

Morphology and Self-Arraying of SDS and DTAB Dried on Mica Surface

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Dewetting phenomena produce interesting patterns that may impart new properties to solid surfaces. Sodium dodecyl sulfate (SDS) and dodecyltrimethylammonium bromide (DTAB) aqueous solutions, dried on mica surfaces under different drying conditions, undergo dewetting events forming structured deposits that were imaged by scanning electron microscopy (SEM), atomic force (AFM) and Kelvin force microscopy (KFM). Dry SDS, in most situations, displays long branched stripes formed due to fingering instability, while DTAB undergoes stick–slip motion forming patterns of parallel continuous or split stripes. In both systems, independently of drying conditions, surfactants pack forming lamellar structures, but with different orientations: SDS lamellae are aligned parallel to the substrate whereas DTAB lamellae are normal to the mica plane. Electric potential maps of SDS obtained by KFM show well-defined electrostatic patterns: surfactant layers deposited on mica are overall negative with a larger excess of negative charge in the interlamellar space than in the lamellar faces.

1. Introduction

Patterns formed by dewetting during fluid droplet drying on solid substrates have been widely studied as a problem in self-organization and also due to their potential applications as templates to promote micro and nanostructuring of surfaces,^{1–3} nanoparticle self-assembly^{4–7} and for printing technologies.^{8,9} In the case of evaporating droplets, the classic “coffee stain” pattern is often obtained, which is formed when a pinned contact line recedes on a substrate, leaving a dense, ring-like deposit along its perimeter.¹⁰ At a later stage of solvent evaporation, the contact line detaches itself from the ring and the thin central film can perform different dewetting movements, giving rise to the formation of various patterns on the solid surface.¹¹

Dewetting generally occurs through spontaneous nucleation of holes, followed by their growth and coalescence,^{12–14} or through an inward motion of the film edge.¹⁵ Woodward¹⁵ noted that when the three-phase line moves quickly from the sample edge, hole nucleation is suppressed, indicating that the predominant dewetting mechanism is either hole formation or three-phase line advance, depending on their respective kinetics.

Studies on the spreading of thin films of surfactant solutions on liquid–liquid^{16–21} and liquid–solid^{22,23} interfaces show that dewetting can occur either by fingering or stick–slip motions. The actual process is dependent on the solution composition, the thickness of pre-existing fluid layers and the surfactant–substrate interaction.

Garoff et al.²² used optical microscopy to observe dewetting motion during the spreading of dip-coated surfactant solutions on silicon oxide and sapphire. Their results revealed the occurrence of finger spreading when both the ionic surfactant and the surface have the same charge sign. On the other hand, when the surfactant molecules carry charge opposite to the ionic substrate, stick–slip motion predominates.

The aim of the present study was to further observe the morphology and structure formed by diluted surfactant solutions drying on solid surfaces, under different experimental conditions, to better understand its formation and properties. This drying phenomenon is present in everyday life when a dilute detergent solution evaporates on different solid surfaces, such as rinsed dishes, hair, and cloth.

Dewetting studies based on the morphology of dry solutes by AFM and SEM are complementary to optical microscopy and they have been applied to polymer films,^{3,24,25} and nanoparticle arrays.^{4,5,26,27} To our knowledge, there is no previous work using these methods to study surfactant dewetting structures, which are thus still not known concerning the morphology features that are uniquely disclosed by these techniques.

2. Materials and Methods

2.1. Sample Preparation and Analysis. Dodecyltrimethylammonium bromide (DTAB) and sodium dodecyl sulfate (SDS)

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(1) Karapanagiotis, I.; Gerberich, W. W.; Evans, D. F. *Langmuir* **2001**, *17*, 3266.
 (2) Bauer, C.; Dietrich, S. *Phys. Rev. E* **2000**, *61*, 1664.
 (3) Lee, L. T.; da Silva, M. C. V.; Galembeck, F. *Langmuir* **2003**, *19*, 6717.
 (4) Lee, L. T.; Leite, C. A. P.; Galembeck, F. *Langmuir* **2004**, *20*, 4430.
 (5) Rezende, C. A.; Lee, L. T.; Galembeck, F. *Langmuir* **2007**, *23*, 2824.
 (6) Huwiler, C.; Halter, M.; Rezwan, K.; Falconnet, D.; Textor, M.; Vörös, J. *Nanotechnology* **2005**, *16*, 3045.
 (7) Harada, T.; Hatton, T. A. *Langmuir* **2009**, *25*, 6407.
 (8) Gans, B. –J.; Schubert, U. S. *Langmuir* **2004**, *20*, 7789.
 (9) Soltman, D.; Subramanian, V. *Langmuir* **2008**, *24*, 2224.
 (10) Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A. *Nature* **1997**, *389*, 827.
 (11) Deegan, R. D. *Phys. Rev. E* **2000**, *61*, 475.
 (12) Seemann, R.; Herminghaus, S.; Jacobs, K. *Phys. Rev. Lett.* **2001**, *86*, 5534.
 (13) Sharma, A.; Jameel, A. T. *J. Colloid Interface Sci.* **1993**, *161*, 190.
 (14) Sharma, A.; Khanna, R. *Phys. Rev. Lett.* **1998**, *81*, 3463.
 (15) Woodward, J. T.; Schwartz, D. K. *Langmuir* **1997**, *13*, 6873.
 (16) Afsar-Siddiqui, A. B.; Luckham, P. F.; Matar, O. K. *Langmuir* **2003**, *19*, 703.
 (17) Afsar-Siddiqui, A. B.; Luckham, P. F.; Matar, O. K. *Langmuir* **2004**, *20*, 7575.
 (18) Afsar-Siddiqui, A. B.; Luckham, P. F.; Matar, O. K. *Adv. Colloid Interface Sci.* **2003**, *106*, 183.

(19) Hamraoui, A.; Cachile, M.; Poulard, C.; Cazabat, A. M. *Colloids Surf. A* **2004**, *250*, 215.
 (20) Cachile, M.; Schneemilch, M.; Hamraoui, A.; Cazabat, A. M. *Adv. Colloid Interface Sci.* **2002**, *96*, 59.
 (21) He, S.; Ketterson, J. B. *Phys. Fluids* **1995**, *7*, 2640.
 (22) Frank, B.; Garoff, S. *Langmuir* **1995**, *11*, 87.
 (23) Qu, D.; Suter, R.; Garoff, S. *Langmuir* **2002**, *18*, 1649.
 (24) Zhang, Z.; Wang, Z.; Xing, R.; Han, Y. *Surf. Sci.* **2003**, *539*, 129.
 (25) Burtovyy, R.; Luzinov, I. *Langmuir* **2008**, *24*, 5903.
 (26) Shenhar, R.; Jeoung, E.; Srivastava, S.; Norsten, T. B.; Rotello, V. M. *Adv. Mater.* **2005**, *17*, 2206.
 (27) Fan, F. Q.; Stebe, K. J. *Langmuir* **2004**, *20*, 3062.

(99% pure) were purchased from Sigma and used without further treatment. Surfactant solutions were prepared with MilliQ water at 0.5, 2, and 10 mM concentrations. Samples were obtained by depositing a drop of the surfactant solution on freshly cleaved mica (Ted Pella), followed by drying at controlled relative humidity ($15 \pm 2\%$ or $50 \pm 2\%$) and temperature ($20 \pm 2^\circ\text{C}$ or $50 \pm 2^\circ\text{C}$). Most experiments were done drying 2 mM surfactant solutions under $20 \pm 2^\circ\text{C}$ and $50 \pm 2\%$. Drop volume used was $10\ \mu\text{L}$ except when indicated otherwise.

Drop evolution during the drying process was imaged and recorded using an Edmund optical microscope coupled to a SSC-C350 Sony camera. Images were processed in the AVerTV program and analyzed using the IMAGE-PRO PLUS 4.0 (Media Cybernetics) software to obtain the wetted area and the contact angle.

Dewetting patterns were imaged in samples dried for 24 h prior to examination in the microscope. Images from large areas of DTAB/mica and SDS/mica samples were recorded in a scanning electron microscope (SEM, JEOL LV-JSM 6360), operating at 15 kV. Samples were mounted on brass stubs and coated with Au/Pd using a MED 020 equipment (Bal-Tec). Image processing was performed using the IMAGE-PRO PLUS 4.0 (Media Cybernetics) software.

Dry samples were also imaged by atomic force microscopy in two electric scanning modes: electric force microscopy (EFM) and electric potential microscopy, also known as Kelvin force microscopy (KFM). In both cases, a Pt-coated tip scans the sample in noncontact mode and electrical and topography images are simultaneously obtained.

In EFM, the tip scans the sample passing twice at every line: a first scan is performed close to the surface (typically 10 nm) to measure the sample topography, considering the short-range van der Waals interaction forces; the same line is then rescanned at a constant height (about 60 nm apart from the sample), where the electrostatic forces predominate. The probe is kept under constant bias but as it crosses over an electrically charged region, an extra voltage is applied to maintain constant its oscillation frequency and to compensate phase shift. The micrograph is a false-color map of applied voltage as a function of pixel position, showing different electric domains on the surface.²⁸

The KFM mode also maps electrostatic domains on the sample surface, with the advantage of being able to quantify these domains in terms of electrostatic potential variations. It operates based on the Kelvin method, except that electrostatic forces acting on the cantilever are measured instead of ac currents.²⁹ Scanning is performed in only one step at a 10 nm height by a conductive tip connected to dc and ac (40–70 kHz) power supplies. The dc power supply is used to bias the probe, while the ac source introduces an alternating force component in the cantilever, which depends on the potential derived from fixed charges on the surface. Whenever the surface and the probe potential differ, a dc voltage is applied to nullify this difference, and the surface potential can thus be quantified.³⁰

EFM images presented in this work were obtained in a Topometrix Discoverer TMX 2010 instrument using a cantilever with resonance in the 60–100 kHz range and stiffness constant between 1 and 5 N/m (as informed by the manufacturer). KFM images were obtained in a Shimadzu SPM 9600 microscope equipped with an environmental chamber that allows temperature ($25 \pm 2^\circ\text{C}$) and relative humidity ($50 \pm 2\%$) to be controlled during image acquisition. A Pt-coated silicon nitride cantilever was used, with nominal resonance frequency of $82 \pm 16\ \text{kHz}$ and $2.9 \pm 0.6\ \text{N/m}$ stiffness constant, according to the manufacturer's calibration data. Resonance frequency was redetermined in this laboratory as 69.9 kHz, in agreement with the expected value.

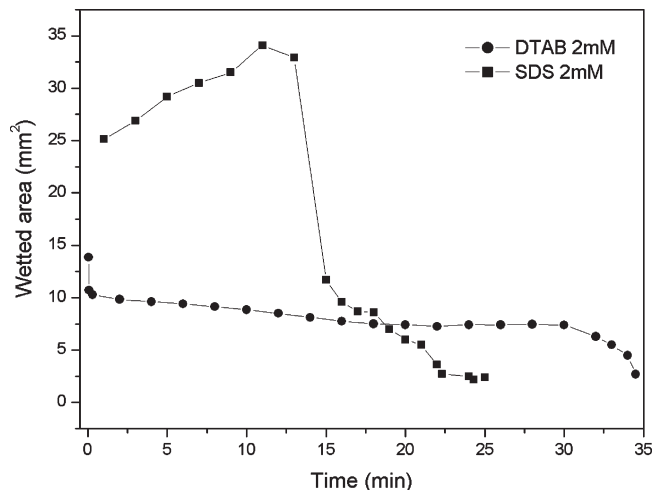


Figure 1. Wetted area as a function of time for a $10\ \mu\text{L}$ drop deposited on mica at 20°C and 50% RH: (●) DTAB 2 mM; (■) SDS 2 mM.

2.2. Evaluation of the Surface Charge Density (σ). The distribution of excess charge on SDS dried on mica was evaluated using a procedure described in a previous paper.^{31,32} This is based on comparison of the electric potential measured at any point close to an electrostatically patterned surface to the potential calculated applying the superposition principle to a virtual charge distribution.³³ The total electrostatic potential (V_T) generated by all surface charges at the plane 10 nm away from the charge-carrying surface is calculated using a C^{++} code for eq 1

$$V_T = \sum_{i=1}^n V = \frac{1}{4\pi\epsilon\epsilon_0} \sum_{i=1}^n \frac{q_i}{r_i} \quad (1)$$

where q is the electric charge, ϵ_0 is the permittivity of free space, and ϵ is the dielectric constant of the medium.

A squared area ($200 \times 200\ \text{nm}$) of an electrostatic map obtained by KFM (indicated by the arrow in Figure 4) is represented by a 10×10 pixel matrix and compared to the potential calculated for a virtual charge matrix of the same size created in MS Excel, carrying definite numbers of charges per pixel. The virtual charge distribution on the matrix is adjusted by trial and error, until the calculated and the experimental electric potentials match. The surface charge density was calculated considering the charge distribution within this $0.04\ \mu\text{m}^2$ area.

3. Results

3.1. Drying Process. Optical images for SDS and DTAB droplets drying on mica were obtained during water evaporation and drop area change with time could be followed. Figure 1 shows how the wetted area changes as a function of time for 2 mM DTAB and SDS solutions, during drying at 20°C and 50% RH.

DTAB Solution Deposited on Mica. In the DTAB/mica system, the droplet spreads fast on the substrate as soon as it is deposited, but in a few seconds, it spontaneously retracts (see Figure 1), forming a drop with high contact angle (55°). Then, the wetted area and the contact angle slowly reduce further with time, suggesting that drop retraction at this stage is caused by solvent evaporation. The dry material is mainly accumulated in the final

(28) Rezende, C. A.; Gouveia, R. F.; da Silva, M. A.; Galembeck, F. J. *Phys. Cond. Matt.* **2009**, *21*, 263002.

(29) Nonnenmacher, M.; O'Boile, M. P.; Wickramasinghe, H. K. *Appl. Phys. Lett.* **1991**, *58*, 2921.

(30) Galembeck, F.; Costa, C. A. R. *Encyclopedia of Surface and Colloidal Science*; Dekker Encyclopedias: New York, 2006.

(31) Gouveia, F. G.; Costa, C. A. R.; Galembeck, F. J. *Phys. Chem. B* **2005**, *109*, 4631.

(32) Gouveia, F. G.; Costa, C. A. R.; Galembeck, F. J. *Phys. Chem. C* **2008**, *112*, 17193.

(33) Griffiths, D. J. *Introduction to Electrodynamics*, 3rd ed.; Prentice Hall: Englewood Cliffs, NJ, 1999.

wetted area. A thick edge, visible to the naked eye, delimits the dry surfactant droplet.

SDS Solution Deposited on Mica. SDS droplets spontaneously spread on the substrate soon after its deposition (see Figure 1). The contact angle at this point is ca. 22° . In the first part of the curve (until ca. 13 min after solution deposition), the wetted area increases by 30% and the three-phase-line advances on the substrate as the contact angle decreases to 12° .

Following the initial slow drop expansion, an abrupt change is verified, as shown in Figure 1: the deposited solution suddenly retracts to a small drop, decreasing the wetted area to ca. one-third. In the last minutes of the drying process, the three-phase line recedes on the substrate and the wetted area continuously decreases, while the contact angle is almost constant (ca. 10°). As in DTAB/mica system, the SDS dry droplet presents a thick edge, which is visible to the naked eye.

Time to evaporate to dryness under the specified conditions is usually in the range of 20–25 min for SDS solution and 30–35 min for DTAB. This shows that the different types of DTAB and SDS adsorption on mica and also the drop shape affect the kinetics of drying and dewetting. Drying time is still within these ranges when the experimental conditions (surfactant concentration, drop volume, and relative humidity) change, as described in the sample preparation section. However when the drying temperature increases to 50°C , this time is reduced to ca. 10 min.

3.2. Surfactant Patterns on Substrates. Aqueous surfactant solution thin films dewet the mica surface upon drying, forming characteristic patterns. The use of SEM for pattern examination is quite convenient due to its broad magnification range and large observation field, producing representative images of the system under many scales. SEM, AFM, and KFM were thus jointly used to image dewetting patterns.

SDS Deposited on Mica. SEM micrographs obtained for the SDS 2 mM solution dried at 20°C and 50% RH are shown in Figure 2. Low magnification image from backscattered electrons (BEI) (Figure 2a) confirms that the dry material forms a region ca. 5.5 mm^2 delimited by a thick edge. Three distinct regions are observed as indicated in Figure 2a: 1) the flat mica surface; 2) the thick edge of the dry droplet and 3) the inner droplet region.

BEI images in Figure 2b–d present dewetting patterns in region 3, showing long surfactant fingers on mica surface branching out from the edge to the center of the droplet. The same branched pattern delimited by a thick ring was observed under different experimental conditions, using lower SDS concentration (0.5 mM), lower volume of the deposited drop ($5\text{ }\mu\text{L}$) or low humidity (15% RH). Examples of patterns obtained under these conditions (changing one at a time) are shown in Figures S2a–d and S3a of the Supporting Information.

The branched morphology is modified when higher drying temperature (50°C) is used. In this condition, various rings are formed instead of the single one observed at 20°C , and small fingers grow from these rings, as shown in Figure S5a,b of the Supporting Information. Moreover, by increasing surfactant concentration to 10 mM, a continuous thick film is obtained (Figure S3b,c, Supporting Information), without exposing the naked substrate, indicating that dewetting does not occur at this higher initial concentration condition.

Branched patterns are also observed by AFM, as presented in Figure 3a for a 2 mM solution dried at 20°C and 50% RH. Moreover, this image shows that the deposited fingers are made up of smooth flat layers with a few holes. Height along different regions of dry SDS droplet presents a strong variation, as observed in various images obtained by AFM. Close to the edge,

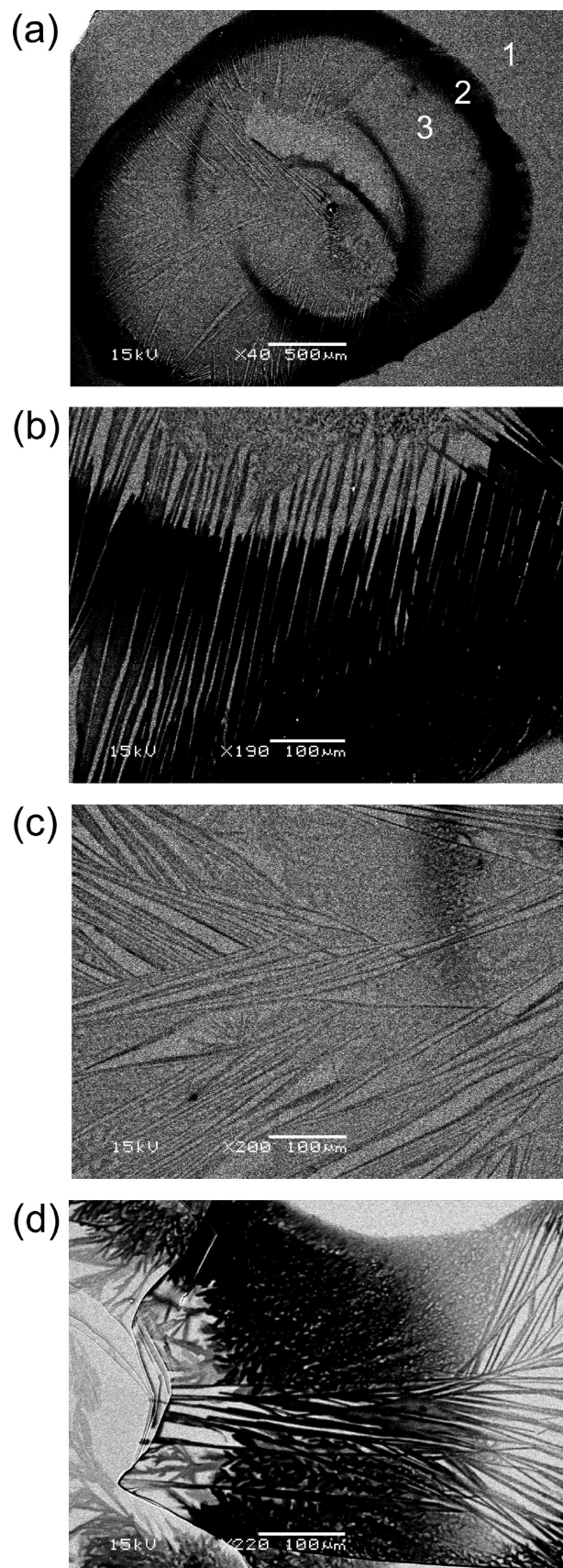


Figure 2. SEM images of SDS 2 mM dried on mica at 20°C and 50% RH: (a) BEI image, scale bar = $500\text{ }\mu\text{m}$; (b–d) BEI images, scale bars = $100\text{ }\mu\text{m}$.

the deposited material height reaches ca. 700 nm. Height decreases toward the droplet center, where regions with very thin

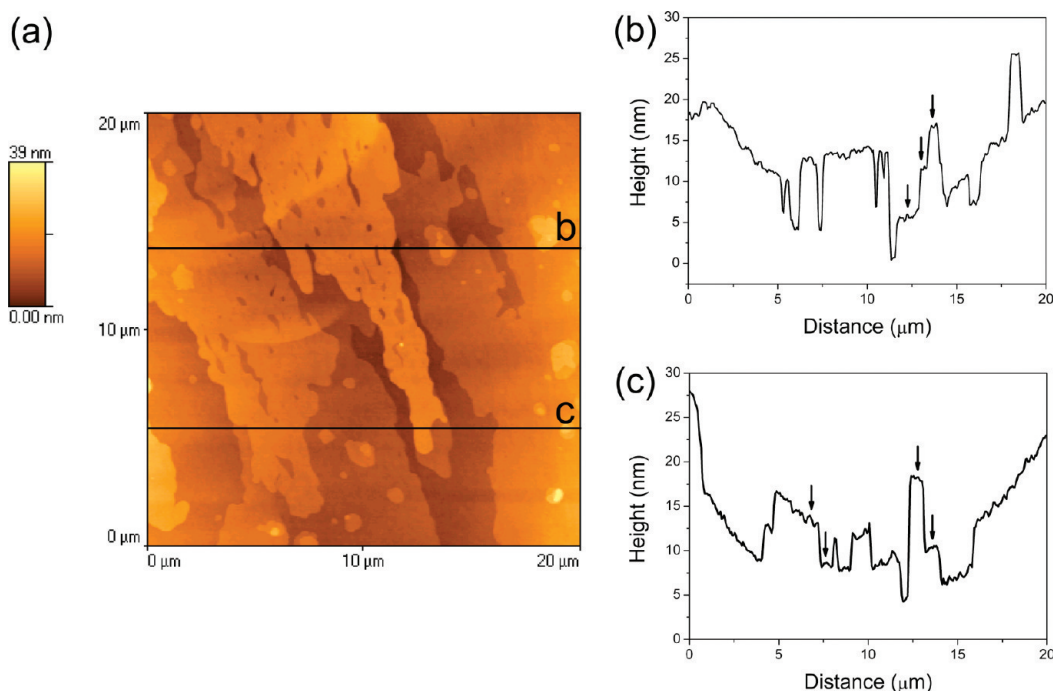


Figure 3. AFM results for SDS 2 mM deposited on mica, dried at 20 °C and 50% RH (a) topography image; (b and c) height profiles of lines indicated in (a).

surfactant coverage are found, as shown in Figure 3a. Line profiles b and c, traced along two lines in Figure 3a, show that the thickness difference between two neighboring layers is nearly constant (ca. 6 nm).

Parts a and b of Figure 4 show beautiful examples of the branched pattern obtained in a relatively thick region of the sample (maximum height ca. 650 nm). The fingers are formed by superimposed surfactant layers horizontally displaced on the surface, with discernible steps topped by a flat surface. Electric potential images simultaneously obtained by KFM on the same sample area are presented in Figure 4, parts c and d, displaying a characteristic electric contrast. Steps between surfactant layers are electrically negative, relative to the layer surfaces or terraces.

The sample area presented in this image has a total, slightly negative electric potential, varying between 0 and −200 mV. This indicates a small negative charge excess on the overall surfactant deposit, calculated as -3×10^{-3} C/m² by using the method described in the experimental section.

The small potential difference also helps to highlight the sample layered structure, since the pattern is highly ordered and the positions of the potential differences correlate well with the steps between terraces. Line profiles traced on the KFM images reveal that every step has an electric potential −60 to −100 mV lower than the respective surface.

In Figure 5, two calculated electric potential profiles, based on the calculated virtual charge distribution are plotted together with the corresponding experimental potential profiles obtained from the small squared area indicated by the arrow in Figure 4. Reasonable agreement is thus observed between the experimental and the calculated curves.

Layered arrays were observed in any of the SDS samples studied in this work, prepared under different experimental conditions, as shown in Figure S6a–c (Supporting Information) for samples dried at 15% RH or 50 °C. Even when the overall morphology of the dewetting patterns change, as when the drying temperature is increased from 20 to 50 °C, layers observed at a smaller size scale are preserved. This is thus a robust supramole-

cular structure formed even under rather drastic drying conditions.

DTAB Deposited on Mica. The low magnification image obtained by BEI for the DTAB/mica system (Figure 6a) agrees with optical images: the dry surfactant forms a delimited region of ca. 2 mm² enclosed within a thick ring. This sample was prepared by depositing 10 μL of a 2 mM DTAB solution on mica, followed by drying at 20 °C and 50% RH. The bordering ring was also observed for DTAB samples with lower (0.5 mM) and higher (10 mM) initial concentrations of surfactant, as shown in Figure S4a,b of the Supporting Information.

In Figure 6b, an image with higher magnification shows three distinct regions on the substrate: (1) the flat mica surface, (2) the thick edge, and (3) the region inside the dry drop, the same as in SDS. The amount of surfactant in the droplet center is thus lower than at its edge.

In region 3, the dry material forms long parallel, highly ordered stripes that can be observed in Figure 6c. These are mainly distributed within two intercalated populations: the first is formed by long stripes (45–65 μm length), and the second one by stripes within the 8–16 μm length range. Between the rows of long and short stripes, material with perpendicular orientation and complex morphology is observed. Furthermore, a region with broader stripes is also detected in the lower right corner of the image.

A secondary electron (SEI) micrograph of DTAB dried on mica is presented in Figure 6d and highlights the parallel, regular spacing of DTAB stripes. In this region of the sample, long stripes break into circular structures with areas ranging from 3 to 5 μm². An elongated structure with bottlenecks can be seen on the left-hand side of a split stripe (indicated by the arrow in Figure 6d). Neck formation is a preliminary step to full stripe breakdown. Completely split stripes are observed in DTAB samples prepared at higher surfactant concentration (10 mM), as shown in Figure S4c (Supporting Information).

Topography images obtained by noncontact AFM also show the presence of circular and elongated structures in the DTAB/mica system, as seen in Figure 7a. Maximum height of the deposited

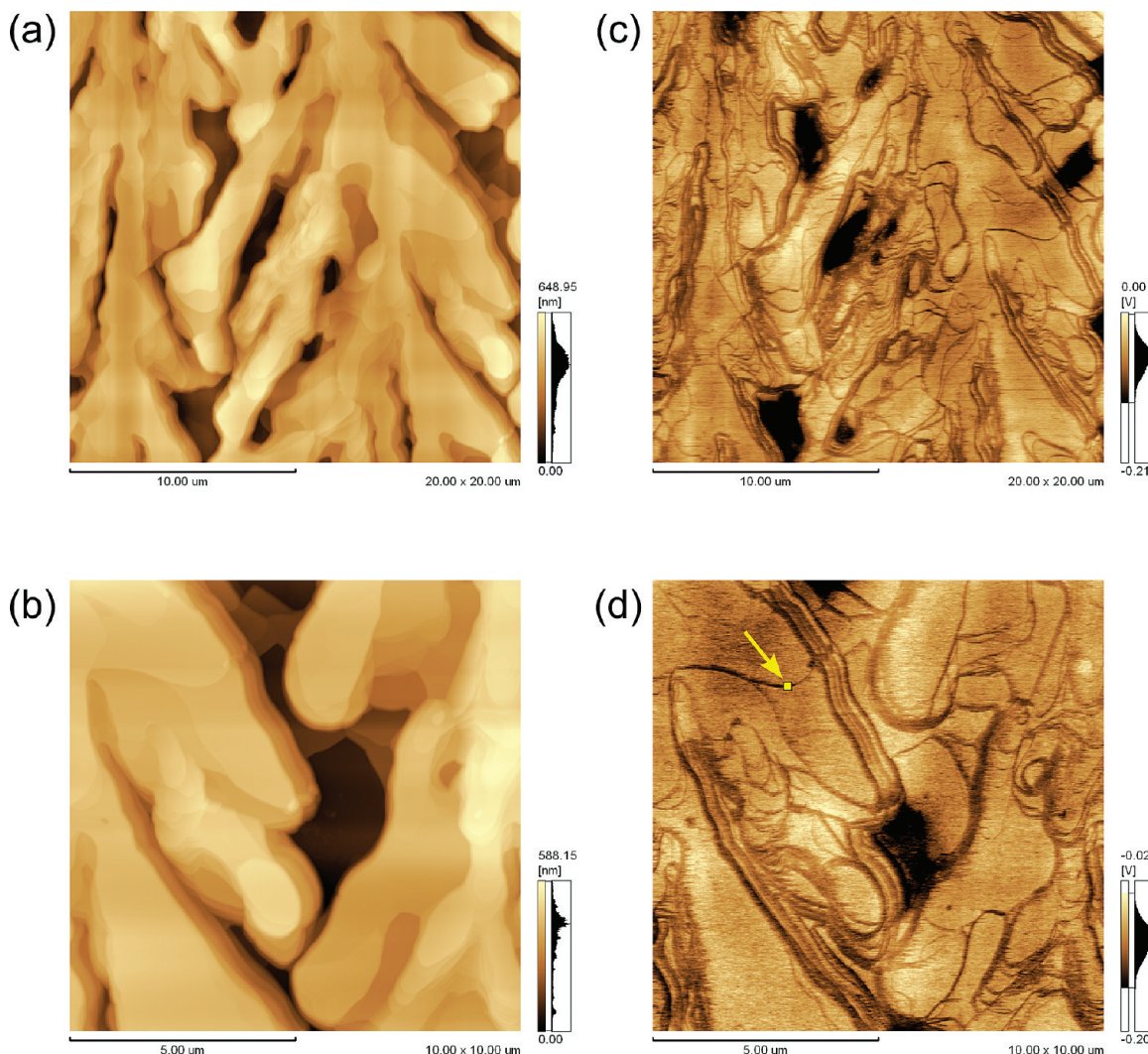


Figure 4. (a and b) topography images; (c and d) electric potential images (KFM) obtained for SDS 2 mM dried on mica at 20 °C and 50% RH.

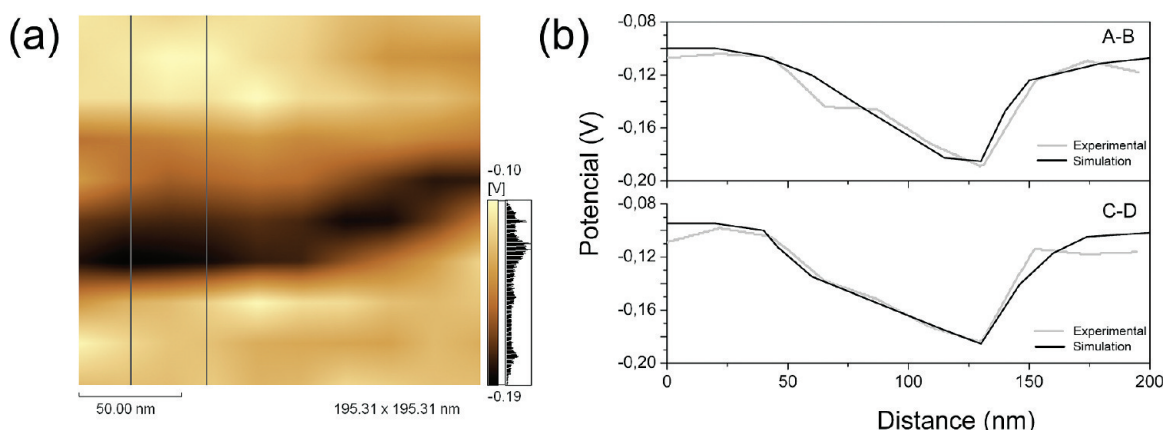


Figure 5. (a) amplified region of the KFM image shown in Figure 4d (indicated by the arrow); (b and c) calculated and experimental electric potential profiles A–B and C–D inside this region.

material in this image is ca. 1.3 μm . The same area was imaged by electric force microscopy (EFM) and the result (Figure 7b) shows an electric pattern superimposed to morphology features, as in the previously shown results for SDS.

However, DTAB does not form parallel flat layered structures similar to SDS. Other samples imaged in the KFM mode also

showed elongated and circular structures, but the layer edges were not as evident as in SDS/mica. Parts a and b of Figure 8 show topography and electric potential images of a region formed by quasi-elliptical drops about 2 μm high, distributed on the substrate. The overall image potential is also negative, ranging from -620 to -450 mV, with surfactant domains more positive than the mica substrate.

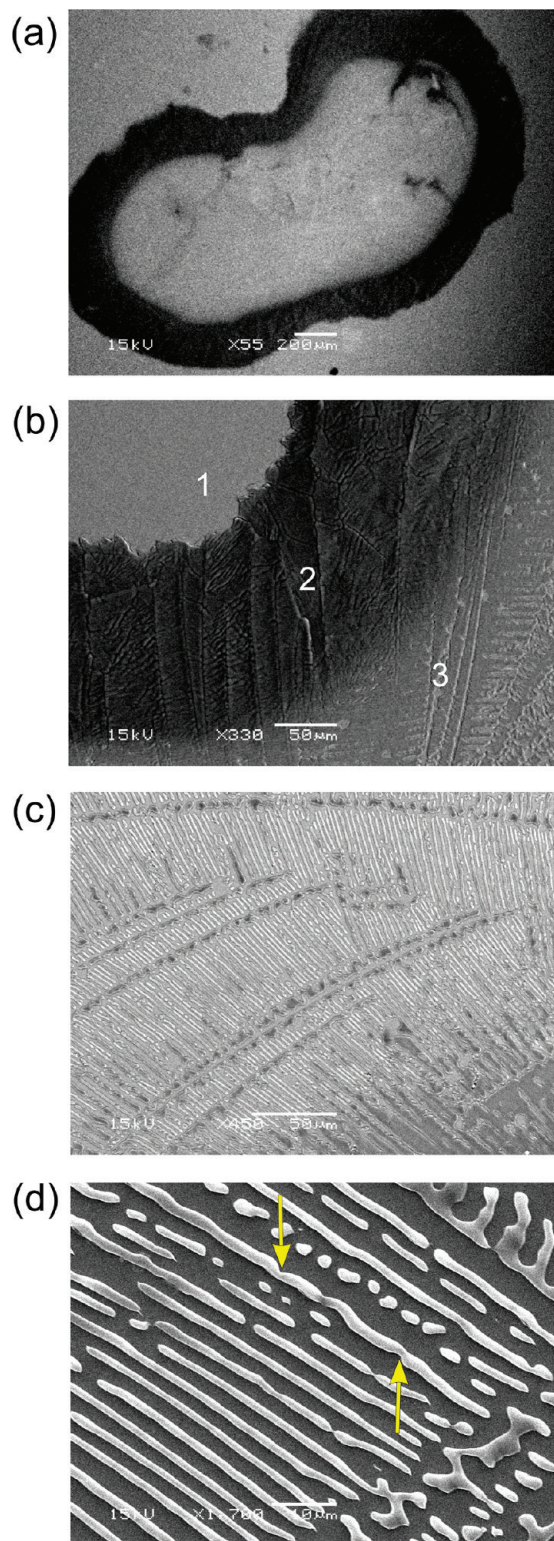


Figure 6. SEM images of DTAB 2 mM dried on mica at 20 °C and 50% RH: (a) BEI image, scale bar = 200 μm ; (b and c) BEI images, scale bars = 50 μm ; (d) SEI image, scale bar = 10 μm .

Parts a and b of Figure 9 show 3D reconstructions of the topography images for SDS and DTAB dried on mica, allowing a better visualization of the differences between the deposits formed by the two surfactants. Overall, SDS deposits resemble geological arenite formations with canyons while DTAB formations look like sierras or mountain ranges.

4. Discussion

The solid patterns formed by each surfactant on mica reflect the different dewetting motions of the thin aqueous films at a later drying stage. Several papers in literature describe dewetting mechanisms of different surfactant solutions based on real time optical microscopy analysis or direct observation of the films.^{17–23} Using different microscopy techniques with resolution in the nanometer range, the present work shows marked differences between dry solid surfactant morphology in the colloidal range, correlating it to dewetting motion. Moreover, hitherto undisclosed electric patterns formed by dewetting are also evidenced and interpreted based on known supramolecular surfactant arrangements.

4.1. Droplet Drying. During the drying process of diluted surfactant solutions, the three-phase contact line moves causing the drop shape changes shown in Figure 1 and in previous literature.²² These movements can be assigned to the various concurrent processes of surfactant adsorption, aggregation and water evaporation.³⁴ In the DTAB/mica system, surfactant adsorption follows the four-step “Somasundaran–Fuerstenau” isotherm during the drying process. Drop retraction in the early drying stages is also described as autophobing,^{16–18,23} the result of surfactant adsorption driven by attractive electrostatic interaction between DTA^+ and mica. This is schematically represented in Figure 10a.

Regarding the SDS/mica system, an initial increase in wettability is observed in Figure 1. Since both DS^- and mica have negative charge, the first surfactant layer is adsorbed on the substrate by its tails, directing the head groups toward the solution and increasing the surface hydrophilicity.²²

Drop retraction only occurs ca. 15 min after liquid deposition on mica, suggesting a change in surface hydrophobicity at this drying stage. The presence of hydrophobic areas on mica, inside the region that was previously wet by the liquid droplet, was confirmed by experiments on water condensation (available as Supporting Information). As the SDS solution dewets and dries on mica, surface hydrophilicity changes due to the adsorption of other surfactant layers, forming aggregates in which hydrophobic tails make up a significant part of the outer surface layer. This can be evidenced in the structures revealed by AFM, EFM, and KFM. The formation of hydrophobic SDS surface is schematically shown in Figure 10b.

4.2. Surfactant Patterns on Substrate. Formation of a surfactant layer enclosed by a thick ring was assigned by Deegan et al.¹⁰ to capillary flow. Pinning of the drying droplet contact line ensures that the liquid evaporating from the edge is replaced by the liquid from within, leaving the inner part of the drying droplet depleted from surfactant. The ring has a variable width, since denser deposits are formed in highly convex regions, where the evaporating flow is more intense.¹⁰

Dry patterns observed on the SDS and DTAB samples are both a result of spreading and retraction of the deposited droplets but at different times, for different reasons. In the case of SDS on mica, the characteristic finger pattern (shown in Figures 4, S2b–d, and S3a (Supporting Information)) can be assigned to nonuniform distribution of surfactant molecules at the liquid–air interface. SDS monomers are mainly adsorbed at the liquid–air interface, since their adsorption on mica is unfavorable due to the charge repulsion. As the solvent evaporates, the droplet surfactant concentration increases as well as the gradients of surfactant concentration on its surface. Fingers are thus developed at the

(34) Soboleva, O. A.; Summ, B. D. *Colloid J.* **2003**, *65*, 89.

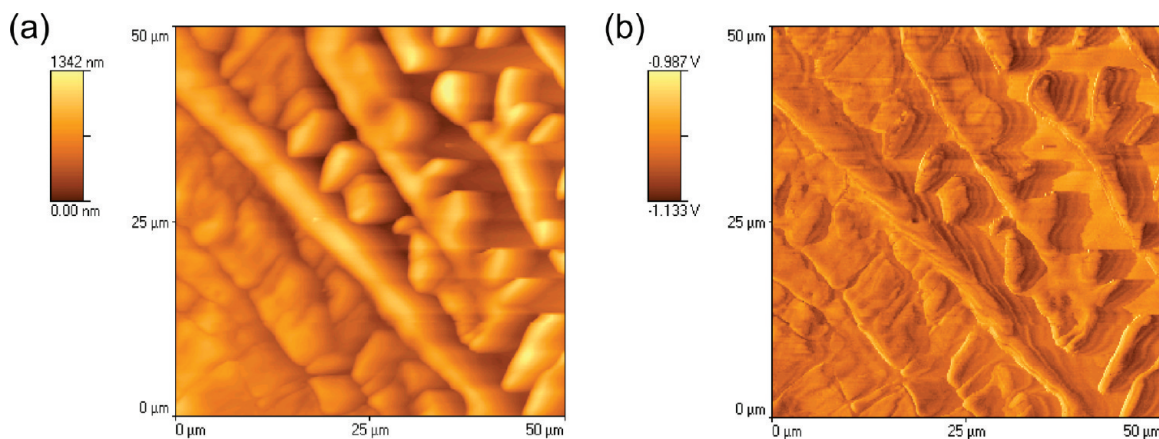


Figure 7. (a) Topography and (b) electric force images (EFM) simultaneously obtained for DTAB 2 mM dried on mica at 20 °C and 50% RH.

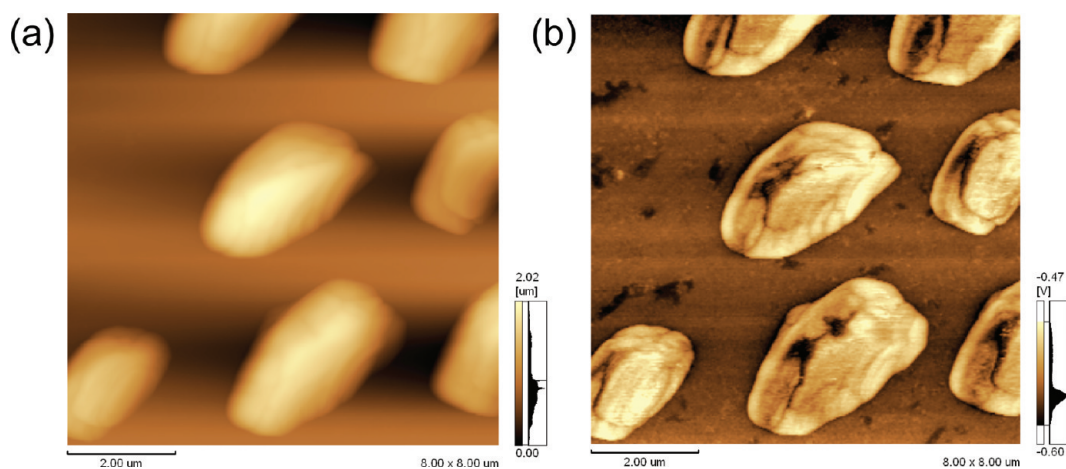


Figure 8. (a) Topography and (b) electric potential images (KFM) obtained for DTAB 2 mM dried on mica at 20 °C and 50% RH.

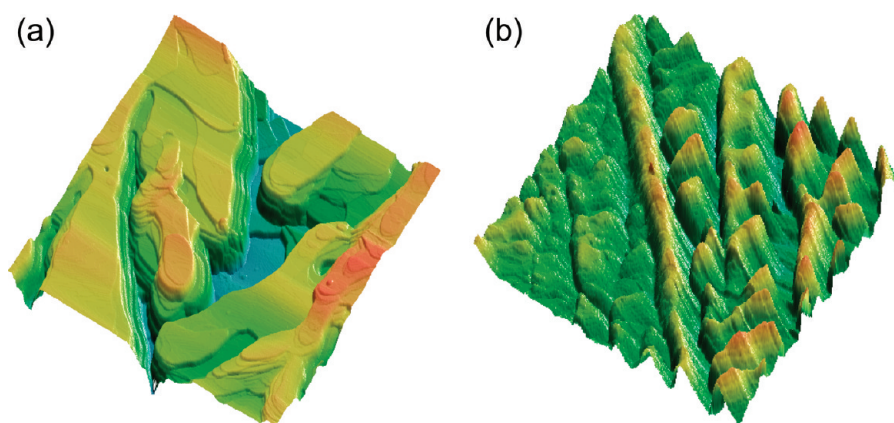


Figure 9. 3D reconstruction of topography images for (a) SDS and (b) DTAB, both dried on mica.

drying front^{18,35} as a consequence of Marangoni instability and the dewetting film takes on a dendritic morphology templating the solid structure.

Fingering patterns were also observed by other authors^{16,19,22,36} who studied the spreading of surfactant solutions on uncoated or prewetted substrates when the surfactant-substrate interaction is repulsive or weakly attractive.

On the other hand, DTAB is strongly electrostatically attracted to mica, and in this case, the three-phase line recedes by stick–slip motion. A liquid bump is formed along the three-phase-line and the film moves by quickly receding followed by pinning and receding again. This bump can also be broken by fingering instability,³⁷ giving rise to the long stripes observed in Figure 6. This movement is repeated many times, leaving several ordered

(35) Vuilleumier, R.; Ego, V.; Neltner, L.; Cazabat, A. M. *Langmuir* **1995**, *11*, 4117.

(36) Leizerson, I.; Lipson, S. G.; Lyushnin, A. V. *Langmuir* **2004**, *20*, 291.

(37) Karthaus, O.; Gräsjo, L.; Maruyama, N.; Shimomura, M. *Chaos* **1999**, *9*, 308.

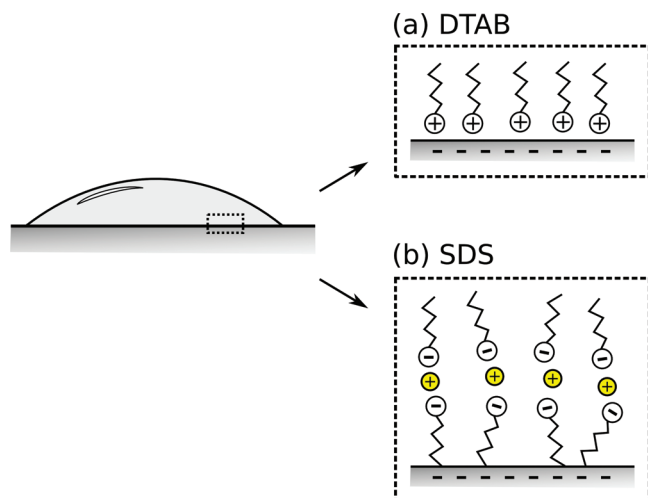


Figure 10. Scheme showing possible surfactant adsorption mechanisms on mica surface: (a) DTAB monolayer adsorbs on the substrate driven by electrostatic interaction; (b) SDS molecules aggregate on the surface at higher surfactant concentration. In both cases, surfactant hydrophobic tails face the solution, resulting on the retraction of the liquid droplet during drying.

lines of surfactant on the substrate with regular spaces between them (Figure 6, parts c and d). Rayleigh instability on the liquid stripes leads to their breaking into droplets, as can be seen in SEM (Figure 6d) and AFM images (Figures 7a and 8a). Stripe rupture is favored at higher concentrations (Figure S4c, Supporting Information), producing lines of small circular spots due to the formation of a dense surfactant monolayer at the liquid–gas interface, where short-range forces take on an important role, decreasing the surface film elasticity.³⁸

Garrof and co-workers previously observed the strong influence of the surfactant–substrate interaction on the motion of the drying film.²² These authors observed organized structures in dip-coated samples, but only a thick ring containing disorganized surfactant patterns was obtained when the coffee-stain drying was used.³⁹ Ordered patterns obtained by coffee-stain depend on surfactant concentration, and they may not be observed below (Figure S4a, Supporting Information) or above (Figure S3a,b, Supporting Information) a defined concentration range, as verified in the present study.

4.3. DTAB and SDS Multibilayers. In addition to showing the overall morphology of DTAB and SDS dried on mica, AFM images revealed that the dewetting patterns are formed by stacks of uniform layers that align parallel to mica, in the case of SDS, while DTAB deposits are normal to the mica surface (see Figure 9). This was assigned to different movements performed by the receding solutions. It is known that high shear rates can induce orientation transition (from parallel to perpendicular) in surfactant lamellar systems.^{40,41} Stick–slip motion of DTAB drying solution is thus responsible for reorienting lamellae stacks while fingering only breaks flat lamellae thin layers into smaller pieces.

Uniform height difference between two neighboring SDS layers (6 nm) is consistent with the height of one surfactant bilayer plus the aqueous channel, which is the unit cell of the

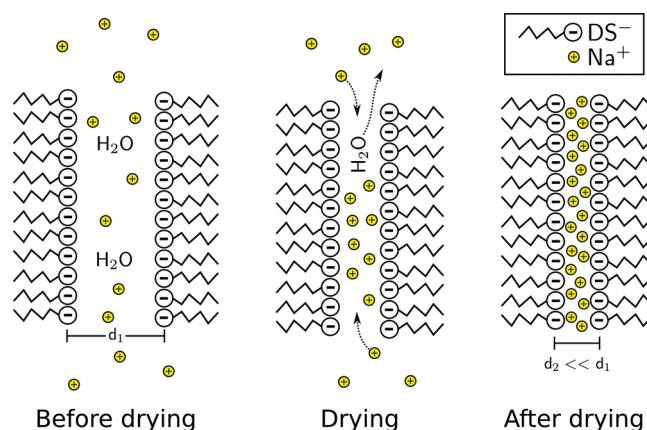


Figure 11. Scheme showing the charge regulation mechanism to explain the charge density decrease in SDS sample with drying. Na^+ ions compensate the charge repulsion between negatively charged SDS bilayers, forced to approach due to water evaporation.

lamellar phase.⁴² Coiro et al.⁴³ determined that the hydrophobic part of one SDS bilayer at low water content (1:8 water: SDS) is about 4 nm, which implies that the aqueous channel (water, surfactant headgroups and counterions) in the deposited bilayers is ca. 2 nm. An estimate using van der Waals volumes⁴⁴ shows that each sulfate group can contribute ca. 0.6 nm to the aqueous channel thickness, thus being in agreement with the measured thickness. In the DTAB system, the bilayer thickness could not be obtained because the films are too thick and mainly perpendicular to the substrate.

The electrostatic patterns observed by KFM in the dry SDS sample and the excess charge calculations yield a small negative charge density ($\sigma = 3 \times 10^{-3} \text{ C/m}^2$), much less than $\sigma = 0.2 \text{ C/m}^2$ ^{45–48} determined in the presence of excess water by sodium diffusion measured by nuclear magnetic resonance (Na-NMR). The charge density in wet conditions is assigned to the Na^+ entropy of mixture in water and this factor is not present in the dry film. Counter ion dissociation causes repulsion between the charged surfactant bilayers, which explains swelling without phase separation.

SDS bilayers dried on mica have thus an approximately only 1/70 of the charge density reported for lamellar phases with higher water contents, but the residual charge density shows that the surfactant layers are not electroneutral. The mechanism proposed to explain the decrease in charge density with drying is schematically represented in Figure 11. During drying, water evaporation forces the approximation of the two negatively charged surfaces, so that their electric double layers increasingly overlap, creating a potential well for Na^+ counterions.

According to calculations by Guldbrand et al.,⁴⁵ if σ were kept constant (0.2 C/m^2) despite water evaporation, the osmotic pressure between the two charged surfaces would take on very high positive values at a 2 nm separation, making surface

(38) Langevin, D. *Adv. Colloid. Interf. Sci.* **2000**, *88*, 209.

(39) Beppler, B. K.; Varanasi, K. S.; Garoff, S.; Evmenenko, G.; Woods, K. *Langmuir* **2008**, *24*, 6705.

(40) Winey, K. I.; Patel, S. S.; Larson, R. G.; Watanabe, H. *Macromolecules* **1993**, *26*, 4373.

(41) Guo, H. X. *J. Chem. Phys.* **2006**, *124*, 054902.

(42) Evans, D. F.; Wennerström, H. *The Colloidal Domain: Where Physics, Chemistry, Biology and Technology Meet*, 2nd ed.; John Wiley & Sons: New York, 1999.

(43) Coiro, V. M.; Manigrasso, M.; Mazza, F.; Pochetti, G. *Acta Crystallogr.* **1987**, *C43*, 850.

(44) Edward, J. T. *J. Chem. Educ.* **1970**, *47*, 261.

(45) Guldbrand, L.; Jönsson, B.; Wennerström, H.; Linse, P. *J. Chem. Phys.* **1984**, *80*, 2221.

(46) Turesson, M.; Forsman, J.; Akesson, T.; Jönsson, B. *Langmuir* **2004**, *20*, 5123.

(47) Linse, P.; Lobaskin, V. *Phys. Rev. Lett.* **1999**, *83*, 4208.

(48) Forsman, J. *Langmuir* **2006**, *22*, 2975.

approach at this distance very unlikely to occur. Our results support the idea of repulsive electrostatic interaction influencing the dissociation degree of the surface groups, a condition known as charge regulation.⁴⁹ The small negative charge density suggests that a small portion of sodium ions is left on the mica surface during the drying process.

To sum up, SDS and DTAB dried on mica surface present two levels of organization: the first one derives from the dewetting patterns and the second is a consequence of surfactant self-assembly. Dewetting pattern variations are obtained by changing experimental conditions, but organization at the supramolecular scale (lamellae formation) is persistent. Interaction between the two organization levels causes the formation of completely different topography and electrical patterns for these two surfactants deposited on mica surfaces.

5. Conclusion

SDS and DTAB dried on mica from aqueous solutions are templated by dewetting movements performed by the solutions. Liquid motion and thus the resulting patterns may be altered by changing the drying conditions and the surfactant concentration.

(49) Hunter, R. J. *Foundations of Colloidal Science*, 2nd ed.; Oxford University Press: New York, 2005.

Long polyhedral or needle-shaped branched SDS stripes were observed, forming a dendritic morphology as a result of fingering instability in the receding surfactant solution. Long DTAB parallel stripes are deposited orderly during the stick–slip solution motion, forming regularly spaced arrays.

At supramolecular scale, surfactant molecules pack into organized layers, independently of the drying conditions. Electrostatic patterns are also obtained, correlated to topography: overlaid SDS surfactant lamellae form terraces that are more positive than steps while the overall surfactant deposits are not electro-neutral, showing small but easily detectable negative excess charge.

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Supporting Information Available: Text discussing experiments on water condensation on SDS layers deposited on mica and figures showing images from samples dried under different experimental conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>.