Colloid Polym Sci (2006) 284: 1191–1196
DOI 10.1007/s00396-006-1511-x

SHORT COMMUNICATION

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

Received: 1 February 2006
Accepted: 2 April 2006
Published online: 24 May 2006

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Abstract Sedimentation and drying dissipative structural patterns formed in the course of drying aqueous suspensions of colloidal silica spheres (1.2 μm in diameter) were observed in the various sizes of watch glasses. The macroscopic broad ring patterns were formed on the inner inclined watch glass in suspension state within a short time after suspension was set. The important role of the convectional flow of water and colloidal spheres for the pattern formation is supported. The influence of sodium chloride was also studied. It was clarified that the sedimentary spheres move toward upper and outer edges along the inclined cell wall by the cell convection and hence the patterns are formed by the balancing between the outside movement and the downward sedimentation of the spheres. Beautiful microscopic drying patterns were also observed from the optical microscopy.

Keywords Sedimentation pattern · Drying pattern · Broad ring · Microscopic structure · Colloidal silica sphere

Introduction

Many kinds of patterns are formed spontaneously by self-organization mechanism, and they are grouped into the dissipative structures in the open systems and the conservative ones in the closed systems. 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 in nature are complex and are therefore hard to study. Thus, several studies on the pattern formation in the course of drying the monodisperse colloidal suspensions were reported hitherto [1–17]. Electrostatic interparticle interactions were pointed out as one of the important factors for the dissipative pattern formation. Hydrophobic and hydrophilic interactions are also important for the drying processes [14–16].

Recently, the dissipative structures of colloidal silica spheres on a cover glass were 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, similar macroscopic broad ring patterns were observed irrespective of the kind of the suspensions and solutions. On the other hand, 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 substances. Furthermore, it was clarified that the vague and primitive microscopic patterns are already formed in the liquid phases before the dry phase. The important role of the microscopic cell convection in the liquid phase was strongly supported for the pattern formation of suspensions and solutions.

Quite recently, the author observed a series of convectional, sedimentation, and drying dissipative patterns for aqueous suspensions of colloidal silica spheres (1.2 μm in diameter) in a glass dish and polystyrene dish [28]. In this paper, we further observe the patterns for aqueous suspensions of the same silica spheres (1.2 μm in diameter) in a watch glass. The watch glass has the inclined bottom surface having the deepest central point and is very convenient for studying the influence of the kinds of

containers upon the convectional flow of water and colloidal spheres.

Experimental

Materials

CS1000A silica spheres were donated by Catalysts & Chemicals Industry (Tokyo). Diameter, standard deviation from the mean diameter, and polydispersity index of the spheres were 1.205 μm, 14 nm, and 0.012, respectively. These size parameters were determined on a transmission electron microscope (Hitachi, H8100) in our laboratory. The spheres were carefully purified by repeated decantation more than 30 times. Then the sample was treated on a mixed bed of cation- and anion-exchange resins [BioRad, AG501-X8(D), 20–50 mesh] for 6 years before use because newly prepared 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

In most cases, 4 ml of the aqueous suspension of CS1000A sample was put carefully and gently into a medium-sized watch glass (70 mm in diameter, TOP, Tokyo). The very small (30 mm in diameter, TOP), small (50 mm, TOP), and large watch glass cells (100 mm, TOP) were also used and 0.4, 1.5, and 15 ml of the sample suspensions were put into these cells, respectively. Observation of the sedimentation and drying patterns was made for the suspensions in a watch glass until the suspensions were 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 0.00129 to 0.0129 in volume fraction (φ) and from 0.0001 to 0.01 M, respectively.

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

Results and discussion

Influence of watch glass size on the sedimentation and drying dissipative patterns

Figure 1 shows the change in the sedimentation patterns with time when the very small watch glass cell is used. Clearly, within 2 h, sedimentation of the colloidal spheres, especially at the upper layers of suspension, took place and a broad ring pattern was observed clearly with the naked eyes at the central area of the watch glass. The suspensions dried up after 13 h (see Fig. 1f). A main cause for the broad ring formation is the convectional flow of water and CS1000A spheres in the different rates and due to the evaporation of water from the outer edges. The diffusion rate of spheres will be slower than that of water. 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 high-definition microscope directly from the movement of the very rarely occurred aggregates of the colloidal particles of Chinese black ink (not CS1000A spheres), is especially important [20]. Clearly, the convectional flow is enhanced by the evaporation of water at the air–liquid interface, resulting in the lowering of the suspension temperature in the upper region of the suspension. When the colloidal spheres reach the edge of the wall of the dish at the outside region of the liquid, a part of the spheres will remain at the drying frontier by the evaporation of water. This process must be followed by the broad ring accumulation of the spheres near the round outside

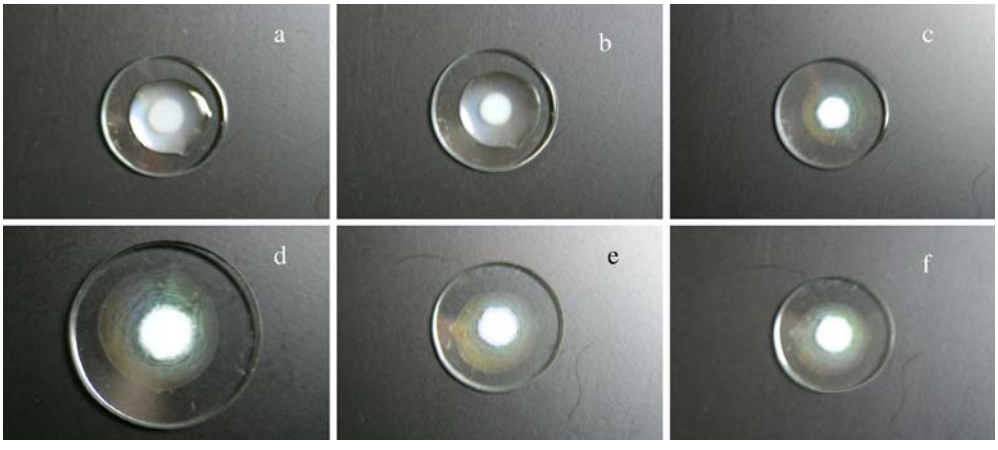

Fig. 1 Sedimentation patterns of CS1000A suspension in a very small watch glass at 24 °C. φ=0.00129, code 132, 0.4 ml; after **a** 1.7, **b** 3.8, **c** 13.1, **d** 29.8, **e** 47.3 h, and **f** dry (60.5 h)

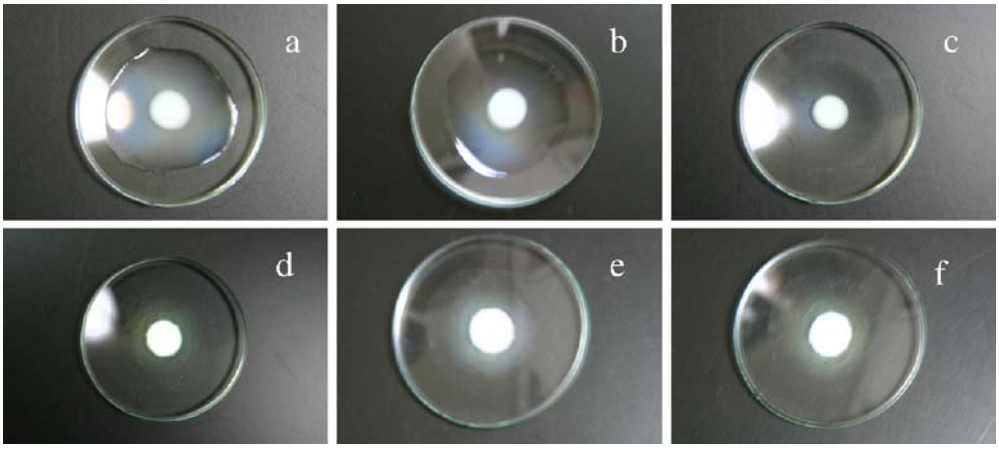

Fig. 2 Sedimentation and drying patterns of CS1000A suspension in a small watch glass at 24 °C. φ=0.00129, code 134, 1.5 ml; after **a** 1.7, **b** 3.8, **c** 13.1, **d** 29.8, **e** 47.3 h, and **f** dry (60.5 h)

edges. It should be noted that the sphere accumulation at the deepest central point did not take place so much compared with the upper broad ring area. It should be mentioned further here that many fine multiple-ring patterns were formed in the outer region of the broad ring. Fine ring patterns will be due to the heterogeneous evaporation rates mainly due to the disturbance of air near the liquid surface.

It is quite interesting to note that the broad sedimentation rings in the liquid phase reported here were also observed in a glass dish and a polystyrene dish [28], irrespective of the shape of vessel cell. The drying patterns shown in Fig. 1d–f shows a clearer broad ring in the dried film than that in the liquid phase. The broad ring formation was observed so often in the dried film patterns for most of the solutions and suspensions examined by our group [18–27] 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 (A. Tsuchida et al., in preparation). It is surprising to note that the broad ring patterns did not disappear even in microgravity. This strongly supports that both the gravitational and the Marangoni convections contribute to the broad ring formation on earth, and the latter is still important in microgravity.

We should note here that the broad ring patterns in a watch glass, which are generally observed for all drying patterns of suspensions and solutions on a cover glass, are already formed in the process of convectional flow of water and solutes in suspension state. As previously reported, the broad ring sedimentation patterns were also formed in a glass dish and a polystyrene dish [28]. It is interesting to note that the broad ring structures were observed even in a deep bowl (Ochawan) for green tea (T. Okubo, in preparation).

Figures 2, 3, and 4 show the sedimentation and drying patterns in the course of dryness of CS1000A spheres in the small, medium, and large watch glasses, respectively. Amounts of the suspension were 1.5, 4, and 15 ml, respectively. The initial sphere concentration was 0.00129 in volume fraction irrespective of the size of the watch glass used. Clearly, quite similar patterns were observed irrespective of size of the watch glass and also of the amount of the suspension when the sphere concentrations were the same with each other. It should be noted here that beautiful spoke-like patterns were already observed in the outer edges of the liquid phase as is shown in Fig. 4d, though the picture is not taken so clearly. This will be due to the sliding of the spheres along the inclined plane of a large watch glass, induced by the extremely slight vibration

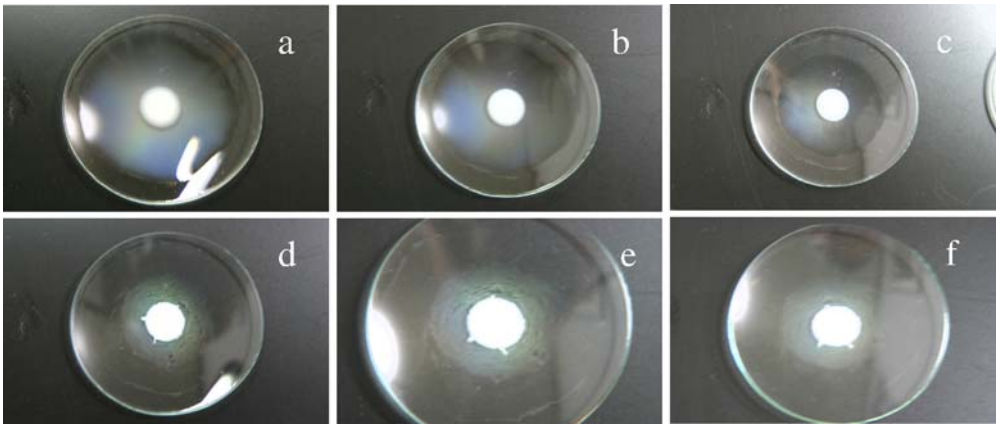

Fig. 3 Sedimentation and drying patterns of CS1000A suspension in a medium watch glass at 24 °C. φ=0.00129, code 121, 4 ml; after **a** 1.7, **b** 3.8, **c** 13.1, **d** 29.8, **e** 47.3 h, and **f** dry (60.5 h)

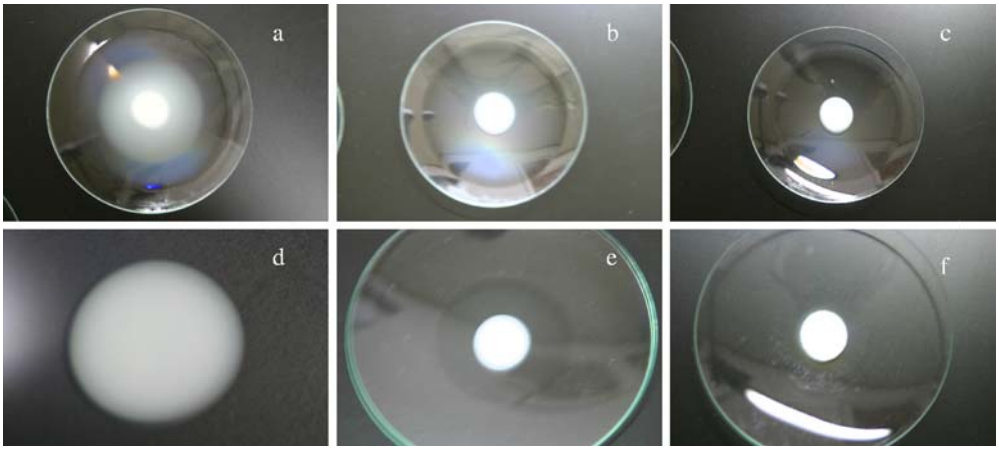

Fig. 4 Sedimentation patterns of CS1000A suspension in a large watch glass at 24 °C. φ=0.00129, code 138, 15.0 ml; after **a** 1.7, **b** 3.8, **c** 13.1, **d** 29.8, **e** 47.3 h, and **f** dry (60.5 h)

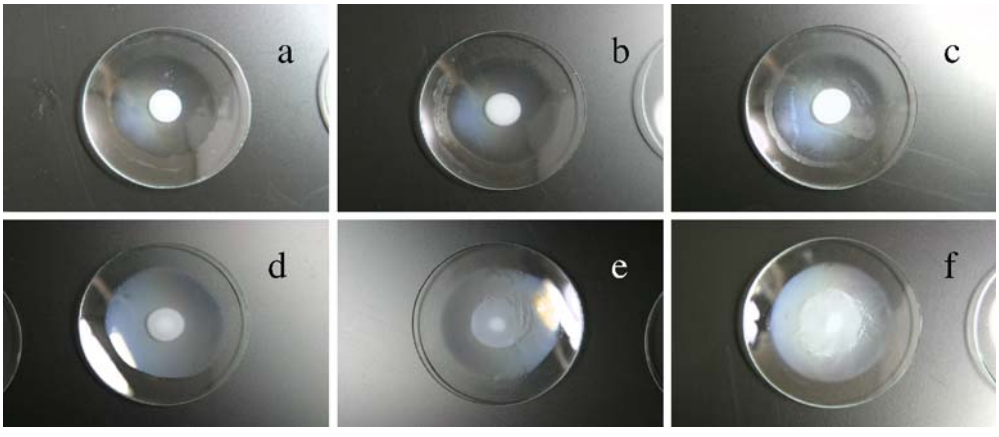

Fig. 5 Sedimentation and drying patterns of CS1000A suspension in a medium-sized watch glass at 24 °C. φ=0.0129, 4 ml, 13.1 h; [NaCl] is equal to **a** 0, **b** 0.0001, **c** 0.001, **d** 0.003, **e** 0.006, and **f** 0.03 M

of the experimental desk in the course of sedimentation equilibrium.

Influence of salt on the sedimentation and drying dissipative patterns

Figure 5 shows the macroscopic sedimentation and drying patterns of CS1000A spheres at 0.00129 in volume fraction in the presence of sodium chloride at the concentrations from 0 to 0.03 M and 13.1 h after suspension was set. Broad rings were formed irrespective of the salt concentrations, but suspensions containing rather large amount of the salt became turbid. Thinning of the electrical double layers around the colloidal spheres will be one of the main reasons for this salt effect. Colloidal spheres surrounded with the thin layers will fluctuate much strikingly with the translational and rotational modes and will still be in the stage of

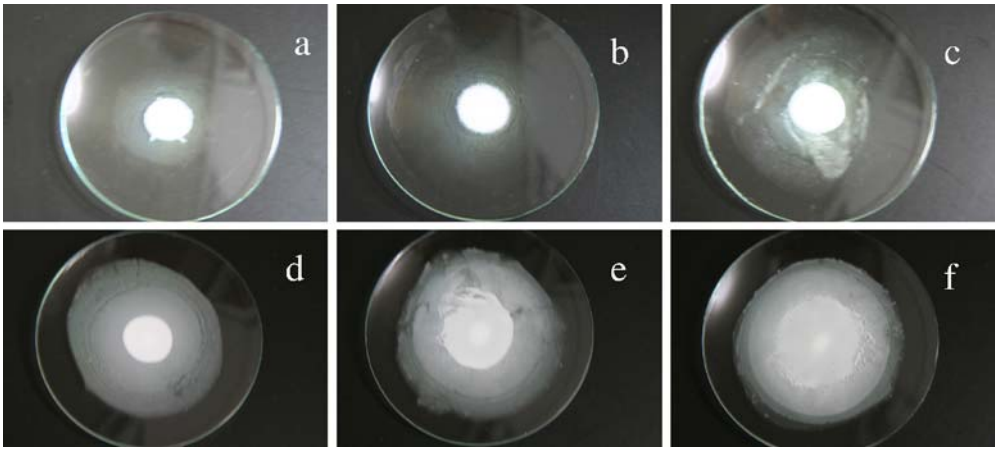

Fig. 6 Drying patterns of CS1000A suspension in a medium-sized watch glass at 24 °C. φ=0.0129, 4 ml, dry (60.5 h); [NaCl] is equal to **a** 0, **b** 0.0001, **c** 0.001, **d** 0.003, **e** 0.006, and **f** 0.03 M

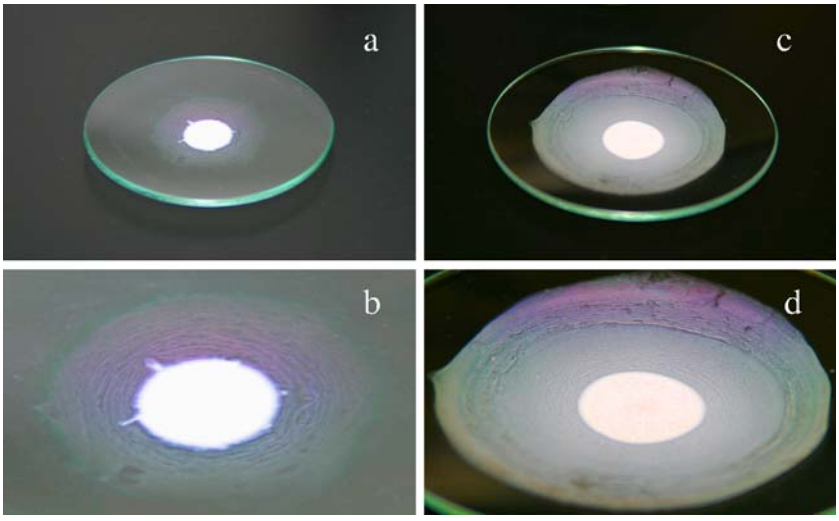

Fig. 7 Drying patterns of CS1000A suspension in a medium-sized watch glass at 24 °C. φ=0.0129, 4.0 ml; **a** code 121, [NaCl]=0 M, dry (after 60.5 h); **b** code 121, extended; **c** code 126, [NaCl]=0.003 M; and **d** code 126, extended

incomplete sedimentation of spheres, which means the convectional flow of the thinning spheres will be more vigorous than the thickened spheres with the electrical double layers in the deionized suspension. The other reason will be the aggregation of the colloidal spheres in the presence of a large amount of the salt, i.e., salting out effect, especially in the final stage of the solidification.

It should be mentioned here that the sedimentary spheres do not make contact with each other because the electrical double layers formed around each spheres extend especially in the deionized suspension. Thus, the sedimentary spheres always move in the translational mode by the convectional flow and the broad ring patterns become sharp with time. The sedimentary spheres accumulate on the inclined plane of the watch glass, keeping the balance between upward convectional flow of the spheres and downward sedimentation of spheres by the gravitational forces. It should be mentioned further that the electrostatic repulsive interaction intermediated with the double layers plays an important role for the stability of the suspensions in the course of drying processes.

Figure 6 shows the drying patterns for the suspensions containing sodium chloride where the initial sphere concentration was 0.0129 in volume fraction and salt concentrations range from 0 to 0.03 M. Broad rings became vague by the addition of the salt. Furthermore, the most significant change of the drying patterns by the addition of salt was the formation of the triple or quadruple broad rings as is shown in the figure, and the accumulation of the spheres took place in the deepest central point. This will support the idea that the aggregation of spheres takes place by the addition of salt especially in the final solidification stage of dryness.

Figure 7 shows the usual and the close-up pictures of the drying patterns for the suspensions in the presence of sodium chloride at 0.003 M and in its absence, respectively. Patterns were composed of the multiple-ring structures in the upper area and the white broad ring in the central area. The former emitted the beautiful Bragg diffraction colors.

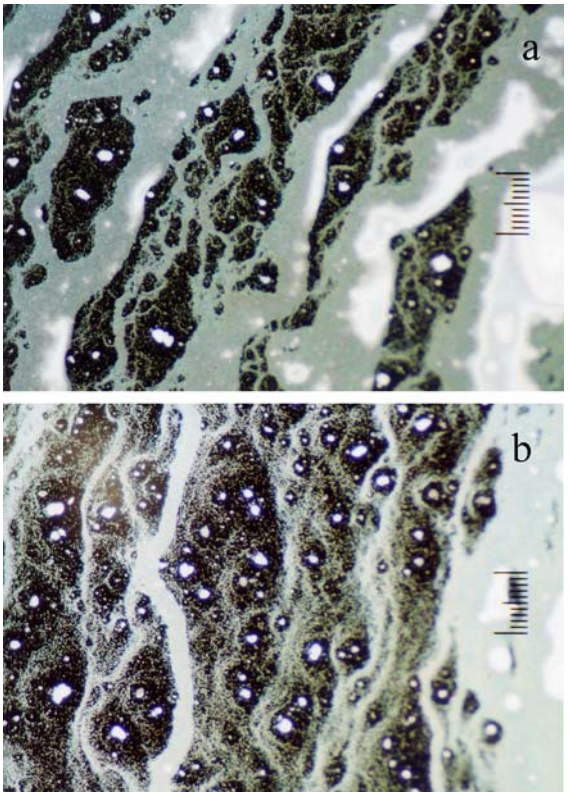

Fig. 8 Microscopic drying dissipative patterns of CS1000A suspension in a watch glass at 24 °C. φ=0.00129; **a** very small watch glass 0.4 ml and **b** small watch glass 1.5 ml; full scale=0.2 mm

Microscopic drying dissipative patterns

Figure 8 shows the microscopic pictures of the drying patterns in the upper area from the central area to the right edge for the deionized CS1000A suspensions in a very small glass (Fig. 8a) and a small watch glass (Fig. 8b), respectively. Similar fine and white string-like ring structures were observed irrespective of the cell size. These patterns clearly show the traces of the movement of the drying frontier zones toward the center. It should be noted here that the beautiful star-like complex patterns composed of colloidal spheres and sodium chloride were not observed, though these patterns were observed in a glass dish [28]. The reason for this difference is not so clear yet.

Acknowledgements Financial support from the Ministry of Education, Science, Sports, and Culture, Japan is gratefully acknowledged for Grants-in-Aid for Scientific Research on Germ Area (17655046), "Direct observation of sedimentation dissipative structure of polymer colloidal suspensions." The author appreciates the donation of the silica sphere sample, CS1000A, by Catalyst & Chemical Industry (Tokyo). Professor Akira Tsuchida of Gifu University is thanked for his support of the author's experiments. Dr. Mitsuhiro Suda of Kanazawa University is acknowledged for his electron microscopic measurements.

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