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ABSTRACT

We use contact angle goniometry, imaging ellipsometry and atomic force microscopy to study the stability and wettability of Langmuir-Blodgett (LB) monolayers of stearic acid on silica substrates, upon drying and exposure to aqueous solutions of varying salinity. The influences of Ca\(^{2+}\) and Na\(^{+}\) ions are compared by varying their concentrations, both in the subphase before the LB transfer, and in the droplets to which the dried LB layers are exposed. Ca\(^{2+}\) ions in the subphase are found to enhance the stability, leading to contact angles up to 100 degrees, as compared to less than 5 degrees for Na\(^{+}\). Consistent with the macroscopic wettability, AFM images show almost intact films with few holes exposing bare substrate when prepared in presence of Ca\(^{2+}\) while subphases containing Na\(^{+}\) result in large areas of bare substrate after exposure to aqueous drops. The observations on varying the composition of the droplets corroborate the stabilizing effect of Ca\(^{2+}\). We attribute these findings to the cation-bridging ability of Ca\(^{2+}\) ions, which can bind the negatively charged stearate groups to the negatively charged substrates. We discuss the relevance of our findings in the context of enhanced oil recovery.

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Introduction

The interaction of organic matter with solid surfaces in an ambient aqueous environment plays a key role in many processes and phenomena in nature, science, and technology including ground water-soil interaction, water purification, lubrication, corrosion inhibition, colloidal stability, Langmuir Blodgett (LB) films, (membrane) fouling, and enhanced oil recovery.\textsuperscript{1-5} Two processes are crucial: the binding of the amphiphilic molecules to the substrate, and their assembly into an interfacial layer.

Since most solid surfaces, including in particular mineral and glass surfaces, assume a finite surface charge in water, usually electrostatic effects contribute strongly to the interactions with polar and/or charged organic molecules. Divalent ions as well as higher multivalent ions are known to be particularly efficient ‘glues’ that stick organic molecules to solid surfaces.\textsuperscript{5-6} For instance, biophysicists make extensive use of this mechanism to immobilize DNA and proteins onto solid surfaces, for example to enable their visualization by Atomic Force Microscopy.\textsuperscript{7} Monovalent ions, in contrast, are unable to provide such strong immobilization.

Additionally, organic films can also undergo rearrangements in three dimensions when they are exposed to aqueous solutions of multivalent ions. It has been reported that mobile counterions\textsuperscript{8-10} embedded into layers of fatty acids can trigger structural rearrangements of molecules. A particularly dramatic example involves a so called ‘flip-over’, in which the molecules form a bilayer which exposes the polar head groups to the substrate and to the aqueous phase.\textsuperscript{11-12}

Both (un)binding events and rearrangements can have a tremendous influence on the chemical affinity of the surface that is exposed to the aqueous liquid: the difference between
hydrophilic and charged (for bare substrate), and hydrophobic (for coated substrates) gives rise to a completely different water wettability. Also the interactions between two such surfaces immersed in water change: from DLVO-type for the bare surfaces, to long-range attractive in case of some hydrophobized surfaces.\textsuperscript{11,13-16} In the present study we focus on the question, how the wettability of an adsorbed organic layer can be changed via exposure to aqueous solutions with different overall salinity and ionic compositions. While this is of interest for many applications (as indicated), the present paper is inspired in particular by recent observations in the field of enhanced oil recovery (EOR).

In traditional (i.e. secondary) oil recovery, highly saline seawater is pumped into the ground to expel oil from pores in the rock.\textsuperscript{5,17} However this process is not very efficient. Evidence has been growing that reducing the overall salinity (and in particular the concentration of divalent ions) of the injected water can substantially increase the oil recovery rate.\textsuperscript{5,17} A possible explanation of this observation assumes that over geological time scales, the intrinsically hydrophilic rock was turned into hydrophobic via the adsorption of polar components from the crude oil. In this picture, the hydrophobic layers become bound (at least partly) via electrostatic interactions. In particular multivalent ions like Ca\textsuperscript{2+} and Mg\textsuperscript{2+} are supposed to play a role, since these can bind acid groups from the oil to negatively charged sites on the surface via an ion bridging mechanism.

The effectiveness of using low salinity water then lies in weakening the bonding between the hydrophobic layers and the rock. As a consequence, the organic layers can be (partially) released. This renders the rock more hydrophilic, and facilitates the expulsion of oil from the narrow pores via a reduction in the required Laplace pressure. Ultimately this would explain the increased efficiency of the oil recovery process. Since the characteristic flow rates in oil recovery are of order one foot per day, corresponding to approximately 1 \( \mu \text{m/s} \), the
decomposition of the hydrophobic layers should take place on much shorter time scales that are much more accessible in the laboratory.

The purpose of the present study is to develop a model system and to test various aspects of the scenario described above. In particular, we want to correlate macroscopic variations of the wettability with the microscopic decomposition or rearrangement of the hydrophobic layers and elucidate the relevance of divalent ions in this process. To this end, we choose one of the best characterized model systems of thin organic layers, namely monolayers of stearic acid (SA) that we deposit onto solid surfaces using the Langmuir Blodgett (LB) technique. While the details of this deposition are of course very different compared to the gradual adsorption from crude oil, LB transfer offers unique control of the physico-chemical parameters that govern the stability of the resulting film.

Monolayers of SA and other fatty acids have been investigated in great detail in the past, both as Langmuir layers at the air-water interface\textsuperscript{18,20} and as LB films deposited onto solid surfaces\textsuperscript{12,21} dating back all the way to the original work of Blodgett\textsuperscript{22} and Langmuir.\textsuperscript{23} It is well known that both the physical and chemical properties of such layers depend very much on pH and on the ion content of an adjacent aqueous phase.\textsuperscript{24-25} A summary of early work based to an important extent on surface potential measurements has been summarized by Goddard.\textsuperscript{26} At low pH, the carboxylic acid groups and solid surfaces like silica remain protonated and the affinity to ions (and interfaces) is weak. In contrast, at high pH, they are deprotonated and interact strongly with the ions.\textsuperscript{8,25,27-28} This affects amongst other things the transferability of Langmuir monolayers in the LB process\textsuperscript{10,29} and the stability of the layers.\textsuperscript{25} More recently, Graber et al.\textsuperscript{30} studied the consequences of these ideas for the macroscopic water-repellency of soils hydrophobized by fatty acids upon exposure to water of variable pH and salt contents. They demonstrated that such soils indeed resist the penetration of water.
drops more efficiently upon increasing the pH and calcium concentration. The mechanisms invoked to explain these observations are very similar to the proposed mechanism of enhanced oil recovery by low salinity water flooding. All these previous observations suggest that SA is a suitable model compound for our purpose.

In this work, we study the influence of Ca\(^{2+}\) and Na\(^{+}\) ions on the stability and wettability of stearic acid monolayers. The layers are deposited onto oxidized silicon wafers mimicking silica surfaces using LB transfer. Subsequently we expose the surfaces to drops of variable salinity. Occasionally, mica is used as an alternative substrate representing clays. We investigate the effect of ions on the film stability in two complementary ways. First, we vary the ion contents of the subphase during LB transfer. Second, we vary the ion contents of the aqueous phase to which the LB films are exposed after the transfer. In both cases we focus on Na\(^{+}\) and Ca\(^{2+}\) ions representing the prevalent mono- and divalent cations of sea water, respectively. Macroscopic contact angle goniometry, imaging ellipsometry, and Atomic Force Microscopy (AFM) consistently show that Ca\(^{2+}\) has a pronounced stabilizing effect on the SA films exposed to water. Microscopic AFM images demonstrate the partial decomposition of the LB films upon exposure to water. In the absence of multilayer formation, the contact angle of sessile drops on partially decomposed LB films is found to agree with the expectations based on the AFM data using Cassie’s equation.

**MATERIALS AND METHODS**

**Chemicals and solutions:**

All solvents and reagents are obtained from Sigma-Aldrich and used without further purification. Solution of stearic acid (SA) (octadecanoic acid, CH\(_{3}\)(CH\(_2\))\(_{16}\)COOH, grade 1, approx. 99\%) is prepared in chloroform (CHCl\(_3\), ACS reagent) at a concentration of 1 mg/mL.
Aqueous subphases for the LB-transfer are prepared by dissolving sodium chloride (NaCl) and/or calcium chloride dihydrate (CaCl$_2$·2H$_2$O) (both ACS reagent grade) in deionized water (Synergy UV, Millipore, resistance 18.2 MΩ·cm). Three different types of subphases are used containing 0.5 M NaCl, 0.01 M CaCl$_2$, and a mixture of 0.5 M NaCl, and 0.01 M CaCl$_2$, respectively. These values of concentrations are chosen to mimic typical concentrations in seawater as it is used in secondary oil recovery. In all cases, the pH of these subphases is adjusted to 9.5 ± 0.1 with 0.1 M standard solution of NaOH, to ensure that the carboxylic acid groups of stearic acid are largely deprotonated and to prevent substantial dissolution of stearate molecules in the bulk water, which occurs for pH >10.

**Substrate preparation and LB film deposition:**

As substrates, we use commercial silicon (100) wafers with a thermally grown oxide layer of ~35 nm thickness. The wafers are cut into pieces of $1 \times 5$ cm$^2$. The substrates are cleaned by the following procedure: firstly, samples were extensively rinsed with successively Millipore water, iso-propanol, and ethanol, then gently dried with N$_2$ gas; secondly, wafers were exposed to ambient air plasma (PDC-32G-2, Harrick plasma) for 30-40 min. This procedure assures good hydrophilicity of the substrate (water contact angle: $\theta<5^\circ$). AFM is used to verify the smoothness of the substrate. The typical RMS (root means square) roughness is found to be <0.2 nm.

LB film deposition is performed using a computer-controlled trough from Nima Technology. Prior to the experiment, the trough is rigorously cleaned with pure water, ethanol and chloroform. The system is assumed to be clean if the surface pressure of the bare subphase (i.e. prior to spreading the SA solution) varies by no more than 0.1 mN/m upon moving the barriers back and forth. Subsequently, a drop (50 µL) of the SA solution in chloroform is deposited on the subphase. Around 30 min are allowed for the solvent to
evaporate and for the SA layer to spread before initiating the LB transfer. All LB transfers are performed at a constant surface pressure of 30 mN/m, just above the kink in the pressure-area isotherm that indicates the apparition of a compact solidified layer (see Fig. 1). The pulling speed is 2 mm/min. Under these conditions, the transfer ratio for the monolayers is unity implying that the substrates become completely covered by the monolayers. Qualitatively similar results were obtained in a few test measurements at a somewhat higher transfer pressure (45 mN/m).

In the following, we denote the LB layers transferred with the three different types of subphases as SA-Na, SA-Ca, and SA-Ca+Na films, respectively, to indicate the type of cation present during the transfer. Before further characterization using contact angle goniometry, ellipsometry and AFM, the samples are stored in a glove box under a continuous flow of dry nitrogen for 20 hours. All experiments are performed within 2-3 days of preparation.

**Contact angle measurements:**

An optical contact angle goniometer with automated data analysis software (OCA 20L; Dataphysics) is used to assess the macroscopic wettability and to determine static water contact angles on the samples with measurement accuracy of ± 0.5°. Droplets of 5–10 µL of pure water or saline solutions are placed on the surfaces in ambient environment. Goniometry measurements are performed after 20 hours of sample preparation at least at 3-4 different locations on each sample. For any given sample the contact angle values are reproducible within ± 3°.

**Ellipsometry imaging:**

The morphology of the transferred monolayers is analyzed after drying using an imaging ellipsometer at a wavelength of 658 nm (EP3 Nanoscope, Accurion). Absolute
thickness maps of the material are obtained by measuring the ellipsometric angles $\psi$ and $\Delta$ as a function of the position on the substrate, and using the (complex) refractive indices $n_i$ of both layer and substrate along with the Fresnel equations to translate ($\psi$, $\Delta$) into a thickness $d_i$. Fitting $\psi$ and $\Delta$ for the bare substrate with a two-layer model (Si: $d \to \infty$, $n_{Si} = 3.96-0.02i$ and SiO$_2$: $n_{SiO2} = 1.5$) yields the exact value of the oxide thickness (with precision of 0.1 nm).

The thickness of the transferred SA layers is then calculated using a three-layer model using the previously determined oxide thickness as a fixed input and assuming a refractive index of $n_{SA}=1.43$ for SA.

**AFM imaging:**

The topography of treated and untreated SA layers on the nanometer scale is obtained under ambient conditions (unless otherwise noted) with a commercial atomic force microscope (Dimension Icon AFM with Nanoscope V controller, Bruker AXS). All images are collected in tapping mode with ScanAsyst Air and ScanAsyst fluid silicon probes purchased from Bruker with sharp tips. Nominal cantilever and tip properties are as follows: tip radius <10 nm; tip height, 0.5 – 0.75 µm; cantilever spring constant 0.4 N/m. The AFM is operated under “gentle” conditions with small cantilever oscillation amplitudes (<10 nm) and weak damping (i.e. high amplitude setpoint values) to protect both tip and sample against damage. Around 3-4 topography and phase images are recorded at representative neighbouring locations on each surface. Image analysis is performed using Bruker’s standard Nanoscope Analysis 1.4 package.

**Monolayer characterization:**

Initial images of the SA layers after preparation and drying show a flat topography with both AFM and ellipsometry in ambient air under all preparation conditions. Inset Fig. 1b
shows a representative AFM image with a typical roughness of approximately 0.15 nm rms. The Fig. 1c and 1d show the typical ellipsometry thickness map and profile. The observed average thickness of ~2 nm is consistent with the length of SA molecules and thus with the expected molecular structure as sketched in the inset Fig. 1a'. Yet, the topography, thickness and roughness of these monolayers highly depend on details of sample cleaning, preparation and drying protocols. For the non-optimized conditions, the monolayer could also have some holes in it or dirt sticks to it just after the preparation (supporting information). We have discarded all such monolayers from further analysis in the present study.

**Figure 1.** (a) Surface pressure versus area (π-Å) isotherm of stearic acid with 0.5 M NaCl aqueous subphase. (a’) Schematic illustration of deposited monolayer (b) AFM image (c) Ellipsometry thickness map and (d) corresponding profile of a SA-Na monolayer.

**RESULTS**

To study the stability of the SA monolayers, we expose all layers to drops of an aqueous “exposure” solution with variable concentrations of NaCl and CaCl₂ at pH ~6. Drops with a
volume of 10 µL are deposited onto the substrates and left there for a period of 10 min. During this period we continuously monitor the contact angle. Subsequently the drops are removed from the substrate and the samples are blown dry using dry nitrogen. AFM and ellipsometry images are recorded both in the center and at the edge of the region previously covered by the drops. We discuss first the influence of the composition of the subphase on the layer stability upon exposure to pure water and subsequently, the effect of various salts added to the drop destabilizing the film.

1. Influence of the subphase composition

The contact angle $\theta$ of the (pure) water drop is found to decrease from an initial value $\theta_0$ to a significantly smaller equilibrium value $\theta_e$ within a few seconds. The latter value is stable for several minutes until it begins to decrease slowly due to evaporation. This qualitative behavior is similar for all samples. The absolute values of $\theta_0$ are difficult to determine due to the limited time resolution of the data acquisition and due to inertial effects that are known to affect the drop dynamics within the first fraction of a second of contact.\(^{33}\) For the present study, however, the quantity of interest is the limiting contact angle $\theta_e$ at long time scales.

As shown in Fig. 2, $\theta_e$ depends very strongly on the composition of the subphase and decreases from approximately 80° for SA-Ca layers to ~30° for SA-Ca+Na layers to <5° for SA-Na layers. This very strong dependence of the contact angle on the counter ion species is the key observation of the present study. Since the contact angles of water on stable self-assembled monolayers such as alkylsilane layers on glass and alkylthiol layers on Au with a comparable length of the alkyl chain are known to be close to 110°\(^{34}\) these results clearly show that the LB films of SA in our experiments do not remain intact upon exposure to water but decompose at least partially. The large variation of $\theta_e$ for the three different subphases suggests that the degree of decomposition varies substantially depending on the specific
cation present in the subphase: SA-Ca layers seem to remain largely intact, SA-Na layers seem to be largely removed, and SA-Ca+Na layers show an intermediate behavior.

Qualitatively similar results were obtained for a large number of samples, also including mica substrates instead of oxidized silicon wafers. The trends regarding the stabilizing effect of Ca$^{2+}$ in the subphase on $\theta_e$ were consistently found (see Fig 2a). Yet, the absolute values of $\theta_e$ vary substantially depending on details of the sample cleaning, preparation, and drying protocol. Occasionally, $\theta_e$ could be as low as 30° even for SA-Ca monolayers (supporting information).

**Figure 2.** (color online) Macroscopic wettability of three monolayers: SA-Ca (green), SA-Ca+Na (blue), and SA-Na (red). (a) Time evolution of the contact angle and (b) snapshots of drops in the final state showing the equilibrium contact angles ($\theta_e$). Note: the axis break in (a) showing the final equilibrium angle.

These wettability changes could originate from different processes at the microscopic level. For example they could be due to desorption of the SA molecules upon exposure of the layer to the aqueous drop. But alternatively they might also result from structural rearrange-
ments within the layer, such that hydrophilic headgroups become exposed to the aqueous liquid. To distinguish between the different possible scenarios, we performed additional characterizations aimed at the surface morphology. Images of the layers (after removing the drop and drying the samples) obtained with ellipsometry and AFM are shown in Fig. 3.

For the SA-Ca and SA-Ca+Na samples, both ellipsometry and AFM images recorded in the central area of the original drop look similar, as can be seen in Fig. 3a, b) and 3a’, b’). Ellipsometry indicates a more or less homogeneous coverage with an average thickness of about 1 nm in the former case and approximately 0.5 nm for the latter samples. Both values are substantially lower than the 2 nm corresponding to the all-trans length of SA molecules before they were exposed to the water drop. Hence we conclude that the LB monolayers must have been partially desorbed.

For SA-Na samples (Fig. 3c and c’), the situation is clearly different and the residual thickness after water exposure is essentially zero. When we image the edge of the region exposed to the water drop, a clear contrast is seen between the exposed area with now bare substrate and the intact monolayer around it. Also the shape of the edge of the drop is observed for larger scan size (20-30 µm) AFM images (not shown) as seen with ellipsometry in Fig. 3c. While the poor lateral resolution of imaging ellipsometry precludes a more detailed analysis, AFM imaging reveals the details of the decomposition process: the monolayers partially desorb from the substrate, leaving behind areas covered by the original SA film (bright in Fig. 3a’ and b’) and holes (dark) exposing what seems to be the bare substrate. The phase image (Fig. 4a) also reveals a clear contrast between the high and the low level, which discriminate between different types of materials, supporting the interpretation that the lower level is indeed the bare substrate. From histograms of the height distribution (right part of Fig. 3 a’, b’, and c’) we extract the area fraction and the thickness of the residual film. The latter is
approximately 2 nm, in agreement with the all-trans length of the SA molecules. Since the missing SA molecules are not found at the surface and they are insoluble in water at pH=6, we think that they migrated to the air-water interface and were washed away upon removal of the drop.
Figure 3. (color online) Macroscopic and microscopic images of SA-Ca (a and a’), SA-Ca+Na (b and b’) and SA-Na monolayer (c and c’) after exposure to water. a, b and c: imaging ellipsometry; a’, b’ and c’: AFM). Inset images are height profiles corresponding to the white scan line (abscissa in µm; ordinate in nm). Histograms in a’, b’, and c’ show the frequency and cumulative bearing area of the height levels.

For the SA-Na samples, AFM images confirm the results of the ellipsometry measurements. Within the previous contact area of the drop, the samples are perfectly flat. As we image the edge of the contact area, a clear topographic step is found with a height of ~1.5 nm, as in the case of the holes in the layers on the SA-Ca and SA-Ca+Na samples. Again, the topographic step is accompanied by a jump in the phase images, confirming the idea of different material compositions.

Figure 4. AFM height and phase images along with section profiles for (a) SA-Ca monolayer
exposed to water and (b) SA-Ca+Na monolayer exposed to 0.01 M CaCl$_2$ solution. The different contrasts correspond to bare substrate, monolayer and multilayer.

These observations unequivocally demonstrate that our LB layers of SA partially decompose upon exposure to water. The somewhat reduced height (as compared to the all-trans length of the SA molecules) of the steps in the AFM images suggests that the molecules in the residual layer are either slightly tilted or that the ‘bare’ substrate in the holes is in fact still covered by a sub-monolayer of hydrocarbon chains oriented parallel to the substrate. The present data do not allow drawing a definite conclusion in this respect. Notwithstanding this uncertainty, all data clearly and consistently demonstrate that Ca$^{2+}$ ions in the subphase have strong stabilizing effect on the SA layers, whereas Na$^+$ ions do not.

2. Effects of salinity of exposure water on monolayer stability:

Having demonstrated the stabilizing effect of Ca$^{2+}$ ions in the subphase during preparation of the LB layers, we now address the effects of ions in the exposure solution. We focus again on Na$^+$ and Ca$^{2+}$ ions. In addition to the pure water discussed in the previous section, 0.01 M and 0.1 M NaCl, as well as CaCl$_2$ are used as the exposure solutions.

Figure 5a shows the time evolution of the contact angle for the five different exposure solutions on SA-Ca monolayers. The data for pure water are the same as in Fig. 2a. The other exposure solutions display the same qualitative behavior, yet it is clear that $\theta_c$ is larger for higher salt concentrations. The highest value of $\theta_c \sim 95^\circ$ is obtained for the 0.1 M CaCl$_2$ solution. The contact angle after 10 min (not shown) is only slightly smaller than after 30 s, like in Fig. 2. Similar results are found for samples prepared with the two other subphase compositions. As summarized in Fig. 5b, more ions in the exposure solution lead to larger contact angles on the SA layers in all cases. Again, Ca$^{2+}$ ions are - by and large - more
efficient than Na$^+$ ions at stabilizing the LB films. Note, however, that the overall effect of ions in the exposure solution is only of order 10$^9$ and thus much less pronounced than for ions in the subphase.

![Figure 5.](image)

**Figure 5.** (a) Contact angle vs. time on SA-Ca monolayer for various compositions of exposure solution. (b) Equilibrium contact angles for all compositions of subphase and exposure solution (bars: experimental results from contact angle goniometry; symbols: values extracted from AFM images in combination with Cassie equation (see text for details).

In Fig. 6 we show an overview of AFM micrographs obtained for all combinations of the composition of subphase and exposure solution investigated in this study. Desorbed area fractions are calculated from histograms of the height distribution as in Fig. 3. Comparing the different subphases, it is clear that LB films prepared on the subphase containing CaCl$_2$ are the most stable. We find that for an exposure solution of 0.1 M CaCl$_2$, as little as $A_{des} = 6\%$ of the SA-Ca film decomposes. This percentage increases for exposure solutions containing less Ca$^{2+}$ or containing Na$^+$. The depth of the holes remains close to 2 nm, with only very small area fractions of thicker films in the case of NaCl exposure solutions. The maximum desorbed
area amounts to 38%, indicating a fairly good stability of the LB film upon contact with water. The value of 38% is reproducible within ± 3% for at least 5 consecutive experiments.

For subphases containing 0.5 M NaCl (with or without additionally 0.01 M CaCl₂), a dramatically different picture is found. For exposure solutions containing NaCl, the LB films are decomposed more or less completely, indicated by desorption ratios $A_{\text{des}}$ close to 100%. For exposure solutions containing CaCl₂ we also find large areas of bare substrate but still a finite amount covered by a layer. Interestingly, in this case the thickness of the residual layers largely exceeds the initial 2 nm. We attribute this to the formation of double or multilayers. Substrates with bare areas, monolayers and multilayers were already shown in Fig. 4b for one of these samples. The chemical nature and in particular the termination of the multilayers are not clear. Yet, we suspect that the multilayers contain calcium stearate and that they expose the hydrophilic head groups to the aqueous phase (see discussion below). This compound is known to be a particularly stable, which was – amongst others – found to precipitate easily at oil-water interfaces if dissolved in oil.⁸ (Few images also display very high round features that look very different from the decomposed areas of the film. We identify these features as salt crystallites that appear as we blow off the residual drop and dry the sample).

To examine the consistency between our macroscopic contact angle measurements and the microscopic characterizations using AFM, we calculate theoretical contact angles, by combining the area fraction obtained from the AFM images with Cassie’s equation for the contact angle of heterogeneous surfaces $\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2$ ($f_i$, $\theta_i$: area fraction and contact angle of phase $i$; $i=$LB film, substrate.) Using a Young angle of $\theta_1=100^\circ$ for the LB film and $\theta_2=5^\circ$ for the bare substrate and taking $f_i=1-A_{\text{des}}$ and $f_2=A_{\text{des}}$ from Fig. 6, we find the contact angles indicated by the round symbols shown in Fig. 5b. (Here, the values of $\theta_1$ and $\theta_2$ are typical values for the contact angle of compact layers of self-assembled monolayers and
cleaned silica surfaces, respectively.\textsuperscript{35-36} Note that the absolute values are not very critical and may be varied by 5° without substantial impact on the agreement with the experimental data.) Despite the rather wide range of $A_{\text{des}}$ covered for the various conditions, the values for $\theta$ calculated from the AFM images agree within 10% with the macroscopic measurements. Note that the success of the Cassie equation is not trivial. It implies in the first place that the variations observed in the center of the solid-liquid interfacial area are representative of the local (de)composition at the contact line, \textit{i.e.} at the location where the contact angle is determined. (This aspect has been discussed intensively in recent years following up a critical note by Gao and McCarthy).\textsuperscript{37-39} Second, the agreement suggests that the advancing contact angle that we measure under the conditions of our slowly spreading drops is indeed close to the equilibrium angle, as determined by Cassie’s equation. This is again not trivial since the closeness of the Cassie angle to the advancing and receding angle depends on the nature of the defects with respect to the majority species on the surface as pointed out by Priest et al.\textsuperscript{40}

The SA-Ca+Na and SA-Na films exposed to CaCl\textsubscript{2} solutions (symbols in parenthesis) deviate from this general trend. These, however, are the samples shown in the bottom right quadrant of Fig. 6, which display the formation of multilayers after exposure to the electrolyte solution. Their experimental contact angle is much smaller than the one predicted by Cassie’s law under the assumption $\theta_1=100^\circ$. This apparent discrepancy disappears however, if we assume that the multilayers are not terminated by the hydrophobic tail but rather expose the hydrophilic carboxylic acid group towards the solution, leading to a much smaller value of $\theta_1$ (see phase contrast corresponding to multilayer formation in Fig. 4b). This behavior is consistent with observations in other experiments with decomposing surfactant layers.\textsuperscript{13}
Figure 6. AFM viewgraphs of LB films prepared with all combinations of subphases after exposure to water and liquid compositions. Image size: $5 \times 5\mu m^2$. Desorption area $A_{des}$ indicates area fraction of exposed bare substrate. Insets show representative cross sections. Vertical scale: in nm. Horizontal scale: 5 μm.
The behavior of the SA-Ca+Na films in pure water cannot be explained in this manner. The thickness of the residual film is close to 2 nm, as concluded from the depth of the holes in film. The desorption ratio suggests that approximately one third of the layer should still be present in its original form with a hydrophobic termination exposed to the water. It leads to a contact angle of approximately 50° by calculating with Cassie’s equation, exceeding the experimental value by ~20°. We do not have any explanation for this deviation, which has been found to persist over several independent measurements spread over a period of several months.

DISCUSSION

Overall, our experiments clearly show that the presence of Ca\(^{2+}\) ions (whether from the subphase or from the exposure solution) strongly stabilizes LB films of stearic acid deposited on silica surfaces.\(^{24, 41-46}\) To discuss the stabilization mechanism, we consider the preparation of the LB film and its subsequent decomposition upon exposure to aqueous liquid separately. Fig. 7 sketches the relevant processes during adsorption-desorption of the monolayer. The Langmuir film initially residing on the subphase consists of a close-packed layer of stearate molecules (Fig. 7a). The structure and stability of this Langmuir monolayer are known to change in different ways, depending on the presence of mono- and divalent ions, as well as the pH in the subphase. At sufficiently high pH, monovalent cations in the subphase cause the monolayer to become less ordered. Divalent cations (at sufficiently high pH) have the opposite effect: they effectively compress the monolayer into a tightly packed untilted structure, leading to enhanced crystalline order\(^{47}\), changes in viscoelastic response\(^{48}\), and make it more easily transferable to solid substrates.\(^{29}\)
In this work, the subphase pH is chosen high enough to ensure that the carboxylic acid groups are largely deprotonated. The ionization fraction of the molecules at the interface ($\chi$) has been related to the pH of the subphase by the Gouy-Chapman equation\textsuperscript{24,49}

$$\text{pH}_{\text{subphase}} = \text{pK}_a + \log \left( \frac{\chi}{1-\chi} \right) + \frac{0.87}{z} \sinh^{-1} \left( \frac{136 \chi}{A \sqrt{c}} \right),$$

where $z$ is the valency of the ions, $A$ is the molecular area ($\text{Å}^2$) and $c$ is the concentration of the counterions (moles/L). Inserting $\text{pK}_a = 5.6$\textsuperscript{50} and using the aqueous compositions in our experiments, we obtain a deprotonation ratio of 86.4% for 0.01 M CaCl$_2$ and 82.3% for 0.5 M NaCl solutions at pH 9.5. According to literature, divalent cations ($D^{2+}$) can form different complexes with ionized stearic acid ($R^- = \text{CH}_3(\text{CH}_2)_{16} \text{COO}^-):$ positive $RD^+$, neutral $R_2D$ or both of these complexes simultaneously.\textsuperscript{51-54} The presence of both $R^-$ and $RD^+$ can make the Langmuir layer electrically neutral at high pH, as has been found for Ca$^{2+}$ both theoretically\textsuperscript{51, 53} and experimentally.\textsuperscript{55-56} In contrast, monovalent cations only form neutral $RM$ complexes and therefore the monolayer remains mainly negatively charged because of dissociated $R^-$.\textsuperscript{51}

When we transfer these neutral or negatively charged layers to our silica substrates, they come in contact with a negatively charged surface\textsuperscript{43-44,57} (Fig. 7b). Under these conditions, positively charged SACa$^+$ ($RD^+$) moieties can associate with negatively charged sites on the silica surface to form strongly bound neutral complexes. Neutral SA$_2$Ca ($R_2D$) can be stabilized by lateral interactions (van der Waals and hydrophobic forces) between alkyl chains which can also lead to a strongly bound LB film.\textsuperscript{58} In the contrasting case of sublayers containing only Na$^+$ cations, a partially dissociated Langmuir layer, carrying some negative charges, is deposited onto a strongly negatively charged solid surface. This precludes the collective self-assembly of cation-stabilized complexes between stearate molecules and deprotonated silanol (SiO$^-$) groups. Moreover, charge neutrality will require the incorporation
of even more cations between the film and the substrates to compensate for the excess negative charges. The combination of both aspects leads to an LB film which can only be weakly bound to the substrate and stabilized by only lateral interactions within the film presumably.

**Figure 7.** Schematic illustration of monolayer adsorption-desorption process (a) formation of salt complexes with dissociated fatty acid at air–water interface (b) negatively charged substrate dipped under subphase (c) desorption of monolayer after water exposure.
The behavior of the SA-Ca+Na films with the mixed subphases is more complex. The partial stability of the layers upon exposure to pure water suggests that some adsorbed Ca\(^{2+}\) is present and able to stabilize the LB films. However, this stabilization is clearly not as strong as in the case of a pure 0.01 M CaCl\(_2\) subphase. The competition between the stronger binding Ca\(^{2+}\) ions and the 50 times more concentrated Na\(^+\) ions in the subphase leads to a mixed association of R\(^-\) and SiO\(^-\) with the two cationic species. Upon exposure to pure NaCl solutions, the gradients in chemical potential for Ca\(^{2+}\) and Na\(^+\) apparently lead to a complete destabilization of the films, suggesting that Ca\(^{2+}\) and/or SACa\(^+\) ions initially stabilizing the LB film can be exchanged with Na\(^+\) ions from the bulk exposure solution resulting in the complete decomposition of layer. The behavior upon exposure to pure Ca\(^{2+}\) solutions again suggests an exchange of ions between the bulk solution and loosely bound parts of the LB monolayer.

Such rearrangements are not uncommon. For multilayer LB films, they have been studied in great detail.\(^{10,12,29}\) In particular, X-ray reflectivity and X-ray photoemission spectroscopy demonstrated a very strong mobility and exchange of cations bound in LB multilayers.\(^9\) These studies also suggest that ion exchange is facilitated by swelling of the LB films. To explore this possibility, we performed some additional ‘in-situ’ AFM experiments, in which the LB films were imaged under aqueous liquid (instead of air). These experiments showed film decomposition patterns that are consistent with the ex-situ experiments (see Supporting Information). However, the depth of the holes in the LB films is more than twice as large as in the ex-situ images recorded on the same surface after drying. Explanations for this swelling behavior and other possible rearrangements (e.g. tilting as a result of partial desorption) are the subject of an ongoing follow-up study.
The Ca$^{2+}$-induced stabilization of LB films might also provide a strategy to develop more stable hydrophobic layers for surface forces measurements. Investigations of fundamental interaction forces between hydrophobic surfaces immersed into water have long been compromised by problems with the stability of hydrophobic layers.$^{13,16}$ LB films stabilized by Ca$^{2+}$ or even higher valence cations might provide a route to overcome these problems.

Overall, the observations described in this work are consistent with the multiple ion exchange mechanism of the low salinity water flooding process as proposed by Lager et al.$^5$ Ionically bound layers of SA on silica surfaces indeed partially come off the solid surface and render it more hydrophilic if exposed to pure water rather than highly saline electrolytes. As in core flooding oil recovery experiments divalent ions also play a crucial role in the present generic model system. It is interesting to note, though, that ions present in the subphase during the preparation of the LB films have a stronger influence than those added subsequently to the exposure solution. This might suggest that the salinity of the formation water, which was present when the oil invaded a certain initially water saturated reservoir rock, plays an important role for the stability of the hydrophobizing layers and thus for the subsequent success of low salinity water flooding. While it is encouraging that the same qualitative behavior is also found on mica substrates (serving as a model for clays that are typically present in many rock formations), more extensive experiments involving different classes of polar organic components from crude oil obviously need to be performed to confirm the general applicability of the multivalent ion exchange concept.

CONCLUSIONS

The stability of Langmuir Blodgett films of stearic acid upon exposure to water is strongly enhanced by the presence of Ca$^{2+}$ ions. Strongly bound LB films transferred in the presence of an excess of Ca$^{2+}$ are very stable independent of the composition of the aqueous phase it is
exposed to, suggesting that Ca\(^{2+}\) can efficiently bind negatively charged SA to negatively charged surfaces. In contrast, Na\(^{+}\) ions are unable to provide such stabilization. For weakly bound LB films transferred in the presence of mixtures of Na\(^{+}\) and Ca\(^{2+}\), high concentrations of Na\(^{+}\) in the ambient exposure fluid can even destabilize ionically bound organic layers. This destabilization can be rationalized by the replacement of initially present stabilizing Ca\(^{2+}\) ions implying a rapid exchange of ions between the ionic layer binding the LB film to the substrate and the ambient electrolyte. Clearly, the competition of several simultaneously present ionic species, which is characteristic for most geological, biological, and technological environments, adds substantial complexity and deserves additional attention in future research.

From an applied perspective, the Ca\(^{2+}\)-induced stabilization reported here implies a destabilization and easy removal of ionically bound organic layers in the absence of divalent ions. This is desired in the context of enhanced oil recovery. We anticipate that the fatty acid layers investigated can indeed be exploited as a model system for further studies of various complex geophysical and technological processes in well-defined laboratory experiments.

**Acknowledgements:** We thank Daniel Wijnperle and Mariska van der Weide for technical support, and Dirk van den Ende for critical reading of this manuscript. We acknowledge financial support within the ExploRe research program of BP plc.

**Supporting Information Available:** Effects of preparation conditions on the water contact angle and the morphology (in air and under water) of Langmuir-Blodgett layers of Stearic Acid on silica substrates. This material is available free of charge via the Internet at [http://pubs.acs.org](http://pubs.acs.org).
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(a) Surface pressure versus area (n-A) isotherm of stearic acid with 0.5 M NaCl aqueous subphase. (a') Schematic illustration of deposited monolayer (b) AFM image (c) Ellipsometry thickness map and (d) corresponding profile of a SA-Na monolayer.
Macroscopic wettability of three monolayers: SA-Ca (green), SA-Ca+Na (blue), and SA-Na (red). (a) Time evolution of the contact angle and (b) snapshots of drops in the final state showing the equilibrium contact angles ($\theta_e$). Note: the axis break in (a) showing the final equilibrium angle.

201x176mm (150 x 150 DPI)
Macroscopic and microscopic images of SA-Ca (a and a'), SA-Ca+Na (b and b') and SA-Na monolayer (c and c') after exposure to water. a, b and c: imaging ellipsometry; a', b' and c': AFM. Inset images are height profiles corresponding to the white scan line (abscissa in µm; ordinate in nm). Histograms in a', b', and c' show the frequency and cumulative bearing area of the height levels.

233x280mm (150 x 150 DPI)
AFM height and phase images along with section profiles for (a) SA-Ca monolayer exposed to water and (b) SA-Ca+Na monolayer exposed to 0.01 M CaCl2 solution. The different contrasts correspond to bare substrate, monolayer and multilayer.
(a) Contact angle vs. time on SA-Ca monolayer for various compositions of exposure solution. (b) Equilibrium contact angles for all compositions of subphase and exposure solution (bars: experimental results from contact angle goniometry; symbols: values extracted from AFM images in combination with Cassie equation (see text for details). 246x104mm (150 x 150 DPI)
Figure 6. AFM viewgraphs of LB films prepared with all combinations of subphases after exposure to water and liquid compositions. Image size: 5×5µm². Desorption area $A_{des}$ indicates area fraction of exposed bare substrate. Insets show representative cross sections. Vertical scale: in nm. Horizontal scale: 5 µm.

<table>
<thead>
<tr>
<th>Exposure solution</th>
<th>0.01 M Ca^{2+}</th>
<th>0.5 M Na^{+}</th>
<th>0.5 M Na^{+} 0.01 M Ca^{2+}</th>
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<td>$A_{des}=38%$</td>
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<td>0.01 M CaCl₂</td>
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<td>$A_{des}=54%$</td>
<td>$A_{des}=82%$</td>
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<tr>
<td>0.1 M CaCl₂</td>
<td>$A_{des}=6%$</td>
<td>$A_{des}=32%$</td>
<td>$A_{des}=65%$</td>
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</tbody>
</table>
Schematic illustration of monolayer adsorption-desorption process (a) formation of salt complexes with dissociated fatty acid at air–water interface (b) negatively charged substrate dipped under subphase (c) desorption of monolayer after water exposure.

260x237mm (150 x 150 DPI)
Table of Contents Graphic
249x175mm (150 x 150 DPI)