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Propagating Precipitation Waves in Hydrogels

Darrell Collison

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Propagating Precipitation Waves in Hydrogels

Darrell Collison

DISSERTATION

Submitted to the Eberly College of Arts and Sciences at
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in
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ABSTRACT

Propagating Precipitation Waves in Hydrogels

Darrell Collison

In 1896, Raphael E. Liesegang discovered that precipitation reactions may produce striking precipitation rings and bands. More than a century later, propagating precipitation waves were discovered in similar reactions. The bands and rings discovered by Liesegang are static, but traveling precipitation waves exhibit complex spatiotemporal dynamics. Traveling waves are widespread and occur in both living and nonliving systems. Examples include calcium waves propagating through *Xenopus laevis* oocytes, cyclic AMP waves in colonies of *Dictyostelium discordium* cells, and spiral waves in propagating flames fronts. Recently, traveling waves were identified in a precipitation reaction involving AlCl_3 and NaOH . The propagating precipitation waves observed in this reaction are the first of their kind to be reported. Since their discovery, other reactions have been shown to produce traveling precipitation waves. Examples of reactions that produce these waves are: $\text{NaAl}(\text{OH})_4/\text{HCl}$, $\text{GaCl}_3/\text{NaOH}$, $\text{ZnCl}_2/\text{NaOH}$, and HgCl_2/KI . In some configurations, propagating precipitation waves are remarkably similar to the propagating reaction-diffusion waves seen in the Belousov-Zhabotinsky (BZ) reaction. However, precipitation waves are distinctly different from reaction-diffusion waves, in both structure and dynamics.

A two-dimensional model is developed to characterize the behavior of precipitation waves in a cross-sectional configuration. The model is a modified sol-coagulation model that is based upon

models of Liesegang bands and redissolution systems. The dynamics of precipitation waves is characterized in terms of growth and redissolution of a precipitation feature that travels through a migrating band of colloidal precipitate. Precipitation waves are fundamentally 3D in nature; thus, a 3D model is also developed. The 3D model refines the 2D model by identifying dominant processes and extending them to 3D. The 3D model is a general model of precipitation waves that it is capable of describing wave behavior in multiple precipitation systems.

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Chapter 1

Reaction-Diffusion Systems

1.1 Introduction

The coupling of reaction with diffusion is responsible for a wide range of spatiotemporal patterns that occur not only in chemistry but in biology, mathematics, physics and nanotechnology [1–5]. Interest in developing an understanding of these patterns, especially in biological systems, has expanded over the last century; examples include the formation of stripes on a zebra [6], the patterns found in some species of tropical fish [7, 8], the aggregation of the microscopic organism *Dictyostelium discoideum* [9], the electromechanical waves in heart tissue [1, 10], spiral waves in propagating flame fronts [11–13] and the periodic precipitation patterns known as Liesegang bands [14]. In all of these different patterns, it is the coupling of reaction with diffusion that leads to their formation.

Theoretical studies have provided important insights into reaction-diffusion systems. In 1952, Alan Turing presented the first model of pattern formation based on a biological system [15]. Turing's paper was possibly the most influential publication in far-from-equilibrium systems to date. He proposed that a set of nonlinear reaction-diffusion equations could explain why a spatially uni-

form state could lose its stability and result in a nonuniform state. Diffusion driven instabilities, i.e. Turing patterns, can be observed in a simple two-component system, where one of the components acts as an activator and increases the rate of reaction and one acts as an inhibitor and decreases the rate of reaction. For Turing instabilities to occur, the inhibitor must diffuse faster than the activator. Following a small perturbation in the system, a local increase in both the activator and inhibitor occurs. However, because of the greater diffusion coefficient of the inhibitor, it will spread to the surroundings, keeping the concentration of the activator low. Locally, the activator is in excess, leading to the decoupling of the two components. This results in an inhomogeneous distribution of concentrations, leading to the formation of patterns. The work of Turing has been highly influential in the field of pattern formation, and Turing patterns are still being investigated today [16, 17]. The work of Turing describes stationary pattern formation; however, dynamic pattern formation is also of great interest. The discovery of Liesegang bands in 1886 provided an example of a chemical system that can exhibit both static and dynamic pattern formation.

1.2 Liesegang Bands

In 1886, the German chemist Raphael Liesegang first observed the Liesegang band phenomenon when he poured a small amount of silver nitrate solution onto a gel saturated with potassium dichromate. After a few hours, Liesegang noted the formation of concentric circles moving outward from the location where the solution of silver nitrate was poured. The circles were bands of insoluble silver dichromate. If the gel containing potassium dichromate is allowed to set in a test tube and a solution of silver nitrate is placed on top, a series of bands will form vertically in the tube. A typical Liesegang experimental setup consists of a gel containing one of the precipitating ions, known as the inner electrolyte, and a solution with the diffusing ion that is placed on top of the

Figure 1.1. (a) Side-by-side images of regular Liesegang banding with helical Liesegang banding in a test tube configuration. Experimental conditions: A 1.0% agarose gel containing 0.01 M potassium chromate as the inner electrolyte and 0.5 M copper(II) chloride as the outer electrolyte [18]. (b) Band formation in the cobalt chloride and ammonia system at increasing times, from left to right, showing what appears to be moving precipitation bands in a Liesegang system [19].

gel, known as the outer electrolyte. The formation of the precipitation structures is, in part, due to the use of a hydrogel, which prevents convective mixing. Notable features of Liesegang bands include an increase in the distance between the bands as they propagate further from solution/gel interface, as well as an increase in band thickness. Since the discovery of the banding phenomenon, many different co-precipitating ion pairs have been shown to produce Liesegang bands [20–23]. From these ion pairs, several different types of banding structures have been observed. Two notable structures are helical patterns and inverse banding. With inverse banding, the separation distance between the bands decreases as the distance from the solution/gel interface increases [24].

Helical patterns corkscrew downward through the gel and the distance between the precipitate bands increases the further from the solution/gel interface the reaction has progressed [18, 25]. A complete model of Liesegang band formation is still being developed, as no single theory has been able to describe all of the experimental findings. However, two theories, the supersaturation theory and the sol coagulation theory, explain some of the experimental findings.

1.2.1 Supersaturation Theory

Supersaturation theory was the first theory set forth to describe the mechanism of Liesegang banding and was developed by Wilhem Ostwald in 1897 [26]. The basic idea of this theory is that in order for precipitation to occur, the ion product (Q_{sp}) of the precipitate must be above the solubility product (K_{sp}), meaning that the system is supersaturated. For precipitation to occur, the concentration of particles present must reach a nucleation threshold. With this model, as the outer electrolyte, B , diffuses into the gel, it reacts with the inner electrolyte A . As B continues to diffuse, its concentration will increase until the solubility product is exceeded and the system is considered supersaturated. Once the nucleation threshold is reached, precipitation will occur. Since the nucleation threshold is higher than K_{sp} , precipitation will occur very rapidly until all of the ions in the region have been depleted. This occurs because the diffusion of B is slow compared to the rapid precipitation process. Since the precipitation mechanism was halted, the nucleation threshold must once again be reached. This will cause zones in the gel devoid of precipitate.

1.2.2 The Spacing and Time Laws

The spacing law of Liesegang banding was first proposed in 1923 by Jablczynski [27]. Jablczynski noted that the distance between the bands usually produces a geometric series. This gives rise

to the spacing law

$$x_n \approx (1 + p)^n, \quad (1.1)$$

where x_n is the distance to the n^{th} band as measured from the gel surface, and p is the spacing coefficient. The value of the spacing coefficient has been determined for many systems and ranges from 0.05-0.4 [28]. Matalon and Packter observed that the spacing coefficient is not a universal constant; it depends on the specifics of the system, such as the initial concentrations of both the inner and outer electrolytes [29]. The relations for the spacing coefficient are given by

$$p = F(A_o) + \frac{G(A_o)}{B_o}, \quad (1.2)$$

where A_o and B_o are the inner and outer electrolyte concentrations, respectively, with $F(A_o)$ and $G(A_o)$ being decreasing functions of A_o . The function $F(A_o) \approx A_o^{-\delta}$, with $0.2 \leq \delta \leq 2.7$, and $G(A_o)$ is not fully understood but generally decreases as A_o increases [30].

The time law was first reported by Morse and Pierce in their 1903 publication [31]. It is observed that

$$x_n \approx \sqrt{t_n}, \quad (1.3)$$

where x_n is the distance measured to the n^{th} band from the top of the gel, and t_n is the time of formation of the n^{th} band. This equation is directly related to the diffusion driven dynamics of the system.

1.2.3 Sol Coagulation Theory

The sol coagulation theory is similar to the supersaturation theory, except that in this theory an intermediate sol or colloidal species C is formed. A general scheme for band formation with

this theory is given by the following reactions:

where A , B , C and P are the inner electrolyte, outer electrolyte, sol and precipitate, respectively. With this precipitation mechanism, the second step, Eq. 1.5, will only occur once the concentration of C is above a critical threshold C^* . Once again, the system must be supersaturated in C before the critical threshold C^* is reached. After C^* is reached, the production of P will occur. Once P is present, C can then react directly with P to form two P s via the third step, Eq. 1.6. This process is known as autocatalysis; for every one mole of P used in the reaction, two moles are produced. The autocatalytic step causes the formation of P to occur very rapidly once $C \geq C^*$. It is the autocatalytic step that leads to band formation. Once all of the available C has been consumed, P is no longer produced locally, and the third step is turned off. In order for P to be produced again, the critical threshold C^* must be reached. This model describes normal Liesegang band formation; however, there are Liesegang systems that produce dynamic banding, where a moving precipitation pattern is observed.

1.2.4 Dynamic Liesegang Bands

Dynamic Liesegang band formation occurs when the precipitate formed has the ability to be redissolved by the outer electrolyte to form a soluble complex. Depending on the kinetics of the system, a stratum of bands can be formed with the same periodicity as observed in static band formation [19, 32], or a single traveling band of precipitate can be formed. If a stratum of bands is observed, the bands appear to be moving downward through the gel. However, as a new band

is formed, when $C \geq C^*$, previously formed bands are dissolved by excess outer electrolyte. The purpose of having excess outer electrolyte ensures that enough ions are present for redissolution to occur. The bands are not actually moving, but appear to move due to the continuous formation and redissolution of bands. An example of this type of Liesegang system is the $\text{Co}^{2+}/\text{NH}_3$ reaction [33]. As ammonia diffuses into the gel containing Co^{2+} ions, reaction occurs to produce sol. Once the sol concentration is above the critical threshold, autocatalytic production of $\text{Co}(\text{OH})_2$ occurs. As the reaction continues, solid $\text{Co}(\text{OH})_2$ reacts with excess ammonia to produce the soluble hexaamminecobalt complex ion, $\text{Co}(\text{NH}_3)_6^{2+}$. This reaction can be modeled via a mechanism much like the one described for the sol coagulation theory, with the addition of a dissolution step [34]:

The second type of dynamic banding is also caused by redissolution behavior, where a single propagating band of precipitate is observed, which can be seen in the $\text{Cr}^{3+}/\text{OH}^-$ system [19, 22]. In this type of system, instead of the formation of multiple bands precipitate, a single band is formed that gradually thickens as it propagates through the gel. The model for dynamic banding can also describe the propagating single precipitation band, except the autocatalytic production of P described in Eq. 1.9 is removed. Without the autocatalytic production of P , the concentration of C is never rapidly depleted and the diffusion front is able to maintain the concentration $C \geq C^*$ so that Eq. 1.8 occurs continuously [23].

1.3 The Belousov-Zhabotinsky Reaction

Boris Belousov discovered the Belousov-Zhabotinsky reaction in 1951, but at the time the scientific community did not understand the reaction. Belousov was looking for an inorganic equivalent to the Krebs cycle [35]. He discovered a reaction that exhibits oscillations in its intermediate species. By choosing an appropriate catalyst, the mixture changes color depending whether it is oxidized or reduced. It was believed that the oscillatory behavior reported violated the second law of thermodynamics; however, this was later proven not to be the case. It was not until 1961 and the work of A. M. Zhabotinsky that the now famous reaction, often referred to as the BZ reaction, began to be understood [36]. The BZ reaction takes place far from chemical equilibrium and oscillates between the oxidized and reduced states of a metal catalyst. The overall chemical reaction is as follows:

However, this overall reaction is not sufficient to describe the behavior that is observed in this system. The reaction mechanism for the BZ is complex and involves many reaction intermediates. The first mechanism was proposed by Zhabotinsky [36], but it was later improved upon by others. In 1972, Field, Körös, and Noyes proposed a ten elementary step reaction mechanism for the BZ reaction [37], known as the FKN model. Since then, other groups have proposed models for the BZ reaction, such as the Oregonator [38] and the ZBKE model [39].

1.3.1 The Oregonator Model

The Oregonator model is based on the FKN mechanism and includes five irreversible steps to describe the oscillations [35, 40]:

where $X = \text{HBrO}_2$, $Y = \text{Br}^-$, $P = \text{HOBr}$, $A = \text{BrO}_3^-$, and $Z = \text{Ce}^{4+}$. In the simplified model, an oscillation takes place via the following scheme: Eq. 1.12 represents the removal of the inhibitory species Br^- and the production of the autocatalyst HBrO_2 ; Eq. 1.14 gives the autocatalytic reaction, with the production of 2 moles of HBrO_2 from 1 mole of HBrO_2 and the oxidation of the metal catalyst; the autocatalytic production of HBrO_2 continues until the concentration of Br^- , which is produced in Eq. 1.16 by the reduction of the metal catalyst, increases to consume HBrO_2 and inhibit the autocatalytic process. As long as the concentration of Br^- is above a critical threshold, the autocatalytic step is inhibited. The concentrations of the species in the overall reaction are only slightly depleted during an oscillation cycle, which allows numerous oscillations to occur over the course reaction.

1.3.2 Pattern Formation in the BZ Reaction

Pattern formation can be seen in spatially extended experimental setups. Originally, Belousov studied the reaction in well-stirred solutions. For a non-stirred system, the reaction intermediates propagate outward via diffusion, causing reaction to occur as they move through the system. In a 2-D configuration, the coupling of reaction and diffusion gives rise to chemical waves. Chemical waves in the BZ reaction were first studied by A. Zaikin and A. M. Zhabotinsky [41]. In thin solutions,

trigger waves develop and propagate as the autocatalyst diffuses ahead to initiate autocatalysis [42, 43]. The trigger waves propagate with a constant velocity that is dependent on the initial concentrations of the reactants [38]. Trigger waves that are formed in thin solutions can produce either target patterns or spiral waves [42–44]. Target patterns are formed from a pacemaker source that generates waves at a given frequency, and, in a given system, more than one pacemaker may be formed. The pacemaker with the highest frequency will overtake any other pacemaker source that oscillates with a slower frequency. Breaking or cutting a target wave gives rise to spiral wave formation. This can be carried out by tilting the solution or dragging a thin wire through a pacemaker source. The result is two free wave ends, which will produce counterrotating spiral waves. Traveling waves in the BZ reaction are propagating concentration gradients that arise from the oscillatory chemical reaction. Wave propagation is also dependent on the size of the perturbation to the system. If the perturbation to the system is too small, the system will relax back to its steady state. However, if the perturbation is above a critical threshold, wave propagation can occur. With diffusion, the intermediate species enter neighboring regions to cause the continuation of the reaction. For this to occur, the reaction time scale and diffusion time scale must be comparable.

A generic mathematical description of a traveling wave is given by the following reaction-diffusion equation:

$$\frac{\partial u_i}{\partial t} = D_i \nabla^2 u_i + f(u_i) \quad (1.17)$$

where D_i is the diffusion coefficient for the i^{th} species of interest, ∇^2 is the Laplacian operator, u_i is the local concentration of the i^{th} species, and represents the rate of reaction in the homogeneous system [45]. For systems with multiple propagating waves fronts, such as the BZ reaction, an activator/inhibitor model is used to describe the wave behavior. While activator/inhibitor

models describe wave behavior of oscillating chemical reactions, they fail to describe propagating precipitation waves.

1.4 Overview

The studies outlined in this dissertation focus on the development of an understanding of propagating precipitation waves. Propagating precipitation waves involve the formation and dissolution of a precipitate in a gel medium. However, they also require multiple phases of precipitate to be present at the same time. Without multiple phases of precipitate, wave formation and propagation would not be possible. One type of precipitate forms a moving band while the other type grows diagonally through the band and acts as a barrier to the diffusion of the outer electrolyte. Chapter 2 presents an introduction to propagating precipitation waves and will include a description of a novel 2-D model used to simulate experimental findings. Chapter 3 discusses the development of a generalized 3-D model, which can describe both the circular and spiral waves that are experimentally observed. Chapter 4 outlines new experimental features of traveling precipitation waves, along with the discovery of two novel systems that produce the traveling precipitation wave phenomenon.

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Chapter 2

Propagating Precipitation Waves

2.1 Introduction

Propagating waves are pervasive in living and nonliving dynamical systems, occurring on a wide range of space and time scales and taking a variety of forms, from electromechanical waves in heart tissue [1, 2] to spiral waves in propagating flame fronts [3–5]. The mechanism of propagation, generally, is the coupling of a positive feedback process with transport, such as the coupling of autocatalytic chemical reaction with diffusion in the Belousov-Zhabotinsky (BZ) reaction [6]. Physical processes, such as phase changes, also play a role in propagating waves [7], for example, surface reconstruction is an essential process in the wave dynamics of the oxidation of CO on a single-crystal Pt [8]. Propagating precipitation waves are another example where multiple phases are essential for wave propagation. They were first discovered in the reaction of aluminum chloride with sodium hydroxide in a hydrogel medium [9]. It was shown that, given the appropriate initial concentrations of the inner and outer electrolyte, dynamic pattern formation occurs. The coupling of reaction with diffusion plays an important role in wave propagation; however, phase changes and the physical properties of the phases are dominant in the wave propagation for this system.

Experiments have shown that the patterns observed in this reaction are similar in appearance to the traveling waves observed in the BZ reaction if viewed from above. However, if vertical gel slabs are used, we observe that the traveling wave appears within the precipitation band that is simultaneously moving downward in the gel [9].

In this chapter, experimental findings in the $\text{AlCl}_3/\text{NaOH}$ system are reported and key structural features of propagating precipitation waves are defined. On the basis of the experimental findings, a 2-D model capable of describing the qualitative features of the traveling waves in a gel slab configuration is developed. Previous computational studies of redissolution Liesegang systems have led to models that describe the experimentally observed stratum of precipitation bands [10, 11], as well as a single moving precipitation band [11, 12], as discussed in Chapter 1. The model presented here incorporates approaches used in these studies to develop a modified sol coagulation model by introducing a second form of precipitate with physical properties different from those of the migrating precipitation band. Models that have two forms of precipitate have been used to describe spatial structure formation in nonamphoteric hydroxide precipitation systems [13]. The interaction of this precipitate with other species in the system yields a model that captures both the migrating precipitation band and the traveling precipitation waves that occur within the band.

2.2 Experimental Setup

An agar gel mixture is prepared by dissolving 1.0 g of agar in 100 mL of distilled water. The solution is heated and stirred until the mixture reaches a temperature of 90° C. The mixture is stirred for an additional 10 minutes without heating. Powdered aluminum chloride hexahydrate is added and the mixture is stirred until it is homogeneously mixed and the solid aluminum chloride is fully dissolved. Experiments are carried out in either a gel disk or a gel slab configuration.

In the disk configuration, the gel mixture is poured into a glass petri dish with a radius of 45 mm. Approximately 30 mL of the gel mixture is poured in the petri dish and allowed to cool to room temperature, which causes it to solidify. If the gel slab setup is used, the mixture is injected between two glass microscopes slides (50 mm x 75 mm) that are separated by a 1.0 mm thick Teflon spacer and clamped together to prevent leakage. The gel is again cooled to room temperature, which causes the gel mixture to solidify. The gel disk allows for visualization of the spiral waves, whereas the gel slab configuration offers a cross-sectional view of the waves propagating within the precipitation band. A variation of the gel slab experiment utilizes a 10 mm separation distance between the glass slides, which allows simultaneous images from above and from the side to be captured. This experiment allows the features of the traveling wave to be matched from the above and side views. All of the experimental setups utilize back lighting (unless otherwise noted) and are imaged with a CCD camera that is connected to a computer.

2.3 Characteristics of the Propagating Band and Traveling Waves

The chemistry involved in this system is dependent upon the formation of a precipitate followed by the formation of a soluble complex ion. The reaction scheme is as follows:

As hydroxide ions diffuse into the gel from above, they react with aluminum ions that are trapped within the gel to form a thin layer of colloidal aluminum hydroxide precipitate that constitutes the propagating precipitation band. The thin band of colloidal precipitate travels downward into the

gel and is driven by the diffusion of hydroxide ions. Sharp leading and trailing edges characterize the band, which indicates that the reaction kinetics of precipitation and dissolution are fast compared to diffusion within the gel. The formation of a propagating precipitation band is not unexpected; many systems have been shown to produce this behavior. However, the formation of propagating precipitation waves within the precipitation band is a novel dynamical behavior that was first reported by Volford et al [9]. Spontaneously formed waves occur within a narrow range of inner and outer electrolyte concentrations. Figure 2.1 shows a plot of concentration of inner electrolyte vs. concentration of outer electrolyte. The yellow color indicates a region of concentrations where there is no wave behavior. This occurs at low inner electrolyte concentrations; however, by decreasing the concentration of the outer electrolyte, wave behavior is observed at concentrations of inner electrolyte where spontaneous formation of waves was previously not observed. This indicates that the ratio of inner/outer electrolyte concentration plays a role in the formation of propagating precipitation waves. The green region indicates concentrations where propagating precipitation waves are spontaneously formed. This region is the largest on the plot; however, it should be noted that the range of concentrations where waves are formed is still small. The purple region indicates turbulent-like behavior, which will be discussed in greater detail in Chapter 4.

The waves that occur within the concentration range outlined by the green region in Figure 2.1 propagate outward from spontaneously formed pairs of counterrotating spiral tips to form expanding quasi-circular waves. This behavior is observed in Figure 2.2(a), which shows a top view of expanding waves in a gel disk configuration. Figure 2.2(b) shows simultaneous top and side view images of a wave in a 10 mm thick gel slab configuration. The top image shows a wave that is observed from above, much like in the gel disk configuration, and the second image is the same wave captured from the side. The simultaneous images of the same wave allow us to identify key features of a propagating precipitation wave. The diagonal precipitation feature that

Figure 2.1. Plot of concentration of inner electrolyte vs. concentration of outer electrolyte. The yellow color corresponds to no wave formation, green corresponds to spontaneous wave formation and purple corresponds to turbulent-like pattern formation.

is observed in the bottom image of Figure 2.2(b) is the traveling precipitation wave, and plays an essential role in the wave dynamics.

Wave propagation can be characterized in terms of the diagonal precipitation feature, which has a wave tip and wave back within the precipitation band, shown in Figure 2.2(b). The wave front exists at the leading edge of the precipitation band, and in a side view image appears as a wave tip of the diagonal feature. As the wave front propagates through the precipitation band, it leaves behind a thin line of precipitate to form the diagonal feature. In 3-D, the diagonal feature becomes a surface and the wave front is the leading edge of this surface. The wave front can be seen in the above view image as well; in the top image of Figure 2.2(b) it appears as the dark region ahead of the light region of the wave. The wave back consists of the reattachment of the precipitation band to the diagonal precipitation feature. It is identified as the concave region of colloidal band precipitate beneath the wave middle. The wave back precipitate has the same appearance and dissolution properties as the precipitation band; hence, it can be viewed as the reattachment of the precipitation band with the diagonal wave precipitate.

Matching the features the precipitation wave in the above and side-view images in Figure 2.2(b) (see red vertical dashed lines) shows that the wave back is associated with the light region in the above view image. The colloidal precipitate is visually less dense in the wave back than in other regions of the precipitation band. Since the gel is illuminated from below, more light is allowed to travel through this region, which allows for a greater intensity of transmitted light. The dark region of the wave in the above-view image matches with the diagonal precipitation feature in the side-view image, and the leading edge matches with the wave tip of the diagonal feature, the wave front.

The dynamics of a propagating wave in a gel slab is illustrated in Figure 2.3(a), with three images of a wave taken at successive times. The wave front propagates at an angle of approximately

Figure 2.2. (a) Image, taken from above, of waves in a gel disk within a petri dish. (b) Simultaneous images taken from above and from the side of a wave in a 10.0 mm gel slab. The bottom image is taken with front illumination. The structural features, the wave front A and the wave back B, are indicated, as well as the migrating precipitation band C. Arrows in the bottom panel near the wave front show relative horizontal and vertical wave velocities and the vector sum showing the overall wave velocity of $5.76 \times 10^{-3} \text{ mm s}^{-1}$. Experimental conditions: (a) A 20.0 mL solution 2.5 M NaOH is poured on top of 25 mL of gelled agar mixture. The agar mixture contains 6.5 g of AlCl_3 per 100 mL of deionized water and 1.0 g of agar. (b) A 10.0 mL solution of 2.5 M NaOH is poured on top of a 15.0 mL of gelled agar mixture with the same composition as in (a). Images are taken at 725 s (a) and 2100 s (b). In the bottom image of (b), the surface of the precipitation feature can be discerned below the diagonal feature in the foreground, which is visible because the wave curves to the right, as shown in the top image of (b). Vertical and horizontal scale bars in (a) and (b) are 1.0 mm. Figure adapted from reference [14].

22° with respect to the leading edge of the horizontal precipitation band. As can be seen in the images, this angle is effectively constant, indicating that the ratio of the horizontal and vertical components of wave velocity is constant. As the experiment progresses, the precipitation band gradually broadens and its velocity decreases as it propagates downward through the gel, which is accompanied by a decrease in the velocity of the precipitation wave. The essentially constant ratio of the vertical to horizontal velocities reflects the strongly coupled dynamics of the propagating waves and precipitation band. As the features of the precipitation band change as a function of time, some aspects of the precipitation wave also vary. For example, waves formed early in the experiment exhibit only a small extension of the precipitation feature beyond the wave back. This region lengthens to form an extended feature as the precipitation band descends in the gel, which we refer to as the wave tail.

Figure 2.3(b) shows a side view image of a wave in which the pH indicator bromothymol blue was added to the gel. The image shows the gel to be basic above the precipitation band and acidic below the band, as is expected. The low pH immediately below the diagonal precipitation feature between the wave front and wave back indicates that the thin line of precipitate acts as barrier to the diffusion of OH^- . The characteristics of the precipitation feature in this system are similar to those of passive borders observed in studies of nonamphoteric hydroxide precipitate systems [15]. Such barriers have been found to behave as ion-selective membranes, restricting the diffusion of the outer and inner electrolytes. These studies have also shown that the pH within the passive barrier is high, which indicates that although the OH^- ion is not able to cross the barrier, it is able to diffuse into the barrier.

Figure 2.3. (a) Images the spatiotemporal development of a wave in a 1.0 mm gel slab at 375, 1050, and 2050 s. (b) Image of a wave traveling in a gel containing the pH indicator bromothymol blue (with front illumination). The wave structure is labeled to indicate the wave front A and the wave back B. Experimental conditions: A 1.0 mL solution of 2.5 M NaOH is added to the top of 2.0 mL of gelled agar mixture. The agar mixture contains 6.5 g of AlCl_3 per 100 mL of deionized water and 1.0 g of agar. Vertical and horizontal scale bars in (a) and (b) are 0.5 mm. Figure adapted from reference [14].

2.3.1 Characterization of the Band and Wave Precipitates

Scanning electron microscopy (SEM) is used to gain further experimental evidence that the wave precipitate and the band precipitate are two different structural forms of aluminum hydroxide. Other researchers have used this technique to observe structural details of precipitates that are not visible with traditional light based microscopes [16–19]. Most SEM's, including the type used in this study, operate under high vacuum conditions, which means that the sample must be free of water. Since the precipitate to be observed is contained in a hydrogel, the water in the hydrogel must be removed without altering the structure of the precipitate. To accomplish this, a critical point drier is used. Critical point drying is a technique used to remove water from a biological sample while leaving the structure of the sample unchanged. Due to the high surface tension in water and the finite time required to convert a liquid into a gas, air-drying will cause the structure of the gel to collapse. To avoid this, critical point drying utilizes a supercritical fluid, in this case based on CO_2 . The critical point of a substance is in the high pressure and high temperature region of the phase diagram, which is seen in Figure 2.4. Here the substance is no longer considered a liquid or a gas but what is known as a supercritical fluid, which has a very low surface tension. Once in the transitional supercritical fluid state, the pressure and the temperature are lowered back to standard temperature and pressure. The advantage of drying a sample in this manner is that a phase boundary is not crossed and is therefore less damaging to delicate samples. The critical point of water occurs at 647 K and 22.06 MPa, which is less convenient. Water in the sample must first be replaced with ethanol, since CO_2 and water are not miscible liquids.

SEM images are obtained by collecting secondary electrons that are ejected from the sample after being hit with electrons from the electron gun, which are translated into a topographical image. However, if the sample is an insulator and hence not conductive, charge will build up on its

Figure 2.4. The phase diagram of CO₂

surface, causing electrons from the electron gun to be deflected from the surface, which is known as charging. To prevent charging, a thin coating of metal is applied to the sample by sputter deposition. Sputter deposition is a physical vapor deposition method which accelerates particles of a plasma at a target to erode the material and coat samples with a very thin film of the target material. In short, the sample is placed into a vacuum chamber and a carrier gas is pumped in. A negative charge is then applied to the target material, which causes free electrons to accelerate away from the target material. The accelerated electrons will collide with the carrier gas in the chamber, in this case argon, and cause argon atoms to lose an outer shell electron, making Ar^+ ions. These ions will be attracted to the negatively charged target material and will collide with

Figure 2.5. SEM images of the band and wave precipitates. (a) Image of the band precipitate at 7000 times magnification. (b) Image of the wave precipitate at 7000 times magnification.

the material, causing atoms of the material to be knocked free. These atoms, since they are not charged, will travel in a straight line from the target through the chamber and coat the sample with the target material.

Samples were taken from the gel slab configuration. Once the precipitation band and wave forms, the outer electrolyte solution is removed from the top of the gel, stopping further reaction. The clamping device is then removed and one of the glass slides is removed to allow access to the gel. A sample is cut from the gel that includes both the band and wave precipitates and is placed in a solution of ethanol to prepare it for critical point drying. The samples are dried using a Tousimis Autosamdri-815 CO₂ critical point dryer. Once the sample is dry, it is attached to a stub that has double-sided carbon tape to insure that the sample does not move when placed in a vacuum. Then it is sputtered using a Denton Desk V sputter coater with a gold/palladium alloy. The sample is then ready to be imaged with the JEOL JSM-7600F scanning electron microscope.

The images obtained from this study proved to be inconclusive. After drying the band and wave precipitates in the gel medium, the gel itself turned white in color, the same as the precipitates. Once the sample was placed in the SEM, identification of what part of the sample was being viewed

proved to be extremely difficult. To resolve this issue, the band and wave precipitates were cut from the gel and placed in boiling water to remove any possible gel that was remaining on the samples. The samples were then allowed to air dry before being sputtered. After examining these samples with the SEM, a significant difference in structure could not be identified. However, this result does not provide evidence that a structural difference is not present. Figure 2.5 shows images of the band and wave precipitate that were obtained from SEM imaging. Figure 2.5(a) shows the band precipitate and Figure 2.5(b) shows the wave precipitate. These images were taken of the band and wave precipitates that had the gel layer removed by placing the precipitates in boiling water. The samples were sputter coated with gold/palladium to prevent charging. On examining the two images, no significant differences can be observed. Heating the two samples in water and air drying may have changed the structure of the precipitates. Raman spectroscopy may be a possible alternative method to observe the differences between the two precipitates, which allows the identification of different polymorphs of chemical compounds [20, 21].

2.4 Spatiotemporal Model

2.4.1 Precipitation Band

A model that captures the spatiotemporal dynamics of the $\text{AlCl}_3/\text{NaOH}$ system should be able to describe both the migrating precipitation band and as well as the traveling waves within the band. This section will address the first of these requirements using a modified sol-coagulation model of Liesegang band formation. A number of approaches for modeling Liesegang band behavior have been developed [22, 23], and many use a diffusive intermediate species known as a sol, combined with a threshold above which a precipitate can form and growth can occur [23]. A characteristic feature of these models is the autocatalytic production of the final precipitate, once

the intermediate or "smaller" type of precipitate has formed. This autocatalysis leads to the local decrease in the intermediate, and precipitate growth does not occur in the adjacent regions, thus giving rise to the formation of successive stationary precipitation bands. An example of such an approach is the CMP model [24, 25], which uses three principle components: sol, small precipitate, and large precipitate. The sol is allowed to diffuse, while the two types of precipitate are assumed to be stationary. The sol is continuously formed in the system through the reaction of the outer and inner electrolytes.

A modified CMP model allows for the dissolution of both types of precipitate through the direct reaction with the outer electrolyte to form a soluble product [11]. This model can account for the experimental observations in redissolution Liesegang systems, such as the stratum of Liesegang bands forming and redissolving, or a single band that moves down through the gel [11].

We apply an approach similar to the sol-coagulation model of Liesegang band formation [22, 26], by the introducing dissolution of the precipitate and sol components in the description of the $\text{AlCl}_3/\text{NaOH}$ system,

where A , B , C and P_1 represent the inner electrolyte, outer electrolyte, sol and precipitate, with concentrations a , b , c and p_1 , respectively. The species A , B and C are free to diffuse with equal diffusion coefficients D . The rates of the four processes are given by k_1ab , $k_2(c-c^*)H(c-c^*)$, k_3p_1b , and k_4p_1b , respectively. The step function $H(s)$ is defined as $H(s) = 1$ for $s > 0$ and $H(s) = 0$ for $s < 0$. The concentration c^* is the threshold value at which coagulation occurs. This model

produces a single moving band of precipitate, migrating downward through the medium, much like the redissolution Liesegang experiments.

2.4.2 Propagating Precipitation Waves

The second component of the model involves the dynamics of the propagating precipitation waves within the migrating precipitation band. As described above, experimental observations show that the diagonal feature plays an essential role in the dynamics of the propagating wave. The precipitate is continuously formed at the wave front, moving diagonally through the gel, with both vertical and horizontal components. The resultant narrow region of precipitate dissolves slowly along its length, as it is exposed to the downward diffusion of the OH^- ion. The preferential growth in the vicinity of the wave front and slow dissolution is convincing evidence that this precipitate is of a different physical form than the colloidal band precipitate. It also has a different visual appearance, as is evident in Figures 2.2 and 2.3. The wave precipitate is labeled P_2 with concentration p_2 .

The formation of the thin region of P_2 precipitate involves preferential directional growth, which has been seen in the formation of needle crystals and dendritic structures in supersaturated solutions and undercooled melts [27]. Microscopic models of directional growth, involving front curvature and surface energy considerations, are well developed [28, 29]. For the purpose of developing a model for the overall spatiotemporal behavior of the $\text{AlCl}_3/\text{NaOH}$ system, a mesoscopic representation of wave front growth and movement is developed. Each precipitation wave has an active wave front at which P_2 growth occurs, and this growth moves the wave front forward along its diagonal trajectory and leaves behind a thin region of P_2 precipitate.

A wave is initiated in the 2-D model simulations of the cross section representation by switching on P_2 formation at an arbitrary point in the leading edge of the precipitation band. This location

constitutes the initial position of the wave front and is typically chosen to be near the system boundary to allow the largest distance of propagation. The growth of P_2 at the wave front is governed by a process analogous to process 2.4 but with C directly producing P_2 rather than P_1 ,

at a rate $k_5 H(c - c^*)$. The directed growth of the P_2 precipitation feature is modeled as the growth of a solid from the available sol C . In the discretized two-dimensional medium, the diffusing species A , B , and C are described by the reaction-diffusion equations with a discrete approximation of the Laplacian operator. The wave front or tip of the P_2 precipitation feature, however, grows as a solid into the neighboring grid point that is determined by the highest concentration c of sol. The wave front advances as p_2 at a particular point exceeds the threshold p_2^* . Equation 2.7 requires that $c > c^*$ at any grid point into which the wave front grows, as sol must be above a critical concentration for P_2 growth. A further requirement is that p_1 must be below the threshold p_1^* . Hence, in this scheme, the two precipitates compete for the sol, with P_2 formation preferred when p_1 is small. Growth is restricted to the wave front or wave tip, and when more than one neighboring point satisfies the conditions for growth, the wave front grows into the point with the largest sol concentration c .

The formation of P_2 occurs only at the wave front, and the growth of the wave front gives rise to the thin diagonal line of precipitate. The precipitate P_2 is subject to dissolution in the presence of the downward diffusing OH^- ion in a process analogous to reaction 2.6,

at rate $k_6 b p_2$. On the basis of the different physical properties of the precipitate P_2 , the diffusion of the inner electrolyte and sol does not occur into or out of this narrow region when the concentration of P_2 is above a permeability threshold ($p_2 > p_{2,perm}$). The absence of P_1 formation below the

thin line of P_2 precipitate indicates that it serves a barrier to the downward diffusion of the hydroxide ion; therefore, diffusion across the precipitation feature does not occur when P_2 is above the threshold concentration $p_{2,perm}$. However, the eventual dissolution of the diagonal feature requires the presence of the hydroxide ion, and therefore, it must be able to diffuse into the thin line of precipitate. The dissolution of P_2 eventually leads to the line of precipitate to become permeable, and all species undergo diffusion across this feature once p_2 has become sufficiently small ($p_2 \leq p_{2,perm}$).

Two-dimensional simulations of the spatiotemporal behavior are carried out using processes 2.3-2.8 with diffusion terms. The integration for width X and height Z utilizes no-flux boundary conditions for all species apart from the fixed (Dirichlet) boundary condition for the outer electrolyte, $b(t, x, 0) = b_0$, $\forall x$ and $\forall t$. Initial conditions are given by $c(0, x, z) = 0$, $p_1(0, x, z) = 0$, $\forall z$ and $\forall x$; $b(0, x, z) = b_0$, $a(0, x, z) = 0$, $\forall x$ and $0 < z < Z_s$; $b(0, x, z) = 0$, $a(0, x, z) = a_0$, $\forall x$ and $Z_s < z < Z$, where Z_s is the location of the liquid-gel interface.

2.5 Modeling Results

Figure 2.6(a) shows images of the P_1 precipitation band and the propagating P_2 wave at successive time intervals. The migrating precipitation band can be seen on the left in the top image; on the right, a recently initiated P_2 wave is beginning to grow and propagate. The successive images show the progress of the wave and its impact on the precipitation band. The filled in circles show the impermeable region of the P_2 precipitation feature, whereas open circles show the permeable region. In the second image, in the tail of the wave, p_2 has decreased sufficiently from the dissolution that the diffusion of hydroxide ions across the P_2 feature occurs, and a new P_1 precipitation band begins to form on the right. The new precipitation band connects to the

underside of the thin line of P_2 precipitate. A small region of the P_2 feature can be seen behind the wave back through which diffusion is still prohibited. Much like the experiment behavior, the wave front travels at essentially the same angle with respect to the precipitation band ($\sim 31^\circ$), indicating that the ratio of the horizontal and vertical components of velocity is virtually constant. However, the velocities of both the precipitation band and the traveling waves within the band decrease as the band migrates downward through the gel.

A more detailed image of the P_1 precipitation band and the P_2 wave is shown in Figure 2.6(b), with p_1 indicated in a concentration map. Figure 2.6(c) shows the same precipitation band and wave but with the concentration of sol c . In the absence of P_2 , hydroxide ions diffuse freely downward in the medium. The sol concentration rises and coagulates to form P_1 , once $c > c^*$. Dissolution of P_1 follows, with increasing hydroxide ion concentration, resulting in a band of P_1 that propagates by diffusion downward through the medium. The sol concentration is higher near the wave front at the leading edge of the precipitation band. When $c > c^*$, which first occurs immediately ahead of the precipitation band, P_2 growth occurs by process 2.7, and the wave front moves ahead into a region of low p_1 and high sol. Figure 2.6(b) (inset) shows a time series plot of p_2 at a point which the wave front grows through and leaves behind in the line of P_2 precipitate. There is an initial sharp rise due to process 2.7, and the influx of B , due to diffusion, leads to the dissolution of P_2 along the line of precipitate. Figure 2.6(b) also shows an increased concentration of P_1 in the vicinity of the wave front. The inability of the sol to diffuse through the line of P_2 precipitate leads to an increase in the production of P_1 , because there is a buildup of c in this region.

An interesting emergent feature of the model is the selection of the direction of wave propagation and the angle of the diagonal feature. Analysis of Figure 2.6(c) shows that the sol concentration c is lower to the right of the wave front and higher to the left due to the restricted diffusion of B

Figure 2.6. (a) Simulations of the P_1 precipitation band and the P_2 precipitate wave at times 3.78×10^5 , 6.58×10^5 , 1.03×10^6 , and 1.47×10^6 . (b) Detail of the wave structure in p_1 at time 6.58×10^5 . Inset: p_2 in a point within the diagonal precipitation feature as a function of time (where times are multiplied by 10^5). This curve also approximately corresponds to the spatial profile of p_2 from the wavefront through the wave back along the line of P_2 precipitate. (c) Detail of the wave structure in c at time 6.58×10^5 . In each image, grid points ($p_2 > p_{2,perm}$) are indicated with filled circles; grid points with ($p_2 < p_{2,perm}$) are indicated with open circles. Model parameters: $k_1 = 10^{-3}$, $k_2 = 0.02$, $k_3 = 2.5^{-6}$, $k_4 = 2.5 \times 10^{-5}$, $k_5 = 2.0 \times 10^{-3}$, $k_6 = 2.5 \times 10^{-5}$, $c^* = 2.1$, $p_1^* = 1.2$, $p_2^* = 0.4$, $p_{2,perm} = 0.01$. The simulation utilized 400×1000 grid points, with $dx = 6.3$, $dt = 5.0$, $Z_I = 200$, $a_0 = 10$, $b_0 = 100$, and $D = 1.0$. Vertical and horizontal scale bars in (a) are 20 grid points. Time, distance, and concentration are dimensionless in the nondimensional model 2.3-2.8. Figure adapted from reference [14].

across the line of P_2 precipitate. Thus, once the direction of the wave front motion is selected, it is maintained by this concentration difference, because there is preferential wave front propagation into regions of higher sol concentration. The magnitude of the propagation angle is related to the threshold values of p_1^* and c^* . For example, a lower value of p_1^* tends to increase the horizontal component of the wave front velocity and thus decrease the angle of propagation with respect to the precipitation band.

The restricted diffusion, due to the presence of the thin line of P_2 precipitate, prevents the formation of sol C and precipitate P_1 below the thin line, as is shown in Figure 2.6(b,c). Outer electrolyte B increases on the upper side of the diagonal P_2 feature, and when p_2 decreases sufficiently to allow diffusion, the wave back rapidly forms. The presence of a steep gradient in B in this vicinity causes the reconnection of the P_1 precipitation band to the underside of the line of P_2 precipitate, in a region where the diffusion across the feature does not occur. The diffusion of B , therefore, has both vertical and horizontal components, as shown by the concaved wave back reconnecting to the diagonal P_2 feature. The precipitation band is slightly offset vertically, in both experiments and simulations, relative to the band ahead of the wave. However, the band approaches the same vertical level further behind the traveling wave.

The model also describes more complex behavior observed in the experimental system. Much like the waves observed in excitable reaction-diffusion systems, such as the BZ reaction [30–32], the propagating precipitation waves annihilate upon collision. An example of the behavior is shown in Figure 2.7(a), where the left and right propagating waves collide, leaving a characteristic V-shape region in the precipitation band. This feature eventually disappears, giving rise to the appearance of an undisturbed precipitation band.

Figure 2.7(b) shows a simulation of two precipitation waves propagating towards each other from the left and right system boundaries. When the wave fronts approach each other an eventually

Figure 2.7. (a) Successive images showing two precipitation waves colliding and subsequently annihilating. Images taken at times 875, 1659, and 2350 s; the experimental conditions are the same as in Figure 2.3(b). (b) Model simulation of colliding and annihilating precipitation waves. Two waves are started at the same time at the left and right boundaries. Images are at times 4.55×10^5 , 7.00×10^5 , and 8.89×10^5 ; all parameters are as in Figure 2.6. Vertical and horizontal scale bars in (a) and (b) are 0.5 mm and 20 grid points, respectively. Figure adapted from reference [14].

collide, they can no longer advance due to the depletion of sol. The wave backs then catch up with the respective wave fronts and merge together, with a single, continuous precipitation band emerging, much like the wave collision behavior observed in the experiment.

2.6 Discussion

The precipitation waves described in this chapter occur through a spontaneous transition in the precipitation process that gives rise to a self-assembling dynamical structure. The physical appearance of the P_2 precipitate is unlike that of the P_1 precipitate, apparently due to a different microstructure, and acts as a barrier to diffusion. The stationary structures that have been reported in a number of nonamphoteric hydroxide precipitation systems as well as in the $\text{CuCl}_2/\text{K}_3\text{Fe}(\text{CN})_6$ Liesegang band system arise through a transition to a secondary precipitation process and have similar features. A major difference between the precipitation waves and the stationary structures is that in the latter case the secondary precipitate does not dissolve to allow the formation of new traveling waves.

The basic wave structure produced by the model is in excellent agreement with the wave profiles observed in the experiments. There is essentially no P_1 precipitation band formation below the P_2 feature, from the wave front to the wave back, due to the restricted diffusion of the OH^- ions. The wave back displays the same attachment of the P_1 precipitation band to the underside of the P_2 feature, with similar concave curvature and a slight delay in downward propagation. Although certain details of the shape are sensitive to the model parameters, the basic wave structure is robust and is maintained across a broad range of parameter values.

The mesoscopic model of traveling precipitation waves is consistent with the detailed models for Liesegang and redissolution systems [10, 11, 25]. A common feature of these systems is the

autocatalytic growth of the final "large precipitate" in the band formation. In the model presented here, a second form of precipitate is also produced, with the formation and subsequent production of P_2 in process 2.7. The directed growth of the precipitation feature occurs with the addition of P_2 to the wave front or wave tip from the surrounding sol C . Hence, although this growth process requires the presence of P_2 , the rate of the process depends only on the concentration of c . The P_2 growth takes place at the leading edge of the precipitation band, where the sol concentration is at its maximum, as observed in the experiment.

This model best represents the behavior observed early in an experiment. As the experiment progresses and the precipitation band propagates further downward, there is significantly more P_2 growth, which is clearly visible in the experimental side view images. This contributes to an increasing length of the P_2 feature. The model does not describe this variation, because there is a maximum extent of P_2 formation at the wave front. Inclusion of the conversion of P_1 to P_2 , either by direct means or through re-formation of P_1 via C , along with the relaxation of the maximum P_2 formation, might allow these features to be captured. The model also does not describe the increasing thickness of the precipitation band as it moves deeper into the gel. Modifications of the model to better represent this feature may also lead to improvements in the description of the P_2 formation with increasing depth.

An important similarity between propagating precipitation waves and reaction-diffusion waves is that they both can be defined as propagating concentration disturbances. A wave front develops in the precipitation band by a nucleation process and proceeds to grow, leaving behind the prominent P_2 precipitation feature. The wave advances by directional growth at the wave front. The recovery of the precipitation band from this disturbance arises from the physiochemical properties of the P_2 precipitation feature, which blocks downward diffusion when first formed but then allows diffusion as it undergoes dissolution from the accumulating hydroxide ion. The resumption

of downward diffusion of the hydroxide ion allows for the reestablishment of the P_1 precipitation band, which attaches to the underside of the P_2 precipitation feature, remarkably, in a region where hydroxide ion does not diffuse across the feature. The overall wave propagation can be viewed as a concentration disturbance propagating through the precipitation band, which is the same ahead and behind the traveling precipitation wave. The concentration disturbance involves the growth and eventual dissolution of the P_2 feature and the disturbance in the P_1 precipitation band.

Though there are similarities between the propagating precipitation waves and reaction-diffusion waves, there are also important differences. Perhaps the most apparent is that the medium, the precipitation band, is itself propagating downward, driven by diffusion of the OH^- ion. A similar case of a system with a moving medium is the downward propagating flame fronts in premixed oxygen-butane mixtures, which displays spiral and target waves within the flame front [3–5]. Another important difference is that the constant waveform, constant velocity propagating waves in reaction-diffusion systems are sustained by autocatalysis, whereas the precipitation wave front grows via process 2.7, with kinetics dependent on the concentration of sol, which is sustained by the downward diffusion of the hydroxide ion. These waves are also not constant waveform, constant velocity waves but exhibit velocities and waveforms that vary with the vertical propagation distance of the precipitation band.

2.7 Conclusion

Valuable insights into many types of propagating waves have been obtained from studies of reaction-diffusion waves, from spiral and scroll waves in cardiac tissue [1, 2] to spreading depression (depolarization) in the brain [33]. It is apparent, however, that most propagating waves in biological systems involve processes other than the coupling of reaction with diffusion. It seems

unlikely that any biological waves involve the processes in the precipitation waves described here; however, the wave propagation mechanism might offer insights into similarly complex waves in biological systems. Directed growth is common in biological systems, and the formation of a substance that impedes diffusive transport seems quite plausible in the complex cytoplasm of living cells.

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Chapter 3

3-Dimensional Modeling of Precipitation Waves

3.1 Introduction

A 2-D model of propagating precipitation waves was presented in Chapter 2 that describes the wave behavior observed in the $\text{AlCl}_3/\text{NaOH}$ system in thin gel slabs. A precipitation band travels downward in the thin slab of gel sandwiched between glass plates in this experiment. Precipitation waves spontaneously form within this band and travel diagonally at an approximately constant angle, moving within the plane of the band but also moving downward with the band. The model qualitatively describes both the precipitation band and the precipitation wave within the band by introducing two forms of $\text{Al}(\text{OH})_3$ precipitate with differing physicochemical properties.

Careful investigations of the propagating precipitation waves have shown that they have a number of unique features that differ from familiar reaction-diffusion waves [1, 2]. For example, spiral waves and target patterns in the BZ reaction occur in quasi-2D reaction mixtures or gels [3], whereas the precipitation waves move within a precipitation band that is itself moving downward

through the gel. Hence, the precipitation waves are fundamentally 3-D in nature. Furthermore, the precipitation waves involve both solution phase and solid phase in their propagation mechanism, in contrast to solutions or solution-like gels in reaction-diffusion wave systems. In this chapter, the 2-D model described in Chapter 2 is refined by identifying dominant processes and extended to 3-D. The 3-D model that is presented is considered to be a general model of propagating precipitation waves, as it describes wave behavior in both the $\text{AlCl}_3/\text{NaOH}$ system and the novel $\text{NaAl}(\text{OH})_4/\text{HCl}$ system.

3.2 Experimental Methods

The $\text{AlCl}_3/\text{NaOH}$ system is prepared according to the methods previously described in Chapter 2. In brief, a 1.0 % agar gel solution is prepared by dissolving 1.0 g of agar in 100.0 mL of distilled water. The solution is heated and stirred to a temperature of 90.0 °C. Heating is discontinued and the mixture is stirred for an additional 10.0 min. Reagent grade aluminum chloride hexahydrate is added and the mixture is stirred until the solid dissolves.

In the $\text{NaAl}(\text{OH})_4/\text{HCl}$ system, the gel/inner electrolyte mixture is prepared by first dissolving the aluminum chloride hexahydrate in 50.0 mL of distilled water, followed by the addition of solid sodium hydroxide. By doing this, solid $\text{Al}(\text{OH})_3$ is formed from the reaction of Al^{3+} with OH^- but sufficient OH^- ions are added to continue the reaction and cause the solid $\text{Al}(\text{OH})_3$ to dissolve and form aqueous $\text{NaAl}(\text{OH})_4$. A 2.0 % agar gel mixture is then produced by dissolving 1.0 g of agar in 50.0 mL of distilled water. Both solutions are heated and stirred until a temperature of 90.0 °C is reached. The two solutions are then combined, resulting in a 1.0 % agar gel solution containing $\text{NaAl}(\text{OH})_4$.

Two experimental configurations are used. In the gel disk configuration (3D experiment),

Figure 3.1. Illustrations of both experimental set-ups. (a) The 3D gel disk configuration with camera above the disk. (b) The gel slab configuration with camera viewing from the side.

the appropriate gel mixture is poured into a petri dish (45 mm radius) and allowed to return to room temperature, setting as it cools. The outer electrolyte solution is then poured on top of the gel. In the gel slab configuration (quasi-2D experiment), the gel mixture is poured into a container constructed from two glass slides (50 mm $\times$ 75 mm) positioned 1.0 mm apart. Images of wave behavior in the gel disk and the gel slab experiments are taken from above and from the side, respectively, using a CCD camera. In both cases, back illumination is utilized. Figure 3.1 shows both experimental set-ups. Figure 3.1(a) illustrates the gel disk configuration and 3.1(b) illustrates the gel slab configuration.

Previous studies of the $\text{AlCl}_3/\text{NaOH}$ system revealed that, at appropriate reactant concentrations, spiral waves spontaneously form in a gel disk [1]. The modeling studies presented here initially focus on circular waves, which can be initiated by mechanically perturbing the precipitation band, in this case with a thin piece of platinum wire. A typical circular wave is shown in Fig. 3.2(a), where the wave moves outward from the initiation location. Figure 3.2(b) shows a cross-section image of a precipitation wave in a thin gel slab with the same concentrations of reactants. Figures 3.2(c) and 3.2(d) show corresponding images for the $\text{NaAl}(\text{OH})_4/\text{HCl}$ system.

Figure 3.2(c) shows a somewhat wider wave traveling outward from the initiation site, and a wave cross section in a thin gel slab with the same reactant concentrations is shown in Fig. 3.2(d). Circular waves occur spontaneously in the $\text{NaAl}(\text{OH})_4/\text{HCl}$ system; however, we have not observed spiral waves in this system.

In both the $\text{AlCl}_3/\text{NaOH}$ and $\text{NaAl}(\text{OH})_4/\text{HCl}$ systems, a precipitation band of $\text{Al}(\text{OH})_3$ moves down through the gel, resulting from the diffusion of the outer electrolyte. The reaction can be represented as $A + B \rightarrow P$, where A , B , and P are the inner electrolyte ion, outer electrolyte ion, and precipitate, respectively. In the $\text{AlCl}_3/\text{NaOH}$ system, A and B represent Al^{3+} and OH^- , whereas in the $\text{NaAl}(\text{OH})_4/\text{HCl}$ system they represent $\text{Al}(\text{OH})_4^-$ and H^+ , respectively. In both systems, P corresponds to the precipitate $\text{Al}(\text{OH})_3$. This precipitate dissolves in excess outer electrolyte to give products, $B + P \rightarrow$. The product species, $\text{Al}(\text{OH})_4^-$ and Al^{3+} , for the $\text{AlCl}_3/\text{NaOH}$ and $\text{NaAl}(\text{OH})_4/\text{HCl}$ systems, play no further role in the reaction.

A precipitation wave forms within the region occupied by the precipitation band. Images of waves in thin gel slabs, shown in Figs. 3.2(b) and 3.2(d), allow the identification of key features of the precipitation wave structure: the wave front or wave tip (A), wave middle (B), wave back (C) and wave tail (D). The wave front or wave tip is the leading edge of the wave in 3D or leading tip of the wave in 2D, which occurs at the leading front of the moving precipitation band (E). The wave grows from this tip at a nearly constant angle to the precipitation band, leaving a diagonal precipitation feature, as shown in Figs. 3.2(b) and 3.2(d). The wave middle is the region of the diagonal feature behind the tip, and is located along the path traveled by the wave tip. The wave back is defined as the region where the precipitation band reconnects to the diagonal precipitation feature. Behind this region is the wave tail. The length of the wave tail increases as the wave descends through the gel.

In the above view images, Figs. 3.2(a) and 3.2(c), the wave front is associated with a slightly

Figure 3.2. Images of the $\text{AlCl}_3/\text{NaOH}$ (a,b) and the $\text{NaAl}(\text{OH})_4/\text{HCl}$ (c,d) precipitation wave systems taken from above in a gel disk configuration (a,c) and from the side in a gel slab configuration (b,d). Experimental conditions: (a,b) A 1.0 % agar gel containing 0.25 M AlCl_3 as the inner electrolyte and 2.5 M NaOH as the outer electrolyte; (c,d) a 1.0 % agar gel containing 0.25 M $\text{NaAl}(\text{OH})_4$ as the inner electrolyte and 2.0 M HCl as the outer electrolyte. The structural features, wave front A, wave middle B, wave back C, and wave tail D are indicated as well as the migrating precipitation band E. The scale bars represent 1.0 mm. The images (a)-(d) were taken in four separate experiments. Figure adapted from reference [4].

darker region just ahead of the bright region of the main wave structure. The brighter wave middle is considerably longer in the $\text{NaAl}(\text{OH})_4/\text{HCl}$ system. Concentric circles are visible in the vicinity of the wave back, Fig. 3.2(c), due to the transmitted light passing through the precipitation band or both the precipitation band and wave tail.

3.3 Model development

The propagating precipitation waves can be modeled by including the two forms of precipitate that are present in the system, P_1 , associated with the precipitation band, and P_2 , associated with the propagating precipitation wave [2, 5]. These different precipitates are both forms of $\text{Al}(\text{OH})_3$ but with different physical properties. Following the previous modeling study outlined in Chapter 2, based in part on earlier studies of Liesegang systems [6–8], the formation of P_1 occurs via a diffusive intermediate species C according to

where A , B , C , and P_1 represent the inner electrolyte ion, outer electrolyte ion, the diffusive intermediate, and precipitate, with concentrations a , b , c , and p_1 , respectively [2, 9]. Both C and P_1 can react with the outer electrolyte ion B ,

These reactions correspond to conversion of the diffusive intermediate and redissolution of the precipitate P_1 to the inactive product. The species A , B , and C are free to diffuse with, for simplicity, equal diffusion coefficients D . The rates of the above four processes are given by k_1ab , $k_2(c - c^*)H(c - c^*)H(p_{2,perm} - p_2)$, k_3cb , and k_4p_1b , respectively. The Heaviside step function $H(s)$ is defined as $H(s) = 1$ for $s > 0$ and $H(s) = 0$ for $s \leq 0$. The concentration c^* is the threshold value at which precipitation occurs.

The precipitate P_2 follows similar kinetics as P_1 ,

with the concentration of P_2 given by p_2 . The rates of these two processes are given by $k_5(c - c^*)H(c - c^*)H(p_2^* - p_2)g$ and k_6p_2b , respectively. The growth of P_2 is additionally constrained. Growth occurs only if P_2 is either already present at a location or a neighboring location has $p_2 = p_2^*$. The modeling study outlined in Chapter 2 allowed growth only at a single tip of the wave, with the tip conditionally moving once p_2 reached a critical value p_2^* [2]. The new approach relaxes this condition by allowing simultaneous P_2 growth and movement at multiple locations, with movement occurring through direct attachment to the preexisting P_2 structure, which we refer to as template growth. The concentration c^* is the threshold value at which template growth occurs. Anisotropy associated with the use of Cartesian computational grids in simulations of solid growth from liquid phase is a known concern and is often addressed with empirical approaches [10–12]. We reduce anisotropy in template growth of P_2 with the growth rate scaling factor g . The growth rate scaling factor g is empirically determined based on the separation distance of active P_2 growth sites. Each active P_2 growth site has 26 neighbors in a $3 \times 3 \times 3$ grid, with each neighbor

Figure 3.3. Side-view image of the $\text{AlCl}_3/\text{NaOH}$ system with the pH indicator bromothymol blue added to the gel. Figure adapted from reference [2].

at a distance of either 1, $\sqrt{2}$ or $\sqrt{3}$ from the active site. When new growth occurs in one of these neighboring sites, a g value of 1, $1/2$ or $1/9$, respectively, is assigned according to the separation distance of the active site and the new growth site. The term $H(p_2^* - p_2)$ restricts the maximum amount of P_2 that can be formed at a given location.

Our experiments show that the wave middle, composed of P_2 , acts as a barrier to diffusion, as can be seen in Fig. 3.3. Here, the indicator bromothymol blue is added to the gel. The blue color above the white precipitation layer indicates that the gel is basic and has a high concentration of OH^- , and the yellow color below the precipitation layer indicates that the gel is acidic. Directly below the P_2 precipitation wave, the gel is acidic, indicating that OH^- ions are unable to diffuse through this region. However, the reattachment of the precipitation band to the wave back indicates that, at some point, diffusion through the P_2 structure occurs, due to its redissolution by the outer electrolyte. These features are incorporated into the model by initially preventing the diffusion of species A or C into or out of a region containing P_2 precipitate. However, in order to facilitate consumption of P_2 via process (3.6), we allow diffusion of B into a region containing P_2 . Diffusion of all species is resumed through the remaining P_2 precipitate once its redissolution by process (3.6) has lowered p_2 below a critical threshold, $p_{2,perm}$. The production of P_1 and P_2 are alternative paths for the consumption of C .

Three-dimensional simulations of the spatiotemporal behavior are carried out using reactions (3.1)-(3.6) with the following differential equations:

$$\frac{\partial a}{\partial t} = D\nabla^2 a - r_1, \quad (3.7)$$

$$\frac{\partial b}{\partial t} = D\nabla^2 b - r_1 - r_3 - r_4 - r_6, \quad (3.8)$$

$$\frac{\partial c}{\partial t} = D\nabla^2 c + r_1 - r_2 - r_3 - r_5, \quad (3.9)$$

$$\frac{\partial p_1}{\partial t} = r_2 - r_4, \quad (3.10)$$

$$\frac{\partial p_2}{\partial t} = r_5 - r_6, \quad (3.11)$$

where $r_1 = k_1 ab$, $r_2 = k_2(c - c^*)H(c - c^*)H(p_{2,perm} - p_2)$, $r_3 = k_3 cb$, $r_4 = k_4 p_1 b$, $r_5 = k_5(c - c^*)H(c - c^*)H(p_2^* - p_2)g$ and $r_6 = k_6 p_2 b$, respectively. In keeping with standard models for Liesegang band formation, neither P_1 nor P_2 are allowed to diffuse [13]. The integration utilizes the Euler method for width X , length Y , and depth Z , with no-flux boundary conditions for all species except the fixed (Dirichlet) boundary condition for the outer electrolyte, $b(t, x, y, 0) = b_0$, $\forall x, \forall y$ and $\forall t$. Initial conditions are given by $c(0, x, y, z) = 0$, $p_1(0, x, y, z) = 0$, $\forall x, \forall y$ and $\forall z$; $b(0, x, y, z) = b_0$, $a(0, x, y, z) = 0$, $\forall x, \forall y$ and $0 \leq z < Z_I$; $b(0, x, y, z) = 0$, $a(0, x, y, z) = a_0$, $\forall x, \forall y$ and $Z_I \leq z \leq Z$, where Z_I is the location of the liquid-gel interface.

3.4 Results

Figure 3.4 illustrates the wave behavior generated by reactions (3.1)-(3.6) at four successive times following initiation of the wave by the seeding of P_2 at a single point. Initially, a cone of P_2 grows, Fig. 3.4(a), with the height of the cone increasing as further P_2 is formed at the base of the cone, i.e., the wave front. This wave front tracks the leading edge of the precipitation band, which

moves downward, driven by the diffusion of the outer electrolyte from above. In Fig. 3.4, the P_2 structure is colored according to the value of p_2 , where only values of $p_2 > p_{2,perm}$ are shown. In Figs. 3.4(b)-3.4(d), the top of the cone is truncated due to the dissolution of P_2 , leading to a frustum shaped structure. The radius of the conical frustum increases while its height remains approximately constant as the structure migrates downward.

The wave behavior in the 3D system can be further analyzed by considering a vertical cross section through the structure that incorporates the initial seed point, Fig. 3.5(a). Following the wave initiation, the precipitation waves spontaneously travel in opposite directions, with the same, approximately constant angle with respect to the horizontal precipitation band. This angle arises through a combination of restricted diffusion, preventing growth into the region behind the wave front, and the requirement that $c > c^*$ in the region where template growth occurs. Each precipitation wave has a finite thickness, with the lower edge of the wave advancing by the template growth mechanism. These waves correspond to the conical precipitation wave structure shown in Fig. 3.4(a). The apex of this cone coincides with the initiation point of the wave. Diffusion of the outer electrolyte into the wave middle leads to continuous dissolution of P_2 . Eventually, p_2 drops below the critical threshold $p_{2,perm}$ and diffusion across the P_2 precipitate occurs. The wave back is formed as the outer electrolyte rapidly diffuses into this region, reacting with the inner electrolyte to form P_1 by processes (3.1) and (3.2). Figure 3.5(b) shows the cross section of the wave structure after the wave back has formed. Also shown is the P_2 that is present beyond the wave back at concentrations below $p_{2,perm}$, which corresponds to the wave tail seen in the experiment.

Figure 3.5(c) shows a 2D image of the 3D precipitation wave viewed from above. From this perspective, the wave structure appears to start as a point and grows as a disk of increasing radius. If the values of only p_2 for which $p_2 > p_{2,perm}$ are plotted, this disk becomes ring shaped, as p_2 drops below $p_{2,perm}$ at the wave back.

Figure 3.4. Three-dimensional simulations showing the evolution of the P_2 precipitation wave structure at successive times: 36250, 52500, 68750 and 85000. The color coding represents the concentration p_2 , where only values of $p_2 > p_{2,perm}$ are shown. (a) Conical region of P_2 grows following seeding. (b)-(d) Redissolution of P_2 leads to truncation of the growing cone, and the resultant frustum structure progresses downward through the medium. The two (pink) planes indicate the approximate location of the front and back of the precipitation band. Model parameters: $k_1 = 1.0 \times 10^{-3}$, $k_2 = 0.02$, $k_3 = 2.5 \times 10^{-6}$, $k_4 = 2.5 \times 10^{-5}$, $k_5 = 0.02$, $k_6 = 7.5 \times 10^{-5}$, $c^* = 2.2$, $p_2^* = 0.3$, $p_{2,perm} = 0.01$. The simulation utilized $200 \times 200 \times 200$ grid points, with $dx = 0.02$, $dt = 5.0$, $Z_I = 20$, $a_0 = 5.0$, $b_0 = 55$, and $D = 1.0 \times 10^{-5}$. Figure adapted from reference [4].

Figure 3.5. (a),(b) Vertical cross-section through Figs. 3.4(a) and 3.4(d), simulations of the $\text{AlCl}_3/\text{NaOH}$ system. The concentration $p_2 > p_{2,perm.}$ is indicated by purple; the concentration $p_2 < p_{2,perm.}$ is indicated by violet. (c) Above view of Fig. 2(d) showing $p_2 > p_{2,perm.}$ by purple. (d)-(f) Analogous simulations of the $\text{NaAl}(\text{OH})_4/\text{HCl}$ system. All parameters as in Fig. 2 except $k_6 = 1.88 \times 10^{-5}$. The P_2 precipitation wave structures in (a),(b) and (d),(e) are approximately 3 grid points thick. Figure adapted from reference [4].

Figure 3.6. Images showing wave annihilation in the experimental $\text{AlCl}_3/\text{NaOH}$ system. Two waves are initiated mechanically at $t = 0$. The waves spread in a circular fashion, and then collide and annihilate. Images taken at times $t = 400$ s, 1100 s, 1450 s, and 2075 s in (a)-(d), respectively. Experimental conditions: gel composed of 1.0 % agar with a concentration of 0.25 M AlCl_3 as the inner electrolyte and 2.5 M NaOH as the outer electrolyte. Figure adapted from reference [4].

A comparison of Fig. 3.5(c) with Fig. 3.4 shows that the apparent expansion of the precipitation wave, seen from above in either the numerical or experimental systems, actually corresponds to an expanding conical frustum progressing down through the gel. As in the experimental images, the depth of the P_2 precipitate leading to the visible ring is not evident from Fig. 3.5(c).

The model presented here is general in the sense that the symbols A and B represent the reactant chemical species in either the $\text{AlCl}_3/\text{NaOH}$ system or the $\text{NaAl}(\text{OH})_4/\text{HCl}$ system. The most apparent difference between the two experimental systems is the longer wave middle associated with the $\text{NaAl}(\text{OH})_4/\text{HCl}$ system. The increase in length of this region is achieved in our simulations by either reducing $p_{2,perm}$ or by reducing k_6 , affecting the rate of consumption of P_2 . An example of a longer wave middle obtained by decreasing k_6 is shown in Figs. 3.5(d)-3.5(f). The view from above, Fig. 3.5(f), shows a thickening of the propagating wave, and the side view, Fig. 3.5(e), demonstrates that this arises due to an increase in the length of the wave middle.

An experimental example of propagating precipitation waves annihilating on collision is shown in Fig. 3.6. Two waves were initiated by mechanically perturbing the precipitation band, and the resulting circular wave fronts propagate outward until they meet and annihilate. This behavior appears to be very much like wave behavior seen in other reaction-diffusion systems, such as the BZ reaction [14–17]; however, it is not apparent from the above view in Fig. 3.6 that while each wave is moving outward, it is also moving downward through the gel medium.

Figure 3.7 shows an example of wave annihilation in a numerical simulation, where two waves are initiated and move outward from their initiation sites as circular fronts. In this above view, the waves are color coded according to the vertical depth of the P_2 precipitate in the wave structure. This color coding permits the downward and outward progression of the waves to be seen as they propagate, collide and annihilate. Figure 3.8 shows the annihilation behavior in a 3D representation, now with the color coding representing the concentration p_2 . The collision occurs at the

Figure 3.7. Simulations of two waves shown at successive times: (a) 36250, (b) 48750, (c) 61250 and (d) 75000. The waves are initiated at $t = 31000$ and each wave propagates outward. The waves then collide and annihilate. The color coding corresponds to the depth of the P_2 wave structure. The simulation utilized $260 \times 260 \times 200$ grid points with $k_6 = 7.5 \times 10^{-5}$. All other parameters as in Fig. 3.4. Figure adapted from reference [4].

leading edge of the conical frustum associated with each wave structure, as shown in Fig. 3.8(c). Annihilation occurs because each region of an active wave front requires a continuous supply of outer electrolyte to propagate. As the two wave fronts approach each other and connect, they restrict this supply of reactant due to the impermeable wave middle. Thus, the fronts stop propagating locally, as P_2 can no longer be formed in the vicinity of the collision. The annihilation is completed as the remaining P_2 is consumed by the outer electrolyte, and the wave backs of the respective waves join to form a continuous precipitation band in the collision region, as shown in Fig. 3.8(d).

Spiral wave behavior is observed in the $\text{AlCl}_3/\text{NaOH}$ system [1, 2], and simulations of this behavior with the 3D model (3.1)-(3.6) were also carried out. Spiral waves can be initiated in reaction-diffusion systems by breaking a circular wave such that free ends are formed [18]. This is achieved in simulations of propagating precipitation waves by setting $p_2 = 0$ at any point where $p_2 > 0$ in a segment of the conical frustum wave structure at a given time. To prevent immediate regrowth, no further formation of P_2 is allowed at these points. This affects P_2 growth only in the plane of the wave front during the wave break. The wave front immediately leaves this plane as it propagates downward, where P_2 growth is not restricted. Figure 3.9(a) shows a broken wave at the time step immediately following the break. The absence of P_2 near the free ends results in an increase of C in this region, as inner and outer electrolytes react, and new growth begins. The free ends curl and rotating spiral tips develop, as shown in Figs. 3.9(c) and 3.9(d). The spontaneous development of this high curvature region is a significant emergent property of the model. The spiral tips, however, are found to be unstable, typically lasting only one or two rotations. This instability arises because the spiral tip grows into the back of the previous wave. The stability can be improved by decreasing the threshold for template growth, c^* , occurring in the direction of increasing z . This modification promotes downward growth of the wave and leads to spiral tips

Figure 3.8. Three-dimensional representation of the waves shown in Fig. 3.7. The color coding corresponds to the concentration p_2 , as shown in Fig. 3.4. The two waves are separately initiated (a) and each wave propagates outward (b). The waves collide (c) and annihilate (d). All parameters as in Fig. 3.6. Figure adapted from reference [4].

Figure 3.9. Simulation of the development of a pair of counter rotating spiral waves. Successive images taken at $t =$ (a) 67500, (b) 97500, (c) 115000 and (d) 125000. The first image corresponds to behavior immediately after the wave is cut. All parameters as in Fig. 3.4 with the additional modification that $c^* = 1.8$ for template growth occurring in the direction of increasing z . For clarity, only values of p_2 satisfying $p_2 > 0.29$ are shown. The wave is broken by setting $p_2 = 0$ in cells with $p_2 > 0$ and $y > 109$. The color coding corresponds to the depth at which the P_2 is formed, as in Fig. 3.7. All parameters as in Fig. 3.7, except $a_0 = 6.0$, $k_6 = 5.0 \times 10^{-6}$, $p_{2,perm} = 1.0$. Figure adapted from reference [4].

that are stable for up to four rotations.

Figure 3.10(a) shows experimental examples of counterrotating spiral waves, as described in the simulations shown in Figure 3.9. We note that as the AlCl_3 concentration is increased, the spiral waves exhibit instabilities, as shown in Figure 3.10(b). On further increasing the AlCl_3 concentration, turbulence-like behavior is exhibited, as shown in Figure 3.10(c). The transition from regular spiral behavior to the turbulence-like behavior is discussed further in Chapter 4.

3.5 Discussion

A fundamental feature of the propagating precipitation waves in both the $\text{AlCl}_3/\text{NaOH}$ and $\text{NaAl}(\text{OH})_4/\text{HCl}$ systems is the presence of two forms of $\text{Al}(\text{OH})_3$ precipitate with different physical properties. The two forms are designated P_1 and P_2 for the $\text{Al}(\text{OH})_3$ in the moving precipitation band and the propagating precipitation wave, respectively. The P_1 form has the characteristics of an ordinary colloidal precipitate, while P_2 has physicochemical properties that play an essential role in the wave propagation. We do not know the exact structural nature of P_2 ; however, our experiments have revealed properties that provide insights into the essential features of the precipitate. There is a distinctly slower redissolution of the P_2 precipitation wave structure compared to the P_1 precipitation band, which is particularly evident in cross-section images of the waves, such as in Figs. 3.2(b) and 3.2(d). There is also preferential growth of the P_2 precipitation wave structure at its front at an approximately constant angle with respect to the leading edge of the P_1 precipitation band, which moves downward with the formation of colloidal $\text{Al}(\text{OH})_3$ precipitate from the diffusive flux of outer electrolyte. Part of the P_2 precipitation wave structure, the wave middle, serves as a barrier to the downward diffusive flux of outer electrolyte, which can be seen in the cross-section images of the waves, Figs. 3.2(b) and 3.2(d). No colloidal P_1 precipitate is

Figure 3.10. Experimental images of precipitation wave behavior with different concentrations of inner electrolyte, AlCl_3 . (a) Counterrotating spiral waves with $[\text{AlCl}_3] = 0.28 \text{ M}$ at 530 s after initiating the experiment. (b) Spiral waves becoming unstable with $[\text{AlCl}_3] = 0.34 \text{ M}$ at 1800 s. (c) Turbulence-like wave behavior with $[\text{AlCl}_3] = 0.37 \text{ M}$ at 425 s. All experiments were carried out with a 1.0 % agar gel and 2.5 M NaOH as the outer electrolyte. Figure adapted from reference [4].

formed below the wave middle because the outer electrolyte is not present. A plausible mechanism for the prevention of diffusion of OH^- across the P_2 precipitation structure is that some of the $\text{Al}(\text{OH})_3$ precipitate reacts with the entering OH^- to form $\text{Al}(\text{OH})_4^-$. If some of the anions remain immobilized in the precipitate, the P_2 precipitation structure becomes negatively charged, which retards further penetration by OH^- ions. As the OH^- concentration increases from the downward flux of outer electrolyte, more $\text{Al}(\text{OH})_4^-$ is formed, with the redissolution of P_2 , until diffusion of OH^- across the precipitation structure occurs and the wave back is formed. The diffusive flux of outer electrolyte across the wave back and wave tail allows the P_1 precipitation band to be reestablished. We note that our computational model is fully consistent with this mechanism. A similar mechanism can be envisioned for the $\text{NaAl}(\text{OH})_4/\text{HCl}$ system, except now the P_2 precipitation structure becomes impermeable to the diffusive flux of H^+ , arising from the formation of immobilized aluminum cations. The formation of a second type of precipitate that acts as a barrier to the diffusive flux of outer electrolyte has been observed in several other precipitation systems [5, 19, 20].

We note that recent experimental studies have reported similar propagating precipitation waves in a system with HgCl_2/KI as the inner/outer electrolyte pair [20]. The precipitation bands and waves in this system have the tetragonal and orthorhombic polymorphs of HgI_2 [21]. This suggests that the differences in the physical properties of precipitates in precipitation wave systems arise from their underlying polymorphic structures.

3.6 Conclusion

The 3D propagating precipitation wave model presented here, reactions (3.1)-(3.6), follows from our earlier 2D model [2] and provides significant advances. The 3D simulations offer insights into

the actual conical and conical frustum structures of the experimental precipitation waves. Related conical structures have been reported in non-amphoteric hydroxide precipitate systems, such as NaOH/AgNO₃, in which an impermeable conical barrier is formed, preventing diffusion of the outer electrolyte [19]. The longer length of the P_2 precipitation wave structure in the NaAl(OH)₄/HCl system, for some conditions, gives rise to complete cones similar to the non-amphoteric hydroxide system. This similarity provides additional evidence for the role played by the impermeable P_2 wave middle in the propagating waves of both the AlCl₃/NaOH and NaAl(OH)₄/HCl systems.

In addition to expanding the dimensionality, the 3D model introduces significant improvements on the earlier 2D model. There are fewer constraints imposed in the 3D model, which allows the propagating wave behavior to emerge from the reaction-diffusion dynamics combined with template growth. For example, in the 2D model, preferential growth of P_2 is imposed by allowing it to occur only at the wave tip. In contrast, growth of P_2 in the 3D model is allowed at any location satisfying the template growth conditions, and preferential growth emerges from the underlying mechanism.

Our simulations of spiral wave behavior demonstrate that curvature at a free end of a wave occurs spontaneously in the 3D model. However, experimental studies of spiral waves in the AlCl₃/NaOH system show that the wavelength is an increasing function of rotation angle. The current 3D model does not reproduce this behavior, suggesting that the rotating spiral tip is not slowing sufficiently at the regions of higher curvature [22]. The spiral tip rotation and the inherent eikonal relationship [23] controlled by the template growth dynamics are still being investigated.

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Chapter 4

Experimental Studies of Propagating Precipitation Waves

4.1 Introduction

Interest in propagating precipitation waves has continued to grow since their discovery in 2007 by Volford et al. [1–6]. However, the discovery of new systems that produce this phenomenon has been limited to 3 different reactions, aluminum chloride reacting with sodium hydroxide [1, 2], zinc chloride reacting with sodium hydroxide [5], and mercury chloride reacting with potassium iodide [5, 7]. In order to determine how robust this phenomenon is, new reactions that exhibit traveling precipitation waves are discussed in this chapter. We present two novel precipitation systems that produce traveling precipitation waves: gallium chloride reacting with sodium hydroxide and sodium tetrahydroaluminate(III) reacting with hydrochloric acid. Both of these reactions, given the appropriate initial conditions, will produce traveling precipitation waves that are characterized by the same methods discussed in Chapter 2.

In this chapter, experimental findings of these two systems are reported, and the key features

used to characterize traveling waves in Chapter 2 are identified. Also discussed are new experimental findings in the $\text{AlCl}_3/\text{NaOH}$ system, a new feature of traveling waves, known as wave catch-up, and the effects of different gel media.

4.2 Experimental Section

The experimental procedures to produce gels in the $\text{AlCl}_3/\text{NaOH}$ and $\text{NaAl}(\text{OH})_4/\text{HCl}$ systems are reported in Chapters 2 and 3, respectively. To produce gels in the $\text{GaCl}_3/\text{NaOH}$ system, a 2.0% agar gel solution is prepared by dissolving 0.2 g of agar powder in 10.0 mL of distilled water. A GaCl_3 solution is also prepared by dissolving the desired concentration of GaCl_3 in 10.0 mL of distilled water. Both solutions are heated with continuous stirring to a temperature of 90°C . The two solutions are then combined and stirred without heat for an additional 10 minutes. The resulting mixture is a 1.0% agar gel solution containing GaCl_3 .

Two experimental configurations are used in this study, a gel disk and gel slab. A smaller petri dish is used for experiments using the $\text{GaCl}_3/\text{NaOH}$ system, since a smaller quantity of agar gel solution is prepared. For the gel disk in this system, approximately 15 mL of the gel solution are poured into a petri dish with a radius of 27.5 mm. The mixture is allowed to cool to room temperature, which causes the gel to solidify. The outer electrolyte is placed on top of the gel disk and images of the resulting reaction are captured from above with a CCD camera utilizing back illumination. The gel slab configuration is the same as that described in Chapter 2. In short, two glass microscope slides (50 mm x 75 mm) are separated by a spacer of desired thickness, normally 1.0 mm. The slides and spacer are then clamped together and the gel mixture is injected between the two slides and allowed to cool to room temperature, causing the gel to solidify. The outer electrolyte is added to the top of the gel to begin an experiment. Back illumination is also utilized

in this configuration unless otherwise noted.

4.3 Results

4.3.1 Characteristics of the $\text{Ga}(\text{OH})_3$ system

The chemistry in the $\text{GaCl}_3/\text{NaOH}$ system is much like that of the $\text{AlCl}_3/\text{NaOH}$ system that was reported in Chapter 2. Here, gallium ions react with diffusing hydroxide ions to produce gallium hydroxide, which is then dissolved in the presence of excess hydroxide to form the soluble gallate complex ion, $\text{Ga}(\text{OH})_4^-$,

In an experiment, reaction begins after the addition of sodium hydroxide to the top of the gel containing the gallium ions. Once the nucleation threshold of $\text{Ga}(\text{OH})_3$ is reached, colloidal $\text{Ga}(\text{OH})_3$ is formed. The colloidal $\text{Ga}(\text{OH})_3$ forms a thin band of precipitate that propagates down through the gel and is driven by the diffusion of hydroxide ions. The thin band of colloidal precipitate has sharp leading and trailing edges as observed in Figure 4.1(c), which is similar to that seen in the $\text{AlCl}_3/\text{NaOH}$ system. This is an indication that the reaction kinetics of precipitation are fast compared to diffusion within the gel. The thickness of the propagating band is dependent upon the length of the experiment, with a longer experiment giving rise to a thicker precipitation band. The propagating band is observed over a wide range of inner electrolyte concentrations. However, if the appropriate inner electrolyte concentration is used, spontaneous traveling waves are observed within the propagating precipitation band. Traveling waves in this system occur within a very narrow range of inner electrolyte concentrations, 0.13 M - 0.20 M.

Traveling precipitation waves in 3-D can be viewed from above, which is accomplished using the gel disk experimental setup. They are characterized by counter rotating spiral tips, which are surrounded by quasi-circular expanding waves, as seen in Figure 4.1(a). On increasing the concentration of the inner electrolyte, wave activity increases and more wave centers are formed, as seen in Figure 4.1(b). As the wave activity increases, so does the frequency of the spiral tips. Evidence of this is illustrated in Figure 4.1(a) and (b). The wavelengths observed in Figure 4.1(a) are much larger than those observed in Figure 4.1(b), owing to the increase in frequency of the rotating spiral tips. The same increase in frequency and wave activity is observed in the $\text{AlCl}_3/\text{NaOH}$ system. Further wave characterization is achieved by examining a cross sectional view of the waves. Cross section images are obtained from the gel slab configuration. This experimental setup produces a quasi 2-D representation of the wave and allows us to identify key components of the waves structure, such as the wave tip, wave middle, wave back, and wave tail. Figure 4.1(c) illustrates the anatomy of a wave.

The tip of the wave is located at the leading edge of the colloidal precipitation band. Propagation of the wave is characterized by growth of the wave tip. Since growth of the wave is limited to its tip, it is considered to be directed or templated growth, and is similar to that observed in crystal needle growth. As the tip grows, it leaves behind a thin layer of wave precipitate. The precipitate directly behind the wave tip is the wave middle. The region below the wave middle contains no precipitate. This indicates that the wave middle is blocking the diffusion of OH^- ions as is observed in the original $\text{AlCl}_3/\text{NaOH}$ system. However, for a wave back to form, OH^- ions must eventually diffuse through the wave middle. The wave back is characterized by the concave reattachment of the colloidal precipitation band to the wave middle. Behind the wave back is the wave tail. Even though the wave middle becomes permeable to OH^- ions, it does not initially redissolve as the precipitation band does and a wave tail remains in the gel after the precipitation

Figure 4.1. (a,b) Top view images of traveling waves in the $\text{GaCl}_3/\text{NaOH}$ system obtained in the gel disk configuration. (c) A side view image of a propagating wave in a gel slab configuration. The structural features, the wave tip A, wave middle B, wave back C, and wave tail D are indicated. Experimental conditions: (a) A 1.0% agar gel with an inner electrolyte concentration of 0.13 M and an outer electrolyte concentration of 2.5 M. (b) A 1.0% agar gel with an inner electrolyte concentration of 0.18 M and an outer electrolyte concentration of 2.5 M. (c) A 1.0% agar gel with an inner electrolyte concentration of 0.15 M and an outer electrolyte concentration of 2.5 M.

band has moved past the wave back. However, given enough time the wave tail will redissolve to form the gallate complex.

Wave annihilation also occurs in the $\text{GaCl}_3/\text{NaOH}$ system. As two wave fronts come together, growth is inhibited due to insufficient sol, which is needed to produce the wave precipitate. The concentration of sol is low in this region due to the wave precipitate acting as a barrier to the diffusion of hydroxide ions. The concave wave back continues propagating down the wave middle. This occurs because the permeability threshold of the wave middle continues to be reached as more hydroxide diffuses into it. Eventually, the two wave backs reach the two stationary wave tips, at which point the wave backs merge together to form a continuous layer of band precipitate.

Comparing the $\text{GaCl}_3/\text{NaOH}$ and $\text{AlCl}_3/\text{NaOH}$ systems shows that they both exhibit the same experimental features on a short time scale, approximately 1 hour. However, if an experiment is allowed to progress for a longer period of time, up to twelve hours, then differences between the two systems emerge. During a long experiment, the waves observed in the $\text{AlCl}_3/\text{NaOH}$ system develop a large wave tail that persists in the gel and does not dissolve as previously observed on a short time scale. In the $\text{GaCl}_3/\text{NaOH}$ system, while the wave tail does lengthen, it does not become as long as that observed in the $\text{AlCl}_3/\text{NaOH}$ system, and it will eventually dissolve. A plausible explanation of the observed effect is that the permeability threshold in the $\text{GaCl}_3/\text{NaOH}$ system is lower than that in the $\text{AlCl}_3/\text{NaOH}$ system. If this is the case, the diffusing hydroxide ions would dissolve the wave precipitate more rapidly, causing the wave tail to be shorter.

4.3.2 Characteristics of the $\text{Al}(\text{OH})_4^-$ system

The chemistry involved in this system focuses on the amphoteric nature of $\text{Al}(\text{OH})_3$, which is formed as a precipitate from the reaction of $\text{NaAl}(\text{OH})_4$ with HCl and then redissolved to form Al^{3+} ions in the presence of excess HCl ,

In an experiment, reaction begins once acid is poured on top of a gel containing NaAl(OH)_4 . As the nucleation threshold is reached, a thin band of colloidal aluminum hydroxide is formed with sharp leading and trailing edges. This feature of the precipitation band occurs in all of the systems that have been shown to exhibit precipitation waves. A second type of aluminum hydroxide precipitate also forms, which gives rise to traveling waves. However, the traveling waves observed in this reaction differ slightly from those in the $\text{AlCl}_3/\text{NaOH}$ and $\text{GaCl}_3/\text{NaOH}$ reactions. Here, two different types of patterns can form; one in which a wave back forms and one in which a wave back does not form. The formation of the wave back is dependent upon the redissolution of the wave middle, which does not always occur in this system. It is observed that the concentration of inner electrolyte does not affect which type of pattern occurs in an experiment. It is expected that the concentration of the outer electrolyte will affect the pattern formation. If the concentration of the outer electrolyte is increased, the formation of a wave back would be expected. Since the formation of a wave back is dependent on the diffusive flux of the outer electrolyte into the region, an increase in the concentration of the outer electrolyte will cause an increase in the diffusive flux of H^+ ions, causing further reaction with the wave middle. Once sufficient reaction has occurred, the permeability threshold will be reached and the diffusion of the outer electrolyte through the wave back will occur, along with the formation of the precipitation band. Propagation of the wave front occurs through the template growth mechanism that is presented in Chapter 3. The front propagates through the gel at the leading edge of the precipitate band, which is itself propagating downward through the gel.

Figure 4.2. Images of the $\text{NaAl(OH)}_4/\text{HCl}$ system. (a,c) Top view images taken from the gel disk configuration and (b,d) side view images taken in the gel slab configuration. Experimental conditions: (a,b) A 1.0% agar gel containing 0.25 M NaAl(OH)_4 as the inner electrolyte and 2.0 M HCl as the outer electrolyte. (c,d) A 1.0% agar gel containing 0.23 M NaAl(OH)_4 as the inner electrolyte and 2.0 M HCl as the outer electrolyte.

Figure 4.2(a) and 4.2(c) show top view images of both types of patterns formed in this system. Figure 4.2(c) is an image illustrating the pattern when a wave back is not formed. The gel is illuminated from below, with light regions corresponding to areas of low precipitate concentration and dark regions corresponding to areas of high precipitate concentration. The light colored expanding circles show the region where the wave precipitate has formed. Figure 4.2(d) allows us to examine a cross section of the pattern formed without a wave back. Here we observe that the front of a wave is formed and grows via template growth; however, the wave middle fails to become permeable to the outer electrolyte, which does not allow for the formation of a wave back. If this structure were observed in 3D, a cone of wave precipitate would be seen with unreacted gel in the interior. Figure 4.2(a) shows the pattern observed when a wave back is formed. The tip of this front or wave can be seen in the image as a dark band propagating slightly ahead of the lighter region of wave precipitate, which is the wave middle. The wave middle appears to be bright because the precipitate that is present there is very thin, which can be observed in the cross section image, Figure 4.2(b). Figure 4.2(a) also shows the formation of a dark region inside the light region. This is evidence that the top of the cone has been redissolved by the excess H^+ ions, which are continuously diffusing into the region. This causes the formation of the wave back. The newly formed band of colloidal precipitate propagates vertically and expands along the edge of the structured precipitate. Since the tip of the circular front continues to expand as the new colloidal band propagates along its boundary, the system can be said to have formed two traveling waves. Structurally, these waves appear to be the same as the waves seen in the $AlCl_3/NaOH$ system, except the wave middle is considerably larger in length, which is discussed in Chapter 3.

Figure 4.3. Plot of wave centers vs. inner electrolyte concentration.

4.3.3 New Experimental Findings in the $\text{AlCl}_3/\text{NaOH}$ system

As previously discussed, increasing the inner electrolyte concentration also increases the activity of the system, which will cause more wave centers to form. Figure 4.3 shows a plot of the number of wave centers formed as a function of inner electrolyte concentration. An imaging area of $38.0 \text{ mm} \times 29.0 \text{ mm}$ is used to determine the number of wave centers, which is kept constant for each inner electrolyte concentration. An increase in activity also causes spiral wave centers to rotate at a higher frequency. The increased rotation frequency causes more waves to be generated at a given time, which leads to a decrease in wavelength.

Figure 4.4 is a plot of wavelength as a function of inner electrolyte concentration. As the inner electrolyte concentration is increased, the wavelength decreases, illustrating that the rotation frequency has increased. An observable consequence of the higher rotation frequency is wave “catch-up”. Wave catch-up is observed only when the frequency of rotation is high, which produces wavelengths that are 1.0 mm or shorter. If the wavelength between two waves is greater than 1.0 mm , wave catch-up does not occur.

Figure 4.4. Plot of wavelength vs. inner electrolyte concentration.

Wave catch-up occurs when a wave formed by a rotating spiral tip catches up with a wave previously formed by the same spiral tip. Wave catch-up was first observed in the $\text{AlCl}_3/\text{NaOH}$ system; however, it can also be observed in the $\text{GaCl}_3/\text{NaOH}$ system. In the reaction of Al^{3+} ions with OH^- ions, wave catch-up is only observed during the first two rotations of a spiral tip. However, in the $\text{GaCl}_3/\text{NaOH}$ system, it can be observed for the lifetime of the rotating tip. A possible explanation for this is that the wave centers in the $\text{GaCl}_3/\text{NaOH}$ rotate at a higher frequency, thus producing waves at a faster rate, which allows for smaller wavelengths as compared to the $\text{AlCl}_3/\text{NaOH}$ system, allowing for multiple waves to catch-up. Figure 4.5 shows a series of images taken in the gel slab configuration in the $\text{AlCl}_3/\text{NaOH}$ system. Figure 4.5(a) shows two waves that are propagating through the gel. Figure 4.5(b) shows the same two waves; however, the second wave has moved closer to the first wave. This indicates that the second wave is catching up to the first wave. As this occurs, the second wave's tip will propagate through the colloidal band and into the concave wave back of the wave in front of it, which can be seen in figure 4.5(c).

The angle with respect to the propagating band of the second wave is much smaller within the concave region as compared to the first wave. This provides the second wave with a larger

Figure 4.5. Images of the $\text{AlCl}_3/\text{NaOH}$ system showing wave “catch-up” in the gel slab experimental configuration. The second wave visible in image (a) catches the wave in front of it and is then annihilated. Images taken at times $t = 565$ s, 850 s, 1355 s, and 2150 s in (a)-(d), respectively. Experimental conditions: A gel is composed of 1.0% agar with 0.28 M AlCl_3 as the inner electrolyte and 2.5 M NaOH as the outer electrolyte.

horizontal velocity as compared to the first wave. As the wave tip of the second wave approaches the first it accelerates. When the tip of the second wave reaches the wave middle of the first, it stops propagating and is annihilated by colliding with the first wave. In order for a wave tip to continue to grow, a continuous supply of OH^- ions must be present. As the wave tip collides with the wave middle of the first wave, the constant supply of OH^- ions is interrupted because OH^- ions cannot diffuse through the wave middle of the first wave. This means that sufficient sol is not available to be converted into the wave precipitate. As the concentration of OH^- ions continues to increase in the wave middle of the first wave, it will eventually reach a critical threshold that allows OH^- ions to diffuse into the region where the second wave was to form new colloidal band precipitate. The wave tail of the second wave remains in the gel as an indicator of the trajectory of the second wave. An arrow in Figure 4.5(d) indicates the wave tail after collision with the wave middle of the first wave.

Figure 4.6 shows top view images of wave catch-up. The same mechanism that is described for the cross sectional view can be applied to the top view. Figure 4.6(a) shows two waves that have a sufficiently small wavelength for catch-up to occur. The first and second waves created by the rotating spiral tips have a sufficiently small wavelength. It should be noted that the next waves have much larger wavelengths, which prevents wave catch-up. Figures 4.6(b) and 4.6(c) show the second wave as it gets closer to the first. Figure 4.6(c) shows the second wave right before the wave tip collides with the wave middle of the first wave. This is comparable to Figure 4.5(c), which shows a cross-sectional view of the second wave's tip before collision. Figure 4.6(d) shows that after collision, the second wave has been annihilated, and the first wave continues to propagate, unaffected by the collision.

Single tipped spiral waves are observed in both the $\text{AlCl}_3/\text{NaOH}$ and $\text{GaCl}_3/\text{NaOH}$ systems. Single spirals occur when the concentration of the inner electrolyte is increased, causing the fre-

Figure 4.6. Images of the $\text{AlCl}_3/\text{NaOH}$ system showing wave “catch-up” in the gel disk experimental configuration. The second wave generated by the counterrotating spiral tips visible in image (a) catches up to the first wave and is then annihilated. Images taken at times $t = 450$ s, 950 s, 1200 s, and 2075 s in (a)-(d), respectively. Experimental conditions: A gel is composed of 1.0% agar with 0.28 M AlCl_3 as the inner electrolyte and 2.5 M NaOH as the outer electrolyte.

Figure 4.7. Images that show the formation of a spiral wave (a)-(c) and images that show the formation of a turbulent-like pattern (d)-(f). Experimental conditions: (a)-(c) A 1.0% agar gel containing 0.30 M AlCl_3 as the inner electrolyte and 2.5 M NaOH as the outer electrolyte. Images were taken at times $t = 300$ s, 950 s, and 1800 s in (a)-(c), respectively. (d)-(e) A 1.0% agar gel containing 0.34 M AlCl_3 as the inner electrolyte and 2.5 M NaOH as the outer electrolyte. Images were taken at times $t = 350$ s, 925 s, and 2050 s in (d)-(f), respectively.

quency of the spiral tips to increase. Initially, a pair of counterrotating spiral tips are formed; however, one of the tips may have a slightly higher frequency than the other tip. When the frequency of one of the spiral tips is higher than the other, the higher frequency tip will overtake the other, leaving a single rotating spiral tip. Figure 4.7(a-c) shows the formation of a single spiral tip in the gel disk configuration. An early experimental image is shown in Figure 4.7(a), which shows the counterrotating spiral tips that are initially formed. In Figure 4.7(b), the tip with the higher frequency has annihilated the second tip. Figure 4.7(c) shows the continued formation of waves from the single remaining spiral center.

As the concentration of the inner electrolyte is increased, spiral tips become unstable. The instability is caused by a spiral tip growing into the back of a previously formed wave. Figure 4.7(d) shows a typically experimental image where spirals may become unstable. Here, there are a number of wave centers with high rotation frequency present. Figure 4.7(e) shows an image where some of the spiral cores have broken up leaving behind wave fragments and others with the tip of the spiral about to collide with a wave back. The formation of wave fragments in the gel causes a turbulent-like pattern to be exhibited. Figure 4.7(f) shows a typical image of the turbulent-like patterns observed in these systems. A brief analysis of the turbulent-like pattern is presented in the discussion section.

4.3.4 Effects of the Gel Medium

The precipitation systems that have been described thus far have been produced in an agar gel medium. To ensure that the wave behavior observed in these systems is not a product of the type of gel used, experiments with different gel media were conducted. In addition to agar, gels were produced using polyvinyl alcohol (PVA), polyacrylamide, gelatin, and agarose. These gelling agents were chosen based on their use in other precipitation systems, such as in the formation

of Liesegang bands [8–15]. Traveling precipitation waves were observed using polyvinyl alcohol, gelatin, and agarose; however, polyacrylamide did not yield traveling waves due to solidification issues after the addition of the inner electrolyte to the gel mixture.

Agar is a mixture of agaropectin and agarose, the linear polysaccharide that causes gelation to occur [16]. Therefore, gels produced with agarose as the gel medium do not need any modification to the experimental procedure and produce waves that are identical to those observed in agar. However, to produce gels with polyvinyl alcohol and gelatin, some modifications are required. Gelatin gels are produced by dissolving 2.0 grams of gelatin in 100 mL of distilled water. The mixture is then heated and stirred until a temperature of 90 °C is reached. The mixture is stirred for an additional 10 minutes without heat. The inner electrolyte is added and the mixture is stirred until it is completely dissolved. All of the gel mixtures discussed in this section use aluminum chloride hexahydrate as the inner electrolyte. The experimental configurations are the same as outlined in the experimental section. The gel dish or slab is then placed in the refrigerator to allow the gelatin to completely solidify. The gel is removed from the refrigerator and immediately used. A 2.0% gel was used because a lower percentage of gelatin proved to be too weak to support the addition of the outer electrolyte. Figure 4.8(a) shows a top view of wave formation using gelatin. The waves formed are essentially the same as those observed in the agar gel medium. Figure 4.8(b) shows a cross sectional view of the waves as observed in the gel slab configuration, with the concentration of gelatin increased to 5.0%. At this concentration of gelatin, there are noticeable differences from the agar system. The precipitation band is much lighter in color, indicating that less of the colloidal band precipitate is present. However, the leading edge of the band is characterized by a dark edge that extends into the wave back, a feature not present in agar. The precipitation band that appears when using PVA also has the characteristic dark leading edge, as seen in Figure 4.7(d), along with a dark trailing edge. The waves that are observed here appear

to be similar to those seen in agar but are more translucent.

PVA gels are produced by adding 4.0 g solid polyvinyl alcohol to 100 mL of distilled water. The mixture is heated to a temperature of 70—80°C for a time period of 2 hours or until all of the solid polyvinyl alcohol is dissolved. After the polyvinyl alcohol is dissolved, a 2.0 M solution of AlCl_3 is added to the mixture until the desired concentration of AlCl_3 is reached. In order for the gel to solidify, a cross-linking agent must be used. Adding 2.0 mL of 12 M HCl and 1.0 mL of 1.0 M glutaric dialdehyde causes the solidification of the gel. The entire mixture is then diluted to 200 mL with distilled water. Figure 4.8(b) shows a top view of the PVA gel system with bromophenol blue added. Although waves are visible in this gel medium, they are much more difficult to observe, as they appear to be translucent. A plausible explanation for the difference in appearance of the waves observed with PVA is the density of the gel. The diffusive flux of hydroxide ions into the gel will be smaller due to the denser gel. This will cause less precipitate to form due to the limited amount of hydroxide that is diffusing into the gel. Figure 4.8(d) shows a cross sectional image of waves that occur using PVA as the gel medium. The precipitation band appears with characteristic sharp leading and trailing edges that appear darker than the rest of the band. We can identify all of the characteristics of traveling precipitation waves, including a wave tip, wave middle, wave back, and wave tail.

4.4 Discussion

The experimental results that are presented in this chapter provide evidence that two novel systems, $\text{GaCl}_3/\text{NaOH}$ and $\text{NaAl}(\text{OH})_4/\text{HCl}$, produce propagating precipitation waves. The waves are characterized based on our previous studies of precipitation waves [2] and exhibit corresponding structural features. A propagating band of precipitate is formed and propagates vertically through

Figure 4.8. Images of gels produced with gelatin and PVA. Images (a) and (b) are gel disk and gel slab images taken with gelatin as the gel medium, and images (c) and (d) are gel disk and gel slab images taken with PVA as the gel medium. Experimental conditions: (a) A 2.0% gelatin gel containing 0.28 M AlCl_3 as the inner electrolyte and 2.5 M NaOH as the outer electrolyte. (b) A 5.0% gelatin gel containing 0.28 M AlCl_3 as the inner electrolyte and 2.5 M NaOH as the outer electrolyte. (c,d) A 2.5% PVA gel containing 0.28 M AlCl_3 as the inner electrolyte and 2.5 M NaOH as the outer electrolyte.

the gel. Within the precipitation band, waves are formed due to two types of precipitate with differing physicochemical properties. Experiments with the $\text{GaCl}_3/\text{NaOH}$ system produced waves that were remarkably similar to the waves observed in the $\text{AlCl}_3/\text{NaOH}$ system. The general 3D model that is presented in Chapter 3 also describes the experimental results obtained with this system. The $\text{NaAl}(\text{OH})_4/\text{HCl}$ system also produced traveling waves; however, some differences from the $\text{AlCl}_3/\text{NaOH}$ system can be identified. With the $\text{NaAl}(\text{OH})_4/\text{HCl}$ system, a longer wave middle is observed and the formation of a wave back does not always occur, leaving cones of precipitate in the gel. The formation of traveling waves is due to the formation of two types of precipitate with differing physicochemical properties. Although we do not know the exact structure of these two precipitates, we have convincing experimental evidence of their differing properties. Recent studies of the HgCl_2/KI system show that two precipitates are key to the formation and propagation of precipitation waves [7, 17]. It was shown that waves of HgI_2 form from two different colored precipitates and that propagation is based on the growth of one type over the other. This is much like the experimental observations described here, except that the precipitates formed are the same color. The mathematical models of propagating precipitation waves that are presented in Chapters 2 and 3 provide further support of the two precipitate mechanism.

The formation of the turbulent-like pattern that occurs at high inner electrolyte concentration is currently under investigation. In order to characterize the behavior observed here, we use a 2-Dimensional Fourier transform. We performed the Fourier transform on two different images with different inner electrolyte concentrations. The first image is of well defined rotating spirals. Figure 4.9(a) shows this image and the corresponding Fourier transform is seen in Figure 4.9(b). The pattern that is observed contains a very distinct ring around the center frequency with a definable structure. In comparison, Figure 4.9(c) shows a turbulent-like pattern, and its corresponding Fourier transform is seen in Figure 4.9(d). Here we notice that the definable ring

Figure 4.9. Experimental images and their corresponding 2D Fourier transforms. Images (a) and (c) are of a structured pattern and a turbulent-like pattern, respectively. Images (b)-(d) are the corresponding Fourier transforms. Experimental conditions: (a) A gel composed of 1.0% agar with 0.28 M AlCl_3 as the inner electrolyte and 2.5 M NaOH as the outer electrolyte. (c) A gel composed of 1.0% agar with 0.34 M AlCl_3 as the inner electrolyte and 2.5 M NaOH as the outer electrolyte.

structure indicating periodic behavior is missing. This does not definitively tell us that the pattern observed at high inner electrolyte concentration is turbulent, but it shows that there is a notable difference between the two types of behavior, with one showing periodicity and the other showing little periodicity.

4.5 Conclusion

The behavior of propagating precipitation waves presented in this chapter provide new insights into the phenomenon. We have shown that traveling precipitation waves occur in a number of precipitation reactions and that wave behavior can be observed in different types of gel media. While the gel itself may play a role in wave propagation, the type of gel used does not prevent wave formation from occurring. We have also provided evidence for the formation of a turbulent-like pattern that is observed at high inner electrolyte concentration. However, we are still investigating the pattern to determine if it is indeed spatiotemporal turbulence.

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Mikel Holcomb, Ph.D.

Charles Jaffé, Ph.D.

Justin Legleiter, Ph.D.

7/21/2015
Date