant
 469 of aroma compounds. As expected, the other contributing factors
 470 are large thicknesses and low partition coefficients. PVC and
 471 PET should every time meet these conditions and behave as
 472 inert packaging toward aromas, which is generally the case.
 473 However, negative effects can be attributed to oxygen perme-
 474 ation, which is not taken into account in this paper. Positive
 475 effects (Ducruet 2001) can be attributed to high interaction
 476 between polymer and aroma (e.g., specific interactions such as
 477 those of cinnamates with PET, by plasticization of the matrix)
 478 leading to DA values larger than 10^{-11} cm^2/s , and K_{PL} values
 479 larger than 10.

480 *Ratio Lower Than 1.* Low ratios correspond mainly to
 481 permeation effects. They are favored by large diffusion coef-
 482 ficients, low thickness, and large K_{PL} . We must remark that these
 483 losses are probably overestimated compared to real situations,
 484 since we have assumed instantaneous evaporation at interface
 485 with air.

486 *Ratio Larger Than 1.* In the best conditions, the ratio can
 487 reach very high values (until 10^5). The “regulating” effect of
 488 the polymer is observed mainly on systems with a large aroma

Stabilization of Aroma Compounds

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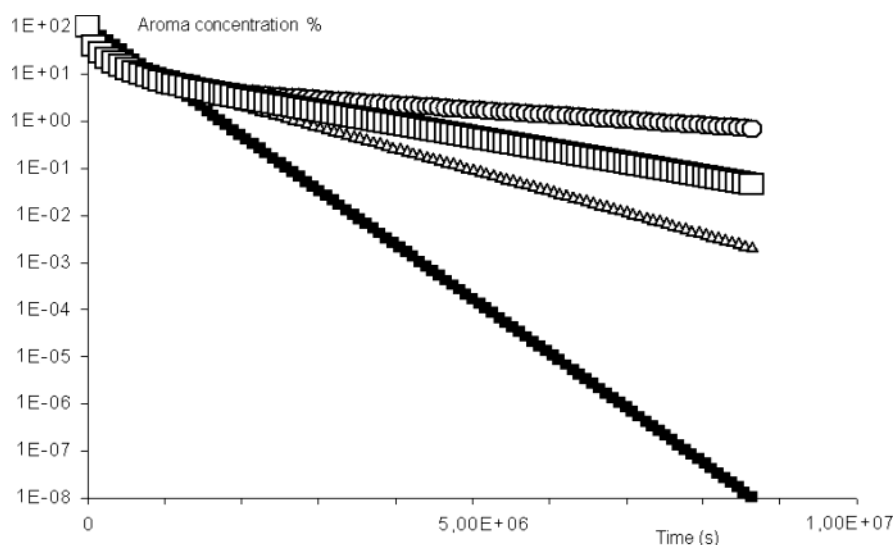


Figure 10. Simulated aroma concentration in the solution in function of time. ■, $K_d = 2.7 \times 10^{-6} \text{ s}^{-1}$ and no interaction with a polymer; △, $K_d = 2.7 \times 10^{-6} \text{ s}^{-1}$, $DA = 10^{-8} \text{ cm}^2/\text{s}$, thickness 2 mm, $K_{P/L} = 50$, $CA_{X=L} = 0$ (instantaneous evaporation at polymer air interface; this was the limit condition used in all simulations of Table 1). □, $K_d = 2.7 \times 10^{-6} \text{ s}^{-1}$, $DA = 10^{-8} \text{ cm}^2/\text{s}$, thickness 2 mm, $K_{P/L} = 50$, $HA_{P-Air} = 1 \times 10^{-7} \text{ cm/s}$. ○, $K_d = 2.7 \times 10^{-6} \text{ s}^{-1}$, $DA = 10^{-8} \text{ cm}^2/\text{s}$, thickness 2 mm, $K_{P/L} = 50$, $HA_{P-Air} = 0$ (no evaporation at polymer air interface).

489 degradation constant. The sorbed quantity must be large, but
 490 the permeated quantity must be low. This is why the higher
 491 ratios correspond to high K_{PL} , high thicknesses, but also to
 492 intermediate values of DA. This request that DA is not too large
 493 is only a consequence of the assumption about polymer air
 494 interfaces used in simulations: as we have assumed
 495 instantaneous mass transfer at polymer air interface, a fast
 496 diffusion is associated to a fast evaporation. Another conse-
 497 quence is that losses by permeation are overestimated compared
 498 to real cases. **Figure 10** corresponds to the example of a thick
 499 polymer, with a large diffusion coefficient, a large K_{PL} , and
 500 varying mass transfer conditions at polymer/air interface:
 501 instantaneous transfer, no transfer ($HA_{P-Air} = 0$), and intermedi-
 502 ate case ($HA_{P-Air} = 10^{-7} \text{ cm/s}$), simulating a permeation
 503 controlled mainly by evaporation rate. The slope of the apparent
 504 first-order degradation increases with decreasing HA_{P-Air} . Of
 505 course, the regulating effect of the polymer is larger when no
 506 permeation occurs. This corresponds to aromas of low volatility
 507 or to multilayer films containing a barrier inner layer (no
 508 exchange assumed with and through this layer). In this case,
 509 the larger is the diffusion coefficient, the better is the regulating
 510 effect.

511 **How Can the Sensory Quality of Food be Improved**
 512 **through Packaging Materials?** The simulation experiments
 513 have shown that plastic packaging could sometimes decrease
 514 the apparent degradation of aromatic compounds in aqueous
 515 solution, by sorption and desorption phenomena (ratio higher
 516 than 1: high DA, high K_{PL} , no permeation). However, the
 517 regulating effect was really important when concentration was
 518 close to zero in the solution. If the curve of **Figure 10**
 519 was expressed with a linear Y scale, the polymer regulating effect
 520 could obviously look less important. However, it should be
 521 emphasized that sensory effects are not linear either with the
 522 concentration.

523 There are few papers claiming a positive effect of plastic
 524 packaging. This is explained by the fact that classical polymers
 525 and packaging thicknesses are not well adapted to observe this
 526 effect: in the first instance, they have to comply with food
 527 contact regulations, which implies that migration is below given
 528 limits and that the exchanges between polymer and food are
 529 low. On the other hand, they also have to comply with source

530 reduction requirements. One should seek larger solubilities rather
 531 than increasing the packaging thickness. Therefore, barrier
 532 polymers with high percentages of cristallinity (lower quantity
 533 of phase in equilibrium with the solution) are often preferred.
 534 To enhance the aroma/polymer interaction, materials such as
 535 elastomers, which have the opposite characteristics, could be
 536 used as contact layer; to prevent permeation, they could be
 537 associated to structures with an inner barrier layer.

538 Another route to obtain high diffusion coefficients could
 539 consist of using hydrophilic polymers in direct contact. In
 540 practice, as these polymers behave as good barriers when they
 541 are anhydrous, they are not used in direct contact with food.
 542 Swelling by water increases diffusion coefficients, and such
 543 polymers could give rise to very fast aroma capture. The
 544 problem would be that polar polymers are associated to low
 545 partition coefficients with aqueous foods. To combine fast
 546 sorption and high partition, blends with polyolefins or block
 547 copolymers should be tested.

548 In conclusion, we have shown here that the limonene/low-
 549 density polyethylene system has a very interesting behavior, as
 550 the packaging material has a regulating role: in the early stage
 551 of contact, the polymer sorbs limonene, and when its concentra-
 552 tion in food becomes low, the packaging liberates back limonene
 553 into the solution. This is due to an efficient competition between
 554 sorption/desorption and degradation. To define which aroma
 555 packaging systems could also display this interesting behavior,
 556 we have simulated all types of possible interactions, using
 557 thermodynamic and kinetic parameters describing most practical
 558 situations.

559 For that purpose, 35 values of reference diffusion coefficients
 560 and 35 partition coefficients of usual aroma compounds between
 561 polymers and water have been measured and combined with
 562 the few available data from literature.

563 Four types of behavior are recognized:

- 564 (i) No sensible evolution of aroma concentration: no
 565 degradation, no sorption, no permeation.
- 566 (ii) Sensible evolution mainly due to degradation.
- 567 (iii) Sensible evolution mainly due to permeation.
- 568 (iv) Regulating function of the polymer, decreasing the
 569 apparent degradation constant.

570 This last type of behavior corresponds to large partition
571 coefficients (above 10), large diffusion coefficients ($> 10^{-9} \text{ cm}^2$
572 $\times \text{s}^{-1}$) and large degradation constants. Such systems open new
573 fields of applications, where plastic packaging could contribute
574 positively to the sensory quality. Such effect has not been
575 reported on real systems up to now, as the materials available
576 on the market do not cover a range of interaction parameters
577 (DA, K_{PL}) as broad as those which have been investigated here.
578 On the basis of the work presented here, it is possible to envisage
579 packaging systems that could be much more efficient for aroma
580 preservation.

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587 LITERATURE CITED

- 588 (1) Kwapong, O. Y.; Hotchkiss, J. H. Comparative sorption of
589 aroma compounds by polyethylene and ionomer food contact
590 plastics. *J. Food Sci.* **1987**, *52*, 761.
- 591 (2) Landois Garza, J.; Hotchkiss, J. H. Plastic packaging can cause
592 aroma sorption. *Food Eng.* **1987**, April, 39–42.
- 593 (3) Pieper, G.; Borgudd, L.; Akermann, P.; Fellers, P. Absorption
594 of aroma volatiles of orange juice into laminated carton did not
595 affect sensory quality. *J. Food Sci.* **1992**, *57*, 1408–1411.
- 596 (4) Sizer, C. E.; Waugh, P. L.; Edstam, S.; Akerman, P. Maintaining
597 flavour and nutrient quality of aseptic orange juice. *Food*
598 *Technol.* **1988**, *42*, 152–159.
- 599 (5) Ayhan, Z.; Yeom, H. W.; Zhang, Q. H.; Min, D. B. Flavor, Color,
600 and Vitamin C Retention of Pulsed Electric Field Processed
601 Orange Juice in Different Packaging Materials. *J. Agric. Food*
602 *Chem.* **2001**, *49*, 669–674.
- 603 (6) Strandburg, G.; Delassus, P. T.; Howell, B. A. Diffusion and
604 sorption of Linear esters in selected polymer films, Barrier
605 Polymers, and structures. *ACS Symposium Series 423*; Koros,
606 W. J., Ed.; American Chemical Society: Washington, DC, 1990;
607 pp 333–348.
- 608 (7) Franz, R. Permeation of Volatile Organic Compounds across
609 Polymer Films—Part I: Development of a sensitive test method
610 suitable for High Barrier Packaging films at very low Permeant
611 Vapour pressures. *Packag. Technol. Sci.* **1993**, *6*, 91–102.
- 612 (8) Delassus, P. T.; Strandburg, G. Flavor and aroma permeability
613 in plastics. *Food Packaging Technology, ASTM STP 1113*;
614 Henyon, D., Ed.; American Society for Testing and Materials:
615 Philadelphia, PA, 1991; pp 64–73.
- 616 (9) Siegmund, B.; Derler, K.; Pfannhauser, W. Changes in the Aroma
617 of a Strawberry Drink during storage. *J. Agric. Food Chem.* **2001**,
618 *49*, 3244–3252.
- 619 (10) Clarck, B. C.; Chamblee, T. S., Jr. Acid-catalysed reactions of
620 citrus oils and other terpene-containing flavors. In *Off-Flavors*
621 *in Foods and Beverages*; Charalambous, Ed.; Elsevier Science
622 Publishers B. V.: Oxford, 1992; pp 229–285.
- 623 (11) Nagy, S.; Rouseff, R. L.; Lee, H. S. Thermally Degraded Flavors
624 in Citrus Juice Products. In *Thermal Generation of Aromas*;
625 Paliment, T. H., Ed.; *ACS Symposium Series 409*; American
626 Chemical Society: Washington, DC, 1989; *31*, pp 331–345.
- 627 (12) Pokorny, J.; Pudil, F.; Volfová, J.; Valentová, H. Changes in
628 the flavour of monoterpenes during their autoxidation under
629 storage conditions. In *Food Flavors: Formation, Analysis, and*
630 *Packaging Influences*; Contis, E. T., et al., Eds.; Elsevier Sciences
631 B. V.: Oxford, 1998; pp 667–677.
- (13) Peacock, V. E.; Kuneman, D. W. Inhibition of the formation of
632 dimethylstyrene and *p*-cymen-8-ol in carbonated citral containing
633 beverage system. *J. Agric. Food Chem.* **1985**, *33*, 330–335. 634
- (14) Lebosse, R.; Ducruet, V.; Feigenbaum, A. Interactions between
635 reactive aroma compounds from model citrus juice with polypro-
636 pylene packaging film. *J. Agric. Food Chem.* **1997**, *45*, 2836–
637 2842. 638
- (15) Ducruet, V.; Fournier, N.; Saillard, P.; Feigenbaum, A.; Guichard,
639 E. Influence of packaging on the aroma stability of strawberry
640 syrup during shelf life. *J. Agric. Food Chem.* **2001**, *49*, 2290–
641 2297. 642
- (16) Moisan, J. Y. Diffusion des additifs du polyéthylène – IV Etude
643 de matériaux modèles. *Eur. Polym. J.* **1981**, *17*, 857–864. 644
- (17) Reynier, A.; Dole, P.; Humbel, S.; Feigenbaum, A. Diffusion
645 coefficients of additives in polymers. I. Correlation with
646 geometric parameters. *J. Appl. Polym. Sci.* **2001**, *82*, 2422–2433. 647
- (18) Reynier, A.; Dole, P.; Feigenbaum, A. Migration of additives
648 from polymers into food simulants: numerical solution of a
649 mathematical model taking into account food and polymer
650 interactions. *Food Addit. Contam.* **2002**, *19*, 89–102. 651
- (19) Reynier, A.; Dole, P.; Feigenbaum, A. Integrated approach of
652 migration prediction using numerical modelling associated to
653 experimental determination of key parameters. *Food Addit.*
654 *Contam.* **2002**, *19* (Suppl.), 42–55. 655
- (20) Nielsen, T. Aroma sorption by food packaging polymers, Ph.D.
656 thesis, 1994, Lund (Sweden). 657
- (21) Gavara, R.; Hernandez, R. J.; Giacini, J. R. Methods to determine
658 partition coefficients of organic compounds in water polystyrene
659 systems. *J. Food Sci.* **1996**, *61*, 947–952. 660
- (22) Steffen, A.; Pawliszyn, J. Analysis of flavour volatiles using
661 headspace solid-phase microextraction. *J. Agric. Food Chem.*
662 **1996**, *44*, 2187–2193. 663
- (23) Hernandez, P.; Catala, R.; Gavara, R. Food aroma partition
664 between packaging materials and fatty food simulants. *Food*
665 *Addit. Contam.* **2001**, *18*, 673–682. 666
- (24) Apostolopoulos, D.; Winters, N. Measurement of permeability
667 for packaging films to *d*-limonene vapour at low levels. *Packag.*
668 *Technol. Sci.* **1991**, *4*, 131–138 669
- (25) Brandsch, J.; Mercea, P.; Piringer, O. Modeling of additive
670 diffusion coefficients in polyolefin. *ACS Symposium Series 753*
671 (*Food Packaging*); American Chemical Society: Washington,
672 DC, 2000; pp 27–36. 673
- (26) Brandsch, J.; Mercea, P.; Ruter, M.; Tosa, V.; Piringer, O.
674 Migration modelling as a tool for quality assurance of food
675 packaging. *Food Addit. Contam.* **2002**, *19* (suppl.), 29–41. 676
- (27) Piringer, O. G. Modeling of additive diffusion coefficients in
677 polymers. Book of Abstracts, 215th ACS National Meeting,
678 Dallas, TX, March 29–April 2 1998; American Chemical
679 Society, Washington, DC, 1998. 680
- (28) Pennarun, P. Y.; Dole P.; Feigenbaum A. Functional barriers in
681 PET recycled bottles. Part I: determination of diffusion coef-
682 ficients in bi-oriented PET with and without food simulant
683 contact. *J. Appl. Polym. Sci.* **2004**, *92*, 2845–2858. 684
- (29) Pennarun, P. Y.; Dole, P.; Feigenbaum, A. Functional barriers
685 in PET recycled bottles. Part III: simulation of migration kinetics
686 using overestimated diffusion coefficients, submitted to *Packag.*
687 *Technol. Sci.* 688
- (30) Vergnaud, J. M. *Liquid Transport Processes in Polymeric*
689 *Materials. Modelling and Industrial Applications*; Prentice
690 Hall: Englewood Cliffs, NJ, 1991. 691

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