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ORIGINAL CONTRIBUTION

Sedimentation and drying dissipative structures of green tea

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Abstract Sedimentation and drying dissipative patterns formed in the course of drying green tea (Ocha) have been studied in tea cup (Ochawan), glass dish, polystyrene dish, and watch glass. The broad-ring patterns are formed within several tens of minutes in suspension state by the convectional flow of water and colloidal particles of green tea (7 μm in mean size and 5 μm in its dispersion from the mean size). Formation of the broad-ring patterns is retarded when a tea cup is covered with a watch glass, which demonstrates the important role of the convectional flow of tea particles and water induced by the evaporation of water at the air-suspension interface under the gravity. The sedimentary particles are suspended above the substrate plate and always move by the convectional flow of water. The broad-ring patterns become sharp just before the solidification occurs. The broad rings are formed even in an inclined glass dish, though the rings are transformed slightly, which demonstrates the strong convectional flow of the particles. The drying broad rings and the microscopic fine structures are formed in the solidification processes on the bases of the convectional and sedimentation patterns in suspension state.

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Introduction

In most Japanese hotels, a guest will find in his or her room a set of green tea, which is composed of green tea granules in a paper filtering bag, a tea cup (Ochawan in Japanese), and hot water. The green tea is prepared conveniently by shaking the tea bag dipped into a hot water in an Ochawan. The author was excited to find that the broad ring always formed within several tens of minutes when green tea in a cup stood still on a disk. Pictures of Fig. 1 show the broad-ring patterns of green tea in the hotels of Yonezawa (a), Sapporo (b), Kumamoto (c), and Ishigaki cities (e). Pictures (d) and (e) are the side views of the cups in Yonezawa and Kumamoto, respectively. The broad ring, which is the hill accumulated with green tea colloids, was formed in the inclined inner wall of the cup and not in the deepest central area. To clarify the reasons, the sedimentation patterns and also the drying dissipative patterns of the monodispersed colloidal silica spheres in glass dish, polystyrene dish, and several sizes of watch glasses have been studied hitherto in the course of drying aqueous and ethanol suspensions [1–3]. The broad-ring patterns were always formed unexpectedly fast in the suspension state irrespective of the cells used. The broad-ring structures were clarified to be formed by the delicate balancing of the upward (and/or outer ward) convectional flow of the colloidal particles in an inner wall and downward gravitational sedimentation (and/or inner ward convectional flow). Important role of the microscopic cell convection in the liquid phase was supported for the broad-ring formation of suspensions and solutions.

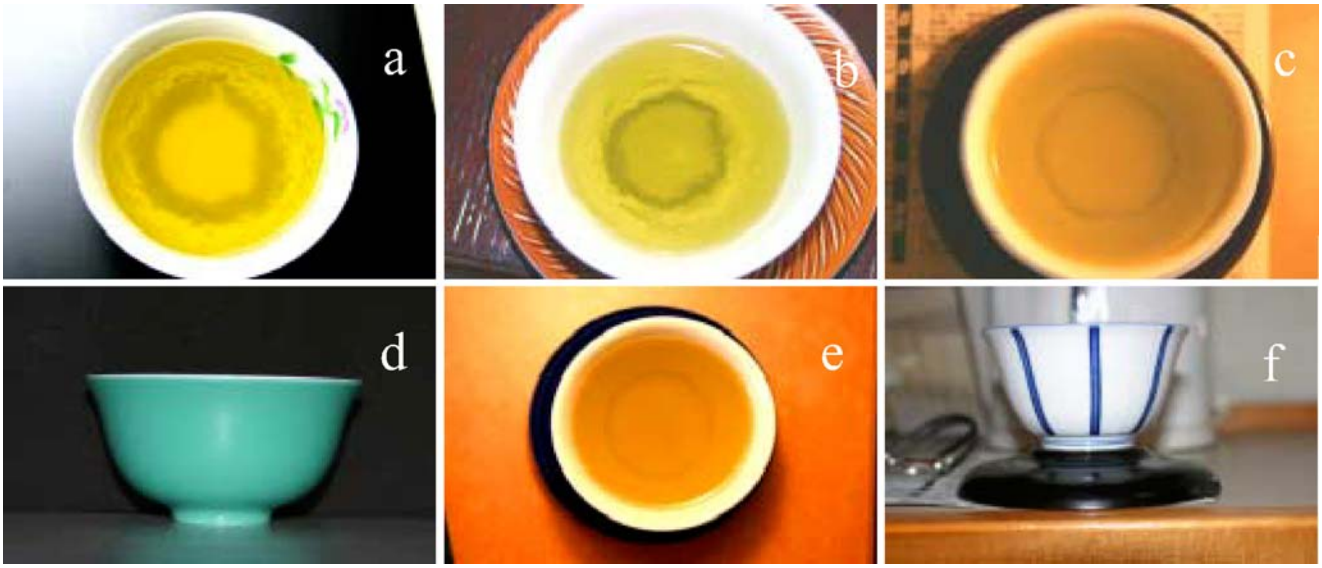

Fig. 1 Sedimentation patterns of green tea in a tea cup at 24 °C. **a** From a hotel in Yonezawa, **b** in Sapporo, **c** in Kumamoto, **d** side view of the tea cup from a hotel in Yonezawa, **e** in Ishigaki, **f** side view of tea cup from a hotel in Kumamoto

As is well known, many kinds of patterns are formed spontaneously by self-organization mechanism, and they are grouped into *dissipative* structures in the free energy of the systems and the *conservative* ones. It is quite difficult to find the energy conservative structures in nature. Most patterns in nature are formed in the *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 much simple drying pattern formation in the course of dryness of the monodispersed colloidal suspensions have been reported hitherto [4–20]. 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 [17–19].

The drying 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 [21–25], solutions of ionic and nonionic surfactants [26–28], polyelectrolyte solutions [29], and solutions of water-soluble neutral polymers [30]. The macroscopic broad-ring patterns of 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 sedimentation patterns formed already in the liquid phases before dryness.

In this paper, we observe the sedimentation dissipative structures of green tea in a tea cup, a glass dish, a polystyrene dish, and a watch glass as systematically as possible.

Experimental

Materials

Green tea granules used in this work are the high-quality Sencha bag sealed in an aluminum film made by Hishidai Seicha, Shizuoka. Typical example of the optical microscopic pictures is shown in Fig. 2. The shape of the particles was plate-like. The size and the standard deviation from the mean size were 7 and 5 µm, respectively. 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).

Fig. 2 Optical microscopic picture of colloidal particles of green tea. *Objective lens* ×40, *eye lens* ×10, *length of the bar* 25 µm

Observation of the dissipative structures

Sixty milliliters of green tea was poured into an Ochawan, which was the same as the one used in the hotel of Yonezawa shown in Fig. 1a,b (90 mm in highest diameter and 51 mm in height). Ten milliliters of green tea was carefully put into a glass dish (42 mm in inner diameter and 15 mm in height, code 305-02, TOP, Tokyo) and a polystyrene dish (Petri dish, 52 mm in inner diameter and 10 mm in height, As One, Tokyo). Some 0.4, 1.5, 4, and 15 ml of tea suspensions were poured carefully into the very small, small, medium, and large watch glasses (30, 50, 70, and 100 mm in outer diameter, respectively, TOP, Tokyo). The initial temperature of the green tea was ca. 60 °C, and the suspensions were cooled down and kept at 24 °C in the air-conditioned room. The sedimentation and drying patterns were observed until the suspensions were dried up completely in a room air-conditioned at 24 °C and 60% in humidity.

Macroscopic dissipative structures were observed on a Canon EOS 10D digital camera (Canon, Tokyo) with a lens (EF 28–200 mm, *f*=3.5–5.6 USM, Canon). The shape and size of green tea colloids and the microscopic patterns were observed with a metallurgical microscope (PME-3, Olympus, Tokyo, Japan).

Results and discussion

Shielding effects on the sedimentation patterns of green tea in an Ochawan

Figure 1 shows the typical examples of the sedimentation patterns of green tea in the hotels in several cities from northern Hokkaido (Sapporo) to southern Okinawa of Japan (Ishigaki). Clearly, broad-ring patterns were always observed for the suspensions without cap in the suspension phase within 20 min. It should be noted that the broad ring, which is the accumulated layer of tea colloids, formed even on an inclined inner wall of Ochawan. The tea's colloidal particles were filtrated with the course filtering paper, and their sizes distributed widely from several micrometers to several tens of micrometers. A main cause for the broad-ring formation is undoubtedly the convectional flow of water and colloidal particles. Especially, the flow of the particles from the central area toward the outside edges in the lower layer of the liquid in a glass dish, 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 [20], is very important. Clearly, the convectional flow is enhanced by the evaporation of water at the liquid surface, resulting in the lowering of the suspension temperature in the upper region of the suspension. The broad ring in a watch glass was formed in the delicate balancing of the upward flow of tea colloids and the gravitational sedimentation of the particles.

It should be noted here that the broad-ring patterns *in the liquid phase* reported in this study were observed firstly for colloidal silica suspensions as the author knows [1–3]. However, the broad rings have been observed so often in the dried films from the solutions and suspensions examined by our group [18–28] and further by other researchers [4, 5, 7]. Recently, microgravity experiments were made for the drying dissipative patterns of deionized suspensions of colloidal silica spheres (Tsuchida et al., in preparation). Surprisingly, the broad-ring drying patterns did not disappear even in microgravity. This supports strongly that both the gravitational and the Marangonil convections contribute to the broad-ring formation in normal gravity, and the latter is still important in microgravity. We should further 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 [25].

Figure 3 shows the sedimentation patterns of green tea 30 min after the tea was set in an Ochawan and a glass dish. Pictures (a) and (c) were patterns when the suspensions were open, whereas (b) and (d) were the pictures when the suspensions were covered with a large watch glass and capped with a glass dish cover, respectively. Here, these covers were dispatched when pictures (b) and (d) were taken. The broad ring was clear and fine for the open samples, whereas the patterns were broad and vague for the capped ones. One of the main reasons why the broad rings formed rather fast even in the shield conditions was the fact that the initial temperature was high, ca. 60 °C, and the convectional flow of water and tea colloids was still vigorous. The other reason would be the fact that the shielding of the suspensions was not so complete for preventing evaporation of water. It should be mentioned in this study that the shielding effects for the colloidal silica suspensions were much significant [1].

Sedimentation patterns of green tea in a glass dish and polystyrene dish

Figure 4 shows the typical examples of the macroscopic sedimentation patterns of green tea in a glass dish from 1.5 to 18 h after the suspension was set. Broad ring formed rather quickly 30 min after the suspension was set, which again demonstrates that the convectional flow of water and colloidal particles was vigorous in our experimental conditions. It should be mentioned in this study that the sedimentary particles did not make contact with the bottom

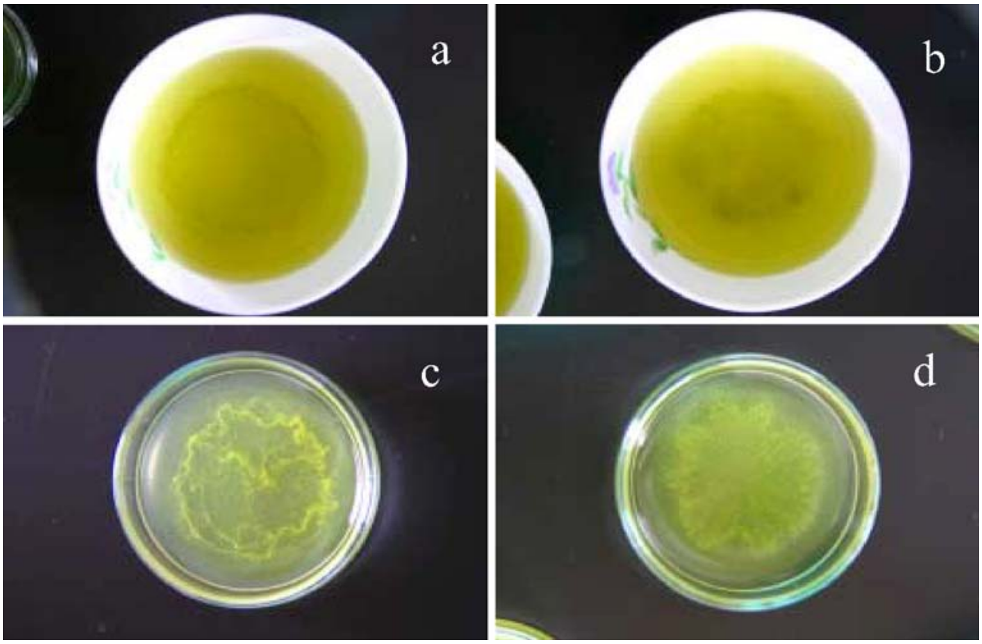

Fig. 3 Sedimentation patterns of green tea in a tea cup and a glass dish with and without shield at 24 °C. After 30 min, **a** tea cup, without shield, 60 ml, **b** tea cup, with shield, 60 ml, **c** glass dish, without shield, 10 ml, **d** glass dish, with shield, 10 ml

cell wall because the electrical double layers being formed around each particle and the cell wall were extended especially in the absence of the foreign salt. Thus, the sedimentary particles always moved by the convectional flow of water and the broad-ring patterns became sharp with time. In this study, the colloidal particles were observed to be aggregated slightly, which means that the green tea colloidal particles were not so stable in suspension state.

The sedimentation and the drying patterns were also observed in a polystyrene dish, though the pictures showing these were omitted in this report. The sedimentation patterns in a polystyrene dish were quite similar to those in a glass dish, and the broad ring was observed clearly. The inner cell wall of the polystyrene dish was highly hydrophobic, whereas that of the glass dish was hydrophilic. The patterns were, therefore, not influenced so much by the nature of the cell wall. It should be noted that the drying patterns in our experiments were not observed accurately in both dishes because the suspensions got musty within several days before complete dryness. However, the broad-ring drying patterns were formed clearly.

Sedimentation patterns of green tea in an inclined glass dish

Figure 5 shows the macroscopic sedimentation patterns of green tea in an inclined glass dish 2 to 17.5 h after the

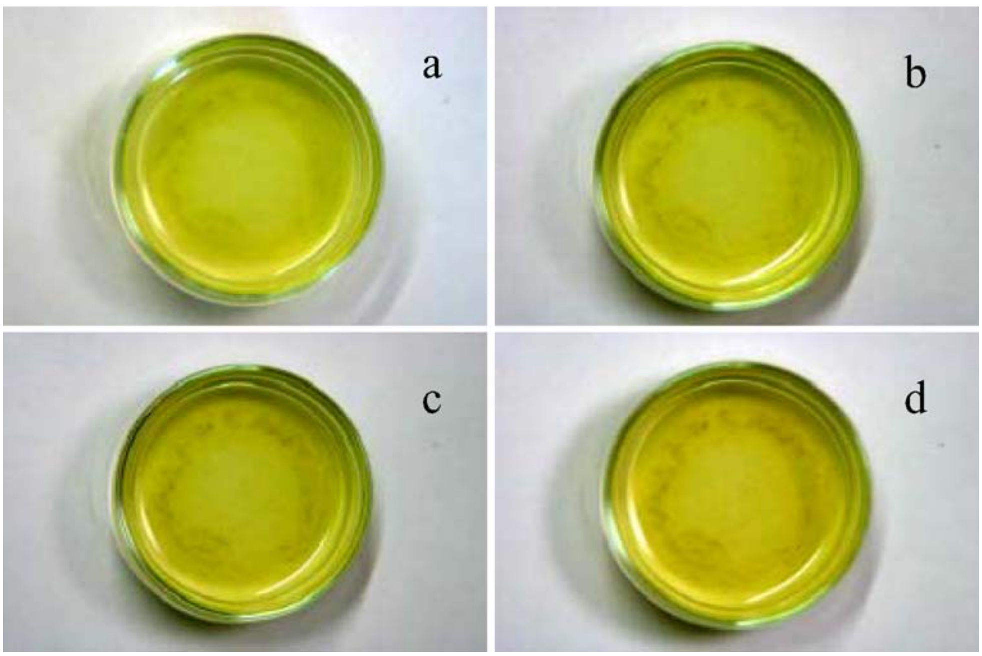

Fig. 4 Sedimentation patterns of green tea in a glass dish at 24 °C. Code 12, 10 ml, **a** after 1.5 h, **b** 5 h, **c** 10.3 h, **d** 18 h

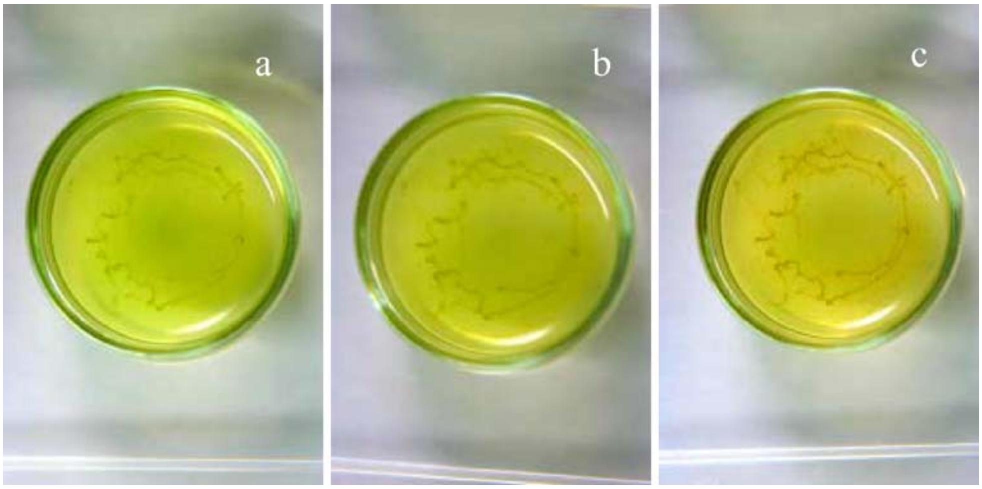

Fig. 5 Sedimentation patterns of green tea in an inclined glass dish at 24 °C. Code 21, 10 ml, *inclined angle* 5°, **a** after 2 h, **b** 8 h, **c** 17.5 h

suspensions were set. The inclined angle was 5°, and the right-hand side was lower. It is impressive that the broad ring was not transformed so significantly but shifted to the lower side slightly. This shows again that the convectional flow of the particles and water was striking compared with the sedimentation of the particles by the gravity even in room temperature.

Sedimentation patterns of green tea in a watch glass

Typical examples of the sedimentation and drying patterns formed in the course of dryness of green tea without salt in a watch glass are shown in Fig. 6. The accumulation of the particles occurred at the central area in addition to the broad ring, though the amount of the colloidal particles in the central area was small compared with that in the broad-ring area. The accumulation of the colloidal particles has been observed for the drying patterns of nonspherical particles and associated colloids on a cover glass hitherto [25]. Green tea colloids are plate-like, and a part of the colloids are aggregated. Furthermore there should be rather large particles of green tea because their polydispersity is very large. The rotational movement of the particles along the bottom cell plane must be highly restricted for the anisotropic-shaped particles, and the sliding movement will be in major form especially in the area close to the substrate plane. This restricted Brownian movement of the particles toward the outer and upper direction by the convectional flow must be correlated deeply to the appearance of the hill in the central area. It should be noted further that the broad-ring pattern in a watch glass was formed rather in inner area compared with the glass dish, which supports the sedimentation of the particles being not negligibly small.

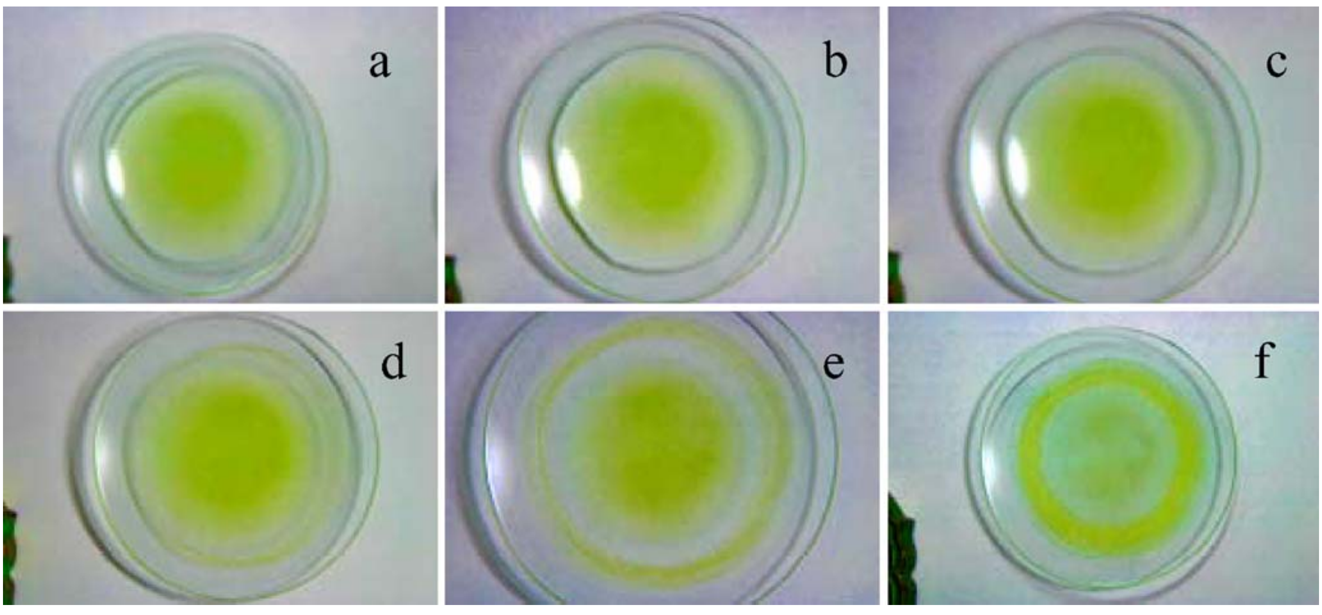

Fig. 6 Sedimentation and drying patterns of green tea in a watch glass at 24 °C. Code 141, 4 ml, **a** after 0.33 h, **b** 1.1 h, **c** 1.8 h, **d** 10 h, **e** 17.3 h, **f** 100.5 h, dry

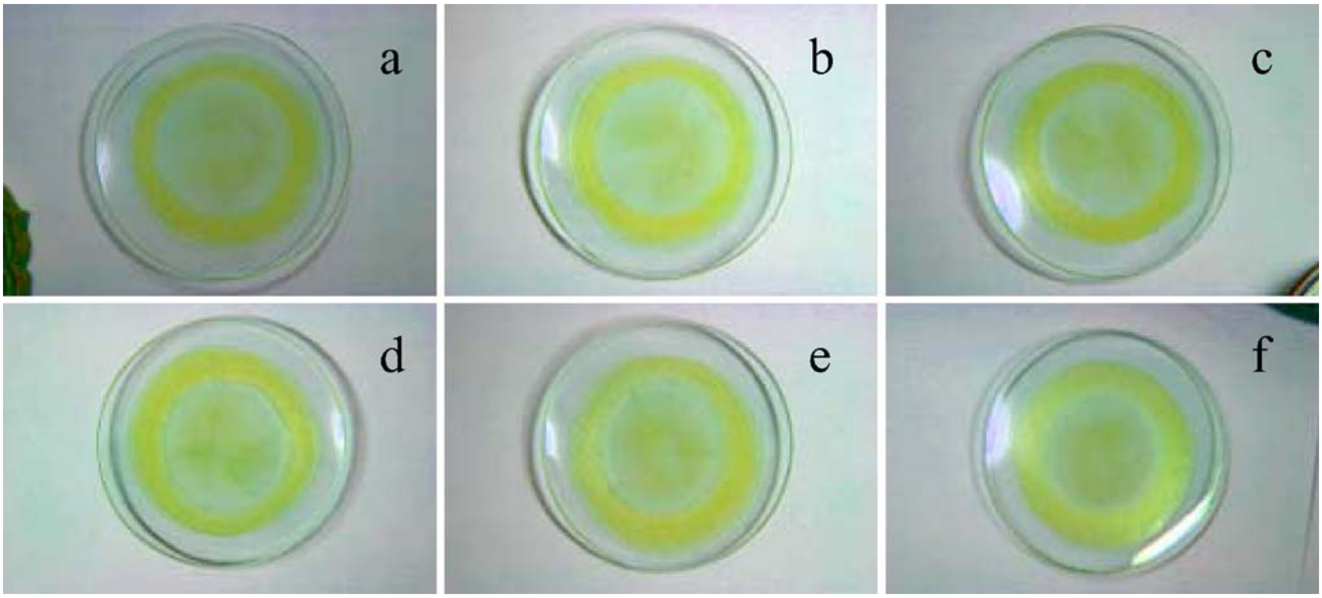

Fig. 7 Sedimentation and drying patterns of green tea in a watch glass at 24 °C. After 100.5 h, dry, 4 ml, **a** [NaCl] = 0 M, **b** 0.0003 M, **c** 0.001 M, **d** 0.003 M, **e** 0.006 M, **f** 0.01 M

Figure 7 shows the influence of sodium chloride added upon the drying patterns of green tea. The patterns were rather insensitive to the addition of the salt, but the accumulation of the particles in the central area looked like more significant in the presence of the salt. The sedimentation patterns were also quite insensitive to the salt addition, though the pictures demonstrating these were omitted in this report.

Figure 8a–e shows the sedimentation dissipative structures of 0.5 ml of the green tea in a very small watch glass. It is clear that the patterns were quite insensitive to the size of watch glasses used. Figure 8f shows one of the typical examples of the microscopic drying pattern close to the broad-ring area observed with the optical microscopy. The number density of the tea colloids was not so high unexpectedly.

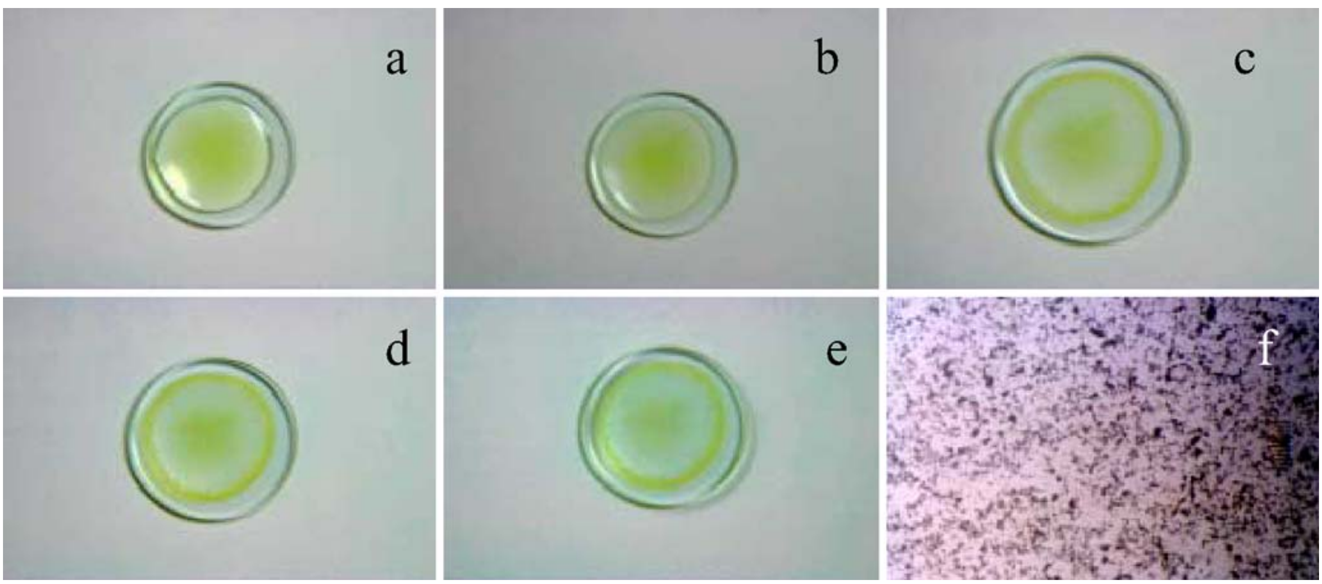

Fig. 8 Sedimentation and drying patterns and microscopic drying patterns of green tea in a very small watch glass at 24 °C. Code 151, 0.4 ml, **a** after 0.33 h, **b** 1.8 h, **c** 10 h, **d** 17.3 h, **e** 100.5 h, dry, **f** microscopic drying pattern close to the broad-ring area, *full scale* 0.2 mm

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