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Olivier Vitrac and Daniel Goujot

Introduction

Although the EU regulation is still in a consolidation phase, 502 substances (including 230 monomers and 272 additives) among the 937, which are positively listed in EU directives on plastics in contact with food, are subjected to specific migration limits (SML) due to toxicological concern. To face such legal obligations, mathematical modeling, as introduced in article 8 of 2002/72/EC, is a competitive alternative to time-consuming migration tests. As materials became more sophisticated (multi-layer multi-materials) or as modeling in semi-solid food was required (e.g. for consumer exposure assessment), only numerical techniques were available up to few years via commercial or freely available software. However, numerical techniques have several drawbacks for end-users with mainly a chemical background: i) they may be computationally burdensome with non-optimized discretization schemes, ii) they may lead to unreliable accuracies for particular stiff problem (e.g. strong partitioning, very thin layers such as adhesive layers), iii) their implementation for legal purposes requires a validation procedure, which is not available. To tackle the limitations of most of available software, this work addresses new exact analytical solutions i) to validate any migration software, ii) to implement efficient probabilistic modeling, iii) to allow real time calculations and transport coefficients identification.

Generic mathematical formulation for multilayer materials in contact with a semi-solid food

The canonical solution for the one-dimension migration of packaging substances into a continuously stirred liquid with a finite volume was proposed by Crank [1] with additional refinements discussed by Vergnaud [2]. The first analytical solution for a semi-solid or for a liquid including a mass transfer resistance (i.e. mass Biot or Sherwood number) was proposed by Sagiv [3] twenty-six years later. As the last solution involves a slow convergence with the number of terms, an equivalent but still approximated analytical solution was proposed by Vitrac and Hayert [4]. Very recently, we reformulated the "Sagiv problem" by introducing an efficient mathematical method known as "energy method" already used to solve multicomponent convection-diffusion problem to derive exact analytical solutions for problems previously renowned "without analytical solution" [5].



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Our approach

INRA is contributing to develop basic scientific and engineering supports for a reliable implementation of migration modeling for the packaging community (packaging and food industries, control and regulatory authorities, food safety agencies). As the approach was motivated by Chemical Engineering concepts, our work was concerned with pioneering valuable techniques of prediction from molecular mechanisms to a macroscopic description of foodpackaging interactions. Three fields were particularly investigated with possible applications beyond the sole food packaging application: molecular mechanisms involving in the control of transport coefficients (partition, diffusion coefficients) and in their activation with temperature and plasticizing effects;

The physical dimensionless formulation is introduced on a comprehensible case consisting in a bilayer material with a whole thickness Is in contact with a semi-solid food on the right side. This formulation can be straightforwardly downgraded to a monolayer material or generalized to n-layer materials.



exact mathematical solutions of transport equations for punctual assessment and probabilistic assessment of the contamination of food products by materials intended to be in contact;

design of decision tools, which act as expert systems and which can handle both missing properties and large uncertainties on input parameters.

Free implementation of last algorithms and methodologies on the SAFE FOOD PACKAGING PORTAL: http://h29.univ-reims.fr

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 $c(x,t) = a_0 + \sum_{n=1}^{\infty} a_n \cdot \cos(\lambda_n \cdot x) \exp\left(-\lambda_n^2 \cdot t\right)$

It is worth to notice that all solutions are self-similar for any triplet ((Bi·L, K/L, t)

guarantees a rapid decrease of the number of terms when the dimensionless diffusion time (t) increases. This property is related to the energy of the solution, which was proven to be strictly decreasing with t. In other words, the high frequency terms vanish rapidly with increasing *t*, whatever *Bi*·*L* and *K*/*L* values.

validate a software for any migration

Only the Goujot-Vitrac's solution [5]

condition, that is for any triplet ($Bi \cdot L, K/L, t$).



less than

chemical affinity for food

K=10

L=0.01

L=0.05

L=0.1

L=0.2

L=0.5

L=1

dimensionless

volume of food

3 terms

Approximated analytical solution for **monolayer** materials

in contact with a semi-solid food

Exact solutions suffer from transcendental equations, whose zeros cannot be expressed in terms of a finite sequence of algebraic operations. The Vitrac-Hayert's solution derived in [4] solves this issue by approximating the initial set of partial differential equations by a simple conditional ordinary differential equation, while providing an accurate estimate of the mass flux density at the interface. It has been shown that this class of solution has efficient properties to help the identification of transport coefficients from noisy or truncated



Exact analytical solution for **multilayer** materials | Illustration on a bilayer material



Literature cited

[1] Crank J. The mathematics of diffusion, 2nd Ed. Oxford University Press, 1975.

[2] Vergnaud JM. Liquid transport processes in polymeric materials. Englewood Cliffs: Prentice-Hall, 1991.

How accurate is the approximated solution ?

0.1

0.08

0.06

0.04

0.02

t=<mark>10⁻¹</mark>

for any contact condition

Vitrac-Hayert's solution leads to accurate results without any bias on Bi=1residual concentration (C_s) and interface mass flux (j) for any contact condition, while providing an easy numerical implementation in any programming

in contact with a semi-solid food (the first exact solution ever published)

An exact solution for multilayer materials has been recently derived [6] from the generalization of the scalar product defined in [5]. The solution expands on a basis of eigenfunctions, which depends on the considered layer. For concision, the solution for a bilayer material is presented here.



How does the analytical solution expands over several layers?

 $C_s/C_s^{(t=0)}$

K=0.1

exact solution

approximated solution

The example illustrates four practical cases with a same initial amount of migrant in the entire packaging. The scenarios are coded by the paired values: $[C_1^{t=0} C_2^{t=0}] - [K_1 K_2]$:

(**a**) monolayer, (c) bilayer including similar materials, (**b**) material including a functional barrier (d-e) bi-materials.



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