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ORIGINAL CONTRIBUTION

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Sedimentation and drying dissipative structures of colloidal silica (1.2 μm in diameter) suspensions in a glass dish and a polystyrene dish

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Abstract Sedimentation and drying dissipative structural patterns formed in the course of drying colloidal silica spheres (1.2 μm in diameter) in aqueous suspension have been studied in a glass dish and a polystyrene dish. The broad ring patterns are formed within a short time in suspension state by the convection flow of water and colloidal spheres. The broad ring patterns are not formed when a dish is covered with a cap, which demonstrates the important role of the convectional flow of silica spheres and water accompanied with the evaporation of water on the air-suspension interface. The sedimentary spheres always move by the convectional flow of water, and the broad ring patterns became sharp with time. Broad ring and microscopic fine structures are formed in the solidification processes on the bases of the convectional and sedimentation patterns. Drying patterns of the colloidal suspensions containing sodium chloride are star-like ones, which strongly supports the synchronous cooperative interactions between the salt and colloidal spheres.

Keywords Sedimentation dissipative structure · Drying dissipative structure · Pattern formation · Colloidal silica spheres · Broad ring pattern · Star-like pattern

Introduction

As is well known, many kinds of patterns are formed spontaneously by self-organization mechanism, and they are grouped into dissipative structures and the conservative ones. It is quite difficult to find the energy conservative structures in nature. Most patterns in nature are formed in nonequilibrium state. Honeycomb structure of honeybee is one of the typical examples of the dissipative structures in nature. However, patterns themselves in nature are complex to study. Thus, several studies on the pattern formation in the course of drying of the monodispersed colloidal suspensions have been reported hitherto [1–17]. Electrostatic interparticle interactions have been pointed out as one of the important factors for the dissipative pattern formation. Hydrophobic and hydrophilic interactions are also demonstrated to be important for the drying processes [14–16].

Recently, the dissipative structures on a cover glass have been studied in our laboratory in the course of dryness of suspensions and solutions, i.e., colloidal suspensions including colloidal crystals [18–22], solutions of ionic and nonionic surfactants [23–25], polyelectrolyte solutions [26] and solutions of water-soluble neutral polymer [27]. From our studies on the drying dissipative structures, macroscopic broad ring patterns for various suspensions and solutions were surprisingly similar to each other. It is interesting to note that most of the microscopic patterns such as branch-like, string-like, arc-like, and small block-like ones were reflected from the shape, size, and flexibility of the solute molecules. Furthermore, it was clarified that the vague and primitive microscopic patterns are formed already in the liquid phases before dryness. The important role of the microscopic cell convection in the liquid phase was supported for the pattern formation of suspensions and solutions.

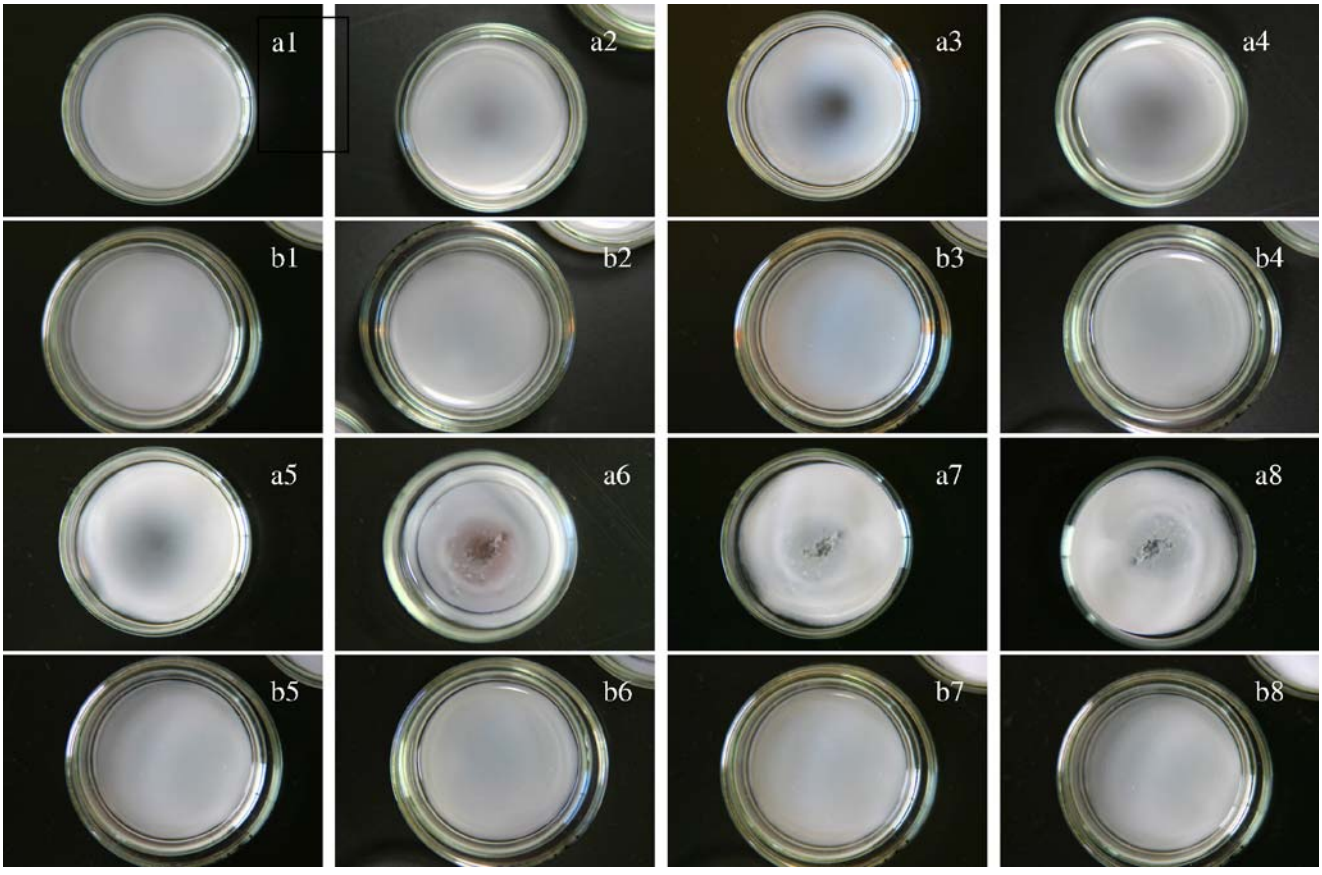

Fig. 1 Sedimentation and drying patterns of CS1000A suspensions with and without cap shield at 24 °C. ϕ=0.00129, **a** without cap shield, **b** with, (*1*) after 2.75 h, (*2*) 7 h, (*3*) 1 day, (*4*) 4 days, (*5*) 4.5 days, (*6*) 5 days, (*7*) 6 days, and (*8*) 14 days

In this paper, we observe the convectional and sedimentation dissipative structures, which must play an important role for the macroscopic and microscopic drying patterns, for aqueous suspensions of colloidal silica spheres (1.2 μm in diameter) in a glass dish and a polystyrene dish. Frankly speaking, the author became aware of the importance of the convectional flow for the broad ring formation of Ocha (plate-like and colloidal size of Japanese green tea particles, ca. 20 μm in their size) accumulating on the slope of the inner surface of an Ochawan (tea bowl) (Okubo T., publication in preparation). The broad rings have been always observed when Ocha was prepared by swinging a tea bag in an Ochawan containing hot water.

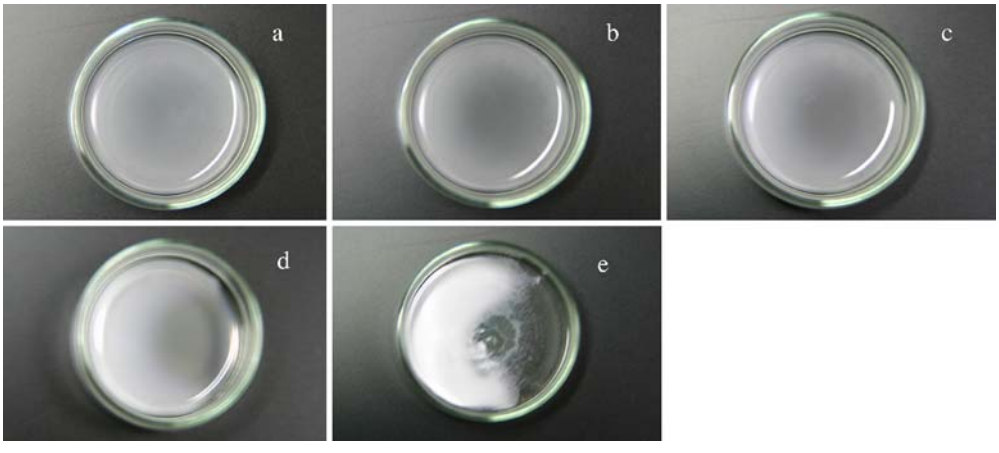

Fig. 2 Sedimentation patterns of CS1000A silica spheres (1.2 μm in diameter) in a glass dish at 24 °C. ϕ=0.00129, code 084, **a** after 6 h, **b** 14 h, **c** 22 h, **d** 134 h, and **e** dry (382 h)

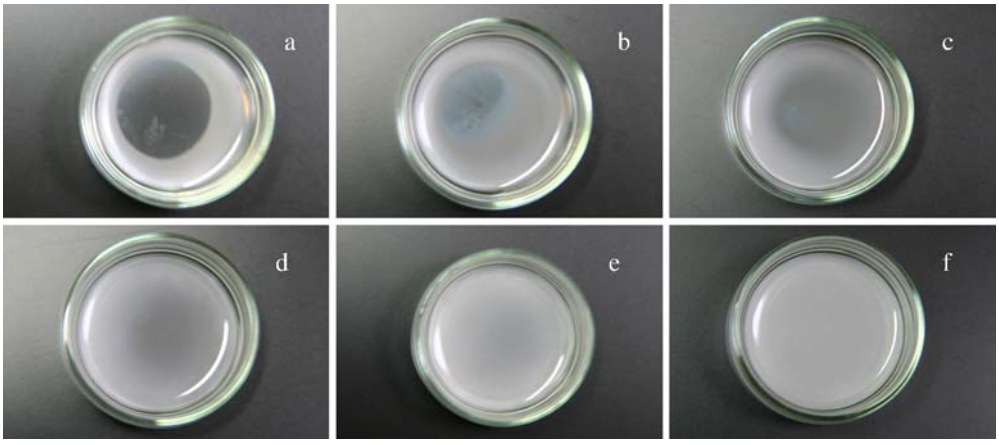

Fig. 3 Sedimentation patterns of CS1000A silica spheres (1.2 μm in diameter) in a glass dish at 24 °C. After 22 h, **a** ϕ=0.000216, **b** 0.000431, **c** 0.00086, **d** 0.00129, **e** 0.00216, and **f** 0.00431

Experimental

Materials

CS1000A silica spheres were kindly donated from Catalysts & Chemicals Ind. (Tokyo). The diameter, the standard deviation from the mean diameter, and the polydispersity index of the spheres were 1.205 μm, 14 nm, and 0.012, respectively. These size parameters were determined from an electron microscope. The spheres were carefully purified by repeated decantation for more than 30 times. Then, the sample was treated on a mixed bed of cation- and anion-exchange resins [Bio-Rad, AG501-X8 (D), 20–50 mesh] for 6 years before use because newly produced silica spheres always released a considerable amount of alkali ions from the porous sphere surfaces for a long time. Water used for the sample preparation was purified by a Milli-Q reagent grade system (Milli-RO5 plus and Milli-Q plus, Millipore, Bedford, MA, USA).

Observation of the dissipative structures

Ten milliliter of the aqueous suspension of CS1000A sample was put carefully and gently into a glass dish (42 mm in inner diameter and 15 mm in height, code 305-02, TOP, Tokyo, Japan) and a polystyrene dish (Petri dish, 52 mm in inner diameter and 10 mm in height, As One, Tokyo, Japan). Observation of the sedimentation and drying patterns was made for the suspension set on a desk until dried up completely in a room air-conditioned at 24 °C and 64% in humidity of the air. Concentrations of CS1000A and NaCl ranged from 0.0002 to 0.004 in volume fraction and from 0.0003 to 0.01 M, respectively.

Macroscopic dissipative structures were observed on a Canon EOS 10D digital camera (Canon, Tokyo, Japan) with a lens (EF 28–200 mm, f=3.5–5.6 USM, Canon). Microscopic structures were observed with a metallurgical microscope (PME-3, Olympus, Tokyo, Japan).

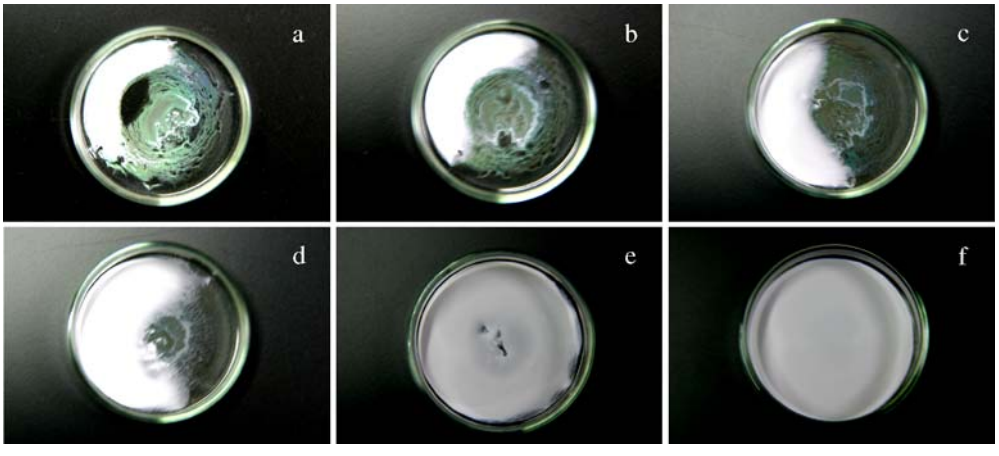

Fig. 4 Drying patterns of CS1000A silica spheres (1.2 μm in diameter) in a glass dish at 24 °C. After 382 h, **a** ϕ=0.000216, **b** 0.000431, **c** 0.00086, **d** 0.00129, **e** 0.00216, and **f** 0.00431

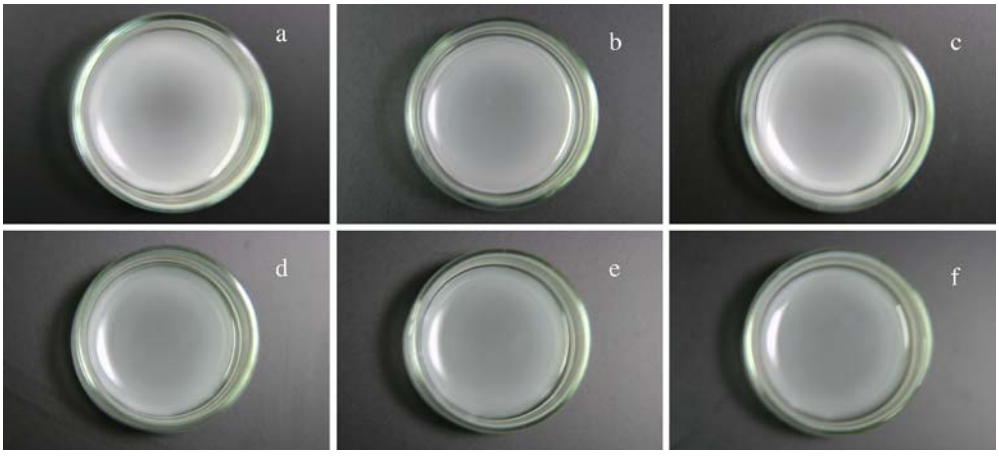

Fig. 5 Sedimentation patterns of CS1000A silica spheres (1.2 μm in diameter) in a glass dish at 24 °C. ϕ=0.00129, after 22 h, **a** [NaCl]=0 M, **b** 0.0003 M, **c** 0.001 M, **d** 0.003 M, **e** 0.006 M, and **f** 0.01 M

Results and discussion

Importance of the convectional flow of suspension accompanied with the evaporation for the sedimentation pattern formation

Figure 1 shows comparison of the evaporation and drying processes for CS1000A suspensions in a glass dish without cap (from a1 to a8) and with cap shield (from b1 to b8). Clearly, broad ring patterns were observed for the suspensions without cap in the suspension phase, and the suspensions dried up after 14 days, whereas the broad ring patterns did not appear at all in a dish with cap for 2 weeks. A main cause for the broad ring formation is due to the convection flow of water and CS1000A spheres in the different rates, where the rate of the latter will be slower than that of the former under gravity. Especially, the flow of the spheres from the center area toward the outside edges in the lower layer of the liquid, which was observed on a digital HD microscope directly from the movement of the very rarely occurring aggregates of the colloidal particles of Chinese black ink (not CS1000A spheres in this work), is important [20]. Clearly, the convectional flow is enhanced by the evaporation of water at the liquid surface, resulting to the lowering of the suspension temperature in the upper region of the suspension. When the colloidal spheres reach the edge wall of the dish at the outside region of the liquid, a part of the spheres will turn upward and go back to the center region. However, many large and heavy spheres may drop downward on the cell bottom, close to the outside cell wall, where the effective horizontal flow of the spheres may stop temporarily. This process must be followed by the broad ring accumulation of the spheres near the round outside edges.

It should be noted that the broad ring patterns in the liquid phase reported in this study were observed first in this paper as the author knows. However, the broad ring formation in the dried film has been observed so often for most of the solutions and suspensions examined by our group [18–27] (Okubo T., publication in preparation) and further by other researchers [4, 5, 7]. Recently, microgravity experiments were made for the observation of the drying dissipative patterns of deionized suspension of colloidal silica spheres (Tsuchida et al., publication in preparation). Surprisingly, the broad ring patterns did not disappear even in microgravity. This supports strongly that both the gravitational and the Marangonil convections

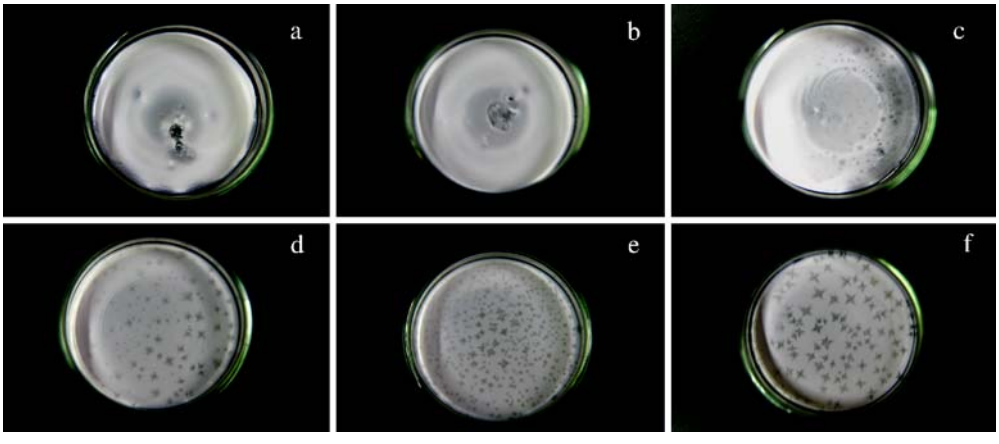

Fig. 6 Drying patterns of CS1000A silica spheres (1.2 μm in diameter) in a glass dish at 24 °C. ϕ=0.00129, after 382 h, **a** [NaCl]=0 M, **b** 0.0003 M, **c** 0.001 M, **d** 0.003 M, **e** 0.006 M, and **f** 0.01 M

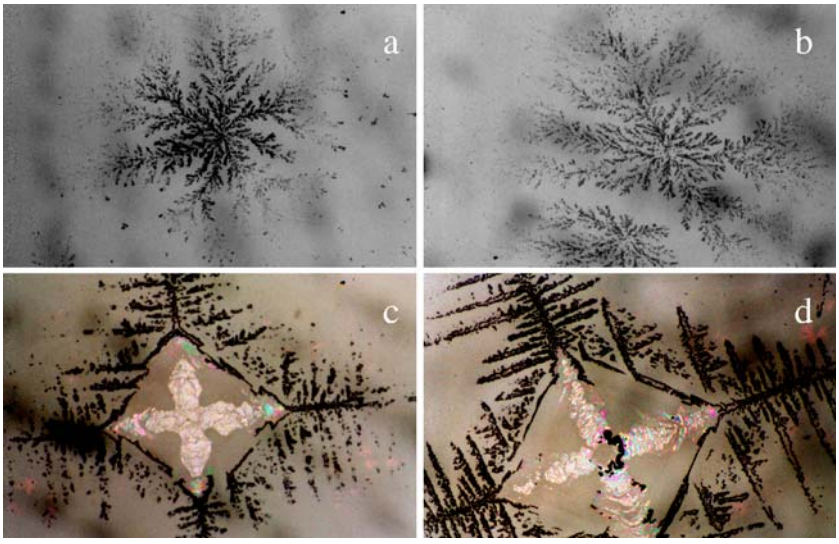

Fig. 7 Microscopic drying patterns of CS1000A silica spheres in a glass dish at 24 °C. ϕ=0.00129, 10 ml, **a** [NaCl]= 0.0003 M, **b** 0.0006 M, **c** 0.001 M, **d** 0.003 M, codes 93–96, length of the scale bar is 0.2 mm

contribute to the broad ring formation on earth, and the latter is still important in microgravity.

We should note in this study that the broad ring patterns, which are generally observed for all drying patterns of suspensions and solutions on a cover glass, are formed already in the process of convectional flow of water and solutes in suspension state in a glass dish. As reported below, in this paper, the broad ring sedimentation patterns were formed also in a polystyrene dish. The broad ring structures have been observed also in a watch glass and even in a deep bowl (Okubo T., publication in preparation).

It should be mentioned further in this study that 10 ml of the aqueous suspensions of silica spheres, 352 nm in diameter and 0.00228 in volume fraction, in a glass dish with cap were dried up after 110 days at room temperature (Okubo T., unpublished results). In comparison, the same suspension was dried up after 8.4 days without cap. In suspension state with cap they also exhibited the broad ring patterns, and dried film showed very strong iridescent colors. Very fine and beautiful fractal structures were observed for the dried film on a microscope. It is clear that shielding of a glass dish with a cap is not so complete for preventing evaporation. However, evaporation and the resulted convectional flow are, of course, retarded efficiently.

Influence of sphere concentration on the sedimentation and drying dissipative patterns

Figure 2 shows the macroscopic sedimentation and drying patterns of CS1000A spheres at 0.00129 in volume fraction from 6 to 382 h (dried) after suspension was set. Broad ring formed rather quickly several tenth minutes after suspension was set and in the stage of incomplete sedimentation of spheres, which shows that the convectional flow of

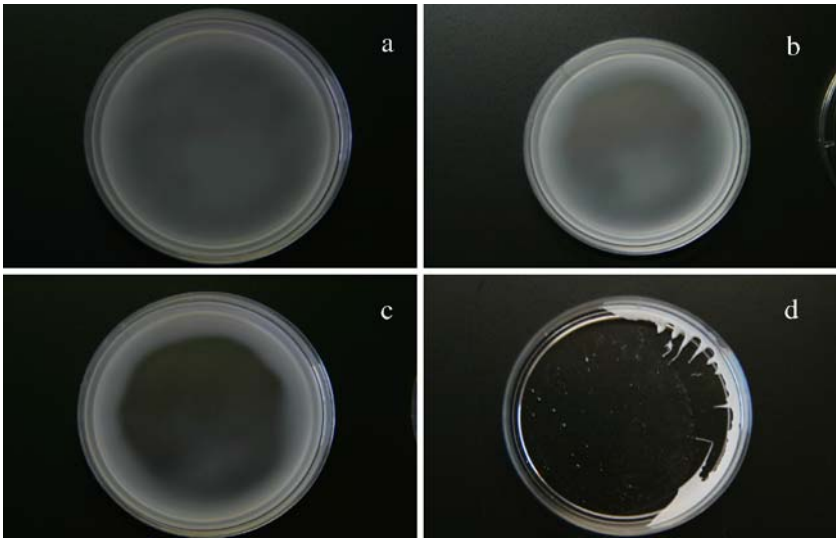

Fig. 8 Sedimentation and drying patterns of CSPA1000 silica spheres (1.2 μm in diameter) in a polystyrene dish at 24 °C. ϕ=0.00129, code 040. **a** After 5 h, **b** 9.25 h, **c** 21.5 h, and **d** dry

water and spheres are vigorous even at room temperature. It should be mentioned in this study that the sedimentary spheres do not contact to each other because the electrical double layers being formed around each spheres are extended especially in the deionized suspension. Thus, the sedimentary spheres always move by the convectional flow of water and became sharp with time. The sedimentary spheres also flow downward easily when the bottom plane of the dish is inclined even slightly. It should be mentioned further that the electrostatic repulsive interaction, which intermediated with the double layers, plays an important role for the stability of the suspensions in the course of drying processes.

Measurements of the width and the thickness of the broad ring in the sedimentation patterns were extremely difficult. Very rough values of the ratio of the width to the inner cell radius were, however, evaluated with the naked eyes. The values were 0.75, 0.70, 0.42, and 0.25 at 355, 845, 1,330 min, and 133.5 h, respectively, for the suspensions at ϕ=0.000216. The width of the broad ring decreased with time. This observation also supports that the sedimentary particles move even after sedimentation is completed and becomes sharp by the convectional flow of water molecules and then colloidal spheres.

Figure 3 shows the sedimentation patterns 22 h after setting, where the sphere concentrations range from 0.000216 to 0.00431. Broad rings were clearly observed with the naked eyes irrespective of the sphere concentration, though the broad rings became vague when the sphere concentration was high. This is due to the strong multiple scattering of light by the colloidal spheres even in the central area, where the sphere concentration is still high.

Figure 4 shows the drying patterns for the suspensions at sphere concentrations from 0.000216 to 0.00431 in volume fraction. The macroscopic drying patterns were broad ring irrespective of sphere concentration. Multiple-ring structures, which emitted the weak Bragg diffraction colors, were observed for the films of sphere concentrations lower than 0.00129 in volume fraction.

Influence of salt concentration on the sedimentation and drying dissipative patterns

Figure 5 shows the macroscopic convection and sedimentation patterns of CS1000A suspensions in the presence of salt and in their absence 22 h after suspensions were set. For a first glance, distinct difference was not observed among the broad ring patterns of the suspensions containing different amounts of sodium chloride. However, it looks with the naked eyes that the broad ring is sharp for the salt-containing suspension. The electrical double layers around the spheres are thin when the ionic concentration is high. Thus, the translational diffusion of the spheres will be much vigorous because the effective size of spheres including the double layers decreases.

Figure 6 shows the drying patterns of CS1000A suspensions containing different amounts of sodium chloride ranging from 0 to 0.01 M. Macroscopic broad-ring patterns were observed clearly for all the samples. Surprisingly, star-like microscopic patterns appeared for the suspensions containing sodium chloride higher than 0.001 M. The extended pictures of the star-like patterns observed on a microscope are shown in Fig. 7. Concentrations of sodium chloride in Fig. 7a–d are 0.0003, 0.0006, 0.001, and 0.003 M, respectively. Black patterns in the pictures are composed of the silica spheres and never observed for the deionized suspension. The colorful cross-like patterns, which are surrounded with the patterns of silica spheres, in Fig. 7c,d are composed of sodium chloride. These beautiful characteristic patterns of the colloidal spheres and sodium chloride demonstrates clearly that the synchronous (cooperative) interactions between sodium chloride and silica spheres play an important role for the pattern formation in the processes of solidification of colloidal spheres and sodium chloride.

Sedimentation and drying dissipative patterns of CS1000A in a polystyrene dish

Typical examples of the patterns formed in the course of dryness of CS1000A suspension in a polystyrene dish are shown in Fig. 8. The broad rings were formed clearly within 5 h as is clear in the figure. It should be mentioned in this study that the suspensions moved quickly and gathered at the certain outer edge before dryness is completed. This is mainly due to the polystyrene dish being highly hydrophobic in its surface. In conclusion, the convectional sedimentation patterns in a polystyrene dish were similar to those in a glass dish. However, the drying dissipative patterns were different between glass and polystyrene dishes.

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