

The effect of an electric field on reaction fronts in autocatalytic systems

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Received 5 May 2005; revised 2 June 2005

The effects of applying a constant electric field E to an ionic autocatalytic reaction with a general power p ($p \geq 1$) are discussed through a consideration of the equations for the corresponding travelling waves. It is shown that, when the ratio of diffusion coefficients D of autocatalyst and substrate is less than some value D_0 (which depends on p), the effect of a negative electric field is to increase the wave speed of the reaction front over its field-free value. This is in contrast to previous results for cubic autocatalysis ($p = 2$) [J.H. Merkin and H. Ševčíková. *J. Math. Chem.* 25 (1999) 111.] for $D > D_0$, where the effect is to decrease the wave speed. This feature, seen in the numerical solutions of the travelling wave equations, is confirmed by an expansion for small E and in an asymptotic analysis for p large.

KEY WORDS: reaction–diffusion fronts, autocatalytic reactions, electric field effects, range of existence

AMS subject classification: 35K57, 35B35, 74J30

1. Introduction

Much of the previous work on the effects that electric fields have on reaction fronts in ionic autocatalytic systems has been concerned with quadratic autocatalysis, see [1]–[6] for example. In this somewhat special case (and perhaps degenerate case, see [7] and the full discussion on fractional orders of autocatalysis in [8]), the wave speed can be found explicitly and hence the conditions for the existence of a reaction front can be established in terms of the (dimensionless) electric field strength E and D , the ratio of the diffusion coefficients of autocatalyst and substrate, see particularly [2]. This analysis is based on waves which have the their “minimum possible” or “linearly determined” speed. It is these waves that evolve as the large time solutions in the numerical simulations for localised initiation. This is not the case when effects of a complexing agent (e.g., starch) are included, in this case waves with speeds faster than those with the linearly determined speed can arise as the large time solutions [9, 10]. When conditions on D and E are such that travelling wave solutions do not exist,

the complete electrophoretic separation of the reaction species is observed in the numerical simulations, see [1,2].

Previous work on higher-order autocatalysis is much more limited. A previous study [11] for cubic autocatalysis has shown that the wave speed has to be determined numerically from the travelling wave equations, at least for $D \neq 1$, and that there are distinct differences in the behaviour of solution between the cases $D > 1$ and $D < 1$. For $D < 1$, there is a positive upper bound on E for the existence of travelling wave solutions, with these existing for all negative E . The opposite is the case for $D > 1$, here there is a negative lower bound on E for waves to exist, with waves existing for all positive electric field strengths. Outside these ranges electrophoretic separation of the reacting species is seen. An important feature of the wave speeds for quadratic autocatalysis and for the specific results given in [11] is that a positive field, in the sense that the ionic species are propagating towards an electrode of the opposite polarity, increases the wave speed over what it would be in field-free conditions, with the converse being the case in a negative field. This is generally accepted as being "intuitively obvious" for these simple systems; the electrode, depending on its polarity, either enhances or reduces transport in the direction of propagation. However, we find that this is not always the case, for values of D sufficiently less than unity (in fact not much less than the value $D = 0.5$ used in [11]) the electric field has a counter-intuitive effect. A negative field, in the sense described above, increases the wave speed and a positive field reduces it, at least for moderate field strengths.

To demonstrate this, perhaps unexpected, result is the main purpose of this paper. To do so we consider a general order for the autocatalytic reaction



where assume that $p \geq 1$ and where a and b are the concentrations of substrate A and autocatalyst B and k_0 is a constant. The dimensionless travelling wave equations corresponding to equation (1) are, see [11] for example,

$$a'' + (c - E)a' - ab^p = 0, \quad (2)$$

$$Db'' + (c - DE)b' + ab^p = 0 \quad (3)$$

(primes denote differentiation with respect to the travelling co-ordinate y). In equations (2 and 3) $c(>0)$ is the (constant) wave speed, $D = D_B/D_A$ is the ratio of the diffusion coefficients of reactant species B and A and E is the (dimensionless) electric field strength. Equations (2 and 3) are subject to the boundary conditions

$$a \rightarrow 1, b \rightarrow 0 \quad \text{as } y \rightarrow \infty, \quad a \rightarrow 0, b \rightarrow b_s \quad \text{as } y \rightarrow -\infty \quad (4)$$

where b_s is a constant to be determined, in general $b_s \neq 1$.

Equations (2 and 3) are based on the high ionic strength approximation normally used in this context, see [2] for a formal justification for making this approximation. The electric field depends on the concentrations of all the ionic species present. Usually experiments are performed with the reactants dissolved at relatively small concentrations in water, so that the reactant species have concentrations which are then small relative the other ionic species present (usually arising from the dissociation of water). This means that, to a good approximation, we can regard the electric field as a constant. A case when this assumption is not made (and a more general derivation of the travelling wave equations for reaction fronts in ionic systems) and in which the applied electric current is taken as constant with the electric field varying with the concentrations of the reacting species, has been discussed in [12, 1]. We start by giving some general properties that can be derived directly from equations (2–4).

2. General results

If we add equations (2 and 3), integrate and apply the boundary conditions as $y \rightarrow \infty$, we obtain

$$a' + (c - E)(a - 1) + Db' + (c - DE)b = 0 \tag{5}$$

from which it follows, on letting $y \rightarrow -\infty$, that

$$b_s = 1 + \frac{(D - 1)E}{c - DE}. \tag{6}$$

This gives a relationship between b_s and c for general orders of autocatalysis p and shows, for $D \neq 1, E \neq 0$, that $b_s \neq 1$. The wave speed c has to be determined from equations (2 and 3). However, for quadratic autocatalysis ($p = 1$), equation (3) gives, on linearising about $a = 1, b = 0$, a “minimum possible” wave speed

$$c = 2\sqrt{D} + DE \tag{7}$$

Expression (7) can then be applied in (6) and the conditions for a “linearly determined” wave established, requiring $b_s > 0$, as

$$E < \frac{2\sqrt{D}}{(1 - D)}, \quad (D < 1) \quad \text{or} \quad E > -\frac{2\sqrt{D}}{(D - 1)}, \quad (D > 1) \tag{8}$$

From (6) (or (8)), it is clear that $D = 1$ is a special case, which we now consider.

$D = 1, D_A = D_B$. In this case we can use expression (5) to show that $a + b = 1$ for all y , so that $b_s = 1$ (as confirmed by (6)). Equations (2–4) can then be reduced to

$$b'' + (c - E)b' + (1 - b)b^p = 0, \quad b \rightarrow 0 \quad \text{as } y \rightarrow \infty, \quad b \rightarrow 1 \quad \text{as } y \rightarrow -\infty \tag{9}$$

The solution to problem (9) is essentially independent of the electric field strength E , in the sense that, if we solve the problem in the field-free $E = 0$ case to obtain a wave speed c_0 (say), the wave speed (and the solution in general) is obtained from this one just by replacing c_0 by $c - E$. Thus, when $D = 1$ (equal diffusion coefficients), the effect of the electric field is only to increase ($E > 0$) or to decrease ($E < 0$) the wave speed by an amount $|E|$ without changing the wave profile. A plot of c_0 (or $c - E$) against p is shown in figure 1. The figure shows the singularity in the solution as $p \rightarrow 1$ derived in [7] and has the asymptotic form $c \sim \sqrt{2}/p$ for p large [13].

The above discussion shows that, at a field strength $E = -c_0$, the wave will become steady and will propagate in the negative direction if $E < -c_0$. We can extend this result for steady waves to the general case, and from now on we will assume that $D \neq 1$.

Steady waves. These are waves for which $c = 0$, i.e., have been brought to rest by the applied electric field. Suppose this occurs at a field strength $E = E_0$, from equations (2 and 3), $E_0 < 0$. Hence E_0 is determined by solving equations (2–4) with c put to zero. Note that, in this case, expression (6) gives $b_s = D^{-1}$, suggesting a transformation (see also [11])

$$b = D^{-1}\bar{b}, \quad \bar{y} = D^{-\frac{p}{2}}y, \quad E_0 = D^{-\frac{p}{2}}\bar{E}_0 \quad (10)$$

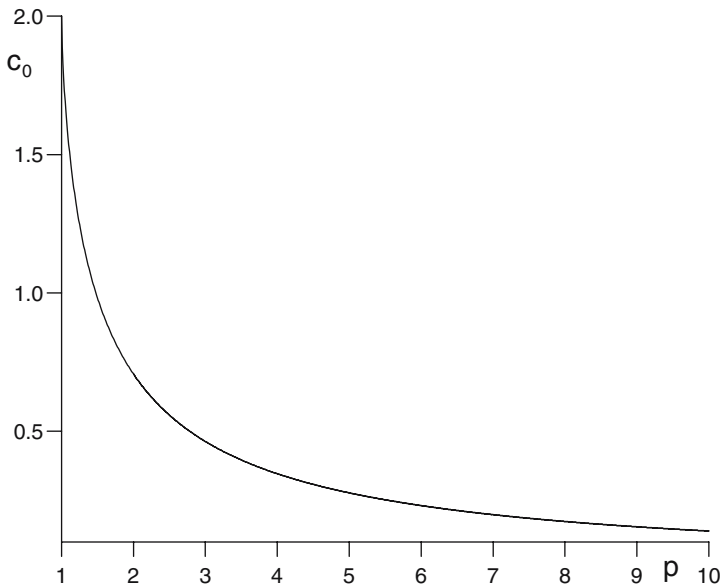


Figure 1. The wave speed c_0 for field-free conditions ($E = 0$) and equal diffusivities ($D = 1$), as given by (9) plotted against the order of autocatalysis p . The application of an electric field is to change the wave speed to $c_0 + E$.

Applying (10) in the original equations (2,3) with $c = 0$ gives

$$\begin{aligned}
 a'' - \bar{E}_0 a' - a\bar{b}^p &= 0, & \bar{b}'' - \bar{E}_0 \bar{b}' + a\bar{b}^p &= 0 \\
 a \rightarrow 1, \bar{b} \rightarrow 0 & \text{ as } \bar{y} \rightarrow \infty, & a \rightarrow 0, \bar{b} \rightarrow 1 & \text{ as } \bar{y} \rightarrow -\infty
 \end{aligned}
 \tag{11}$$

(In (11) primes denote differentiation with respect to \bar{y} .) Problem (11) is, in effect, problem (9) for the case when $D = 1$. Thus we have $\bar{E}_0 = -c_0$ or

$$E_0 = -c_0 D^{-\frac{p}{2}} \tag{12}$$

where c_0 is the field-free wave speed for $D = 1$.

We now consider the solution to the travelling wave equations (2–4) in more detail.

2.1. Travelling waves

In general, equations (2–4) have to be solved numerically, with the solution determining the wave speed c in terms of D , the electric field strength E and the order of the autocatalysis p (as well as determining the corresponding wave profiles). Results for cubic autocatalysis ($p = 2$) have already been given in [11] for $D = 2.0$ and $D = 0.5$ and here we concentrate on smaller values of D . Results, wave speed c plotted against E , are shown in figure 2a for $D = 0.1$. As in [11] for $D = 0.5$, there is a (positive) upper bound E_c on E for the existence of a solution, with two solution branches for $0 < E < E_c$. This can be seen more easily in figure 2b, where we re-plot the results shown in figure 2a for small values of E to highlight this behaviour. In this case $E_c = 0.0321$, a relatively small value compared to that seen in [11] for $D = 0.5$. However, there is an important difference between the results shown in figure 2a with those in [11], in that here the wave speed *increases* for negative E , whereas in [11] it *decreased*. This can, perhaps, be more easily seen in figure 2b. Figure 2a shows that, for $D = 0.1$, the maximum value of the wave speed $c = 0.244$ is achieved with $E = -1.5$. So that for this value of D , a wave can travel *faster* in a negative field than it does in field-free conditions. In fact, speeds of up to three times the field-free value can be achieved in the appropriate negative fields.

To examine this point further, we now construct a solution to the travelling wave equations (2–4) valid for small E . We look for a solution by expanding

$$\begin{aligned}
 a(y; E) &= a_0(y) + E a_1(y) + \dots, & b(y; E) &= b_0(y) + E b_1(y) + \dots, \\
 c(E) &= c_0 + E c_1 + \dots
 \end{aligned}
 \tag{13}$$

At leading order we obtain the equations for the field-free case

$$\begin{aligned}
 a_0'' + c_0 a_0' - a_0 b_0^p &= 0, & D b_0'' + c_0 b_0' + a_0 b_0^p &= 0 \\
 a_0 \rightarrow 1, b_0 \rightarrow 0 & \text{ as } y \rightarrow \infty, & a_0 \rightarrow 0, b_0 \rightarrow 1 & \text{ as } y \rightarrow -\infty
 \end{aligned}
 \tag{14}$$

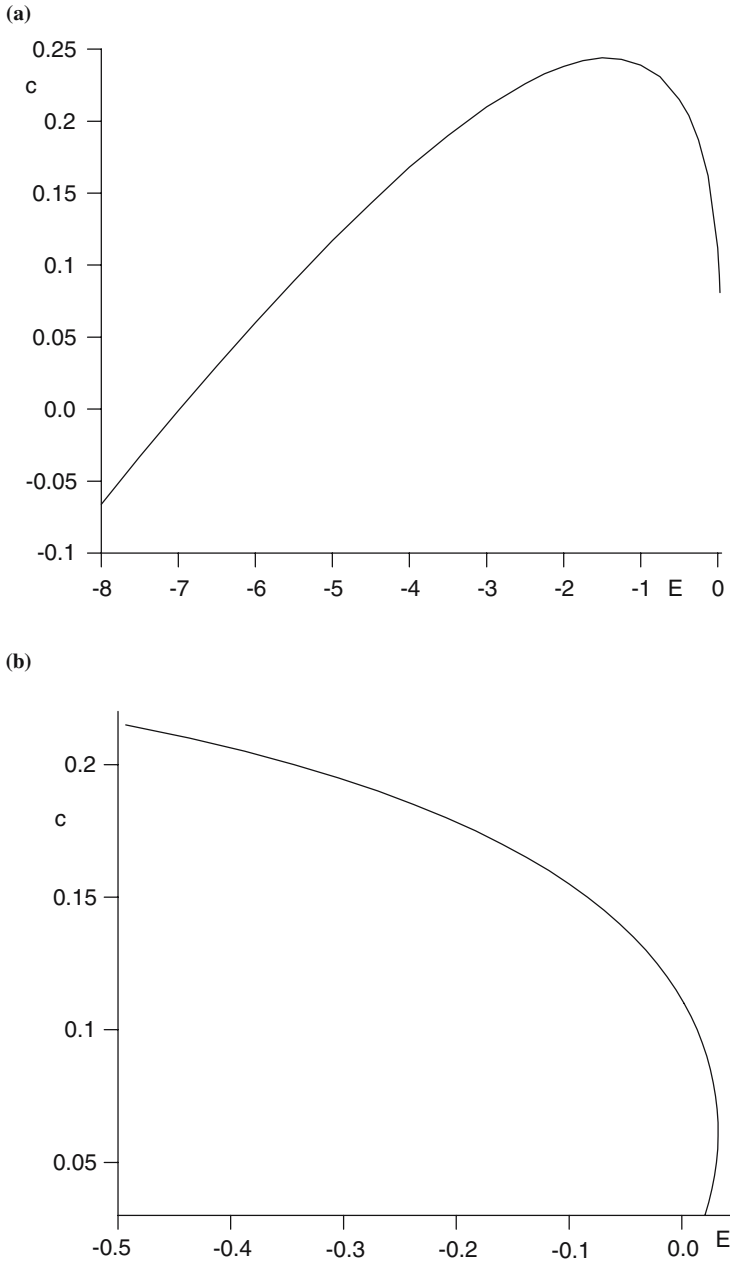


Figure 2. (a) The wave speed c of the reaction fronts for cubic autocatalysis ($p = 2$), as given by (2–4), plotted against E for $D = 0.1$, showing the increase in wave speeds in negative fields. (b) Wave speeds for smaller values of E , showing the multiple solutions for $0 < E < E_c$ and no solutions for $E > E_c$, with $E_c = 0.0321$ for $D = 0.1$.

At $O(E)$ we have

$$\begin{aligned} a_1'' + c_0 a_1' - b_0^p a_1 - p a_0 b_0^{p-1} b_1 &= (1 - c_1) a_0' \\ D b_1'' + c_0 b_1' + b_0^p a_1 + p a_0 b_0^{p-1} b_1 &= (D - c_1) b_0' \end{aligned} \tag{15}$$

$$a_1, b_1 \rightarrow 0 \quad \text{as } y \rightarrow \infty, \quad a_1 \rightarrow 0, \quad b_1 \rightarrow \frac{(D-1)}{c_0} \quad \text{as } y \rightarrow -\infty$$

We note, from equations (15), that

$$a_1' + c_0 a_1 + (1 - c_1)(1 - a_0) + D b_1' + c_0 b_1 - (D - c_1) b_0 = 0 \tag{16}$$

giving the boundary condition on b_1 consistent with (6) for small E .

We construct a solution to equations (15) in the form

$$a_1 = \frac{(D - 1)}{c_0} \bar{a}_1 + A_1, \quad b_1 = \frac{(D - 1)}{c_0} \bar{b}_1 + B_1 \tag{17}$$

In (17) (\bar{a}_1, \bar{b}_1) satisfy the homogeneous equations arising from (15) and subject to the boundary conditions

$$\bar{a}_1 \rightarrow 0 \quad \text{as } |y| \rightarrow \infty, \quad \bar{b}_1 \rightarrow 0 \quad \text{as } y \rightarrow \infty, \quad \bar{b}_1 \rightarrow 1 \quad \text{as } y \rightarrow -\infty \tag{18}$$

and (A_1, B_1) satisfy the full equations, but subject to the homogeneous boundary conditions

$$A_1, B_1 \rightarrow 0 \quad \text{as } |y| \rightarrow \infty \tag{19}$$

Now equations (15) have a solution $a_1 = a_0', b_1 = b_0'$ which satisfies the homogeneous problem and homogeneous boundary conditions. From this it follows that a compatibility condition is required for the non-homogeneous problem (15) to have a solution satisfying all the boundary conditions. This, in turn, determines the constant c_1 . To derive this condition we need to consider the adjoint problem [14] (Theorem 2.2., p. 307) and to do so we start by writing equations (15) in the form

$$\begin{aligned} \frac{d}{dy} (e^{c_0 y} A_1') - (b_0^p A_1 + p a_0 b_0^{p-1} B_1) e^{c_0 y} &= (1 - c_1) e^{c_0 y} a_0' \\ \frac{d}{dy} (D e^{\frac{c_0 y}{D}} B_1') + (b_0^p A_1 + p a_0 b_0^{p-1} B_1) e^{\frac{c_0 y}{D}} &= (D - c_1) e^{\frac{c_0 y}{D}} b_0' \end{aligned} \tag{20}$$

and then following [14] we construct the corresponding adjoint problem for $(U(y), V(y))$

$$\begin{aligned} \frac{d}{dy} (e^{c_0 y} U') - b_0^p (e^{c_0 y} U - e^{\frac{c_0 y}{D}} V) &= 0 \\ \frac{d}{dy} (D e^{\frac{c_0 y}{D}} V') - p a_0 b_0^{p-1} (e^{c_0 y} U - e^{\frac{c_0 y}{D}} V) &= 0 \end{aligned} \tag{21}$$

subject to

$$U, V \rightarrow 0 \quad \text{as } y \rightarrow \pm\infty \quad (22)$$

If we now multiply (20)_a by U and (20)_b by V , add and integrate from $-\infty$ to ∞ , we obtain, after integrating by parts and applying the boundary conditions (19) on (A_1, B_1) , the compatibility condition

$$(1 - c_1) \int_{-\infty}^{\infty} e^{c_0 y} a'_0 U dy + (D - c_1) \int_{-\infty}^{\infty} e^{c_0 y/D} b'_0 V dy = 0 \quad (23)$$

It is from condition (23) that we determine c_1 . Problem (20) and the adjoint problem (21 and 22) have to be solved numerically, with (23) then being used to calculate c_1 . A graph of c_1 against D is shown in figure 3 for cubic autocatalysis ($p = 2$). The figure shows that there is a value D_0 (which will depend on p) such that $c_1 < 0$ for $D < D_0$ and that $c_1 > 0$ for $D > D_0$, with $D_0 \simeq 0.435$ for $p = 2$. Also the figure suggests that $c_1 \rightarrow 0$ as $D \rightarrow 0$, having a minimum value of $c_1 \simeq -0.336$ at $D \simeq 0.157$. Thus for $D < D_0$, the wave speed starts by *increasing* as the field changes from positive to negative and we can expect (as in figure 2a) a range of (negative) E over which the wave speed is greater in a negative field than in field-free conditions.

We solved the adjoint problem (21 and 22) for higher values of p , having first calculated the corresponding travelling wave solution. The results are shown

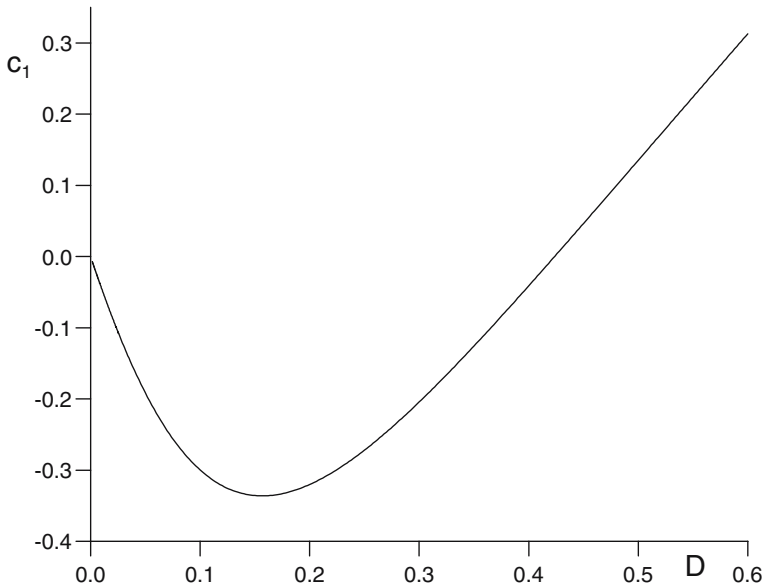


Figure 3. The solution for small E , a plot of the constant c_1 , which indicates how the applied electric field alters the field-free wave speed c_0 , obtained from the compatibility condition (23) for cubic autocatalysis ($p = 2$) against D . The wave speed $c \sim c_0 + c_1 E$.

in figure 4, with plots of c_1 against D for $p = 3, 5, 10$. This figure shows the same effect seen for cubic autocatalysis, in that, for smaller values of D , i.e., $D < D_0(p)$, the wave speed starts by increasing in a negative field over that which arises in field-free conditions. The value of D_0 (where c_1 changes from positive to negative) increases with p , from $D_0 = 0.551$ for $p = 3$ to $D_0 = 0.644$ for $p = 5$ and to $D_0 = 0.672$ for $p = 10$. Also, the minimum value of c_1 increases over that for cubic autocatalysis for $p = 3$ and $p = 5$, to $c_1 = -0.434$ and $c_1 = -0.368$, respectively, though for $p = 10$ this minimum value has decreased to $c_1 = -0.186$.

Figure 4 suggests that, as the order of the autocatalysis increases, the effect of a negative field to increase the wave speed becomes more pronounced, in that it is seen for greater range of D . To examine this further we next construct an asymptotic analysis of the travelling wave equations (2–4) for p large. This analysis also reveals further qualitative information about the nature of the solution.

2.2. Solution for p large

The asymptotic solution of equations (2–4) for p large follows that for the field-free case, see [13,15] for example. We require two regions, an inner region where the reaction terms are significant and an outer, purely diffusive region. To get a consistent asymptotic solution we need to scale c and E (as in [13,15]) by

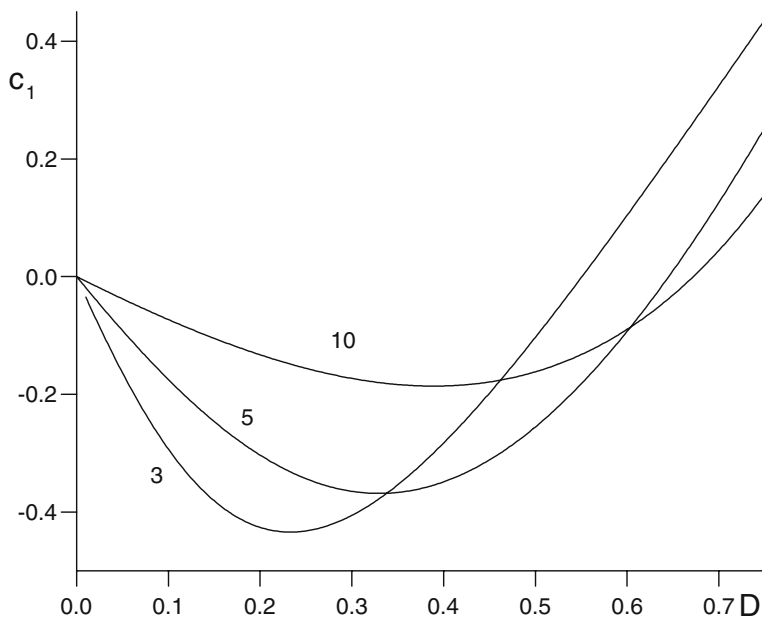


Figure 4. A plot of the constant c_1 obtained from the compatibility condition (23) for powers of autocatalysis $p = 3, 5, 10$ against D . The wave speed $c \sim c_0 + c_1 E$ for E small.

$$c = \bar{c}p^{-1}, \quad E = \bar{E}p^{-2} \quad \text{with } \bar{c}, \bar{E} \text{ of } O(1) \text{ for } p \text{ large.} \quad (24)$$

We start in the inner region where we leave y unscaled and write

$$b = 1 - p^{-1}B, \quad a = p^{-1}A \quad (25)$$

and look for a solution by expanding A, B and \bar{c} in inverse powers of p . The leading order terms A_0, B_0 and c_0 in this expansion satisfy the equations

$$A_0'' - A_0e^{-B_0} = 0, \quad DB_0'' - A_0e^{-B_0} = 0 \quad (26)$$

We solve equations (26) subject to

$$A_0 \rightarrow 0, \quad B_0 \rightarrow T_0 \quad (\text{and } B_0' \rightarrow 0) \quad \text{as } y \rightarrow -\infty \quad (27)$$

where T_0 is a constant to be determined. This leads to $A_0 = D(B_0 - T_0)$ and hence

$$B_0'^2 = 2[e^{-T_0} - (B_0 - T_0 + 1)e^{-B_0}] \quad (28)$$

As $y \rightarrow \infty$, B_0 becomes large, with (28) then showing that

$$B_0 \sim \sqrt{2}e^{-\frac{T_0}{2}}y + \dots, \quad A_0 \sim \sqrt{2}De^{-\frac{T_0}{2}}y + \dots \quad \text{as } y \rightarrow \infty \quad (29)$$

We now turn to the outer (diffusive) region. Expressions (25 and 29) suggest an outer variable $Y = p^{-1}y$. Then, leaving a and b unscaled and noting that, since $b < 1$ in this region, the reaction terms are negligible for $p \gg 1$, we obtain the equations for the leading order terms $a_0(Y), b_0(Y)$ as, on using (24),

$$a_0'' + c_0a_0' = 0, \quad Db_0'' + c_0b_0' = 0 \quad \text{with } a_0 \rightarrow 1, b_0 \rightarrow 0 \text{ as } Y \rightarrow \infty \quad (30)$$

and, subject to matching with (29), that

$$a_0 \sim \sqrt{2}De^{-\frac{T_0}{2}}Y, \quad b_0 \sim 1 - \sqrt{2}e^{-\frac{T_0}{2}}Y \quad \text{as } Y \rightarrow 0 \quad (31)$$

The required solution is

$$a_0(Y) = 1 - e^{-c_0Y}, \quad b_0 = e^{-c_0Y/D} \quad (32)$$

with the matching conditions (31) then giving

$$c_0 = \sqrt{2}De^{-\frac{T_0}{2}} \quad (33)$$

We need a further relation between T_0 and c_0 . This can be determined by looking at the equations that arise at $O(p^{-1})$ in the inner region and matching with the solutions corresponding equations in the outer region. However, a more straightforward approach is to use expression (6), which holds for all p .

Applying the scalings (24) in (6) and expanding, gives $T_0 = -\frac{(D-1)\bar{E}}{c_0}$, with (33) then giving

$$c_0 = \sqrt{2}D \exp\left(\frac{(D-1)\bar{E}}{2c_0}\right) \tag{34}$$

For $D = 1$, expression (34) gives $c_0 = \sqrt{2}$, independent of \bar{E} .

To examine expression (34) for $D \neq 1$, we write it as

$$\bar{E} = \frac{2c_0}{(D-1)} \left[\log c_0 - \log(\sqrt{2}D) \right] \tag{35}$$

Expression (35) shows that $\bar{E} \rightarrow 0$ as $c_0 \rightarrow 0$ and $\bar{E} = 0$ at $c_0 = \sqrt{2}D$, with a turning point at

$$c_0 = \sqrt{2}De^{-1}, \quad \bar{E} = -\frac{2\sqrt{2}De^{-1}}{(D-1)}$$

These expressions show that the forms for $D < 1$ and $D > 1$ are qualitatively different. This can be seen in figure 5, where we give representative plots of c_0 against \bar{E} for $D > 1$ (figure 5a) and for $D < 1$ (figure 5b). The forms shown in figure 5 are qualitatively the similar to those given in [11] and in figure 2. For $D > 1$ there is a lower bound $\bar{E}_c < 0$ on \bar{E} for the existence of a solution, with solutions existing for all $\bar{E} > \bar{E}_c$, whereas for $D < 1$ there is an upper bound $\bar{E}_c > 0$ on \bar{E} , with solutions existing for all $\bar{E} < \bar{E}_c$. Also, for $D < 1$, c_0 increases as \bar{E} changes from positive to negative (as seen in figure 2) suggesting that negative fields increase the wave speed over the field-free value for all $D < 1$ in the large p limit, which is consistent with the results shown in figure 4. Finally, (35) gives the bound on existence

$$E_c \sim -\frac{2\sqrt{2}De^{-1}}{(D-1)}p^{-2} + \dots \quad \text{as } p \rightarrow \infty \quad (D \neq 1) \tag{36}$$

Expression (36) shows that, for high powers of autocatalysis, the effect of applying an electric field is strongly inhibitory on wave formation, in positive fields when $D < 1$ and in negative fields when $D > 1$.

3. Conclusions

We have seen that, when $D < D_0(p)(<1)$, the effects of a negative field, in the sense that the ionic species are propagating towards an electrode of the same polarity, is to increase the speed of the reaction front from what would arise in field-free conditions. Wave speeds considerably greater than the field-free value can be achieved for appropriate values of D and E (as seen in figure 2). This

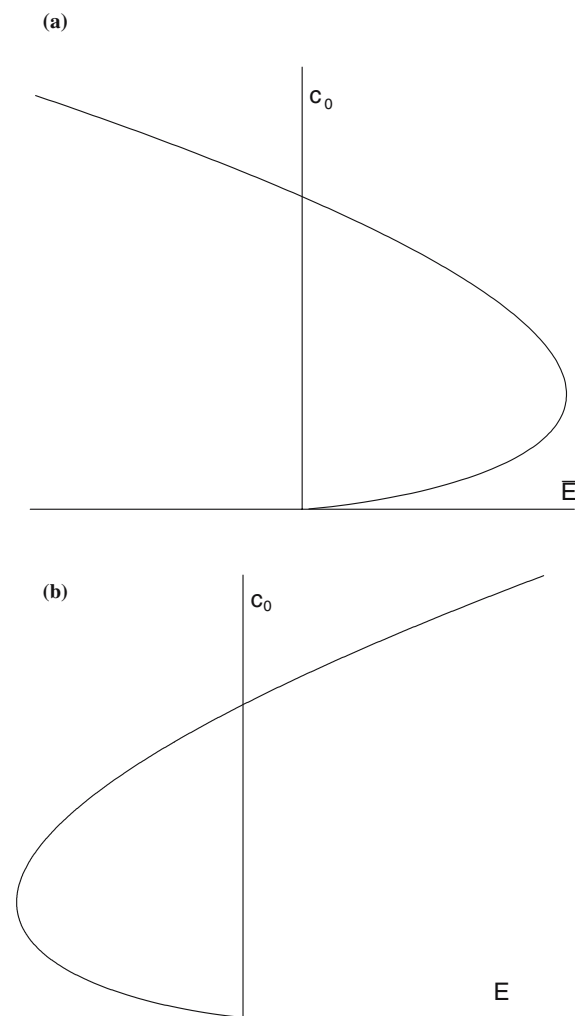


Figure 5. Representative plots of the wave speed c_0 against the electric field strength \bar{E} in the large p limit obtained from expression (35) for (a) $D > 1$, (b) $D < 1$.

result is contrary to what, at first, might be thought to happen. The effect of a negative field is to slow down the transport of the ionic species towards the electrode and thus a slow down in the propagation speed could be expected. This is what is observed [11] if the diffusion coefficient of the autocatalyst B is greater than, or not too much less than, that of the substrate A . A propagating reaction front is a balance between the production of B from A by the autocatalytic reaction and the diffusion and ionic transport of A into and of B away from the reaction zone. Hence, when $D < D_0$, the reduced rate of diffusion and transport of B over that of A enhances the reaction rates within the front and, as a consequence, the speed of propagation. Very large (negative) fields are needed to

overcome this effect, to slow down and even reverse the direction of propagation of the wave (see result (12)).

Our numerical solutions of the travelling wave problem (2–4) were mainly for cubic autocatalysis ($p = 2$) and complement those given previously [11]. Our results for $D = 0.1$ (figure 2) clearly show the enhancing effect of a negative field. To discuss this point in more detail we considered how the solutions to the travelling wave problem (2–4) behaved for small E . To this end we calculated c_1 , where the wave speed $c \simeq c_0 + c_1 E$ for $|E| \ll 1$ (c_0 being the field-free value). This calculation determined $D_0 = D_0(p)$, the value of D where $c_1 = 0$ and so where there was a change from a decrease in wave speed ($c_1 > 0, D > D_0$) to an increase in wave speed ($c_1 < 0, D < D_0$) as E changed from positive to negative (see figure 3). We also performed this calculation to find c_1 for a range of values of p , finding that the value of D_0 increased as p was increased (see figure 4).

A point to note about how c_1 was calculated (equations (15, 20–23)) is that it is the same as that used to calculate the growth rate σ (say) in the linear stability analysis for transverse instabilities of reaction fronts in autocatalytic systems (1) [16] (without an applied electric field). In this case, the calculation determines how σ behaves for small wavenumbers k , with $\sigma \simeq -c_1 k^2$. Thus the condition for a negative field to increase the wave speed is the same as that for a transverse diffusional instability in a field-free environment, with our calculations suggesting that the reaction front will become unstable over a greater range of D as the order p of the autocatalysis is increased.

We performed an asymptotic analysis for p large. These results gave a qualitative confirmation of the wave speed curves for $D > 1$ and $D < 1$ computed previously (figure 5), showing the inhibition in positive fields for $D < 1$ and in negative fields for $D > 1$ (as seen in [11] and figure 2). They also suggested that $D_0 \rightarrow 1$ in the limit as $p \rightarrow \infty$ and gave a very weak, of $O(p^{-2})$, field strength for inhibition (result (36)). This effect can also be seen in (12), which gives a field strength $E_0 \sim -\frac{\sqrt{2}}{p} D^{-p/2}$ for p large at which the direction of propagation changes, showing that E_0 is very small (and the range of existence in negative fields severely limited) when $D > 1$ but takes very large (and negative) values when $D < 1$.

Acknowledgments

The author wishes to thank Brian Sleeman for pointing out how to calculate the adjoint problem (21).

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