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Phil. Trans. R. Soc. Lond. A 1995 **350**, 379-406
doi: 10.1098/rsta.1995.0021

Migration from plastic packages into their contents. I. The role of mathematical models

By J. A. Lum Wan[1], P. C. Chatwin[2] and L. L. Katan[3]

[1] *29 Canberra Street, Brunswick, Victoria 3056, Australia*

[2] *Applied Mathematics Section, School of Mathematics and Statistics, University of Sheffield, Sheffield S3 7RH, U.K.*

[3] *I.F.P.S. Ltd, P.O. Box 410, Kingston-upon-Thames, Surrey KT1 4YE, U.K.*

Materials contained in plastic packages can transfer (migrate) into the contents. In some circumstances, such as packages of food, drink or medicine, the consequences of this migration can be unpleasant or even harmful. Many countries, and the European Community, have adopted legal regulations designed to limit the amount of migration. It is shown, partly by discussing one example in some detail, that certain quantitative criteria in such regulations are unsatisfactory. The reasons include (*a*) improper recognition of the importance of package geometry, (*b*) invalid assumptions about a correspondence between concentrations in the contents and mass transfer per unit area of the package–contents interface and (*c*) failure to account, in an adequate manner, for the inevitable variability between nominally identical package systems. The principal theme of the paper is that these faults could have been, and can be, substantially ameliorated by proper use of mathematical models. Common shortcomings in the previous (but very limited) use of mathematics are exposed partly by detailed examination of a recent research paper. The paper discusses the requirements of a successful model and considers the simplest type, namely diffusion equations with diffusion coefficients that are independent of the concentrations of the migrant in either the plastic or the contents. Particular solutions are chosen to illustrate faults in existing legislation and practice, and because they are thought to be good candidates for testing against data. It is argued that future experiments would be more successful and more useful if they were planned and conducted in teams involving mathematicians.

1. Introduction

(*a*) *Background*

Plastics used in packaging usually contain substances that may migrate into the package contents. Examples are residual monomers or reagents, additives such as antioxidants or plasticizers, colouring materials, and reaction products formed in manufacture or work-up. Some migrants have undesirable effects if they are present in the contents in sufficient quantities. In food (including drink) and medicines, such effects range from unpleasant, but harmless, taste or smell (e.g. styrene in orange juice or coleslaw) to toxicity if potentially dangerous substances, such as vinyl chloride monomer (VCM) or heavy metals, migrate in sufficient quantities. A famous example of the latter arose when airlines used to serve spirits in miniature bottles made of PVC (Katan 1992).

Phil. Trans. R. Soc. Lond. A (1995) **350**, 379–406
Printed in Great Britain

In view of the enormous and continuing growth in the use of plastic packaging for food, regulatory authorities have inevitably had to pay increasing attention to migration. Many nations now have regulations and the Commission of the European Communities (CEC 1990) has adopted a Directive 'relating to plastics materials and articles intended to come into contact with foodstuffs', having earlier adopted other Directives, such as 78/142/EEC dealing specifically with VCM. These regulations and Directives impose legal duties on both suppliers and governmental authorities; in particular the latter are charged with surveillance and enforcement.

Unfortunately the scientific basis of existing regulations and Directives is inadequate in some important respects. The main purposes of the present paper are:

(i) to expose these inadequacies;

(ii) to demonstrate that they can be ameliorated by mathematical modelling;

(iii) to argue for a multidisciplinary research programme whose adoption would lead to scientifically sounder regulations and, hence, enhanced consumer safety. A largely non-technical summary of some of the themes developed here is given by Chatwin & Katan (1989).

Later papers will deal with another more general mathematical model and its comparison with data sets.

In this paper the word 'food' will be used to denote both solid and liquid food, including drinks. While the work was motivated by applications to food packaging, and all the examples will refer to this area, it is clear that much of it applies whatever the package contents.

(*b*) *Scientific basis of existing legislation*

The scientific research on migration that has underpinned existing regulations and Directives has been almost entirely in the field of analytical chemistry. (No account need be taken here of related research areas, such as toxicology and estimation of consumer exposure, since these are concerned not with the phenomenon of migration *per se* but with its effects.) Thus each available migration data set is specific to:

(i) the materials used – plastic, migrant(s), food (or food simulant);

(ii) the geometry of the system tested – size, shape;

(iii) experimental conditions such as temperature.

These limitations are of course inevitable. But the experiments ought, ideally, to have formed parts of concerted, multidisciplinary, research programmes designed to enable quantitative assessments of migration to be made across the whole vast range of circumstances relevant to consumer safety. Because of factors such as inherent variability in food and plastic structure, and ignorance of the exact temperature history of any one package since containment, no quantitative assessment of migration can be completely accurate even for a system whose nominal twin had been specifically examined in a laboratory test. But such situations are widespread, even normal, in our world and a key scientific skill is to provide best possible and scientifically well founded estimates under these circumstances. All such estimates will make full use of available information, especially experimental results, on relevant specific cases. Sometimes, of course, lack of information will mean that 'best possible' is only correct to an order of magnitude, or worse.

But, unfortunately, there is little sign that those responsible for advising on migration legislation have recognized the desirability, indeed necessity, of involving experts in fields other than analytical chemistry in their research programmes. (This is surprising not only for the positive reasons summarized above but also because of

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the manifest impossibility of conducting a specific test for each package system available to the consumer.)

It is important to prove this contention, namely that the scientific base of migration research has been too narrow, till now at least. Evidence is easy to find, and two examples are discussed in detail in the two appendices. Appendix A demonstrates that an existing Directive does not provide the protection to the consumer that is its intention. A major reason is that package size and shape are totally ignored; additionally the Directive makes some implicit, but erroneous, assumptions about basic science. Appendix B points out some of the serious errors made in a recent research paper, errors of both understanding and technique in simple physics and mathematics. Although the particular paper discussed is perhaps an extreme example, all the types of error listed have appeared many times in the research literature.

(*c*) *Use of mathematics in previous migration research*

The potential of mathematics to quantify, generalize and predict has hardly been exploited by migration research workers. There are numerous examples in which a mathematical formula for the concentration of a migrant, or its total transferred mass, is quoted in an otherwise experimental paper and then is not referred to again. On some other occasions, attempts made to compare such formulae with the experimental results are scientifically invalid, often because the quoted formula does not apply for the geometry of the experiment.

This lack of recognition of the potentially crucial importance of geometry is a common fault in papers on migration, but there are others that are arguably as serious.

Little use is made of non-dimensional plots to collapse data and thereby most efficiently to facilitate intercomparisons of data sets from different experiments and laboratories, and with different materials. A consequence is that claims are often made, on the basis of graphs of, for example, dimensional concentration against dimensional time, that two (or more) systems behave differently when appropriate dimensionless plots might well demonstrate the opposite, i.e. that they are controlled by the same physics. Unfortunately, however, key information is often omitted from such papers so that the data given in them cannot be replotted in dimensionless form.

This criticism illustrates a more general fault. Most experiments on migration do not involve chemical change so that what is observed is essentially a result of physics. Accordingly, more emphasis on physics would usually be in order.

Finally it does not appear to be generally understood that a mathematical formula expressing concentration as a function of position and time does not constitute an effective mathematical model since, of course, such a formula can be valid only for one geometry and only for one set of initial and boundary conditions. Since the formula concerned is invariably an elementary solution of a partial differential equation, the effective mathematical model would then be this equation together with the appropriate boundary and initial conditions. Numerical predictions for realistically shaped food package systems would require the use of numerical analysis and computers, nowadays a standard task (but not necessarily a trivial one).

The points above are discussed at greater length in Chatwin & Katan (1989). Also, of course, there are exceptions to the general criticisms and some will be referred to later.

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(d) Plan of the paper

The rest of this paper discusses the structure, and some details, of mathematical models that seem promising candidates for further investigation. A simple result giving an absolute maximum limit on the mass of migrant that can be present in food is discussed in §2, while models giving more detailed predictions are considered in §3.

However, as emphasized elsewhere (Chatwin & Katan 1987, pp. 3/1/56–3/3/56; 1989), mathematical models of migration – indeed of any phenomenon – have little or no practical value unless they have been tested against data and, where necessary, refined or changed. Unfortunately, as explained in §1*c* above and illustrated by appendix B, very few available data sets have the detail or, sometimes, the quality required for this task. Therefore the main aim of §3 is to provide a reference and, perhaps, a guideline for testing and validation by future experimenters, working in collaboration with mathematicians. However, in a later paper (Lum Wan *et al.* 1996) one data set will be discussed in depth that is an exception to those criticized immediately above, and shows that it agrees well with the predictions of a mathematical model.

2. The maximum possible migrant concentration in the food

In this paper, italic capital letters (e.g. M, C, V) denote quantities that refer to the food (mass of migrant, migrant concentration, volume respectively) and lower case letters (e.g. m, c, v) denote the corresponding quantities for the plastic package. In particular, note that v is the volume of plastic forming the package, whereas V is the capacity of the package when full. (When necessary, concentrations will be expressed as mass/volume – kg m^{-3} in SI units – but conversions to a system using mass ratio can easily be made if needed.)

Suppose that, at containment, the mass of migrant in the plastic package is m_0. To obtain a 'fail safe' assessment, it is clearly legitimate to ignore any loss of migrant to the environment outside the food package system (and it is difficult to estimate such losses when they are caused, for example, by handling). It will also be assumed here that the system is not affected by chemical or biological change.

Whatever its precise mechanism, mass transfer of migrant from the package to the food would result (if the food were not consumed first) in an eventual equilibrium provided that conditions like temperature and pressure were ultimately steady. Let the masses of migrant in the food and package at this equilibrium be M_∞ and m_∞ respectively. By mass conservation,

$$M_\infty = m_0 - m_\infty. \tag{1}$$

Normally, at equilibrium, the concentrations C_∞ and c_∞ of the migrant in the food and plastic respectively will be uniform (i.e. independent of position). This will always be true, for example when the mass transfer mechanism is a diffusion process, even if the diffusion coefficient depends on concentration. Thus, from (1),

$$C_\infty = (c_0 - c_\infty)\, v/V, \tag{2}$$

based on the assumption (see §3) that any change in volume of either food or plastic due, for example, to penetration of the plastic by the food can be neglected.

It follows from (2) that

$$C_\infty < c_0\, v/V. \tag{3}$$

Hence it can be guaranteed that the final concentration of migrant in the food will be less than any prescribed (e.g. toxicologically hazardous) limit, C_T say, by choosing one (or more) of c_0, v and V so that

$$c_0 v/V < C_T. \tag{4}$$

This result is not new and refinements involving partition coefficients and solubility can be introduced. (Note, for example, equation (14) below.) See Garlanda & Masoero (1966), Katan (1979), Sanchez *et al.* (1980) and Chatwin & Katan (1989) where many details, including numerical examples, are discussed. These refinements result in a lowering of the maximum possible value of C_∞, given by (3), but at the cost of introducing physical constants of usually unknown values.

An absolute insistence that (4) must be satisfied would generate technological or economic problems that are deemed to be unacceptable in many cases. It may also result in food packages that are not attractive to the consumer, a drawback that could be substantially alleviated by more public information. However, even with these caveats, there is little doubt that the degree of safety could be improved by adopting regulations that take more account of (4) than is presently so. This would also have the advantage of tending to reduce the mass of plastic needed for a given mass of food.

3. Some types of mathematical model

(*a*) *Deterministic or stochastic?*

With a few exceptions (e.g. some liquid foods), foodstuffs sold commercially do not have spatially uniform (homogeneous) structures. Moreover, the degree of non-uniformity (heterogeneity) within any one item of food (e.g. a piece of cheese or meat) is often large and unpredictable as far as factors like location, spatial extent and magnitude are concerned; different samples of any single item of most foods will differ from one another in a random manner. Randomness is also inevitable in the structure of the plastic packages (but usually to a significantly smaller extent) and in the geometry (e.g. air pockets) of the interface between the food and the plastic. There are other factors that cause the quantity of migration in any one food package system to be unpredictable; one important example is its temperature history since containment.

The effects on migration of this inherent randomness (variability) can be quantified only by conducting repeat experiments with random samples (of e.g. 20 or more nominally identical packages each containing 0.25 kg of Cheshire cheese). On grounds of cost, it is perhaps superficially understandable why few such investigations have been undertaken. But the quantitative result of a single migration test on a single food package system can have little meaning; it may not be close to the statistical mean for all such packages and may even be an outlier (Barnett & Lewis 1984).

What little experimental evidence there is amply confirms that this inherent variability has substantial consequences for migration assessment. Schwope *et al.* (1987) note that 'satisfactory replication of results could not be achieved in migration measurements of BHT from LDPE into water at 49 °C' and 'the results show a disconcerting scatter'. An estimate by eye from figure 4 of their paper shows that after about 110 h the maximum mass of BHT in water over 15–20 repeat experiments is about three times higher than the minimum. Moreover, it is important to observe that these experiments must substantially underestimate real life

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variability because (*a*) they were done under closely controlled laboratory conditions, including temperature, and (*b*) the 'food' was water so that the random structure of most real foods was not a factor.

The most substantial study of variability was organized by the EC Joint Research Centre at Petten in the Netherlands and is reported by Haesen *et al.* (1984). A total of nine laboratories, from various member countries of the EC and from Switzerland, took part in a project with four phases, of which only the first two need be considered here.

Migration was not investigated in the first phase, which dealt only with the reliability of the technique used to measure migrant concentrations. Each of eight laboratories used high performance liquid chromatography (HPLC) to analyse each of a set of 12 nominally identical samples centrally prepared at Petten. The 12 samples involved two different food simulants (water and HB 307, a synthetic fat), two plastic additives (Irganox 1010 and DHBP) and three different concentrations in the parts per million range. The most striking feature of the results was that in all cases the average measured concentration was substantially below the actual (i.e. nominal) concentration by amounts between 10% and 50%; this feature, clear from table 1 of Haesen *et al.* (1984), was not commented on. From the point of view of immediate concern, there was, additionally, considerable scatter in the results with standard deviations ranging from 11–16% for DHBP in HB307 to greater than 70% for Irganox 1010 in HB307. Not unreasonably, it was concluded that 'The considerable scatter observed showed a major problem ... another identification method had to be found to obtain satisfactory repeatability and reproducibility'. (In fact, the strongest reason for rejecting the method is not the scatter but the large and systematic shortfall in the measured concentrations.) The scatter could be due at least in part to real differences between the nominally identical samples. There is a lot of other evidence – for example the data discussed in appendix B of the present paper – to suggest that the variability between nominally identical samples can produce scatter of the observed order of magnitude.

The second phase was principally concerned with examining the repeatability (experiments within a single laboratory) and reproducibility (experiments in different laboratories) of migration data. The measurement problems in the first phase were stated to be eliminated by the use of ^{14}C labelled additives; certainly the results were no longer consistently low. The central laboratory at Petten distributed samples of HDPE, each sample containing one of the two additives used in phase one, to the participating laboratories. Migration tests, each for 10 days at 40 °C, were conducted in Petri dishes with three test liquids: 90:10 v/v water–ethanol; HB307; olive oil. Samples of the resulting liquids were in each case analysed both at the laboratory conducting the test and at Petten. There were some problems with ethanol evaporation and about 15% of the results were rejected as outliers. (The proper statistical treatment of outliers is a controversial topic (Barnett & Lewis 1984); accordingly it would have been useful to state the precise criteria used for defining an outlier.) The standard deviations for repeatability ranged from 2 to 9% and this was judged to be acceptable. However the standard deviations for reproducibility were generally much larger, ranging from 5 to 47% with an average of about 28%.

It is now clear that even in controlled laboratory experiments (and *a fortiori* under real life conditions) migration ought to be regarded as a statistical phenomenon or, in technical terms, a stochastic process. Ideally, therefore, mathematical models of migration should involve a substantial statistical component. In particular a model

should include an assessment of the degree of uncertainty associated with any one numerical estimate of migration, for example by including a procedure for estimating its standard deviation. Note that such a standard deviation is a net effect of all the factors that contribute to inherent variability, and these can be quantitatively investigated by well designed experimental programmes.

Stochastic models of the type envisaged are being increasingly developed in many fields because it is now recognized that they, and not the traditional deterministic models, correspond to reality; two examples are the assessment of risk consequent upon the accidental release of dangerous gases into the atmosphere, and the monitoring of urban air quality (Chatwin & Sullivan 1990; Chatwin 1991).

However, all the mathematical models used so far in migration research have been deterministic. This is realistic only insofar as the data sets available are so limited that they do not allow any stochastic model to be tested; indeed, and as noted already, they are rarely useful even in conjunction with deterministic models. Nevertheless, although deterministic models will not ultimately prove satisfactory for migration into real foods, they can, more positively, be proposed as providing predictions of the mean (i.e. expected) migration over a population of migration events or, less ambitiously, as providing estimates of the order of magnitude of the migration and its dependence on key quantities like time. This is the justification for considering deterministic models below, but only further experiments can decide whether this approach is practically acceptable.

(*b*) *Diffusion equation models. Principles*

It is good practice to investigate simple deterministic models until there is strong experimental evidence that their predictions are practically inadequate. In the first instance only specific migration (i.e. the migration of one migrant) will be considered.

Contrary to what is usual in real life (albeit not in many experiments), but consistent with the philosophy recommended in the last paragraph of §3*a*, it will be supposed that both the food and the plastic are homogeneous and isotropic. (For packages that are laminates the modelling is valid provided migration occurs only from the layer in contact with the food. So, either the interface between the first two layers is impervious to the migrant or the first layer is effectively of infinite thickness, i.e. the obvious analogues of (7*a*) or (7*b*) respectively are true.)

This paper does not consider situations in which chemical or biological changes occur. Although there is some experimental evidence (Schwope *et al.* 1987) that chemical changes are relevant in certain circumstances, this restriction is generally valid.

When the above conditions hold, migration is a conservative mass transfer process, and it can be argued quite generally (see, for example, Batchelor 1967, pp. 28–37) that changes in the migrant concentrations $C = C(\boldsymbol{x}, t)$ (in the food) and $c = c(\boldsymbol{x}, t)$ (in the plastic), where the notation is consistent with the convention introduced at the beginning of §2, and $\boldsymbol{x}$ and t denote position and time respectively, are described by diffusion equations with diffusivities D and d. Thus

$$\partial C/\partial t = \nabla\cdot(D\nabla C), \quad \partial c/\partial t = \nabla\cdot(d\nabla c). \tag{5}$$

The way in which equations (5) have been written allows the possibility that D and d are not constant. In particular, they may depend on C, c and state variables like temperature (but not separately on $\boldsymbol{x}$ and t in view of the postulated homogeneity); see §3*d* below and Lum Wan *et al.* (1996). (Equations (5) are referred to as 'Fick's

second law' by many who write about migration, but this attribution is not normal in physics, mathematics or engineering. The reason is that the general argument leading to equations (5) applies also to heat, and Fick in 1855 simply recognized the applicability to mass transfer of (5), equations for temperature derived by Fourier in 1822 (see Crank 1975, p. 2, p. 4).)

All the mathematical modelling in this paper will be for cases where, before containment, the migrant is absent from the food and distributed uniformly in the plastic with concentration c_0. The time at which containment (i.e. the formation of the food package system) occurs is chosen to be $t = 0$. Consequently the initial conditions that solutions of (5) must satisfy are:

$$C(\boldsymbol{x}, 0) = 0, \quad c(\boldsymbol{x}, 0) = c_0. \tag{6}$$

The boundary conditions for (5) depend on the circumstances in which migration takes place. These are controlled to a greater or lesser extent by e.g. the food manufacturer, the retailer, the consumer or (for laboratory tests) the experimenter. In general they differ from case to case even with the same materials and same geometry.

One such condition is needed at the exterior boundary of the package where it is in contact with air, for example. In most migration experiments (and for most real life situations if only on the grounds of maximizing consumer safety) it is appropriate to assume no loss of migrant, i.e.

$$\boldsymbol{n} \cdot \nabla c = 0 \tag{7a}$$

everywhere on the exterior boundary, where $\boldsymbol{n}$ is the normal vector. It often happens that $(dt)^{\frac{1}{2}} \ll h$ for all times t of interest, where h is the plastic thickness. In such cases the plastic can be assumed to be infinitely thick as far as migration is concerned and (7a) can be replaced by

$$c \to c_0 \quad \text{as} \quad |\boldsymbol{n} \cdot \boldsymbol{x}| \to \infty. \tag{7b}$$

Mass conservation requires that

$$D\boldsymbol{n} \cdot \nabla C = d\boldsymbol{n} \cdot \nabla c \tag{8}$$

everywhere on the interface between the food and the plastic. To solve (5) a second condition is required at this interface. Under some conditions, when equilibrium is approached,

$$C = \gamma c \tag{9}$$

everywhere on the interface, where γ is the partition coefficient. It will be assumed in this paper that (9) holds throughout the migration process even though this is not an equilibrium state. This assumption is discussed and used by Reid *et al.* (1980) and by Chatwin & Katan (1987, pp. 3/4/56–3/5/56, 3/14/56–3/16/56), but its examination by good experiments is overdue. It will further be supposed here that γ is independent of concentration. Reported values of γ for aqueous foods and lyophilic plastics are typically very small (e.g. $\gamma \approx 7 \times 10^{-6}$ for plasticizers migrating from PVC into 3% acetic acid (Till *et al.* 1982*a*) and $\gamma \approx 7.1 \times 10^{-3}$ for styrene monomer migrating from polystyrene into 50% aqueous ethanol (Till *et al.* 1982*b*)) but they can be much larger, even exceeding one, when oily foods are involved.

Use of (6)–(9) inclusive obviously requires complete specification of the relevant system geometry.

In circumstances when the dependence of D and d in (5) on the migrant concentrations is known (or can be adequately approximated), equations (5)–(9)

inclusive determine C and c uniquely as functions of $\boldsymbol{x}$ and t. Some particular examples that illustrate this assertion will be discussed in §3*c*, *d*.

However, because D, d and γ are, in general, strongly dependent on temperature T, the above statement assumes implicitly that the migration occurs under isothermal conditions. This is true for most laboratory experiments but not in real life. When conditions are not isothermal, the mathematical model given by equations (5)–(9) is not complete and therefore not soluble. Equations, like (5), for the variation of T throughout the food and package, boundary conditions, and formulae giving the dependence on it of D, d and γ must be added. The resulting model would then be very complicated (and, in particular, nonlinear) so that its solution even on a computer would be a major task. From a practical point of view it is doubtful whether the effort would be justified. Realistically the most useful strategy for consumer safety would seem to be to assume isothermal conditions with the temperature equal to the maximum to which the food package is likely to be exposed for any significant period. Only such isothermal models will be considered in this paper.

Except for small t, useful analytic solutions (i.e. mathematical formulae) of equations (5)–(9) can be obtained, if at all, only for geometries much simpler than those used in real food package systems. For realistic geometries, solutions must be obtained by using computers. It is reasonable to suppose that software packages in user friendly form will become available to the food packaging industry and to those responsible for surveillance and for the enforcement of regulations. However the development of such packages is not justified unless the mathematical model has first been validated. This validation is of the physics underlying equations (5)–(9), and does not require the use of complicated geometries. This is the justification for migration experiments with simple (e.g. one-dimensional) geometries and it follows that, to be practically useful, the results of such experiments must be compared with the predictions of mathematical models (which may then be given by mathematical formulae). The results of experiments in test cells with simple geometries cannot be extrapolated to realistic geometries, except for small t, without use of mathematical models and computers.

(*c*) *Diffusion equation models. Some illustrative solutions with constant diffusion coefficients*

(i) *Previous work*

Migration behaviour was classified by Katan in 1971 (Briston & Katan 1974). His Class II systems are those, simply speaking, in which penetration of the plastic package by the food has an insignificant effect on migration, and it is for these systems that constant diffusion coefficient models are the obvious first candidates.

Many solutions of equations (5)–(9) when D and d are constant are known. Among the comprehensive treatments of both methods and analytical solutions are the books by Carslaw & Jaeger (1959) and Crank (1975). The first paper discussing such models in the migration context was by Garlanda & Masoero (1966), and significant contributions were made by an Arthur D. Little/MIT/FDA group in the 1980s (see, for example: Reid *et al.* 1980; Schwope *et al.* 1987).

The remainder of this subsection (§3*a*) will consider some features of diffusion equation models with constant diffusion coefficients that are judged to be potentially important. A critical summary of other work with these models is given by Chatwin & Katan (1987, especially pp. 3/17/56–3/33/56).

(ii) *Small time behaviour*

Let h and H be length scales characteristic of the thickness of the plastic and of the smallest dimensions of the region occupied by the food respectively. For times t such that

$$(dt)^{\frac{1}{2}} \ll h \quad \text{and} \quad (Dt)^{\frac{1}{2}} \ll H, \tag{10}$$

the mass transfer is effectively from a plastic of infinite thickness to a food of infinite thickness.

There is an old one-dimensional solution of equations (5)–(9), quoted on p. 39 of Crank (1975), for which the amount of migration at time t is proportional to $t^{\frac{1}{2}}$. This has appeared in many papers on migration, but it does not seem to have been realized (or at least not stated) that the result applies to packages of any shape. Suppose A is the area of the interface between the plastic and the food, and let $M = M(t)$ be the mass of migrant in the food at time t. Provided (10) is satisfied, the solution gives

$$M \approx \frac{2}{\pi^{\frac{1}{2}}}\left(\frac{1}{1+\alpha}\right) c_0 A (dt)^{\frac{1}{2}} = \frac{2}{\pi^{\frac{1}{2}}}\left(\frac{\alpha\gamma}{1+\alpha}\right) c_0 A (Dt)^{\frac{1}{2}}, \tag{11}$$

where the non-dimensional constant α is defined by

$$\alpha = \frac{1}{\gamma}\left(\frac{d}{D}\right)^{\frac{1}{2}}. \tag{12}$$

(iii) *Final equilibrium*

The mathematical model predicts an approach to an equilibrium as $t \to \infty$. (Note that this requires use of (7*a*), not the approximation to it given by (7*b*), which, as noted earlier, is valid only when $(dt)^{\frac{1}{2}} \ll h$.) As in §2, denote the uniform concentrations of the migrant in the food and the plastic at equilibrium by C_∞ and c_∞ respectively. Mass conservation, ensured in the model by equations (5) and (7*a*), requires that

$$c_0 v = C_\infty V + c_\infty v. \tag{13}$$

Use of (9) then gives

$$C_\infty = c_0 \gamma v/(v+\gamma V). \tag{14}$$

It is easy to see that the right side of (14) is less than $c_0(v/V)$ for all values of γ, so that (14) is consistent with (3). Denote the mass of migrant in the food at equilibrium by M_∞. Since $M_\infty = C_\infty V$, (14) gives

$$M_\infty = \left(\frac{\gamma}{1+\beta}\right) c_0 V, \tag{15}$$

where β is a second non-dimensional constant defined by

$$\beta = \gamma V/v. \tag{16}$$

Effectively β is the ratio of capacities for migrant of the food and plastic respectively.

For later reference, note that (11) and (16) combine to give

$$\frac{M}{M_\infty} \approx \frac{2}{\pi^{\frac{1}{2}}}\left[\frac{1+\beta}{\gamma(1+\alpha)}\right]\frac{A(dt)^{\frac{1}{2}}}{V} = \frac{2}{\pi^{\frac{1}{2}}}\left[\frac{\alpha(1+\beta)}{1+\alpha}\right]\frac{A(Dt)^{\frac{1}{2}}}{V}, \tag{17}$$

provided, still, that (10) holds.

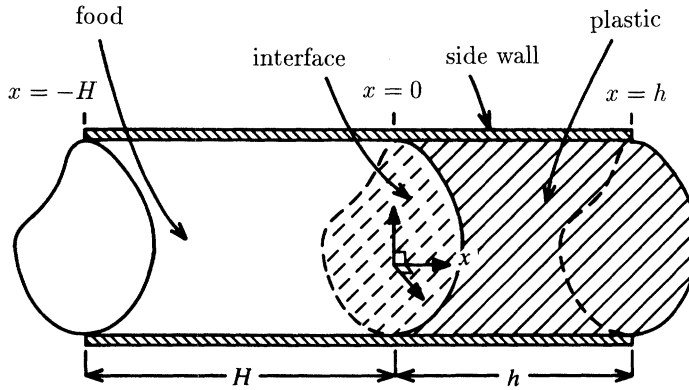

Figure 1. Definition sketch for one-dimensional geometry.

(iv) *The full model solution for one-dimensional geometry*

The importance of the results in (ii) and (iii) is due to the fact that they hold in all geometries.

Clearly it is not possible, for most geometries, to derive formulae from the model equations that are valid for all t. Computers must be used to obtain numerical solutions.

In this expository paper it is appropriate instead to focus upon the physical content of the mathematical model by considering some simple geometries. In the first instance, consider the geometry illustrated schematically in figure 1, which represents essentially all the test cells for which migration data have been reported. (Note that for two-sided migration it is necessary only to reflect the diagram in the plane $x = h$ and to make trivial changes in some of the formulae below.) It is important to note that the interface of area A between the plastic and the food at $x = 0$ can have any shape. Provided the side walls exert a negligible influence, the variations of C and c with y and z can be ignored. The full model equations (5) to (9) can then be approximated by:

$$\left.\begin{gathered} \frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}, \quad \frac{\partial c}{\partial t} = d\frac{\partial^2 c}{\partial x^2}, \\ C(x,0) = 0 \text{ for } -H \leqslant x < 0; \quad c(x,0) = c_0 \text{ for } 0 < x \leqslant h, \\ \partial C/\partial x = 0 \text{ on } x = -H; \quad \partial c/\partial x = 0 \text{ on } x = h, \\ D\,\partial C/\partial x = d\,\partial c/\partial x \text{ on } x = 0, \\ C = \gamma c \text{ on } x = 0. \end{gathered}\right\} \tag{18}$$

For this geometry

$$V = AH, \quad v = Ah, \quad \beta = \frac{\gamma H}{h}, \quad M_\infty = \left(\frac{\gamma}{1+\beta}\right) c_0 AH, \tag{19}$$

with use of (15) and (16).

The solution of the system (18) is a routine task; technical details are analogous to those given for similar systems by Carslaw & Jaeger (1959). The results are most conveniently expressed in terms of one or other non-dimensional times Θ and θ, defined by

$$\Theta = Dt/H^2; \quad \theta = dt/h^2. \tag{20}$$

Since (H^2/D) is a time scale for diffusion in the food, Θ is an appropriate non-dimensional time for this element of the migration process; θ has an analogous interpretation in terms of the plastic.

When expressed in terms of Θ, the exact result for M/M_∞ derived from (18) is:

$$\frac{M}{M_\infty} = 1 - 2\alpha^2\beta(1+\beta)\sum_{n=1}^{\infty}\frac{\tan^2 Q_n}{Q_n^2}\frac{\mathrm{e}^{-Q_n^2\Theta}}{\{\alpha^2(1+\beta)+(1+\alpha^2\beta)\tan^2 Q_n\}}, \tag{21a}$$

where the Q_n for $n = 1, 2, \ldots$, are the positive roots in ascending order of the equation

$$\tan Q = -\alpha\tan(Q/\alpha\beta). \tag{22a}$$

The same result, but expressed in terms of θ, is:

$$\frac{M}{M_\infty} = 1 - 2\left(\frac{1+\beta}{\beta}\right)\sum_{n=1}^{\infty}\frac{\tan^2 q_n}{q_n^2}\frac{\mathrm{e}^{-q_n^2\theta}}{\{(1+\beta)+(1+\alpha^2\beta)\tan^2 q_n\}}, \tag{21b}$$

where the q_n for $n = 1, 2, \ldots$ are the positive roots in ascending order of the equation

$$\tan(\alpha\beta q) = -\alpha\tan q. \tag{22b}$$

Note that the infinite series in (21) tends to zero exponentially quickly as $\theta\to\infty$ (i.e. as $t\to\infty$) so that $M/M_\infty\to 1$, as it must. It can also be shown quickly that (21) predicts that

$$\frac{M}{M_\infty} \approx \frac{2}{\pi^{\frac{1}{2}}}\left[\frac{\alpha(1+\beta)}{1+\alpha}\right]\Theta^{\frac{1}{2}} \quad \text{for} \quad \Theta \ll 1. \tag{23}$$

This is exactly what (17) gives when $V = AH$ – see (19). This agreement between two independent calculations is an important check on the accuracy of both. Note also that $\Theta \ll 1$ is equivalent to the condition given in (10) that was shown to be necessary for (17) to be a valid approximation.

The result in (21) was first derived by two of the present authors (Chatwin & Katan 1987, equation (3.37)), and was believed to be new at that time. Its importance is that it is the most general one-dimensional solution of the mathematical model in equations (5) to (9) when D and d are constants. (Note that it is straightforward to derive expressions for C and c with use of Laplace transforms but these are substantially lengthier than (21) since C and c also depend on x.) Since M/M_∞ in (21) is a function of the two non-dimensional constants α and β, as well as of Θ, it is not practical to plot it here (and the same applies *a fortiori* to the concentrations themselves).

Many important special cases of (21) occur when appropriate limits are taken, and nearly all of these have been quoted in the migration literature (some on many occasions).

Reid *et al.* (1980) point out that in many practical cases the plastic is essentially infinite as far as migration is concerned. They suggest that this approximation is appropriate if 'less than 30–40 %' of the migrant is extracted. From (19), this case corresponds to letting $\beta\to 0$ in such a way that there is no dependence on h so that, also from (19), $M_\infty = \gamma c_0 AH$. The early stages of migration are described by (23) with $\beta = 0$, but, for values of Θ that are not small, the effects of partitioning and the finite food volume are felt. The appropriate limit of (23) can be written (Chatwin & Katan 1987, equation (3.45)):

$$\frac{M}{M_\infty} = 1 - \frac{2\alpha}{\pi}\int_0^\infty \frac{\sin^2 u\,\mathrm{e}^{-u^2\Theta}}{u^2(\sin^2 u + \alpha^2\cos^2 u)}\,\mathrm{d}u. \tag{24}$$

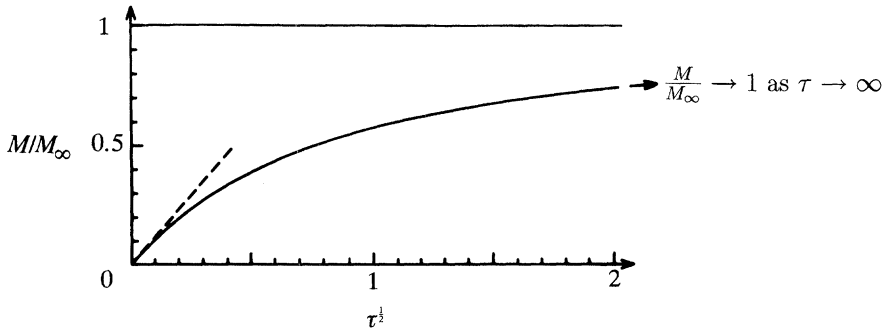

Figure 2. Sketch of M/M_∞ versus $\tau^{\frac{1}{2}}$ for well mixed food and infinite plastic (equation (26)). The dashed straight line is the approximation in equation (27).

Reid *et al.* (1980) give an alternative (but equal) expression for (24) – their equations (23) to (25) – and show plots of M/M_∞ versus non-dimensional time for many values of α in their figure 2.

Another approximation that is valid in many practical cases, especially for liquid foods, is that the migrant diffuses much more rapidly in the food than in the plastic, i.e. that $D \gg d$. This will be termed the 'well mixed food' case. (In real life the same results often occur because real food packages are shaken.) By (12), this corresponds mathematically to letting $\alpha \to 0$ in such a way that D disappears from all formulae. The general case is given by Crank (1975, p. 57) and is discussed by Reid *et al.* (1983); here it is sufficient to note two particular solutions.

If, additionally, the plastic is effectively infinite, the result for M/M_∞ can be obtained by letting $\alpha \to 0$ in (24). Since M/M_∞ can depend neither on D nor on h in this limit, the non-dimensional times Θ and θ can no longer be used. The result is most neatly expressed in terms of another non-dimensional time τ, where

$$\tau = dt/\gamma^2 H^2, \tag{25}$$

and is (Carslaw & Jaeger 1959, p. 306):

$$\frac{M}{M_\infty} = 1 - e^{\tau}\,\mathrm{erfc}\,(\tau^{\frac{1}{2}}). \tag{26}$$

This result is plotted in figure 2, together with the approximation for small time which is obtained from (17) as:

$$\frac{M}{M_\infty} \approx \frac{2}{\sqrt{\pi}}\tau^{\frac{1}{2}} \quad \text{for} \quad \tau \ll 1. \tag{27}$$

Figure 2 illustrates, for this simple case, two characteristic properties of the behaviour of M/M_∞ as a function of time. One is that the approximation for small t given by (17) is good only for a very small fraction of the time needed to achieve near equilibrium conditions; the error in (27) is already 9% when $\tau = 0.01$. The second, complementary, point is that the approach to equilibrium is very slow; even for $\tau = 100$, M/M_∞ is only 0.94.

The final special case to be considered for well mixed food is that when the food is effectively infinite. This important case is also of historical interest in migration,

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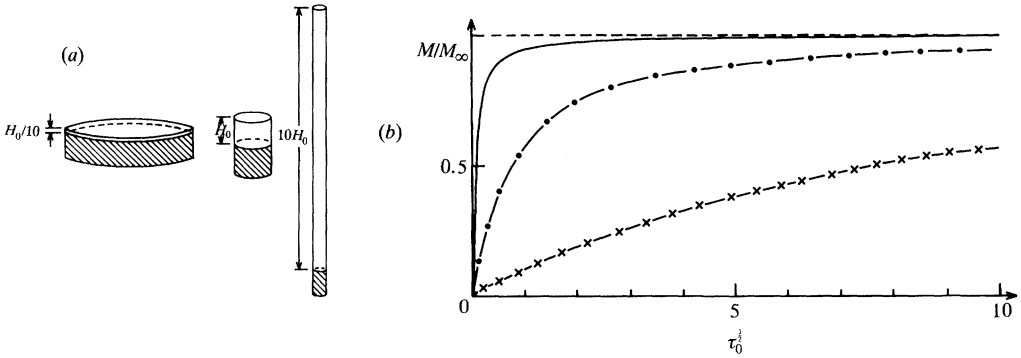

Figure 3. Effect of shape on migration. (*a*) Three differently shaped cells all of food capacity $A_0 H_0$. (*b*) The different behaviour of M/M_∞ with $\tau_0^{\frac{1}{2}}$ for the three cells, where $\tau_0 = dt/\gamma^2 H_0^2$. —— $H = H_0/10$; —·— $H = H_0$; —×— $H = 10H_0$.

since it appears in the pioneering paper by Garlanda & Masoero (1966). The solution must be independent of both D and H, so that M/M_∞ is a function only of θ, the non-dimensional time based on diffusion parameters for the plastic (see (20)). The result is

$$\frac{M}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{\mathrm{e}^{-(2n-1)^2 \pi^2 \theta/4}}{(2n-1)^2}, \tag{28}$$

and the appropriate form of the approximation (23) is

$$\frac{M}{M_\infty} \approx \frac{2}{\sqrt{\pi}} \theta^{\frac{1}{2}} \quad \text{for} \quad \theta \ll 1. \tag{29}$$

A plot of (28) is given in the paper by Garlanda & Masoero. This case illustrates that the effect of the partition coefficient γ on M/M_∞ is low when β is large, essentially because the concentration C of migrant is insignificantly different from zero. It will be noted that γ does not appear in (28) or (29) at all since these correspond to the limit $\beta \to \infty$.

Many other special cases of (21) can be derived, not given here.

(v) *Examples of the effect of shape*

The results in (iv) can be used to provide quantitative illustrations that the shape of a food package is important. It was claimed in §1 above, and is partly illustrated in appendix A, that this point has not yet received the close attention it merits.

As one example, consider three cells of different shapes, but all with the same capacity V. The cells shown in figure 3(*a*), have different heights $H_0/10$, H_0 and $10H_0$ (and therefore different interfacial areas $10A_0$, A_0 and $A_0/10$ respectively, where $A_0 = V/H_0$). To make the main point as simply as possible, suppose that the plastic is effectively infinite (i.e. β in (16) is much less than one) and that the food is well mixed (i.e. α in (12) is also much less than one). Provided, also, that the one-dimensional theory discussed above applies, the mass of migrant in the food satisfies (26). The values of γ, d and $M_\infty = \gamma c_0 V$ are the same for each cell, but the three values of H differ. Note that H appears in the formula (25) for non-dimensional time τ. The three curves in figure 3(*b*) show M/M_∞ for the three cells at the same values of $(dt)^{\frac{1}{2}}/\gamma H_0$, and hence of real time t. The differences are substantial and are due entirely to the

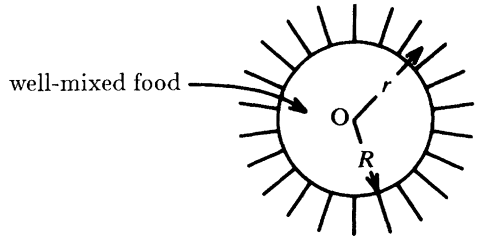

Figure 4. Definition sketch for spherical geometry.

differences in shape. For this geometry the flux of migrant in a cell is, at any time, the same at all points on the interface. Since the cell of smallest height $H_0/10$ has the largest area, equilibrium is reached most quickly in this case.

Many other examples, not (necessarily) involving the simplifying assumptions of infinite plastic and well mixed food, can be given, with use of the results in (iv), to illustrate that changes in shape can, on their own, cause large differences in migration behaviour.

It is valuable briefly to consider shape effects that occur when the package geometry is not one-dimensional. This is, of course, the normal situation in real life. Since C and c then depend on three space coordinates x, y, z (components of $\boldsymbol{x}$) and t, the simplified version of the mathematical model given in (18) cannot then be used (except as a practical approximation in some special cases). Instead the full model equations must be solved. In terms of x, y, z and t, the second equation of (5) is

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(d\frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(d\frac{\partial c}{\partial y}\right) + \frac{\partial}{\partial z}\left(d\frac{\partial c}{\partial z}\right), \tag{30}$$

and the other equations in (5)–(9) are similarly longer and more complicated than the simple versions in (18). Computers will normally have to be used.

Some scientific insights can, however, be obtained by considering a spherical system, sketched schematically in figure 4. (This is actually as relevant to real life as many of the migration cells used in laboratory tests.) For this case, C and c can be expressed as functions of t and r, where

$$r = (x^2 + y^2 + z^2)^{\frac{1}{2}}. \tag{31}$$

As shown in figure 4, r is the distance of a point from the centre O of the sphere containing food. For simplicity, and to facilitate comparisons with the one-dimensional solutions immediately above, it will again be supposed that the plastic is effective infinite, that the food is well mixed and that d in (30) is constant.

Equation (3) can then be written

$$\frac{\partial c}{\partial t} = \frac{d}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right). \tag{32}$$

For this case the model equations can be solved analytically. The solution for M/M_∞ has the form

$$M/M_\infty = F(\eta, \gamma), \tag{33}$$

where η is a non-dimensional time defined by

$$\eta = dt/\gamma^2 R^2. \tag{34}$$

It will be noted that η is the natural analogue of the corresponding variable τ, defined in (25) and used in the one-dimensional solution with the same physics. The function F in (33) is given by

$$F(\eta,\gamma) = 1 - \frac{1}{(\lambda_1 - \lambda_2)}\{\lambda_1 f(\lambda_1^2\eta) - \lambda_2 f(\lambda_2^2\eta)\}, \tag{35}$$

where λ_1 and λ_2 are the roots of the quadratic equation

$$\lambda^2 - 3\lambda + 3\gamma = 0, \tag{36}$$

and

$$f(\eta) = \mathrm{e}^{\eta}\,\mathrm{erfc}\,(\eta^{\frac{1}{2}}). \tag{37}$$

It will be noted that f is the function appearing in the formula (26) for M/M_∞ in the corresponding one-dimensional case, and this is not a coincidence as will be seen below.

These formulae illustrate several points that apply to packages in real life.

Equation (33) shows explicitly that M/M_∞ depends on γ as well as η, i.e. on two non-dimensional groups. This is not true for the corresponding one-dimensional solution as (26) shows. So, for a sphere, M/M_∞ is not determined by the value of η alone; it is necessary also to know the value of γ. This conclusion is not changed if another non-dimensional time (e.g. dt/R^2) is used instead of η. For a general package, the variation of M/M_∞ with non-dimensional time depends also on γ and, additionally, on the non-dimensional numbers needed to fix its shape, e.g. two aspect ratios for a cuboid. This statement is illustrated for a special case by table 1 in appendix A.

It is sometimes implied or assumed (as perhaps in the CEC Directive discussed in appendix A) that shape does not affect the quantity of migration provided the volume V and interfacial area A are fixed. That this is wrong is shown by an example in appendix A; the results above provide another counter example. The one-dimensional cell in figure 1 has the same A and V as a sphere of radius R provided its height H is equal to $R/3$. (In that case, incidentally, $A = 4\pi R^2 = 36\pi H^2$, which is the area of a circle of radius $6H$. So if, for example, the one-dimensional cell has a cylindrical cross section – a common feature of laboratory tests – its shape is also fixed. In real life, such a constraint could well be commercially unacceptable.) Even then, M/M_∞ for the same values of d, t and γ is different for the sphere of radius R than for the one-dimensional cell of height $R/3$; this is clear from the fact that the formula for a sphere is different from (26). Although calculations suggest that the difference is not numerically large in this case (e.g. for $\gamma = 0.75$, M/M_∞ for the sphere is never more than 14% greater than for the one-dimensional cell, with the maximum occurring when $dt/H^2 = 9dt/R^2 \approx 2$), the effect will undoubtedly be much greater for many real packages because of the strong influence of shape parameters (like aspect ratios for a cuboid).

For $\gamma \ll 1$, $C_\infty \ll c_0$ and near equilibrium is achieved relatively rapidly by migration from a layer in the plastic of thickness much less than R. It can then, but only then, be anticipated that the difference in shape between the sphere and the one-dimensional cell with the same A and V would be small for all time. It can readily be verified that (33)–(37) confirm this expectation.

When the food is not well mixed and/or when the plastic is not infinite, the behaviour of M/M_∞ depends also on α and/or β. Again, it is highly unlikely that this dependence will be shape-invariant.

(*d*) *Diffusion equation models. Models of Class III systems*

Katan (1971) (see also Briston & Katan 1974) defined Class III systems as those where migration is controlled by the food with the implication that it is negligible in the absence of the food. In practice the most important group in this class is when the food penetrates the plastic, usually with a change in volume (often called 'swelling'), and also enables substantial migration to occur ('leaching'). This class includes, for example, most additives in most plastics in contact with oily or fatty foods, or in hydrophilic plastics like nylons in contact with aqueous foods. Recent experimental evidence from many sources suggests that penetration is more common than was anticipated by Katan over 20 years ago.

The first discussions of possible mathematical models of Class III systems were given by Knibbe (1971) and Katan (1971). Both authors postulate a sharp penetration front (at, say, $x = b(t) > 0$ with the geometry of figure 1). Rudolph (1979, 1980) uses the same hypothesis and closes the mathematical model by using concentration-dependent diffusion coefficients. Frisch (1978) gives a complete model essentially using equations (5) only (plus boundary conditions) with, again, concentration-dependent diffusion coefficients; there is no separate front in his model. These models will be discussed fully in a later paper (Lum Wan *et al.* 1996), which also proposes a new model of the same type as Frisch's and includes comparisons with data.

It is worth noting that, from a mathematical viewpoint, it is natural to use model equations for Class III systems that include Class II systems as a special case since the division between the two classes is not sharp.

4. Conclusions

At present, mathematical models are not being adequately used in work on migration. As a result, little or usually no attempt is made to extend or generalize the results of a single experiment to other systems with either (*a*) materials with similar physical properties, or (*b*) the same materials but different geometries.

Mathematics alone cannot replace measurements; they will always be essential for proper mathematical modelling. But the other extreme of expecting to make measurements for every geometry, every set of materials, etc. is also impossible; sadly, this appears to be prevailing policy.

This paper has shown the power of mathematical models of migration. Recognition of this power in planning experiments and formulating legislation is overdue. Mathematicians (including statisticians) should be in the relevant teams. This is the only way to ensure consumer safety.

Some of this work was done with support from MAFF in the Department of Mathematics and Statistics at Brunel University. The authors thank Trevor Coomes and John McGuinness of MAFF for their encouragement and Colin Tripp of Brunel for checking some of the mathematical formulae.

Appendix A. An example of migration legislation

Directive 90/128/EEC (CEC 1990) applies to 'plastics materials and articles and parts thereof... which, in the finished product state, are intended to come into contact or are brought into contact with foodstuffs...' (extract from *Article 1*).

Article 2 of the Directive is:

'Plastics materials and articles shall not transfer their constituents to foodstuffs in quantities exceeding 10 milligrams per square decimetre of surface area of material or article (mg/dm²) (overall migration limit). However, this limit shall be 60 milligrams of the constituents released per kilogram of foodstuff (mg/kg) in the following cases:

(*a*) articles which are containers or are comparable to containers or which can be filled, with a capacity of not less than 500 millilitres (ml) and not more than 10 litres (l);

(*b*) articles which can be filled and for which it is impracticable to estimate the surface area in contact with foodstuffs;

(*c*) caps, gaskets, stoppers or similar devices for sealing.'

As explained in *Article 3*, these provisions on overall (or global) migration are supplemented by limits on specific migration, i.e. the migration of a single (chemical) substance from a particular plastic, and §8 of *Annex I* to 90/128/EEC states that 'the sum of all specific migration ... shall not exceed the overall migration limit'. *Annex II* lists those 'monomers and other starting substances' that, as from 1 January 1993†, 'may be used for the manufacture of plastics materials and articles ...'.

Article 4 of 90/128/EEC is:

'The specific migration limits in the list set out in *Annex II* are expressed in mg/kg. However, such limits are expressed in mg/dm² in the following cases:

(*a*) articles which are containers or which can be filled, with a capacity of less than 500 ml or more than 10 l;

(*b*) sheet, film or other materials which cannot be filled or for which it is impracticable to estimate the relationship between the surface area of such materials and the quantity of foodstuff in contact therewith.

In these cases, the limits set out in *Annex II*, expressed in mg/kg shall be divided by the conventional conversion factor of 6 in order to express them in mg/dm².'

Annex I is concerned with migration testing procedures. Earlier Directives have authorized the use of food simulants, instead of the intended actual food, in these experiments. One such simulant is rectified olive oil. This is a difficult material with which to do reproducible or repeatable experiments (which, incidentally, suggests that it was not a wise choice as an authorized simulant). This is recognized in §7 of *Annex I* which states that:

'A material or article that exceeds the overall migration limit by an amount not greater than the analytical tolerance mentioned below should therefore be deemed to be in compliance with this Directive.

The following analytical tolerances have been observed:

– 20 mg/kg or 3 mg/dm² in migration tests using rectified olive oil or substitutes,

– 6 mg/kg or 1 mg/dm² in migration tests using the other simulants referred to in Directives 82/711/EEC and 85/572/EEC.'

Thus the overall migration limits of 10 mg dm^{-2} and 60 mg kg^{-1} in *Article 2* of the Directive (see above) can be increased in practice to 13 mg dm^{-2} and 80 mg kg^{-1} respectively for rectified olive oil or substitutes, and to 11 mg dm^{-2} and 66 mg kg^{-1} respectively for other simulants.

It is expected that most readers will immediately recognize from the above extracts that, in parts, the Directive is scientifically nonsensical. But, obviously, this has not been apparent to those involved in writing and approving the Directive or, if apparent, has not been thought important. It is necessary to expose the errors in the interest of consumer safety.

† From time to time, *Annex II* is updated by Amendments which involve changes to this date in some circumstances.

It was pointed out some years ago (Chatwin & Katan 1987, pp. 4/1/11–4/6/11) that migration limits, both overall and specific, should be given in dimensionally sensible terms. This requirement would be satisfied if all limits were on concentration(s) of the migrant(s) in the food expressed as mass ratio(s). There is therefore no *a priori* objection to a limit of 6×10^{-5} (60 mg kg^{-1}). What is of course inexcusable is to assume (as is done throughout the Directive, and as is clear from the extracts above) that this can be equated to a flux (mass per unit area) of migrant across that part of the surface area of the package that is in contact with food. The statement at the end of *Article 4* (quoted above in full) that 'limits expressed in mg/kg shall be divided by the conventional conversion factor of 6 in order to express them in mg/dm^2' is absurd.

For example, consider a manufacturer of cubic packages to contain food of the same density as water (10^3 kg m^{-3}) who, in compliance with *Article 4* of the Directive, 'converts' a specific migration limit of say, 6×10^{-5} (60 mg kg^{-1}) into 10^{-3} kg m^{-2} (10 mg dm^{-2}). For a cube of side 3×10^{-2} m ($\Rightarrow$food volume $V = 2.7 \times 10^{-5}$ m^3 = 27 ml, typical, for example, of the quantities in which food flavouring like vanilla essence is sold to consumers), the total mass of migrant in the food after migration to the allowed limit has occurred will be (surface area in m^2) $\times 10^{-3}$ kg m^{-2} = $6 \times 9 \times 10^{-4} \times 10^{-3}$ kg = 5.4×10^{-6} kg. So, as a mass ratio, the concentration of the migrant in the food is 5.4×10^{-6} kg/(mass of food in kg) = $5.4 \times 10^{-6}/(10^3 \times 27 \times 10^{-6})$ = 2×10^{-4}. This is 200 mg kg^{-1}, different from, and much higher than, the nominal limit of 60 mg kg^{-1} that provided the manufacturer's starting point! On the other hand, if the cubic package has side 3×10^{-1} m ($\Rightarrow V = 2.7 \times 10^{-2}$ m^3 = 27 l, i.e. of the order of magnitude of, say, commercial containers of cooking oil) an analogous calculation yields a concentration of migrant in the food as 2×10^{-5} (20 mg kg^{-1}). Only if the cube has side 10^{-1} m (1 dm) does the concentration equal the nominal limit of 6×10^{-5}.

This illustrative example (and the conclusion would be reached irrespective of shape, food density or migration limit) confirms the obvious fact that: it is not possible to 'convert' mg kg^{-1} to mg dm^{-2}. Thus *Article 4* is potentially dangerous; its use will permit concentrations far higher than the legal maxima which the Directive is intended to ensure.

Another serious error in the Directive, but one that is perhaps less obvious because it is implicit, is the assumption of uniformity, i.e. that conditions are the same at every point. The Directive presumes that migration from the surface area of a package occurs at the same rate everywhere on the surface and that it results in a migrant concentration that is the same everywhere in the food. Neither of these assumptions is correct even for food (like water) of homogeneous structure. There is a variation with position that is determined by physics and by the system geometry in a way that is not easy to predict without the use of calculus and other basic mathematical techniques. The degree of variation is often likely to be substantial, even by an order of magnitude or more, especially for foods of strongly heterogeneous structure like meat or cheese. So the status of the migration limits in the Directive ought to have been defined as e.g. maxima or averages. And, given the practical intentions of this Directive, there is a need to state how a maximum, or an average, limit is to be estimated by experiment, a point of central importance that is not easy to resolve.

The Directive mentions package size in *Articles 2* and *4* (see quoted extracts above) and the illustrative calculations above show that what is written does not ensure

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Table 1. *Values of average migrant concentration given by (A 1)*

κ	approximate package dimensions/(10^{-2} m)	C/(mg kg^{-1})
1	$7.9 \times 7.9 \times 7.9$	75.6
3	$23.8 \times 7.9 \times 2.6$	109.2
5	$39.7 \times 7.9 \times 1.6$	156.2
10	$79.4 \times 7.9 \times 0.8$	279.7

consumer safety. Moreover, no mention is made of an equally important geometrical feature, namely package shape. Consider, for example, packages containing food of the same density as water and of capacity 5×10^{-4} m^3 (500 ml). A cube with this capacity has internal side l_0, where $l_0 = (5 \times 10^{-4})^{\frac{1}{3}}$ m $\approx 7.937 \times 10^{-2}$ m. As an illustration of the importance of shape, it suffices to consider packages with the same capacity in the form of a cuboid with internal sides κl_0, l_0, $\kappa^{-1} l_0$ where κ is a constant. It will not change the main conclusion of this paragraph to assume that all faces of the package are in contact with the food, so that the total surface area across which migration occurs is

$$2l_0^2(\kappa + 1 + \kappa^{-1}) \approx 1.260\ (\kappa + 1 + \kappa^{-1}) \times 10^{-2}\ \text{m}^2.$$

With migration across each point of the internal surface area having occurred to the upper limit of 10^{-3} kg m^{-2} (10 mg dm^2) laid down in *Article 2* of the Directive (see above), the average concentration C of migrant in the food is easily found to be given by

$$C \approx 25.20(\kappa + 1 + \kappa^{-1})\ \text{mg kg}^{-1}, \tag{A 1}$$

and so depends on κ, which determines the precise package shape. Some typical values given by (A 1) are shown in table 1. Note that:

(i) the minimum value of C is 75.6 mg kg^{-1} when the package is a cube ($\kappa = 1$);

(ii) for all other values of κ, C is greater than 75.6 mg kg^{-1};

(iii) C tends to infinity as κ tends to infinity;

(iv) C is greater than 60 mg kg^{-1} for all κ, yet one more example of the impossibility of converting from mg kg^{-1} to mg dm^{-2};

(v) since C in (A 1) is an average concentration, the maximum concentration will be greater.

The conclusion is clear, and independent of the particular shape considered in this example. Migration limits expressed as mass per unit area without specification of the package shape do not ensure that any specified concentration of migrant in the food expressed as a mass ratio is not exceeded.

Lack of scientific rigour apart, some statements in the Directive are unclear. For example, it is difficult to understand what is meant by (*c*) of *Article 2* (see above).

Appendix B. Some comments on a research paper on migration

A paper by Mercer *et al.* (1990) deals with the migration of DEHA (di-(2-ethylhexyl) adipate) plasticizer in cheese. This paper will be denoted by MCCG in the rest of this Appendix. Some corrections to it are given in Mercer *et al.* (1991).

In brief, some Cheddar cheese was contaminated with DEHA to a nominally uniform concentration C_0. As a mass ratio, C_0 was stated to have the value 1.930×10^{-3}(1930 mg kg^{-1}). Four cylinders of cheese of internal diameter

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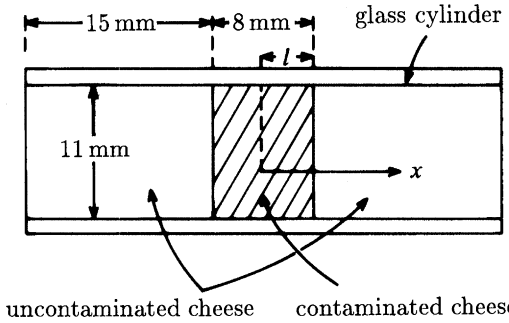

Figure 5. The geometry of the cell used in the experiments reported in MCCG.

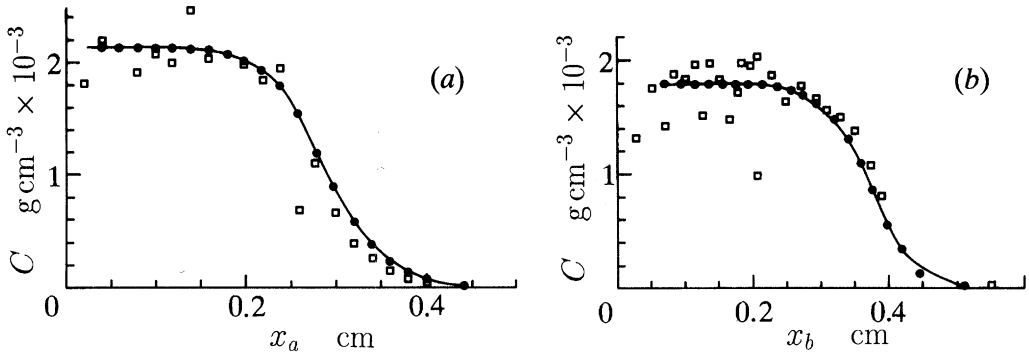

Figure 6. Data (□) from two experiments at 5 °C (MCCG) with $t = 6$ d. Adapted without change of units or relative scaling from figure 1 of MCCG. The solid circles (●) are claimed to be evaluations of (B 1) with $D = 3 \times 10^{-13}$ m^2 s^{-1} in (*a*) and $D = 2 \times 10^{-13}$ m^2 s^{-1} in (*b*). The solid curve is claimed to be a graph of (B 1).

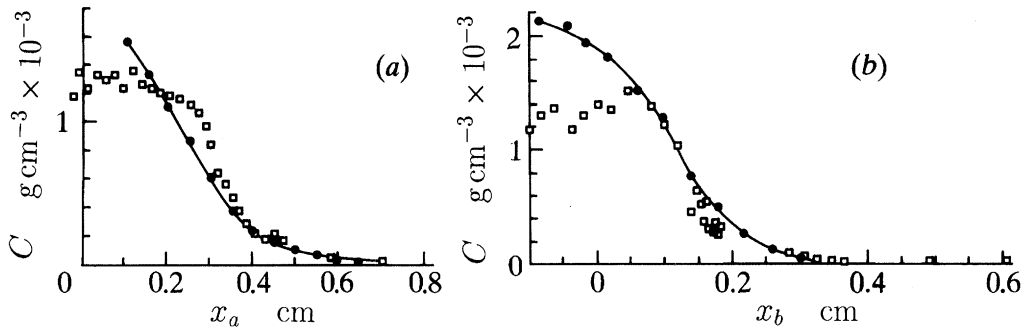

Figure 7. As for figure 6 except that the temperature was 25 °C, $t = 4$ d, and the values of D were stated to be 4×10^{-12} m^2 s^{-1} in (*a*) and 1×10^{-12} m^2 s^{-1} in (*b*). Adapted without change of units or relative scaling from figure 2 of MCCG.

1.1×10^{-2} m and total length 3.8×10^{-2} m were formed; contaminated cheese occupying the central 8×10^{-3} m of the cylinder was sandwiched between two sections of uncontaminated cheese each of length 1.5×10^{-2} m as shown in figure 5. Each cylinder of cheese was contained within a glass tube. Two of the cylinders were maintained at 5 °C for 6 days, and two at 25 °C for 4 days. After storage, portions of each cylinder of length 1.3×10^{-2} m were microtomed at −40 °C into slices of thickness 2×10^{-5} m, and the DEHA concentrations were determined by gas chromatography.

The results for the two experiments at 5 °C are shown in figure 6, and those for 25 °C are shown in figure 7. These figures have been adapted from figures 1 and 2 of MCCG, but without change of units or relative scaling. While the use of dimensional units is not to be commended, a worse fault is the use, in each figure, of different scalings for the duplicate experiments. Easy visual comparison is therefore impossible. Also shown in each diagram is a 'theoretical' curve, claimed in the paper to be an evaluation of

$$C = \tfrac{1}{2}C_0\left\{\operatorname{erf}\left(\frac{l-x}{2\sqrt{(Dt)}}\right)+\operatorname{erf}\left(\frac{l+x}{2\sqrt{(Dt)}}\right)\right\}, \tag{B 1}$$

where l and x are as shown in figure 5, t is diffusion time and the four different values of the constant D are given in the figure captions.

Some obvious comments on the data can be made immediately.

1. Given that the relative standard deviation of the gas chromatography method used to determine DEHA concentrations is only 2%, the considerable scatter in the data points must have other cause(s). One possibility is inaccurate microtoming (see the discussion of another data set in Lum Wan *et al.* (1996). Another is that the homogenization process applied to the contaminated cheese was inadequate; indeed MCCG describes a microscopic examination of contaminated cheese samples that confirms this. (Given that cheese sold commercially is likely to have a much less homogeneous structure than the specially prepared samples used in these experiments, the data provide rather strong evidence in support of the proposal in §3*a* of the present paper (see also Chatwin & Katan 1987, 1989) that practically useful mathematical models of migration will eventually have a large stochastic component.)

2. It is evident from the figures that the zeros of x do not coincide either with one another or with the zero of x in equation (B 1), which is the midpoint of the cylinder of length 8×10^{-3} m initially containing all the DEHA. The practical difficulty of locating $x = 0$ absolutely is understandable with the microtoming procedure used, but the failure to refer to it is not.

3. Another shortcoming is the relative paucity of measurements, in at least three of the diagrams, in the region where the concentration is changing most rapidly.

MCCG states that 'For the sample geometry used in the migration experiments the solution of Fick's second law of diffusion (Crank 1975) given in equation (B 1) was applicable'. Leaving aside the points that a 'law' does not have a 'solution', and that no evidence is given to support the assumption, made categorically, that migration in the experiments is governed by the diffusion equation

$$\partial C/\partial t = D\,\partial^2 C/\partial x^2, \tag{B 2}$$

of which (B 1) is an elementary solution, there is no recognition that (B 1) applies to the sample geometry only if the initially uncontaminated cheese cylinders of length 1.5×10^{-2} m can be regarded as effectively infinite, i.e. if $2\sqrt{(Dt)} \ll 1.5\times10^{-2}$ m. Fortunately this condition turns out to be satisfied for the data shown in figure 6 and, probably, for figure 7; otherwise another elementary formula can easily be obtained (and is given, for example, on p. 16 of Crank's book).

It will also be immediately apparent that there are several elementary but serious errors in the 'theoretical' curves in figures 6 and 7, i.e. in the numerical evaluation and use of (B 1) by MCCG. Among these are:

1. The second point to the right of the ordinate in figure 7*a*, for $x \approx -0.05$ cm, is

clearly wrong since the curve obtained from (B 1) must be smooth. Closer inspection shows that other points are also wrong, although the errors are of smaller magnitude.

2. In general, the 'theoretical' curves drawn by MCCG do not go through all their calculated points, and not only because some points are wrong (see figure 6*b*).

3. Also, and related to the point made above about $x = 0$, the graph of C versus x given by (B 1) is symmetric about $x = 0$ (and therefore, in particular, flat at $x = 0$), which is totally different from the behaviour of the so-called 'theoretical' curves shown in both diagrams in figure 7.

4. MCCG claims that the values of D given in the figure captions were found by varying this constant until the 'best visual fit' was obtained. This is a proper practice but it was clearly not accomplished for either of the two diagrams in figure 7.

5. Nor did MCCG recognize that if (B 2) is an appropriate model, the value of D must be the same for each of the two experiments in figure 6 and for each of the two experiments in figure 7 (albeit higher in the latter because of the increase in temperature).

6. Finally, MCCG state without explanation that the 'mean' diffusion coefficients were estimated to be 1.5×10^{-13} m^2 s^{-1} at 5 °C and 2.0×10^{-12} m^2 s^{-1} at 25 °C, values that are in neither case the average of the two values given in the figure captions.

Each of these errors is so fundamental that those quantitative conclusions given by MCCG that are supposedly based on (B 1) can have no validity whatsoever.

However it is possible to demonstrate that proper use of (B 1) with MCCG's data can lead to valid conclusions, despite the shortcomings in the data summarized above. Consider first the data from the two experiments in figure 6, and hypothesize that (B 2) describes the DEHA migration.

The following procedures were applied.

(i) Data were transcribed from the graphs by using a ruler (thereby inducing errors of much smaller magnitude than the existing scatter). The results are given in columns (1), (2), (5) and (6) of table 2.

(ii) It is reasonable to suppose from inspection of the data that DEHA has not yet migrated measurably in either case from the centre of the contaminated cheese and that, therefore, the points nearest the ordinate correspond to C_0, the initial concentration of DEHA. Some points, indicated by crosses in table 2, appear to be outliers and were henceforth rejected. The averages of the ticked points were taken as the values of C_0 for the two experiments. (Notice that the average of 1.992 kg m^{-3} and 1.880 kg m^{-3} is 1.936 kg m^{-3}, close to the nominal C_0 of 1.930 kg m^{-3},† and that differences of C_0 between otherwise duplicate experiments are to be expected and cause no difficulty in the application of (B 2) since this is a linear equation.) The two C/C_0 columns (3) and (7) in table 2 were then obtained.

(iii) As shown in figure 8, the data from the two experiments appear consistent (within experimental error) with their being obtained from a single experiment provided the origin in figure 6(*b*) is moved about 1×10^{-3} m to the right. This step is justified because absolute positions could not be located precisely in this experiment as noted above.

(iv) For the same reason it is necessary to estimate the initial position of the doped cheese in relation to the axes used in figure 8. Assume for the moment that (B 1) is the appropriate solution of (B 2). It follows, because it has also been supposed – see

† MCCG assumes without comment that a concentration of 1930 mg kg^{-1} is the same as one of 1.930 kg m^{-3}, i.e. that the cheese has density 10^3 kg m^{-3}, the same as water.

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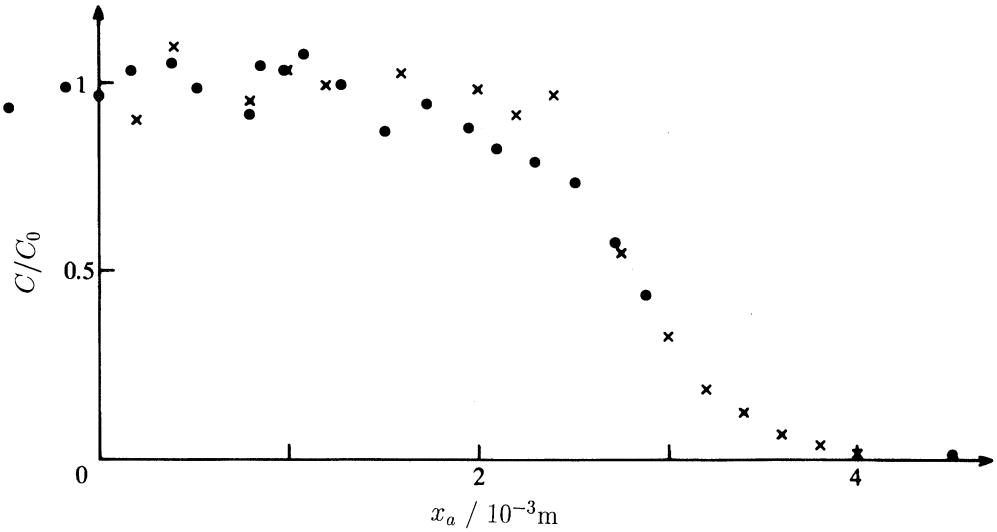

Figure 8. The consolidated data set obtained as explained in the text from the data in both diagrams of figure 6 (columns (3), (4), (7) and (8) of table 2). Data from 6(*a*): ×, 6(*b*): ●.

Table 2. *Data from figure 1 of* MCCG (*figure 6 of present paper*)

(*X*, Rejected outliers; √, values used to calculate, C_0. Column (4): $x = x_a + 1.15 \times 10^{-3}$ m; column (8): $x = x_b + 0.15 \times 10^{-3}$ m.)

		(1) $C/(\text{kg m}^{-3})$	(2) $x_a/10^{-3}$ m	(3) C/C_0	(4) $x/10^{-3}$ m			(5) $C/(\text{kg m}^{-3})$	(6) $x_b/10^{-3}$ m	(7) C/C_0	(8) $x/10^{-3}$ m
(*a*)	√	1.80	0.20	0.90	1.35	(*b*)	*X*	1.30	0.27	—	—
	√	2.18	0.40	1.09	1.55		√	1.74	0.52	0.93	0.67
	√	1.90	0.80	0.95	1.95		*X*	1.40	0.71	—	—
	√	2.06	1.00	1.03	2.15		√	1.87	0.83	0.99	0.98
	√	1.98	1.20	0.99	2.35		√	1.82	1.00	0.97	1.15
	X	2.45	1.40	—	—		√	1.94	1.17	1.03	1.32
	√	2.03	1.60	1.02	2.75		*X*	1.50	1.27	—	—
		1.96	2.00	0.98	3.15		√	1.97	1.39	1.05	1.54
		1.82	2.20	0.91	3.35		√	1.83	1.52	0.97	1.67
		1.92	2.40	0.96	3.55		*X*	1.46	1.65	—	—
	X	0.66	2.60	—	—		√	1.71	1.80	0.91	1.95
		1.07	2.75	0.54	3.90		√	1.96	1.85	1.04	2.00
		0.64	3.00	0.32	4.15		√	1.94	1.99	1.03	2.14
		0.36	3.20	0.18	4.35		*X*	0.97	2.07	—	—
		0.24	3.40	0.12	4.55		√	2.02	2.08	1.07	2.23
		0.12	3.60	0.06	4.75			1.86	2.28	0.99	2.43
		0.06	3.80	0.03	4.95			1.63	2.51	0.87	2.66
		0.02	4.00	0.01	5.15			1.76	2.72	0.94	2.87
								1.65	2.95	0.88	3.10
								1.55	3.10	0.82	3.25
								1.49	3.30	0.79	3.45
								1.37	3.51	0.73	3.66
								1.07	3.71	0.57	3.86
								0.80	3.89	0.43	4.04
								0.02	5.52	0.01	5.66

(*a*) $C_0 = 1.992$ kg m^{-3}; (*b*) $C_0 = 1.880$ kg m^{-3}.

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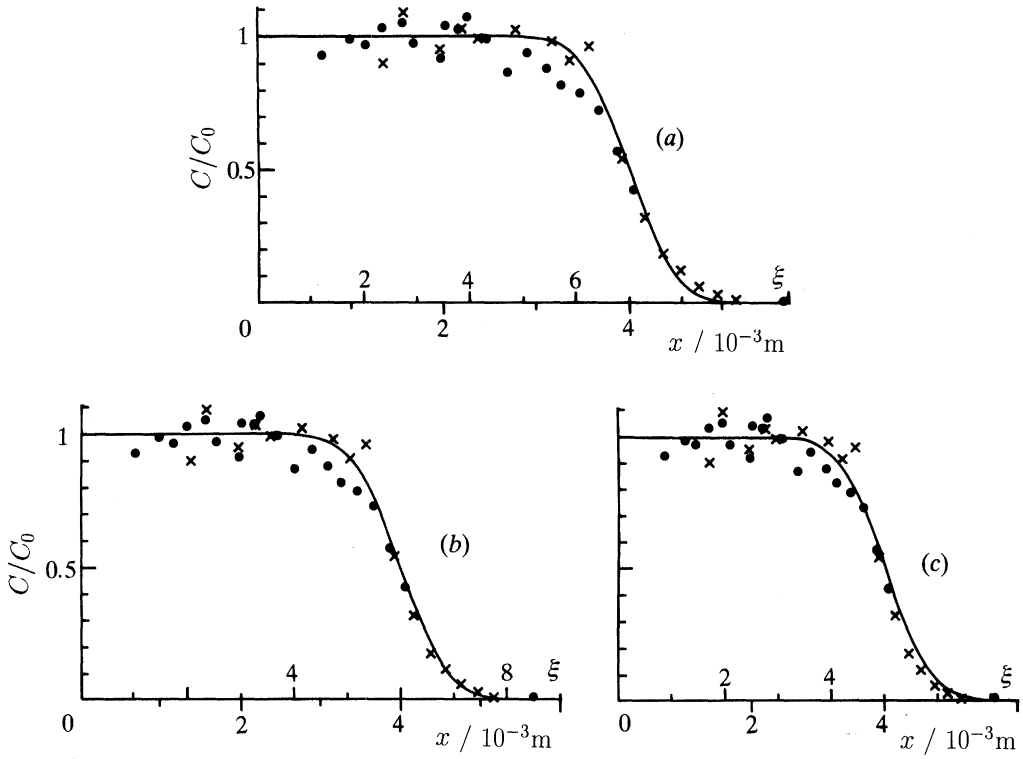

Figure 9. Fits of (B 1) to data in figure 8 with $\xi = x/2(Dt)^{\frac{1}{2}}$ and $D =$ (*a*) 1.57×10^{-13} m^2 s^{-1}, (*b*) 2.14×10^{-13} m^2 s^{-1}, (*c*) 3.09×10^{-13} m^2 s^{-1}.

(ii) above – that DEHA has not yet migrated in measurable quantities from the centre, that the value of C/C_0 is essentially $\frac{1}{2}$ where $x = \pm l = \pm 4 \times 10^{-3}$ m, i.e. at either end of the initial cylinder of doped cheese (see figure 5). Visual inspection of figure 8 then shows that its origin has to be moved about 1.15×10^{-3} m to the left.

(v) These steps lead to a single table of C/C_0 versus x, where, following step (iv), $x = 0$ is (within experimental error) at the centre of the initially contaminated cheese. This table comprises columns (3) and (7) – for C/C_0 – and (4) and (8) – for x of table 2.

(vi) Only now can a sensible attempt be made to apply (B 1) to the data. Figure 9 shows the fit between (B 1) and the consolidated data set for three different values of the constant diffusion coefficient D. It is claimed that the quality of fit in all three graphs is better than that obtained by MCCG and shown in figure 6. The quality of fit is good enough to assert that (B 2) is a satisfactory mathematical model. Since the best of the three fits is (*b*), it can also be tentatively concluded that D is of order 2×10^{-13} m^2 s^{-1} but the scatter in, and the limited number of, data points are such that this estimate could turn out to be substantially in error.

With this value of D and with $t = 6$ d $= 5.184 \times 10^5$ s, the half thickness of the two layers (one at each end of the initial cylinder containing contaminated cheese) over which migration has occurred is of order $4\sqrt{(Dt)} \approx 1.3 \times 10^{-3}$ m. That this is much less than the lengths of any of the cheese cylinders confirms the consistency of the above working.

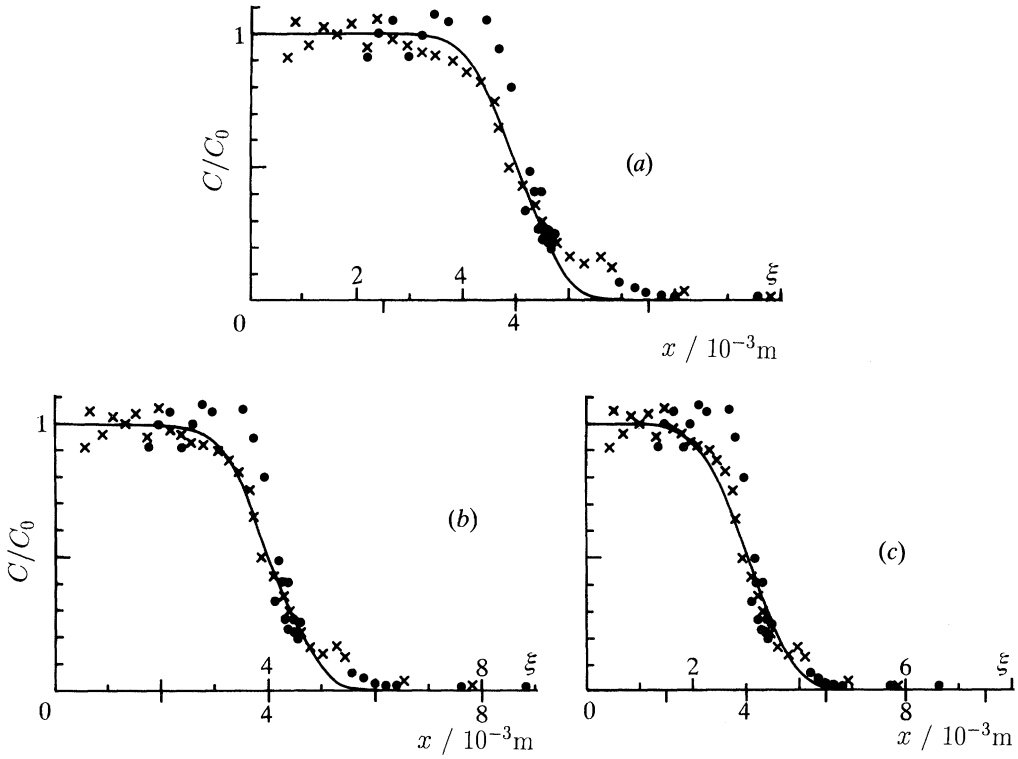

Figure 10. Fits of (B 1) to data in figure 7. Data from 7(*a*) ×, from 7(*b*) ●. D = (*a*) 4.63×10^{-13} m^2 s^{-1}, (*b*) 7.23×10^{-13} m^2 s^{-1}, (*c*) 1.29×10^{-12} m^2 s^{-1}.

Consider now the data in figure 7. Suppose first that (B 2) is still a satisfactory mathematical model, and that (B 1) is the appropriate solution. A problem arises almost immediately. The maximum concentration in both diagrams of figure 7 is about 1.35 kg m^{-3}, substantially below the nominal C_0 which is stated to be about 1.93 kg m^{-3}. For $x = 0$, (B 1) gives

$$1.35 \approx 1.93\ \mathrm{erf}\{l/2\sqrt{(Dt)}\}. \tag{B 3}$$

With $l = 4\times10^{-3}$ m and $t = 4$ d $= 3.456\times10^5$ s, this gives $D \approx 2.16\times10^{-11}$ m^2 s^{-1} with use of a table of the error function. According to (B 1), the half thickness of the migration layer is then of order $l+4\sqrt{(Dt)} \approx 1.5\times10^{-2}$ m. This is, however, substantially greater than the data show, so there is a contradiction. It is easy to show that the contradiction persists if (B 1) is replaced by the solution of (B 2) for a finite cylinder that was referred to earlier and is quoted on p. 16 of Crank (1975).

Unless either the mathematical model (B 2) or both data sets in figure 7 are to be rejected entirely, there is one other possibility. This is that, for these data sets, the value of C_0 is of order 1.35 kg m^{-3}, and that MCCG have omitted mention of this distinction between figures 6 and 7. When this assumption was made, the procedure described above was applied to the data sets in figure 7 (rejecting only one point as an outlier from the bottom diagram). The comparisons with (B 1) are shown in figure 10 for three values of D. The agreement between the data and (B 1) is reasonable, but perhaps not quite as good as in figure 9. (The agreement is much better than that shown by MCCG.) An estimate for D is that it is of order 1×10^{-12} m^2 s^{-1}, the average of the values used in figure 10(*b*), (*c*). This estimate is one-twentieth of the value

obtained by using the inconsistent (B 3). Note also that $D \sim 10^{-12}$ m^2 s^{-1} gives a migration layer with half thickness of order 2.4×10^{-3} m, consistent with the data and small enough to ensure that (B 1) is the appropriate solution of (B 2).

According to standard Arrhenius theory, D depends on absolute temperature T according to

$$D = D_\infty \exp(-E/RT), \tag{B 4}$$

where E is the activation energy per mole, $R \approx 8.31$ J K^{-1} mol^{-1} is the gas constant, and D_∞ is a constant. With the above estimates of $D \approx 2 \times 10^{-13}$ m^2 s^{-1} at $T = 278$ K and $D \approx 10^{-12}$ m^2 s^{-1} at $T = 298$ K, D_∞ and E in (B 4) are found to be approximately 5.2×10^{-3} m^2 s^{-1} and 5.6×10^4 J mol^{-1}. The latter value is of the same order as those quoted by Moisan (1980) for some stabilizers in LDPE.

The data analysis has shown up further shortcomings in the experimental design. Given the inability of the data published in MCCG to determine D with precision, the periods allowed for migration should have been lengthened in each experiment. Had more samples been prepared, results for a range of migration times could have been collected. It is also curious that the microtomed samples were taken only from one side ($x > 0$ in figure 5) of the composite cheese cylinders when twice as much data could have been obtained by microtoming samples from both sides of the centre. As the experiments were conducted, there was never any need for the left cylinder of uncontaminated cheese in figure 5.

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Received 5 November 1992; accepted 23 July 1993

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