Modelling complex spatiotemporal behaviour in a Couette reactor

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The development of spatiotemporal complexity in a chemical reaction in a ‘Couette reactor’ is analysed through the Lengyel–Epstein model for the chlorine dioxide–iodine–malonic acid (CDIMA) reaction which is characteristic of a system showing instability through supercritical Hopf bifurcation (as opposed to excitable systems). The Couette reactor comprises the annular gap between two concentric cylinders, the inner of which is rotated at a controlled rate so as to establish Taylor–Couette flow, which dominates the transport of molecules along the reactor. The ‘boundary conditions’ for the Couette reactor are set by well-stirred continuous flow reactors (CSTRs), which may be operated with different chemical inputs, so imposing background reactant concentrations along the Couette reactor. We examine this system analytically and numerically using a simplified representation of the Taylor–Couette flow through an ‘enhanced’ reaction–diffusion model and restrict ourselves at this stage to operating conditions such that the steady states in the CSTRs are stable rather than oscillatory. Despite this, and the stabilising effects of the boundary conditions thus imposed, complex spatiotemporal responses develop within the Couette reactor for a range of parameter values. We determine the variation in stability of the (spatially-dependent) steady state concentration profiles and observe both saddle-node and Hopf bifurcations. The unsteady solutions that emerge from the Hopf bifurcations show subsequent instabilities, possibly through a period-doubling–mixed-mode sequence to more complex structures.

1 Introduction

In the search for new types of spatiotemporal chemical patterns, several different types of chemical reactor have been developed recently.^{1–4} Many of these, driven by the pattern formation mechanism suggested originally by Turing,⁵ have sought to attain a situation of ‘differential diffusion’, in which selected species have reduced or enhanced diffusion rates compared to the remaining species. In some cases, this has been achieved by reversible complexation with an immobilized species (iodine–starch is often used in this context): in other cases, electric field effects have been exploited.^{6–10} Somewhat less attention has been paid to patterns arising in situations for which all reacting species have diffusion coefficients of similar magnitude: indeed there is something of a mythology that states that patterns actually require differential diffusion, despite compelling experimental and theoretical evidence to the contrary. One interesting experimental configuration which has clearly demonstrated the possibility of spatial structure with equal diffusivities is the ‘Couette reactor’ (CR) introduced by the groups in Bordeaux and Texas.^{11–16}

The main feature of the CR comprises two horizontally-mounted concentric cylinders, the inner of which is rotated at a controlled rate. Reaction occurs in the annular gap between these cylinders. In a typical ‘Bordeaux’ configuration, constant-flow well-stirred reactors (CSTRs) are connected at each end of the cylinders providing a continuous supply of reactants and removal of products such that the system as a whole is thermodynamically open. A schematic representation of the reactor is shown in Fig. 1. The pertinent similarity

parameter of the Couette flow problem is the Taylor number that represents the relative importance of the centrifugal over the viscous effects.¹⁷ Above a critical rotation rate, corresponding to a sufficiently high Taylor number, the fluid in the cylindrical reaction zone becomes sufficiently turbulent and well-mixed in both the radial and azimuthal directions. Mass transport along the cylinder is then dominated by turbulent mixing rather than by simple molecular diffusion. This results in substantially higher ‘diffusion’ rates, all species are transported at essentially the same rate and renders the ‘diffusion coefficient’ as a tuneable parameter, dependent on the rotation rate of the inner cylinder.

In a series of experiments, two different chemical reactions were investigated: the Belousov–Zhabotinsky (BZ) reaction and the chlorite–iodide–malonic acid (CIMA) reaction. The former is the classic chemical example of an excitable medium, whereas the latter has a different character, the main feature of which are sustained oscillatory responses arising typically through a supercritical Hopf bifurcation. Ouyang *et al.*^{11,13}

Fig. 1 A schematic representation of the Couette reactor.

and De Kepper *et al.*¹² report a series of increasingly complex spatiotemporal structures along the CR as the concentration of one of the major species (ClO_2^-) in one of the CSTRs is varied, ranging from a simple front, through single and multiple oscillating fronts, to complex colliding fronts. Interesting spatiotemporal behaviour is seen to occur even if the two reactors are operating under identical experimental conditions, *i.e.* so that the system is symmetric. Many of these results were subsequently modelled through numerical computation¹³ using the Citri–Epstein mechanism¹⁸ in the CR.

Lengyel *et al.*¹⁹ have recently proposed a reduced, two-variable model for the chloride–dioide–iodine–malonic acid (CDIMA) reaction and have demonstrated its connection to the CIMA system. In this paper we seek to exploit this simple model in the CR context with the aim of achieving a deeper analytical understanding of the basic pattern formation mechanism operating in this situation. Although guided by the experimental results, our objective is to determine generic features of systems with Hopf bifurcation structures in the CR. A complementary analysis for excitable systems based on a representation of BZ-type kinetics has been presented previously by Arneodo and Elezgary.²⁰ In Section 2 the model is introduced and the governing equations cast in an appropriate dimensionless form. Some analytical results are presented in Section 3 and the linear stability analysis of the stationary concentration patterns is given in Section 4. A numerical survey of the range of possible spatiotemporal structures is offered in Section 5. We conclude with comments summarising the general features and also the relevance and implications of our results to the modelling of the CIMA reaction in general.

2 Model and governing equations

In order to simplify the representation of the CR as far as possible, we make the following assumptions:

- The important reacting species in the annular section of the reactor are iodide ion (I^-) and chlorite ion (ClO_2^-).
- The kinetics of the reactions involving these species are adequately described by the Lengyel–Epstein model.
- Mass transport within the reactor is governed by a diffusion-like term with equal diffusion coefficients for each species.
- The exchange between the CSTRs and the reactor is much faster than the chemical reaction rates. Hence, the CSTRs impose boundary conditions on the CR in the form of constant concentrations of I^- and ClO_2^- (Dirichlet boundary conditions).

(v) These boundary conditions are determined from the governing equations appropriate for the Lengyel–Epstein model in a flow reactor.

We note that the two CSTRs could have different inflow concentrations and, hence, impose different boundary conditions at each end of the CR, thus introducing a spatial gradient into the problem.

The Lengyel–Epstein model involves the following representation of the chemical kinetics:

$$-\frac{d[\text{ClO}_2^-]}{dt} = k_{3\alpha}[\text{ClO}_2^-][\text{I}^-][\text{H}^+] + k_{3\beta} \frac{[\text{ClO}_2^-][\text{I}_2][\text{I}^-]}{k_{3\gamma} + [\text{I}^-]^2} \quad (1c)$$

Following Lengyel *et al.*²¹ and Lengyel and Epstein,²² the final term in eqn. (1c) has been modified slightly from the original literature, introducing the coefficient $k_{3\gamma}$. The original form is obtained by setting this quantity to zero, so the rate law becomes inverse first-order in the iodide ion, revealing the self-inhibition through which feedback operates in the reaction. The modified form prevents this rate becoming infinite as the I^- concentration tends to zero.

In the model, ClO_2 , I_2 , MA and H^+ are taken as ‘pool chemicals’ so their concentrations do not vary with time. In the experiments to be modelled here, the concentrations of I_2 , MA and H^+ are the same in each CSTR and hence independent of position along the CR, but spatial gradients in $[\text{ClO}_2]$ may be imposed by employing different feed concentrations to the CSTRs, in which case $[\text{ClO}_2]$ varies with $\bar{x}$, the distance along the reactor, but not time. Also, under typical operating conditions, the first term in rate law (1c) is considered to be negligible²² and so is ignored here.

This leads to our model for the CR as

$$\frac{\partial \bar{u}}{\partial \bar{t}} = D_T \frac{\partial^2 \bar{u}}{\partial \bar{x}^2} + k_{1\alpha} \frac{[\text{MA}][\text{I}_2]}{k_{1\beta} + [\text{I}_2]} - k_2[\text{ClO}_2]\bar{u} - 4k_{3\beta} \frac{[\text{I}_2]\bar{u}\bar{v}}{k_{3\gamma} + \bar{u}^2} \quad (2a)$$

$$\frac{\partial \bar{v}}{\partial \bar{t}} = D_T \frac{\partial^2 \bar{v}}{\partial \bar{x}^2} + k_2[\text{ClO}_2]\bar{u} - k_{3\beta} \frac{[\text{I}_2]\bar{u}\bar{v}}{k_{3\gamma} + \bar{u}^2} \quad (2b)$$

on $0 < \bar{x} < l$, where $\bar{u} = [\text{I}^-]$, $\bar{v} = [\text{ClO}_2^-]$ and D_T is a ‘diffusion coefficient’ arising from the strong turbulent mixing within the annular region of the reactor, of length l , and characterises the transport of the species by the turbulent eddies for fully developed turbulent flow. The concentrations of ClO_2 can be different in the CSTRs at $\bar{x} = 0$ and at $\bar{x} = l$, with the strong mixing within the reactor producing a steady linear variation of this species along the reactor, so that

$$[\text{ClO}_2](\bar{x}) = \left(1 - \frac{\bar{x}}{l}\right)[\text{ClO}_2]_0 + \frac{\bar{x}}{l}[\text{ClO}_2]_l \quad (3)$$

where the subscripts refer to conditions at $\bar{x} = 0$ and at $\bar{x} = l$ respectively.

We start by making eqn. (2a, b) dimensionless by writing

$$\bar{u} = U_s u, \quad \bar{v} = V_s v, \quad x = \bar{x}/l, \quad t = k_2[\text{ClO}_2]_0 \bar{t} \quad (4)$$

where U_s and V_s are scales for the concentrations of $[\text{I}^-]$ and $[\text{ClO}_2^-]$ respectively, given by

$$U_s = \frac{k_{1\alpha}[\text{MA}][\text{I}_2]}{k_2[\text{ClO}_2]_0(k_{1\beta} + [\text{I}_2])}, \quad V_s = \frac{(k_{1\alpha}[\text{MA}])^2[\text{I}_2]}{k_{3\beta}k_2[\text{ClO}_2]_0(k_{1\beta} + [\text{I}_2])^2}$$

Applying eqn. (4) in eqn. (2) leads to the dimensionless version of our model as

$$\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial x^2} + 1 - f(x)u - \frac{4uv}{\beta + u^2} \quad (5a)$$

$$\frac{\partial v}{\partial t} = D \frac{\partial^2 v}{\partial x^2} + \alpha \left\{ f(x)u - \frac{uv}{\beta + u^2} \right\} \quad (5b)$$

on $0 < x < 1$, $t > 0$, where

$$f(x) = 1 - (1 - \gamma)x; \quad 0 \leq x \leq 1 \quad (5c)$$

represents the dimensionless variation of $[\text{ClO}_2]$ along the reactor. The dimensionless parameters are

$$D = \frac{D_T}{k_2[\text{ClO}_2]_0 l^2}, \quad \alpha = \frac{k_{3\beta}(k_{1\beta} + [\text{I}_2])}{k_{1\alpha}[\text{MA}]} \left(= \frac{U_s}{V_s} \right),$$

Fig. 2 Hopf bifurcation curves for the CSTRs. Plots of α against ϕ on which supercritical Hopf bifurcations occur, for $\gamma = 1.0$ and $\gamma = 0.5$. The operating states of the CSTR are stable outside these curves and have an oscillatory response inside.

$$\beta = \frac{k_{3\gamma}}{U_s^2}, \quad \gamma = \frac{[\text{ClO}_2]_l}{[\text{ClO}_2]_0}$$

It is worth mentioning that the dimensionless scalings adopted here differ slightly from those used previously,^{22,23} in particular the explicit appearance of the parameter β in the present form. The influence of this parameter will be addressed below.

Before considering the boundary conditions to be applied in our model, it is useful to have some estimates for the sizes of the dimensionless parameters given above. The value of α depends essentially on the ratio of the (constant) concentrations of I_2 and MA in the reactor. Using values for the rate constants, from ref. 19 suggests that $\alpha \simeq 0.2$, though higher (or even slightly lower) values of α are within the operating range of the CR. γ depends only on the inflow concentrations of ClO_2 in the CSTR and could range from $\gamma = 1$ (symmetric operating conditions) down to $\gamma = 0.1$ (say). To a large extent the rate constant $k_{3\gamma}$ is an artificially introduced quantity and taking the value $k_{3\gamma} = 10^{-14} \text{ M}^2$ suggested in ref. 19 we obtain $\beta \simeq 10^{-4}$. The main point is that β is to be regarded as a small parameter.

The effective diffusivity D_T depends on the turbulent intensity in the annular region of the reactor, which, in turn, is controlled by the rotation rate of the inner cylinder, and is expected to increase with increasing rotation rates. Values for

Fig. 3 Local stability analysis in the $\alpha - \beta$ parameter plane: In region I the steady-states are locally stable for all x and locally unstable for all x in region III. In region II the steady-states are locally unstable for $1 \geq x > x_H$ with x_H given by eqn. (10).

D_T in the range 10^{-2} to $10 \text{ cm}^2 \text{ s}^{-1}$ are suggested²⁰ as reasonable values. With l in the range 10–20 cm, this gives values for D in the range 10^{-5} to 10^{-1} .

(a) Boundary conditions

The boundary conditions at $x = 0$ and $x = 1$ are imposed by the CSTRs, which we assume are operating under steady-state conditions. The dimensionless concentrations (u_s , v_s) at the ends of the reactor satisfy the spatially invariant versions of eqn. (5a, b) with their right hand sides modified to include the extra terms $-\phi u$ and $-\phi v$ to account for the flow of I^- and ClO_2^- respectively out of the CSTR. Here ϕ represent the dimensionless flow rate, which we assume to be the same in each CSTR. In the CSTR equations $f = 1$ for conditions at the $x = 0$ end and $f = \gamma$ for $x = 1$. The steady-states in the CSTRs are then given by

$$\phi(1 + \phi)u_s^3 + [\alpha(5 + \phi) - \phi]u_s^2 - [\alpha - \phi\beta(1 + \phi)]u_s - \phi\beta = 0$$

$$v_s = \frac{(u_s^2 + \beta)}{4u_s} [1 - (1 + \phi)u_s] \quad (6)$$

at $x = 0$, and at $x = 1$ by

$$\phi(\gamma + \phi)u_s^3 + [\alpha(5\gamma + \phi) - \phi]u_s^2 - [\alpha - \phi\beta(\gamma + \phi)]u_s - \phi\beta = 0$$

$$v_s = \frac{(u_s^2 + \beta)}{4u_s} [1 - (\gamma + \phi)u_s] \quad (7)$$

We also need to determine the stability of the steady-states as given by eqn. (6) and (7). This is easily achieved using a standard continuation method based on a secant iteration. The results are presented in Fig. 2, which show $(\alpha - \phi)$ curves on which supercritical Hopf bifurcations occur for two representative values of γ . The CSTR at $x = 1$ is stable for parameter values outside the curve and has an oscillatory response inside. In essence these Hopf curves form a nested sequence as γ is reduced, since the equations for the CSTR can be rendered independent of γ by the transformation $(u, v, t, \phi) \rightarrow \gamma^{-1}(u, v, t, \phi)$ provided β is replaced by $\beta\gamma^2$. As this is only a small term it makes no noticeable difference to bifurcation curves.

The points where the curves of Fig. 2 intersect the α axis can be obtained analytically: an asymptotic expansion of the Hopf condition,

$$-\gamma - 2\phi + 4\frac{v_s}{u_s^2} - \frac{\alpha}{u_s} = 0$$

for $\phi \ll 1$ gives $\alpha \sim \frac{3}{5} + O(\phi)$ and

$$\alpha \sim \frac{1}{6\gamma} \phi + O(\phi^2).$$

The main feature to note from Fig. 2 is that there is a critical flow rate $\phi_c(\gamma)$ above which the CSTR is stable for all parameter values for flow rates $\phi > \phi_c$, where, for small β , $\phi_c(\gamma) = \gamma\phi_c(1)$, with $\phi(1) \simeq 0.4147$.

We now limit our attention to parameter values outside the Hopf curve for $\gamma = 1$ shown in Fig. 2, where both CSTRs have stable steady-states.

3 Local stability analysis

For the CR, we may initially suppose that the effects of diffusion and boundary conditions are small, for $D \ll 1$ at least. On neglecting the diffusion terms in eqn. (5a, b) we find that the

'equivalent batch problem' has the following spatially dependent steady-states:

$$u = \frac{1}{5f(x)}, \quad v = \frac{1 + 25\beta f(x)^2}{25f(x)} \quad (8)$$

If $f(x)$ is now treated as a 'slowly varying' parameter, a local stability analysis indicates that there is a Hopf bifurcation when

$$\alpha = \frac{3}{5} - 25\beta f(x)^2 \quad (9)$$

Hence, there exist two Hopf lines on the $\alpha - \beta$ parameter plane, obtained from eqn. (9) for $f = 1$ and γ , the two extremal values of $f(x)$. These lines divide the parameter plane into three regions as shown in Fig. 3. In region I with $\alpha > 0.6 - 25\beta\gamma^2$, the steady-state is locally stable for all x . In region III, with $\alpha < 0.6 - 25\beta$, the steady-state is locally unstable for all x . In region II there is a position x_H for a Hopf bifurcation within the reactor given by

$$x_H = \frac{1}{1 - \gamma} \left\{ 1 - \frac{(\frac{3}{5} - \alpha)^{1/2}}{5\beta^{1/2}} \right\}, \quad \alpha < \frac{3}{5} \quad (10)$$

such that the steady state is locally stable/unstable for $x < /> x_H$.

4 Steady-states and their stability

(a) Steady state profiles

The spatially dependent steady-states given by eqn. (8) are essentially the leading order terms of a perturbation expansion of u and v in eqn. (5a, b) for $D \ll 1$. Such an expansion will not, in general, satisfy the boundary conditions (6) and (7) at $x = 0, x = 1$ respectively imposed by the CSTRs and hence is non-uniformly valid as $x \rightarrow 0, 1$. The boundary conditions at $x = 0, 1$ are then satisfied by the inclusion of boundary layer regions at $x = 0, 1$, of width $O(D^{1/2})$. The need for these boundary layers depends on there being a difference between eqn. (6), (7) and (8) at $x = 0, 1$. The values u_s, v_s given by eqn. (6) and (7) can coincide with the values obtained from the u, v distributions in eqn. (8) at $x = 0, 1$: a comparison of eqn. (6), (7) and (8) at the boundaries indicates that this is the case when $\phi = 0$ and $\gamma = 1$. We therefore expect that for values of ϕ slightly larger than zero and values of γ slightly smaller than 1—in which case $f(x)$ is a weak function of x as it depends on the slow spatial scale $(1 - \gamma)x$ —the boundary layers disappear and the analysis presented in the previous section determines accurately the stability characteristics of the CR.

In general, however, ϕ and γ may be substantially different from 0 and 1 respectively. In addition, as we shall demonstrate, the effective diffusivity D has to be very small, $\leq 10^{-4}$, for eqn. (8) to be an accurate representation of the concentration profiles within the reactor. Hence, there is a need for a systematic treatment of the stability of the reactor. For this purpose we first construct the steady-states by solving numerically the time-independent versions of eqn. (5a, b) as a two-point boundary-value problem subject to the boundary conditions supplied from eqn. (6) and (7).

The method we adopted for the construction of the steady-states is based on a finite-difference technique with deferred correction allied with a Newton iteration to solve the finite-difference equations. Accuracy is tested by a convergence criterion with respect to mesh refinement. Typically 100 mesh points were used in the domain $0 < x < 1$. Representative concentration profiles are depicted in Fig. 4. These show that the concentrations of both v and more markedly u are not monotone across the reactor as might be intuitively expected [also from eqn. (8)]. There are considerable differences between the calculated profiles and those given by eqn. (8) for the larger values of D (Fig. 4a, with $D = 0.02$). Reasonable

Fig. 4 Concentration profiles obtained from the solution of the steady-state versions of eqn. (5a, b) subject to the CSTR boundary conditions of eqn. (6) and (7). (a) $\alpha = 0.05$, $\beta = 10^{-4}$, $\gamma = 0.1$, $D = 0.02$ and $\phi = 0.5$; (b) $\alpha = 0.5$, $\beta = 10^{-4}$, $\gamma = 0.1$, $D = 10^{-4}$ and $\phi = 0.5$. The dotted lines are the concentration profiles given by eqn. (8). Note the diffusive boundary layers at $x = 0$ and 1; (c) $\alpha = 0.12$, $\beta = 10^{-4}$, $\gamma = 1.0$, $D = 0.013424$ and $\phi = 1.0$.

agreement between the two requires much smaller values of D (Fig. 4b, with $D = 10^{-4}$), though note the diffusive boundary layers near the ends of the reactor in this case. The concentration profiles can be very different to eqn. (8). Notice the presence of a 'dimple' in the profiles of Fig. 4c associated with the presence of a sharp gradient for the u -profile at $x = 0.5$. Such dimples exist also for $\gamma \neq 1$ and move towards $x = 0$ as $\gamma \rightarrow 0$.

(b) Linear stability analysis

The linear stability of the steady-states is then determined by the eigenvalue problem obtained by linearising eqn. (5a, b) about these spatially varying steady-states. The eigenvalue problem was solved numerically using a second-order central

Fig. 5 The stability boundary in β - α parameter space for $D = 0.02$, $\phi = 0.5$ and $\gamma = 0.1$. The regions where the steady-state is stable S, unstable U and where no steady states exist N are indicated in the figure.

finite-differencing scheme to approximate the linearised equations with their discrete analogues, in effect replacing a complicated differential eigenvalue problem with a simpler matrix eigenvalue problem. The eigenvalues of the associated matrix were obtained by reducing the matrix to an upper Hessenberg form followed by a standard QR algorithm. Typically 300 mesh points (corresponding to 600×600 matrices) in the domain $0 < x < 1$ were found necessary for the first few eigenvalues with largest real parts to converge.

We found that, in all cases, the dominant eigenvalues were complex conjugates, with the loss of stability arising through the real part of the least stable pair of eigenvalues going through zero (Hopf bifurcation). Fig. 5 depicts the stability boundary in β - α parameter space. Notice the presence of a region where no steady-states satisfying the CSTR boundary conditions in eqn. (6) and (7) exist. This region appears at a critical ϕ value (< 1) and grows as ϕ decreases until another critical ϕ value where it crosses the U-S stability boundary and starts to penetrate the S region. A further feature to note is that, as the N region is approached from above or below for fixed β , the imaginary parts of the dominant complex conjugate eigenvalues decay to zero and a pair of real and positive eigenvalues then emerges. These two eigenvalues diverge rapidly from each other with one of them eventually becoming negative. As can also be seen from the figure, for these particular values of D , ϕ and γ , the system is always stable for

Fig. 6 The stability boundary in α - D parameter space for $\beta = 10^{-4}$, $\phi = 0.5$ and $\gamma = 0.1$. The regions where the steady state is stable S, unstable U and where no steady states exist N are indicated in the figure.

Fig. 7 Time series plots of $u(\frac{1}{2})$, the dimensionless concentration of I^- at the centre of the reactor for $\phi = 0.5$, $\alpha = 0.25$, $\gamma = 0.1$, $\beta = 10^{-4}$ and (a) $D = 0.02$ (showing single period oscillations), (b) $D = 0.012$ (showing aperiodic behaviour), (c) $D = 0.011$, (d) $D = 0.01$ (showing a period-two response), (e) $D = 0.008$ (showing period-three made up of two regular and one 'peak-fluctuation' oscillations), (f) $D = 0.007$ (showing period-two 'peak-fluctuation' oscillations), (g) $D = 0.001$ (fully irregular behaviour).

$\beta \geq 3.5 \times 10^{-2}$ and $\alpha \geq 0.41$ while extrapolation of the U-N, N-U and U-S stability boundaries towards $\beta \rightarrow 0$ indicates asymptotes of 0.19, 0.06 and 0.04 respectively.

The stability boundary in D - α parameter space is shown in Fig. 6. As expected, for large values of D (≥ 0.056) corresponding to small reactor lengths l , the steady-states are stable. There is a sharp dip in the upper S stability boundary at $D \approx 0.01$ leading to somewhat smaller values of α being needed to destabilize the system for D around this value. Notice that for $D \ll 1$ the N-U boundary approaches an asymptote of 0.1 while the U-S boundary tends to an asymptotic value ≈ 0.6 as predicted by eqn. (9).

5 Spatio-temporal behaviour

(a) Numerical method

The reaction-diffusion eqn. (5a, b) subject to the CSTR boundary conditions (6) and (7) were solved numerically using a Crank-Nicolson-type implicit scheme with the x -derivatives approximated by central finite differences. The time discretization uses a two-level scheme. In advancing from time t to time $t + \Delta t$ we replace the time derivative terms by difference quotients involving the solution at the old time level (time t) and the, as yet unknown, solution at the new time

Fig. 8 Profile plots of u at equally spaced time intervals for $D = 0.02$ (and $\phi = 0.5$, $\alpha = 0.25$, $\gamma = 0.1$, $\beta = 10^{-4}$).

level ($t + \Delta t$). We evaluate the other terms using a weighted average of the solution at the two time levels; a typical weight is $\theta = 0.55$ on the advanced time level and $1 - \theta = 0.45$ on the old time level. At each time level, the fully discrete system is a set of nonlinear algebraic equations which we solve using Newton's method.

We dynamically choose the time step Δt to control several aspects of the simulation, while the spatial grid is fixed (typically 100 points in the domain $0 < x < 1$ were used). If the result of the time step violates any of a list of constraints, it rejects this step and tries again with a smaller step size. To avoid using unnecessarily small time steps, if we easily meet all the constraints for several steps, we increase the step size by about 50% at the next step. The constraints involve local time truncation and the rejection of a step for which the minimum of u , v decreases by more than 10%. The accuracy of the numerical simulations was determined by mesh refinement and time step sizing.

(b) Numerical results

We consider the behaviour of the system when the spatial steady-state profiles are unstable (or none exist), starting by investigating what changes in behaviour result when D is decreased for fixed values of the other parameters (taking $\phi = 0.5$, $\alpha = 0.25$, $\gamma = 0.1$, $\beta = 10^{-4}$). For these parameter values the CSTR solutions are stable and, for $D < 0.056$, the steady-state configuration of the reactor is unstable (Fig. 6). We illustrate the behaviour of the system mostly through time series plots of $u(\frac{1}{2})$, the (dimensionless) concentration of I^- at the mid-point of the reactor, sampled after any transients had died out. For larger values of D (but still with $D < 0.056$) the response is oscillatory with a single period, as is shown in Fig. 7a for $D = 0.02$. Values larger than the corresponding steady-states are achieved by both I^- and ClO_2^- though, perhaps, the more important feature to note is the comparatively long time (nearly half the period) during which the concentration of I^- is very low, taking values of $O(\beta)$.

The sequence of events giving the single-period oscillations shown in Fig. 7a is illustrated in Fig. 8, where we give profile plots of u at equally spaced time intervals. A region of low u

concentration forms at $x \simeq 0.2$ ($t = 27$). This effect becomes enhanced and a large region where there is virtually no iodide develops ($t = 28$, where $u \simeq 2 \times 10^{-4}$ for $0.1 < x < 0.55$). At the same time a region of relatively high u is formed towards the $x = 1$ boundary. The region of low u spreads across the reactor until waves of higher u form near both ends of the reactor as a consequence of the concentrations of I^- and ClO_2^- maintained in the CSTRs. These waves propagate rapidly from both the $x = 0$ and 1 boundaries ($t = 29$) filling the whole reactor ($t = 30, 31$) after which the whole process starts again ($t = 32$).

This single-period response continues as D is decreased, with the amplitude of the oscillations in both u and v decreasing slightly with D , until at $D \simeq 0.013$ weak period-two oscillations are seen. This leads to fully aperiodic behaviour by $D = 0.012$, as is shown in Fig. 7b. By reducing D slightly ($D = 0.011$, Fig. 7c) a somewhat unusual periodic behaviour results. In this a sequence of regular oscillations is interspersed with a sequence of oscillations which have a small period-two oscillation about their peak values. This behaviour is seen only for a narrow range of D and by $D = 0.01$ (Fig. 7d) period-two oscillations are again seen. On reducing D a little more, further unusual-looking periodic behaviour results. This is illustrated in Fig. 7e, for $D = 0.008$ (compare this with Fig. 7c). Here a period-three response is seen, made up of two regular oscillations and a 'peak-fluctuation' oscillation.

This trend continues with the regular part of the oscillations breaking into the 'peak-fluctuation' oscillations seen in Fig. 7c, e. The periodicity of these fully 'peak-fluctuation' oscillations decreases to period-two (Fig. 7f, for $D = 0.007$). This period-two response then persists until relatively low values of D , for which the behaviour becomes completely irregular. This is illustrated in Fig. 7g for $D = 0.001$. Finally, we note that a feature common to all the plots shown in Fig. 7 is the relatively long periods over which the concentration of I^- is very low, typically of $O(\beta)$.

We complement these time series plots of $u(\frac{1}{2})$ with contour plots of u for some representative cases. Period-one behaviour, typical of the higher values of D , is shown in Fig. 9a (taking $D = 0.02$, compare with Fig. 7a, 8). In this simple response, contours represented by any colour show a similar overall response. For the regular 'peak fluctuation' oscillations shown in Fig. 9b corresponding to $D = 0.007$ to compare with Fig. 7f, the 'islands' of highest u concentration, corresponding to the blue colour in the figure, are more evident in the vicinity of $x = 0.9$. A more complex structure in the orange and red contours in the region of $x = 0.5-0.6$ is also observed. This latter feature develops more fully in Fig. 9c, corresponding to $D = 0.001$ and Fig. 7g, in which fully irregular behaviour is evident. The appearance of islands of higher u (orange) among the yellow in the region around $x = 0.5$ may be evidence for similar isolated patches of high iodide ion concentration revealed by the chemical indicator in experiments. The 'propagation' of the spatial structure along the CR is evident from the departure of the contours from the vertical (this occurs in all the plots, but is clearest in this particular case).

We now consider the effect of changing α for fixed values of the other parameters. For the larger values of D the system undergoes only period-one oscillations throughout its unstable regime. The period of these oscillations increases monotonically as α is decreased, whereas their amplitude decreases slightly as α is decreased. This is illustrated in Fig. 10 (for $D = 0.02$, $\phi = 0.5$, $\gamma = 0.1$, $\beta = 10^{-4}$) with a plot of the amplitude of the oscillations in $u(\frac{1}{2})$ against α , as obtained from the numerical simulations of the full initial-value problem [eqn. (6a, b), (7) and (8)]. These results show that the oscillatory response persists for values of α slightly above and below the upper and lower bifurcation points respectively. This, in turn, suggests that there is a 'hard excitation' (subcritical bifurcation) to the oscillatory response, with the

Fig. 9 Contour plots of u for $\phi = 0.5$, $\alpha = 0.25$, $\gamma = 0.1$, $\beta = 10^{-4}$ and (a) $D = 0.02$, (b) $D = 0.007$, (c) $D = 0.001$.

Fig. 10 The amplitude of the oscillations in $u(\frac{1}{2})$ against α for $D = 0.02$, $\phi = 0.5$, $\gamma = 0.1$, $\beta = 10^{-4}$.

evidence for this being much clearer at the lower bifurcation point than at the upper bifurcation point, where there is only a very narrow region of α above the bifurcation value where oscillations are seen in the numerical solutions.

6 Discussion

The numerical results presented in the previous sections add to the growing body of evidence for spatiotemporal complexity in chemical systems with equal diffusion coefficients for all reacting species. They also confirm the generic nature of such responses in chemical systems for which the kinetics support oscillatory behaviour originating through supercritical Hopf bifurcations ('soft excitation'). The space-time plots shown have strong qualitative connections to the patterns reported experimentally.^{11–13}

The simplest representation of the mass transport between the Taylor–Couette cells along the reactor has been considered here through an effective diffusion coefficient which differs from the traditional coefficient only through its magnitude. Similarly, the two CSTRs at the ends of the CR are taken to be under steady state operation, imposing 'boundary conditions' on the CR: the behaviour in the reactor does not feed back to the CSTR dynamics in our model. The simple stability analysis based on a 'slow' spatial variation given in Section 3 suggests the possibility of non-trivial spatial structure developing through Hopf bifurcation along the CR axis. This analysis does not take the boundary conditions into consideration sufficiently. Comparison of Fig. 3 produced through this analysis with Fig. 5 obtained from a numerical stability analysis of the full governing equations indicates that the region of instability for the CSRT + CR system occurs in a much narrower region of the α – β parameter plane (for comparison, $3/125 = 0.024$ and $3/(125\gamma^2) = 2.4$ with $\gamma = 0.1$).

Instability does indeed arise initially through a Hopf bifurcation, but further instabilities develop. Although we have not been able to fully characterise the bifurcation sequence, it seems to have strong elements of a progression through a series of 'mixed mode' states, with each state losing stability through a period-doubling cascade. Such sequences have been studied in ordinary differential equation models of chemical systems²⁴ with the various mixed mode states shown to lie on separate 'isola' solution branches. The occurrence of mixed-mode states in reaction–diffusion systems is not uncommon, with examples in thermal flames,²⁵ isothermal chemical waves²⁶ and solid combustion,²⁷ although in those cases the instability is crucially dependent on having unequal diffusivities.

More remarkable, perhaps, are the regions in Fig. 5 and 6 for which apparently no steady state profile exists. From the change in the eigenvalues of the steady state profile at the boundary of this region (real eigenvalue passing through zero), we may presume there is a turning point in the steady state locus as α is increased or decreased along the lower or upper boundaries respectively. Further, we might conjecture that the two saddle branches have further saddle-node points leading to another branch of (possibly stable) steady states, leading to an overall 'mushroom' locus in terms of the parameters α . We have not, however, been able to follow the unstable branches using any of the standard numerical packages available, so this conjecture is, as yet, unconfirmed. If it is so, the bifurcation locus plotted against the parameter β would be of interest as it would have the character of a 'disjoint' bifurcation.²⁸

The role of the 'parameter' β is of some considerable interest. Its origin is in a perfectly sensible modification of the empirical rate law for step 1(c) in which I^- plays an inhibitory role. The original empirical form simply shows an inverse first order dependence on $[I^-]$, but such an equation would lead to an infinite rate as $[I^-]$ approaches zero. The incorporation of the extra coefficient $k_{3\gamma}$ and raising the power of the iodide ion concentration in both the numerator and denominator yields a rate that remains finite (and, in fact, tends to zero) as $[I^-]$ tends to zero, but which tends to the empirical rate law at iodide ion concentration that are high compared to $(k_{3\gamma})^{1/2}$. Although β is not a parameter that could be controlled experimentally, we have determined the effect of this parameter on the response of the system—see Fig. 5a. This calculation is worthwhile to show that the responses are not artefacts of the specific choice of β but are robust to different estimates of this parameter. In principle, one would hope to choose a sufficiently small value for $k_{3\gamma}$ such that the iodide ion concentration remains sufficiently high so this modification is not important. However, as calculations with this model here and in other scenarios show, the minimum value for $[I^-]$ is strongly determined by the choice of $k_{3\gamma}$ (i.e. the minimum is u is determined by β in dimensionless terms). Furthermore, the computed concentration shows long periods for which this concentration remains close to this minimum value. This point is revealed very clearly in the present work, with the scalings as given in eqn. (4). In previous scalings, $k_{3\gamma}$ has typically been used as the basis for the dimensionless concentrations, so its influence is only revealed when the results are cast back into dimensional form. Despite this one concern, it is clear from Fig. 5 that the complex responses reported here occur for at least a very wide range of sufficiently small β , and the near horizontal nature of the bifurcation loci on this diagram suggest that the responses persist as $\beta \rightarrow 0$ and so are in no way an artefact of this modification of the empirical rate law. It should be noted that a more recent model²⁹ for this system has been proposed and which includes the reversibility of all the reaction steps. That model generally shows qualitatively similar behaviour to the present, simpler scheme, under a variety of reactor scenarios, but avoids predicting unrealistically low iodide ion concentrations.

The Lengyel–Epstein model provides an ideal vehicle for theoretical test of various, more advanced features generic to chemical systems in the Couette reactor. Obvious extensions include allowing the CSTRs to operate in periodic mode: this provides an approach for studying the effects of forcing on spatial patterns, guiding experiments in an area considered to be of interest in biological systems. Closer matching with experiment may require the issue of feedback from the CR to the CSTRs to be addressed. There are also, several more sophisticated, but still relatively simple, representations of the fluid exchange in various regimes of Taylor–Couette flow which could be incorporated into the governing mass-balance equations. These issues are currently under consideration.

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