

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

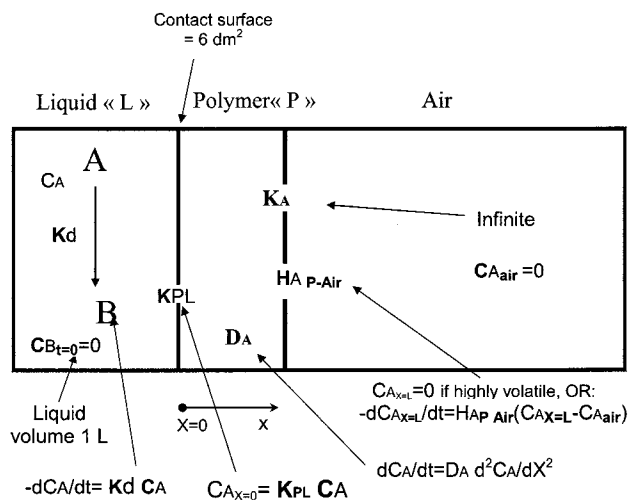


Figure 1. Basic equations and assumptions used in the numerical model.

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 in 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).

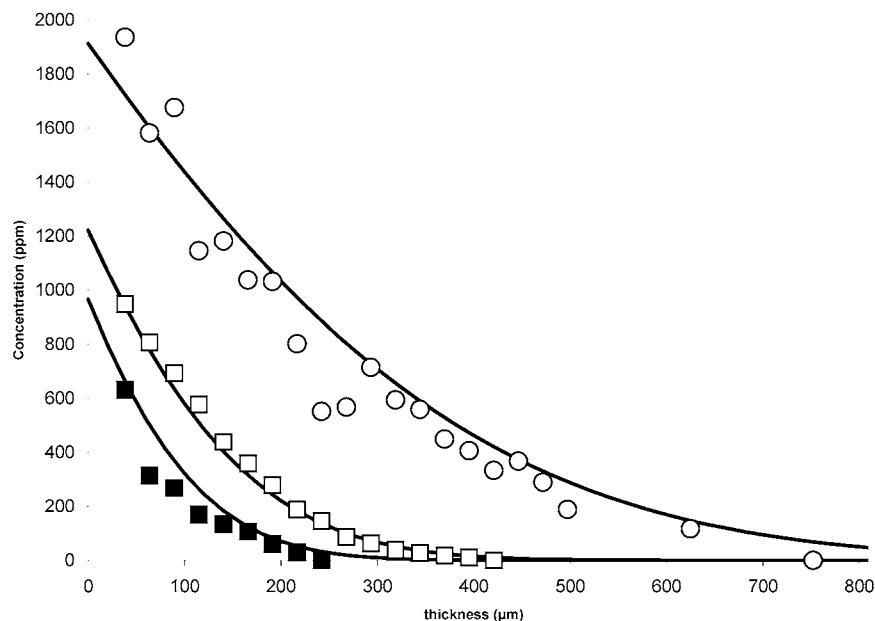


Figure 2. Limonene concentration profiles in the thickness of LDPE stack—Initial concentration of limonene in the *stabilized* solution is 80 ppm—experimental data: ■, $t = 2.88 \cdot 10^4$ s, □, $t = 5.37 \cdot 10^4$ s, ○, $t = 2.59 \cdot 10^5$ s. Black curve is the best fit with the following parameters: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

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

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

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

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

Results of the calculations are expressed in **Table 1** as a function of L (thickness of the polymer in μm), DA (in cm^2/s), K_{PL} partition coefficient, and K_d (in s^{-1}). The results are given only for systems leading to the most important losses: $CA_{t=100} < 70\%$ of the initial concentration.

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

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

RESULTS AND DISCUSSION

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/reativity 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 (equilibrium) 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: $K_{PL} = 38.2$, $H = 1.3 \times 10^{-7}$ cm/s , $DA = 3 \times 10^{-9}$ cm^2/s .

As expected, the values of DA and K_{PL} are quite high, since LDPE is sorbed quickly and strongly by limonene.

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-08	50	2.7E-08	++	---	2000	1E-08	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 (cm²/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 < ratio < 10000; (+++), 100 < ratio < 1000; (++) 10 < ratio < 100; (+), 1 < ratio < 10; (1), ratio ≈ 1; (-), 0.1 < ratio < 1; (---), 0.01 < ratio < 0.1, (---), ratio < 0.01.

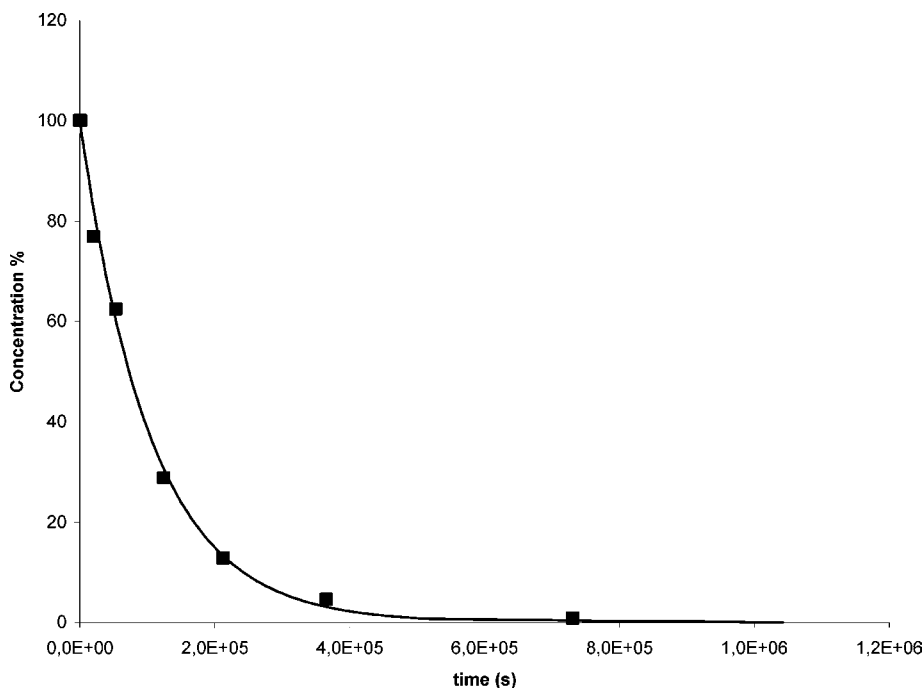


Figure 3. Limonene degradation kinetics in unstabilized conditions; initial concentration is 80 ppm. Black curve is the best fit, assuming first-order degradation: $K_d = 9.5 \cdot 10^{-6} \text{ s}^{-1}$.

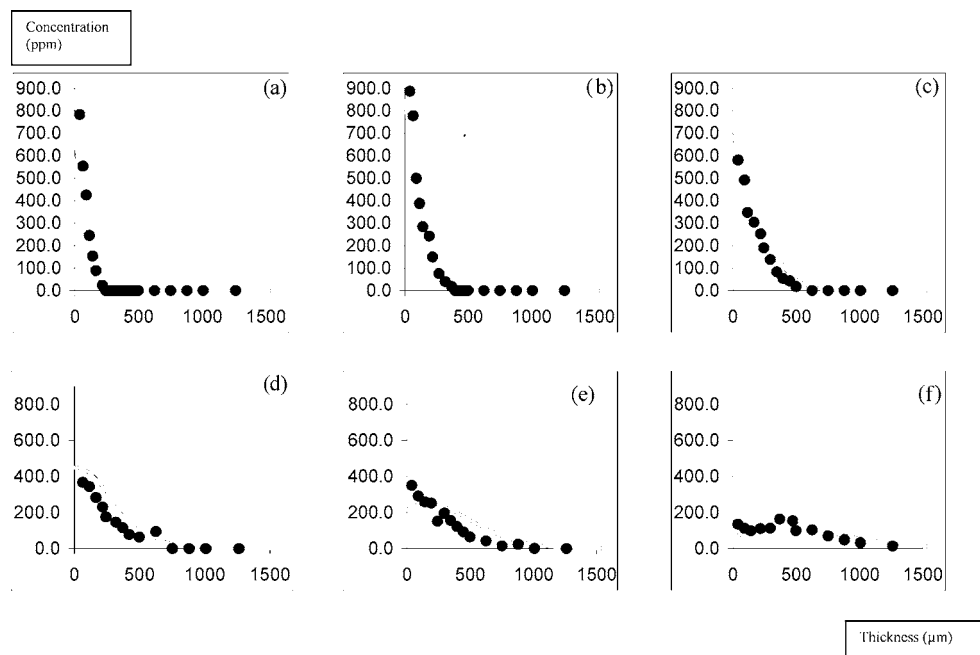


Figure 4. Limonene concentration profiles in the thickness of LDPE stack. Initial concentration of limonene in the *UNstabilized* solution is 80 ppm. (a) $t = 5.58 \text{ h}$, (b) $t = 14.75 \text{ h}$, (c) $t = 34.58 \text{ h}$, (d) $t = 58.92 \text{ h}$, (e) $t = 101.42 \text{ h}$, (f) $t = 202.92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

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

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

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

The parameters obtained previously can be used to simulate (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 simplified 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

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

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

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

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

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

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

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

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

With the polymers studied here, there is little effect of polymer polarity. However, Nielsen (20) determined partition coefficients for a broader range of polymer polarity: when their polarity increases, K_{PL} tends to 1.

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

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

$$\log D = A - BM - C/T,$$

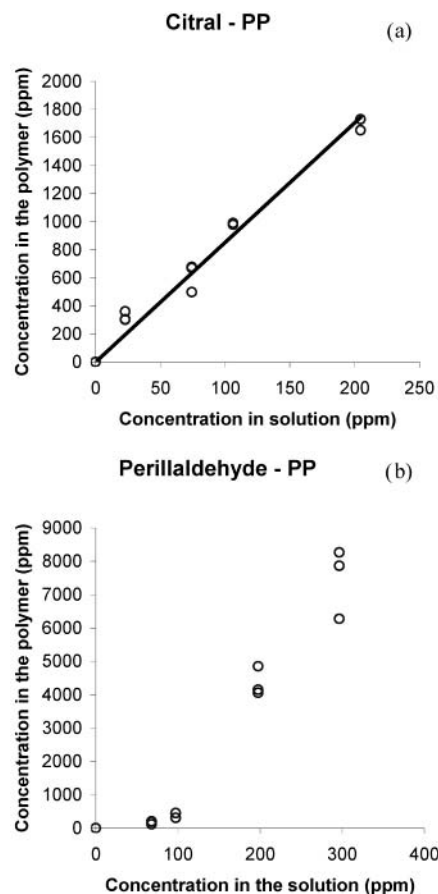


Figure 5. Determination of partition coefficients. Examples of the two types of behavior observed. The case (a) (linear relation, constant partition coefficient) is the more common case. Case (b) (non linear) was observed for perillaldehyde in PP, EVA and LDPE

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

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

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

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

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

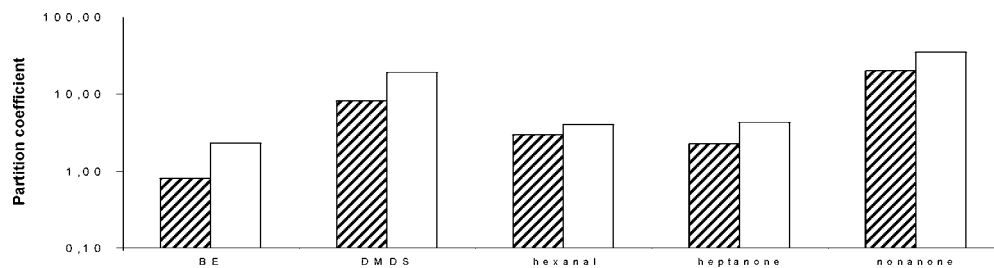


Figure 6. Partition coefficients (K_{pl}) in LDPE (lined bar) and OPP (white bar). BE, ethyl butyrate; DMS, dimethyl disulfide.

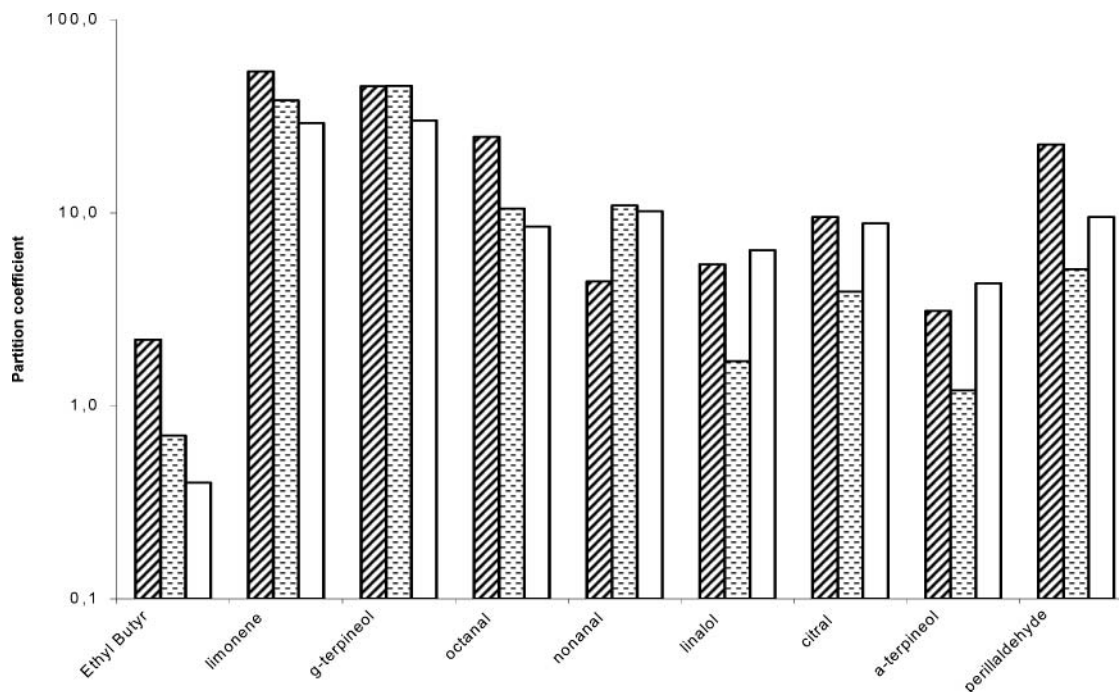


Figure 7. Partition coefficients (K_{pl}) in PP (lined bar), LDPE (hatched bar), and EVA (white bar).

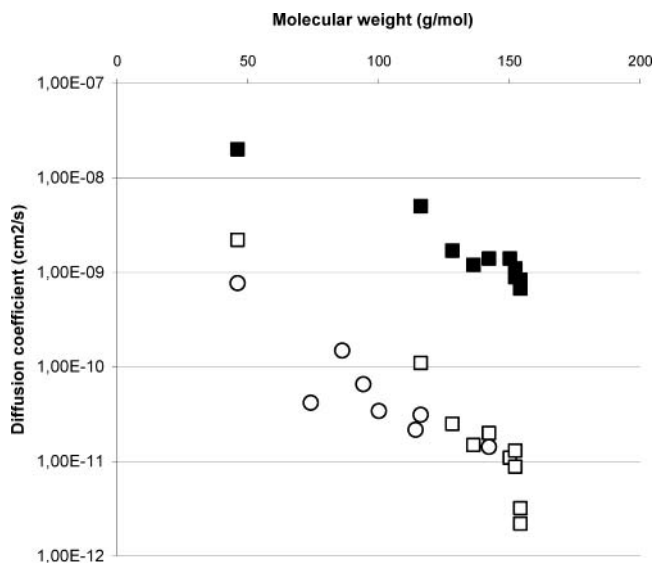


Figure 8. Diffusion coefficients at 23 °C in LDPE ■, PP □, and OPP ○.

PET of model contaminants, in the same range of molecular weight as aroma: values extrapolated at 25 °C are lower than 10^{-13} cm^2/s .

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

Diffusion Coefficients Vary between 10^{-8} and 10^{-14} cm^2/s . Schematically, the aroma diffusion coefficient is between 10^{-8}

and 10^{-11} cm^2/s for rubbery polymers and between 10^{-11} and 10^{-14} cm^2/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 K_d : 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 ($K_d = 0$) can be taken as a reference for degradation constants below 10^{-8} cm^2/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-

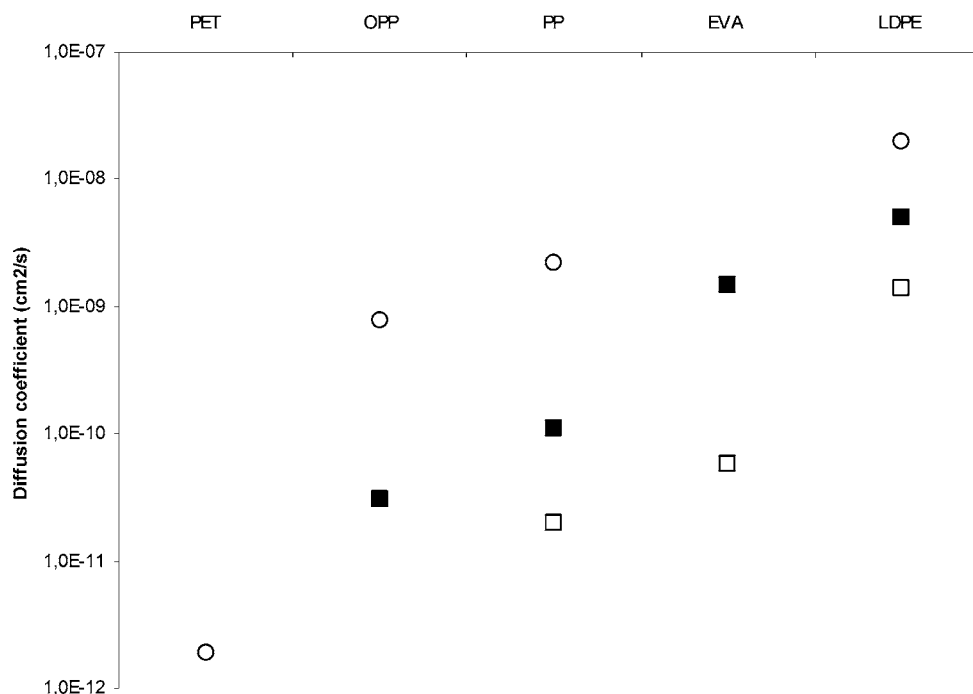


Figure 9. Diffusion coefficients at 23 °C of ethanol ○, ethyl butyrate ■, and nonanal □.

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

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

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

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

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

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

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

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

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

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

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

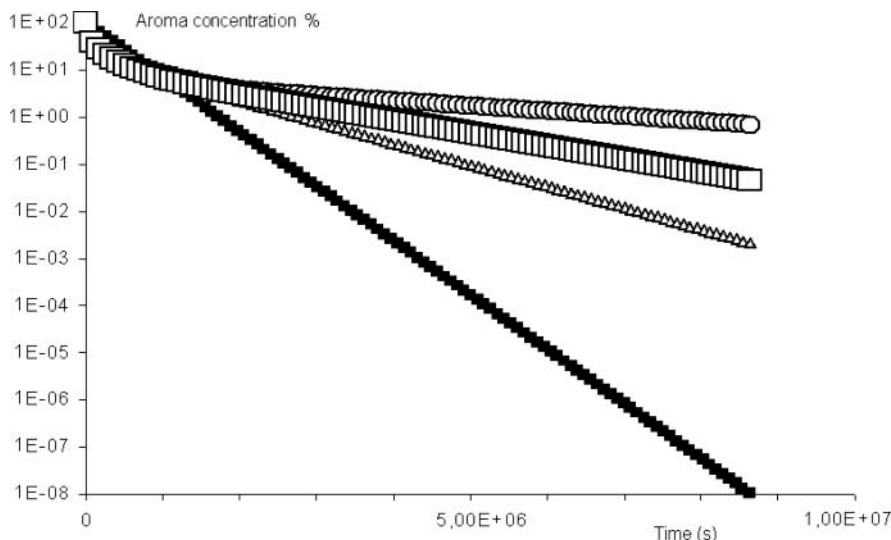


Figure 10. Simulated aroma concentration in the solution in function of time. ■, $K_d = 2.7 \times 10^{-6} \text{ s}^{-1}$ and no interaction with a polymer; △, $K_d = 2.7 \times 10^{-6} \text{ s}^{-1}$, $DA = 10^{-8} \text{ cm}^2/\text{s}$, thickness 2 mm, $K_{P/L} = 50$, $CA_{X=L} = 0$ (instantaneous 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).

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

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

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

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

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

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

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.

Four types of behavior are recognized:

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

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

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