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Three-dimensional modeling of propagating precipitation waves

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A general three-dimensional model for propagating precipitation waves is presented. Structural features identified in experimental studies of propagating waves in the AlCl3/NaOH and NaAl(OH)4/HCl systems are described by the 3D model. Two forms of precipitate with different physical properties play key mechanistic roles in the wave propagation. Experimentally observed circular and spiral waves are simulated by the 3D model, as well as wave annihilation on the collision of two waves. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4921695]

INTRODUCTION

Liesegang bands are periodic precipitation patterns formed when ionic species diffusively mix to produce an insoluble compound. A typical experimental system consists of two, initially separate, reaction mixtures: the inner electrolyte, dissolved in a hydrogel such as agar or gelatin, and the outer electrolyte, dissolved in a separate aqueous solution, usually at a higher concentration. The outer electrolyte solution is placed on top of the hydrogel containing the inner electrolyte. As the outer electrolyte diffuses downward through the gel, a precipitate is formed due to the low solubility of the product species. Under most conditions, continuous precipitation is observed; however, it is not difficult to find concentrations of the inner and outer electrolytes where the continuous behavior is unstable and, instead, periodic precipitation bands are formed.

In a redissolution Liesegang system, the precipitate is capable of dissolving in an excess of outer electrolyte. Examples of inner/outer electrolyte pairs in these systems include Cr(NO3)3/NaOH and CoCl2/NH4OH, which react to form the Cr(OH)3 and Co(OH)2 precipitates, respectively. These precipitates then dissolve in higher concentrations of the outer electrolyte to form the tetrahydroxochromate(III) and hexaamminecobalt(II) complex ions, respectively.

Redissolution Liesegang systems produce either quasi-traveling Liesegang bands, in which new bands form ahead while the bands behind dissolve, or a single moving precipitation band.

A new type of spatiotemporal behavior in precipitation systems was reported in 2007 by Volford et al. Propagating precipitation waves were found in the redissolution AlCl3/NaOH system, including spiral and circular waves. The reaction produces a single moving precipitation band, as Al(OH)3 is first precipitated and then redissolved in excess hydroxide to form the tetrahydroxoaluminate(III) complex ion, Al(OH)4−. The traveling waves occur within this moving precipitation band, and when viewed from above, they have a striking resemblance to the reaction-diffusion waves observed in the BZ reaction.

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

A 2D model was developed to describe the wave behavior observed in the AlCl3/NaOH system in thin gel slabs. A precipitate 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 propagation wave within the band by introducing two forms of Al(OH)3 precipitate with differing physicochemical properties. In this work, we refine the model by identifying dominant processes and extend the 2D description to 3D.

We also report on our observations of precipitation waves in a modified version of the system. The propagating wave behavior observed in the AlCl3/NaOH system is also
observed in the NaAl(OH)$_4$/HCl system, which exploits the amphoteric properties of Al(OH)$_3$ by using NaAl(OH)$_4$ as the inner electrolyte and HCl as the outer electrolyte. The precipitate Al(OH)$_3$ is again formed as the acid diffuses downward through the gel; however, now the precipitate dissolves in an excess of the acid to form the soluble hydrated aluminum ion Al$^{3+}$. The 3D model presented here also describes the NaAl(OH)$_4$/HCl system and we use it to explore the differences between the two systems.

**EXPERIMENTAL METHODS**

The AlCl$_3$/NaOH system is prepared according to the methods previously described. 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 NaAl(OH)$_4$/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. 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 NaAl(OH)$_4$.

Two experimental configurations are used. In the gel disk configuration (3D experiment), 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 × 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. The two configurations, with images taken from above and from the side, can be seen for a single experiment in Figure 1 of Ref. 9.

Previous studies of the AlCl$_3$/NaOH system revealed that, at appropriate reactant concentrations, spiral waves spontaneously form in a gel disk. Our modeling studies here initially focus on circular waves, which can be initiated by mechanically perturbing the precipitation band. A typical circular wave is shown in Fig. 1(a), where the wave moves outward from the initiation location. Figure 1(b) shows a cross-section image of a precipitation wave in a thin gel slab with the same concentrations of reactants. Figures 1(c) and 1(d) show corresponding images for the NaAl(OH)$_4$/HCl system. Figure 1(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. 1(d). Circular waves occur spontaneously in the NaAl(OH)$_4$/HCl system; however, we have not observed spiral waves in this system.

In both the AlCl$_3$/NaOH and NaAl(OH)$_4$/HCl systems, a precipitation band moves down through the gel, resulting from the diffusion of the outer electrolyte. The reaction can be represented as $A + B ightarrow P$, where $A$, $B$, and $P$ are the inner electrolyte ion, outer electrolyte ion and precipitate, respectively. In the AlCl$_3$/NaOH system, $A$ and $B$ represent Al$^{3+}$ and OH$^-$, whereas in the NaAl(OH)$_4$/HCl system they represent Al(OH)$_4^-$ and H$^+$, respectively. In both systems, $P$ corresponds to the precipitate Al(OH)$_3$. This precipitate dissolves in excess outer electrolyte to give products, $B + P ightarrow$. The product species, Al(OH)$_4^-$ and Al$^{3+}$, for the AlCl$_3$/NaOH and NaAl(OH)$_4$/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. 1(b) and 1(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. 1(b) and 1(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. 1(a) and 1(c). The wave front is associated with a slightly darker region just ahead of the bright region of the main wave structure. The brighter wave middle is considerably longer in the NaAl(OH)$_4$/HCl system. Concentric circles are visible in the vicinity of the wave back, Fig. 1(c), due to the transmitted light passing through the precipitation band or both the precipitation band and wave tail.

**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.9,11 These different precipitates are both forms of Al(OH)$_3$ but with different physical properties. Following our previous modeling study, based in part on earlier studies of Liesegang systems,5-8 the formation of $P_1$ occurs via a diffusive intermediate species $C$ according to

$$A + B ightarrow C, \quad (1)$$

$$C ightarrow P_1, \quad (2)$$

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.9,12 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 $k_1ab$, $k_2(c - c^*)H(c - c^*)H(p_{2,\text{perm}} - p_2)$, $kscb$, and $kgpq_b$, 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 $P_1$:

$$C + B \rightarrow \text{,}$$

$$P_1 + B \rightarrow \text{.}$$

with the concentration of $P_2$ given by $p_2$. The rates of these two processes are given by $k_3(c - c^*)H(c - c^*)H(p_{2,\text{perm}} - p_2)$ and $kgpq_b$, 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 $p_2 = p_2^*$. Previous modeling studies allowed growth only at a single tip of the wave, with the tip conditionally moving once $p_2$ reached a critical value $p_2^*$.13 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. The growth rate scaling factor $g$ is empirically determined based on the separation distance of active $P_2$ growth sites.13 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 (see, e.g., Fig. 2(b) in Ref. 9). 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 (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 (6) has lowered $p_2$ below a critical threshold, $p_{2,\text{perm}}$. 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 (1)–(6) with diffusion terms. In keeping with standard models for Liesegang band formation, neither $P_1$ nor $P_2$ are allowed to diffuse.14 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, $b(i, x, y, 0) = b_0$, $\forall x, y$, and $\forall t$. Initial conditions are given by $c(0, x, y, z) = 0$, $p_1(0, x, y, z) = 0$, $\forall x, y$, and $\forall z$; $b(0, x, y, z) = b_0$, $a(0, x, y, z) = 0$, $\forall x, y$ and $0 \leq z < Z_I$; $b(0, x, y, z) = 0$, $a(0, x, y, z) = a_0$, $\forall x, y$ and $Z_I \leq z \leq Z$, where $Z_I$ is the location of the liquid-gel interface.
correspond to the conical precipitation wave structure shown in Fig. 2(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 \( p_{2,\text{perm}} \) 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 (1) and (2). Figure 3(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 \( p_{2,\text{perm}} \), which corresponds to the wave tail seen in the experiment.

Figure 3(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 \( p_2 > p_{2,\text{perm}} \) are plotted, this disk becomes ring shaped, as \( p_2 \) drops below \( p_{2,\text{perm}} \) at the wave back.

A comparison of Fig. 3(c) with Fig. 2 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(c).

The model presented here is general in the sense that the symbols \( A \) and \( B \) represent the reactant chemical species in either the AlCl\(_3\)/NaOH system or the NaAl(OH)\(_4\)/HCl system. The most apparent difference between the two experimental systems is the longer wave middle associated with the NaAl(OH)\(_4\)/HCl system. The increase in length of this region is achieved in our simulations by either reducing \( p_{2,\text{perm}} \) 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(d)–3(f). The view from above, Fig. 3(f), shows a thickening of the propagating wave, and the side view, Fig. 3(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. 4. 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,\(^3\)–\(^5\) however, it is not apparent from the above view in Fig. 4 that while each wave is moving outward, it is also moving downward through the gel medium.

Figure 5 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 6 shows the annihilation behavior in a 3D representation, now with the color coding representing the concentration \( p_2 \). The collision occurs at the leading edge of

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**FIG. 2.** Three-dimensional simulations showing the evolution of the \( P_2 \) precipitation wave structure at successive times: 36 250, 52 500, 68 750, and 85 000. The color coding represents the concentration \( p_2 \) at any given time. The concentration \( p_2 \) is approximately 3 grid points thick.

**FIG. 3.** (a),(b) Vertical cross-section through Figs. 2(a) and 2(d), simulations of the AlCl\(_3\)/NaOH system. The concentration \( p_2 > p_{2,\text{perm}} \) is indicated by purple; the concentration \( p_2 < p_{2,\text{perm}} \) is indicated by violet. (c) Above view of Fig. 2(d) showing \( p_2 > p_{2,\text{perm}} \) by purple. (d)–(f) Analogous simulations of the NaAl(OH)\(_4\)/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.
the conical frustum associated with each wave structure, as shown in Fig. 6(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. 6(d).

Spiral wave behavior is observed in the AlCl\(_3\)/NaOH system\(^{2,9} \) and simulations of this behavior with the 3D model (1)–(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.\(^{15} \) This is achieved in simulations of propagating precipitation waves by setting \( p_2 = 0 \) at any point where \( p_2 \) 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 7(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. 7(c) and 7(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 $z$. 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. 5. All parameters as in Fig. 5, except $a_0 = 6.0$, $k_6 = 5.0 \times 10^{-6}$, $P_2_{\text{perm}} = 1.0$.

FIG. 7. Simulation of the development of a pair of counter rotating spiral waves. Successive images taken at $t =$ (a) 67 500, (b) 97 500, (c) 115 000, and (d) 125 000. The first image corresponds to behavior immediately after the wave is cut. All parameters as in Fig. 2 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. 5. All parameters as in Fig. 5, except $a_0 = 6.0$, $k_6 = 5.0 \times 10^{-6}$, $P_2_{\text{perm}} = 1.0$.

Figure 8(a) shows experimental examples of counterrotating spiral waves, as described in the simulations shown in Figure 7. We note that as the AlCl$_3$ concentration is increased, the spiral waves exhibit instabilities, as shown in Figure 8(b). On further increasing the AlCl$_3$ concentration, turbulence-like behavior is exhibited, as shown in Figure 8(c). The transition from regular spiral behavior to the turbulence-like behavior is currently under investigation.

FIG. 8. Images of experimental precipitation wave behavior with different concentrations of inner electrolyte, AlCl$_3$. (a) Counterrotating spiral waves with [AlCl$_3$] = 0.28 M at 530 s after initiating the experiment. (b) Spiral waves becoming unstable with [AlCl$_3$] = 0.34 M at 1800 s. (c) Turbulence-like behavior with [AlCl$_3$] = 0.37 M at 425 s. All experiments were carried out with a 1.0% agar gel and 2.5 M NaOH as the outer electrolyte.

**DISCUSSION**

A fundamental feature of the propagating precipitation waves in both the AlCl$_3$/NaOH and NaAl(OH)$_4$/HCl systems is the presence of two forms of Al(OH)$_3$ precipitate with different physical properties. The two forms are designated $P_1$ and $P_2$ for the Al(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. 1(b) and 1(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. 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. 1(b) and 1(d). No colloidal $P_1$ precipitate is 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 in the AlCl$_3$/NaOH system is that some of the Al(OH)$_3$ precipitate
reacts with the entering $\text{OH}^{-}$ to form $\text{Al(OH)}_{3}^{+}$. If some of the anions remain immobilized in the precipitate, the $P_2$ precipitation structure becomes partially negatively charged, which retards further penetration by $\text{OH}^{-}$ ions. As the $\text{OH}^{-}$ concentration increases from the downward flux of outer electrolyte, more $\text{Al(OH)}_{3}^{+}$ is formed, with the redissolution of $P_2$, until diffusion of $\text{OH}^{-}$ 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 NaAl(OH)$_4$/HCl system, except now the $P_2$ precipitation structure becomes impermeable to the diffusive flux of $\text{H}^{+}$, 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.\textsuperscript{11,16,17}

The 3D propagating precipitation wave model presented here, reactions (1)–(6), follows from our earlier 2D model\textsuperscript{9} 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 the NaOH/AgNO$_3$ system, in which an impermeable conical barrier is formed, preventing diffusion of the outer electrolyte.\textsuperscript{16} 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 AlCl$_3$/NaOH and NaAl(OH)$_4$/HCl systems.

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.\textsuperscript{17} The precipitation bands and waves in this system contain the tetragonal and orthorhombic polymorphs of HgI$_2$.\textsuperscript{18} This suggests that the differences in the physical properties of precipitates in precipitation wave systems arise from their underlying polymorphic structures.

In addition to expanding the dimensionality, the 3D model introduces significant improvements on the earlier 2D model.\textsuperscript{9} 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 AlCl$_3$/NaOH system show that the wavelength is an increasing function of rotation angle.\textsuperscript{19} 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.\textsuperscript{20} The spiral tip rotation and the inherent eikonal relationship\textsuperscript{21} controlled by the template growth dynamics is currently under investigation.

ACKNOWLEDGMENTS

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APPENDIX: 3D MODEL SYSTEM

The model for propagating precipitation waves is made up of the following six processes:

\begin{align}
A + B & \rightarrow C, \\
C & \rightarrow P_1, \\
C + B & \rightarrow, \\
P_1 + B & \rightarrow, \\
C & \rightarrow P_2, \\
P_2 + B & \rightarrow,
\end{align}

where $A$, $B$, $C$, $P_1$, and $P_2$ represent the inner electrolyte, outer electrolyte, diffusive intermediate, precipitate type 1, and precipitate type 2, respectively. The rates of these six processes are given by $r_1 = k_{1ab}$, $r_2 = k_{2}(c-c^*)H(c-c^*)H(p_{2,\text{perm}} - p_2)$, $r_3 = k_{3}cb$, $r_4 = k_{4}p_1b$, $r_5 = k_{s}(c-c^*)H(c-c^*)H(p_{2,\text{perm}} - p_2)g$ and $r_6 = k_{d}p_2b$, respectively. The step function $H(s)$ is defined as $H(s) = 1$ for $s > 0$ and $H(s) = 0$ for $s \leq 0$. Species $A$, $B$, and $C$ are, in general, free to diffuse with equal diffusion coefficients $D$. The concentration $c^*$ is the threshold value at which precipitation occurs.

The associated reaction-diffusion equations are written as

\begin{align}
\frac{\partial a}{\partial t} &= D\nabla^2 a - r_1, \\
\frac{\partial b}{\partial t} &= D\nabla^2 b - r_1 - r_3 - r_4 - r_6, \\
\frac{\partial c}{\partial t} &= D\nabla^2 c + r_1 - r_2 - r_3 - r_5, \\
\frac{\partial p_1}{\partial t} &= r_2 - r_4, \\
\frac{\partial p_2}{\partial t} &= r_5 - r_6.
\end{align}

Additional constraints associated with the presence and growth of the precipitate $P_2$ are given by the following:

\begin{enumerate}[a)]
\item If $p_2 \geq p_{2,\text{perm}}$ at a location, then species $A$ and $C$ do not diffuse into or out of the location. However, species $B$ may diffuse into the location.
\item Growth of $P_2$ can occur at a location if $P_2$ is either already present or one of the neighboring sites has $p_2 = p_{2,\text{max}}$.
\end{enumerate}
(c) Each active $P_2$ growth site has 26 neighbors in a $3 \times 3 \times 3$ grid, with each neighbor 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.13,22–24

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13Anisotropy associated with the use of Cartesian computational grids in simulations of solid growth processes from liquid phase is a known concern and is often addressed with empirical approaches.22–24 We reduce anisotropy in template growth of $P_2$ with a growth rate scaling factor $g$ (see the Appendix).