

Analysis of reaction–diffusion waves in the ferroin-catalysed Belousov–Zhabotinsky reaction

Annette F. Taylor,^a Vilmos Gáspár,^b Barry R. Johnson^a and Stephen K. Scott^a

^a School of Chemistry, University of Leeds, Leeds, UK LS2 9JT

^b Institute of Physical Chemistry, Kossuth L. University, H-4010 Debrecen, P.O. Box 7, Hungary

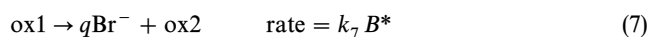
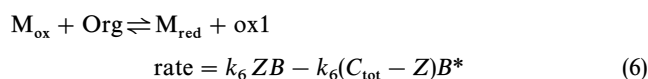
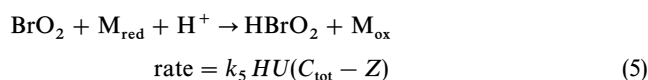
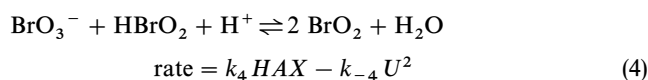
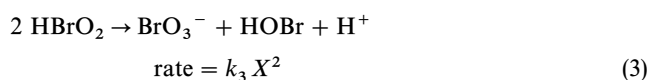
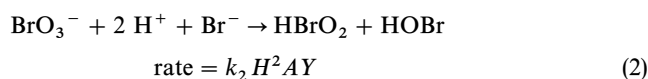
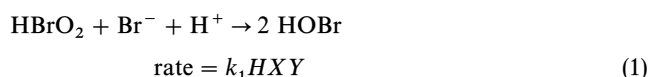
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The Oregonator model is used to analyse reaction–diffusion waves in the ferroin-catalysed Belousov–Zhabotinsky reaction. The value of the effective rate constant of ferroin reduction k_j is determined from experimental wave profiles of the oxidised catalyst obtained from solutions open to air, nitrogen or sealed with a perspex lid. The value of k_j is found to be lower in systems affected by O_2 . The dependence of the wave speed c on the concentration of ferroin in the wave profiles is analysed. An alternative method for the determination of k_j from a relationship between the period of target initiation T and $[Fe(III)]$ is presented. The effect of these results on the ‘universal dispersion relation’ is also discussed.

1. Introduction

Although much data have been accumulated in recent years on the rate constants of the inorganic subsections of the Belousov–Zhabotinsky (BZ) reaction, still little is known with regard to the steps involving the organic species. The few kinetic measurements of the reaction between ferroin and MA/BrMA are contradictory.^{1–4}

It is reasonable to assume that information regarding the rates of reactions could be gleaned from concentration profiles of the reactants since the distribution of species in space and time is determined by these reactions combined with diffusion, and diffusion effects are small unless the gradient of the profile is changing rapidly. A recent publication by Ungvárai *et al.*⁵ suggests that the rate constant for ferroin reduction, k_j , could be calculated from an analysis of the rate of relaxation in the wave tail. They employ the following modified Oregonator model for the ferroin-catalysed BZ reaction



where $A = [BrO_3^-]$, $B = [Org]$ with $Org = [MA] + [BrMA]$, $H = [H^+]$, $U = [BrO_2]$, $B^* = [ox1]$ ($ox1$ and $ox2$ are oxidation products), q is the stoichiometric coefficient, $X = [HBrO_2]$, $Y = [Br^-]$, $Z = M_{ox}$ ($[Fe(III)]$) and $C_{tot} = \{M_{ox} + M_{red}\}$ is the total catalyst concentration.

In the classical Oregonator model, the large value of the redox potential for the cerium(IV)/cerium(III) couple (1.44 V) allows the reversibility of step (6) to be ignored. Therefore, from the point of view of the reaction kinetics, the sum of reactions (6) and (7) can be considered as a single step (8)



For the ferroin system, step (6) is essentially reversible and usually assumed to be in pre-equilibrium due to the low redox potential of the ferroin/ferroin couple (1.06 V). Assuming that the rate of relaxation in the tail of BZ waves is governed by steps (6), (–6) and (7) only, the following kinetic equation for $[Fe(III)]$ in the wave tail can be derived¹ by application of a pseudo steady state approximation on B^*

$$\frac{dZ}{dt} = -\frac{k_6 k_7 BZ}{k_7 + k_{-6}(C_{tot} - Z)} \quad (9)$$

In the work of Ungvárai *et al.* the term k_7 in the denominator of this equation was ignored with respect to the term $k_{-6}(C_{tot} - Z)$ on the basis of the argument that $k_{-6} \gg k_7$.⁶ They then integrate eqn. (9) from 0 to t assuming $Z_{(t=0)} = C_{tot}$. Here we integrate taking $Z_{(t=0)} = Z_0$ where Z_0 is the maximum value of $[Fe(III)]$, since the assumption $Z_{(t=0)} = C_{tot}$ was not found to be true in all of the extracted concentration profiles we used. We also retain the term k_7 in the denominator as it cannot really be ignored with respect to the term $k_{-6}(C_{tot} - Z)$ since initially Z_0 is close to C_{tot} . The following equation is obtained

$$\left(C_{tot} + \frac{k_7}{k_{-6}}\right) \ln(Z/Z_0) - Z + Z_0 = -k_j Bt \quad (10)$$

where

$$k_j = \frac{k_6 k_7}{k_{-6}} \quad (11)$$

From the arguments of Rovinsky and Zhabotinsky,⁶ C_{tot} is likely to be much greater than k_7/k_{-6} and eqn. (10) simplifies to

$$C_{tot} \ln(Z/Z_0) - Z + Z_0 = -k_j Bt \quad (12)$$

From eqn. (8) which is representative of the organic step in the

classical Oregonator model, the following relationship between Z and t would be established

$$\ln(Z/Z_0) = -k_6 Bt \quad (13)$$

Thus $C_{\text{tot}} \ln(Z/Z_0) - Z$ vs. t is plotted from the calibrated wave profiles of the oxidised form of the metal catalyst. The value of the rate constant of ferriin reduction k_7 is calculated from the slope of the linear fit. The determination of k_7 using the method described above is compared with an alternative approach presented in section 4, involving the dependence of the period of target initiation on $[\text{Fe(III)}]$. The results of these analyses have consequences for the derivation of the universal dispersion relation which will be discussed in the final section.

2. Experimental procedure

The method and apparatus were described in detail previously.⁷ Experiments were performed in a specially constructed Petri-dish illuminated from below. BZ solutions were mixed to give initial concentrations $[\text{KBrO}_3]_0 = 0.2 \text{ M}$, $[\text{H}_2\text{SO}_4]_0 = 0.25 \text{ M}$, $[\text{MA}]_0 = 0.02 \text{ M}$ or 0.04 M , $[\text{Ferriin}]_0 = 1 \times 10^{-3} \text{ M}$ and depths of 0.7, 1, 1.5 and 2 mm. The solution layers were maintained at room temperature (approximately $25 \pm 0.2^\circ\text{C}$) using a heated water jacket, and were either open to the atmosphere, open to N_2 or sealed with a Perspex lid. Digital images were spatially calibrated using graph paper in order to calculate the wave speed. The intensity profiles were calibrated using an extension of the Beer-Lambert law to determine the spatial distribution of $[\text{Fe(III)}]$. Both initial sets of concentrations ($[\text{MA}]_0 = 0.02 \text{ M}$ and $[\text{MA}]_0 = 0.04 \text{ M}$) gave reactant mixtures which were oscillatory under well-stirred batch conditions and all target initiation was spontaneous.

3. Determination of k_7 from wave profile analysis

Following the discussion outlined in the introduction, plots of $C_{\text{tot}}[\ln(Z/Z_0) - Z/C_{\text{tot}}]$ were constructed from the wave profiles and compared with $C_{\text{tot}} \ln(Z/Z_0)$ plots. Concentration profiles for the oxidised form of the metal catalyst were obtained from the experiments as discussed in ref. 7. Examples of these plots from typical wave profiles are shown in Fig. 1. In agreement with the results of Ungvárai *et al.*, it was found

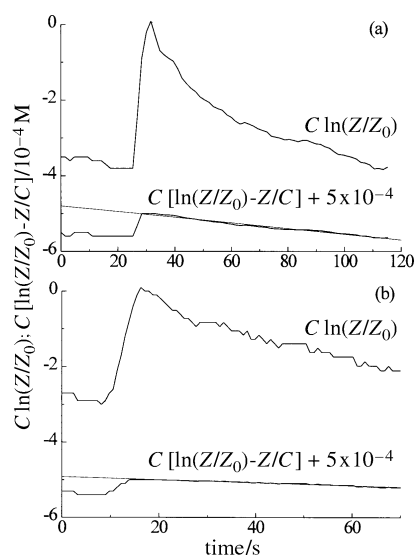


Fig. 1 Example plots of the ferriin profile in time, comparing the classical Oregonator decay in the wave tail, $C \ln(Z/Z_0)$, with reversibility included in the decay in the wave tail, $C[\ln(Z/Z_0) - Z/C]$, in (a) Perspex system (b) nitrogen system ($C = C_{\text{tot}}$). The value of $[\text{MA}]_0 = 0.04 \text{ M}$ in both cases and the values of the other reactant concentrations are specified in the text.

Table 1 Determined values of the kinetic constant k_7 for the systems exposed to air, N_2 , or sealed with a Perspex lid

System	Depth/mm	$[\text{MA}]/\text{M}$	$k_7/10^{-5} \text{ s}^{-1}$
Air	1.5-2	0.02 and 0.04	2.7 ± 0.3
Nitrogen	1-2	0.02 and 0.04	2.0 ± 0.2
Sealed	1-2	0.02 and 0.04	3.8 ± 0.4
Air	1	0.04	0.44 ± 0.09

that fitting a simple exponential decay (eqn. (13)) to the wave tail did not give a straight line, but the slightly more complex relationship did (eqn. (12)). For each system (open to air, N_2 or sealed by a Perspex lid), six profiles of waves with various speeds were chosen and the average value of k_7 taken. Some of the profiles, particularly those with a small difference between the minimum and maximum were noisy. In these cases k_7 was calculated from spline fits. The results are shown in Table 1, along with the estimated errors.

The first three values of k_7 in Table 1 were calculated from systems which were unaffected by oxygen,⁷ and are of a similar order $\sim 10^{-5} \text{ s}^{-1}$. The difference between the two open to atmosphere and the one sealed by a Perspex lid suggests that the evaporation of bromo-derivatives may have an effect on the processes that take place in the relaxation tail of the wave. At 25°C , the value of $k_7 = (3.1 \pm 0.2) \times 10^{-5} \text{ s}^{-1}$ calculated by Ungvárai *et al.* agrees well with the value in air calculated from the experiments presented here. The experiments of Ungvárai *et al.* can be assumed to be unaffected to any great extent by oxygen as although the experiments were performed in air, the wave speeds did not change as $[\text{MA}]_0$ was increased and all remained within a few percent of the maximum speed calculated for their system. The profiles also displayed 100% extent of conversion in the wave back, indicating a lack of the inhibited layer at the surface, which has previously been demonstrated to exist under certain initial conditions.⁷

Earlier work suggests the validity of including the reversible reaction. Wood and Ross⁸ found that a simple exponential decay did not fit the tail of wave profiles in their experiments. The relaxation rate from the peak of the profile back to the steady state value of Fe(III) was up to 10 times faster in predictions they made using the Oregonator, than in the experiments. The slower, more complex decay in the ferriin system can be accounted for by allowing the reversibility of step (6). Rovinsky and Zhabotinsky^{2,6} calculated the rate constant of ferriin reduction by BrMA by following the concentration of Fe(III) spectrophotometrically in well stirred solution mixtures. They assumed that steps (6) and (7) took place with $\text{org} = \text{BrMA}$ and $\text{ox1} = \text{BrMA}^{\cdot}$. The value of h_0 was not incorporated into k_{-6} in this work. Since the method of synthesis of BrMA has since been shown⁹ to result in mixtures of MA , BrMA and Br_2MA , the rate constant they determined $K = (1.9-3) \times 10^{-5} \text{ M s}^{-1}$ is equivalent to $k_7 \times h_0$. As $h_0 = 3.65 \text{ M}$ in their experiments this gives a value of $k_7 = (5-8) \times 10^{-6} \text{ s}^{-1}$ at 40°C . It is not clear whether these experiments were performed in air. Aliev and Agladze¹⁰ estimated a value for $k_7 = 2 \times 10^{-6} \text{ s}^{-1}$ at 20°C assuming the rate constant has an Arrhenius temperature dependence.

The reversibility of reaction (6) was also confirmed by Chou *et al.*⁴ in experiments where they determined the values of k_6 for reactions between Fe(III) and MA or BrMA alone. The values of k_6 and k_7 have also been determined for the reaction between Ce(IV) and MA , where ox1 in reaction (6) corresponds to MA^{\cdot} and ox2 in reaction (7) to ETA .^{11,12} However it is impossible to compare the individual values of k_6 , k_{-6} and k_7 mentioned above with the value of k_7 determined in this work since those experiments involved a subset of the BZ reaction, with reaction (6) and (7) corresponding to the formation and recombination of MA radicals respectively. The species ox1

and ox2 in the model presented here do not correspond with specific reaction products but incorporate the mixture of organic species and radicals likely to be present in the full BZ reaction.

For the system in Table 1 which was affected by O₂, the value of k_j is almost a factor of 10 lower than those unaffected. This value is close to that determined by Aliev and Agladze from the experimental work of Rovinsky, and suggests that their experiments were also affected by O₂. Chou *et al.* found that k_6 increased in air, but again this result is impossible to compare with the systems discussed here since their experiments involved either MA or BrMA only and not a mixture of the two, and also the values of k_{-6} and k_7 are not known. The reduction in k_j can be explained by the model for oxygen effects in the ferriin-catalysed BZ reaction suggested by Taylor *et al.*¹³ The model introduces a chain branching step in addition to reaction steps (6) and (7), the net effect of which will increase the level of Br⁻



and the reaction has a rate constant k_{10} . Eqn. (9) will then become

$$\frac{dZ}{dt} = \frac{k_6 BZ[\phi k_{10} O_2 - k_7]}{k_{-6}(C_{tot} - Z) + k_7 - \phi k_{10} O_2} \quad (15)$$

where $\phi k_{10} O_2 < k_7$ ($O_2 = [O_2]$). Using the same arguments as above, k_{-6} is likely to be much greater than $(k_7 - \phi k_{10} O_2)$, so eqn. (15) becomes

$$\frac{dZ}{dt} = -\frac{k_6 BZ[k_7 - \phi k_{10} O_2]}{k_{-6}(C_{tot} - Z)} \quad (16)$$

and k_j now has a value

$$k_j = \frac{k_6(k_7 - \phi k_{10} O_2)}{k_{-6}} \quad (17)$$

Since $\phi k_{10} O_2$ is less than k_7 , this results in an overall reduction in k_j when the system is exposed to O₂, consistent with the result above. This analysis suggests that the value of k_j in systems affected by oxygen is independent of the initial acid and bromate concentrations although it has been demonstrated that the extent of the oxygen effect does depend on the values of $[H^+]_0$ and $[BrO_3^-]_0$.¹⁴ However, the value of ϕ may depend on the initial solution composition.

4. Dependence of the wave speed c and period T on [Fe(III)]

An alternative method for the determination of k_j is presented in this section from a combination of the experimentally determined wave speeds and target periods, and the concentration profiles of the oxidised form of the catalyst, [Fe(III)]. Tyson and Keener¹⁵ have shown that the wave speed c and direction of a wave in the Oregonator model is determined by the level of the oxidised form of the catalyst in a wave front (represented by the non-dimensional variable v in their work). The wave speed c is a monotone decreasing function of v . The concentration of Fe(III) in front of the wave is represented by v_f (the wave front is defined here as the rapid change in Fe(III), not HBrO₂ as is often assumed) and in the wave back v_b . The value of $c(v_f)$ is positive, $c(v_b)$ is negative so there exists a value v^* for which $c(v^*) = 0$ (Fig. 2(a)). If v_f and v_b are close to v^* they will be in the approximately linear portion of the curve in Figure 2(a) (see Fig. 2(b)).

For periodic perturbations the values of v_f and v_b become constant over successive waves and the speed of the wave front and back is equal. The period of wave initiation T can be approximated by the sum of T_+ , the time taken for v to

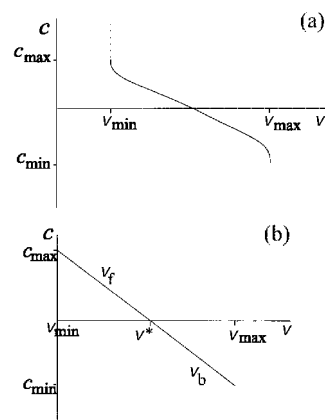


Fig. 2 (a) The wave speed c as a function of the ferriin concentration v , taken from ref. 9. (b) Graph to show the linear approximation to the dependence of c on v .

jump from v_f to v_b and T_- , the time taken for v to fall from v_b back to v_f . An approximate value of the period can be calculated by assuming that for typical wave profiles $T_+ \ll T_-$ so that

$$T \approx T_- = \int_{v_b}^{v_f} \frac{dv}{(dv/dt)_-} \quad (18)$$

During the jump from v_b to v_f the concentration of HBrO₂ is likely to be much less than [Fe(III)], so for the classical Oregonator (ignoring diffusion), the rate of change of v can be approximated by

$$dv/dt \approx -\frac{v}{\tau} \quad \text{with } \tau = \frac{1}{k_6 B} \quad \text{where } B = [MA] \quad (19)$$

(Note that all variables and parameters are dimensional from this point onwards.) If the reversibility of step (6) is incorporated then

$$dv/dt \approx -\frac{v}{(C_{tot} - v)\tau'} \quad (20)$$

with C_{tot} = total catalyst concentration and $\tau' = 1/k_j B$. The equation for k_j is given by (11).

Since the concentration profiles seem to confirm that the relaxation in the wave tail is not a simple exponential decay but slightly more complex, then substituting eqn. (20) into (18) and evaluating leads to the following relationship between T and v

$$T = \int_{v_b}^{v_f} \frac{-\tau'(C_{tot} - v)}{v} dv = -\tau' \left[C_{tot} \ln \frac{v_f}{v_b} - (v_f - v_b) \right] \quad (21)$$

or alternatively, assuming $|v_f - v_b| = |v_b - v^*|$,

$$T = -\tau' \left[C_{tot} \ln \left(\frac{v_f}{2v^* - v_f} \right) + 2(v^* - v_f) \right] \quad (22)$$

where T is the period of the target, $v = [Fe(III)]$, $C_{tot} = [Fe(III)] + [Fe(II)]$, v_f is the concentration of the oxidised form of the catalyst in front of the wave, v_b is [Fe(III)] in the wave back and v^* is the [Fe(III)] at which the wave speed c turns from positive to negative.

Plots of T vs. v_f were constructed from the results presented previously, where T was calculated from the wave speed and wave length and v_f was determined from profiles in each of the systems, open to air (depths 1.5–2 mm therefore unaffected by oxygen), N₂ or Perspex (Fig. 3(a)–(c)). The terms τ' and v^* were used as fitting parameters, and k_j was determined from τ' . Plots of the wave speed c vs. v_f and v_b were also produced to test the validity of the assumption of a linear relationship

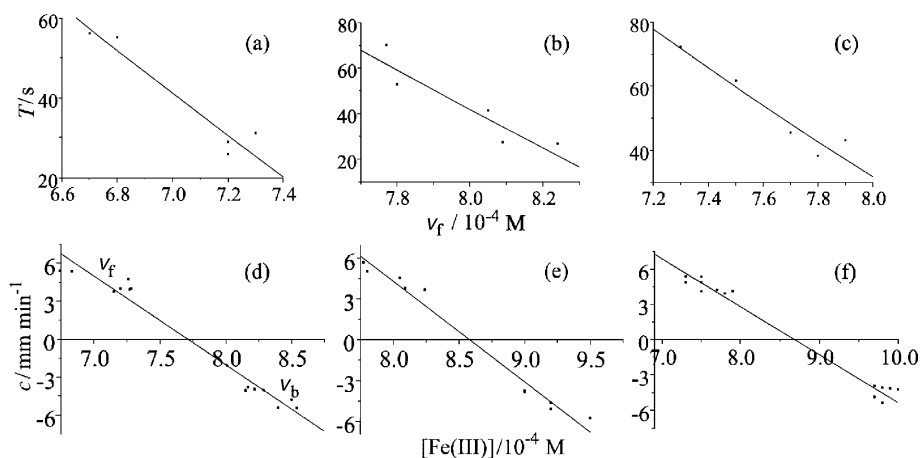


Fig. 3 Determination of v^* and k_j . 3(a)–(c) are plots of T vs. v_f fitted with eqn. (22). 3(d)–(f) are plots of c vs. v_f and v_b fit with a linear function $c = a - bv$. The data from both these sets of graphs are displayed in Table 2. (a) and (d) correspond to systems open to air, (b) and (e) to systems open to N_2 , and (c) and (f) to systems sealed with a Perspex lid.

by comparing v^* in these plots with the ones determined from the fitted relationship. The results of these plots are tabulated in Table 2.

There is clearly a good agreement in the values of v^* shown in Table 2, between the two sets of plots, c vs. v_f and v_b , and T vs. v_f . The values of k_j calculated from the fitted values of τ' agree very well with those calculated from the relaxation tail of the concentration profiles, lying within the determined error range in the systems open to N_2 and air, and slightly below this range in the Perspex system. However, the experimental data is quite scattered in these plots, due to the noise in the profiles which makes accurate determination of v_f and v_b difficult. In order to improve this data, a more extensive analysis would be necessary than is possible here, involving solutions of different initial concentrations of bromate and acid.

5. Consequences for the universal dispersion relation

Flesselles *et al.*¹⁶ derived the following equation for the dispersion relation using the classical Oregonator model

$$c(T) = c_\infty \tanh(T/T^*) \quad (23)$$

where c_∞ is the speed of the wave propagating into a fully recovered medium and T^* is a characteristic time period which was found to correspond closely to the rotational period of a spiral in a given medium. Flesselles *et al.* compared data from various other published work with their own by plotting $M(\xi)/M(1)$ vs. ξ where

$$\xi = T/T^* \quad (24)$$

$$M = \frac{\lambda^2}{DT} \quad (25)$$

λ is the wavelength of the target and D is the diffusion coefficient of species in the BZ reaction. Substituting eqn. (25) into eqn. (23) gives the following scaling form for M

$$M = \beta \xi \tanh^2 \xi \quad \text{where} \quad \beta = c_\infty^2 T^*/D \quad (26)$$

All the data were found to fall on the same dimensionless curve. This prediction was tested against our recent experimental data¹³ and again the results indicate that all experimentally determined dispersion data can be rescaled onto a single curve (Fig. 4). However, the derivation of Flesselles *et al.* was based upon several assumptions which become subject to question in the light of results presented here. They did not include the reversibility of step (6), which is essential for modelling the ferroin-catalysed BZ reaction. They also assumed the following linear relationship between c and v

$$c(v) \approx \alpha(v^* - v) \quad \text{where} \quad \alpha = c_\infty/v^* \quad (27)$$

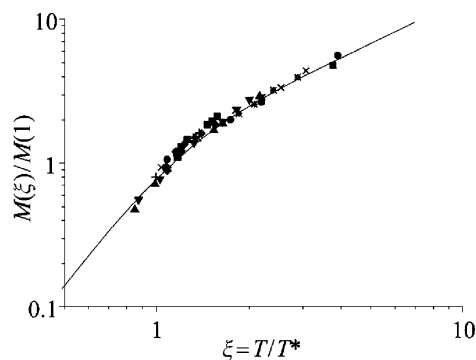


Fig. 4 Dimensionless plot of $M(\xi)/M(1)$ vs. $\xi = T/T^*$ for all the data in ref. 7. The solid line corresponds to the theoretical curve.

Table 2 Dependence of c and T on v_f and v_b according to the two theoretical approaches outlined in the text (linear fit and eqn. (22))—data from Fig. 3^a

	c vs. v_f and v_b ($c = a - bv$)			T vs. v_f (eqn. (22))		
	$a/\text{mm min}^{-1}$	$b/\text{mm min}^{-1} \text{ M}^{-1}$	$v^*/M (= a/b)$	$\tau'/\text{s M}^{-1}$	k_j/s^{-1}	v^*/M
Air 1.5–2 mm	54	6.96×10^4	7.7×10^{-4}	8.97×10^5	2.8×10^{-5}	7.8×10^{-4}
Nitrogen 0.7–2 mm	63	7.32×10^4	8.6×10^{-4}	2.35×10^6	2.1×10^{-5}	8.5×10^{-4}
Sealed 0.7–2 mm	35	4.0×10^4	8.7×10^{-4}	1.61×10^6	3.1×10^{-5}	8.6×10^{-4}

^a $[\text{MA}]_0 = 0.02 \text{ M}$ in the systems open to N_2 /perspex and 0.04 M in the system open to air.

It is clear that in the linear plots of c vs. v_f and v_b (Fig. 3(d)–(e), Table 2), extrapolation to the y axis does not yield c_∞ , and therefore the gradient does not correspond to c_∞/v^* as assumed. The value of c_∞ actually occurs at some finite value of v , not $v = 0$ (c_{\max} , Fig. 2(a)). A more accurate description of α might be $\alpha = c_\infty/(v^* - v_{\min})$ (see Fig. 2(b)). Incorporating the reversibility of step (6) and the above definition of α into the derivation for the universal dispersion relation results in the following equation

$$T = -\tau \left[C_{\text{tot}} \ln \left(\frac{v^* - c/\alpha}{v^* + c/\alpha} \right) + 2c/\alpha \right] \quad (28)$$

This formula does not yield simple relationship between c and T , but T calculated using eqn. (28) compares well with the experimentally determined values. For example, in the system sealed by a Perspex lid with $[\text{MA}]_0 = 0.02$ M and wave speed $c = 4$ mm s⁻¹, T can be determined using $v^* = 8.6 \times 10^{-4}$ M and $v_{\min} = 7.2 \times 10^{-4}$ M with the values of $k_j = 3 \times 10^{-5}$ s⁻¹ and $c_{\max} = 5.5$ mm min⁻¹. The calculated value of T was found to be 47 s, in good agreement with the experimental result of ~ 45 s.

6. Summary and conclusions

The importance of the reversibility of the reaction of ferriin reduction was demonstrated in this work. The rate constant of ferriin reduction k_j was calculated from the Fe(III) wave profiles in good agreement with other experimental results. Oxygen was found to reduce the value of k_j , which can be justified from the predictions of the simple model for oxygen effects presented previously. An analysis of the dependence of the wave speed c and period T on $[\text{Fe(III)}]$ provided an alternative method for the determination of k_j , resulting in values which were close to the values determined from profile analysis.

The derivation of the universal dispersion result was found to depend on several assumptions which seem unlikely to be true from results presented here. Therefore although it remains an excellent empirical result with all data from experimentally determined dispersion curves collapsing onto a single dimensionless curve, a revision of the derivation is necessary.

An attempt to take into account the failings of previous assumptions did not result in a simple relationship between the wave speed c and the period of target initiation T .

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