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ORIGINAL CONTRIBUTION

Convectional, sedimentation, and drying dissipative structures of ethanol suspension of colloidal silica (110 nm in diameter) spheres

Tsuneo Okubo

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Abstract Convectional, sedimentation, and drying dissipative structural patterns formed in the course of drying ethanol suspensions of colloidal silica spheres (110 nm in diameter) were studied in a glass dish and a watch glass. Vigorous cell convectional flow was observed with the naked eye, and the patterns changed dynamically with time. Broad-ring-like sedimentation patterns were observed in the suspension state just before the suspension was dried up, and the principal macroscopic patterns of the drying patterns were also broad-ring, though the colorful and fine microscopic structures were observed from optical microscopy.

Keywords Dissipative structure · Convectional pattern · Ethanol suspension · Drying pattern · 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 the nonequilibrium state. The honeycomb structure of the 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 dissipative pattern formation in the course of drying 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 important for the drying processes [14–16].

Recently, the dissipative structures of colloidal silica spheres on a cover glass have been studied in our laboratory in the course of drying 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 polymers [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 patterns, were reflected from the shape, size, and flexibility of the solute substances. 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 strongly supported for the pattern formation of suspensions and solutions. Studies on the drying patterns have supported strongly that the convectional flow of water and the colloidal particles are significant.

Thus, recently, the author observed a series of the sedimentation and drying dissipative patterns for aqueous suspensions of colloidal silica spheres (1.2 μm in diameter) in a glass dish and a polystyrene dish [28], and also in a watch glass [29]. These experiments clarified that the

T. Okubo (✉)
Institute for Colloidal Organization,
Hatoyama 3-1-112,
Uji, Kyoto 611-0012, Japan
e-mail: okubotsu@ybb.ne.jp

T. Okubo
Cooperative Research Center, Yamagata University,
Johnan 4-3-16,
Yonezawa 992-8510, Japan

macroscopic broad ring patterns are formed in the beginning stage in the drying processes both in a dish and a watch glass.

It should be noted here that the convectional and sedimentation structures are patterns formed in the suspension state, where most colloidal particles are suspended in the bulk and in the sedimentation state, respectively. The distinction between the two structures is not always very clear because the boundary region between them is rather wide. The dissipative structures are often observed for the colloidal suspensions, where most particles still remain in the bulk. In this case, it is hard to identify the structures as being convectional or sedimentation.

To study the convectional effect more in detail, the convectional, sedimentation, and drying dissipative structures are observed in ethanol suspensions of colloidal silica spheres in this work. It is well known that there are two kinds of convectional flow: gravitational and Malangonyl convections. The former will vanish in microgravity, though the latter still remains in microgravity. The author's group has conducted microgravity experiments for the drying dissipative patterns for very small liquid drops of the colloidal suspensions in ethanol [30]. Interestingly, quite similar patterns were observed between microgravity and gravity gravitational and Malangonyl, respectively, though the convectional flows are different.

Experimental

Materials

Ethanol suspensions of CS91 silica spheres were kindly donated by Catalyst & Chemicals (Tokyo, Japan). Diameter, polydispersity index (standard deviation divided by the mean diameter), and charge density of the spheres were 110 nm, 0.041, and 0.40 $\mu C/cm^2$, respectively. These parameters were determined on an electron microscope (TEM, Hitachi, Tokyo, Japan, H8100) and a Horiba model DS-14 conductivity meter (Kyoto, Japan) in our laboratory. The suspensions were treated on a mixed bed of cation- and anion-exchange resins [Bio-Rad, Hercules, CA, USA, AG501-X8(D), 20–50 mesh] and on molecular sieves [code 3A 1/8, Wako Chemicals (Osaka, Japan)] more than 7 years before use. It should be noted that newly prepared silica spheres always release a considerable amount of alkali ions and water molecules from the porous sphere surfaces for a long time. Ethanol was spectroscopic grade purchased from Wako Chemicals and treated with the mixtures of ion-exchange resins and the granules of molecular sieves more than 5 years before being used for the experiments to delete ionic impurities and water molecules from the sample suspensions as thoroughly as possible. 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 and 4 mL of the ethanol suspensions of CS91 spheres were placed 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 medium-sized watch glass (70 mm in diameter, TOP, Tokyo, Japan), respectively. Observation of the convectional, sedimentation, and drying patterns was made until the suspensions were dried up completely in a room air-conditioned at 24 °C with 64% humidity of the air.

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

Results and discussion

Macroscopic patterns in a glass dish

Figure 1 shows a series of convectional (Fig. 1a–d), sedimentation (Fig. 1c–e), and drying dissipative patterns (Fig. 1e,f) in 100% ethanol suspension of CS91 spheres at ϕ=0.00427 in a glass dish. The sphere concentrations ranged from 0.00085 to 0.0256. Assignment of Fig. 1a–f to the type of patterns was made roughly with naked eyes. Evaporation of ethanol from the air-suspension interface was substantial and the drying processes completed 10.8 h after suspension was set. The convectional flow of the whity and turbid suspension was not observed clearly with the naked eye, but the broad ring appeared soon after the suspension was set (see Fig. 1a, for example). Then, the suspension became bluish with time, accompanied with the enrichment of spheres in the broad ring region, as is shown in Fig. 1b–d. The bluish color originated from the Bragg diffraction of light by the colloidal crystal lattices. Furthermore, the suspension layer in the central area became thin, but significant convectional flow of the suspensions was observed in the central area. On the other hand, the thick ring remained in the region of the outside edge. Figure 1c,d shows the appearance of the "islands in sea"-like convectional and sedimentation patterns, though the patterns are not so clear when compared with the patterns shown in Fig. 2c,d. After 9.9 h, a whity dry area with fine and long, straight, fiber-like patterns appeared, as shown in Fig. 2e. After 10.8 h, the suspension dried up and many spoke-like fine cracks appeared. These patterns

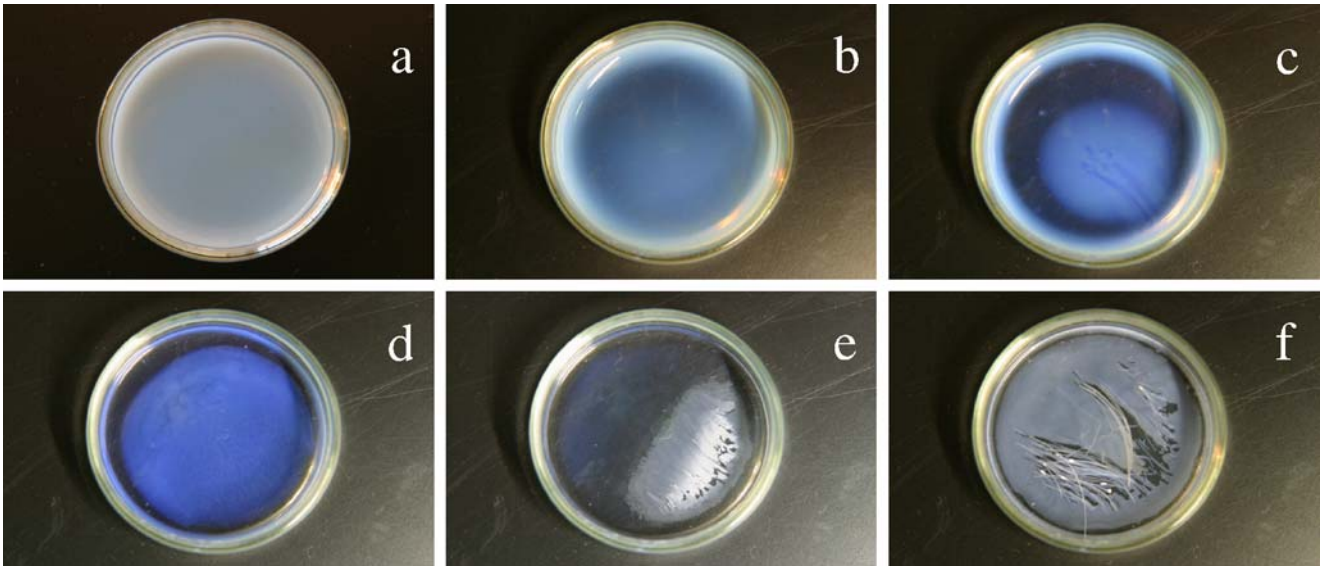

Fig. 1 Convectional, sedimentation, and drying patterns of 100% ethanol suspension of CS91 spheres in a glass dish at 25 °C. ϕ (volume fraction)=0.00427, 10 mL, code Y021, **a** after 7.5 h, **b** 9 h, **c** 9.17 h, **d** 9.4 h, **e** 9.9 h, and **f** 10.8 h, dry

support that (1) a large number of fine cell convections are formed before dryness by the strong convectional flow in ethanol suspensions [18, 21] and (2) the rigidity of the dried film is low because the number of colloidal spheres is low.

It should be noted that drying times, *T*, increased as the sphere concentration increased. The *T*-values were sensitive to the humidity surrounding the sample suspension.

Figure 2 shows the typical example of the dissipative patterns for the suspension at a higher sphere concentration (ϕ=0.0256) than that of the suspension shown in Fig. 1 (0.00427). Now, broad ring was formed in the whity suspension in a glass dish, and the convectional patterns are observed clearly (see Fig. 2c, for example). It should be mentioned here that the convectional patterns shown in Fig. 2c changed with time, which is ascribed to the nonhomogeneity in the local concentrations of spheres and ethanol in the suspension area. The drying patterns in Fig. 2e,f showed spoke-like cracks, but the number of cracks decreased significantly at high sphere concentrations.

The convectional, sedimentation, and drying dissipative patterns were also observed in the aqueous ethanol mixtures at 100, 80, 60, 40, 20, and 0 vol% in volume percent of ethanol. A typical example is shown for 60 vol% ethanol in Fig. 3. The convectional flow looks slow in the presence of water, and the convectional and sedimentation patterns shown in Fig. 3a–c are quite similar to those in 100%

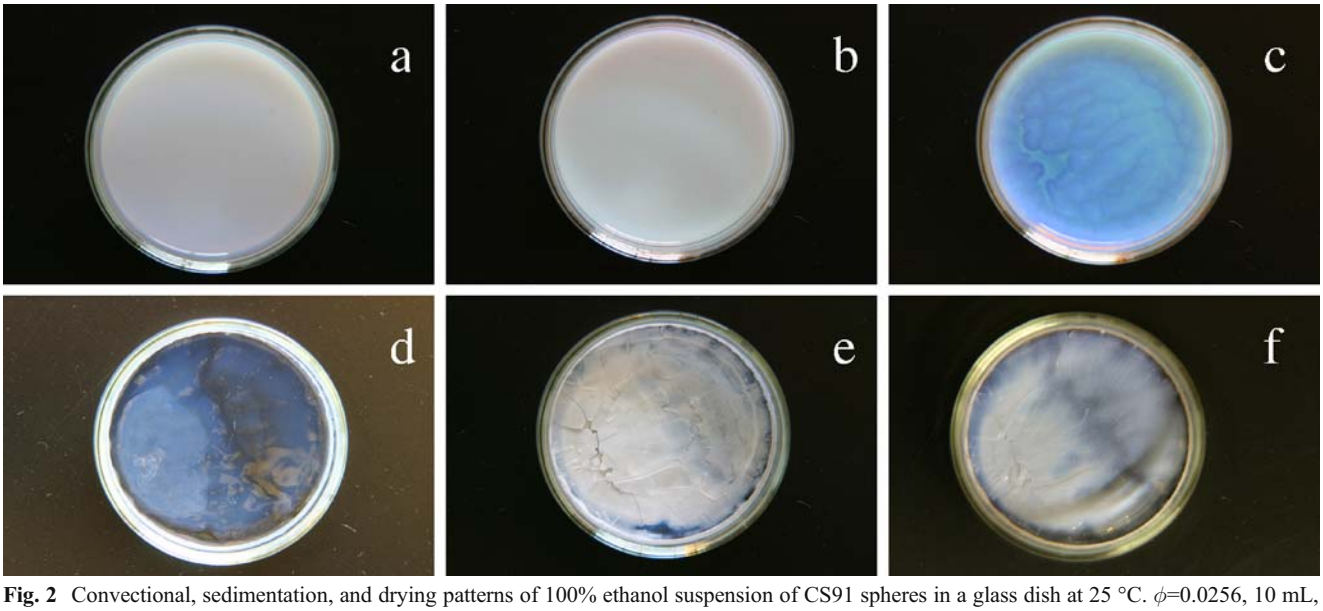

Fig. 2 Convectional, sedimentation, and drying patterns of 100% ethanol suspension of CS91 spheres in a glass dish at 25 °C. ϕ=0.0256, 10 mL, code Y006, **a** after 15 min, **b** 4.25 h, **c** 5.4 h, **d** 7.6 h, **e** 8.0 h, and **f** 10.2 h, dry

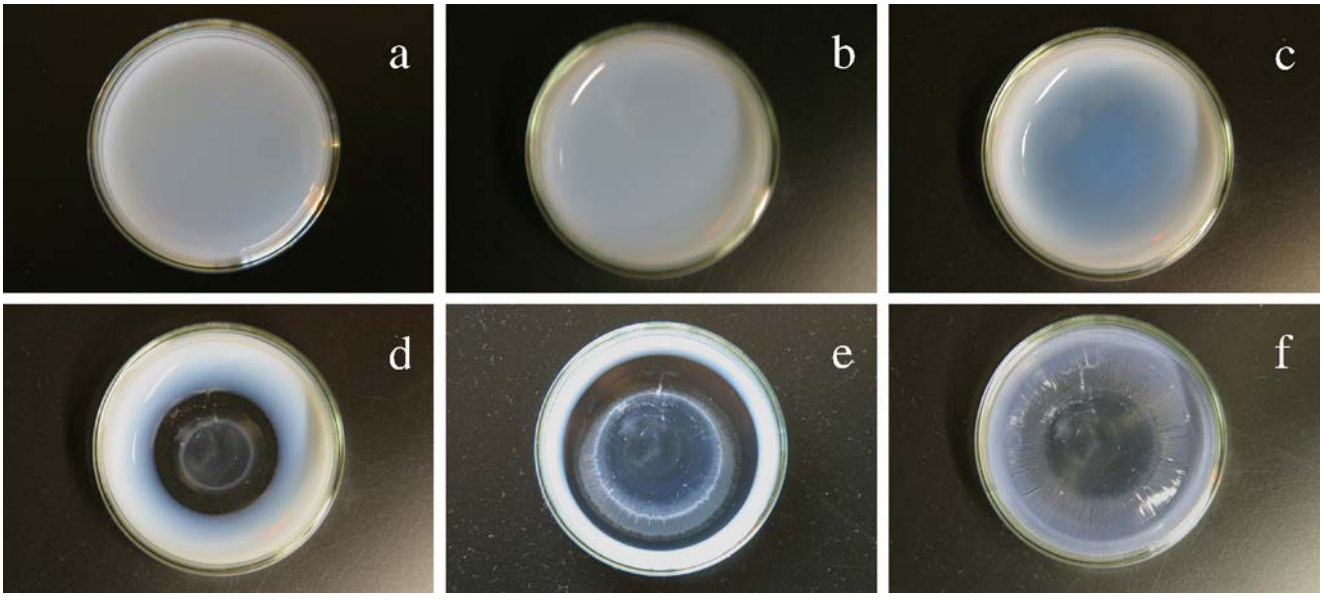

Fig. 3 Convectional, sedimentation, and drying patterns of aqueous ethanol suspension of CS91 spheres in a glass dish at 25 °C. 60 vol% EtOH, ϕ=0.00427, 10 mL, code Y023, **a** after 7.5 h, **b** 11.7 h, **c** 32.3 h, **d** 35 h, **e** 49.5 h, and **f** 53.8 h, dry

aqueous systems of colloidal silica spheres (Okubo submitted for publication). The final pattern of dryness shown in Fig. 3f was also similar to that of aqueous suspension, i.e., broad ring and spoke-like cracks in the macroscopic patterns. It should be mentioned here that the dried film for aqueous ethanol was hygroscopic, and the humidity of the room air played an important role for the patterns.

The *T*-values were 10.8 to 11.7 h, 31.1, 53.8, 80.5, 108.1, and 118.7 h after the suspensions were set for 100, 80, 60, 40, 20, and 0 vol% of ethanol, respectively. *T* increased substantially as water content increased.

Macroscopic patterns in a watch glass

Figure 4 shows a series of the convectional, sedimentation, and drying dissipative patterns of ethanol suspension of CS91 spheres in a watch glass. Sphere concentration was 0.00427 in volume fraction. Vigorous convectional flow

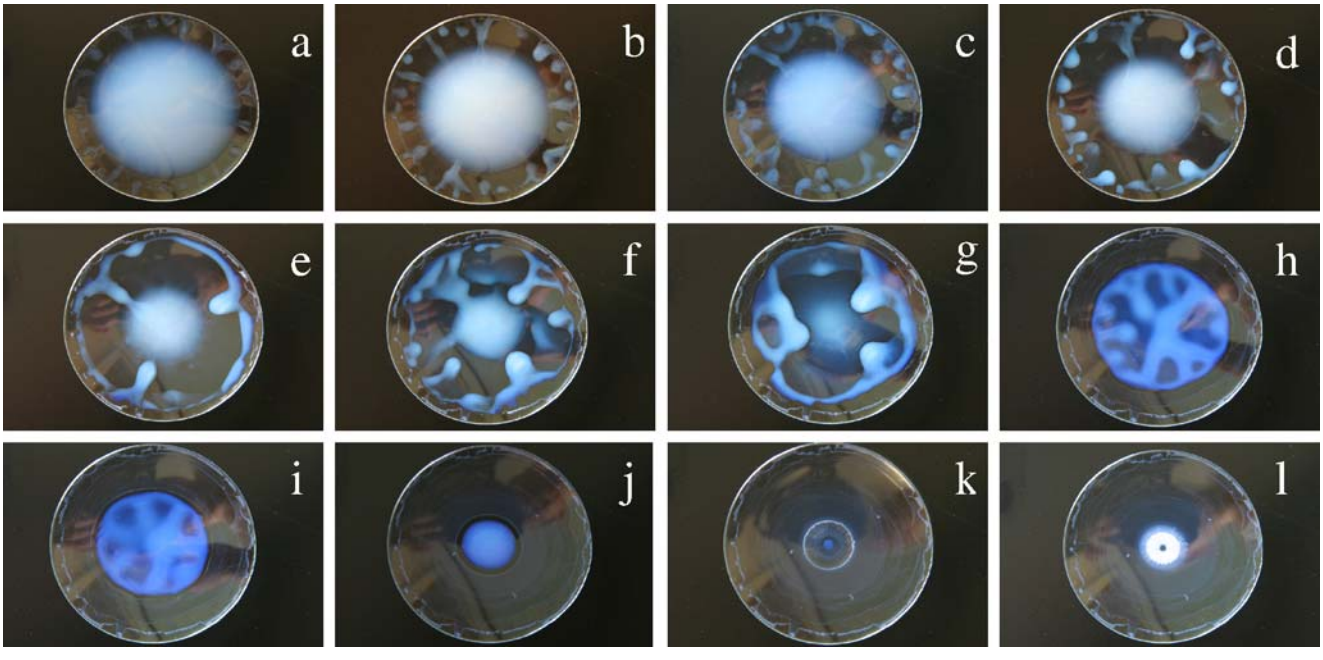

Fig. 4 Convectional, sedimentation, and drying patterns of 100% ethanol suspension of CS91 spheres in a watch glass at 25 °C. ϕ=0.00427, 4 mL, code Y013, **a** after 7 min, **b** 25 min, **c** 40 min, **d** 50 min, **e** 60 min, **f** 62 min, **g** 65 min, **h** 70 min, **i** 75 min, **j** 90 min, **k** 122 min, and **l** 125 min, dry

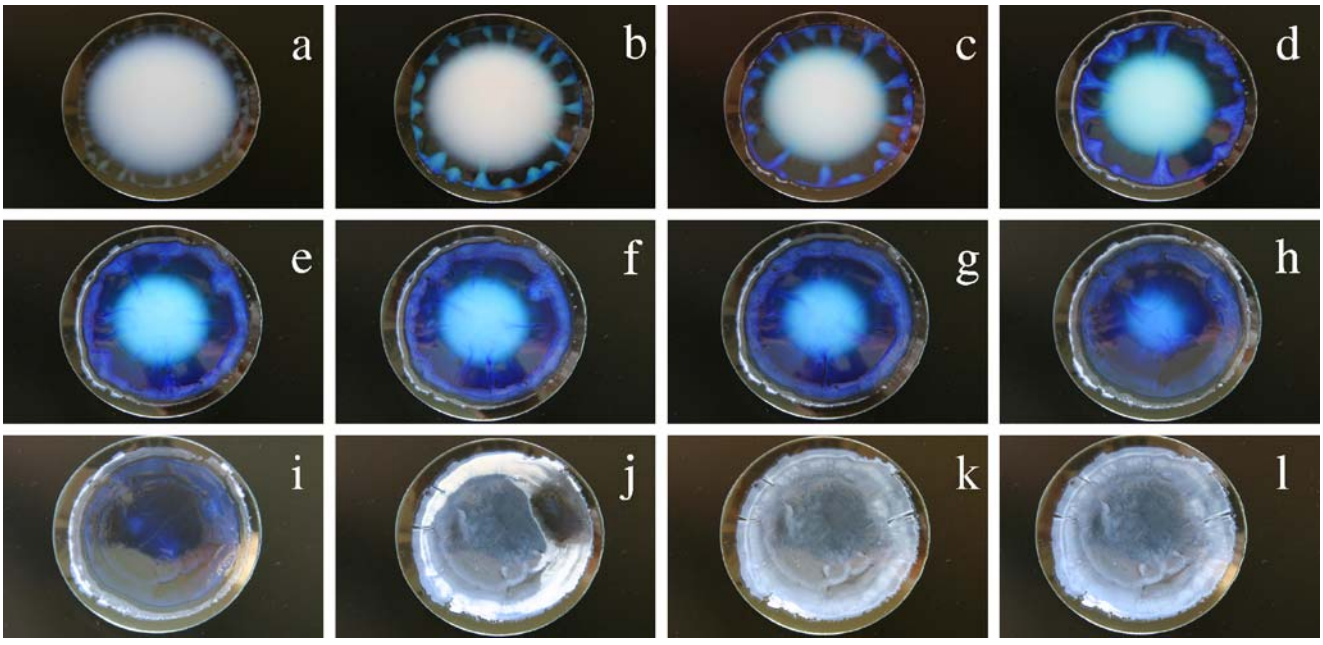

Fig. 5 Convectional, sedimentation, and drying patterns of 100% ethanol suspension of CS91 spheres in a watch glass at 25 °C. ϕ=0.0213, 4 mL, code Y016, **a** after 7 min, **b** 25 min, **c** 40 min, **d** 50 min, **e** 60 min, **f** 62 min, **g** 65 min, **h** 70 min, **i** 75 min, **j** 90 min, **k** 102 min, and **l** 125 min, dry

gave the beautiful dynamic change in the convectional patterns. In the beginning state, within 50 min after suspension was set, the spoke-like patterns formed outside of the mother suspension in the central area. The suspensions in the spoke-like suspension drops in the outer region were sometimes bridged with the mother suspension in the central area and disappeared when most of the drop suspensions flowed down to the mother suspension, and the suspension flow took place from the mother suspension pool toward the outside edge, resulting again in the appearance of the spoke-like suspension drops. These dynamic changes in the patterns and the bluish Bragg diffraction colors are beautiful and impressive. Between 60 and 75 min after the suspension was set, the mother suspension area decreased with time and the initial patterns changed drastically to the different kinds of patterns, like the section of lotus-root. After 90 min, the suspension remained in the central area only, and the broad rings were formed in the final course of dryness, which are quite similar to the patterns observed previously for the aqueous suspensions (Okubo submitted for publication). Interestingly, colloidal particles disappeared just at the central deepest point, as is

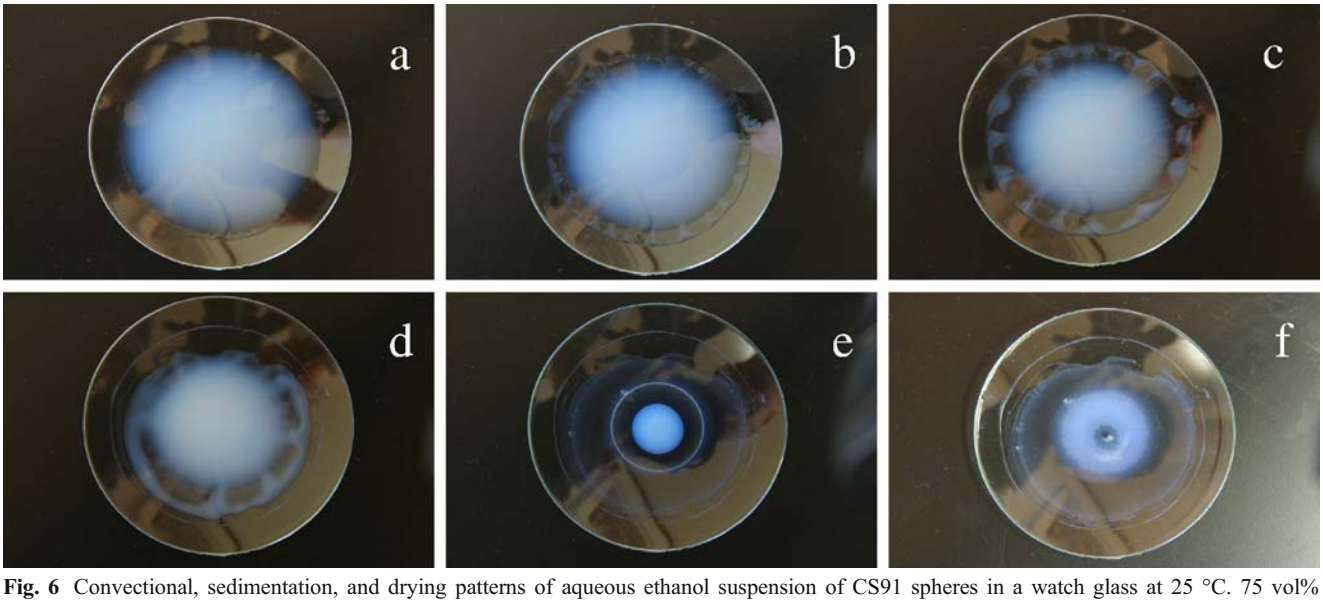

Fig. 6 Convectional, sedimentation, and drying patterns of aqueous ethanol suspension of CS91 spheres in a watch glass at 25 °C. 75 vol% EtOH, ϕ=0.00427, 4 mL, code Y033, **a** 30 min, **b** 60 min, **c** 82 min, **d** 120 min, **e** 4.67 h, and **f** 5.1 h, dry

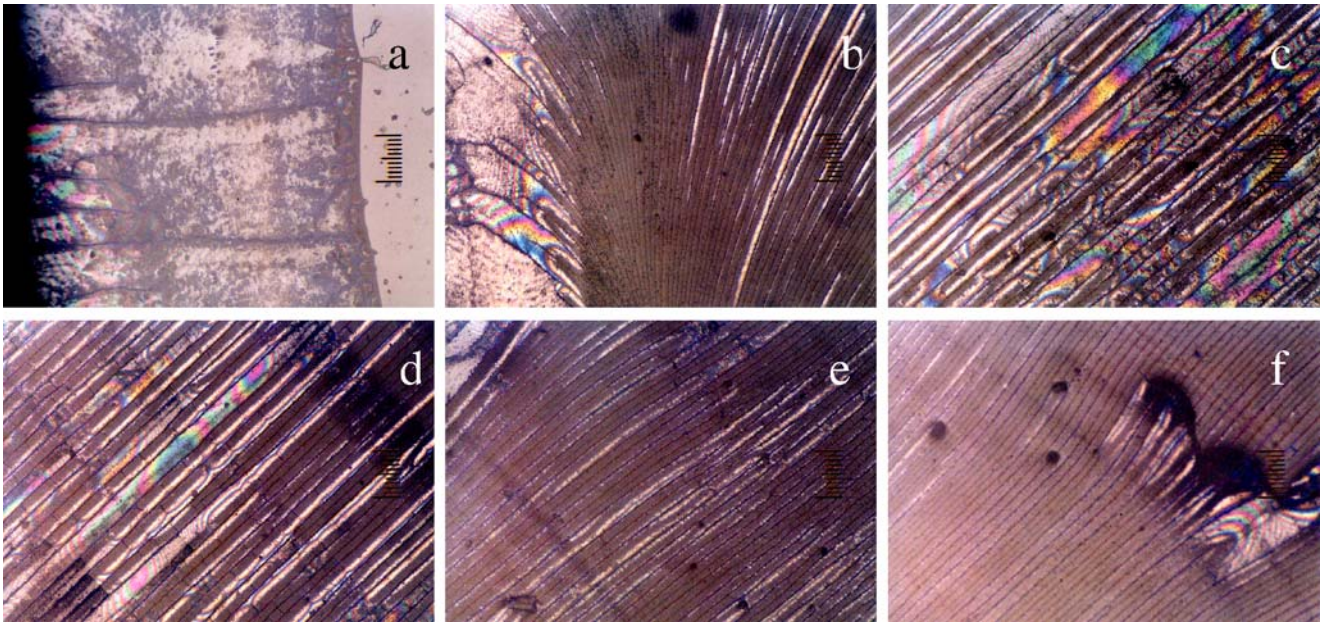

Fig. 7 Microscopic drying patterns of 100% ethanol suspension of CS91 spheres in a glass dish at 25 °C. ϕ=0.00427, 10 mL, dry, code Y003, from left edge (**a**) to center (**f**), full scale=0.2 mm

clear in Fig. 4l. *T* increased from 1.5 to 2.1 h as sphere concentration increased from 0.00064 to 0.0213 in volume fraction.

Figure 5 shows the dissipative patterns in 100% ethanol suspensions at 0.0064 in volume fraction. It should be noted here that the patterns at ϕ=0.0064 were quite similar to those shown in Fig. 4. The final drying patterns at a high sphere concentration of 0.0213 (Fig. 5) were large broad ring patterns and different from those shown in Fig. 4.

The convectional, sedimentation, and drying patterns for the aqueous–ethanol suspensions, 100, 95, 75, 50, 25, and 5 vol% in alcohol volume percent, were observed at ϕ=0.00427. Figure 6 shows the dissipative patterns of silica suspensions in the 75-vol% ethanol–water mixtures. Spoke-like patterns are observed in the outside area from the central mother suspension region, which are quite similar to those in the 100-vol% ethanol system (see Figs. 4 and 5, for example). Rather vigorous movements of spheres and solvent molecules are highly plausible. It is interesting to note that the patterns changed drastically just before the liquid–solid transition, as is shown in Fig. 6e,f.

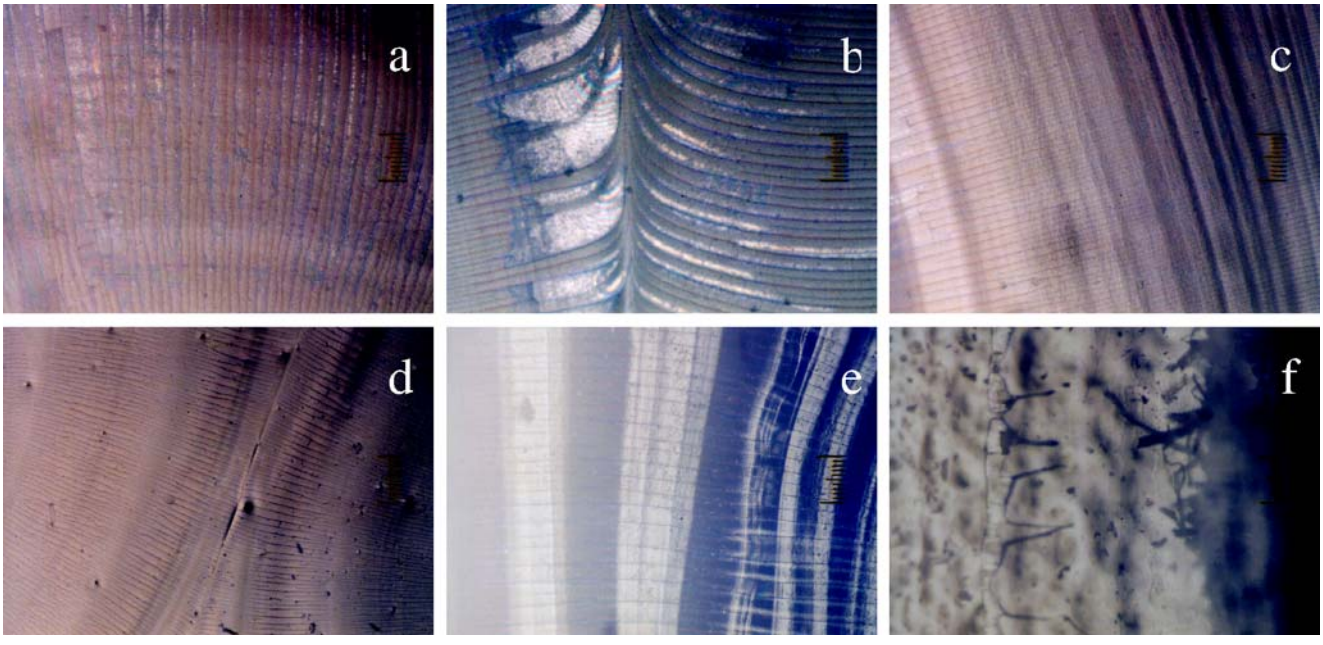

Fig. 8 Microscopic drying patterns of 100% ethanol suspension of CS91 spheres in a watch glass at 25 °C. ϕ=0.00427, 4 mL, dry, code Y031, from center (**a**) to right edge (**f**), full scale=0.2 mm

Microscopic drying dissipative patterns

Figures 7 and 8 show the microscopic drying patterns of 100% ethanol suspensions in a glass dish and in a watch glass, respectively. The fine spoke-like and ring-like cracks are beautiful. The curved patterns correspond to the dried film bent backward from the surface of the glass cell.

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