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Stochastic modelling of migration from polyolefins

Erika Helmroth,[1] Chris Varekamp[2] and Matthijs Dekker[3]*

[1] *TNO Nutrition and Food Research, Packaging Research and Sensortechnology, PO Box 360, 3700 AJ Zeist, The Netherlands*
[2] *Nijverheidslaan 32, 5506 EE Veldhoven, The Netherlands*
[3] *Wageningen University, Product Design and Quality Management Group, Agrotechnology and Food Sciences, PO Box 8129, 6700 EV Wageningen, The Netherlands*

Abstract: A method is presented to predict diffusion coefficients in polyolefins using stochastic modelling. A large number of experimental diffusion coefficients, published in the literature as one dataset, was used to derive probability distributions of diffusion coefficients in the polymers low-density polyethylene and linear low-density polyethylene, medium- and high-density polyethylene, and polypropylene. An equation is proposed to describe the diffusion coefficient as a function of the molar mass of the migrant. Model parameters and standard deviations are predicted by minimizing the sum of squared errors and the residuals are used to check the assumed types of probability distribution. The experimental data can be described by a log–normal distribution. It is shown how the derived probability distributions can be used as input for migration predictions. The method presented provides information about the most likely migration results for a given packaging–food simulant combination. This is important for prediction of the probability that a given migration limit may be exceeded.

Keywords: packaging; migration; diffusion; polyolefins; stochastic modelling

INTRODUCTION

Research during the second half of the nineteenth and first half of the twentieth century, as reviewed by Crank and Park,[1] shows that the transport of small molecules through polymers can be described as a diffusion process. This rate of this process depends on the value of the diffusion coefficient and the distribution of the small molecular compound between the polymer and the contacting phase (usually expressed as a partition or solubility coefficient). This was later shown also to be the case for migration of larger molecules (such as monomers and additives) from plastic packaging materials to foods or food simulants.[2–5] By using an appropriate diffusion model, it is possible to predict migration as a function of time. Such models are useful for predicting exposure risks of toxic compounds in packaging materials and may in some cases replace time-consuming and expensive migration experiments currently required for demonstrating compliance with food packaging regulations. The key question, however, is how to obtain values for the model parameters that are characteristic of each combination of migrant, packaging material and food simulant. *A priori* prediction from physical properties alone is impossible, since the precise factors determining migration are not known. The use of semi-empirical relationships derived from experimental data is therefore inevitable.

A relatively simple migration model is given by a solution of Fick diffusion equations containing two model parameters: a diffusion coefficient (D) and a partition coefficient (K). The diffusion coefficient represents the migration rate in the polymer and the partition coefficient represents the distribution of migrant over packaging and food simulant at equilibrium. Empirical relations for the diffusion coefficient as a function of the molar mass of the migrant and temperature have been proposed.[6,7] The latter used a 'worst-case' approach based on a large number of experimental diffusion coefficients found in the literature. This equation has been shown to overestimate migration from polyolefins in most cases.[8,9] However, the disadvantage of a 'worst-case' approach is that no information is obtained about the uncertainty of the prediction. Using the large number of experimental data available, stochastic modelling can be applied to determine probability distributions, ie curves that show the probability of finding a given diffusion coefficient. From the probability distribution of the diffusion coefficient (and if available the partition coefficient), the probability of exceeding a certain migration limit can be calculated. Probability

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* Correspondence to: Matthijs Dekker, Wageningen University, Product Design and Quality Management Group, Agrotechnology and Food Sciences, PO Box 8129, 6700 EV Wageningen, The Netherlands
E-mail: Matthijs.Dekker@wur.nl

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distributions of migration are also needed as input in stochastic models that predict exposure from food packaging based on the concentration of a toxic compound in the food, food consumption and absorption by the body.[10]

The goals of this paper are to show (1) how probability distributions can be derived for diffusion coefficients of migrants in polyolefins, and (2) how these distributions can be used for migration prediction.

THEORY

Migration of a compound from plastic to a contacting food simulant is often calculated as a function of time by solution of the second diffusion equation of Fick. This analytical solution is given by:[11]

$$\frac{M_{\mathrm{F},t}}{M_{\mathrm{P},0}} = \left(\frac{\alpha}{1+\alpha}\right) \left[1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp\left(-Dt\frac{q_n^2}{L^2}\right)\right] \quad (1)$$

where $M_{\mathrm{F},t}$ is the migrant mass in the food simulant (kg) after time t (s), $M_{\mathrm{P},0}$ the initial migrant mass in the polymer (kg), D the diffusion coefficient ($\mathrm{m^2\,s^{-1}}$), L the polymer thickness (m), $\alpha = V_\mathrm{S}/(V_\mathrm{P} \cdot K)(-)$, V_P and V_S are the volumes of plastic and food ($\mathrm{m^3}$), $K = C_\mathrm{P}/C_\mathrm{F}(-)$ is the partition coefficient, C_P and C_F are the migrant concentrations in the plastic and food at equilibrium ($\mathrm{kg\,m^{-3}}$) and q_n are the non-zero, positive roots of equation $\tan(\alpha) = -q_n\alpha$ where n is an index variable.

Equation (1) assumes that (1) the migrant is homogeneously distributed in the polymer, (2) there is no mass transfer resistance at the interface between polymer and solvent, (3) there is no diffusion from the polymer surface that is not in contact with the food simulant, (4) the food simulant is well mixed, and (5) the polymer matrix does not change (no swelling).

EXPERIMENTAL DATA

In this study, we used the diffusion coefficient values at 23 °C collected from literature by Mercea[12] for the groups of polymer types LDPE [low-density ($\leqslant 0.925\,\mathrm{g\,cm^{-3}}$) polyethylene] and LLDPE (linear low-density polyethylene), MDPE [medium-density (0.926–$0.940\,\mathrm{g\,cm^{-3}}$) polyethylene] and HDPE [high-density ($>0.940\,\mathrm{g\,cm^{-3}}$) polyethylene], and PP (polypropylene). The diffusion coefficient values have been measured by a number of different researchers during the past four decades using different measurement methods. They were either measured directly at 23 °C or extrapolated by Mercea[12] to 23 °C from other temperatures.

DIFFUSION COEFFICIENTS AND MOLAR MASS

The first step was to find a relationship between the diffusion coefficient and properties of additive and polymer. A polymer matrix can be regarded as a network of polymer molecules containing holes with different sizes and shapes. The diffusion rate in this matrix depends on the size and shape of the migrants and on the size and shape of the holes. The size and shape of the holes in a polymer will depend on properties like chemical structure, density, temperature and orientation of the polymer chains. The smaller the molecule, the higher the chance of finding a hole that is large enough for it to pass through and thus the higher the diffusion coefficient.[13] Similarly, the smaller and less frequent the holes, the smaller the diffusion coefficient. According to the free-volume theory of diffusion,[14] the diffusion rate of a migrant is proportional to the probability of finding a neighbouring hole with a volume equal to or larger than the volume of the migrating molecule. This probability is a negative exponential function of the molecular volume of the migrant and the available space.[15] An exponential dependency of the diffusion coefficient as a function of molecular diameter or volume has been confirmed by direct measurements.[16,17] In migration predictions the volume is often replaced by the molar mass for simplicity.[6,17,18]

The free-volume theory motivated us to assume the following semi-empirical relationship between the diffusion coefficient ($\mathrm{cm^2\,s^{-1}}$) and molar mass:

$$D = a \exp\left[-\left(\frac{M}{M_0}\right)^b\right] \quad (2)$$

where M is the molar mass ($\mathrm{g\,mol^{-1}}$), M_0 is a reference value of $1\,\mathrm{g\,mol^{-1}}$ and a and b are model parameters. This expression resembles the free volume equation (Duda and Zielinski,[15] p 145). However, an extra parameter, b, was introduced since this improves the fit with the experimental data. Because the hole frequency in the polymer matrix depends on polymer properties such as density and crystallinity, a and b differ for different polymers.

STOCHASTIC MODEL

In any set of experimental data there will be a distribution around a mean. In this case, differences between experimental diffusion coefficient values and the mean diffusion coefficient as calculated by equation (2) depend on two types of errors. The first type is experimental measurement error and variation in experimental set-up (method, temperature, etc). The second type is caused by physical variation due to small differences in the properties of additive, polymer and food simulant, such as in polarity, density, crystallinity and shape. The approach in stochastic modelling is to assume that the diffusion coefficient is a random variable with a given probability distribution. Assuming that this is a normal distribution, parameters a and b of equation (2) were estimated from the experimental data for LDPE and

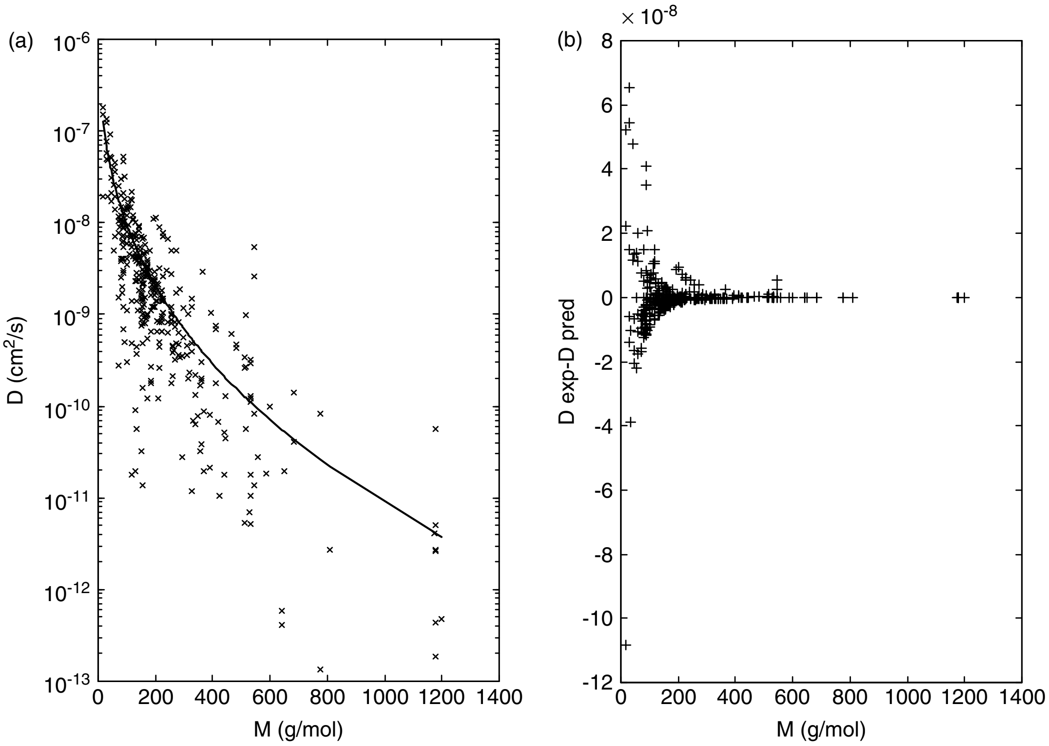

Figure 1. Result of minimization procedure of diffusion coefficient with experimental data for polymer group LDPE and LLDPE assuming a normal distribution of errors: (a) experimental data shown by '×' and best fit by a solid line; (b) residuals.

LLDPE by minimizing the sum of squared errors given by

$$SS = \sum_{i=1}^{N} (D_{\mathrm{exp},i} - D_{\mathrm{pred},i})^2 \qquad (3)$$

where N is the number of experimental data. A Simplex iteration method was used for the minimization procedure.[19] The smallest SS was found for a equal to 2.0×10^{-6} and b equal to 0.36. With these values equation (2) is plotted in Fig 1(a) together with the experimental data. Figure 1(b) shows that the residuals, calculated as the difference between experimental and predicted diffusion coefficients, depend on the molar mass of the migrant. The residuals are larger for smaller than for larger migrants.

Taking the natural logarithm of the diffusion coefficient values makes the residuals approximately independent of molar mass [see Fig 2(b)]. Ln(D) is assumed to be normally distributed, from which it follows that the diffusion coefficient itself has a log–normal distribution.[20] Parameters a and b were determined from the experimental data by minimizing the sum of squared errors, now given by

$$SS = \sum_{i=1}^{N} (\ln D_{\mathrm{exp},i} - \ln D_{\mathrm{pred},i})^2 \qquad (4)$$

The best fit is shown in Fig 2(a) together with the experimental data; values of the parameters a and b are given in Table 1. Figure 2(c) shows the histogram of the residuals, derived by classification of the residuals by size and counting the number of times that the residuals fall within a given bin in a range of bins with defined edges. The histogram was normalized by dividing the frequency counts by the total number of experimental values and by the bin size, to enable comparison with the predicted (normal) probability distribution (shown by a solid line). The histogram shows that the residuals approximately follow a normal distribution. A log–normal distribution therefore seems to be a reasonable assumption.

Table 1. Estimated model parameters a and b in equation (2) and standard deviation s for different groups of polyolefins

Polymer group	a	b	s
LDPE and LLDPE	1.2×10^{-6}	0.37	1.3
MDPE and HDPE	7.2×10^{-7}	0.39	1.6
PP	1.9×10^{-8}	0.36	2.0

The standard deviation (σ) is estimated by[20]

$$s = \sqrt{\frac{1}{N-1}\left\{\begin{array}{l} \sum_{i=1}^{N} (\ln D_{\mathrm{exp},i} - \ln D_{\mathrm{pred},i})^2 \\ - \left[\sum_{i=1}^{N} (\ln D_{\mathrm{exp},i} - \ln D_{\mathrm{pred},i})\right]^2 \end{array}\right\}} \qquad (5)$$

and is shown in Table 1.

The 95% confidence limits were approximated by $D_{\mathrm{mean}} \pm 2\sigma$ [21] and are shown in Fig 2(a) by dotted lines. The probability that a diffusion coefficient lies within the interval defined by these limits is about 95%. In a worst-case approach, the upper limit curve

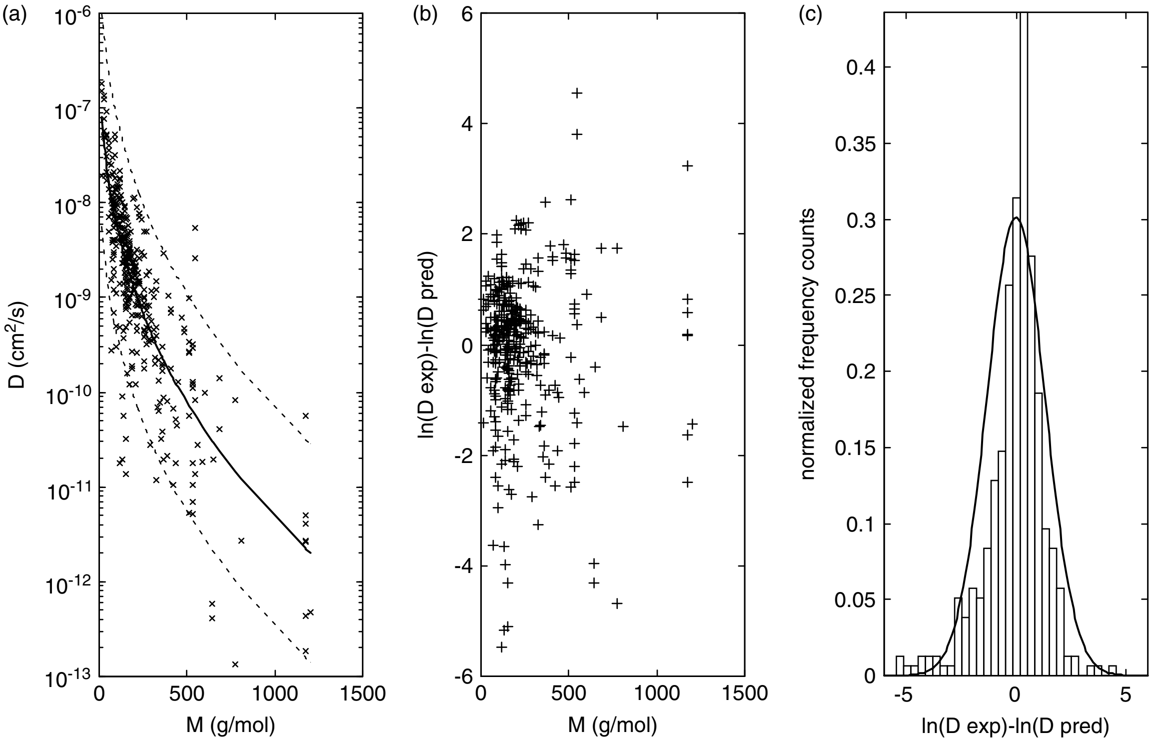

Figure 2. Result of minimization procedure of diffusion coefficient for experimental data for LDPE and LLDPE polymers assuming a log–normal distribution of errors: (a) experimental data shown by '×', best fit by a solid line and the 95% confidence limits (see text) by a dotted line; (b) residuals; and (c) histogram of the residuals (bars) and normal curve with zero mean and σ equal to 1.3 (solid line).

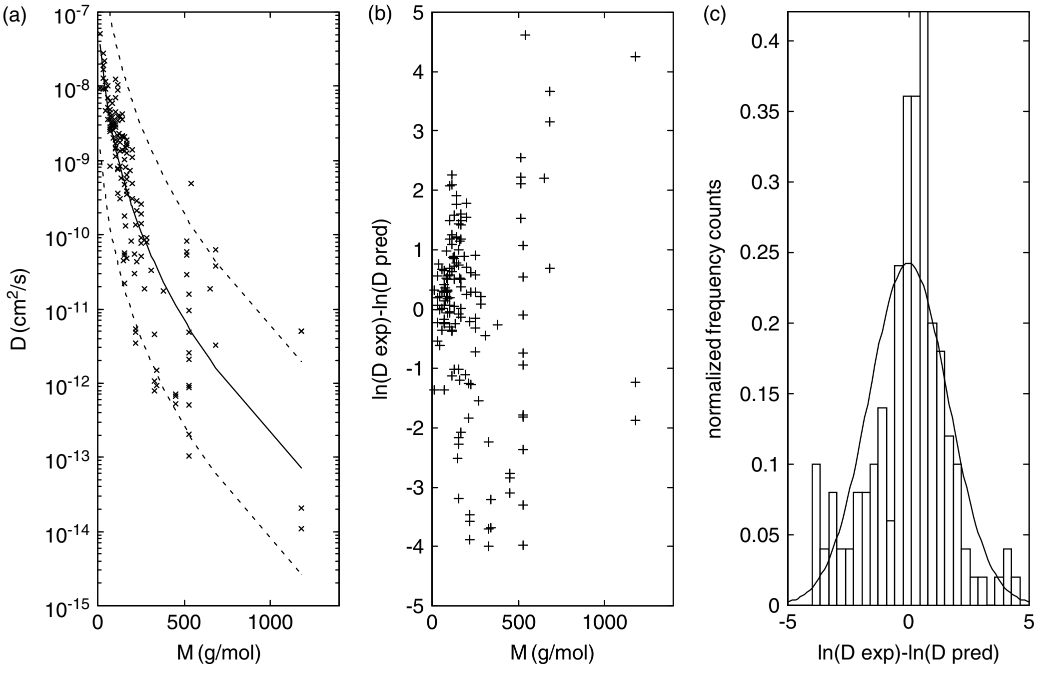

Figure 3. Result of the minimization procedure of diffusion coefficient for experimental data for polymer group HDPE and MDPE assuming a log–normal distribution of errors: (a) experimental data shown by '×', best fit by a solid line and the approximate 95% confidence limits (see text) by a dotted line; (b) residuals; and (c) histogram of the residuals (bars) and normal curve with zero mean and σ equal to 1.6 (solid line).

(or a limit given by any other probability value) can be used for the prediction of an upper value of the diffusion coefficient.

For the polymer groups MDPE and HDPE, and PP, probability distribution models were determined in the same way. Figures 3 and 4 show the results, and values for a, b and s are given in Table 1. Also for these polymer groups, the assumption of a log–normal distribution of the diffusion coefficient is reasonable.

A closer look at the experimental data in Figs 2(a), 3(a) and 4(a) shows that most values of the migrant molar masses lie in the range from 0 to

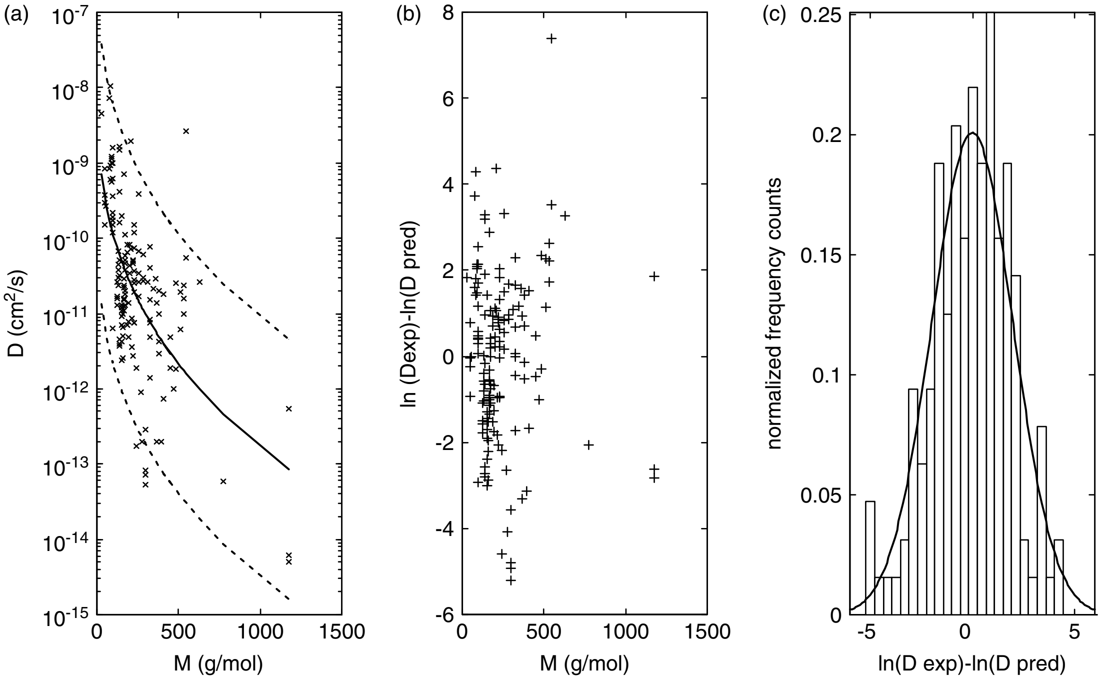

Figure 4. Result of the minimization procedure of diffusion coefficient for experimental data for polymer group PP assuming a log–normal distribution of errors: (a) experimental data shown by '×', best fit by a solid line and the approximate 95% confidence limits (see text) by a dotted line; (b) residuals; and (c) histogram of the residuals (bars) and normal curve with zero mean and σ equal to 2.0 (solid line).

200 g mol^{-1}. This is because most research on diffusion in polymers has been carried out with small molecules. However, most polymer additives have a molar mass between 300 and 1000 g mol^{-1}. Equations for estimating diffusion coefficients for migration calculations based on literature data therefore extrapolate to high molar masses. Some additives are used more often for research than others. For example, many data points for a migrant molar mass of 521 g mol^{-1} are available in all polymer groups. This is the antioxidant Irganox 1076, which is frequently used in polyolefins and also in experiments to determine diffusion coefficients. The large variation in the values of this component shows that the experimental method and the conditions of measurement have a large influence on the diffusion coefficient.

MIGRATION SIMULATIONS

Finally, the probability distributions of the diffusion coefficients were used for migration prediction. The partition coefficient was assumed for simplicity to have one value with no error. According to Baner,[22] the partition coefficient, defined as the ratio of concentration in packaging to concentration in food simulant, is 1 for migrants with a high solubility in the food simulant and 1000 for a low solubility.

To obtain migration probability distributions we used a Monte Carlo procedure with the following steps:

(1) select a molar mass of the migrant;
(2) calculate the mean diffusion coefficient using equation (2) and corresponding parameter values for *a* and *b* from Table 1;
(3) draw a random diffusion coefficient from the probability distribution given by the mean diffusion coefficient and *s* using

$$\ln D = \ln D_{\text{mean}} + sR \tag{6}$$

where R is a random number from a normal distribution with zero mean and standard deviation equal to 1;

(4) calculate the migration using equation (1);
(5) repeat steps 3 and 4 a large number of times (here 10 000 times);
(6) plot a histogram of the obtained migration values.

To illustrate the method, the migration of Ultranox 640 (PM/REF 95 270) with a molar mass of 450 g mol^{-1} from a 200 µm thick PP polymer film at 23 °C is calculated. The initial additive concentration is assumed to be 500 mg kg^{-1} and the dimensions of a standard EC packaging (6 dm^2 contact area per kg food) are used. Polymer density is assumed to be 0.95 kg dm^{-3} and food simulant density 1 kg dm^{-3}. The specific migration limit of Ultranox 640, according to EC Directive 90/128/EEC and its amendments,[23] is 2 mg kg^{-1} food. Test conditions are officially 10 days at 40 °C, but since our model is only applicable at 23 °C, we arbitrarily assumed test conditions of 20 days at 23 °C.

Figure 5 shows the results of the Monte Carlo procedure for a fatty food simulant ($K = 1$). The distribution of migration values is broad, which means that both low and high migration values are possible. This is due to the large variation in the experimental diffusion coefficients (included in

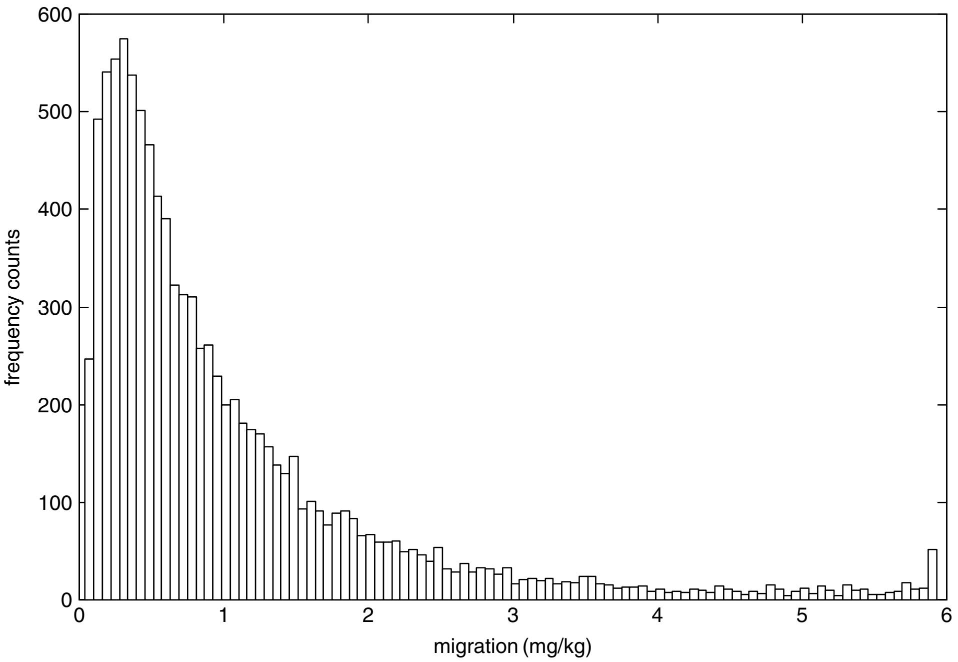

Figure 5. Probability distribution of the migration of Ultranox 640 from a PP polymer film at 23 °C during 20 days of incubation (see text for further details).

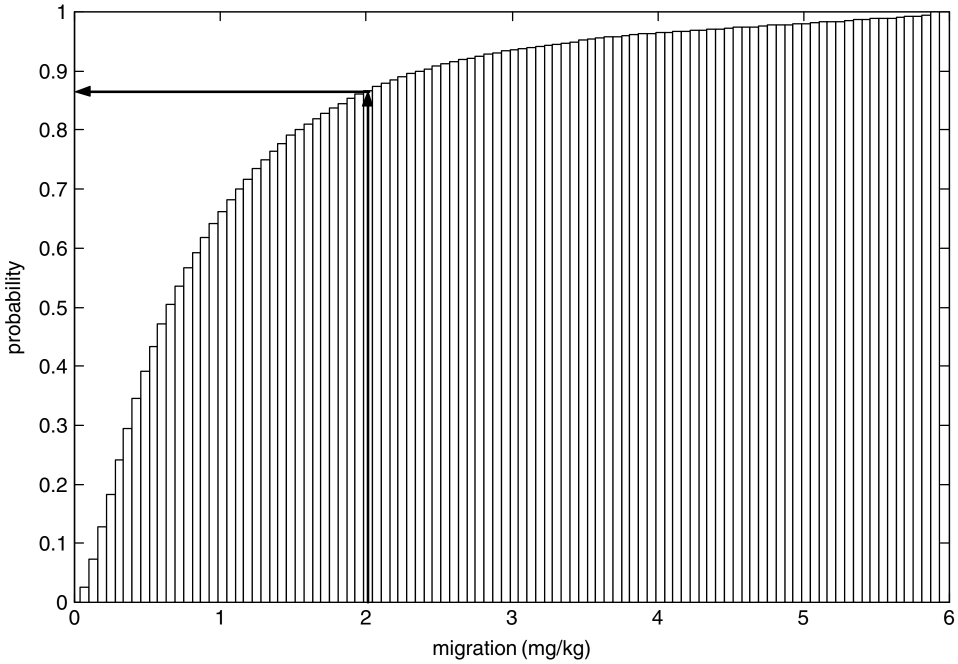

Figure 6. Probability of finding a migration value less than or equal to the migration value given on the *x*-axis for the migration situation described in the text and shown in Fig 5. The arrows indicate the probability of finding a migration value less than 2 mg ml^{-1}.

the standard variation). According to the results, a migration value in the range 0–1 mg kg^{-1} is most likely to be found. However, higher migration values are possible. The shape of the curve results from the log–normal distribution of the diffusion coefficient. If the partition coefficient in equation (1) was also provided with a probability distribution, then another distribution of migration values may be found. The peak at 5.9 mg kg^{-1} is due to the fact that the maximal concentration in the food simulant (according to the thermodynamic equilibrium) has already been reached for all of the highest diffusion coefficient values.

The cumulative of the frequencies shown in Fig 5 gives the probability of finding a migration value less than or equal to a given limit (Fig 6). In our example, the probability that the migration is less than or equal to 2 mg kg^{-1} is 0.86, which corresponds with a chance of 0.14 of exceeding this limit.

In principle, the estimated parameters *a* and *b* also have an uncertainty, which may be included in the predictions by introducing a probability distribution for each parameter as well. A method to include uncertainty in the parameters is given in Press *et al*[19] (p 689).

DISCUSSION

The derived probability distributions are for a temperature of 23 °C. To include other temperatures, there are two options. The first is to collect diffusion coefficients at another temperature, for example 40 °C, and again derive the parameters *a* and *b* and standard deviation *s*. The other is to include a temperature dependency in equation (2) or use another expression for the diffusion coefficient as a function of temperature. However, this requires many experimental diffusion coefficient values of different migrants at different temperatures. Sufficient values have not yet been measured, especially at higher temperatures and for higher molar masses, to allow this type of stochastic approach.

The choice of a type of distribution is the most important and difficult part of stochastic modelling, since this determines the probability of a given diffusion coefficient. The log–normal distribution gives a reasonable, although not perfect, fit of the experimental data. It is important to remember that the diffusion coefficients have been determined by many different methods and under very different conditions. Since the available data are rather noisy, it does not seem worthwhile to apply more complex distributions, or even different distributions for each polymer group, until this is justified by more experimental data.

An approach to reducing the variation in predicted diffusion coefficients is to sort the diffusion data of the various polymer into more classes as has been done in this research. In particular, using more specific information on the molecular structure differences might reduce the scattering of the reported diffusion coefficients. However, due to a lack of information on these properties in the reported diffusion coefficients this was not possible at this point.

Since the migration rate depends not only on the value of the distribution coefficient but also on the value of the partition coefficient, a similar treatment of the effects in variation in predicted partition coefficient would be justified. For this it is required to have models relating the value of the partition coefficient to a molecular property of the migrant. Few attempts on this have been presented in literature.[24] These are based upon the polarity (log P) of compounds,[25] or provide only a rough separation[22] in two catagories with high (1000) or low (1) values for the partition coefficients. A more systematic investigation into measuring and modelling partition coefficients is required for this purpose.

CONCLUSIONS

The purpose of this paper has been to show how stochastic modelling can be applied to derivation of probability distributions of diffusion coefficients of migrants in polyolefins based on results of diffusion experiments reported in the literature. The probability distributions can be used to simulate migration processes and predict the probability of exceeding a given migration limit. The model presented can be used for migration prediction in polyolefins at 23 °C. More experimental data may allow extension to other temperatures and to a more justified choice of type of probability distribution.

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