Attenuation of Cracks Pattern in Dried Silica Colloidal Droplets by Anionic Surfactant Addition

Mahoulo Ahouansou*[1]*, Simon Biggs*[2] *and Olivier J. Cayre*[1]*; [1] School of Chemical and Process Engineering, Leeds, University of Leeds, United Kingdom, [2] Faculty of Engineering, Architecture and Information Technology, The University of Queensland; Brisbane, Australia

Abstract

The influence of the anionic surfactant sodium dodecyl sulfate (SDS) on the evaporation of drying silica colloidal droplets is investigated. The addition of SDS leads to an attenuation of cracks patterns after evaporation (i.e., the presence of cracks in the structure are dramatically altered). We understand that this phenomenon could be induced by radial Marangoni flows induced by the variation of SDS concentration along the air-water interface along with a depletion flocculation.

Introduction

The drying of small solid particle in liquid typically leaves the well-known pattern of a ring-shaped stain upon solvent evaporation, this phenomenon also known as the "coffee-ring effect"[1] is identified with most of the solid material deposited at the periphery of the initial deposit. This non uniform deposit is observed when the contact line is pinned and a capillary flow[1-2] is generated carrying the suspended solutes from the drop center towards the edges in order to compensate the fast solvent evaporation at the edges. This effect is observed regardless of the particles sizes (i.e., from micrometer-sized particles down to macromolecules)[3,4,5] or the substrates used (i.e., hydrophobic or hydrophilic substrates)[1,4,6]). Another phenomenon leading to a non-uniform particle distribution is the formation of cracks [7-10]. These cracks are due to stress release upon solvent evaporation[7-10].

To overcome these phenomena, promising alternatives to control the final pattern of colloidal droplets have been studied including tuning the temperature and relative humidity[11], addition of electrolyte[12], generating a Marangoni flow by addition of a cosolvent[13-17], polymer[18,19] or surfactants[6,13,14,20], the use of a sol-gel transition[21] , by surface modification[4,22,23] and by particle shape modification[24,25].

In this contribution, we investigate the drying behavior of colloidal suspensions of silica nanoparticles by addition of SDS above and below the critical micelle concentration (cmc). This has indeed been proven to be an efficient technique to suppress the “coffee ring effect”[13,14] as well as formation of cracks[10] for polystyrene (PS) and polytetrafluoroethyleme (PTFE). Focus is placed on the dried deposit structure and the explanation of how the cracking behavior is attenuated by surfactant addition is also discussed in details.

Experimental methods

The experiments employed aqueous suspension of colloidal Ludox-AS® (Sigma-Aldrich, UK) silica particles with diameter *d*~21 nm. Amberlite MB-150 resin (MB Biomedicals, UK) was used to purify the Ludox-AS® by ion exchange to remove residual soluble ions from the commercial sample. Sodium dodecyl sulfate solutions (VWR Prolabo, ≥98%) is added to Ludox-AS® and the suspensions are stirred for 5 minutes before the droplets deposition, with a final SDS concentration from 0 to 30 mM and Ludox-AS® at 2 wt%.

The drying of the droplets was performed using KSV CAM 200 goniometer (KSV Instruments). Clean glass slides (Thermo Scientific, hydrophilic) were used as evaporation substrates. The drop volumes were 10.5±0.8 μL, leading to deposition coatings with diameters of 7.2 to 8.6 mm. Total evaporation times ranged between 5 and 68 min. All the experiments and observation were carried out at room temperature ~ 25°C with a relative humidity of ~ 28%.

To obtain more information of the morphology and structure of the evaporated deposition, the deposition patterns were studied using an optical microscope, (Olympus, U-MNUA2), a Canon camera (EOS 550D).

Results and discussion

Stability and Surface Tension Analysis

The size of Ludox-AS® increases when SDS is added to the system (Figure 1). The size switches from 21 nm in pure MilliQ-water to 36 nm between 7.5 and 15 mM to 47 nm at 30 mM , this size increase could be explained by the adsorption of SDS onto the Ludox-AS®. The suspensions are stable in the different SDS concentration, the Zeta potential is measured -30mV.

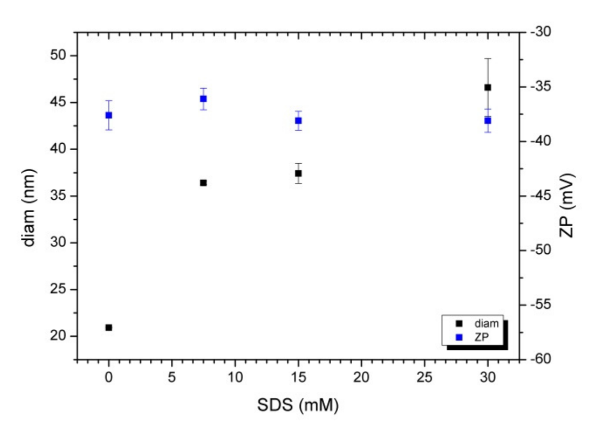

Figure 1. Stability and size variations of Ludox-AS® at different SDS concentration in water at 25°C.

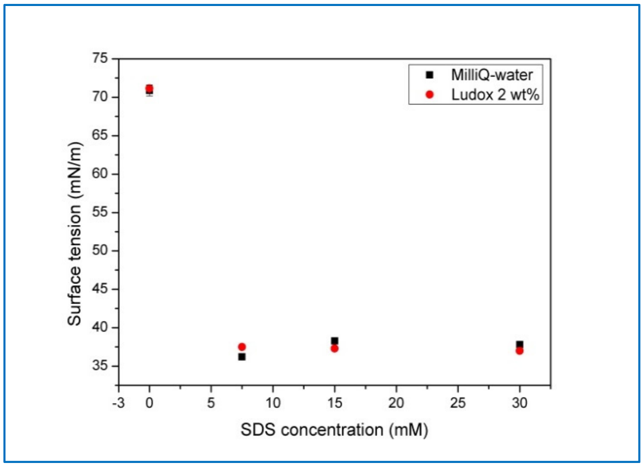

Figure 2. Surface tensions of Ludox-AS® with and without addition of SDS in water at 25ºC.

The pure Ludox-AS® in aqueous suspension is not surface active, the initial surface tension is at 71.1 mN/m which is close to the experimental surface tension of pure MilliQ-water at 70.9 mN/m at 25°C. When SDS is added to the system the surface decreases dramatically to reach ~ 37.3 mN/m. Hence, the surface tension is nearly constant and consistent with a pure system of SDS considering that the critical micelle concentration for SDS is at 8.3 mM and thus the surface tension will show a small variation (cf. Figure 2).

Wetting Properties

In order to examine the influence of surfactant concentration, the wetting property of a drop containing Ludox-AS® at 2 wt% is investigated.

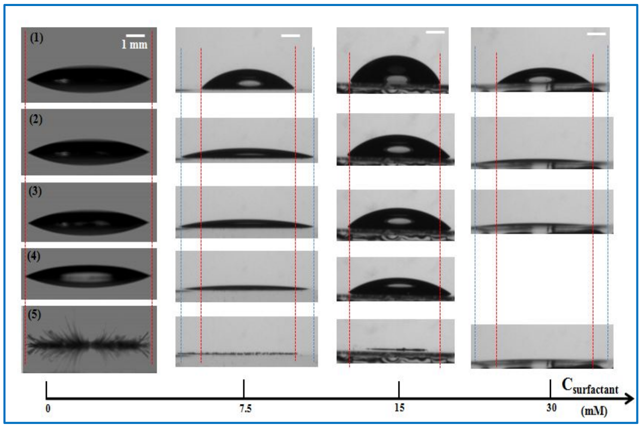

Figure 3. Drying sequence of a drop of Ludox-AS® as a function of SDS concentration at (1) 0, (2) 50, (3) 150, (4) 600 seconds and (5) dried deposit.

Viewing droplet evaporation from the side showed that the Ludox-AS® in 0 mM SDS has a pinned contact line. The contact diameter increases with the addition of SDS cf. Figure 3.

The contact diameter increases is due to charge of negative charge of the SDS and the glass slide, this same charge causes the contact radius not to be pinned[26].

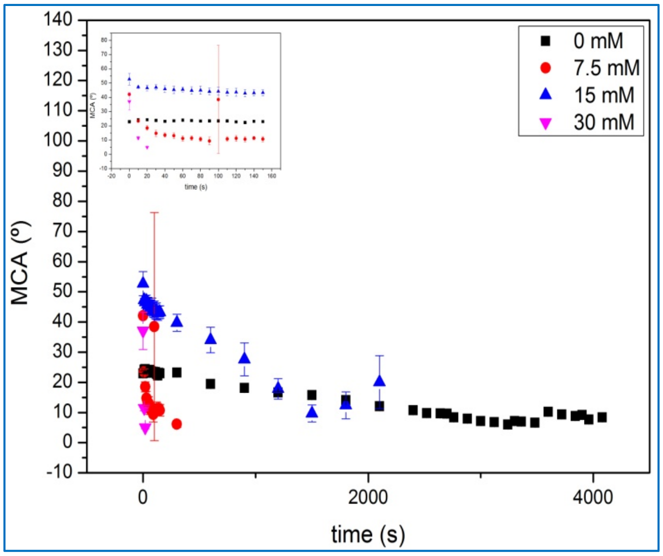

Figure 4. Variation of the mean contact angle (MCA) of Ludox-AS® as a function of SDS concentration, inset zoom of the mean contact angle variation between 0 to 160 seconds.

The addition of the SDS decreases the evaporation rate of the drying droplet dramatically[26]. When the system is a pure Ludox-AS® the evaporation takes 68 minutes while when the SDS is at 30 mM the evaporation takes around 5 minutes. Though, this evaporation decrease is not linear with the SDS variation increases. The initial mean contact angle increases with the SDS addition and overtime we observe a clear mean contact angle decreases which is coherent with the solvent evaporation cf. Figure 3. Though usually a decrease of the contact angle is observed when SDS is added [26].

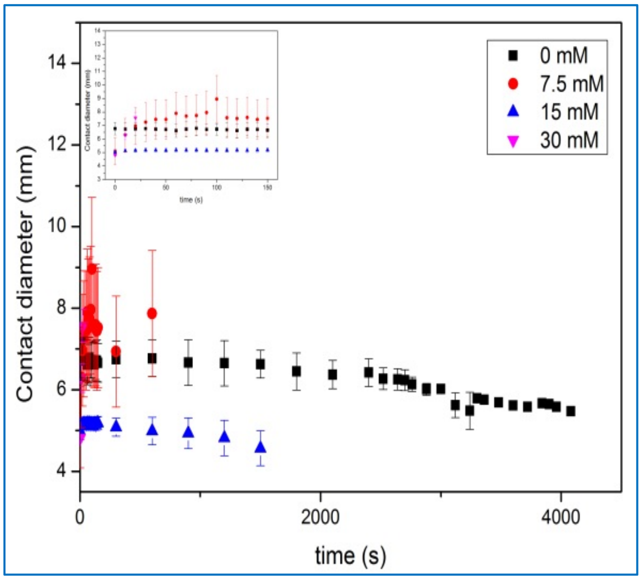

Figure 5. Contact diameter variation of Ludox-AS® as a function of SDS concentration, inset zoom of the diameter variation from 0 to 150 seconds.

As illustrated in Figure 3,4 and 5, the contact diameter is nearly constant for the Ludox-AS® at 0 mM and we observed a decrease of the mean contact angle which consistent with a pinned contact which would lead to a coffee ring stain cf. Figure 3,4 and 5. For 7.5 mM, the contact diameter increase slightly which correspond to a spreading of the drop with a decreasing contact though we do not observed a combination of constant contact diameter and mean contact angle which could explain the apparition of several concentric ring in the dried structure. At 15 mM, we also observe a slight contact diameter increase at the beginning (toward the end the diameter changes due to nearly complete solvent evaporation) with a decreasing mean contact angle, this should give use an pinned contact line though the dried deposit structure give an outer ring with lumps of particle in the center of the dried deposit. Finally for the 30 mM SDS concentration, an increase of the contact diameter is observed with a decreasing mean contact diameter (at 30 mM the mean contact angle and contact diameter cannot be determined after 20 seconds hence the three data points), while an outer ring is observed while a distribution with the particle in the middle of drop. The contact diameter variation and mean contact angle variation should be indicative of a Marangoni flow [13-17], despite the difference in dried deposit structure at 15 mM and 30 mM which are both well above the cmc are very different both in term of evaporation rate-much faster at 30 mM- and droplet spreading on a smooth substrate.

Deposit Structure

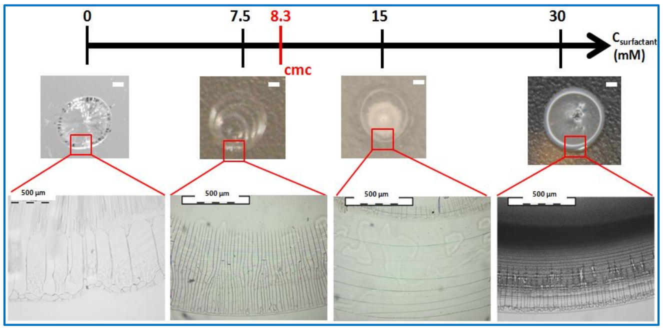

Figure 6. Set of depositions from dried water drops containing 2 wt% Ludox-AS® silica nanoparticles as a function of SDS concentration. Top pictures scale bars represents 2 mm. Bottom zoom-in optical microscopy images of the corresponding regions marked by the boxes of the deposit).

With the SDS addition, the dried deposit structure switch from a coffee ring stain at 0 mM, to several concentric ring at 7.5 mM, then several ring with a particle agglomeration at the centre at 15 mM to a thick outer ring at 30 mM with a fine particle distribution in the centre. We also observe that the particle are not raising above the substrate when the concentration of SDS increases. The cracks no longer propagate toward the centre at 30 mM compare to 7.5 and 15 mM cf. Figure 6 and 7.

The fast evaporation of the drop and the affinity of the SDS for the glass slide could create a depletion flocculation separation[27] the Ludox-AS® and the SDS attenuate the cracks[27].

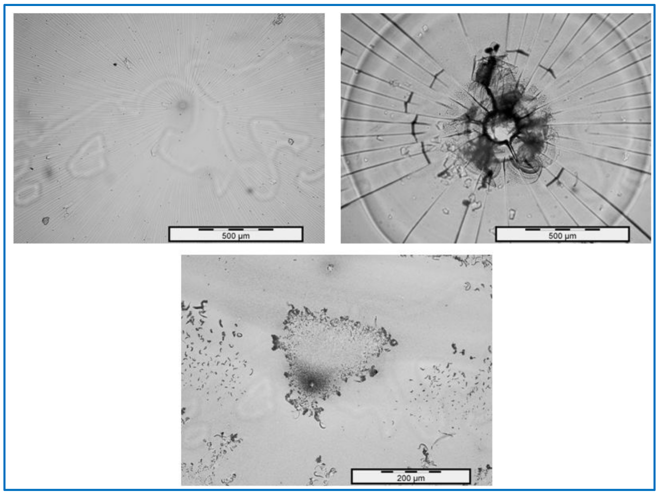

Figure 7. Set of depositions from dried centre of water drops containing 2 wt% Ludox-AS® as a function of SDS concentration (a) 7.5, (b) 15 and (c) 30 mM).

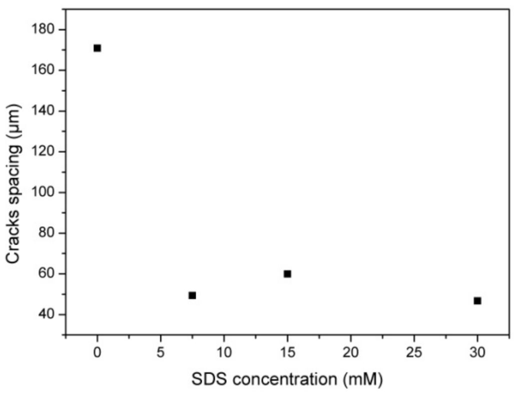

Figure 8. Cracks spacing with SDS concentration variation

The addition of SDS to the system decrease the cracks spacing cf. Figure 6 and 7. The addition of SDS does affect the stress formation during the drying process hence the final dried deposit structure[7,8,10].

The study of the wetting properties are not able to corroborate the dried deposit structure. Especially at 7.5 and 15 mM, a depinning effect is not observed which could explain the formation of several concentric rings in the dried deposit structure. When the droplet is pinned unless the system is surfactant free, a coffee ring stain is not observed upon solvent evaporation.

The difference in the dried deposit structure could be explain with the generation of a depletion flocculation in the system at concentration above the cmc.

The attenuation of cracks patterns could be explain by a faster drying of the suspensions which could prevent the formation of tensile stress toward the end of the evaporation . Thus, the observation of cracks patterns at the edges at 30 mM and the absence of cracks in the centre of the drop compare to radial cracks towards the centre at the other concentration (7.5 and 15 mM).

Conclusions

We have demonstrated that the addition of anionic surfactants, such as SDS, can lead to difference dried deposit structure of drying aqueous colloidal drops of spherical Ludox-AS®. The increase of SDS concentration generates a depletion flocculation SDS which leads to aggregation of particles at the center of the drop and attenuate the stress release hence the formation of cracks patterns in the centre of the drop especially at 30 mM. Additionally, the addition of the SDS decrease dramatically the cracks spacing in the dried deposit of the drops. Because, the use of surfactants is observed in several industrial applications involving drying suspensions, this knowledge offer new insight in the complex system of drying suspensions and suggests more specific utilization of surfactants to attenuate cracks patterns in drying suspensions with underlying application in ink jet printing or painting for example.

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Author Biography

Mahoulo Ahouansou received her MSc in chemistry from the University of Pierre and Marie Curie (Paris VI, in 2011). She is doing her PhD with Dr Olivier J. Cayre (School of Chemical and Process Engineering, University of Leeds) and Prof Simon Biggs (Executive Dean, Faculty of Engineering, Architecture and Information Technology, University of Queensland). Her main focus is to investigate the morphology and particle distribution upon solvent evaporation of colloidal suspensions in different formulation.