

Precipitation Behavior in Liesegang Systems under Microwave Irradiation

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Abstract

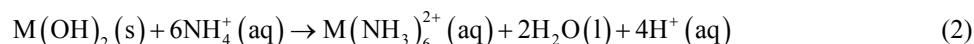
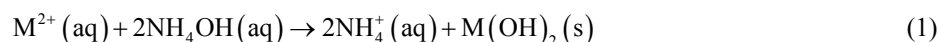
We studied precipitation patterns in a Liesegang system under microwave irradiation in order to investigate metal salt diffusion in an electrolyte gel. The salt species and microwave irradiation power were varied. Microwave irradiation induced periodic patterns of precipitation because polar molecules vibrate and rotate in an electromagnetic field. For example, the number of patterns increased with the irradiation power. Accordingly, microwave irradiation nonlinearly accelerated the diffusion of ionic molecules.

Keywords

Component, Microwave, Liesegang, Diffusion, Precipitation

1. Introduction

Liesegang phenomena, a function of diffusion and reaction conditions, form attractive and unique periodic stripe patterns. Such pattern formation frequently inspires microstructural design in materials science. Moreover, morphological pattern transitions between periodic precipitation and tree-like crystal aggregates are scientifically interesting [1] [2]. Liesegang phenomena usually manifest themselves when a concentrated salt solution diffuses through a gel that contains another electrolyte at a lower concentration. Diffusion and chemical reactions cause little precipitation of otherwise soluble salts in a periodic manner. The precipitation and redissolution reactions for a generic metal ion M^{2+} are as follows:



When NH_4OH diffusion causes metal ions to precipitate in the form of $M(OH)_2$, redissolution at the top of the

pattern induces a Liesegang band.

Recent research indicates that spontaneous diffusion-related self-organization dynamics and irreversible reactions or precipitation systems based on Ostwald supersaturation theory explain Liesegang pattern formation [3]. However, nonlinearly hinders elaboration of the exact mechanism.

Microwave radiation may be helpful in this context. Microwave radiation has recently been a very active area of research due to the many advantages of nonthermal effects such as reaction promotion, nucleation induction, and diffusion facilitated by the molecular vibration of polar molecules [4] [5]. We hypothesized that the reaction and diffusion characteristics of a Liesegang system could be modulated or explained via various microwave properties. In addition, Liesegang phenomena may suggest a new application of microwave radiation and suitable operating conditions for highly functional inorganic nanomaterials. Salt and gel concentration [6], inner electrolyte species, and so on are essential for solving the diffusion challenge of Liesegang phenomena. In this study, we varied salt species and microwave output to understand the microwave effect. We used a microwave reactor equipped with an *in situ* observation system to analyze the dynamic growth behavior of the periodic pattern.

2. Experimental

To form a Liesegang pattern, we used a gel because it can prevent precipitate sedimentation and hydrodynamic turbulence. A salt was added to a prepared gelatin-based gel [7] [8]. In this study, gelatin and salt concentration were constant, and we used three salt species containing the same metal ion: $\text{Co}(\text{NO}_3)_2$, CoCl_2 , and CoSO_4 (Table 1). These salts were selected because counterion species is a major controlling factor in pattern formation. The counterion modulates the solubility, diffusion coefficient, and dielectric constant of each salt, which is a function of microwave adsorption. We first heated a solution (*i.e.*, gel and salt) to 90°C . We then poured the solution into a glass test tube (ϕ : 13 mm; height: 100 mm; volume: 5 mL) and gradually cooled it to room temperature to impart a homogeneous gelatin network structure. Temperature is the most important factor for pattern formation; we used two different methods, microwave irradiation (MW) and conventional heating (oil bath, OB) for maintaining solution temperature. After we poured 2 mL of a 28% ammonium solution at the gel surface, we covered it with a silicon rubber lid. Ammonium salt precipitates via ammonium ion diffusion into the gel, and Liesegang stripe-pattern formation starts from the top surface to the bottom of the tube. We measured the stripe number and length for the two heating methods.

2.1. Microwave Heating

Figure 1 shows a tube-guide microwave reactor (Shikoku Instrumentation), which is specially designed for preventing microwave leakage and equipped with a microscope camera (Sigma Koki, model SK-TC202USB-AT) for *in situ* observation [9] [10]. We hung a test tube containing the solution by a thread at the center of the reactor. Immediately after pouring the ammonium solution onto the gel surface, we initiated microwave irradiation for 30 min. Because the stripe pattern grows from the surface to the bottom, we gradually lifted up the test tube at a controlled speed to acquire photographs around the vertical stripe center, through the side of the reactor, with the fixed microscope. We measured the Liesegang pattern length via the pixel number between the top and bottom of the precipitation region, and we counted the stripes through the photographs every 5 min. This approach enables dynamic evaluation of Liesegang pattern propagation with respect to microwave radiation. After 30 min, we measured the final temperature with an optical fiber (Anritsu Meter) because the solution temperature increases under irradiation.

2.2. Conventional Heating

We used an oil bath to maintain the solution temperature. The bath temperature was increased over the course of

Table 1. Experimental conditions.

| | Gel conc. [w%] | Salt conc. [mol/L] | MW output [W] |
|----------------------------|----------------|--------------------|---------------|
| $\text{Co}(\text{NO}_3)_2$ | 1.0 | 0.3 | 22, 23, 24 |
| CoCl_2 | 1.0 | 0.3 | 22, 23, 24 |
| CoSO_4 | 1.0 | 0.3 | 22, 23, 24 |

30 min to the final temperature observed in the microwave experiment. We poured ammonium solution into the test tube immersed in the oil bath, and photographed the stripe pattern after 30 min with the microscope camera.

3. Results and Discussions

Figures 2-7 show photographs of the stripe pattern near the gel surface for each salt under MW or OB conditions after 30 min. The experiment involves precipitation after the salt concentration in the gel exceeds the critical values (*i.e.*, the solubility due to ammonium ion diffusion). We observed a stripe pattern in the case of $\text{Co}(\text{NO}_3)_2$

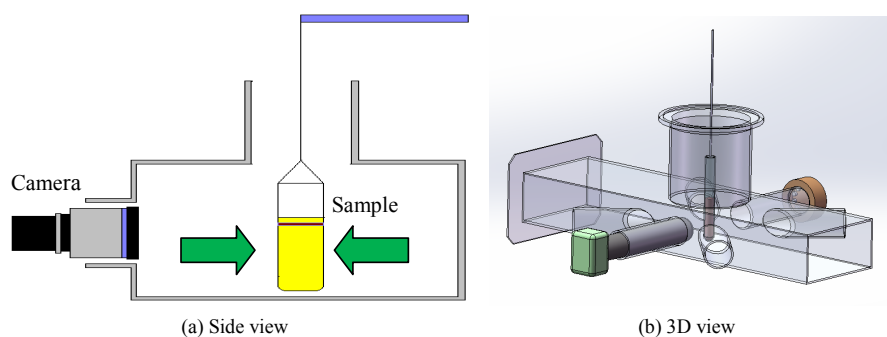


Figure 1. Microwave reactor.

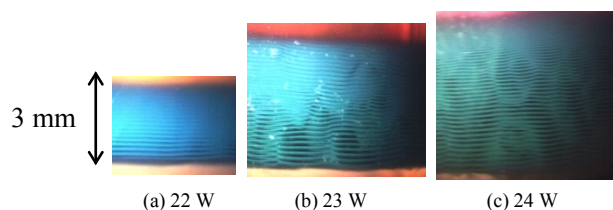


Figure 2. $\text{Co}(\text{NO}_3)_2$ stripe pattern under MW.

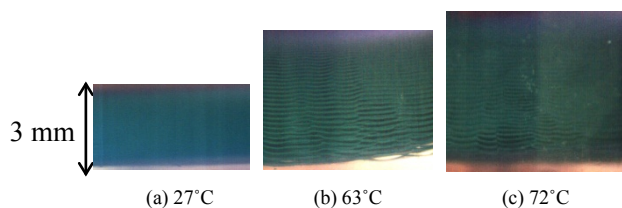


Figure 3. $\text{Co}(\text{NO}_3)_2$ stripe pattern in OB.

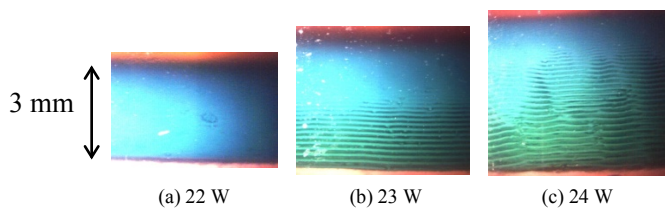


Figure 4. CoCl_2 stripe pattern under MW.

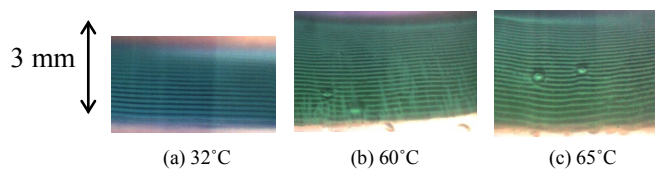


Figure 5. CoCl_2 stripe pattern in OB.

and CoCl_2 . However, the pattern induced by CoSO_4 was not clear; 30 min may be insufficient for stable precipitation because of its higher solubility. We did not observe an expected pattern transition (e.g., a tree-like pattern [1]) in this experiment, and the parallel stripe pattern remained even under microwave irradiation.

To aid in understanding the mechanism of stripe-pattern formation, **Figures 8 and 9** plot the stripe number and length, respectively, in relation to reaction time. Filled and open symbols indicate MW and OB conditions,

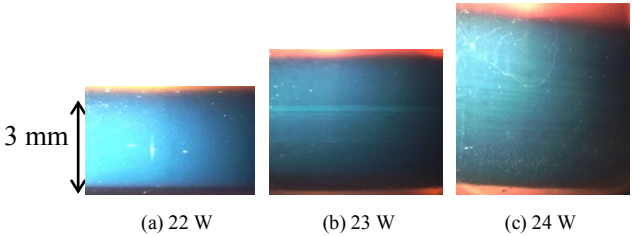


Figure 6. CoSO_4 stripe pattern under MW.

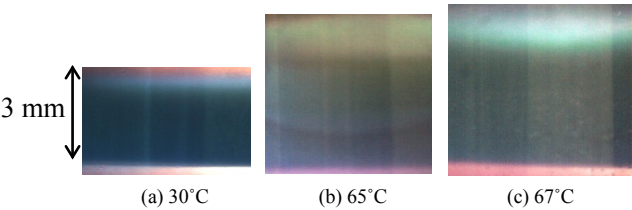


Figure 7. CoSO_4 stripe pattern in an OB.

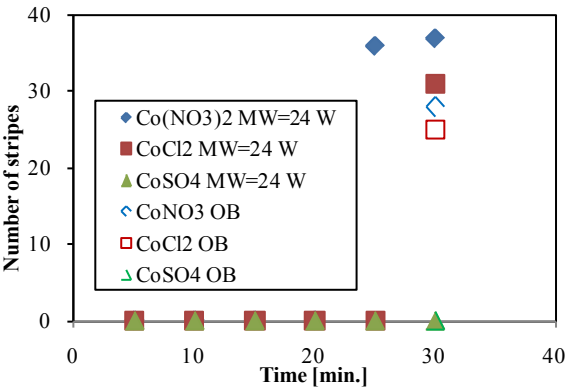


Figure 8. Stripe number versus time.

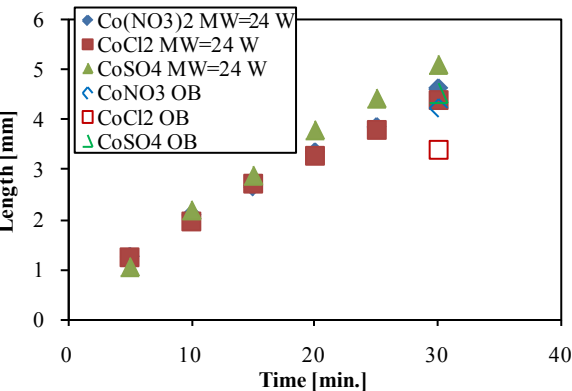


Figure 9. Liesegang pattern length versus time.

respectively. Although precipitation starts just after contact with the ammonium solution, either the stripes do not immediately form or the camera resolution limit precludes sufficiently fast and precise image acquisition; accordingly, we assigned the initial number of stripes as 0. We counted the number of stripes after approximately 25 min. The stripe length linearly increased with reaction time (Figure 9). After 30 min of reaction time, nonthermal effects induced by microwave irradiation caused the stripe number and length to increase more rapidly for MW relative to OB. This is attributable to enhanced molecular diffusion and facilitated supersaturation. Molecular vibration induced by microwave irradiation accelerates ionic diffusion. Moreover, such vibration readily induces supersaturation of the precipitate. Consequently, cyclic periods of supersaturation, nucleation, and depletion become faster. However, temperature must be carefully controlled to modulate such cycling.

Figure 10 and Figure 11 show an almost linear relation of stripe number and length, after 30 min of irradiation, with respect to microwave power for $\text{Co}(\text{NO}_3)_2$ and CoCl_2 . MW imparted a greater effect than OB. Consequently, microwave irradiation more effectively induced precipitation via supersaturation. Strip pattern formation did not proceed readily for CoSO_4 , even at a higher microwave irradiation power.

4. Conclusion

To understand the mechanisms of precipitation and diffusion in Liesegang patterns, experiments varying the salt species and microwave power were conducted in an oil bath and microwave reactor equipped with *in situ* observation system. Stripe length and number increased more quickly with respect to time under microwave irradiation than oil bath heating, and also increased with respect to microwave irradiation power. We explained these findings in the context of nonthermal effects (*i.e.*, higher molecular diffusion and facilitated supersaturation) that are accelerated by radiation-induced molecular vibration. Microwave irradiation can modulate the diffusion and

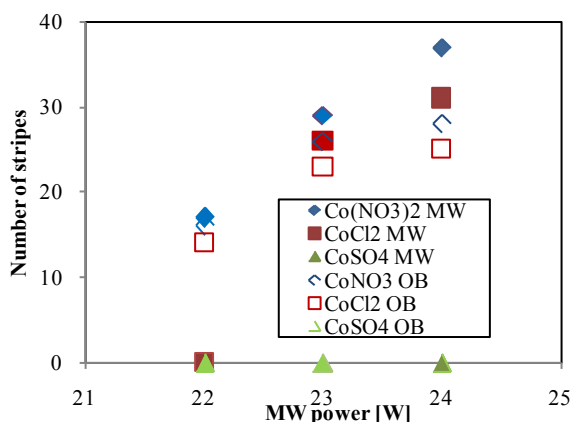


Figure 10. Stripe number versus MW power

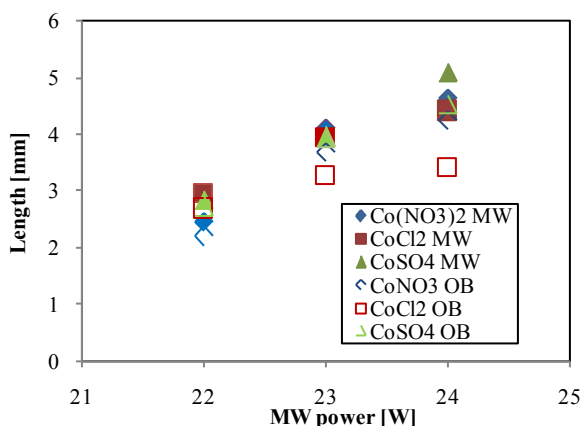


Figure 11. Liesegang pattern length versus MW power.

manifestation of Liesegang patterns, and may be a useful tool in other fine-scale, nonequilibrium self-organization processes that involve precipitation and nonlinearity.

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