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ORIGINAL CONTRIBUTION

Convectional, sedimentation, and drying dissipative structures of black tea in the presence and absence of cream

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Abstract Convectional, sedimentation, and drying dissipative structures of black tea with and without cream were studied in a tea cup, a cover glass, a watch glass and a glass dish on macroscopic and microscopic scales. The convectional patterns were vigorous and irregular at the initial stage but soon highly distorted Bernard cells grew. The global integrated flows of the tea particles coated with cream at the air–suspension interface were observed vaguely from the central area toward outside edge at the initial stage in a tea cup and a large watch glass, but the flow direction turned oppositely from the outside to the central area. At the similar time, the short and few spoke lines appeared at the outside edge and grew long toward the central area. Then, the cooperative formation of clusters and bundles of the spoke lines took place at the middle and final convectional stages, and then the dynamic sedimentation patterns appeared. The drying patterns of tea with and without cream were composed of the broad ring at the outside edge and a round hill accompanied sometimes with the bundles of spoke lines. These features are consistent with those of suspensions of non-spherical particles. The pinning effect is not always supported by this work, but importance of the gravitational and Marangoni convectional flows is proposed instead.

Keywords Black tea · Black tea with cream · Convectional pattern · Sedimentation pattern · Drying pattern · Dissipative structure · Clusters · Bundles

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Introduction

In general, most structural patterns in nature form via self-organization accompanied with the *dissipation* of free energy and in the non-equilibrium state. In order to know the mechanisms of the dissipative self-organization of the simple model systems instead of the much complex nature itself, the authors have studied the *convectional*, *sedimentation*, and *drying* dissipative patterns during the course of drying colloidal suspensions and solutions as systematically as possible, though the three kinds of patterns are correlated strongly and overlapped to each other.

The most famous convectional pattern is the *hexagonal circulating* one, *Benard cell*, and has been observed when liquids contain plate-like colloidal particles as monitors and are heated homogeneously in a plain pan [1–3]. Another typical convectional dissipative pattern is the spoke-like lines, which were observed in the whole area at the liquid surface and also appeared in various substrates sometimes accompanied with the huge number of small *cell convections*. The spoke patterns with cell convections were observed formerly for the Chinese black ink by Terada et al. [4–7]. Authors like to call these patterns as *Terada cells*. The convectional patterns, especially Terada cells, were observed directly in the initial course of dryness of the Chinese black ink in a glass dish [8], the 100% ethanol suspensions of colloidal silica spheres [9], a cup of

Miso-soup [10], coffee [11], and colloidal crystals of poly (methyl methacrylate) (PMMA) spheres on a cover glass and a watch glass [12, 13]. Distorted Benard cells were often observed for Miso-soup, coffee, and black tea. For the 100% ethanol suspensions of colloidal silica spheres, Terada cell-type convectional flow was observed clearly, with the naked eye, and these convectional patterns changed dynamically with time. Deegan et al. [14, 15] have reported the traces of spoke-like patterns in the suspensions of polystyrene spheres (1 μm in diameter) under a microscope. They introduced the capillary flow theory accompanied with the pinning effect of the contact line of the drying drop. From our series of drying experiments for suspensions and solutions, however, the pinning effect was not always supported except experiments at high particle concentrations and/or for small colloidal particles and in the final stage of convections. In general, at low solute concentrations, the broad-ring-like drying patterns were always formed irrespective of the substrates used among a cover glass, a watch glass, and a glass dish, but they moved toward central area, and their size became small until the solute–solute *repulsive* or *attractive* interactions are strong enough to form the inter-solute structures on substrates such as critical concentration of the structure formation of colloidal crystals [12, 13], helix and sheet structures of biopolymers [16], or micelles [17, 18]. For typical anisotropic-shaped particles, furthermore, broad ring at the outside edge disappeared, and round hill appeared instead as described below. Calchile et al. [19, 20] reported that the droplets of completely wetting liquids deposited on a thoroughly smooth and wetting surface for which no contact line anchoring occurs. The author believes that the convectional flow of solvent and solutes is essentially important throughout the convectional, sedimentation, and drying pattern formation. The pinning effect was not supported in a glass dish, where drying frontier starts from the central area of a vessel substrate and developed toward outside. In conclusion, the broad-ring drying patterns were formed at the outside area. However, the broad rings became small when the solute concentration decreased. It should be mentioned further that theoretical and experimental studies for the convectional patterns have been made hitherto, but these are not always successful yet [12, 14, 15, 21–28]. It should be noted further that information on the *size*, *shape*, *conformation*, and/or *flexibility* of particles and polymers, for example, is transformed cooperatively and further accompanied with the *amplification* and *selection* processes toward the succeeding sedimentation and drying patterns during the course of dryness of solutions and suspensions [17, 18, 29, 30].

Recently, the whole growing processes of the convectional patterns were summarized in seven steps [10–13]. Firstly, at the initial stage of convection, appearance and disappearance of the circulating lines (*irregular circulations*) are formed at random in their direction accompanied with the *gravitational* upward transportation of heat. Secondly, global flow of the convection takes place at the surface layers from the center toward outward edge of the liquid. Thirdly, the cooperated distorted Benard cells form at the liquid surface. Fourthly, the reversed global flow of convection from the outside edge to the central area is observed at the liquid surface at the middle stage of convection. The reversal takes place mainly by the Marangoni convection. Fifthly, growing of the spoke lines from the outside edge to the central area takes place at the liquid surface layers. Sixthly, the clusters and further bundles of the spoke lines are formed at the final stage of convection. The bundles at the final stage of convection are also considered to be the sedimentation patterns and are further transformed to the drying patterns with fine structures. Growing of the broad-ring sedimentation and drying patterns are formed in the middle and/or final stage of convections. Seventhly, the convectional flow by the pinning effect proposed by Deegan et al. [14, 15] comes important at the final stage of convections.

Sedimentation dissipative patterns in a glass dish, a cover glass, a watch glass, and others have been studied in detail in the course of drying suspensions of colloidal silica spheres (183 nm to 1.2 μm in diameter) [31–36], size-fractionated bentonite particles [37], green tea (Ocha) [38], and Miso-soup [10], for the first time, in our laboratory. The broad-ring patterns were formed within several 10 min in suspension state by the convectional flow of water and the colloidal particles. It was clarified that the sedimentary particles were suspended above the substrate by the electrical double layers and always moved by the balancing of the external force fields, including convectional flow and sedimentation. Sharpness of the broad rings was sensitive to the time gradients in the room temperature and/or humidity [31]. The main cause for the broad-ring formation is due to the convectional flow of water and colloidal particles at the different rates, where the rate of the latter is slower than that of the former. Quite recently, it was clarified that the dynamic bundle-like sedimentation patterns formed cooperatively from the spoke line-like convectional structures of colloidal particles for coffee [11], colloidal crystals of PMMA spheres [12, 13], and black tea (this work).

Drying dissipative patterns have been studied for suspensions and solutions of colloidal particles [8–11, 31–55], linear-type synthetic and bio-polyelectrolytes [16, 29], water-soluble neutral polymers [56, 57], ionic and nonionic detergents [17, 18, 30], gels [58], and dyes [59] mainly on a cover glass. The macroscopic broad-ring patterns of the hill accumulated with the solutes in the outside edges formed on a cover glass, a watch glass, and a glass dish. Size of the broad rings decreased when solute concentration and/or solute size decreased. For the non-spherical particles, the round hill was formed in the center area in addition to the broad ring [37]. Macroscopic spoke-like cracks or fine hills, including flickering spoke-like ones, were also observed for many solutes. Furthermore, beautiful microscopic fractal patterns such as earth worm-, branch-, arc-, block-, star-, cross-, and string-like ones were observed. These microscopic drying patterns were often reflected from the shape, size, and/or flexibility of the solutes themselves. Microscopic patterns also formed by the translational Brownian diffusion of the solutes and the electrostatic and/or the hydrophobic interactions between solutes and/or between the solutes and the substrate in the course of the solidification. One of the very important findings in our experiments is that the primitive vague sedimentation patterns were formed already in the liquid phase before dryness, and they grew toward fine structures in the process of solidification [37].

In this work, the convectional patterns of black tea were observed clearly with the naked eyes by addition of cream like coffee plus cream system [11]. Convectional, sedimentation, and drying dissipative patterns of black tea with and without cream have been studied on the macroscopic and microscopic scales. One of the main purposes of this work is clarification of the convectional pattern formation processes with a help of the experimental data of black tea plus cream on the various substrates.

Experimental

Materials

Black tea bags (Lipton, Yellow Label Tea, Unilever Japan, Tokyo) were available commercially. Each bag contained 2 g of crushed tea leaves. Cream was coffee flesh (Sujahta, 5 ml pack, vegetable oils and fats, Nagoya Seiraku, Nagoya). Hot tea was prepared by swing three bags in a tea pot (Sweet Plum, Wedgwood, England) containing hot water (ca. 450 ml). Tap water of Uji city (Kyoto) was used for tea preparation, and the dilution of the black tea was made with water purified by a Milli-Q reagent grade system (Milli-RO plus and Milli-Q plus, Millipore, Bedford, USA).

Observation of the dissipative structures

Tea (130 ml) with or without cream was put into a tea cup (105 mm in upper outside diameter and 55 mm in height, Blue Plum, Wedgwood). Aliquot (0.1 ml) of tea without or with cream was carefully and gently placed onto a micro-cover glass (30 mm×30 mm, thickness 0.12 to 0.17 mm, Matsunami Glass, Kishiwada, Osaka, Japana) set in a plastic dish (type NH-52, 52 mm in diameter, 8 mm in depth, As One, Tokyo). The cover glasses were used without further rinse. Tea suspensions (40 and 1 ml) with and without cream were set on the large (150 mm in diameter, TOP, Tokyo) and small watch glasses (50 mm, TOP), respectively. The suspensions (3 ml) were put into a medium glass dish (42 mm in inner diameter and 15 mm in height, code 305-02, TOP, Tokyo). The disposable serological pipets (1 and 10 ml, Corning Lab. Sci.) were used for the putting the suspension in the substrates. The convectional, sedimentation, and drying patterns were observed for the suspensions on a desk covered with a black plastic sheet in most experiments and also covered with a white luster paper for ink-jet printing (type IT-122GH 46-135, Plus Stationary, Tokyo). The room temperature was regulated at 25 °C. Humidity of the room was not regulated and between 40% and 60%.

Macroscopic patterns were observed on a Canon EOS 10 D digital camera with a macro-lens (EF 50 mm, f=2.5) plus a life-size converter EF and a zoom-lens (Canon, EF28-70 mm, 1:2.8) on a cover glass, a medium glass dish or a small watch glass, and a tea cup or a large watch glass, respectively. Microscopic drying patterns were observed with a metallurgical microscope (PME-3, Olympus, Tokyo). Thickness profiles of the dried films were measured on a laser 3D profile microscope (type VK-8500, Keyence, Osaka, Japan).

DLS and electrophoresis light-scattering measurements

The dynamic light-scattering (DLS) measurements were made on a DLS-7000 spectrophotometer (Otsuka Electronics, Osaka) at 25±0.02 °C. The sample of 5 ml was set in a Pyrex tube cell (12 mm outside diameter and 130 mm long). Data analysis was made with the cumulant analysis. Histogram methods, including the non-negative least square and the Marquadt analyses, were also made for discussing the size distribution of tea particles with cream. The zeta-potential measurements were made on an electrophoresis light-scattering spectrophotometer (LEZA-6000, Otsuka Electronics). The reproducibility of the ζ potential was within 5%.

Results and discussion

Characterization of colloidal particles of black tea with and without cream

Compositions of the tea leaves are carbohydrate (51.7% in weight), protein (20.3%), lipid (2.5%), ash (5.4%), caffeine (2.9%), tannin (11%), and water (6.2%) [60]. The flesh cream is composed of vegetable oils and fats, dairy products, sugar, casein (originated in milk), and emulsifier (originated in bean) as reported by the manufacturer. Table 1 shows size and zeta-potential values of the tea colloids with cream. The mean size was obtained with cumulant data treatment of the dynamic light-scattering data. Mean size of tea plus cream colloidal particles was 319 nm. It should be recalled that the mean sizes of coffee and coffee plus cream colloidal particles were 455 and 212 nm, respectively, and the former was twice as large compared with the latter [11]. This supports that the tea particles apt to aggregate in suspension state, though the colloidal size of tea without cream was not measured in this work. On the other hand, tea particles are coated with the cream layers (mainly composed of oils and fats) and forms small and stable dispersions. Zeta potentials of black tea without and with cream were negative and −20 and −54 mV, respectively. These values in the zeta potential also supports that the black tea particles coated with cream are more stable than the bare tea particles in suspension state since the colloidal particles having large absolute values of zeta potential are more stably dispersed in general. It should be noted here that the biological decomposition of the black tea took place after 2 days at 25 °C whether the cream coexisted or not.

Convectional patterns of black tea with cream in a tea cup

Tea without cream in a cup did not show any convectional patterns during 24 h after setting the suspension on a desk. However, when a 5 ml pack of cream was added into the tea and mixed homogeneously in a cup, the convectional patterns appeared at the liquid surface and changed dynamically with time during observation period. These features of tea suspensions are quite similar to those of coffee with and without cream [11]. Figure 1 shows a typical example of the convectional patterns of tea plus cream system during 12 h after setting. After 2 min, irregular convectional circulating patterns were formed. However, size of the patterns was small. The cooperation seems not to operate among the small patterns. The gravitational upward transfer of heat also takes place at the similar time. Within 1 h, the global convectional flow of suspension from the central area to the outside edge along the liquid surface was observed, and the circulating patterns had some regular structure like the distorted Benard cell whole the air–liquid surface. The cooperative pattern formation takes place between the neighboring convection cells. It should be noted here that temperature gradient in the bulk phase of liquid, higher temperature at higher layers, is formed. Furthermore, the liquid temperature at the air–liquid interface is lowered sharply by the water evaporation at the interface. This temperature gradient was observed and discussed already in the coffee suspensions [11]. After 4 h, a broad ring and a large number of spoke lines formed in the inner region and the areas between the ring and outside edge of the liquid surface, respectively. The reversal of the global integrated flow was observed rather vaguely compared with those of coffee [11] and Miso-soup systems [10]. The broad ring did not keep its position with time and moved very slowly and repeatedly between the center and the outside area. Several other experiments in a cup were made in this work at different initial liquid temperatures between 40 and 80 °C. The similar convectional patterns formed to each other.

The most plausible reason why the convectional patterns were observed for tea plus cream systems is that the tea colloids coated with the cream are suspended in the thin layer of cream. It should be recalled that Chinese black ink is quite similar to the black tea or coffee plus cream. The carbon particles originated in soot of the Chinese ink are coated with glue and also floated in the thin layer of glue at the interface [4–6]. The convectional patterns of Chinese black ink were also observed clearly [8]. The authors believe that the tea plus cream colloidal particles also apt to aggregate each other but very *weakly* and *reversibly* like Chinese black ink and coffee. Then, the significant flow birefringence effects of large-sized temporal aggregates play an important role for the pattern formation observable with the naked eyes. It should be mentioned further that colloidal crystals of PMMA spheres, which are weakly hydrophobic in water and also apt to aggregate reversibly, showed the clear convectional patterns at the air–liquid interface on a cover glass and a watch glass [12, 13].

A main cause for the broad-ring formation is due to the convectional flow of water and colloidal particles in the different rates, i.e., the translational motion of colloidal particles are slower than water molecules. Especially, flow of the spheres from the central area toward the outside edge in the lower layer of the liquid, which was observed with the naked eyes for suspensions of Chinese black ink in a glass dish [8] and PMMA on a cover glass and a watch glass [8, 12, 13], is important. The convectional flow in a

Table 1 Size and zeta-potential data of black tea colloids that coexisted with and without cream

Suspension	Mean size (nm)	Size distribution (nm)		Zeta potential (mV)
		First peak	Second peak	
Black tea	–	–	–	−20.4
Black tea+cream	319±0.2	316±60	None	−54.2

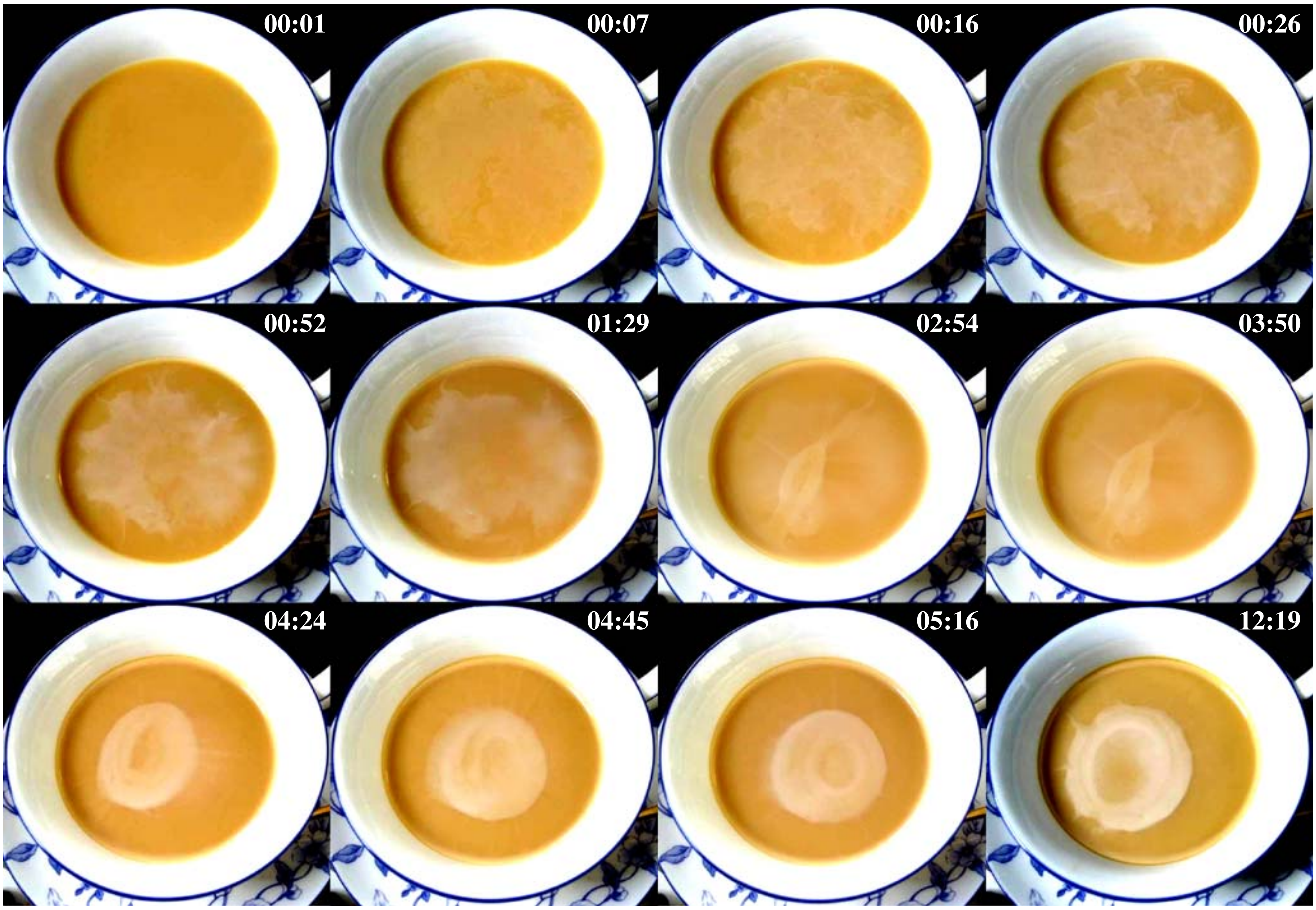

Fig. 1 Convectional patterns of black tea with cream in a tea cup. Exp. 1, w=1.6 wt.% (black tea 0.3 wt.%, cream 1.3 wt.%), 130 ml, liquid temperature decreases from 70 to 25°C, times show [hours/minutes]

cup is enhanced by the evaporation of water at the liquid–air surface, resulting in the lowering of suspension temperature in the interface region of the suspension. When the colloidal particles reach the outside edge of the liquids at the lower layers along the cell wall, a part of the particles will turn upward and go back to the central region at the air–liquid interface. It should be noted that the spoke lines grew mainly from the outside edge *toward center* at the air–liquid interface accompanied with a large number of cell convections in the normal direction to the spoke lines, "Terada cell". It should be further noted here that the broad-ring-like sedimentation patterns must be formed on the bottom layers of liquid in a cup [29–36], though the direct observation was impossible because the cup was made of porcelain.

Dissipative patterns of black tea with and without cream on a cover glass

Tea without cream did not show any clear convectional patterns during the course of dryness as is shown in Fig. 2*a* (in the Electronic supplementary materials). On the other hand, the rather clear convectional patterns appeared by the addition of cream into tea (see Fig. 2 and Fig. 2*b* (in the Electronic supplementary materials)). Here, room temperature was kept at 25°C during observation. The concentrations of the tea with and without cream in Fig. 2 were lowered by addition of pure water. Fifteen minutes after setting, the vague block- or broad-ring-like patterns appeared around the central area to the outside region of the air–liquid interface (see Fig. 2 and Fig. 2*b* (in the Electronic supplementary materials)). Furthermore, a large number of short spoke lines were observed at the outside edge of the liquid. The cooperative convectional patterns of the spoke lines are clearly formed. After 1 h and 5 min (see Fig. 2, for example), cooperative clustering of the several spoke lines started, and number of spoke lines decreased but the spoke lines became thick and clear. Furthermore, bundles of the cluster were recognized in the inner area of the liquid surface (see Fig. 2 and Fig. 2*b* (in the Electronic supplementary materials)). The bundles from the clustered spoke lines grew with time, and about 12 main bundles

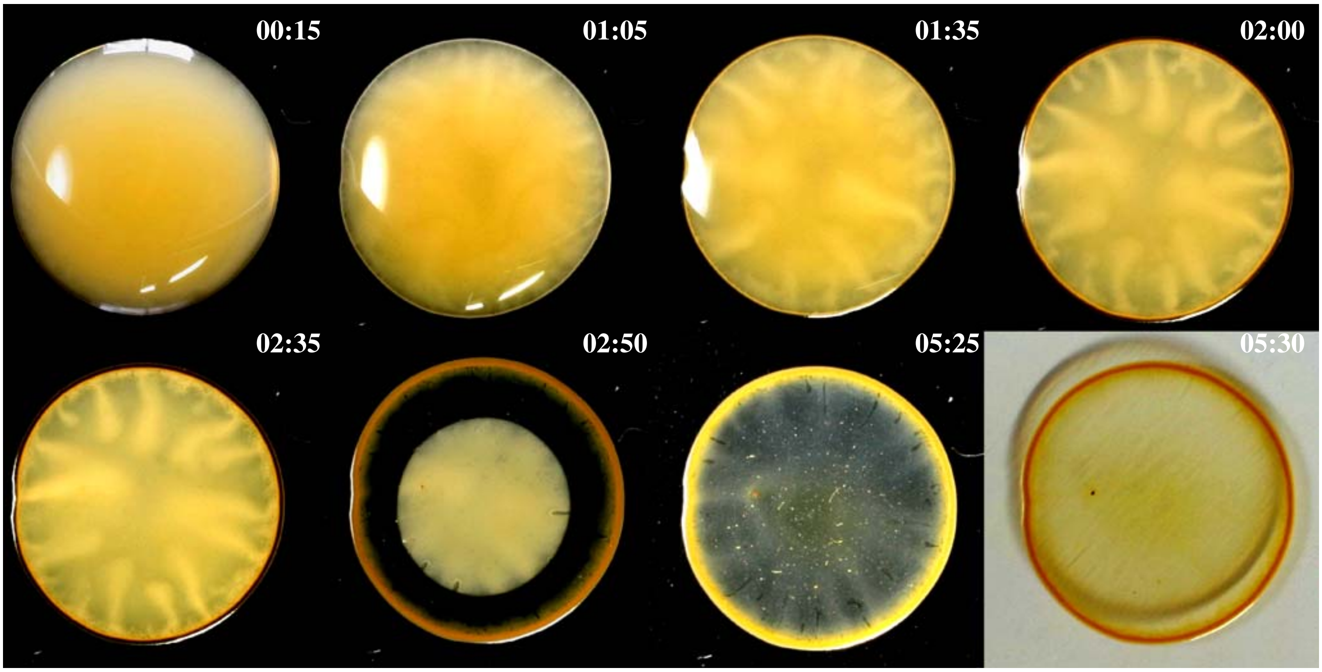

Fig. 2 Convectional, sedimentation, and drying dissipative patterns of black tea with cream on a cover glass at 25°C. w=0.8 wt.% (black tea 0.15 wt.%, cream 0.65 wt.%), code 1034, 0.1 ml, times show [hours/minutes]

were formed after 1 h and 35 min (see Fig. 2*b* (in the Electronic supplementary materials)). These bundles further grew, and seven main bundles are observed after 2 h and 40 min (see Fig. 2*b* (in the Electronic supplementary materials)). Convectional patterns showing the clusters and bundles were observed also for other tea plus cream suspensions, i.e., the stock suspensions and their diluted ones, where one part of the stock suspensions were diluted with nine parts of pure water, for example.

The formation of the clusters and the bundles from the spoke lines were observed clearly in this work and for coffee plus cream [11]. Furthermore, quite similar patterns have been observed for colloidal crystals of PMMA spheres in a watch glass (see Figs. 4f and 5f of Ref. [13]). Furthermore, the vigorous changes in the convectional flow of colloidal silica spheres in ethanol also support the formation of the clusters and bundles [9]. Figure 2 and Fig. 2*b* (in the Electronic supplementary materials) show the pictures, where dryness was almost completed at the broad-ring area, but the inner area is still liquid state, though the completion of dryness is very immediate. In other words, the bundle-like patterns in the final stage of convection are already sedimentation patterns. It should be noted that the clusters and then bundles in the sedimentation state are originated in the spoke lines and always change their forms *dynamically* and *cooperatively.*

Figure 3 shows the thickness profiles of the dried films of tea without cream. Figure 3 c and d are profiles with cream. Two high peaks at the outside edges correspond to

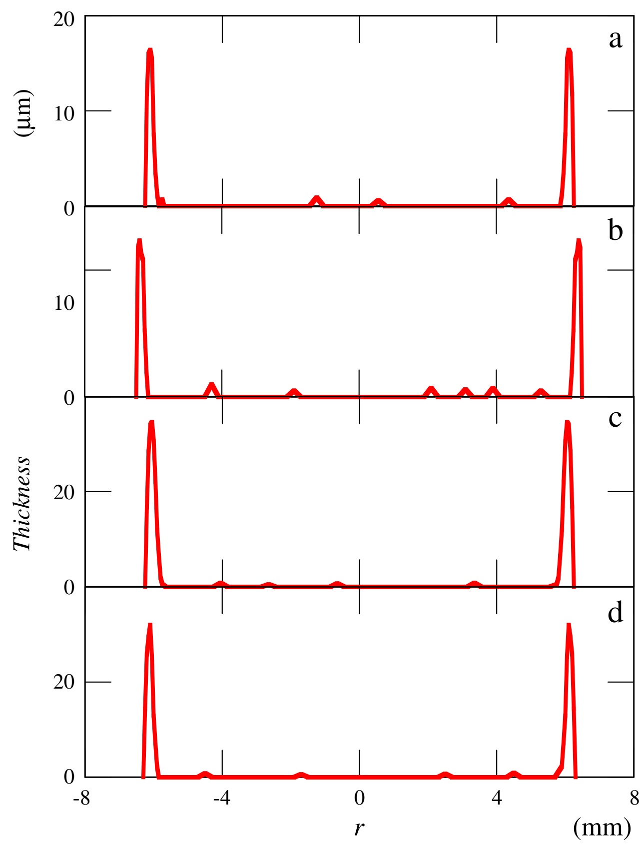

Fig. 3 Thickness profiles of the dried film of black tea without cream (*a*, *b*) and with cream (*c*, *d*) on a cover glass as a function of the distance from the center at 25°C. *a* w=0.3 wt.%, *b* 0.15 wt.%, *c* 1.6 wt.%, *d* 0.8 wt.%

the broad ring. We should note here that the small hills or rings always coexisted at the inner area of the film. This supports that the large and non-spherical colloidal particles of tea distribute at the almost all areas in addition to the broad rings. Figure 2*a* (in the Electronic supplementary materials) also shows clearly the coexistence of the broad ring and the particle accumulation at the outside edge and the central area, respectively. Shape of the colloidal particles of tea with and without cream must not be spherical. The authors have observed the round-hill-like accumulation of the non-spherical bentonite particles that took place at the central areas of the dried film in addition to the broad ring [37]. Furthermore, the segregation effect in the drying patterns was also observed for the binary and ternary mixtures of colloidal silica spheres [35, 36]. Here, the small and large spheres were separated toward outside and inside areas, respectively.

Accumulation of the tea colloids at the inner area of the film (bundle-like pattern sometimes) in addition to the brown broad ring at the outside edge was also clearly observed irrespective of cream addition by the microscopic observation of the dried film shown in Fig. 4a and b. It should be mentioned here that patterns of the dried film of tea plus cream systems shown in Fig. 4b seem to be much fine in their textures than those of the film without cream shown in Fig. 4a. This

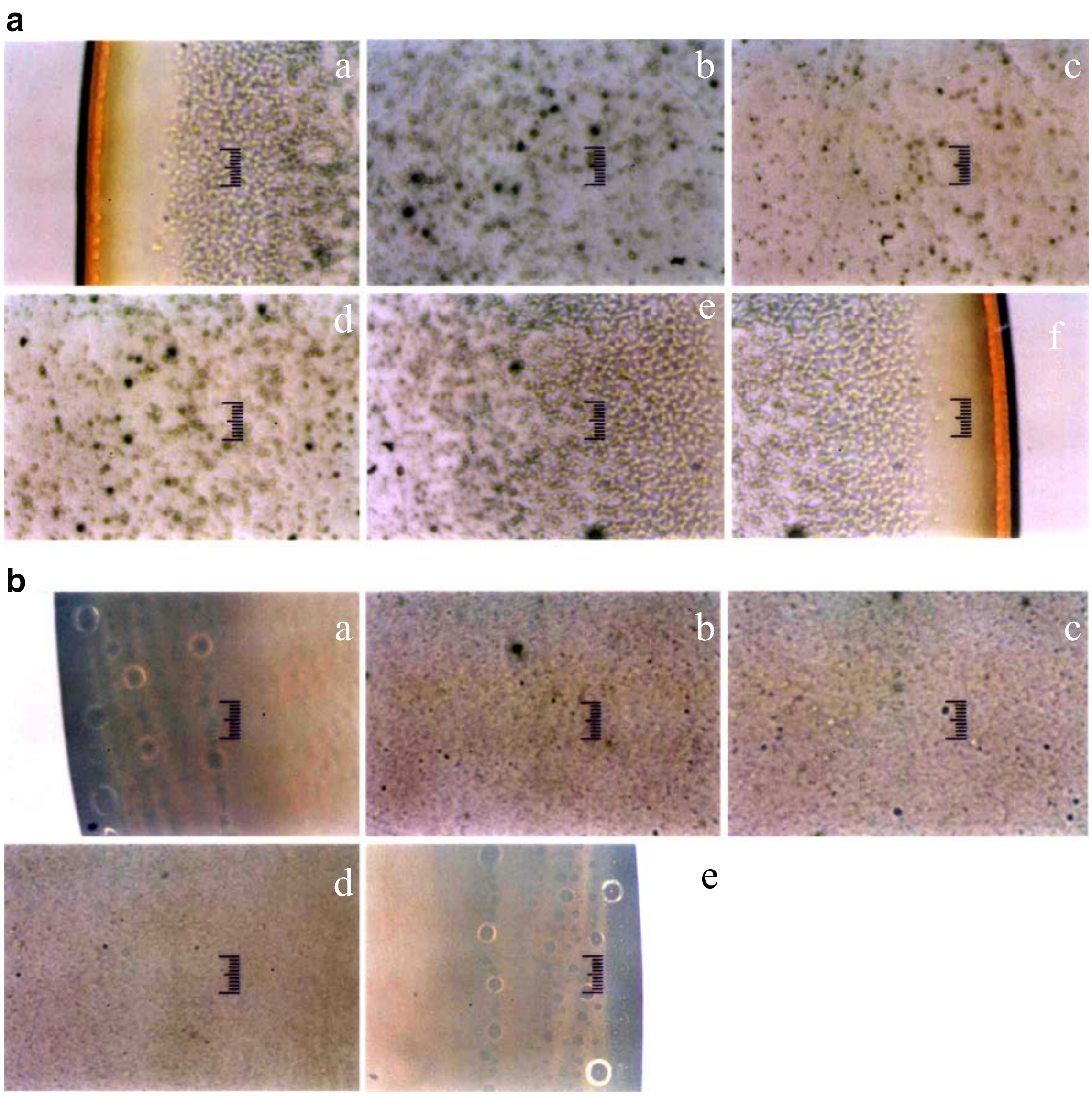

Fig. 4 **a** Microscopic drying patterns of black tea without cream on a cover glass at 25°C. w=0.3 wt.%, code 901, 0.1 ml, from left edge (*a*) to right (*f*), full scale=100 μm. **b** Microscopic drying patterns of black tea with cream on a cover glass at 25°C. w =1.6 wt.% (black tea 0.3 wt.%, cream 1.3 wt.%), code 902, 0.1 ml, from left edge (*a*) to right (*f*), full scale=100 μm

observation is consistent with the fact that size of the coffee colloids with cream is less than that of the colloids without cream.

Let us discuss the positions of the broad rings in the dried film of tea suspensions. The ratios of the final size of the broad rings in diameter (d_f) against the initial size of the liquid in diameter (d_i) were measured on a cover glass. The size of the broad ring was measured as the distance between outside positions, not the peak center positions of the rings (observed in Fig. 3, for example). The d_f/d_i values in the range of particle concentrations measured were very close to unity irrespective of the particle concentration examined. This constancy was also observed for coffee suspensions [11] and looks to support the pinning hypothesis of the contact line proposed by Deegan et al. [14, 15]. However, we have often observed hitherto that the ratio d_f/d_i decreased substantially from unity when the solute concentrations decreased sharply. For example, the d_f/d_i values of colloidal silica suspensions of CS45 (56.3 nm in diameter) [47], CS82 (103 nm) [45], and CS301 (311 nm) [47] were ca. 0.1, 0.2, 0.4, 0.5, 0.9, and 1.0 when sphere concentrations were 1.33×10^{-9}, 1.33×10^{-7}, 1.33×10^{-5}, 0.00133, 0.0133, and 0.0333, respectively, in volume fraction. The similar concentration effect on the broad rings has been observed for suspensions or solutions of polystyrene spheres [46], ionic detergents [17], neutral and water-soluble detergents [18], biological polyelectrolytes such as sodium poly-α-L-glutamate, poly-L-lysine hydrobromide [16], and polyethylene glycol (PEG) [57]. It should be mentioned here that the d_f/d_i values of polystyrene sphere suspensions were rather insensitive to sphere concentration, i.e., d_f/d_i values were 0.95, 0.97, 0.97, 0.97, and 1.0 when sphere concentrations were 0.0089, 0.021, 0.044, 0.050, and 0.066, respectively [46]. Clearly, d_f/d_i values of the suspensions and the solutions were quite insensitive to the high solute concentrations ranging 0.001 to 0.05 in volume fraction. Thus, it is highly plausible that the shift of the broad ring takes place at the very low particle concentrations, though the observation of the broad rings at the very low concentrations was impossible in this work. In conclusion, the observations hitherto show the shift of the broad ring certainly as solute concentration decreases, and then the pinning effect is not supported. It should be mentioned here further that the d_f/d_i values are also sensitive to other several experimental parameters in addition to the solute concentration described above. d_f/d_i values of PEG solutions decreased from unity as molecular weight of PEG decreased [57]. The d_f/d_i values of thermo-sensitive gel spheres of poly (*N*-isopropyl acryl amide) decreased sharply and transitionally at low temperature [58]. The broad rings shifted toward inner area of the dried film for the ethyl alcohol and ethyl alcohol plus methyl alcohol mixture suspensions of colloidal silica spheres on a cover glass [51]. Furthermore, the broad rings of aqueous colloidal silica suspensions formed at the inner area in addition to the outside edge when the dryness proceeded at high humidity atmosphere [53]. In the binary and ternary mixtures of colloidal silica spheres, the broad rings of larger spheres always appeared at the inner area of a dried film [35, 36]. Thus, the pinning effect is not so important in general for the drying pattern formation. However, in the final stage of convections, liquid flow will take place by the pinning effect induced by the drying area within the broad ring. Quite recently, the authors observed that the small single crystals are formed around the large crystals by the pinning effect.

Dissipative patterns of black tea with and without cream in a watch glass

In a small watch glass, the dissipative patterns of tea with and without cream were observed (see Fig. 5). Tea without cream did not show any clear convectional patterns (see Fig. 5*a* (in the Electronic supplementary materials)). However, broad-ring-like sedimentation patterns were observed even without cream as shown in the pictures at 19:10 and 20:15 in Fig. 5. The drying patterns of tea without cream showed rather sharp ring structure at the outside edge and the thick broad ring at the inner area from the outside edge. The main reason for the broad-ring formation at the inner area is the fact that the tea particles are non-spherical and highly polydispersed in their size and shape.

In the presence of cream, the convectional patterns were observed in a small watch glass as is shown in Fig. 5 and Fig. 5*b* (in the Electronic supplementary materials). Several important convectional patterns like those on a cover glass described above were again observed. Firstly, spoke lines appeared at the outside edge. Secondly, they grew long and a number of them increased. Thirdly, the clustering of the spoke lines accompanied with decrease in the number of the spoke lines took place. Fourthly, the bundles were further formed from the clusters. Pictures at 20:15 and 19:10 of Figs. 5 and 5*b* (in the Electronic supplementary materials) are the final drying patterns on the black and white sheets, respectively. Impressively, the cluster and the bundle structures remained clearly on the drying patterns especially when the suspension concentration was low.

When a large amount of tea plus cream suspensions was set in a large watch glass, (a) the irregular circulating line patterns were observed within 30 min (see pictures at 00:01 to 00:32 in Fig. 6). (b) Between 5 and 15 min, global flow of suspension at the liquid surface was in the direction from center to outside edge. (c) Then, global flow was reversed

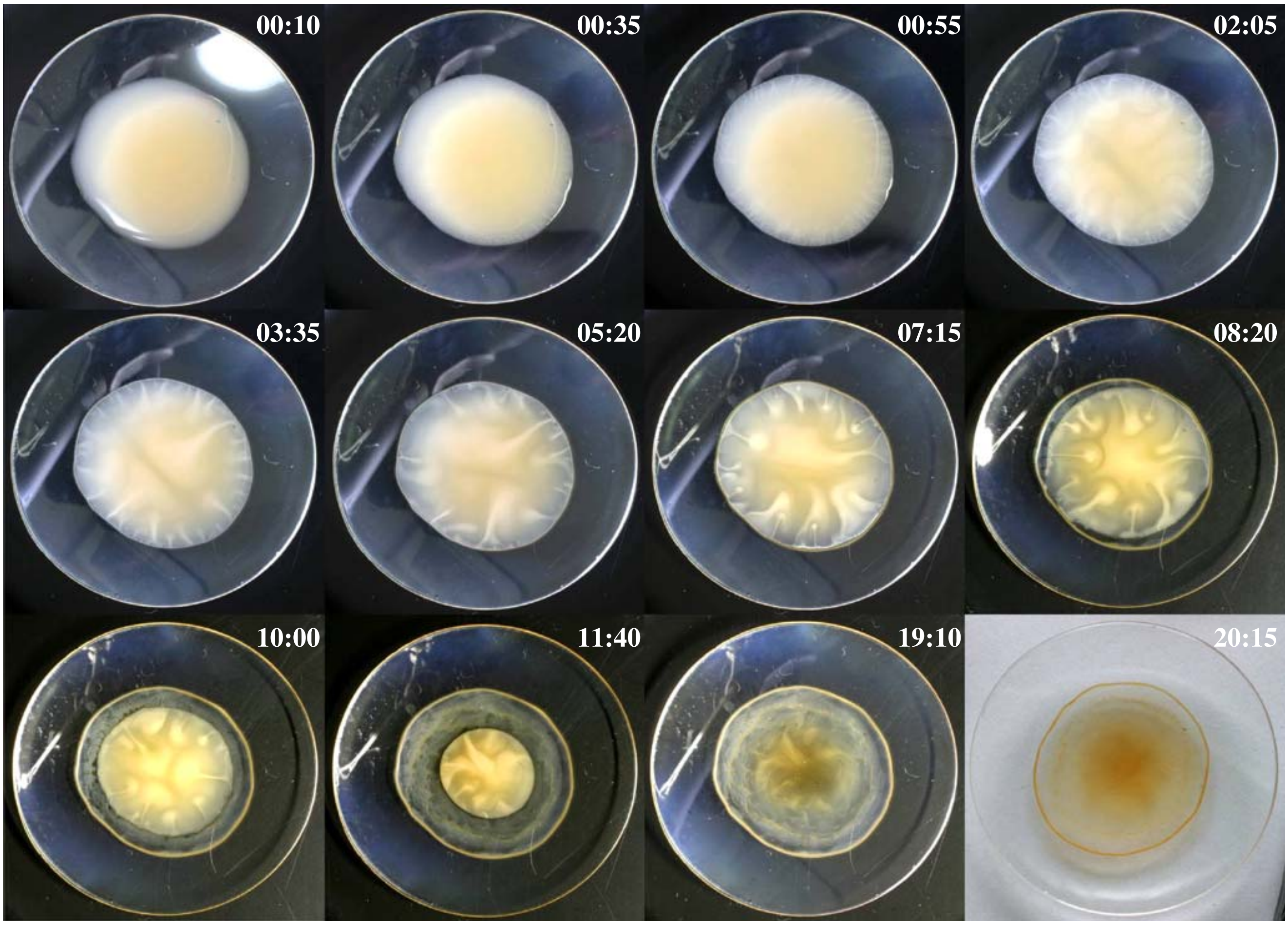

Fig. 5 Convectional, sedimentation, and drying dissipative patterns of black tea with cream in a small watch glass at 25°C. w=0.48 wt.% (black tea 0.09 wt.%, cream 0.39 wt.%), 1 ml, picture after 20 h 15 m: on a white sheet, times show [hours/minutes]

from outside edge toward center after 22 min, and (d) at the similar time, growth of the spoke lines toward central area and formation of the clusters and bundles were observed. (e) After about 3 h, the clusters of the spoke lines and the bundles were further formed. Change in the convectional patterns is quite similar to that of coffee plus cream systems [11]. We should note here that the reversal of the total flow is correlated deeply with the Marangoni effect [26, 61].

Summarizing our observations of convectional patterns of tea with cream in a large watch glass, (1) at the initial stage within 5 min, appearance and disappearance of the circulating lines took place at random in their direction. (2) During time between 5 to 15 min, total flow of convection at the surface layers was from the center toward outside edge. (3) Around 20 min after setting, few and short spoke lines appeared at the outside edge. Then, the number of the spoke lines increased. (4) At the similar time of the spoke line formation, total flow of convection was reversed from outside edge to the central area, and the outward flow remained until solidification started. (5) Growth of the spoke lines and formation of the clusters and bundle took place during time from 3 min to 7 h or more, though the observation ceased at that time in Fig. 6.

Dissipative patterns of black tea with and without cream in a glass dish

A typical example of the dissipative patterns of tea with and without cream during the course of dryness in a glass dish is shown in Fig. 7. In the absence of cream, any convectional pattern was not observed as is shown in Fig. 7*a* (in the Electronic supplementary materials), but the patterns appeared in their presence. In the initial stage of convections before 45 min shown in Figs. 7 and Fig. 7*b* (in the Electronic supplementary materials), quite vigorous circulating lines appeared like those in a watch glass. These irregular convection cells were interacted cooperatively after 45 min, and the distorted Bernard cells were formed in the inner region at the surface of the dish. The distorted Bernard cells changed dynamically to the very big single bundle of the spoke lines after passing about 20 h.

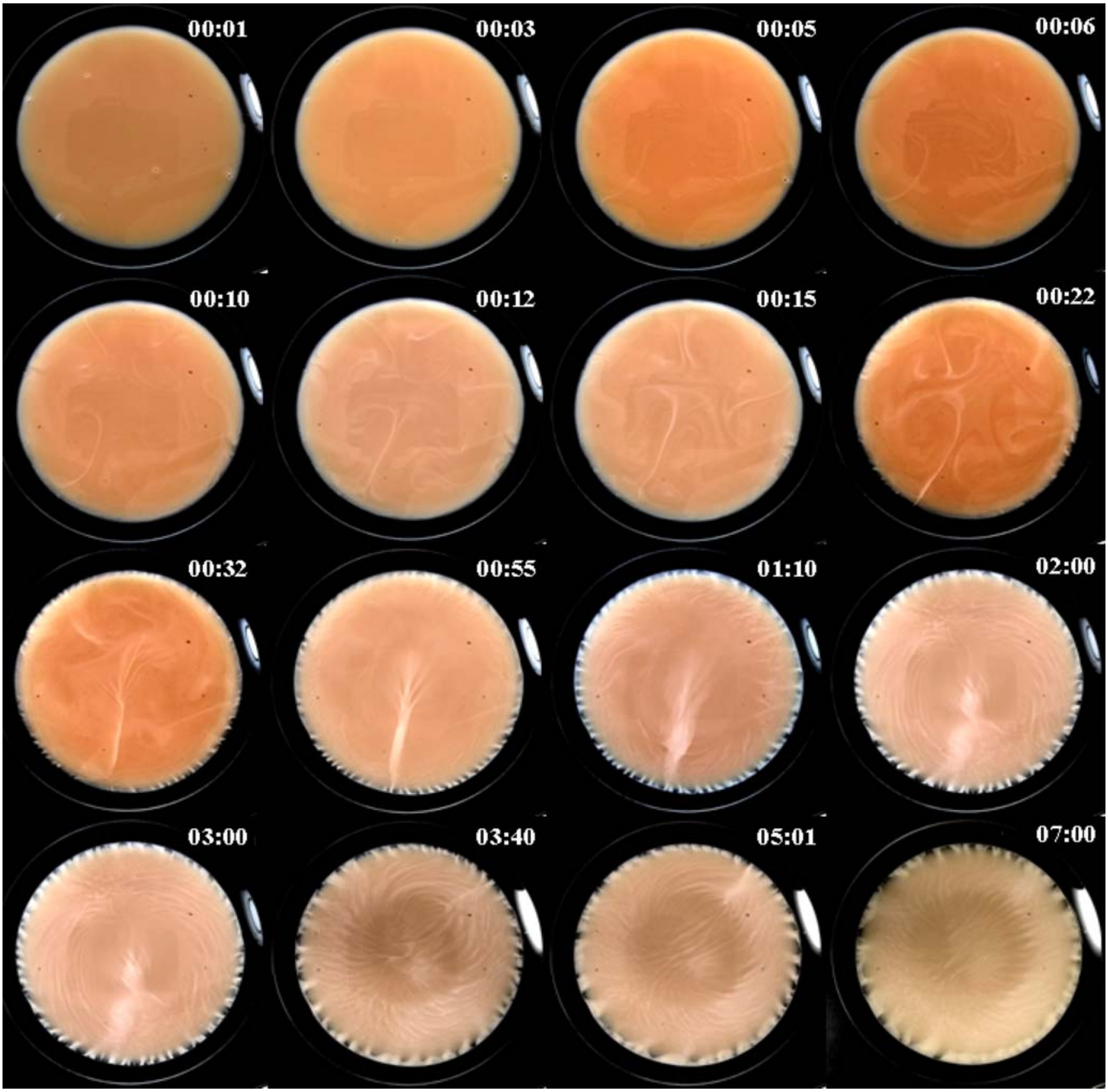

Fig. 6 Convectional, sedimentation, and drying dissipative patterns of black tea with cream in a large watch glass. Liquid temperature decreases from 40 to 25°C. w=1.6 wt.% (black tea 0.3 wt.%, cream 1.3 wt.%), 40 ml, times show [hours/minutes]

However, growth of the spoke lines at the outside edge of the dish was not recognized directly and clearly with the naked eyes. However, the spoke line formation was easily deduced from the traces of many spoke lines at the outside edges in the dried film. Interestingly, the big bundle pattern is quite similar to the drying pattern. This observation supports that the big bundle is already dynamically stable sedimentation pattern, and further, the drying patterns are originated in the sedimentation pattern. It is clearly recognized that the broad ring and a round hill patterns coexisted at the inner region from the cell wall and central region, respectively, in the dried film. This observation again supports that the tea with cream colloidal particles are non-spherical like bentonite particles studied previously [37].

It should be mentioned here that aerobic bacteria often lived in thin layers near substrate–air–water contact lines [62]. Surprisingly, the bacteria made the spoke lines and

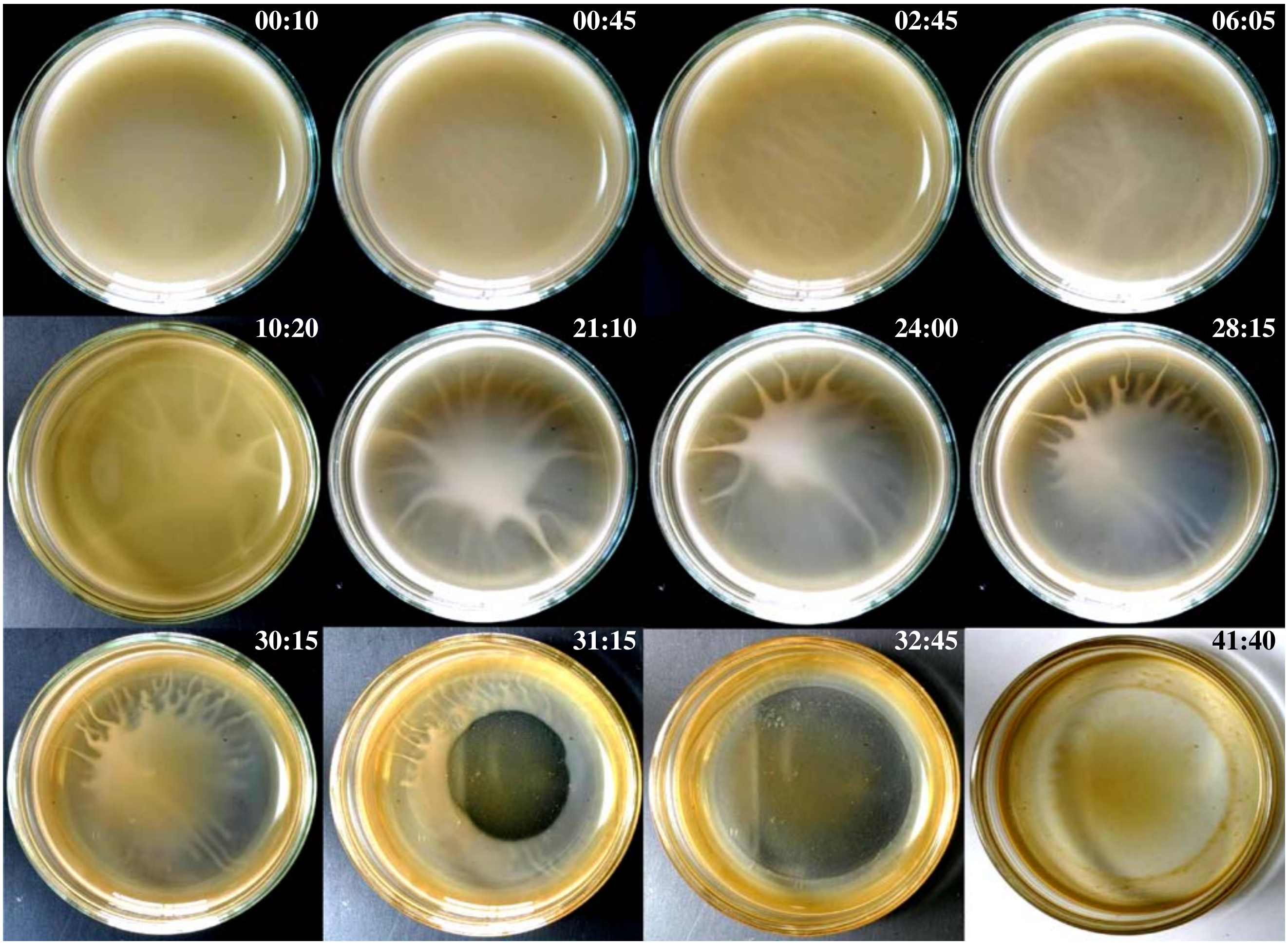

Fig. 7 Convectional, sedimentation, and drying patterns of black tea with cream in a medium glass dish at 25°C. w=0.48 wt.% (black tea 0.09 wt.%, cream 0.39 wt.%), 3 ml, times show [hours/minutes]

bundles patterns at the outside edge of the liquids and in the inner area, respectively. Furthermore, these patterns of bacteria were successfully explained theoretically by the fluid dynamics, including oxygen diffusion and consumption and further convectional flow. However, in our experiments, these bacterial effects are neglected safely since most experiments were achieved within 15 h after setting, where tea and cream do not rot. However, few experiments especially in a glass dish continued for 42 h. In these cases, it is highly plausible that the bacterial effects may change more or less the dissipative patterns.

Concluding remarks

In this work, the growing processes of the convectional patterns were mainly studied from the macroscopic and microscopic pattern observation of tea with and without cream on the various substrates. The convectional patterns from the irregular circulating lines to the bundles were observed. Figure 8 shows the most plausible convectional patterns derived from a series of observations in the authors' laboratories [8–13, this work]. The convectional processes are analyzed in seven steps: (1) At the initial stage, appearance and disappearance of the circulating lines

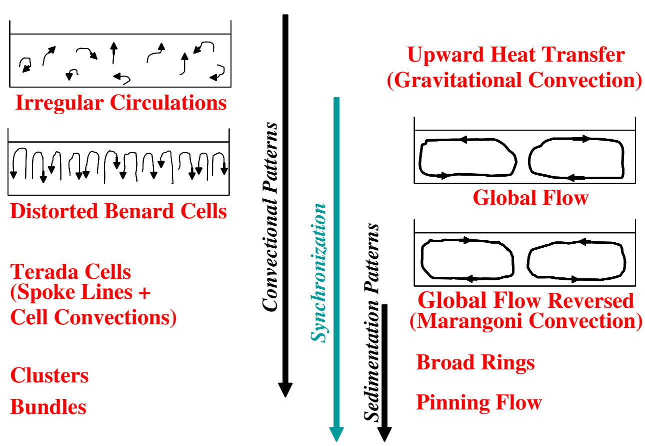

Fig. 8 Schematic presentation of change in the convectional patterns with time

("irregular circulations") took place at random in their direction accompanied with the gravitational upward heat transformation. (2) Global integrated flow of convection at the surface layers at the initial stage is from the center toward outside edge. (3) Distorted Benard cells are formed. (4) Meanwhile, at the middle stage of convections, few and short spoke lines appeared at the outside edge. Then, number of the spoke lines increases. (5) At the similar time, total flow of convection was reversed in direction from outside edge to the central area, and the outward direction remained for a long time until solidification takes place and also induced the broad-ring-like sedimentation structure. The main driving force of the reversal is the Marangoni convection. (6) The clusters and bundles of the spoke lines are formed in the middle and/or final stages of convections. (7) In the final stage of convections, flow of the suspensions will take place by the pinning effect induced by the dried broad-ring area. The sedimentation and drying patterns were also observed in tea plus cream suspensions. The bundle pattern formation at the final stage of convection is also considered to be the sedimentation pattern and is further transferred to the drying patterns. In the absence of cream, the convectional patterns were not recognized with the naked eyes. However, of course, the quite similar growing processes of dissipative patterns to tea plus cream should take place for all kinds of liquids in the almost all substrates.

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