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Transition between Periodic Precipitation and Tree-Like Crystal Aggregates: A Detail Experimental Study

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Abstract. Transitions between periodic patterns and tree-like patterns in lead iodide precipitation systems were found with varying agar concentration in diffusion media. At high agar concentrations, periodic patterns (Liesegang band) of lead iodide precipitates form whereas at low agar concentrations, tree-like crystal aggregates similar to diffusion-limited aggregation (DLA) develop in the entire system. At an intermediate agar concentration, Liesegang band forms near the contact surface, while tree-like aggregates appear suddenly at some distance from the contact. The influence of agar concentration and lead-iodide concentration ratio was represented as the morphological phase diagram. Together with examinations of diffusion coefficient, nucleation threshold, internal structure of agar media and crystal number densities with varying agar concentration, it is concluded that the effect of agar concentration on nucleation kinetics, rather than on diffusion coefficient, controls the morphological transition.

1. Introduction

During crystallization in solution, various types of structures can be found. Periodic precipitation, otherwise known as Liesegang band or ring, has been studied to understand non-equilibrium pattern formation, especially the mechanism of periodic pattern formation since its discovery (HENISCH, 1988). The formation of a periodic pattern is basically understood by the Ostwald supersaturation theory (OSTWALD, 1897; WAGNER, 1950; PRAGER, 1956) in which the coupling between diffusion and the reaction with supersaturation is essential. Another well-known precipitation pattern exists called tree-like crystal aggregates or diffusion-limited aggregation (DLA) (VICSEK, 1989). Both periodic precipitation and tree-like aggregate patterns have been studied separately (based on different experiments and theories to understand the pattern formation) in a non-equilibrium system despite their common features of diffusion and irreversible reactions (KAI, 1993).

Recently we found the morphological transition between Liesegang Ring and tree-like crystal aggregates (TORAMARU and IOCHI, 1997). In the present study, we examine in detail the morphological transition with varying agar concentrations under a macroscopic concentration gradient in a lead iodide precipitation reaction. The morphological transition

suggests that, in addition to the macroscopic concentration gradient, the agar concentration systematically influences the nucleation and growth rates, which is another important factor in controlling the precipitation patterns. Firstly, we demonstrate the experimental results showing typical variation in morphology. The experimental results are presented in a morphological phase diagram with two variables: agar concentration and ion-anion concentration ratio, $[I^-]/[Pb^{2+}]$. Secondly, we report supplemental experiments carried out to clarify the cause of the transition. Finally we discuss the mechanism of the morphological transition between periodic precipitation and tree-like crystal aggregate patterns.

2. Experiment and Results

The experiment consists of an inorganic reaction with diffusion of the reacting components. A gel containing iodide anion was placed above a gel containing lead cation in a glass tube. Diffusion of iodide anions into the lead cation gel results in monomer formation; $2I^- + Pb^{2+} \rightarrow PbI_2$ immediately after the concentration product exceeds a critical value ($[I^-]^2[Pb^{2+}] = 7.5 \times 10^{-9}$ (mol/l)^3) at 15°C from a data book (THE JAPAN SOCIETY FOR ANALYTICAL CHEMISTRY, 1994). When the concentration of monomer PbI_2 exceeds the critical value for nucleation, which is considered to be an important factor in the present investigation, the nucleation of PbI_2 crystals takes place (this monomer hypothesis will be discussed in Subsec. 3.2). As iodide anions diffuse into the gel, the reaction proceeds periodically in space and time to form a Liesegang band.

The concentrations of KI and $Pb(NO_3)_2$ were 2.6 wt% (0.16 mol/l), and 0.32 wt% (0.010 mol/l), respectively. An agarose compound (product of Sigma Company) was used as a diffusing medium to prevent hydrodynamic disturbance. Agar media were prepared by microwave heating until all agar powder was completely dissolved in water and had formed a homogeneous solution. First agar solution of $Pb(NO_3)_2$ was poured into a glass tube (1.4 cm in diameter and 12 cm in length). After gelation of $Pb(NO_3)_2$ solution had been completed (gelation temperature of the agarose is 36°C), the agar solution of KI was added. The timing of addition of KI solution was just before gelation of KI solution to minimize the thermal influence on $Pb(NO_3)_2$ agar. During precipitation pattern development, the glass tubes were maintained at a constant temperature of 18°C in a thermal bath.

In the experiment with 3 wt% agar, only a periodic precipitation was observed over the entire distance of the glass tube (8 cm in height) (Fig. 1a). Increase in a band width with distance was observed, and can be approximately described by the well-known asymptotic spacing law [1] (the ratio, $\Delta x_{n+1}/\Delta x_n$, is constant for large n where Δx_n is the n-th spacing between two succeeding bands).

In the experiment with 2.0 wt% agar, periodic precipitation occurred near the contact interface between two gels. The tree-like crystal aggregates appeared (Fig. 1b) after periodic precipitation continued to a distance of 0.7 cm from the contact interface. Some of the crystal aggregates were initiated from band defects, and others grew from crystals on the final band. A tree-like crystal aggregate is composed of a number of plate-like single crystals. This fact suggests that surface nucleation takes place concurrently with growth of each grain. Assuming that the crystal aggregate is a kind of fractal crystal-aggregate, the fractal dimension, d, can be estimated at approximately 1.6 to 1.5 (Fig. 2) in the quasi-2 dimensional experiment.

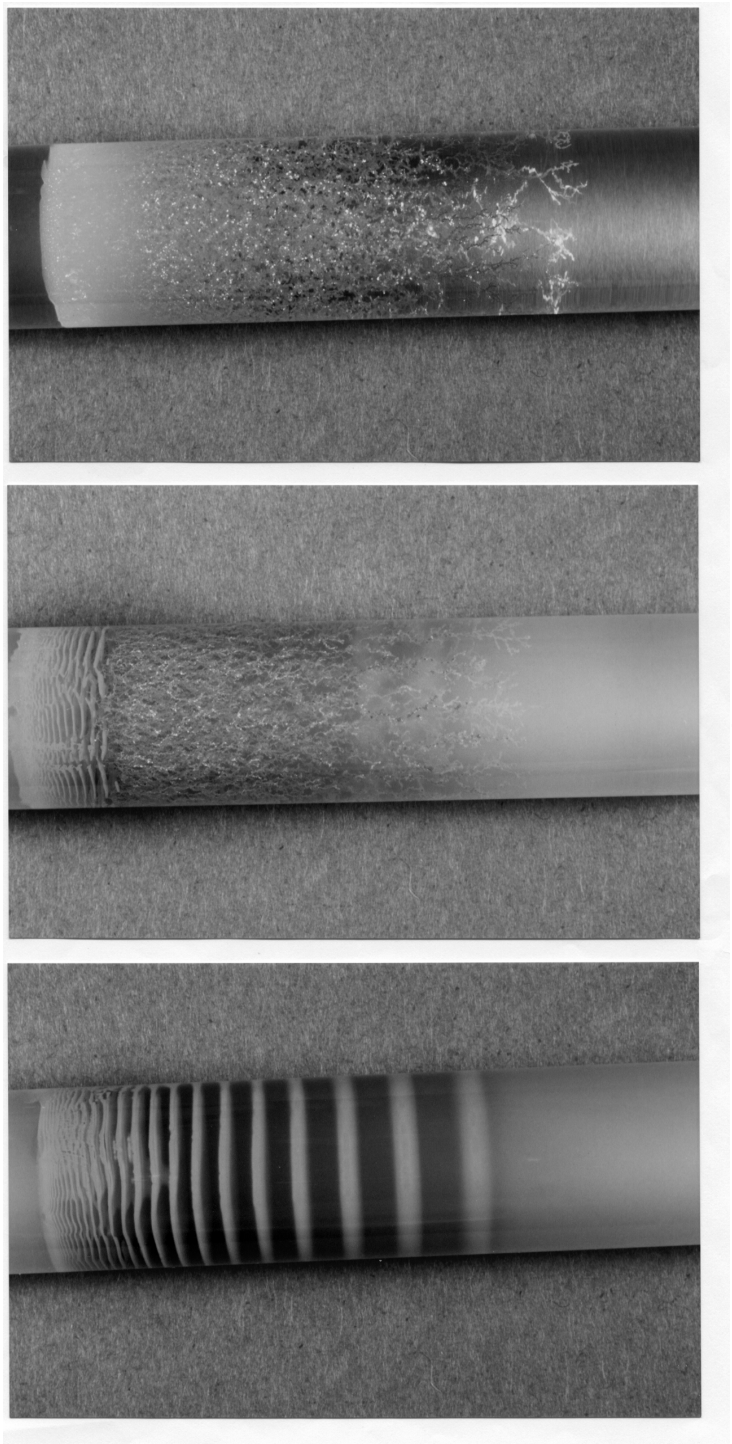

Fig. 1. The Liesegang experiment showing morphological transition. (a) Agar concentration is 3 wt%. A periodic precipitation pattern is observed. (b) Agar concentration is 2 wt%. The transition from periodic precipitation to tree-like crystal aggregates is observed. (c) Agar concentration is 0.5 wt%. Tree-like crystal aggregates develop directly from the contact surface without any ordinary Liesegang Band. Width of glass tube is 1.8 cm.

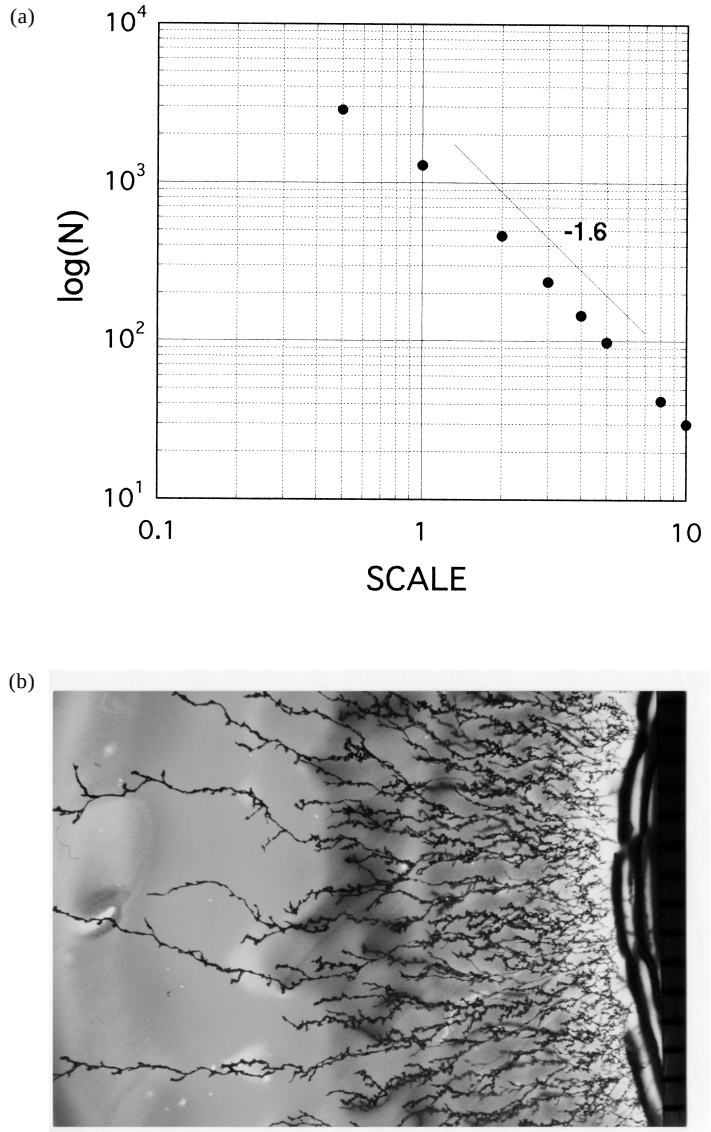

Fig. 2. (a) A result of box counting for tree-like crystal aggregates in the quasi-2 dimensional experiment. (b) A photograph of the quasi-2 dimensional experiment (concentrations are 1.0 wt% agar, 0.16 mol/l KI, and 0.01 mol/l $Pb(NO_3)_2$, respectively). In this experiment, $Pb(NO_3)_2$ agar was made 0.5 cm in thickness on a petri dish of 10 cm in diameter. A chip of KI agar (2 cm in diameter and 0.5 cm in thickness) was placed on the surface at the center of the petri dish. The photo is the pattern after 9 days from the onset of experiment. The width of this photo is 2 cm. Note that in this experimental situation, even for 1.0 wt% agar concentration, periodic pattern appears near the contact.

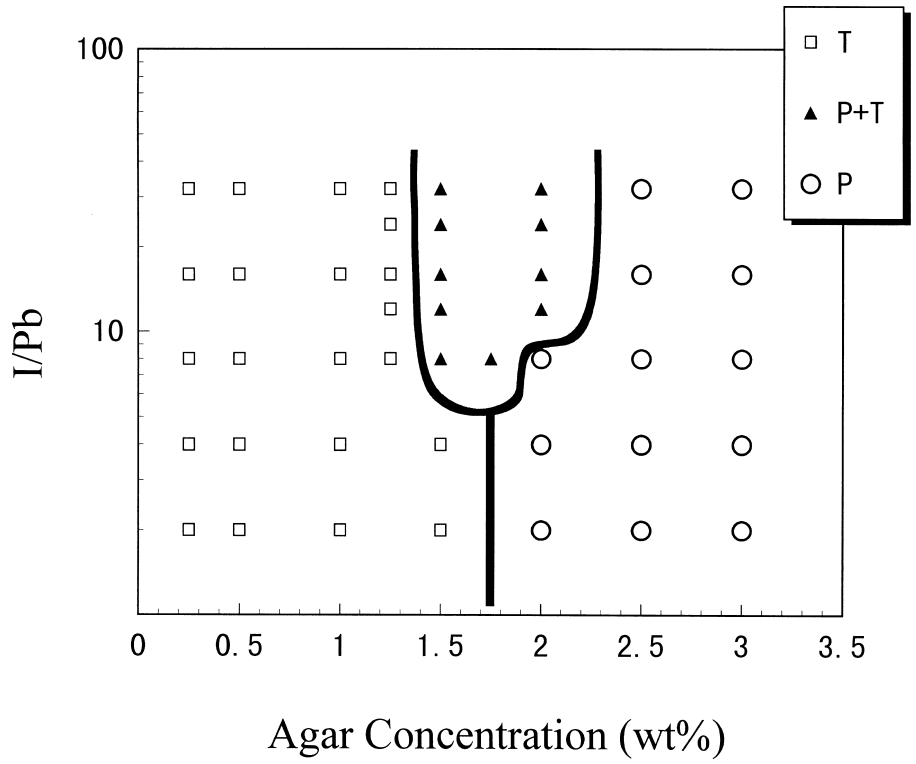

Fig. 3. The morphological phase diagram as functions of agar concentration and I/Pb. The concentration of Pb is kept constant at 0.01 mol/l. The open circle indicates the appearance of periodic precipitation (P). Solid triangles indicate the transition between periodic precipitation and tree-like crystal aggregates (P + T). Open squares represent the tree-like crystal aggregates. Approximate phase boundaries are represented by thick lines.

At approximately 1.4 wt% or less agar concentration, tree-like aggregates were initiated directly from the contact plane and developed throughout the glass tube (Fig. 1c). Morphological characteristics of the tree-like crystal aggregates vary with agar concentration and also with distance, and depend delicately on the experimental configuration such as the size of glass tube. As the agar concentration decreases, the spacing between branches appears to become narrower.

We investigated the pattern formation by varying the ion-anion concentration ratio. From the experiments conducted, it was found that the morphological transition is not largely influenced by the I/Pb ratio. Figure 3 shows the morphological phase diagram as a function of agar concentration and ion-anion ratio. The qualitative nature of the phase diagram does not depend on other parameters such as the duration of microwave treatment and temperature. However, the detail of phase diagram (e.g., the absolute values of two variables at the phase boundaries) may be influenced by these parameters. For example, at a temperature of 8°C, in 2.5 wt% agar concentration, tree-like crystal aggregates appeared.

Nevertheless the qualitative nature that the transition occurs at a range of intermediate agar concentration does not change.

3. Additional Experiments

The transition between periodic precipitation and tree-like crystal aggregates can be attributed to either the kinetics of nucleation and growth or the diffusion process, both of which depend on agar concentration. In order to discriminate between these two effects, we carried out three sets of additional experiments. The first was the determination of diffusion coefficient as a function of the agar concentration. The second was the determination of supersaturation required for nucleation as a function of agar concentration. The third was the determination of the number densities of crystals in the two patterns.

3.1. Diffusion coefficient

This experiment was based on a simple principle and procedure. The principle is that the diffusion distance is proportional to $\sqrt{Dt}$, where D is the diffusivity of the anion (or ion) and t is the diffusion time. Therefore the method involves measuring the diffusion distance (front) which can be visualized by reaction.

Firstly, we prepared media with agar concentrations of 3 wt% and 0.5 wt% without any reactive components. These reacting component-free agar media (rod shape, 1.4 cm in diameter, approximately 10 cm in length) were overlaid with the iodide-bearing agar media at the same agar concentrations. The iodide ions diffused into the agar media corresponding to the diffusion coefficient dependent on the agar concentration. After 6 hours, the agar media were soaked in a lead nitrate solution and a lead iodide precipitate was formed. Precipitation appeared for a diffusion distance within which the iodide ion concentration exceeded a certain value. The diffusion distances measured show that the diffusion coefficient in 0.5 wt% agar media is approximately two times higher than that in 3 wt% agar; i.e., $D_{0.5} \approx 2D_{3.0}$, where the subscript refers to the agar concentration in weight percent.

3.2. Critical effect of agar concentration on nucleation

The minimum concentration of reacting components required for homogeneous nucleation of lead iodide particles was determined experimentally. It should be noted that the term “homogeneous” nucleation as referred to in the present paper is somewhat different from that in solution, liquid or melt. In agar media “homogeneous” nucleation in the exact sense cannot be applied because agar media have internal structures which provide nucleation sites. In the present paper, for convenience, the term “homogeneous” nucleation is used to distinguish the surface nucleation that new crystals nucleate on the surface of old crystals.

The experimental procedure to examine the critical condition for homogeneous nucleation was as follows. Agar media chips with various concentrations of agar, lead cation and iodide anion were prepared. A lead bearing chip was brought into contact with an iodide bearing chip. We then closely observed the appearance of precipitation near the interface of a pair of iodide and lead agar chips using an optical microscope.

From the results obtained (Fig. 4) it is found that the critical condition for homogeneous nucleation correlates with agar concentration. Namely, in the case of higher agar concentration (3.0 wt%), lower concentrations of reacting components are required for nucleation, and vice versa. However the nucleation process is not simple because the critical condition seems to be mainly controlled by the concentration product $[I^-]^2[Pb^{2+}]$ rather than the monomer concentration. This implies that nucleation process is not simple coagulation process of PbI_2 monomer but the collisional kinetics of I^- and Pb^{2+} particles. Thus this fact requires the reconsideration of the monomer hypothesis that nucleation takes place when the monomer concentration exceeds a critical value. We do not make further discussion here because it is beyond the scope of the present paper.

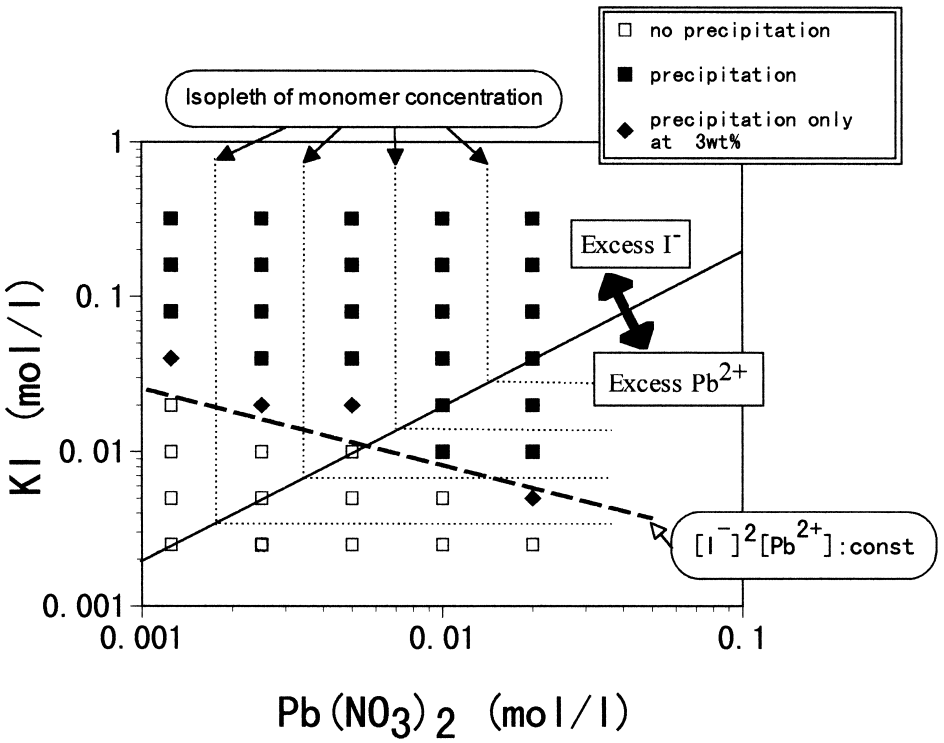

Fig. 4. Diagrams showing the critical condition for precipitation occurrence with variable lead and iodide concentration. For both 3.0 wt% and 0.5 wt% of agar concentrations, the precipitation occurred for the concentration condition indicated by solid squares but did not occur for those indicated by open squares. At the condition indicated by solid diamonds, the precipitation occurred in 3 wt% agar media but not in 0.5 wt% agar media. A solid line indicate the constant concentration ratio, [I]/[Pb] = 2. On this line, anion (I^-) and cation (Pb^{2+}) are equivalently consumed to form PbI_2 monomer. In the upper region of this line, an excess iodide anion exists whereas in the lower, an excess lead ion does. A dashed line indicates the constant value of the concentration product $[I^-]^2[Pb^{2+}]$. Dotted lines indicate the isopleth of monomer concentration.

This result is consistent with the agar structure observed by the scanning electron microscopy (SEM). SEM micrographs (Fig. 5) show that the characteristic spatial scale of the agar structure is smaller in the higher agar concentration medium than in the lower agar concentration medium. This implies that the characteristic spatial scale of the agar

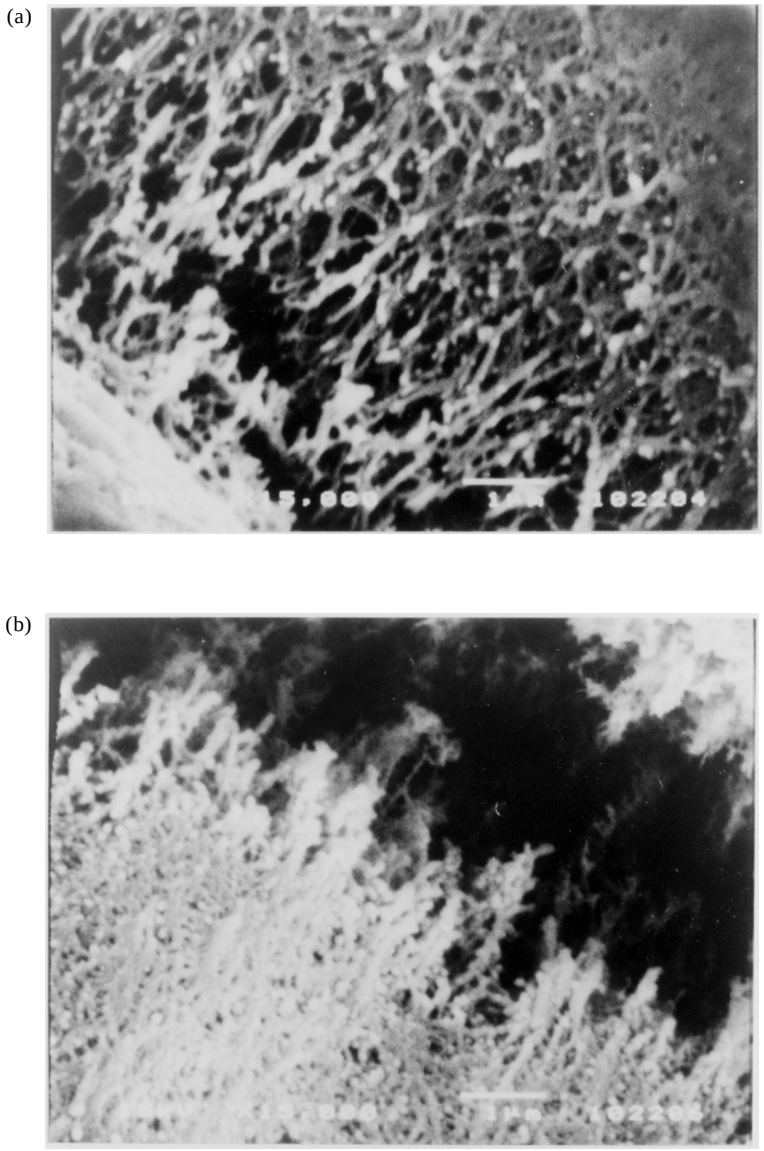

Fig. 5. Micrographs of internal network structure of agar media. SEM micrographs were taken of the agar medium after the critical point dehydration. (a) 0.5 wt%, (b) 3 wt%. Scale bars are 1 μm in both.

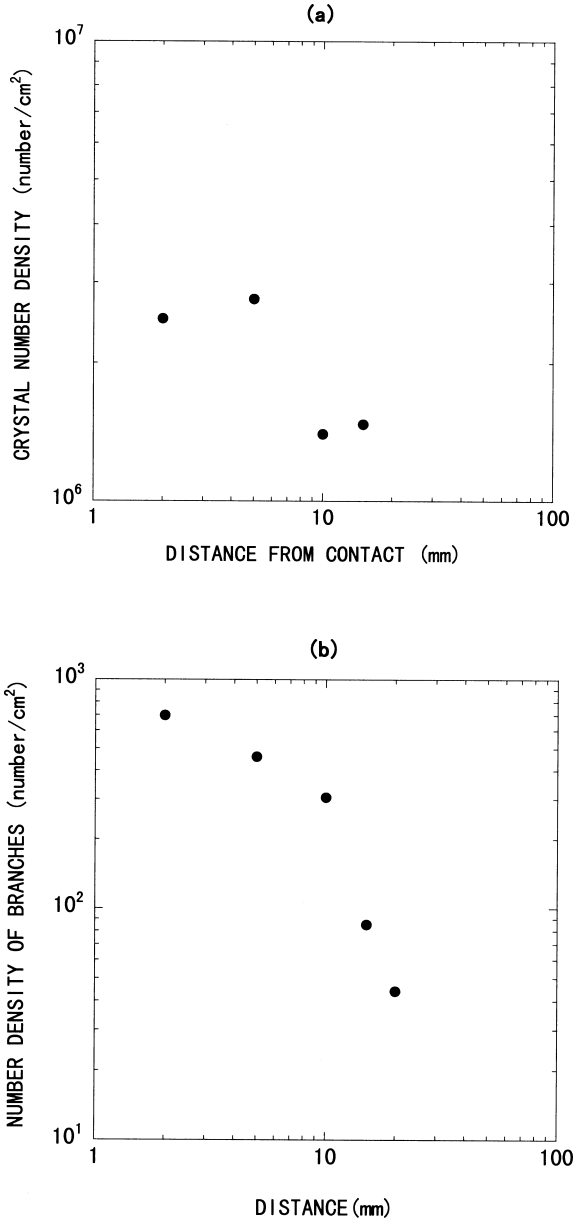

Fig. 6. The results of measurement of number of crystals in periodic precipitation (a) and number of branches in tree-like crystal (b). Agar concentration for periodic precipitation is 2.75 wt%, and that for tree-like crystal aggregate 0.5 wt%.

structure may affect the critical condition for nucleation because an agar medium with a smaller scale has a larger internal surface area, which provides a greater number of nucleation sites. However, it should be noted that the expected contrast of internal surface area with agar concentration is not proportional to the observed contrast in the number density: the internal surface area difference estimated based on micrographs of Fig. 5 is at the most 10 times greater whereas the number density difference is at least 10^3 as shown in the next section.

3.3. Measurement of number densities of crystals

Crystals in periodic precipitation were at most 5 micro meter in diameter even after a few days since the onset of experiment. Therefore we used the SEM observational method similar to those for the agar internal structure observation described above. The numbers of crystals in periodic precipitation were measured on the 2-dimensional cross section. From the measurement, the number denstity of crystals was estimated to be approximately 10^6 per cm^2. In Fig. 6(a) the results are shown as a function of distance from the contact position.

In tree-like crystal aggregates, numbers of crystal branches were measured on the 2-dimensional cross section perpendicular to the axis of glass tube using an optical microscope. In Fig. 6(b) the results are shown as function of distance from the contact. Though each branch in tree-like crystal aggregate is a chain of many platy crystals, the microscopic observation confirmed that a branch cut by the observational cross section corresponds to a platy crystal. Therefore the branch number can approximate the number of crystals. Comparing Fig. 6(a) with 6(b), we found that the number density of crystals in tree-like crystal aggregates is less by 3 to 4 orders of magnitude than that in periodic pattern.

4. Discussion

One major difference between periodic structure and tree-like crystal aggregates is the number density of crystals. Periodic structures have a number density of 10^3 times higher than tree-like crystal aggregates. Another essential difference between periodic structure and tree-like crystal aggregates is surface nucleation. In-site observation under optical microscopy shows that surface nucleation occurs in tree-like crystal aggregate formation but not in periodic precipitation. These two differences in number density and surface nucleation are thought to give rise to the morphological transition. In this section, we discuss how these differences are related to nucleation and growth kinetics and not to diffusion coefficient through the effect of agar concentration.

As well as acting as a diffusion medium inhibiting hydrodynamic disturbance, agar also supplies nucleation sites on the internal surface of the gel structure or under effect of impurities. The impurities effectively reduce the interfacial tension for nucleation. Indeed, as mentioned above, we observed a decrease in critical supersaturation for nucleation with an increase in agar concentration (Fig. 4). This means that at the same supersaturation, the nucleation rate or the consequent number density of particles increases with agar concentration. This dependence of number density on agar concentration was also observed experimentally in a different system (PROVOST and ROBERT, 1992).

The above hypothesis for the effect of agar concentration on nucleation allows us to qualitatively interpret our results as follows. At a higher nucleation rate in higher agar concentration experiments, crystals nucleate with a sufficiently high number density. Consequently, the growth of an individual crystal is relatively suppressed. As a result the ordinary Liesegang Ring consisting of a high number density of tiny crystals is developed. On the other hand, in experiments with lower agar concentration, nucleation is suppressed resulting in a lower number density allowing each nucleated crystal to effectively grow by monomer diffusion to a large plate-like crystal. Such a large crystal can accommodate the surface nucleation to form a tree-like crystal aggregate. Growth of tree-like aggregates reduces the supersaturation at a rate high enough to suppress further homogenous nucleation.

In order to understand the spatial transition from periodic structure to tree-like crystal aggregates in P + T regime at the intermediate agar concentration, we need another factor influencing the number density. The possible factor is the rate of supersaturation, which varies with distance from the contact interface. Near the contact the rate of supersatration is higher than that far from the contact because the increasing rate of iodide anion decreases with distance from the contact due to the diffusion effect. The number density of crystals nucleated increases with the rate of supersaturation (TORAMARU, 1991). Therefore the number density of crystals can be expected to decrease with distance with contact. Indeed, in periodic structure regime, the number density decreases with distance (Fig. 6). We think that this effect of rate of supersaturation causes the spatial transition from periodic structure to tree-like structure.

As diffusivity is also a function of agar concentration, we also have to evaluate the influence of diffusivity on the above hypothesis. It has been reported that the number density of nucleated crystals decreases with the diffusivity proportional to $D^{-3/2}$ for a similar system (TORAMARU, 1991). Based on this, the measured difference ($D_{0.5} \approx 2D_{3.0}$) in anion diffusivity cannot explain the number density difference of 10^3 times between the periodic structure and tree-like crystal aggregates. Thus, we conclude that the complicated coupling among nucleation, growth, and the surface nucleation as functions of agar concentration, can be controlling factors for transition in precipitation patterns under a macroscopic concentration gradient. The detailed mechanism of pattern transition, however, remains to be examined.

In relation to nucleation and growth kinetics, the morphological properties of tree-like crystal aggregates should be noted. The fractal dimension value of 1.6 to 1.5 is close to but slightly smaller than the value of diffusion-limited aggregation (1.7). A numerical study (CHOPARD *et al.*, 1991) showed that a tree-like aggregate made by the diffusion-reaction process may change the fractal dimension depending on the reaction kinetics and concentrations of reacting components. The fractal dimension value of 1.6 to 1.5 implies that the reaction kinetics in our experiment is somewhat different from and more complicated than in simple DLA (this will be discussed later). As well as determining the exact mechanism of formation of these tree-like aggregates through the fractal dimension, it must also be clarified by future work whether this aggregate is exactly fractal or not.

The structure of tree-like aggregates is different from that of DLA. DLA is an aggregate composed of diffusing particles. On the other hand the tree-like aggregates in our experiments are composed of a number of small single crystals (approximately 0.1 mm

size) that cannot diffuse. In addition, in our case, iodide anion, lead ion and PbI_2 monomer diffuse, and the precipitation occurs at the precipitation front which propagates with the iodide anion diffusion. This difference between DLA and our tree-like crystal aggregate implies that the nucleation and growth process in our experiments are far more complex. In our experiments surface nucleation also plays an important role in generating tree-like morphology. Unless surface nucleation is effective, few large single crystals with polyhedral or plate-like shapes will develop. Thus we propose that the coupling of nucleation and growth process sensitive to agar concentration variation, results in the discontinuous change in number density of crystals between the periodic precipitation and the tree-like crystal aggregates.

Finally, we would like to note that examples of pattern transitions observed in various geologic systems such as amethyst, agate with quartz crystals, cress cumulate crystal aggregate in igneous rocks (MCBIRNEY and NOYES, 1979), orbicular structures (MOORE and LOCKWOOD, 1973), and black smoker chimney in Deep Ocean (TIVEY *et al.*, 1995). In these systems, crystal aggregates grow terminating the band structures found near the outer boundary. From the results obtained in the present study, we hope that some key understanding in pattern formation and transition through a common basis of nucleation and growth kinetics under the Laplacian field has been achieved.

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