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ORIGINAL CONTRIBUTION

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Drying dissipative structures of Chinese black ink on a cover glass and in a dish

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Abstract Macroscopic and microscopic dissipative structural patterns are formed in the course of drying a suspension of Chinese black ink on a cover glass and in a dish. The time for the drying and the pattern area increased as the particle concentration increased. The broad ring patterns of the hills accumulated with the particles formed around the outside edges on a macroscopic scale. The height and the width of the broad ring increased as the particle concentration increased. The spokelike patterns of the rims accumulated with particles were also formed on a macroscopic scale. Microscopic patterns of colloidal accumulation were observed over the whole region of the pattern area. Various types of convection cells were observed on a cover glass and in a dish at 25–80 °C. A time-resolved observation of the drying process was also made. The convections of water and the colloidal particles at different rates under gravity and the translational and rotational Brownian movement of the particles were important for the macroscopic pattern formation. Microscopic patterns were determined by the translational Brownian diffusion of the particles and the electrostatic and the hydrophobic interactions between the particles and/or between the particles and the cell wall in the course of the solidification of the particles.

Keywords Drying dissipative structure · Chinese black ink · Pattern formation · Convection cell

Introduction

It is well known that most patterns in nature and in experiments in the laboratory form via self-organization accompanied by the dissipation of free energy and occur in the nonequilibrium state. Among the factors for the free-energy dissipation, evaporation and convection induced by the earth's gravity are very important for the pattern formation. Several papers on pattern formation in the course of drying suspensions of monodispersed colloidal particles have been reported so far [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16]. Most of the works have studied suspensions in the liquidlike distribution of particles and containing more or less ionic species. As important factors of dissipative structures, electrostatic interparticle interactions have been pointed out. Hydrophobic and hydrophilic interactions have also been demonstrated to be important for the drying process [6, 14, 15]. Gelbart and coworkers [4, 5, 7] examined the mechanism of solvent dewetting in annular ring structures formed by drying a diluted metal colloid on a cell wall. Shimomura and Sawadaishi [17] studied intensively the dissipative patterns in the processes of film formation by drying the polymer solutions.

In previous work in our laboratory, dissipative patterns on a cover glass were observed in the course of drying colloidal crystal suspensions of colloidal silica [18] and monodispersed polystyrene spheres [19], which are hydrophilic and hydrophobic in their surfaces, respectively. The colloidal crystal is undoubtedly one of the simplest and most convenient systems for studying dissipative structures on a laboratory scale. For example, accurate structural information on the processes of the dissipative pattern formation is available from reflection spectroscopy of colloidal crystal suspensions. Quite similar macroscopic and microscopic dissipative structural patterns formed between colloidal crystals of silica [18] and polystyrene spheres [19]. Spokelike and ringlike cracks formedon a macroscopic scale. The broad ring patterns of the hill accumulated with spheres formed around the outside edge. Fractal patterns of the sphere association were observed on a microscopic scale. Capillary forces between spheres at the air–liquid interface and the different rates of convection flow of water and solutes at the drying front were important for the macroscopic and microscopic pattern formation. The macroscopic and microscopic dissipative structures formed systematically as a function of sphere size for colloidal crystals of silica spheres of sizes ranging 5 nm to 1 μm in diameter (T. Okubo, T. Yamada, K. Kimura, unpublished results). Fundamental macroscopic patterns such as a broad ring, spokelike and ringlike patterns were observed irrespective of sphere size. Furthermore, the crystal distribution of the colloidal spheres remained constant during the drying process from the suspension state to the solid. The change in the lattice spacing in the course of drying was followed by reflection spectroscopy [18, 19].

Recently, anisotropic colloidal particles of platelike bentonite and rodlike palygorskite were used for studying their dissipative structures (T. Okubo, T. Yamaguchi, A. Ohtake, K. Kimura, A. Tsuchida, unpublished results). For these nonspherical particles, the hill was newly formed in the center of the pattern area in addition to the broad ring at the outside edge, and the spokelike and ringlike patterns disappeared. Drying dissipative structures have been studied for aqueous solutions of linear-type cationic polyelectrolyte, poly(allylamine hydrochloride) [20], and cationic detergent, *n*-dodecyltrimethylammonium chloride [21]. In both cases, macroscopic broad ring patterns formed. Furthermore, several types of beautiful fractal patterns were observed on a microscopic scale. Especially for the solution of ionic detergent, crosslike, branchlike and arclike microscopic patterns formed in the separated block regions.

It should be noted here that macroscopic broad ring patternsalways formed for all kinds of solutions and suspensions which the authors have examined hitherto. The main cause for the pattern formation is the convection flow of the solutes in normal gravity. The macroscopic spokelike and ringlike patterns were also common to all kinds of spherical particles in the suspension state. It is now observed preliminarily that the macroscopic and microscopic structures change quite systematically depending on the shape and size of the molecules or particles.

In this work, drying processes from suspension to film were observed for exhaustively deionized suspensions of Chinese black ink on a cover glass and also in a dish at various experimental conditions, such as particle concentration, temperature and amount of suspension. Chinese black ink is made from soot and glue, and has been used for writing for a long time in China and Japan. Terada and coworkers [22, 23, 24] clarified that Chinese ink was a typical example of a colloidal suspension. Terada and coworkers spread Chinese ink on clean water and compressed the air–liquid interface area by sliding a horizontal bar in a similar manner as in the Langmuir–Blodgett method and observed the liquid and solid structures. Furthermore, they observed the spokelike patterns and the convection cells for their systems.

Experimental

Materials

Two kinds of stock suspensions of Chinese black ink, Fueki FV3612 (Fueki Paste Co., Tokyo, Japan) and Kaimei SE-1702 (Kaimei Co., Urawa, Japan), were purchased. These colloidal particles were highly polydisperse and their mean diameters were 33.0 ± 6.4 and 32.8 ± 9.2 nm, respectively, which were determined from transmission electron microscope measurements(Hitachi type H8100, Tokyo, Japan). The stock suspensions were deionized with a mixed bed of cation-exchange and anion-exchange resins more than 6 months before preparing the sample suspensions. Their concentrations ranged from $1{\times}10^{-6}$ to 0.2 g/mL. The 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

Aliquots (0.1 or 0.2 mL) of the aqueous suspensions of Chinese ink were dropped carefully and gently on a microscope cover glass (30 mm×30 mm, thickness no. 1, 0.12–0.17 mm, Matsunami Glass Co., Kishiwada, Osaka) set in a dish (60 mm in diameter, 15 mm in depth, Petri Co., Tokyo). A syringe (2.5 mL, type SS-02SZ, Terumo Co., Tokyo, Japan) was used for the dropping. The cover glass was used without further rinsing in many cases. The extrapolated value of the contact angle for pure water was $31 \pm 0.2°$ from the drop profile of a small amount of water (0.2, 0.4, 0.6 and 0.8 μL) on the cover glass. Some of the experiments were made on a rinsed cover glass with the mixed acid sulfuric acid solution of potassium dichromate. The extrapolated contact angle of the rinsed glass for pure water was $11 \pm 0.2°$.

In order to observe the convection flow in the sample suspensions directly, 0.5–3.0 mL of the suspensions was set in a dish (30 mm in diameter and 15 mm in height) on a Shamal hotplate (HHP-401, Iuchi Seiei Dou Co., Tokyo, Japan). The suspension temperature was raised and an equilibrium temperature was reached within 10 min at 36, 48, 58, 72 and 80 °C when the temperatures of the plate surface were set at 50, 75, 100, 125 and 150 °C, respectively.

Macroscopic structures were observed with a digital HD microscope (type VH-7000, Keyence Co., Osaka) and with a Handycam Video Hi 8 (CCD-TR3300, Sony Co., Tokyo, Japan). On the other hand, microscopic structures were observed on a laser 3D profile microscope (type VK-8500, Keyence), a metallurgical microscope (Axiovert 25CA, Carl Zeiss, Jena, Germany) and an atomic force microscope (type SPA400, Seiko Instruments, Tokyo, Japan).

Results and discussion

Typical patterns formed in the drying suspensions of Chinese ink at concentrations, w, ranging from 1×10^{-5} to 0.2 g/mL on an unrinsed cover glass are shown in Fig. 1. The broad rings were observed clearly in the pictures at the outer edges irrespective of the concentration. The width of the broad ring regions increased when the ink concentration increased. The changes in the width (W, millimeters) and the maximum height (d_{max}, microns) of the broad rings for Fueki and Kaimei inks are compiled in Table 1. The width increased significantly when the particle concentration increased. W increased linearly as a function of $\log w$, though the

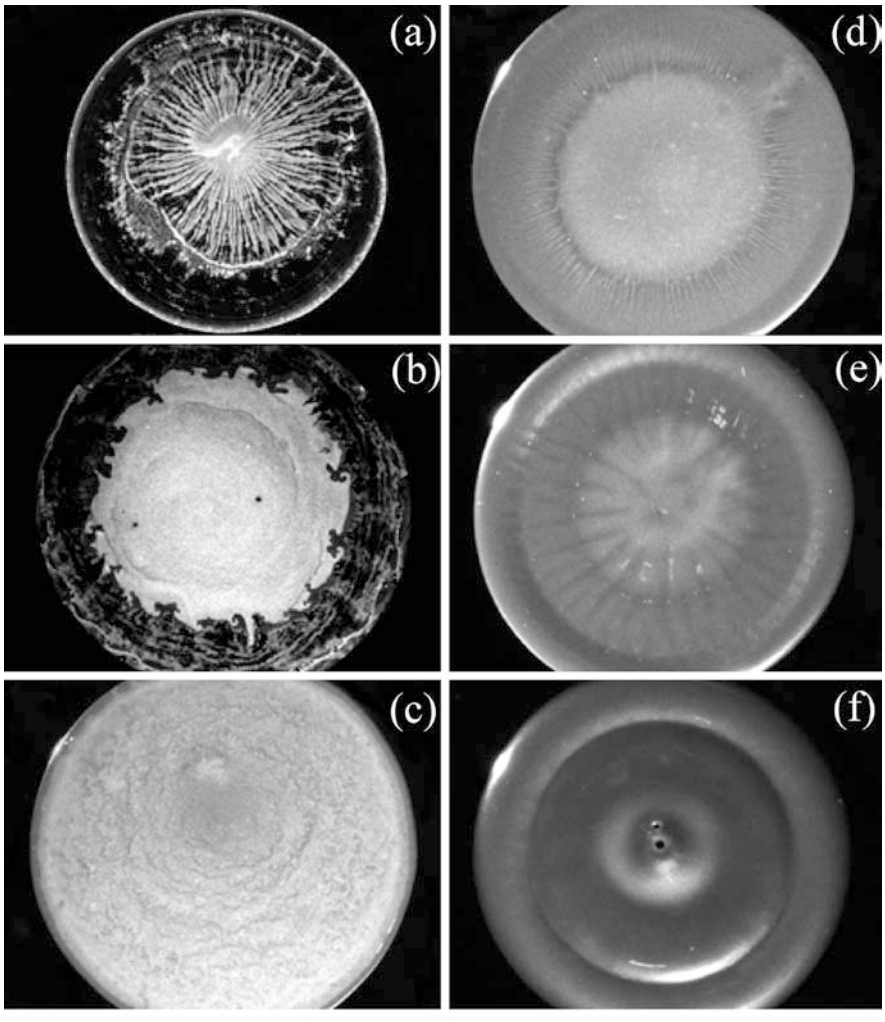

Fig. 1a–f Patterns formed in the drying process of Chinese ink (Kaimei) on an unrinsed cover glass at 25 °C. In water, $V = 0.1$ mL, **a** $w = 1\times10^{-5}$ g/mL, **b** $w = 1\times10^{-4}$ g/mL, **c** $w = 1\times10^{-3}$ g/mL, **d** $w = 0.01$ g/mL, **e** $w = 0.1$ g/mL, **f** $w = 0.2$ g/mL. The length of the *bar* is 2.0 mm

Table 1 The values of S, T, W and d_{max} on an unrinsed cover glass and on a rinsed cover glass (in *parentheses*) as a function of w of Chinese black ink at 25 °C

w (g/mL)	S (mm^2)		T (min)		W (mm)		d_{max} (µm)
	Fueki ink, 0.2 mL	Kaimei ink, 0.1 mL	Fueki ink, 0.2 mL	Kaimei ink, 0.1 mL	Fueki ink, 0.2 mL	Kaimei ink, 0.1 mL	Kaimei ink, 0.1 mL
1×10^{-6}	–	58 (83)	–	–	–	–	0.22 (0.73)
1×10^{-5}	–	58 (83)	–	–	–	2.7	0.66 (0.83)
1×10^{-4}	–	70 (107)	–	106	–	–	10 (1.5)
1×10^{-3}	–	64 (114)	–	152	–	1.3 (0.8)	22 (14)
2.3×10^{-3}	64	–	206	–	0.11	–	–
4.6×10^{-3}	–	–	–	–	0.17	–	–
5.0×10^{-3}	–	65 (109)	–	–	–	–	22 (24)
7.6×10^{-3}	71	–	212	–	1.1	–	–
0.01	–	75 (105)	–	–	–	6.0 (3.5)	33 (28)
0.0228	71	–	211	–	3.6	–	–
0.05	–	62 (113)	–	–	–	–	129 (75)
0.1	–	75 (84)	–	–	–	10.7 (3.5)	189 (150)
0.2	–	95 (177)	–	–	–	15.0 (3.5)	–
0.228	82	–	221	–	–	–	–

graph showing this is omitted in this paper. It should be mentioned here that the macroscopic broad ring patterns were observed for all the suspensions or solutions examined in the author's laboratory: colloidal silica [18], polystyrene spheres [19], ionic detergent of *n*-dodecyltrimethylammonium chloride [21], platelike bentonite, rodlike palygorskite, poly(allylamine hydrochloride) [20], sodium chloride and other simple electrolytes, for example.

The main cause for the broad ring formation is undoubtedly the convection flow of the solvent and the Chinese ink particles. Especially, flow of the particles from the central area toward the outside edges will be enhanced by the evaporation of water at the liquid surface of the outside edges, resulting in a lowering of the suspension temperature in the upper region of the liquid area. When the particles reach the edges of the drying frontier at the outside region of the liquid, some of them will go back to the center. However, the movement of most of the ink particles may be stopped by the solidification at the frontier region owing to the disappearance of water. This process must be followed by the broad ringlike accumulation of the ink particles near the round edges.

The spokelike pattern was clearly observed at a particle concentration at 1×10^{-5} g/mL (Fig. 1a), 0.01 g/mL (Fig. 1d) and 0.1 g/mL (Fig. 1e). It should be recalled that the spokelike patterns of cracks were observed for colloidal crystal suspensions of silica [18] and polystyrene spheres [19]. However, the patterns for Chinese black ink were not cracks but ridge lines. Chinese ink contains the glue component and the film must be strong enough not to make cracks. The origin for the spokelike patterns, whether cracks or ridge lines, is the many circle convection cells formed in the liquid phase in the course of drying the suspension [18, 19, 20 ,21, 22].

The pattern area, S, and the drying time, T, at 25 °C are shown in Table 1. The S values increased first as the particle concentration increased, and saturated to certain critical values. The dependency of the S values suggests that the interfacial tension of Chinese ink on a cover glass decreases as the concentration of the ink particles increases and Chinese ink is slightly surface-active. The T values increased slightly as the particle concentration increased, especially at low suspension temperatures; however, at elevated temperatures above 45 °C, T was quite insensitive to the particle concentration, though the data showing this are omitted from the table. This suggests that at high temperature the water activity (vapor pressure) is high and is not influenced very much by the colloidal particles coexisting.

The drying patterns of the same samples as shown in Fig. 1 but on a rinsed cover glass are shown in Fig. 2. The pattern area increased substantially, about threefold, compared with an unrinsed glass, which is clearly due to the fact that the contact angle of the rinsed glass was 11°, much lower than that of the unrinsed glass, 31°, as described in the Experimental section. Surprisingly, the fundamental features of the patterns on a rinsed glass were almost the same as those on an unrinsed cover glass as is clearly shown by comparing Figs. 1 and 2.

It should be noted here that very fine rings were observed at particle concentrations of 1×10^{-5} g/mL (Fig. 2a) and 1×10^{-4} g/mL (Fig. 2b). These fine rings have often been observed for colloidal spheres [18, 19]. When the particle concentration was high the fine rings became broad as shown in Fig. 2d. The spokelike patterns were also observed on a rinsed cover glass especially at $w=1\times10^{-5}$ g/mL (Figs. 1a, 2a), $w=0.01$ g/mL (Figs. 1d, 2d) and $w=0.1$ g/mL (Figs. 1e, 2e), respectively, irrespective of the rinsing cover glass or not.

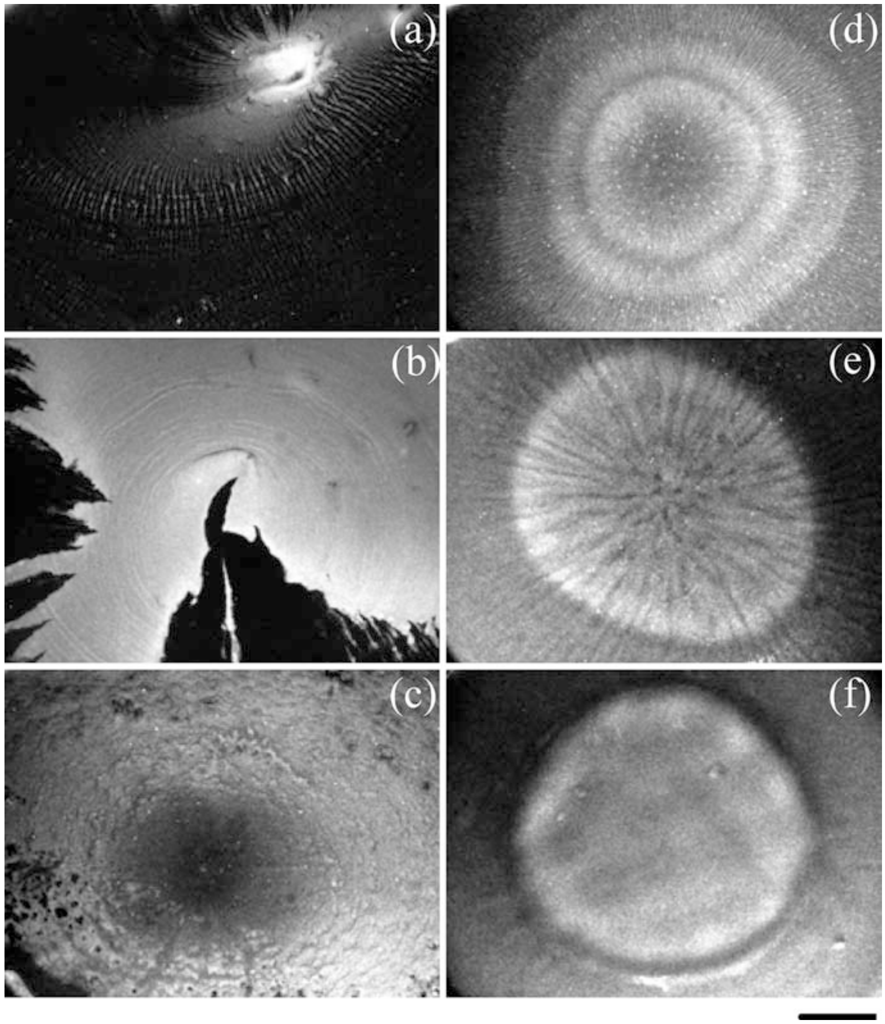

Fig. 2a–f Patterns formed in the drying process of Chinese ink (Kaimei) on a rinsed cover glass at 25 °C. In water, $V = 0.1$ mL, **a** $w = 1{\times}10^{-5}$ g/mL, **b** $w = 1{\times}10^{-4}$ g/mL, **c** $w = 1{\times}10^{-3}$ g/mL, **d** $w = 0.01$ g/mL, **e** $w = 0.1$ g/mL, **f** $w = 0.2$ g/mL. The length of the *bar* is 2.0 mm

At the special experimental condition of $w = 1{\times}10^{-3}$ g/mL on an unrinsed cover glass at 25 °C, the convection flow of the Kaimei particles was visible with the naked eye. The patterns formed in the course of drying 1 min (Fig. 3a), 36 min (Fig. 3b), 115 min (Fig. 3c) and 136 min (Fig. 3d), respectively, after setting the sample suspensions on the cover glass are shown in Fig. 3. At 1 min after setting, Chinese ink particles meet together and the associated particles distribute at random. However, after 36 min, the particles started to orient themselves as a result of the convection flow. Surprisingly, after 136 min, the spokelike lines both in the liquid and in the solid phases just coincided with each other (Fig. 3d). This observation suggests strongly that the spoke lines were already formed in the suspension phase by the convection flow. The drying frontier at the border between gray (center part) and black regions (edges) in Fig. 3d moved inside with time. The clear-cut spoke lines appeared especially around the outside region of the liquid area.

Typical examples of the pattern formation processes of Chinese black ink observed on a metallurgical microscope at 25 °C are shown in Fig. 4. From the top the pictures show 18, 25, 26 and 27.5 min after setting the suspensions. The drying frontier and the central region are shown at the top and at the bottom in the pictures, respectively. The border between black and gray regions is the frontier zone of drying. Just after setting the suspension, fluctuating patterns appeared, but a clear pattern was not visible. After 18 min (Fig. 4a), however, the convection of the particles from the center toward the outside edges was observed clearly with the naked eye. The patterns, which were composed of the accumulated particles, had already formed in the suspension phase, though they were not so fine and clear. As time elapsed, the dry frontier moved to the center as shown in Fig. 4, and the patterns in the liquid phases became clearer. These observations suggest strongly that the patterns grow and are already fixed in the suspension phase. The suspension phases shown in

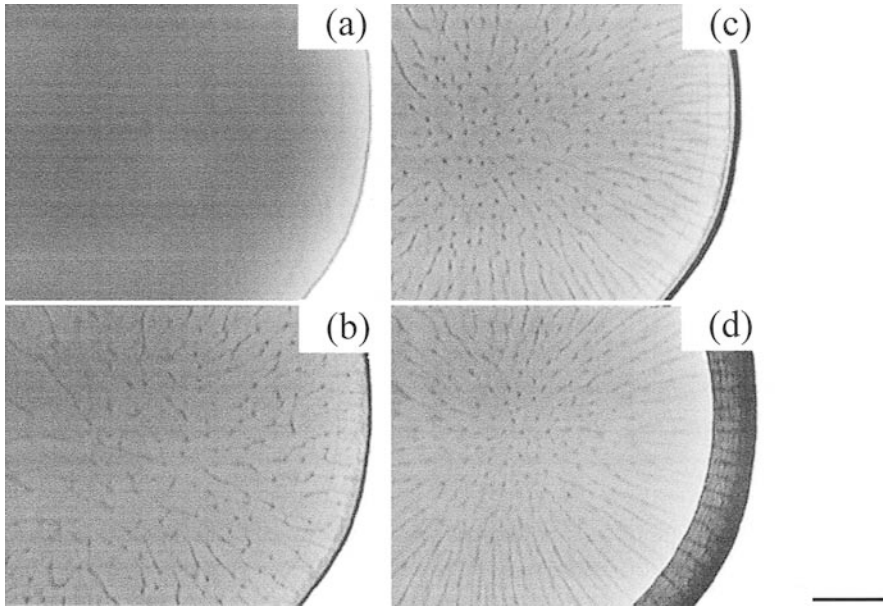

Fig. 3a–d Patterns formed in the drying process of Chinese ink (Kaimei) on an unrinsed cover glass at 25 °C. In water, $V=0.1$ mL, $w=1\times10^{-3}$ g/mL, **a** 1 min after setting, **b** 36 min after setting, **c** 115 min after setting, **d** 136 min after setting. The length of the *bar* is 2.0 mm

Fig. 4b and c must be close to the solid phase though many water molecules are included in the interparticle dead space regions. Figure 4d shows the patterns formed when the drying process was complete. Here, the top black area is the broad ring region. Clearly, the patterns became fine and kept the same structures as those formed in the liquid phase.

A further study on the convection flow in the course of drying was made using a large amount of the ink suspension in a dish on a hot plate keeping the suspension temperatures between 25and 80 °C. The typical patterns observed when the drying was complete at 80 °C for the suspensions at $w=1\times10^{-5}$, 5×10^{-5} and 1×10^{-4} g/mL are shown in Figs. 5, 6 and 7, respectively. The amount of the suspension was 2.0 mL. After setting the sample suspensions on a hot plate for 21, 15 and 21 min, cyclic convection cells around the outside edges of the suspension, grainlike convection patterns and smokelike convection structures were observed in the suspension phases as shown in Figs. 5, 6 and 7, respectively. Interestingly, the patterns of the dried films were spokelike lines, fine circles and the surface patterns of the Japanese earthenware called "Shigaraki Yaki", respectively (Figs. 5b, 6b, 7b, respectively). For the spokelike pattern formation, the number of spoke lines was plotted against number of convection circles (Fig. 8). The linear relationship held with a slope of 2.0. In Fig. 5a, only half of the small circle cells were observed with the naked eye. Thus, this relationship suggests strongly that the spoke lines in the dried film originated from the small circle convection cells in the suspension phase before drying. Now, it is clear that the convection flow of the particles and further the difference in the flow rates between the particles and the solvents play an important role for the pattern formation.

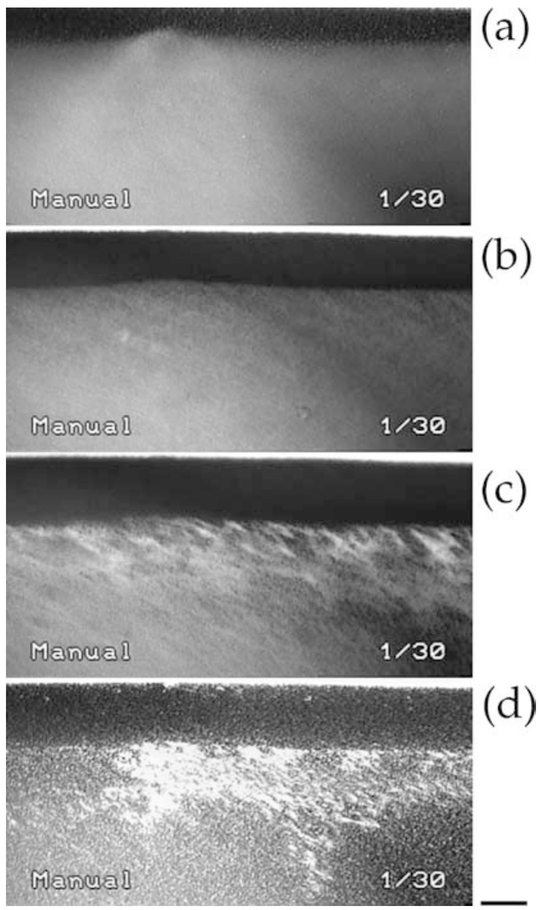

Fig. 4a–d Patterns formed in the drying process of Chinese ink (Fueki) on an unrinsed cover glass at 25 °C. In water, $V=0.1$ mL, $w=2.28\times10^{-3}$ g/mL, **a** 18 min after setting, **b** 25 min after setting, **c** 26 min after setting, **d** 27.5 min after setting. The length of the *bar* is 10 μm

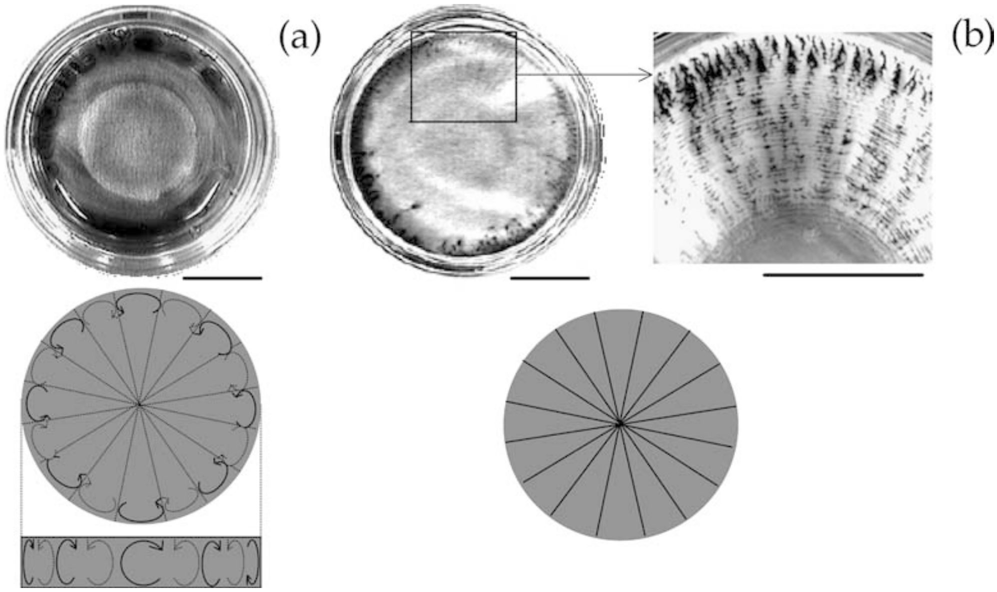

Fig. 5a,b Patterns formed in the drying process of Chinese ink (Kaimei) in a dish at 80 °C. In water, $V = 2$ mL, $w = 1 \times 10^{-5}$ g/mL **a** 21 min after setting, **b** dried film. The length of the *bar* is 10 mm

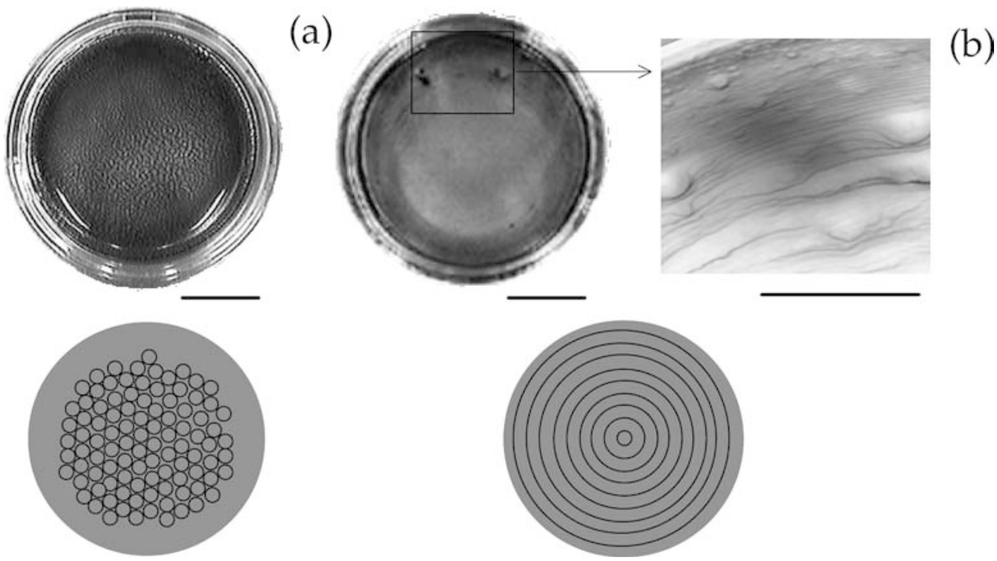

Fig. 6 Patterns formed in the drying process of Chinese ink (Kaimei) in a dish at 80 °C. In water, $V = 2$ mL, $w = 5 \times 10^{-5}$ g/mL **a** 15 min after setting, **b** dried film. The length of the *bar* is 10 mm

The patterns observed in the suspension phase at various experimental conditions are compiled in Tables 2 and 3. Surprisingly, these patterns were observed with the naked eye when the amount of liquid was great, the suspension temperature was high and/or the suspension concentration was in the range between 1×10^{-5} and 1×10^{-4} g/mL. In other words, the convection patterns appeared only when the convection flow of the particles and water is rather fast and the particle concentrations are just in the appropriate range where the convection flow of the particles is most visible with the naked eye. In conclusion, three kinds of convection patterns appeared by the delicate balancing of the hydrodynamic and optical contributions, such as the difference in the flow rates between the particles and water, the viscosity of the solvent, the Reynolds number (correlating to the turbulent flow) of the suspension, the amount and shape of the suspension phase, the size of the particles and the interparticle distance.

Concluding remarks

Macroscopic broad ring patterns were observed for all kinds of the solutes examined including Chinese black ink studied in this work. Some of the microscopic pat-

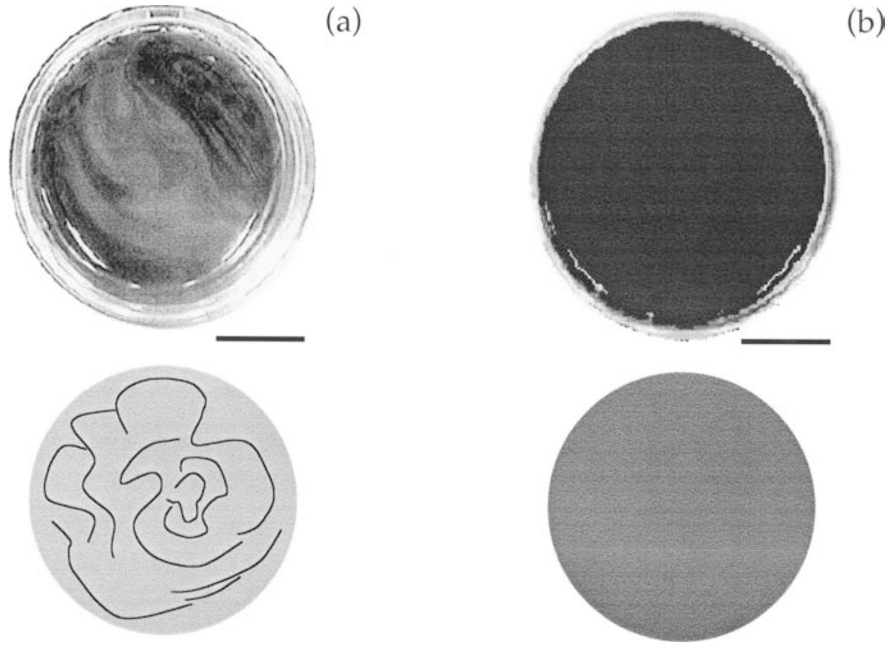

Fig. 7 Patterns formed in the drying process of Chinese ink (Kaimei) in a dish at 80 °C. In water, $V=2$ mL, $w=1\times10^{-4}$ g/mL **a** 21 min after setting, **b** dried film. The length of the *bar* is 10 mm

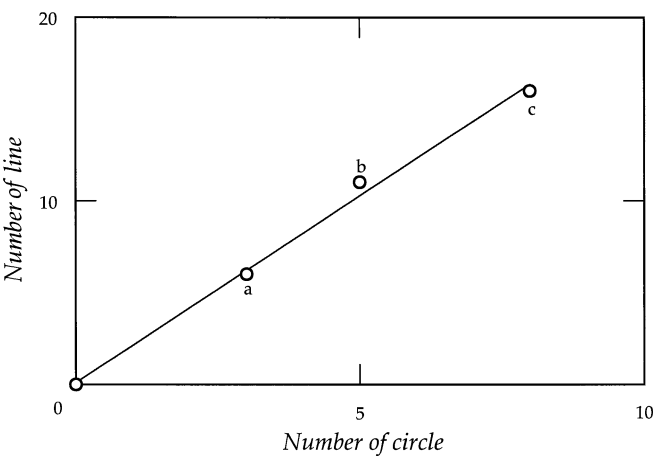

Fig. 8 Number of spoke lines against number of circles. Kaimei ink *a* $w=1\times10^{-5}$ g/mL, 80 °C, $V=2.5$ mL, *b* $w=5\times10^{-5}$ g/mL, 50 °C, $V=3.0$ mL, *c* $w=1\times10^{-5}$ g/mL, 80 °C, $V=2.0$ mL

terns of the ink were quite similar to those of the polymer [20]. The nature of the surface and the size of the colloidal particles were not so essential for the formation of the macroscopic structures. A spherical shape itself was essential instead. However, it should be recalled that for the polymer and *n*-dodecyltrimethylammonium chloride solution, the specific association between the solutes in the course of drying played an important role for the microscopic pattern formation. In other words, microscopic patterns may differ greatly depending on the nature of the solutes and also on the electrostatic and the hydrophobic interactions between the ink particles and/or between the particles and the cell wall in the course of the solidification.

Table 2 Types of convection patterns observed with the naked eye in the suspension phase at 80 °C

V (mL)	w (g/mL)			
	1×10^{-5}	5×10^{-5}	1×10^{-4}	1×10^{-3}
0.5	None	None	None	None
1.0	None	None	None	None
1.5	None	None	None	None
2.0	Smoke	Grain	None	None
2.5	Smoke	Smoke	Smoke	None
3.0	Scroll/smoke	Grain/scroll/smoke	Smoke	None

Table 3 Types of convection patterns observed with the naked eye in the suspension phase at $V=3.0$ mL

T (°C)	w (g/mL)			
	1×10^{-5}	5×10^{-5}	1×10^{-4}	1×10^{-3}
25	None	None	None	None
40	None	None	None	None
50	Smoke	Grain	None	None
70	Scroll/smoke	Grain	Smoke	None
80	Scroll/smoke	Grain/scroll/smoke	Smoke	None

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