

Phase Diagram of Precipitation Morphologies in the Cu^{2+} – PO_4^{3-} System

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We have experimentally investigated the phase diagram of spatiotemporal pattern formation in the precipitation reaction of copper sulfate and sodium phosphate. The system exhibits an unusual variety of both vertically and horizontally growing structures. Quantitative measurements have been used to analyze the transition between the two patterns. The driving forces for the pattern formation have been identified as osmosis, buoyant forces, flow rate, and the mechanical properties of the membrane.

1. Introduction

“Chemical gardens” belong to the same chemical phenomena as chemical oscillations, chemical waves, and Liesegang structures. They were discovered about 100 years ago^{1,2} but have not been the subject of serious scientific study until recently. Chemical oscillations played a basic role in the development of the theory of chaos, the theory of bifurcations, and nonlinear dynamics.³ Chemical waves⁴ have become an important part of modern physical chemistry, and the number of papers devoted to Liesegang rings is increasing exponentially. Recently, similar dynamical developments have occurred in the study of chemical gardens.^{5–20} Chemical gardens are characterized by their unusual complexity, measured as a number of structures, and by the diversity of elements forming these structures. Great varieties of complex patterns, many of them resembling biological structures, are observed in simple two-component inorganic systems. Most papers devoted to chemical gardens focus on detailed studies of a single pattern. In this paper, we concentrate on the phase diagram by discovering as many patterns that exist in the system as possible, and we study the transitions from one pattern to another. The construction of the phase diagram is a crucial step that has to be done to develop the theory of complex self-developing chemical systems. As opposed to the “classical” chemical gardens, we have discovered complex patterns not only in solution but also on the bottom of the experimental dish and on the top of the solution. Overall, more than 20 structures have been observed in a single reaction, including patterns developed on the top of the solution, some of which have not been reported before. The experiments have been conducted in a geometrical arrangement mimicking biological morphogenesis; the inner electrolyte, representing the seed, is pumped into the outer electrolyte, representing the environment.

2. Experimental Method

Solutions of copper sulfate and sodium phosphate were prepared by dissolving the analytical grade salts in distilled water. The concentration of the aqueous metal salt solution was

varied between 0.0500 and 0.800 M, and the concentration range of phosphate solution was between 0.0300 and 0.500 M. The CuSO_4 solution (Sigma, Aldrich, Scharlau) was injected into the Na_3PO_4 solution (Spectrum 3D, Mallinckrodt Chemicals) by a peristaltic pump (Gilson Minipuls 3, Ismatec) at a constant flow rate of 0.50 to 2.00 mL/h.

The copper sulfate solution entered the large volume of sodium phosphate solution contained in a beaker (250 and 500 mL) or a Petri dish (90 and 250 mL) through a flat-tipped needle, attached to the end of the tube with an inner diameter of 0.76 mm (for the Gilson pump) or 0.25 mm (for the Ismatec pump) at room temperature ($22 \pm 1^\circ\text{C}$) as shown in Figure 1. Beakers, Petri dishes, and other containers were prepared by first drilling a small hole in the bottom followed by sealing the holes with a silicone adhesive (Loctite). The sealant was then allowed to dry for 24 h before the flat-tipped needle was placed in the hole prior to filling the solutions for the experiments.

The preliminary experiments were carried out in a 100 mL beaker or Petri dish. For studying horizontally growing patterns, wide Petri dishes or rectangular containers were used to avoid contact of the precipitate with the side walls. For vertical structures, thinner but taller beakers or rectangular containers were selected to avoid boundary effects caused by the surface of the outer electrolyte.

The height of the precipitate formed was measured for most experiments using a standard metric ruler; however, digital photographs were also taken of most experiments at the end of the 20 h running period from both the top and the side using a Canon EOS 350D camera and a scalar USB digital microscope. In a number of cases, a microscopic attachment was also used to take $50\times$ and $100\times$ magnified close-up pictures.

Our experiments involved the variation of one of the following four factors: copper sulfate concentration, sodium phosphate concentration, flow rate, and/or container size. Two flow rates were selected, and data from each one were analyzed independently for the construction of the phase diagram.

3. Results

The discovered patterns may be classified into three groups: patterns that develop on the bottom of the container, vertical patterns that rise in the solution, and horizontal patterns that are formed on the surface of the solution.

At small phosphate concentrations dome structures may form on the bottom of the vessel, which have also been observed

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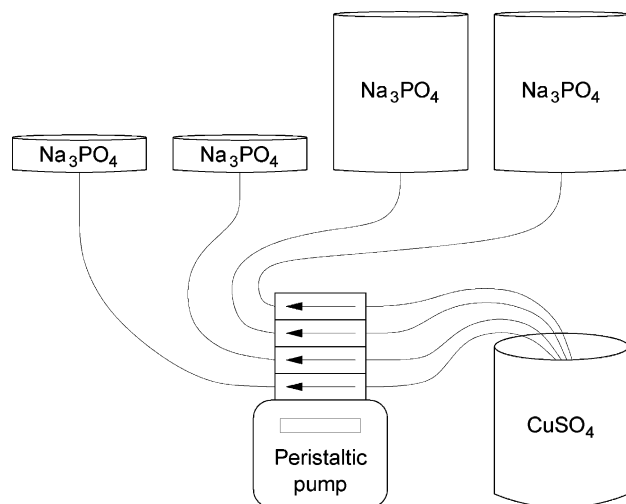


Figure 1. Schematic drawing of the experimental setup.

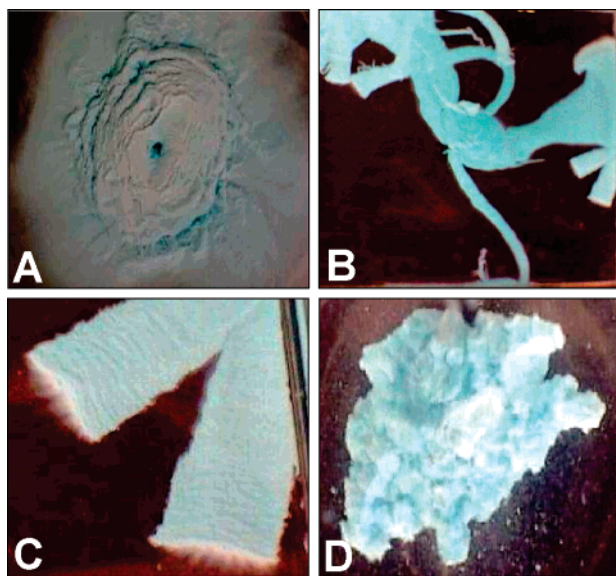


Figure 2. Patterns developed on the bottom of the Petri dish. For chemical compositions and flow rate see Figures 5 and 6, except for 2A where $[\text{PO}_4^{3-}]_0 = 0.03 \text{ M}$ and $[\text{Cu}^{2+}]_0 = 0.80 \text{ M}$ with a flow rate of 0.5 mL/h .

around copper sulfate pellets in previous experiments.¹¹ The precipitate first forms a closure around the inner solution, and pressure inside then starts to increase and eventually lifts the entire precipitate. The inner solution flows outside and reacts with the outer solution by forming a new layer of precipitate. The process repeatedly continues, yielding a dome structure with the characteristic terraces as seen in Figure 2A. When the precipitate becomes too heavy, only the peak of the structure erupts and then a crater forms in the center. The hole remains open upon the depletion of the outer solution. By increasing the concentration of the phosphate solution, precipitation fingers grow out around the perimeter of the dome on the bottom of the container. These fingers (see Figure 2B–C) have an unusual geometry; their tips are squared with sharp edges uncommon in natural systems. A further increase in the phosphate concentration, relative to that of the copper ion, changes the precipitation pattern into the rigid structures shown in Figure 2D.

At greater phosphate concentration, domes are replaced by vertical tubular structures in the solution. The observed morphology is rich; it varies from single vertical tubes, as shown in Figure 3A, to a “chemical forest” composed of numerous tubes, as shown in Figure 3D. A vertical tube may have a cotton-

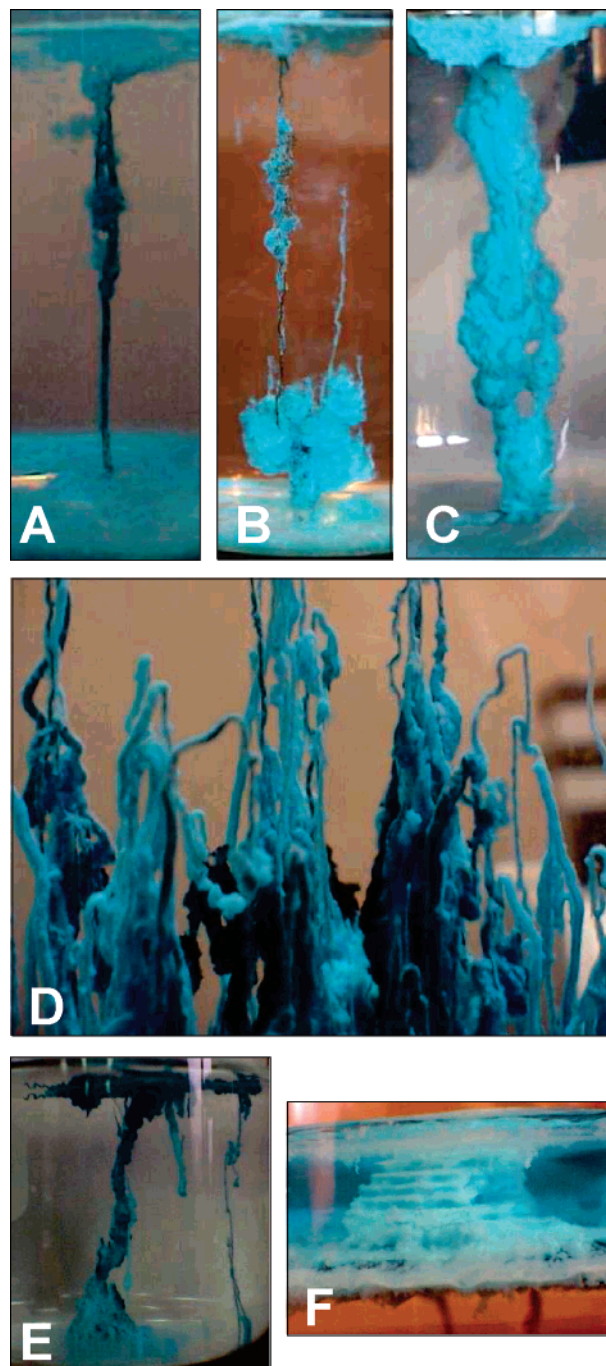


Figure 3. (A–E) Patterns developed inside the phosphate solution. (F) Pattern developed inside the copper solution that is on the top of the phosphate solution. For chemical compositions and flow rate see Figures 5–6.

like structure with thin tubes 10^{-3} – 10^{-2} mm in diameters close to the bottom (see Figure 3B), or the latter may completely cover the tube as in Figure 3C.

Secondary structures may form after vertical tubes reach the surface of the liquid. As the precipitate spreads on the surface with increasing mass, small pieces of copper phosphate precipitate may break from the floating layer and sink to the bottom in a continuous “snow shower”. A precipitate particle separating from the top layer may also draw the inner copper sulfate solution with it, forming a vertical tube growing downward (see the tube on the right in Figure 3E). At higher flow rate, a layer of copper sulfate solution may accumulate above the floating precipitate as the inner liquid is funneled through a vertical tube. With a supply of phosphate ions from the bottom solution, a

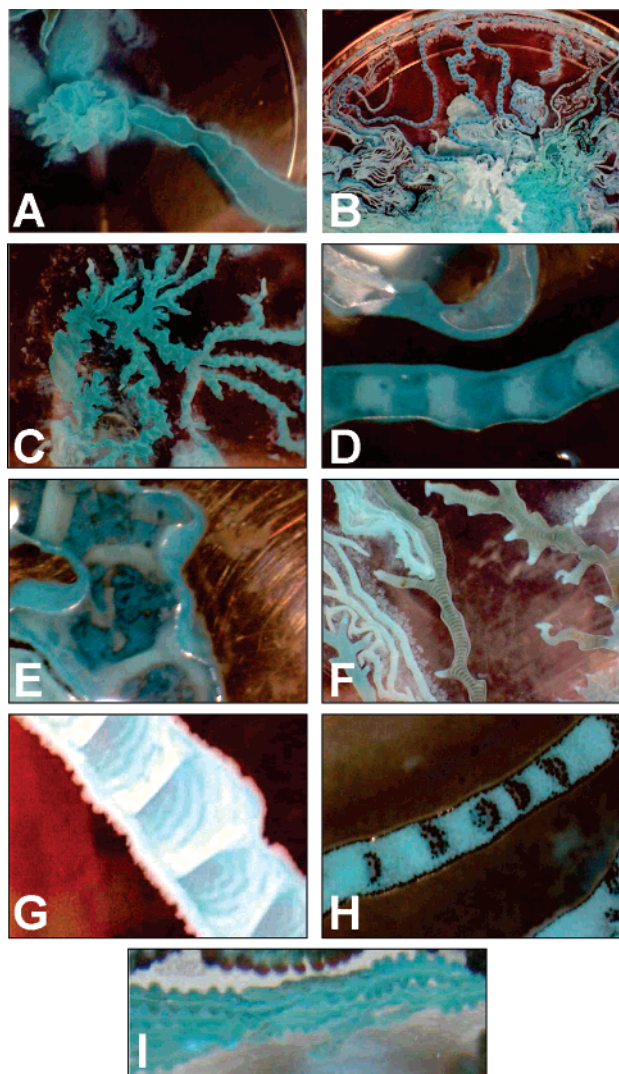


Figure 4. Patterns developed on the top of the phosphate solution. For the chemical compositions and flow rate see Figures 5–6.

layered structure of the precipitate can then be formed in the copper sulfate solution as shown in Figure 3F.

Focusing on the surface of the outer phosphate solution reveals a rich variety of complex precipitate patterns. At low concentrations of reactants, canals develop from the point where the vertical tube surfaces (see Figure 4A). As the copper solution flows in these channels, the fingers grow into different morphologies; “spaghetti-like” patterns with numerous long smooth channels may form (Figure 4B), or “fractal-like” structures may evolve following the successive division of fingers (Figure 4C). A closer look at the individual canals shows that periodic pools filled with copper solution are formed on the millimeter scale as depicted in Figure 4D and that the precipitate may even lead to complex periodic patterns as seen in Figure 4G. At longer times, black copper oxide is formed inside the pools and the membranes (Figure 4H), indicating the chemically complex nature of precipitate structure; at the interface between the copper sulfate and the alkaline sodium phosphate solution, not only copper phosphate but also copper hydroxide and copper hydroxide phosphate may be formed. The determination of the exact chemical structure of the precipitate is, however, beyond the scope of this work. It is important to note that the depth of the canals on the surface also varies periodically, as presented by the side view of the floating precipitate in Figure 4I. The

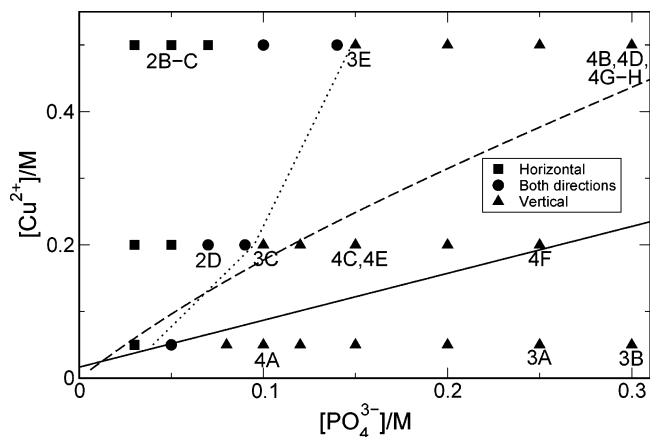


Figure 5. Phase diagram for direction of growth summarizing the results of experiments at flow rate of 0.5 mL/h. Also shown are the locations of the various patterns depicted in Figures 2–4. The dotted line marks the appearance of vertical growth in experiment with horizontal feed. The solid line indicates the line of equal density, and the dashed line is that of equal osmotic pressure.

dynamics of the periodic patterns on the solution surface is under investigation.

3.1. Phase Diagrams. Figure 5 depicts the phase diagram summarizing the results of experiments carried out at a low flow rate of 0.5 mL/h. At three different copper concentrations (0.05, 0.2, and 0.5 M) a rich variety of structures are observed with a trend showing that, for a given copper concentration, an increase in the concentration of sodium phosphate results in a transition from horizontal to vertical growth patterns.

At the lowest phosphate concentration horizontally growing patterns arise in the entire investigated range of copper concentrations. At the 0.05 M copper concentration, the transition from vertical to horizontal growth occurs at the 0.04 M concentration of phosphate, which then shifts to higher values as the concentration of copper is increased.

The most diverse group of precipitate patterns is observed for the 0.5 M copper concentration. The structures, similar to a dome or starfish shape with some splitting observed at the lowest concentrations of phosphate, are replaced by a very unique structure having thick, overlapping arms with square-shaped edges (see Figure 2C) at $[\text{Na}_3\text{PO}_4]_0 = 0.05 \text{ M}$.

It is along the diagonal of the phase diagram where the most interesting patterns evolve on the surface of the solution, once the vertical precipitate surfaces. Medium concentrations lead to distinct splitting of fingers into fractal-like structures, whereas at high concentrations, long curling fingers form, but the periodicity of the precipitate along a single tube remains.

In experiments with a significantly higher flow rate of 2 mL/h, the transition from horizontal to vertical structures shifts to higher values of the phosphate concentration, in general. At higher concentrations, phosphate ions penetrate the thin precipitate film separating the solutions, resulting in the appearance of secondary precipitate with a unique layered structure (see Figure 3F).

In a separate set of experiments in which the copper solution is introduced horizontally through the needle placed at middle height in the side wall of the container, the distinction of growth direction is more pronounced. The results, shown with dotted lines in Figures 5 and 6, are in good agreement with the rest of the experiments.

3.2. Transition to Vertical Structures. For a given concentration of copper sulfate, horizontal growth patterns are favored in systems with low concentrations of sodium phosphate, which

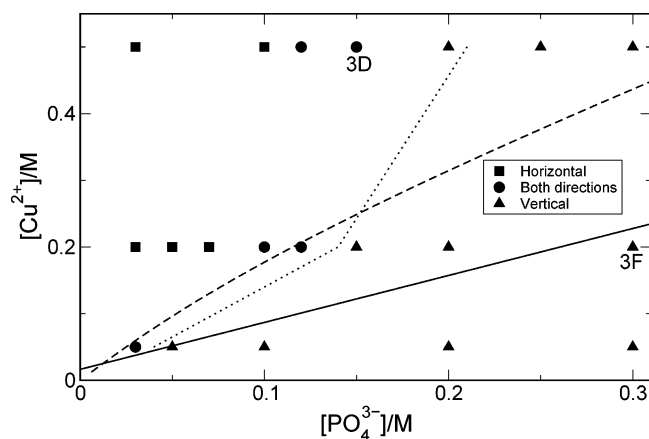


Figure 6. Phase diagram for direction of growth summarizing the results of experiments at higher flow rate (2.0 mL/h). Also shown are the location of the various patterns depicted in Figures 2–4. The dotted line marks the appearance of vertical growth in experiment with horizontal feed. The solid line indicates the line of equal density, and the dashed is that of equal osmotic pressure.

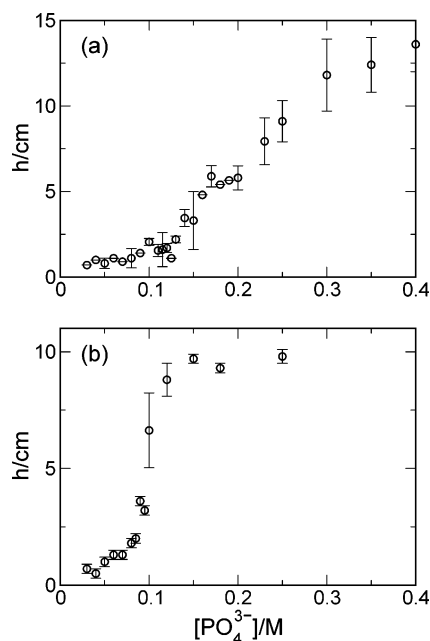


Figure 7. Height of the precipitates as a function of the Na_3PO_4 concentration for experiments carried out with 0.5 M CuSO_4 (top) and 0.2 M CuSO_4 (bottom) at a flow rate of 0.5 mL/h.

then succumb to vertical precipitate patterns with increasing phosphate concentration. This transition is studied in several experiments, where the height of the precipitate pattern developed (horizontal or vertical) is recorded in containers ranging from a 250 mL Petri dish to a rectangular vessel $5 \times 5 \times 22$ cm in size. Figure 7 shows the graph of height versus the sodium phosphate concentration obtained for high (0.5 M) and low (0.2 M) concentrations of inner copper sulfate concentrations, respectively. In the former case, the trend appears continuous; however, in the latter the transition is sharper, resulting in a sigmoidal curve ending at a height of ~ 10 cm. The height of the phosphate solution for vertically growing structures was 20 cm with a volume of 500 mL, which did not change significantly during the experiments.

4. Discussion

In the selection of growth direction, two properties of the solution play an important role: density and osmotic pressure.

Considering the density relation, we can hypothesize that if the density of the outer phosphate solution is greater than that of the inner copper sulfate solution, then vertical structures are favored by the buoyant forces, whereas horizontal growth is expected in the opposite case. To test the role played by the difference in density, we added sodium sulfate to the 0.03 M phosphate solution to increase its density and found that the precipitate grew vertically where it previously grew horizontally. In separate experiments to create the opposite scenario, we added 1.0 M sodium sulfate to 0.50 M copper sulfate solution and found that horizontally growing patterns developed instead of the vertically growing ones.

Density varies linearly at 20 °C in both solutions according to eqs 1 and 2,²¹

$$\rho_{\text{CuSO}_4}/(\text{g cm}^{-3}) = 0.152[\text{CuSO}_4]/\text{M} + 1.00 \quad (1)$$

$$\rho_{\text{Na}_3\text{PO}_4}/(\text{g cm}^{-3}) = 0.107[\text{Na}_3\text{PO}_4]/\text{M} + 1.00 \quad (2)$$

from which the line of equal density may be obtained as the following equation.

$$[\text{CuSO}_4]/\text{M} = 0.704[\text{Na}_3\text{PO}_4]/\text{M}$$

This line only coincides with the transition from horizontal to vertical structures at low copper concentration as indicated by the solid line in Figures 5 and 6.

At higher copper concentrations, however, vertical patterns are also observed in regions where the inner solution has a greater density than the outer phosphate solution (i.e., above the solid line in Figures 5 and 6), which is caused by the influence of the membrane density. In our experiments, the position of the transition curve is above the equal density curve, indicating that the density of the membrane is smaller than that of the inner solution. The other important factor, the osmotic pressure for both solutions is calculated from eq 3,

$$\pi = -\frac{RT}{V_1} \ln(a_1) = \frac{RT}{V_1} \left(\frac{vm\phi}{55.506 \text{ mol/kg}} \right) \quad (3)$$

where V_1 is the partial molar volume of the solvent water, v is the number of ion produced by the electrolyte upon dissolution, m is the molality of the solution, and ϕ is the osmotic coefficient. The value of V_1 can be obtained from the variation of density with solution composition according to eq 4,

$$V_1 = M_1 \left(\rho^{-1} - \frac{d\rho^{-1}}{dw_2} w_2 \right) \quad (4)$$

where M_1 is the molar mass of water, and w_2 is the mass fraction of the solute. For copper sulfate, the osmotic coefficient as a function of molality from ref 22 is applied, whereas for sodium phosphate it is obtained from the activity coefficient (γ) as a function of molality²³ by eq 5.

$$\phi = 1 + \frac{1}{m} \int_0^m m' d \ln(\gamma) \quad (5)$$

The line of equal osmotic pressure is especially important in the experiments conducted with a pellet instead of pumping the inner solution. If the osmotic pressure of the electrolyte inside is lower than that of the outer electrolyte, water diffuses from the cell, and the growth of structure is impossible. In this case, the membrane precipitates around the pellet, preserving its shape.¹¹ Along the line of equal osmotic pressure the amount

(volume) of water that diffuses in (dV_i) and out (dV_o) per unit time must be equal ($dV_i = dV_o$). In the vicinity of this line, dV_o may be slightly greater than dV_i , we may observe a limited growth of the cell around the membrane. The inflow of water will increase the inside pressure by $dp \propto dV/V$, and a new equilibrium will be reached. When the inner pressure becomes greater than the stability of the membrane, the membrane is ruptured, and the ejection of inner copper sulfate solution results in the reaction of copper ion with phosphate to extend the structure, and this process will recommence. In experiments with pellets, the line of equal osmotic pressure defines the area where the growth of structures is possible. When the supply of inner electrolyte is maintained by pumping the solution instead of the application of a solid pellet, the water balance equation will change according to $dV_i + dV_p = dV_o$, where dV_p represents the contribution of pumping to the volume change. The development of structures is possible only above the line of equal flow defined by this equation. As the pumping flow increases, dV_i may decrease for a constant value of dV_o . The line of equal flow will, therefore, shift to lower copper concentrations, and it will lie below the line of equal osmotic pressure in accordance with our experiments, where we see patterns below the equal osmotic line. Calculation of the position of the equal flow line requires knowledge of diffusion coefficients through the membrane and the kinetics of membrane formation and membrane changes. It is beyond the scope of this paper.

Apart from the properties of the two solutions, the applied flow rate at which the inner copper sulfate solution is fed has an effect on the preferred dominant orientation of the precipitate. The higher flow rate increases the range of horizontal and mixed patterns, especially at greater copper concentration (cf. Figures 5 and 6), whereas the orientation of the feed itself (by injecting the solution horizontally through the side wall of the beaker) has no effect on the selection of initial growth direction. The phase diagram can be used to predict the initially developing structure for a set of parameters as long as sodium phosphate is in large excess, because the patterns are very reproducible.

At greater copper sulfate concentration, not only vertical growth is observed at phosphate concentrations lower than predicted by the lines of equal density or osmotic pressure, but the transition region (where mixed growth prevails) also becomes wider, resulting in a gradual increase in the height of the precipitate instead of the sudden change.

It is important to mention that, as time progresses, the outer phosphate solution is gradually depleted. Therefore, a concentration gradient builds up in the solution that may also contribute to the quantitative characteristics of the precipitate. To eliminate this effect, the height measurements have been carried out in the same container with constant, large liquid volume.

We have seen two mechanisms controlling the saturation of the height of vertical structures. One mechanism is presented in Figure 3D. Developing tubes, after reaching some height, curve down. It is probably related to the depletion of copper ion and to the change in chemical and mechanical properties of the membrane. In the second mechanism, we have observed that tubes break after reaching maximum height, and the upper part falls to the bottom. In both cases, the mechanical properties of precipitated structures define maximum height.

5. Conclusion

The construction of phase diagrams has resulted in the discovery of, for a two-compound system, a variety of unusual structures with high complexity. It allows us to study the

transitions between structures, and it is also the necessary step for future modeling and understanding of the causal relations among the various structures and processes. The complexity of structures is outstanding, both in the number of possible structures and in the number of different elements forming the structure. Similar to biological systems, the structures are defined by chemical reactions, hydrodynamics, and mechanics. All of them interact together to form this unusual variety. It is even more outstanding that these structures appear in a very simple two-component inorganic system.

In the study of precipitation patterns in the "chemical garden", three approaches have been developed recently. First is the typical reductionist approach, which chooses one of the structures or phenomena and develops mathematical models that are as accurate as possible.¹⁵

The second approach is concentrated on the processes itself.¹¹ The morphogenesis of structures is studied as a chain of chemical, physical, and mechanical processes that are precisely organized in space and time. Finding these processes and their spatiotemporal organization is the goal of the study. The processes are related to the gradient of different potentials or forces and related fluxes, which in our case are (1) the difference in chemical potential (both between ions in the solution and the membrane, causing membrane precipitation, and between the two sides of the membrane, leading to osmotic pressure), (2) the pressure difference between the inner and outer side of the membrane, (3) and buoyant forces due to gravity. These forces then lead to the formation of the membrane by precipitation, fluid flow across the membrane by osmosis, rupture of membrane due to excessive pressure build-up, and ejection of inner solution, all in a cycle.

The third approach is the study of a phase diagram, which is the basic tool in the dynamically developing field of theoretical morphology, and it is originated from studies of morphology and morphogenesis in biological systems. Theoretical morphology "seeks to reduce complex forms to few generating factors and causal influences".²⁴ The most important tool is the idea of morphospace: the space of all possible structures under given chemical, physical, mechanical, and geometrical constraints.

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