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Integrated approach of migration prediction using numerical modelling associated to experimental determination of key parameters

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The principle of utilizing a computing program describing precisely the migration of additives from a polymer into a food simulant is presented. The model has been validated with a UV absorber in polypropylene migrating into glyceryl tripelargonate, a pure triglyceride whose behaviour and average molecular weight are similar to Myglyol (a synthetic mixture of C8–C12 triglycerides). Six parameters were used to fit the simulant sorption and additive extraction kinetics, and these were determined by independent experiments. The possibility of eliminating any of the parameters is also discussed. This work provides the first consistent set of experimental data that can be used to overestimate the diffusion coefficients of additives both in virgin (without contact with solvent) and in swollen (fat contact) polymer. The influence of mobility increase brought out by temperature or swelling are compared. The effects were more important for high molecular weight compounds.

Introduction

A new approach to evaluate migration from food packaging using mathematical modelling is currently

being discussed by experts in the European Community. The basis for a possible regulatory approach has been laid down by Brandsch et al. (2000): the diffusion coefficient is overestimated using experimental correlations based on the molecular dimensions, and Fick's law is used to calculate the migration kinetics in worst-case conditions. This paper provides an overview of the authors' contribution to the field of migration prediction during the last few years (Reynier et al. 1999. 2001a–c) and indicates improvement of the mathematical models and measurement of reference kinetic parameters using model experiments in the following areas.

- Swelling effects with simulants, and mass transfer kinetics are added to the classical model implying a constant diffusion coefficient.
- Reference data are presented leading to necessary rediscussions about equations overestimating the diffusion coefficient.

Materials and methods

Polymer: polypropylene powder was supplied by Solvay (ELTEX HV0001P).

Diffusing molecules (table 1): for $D = f(M)$ correlation, a large set of molecules with different molecular weights, linear/non-linear structures, flexible/rigid structures, polar/non-polar functional groups and commercial additives.

For easy migration monitoring (UV detection). UVITEX (2,5-bis(5-ter-butyl-benzoxazol-2-yl)thiophen) supplied by CIBA was used.

Liquid simulant: the swelling liquid used for migration tests must have the following characteristics.

- A chemical structure close to official food simulants and to food fats.

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Table 1. Studied molecules for diffusion tests.

Linear alkans	Other molecules	Commercial additives
Undecane	Triphenyl-methane	Tinuvin P
Tridecane	Tetramethyl pentadecane	Chimasorb 81
Pentadecane	Octadecanol	DEHP
Hexadecane	Heptadecyl benzene	Uvitex OB
Heptadecane	Docosanol	Irganox PS800
Octadecane	Squalane	Irganox 1076
Docosane	Trilaurin	Irgafos 168
Tetracosane	Tripalmitin	Irganox 1330
Octacosane		
Hexatria-Contane		
Tetracontane		

● No impurities that can react with the tested molecules or lead to co-elution problems in chromatographic analysis. (This is specially the case of the official food simulant, olive oil, which :s a complex mixture.)

In a first step, the authors have chosen Myglyol 812 (Hüls), a mixture of C8–C12 triglycerides (50–65% C8, 30–45% C10 and < 3% C3, C6 and C14). The advantages of this simulant are its low concentration of impurities and its low average molecular weight. Then, its large swelling effects would be easy to demonstrate. However, the GC/FID analysis revealed the presence of many peaks due to the statistical distribution of the C8 and C10 fatty acids on the glyceryl group.

Thus, Myglyol 812 has been replaced by glyceryl tripelargonate (tri-C9: purity 99%; Synfina Oleofina, Brussels, Belgium), which leads by GC to a single peak. Its molecular weight is close to the average molecular weight of Myglyol, so it can be considered as a 'Myglyol-like' pure component. The methods of determination of the diffusion coefficients have been reported (Reynier *et al.* 2001a–c)

Migration modelling and experimental validation

Mathematical model

The model developed here predicts the migration of a molecule from a polymer to a food simulant. All the phenomena taken into account here have already been described at different places in the scientific literature but they have never been put together for a global model.

The model developed here can be used in the case of a polymer plate of finite dimensions in contact with a food simulant. It is assumed that the food simulant is sufficiently stirred to obtain a perfect homogeneity of migrant in the liquid.

The diffusion in the polymer is assumed to obey Fick's second law (equation 1), valid for the case of concentration-dependent diffusion coefficients (six):

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \tag{1}$$

where C is migrant concentration, t is time, D is the migrant diffusion coefficient and x is the abscissa in polymer thickness.

Phenomena taken into account

Swelling of the polymer

During a migration test and during contact with foodstuffs, the food or food simulant can penetrate into the polymer and swell it. This effect is taken into account in the model by an exponential dependence of all the diffusion coefficients as a function of the local concentration of food simulant (Crank 1975).

Three remarks can be noted.

● Diffusion coefficients of both the migrant and simulant depend on the local simulant concentration. Indeed, if the migrant concentration in the polymer

is assumed low enough, its own effects on the matrix can be neglected.

● It is assumed that swelling of the polymer by the simulant is instantaneous (i.e. a given *local* simulant concentration corresponds to a given additive diffusion coefficient).

● No direct interaction between the food simulant and migrant is taken into account in the polymer this being justified by their low concentration.

Kinetics limitations at the surface

At the surface of the polymer, mass transfer can be limited by a slow dissolution or by evaporation, for example. These effects can have important consequences on global kinetics. They are taken into account by the model.

Partition coefficient

At equilibrium, the migrant is distributed between the polymer and the food simulant according to a partition coefficient. This parameter appears in the model only for the calculation of the concentrations on the surface, but it rules the final equilibrium.

Equations and the principle of resolution

As there are many phenomena taken into account, there is no analytical solution of equation (1). Calculations must be done by numerical analysis. (Free software is available on the INRA website [http://www.inra.fr/Internet/Produits/securite-emballage/].) Its algorithm is based on following equations where X is the considered element in the polymer sample thickness divided into 100 elements (Reynier *et al.* 2001c).

Calculation in polymer bulk

Local concentrations of the migrant and of the simulant are calculated by equation (2):

$$
\begin{cases}
CF_{X,t+\Delta t} = CF_{X,t} + \left[\frac{\partial}{\partial x}\left(DF_{X,t}\frac{\partial CF_{X,t}}{\partial x}\right)\right]\Delta t \\[2ex]
CA_{X,t+\Delta t} = CA_{X,t} + \left[\frac{\partial}{\partial x}\left(DA_{X,t}\frac{\partial CA_{X,t}}{\partial x}\right)\right]\Delta t
\end{cases}
$$

$$(2)$$

with

$$
\begin{cases}
\left[\frac{\partial}{\partial X}\left(DF_{X,t}\frac{\partial CF_{X,t}}{\partial X}\right)\right]_{X,t} = \frac{1}{\Delta X^2} \times \\[1ex]
\quad [CF_{X-1,t}DF_{X-0.5,t} + CF_{X+1,t}DF_{X+0.5,t} - CF_{X,t}(DF_{X-0.5,t} + DF_{X+0.5,t})] \\[2ex]
\left[\frac{\partial}{\partial X}\left(DA_{X,t}\frac{\partial CA_{X,t}}{\partial X}\right)\right]_{X,t} = \frac{1}{\Delta X^2} \times \\[1ex]
\quad [CA_{X-1,t}DA_{X-0.5,t} + CA_{X+1,t}DA_{X+0.5,t} - CA_{X,t}(DA_{X-0.5,t} + DA_{X+0.5,t}]
\end{cases}
$$

and

$$
\begin{cases}
DA_{X,t} = DA_0 \exp\left(BA\,\frac{CF_{X,t}}{CF_\infty}\right) \text{ with } BA = \ln\left(\frac{DA_{SW}}{DA_0}\right) \\[2ex]
DF_{X,t} = DF_0 \exp\left(BF\,\frac{CF_{X,t}}{CF_\infty}\right) \text{ with } BF = \ln\left(\frac{DF_{SW}}{DF_0}\right)
\end{cases}
$$

where

$CF_{X,t}$, $CA_{X,t}$ is the local concentration of food simulant and of additive at time t and distance X,
Δt is the time interval between two iterations of the calculation,
ΔX is the thickness of an element in the polymer,
$DA_{X,t}$, $DF_{X,t}$ is the local diffusion coefficient of additive and of food simulant at time t, at the distance X of the surface,
DA_{SW}, DF_{SW} is the diffusion coefficient of additive and of food simulant in totally swollen polymer,
$DA0$, $DF0$ is the diffusion coefficient of additive and of food simulant in virgin polymer,
BA, BF is the swelling dependence parameters, and
$CF_{X,t}/CF_\infty$ is the relative local concentration of the food simulant at time t.

Calculation at the interface

Kinetic limitation effects occur at the polymer surface. They are mathematically taken into account by equation (4). This corresponds to the case where the additive, for example, in the polymer is not instantaneously in equilibrium with the additive solution in the liquid (slow dissolution). The rate of additive
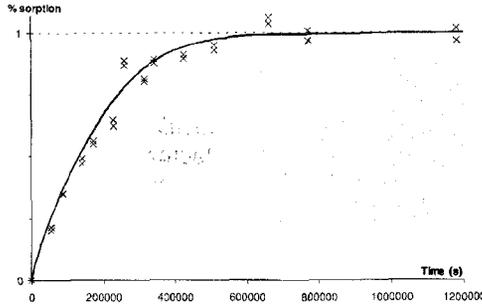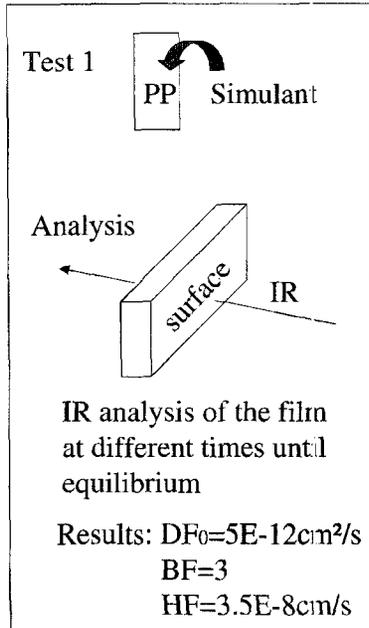
dissolution into the liquid is proportional to the difference between the concentration on the surface at t ($CA_{x=0,t}$), and the concentration which should be in equilibrium with the liquid at t ($CA_{F,t}.K_{P/F}$). The proportionality factor is noted HA. In the calculation, HA plays the same role as a convection factor, although it does not describe exactly the same phenomenon (it is the same for the food sorption at the surface with HF, rate-limiting factor to reach solubility CF_∞):

$$\begin{cases} \phi F_{x=0,t} = \text{HF}(CF_\infty - CF_{X=0,t}) + DF_{X=0,t}\dfrac{dCF_{X=0,t}}{dX} \\ \\ \phi A_{x=0,t} = \text{HA}(CA_{F,t}K_{P/F} - CA_{X=0,t}) \\ \\ \qquad\qquad + DA_{X=0,t}\dfrac{dCA_{X=0,t}}{dX} \end{cases}$$
$$(3)$$

where

$\phi F_{x=0,t}$, $\phi A_{x=0,t}$ is the flux of food simulant and of additive through the surface,
HF, HA is the kinetic limitation parameters for the food simulant and the additive,
V_P, V_F is the volume of polymer and volume of food simulant,
$CA_{F,t}$ is the concentration of additive in the food at time t, and
$K_{P/F}$ is the partition coefficient of additive between polymer and food.

Note that if dissolution is not rate limiting, $CA_{X=0,t+\Delta t} = CA_{F,t}K_{P/F}$.

If simulant sorption is not rate limiting, $CF_{X=0,t+\Delta t} = CF_\infty$.

Calculation of the global concentration

Total concentration of additive in polymer at time t:

$$A_t = \frac{\sum\limits_{X=1}^{X=100} CA_{X,t}}{100} \qquad (4)$$

Total concentration of additive in food simulant at time t:

$$m_{F,t} = (A_{t=0} - A_t)\frac{V_P}{V_F} \qquad (5)$$

Experimental validation

Principle of model validation

The model proposed here is based on seven important parameters:

- DF_0, BF and HF for the liquid.
- DA_0, BA, HA and KA for the additive.

Note that the partition coefficient is not taken into account in the validation tests because the volume for the liquid is assumed to be in all cases much larger than the volume of the polymer. Moreover, it will be experimentally validated that in our studied case, the concentration of the additive in the film at equilibrium is equal to zero.

To validate the model, all the determinant parameters are measured with independent experiments whenever possible. The experimental migration kinetics will then be compared with calculated ones (using the six parameters obtained by independent experiments).

Measurement of the parameters

Study of the liquid sorption. Independent measurements for the three parameters of the liquid are not possible. However, it is possible to define two different tests leading to different fits of experimental data involving the parameters DF_0, HF and BF: sorption kinetic and sorption profiles (Riquet *et al.* 1998).

Sorption is recorded by FTIR in transmission mode (for sorption kinetics) and by IR microspectrophotometry (for sorption profiles).

The quantity of glyceryl tripelargonate sorbed is quantified by measuring the absorbance at $1747\,\text{cm}^{-1}$ (carbonyl triglyceride). To erase the effect of weak variations of the film thickness, this is divided by the absorbance of the weak C-H peak at $2723\,\text{cm}^{-1}$ corresponding to the polymer matrix.

The fitting of the results and the principle of the tests are presented in figures 1 and 2.

The two results (kinetic and profile) are in good agreement.

The BF obtained corresponds to a ratio between DF_0 and $DF_\infty = 20$ ($\ln 20 \approx 3$), showing that strong swel-

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Test 1

PP | Simulant

Analysis

surface   IR

IR analysis of the film
at different times until
equilibrium

Results: DF₀=5E-12cm²/s
BF=3
HF=3.5E-8cm/s

% sorption

Time (s)
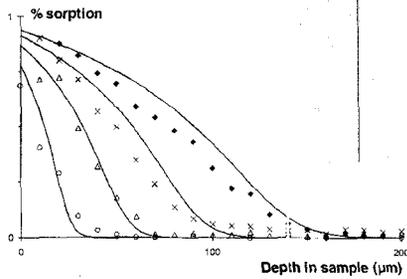
Figure 1. Simulant sorption kinetics in polypropylene at 40°C.

% sorption

Depth in sample (μm)

Test 2

PP | Simulant

Analysis   μIR

Thickness   surface

μIR analyses of the cross
section of the film at
different times

Results: DF₀=3E-12cm²/s
BF=3
HF=2.5E-8cm/s

Figure 2. Simulant sorption profiles in polypropylene plate at 40°C in polypropylene plate (750 μm) at 40°C. Experimental data at 2 (○), 7 (△), 18 (×), and 38 days (◆). Theoretical profiles (—) calculated with $DF_0 = 3 \times^{-12}\ cm^2\ s^{-1}$, $BF = 3$ and $HF = 2.5 \times 10^{-8}\ cm\ s^{-1}$.

ling of PP occurs during glyceryl tripelargonate sorption.

It appears also that mass transfer of glyceryl triperlagonate at the interface has an influence on the sorption kinetics as HF cannot be approximated to ∞.

Study of the additive diffusion

Calculation of the diffusion coefficient. DA_0 in the virgin polymer. An original test (figure 3) was defined to measure DA_0 preventing all mass transfer effects using only polymer/polymer contacts.

Seven trilayer Uvitex filled/virgin/Uvitex filled PP samples are stored at 40°C. At different times the inner layer is analysed to draw the beginning of the sorption kinetic. The plateau can be obtained by the analysis of inner layer at very long contact time or from an experiment made with a very thin inner layer. The diffusion coefficient is obtained by fitting the experimental curve (relative quantity of the inner film versus contact time) with a Fick's law resolution programme: it is assumed there an instantaneous mass transfer at interfaces, constant diffusion coefficient, homogeneous additive repartition in lateral films.

Fitting the data for Uvitex leads to $DA_0 = 5 \times 10^{-12}$ cm^2/s (figure 3).

Determination of the swelling dependence parameter (BA). BA is calculated from the diffusion coefficient of the additive in the swollen polymer (DA_∞), using equation (6) derived from equation (2):

$$BA = \ln\left(\frac{DA_{SW}}{DA_0}\right) \qquad (6)$$

DA_{SW} was determined by monitoring and modelling the sorption of Uvitex by a 60-μm thick sample, which had first been equilibrated with glyceryl tripelargonate.

Assuming that no surface kinetics affects the sorption kinetics (this will be confirmed by the next experiment), this experiment allows to calculate $DA_{SW} = 2.2 \times 10^{-11}$cm^2 s^{-1}, then BA = 1.5. The same value leads to a good fit in the two cases (figure 4).

Kinetic limitations at the surface (figure 5). The concentration profiles of the additive in the thickness of the material allow the extrapolation of the concentrations at the surface as a function of time. The experimental profiles of migration show that after only 1 day of contact, the concentration on the

Test 3
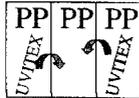
Analysis

Extraction of midle layer at different contact times and fit of the kinetics

Plateau is obtained from experiment with a fine midle layer

Result : DA₀ = 5E-12cm²/s
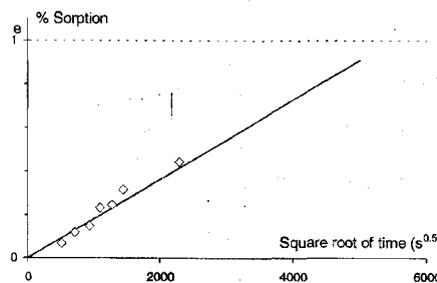
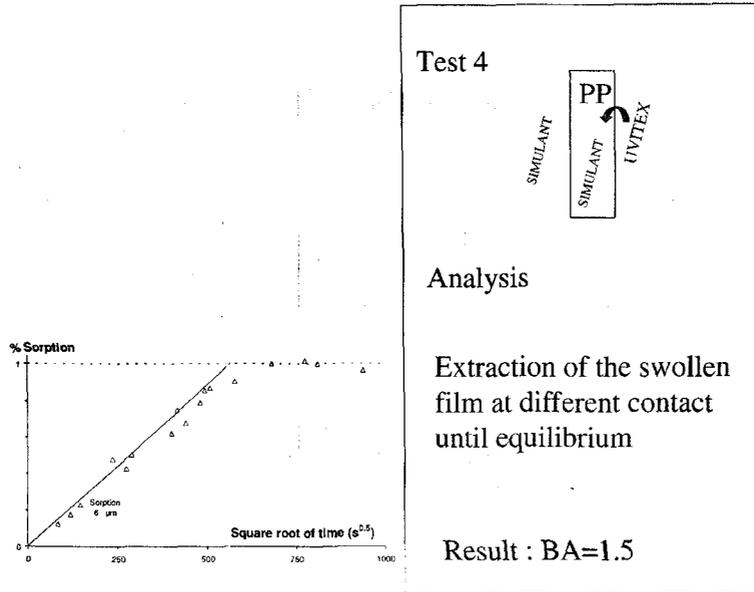*Figure 3. Sorption kinetics of UVITEX (solid/solid contact).*

Figure 4. Uvitex sorp'ion kinetics in totally swollen polypropylene films at 40°C.
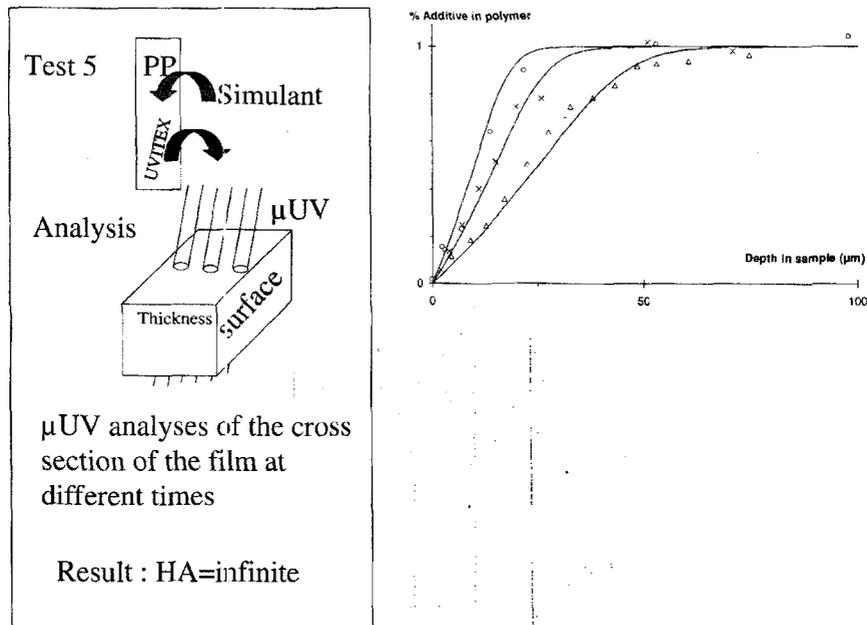

Figure 5. Uvitex migration profiles in a polypropylene plate (750 μm) in contact with simulant at 40°C. Experimental data at 1 (○), 2 (×) and 5 days (△). Theoretical profiles (—) calculated with $DF_0 = 4 \times 10^{-12}\,cm^2\,s^{-1}$, $BF = 3$, $HF = 3 \times 10^{-8}\,cm\,s^{-1}$, $DA_0 = 5 \times 10^{-12}\,cm^2\,s^{-1}$, $BA = 1.5$ and HA infinite.

surface is already equal to zero. If a mass transfer limitation at the surface plays any role, it will be observed for very short contact times (1 or 2 days) and for very thin samples. Since this is not the case studied; HA can be considered infinite.

Note that the concentration at the surface becomes zero, which confirms also that the partition coefficient can be approximated as equal to zero (total migration at equilibrium) when the ratio of the volumes between the liquid and the polymer is important.

Fitting of migration kinetics (figure 6). Two migration experiments have been studied, with 59 and 100 μm thick films. To fit the experimental results, only slightly different DA_0 had to be used. The model experiments are then in good agreement with the fit of the migration kinetics.

Determination/prediction of parameters for modelling

List of constants. The prediction of migration based on mathematical modelling can be envisaged. However, as we have seen already above, the

complete model described here requires the estimation of seven parameters. This model can be used even if interactions between polymer and food simulant occur.

Parameters needed for the food simulant. $DF0$, **BF**, HF. These parameters could be known in advance for classical series of polymer/simulant couples. Of course, the parameters will only be used when swelling effect occurs. The best way should be to agree on a single-swelling simulant for each material. The authors think that glyceryl tripelargonate, which behaves like Myglyol 812 towards polyolefins, but which is simpler for analytical work is concerned, is acceptable, but this choice may be considered as an 'excessively worst case'.

Parameters needed for the additive: DA_0, BA *(via* DA_{SW}). These two parameters must be over-estimated by empirical correlations. The easiest approach is to use a correlation with the molecular weight M, which seems feasible for DA_0, as a sufficient amount of data is available in the literature (Brandsch *et al.* 2000). However, the equation proposed by Piringer to calculate an overestimated diffusivity from M must be improved to take into account the increase of activation energy with the
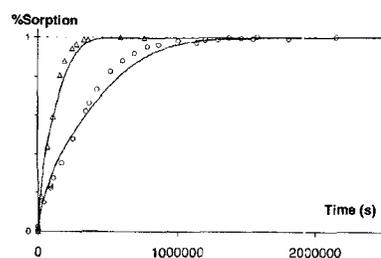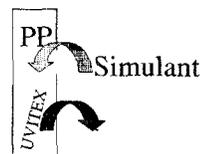
Figure 6. Uvitex migration kinetics in polypropylene films in simulant at 40°C. △, *Thickness 59 μm;* ○, *thickness 100 μm.*

molecular weight of the additive. For the prediction of DA_{SW}, the problem is still the choice of a reference swelling agent or simulant, which should be recognized by the scientific community. More experimental data must be acquired to confirm the parameters of the predictive equation.

For HA, a very high value (no limitation) was found in the validation study. Moreover, as a low HA tends to decrease the migration rate, an infinite HA should be assumed in a worst-case predictive approach.

The influence of KA (polymer/food partition coefficient) is not experimentally observed when the volume ratio between simulant and polymer is high (which is usually the case in migration tests). In a 'worst-case' approach (overestimation of consumer's exposure), migration can be assumed to be complete.

The only factors that must be determined by empiric correlations are also the diffusion coefficients. For a given polymer, three variables (at least) have to be taken into account to establish a correlation for prediction purposes:

- molecular weight;
- temperature; and
- the nature of the triglyceride in contact with the polymer.

It is underlined that swelling does not need to induce either visible changes (dimensions) or a decrease of the mechanical properties of the material. However, it may have a strong effect on migration. Analysts in charge of global migration control experience daily swelling by olive oil, as it is absorbed by most usual packaging polymers, and specially by polyolefins.

Prediction of D at 40°C. Diffusion coefficients of several molecules have been measured using the improved Moisan test (Reynier *et al.* 1999) (figure 7). The correlation of the diffusivity to the molecular weight of the migrants shows different types of behaviours according to the shape and flexibility of the molecules (fast diffusion of linear molecules by reptation, or slower diffusion by jumps in the case of rigid and/or spherical structures) (Reynier *et al.* 2001a). As this represents the first set of high molecular weight compounds, closer examination of the mode of displacement are under study.

Prediction of BA at 40°C. In a migration test, sorption of the simulant into the polymer usually occurs, especially for fatty simulants. Glyceryl tripelargonate was chosen to test swelling effect

because its structure is similar to typical simulants consisting of mixtures of short-chain triglycerides (C8–C12) such as Myglyol 812 and HB307. Furthermore with glyceryl tripelargonate, the analytical procedures are simpler as with these mixtures.

The molecular weight of glyceryl tripelargonate ($M = 513\,\mathrm{g\ mol^{-1}}$) is lower than that of olive oil (average $M = 850\,\mathrm{g\ mol^{-1}}$). Hence, it will induce more swelling than olive oil. On the other hand, it can be expected that Myglyol 812, accepted as an official food simulant by the FDA, which also has a lower molecular weight than olive oil, will also induce stronger swelling. Indeed, since Myglyol is a blend containing up to 50–60% C8 and 3% C6 tri-esters, it may even be more aggressive than pure glyceryl tripelargonate. These swelling properties certainly play an important role on the diffusion and migration behaviours in polyolefins. Swelling by either of these simulants leads to an overestimation of consumer exposure (tri-C9 and Myglyol are more aggressive than olive oil), and this should be considered as a positive point.

The comparison of diffusion coefficients before and after swelling (figure 8) leads to the following conclusions.

- The diffusion coefficients of migrants in the swollen polymer are higher than in the virgin polymer. This is an obvious but important conclusion, often underestimated.
- Whether or not swelling occurs, linear alkanes seem to have the highest diffusivity for a given molecular weight.
- Increasing the mobility leads to a lower influence of the diffusivity to the molecular weight: the slope of the alkanes $D = f(M)$ linear correlation is lower in the swollen polymer than in the virgin one.

The effect of swelling can be quantitatively expressed by the ratio D_{sw}/D_0. Results for linear alkanes are shown in figure 9. As linear alkanes display a linear dependence of log (D) versus M, the ratio of the linear fits has been used to make the calculation instead of using each experimental alcan point.

- The influence of the swelling is higher with higher molecular weight compounds. The ratio varies from 1 (no effect of swelling with low molecular weight compounds) to > 100 when the molecular weight $> 800\,\mathrm{g\ mol^{-1}}$.
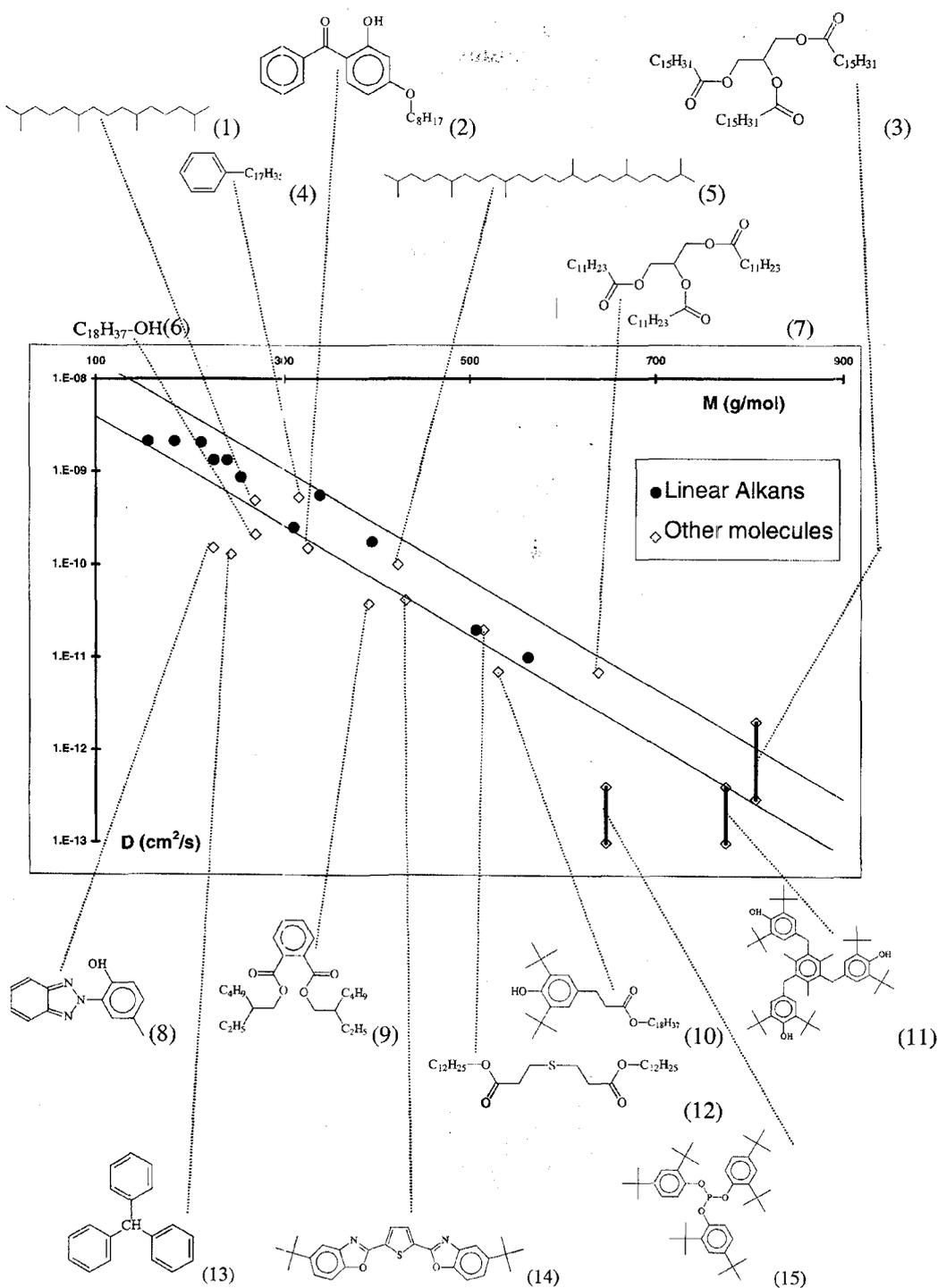
(1)

OH

C_8H_{17} (2)

$C_{15}H_{31}$
$C_{15}H_{31}$
$C_{15}H_{31}$ (3)

$C_{17}H_{35}$ (4)

(5)

$C_{11}H_{23}$
$C_{11}H_{23}$
$C_{11}H_{23}$ (7)

$C_{18}H_{37}$-OH(6)

100   300   500   700   900

1.E-08

M (g/mol)

1.E-09

● Linear Alkans
◇ Other molecules

1.E-10

1.E-11

1.E-12

1.E-13   D (cm²/s)

OH
(8)

C_4H_9 C_4H_9
C_2H_5 C_2H_5 (9)

HO
$O-C_{18}H_{37}$ (10)

OH
OH (11)

$C_{12}H_{25}-O$ S $O-C_{12}H_{25}$
(12)

CH (13)

(14)

(15)

Figure 7. Correlation $\log(DA_0) = f(M)$ *in polypropylene at 40°C.*
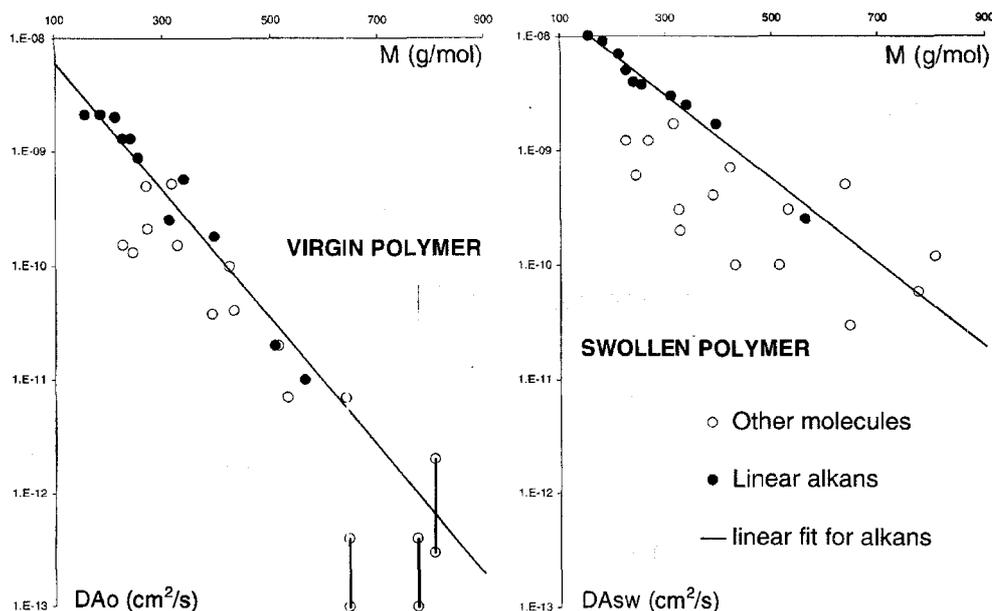
Figure 8. Diffusion coefficients in virgin and swollen polypropylene at 40°C (swelling by glyceryl tripelargonate).
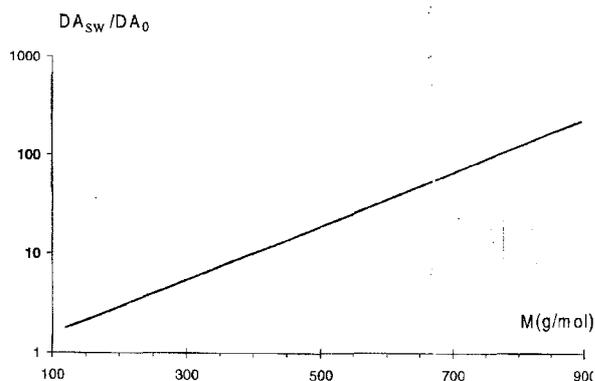
Figure 9. Ratio DA_{SW}/DA_0 for linear alcans in polypropylene at 40°C (ratio of linear fits from figure 8). DA_0, virgin polymer; DA_{SW}, polymer totally swollen with glyceryl tripelargonate.

Hence, the exponential increase is directly due to the difference of the slopes of the straight lines before and after swelling: after swelling, the influence of molecular weight is less important (figure 8).

When the molecular weight is $< 500 \, g \, mol^{-1}$, the DA_{SW}/DA_0 ratio varies from 1 to 20. Piringer's

assumption (1990) that swelling has no effect on substances that have a molecular weight lower than that of the simulant should be rediscussed in light of the experimental results. Nevertheless, it is difficult to give arbitrary criteria to decide if a simple model (not taking into account swelling) is satisfactory. Indeed, many parameters are involved in the differences observed between results of the two models. The ratio

$$\frac{migration_{10 \, days, \, swelling} - migration_{10 \, days, \, no \, swelling}}{migration_{10 \, days, \, swelling}}$$

calculated for different thicknesses of polymer sample and different molecular weights of additives is shown in figure 10. The simulation of all migration kinetics in PP have been obtained with olive oil sorption parameters (DF, HF, BF), and the swelling effect is overestimated taking BA obtained by linear alkanes behaviour in glyceryl tripelargonate (figure 9). The following tendencies are noted. (Note that the absolute values of the ratio are connected to the choice of BA; the purpose here is only to show the link between parameters and potential error and without emphasizing an absolute error.)

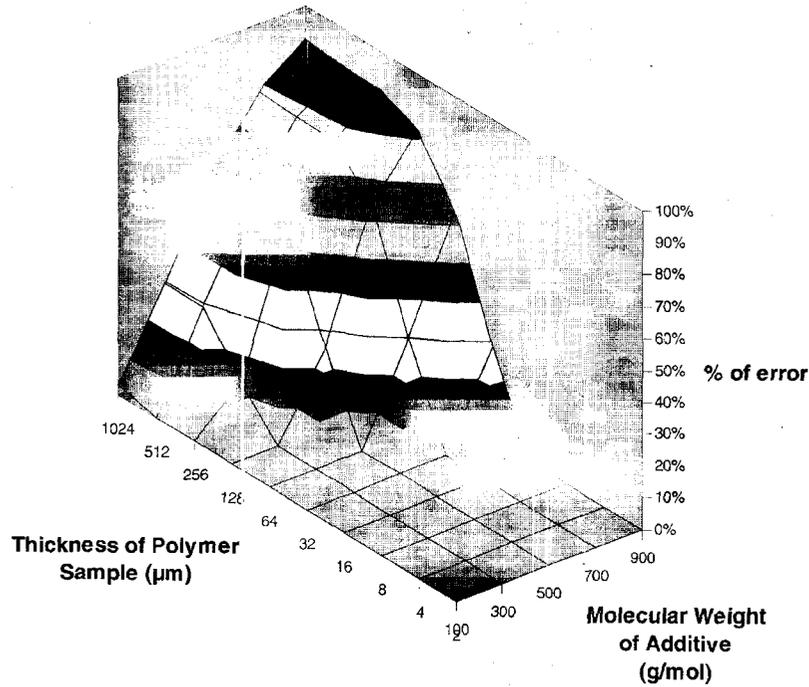● The higher the molecular weight, the higher swelling effect.

Figure 10. Estimation of error on claculated migration (at 10 days) when the swelling effect is not taken into account (polypropylene/olive oil at 40°C).
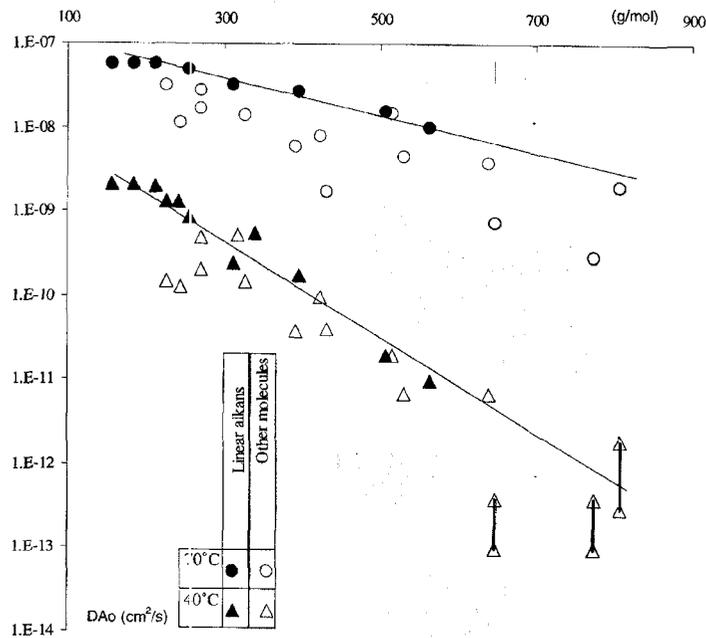

Figure 11. Diffusion coefficients of all the molecules of the panel in virgin polypropylene at 40 and 70°C.
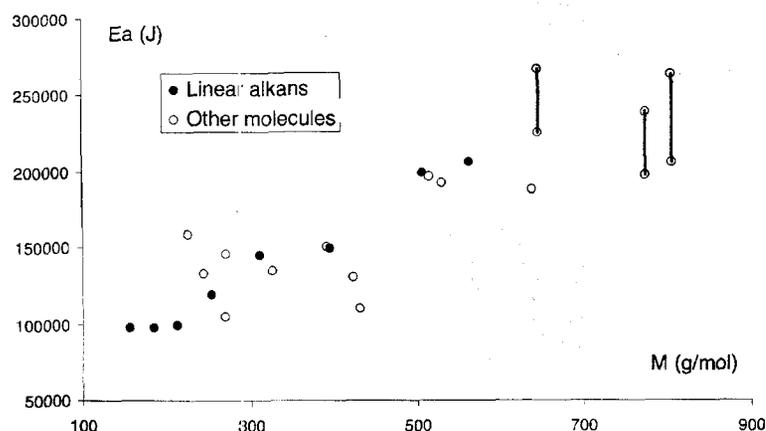
Figure 12. Activation energy E_a *versus* M *in polypropylene.*

● The larger the thickness, the higher the swelling effect for a given additive.

As a general comment, the 'error' tends to zero in the only case when migration reaches the plateau before 10 days (low M and/or thin sample).

Temperature effects

Diffusion coefficients of several molecules have been measured in virgin polypropylene at 70°C. A comparison of diffusivities at 40 and 70°C is presented on figure 11. However, as already observed for the swelling effect, the increase of mobility leads to a lower diffusivity sensitivity to the molecular weight: the slope of the alkanes straight line is lower at 70°C than at 40°C.

It is important to underline that the model used at present for the prediction of the diffusion coefficient is the Piringer model. It considers a *constant* activation energy of 100 kJ (in polypropylene). As shown in figure 12, this energy corresponds to molecular weight $< 450\,g\ mol^{-1}$. So, this approach tends to underestimate temperature influence on diffusion of high molecular weight compounds.

However, experimental tests with high molecular weight *commercial additives* (at high temperature and/or with oil contact) lead generally to values lower than the Piringer prediction. This could be explained considering the shape of these molecules, which are

rather spherical. Their real initial diffusion coefficient (at 40°C in virgin polymer) is very low compared with the calculated value, which also overestimates the fastest molecules (linear ones). It can be supposed that this 'over' overestimation covers the lack of using swelling factors and/or appropriate activation energies. But what about testing the Piringer's model at high temperature or in contact with swelling simulant with LINEAR high molecular weight molecule?

Conclusion

A new mathematical model including previous proposals (Brandsch *et al.* 2000) has been developed. Its practical application (free software http://www.inra.fr/Internet/Produits/securite-emballage) can be used to study migration phenomenon (scientific level) as well to predict migration (industrial level). For both objectives, the approach can be improved. The need for scientific support to legislation is to obtain new data to feed the model. It has been shown that the principal factor estimated by empirical modelling for migration prediction is the diffusion coefficient. Data still need to be obtained to establish a generally recognized correlation involving the diffusion coefficient, molecular weight, temperature and swelling effect. The authors believe that a large study is needed to obtain good reference data, which must be obtained not only by migration tests, but also by

well-designed model experiments leading to the pure parameter values.

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References

BRANDSCH, J., MERCEA, P., and PIRINGER, O., 2000, Possibilities and limitations of migration modeling. *Plastic Packaging Materials for Food: Barrier Function, Mass Transport, Quality Assurance and Legislation*, edited by O. Piringer and A. Baner (Wiley–VCH).

CRANK, J., 1975, *Mathematics of Diffusion*, 2nd edn (Oxford: Clarendon).

PIRINGER, O., 1990, Ethanol and ethanol/water mixtures as test foods for the migration from plastics. *Deutsche Lebensmittel Rundschau*, **86**, 35.

REYNIER, A., DOLE, P., and FEIGENBAUM, A., 1999, Prediction of worst case migration: presentation of a rigorous methodology. *Food Additives and Contaminants*, **16**, 137–152.

REYNIER, A., DOLE, P., and FEIGENBAUM, A., 2001c, Additive migration from polymers by swelling food simulants: modelling by numerical analysis. *Food Additives and Contaminants* (in press).

REYNIER, A., DOLE, P., HUMBEL, S., and FEIGENBAUM, A., 2001a, Diffusion coefficient of additives — Part I: Correlation with geometric parameters. *Journal of Applied Polymer Science* (in press).

REYNIER, A., DOLE, P., HUMBEL, S., and FEIGENBAUM, A., 2001b, Diffusion coefficient of additives — Part II: Effect of swelling and temperature on $D = f(M)$ correlation. *Journal of Applied Polymer Science* (in press).

RIQUET, A. M., WOLFF, N., LAOUBI, S., VERGNAUD, J. M., and FEIGENBAUM, A., 1998, Food packaging interactions: determination of the kinetic parameters of olive oil diffusion in polypropylene using concentration profiles. *Food Additives and Contaminants*, **15**, 690–700.