Colloid Polym Sci (2005) 283: 898–904
DOI 10.1007/s00396-004-1233-x

ORIGINAL CONTRIBUTIONS

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Drying dissipative structures of the aqueous solution of sodium *n*-alkyl sulfates on a cover glass

Received: 17 May 2004
Accepted: 30 September 2004

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Abstract Macroscopic and microscopic dissipative structural patterns formed in the course of drying a series of the anionic detergents, sodium *n*-alkyl sulfate (*n*-alkyl = *n*-hexyl, *n*-octyl, *n*-decyl, *n*-dodecyl, *n*-hexadecyl, and *n*-octadecyl), on a cover glass have been observed. The broad ring patterns of the hill accumulated with the detergent molecules are formed around the outside edges in the macroscopic scale. The microscopic patterns of the small blocks, star-like patterns, and branched strings are formed. The pattern area and the time for the dryness have been discussed as a function of detergent concentration and the number of carbons of the detergents. The convection flow of water accompanied by the detergent molecules, change in the contact angles at the drying frontier between the solution and substrate in the course of dryness, and interactions among the detergents and substrate are important for macroscopic pattern formation. Microscopic patterns are determined mainly by the shape and size of molecules, translational Brownian movement of detergent molecules, and the electrostatic and hydrophobic interactions between detergents and/or between the detergent and substrate in the course of solidification.

Keywords Drying dissipative structure · Pattern formation · Sodium *n*-alkyl sulfate · Broad ring · Microscopic pattern

Introduction

Most structural patterns in nature and experiments in the laboratory form via self-organization accompanied by the dissipation of free energy and in the non-equilibrium state. Among several factors in the free-energy dissipation, evaporation and convection induced by the earth's gravity are very important.

In previous papers from our laboratory [1, 2], drying dissipative patterns on a cover glass have been observed for colloidal crystal suspensions of colloidal silica and monodispersed polystyrene spheres, which are hydrophilic and hydrophobic in their surfaces. The colloidal crystal is undoubtedly one of the most simple and convenient systems for the study of dissipative structures on the laboratory scale. For example, accurate structural information on the processes of dissipative pattern formation is available for colloidal crystal suspensions by use of reflection spectroscopy in real time. Quite similar macroscopic and microscopic dissipative structural patterns formed between the colloidal silica and polystyrene spheres. The broad ring patterns of the hill accumulated with spheres and spoke-like and ring-like cracks formed on the macroscopic scale. From these observations, existence of the small circle convection cells proposed by Terada [3–5] was supported. The primitive patterns of valleys had been formed in the concentrated suspensions before dryness, and they grew toward fine cracks in the course of solidification. Branch-like fractal patterns of the sphere association were observed on the microscopic scale. Capillary forces between spheres at the air–liquid interface and the different rates of convection flows of water and spheres at the drying front were important for these pattern formations.

Macroscopic and microscopic structural patterns were studied in the course of drying the suspension of Chinese black ink on a cover glass and in a dish [6]. The clear broad ring and spoke-like patterns of the rims accumulated with particles were formed especially in the central region of the pattern. The convection of water and colloidal particles in the different rates under gravity and the translational and rotational Brownian movement of the particles were important for the macroscopic pattern formation. Microscopic patterns were strongly influenced by the translational Brownian diffusion of the particles and the electrostatic and/or hydrophobic interactions between the particles and the substrate in the course of solidification of the particles. For Chinese ink, direct observation of the convection flow was made mainly in a dish. Drying dissipative structures have been studied further for the linear-type macrocations, poly(allylamine hydrochloride) [7]. Macroscopic broad ring patterns, where the polymers accumulate densely in the outside edge, formed. Furthermore, beautiful string-like fractal patterns were observed on the microscopic scale.

Quite recently, the drying experiments were made for *n*-dodecyltrimethylammonium chloride (DTAC), which is one of the typical cationic detergent molecules [8]. Broad ring patterns of the hill accumulated with detergent molecules formed around the outside edges of the film in the macroscopic scale. Star-like, blanch-like, arc-like, and small block-like microstructures were also observed. The convection of water and detergents at different rates under gravity and the translational and rotational Brownian movement of the latter were important for macroscopic pattern formations. Microscopic patterns were determined by the translational Brownian diffusion of the detergent molecules and the electrostatic and hydrophobic interactions between detergents and/or between the detergents and substrate in the course of solidification.

From these studies on drying dissipative structures, it was found that macroscopic broad ring patterns for various solutions and suspensions were surprisingly similar to each other. Interestingly, microscopic patterns such as branch-like, string-like, arc-like, and small block-like ones were reflected in the shape, size, and flexibility of the solute molecules. In this work, drying structural patterns were studied for a series of anionic detergent molecules, sodium *n*-alkyl sulfates (*n*-alkyl = *n*-hexyl (S6S), *n*-octyl (S8S), *n*-decyl (S10S), *n*-dodecyl (S12S), *n*-hexadecyl (S16S), and *n*-octadecyl (S18S)). The main purpose of this work is to study the patterns are common and special among a series of detergents.

Experimental

Materials

Sodium *n*-alkyl sulfates (*n*-alkyl = *n*-hexyl (S6S), *n*-octyl (S8S), *n*-decyl (S10S), *n*-dodecyl (S12S), *n*-hexadecyl (S16S) and *n*-octadecyl (S18S)) were purchased from Aldrich Chemical Co. (Milwaukee, WI, USA). They were used without further purification. The water used for the sample preparation was purified by a Milli-Q reagent grade system (Milli-RO5 plus and Milli-Q plus, Millipore, Bedford, MA, USA).

Observation of the dissipative structures

0.1 mL of the aqueous solution of the anionic detergent molecules was dropped carefully and gently on a micro cover glass (30×30mm, thickness No.1, 0.12–0.17 mm, Matsunami Glass Co., Kishiwada, Osaka) in a dish (60 mm in diameter, 15 mm in depth, Petri Co., Tokyo). The cover glass was used without further rinsing in this work. The extrapolated value of the contact angle for pure water was $31 \pm 0.2°$ from the drop profile of a small amount of water (0.2, 0.4, 0.6, and 0.8 μL) on the cover glass. A pipet (1 mL, disposable serological pipet, Corning Lab. Sci. Co.) was used for the dropping. Macroscopic and microscopic observations were made for the film formed after the suspension was dried completely on a cover glass in a room air-conditioned at 25 °C and 65% in the humidity of air. Concentrations of the detergents ranged from 1×10^{-7} to 0.01 M.

Macroscopic dissipative structures were observed with a digital HD microscope (type VH-7000, Keyence Co., Osaka) and a Canon EOS 10 camera with macro-lens (EF 50 mm, $f = 2.5$) and a life-size converter EF. Microscopic structures were observed with a laser 3D profile microscope (type VK-8500, Keyence) and a Metallurgical microscope (Axiovert 25CA, Carl-Zeiss, Jena GmbH). Observation of the microscopic patterns was also made with an atomic force microscope (type SPA400, Seiko Instruments).

Results and discussion

Figure 1 shows the typical patterns formed in drying the S8S solution at concentrations ranging from 1×10^{-6} to 0.01 M. The large fine circles in the figure show the initial solution area on a cover glass. For all the solutions examined, the pattern area shrank at the center and the broad ring regions distributed roundly in the

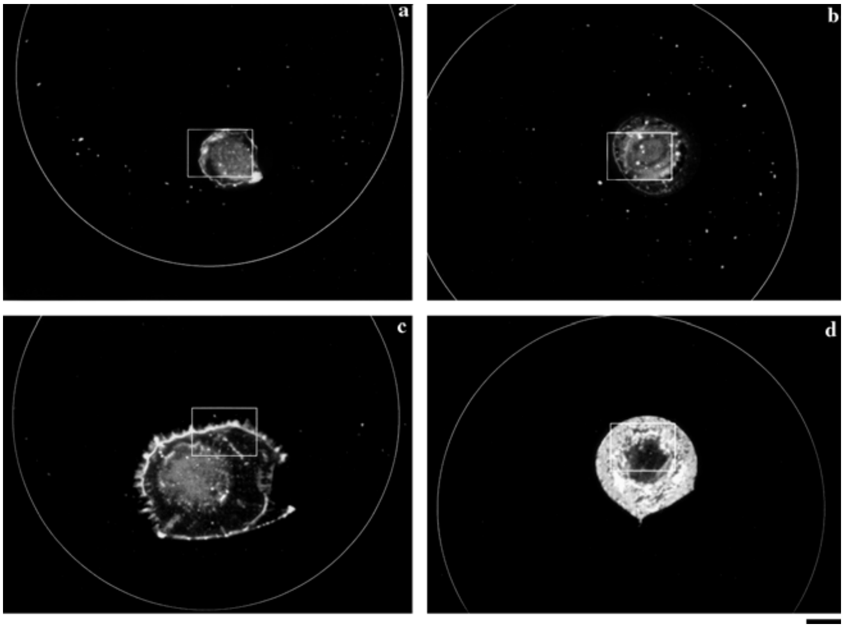

Fig. 1 Patterns formed for S8S on a cover glass at 25 °C. **a** 1×10^{-6} M, **b** 1×10^{-5} M, **c** 1×10^{-4} M, **d** 1×10^{-2} M. In water, 0.1 mL; length of the bar is 1.0 mm

outer edges, which were also observed for low concentrations of the cationic detergent, DTAC [8]. This shrinking phenomenon seems to correlate intimately to the critical micelle concentration (cmc) of the detergent solution. When the solute concentration is lower than the cmc, the initial solution area should shrink without solidification until the solution is concentrated in the course of drying and its concentration reaches the cmc. For concentrations of the detergents higher than the cmc, the shrinking of the solution area stops. In other words, the solution area shrinks when the contact angle between the solution and substrate is large, and the shrinking stops when the angle is small enough at the concentrations of detergents higher than cmc. Shrinking of the solution area was observed clearly in (Fig. 1) for all the solutions of S8S examined. This observation strongly supports the cmc of S8S being higher than 0.01 M. The reference value of the cmc for S8S has been reported to be ca. 0.1 M [9], which agrees with the predicted value from this work. It should be noted here

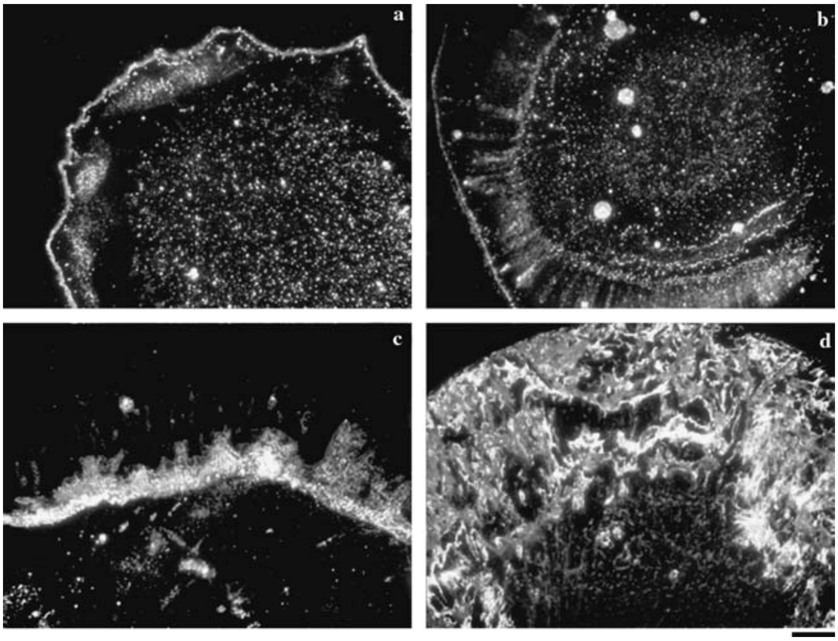

Fig. 2 Patterns formed for S8S on a cover glass at 25 °C. **a** 1×10^{-6} M, **b** 1×10^{-5} M, **c** 1×10^{-4} M, **d** 1×10^{-2} M. In water, 0.1 mL; length of the bar is 200 μm

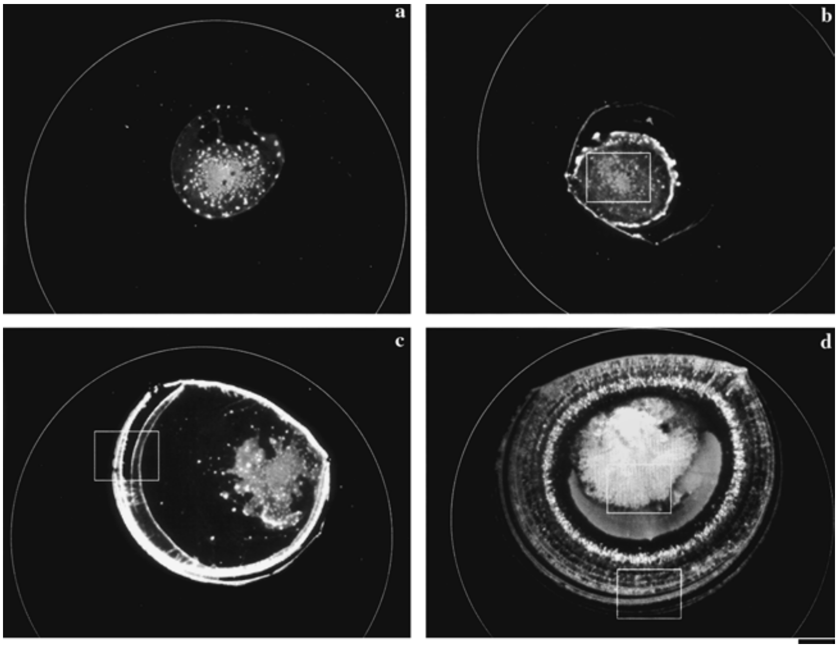

Fig. 3 Patterns formed for S12S on a cover glass at 25 °C. **a** 1×10^{-6} M, **b** 1×10^{-5} M, **c** 1×10^{-4} M, **d** 1×10^{-2} M. In water, 0.1 mL; length of the bar is 1.0 mm

that the pattern area of the sodium poly-α-L-glutamate and hydrochloride of poly-L-lysine shrank when their concentrations were lower than the critical concentration, *m**, where these polymers form the structured conformation at the air–water interface, and their surface tensions start to decrease sharply as polymer concentration increases [10, 11].

A main cause for the broad ring formation is the convection flow of the solvent and the detergent molecules at different rates under gravity. Especially, the flow of detergents from the center area toward the outside edges in the lower layer of the liquid drop (which was observed on a digital HD microscope directly from the movement of the very rarely occurring aggregates of the detergents) is important [8]. The flow will be enhanced by the evaporation of water at the liquid surface, resulting in lowering of the suspension temperature in the upper region. When the detergents reach the edges of

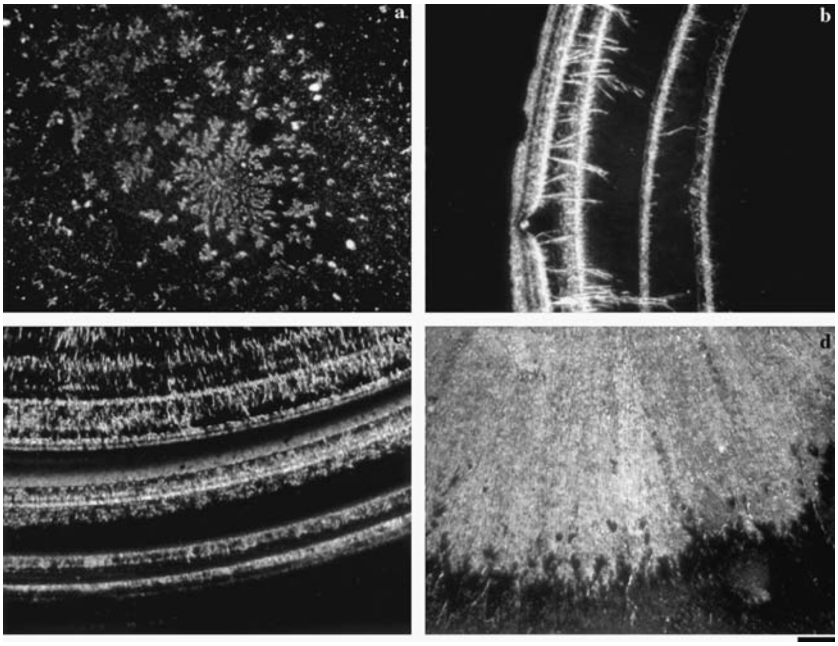

Fig. 4 Patterns formed for S12S on a cover glass at 25 °C. **a** 1×10^{-5} M, **b** 1×10^{-4} M, **c**, **d** 1×10^{-2} M. In water, 0.1 mL; length of the bar is 200 μm

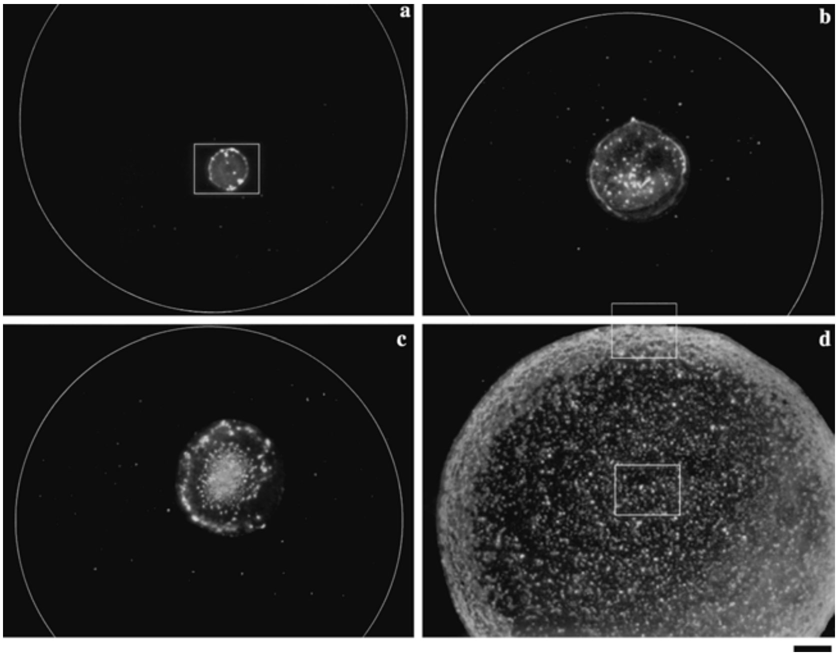

Fig. 5 Patterns formed for S16S on a cover glass at 25 °C. **a** 1×10^{-6} M, **b** 1×10^{-5} M, **c** 1×10^{-4} M, **d** 1×10^{-2} M. In water, 0.1 mL; length of the bar is 1.0 mm

the drying frontier at the outside region of the liquid, a part of the molecules will turn upward and go back to the center region. However, the movement of most detergents may stop at the frontier region by the disappearance of water. This process must be followed by the broad ring-like accumulation of the detergents near the round edges. It should be noted that the broad ring formation was observed for all the solutions and suspensions examined by our group [1, 2, 6–8, 12–15] and further by other researchers [16–18]. Recently, microgravity experiments were carried out for the drying dissipative patterns of deionized suspension of colloidal silica spheres [19]. Surprisingly, the broad ring patterns did not disappear even in microgravity. This supports the fact that both the gravitational and Marangoni convections contribute to the broad ring formation on earth but only the latter is important in microgravity.

Figure 2 shows the close-up detail of the square area shown in Fig. 1a–d; the length of the bar is 200 µm. The broad rings were observed in the outside

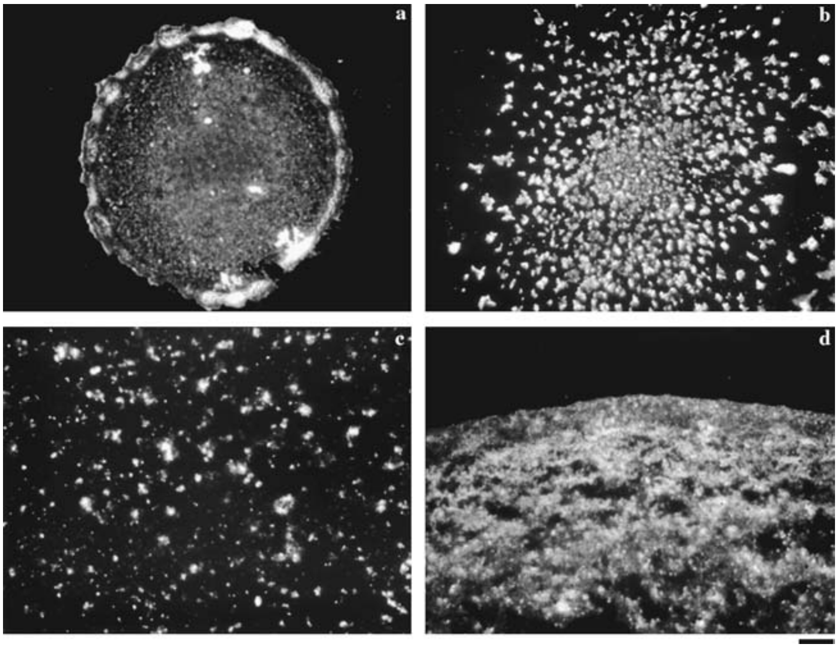

Fig. 6 Patterns formed for S16S on a cover glass at 25 °C. **a** 1×10^{-6} M, **b** 1×10^{-4} M, **c**, **d** 1×10^{-2} M. In water, 0.1 mL; length of the bar is 200 µm

ridges; though they were not so smooth, they were composed of small blocks. The patterns in the central region shown in Fig. 2 are composed of small spots, which must have been formed in the course of solidification above the solubility of S8S. The detergent concentrations may fluctuate and distribute roundly in the course of drying with the dissipative convection flow. Thus, shape and size differ delicately as a function of the distance from the center. The extended pattern in the broad ring region shown in Fig. 2d at a high concentration of S8S (0.01 M) is composed of fine strings, which are crossed or netted to each other. It should be mentioned here that the patterns in Fig. 2d are quite similar to those for aqueous solution of the cationic detergent, DTAC [5]. These microstructures of small blocks and strings form in a semi-equilibrium state above the solubility in the gradient detergent-concentration distribution by the dissipative convection flow.

Figure 3 shows the dried patterns of S12S. The pattern area shrank toward the center and the broad ring regions formed in the outer edges, which are similar to the features of S8S. It should be noted here that the dried pattern area increased as S12S concentration increased and the area at 0.01 M was not so far from the initial liquid area. These observations support the fact that the cmc value of S12S is not far from 0.01 M. The reference value of the cmc for S12S is 0.007 M [9]. Fine multi rings were observed especially in (Fig. 3c, d). Figure 4 shows the close-up detail of the square area shown in Fig. 3. Fractal patterns composed of crosses and branches (Fig. 4a), string-like rings, and spokes (Fig. 4b–d) were observed. These micro-patterns are also quite similar to those of S8S shown in Fig. 2 though the string-like patterns were observed for S12S much more often compared with S8S.

Figure 5 shows the drying patterns of S16S. The pattern area shrank toward the center when the detergent concentrations were between 1×10^{-4} and 1×10^{-2} M. However, no shrinking was observed at 0.01 M, which strongly suggests that the cmc of S16S is in between 1×10^{-4} and 1×10^{-2} M. The reference value of cmc for the S16S solution is ca. 5×10^{-4} M [9], which agrees excellently with the prediction from this experiment. Thus, it is concluded soundly that the shrinking of the pattern area always occurs when the surface tension and then the contact angle between the solution and substrate are high. The broad ring regions were observed for all the solutions of solute concentrations examined, and the macroscopic patterns observed in Fig. 5 are quite similar to those of S8S and S12S.

Figure 6 shows the extended patterns of the S16S detergent observed in Fig. 5. The microscopic patterns composed of small blocks and strings were observed though the patterns tend to change from blocks to strings as the detergent concentration increases.

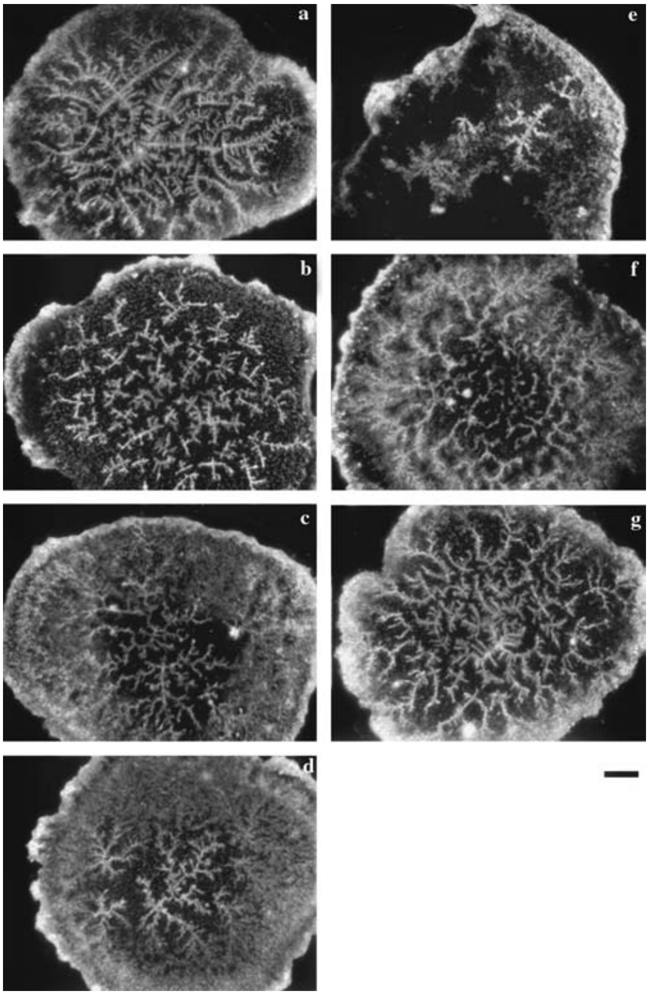

Fig. 7 Patterns formed for detergents on a cover glass at 25 °C. **a** S6S, **b** S8S, **c** S10S, **d** S12S, **e** S16S, **f** S18S, **g** DTAC. In water, 0.1 mL, 1×10^{-7} M; length of the bar is 200 μm

Figure 7 shows the close-up details of the microscopic patterns of a series of anionic detergents from S6S to S18S at 1×10^{-7} M. Surprisingly, patterns of branch-like strings quite similar to each other were observed. This observation supports the fact that the shapes of detergent molecules from S6S to S18S are essentially rod-like and thereafter the similar patterns of branch-like strings were formed. It should be noted that the cationic detergent DTAC also has quite similar patterns of branch-like strings as is clear in Fig. 7g [8].

Figure 8 shows the time for the completion of the dryness observed with the naked eye, *T*, and the initial and final area of dried patterns, S_i and S_f, as a function of detergent concentration. *T*-values decreased as the number of the carbons of the detergent molecules increased and decreased slightly with increasing detergent concentration. It should be noted here that these features of *T*-values are quite similar to those of DTAC [8].

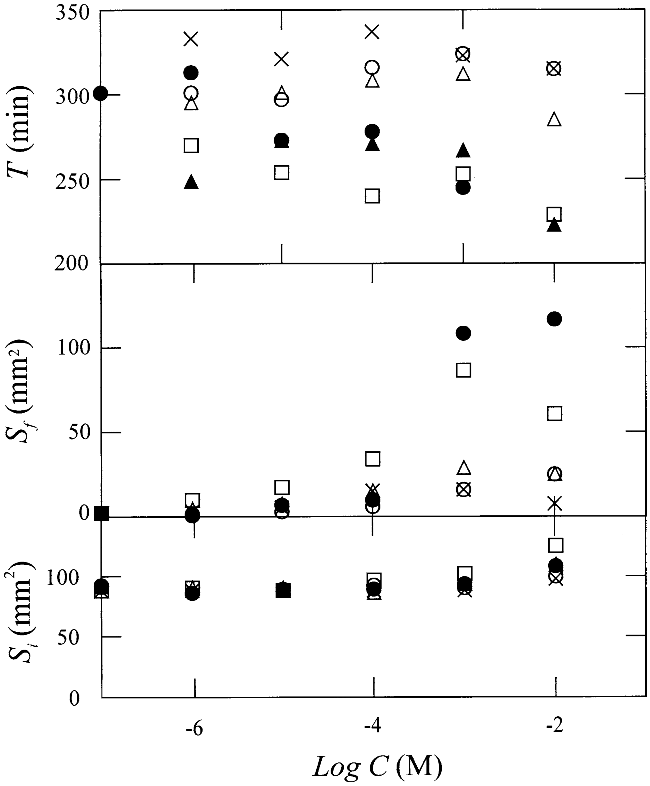

Fig. 8 Drying times (T) and final and initial areas (S_f and S_i) as a function of concentration (C) at 25 °C. In water, 0.1 mL, *open circle* S6S, *cross* S8S, *open triangle* S10S, *open square* S12S, *filled circle* S14S, *filled triangle* S16S

S-values increased sharply as the carbon number of detergents and/or detergent concentration increased. Thus, it is clear that T decreases sharply when S increases, which is quite understandable because the drying process is fast when the liquid film is thin even though the area is large. It should be mentioned here that the inversely proportional relationship between T and S observed in this work supports the important feature in the drying dissipative structures, i.e., the dissipative structures should be formed even for very thin liquid films. This is because the difference in the temperatures at the air–liquid interface and in the bulk liquid is large and the convection flow comes fast in the condition of small T-values. Experimentally, the drying dissipative structures were always observed even for very thin liquid films of detergents hitherto.

In conclusion, macroscopic broad rings were always formed irrespective of the kind of solutes including the anionic detergents studied in this work. The shrinking of the dried patterns occurs when the detergent concentrations are lower than the cmc and the contact angle between solution and substrate are high. For the rod-like molecules like the anionic detergent molecules studied in this work and further for the linear-type polyelectrolytes, block-like, star-like, and string like microscopic patterns were often observed.

Acknowledgements The Ministry of Education, Science, Sports and Culture are thanked for grants-in-aid for Scientific Research on Priority Area (A) (11167241) and for Scientific Research (B) (11450367).

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