Simplification of Micromixing Calculations. I. Derivation and Application of New Model

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ABSTRACT

The micromixing model reported by us in 1984 consists of a set of partial differential equations to express unsteady diffusion and reaction in deforming laminated structures formed by engulfment in a turbulent fluid. This engulfment–deformation–diffusion (EDD) model has been widely applied to interpret experiments showing an effect of mixing on the product distribution of the reactions between 1-naphthol and diazotized sulphamic acid. Theoretical arguments and recent experimental results show how the EDD model can be simplified by neglecting deformation and diffusion provided that $Sc < 4000$ and $F < 1$. The new E model retains fluid engulfment as the rate-determining step in micromixing and contains no arbitrary parameters. Application to two complex reactions has shown that engulfment is also product determining, i.e. the product distribution does not depend on deformation and diffusion. The new E model consists of a set of ordinary differential equations; it is one to two orders of magnitude faster to compute and a wider choice of software is available for its numerical implementation. Micromixing calculations have been simplified and accelerated.

1. INTRODUCTION

The mechanisms involved in micromixing (mixing on a molecular scale) are engulfment, deformation and diffusion [1]. Engulfment of one fluid by another is caused by vorticity. Deformation, which can be resolved into shear and elongation, causes kinetic energy to be dissipated irreversibly to heat and accelerates diffusion. Diffusion is the only mechanism whereby molecules, initially present in separate feed streams, can encounter each other. This description of micromixing, termed EDD after its three mechanisms, has often been used to calculate the effects of all available independent variables on the product distribution of competitive–consecutive reactions (coupling between 1-naphthol and diazotized sulphamic acid).

The EDD model requires the solution of coupled, non-linear, parabolic partial differential equations of the type

$$\frac{\partial c_i}{\partial t} + u(x, t) \frac{\partial c_i}{\partial x} = D_i \frac{\partial^2 c_i}{\partial x^2} + R_i(x, t)$$

(1)

Such equations express unsteady diffusion and reaction within a deforming vortex. In general, complete micromixing requires several vortex generations ($N$) and so the set of equations (1) requires solving $N$ times. Considering a semi-batch reactor, the addition of stream B to solution A, which is present in the reactor, is discretized [2] into $\sigma$ equal parts. For the reactions

$$A + B \rightarrow R \quad (2)$$
$$R + B \rightarrow S \quad (3)$$

$i = A, B$ and $R$, $N \approx 10$ and $\sigma \approx 20$, so that eqn. (1) must be solved some 600 times.

There are two ways of simplifying this substantial numerical task.

(a) If the first reaction is instantaneous (i.e. if its half-life is much shorter than that of the micromixing), A and B cannot coexist. The $W$–$Z$ transformation then reduces the number of components from three to two [2] with a corresponding saving in computer time.

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(b) By a suitable choice of numerical method and software. Spline orthogonal collocation has been found to require one to two orders of magnitude less computer time than a finite difference method [3]. Stiffness, caused by widely differing values of $k_1$ and $k_2$ and hence of the time scales of the two reactions, frequently accentuates the numerical problem. Stiffness disappears if $k_1$ is sufficiently high and the first reaction becomes instantaneous.

Although much remains to be done in choosing suitable numerical methods and software, the physical situation behind the EDD model is re-examined first in order to find a basis for its simplification.

2. ROLE OF DIFFUSION IN MICROMIXING

Three recent results indicate that under certain circumstances diffusion is not the determining step in the EDD formulation.

(a) The measured concentration–distance profiles for single, irreversible, second-order instantaneous reactions are independent of the diffusivities of the reagents [4]. This experimental result is particularly significant since reactions in gas and liquid phases have been considered, and a wide range of diffusivities covered. Since diffusion does not determine the observed reaction rate, and the chemical kinetics, which are asymptotically instantaneous cannot do so, what does? The EDD model predicts the engulfment frequency to be rate determining [5, 6]. For $Sc < 4000$

molecular diffusion should not influence reaction rate.

(b) When $Sc < 4000$ the possibility remains that diffusion might influence product distribution. This is defined by $X_S$ for the reactions given in eqns. (2) and (3), where

$$X_S = \frac{2S}{(R + 2S)} \quad (5)$$

$X_S$ has been evaluated by numerically integrating eqn. (1) using a common diffusivity for A, B and R as well as their individual values. There is no significant effect on $X_S$ [3]. By changing the common diffusivity, but keeping all other independent variables constant, no effect on $X_S$ is seen in the range $640 < Sc < 2560$ [2] (see Table 1, note that $M \approx D^{-1}$ and $Sc \approx D^{-1}$). Doubling the diffusion path length (hence extending the diffusion time by a factor of four) has been computed to have no effect on product distribution, but calculation shows a high sensitivity of product distribution to the rate of engulfment [2].

(c) Local, transient pH gradients can also influence $X_S$, and the diffusivity of protons is an order of magnitude higher than the diffusivities of A, B and R. The same product distribution has nevertheless been computed whether the real proton diffusivity is used or a value equal to the diffusivity of the other species [7]. When mixing a concentrated acidic solution (pH 1.5) with a weakly buffered solution (pH 10), fig. 2 of ref. 7 shows that the transient pH gradient disappears within one vortex generation ($Sc \approx 4000$).

Table 1 gives some further results which also indicate that, as long as eqn. (4) is satisfied, diffusion determines neither reaction rate nor product distribution. (The time scale is introduced by noting that each eddy generation has a lifetime of $12(\nu/v)^{1/2}$ [1].)

In addition to eqn. (4), a further general criterion for engulfment to become rate determining in the whole micromixing process can be derived. Let $N$ be the number of vortex generations needed to mix two fluids completely. If $N = 1$, diffusion between the striations of the vortex can determine the rate of fine scale mixing. If $N > 1$ or, to be more conservative, if $N > 2$ and simultaneously $Sc < 4000$, engulfment frequency will deter-

### Table 1

<table>
<thead>
<tr>
<th>Sc</th>
<th>$M$</th>
<th>$X_S$</th>
<th>$D_{H^+} = 10D$</th>
<th>$D_{H^+} = D$</th>
<th>$N$</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1110</td>
<td>1</td>
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<td>0.0048</td>
<td></td>
<td>11</td>
<td>9.88</td>
</tr>
<tr>
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<td>0.2188</td>
<td>0.2188</td>
<td></td>
<td>9</td>
<td>9.88</td>
</tr>
<tr>
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<td>5.2</td>
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<td>0.0079</td>
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<td>11</td>
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<tr>
<td>3330</td>
<td>520</td>
<td>0.2926</td>
<td>0.2926</td>
<td></td>
<td>9</td>
<td>9.88</td>
</tr>
</tbody>
</table>

Semi-batch reactor, $\sigma = 30$, $a = 100$, $F = 0.011$, $\beta = 3840$, $C_{PA} = 10$, $C_{PB} = 0$, $pH_A = 9.88$, $pH_B = 1.65$. 
mine the rate of micromixing. The further general criterion is therefore

\[ N > 2 \]  

(6)

The EDD model is not subject to the restriction of eqn. (6). For example, it has recently been applied to acid-base (\( N = 1 \)) and to diazo coupling (\( N > 2 \)) reactions in a given turbulent flow within a tubular reactor [8]. The same rate of turbulent energy dissipation was deduced for both reactions.

Equation (6) cannot be used to predict the effect of engulfment, because \( N \) is not known \textit{a priori}. This limitation can be removed by considering the local volume fractions \( X_{i0} \) and \( X_{j0} \) of unmixed reagent solutions (for the species \( j \) and \( i \)). The following cases arise.

(i) \( X_{j0} < X_{i0} \). Mixing proceeds by growth of zone \( j \) in bulk \( i \). For example, reactions (2) and (3) are rapid and can be conducted in a continuously stirred tank reactor (CSTR), whose mean residence time will generally greatly exceed the local mixing time. Thus the steady state concentration of the limiting reagent \( B \) will be vanishingly small, \textit{i.e.} \( B \) will be engulfed by \( A \) (\( B = j \) and \( A = i \) in this case). A second example is reactions (2) and (3) conducted in a semi-batch reactor, where \( A \) (i) is initially charged to the reactor and \( B \) (j) is slowly added as a concentrated solution. Here \( X_{j0} < X_{A0} \) and \( B \) is engulfed by \( A \).

(ii) \( X_{i0} < X_{j0} \). Many engulfments will cause \( i \) to engulf \( j \). Some of the engulfments involving \( j \) will, however, be self-engulfments (\textit{i.e.} \( j \) engulfs \( j \)) and thus contribute nothing to mixing \( i \) and \( j \). The same applies, as in case (i), to \( i \)-\( i \) engulfments. Part II (Chem. Eng. J., 42 (1989) 93) of this study will develop a simple treatment of self-engulfment.

(iii) \( X_{j0} \approx X_{i0} \). Local growth of zones \( i \) and \( j \) by engulfment with surroundings \( j \) and \( i \) respectively must be considered. Calculating the statistics of these events requires a mixing rule, \textit{e.g.} the local average concentration is engulfed or the resulting eddy is termed zone \( i \) or \( j \) if it contains a local excess of \( i \) or \( j \). This will not be treated here because our experimental situation corresponds to (i) and to some extent also to (ii).

For reactions (2) and (3) in a semi-batch reactor, a high yield of the primary product \( R \) requires \( A \) to be initially charged and \( B \) to be slowly added. The stoichiometric ratio will be of order unity and to restrict the volume of \( B \) to be added, \( c_{B0} \gg c_{A0} \). The \( B \)-rich zones will be dilute and \( B \)-\( B \) engulfments infrequent, \textit{i.e.} micromixing proceeds by \( A \) engulfing \( B \). Because equal volumes of \( A \) and \( B \) solutions participate in each engulfment and \( c_{B0} \gg c_{A0} \), more than one engulfment will be needed for mixing. The criterion \( N > 2 \) will be satisfied provided that \( F = c_{A0}/c_{B0} \) is much smaller than unity. In order for engulfment, rather than molecular diffusion, to be the determining step in micromixing, the feed concentrations should satisfy eqn. (7)

\[ F \ll 1 \]  

(7)

When eqns. (4) and (6) are satisfied, the diffusive term in eqn. (1) will be omitted, so that a set of coupled (stiff) ordinary differential equations can be used to calculate micromixing. Physically this means that diffusion between the layers within a vortex is much faster than engulfment and is not the determining step. The EDD formulation reduces to the simpler engulfment (E) model.

3. ENGULFMENT RATE (E)

In this section the previous discrete treatment of engulfment for a single family of eddies is replaced by a continuous version which averages over a large number of families of vortices. Otherwise the same physical description is retained [1].

Mixing by engulfment was previously formulated for the growth of the volume of a single feed eddy having a volume \( V_0 \) over \( N \) generations, whereby on average each engulfment took place between equal volumes of fluid. Thus

\[ V_e(N) = V_0 2^N \]  

(8)

Eddies start their growth at different times and averaging over all these families gives a continuous growth law, the independent variable being the lagrangian age \( \alpha \) since birth. Eddies of substance \( i \) grow exponentially, which is the continuous version of eqn. (8)

\[ \frac{dV_{ei}}{d\alpha} = EV_{ei} \]  

(9)
The hydrodynamic lifetime of a vortex is
\[ \tau_\omega = 12(\nu/\varepsilon)^{1/2} \] (10)
Since eqns. (8) and (9) describe the same growth process
\[ V_e(N) = V_0 2^N = V_0 \exp(EN\tau_\omega) \] (11)
\[ E = \ln 2/\tau_\omega = 0.05776(\varepsilon/\nu)^{1/2} \]
\( E \) is the engulfment rate and applies to the viscous-convective part of the concentration spectrum.

4. DIMENSIONLESS GROUPS FOR MICROMIXING

The EDD model relates \( X_S \) when reaction is complete (and the limiting reagent \( B \) is fully consumed) to the following dimensionless groups for a particular reactor operating mode (plug flow, CSTR, semi-batch, etc.) [2]
\[ X_S = f(k_1/k_2; N_{A0}/N_{B0}; V_A/V_B; Sc; M) \] (12)
The last group \( M \) can be replaced by \( M/Sc \) with no loss of generality.
\[ M = k_2c_{B0}\delta_0^2/D \] (13)
\[ Sc = \nu/D \] (14)
\[ \delta_0 = 0.5(\nu^3/\varepsilon)^{1/4} \] (15)
From eqns. (11) and (13) - (15)
\[ M/Sc = \frac{0.05776 k_2 c_{B0}}{4} \frac{k_2 c_{B0}}{E} \] (16)
The new group is a second Damköhler number, which is the ratio of a characteristic time for mixing to that for reaction. It is conventional (e.g. in combustion theory) to refer this number not to the feed concentration \( c_{B0} \) but to the concentration which \( B \) would have if it were first to mix completely with stream \( A \) before reaction started (\( \bar{c}_B \)).

Defining \( a \) by
\[ a = V_A/V_B \] (17)
a simple dilution calculation shows that
\[ \bar{c}_B = c_{B0}/(1 + a) \] (18)
Thus eqn. (16) can also be written
\[ M/Sc = \frac{0.05776}{4} (1 + a) \frac{k_2 \bar{c}_B}{E} \] (19)

Two forms of the Damköhler number are
\[ \bar{Da} = k_2 \bar{c}_B/E \] (20)
\[ Da = k_2 c_{B0}/E \] (21)
\( M \) in eqn. (12) may be replaced by either of these, if it is more convenient.

5. APPLICATION OF E MODEL TO SEMI-BATCH REACTOR

Semi-batch operation refers to the slow and controlled addition of a reagent \( B \) to a reagent \( A \) which is already present in the reactor. It is widely used industrially in preference to batch or plug flow schemes, since interrupting feed \( B \) can help to limit a thermal run-away. It can be extended to fully continuous operation, e.g. by feeding \( B \) to each tank in a cascade through which \( A \) flows in sequence. Slow addition of \( B \) means that fresh \( B \) mixes and reacts on a much shorter time scale than that of addition, and the concentration of \( B \) averaged over the whole reactor is low. Each fresh quantity of \( B \) is a source of vortices which grow according to eqn. (9) by engulfment of the \( A \)-rich surroundings. A mass balance on substance \( i \) in this growing reaction zone is
\[ \frac{d\langle c_i \rangle}{d\alpha} = EV_i \langle c_i \rangle + Ri V_{ei} \] (22)
\( \langle c_i \rangle \) is the concentration of \( i \) in the local environment of the growing eddy and the first term on the right-hand side of eqn. (22) is the rate of addition of \( i \) by engulfment. The second term is the production of \( i \) by reaction. Because diffusion is rapid relative to engulfment when eqn. (4) is satisfied, \( c_i \) refers to a uniform concentration within the growing reaction zone. Introducing eqn. (9) into eqn. (22) gives the basic E model
\[ \frac{dc_i}{d\alpha} = E(\langle c_i \rangle - c_i) + R_i \] (23)
Dimensionless variables may be defined with particular reference to the second-order reactions (2) and (3)
\[ T = \alpha E \] (24)
\[ C_i = c_i/c_{B0} \] (25)
\[ \beta_{ii} = k_{ii}/k_2 \] (26)
Together with eqn. (21), eqn. (23) may be written as

\[ \frac{dC_i}{dT} = (C_i) - C_i + D_a \sum_j \delta_{ij} C_i C_j \]  

(27)

Equation (23) is similar to a mixing model, defined by eqn. (28)

\[ \frac{dc_i}{dt} = k_m (\bar{e}_i - e_i) + R_i \]  

(28)

In the literature on chemical reactors, excluding combustion, eqn. (28) was suggested in 1962 [9] and again in 1972 [10, 11]. The model, usually known as IEM (interaction by exchange with the mean), has since been extended and applied (see, for example, refs. 12 - 17) yet no derivation seems to be available. Here engulfment is the basis of eqn. (22) and will be the controlling mechanism if eqns. (4) and (7) are satisfied. The E model can thus be related to physical processes (diffusion, deformation, engulfment) and their relative importance suggests limits for its applicability. Equation (28) without the reaction term was also proposed in 1951 by Burgers [18], but there is some doubt whether it can describe turbulent exchange [18]. Apart from the question of similar model structures, relating the parameters \( E \) in eqn. (23) and \( k_m \) in eqn. (28) to physical quantities is important if these equations are to be used predictively. Equation (11) relates \( E \) to the kinematic viscosity and the rate of energy dissipation and thus applies to micromixing in the viscous sub-region. \( k_m \) (or its inverse \( t_m \)) has often been related to Corrsin's analysis of the rate of decay of concentration variance [19] or to impeller characteristics (e.g. power and pumping numbers) in the turbulent regime [13]. In both cases \( k_m \) depends essentially on quantities characterizing the inertial-convective part of the concentration spectrum, e.g. the influence of viscosity is not included. No generally valid equation relating \( k_m \) to all relevant variables could be found in the literature.

\( \langle c_i \rangle \) obviously changes during reaction and is calculated as follows. The volume of solution B added to the semi-batch reactor is discretized into \( \sigma \) equal parts, each of volume \( V_B/\sigma \) and concentration \( c_{BO} \). When any part has been added, the volume of the reaction zone grows according to eqn. (9). Engulfments take place independently with the same environment, having a concentration \( \langle c_i \rangle \) [6]. During application of eqn. (27) to any part of the feed, \( \langle c_i \rangle \) is constant. From one part to the next, however, the concentration in the surroundings is updated by a mass balance, which represents mixing the uniform reaction zone with the surroundings. This fluid remains perfectly mixed because the rate of addition of B is slow relative to the homogenization of the surroundings, i.e. macroscopic concentration gradients are not included in the present analysis. This was also the case for the EDD model in refs. 1 and 2. Updating is as follows. The \( j \)th part of the feed completely reacts in the time \( T \) (i.e. B is fully consumed) and the concentration of \( i \) is then \( c_{i,T} \). The volume of this solution started at \( V_B/\sigma \) and is finally \( (V_B/\sigma)e^T \). The rest of the solution has a volume \( V_A + j V_B/\sigma - (V_B/\sigma)e^T \) and concentration \( c_{ij} \). The surroundings for the \( (j + 1) \)th part have concentrations \( \langle c_i \rangle \). Thus

\[ \langle c_i \rangle_j = \frac{(c_{ij} - \langle c_i \rangle)(aa + j - e^T) + c_{i,T}e^T}{aa + j} \]  

(29)

6. RESULTS

The replacement of partial differential equations by ordinary differential equations leads to reduced computer times and makes it easier and quicker to calculate micromixing for more complex reactions than eqns. (2) and (3). These results are illustrated by comparisons with previous calculations and in Part II by extensions to new problems.

6.1. Case 1: competitive–consecutive reactions following eqns. (2) and (3)

The first diazo coupling reaction is effectively instantaneous and the W Z transformation is used instead of solving eqn. (27) for the concentrations of A, B and R (\( W = C_B - C_A \) and \( Z = C_A + C_R \) [2]). (This technique was probably first used for single reactions by Burke and Schumann [20].)

Thus two and not three coupled ordinary differential equations need to be integrated. A modified Euler finite difference method was employed. Results were compared with
finite difference, global and spline collocation methods applied to integrate the partial differential equation (eqn. (1)) [3], also using a CDC Cyber 180-855. For reactions (2) and (3), the following parameter set had previously been specified: \( Sc = 1000, M = 50, F = 0.021, \alpha = 50, \beta = \infty \) and \( \sigma = 20 \). Thus by numerical integration of eqn. (1), \( X_S = 0.3249 \) or 0.325 (three-figure accuracy is sufficient for comparison with experiments whose analytical error is about \( \pm 0.004 \)). From eqns. (19) - (21), \( Da = 0.1358 \). By integrating eqn. (27), \( W \) and \( Z \) are found when the limiting reagent \( B \) has been consumed. The concentrations of \( R \) and \( S \) are found from \( W \) and \( Z \) [2] and hence \( X_s \) from eqn. (5). Using various step lengths \( H \) from \( 10^{-5} \) to \( 10^{-2} \) expressed in units of \( T_1 \), \( X_S = 0.3301 \) or 0.330. CPU time ranges from 2 to 89 s as the step length decreases. Modelling micromixing with ordinary differential equations gives \( X_S = 0.330 \) in a CPU time of 2 s, whereas solving partial differential equations by spline collocation gives \( X_S = 0.325 \) in a CPU time of 16 s. One possible reason for the difference in \( X_S \) is related to the discretization of the feed, i.e. in assigning a value to \( \sigma \). Physical consideration suggests

\[
\sigma \approx \frac{\text{time to feed solution B}}{\text{bulk mixing time}} \tag{30}
\]

At laboratory scale (few litres) these times may be of the order of several minutes for the feed time and 1 s for the blending time. Thus \( \sigma \approx 10^2 \) - \( 10^5 \). The value \( \sigma = 20 \) used here is too low and increasing \( \nu \) has previously [2, 21] been found to raise \( X_S \) slightly. This however, causes a proportional increase in computer time [3]. Table 2 shows the effect of \( \sigma \) on \( X_S \) determined from eqn. (27) at two levels of \( Da \). They correspond in the EDD model to \( Sc = 1000 \) and \( M = 10 \) and 100. These results show that \( \nu \) should exceed \( 10^2 \) for three-figure accuracy; however, for experimental accuracy \( \sigma = 20 \) is acceptable. CPU times increase from 3 to about 95 s with rising \( \sigma \). Comparing Table 2 with table 3 of ref. 3, the E model predicts a slightly higher value of \( X_S \) than the EDD model, whereas the E model is at least an order of magnitude faster, as measured by CPU time. The growth of the volume within which mixing and reaction occur is described as discrete in eqn. (8) in the EDD model and as continuous in eqn. (9) in the E model and, although these are related through eqn. (11), their details differ slightly. This is considered to be the main reason why the two models predict values of \( X_S \), which in Table 2 differ by no more than 1.8% from those previously published for the EDD formulation [3].

6.2. Case 2: influence of local pH gradients on selectivity

pH gradients influence the concentrations of the reactive species in eqns. (2) and (3) by way of ionic pre-equilibria. Model development is explained elsewhere [7]. The product distribution is determined by the simultaneous solution of six partial differential equations and one algebraic equation using the EDD formulation. When applied to the coupling between 1-naphthol and diazotized sulphanilic acid, the instantaneous first reaction (eqn. (2)) means that \( A \) and \( B \) cannot coexist; therefore, as in case 1, a transformation of variables allows the removal of stiffness from the differential equations and a reduction in the number of differential equations (partial and ordinary in EDD and E models respectively).

\[
U = C_B - C_A \tag{31}
\]
\[
Z = C_A + C_R \tag{32}
\]
\[
V = C_W + C_A \tag{33}
\]

<table>
<thead>
<tr>
<th>( Da )</th>
<th>( X_S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( u = 10 )</td>
<td>( u = 20 )</td>
</tr>
<tr>
<td>0.01358</td>
<td>0.0671</td>
</tr>
<tr>
<td>0.1358</td>
<td>0.3267</td>
</tr>
</tbody>
</table>

Semi-batch, \( \alpha = 50, F = 0.021, \beta = \infty, H = 0.0005 \).
When the first reaction (eqn. (2)) is instantaneous, the concentrations are given by

\[ C_A = \frac{|U| - U}{2} \]  
\[ C_B = \frac{|U| + U}{2} \]  
\[ C_R = Z - \frac{|U| - U}{2} \]  
\[ C_W = V - \frac{|U| - U}{2} \]  

Equation (27) written for this system of variables becomes

\[ \frac{dU}{dT} = (U) - U - A_1A_2DaZ \left(\frac{U + |U|}{2}\right) \]  
\[ \frac{dZ}{dT} = (Z) - Z - A_1A_2DaZ \left(\frac{U + |U|}{2}\right) \]  
\[ \frac{dS}{dT} = (S) - S + A_1A_2DaZ \left(\frac{U + |U|}{2}\right) \]  
\[ \frac{dP}{dT} = (P) - P \]  
\[ \frac{dV}{dT} = (V) - V + A_1A_2DaZ \left(\frac{U + |U|}{2}\right) \]  

The coefficients \( A_1 \) and \( A_2 \) are related to the \( \text{pK} \) values of R and B and to the local pH.

\[ A_1 = K'_R/(K'_R + C_{H^+}) \]  
\[ A_2 = C_{H^+}^2/(K'_B + C_{H^+}) \]  

where, as in eqn. (25), all dimensionless variables are referred to \( c_{BO} \).

After each time step in the integration of eqns. (38) - (42), the concentrations of P (\( P \equiv c_P \)) and S (\( S \equiv c_S \)) are known and those of A, B, R and W follow from eqns. (34) - (37). \( C_{H^+} \) now follows from eqn. (45), which is solved by Newton’s method.

\[ C_W = C_{H^+} - \frac{K'_W}{H^+} + \frac{C_A C_{H^+}}{K'_A + C_{H^+}} + \frac{C_R C_{H^+}}{K'_R + C_{H^+}} \]
\[ + \frac{C_B C_{H^+}}{K'_S + C_{H^+}} - \frac{2C_B K'_B}{K'_B + C_{H^+}^2} \]
\[ + \frac{C_P (2C_{H^+} + K'_P C_{H^+})}{K'_P K'_2 + K'_P C_{H^+} + C_{H^+}^2} \]  

This equation is applied to the growing B-rich reaction zone, where \( C_A = 0 \) when eqn. (2) is instantaneous. Thus the third term on the right-hand side of eqn. (45) is set equal to zero. The initial conditions for this E model apply to B-rich solutions and are

\[ U(0) = 1 \quad P(0) = c_{PB} \]  
\[ Z(0) = 0 \quad V(0) = c_{W0} \]  

(from eqn. (45) with \( C_A = C_R = C_S = C_P = 0 \) at \( T = 0 \))

\[ S(0) = 0 \]

These are then updated for the addition of subsequent parts of the feed (\( j > 1 \)).

In the surrounding solution A the concentrations are initially

\[ \langle U(0) \rangle = -F \quad \langle S(0) \rangle = 0 \]
\[ \langle Z(0) \rangle = F \quad \langle P(0) \rangle = c_{PA} \]
\[ \langle V(0) \rangle = c_{W0} + C_A(0) = c_{W0} + F \]

Again these are updated for each part of the feed.

For \( Sc = 1000, c_{PA} = 0.5, c_{PB} = 0, pH_A = 10.0, pH_B = 1.5, M = 100 \) (\( Da = 0.1358 \)), \( a = 50 \), \( F = 0.021 \), \( c_{B0} = 0.02 \text{ mol dm}^{-3} \) and \( \sigma = 20 [7] \), solution of the EDD model using spline collocation with a total of 20 points gives \( X_S = 0.263340 \) in 7329 s of CPU time. Solution of eqns. (38) - (42) with a modified Euler method (\( H = 10^{-4} \)) and of eqn. (45) with Newton’s method gives \( X_S = 0.263564 \) in 75 s. Extending the step length (\( H = 5 \times 10^{-4} \)) gives \( X_S = 0.263547 \) in 18 s. As in case 1 the E model gives a slightly higher value of \( X_S \) than the EDD model; the CPU time for three- and four-figure accuracy is reduced by more than an order of magnitude.

Table 3 contains the influence of feed discretization (\( \sigma \)) on \( X_S \) at two levels of \( Da \) (or \( M \)), calculated using the E model. Most computations use \( H = 10^{-4} \) and the CPU time increases from 40 s for \( \sigma = 10 \) to 380 s for \( \sigma = 100 \). All these results are directly comparable with spline collocation solutions of partial differential equations in the EDD case [7]. The values of \( X_S \) in Table 3 are about 6% lower when \( Da = 0.01358 \) (\( M = 10 \)), but are within 0.1% of the EDD model (\( M = 100 \)). The E model is 15 - 20 times faster. The EDD calculation of a single point
TABLE 3
Effect of degree of discretization of feed on product distribution

<table>
<thead>
<tr>
<th>Da</th>
<th>(X_S)</th>
<th>(\sigma = 10)</th>
<th>(\sigma = 20)</th>
<th>(\sigma = 30)</th>
<th>(\sigma = 50)</th>
<th>(\sigma = 100)</th>
<th>(\sigma = 200)</th>
<th>(\sigma = 500)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01358</td>
<td>0.0388</td>
<td>0.0400</td>
<td>0.0405</td>
<td>0.0410</td>
<td>0.0411</td>
<td>0.0413</td>
<td>0.0413</td>
<td></td>
</tr>
<tr>
<td>0.1358</td>
<td>0.2592</td>
<td>0.2636</td>
<td>0.2660</td>
<td>0.2662</td>
<td>0.2670</td>
<td>0.2674</td>
<td>0.2677</td>
<td></td>
</tr>
</tbody>
</table>

Semi-batch reactor, \(a = 50\), \(F = 0.021\), \(\beta = \infty\), \(C_{PA} = 0.5\), \(C_{PB} = 0\), \(pH_A = 10.0\), \(pH_B = 1.5\), \(c_{B0} = 0.02\) mol dm\(^{-3}\).

TABLE 4
Effect of SC (or Da) on product distribution (conditions as in Table 3, \(a = 20\), \(M = 100\))

<table>
<thead>
<tr>
<th>Model</th>
<th>(X_S)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Sc = 1000)</td>
</tr>
<tr>
<td>EDD</td>
<td>0.2634</td>
</tr>
<tr>
<td>E</td>
<td>0.2636</td>
</tr>
</tbody>
</table>

requires 3.5 h when \(a = 200\) compared with some 6 - 12 min for the E model.

Table 4 reports the influence of Sc (or Da using eqns. (19) - (21)) on \(X_S\) using the EDD and E formulations. Agreement between them is good provided that Sc < 4000, as expected from eqn. (4). The values in parentheses are inaccurate.

Table 5 shows the effect of buffer concentration on \(X_S\) at two reagent concentration levels. Again direct comparison with the published results for the EDD model is possible. At and above \(C_{PA} = 0.5\) the two models agree within 1% at three figure accuracy. The values of \(X_S\) at \(C_{PA} = 0.1\) from the EDD model are 0.0497 \((c_{B0} = 0.02)\) and 0.0159 \((c_{B0} = 0.01)\) which do not agree well with the E model. With decreasing buffer concentration, the pH at the reaction site falls below the optimum value of 10.0, and reaction slows down thus reducing \(X_S\) (Table 5) [7]. A and B can then coexist and the solution in transformed variables (eqns. (34) - (37)) is no longer valid. Equation (27) is therefore written in the dimensionless concentrations of the various species, which are A, B, R, S, P and W. The six ordinary differential equations are solved numerically together with the algebraic equation eqn. (45)). One more ordinary differential equation and stiffness are the disadvantages of using actual concentrations. The results from the fuller E model (Table 6) agree to within the experimental error in measuring \(X_S\), namely \pm 0.004, over the whole range of \(C_{PA}\) with the EDD model. The CPU time for the results in Table 6 is about 130 s compared with around 80 s in Table 5. A few calculations to determine the effect of \(\beta = k_1/k_2\) were made using the conditions in Table 3 and for \(a = 20\). The results are given in Table 7. As noted earlier [7], increasing \(\beta\) at constant Da slightly promotes the primary coupling and \(X_S\) decreases; over the range of \(\beta\) from 4000 to infinity, this decrease in \(X_S\) is not measurable.

7. CONCLUSIONS

A quantitative description of micromixing is given in eqn. (1), which is based on the processes of engulfment, deformation and

TABLE 5
Effect of buffer concentration on product distribution (conditions as in Tables 3 and 4, solution in transformed variables)

<table>
<thead>
<tr>
<th>(c_{B0}) (mol dm(^{-3}))</th>
<th>(X_S)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(C_{PA} = 0.1)</td>
</tr>
<tr>
<td>0.02</td>
<td>(0.0390)</td>
</tr>
<tr>
<td>0.01</td>
<td>(0.0034)</td>
</tr>
</tbody>
</table>
TABLE 6
Effect of buffer concentration on product distribution (conditions as in Tables 3 - 5, except $\beta = 4000$; solution in actual variables)

<table>
<thead>
<tr>
<th>$c_{BO}$ (mol dm$^{-3}$)</th>
<th>$X_S$</th>
<th>$C_{PA} = 0.1$</th>
<th>$C_{PA} = 0.5$</th>
<th>$C_{PA} = 1.0$</th>
<th>$C_{PA} = 2.0$</th>
<th>$C_{PA} = 10$</th>
<th>$C_{PA} = 20$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>0.0519</td>
<td>0.2653</td>
<td>0.3036</td>
<td>0.3151</td>
<td>0.3145</td>
<td>0.3136</td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>0.0188</td>
<td>0.1967</td>
<td>0.2681</td>
<td>0.3039</td>
<td>0.3153</td>
<td>0.3143</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 7
Effect of $k_I/k_z$ on product distribution (conditions as in Table 3 and $\sigma = 20$)

<table>
<thead>
<tr>
<th>$Da$</th>
<th>$X_S$</th>
<th>$\beta = 4000$</th>
<th>$\beta = 8000$</th>
<th>$\beta = \infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01358</td>
<td>0.0419</td>
<td>0.0412</td>
<td>0.0401</td>
<td></td>
</tr>
<tr>
<td>0.1358</td>
<td>0.2653</td>
<td>0.2645</td>
<td>0.2635</td>
<td></td>
</tr>
</tbody>
</table>

diffusion in turbulent liquids (EDD model). When $Sc$ is sufficiently small (eqn. (4)) and more than two engulfments are needed for complete mixing (eqns. (6) and (7)), it has been shown experimentally and theoretically that deformation and diffusion are not rate limiting. This suggests a simplification of the partial differential equation (eqn. (1)) to an ordinary differential equation with the vortex age as independent variable, thus enabling faster computations and the use of a wider range of software when calculating the effect of micromixing on chemical reactions.

The basic model equation (eqn. (23)) results from a simple mass balance to express the growth of the reaction zone by engulfment and uniform reaction within this zone. The engulfment rate is related to the kinematic viscosity and the energy dissipation rate by eqn. (11). The reaction kinetics also appear in eqn. (23); there are no arbitrary parameters. The dimensionless form (eqn. (27)), applying to second-order reactions, is applied to the semi-batch reactor, for which addition of the feed is discretized (eqn. (29)).

Although the conditions in eqns. (4), (6) and (7) should ensure that diffusion is not rate determining, it was previously unclear whether diffusion could determine product distribution. Thus the simplified E model (involving ordinary differential equations) was applied to two cases of complex reaction, which had previously been studied in detail using the EDD model (involving partial differential equations). Within its range of application the E model gives the same results for the product distribution as the EDD model and is roughly one to two orders of magnitude faster as measured by CPU time. Numerical methods and software for both formulations have not been optimized, rather physical arguments have been applied in order to clarify the modelling. Further improvements in software may be expected.

No specific comparison is made here between models and experiments. All the present computations with the E model refer to typical experimental conditions for the coupling between 1-naphthol and diazotized sulphanilic acid. Since its publication in 1984, applications of the EDD model to experimental results for this reaction have shown its usefulness and value. Under the conditions of its validity the E model yields the same product distribution and thus good agreement between measurements and the EDD model also implies successful application of the E model.

REFERENCES

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APPENDIX A: NOMENCLATURE

\( a \) ratio of volume of solution A to that of solution B (eqn. (17))
\( A_m \) pH-dependent factor (eqns. (43) and (44))
\( \bar{c}_B \) concentration of B averaged over whole reactor (eqn. (18))
\( c_{B0} \) feed concentration of solution B
\( c_i \) concentration of \( i \) (usually in reaction zone)
\( \langle c_i \rangle \) concentration of \( i \) in surroundings near reaction zone
\( C_i \) dimensionless concentration (eqn. (25))

\( C_{PA} \) dimensionless concentration of buffer in solution A
\( C_{PB} \) dimensionless concentration of buffer in solution B
\( D, D_i \) diffusivity of \( i \)
\( Da \) Damkohler number (eqns. (20) and (21))
\( E \) engulfment rate
\( F \) concentration ratio \( c_{A0}/c_{B0} \)
\( H \) dimensionless integration step length
\( j \) discretization variable
\( k_i \) second-order rate constant of \( i \)th reaction
\( K \) dimensionless ionic equilibrium constant
\( M \) mixing modulus (eqn. (13))
\( N \) number of vortex generations
\( N_i \) quantity of substance \( i \)
\( P \) dimensionless buffer concentration
\( R, S \) reaction products (eqns. (2) and (3))
\( R_i \) specific reaction rate
\( Sc \) Schmidt number (eqn. (14))
\( t \) time
\( T \) dimensionless time (eqn. (24))
\( u \) shrinkage velocity
\( U, V, Z \) dimensionless transformed concentrations (eqns. (31)-(33))
\( V_e \) eddy volume
\( V_i \) volume of solution containing \( i \)
\( x \) Cartesian coordinate
\( X_S \) product distribution (eqn. (5))

Greek symbols
\( \alpha \) vortex age
\( \beta \) dimensionless rate constant (eqn. (26))
\( \delta_0 \) initial half-thickness of diffusion layer (eqn. (15))
\( \epsilon \) rate of turbulent energy dissipation
\( \nu \) kinematic viscosity
\( \sigma \) number of parts of feed
\( \tau_\omega \) lifetime of vortex