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ORIGINAL CONTRIBUTION

Convectional, sedimentation, and drying dissipative patterns of coffee in the presence of cream and in its absence

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Abstract Convectional, sedimentation, and drying dissipative structures of coffee with and without cream were studied on macroscopic and microscopic scales. Convectional pattern of colloidal particles of coffee with cream were clearly observed in this work and analyzed in a cup, a cover glass, a watch glass, and a glass dish. The convectional patterns were vigorous and irregular at the initial stage but soon highly distorted Bernard cells grew. The integrated total flows of the coffee particles coated with cream at the air–suspension interface were observed directly with the naked eyes from the central area toward outside edge at the initial stage (3 to 30 min), but the flow direction turned oppositely from the outside to the central area after 30 min. 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 at the air–suspension surface, and then the dynamic sedimentation patterns appeared. The spoke lines of the coffee with cream were analyzed as a function of time elapsed. The drying patterns of coffee with and without cream were composed of the broad ring at the outside edge and a round hill accompanied sometimes with the spoke lines. These features are consistent with those of suspensions of nonspherical particles such as plate-like bentonite particles. The idea of the pinning effect is not supported, but importance of the gravitational and Marangoni convectional flows is clarified instead in this work.

Keywords Coffee · Coffee 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 nonequilibrium 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.

Most famous *convectional* pattern is the *hexagonal circulating* one, *Bernard 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 membranes of Chinese black ink on water by Terada et al. [4–7]. Authors like to call the spoke-like pattern as *Terada cell*. 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 (Okubo, publication in preparation), coffee (this work), black tea (Okubo et al., publication in preparation), and colloidal crystals of poly(methyl methacrylate) (PMMA) spheres on a cover glass and a watch glass [10, 11]. Distorted Bernard 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 the convectional patterns changed dynamically with time. Deegan et al. [12, 13] 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, the pinning effect was not supported except experiments at high particle concentrations and for small colloidal particles. In general, at low solute concentrations, the broad ring-like drying patterns were always formed irrespective of the substrates used, but they moved toward central area and their size became small. For typical anisotropic-shaped particles, furthermore, broad ring at the outside edge disappeared and round hill appeared instead as described below. The author believes that the convectional flow of solvent and solutes is essentially important for the convectional, sedimentation, and drying pattern formation. Furthermore, 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. The broad ring drying patterns, however, were not formed at the outside area. It should be mentioned further that theoretical and experimental studies for the convectional patterns have been made intensively hitherto, but these are not always successful yet [10, 12–21]. Main cause for this is still due to the insufficient experimental studies so far. It should be noted further that information on the *size*, *shape*, *conformation*, and/or *flexibility* of particles and polymers 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.

Sedimentation dissipative patterns in the course of drying suspensions of colloidal silica spheres (183 nm to 1.2 μm in diameter) [22–27], size-fractionated bentonite particles [28], green tea (Ocha) [29], and Miso-soup (Okubo, publication in preparation) have been studied in detail in a glass dish, a cover glass, a watch glass, and others, 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. The sharpness of the broad rings was sensitive to the change in the room temperature and/or humidity [24]. 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 particle is slower than that of the former one. Quite recently, it was clarified that the dynamic bundle-like sedimentation patterns formed cooperatively from the distorted spoke line convectional structures of colloidal particles for coffee (this work), colloidal crystal suspensions of PMMA spheres [11], and black tea (Okubo, publication in preparation).

Drying dissipative patterns have been studied for suspensions and solutions of many kinds of colloidal particles [8–11, 22–47], linear-type synthetic and biopolyelectrolytes [48, 49], water-soluble neutral polymers [50, 51], ionic and nonionic detergents [52–54], gels [55], and dyes [56] 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, when the solute concentration was high. However, the broad rings moved innerward when solute concentration decreased and/or solute size increased. For the nonspherical particles, furthermore, the round hill was formed in the center area in addition to the broad ring [28]. Macroscopic spoke-like cracks or fine hills including flickering spoke-like ones were also observed for many solutes. Furthermore, beautiful fractal patterns such as earthworm-like, branch-like, arc-like, block-like, star-like, cross-like, and string-like ones were observed in the microscopic scale. 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

Table 1 Size and zeta-potential data of coffee colloids coexisted with and without cream

Suspension	Mean size (nm)	Size distribution (nm)		Zeta-potential (mV)
		first peak	second peak	
Coffee	455±1	700±90	25±7	−24
Coffee + cream	212±1	360±70	9±2	−52

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.

In this work, convectional, sedimentation, and drying dissipative patterns of coffee with and without cream have been studied on the macroscopic and microscopic scales. The convectional patterns of coffee were observed clearly with the naked eyes, for the first time, by addition of cream in this work. One of the main purposes of this work is clarification of the pattern formation processes of convection with a help of the experimental data of coffee plus cream on the various substrates, such as a coffee cup, a cover glass, a watch glass, and a glass dish.

Experimental

Materials

Toasted coffee beans were purchased from Ogawa Coffee Creates Co. (Special Mild Blend type in most cases and Special for Iced Coffee in part, Kyoto, Japan). Cream was coffee flesh (Sujahta, 5 ml pack, vegetable oils and fats, Nagoya Seiraku Co. Ltd., Nagoya, Japan). Hot coffee and iced coffee were prepared using an Auto Coffee Maker (VC-A25 type, Matsushita Electric Industrial Co., Osaka, Japan). The coffee maker grinds coffee beans, infuses the powder with boiled water, and then filters out the dregs through a paper filter made of unbleached pulp (Nihon Ryutsu Sangyo Co., Osaka, Japan) automatically. Tap water of Uji city (Kyoto, Japan) was used for coffee preparation, and the dilution of the coffee was made with water purified by a Milli-Q reagent grade system (Milli-RO plus and Milli-Q plus, Millipore, Bedford, MA, USA).

Observation of the dissipative structures

Of coffee with or without cream, 130 ml was put into a coffee cup (90 mm in upper outside diameter and 70 mm in height, Bone China, Royal Albert, UK). Of coffee without or with cream, 0.1-ml aliquot was carefully and gently placed onto a microcover glass (30×30 mm, thickness 0.12 to 0.17 mm, Matsunami Glass, Kishiwada, Osaka, Japan) set in a plastic dish (type NH-52, 52 mm in diameter, 8 mm in depth, As One Co., Tokyo, Japan). The cover glasses were used without further rinse. Of coffee suspensions with and without cream, 40, 4, and 1 ml were set on the large (150 mm in diameter, TOP Co. Tokyo, Japan), medium (70 mm, TOP), and small watch glasses (50 mm, TOP), respectively. Of the suspensions, 3 or 2 ml were put into a

Fig. 1 Convectional patterns of coffee with cream in a cup. Experiment 2, w=2.3 wt.%, 130 ml, liquid temperature goes down from 70 °C to 25 °C, times show [hours:minutes]

medium glass dish (42 mm in inner diameter and 15 mm in height, code 305-02, TOP Co., Tokyo, Japan) and small glass dish (27 mm in inner diameter and 15 mm in height, code 305-01, TOP Co., Tokyo, Japan), respectively. The disposable serological pipets (1 and 10 ml, Corning Lab. Sci., Co.) 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 Co., Tokyo, Japan). The room temperature was regulated at 25 °C or 20 °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 macrolens (EF 50 mm, f=2.5) and a life-size converter EF. Microscopic drying patterns were observed with a metallurgical microscope (PME-3, Olympus Co., Tokyo, Japan). Thickness profiles of the dried films were measured on a laser 3-D profile microscope (type VK-8500, Keyence Co., Osaka, Japan).

DLS and ELS measurements

The dynamic light-scattering (DLS) measurements were made on a DLS-7000 spectrophotometer (Otsuka Electronics, Osaka, Japan) 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 nonnegative least square (NNLS) and the Marquadt analyses were also made for discussing the size distribution of coffee particles with and without cream. The zeta-potential measurements were made on an electrophoretic light-scattering spectrophotometer (LEZA-6000, Otsuka Electronics). The reproducibility of the ζ-potential was within 5%.

Results and discussion

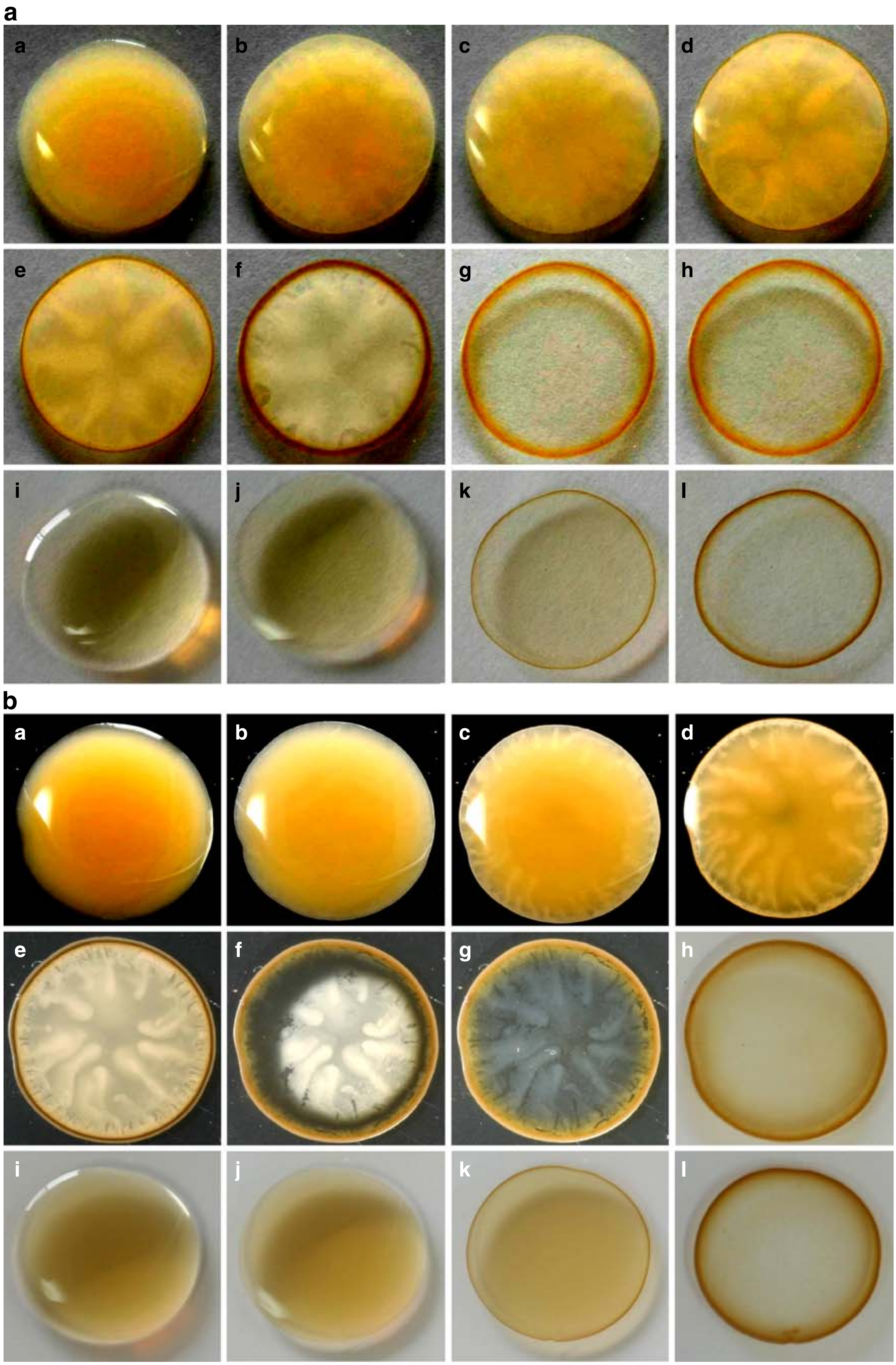
Characterization of colloidal particles of coffee with and without cream

Compositions of the coffee beans are carbohydrate (50% in weight), protein (14%), tannin (18%), caffeine (4%), and ash (14%), when water content is excluded from the calculation [57]. Coffee colloids do not contain oils and fats effectively. 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 coffee colloids without and with cream. The mean size was obtained with cumulant data treatment of the dynamic light-scattering data. The main and second size peaks, which were analyzed with the NNLS size distribution analysis method, are also compiled in the table. Mean sizes of coffee and coffee plus cream colloidal particles were 455 and 212 nm, respectively, and the former particle was twice large compared with the latter one. This strongly supports that the coffee particles apt to aggregate in suspension state. On the other hand, each coffee particles are coated with the cream layers (mainly composed of oils and fats) and forms small and stable dispersions. Zeta-potentials of coffee without and with cream were negative and −24 and −52 mV, respectively. These values in the zeta-potential also supports that the coffee particles coated with cream are more stable than the bare coffee particles in suspension state, since the colloidal particles having large absolute values of zeta-potential are more stably dispersed in general. Actually, no sedimentation of coffee without and with cream in a test tube took place for about 1 and 3 days at 8 °C. It should be noted here that the biological decomposition of the coffee took place after 2 days at 25 °C whether the cream was coexisted or not.

Convectional patterns of coffee with cream in a cup

Coffee without cream in a cup did not show any convectional patterns during 2 days after setting the suspension on a desk. However, when a 5-ml pack of cream was added into the coffee and mixed homogeneously in a cup, the convectional patterns appeared at the liquid surface and changed dynamically with time during observation period of 2 days. Figure 1 shows a typical example of the convectional patterns of coffee plus cream system during 29 h after setting. After 2 min, formation of the irregular convectional circulating patterns are already clear. However, size of the patterns was small and very complex to be analyzed. The cooperation seems not to operate among the small patterns. Within 1 h, the circulating patterns had some regular structure whole the air–liquid surface. The cooperative pattern formation takes place between the neighboring convection cells. After 4 to 5 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 broad ring did

Fig. 2 **a** Convectional, sedimentation, and drying dissipative patterns of coffee with cream (*a–h*) and without cream (*i–l*) on a cover glass at 25 °C. w=0.70 wt.% (with cream), 0.29 wt.% (without cream), 0.1 ml, *a* 20 min after setting, *b* 1 h5 min, *c* 1 h35 min, *d* 2 h10 min, *e* 2 h40 min, *f* 3 h15 min, *g* 3 h35 min, *h* 6 h30 min, *i* 20 min, *j* 2 h10 min, *k* 3 h15 min, *l* 6 h30 min. **b** Convectional, sedimentation, and drying dissipative patterns of iced coffee with cream (*a–h*) and without cream (*i–l*) on a cover glass at 25 °C. w=1.26 wt.% (with cream), 0.70 wt.% (without cream), 0.1 ml, code 1004, *a* 10 min after setting, *b* 25 min, *c* 50 min, *d* 1 h40 min, *e* 2 h40 min, *f* 3 h15 min, *g* 3 h25 min, *h* 6 h40 min, *i* 10 min, *j* 1 h40 min, *k* 2 h40 min, *l* 6 h40 min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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 °C and 80 °C. The similar convectional patterns formed to each other.

The most plausible reason why the convectional patterns were observed for coffee plus cream systems is that the coffee colloids coated with the cream are suspended in the thin layer of cream at the air–liquid interface. It should be recalled that Chinese black ink is quite similar to that of the 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 at the air–liquid surface [8]. The authors believe that the coffee plus cream colloidal particles also apt to aggregate each other but very *weakly* and *reversibly* like the Chinese black ink. 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 aqueous colloidal suspensions of PMMA spheres, which are weakly hydrophobic in water and also apt to aggregate reversibly, showed the clear-cut convectional patterns at the air–liquid interface on a cover glass, a watch glass, and a glass dish [10, 11, 47].

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 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 [10, 11], is important. The convectional flow in a cup is enhanced by the evaporation of water at the liquid–air surface, resulting in the lowering of suspension temperature in the upper region of the suspension. When the colloidal particles reach the outside edge of the liquids, 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 by a large number of cell convections in the normal direction to the spoke lines, which was called as “Terada cell” as was described in the “Introduction” section. It should be further noted here that the broad ring-like sedimentation patterns must be formed on the bottom layers of liquid in the cup [22–29], though the direct observation was impossible because the cup was made of porcelain.

Dissipative patterns of coffee with and without cream on a cover glass

Coffee without cream did not show any convectional patterns during the course of dryness as is shown in Fig. 2a i and j. On the other hand, the rather clear convectional patterns appeared by the addition of cream into coffee (see Fig. 2a a to f). Here, the temperature of the suspensions was kept at 25 °C during observation. The concentrations of the coffee with and without cream in Fig. 2a were lowered by addition of pure water. Twenty minutes after setting (see Fig. 2a a), the vague block-like or broad ring-like patterns appeared from the central area to the outside region of the air–liquid interface. Furthermore, a

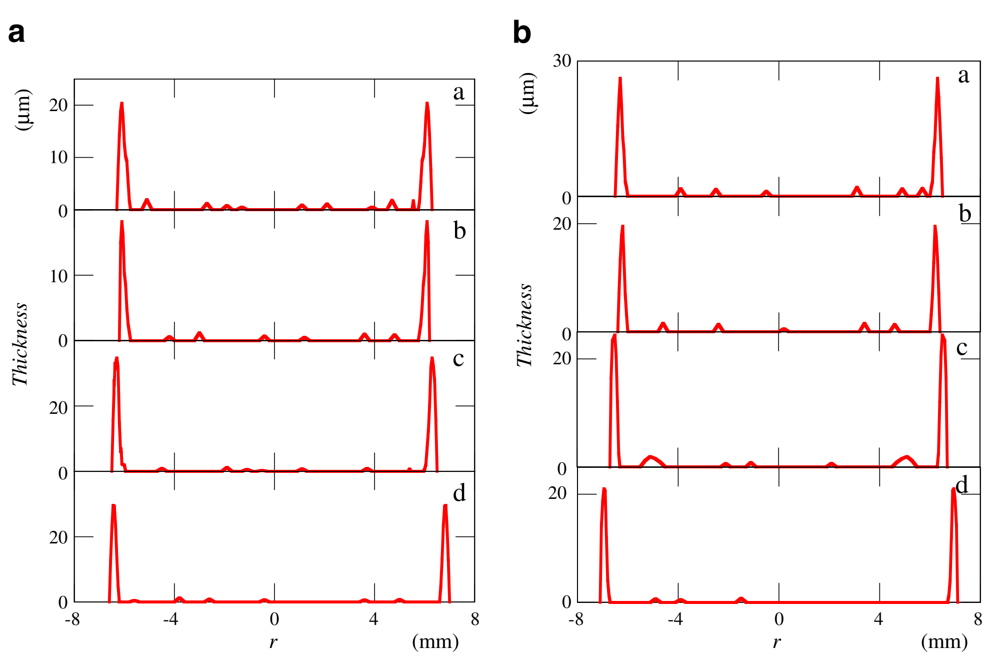

Fig. 3 **a** Thickness profiles of the dried film of coffee without cream (*a*, *b*) and with cream (*c*, *d*) as a function of the distance from the center at 25 °C. *w*=0.96 wt.% (*a*), 0.48 wt.% (*b*), 2.3 wt.% (*c*), 1.2 wt.% (*d*). **b** Thickness profiles of the dried film of iced coffee without cream (*a*, *b*) and with cream (*c*, *d*) as a function of the distance from the center at 25 °C. *w*=1.4 wt.% (*a*), 0.70 wt.% (*b*), 2.5 wt.% (*c*), 1.3 wt.% (*d*)

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. 2a b), 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. The bundles from the clustered spoke lines grew with time and about ten main bundles were formed after 2 h and 40 min (see Fig. 2a e). These bundles further grew and seven main bundles are observed after 3 h and 35 min (see Fig. 2a g). Quite similar convectional patterns showing the clusters and bundles were observed also for other coffee plus cream suspensions, i.e., the stock

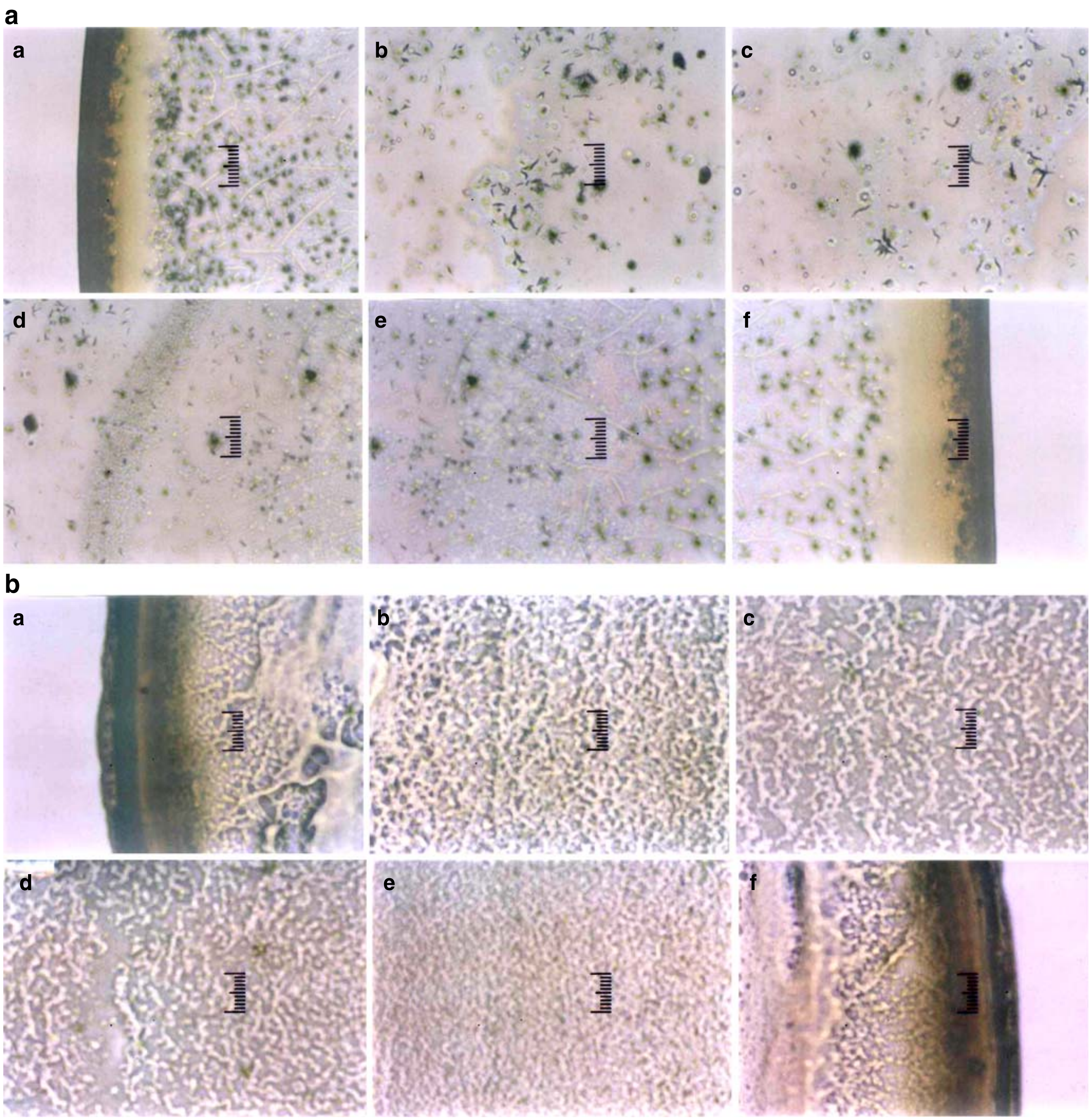

Fig. 4 **a** Microscopic drying patterns of coffee without cream on a cover glass at 25 °C. w=0.0096 wt.%, 0.1 ml, from left edge (*a*) to right (*f*), full scale=100 μm. **b** Microscopic drying patterns of coffee with cream on a cover glass at 25 °C. w=0.0096 g/ml, 0.1 ml, from left edge (*a*) to right (*f*), full scale=100 μm

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. However, quite similar patterns have been observed for colloidal crystal suspension of PMMA spheres in a watch glass (see Figs. 4f and 5f of [11]). 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 2a f shows the picture, 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 soon. In other words, the bundle-like patterns are already sedimentation patterns in the final stage of convection. It should be noted that the clusters and then bundles are originated in the spoke lines and always change their forms *dynamically* and *cooperatively*.

Figure 2b shows the convectional, sedimentation, and drying patterns of iced coffee in the presence of cream (a to h) and in its absence (i to l) on a cover glass. The stock suspension of coffee plus cream was diluted with the same amount of pure water before the observation was made. The formation of clusters from the spoke lines and then further growth of bundles from the clusters from the outside edge toward the central area at the liquid surface is clearly observed, though the distinction between clusters and bundles are difficult to each other. Number of clusters and/or bundles decreased, i.e., 35, 20, 16, 12, and 12 after 50 min, 1 h40 min, 2 h40 min, 3 h15 min, and 3 h25min, respectively. Impressively, these basic forms of bundle-like sedimentation patterns were transferred toward the drying patterns faithfully. The clusters and bundles were also observed for the stock suspensions of iced coffee plus cream, though the patterns were vague slightly by the enhanced multiple scattering of light. However, the pictures showing these features were omitted in this report.

Figure 3a,b shows the thickness profiles of the dried film of coffee and iced coffee, respectively. Pictures a, b and c, d in Fig. 3a,b are profiles without cream and with cream, respectively. Two high peaks at the outside edges correspond to the broad ring. We should note here that the small hills or rings were always coexisted at the inner area of the film. This supports that the large and nonspherical colloidal particles of coffee distribute at the almost all areas in addition to the broad rings. Shape of the colloidal particles of coffee with and without cream must not be spherical. The authors have observed the round hill-like accumulation of the nonspherical bentonite particles took place at the central areas of the dried film in addition to the broad ring [28]. Furthermore, the segregation effect in the drying patterns was also observed for the binary and ternary mixtures of colloidal silica spheres [26, 27]. Here, the small and large spheres were separated toward outside and inside areas, respectively.

Accumulation of the coffee colloids at the inner area of the film in addition to the black and brown broad ring at the outside edge was also clearly observed by the microscopic observation of the dried film shown in Fig. 4a,b. It should be mentioned here that patterns of the dried film of coffee plus cream systems shown in Fig. 4b were much finer in their textures than those of the film without cream shown in Fig. 4a. This 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 coffee suspensions. Table 2 shows the ratio of the final size of the broad rings in diameter (d_f) against the initial size of the liquid in diameter (d_i). Here, the size of the broad ring was measured as the distance between outside positions, not the peak center positions of the rings. The table shows the d_f/d_i values in the range of particle concentrations measured are very close to unity but slightly decrease as particle concentration (w, weight %) decreases even when the experimental errors are taken into account, ±0.01. This constancy keeping unity irrespective of the particle concentration in our experiments looks support the pinning hypothesis of the contact line proposed by Deegan et al. [12, 13]. 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) [39], CS82 (103 nm) [36], and CS301 (311 nm) [39] were approximately 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 [37], ionic detergents [53], neutral and water-soluble detergents [54], biological polyelectrolytes such as sodium poly-α-L-glutamate, poly-L-lysine hydrobromide [49], and polyethylene glycol (PEG)

Table 2 d_f/d_i values of coffee and iced coffee as a function of their concentrations

With cream		Without cream	
w (wt.%)	d_f/d_i	w (wt.%)	d_f/d_i
Coffee			
0.234	0.98±0.01	0.096	0.95±0.01
0.70	0.98	0.29	0.98
2.34	0.99	0.96	0.96
Iced coffee			
1.26	0.98	0.70	0.97
1.26	0.99	0.70	0.99
2.51	1.00	1.39	0.99
2.51	0.99	1.39	0.99

[51]. It should be mentioned here that the d_f/d_i values of polystyrene sphere suspensions [37] 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. 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 [51]. The d_f/d_i values of thermosensitive gel spheres of poly(*N*-isopropyl acrylamide) decreased sharply and transitionally at low temperature [55]. 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 [43]. 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 [45]. 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 [26, 27].

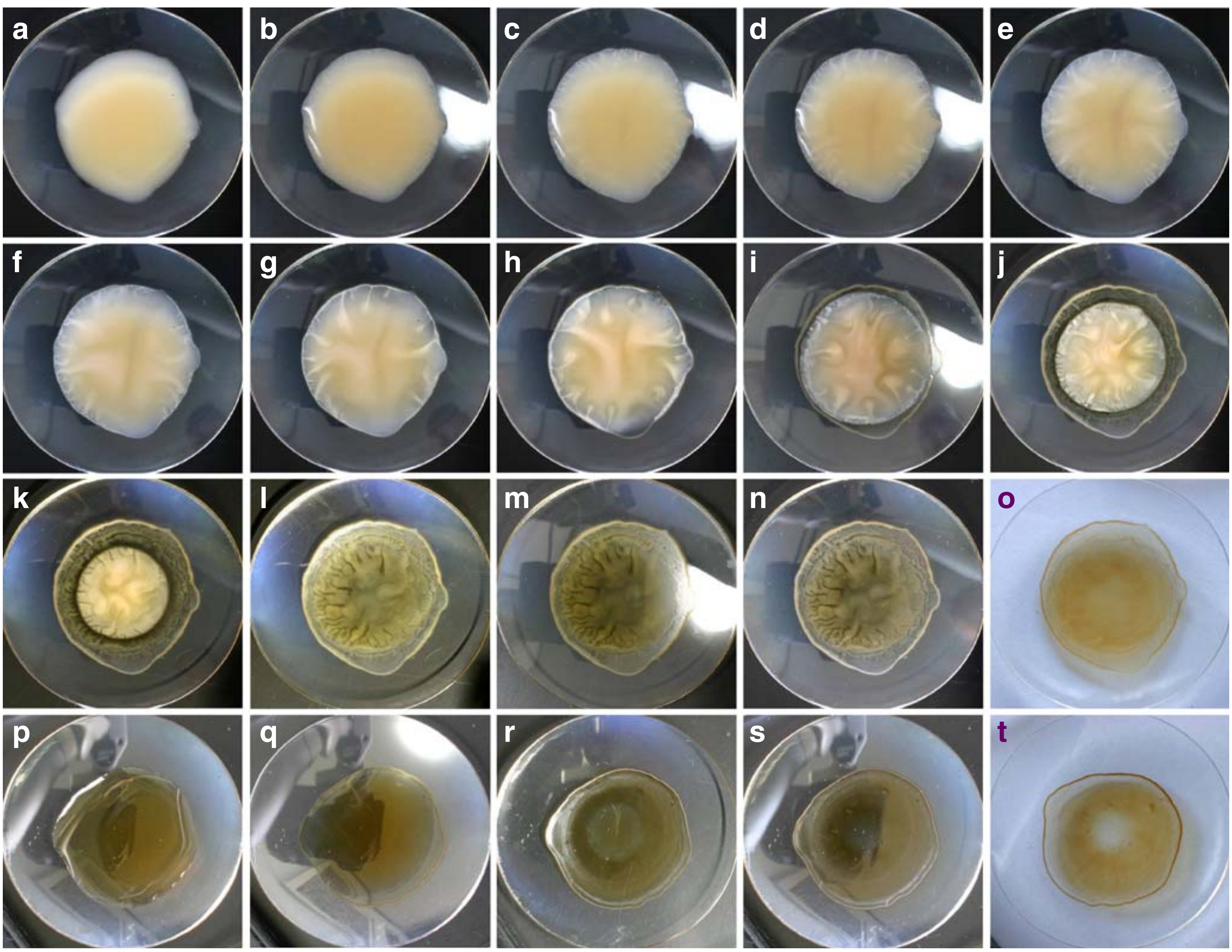

Fig. 5 Convectional, sedimentation, and drying dissipative patterns of coffee with cream (*a*–*o*) and without cream (*p*–*t*) in a small watch glass at 25 °C. w=0.70 wt.% (with cream), 0.29 wt.% (without cream), 1 ml, *a* 10 min after setting, *b* 40 min, *c* 1 h5 min, *d* 1 h35 min, *e* 2 h5 min, *f* 2 h45 min, *g* 4 h50min, *h* 5 h50 min, *i* 8 h, *j* 9 h20 min, *k* 10 h10 min, *l* 11 h30 min, *m* 13 h55 min, *n* 22 h55 min, *o* 23 h5 min (*on a white sheet*), *p* 10 min, *q* 8 h, *r* 11 h30 min, *s* 22 h55 min, *t* 23 h5 min (*on a white sheet*)

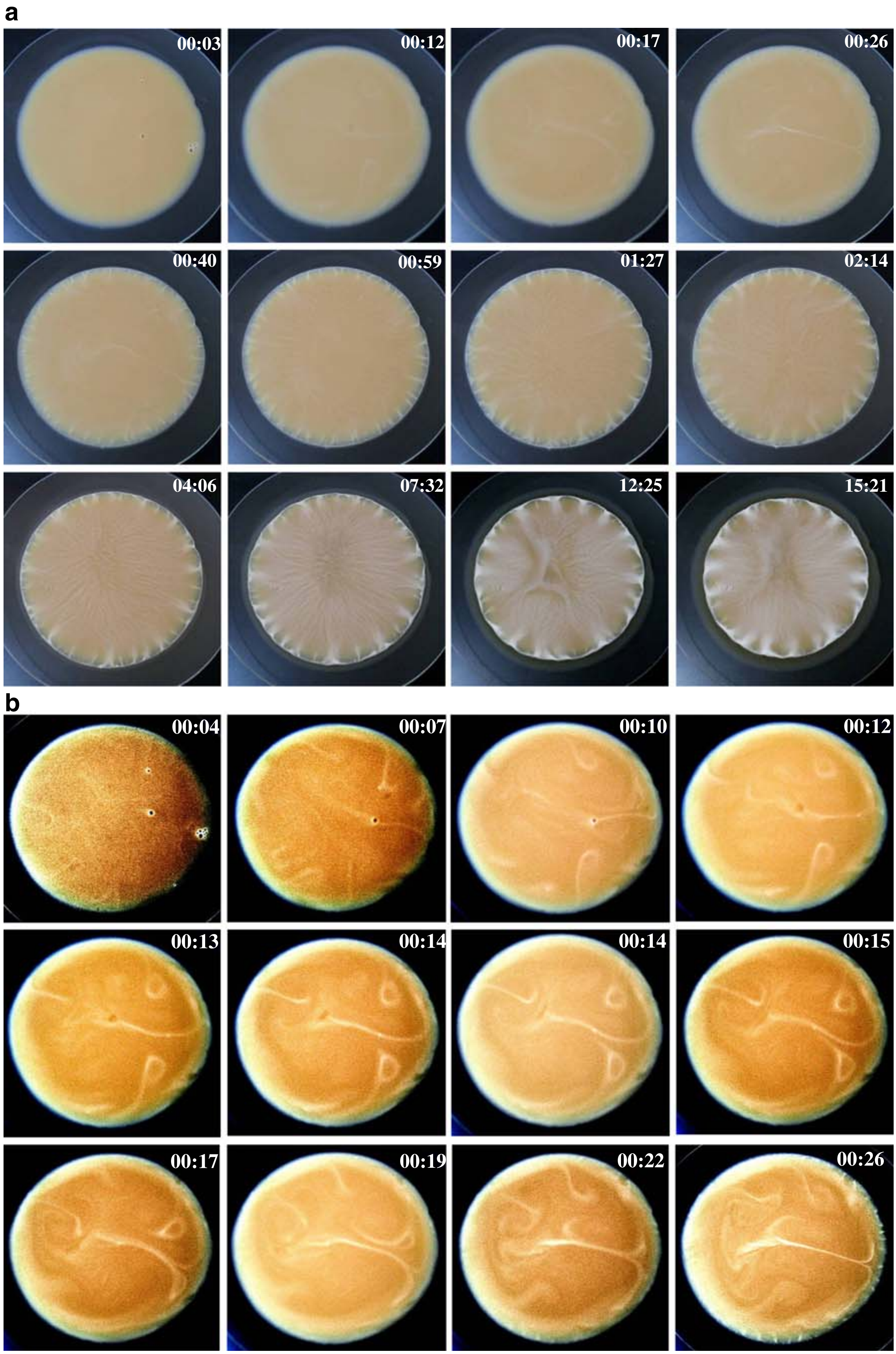
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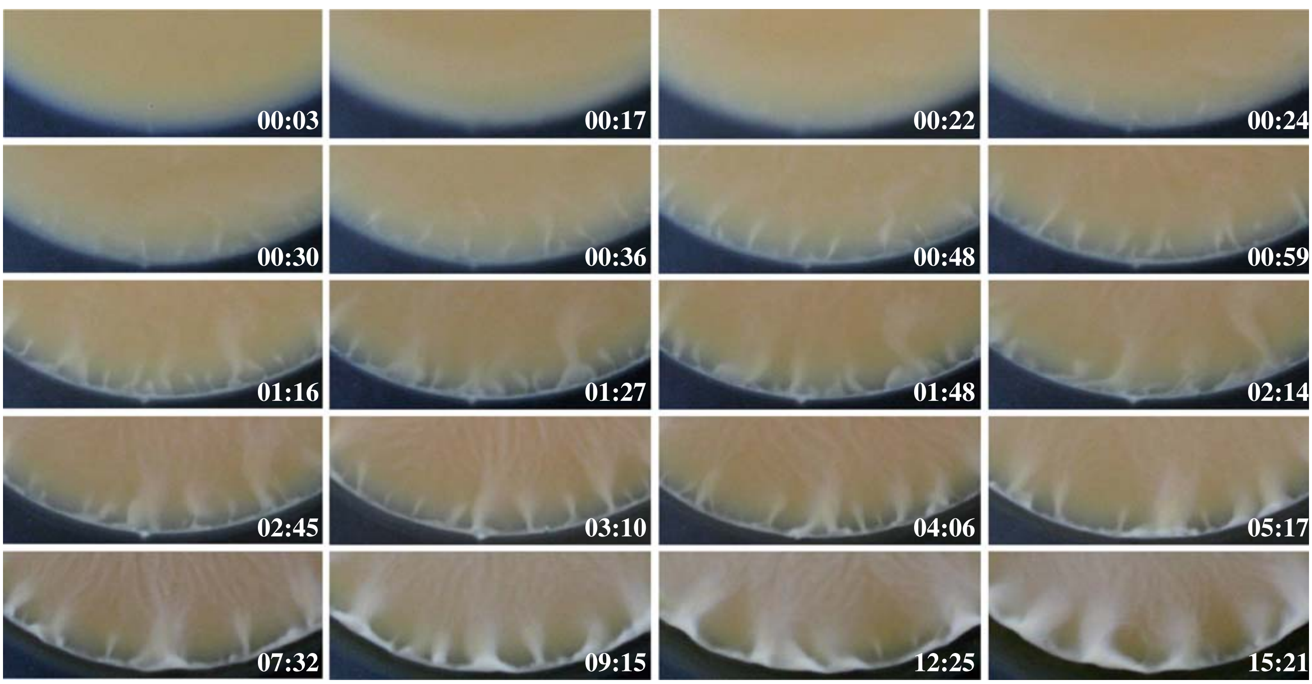
Fig. 6 **a** Convectional patterns of coffee with cream in a large watch glass. Experiment 5, *w*=2.3 wt.%, 40 ml, liquid temperature goes down from 70 °C to 20 °C, times show [hours:minutes]. **b** Convectional patterns of coffee with cream in a large watch glass. Experiment 5, *w*=2.3 wt.%, 40 ml, liquid temperature goes down from 70 °C to 20 °C, times show [hours:minutes]. **c** Convectional patterns of coffee with cream in a watch glass. Lower outside areas of patterns shown in **a** were extended. Experiment 5, *w*=2.3 wt.%, 40 ml, liquid temperature goes down from 70 °C to 20 °C, times show [hours: minutes]. **d** Plots of number of spoke lines against time in the convectional patterns of coffee with cream in a large watch glass. Experiment 5, *w*=2.3 wt.%, 40 ml, liquid temperature goes down from 70 °C to 20 °C, times show [hours:minutes], *circle*: number of long spoke lines, *cross*: number of short spoke lines

Dissipative patterns of coffee with and without cream in a watch glass

In a comparatively small watch glass, the dissipative patterns of coffee with and without cream were observed (see Fig. 5). Coffee without cream did not show any clear convectional patterns (see Fig. 5p–s). However, broad ring-like sedimentation patterns were observed even without cream as shown in Fig. 5r, s. The drying patterns of coffee without cream showed rather sharp ring structure at the outside edge and the thick broad ring at the inner area from the outside edge (see Fig. 5t). The main reason for the broad ring formation at the inner area is the fact that the coffee particles are nonspherical and highly polydispersed in their size and shape. It should be noted here that the

c



d

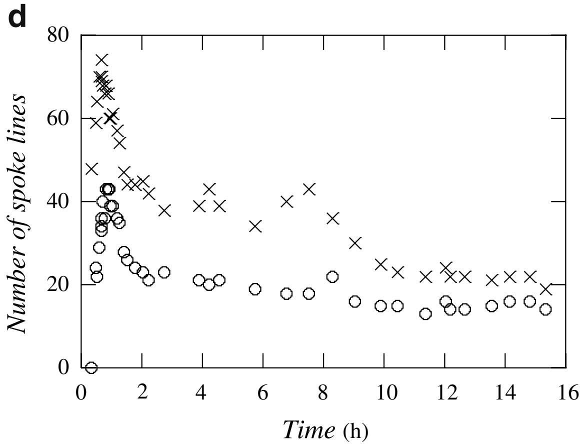


Fig. 6 (continued)

particle-free area at the central region of a watch glass has been often observed for other kinds of colloidal suspensions [9, 11, 22, 24, 26, 46]. The convectional flow of water and the colloidal particles with the different rates from the center area toward outside edge at the lower layers along the watch glass plays an important role for the central particle-free phenomenon.

In the presence of cream, the clear-cut convectional patterns were observed in a small watch glass as is shown in Fig. 5a–k. Several important convectional patterns like on a cover glass described above were again observed. Firstly, spoke lines appeared at the outside edge (b, c). Secondary, they grew long and number of them increased (c, d). Thirdly, the clustering of the spoke lines accompanied with decrease in the number of the spoke lines took place (f, g). Fourthly, the bundles were further formed from the clusters (g–k). Pictures n and o of Fig. 5 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.

When a large amount of coffee plus cream suspensions was set in a watch glass, (a) the circulating line patterns were observed within 30 min (see Fig. 6a,b). (b) Between 4 to 30 min, total flow of suspension at the liquid surface was in the direction from center to outside edge (see Fig. 6b). (c) The total flow was reversed from outside edge toward center after 30 min (see Fig. 6c), and (d) growth of the spoke lines toward central area and formation of the clusters and bundles were observed (see Fig. 6c). (e) After about 7 h, the large bundles further grew into approximately three blocks of bundles (see the pictures at the times 12:25 and 15:21 in Fig. 6a).

The circulating lines in the initial stage of convections were further shown in Fig. 6b. Here, the contrast of pictures was enhanced using a device of the computer soft. At the initial stage within 4 min, appearance and disappearance of the circulating lines took place at random in their direction.

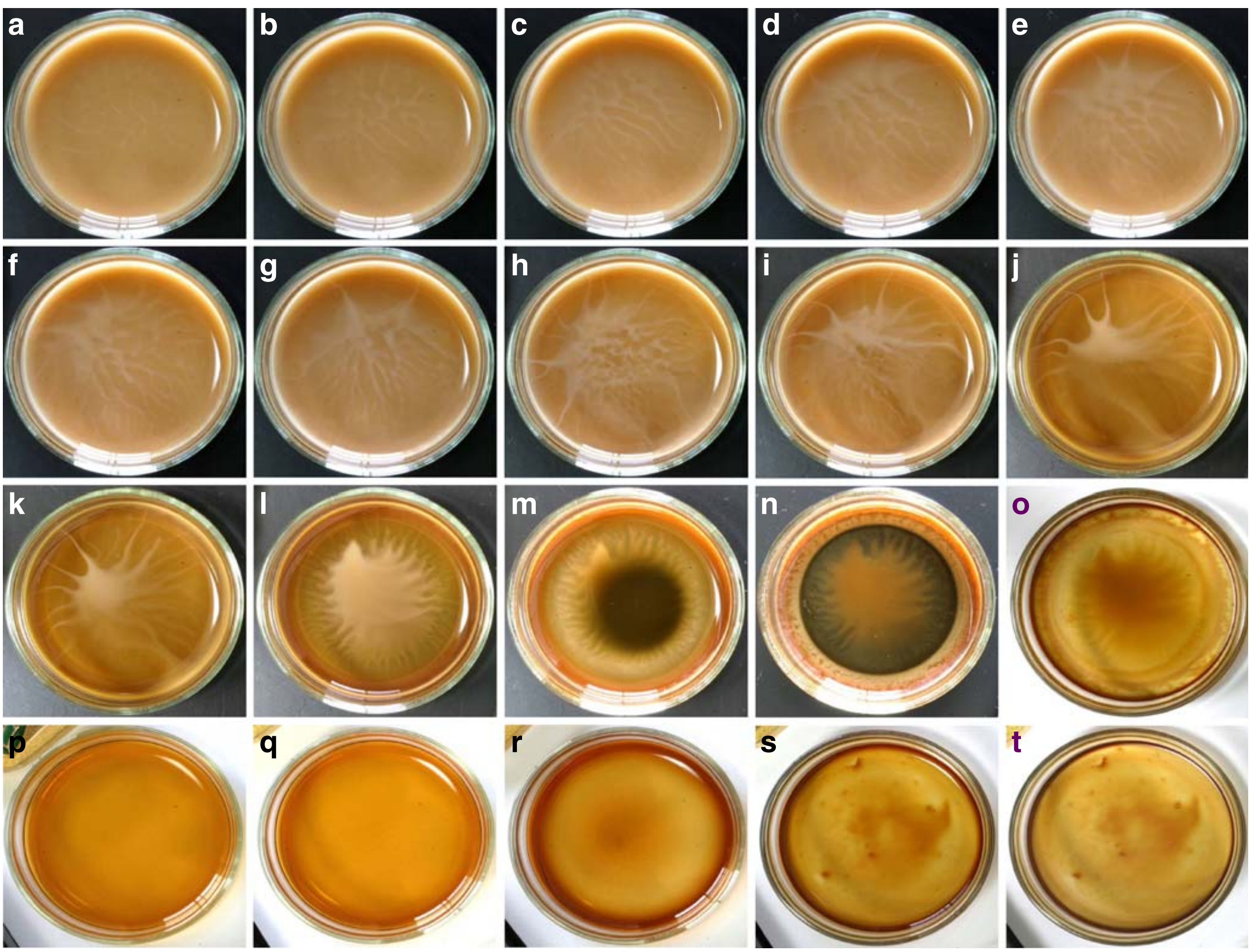


Fig. 7 Convectional, sedimentation, and drying dissipative patterns of coffee with cream (*a*–*o*) and without cream (*p*–*t*) in a medium glass dish at 25 °C. *w*=2.3 wt.% (with cream), 0.96 wt.% (without cream), 3 ml, codes 921–926, *a* 35 min after setting, *b* 50 min, *c* 1 h10 min, *d* 1 h45 min, *e* 2 h30 min, *f* 3 h50 min, *g* 5 h30 min, *h* 7 h55 min, *i* 9 h5 min, *j* 11 h20 min, *k* 13 h, *l* 20 h5 min, *m* 23 h30 min, *n* 26 h20 min, *o* 35 h40 min, *p* 35 min, *q* 7 h55 min, *r* 23 h30 min, *s* 31 h25 min, *t* 35 h40 min, *o*–*t* on a *white sheet*

However, several regularly oriented circulating lines and circles appeared soon. Interestingly, two circles at the right hand side moved together toward the right-hand side outside edge keeping their relative positions. This observation supports that the direction of the total flow of the suspension at the liquid surface is induced toward outside edge from the central by the integration of each convectional circulating lines during time from approximately 13 to 26 min.

Next, growth processes of the spoke lines are further observed in detail using the extended pictures as is shown in Fig. 6c. Around 20 min after setting, few and short spoke lines appeared at the outside edge. Then the number of the spoke lines increased. These spoke lines further grew toward central area accompanied with the dynamical fusion and separation between the neighboring spoke lines and clusters (see the pictures from 48 min to 15 h21 min). Number of short and long spoke lines including clusters and bundles was plotted during the whole time of observation in Fig. 6d. Clearly, both of long and short spoke lines increased sharply with time between 20 and 40 min. However, the number turned to decrease after 1 h. It should be noted that the decrease in number is accompanied with the formation of clusters and bundles. It should be noted here that quite similar change of the number was observed also for the convectional patterns of suspensions of PMMA on a cover glass [10] and a watch glass [11]. Thus, the formation of clusters and bundles is highly plausible to be formed for PMMA suspensions, though the direct observation of the clusters and bundles was not made. On a cover glass, cluster formation was observed (see Figs. 1 and 2 of [10]). However, the clusters and bundles were not observed in a watch glass probably due to the strong multiple scattering of light by a large amount of suspensions. We should note here that the reversal of the total flow is correlated deeply with the Marangoni effect [19, 58].

Summarizing our observations of convectional patterns of coffee with cream in a large watch glass, (1) at the initial stage within 4 min, appearance and disappearance of the circulating lines took place at random in their direction. (2) During time between 4 and 20 min, total flow of convection at the surface layers was from the center toward outside edge. (3) Around 20 to 30 min after setting, few and short spoke lines appeared at the outside edge. Then the number of the spoke lines turned to increase. (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 48 min to 15 h.

Dissipative patterns of coffee with and without cream in a glass dish

A typical example of the dissipative patterns of coffee with and without cream during the course of dryness in a glass dish is shown in Fig. 7. In the initial stage of convections before 35 min shown in a, the quite vigorous circulating lines appeared like those in a watch glass. These irregular convection cells were interacted cooperatively after 35 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 (see picture l). 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 (see Fig. 7n). Interestingly, the big bundle pattern shown in l is quite similar to the drying pattern shown in n and o. 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 from pictures n and o that the broad ring and a round hill patterns are coexisted at the inner region from the cell wall and central region, respectively, in the dried film. This observation again supports that the coffee with cream colloidal particles are nonspherical like bentonite particles studied previously [28].

It should be mentioned here that aerobic bacteria often lived in thin layers near substrate air–water contact lines [59]. Surprisingly, the bacteria made the spoke lines and 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 [59]. However, in our most experiments, these bacterial effects are neglected safely since most experiments were achieved within 15 h after setting, where coffee and cream do not rot. However, few experiments especially in a coffee cup and a large watch

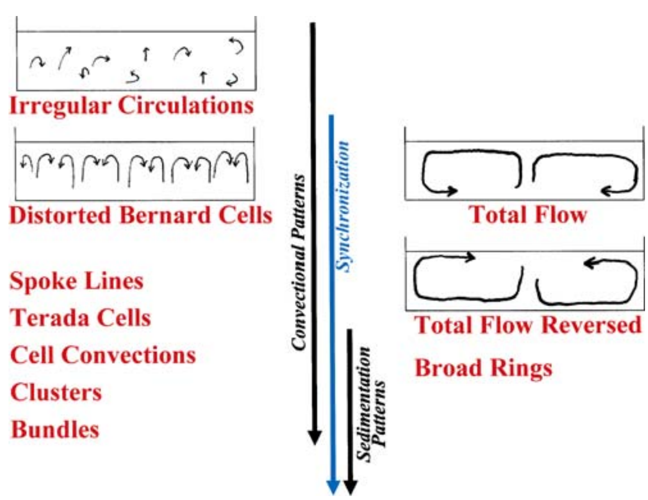


Fig. 8 Schematic presentation of formation processes of convectional patterns with time

glass continued for 2 days. 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 coffee with and without cream on the various substrates. The convectional from the irregular circulating lines to the bundles were observed (see scheme shown in Fig. 8). The convectional processes are analyzed as five steps: (1) At the initial stage, appearance and disappearance of the circulating lines took place at random in their direction. (2) Total flow of convection at the surface layers at the initial stage was from the center toward outside edge. (3) Meanwhile, at the middle stage of convections, few and short spoke lines appeared at the outside edge. Then, number of the spoke lines increased. (4) 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. (5) Growth of the spoke lines and formation of the clusters and bundle took place from the middle to the final stages. The sedimentation and drying patterns were also observed in coffee plus cream suspensions. The bundle patterns at the final stage of convection are considered to be the sedimentation patterns and are further transferred to the drying patterns. In the absence of cream, the convectional patterns were not recognized with the naked eyes. However, of course, it is highly plausible that the quite similar growing processes of dissipative patterns to coffee plus cream take place also for coffee without cream.

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