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Reaction-diffusion travelling waves in the acidic nitrate-ferroin reaction

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A two-variable model proposed for the acidic nitrate-ferroin reaction is considered in the reaction-diffusion context. An initial-value problem in which an amount of nitrate is introduced locally into ferroin at uniform concentration is treated both analytically and numerically. It is shown that the large time structure is a reaction-diffusion travelling wave of permanent form propagating with constant speed. This asymptotic wave speed is shown to be the minimum possible wave speed and the asymptotic approach to this value is estimated. Properties of the permanent-form travelling waves are derived and solutions valid for small and large values of a parameter β, involved in the kinetic mechanism, are obtained.

1. Introduction

In a series of recent papers [1–3], Pota and co-workers have described their work on the development of reaction-diffusion travelling waves in the acidic nitrate-ferroin reaction. In [1,3] the basic kinetic mechanism is obtained and the various appropriate simplifying assumptions and approximations detailed. This reduction leads to essentially a two-variable kinetic scheme from which a pair of reaction-diffusion equations are derived. An expression for the asymptotic wave speed of any travelling waves that may be initiated is then deduced from these equations. This theoretical value for the wave speed is then compared with their experimental results, and the two are found to be in good agreement over most of the operating range of their experiments, and certainly where the approximations made to reduce the kinetic scheme are valid. In [2] the travelling wave profiles that arise are considered further and compared with experimental observations.

In this paper we consider the reaction-diffusion system derived in [1] in more detail. This system involves, as dependent variables, the concentrations of the ferroin and acidic nitrate, which we represent by u and v respectively. We assume different diffusion coefficients, D_u and D_v respectively, for ferroin and the nitrate, previously they were assumed to be the same. We set up an initial-value problem in which it is assumed that ferroin is present at a uniform concentration u_0, with the acidic nitrate being introduced locally (which is effectively how the experiments described in [1,2] were performed). This initial-value problem is analysed in detail and it is shown that the large-time behaviour is a permanent-form travelling wave, propagating with an asymptotic wave speed which is independent of D_u, being dependent only on D_v and the kinetic mechanism.

From [1] the reaction is governed essentially by the scheme

$$NO_3^- + HNO_2 + H^+ \rightleftharpoons 2NO_2 + H_2O\,, \tag{1}$$

$$NO_2 + Fe(phen)_3^{2+} + H^+ \rightarrow HNO_2 + Fe(phen)_3^{3+}\,. \tag{2}$$

Under the assumptions that the steady state approximation can be applied to the NO_2 species and that the initial concentration of NO_3^- is very much larger than that of the ferroin, the overall rate equation is

$$r = \frac{k[HNO_2][Fe(phen)_3^{2+}]}{\bar{\beta} + [Fe(phen)_3^{2+}]}\,, \tag{3}$$

where

$$k = k_1[H^+][NO_3^-] \quad \text{and} \quad \bar{\beta} = \frac{2k_{-1}[NO_2]_{ss}}{k_2[H^+]}$$

are taken to be constant.

The distribution of u and v in space and time is then governed by the equations

$$\frac{\partial u}{\partial t} = D_u \frac{\partial^2 u}{\partial x^2} - \frac{2kuv}{\bar{\beta} + u}\,, \tag{4}$$

$$\frac{\partial v}{\partial t} = D_v \frac{\partial^2 v}{\partial x^2} + \frac{kuv}{\bar{\beta} + u}\,. \tag{5}$$

The equations are to be solved subject to the initial and boundary conditions

$$u = u_0\,, \quad t = 0\,, \quad -\infty < x < \infty\,, \tag{6}$$

$$v = \begin{cases} v_0 g(x)\,, & |x| < l\,, \\ 0\,, & |x| > l\,, \end{cases} \quad t = 0\,, \tag{7}$$

$$u \to u_0\,, \quad v \to 0 \quad \text{as} \quad |x| \to \infty\,, \quad t \geqslant 0\,, \tag{8}$$

where u_0 and v_0 are constants and $g(x)$ is continuous and differentiable on $-l < x < l$ with a maximum value of unity.

To make eqs. (4), (5) and conditions (6)–(8) dimensionless, we introduce the variables

$$u = u_0 U, \quad v = u_0 V, \quad \tau = kt \quad \text{and} \quad X = \sqrt{\frac{k}{D_v}}x. \tag{9}$$

Equations (4), (5) then become

$$\frac{\partial U}{\partial \tau} = \delta \frac{\partial^2 U}{\partial X^2} - \frac{2UV}{\beta + U}, \tag{10}$$

$$\frac{\partial V}{\partial \tau} = \frac{\partial^2 V}{\partial X^2} + \frac{UV}{\beta + U}, \tag{11}$$

where $\delta = D_u/D_v$ and $\beta = \bar{\beta}/u_0$.

The initial and boundary conditions are

$$U = 1, \quad -\infty < X < \infty, \quad \tau = 0, \tag{12}$$

and

$$V = \begin{cases} V_0 G(X), & |X| < \sigma, \\ 0, & |X| > \sigma, \end{cases} \quad \tau = 0, \tag{13}$$

$$V \to 0, \quad U \to 1 \quad \text{as} \quad |X| \to \infty \quad (\tau \geqslant 0), \tag{14}$$

where $V_0 = v_0/u_0$ and $\sigma = \sqrt{kl^2/D_v}$. The function $G(X)$ is assumed to be positive and continuous with a maximum value of unity on $|X| < \sigma$.

An important feature of the system given by (10), (11) is the initiation of reaction-diffusion travelling waves of permanent form and it is with this aspect that we start our discussion.

2. Permanent-form travelling waves

A permanent-form travelling wave (PTW) is a solution of the partial differential equations (10), (11) of the form $U = u(y)$, $V = v(y)$, where y is the travelling coordinate

$$y = X - c\tau, \quad c > 0, \tag{15}$$

i.e. $u(y)$ and $v(y)$ satisfy the ordinary differential equations

$$\delta u'' + cu' - \frac{2uv}{\beta + u} = 0, \tag{16}$$

$$v'' + cv' + \frac{uv}{\beta + u} = 0 \tag{17}$$

satisfying boundary condition (14), namely

$$u \to 1, \quad v \to 0 \quad \text{as} \quad y \to \infty. \tag{18}$$

Furthermore, for a PTW we require a solution to eqs. (16), (17) which is non-negative, non-trivial (i.e. $u \not\equiv 1$ or $v \not\equiv 0$) and for which the derivatives of u and v approach zero as $y \to \pm\infty$. We note that a PTW does satisfy initial conditions (12), (13). We start by noting:

R1. In a PTW, $u \not\equiv 1$ or $v \not\equiv 0$

Clearly, if $v \equiv 0$, eqs. (16), (18) give $u \equiv 1$, and if $u \equiv 1$, eq. (16) gives $v \equiv 0$.

R2. In a PTW, $u(y) > 0$, $v(y) > 0$ on $-\infty < y < \infty$

The proof of this result follows directly from an analogous result in Merkin et al. [4] or Billingham and Needham [5].

We can now determine the conditions as $y \to -\infty$. If we combine eqs. (16), (17), integrate once and apply boundary condition (18) we obtain

$$\delta u' + 2v' + c(u + 2v - 1) = 0. \tag{19}$$

Consequently, we must have

$$u \to 0, \quad v \to 1/2 \quad \text{or} \quad v \to 0, \quad u \to 1 \quad \text{as} \quad y \to -\infty \tag{20}$$

since, from (16), (17), $uv \to 0$ as $y \to -\infty$. Now, suppose $v \to v_s$ as $y \to -\infty$. If we apply $\int_{-\infty}^{\infty} \dots dy$ to eq. (17) and use boundary condition (18), we obtain

$$cv_s = \int_{-\infty}^{\infty} \frac{uv}{\beta + u} dy > 0 \tag{21}$$

from R2. Hence we must have, from (20, 21)

$$u \to 0, \quad v \to 1/2 \quad \text{as} \quad y \to -\infty \tag{22}$$

and this completes the description of the PTW.

We can establish the further results.

R3. In a PTW, $u(y)$ is monotone increasing and $v(y)$ is monotone decreasing

From eq. (16) we have, on multiplying by $e^{cy/\delta}$ and integrating,

$$u'(y) = \frac{2}{\delta} e^{-cy/\delta} \int_{-\infty}^{y} e^{cs/\delta} \frac{u(s)v(s)}{\beta + u(s)} ds. \tag{23}$$

From R2 it then follows that

$$u'(y) > 0 \quad \text{on} \quad -\infty < y < \infty. \tag{24}$$

In a similar way, we can also establish that

$$v'(y) = -e^{-cy} \int_{-\infty}^{y} e^{cs} \frac{uv}{\beta + u} ds, \tag{25}$$

giving

$$v'(y) < 0 \quad \text{on} \quad -\infty < y < \infty, \tag{26}$$

which establishes the result.

We also have

R4. $u + 2v > 1$ *if* $\delta < 1$, $u + 2v < 1$ *if* $\delta > 1$, $u + 2v = 1$ *if* $\delta = 1$

Put $w = u + 2v - 1$, then from eq. (19)

$$w' + cw = (1 - \delta)u'. \tag{27}$$

On multiplying eq. (27) by e^{cy}, integrating and applying boundary condition (22), we obtain

$$w(y) = (1 - \delta)e^{-cy} \int_{-\infty}^{y} e^{cs} u'(s)\, ds. \tag{28}$$

From R3 the integrand in (28) is strictly positive and the results follow.

(a) Behaviour as $y \to \infty$

The behaviour of the solution as $y \to \infty$ is determined by linearizing eq. (17) about (1, 0), the unreacted state ahead of the wave. This equation has a solution of the form $v \propto e^{\lambda y}$, where

$$\lambda = \frac{1}{2}(-c \pm \sqrt{c^2 - 4/(1 + \beta)}). \tag{29}$$

We require λ to be real otherwise negative values of v would result. Hence a necessary condition for the existence of a PTW is that $c \geqslant c_{min}$, where

$$c_{min} = 2/\sqrt{1 + \beta}. \tag{30}$$

We shall establish that any travelling waves which emerge as long-time solutions to the initial-value problem with initial data for v having compact support will travel with their minimum possible speed, i.e. their asymptotic wave speed is $c_{min} = 2/\sqrt{1 + \beta}$. In terms of the original variables this gives an asymptotic wave speed $2(ku_0 D_v)^{1/2}/\sqrt{(u_0 + \bar{\beta})}$. It is important to note that this depends only on the diffusion rate of the autocatalyst (acidic nitrate) and not on that of the ferroin.

Finally we have that

$$v \sim A_0 e^{\lambda + y} \quad \text{as} \quad y \to \infty \tag{31}$$

when $c > c_{min}$ (where λ_+ is the root associated with the positive sign in (31)) and when $c = c_{min}$, $\lambda = -c/2$ and

$$v \sim (A_0 y + B_0)e^{-y/\sqrt{1+\beta}} + \dots \quad \text{as} \quad y \to \infty \tag{32}$$

for constants A_0 and B_0.

2.1. SOLUTION FOR β LARGE

Expression (30) shows that c is $O(\beta^{-1/2})$ for β large. This suggests that to obtain a solution of eqs. (16), (17), (18) and (22) valid for β large we should put

$$c = \beta^{-1/2}\bar{c}\,, \quad Y = \beta^{-1/2}y \tag{33}$$

and leave u and v unscaled. This leads to the equations

$$\delta u'' + \bar{c}u' - \frac{2uv}{1 + u\beta^{-1}} = 0\,, \tag{34}$$

$$v'' + \bar{c}v' + \frac{uv}{1 + u\beta^{-1}} = 0 \tag{35}$$

(primes denote differentiation with respect to Y). Equations (34), (35) suggest looking for a solution by expanding

$$u(Y;\beta) = u_0(Y) + \beta^{-1}u_1(Y) + \dots\,, \tag{36}$$

$$v(Y;\beta) = v_0(Y) + \beta^{-1}v_1(Y) + \dots\,, \tag{37}$$

$$\bar{c}(\beta) = c_0 + \beta^{-1}c_1 + \dots\,. \tag{38}$$

At leading order we obtain

$$\delta u_0'' + c_0 u_0' - 2u_0 v_0 = 0\,, \tag{39}$$

$$v_0'' + c_o v_0' + u_0 v_0 = 0 \tag{40}$$

subject to

$$u_0 \to 1\,, \quad v_0 \to 0\,, \quad Y \to \infty\,, \tag{41}$$

$$u_0 \to 0\,, \quad v_0 \to 1/2\,, \quad Y \to -\infty\,. \tag{42}$$

The system (39)–(42) is essentially the same system (for quadratic autocatalysis) discussed in detail by Billingham and Needham [5] and need not be considered further. The terms of $O(\beta^{-1})$ are solvable with c_1 being determined in terms of c_0. Expansion (36)–(38) is then a regular expansion and no further regions are required. The important point to note from this analysis is that the wave speed becomes small, of $O(\beta^{-1/2})$, and the reaction region becomes large, of lateral extent $O(\beta^{1/2})$, as β increases.

2.2. SOLUTION FOR SMALL β

Putting $\beta = 0$ in eq. (17) leads to a linear equation for $v(y)$ which cannot have a solution satisfying both boundary conditions (18) and (22). Thus we expect the expansion for small β to be singular requiring the matching of inner and outer regions. We start in the inner region at the rear of the wave, where u is small, $v \simeq 1/2$ and c is O(1). A balancing of terms in eqs. (16), (17) then suggest that we write

$$u = \beta U\,, \quad \bar{y} = \beta^{-1/2} y \tag{43}$$

and leave v and c unscaled. This region is thin, having extent of $O(\beta^{1/2})$. When (43) is substituted into eqs. (16), (17), an expansion of the form

$$U(\bar{y};\beta) = U_0(\bar{y}) + \beta^{1/2} U_1(\bar{y}) + \dots\,, \tag{44}$$

$$v(\bar{y};\beta) = \tfrac{1}{2} + \beta^{1/2} v_1(\bar{y}) + \dots\,, \tag{45}$$

$$c(\beta) = c_0 + \beta^{1/2} c_1 + \dots \tag{46}$$

is suggested. At leading order we obtain the equation

$$\delta U_0'' - \frac{U_0}{1 + U_0} = 0 \tag{47}$$

subject to

$$U_0 \to 0\,, \quad \bar{y} \to -\infty\,. \tag{48}$$

Equation (47) can be integrated once to give, on applying (48) and using R3,

$$\frac{dU_0}{d\bar{y}} = \sqrt{\frac{2}{\delta}}\,[U_0 - \log(1 + U_0)]^{1/2}\,. \tag{49}$$

Equation (49) cannot be integrated further to find U_0 explicitly. However, from (49) we have that

$$U_0 \sim \frac{\bar{y}^2}{2\delta} + \dots \quad \text{as} \quad \bar{y} \to \infty\,. \tag{50}$$

At $O(\beta^{1/2})$ we obtain

$$v_1 = 0\,, \tag{51}$$

$$\delta U_1'' - \frac{U_1}{(1 + U_0)^2} = -c_0 U_0' \tag{52}$$

subject to

$$U_1 \to 0 \quad \text{as} \quad \bar{y} \to -\infty. \tag{53}$$

The details of the solution of (52), (53) are not important, we require only the behaviour as $\bar{y} \to \infty$, finding that

$$U_1 \sim -\frac{c_0}{6\delta^2}\bar{y}^3 + \dots \quad \text{as} \quad \bar{y} \to \infty. \tag{54}$$

A consideration of the terms of $O(\beta)$ shows that

$$v_2 \sim -\frac{\bar{y}^2}{4} + \dots \quad \text{as} \quad \bar{y} \to \infty. \tag{55}$$

The solution in the inner region does not satisfy the conditions at the front of the wave and a further, outer region is required in which these boundary conditions are attained. A consideration of the behaviour of u and v as $\bar{y} \to \infty$ suggests that the outer region has an extent of O(1) and that we should leave u, v and y unscaled. An expansion in powers of $\beta^{1/2}$ is then suggested, the leading order terms ($u_0(y)$, $v_0(y)$) of which satisfy

$$\delta u_0'' + c_0 u_0' - 2v_0 = 0, \tag{56}$$

$$v_0'' + c_0 v_0' + v_0 = 0 \tag{57}$$

subject to

$$u_0 \to 1, \quad v_0 \to 0 \quad \text{as} \quad y \to \infty \tag{58}$$

and, on matching with the inner region, that

$$u_0 \sim \frac{y^2}{2\delta} - \frac{c_0 y^3}{6\delta^2} \dots, \quad v_0 \sim \frac{1}{2} - \frac{y^2}{4} + \dots \quad \text{as} \quad y \to 0. \tag{59}$$

The solution of eqs. (56), (57) is readily found as

$$v_0 = \frac{1}{2(\mu_+ - \mu_-)}\left[\mu_+ e^{\mu_- y} - \mu_- e^{\mu_+ y}\right], \tag{60}$$

where $\mu_\pm = \frac{1}{2}\left(-c_0 \pm \sqrt{(c_0^2 - 4)}\right)$, $(0 > \mu_+ > \mu_-)$ together with a somewhat more complicated solution for $u_0(y)$. In the special case when $c_0 = 2$ (equal roots or minimum speed case) we obtain

$$v_0 = \tfrac{1}{2}(1 + y)e^{-y}, \tag{61}$$

$$u_0 = 1 + \frac{1}{(\delta - 2)^2}\left([(\delta - 2)y + (3\delta - 4)]e^{-y} - \delta(\delta - 1)e^{-2y/\delta}\right) \tag{62}$$

for $\delta \neq 2$, and when $\delta = 2$

$$u_0 = 1 - (1 + y + y^2/4)e^{-y}. \tag{63}$$

The structure of the PTW for β small is now clear. At the rear of the wave the concentration u rises rapidly, over a region of $O(\beta^{1/2})$ thickness, from its fully reacted state, while v remains virtually constant. Ahead of this region, the concentration v falls slowly, over a region of O(1) thickness, to its unreacted state, while u slowly attains its value ahead of the wave.

2.3. NUMERICAL RESULTS

We solved eqs. (16), (17) numerically for a range of values of β and δ, throughout we took the minimum wave speed, as given by (30). The results (concentration profiles for u and v) are shown in figs. 1 and 2.

We started by considering the effect of varying β while keeping δ fixed. In figure 1a, we show concentration profiles for the case $\delta = 1$, $\beta = 1$. Note that the spread of u and v from their asymptotic values are comparable in extent. We next took $\delta = 1$ and $\beta = 10$. Here we again see that u and v to have comparable reaction zones, but now, from (33) we expect this region to be more spread out than that for the case $\beta = 1$, as is seen in fig. 1(b).

For small values of β we expect a double-region structure to develop along the lines of the analysis described in the previous section. This can be seen in figure 1c (for $\beta = 0.01$ and $\delta = 1$).

We next explored the change in structure as δ is varied. The results are shown in fig. 2(a), (for $\delta = 10$) and figure 2b (for $\delta = 0.1$), in both cases $\beta = 1$, to compare with fig. 1(a). From R4 $u + 2v > 1$ or < 1 depending on whether $\delta < 1$ or $\delta > 1$, which can be seem to be the case in figs. 2(a) and 2(b). Also, we see that the reaction region becomes more spread out as δ is increased.

3. Initial-value problem

3.1. A PRIORI BOUNDS

It is straightforward to show, using standard results, given, for example, by Britten [6], that

$$U(X,\tau) \geqslant 0\,, \quad V(X,\tau) \geqslant 0 \quad \text{for} \quad -\infty < X < \infty\,, \quad \tau \geqslant 0\,. \tag{64}$$

We can then use (64) to show that $\bar{U} \equiv 1$ is a supersolution for eq. (10) and establish that [6]

$$0 \leqslant U(X,\tau) \leqslant 1\,, \quad -\infty < X < \infty\,, \quad \tau \geqslant 0\,. \tag{65}$$

We are unable to derive an upper bound on V for general values of δ. However, for the special case $\delta = 1$, we have that $W = U + V$ satisfies the diffusion equation on $-\infty < X < \infty$, $\tau \geqslant 0$, subject to

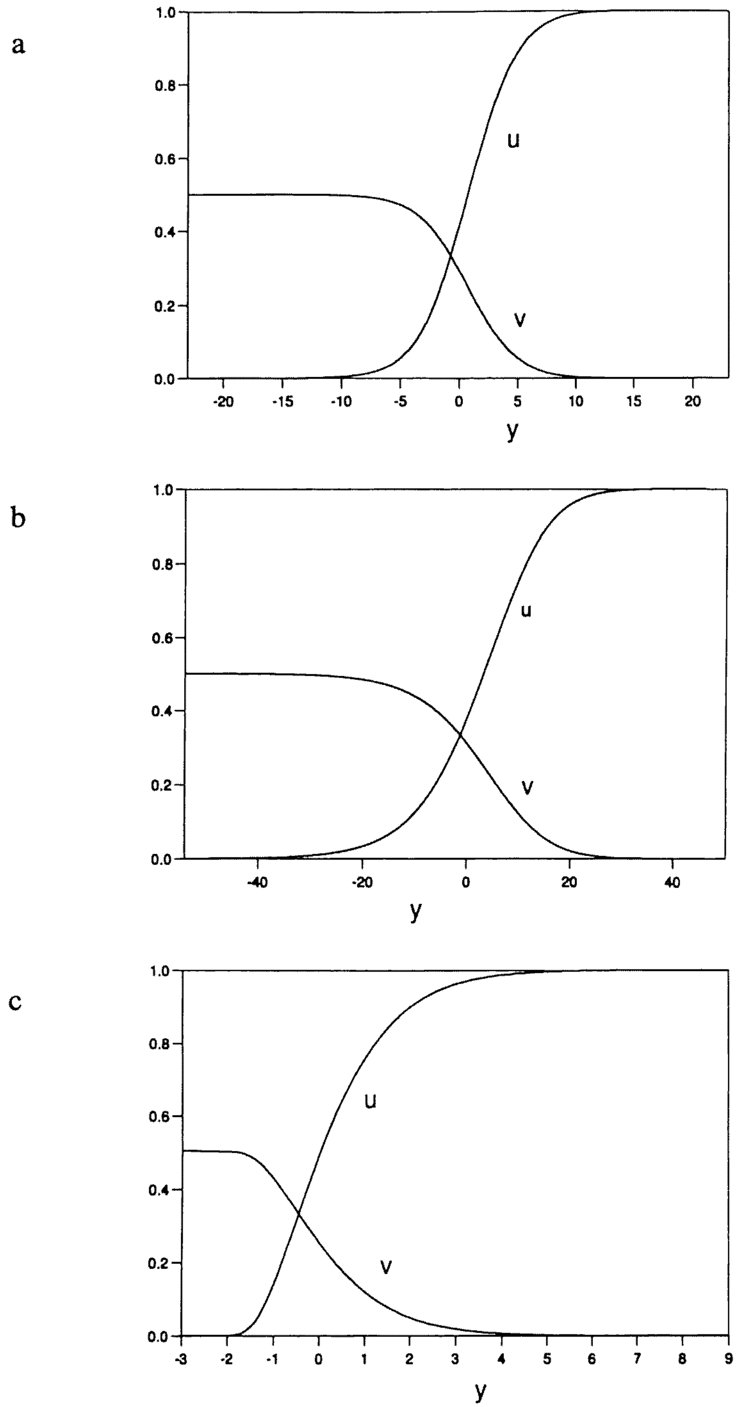

Fig. 1. Concentration profiles, $u(y)$, $v(y)$, obtained from solving eqs. (16), (17) numerically for the minimum speed wave (c given by (32)) for $\delta = 1.0$ and (a) $\beta = 1.0$, (b) $\beta = 10.0$, (c) $\beta = 0.01$.

a

b

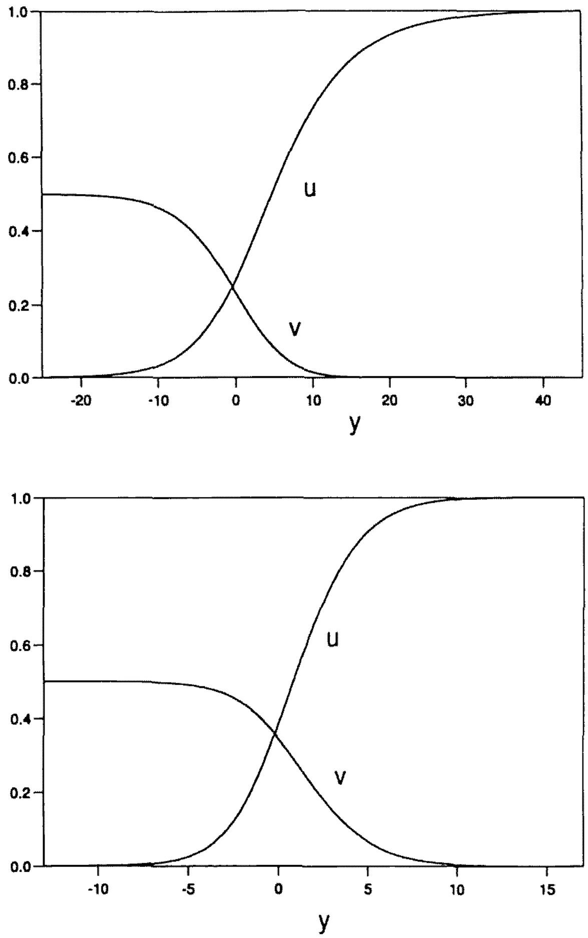

Fig. 2. Concentration profiles, $u(y)$, $v(y)$, obtained from solving eqs. (16), (17) numerically for the minimum speed wave (c given by (32)) for $\beta = 1.0$ and (a) $\delta = 10.0$, (b) $\delta = 0.1$.

$$W(X,0) = 1 + V_0 g(X)\,, \quad -\infty < X < \infty\,, \tag{66}$$

$$W \to 1 \quad \text{as} \quad |X| \to \infty\,, \quad \tau \geqslant 0\,. \tag{67}$$

From the maximum principle for the diffusion equation, we have

$$W(X,\tau) \leqslant 1 + V_0\,, \quad -\infty < X < \infty\,, \quad \tau \geqslant 0\,. \tag{68}$$

It then follows from (65) that, for $\delta = 1$,

$$0 \leqslant V(X,\tau) \leqslant 1 + V_0\,, \quad -\infty < X < \infty\,, \quad \tau \geqslant 0\,. \tag{69}$$

The existence of the invariant rectangle for $U(X, \tau)$, $V(X, \tau)$, given by (65), (69) guarantees the existence of a unique global solution, Smoller [7]. We expect a similar result to hold for $\delta \neq 1$, but are unable to establish it rigorously.

3.2. ASYMPTOTIC ANALYSIS

An asymptotic theory can be developed for initial-value problem (10)–(14) which follows closely that described previously for a similar problem by Billingham and Needham [8] and used to discuss a somewhat different reaction-diffusion problem by Needham et al. [9]. This starts with a solution for τ small, which is then matched to a solution valid for X large and τ of O(1). Finally, this solution is then matched to a solution valid for τ large. It is shown in [8] that the initial development has the Gaussian form, typical of solutions of the diffusion equation on a semi-infinite domain, and that to obtain a solution, valid for X large and τ of O(1), for initial data of the form given by (13), (i.e. having compact support), we should put

$$U = 1 + o(1)\,, \quad V = e^{-X^2\psi(X,\tau)}\,, \tag{70}$$

where $\psi(X,\tau)$ is positive as $X \to \infty$.

When (70) is substituted into eq. (11) an equation for ψ results, a solution of which is sought by expanding, (following [8])

$$\psi(X,\tau) = \psi_0(\tau) + X^{-1}\psi_1(\tau) + X^{-2}\psi_2(\tau) + \dots\,. \tag{71}$$

After a little algebra the equations for the ψ_i $(i = 0,\ 1,\ 2\dots)$ can be solved in turn to get

$$\psi_0 = \frac{1}{4\tau}\,, \quad \psi_1 = \frac{a_1}{2\tau}\,, \quad \psi_2 = -\frac{\tau}{1+\beta} + \frac{1}{2}\log\tau + \frac{a_1^2}{4\tau} - \log a_2 \tag{72}$$

for constants a_1 and a_2. From (70)–(72) it then follows that

$$V \sim a_2 \exp\left[-\frac{(X+a_1)^2}{4\tau} - \tfrac{1}{2}\log\tau + \frac{\tau}{1+\beta}\right] \quad \text{as} \quad X \to \infty\,, \quad \tau \text{ of O}(1)\,. \tag{73}$$

Expression (73) suggests that a travelling wave evolves for τ large with a propagation speed $2/(\sqrt{1+\beta}) + \mathrm{O}(\tau^{-1})$, which will be confirmed below.

As $\tau \to \infty$, expansion (71), (72) remains uniform for $X >> \tau$, but becomes non-uniform when $X \sim \tau$. This suggests that to obtain a solution valid for τ large, we should start by introducing the travelling co-ordinate

$$y = X - S(\tau)\,, \tag{74}$$

where $S(\tau)$ is $\mathrm{O}(\tau)$ as $\tau \to \infty$, and leave U and V unscaled. This results in the equations

$$\delta\frac{\partial^2 U}{\partial y^2} + \frac{dS}{d\tau}\frac{\partial U}{\partial y} - \frac{2UV}{\beta + U} = \frac{\partial U}{\partial \tau}\,, \tag{75}$$

$$\frac{\partial^2 V}{\partial y^2} + \frac{dS}{d\tau}\frac{\partial V}{\partial y} + \frac{UV}{\beta + U} = \frac{\partial V}{\partial \tau} . \tag{76}$$

A solution of eqs. (75), (76) is sought by expanding

$$U = u_0 + \tau^{-1/2} u_1 + \tau^{-1} u_2 + \dots ,$$

$$V = v_0 + \tau^{-1/2} v_1 + \tau^{-1} v_2 + \dots , \tag{77}$$

$$S = c_0 \tau + c_1 \log \tau + \dots .$$

The leading order problem is just the permanent-form travelling wave equations (16), (17) discussed in the previous section. At $O(\tau^{-1/2})$ we obtain

$$u_1 = b_1 u_0' , \quad v_1 = b_1 v_0' \tag{78}$$

for any constant b_1. At $O(\tau^{-1})$ we obtain equations, the solution of which can be expressed in terms of (u_0, v_0). The details are not important, we note only that, as $y \to \infty$,

$$v_2 \sim -\frac{c_1 A_0 \lambda_+}{2 + c_0} y e^{\lambda_+ y} + \dots \tag{79}$$

when $c > c_{min}$, on using the asymptotic form for $v_0(y)$ given by (31), and

$$v_2 \sim c_1 \left[\frac{A_0 y^3}{6\sqrt{1+\beta}} + \left(\frac{B_0}{\sqrt{1+\beta}} - A_0 \right) \frac{y^2}{2} + \dots \right] \exp(-y/\sqrt{1+\beta}) \tag{80}$$

when $c = c_{min}$, on using (32).

Now the present solution has to match with (73) as $y \to \infty$. If we write the exponent in (73) in terms of y, using (74) and expand $S(\tau)$ using (77), we find that this is possible only if

$$\frac{c_0^2}{4} = \frac{1}{1+\beta} \quad \text{i.e.} \quad c_0 = \frac{2}{\sqrt{1+\beta}} = c_{min} .$$

From this we can deduce that, for initial data for V with compact support, the permanent-form travelling wave which emerges as the long time solution of the initial-value problem will travel with its minimum possible speed.

We now proceed with our asymptotic analysis with $c_0 = c_{min}$, when the asymptotic forms for v_0, v_1 and v_2 are given by (32) and (80). We can see that, in this case, expansion (77) becomes non-uniform when y is $O(\tau^{1/2})$ for τ large, and a further region is required in which we write

$$U = 1 + o(1) , \quad V = \tau^{1/2} e^{-c_0 y/2} F(\eta, \tau) , \quad \eta = y/\tau^{1/2} , \tag{81}$$

where $c_0 = 2/(\sqrt{1+\beta})$. On substituting transformation (81) into eq. (76) we obtain, on neglecting exponentially small terms,

$$\frac{1}{2}\left(\frac{4}{1+\beta}-c_0\frac{dS}{d\tau}\right)F+\tau^{-1/2}\left(\frac{dS}{d\tau}-c_0\right)\frac{\partial F}{\partial\eta}$$
$$+\tau^{-1}\left(\frac{\partial^2 F}{\partial\eta^2}+\frac{\eta}{2}\frac{\partial F}{\partial\eta}-\frac{1}{2}F-\tau\frac{\partial F}{\partial\tau}\right)=0\,, \qquad (82)$$

which has to be solved subject to matching with the asymptotic forms for v_0, v_1, $v_2\dots$ as $\eta\to 0$. Equation (82) suggests looking for a solution by expanding

$$F(\eta,\tau)=F_0(\eta)+\tau^{-1/2}F_1(\eta)+\dots \qquad (83)$$

together with expansion (77) for $S(\tau)$.

At leading order, we obtain

$$F_0''+\frac{\eta}{2}F_0'-\left(\frac{1}{2}+\frac{c_0c_1}{2}\right)F_0=0 \qquad (84)$$

subject to

$$F_0\sim A_0\eta+\frac{c_1A_0}{6\sqrt{1+\beta}}\eta^3+\dots \quad \text{as} \quad \eta\to 0\,. \qquad (85)$$

The solution to eq. (84) satisfying (85) can be expressed in terms of confluent hypergeometric functions, [10] as

$$F_0=A_0\eta e^{-\eta^2/4}{}_1F_1\left(\frac{3}{2}+\frac{c_0c_1}{2};\frac{3}{2};\frac{\eta^2}{4}\right). \qquad (86)$$

This solution is only algebraic for η large, and thus violates the asymptotic form (73), unless the series given in (86) terminates which requires $3/2+c_0c_1/2$ to be zero or a negative integer. However in this latter case the solution has ranges of η over which F_0 is negative, unless $3+c_0c_1=0$, giving finally

$$c_1=-\frac{3\sqrt{1+\beta}}{2}\,,\quad F_0=A_0\eta e^{-\eta^2/4}\,. \qquad (87)$$

The solution to equation for F_1, the term of $O(\tau^{-1/2})$, follows very closely the analogous equation given in [8]. The details are not important, only to note that this determines the constant b_1.

The analysis presented above shows that for τ large a travelling wave structure evolves propagating with speed given by

$$\dot{S}\sim\frac{1}{\sqrt{1+\beta}}\left(2-\frac{3(1+\beta)}{2\tau}+\dots\right) \quad \text{as} \quad \tau\to\infty\,. \qquad (88)$$

Expression (88) shows that, though ultimately the wave will propagate with its minimum possible speed as given by (30), the approach to its asymptotic value is relatively slow, being only of $O(\tau^{-1})$ for τ large.

To confirm the above predictions, as well as giving results where the asymptotic theory does not hold, we go on to describe results obtained from numerical integrations of the initial-value problem.

3.3. NUMERICAL RESULTS

Initial-value problem (10)–(14) was solved numerically using essentially the same scheme described in Merkin and Needham [11]. This method is effectively a Crank–Nicolson method using Newton–Raphson iteration to solve the sets of non-linear algebraic equations which arise at each time step. From the numerical integrations, which give concentration profiles at equal steps in X at each time step, we calculated the position of the reaction-diffusion front, which we took to be at that value of X at which $U = 1/2$. This was done using interpolation on the nearest calculated values to this point. This then enabled us to calculate the speed of the travelling front, using central differences.

We started by considering different values of δ for a given value of β. The results for $\beta = 1.0$ and $\delta = 0.1, 1.0$ and 10.0 are shown in figure 3, where we plot the calculated wave speed c against τ. We can see that all three curves are approaching the same constant value of $\sqrt{2}$, as predicted by the theory, confirming that the asymptotic wave speed is c_{min}, independent of the value of δ. We also note from this figure that the approach to this asymptotic value is rather slow, again as suggested by (88). We also monitored the wave profiles for large values of τ and these were seen to be identical to those shown in figures 1 and 2.

We next considered the effects of changing β for a given value of δ. We took $\delta = 1.0$ and obtained results for $\beta = 10.0, 1.0$, and 0.1. The results are shown in figure 4, where we plot the wave speed c against τ for these different cases (the results for $\beta = 1.0$ have already been given in fig. 3). Again these figures show that, for τ

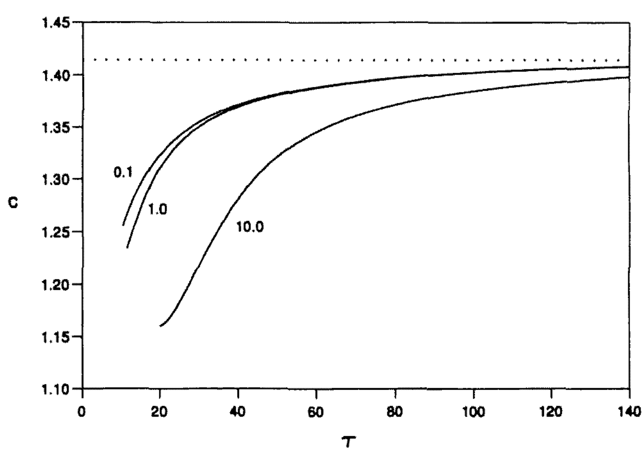

Fig. 3. Wave speed c calculated from the numerical solution of the initial-value problem for $\beta = 1.0$ and $\delta = 0.1, 1.0$ and 10.0.

large, the wave speed approaches c_{min}, which now depends on the value of β, and that the approach to this asymptotic value is rather slow, in line with (88). Note that expression (88) also suggests that the rate of approach of c to c_{min} should decrease as β is increased, as is confirmed by the results shown in fig. 4.

Finally, we monitored the development of the travelling wave profiles from the initial input. The results are shown in fig. 5, for $\beta = 0.5$, $\delta = 1.0$ (though all the other cases we considered have a very similar behaviour) where we plot U and V concentration profiles against X at equal time intervals $\Delta\tau$. In fig. 5(a) ($\Delta\tau = 3.84$) we show initial development of a reaction-diffusion travelling wave in U caused by the local input of V. The first profile plotted (at $\tau = 0.322$) shows a small depletion of U. This deficit in U then increases (by reaction) and spreads (by

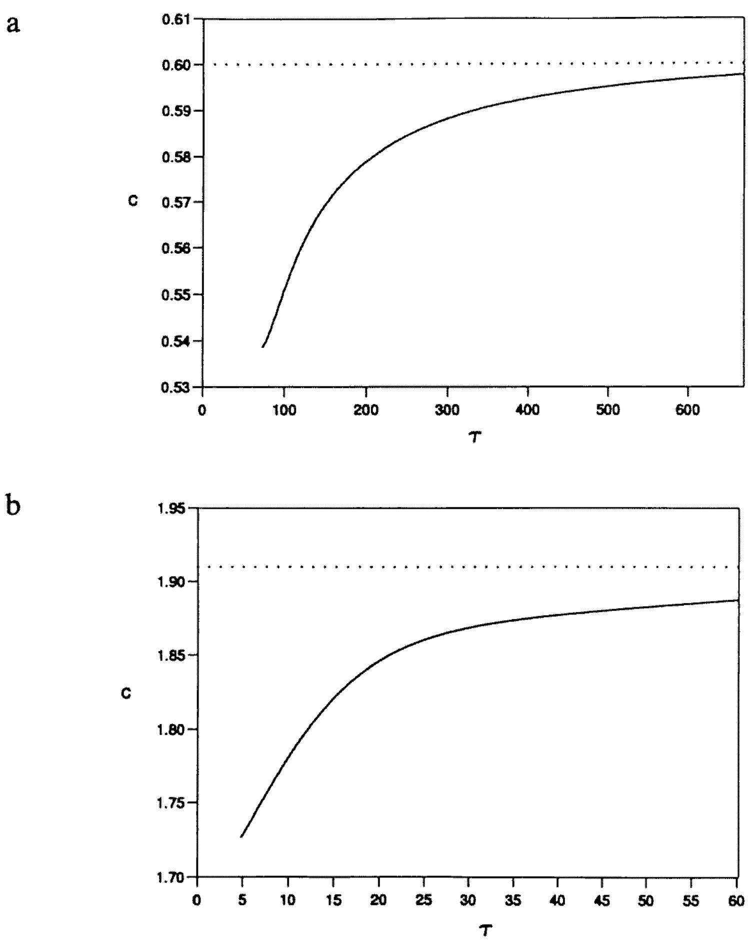

Fig. 4. Wave speed c calculated from the numerical solution of the initial-value problem for $\delta = 1.0$ and (a) $\beta = 10.0$, (b) $\beta = 0.1$.

a

b

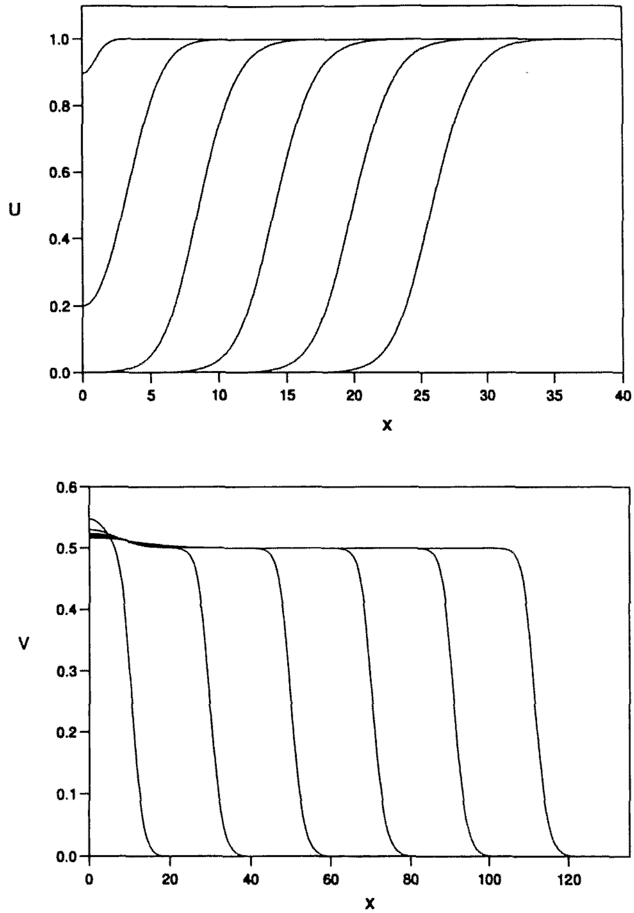

Fig. 5. Concentration profiles U and V plotted at equal time intervals $\Delta\tau$. (a) U profiles, with $\Delta\tau = 3.84$, showing the initial development of the PTW, and (b) V profiles with $\Delta\tau = 12.8$.

diffusion) as τ increases with a travelling wave of permanent form becoming established. This development is more clearly seen in fig. 5(b) where we plot V profiles at longer times ($\Delta\tau = 12.8$). Figure 5(b) shows that an excess in autocatalyst concentration is left behind near the origin due to the initial input. This decays slowly with a slightly increasing spread through purely diffusive effects (here the concentration U is effectively zero). For large times the reaction-diffusion front has become clearly separated from this local diffusive region.

An important feature to note about these concentration profiles is that they appear to attain a permanent-form somewhat more readily than calculations of the wave speed would suggest. This means that the wave profiles have reached the form as given by the solution of the PTW equations (16), (17) at times considerably shorter than is required for c to reach a value of c_{min}.

4. Discussion

We have established that when the acidic nitrate is introduced locally into an otherwise uniform concentration of the other chemical species (notably the ferroin), which react via kinetic scheme (1), (2), the resulting large time structure is a reaction-diffusion travelling wave of permanent form. This wave travels with its minimum possible speed, c_{min}, which, in dimensional terms, is given by

$$\frac{2(ku_0 D_v)^{1/2}}{\sqrt{(u_0+\bar{\beta})}}, \tag{89}$$

where k and $\bar{\beta}$ depend on the details of the kinetics and u_0 is the initial (uniform) concentration of ferroin.

There are two features worth noting about expression (89). Firstly, it is independent of D_u, the diffusion coefficient of the ferroin, and involves only D_v, the diffusion coefficient of the acidic nitrate. Consequently, only values of D_v are required in establishing agreement between experimental and theoretically calculated values of the wave speed. Conversely, if the measurements taken from travelling wave speeds as in the experiments described by Pota et al. [1–3] are to be used to find diffusion coefficients, only values of D_v are accessible by this route. Secondly, the asymptotic wave speed depends on the initial ferroin concentration, and increases from zero (when $u_0 = 0$) monotonically to an upper limit of $2(kD_v)^{1/2}$ as $u_0 \to \infty$. It is also worth noting that the maximum sensitivity of wave speed (89) to changes in u_0 occurs when $u_0 = \frac{1}{2}\bar{\beta}$.

We have also shown that the minimum wave speed is attained only asymptotically and must be regarded as the large time limit. Moreover, we have shown that this asymptotic value is approached only slowly, the perturbation to it being only algebraic in t (of $O(t^{-1})$) for t large. This could well have important consequences in the treatment of experimental observations, which, of necessity, are taken at finite times. Even though these times will generally be large, there could still be a difference between the asymptotic wave speed and the experimentally measured wave speed. This difference could well lead to small, though significant, errors if calculations are performed, or agreement between theory and experiment is sought, using the asymptotic wave speed (89).

When we considered the travelling wave profiles, their asymptotic forms (PTW) were seen to be attained at much shorter times. To illustrate this we observed that, even though there could still be a significant difference (of the order of 5–10%) between the calculated and asymptotic wave speeds, the PTW structure had been attained to within the overall accuracy of the numerical integrations by these times. This suggests that the effects of diffusion and reaction interact over relatively short time scales to produce their ultimate reaction-diffusion front structure and that much longer times have to elapse to allow this front to accelerate slowly to reach its asymptotic speed. As a consequence, experimental measurements taken from the reaction-diffusion wave structures should be in much better agreement with their theoretically calculated counterparts and, perhaps, from a more reliable guide to correlations between theory and experiment.

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