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Magnetic resonance imaging of a magnetic field-dependent chemical wave

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Abstract

The magnetic field dependence of the travelling wave formed during the reaction of (ethylenediaminetetraacetato)cobalt(II) $(Co(II)EDTA^{2-})$ and hydrogen peroxide was studied using magnetic resonance imaging (MRI). The reaction was investigated in a vertical tube, in which the wave was initiated from above. The wave propagated downwards, initially with a flat wavefront before forming a finger. Magnetic field effects were observed only once the finger had formed. The wave propagation was accelerated by a magnetic field with a negative gradient (i.e., when the field was stronger at the top of the tube than at the bottom) and slightly decelerated by positive field gradients.

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1. Introduction

Exploring chemical wave reactions, which can model wave or oscillatory behaviour in biological processes such as chemotaxis or calcium waves, has been an area of increasing interest in recent years [1]. One such reaction is that of (ethylenediaminetetraacetato)cobalt(II) (Co(II)EDTA²⁻) and hydrogen peroxide [2], at pH 4. In this reaction the cobalt complex is oxidised to a Co(III)EDTA⁻ complex (Eq. (1)).

$$2Co(II)EDTA^{2-} + H_2O_2 \rightarrow 2Co(III)EDTA^- + 2OH^-$$
(1)

The reaction is catalysed by hydroxide ions and is therefore autocatalytic. By introducing sodium hydroxide into a localised region of the reaction mixture, it is possible to produce a travelling wave [2]. The local concentration of hydroxide ions is autocatalytically in-

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creased by the reaction then diffuses to neighbouring regions and similarly catalyses the reaction there, thus propagating the wave.

An interesting feature of this reaction is the conversion of paramagnetic Co(II)EDTA²⁻ ions to diamagnetic Co(III)EDTA- ions and the subsequent production of a concentration gradient and hence a magnetic susceptibility gradient. Work by Nagypál and co-workers [2,3] showed that the propagating wave produced in this reaction could be manipulated using magnetic fields. Experiments were conducted by placing a shallow layer of the Co(II)EDTA²⁻ and hydrogen peroxide solution into a Petri dish. A drop of sodium hydroxide solution was then added to the centre of the Petri dish to initiate the autocatalytic reaction. In the absence of a magnetic field, the resulting wave propagated isotropically (Fig. 1a). In the presence of an inhomogeneous magnetic field, such as that produced by the arrangement of bar magnets placed below the Petri dish (Fig. 1c), the wave propagates in the shape of a cross (Fig. 1b). A qualitative explanation for this effect has been postulated [2] and is based on the different

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Fig. 1. Photographs of the reaction of $Co(II)EDTA^{2-}$ with H_2O_2 in a shallow layer in a Petri dish 26 min after mixing, in the absence (a) and presence (b) of an applied magnetic field. Light (pale pink) regions are areas of unreacted $Co(II)EDTA^{2-}$ and the dark (purple) regions are areas of reacted $Co(II)EDTA^{-}$ solution. The orientation of the magnets used for image (b) is shown in (c). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

behaviour of the paramagnetic and diamagnetic cobalt ions in a magnetic field where there is a concentration gradient [3]. As the reaction progresses, diamagnetic $Co(III) EDTA^{-}$ ions are produced and these are pushed down the magnetic field gradient whilst attractive forces cause the $Co(II)EDTA^{2-}$ ions to move into regions of high magnetic field further increasing the concentration gradient. However, discussion of these effects has been based solely on the interpretation of visually obtained results, with no quantitative measurements and no discussion of the forces that drive this behaviour.

It is easily shown that the thermal energy of the cobalt ions in an aqueous solution (k_BT) is much larger than the magnetic energy of the ions in the magnetic fields applied and hence it should not be possible to separate these ions using an inhomogeneous magnetic field. Indeed, it was noted by Boga et al. [3] that Co(II)EDTA²⁻ and Co(III)EDTA⁻ ions cannot be separated from a *homogeneous* solution and it was therefore concluded that inhomogeneity of both the solution and the applied magnetic field is essential for the evolution of the magnetic field effects such as those depicted in Fig. 1b.

The magnetic force, $\vec{F}_{\rm M}$, per unit volume acting on a droplet of pure Co(III)EDTA⁻ solution immersed in a pure Co(II)EDTA²⁻ solution is given by

$$\vec{F}_{\rm M} \propto (\chi_{\rm Co(III)} - \chi_{\rm Co(II)}) (\vec{B} \cdot \vec{\nabla}) \vec{B}, \qquad (2)$$

where \overline{B} is the magnetic flux density and $\chi_{Co(II)}$ and $\chi_{Co(III)}$ are the magnetic susceptibilities of the pure $Co(II)EDTA^{2-}$ and $Co(III)EDTA^{-}$ solutions, respectively. The autocatalytic oxidation reaction described by equation 1, has a complex time and concentration dependence. Consequently, the relative concentrations of Co(II)EDTA²⁻ and Co(III)EDTA⁻ ions vary significantly across the solution with sharp concentration gradients at the reaction front. Susceptibility measurements of Co(II)EDTA²⁻ and Co(III)EDTA⁻ solutions at the concentrations used in Fig. 1 (0.02 M) yielded $\chi_{Co(III)} = -0.741 \times 10^{-10} \text{ m}^3 \text{ kg}^{-1}$ and $\chi_{Co(III)} = -0.925 \times 10^{-10} \text{ m}^3 \text{ kg}^{-1}$, respectively. Hence, both solutions are in fact diamagnetic although the Co(II)EDTA²⁻ solution is less diamagnetic than the Co(III)EDTA⁻ solution resulting in a force down the magnetic field gradient, $F_{\rm M}$, for Co(III)EDTA⁻ containing solution in a $Co(II)EDTA^{2-}$ solution and a force up the magnetic field gradient for the reversed scenario.

The conversion of paramagnetic to diamagnetic ions is not only crucial for the magneto-sensitivity of the wave but it also allows a more quantitative study of the reaction using magnetic resonance imaging (MRI). The protons in the water molecules surrounding the $Co(II)EDTA^{2-}$ and $Co(III)EDTA^{-}$ ions show very different relaxation characteristics, with paramagnetic $Co(II)EDTA^{2-}$ ions significantly reducing both longitudinal, T_1 , and transverse, T_2 , relaxation times. This produces the image contrast necessary to observe the wave using MRI, highlighting where $Co(II)EDTA^{2-}$ or $Co(II)EDTA^{-}$ ions predominate. MRI was used to follow the formation and motion of the travelling wave and to investigate the effect of welldefined applied magnetic field gradients. As the reaction needed to be fitted into the MRI probe the reaction was performed in a narrow vertical tube.

2. Experimental

Sodium hydroxide, EDTA, cobalt chloride and hydrogen peroxide (35% by volume), all of ACS grade, were obtained from Aldrich and were used without further purification. A 0.02 M Co(II)EDTA²⁻ solution was made by dissolving equimolar quantities of EDTA and CoCl₂ in de-ionised water and then adjusting the acidity to pH 4. The reacting solution was made from 0.02 M Co(II)EDTA²⁻ and hydrogen peroxide solutions, in a 9:1 ratio. The concentration of sodium hydroxide solution used to initiate the travelling wave was 0.0284 M.

The reaction was initiated inside the spectrometer magnet, ensuring that the reacting sample was not moved through the enormous stray field associated with the magnet, which would have affected the wave front. A delivery device was constructed which layered a small amount of the sodium hydroxide solution on top of the Co(II)EDTA²⁻ solution. This layer was less dense than the Co(II)EDTA²⁻ solution, thus preventing any initial density fingering.

MRI [4] experiments were performed on a Bruker DMX-300 spectrometer equipped with a 7.0 T superconducting magnet, operating at a proton resonance frequency of 300 MHz. All MRI experiments were carried out at a temperature of 24 ± 0.2 °C. The reaction was imaged inside 5 mm NMR tubes, using a 25 mm radiofrequency coil.

Relaxation times for the water were measured [5] for Co(II)EDTA²⁻ and Co(III)EDTA⁻ solutions using CPMG (transverse relaxation, T_2) and saturation recovery (longitudinal relaxation, T_1) experiments. At 0.02 M, a solution containing paramagnetic Co(II)EDTA²⁻ ions gave relaxation times of 340 ± 1 ms (T₁) and of 33 ± 1 ms (T_2) and a solution containing diamagnetic Co(III)EDTA⁻ ions 622 ± 4 ms (T₁) and 398 ± 3 ms (T_2) . Images were obtained using the fast imaging, multiple spin-echo sequence RARE [6]. Here a single excitation pulse is used to excite the spins in the sample and multiple echoes are acquired, which were encoded for position using magnetic field gradients. The signal was reconstructed using two-dimensional Fourier analysis, producing a two-dimensional image. By collecting multiple echoes, after the initial excitation, T_2 relaxation contrast is possible, where regions of longer T_2 appear brighter than regions of shorter T_2 . As the sampling time for the experiment is comparable with the T_2 relaxation time of the imaged solution a degree of blurring is



Fig. 2. Schematic representing the timings between imaging sequences and gradient trains, which are looped n times.

expected, however it is not significant and its point spread function is less than a pixel.

The vertical images had a slice thickness of 1 mm and were positioned in the centre of the tube. The vertical and horizontal fields of view were 50 and 10 mm, respectively, and were composed of a 256×64 pixel array. The corresponding pixel size was 195 µm (horizontal) by 156 µm (vertical). The relaxation time of the Co(III)EDTA⁻ solution was sufficiently long that an image could be obtained from a single excitation. Just one signal acquisition was required, so the experiment time, for each image, was 1 s.

To follow the effect of magnetic field gradients on the travelling wave, trains of gradient pulses were applied between image acquisitions. Gradient trains were generated by the imaging gradients of the spectrometer and comprised pulses, which were switched on for 2 ms and off for 1 ms, cycled 2000 times, with amplitude of +0.2 or -0.2 T m^{-1} . This produced an average gradient of ± 0.133 T m⁻¹ over a period of 6 s. A constant gradient was not applied, as this could have damaged the gradient coils. A set of three trains was applied, at 5 s intervals and at equidistant intervals between images (Fig. 2). As a control, an experiment was also done in the absence of these additional gradients. As the imaging sequences apply gradients (typically 0.03-0.04 $T m^{-1}$ for a duration of 340 ms), all the experiments using -0.2, 0 and +0.2 T m⁻¹ gradient trains were acquired at the same time intervals of 51 s, thus allowing comparison between experiments. The relatively long time interval of 51 s was chosen to minimise the influence of the magnetic field gradients involved in the imaging sequence. For negative gradients, the field decreases from top to bottom of the sample/image and increases for positive gradients. Heating of the sample due to the imaging sequence and gradient pulses was negligible.

3. Results

3.1. Flat wave fronts

After initiation of the reaction with NaOH solution, a flat interface for the wave formed. Fig. 3 shows typical images of the wave. The figure depicts the wave front just after the reaction was initiated (a), with two further images at 102 s (b) and 204 s (c), in the absence of any



Fig. 3. MRI images of a travelling wave in the reaction of $Co(II)EDTA^{2-}$ with H_2O_2 . Image (a) was taken immediately after the reaction was initiated, through the addition of NaOH solution. Images (b) and (c) were taken 102 and 204 s, respectively, afterwards. No magnetic field gradients were applied in between images. Signal intensity is high (bright) where $Co(III)EDTA^{-}$ ions predominate and low (dark) where $Co(II)EDTA^{2-}$ predominate.

applied magnetic field gradients, except those required for imaging. Similar images were found for experiments when additional magnetic field gradients were applied, as described in Section 2. The signal intensity at 50% of its maximum value (corresponding to the fully reacted Co(III)EDTA⁻ solution), served as a parameter to define the position of the wave front and facilitated the determination of the wave velocity. Table 1 gives the velocity of waves, for the three magnetic field gradient conditions (-0.2, 0, +0.2 T m⁻¹). The velocities of the waves in each experiment were small and constant, and approximately 8×10^{-6} m s⁻¹. There appears to be only a coupling between reaction and diffusion at this stage [7]. Also, no significant dependence of the wave

Table 1 Wave velocities, where the interface remains flat and is unaffected by fingering

Gradient pulse strength (T m ⁻¹)	Wave velocity $(10^{-6} \text{ m s}^{-1})$
-0.2	8.5 ± 1.3
0	8.0 ± 0.9
+0.2	8.3 ± 0.5

velocity on the sign or indeed presence of the magnetic field gradient was observed.

3.2. Fingering

By investigating the reaction in a vertical tube, rather than a shallow layer, there is an increased risk of hydrodynamic effects, where density differences associated with the reaction may cause convection. This type of behaviour has been observed in a number of travelling wave reactions [1,8,9] and also appears to be present in this system after the initial period in which the flat wave front is dominant. The flat wave front persists for typically 10-20 min after initiation of the reaction, then a perturbation of the interface occurs, which develops into a finger or tendril. Fig. 4 shows a typical set of images after fingering occurred. This experiment was performed without additional gradients; similar images were obtained for fingers formed in experiments in which positive or negative gradients were applied. The origins of this fingering are uncertain. Experiments have been done where the reaction is initiated from the bottom: no tendrils were observed propagating upwards. This suggests that fingering is a manifestation of density differences, arising from compositional differences $(\Delta \rho_{\rm C})$ or temperature differences $(\Delta \rho_{\rm T})$. As the reaction mixture used in this Letter is exothermic ($\Delta H = -8.15 \pm$ 1.25 kJ l⁻¹) a decrease in density ($\Delta \rho_T < 0$) for the reacted Co(III)EDTA⁻ solution is expected. To calculate $\Delta \rho_{\rm C}$, the densities of typical unreacted and fully oxidised



Fig. 4. MRI images after the development of fingering, in the reaction of $Co(II)EDTA^{2-}$ with H_2O_2 . No magnetic field gradients were applied in between the images. Image (a) was taken when the fingering distortion became fairly large and images (b)–(d) were taken at 51, 102 and 153 s after image (a), respectively.

Table 2Wave velocities, after the development of fingering

Gradient pulse strength (T m ⁻¹)	Wave velocity $(10^{-6} \text{ m s}^{-1})$
-0.2	173.2 ± 17.7
0	135.1 ± 3.3
+0.2	125.8 ± 3.6

solutions were measured giving values of $\rho_{Co(II)} = 1.077 \pm 0.001$ g ml⁻¹ and $\rho_{Co(III)} = 1.0378 \pm 0.001$ g ml⁻¹, respectively. This leads to a $\Delta \rho_{C}$, which like $\Delta \rho_{T}$, is negative. However as a dicobalt species is formed during this reaction [10], an increase in density is possible before the solution fully reacts and its density eventually falls. From observations of the wave propagating upwards and downwards it seems likely that this possible contribution to the $\Delta \rho_{C}$, gives rise to the fingering. The presence of the negative $\Delta \rho_{T}$ will not prevent this, but may lead to *multicomponent* or *double-diffusive* convection [1].

The velocities of the waves were measured from the MRI and again three sets of experiments were done, in which gradient trains of 0, +0.2 and -0.2 T m⁻¹ were applied. The development of these fingers was followed, by taking consecutive images until the wave front propagated out of the observable region of the imager. By measuring the position of the leading edge of the finger, in a similar way to measurement of the flat interface, its displacement was measured. Table 2 shows velocities, measured from typical experiments once the finger had developed. Once the finger had formed, its velocity was constant. As expected [1] these velocities are greater for the displacing finger than for the flat interface. More importantly there is a difference in behaviour depending on the magnetic field gradient applied. The velocity of the finger is significantly greater when a negative gradient is applied and a positive gradient slightly hinders the progression of the wave.

An explanation for the acceleration of the wavefront in a negative gradient most likely lies with an increase in the transport of the autocatalytic hydroxide ions. The finger, being more diamagnetic than the surrounding solution, experiences a magnetic force directed *down* the field gradient that would bring hydroxide ions to the reacting front, thus propagating the wave more quickly.

4. Conclusions

The MRI technique used here requires differences in the relaxation time of the solvent molecules, produced through a change in oxidation state of a transition metal ion, to image the wave. In this case there is a conversion from paramagnetic reactants to diamagnetic products, which produces a large change in the T_2 of the water molecules surrounding the ions. Changes in oxidation number of transition metal ions have been used to image other wave-forming reactions using MRI, the most-well known being the Belousov–Zhabotinsky reaction [11] and the 1,4-cyclohexanedione-acidbromate reaction [12]. In addition to the measurement of wave front behaviour, MRI can be used to measure the hydrodynamic influences on the wave [13] and can also provide a unique opportunity to investigate these types of reactions in optically opaque systems, such as packed beds.

This Letter presents the first quantitative measurements of wave velocity and magnetic field effects for this travelling wave reaction. The work by He et al. [2] showed that the direction of wave propagation is controlled by the properties of the applied magnetic field. The experiments described here demonstrate clearly that the velocity of the wave can be affected by the presence and direction of a magnetic field gradient in conjunction with a strong uniform magnetic field. We have shown that the geometry of the interface is important: no magnetic effects were observed for a flat interface. It appears that some sort of 'symmetry-breaking' [14] process is required, achieved here by the formation of chemical fingers, before the wavefront becomes sensitive to the applied magnetic field.

It seems plausible that similar magnetic convection effects may be observable in other autocatalytic reactions that show wave behaviour. A pre-requisite is that the reactants and products, and possibly the reaction intermediates, have significantly different magnetic susceptibilities and that large concentration gradients are present.

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