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Calcium Carbonate-Modified Surfaces by Electrocrystallization To Study Anionic Surfactant Adsorption

Zilong Liu,* Hayati Onay, Fengzhi Guo, Junqing Chen, Lukasz Poltorak, Pegah Hedayati, and Ernst J.R. Sudhölter*

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1. INTRODUCTION

Generally, less than 30% of original oil in place can be extracted from oil reservoirs using conventional primary and secondary recovery techniques, varying in the type of hydrocarbons and reservoir drives.1–5 Thus, various enhanced oil recovery (EOR) methods have been proposed and employed to increase the efficiency of obtaining residual oil.5 One such technique is chemical EOR (cEOR), where a solution containing chemicals is injected into a petroleum reservoir to mobilize the trapped oil for more efficient recovery. As an important part of cEOR, surfactant flooding has received much attention because of its capabilities to reduce the interfacial tension between oil and water and to alter the wettability of the mineral surface to a more water-wet state.6–8 However, the main issue associated with surfactant flooding is surfactant loss through adsorption to porous rock surfaces.9,10 As a result, the effectiveness and economic attractiveness of this method suffers. Therefore, to optimize and find suitable surfactant flooding parameters, it is important to investigate the factors governing surfactant adsorption on mineral surfaces.

The most common rock surfaces encountered in oil reservoirs consist of sandstone and carbonate minerals, with the latter occurring in over half of the Earth’s oil reservoirs.11 Sandstone reservoirs are typically composed of quartz (silica, SiO₂) and other silicate minerals. Carbonate reservoirs are composed of calcite (CaCO₃), dolomite (CaMg(CO₃)₂), and magnesite (MgCO₃) minerals, and these often show a less efficient oil recovery than sandstone.12 Also, carbonates are more difficult to study because of their chemical reactivities, matrix pore structures, fracture densities, complex surface properties, and partly dissolution in the presence of an aqueous environment.13 Bearing in mind the challenges of the complexity of carbonates, less than 20% of cEOR projects were implemented in carbonate reservoirs.14 Although a vast majority of research is focused on minerals typical for sandstone reservoirs, surfactant adsorption on carbonate rocks is still not yet well understood and needs to be investigated further.

With the aim of clarifying the surfactant adsorption process on mineral surfaces, the traditional depletion measurements of static tests (batch equilibrium tests on crushed core grains) and dynamic tests (core flooding measurements) are often used to determine the adsorbed amounts of surfactants.15–19 However, these methods cannot monitor the kinetic processes in real-time and cannot quantify the structure of the adsorbed surfactant layer. More recently, quartz crystal microbalance
with dissipation (QCM-D) monitoring has been extensively applied to study the adsorption behavior of surfactants, allowing for the real-time quantitative analysis of adsorption and desorption processes onto model mineral surfaces with nanogram sensitivity.  

Sensors covered with model minerals can be obtained commercially, fabricated by covering with core-shell microparticles, or prepared using different processing methodologies such as layer-by-layer deposition and electrochemical techniques. In the latter, the formed mineral deposit is a product of electrochemically assisted reactions (acid–base reaction), followed by the electrochemically controlled redox reaction. For example, electrochemical pH modulation allowing for the formation of CaCO3 coating on stainless steel substrates and silica deposition derived from sol–gel processing. In addition to electrochemically controlled deposition, the electrochemical toolbox offers a wide range of electroanalytical techniques that can be directly used to study surface properties. Therefore, the electrochemically assisted methods offer a powerful methodology to prepare model rock surfaces for surfactant adsorption studies. Combining electrochemical techniques with QCM-D into one analysis setup (EQCM-D) offers a new methodology to study the complex surfactant adsorption processes. One of our aims is to fabricate uniform and well-covered model CaCO3 surfaces on gold (Au) and platinum (Pt) sensor surfaces to mimic carbonate reservoir rocks. We improved our initial study where the CaCO3 particles were deposited on Au-covered QCM-D sensors. In this work, the CaCO3 electrochemically assisted deposition process was improved, which in turn allowed for the comprehensive description of the mass and structure of the adsorbed surfactant layer. Electrocrystallization conditions were optimized, and a high CaCO3 coverage having rough surface properties was obtained. The performance of the created platform and the surfactant adsorption behavior under varying CaCl2 concentration conditions were then studied and compared with the results obtained using the commercially available sensor covered with a smooth CaCO3 layer. The quantitative description of the surfactant adsorption processes obtained from the electrocrystallized and commercially available CaCO3 surfaces revealed significant differences. This underlines the necessity of developing complex model interfaces that will allow a better understanding of surfactant adsorption on different rock surfaces.

2. EXPERIMENTAL METHODS

2.1. Chemicals and QCM-D Sensors. CaCl2·2H2O (147.01 g mol⁻¹, ≥99% purity) and NaHCO3 (84.01 g mol⁻², ≥99.5% purity) were purchased from Sigma Aldrich. NaNNO3 (84.99 g mol⁻¹, ≥99.5% purity), HCl (1 M), and NaOH (1 M) were purchased from Merck. Ethanol (≥96% purity), isopropanol (≥98% purity), and centrifugal tubes (50 mL) were purchased from VWR International. Whatman filter papers (11 µm pore size) were purchased from Fischer Scientific. All salt solutions were prepared by dissolving an appropriate amount of solute in deionized water (Milli-Q, resistivity of >18.2 MΩ cm and 5.3 ppb TOC). The anionic alcohol alkoxylate (AAS) surfactant having a molecular weight of 700 g mol⁻¹ was provided by Shell Global Solutions. This surfactant contained mainly C12/C14 alkyl tails connected via seven propoxy units to a sulfate head group. AAS surfactant is commonly used in eOR with excellent divalent cation tolerance and is relatively inexpensive compared to other types of EOR surfactants. The used Au (QS-QSX30), Pt (QS-QSX314), and CaCO3 (QS-QSX 999) covered QCM-D sensors (diameter = 14 mm, thickness = 0.3 mm) were purchased from Q-Sense Biolin Scientific.

2.2. Electrocrystallization of CaCO3. In this study, electrochemically assisted deposition is used to produce in situ CaCO3 coatings on Au and Pt QCM-D sensor substrates, which acted as a cathode (negative electrode) in an aqueous solution containing calcium and bicarbonate ions. For this purpose, the Q-Sense QCM-D and Q-Sense Explorer electrochemistry module from Biolin Scientific were used. An electroanalytical analyzer from CH Instruments (CHI660D) was coupled to a three-electrode flow cell. The Au or Pt-covered QCM-D sensor was mounted on the electrochemical cell module and served as the working electrode. A Pt counter electrode and an Ag/AgCl (3 M KCl saturated) reference electrode were used. In- and out-flow of solutions through the flow module were modulated by a REGLO digital peristaltic pump from Ismatec. The PDC-002-CE plasma cleaner from Harrick Plasma and RET Basic magnetic stirrer from IKA were used to remove any possible contaminants from the Au or Pt sensors surface. All EQCM-D measurements were performed at room temperature with a supporting electrolyte containing an excess of 500 mM sodium nitrate. All the potential difference values given in this study are quoted against Ag/AgCl (3 M KCl). Before conducting the CaCO3 deposition experiments, the linear sweep voltammogram (LSV) was recorded to find the optimal reduction potential difference that was further applied to the working electrode during the chronamperometrically and electrochemically assisted CaCO3 deposition process. For this purpose, a solution containing 500 mM NaNO3 was prepared. An iR-compensation was performed before measuring the LSV of a metal sensor. The voltage was swept linearly from 0 to −1.4 V for the Au sensors and from 0 to −1.2 V for the Pt sensors at a scan rate of 20 mV s⁻¹.

The CaCO3 deposition solution was prepared by first preparing two precursor solutions, one containing CaCl2 (solution A) and the other containing NaHCO3 (solution B), as shown in Table 1. These solutions also contained NaNNO3 that acts as a background electrolyte and OH⁻ supplier via electrochemistry (see section 3.1). The pH of these solutions were adjusted to 7 ± 0.1 to minimize CaCO3 precipitation upon mixing. Then, solution B was added to solution A in a dropwise manner while magnetically stirring at 1500 rpm in order to prepare the CaCO3 deposition solution. The CaCO3 deposition solution was filtered into a centrifugal tube to remove any possible precipitated CaCO3. The following step was to load the unmodified QCM-D sensor into an appropriate module attached to all the necessary connections (electrochemical and tubing from the pump).

Next, the pump was turned on, and the measurement was started. Across all depositions, the CaCO3 deposition solution was fed to the flow module for 10 min to establish a stable reference frequency. Then, a negative voltage was applied in the potentiostatic mode of the electroanalytical apparatus. The frequency shift was monitored as deposition progressed. After the applied voltage was turned off, the sensor was left to equilibrate until a final, stable frequency signal was reached. The resonance frequency was considered to be stable if the resonance frequency shift was less than 1% of the total resonance frequency shift over a 20 min period. Then, the deposited CaCO3-metal sensor was directly taken out of the flow module and placed on a petri dish, after which it was placed inside an oven set at a temperature of 60 °C to dry overnight.

Table 1. Composition of the Solutions Used To Prepare CaCO3 Deposits

<table>
<thead>
<tr>
<th></th>
<th>CaCl2 (mM)</th>
<th>NaHCO3 (mM)</th>
<th>NaNNO3 (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>solution A</td>
<td>100</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>solution B</td>
<td>100</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>CaCO3 deposition solution</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

2.3. Surface Characterizations. A JSM-IT200 Intlosscope scanning electron microscope from JEOL was used to study the
electron beam voltage of 20 kV was used, and the spot size was dispersive X-ray analysis (EDX) was performed for elemental the sensors. Scanning electron microscopy (SEM) with energy frequency, CaCO3-Au and CaCO3-Pt sensors, which are used in the surfactant adsorption measurements.

2.4. QCM-D Principle. The working principle behind QCM-D is the converse piezoelectric effect. When an alternating voltage is applied, shear stress is generated across a piezoelectric material, resulting in the oscillation of the crystal at its resonance frequency. Quartz crystals are often used as the piezoelectric material because they vibrate with minimal energy dissipation, making them ideal oscillators. Once a stable resonance frequency is obtained, it can be calculated with eq 1. In a rigid system, \( \Delta f \) should be much less than \( \Delta D \). According to the QCM-D manufacturer (Q-Sense), for 5 MHz sensors, an empirical limit of \( \Delta D/(-\Delta f) \sim 1 \times 10^{-7} \) Hz\(^{-1}\) or lower. This may not be always the case, especially when the adsorbed film is relatively soft. Thus, the Voigt model can be used to derive the adsorbed amount, and it has been implemented in the D\text{\textregistered} software from Q-sense.\(^{20,48}\) The Voigt model is usually applied to the adsorbed molecules, which conserve their shapes under shear deformations and do not flow. When Newtonian fluids flow over the oscillating crystal, the frequency shifts because the changes in the viscosity and density of the solution were estimated using eq 2. The viscosity and density of the salt solutions were found to be similar to those of the salt solution in the presence of small amounts of 0.15 wt % (2.1 mM) surfactant. Under these conditions, the frequency shifts were attributed to the surfactant adsorption when the salt solution was changed to a surfactant solution. The surface roughness of the crystal can also influence the frequency shift because of liquid trapping by the present interfacial cavities and pores,\(^{49}\) and this contribution was calculated using eq 3. The effect of liquid trapping was neglected for the commercial sensors because they were atomically flat.

2.5. Surfactant Adsorption. Before using the commercial CaCO3 sensors and the self-made electrocrystallized CaCO3-metal sensors, they were subsequently rinsed with ethanol and iso-propanol and dried under a flow of dry nitrogen gas. The contacting parts of the flow module were also subsequently rinsed with Milli-Q water, ethanol, and iso-propanol and dried with nitrogen gas prior to each measurement. All surfactant adsorption measurements started with the highest concentration of the background salt. After the next surfactant adsorption and desorption processes, the surfactant adsorption experiments were repeated with a lower salt background concentration. This was performed to prevent the dissolution of the CaCO3 coating because CaCO3 can be easily flushed by injecting a lower salt concentration solution. Then, the sensor was loaded in the flow module, and all the remaining parts were attached. Three kinds of CaCO3 sensors were used: a commercial CaCO3 sensor and the deposited CaCO3-Pt and CaCO3-Au sensors. Upon loading the electrocrystallized CaCO3-metal sensors, only the third harmonic overtone was found. Because of the presence of the CaCO3 deposits, signals from higher overtones were not processable. However, upon loading the commercial CaCO3 sensor, all the overtones (3rd to 13th) were found before starting the adsorption measurement. Prior to

\[ \Delta f_{\text{ads}} = \frac{2f_0^2}{\rho_l v_l^3} \Delta m = \frac{-n\Delta m}{C} \]  

\[ \Delta f_{\text{liquid loading}} = \frac{2f_0^2}{\rho_l v_l^3} \left( \sqrt{\rho_l \rho_i} - \sqrt{\rho_i \rho_l} \right) \]  

\[ \Delta f_{\text{liquid trapping}} = \frac{-2f_0^2}{\rho_l v_l^3} h_i (\rho_i - \rho_l) \]  

where \( \Delta m \) is the adsorbed mass, \( f_0 \) is the fundamental resonant frequency, \( n \) is the overtone number (1, 3, 5, etc.), \( C \) is the sensitivity constant of the quartz crystal (0.177 mg m\(^{-2}\) Hz\(^{-1}\)), \( \rho_l \) is the specific density of quartz (2650 kg m\(^{-3}\)), \( v_l \) is the shear wave velocity (3340 m s\(^{-1}\)), and \( h_i \) is the thickness of the trapped liquid. Subscripts 1 and 2 refer to different solution densities and viscosities, whereas the subscripts 0 and 1 refer to the solvent and liquid mixtures, respectively.
feeding the solutions through the flow module, the pH of both the salt and AAS solutions was adjusted to 9.5 ± 0.1 with drops of dilute NaOH and/or HCl. Next, the temperature control was set to 23 °C, the pump was turned on with a constant flow rate of 200 μL min⁻¹, and the measurement was started. First, the salt solution was fed through the flow module to establish a stable baseline frequency. Next, the inlet tube was switched to the AAS solution, and the frequency shift (due to AAS adsorption) was monitored. Then, the surfactant was desorbed again by flushing with the next lower concentration of salt until the lowest studied salt and surfactant concentration was reached. The measurements were repeated 2–4 times, and the averaged values of the QCM-D data have been used for the calculations presented in this work.

3. RESULTS AND DISCUSSION

3.1. Electrochemically Assisted Deposition of CaCO₃ on Pt and Au. LSVs have been recorded in the clean Pt and Au sensors in 500 mM NaNO₃, as shown in Figure 1a. An iR-compensation was performed for each metal sensor prior to the LSVs. For the Pt sensor, the voltage was linearly swept from 0 to −1.2 V, while for the Au sensor, it was linearly swept from 0 to −1.4 V at the same scan rate of 20 mV s⁻¹. The electrogeneration of hydroxide ions at the electrode surface occurred because of the following reduction reactions:

Oxygen reduction:

\[ \text{O}_2 (aq) + 2H_2O (l) + 4e^- \rightarrow 4OH^- (aq) \]  

(Nitrate reduction:

\[ \text{NO}_3^- (aq) + H_2O (l) + 2e^- \rightarrow \text{NO}_2^- (aq) + 2OH^- (aq) \]  

Water reduction:

\[ 2H_2O (l) + 2e^- \rightarrow H_2 (g) + 2OH^- (aq) \]  

Both LSVs exhibit the likely onset of hydrogen evolution at lower applied voltages, approximately at −0.8 V for Pt and −1.1 V for Au. This voltage is dependent on the catalytic properties of the used metal substrates. Bubbles were observed in the outlet tube of the flow module when a potential < −0.8 V for Pt and < −1.1 V for Au was applied, indicating the formation of hydrogen gas. As hydrogen gas formation can cause that parts of the CaCO₃ layer detach from the metal substrate and disturb the uniformity of the coating, the optimal potential for the electrochemically assisted deposition process should be larger than the potential at which significant bubbling will occur at the same time, being low enough to provide sufficient amounts of OH⁻ ions. The production of OH⁻ ions leads to an increase in pH near the cathode (QCM-D sensor surface), converting bicarbonate into carbonate (eq 7) and resulting in the precipitation of CaCO₃ on the metal sensor surface (eq 8):

\[ \text{HCO}_3^- (aq) + \text{OH}^- (aq) \rightarrow \text{H}_2\text{O} (l) + \text{CO}_3^{2-} (aq) \]  

\[ \text{Ca}^{2+} (aq) + \text{CO}_3^{2-} (aq) \rightarrow \text{CaCO}_3 (s) \]  

The CaCO₃ deposition process was run in the potentiostatic mode (chronoamperometry) to trigger the reduction reactions described above (eqs 4–6). The selected potentials for electrodeposition were −0.7 and −1.0 V for Pt and Au sensors, respectively. Because of the catalytic properties of Pt, the potential applied to the Pt electrodes was significantly lower. By coupling the chronoamperometry experiments to QCM-D, the extent of deposition on the sensor surface can be monitored in real-time via the change in the resonance frequency of the quartz crystal (Figure 1b). In the first 10 min, the CaCO₃ deposition solution was fed to the flow module in order to obtain a stable baseline frequency. Then, the potential was applied for 20 min, giving rise to a significant frequency drop that is associated with the CaCO₃ deposition process. From the pattern of the frequency drop, two major stages for the crystallization of CaCO₃ can be deduced: nucleation and growth. Nucleation most probably starts with the arrangement of the Ca²⁺ and CO₃²⁻ ions into small clusters, and this process is relatively fast (see first 60 s in Figure S1). The agglomeration of such clusters formed sites upon which additional particles and ions were deposited that make the crystal grow. Additionally, the growth of the crystals was often accompanied by Ostwald ripening. Ostwald ripening is a spontaneous, thermodynamically driven process in which the larger crystals grow at the expense of the dissolution of the smaller crystals. This is a favorable effect because of the overall reduction of the surface area to volume ratio, thus reducing the overall surface energy. The CaCO₃ deposits cover the metal electrode progressively, resulting in a nonlinear decrease in the resonance frequency as the constant potential is applied over time to the sensor surface. Finally, the applied voltage was turned off after a period of 30 min. Next, the sensor was allowed to stabilize until the frequency leveled off, as shown in Figure 1b. During the stabilization period (t = 20 to 60 min), the CaCO₃ deposition solution was still flowing through the flow module, exhibiting only small changes in the observed resonance frequency. This observation suggests that the applied CaCO₃ coating was stable and did not dissolve or detach when being in direct contact with the flowing liquid. The optical micrographs of the resulting modified CaCO₃-Pt and CaCO₃-Au sensors are shown in Figure 1c. There were no significant visible differences in the electrocrystallized CaCO₃ on these two metal substrates. However, the use of Pt as the metal was observed to produce a somewhat more stable sensor compared to using Au as the metal while performing surfactant adsorption measurements.

Electrochemically assisted CaCO₃ deposition and the corresponding experimental parameters, the applied voltage, deposition time, frequency shift, deposited mass, deposited thickness, and coverage for the CaCO₃-metal sensors, are summarized in Table 2. The deposited mass and coating thickness of CaCO₃ were calculated with the Sauerbrey model, assuming a high rigidity of the deposited CaCO₃ (see section 2.4). From the frequency shift, the derived mass and thickness for CaCO₃-Au and CaCO₃-Pt sensors were 69.0 and 74.3 μg cm⁻² and 331 and 357 nm, respectively. The SEM images taken in the backscatter electron image mode were analyzed and used for the coverage determination. For this purpose, five different micrographs were taken on four different spots and

### Table 2. Applied Voltage, Deposition Time, Frequency Shift, Deposited Mass, Thickness, and Coverage of the Deposited CaCO₃-Metal Sensors

<table>
<thead>
<tr>
<th>Material</th>
<th>Voltage (V)</th>
<th>Time (min)</th>
<th>Δf (Hz)</th>
<th>Δm (μg/cm²)</th>
<th>Thickness (nm)</th>
<th>Coverage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃-Pt</td>
<td>−0.7</td>
<td>20</td>
<td>3900</td>
<td>69.0</td>
<td>331</td>
<td>35</td>
</tr>
<tr>
<td>CaCO₃-Au</td>
<td>−1.0</td>
<td>20</td>
<td>4200</td>
<td>74.3</td>
<td>357</td>
<td>40</td>
</tr>
</tbody>
</table>

*Coverage is based on the SEM micrographics analysis.*
Figure 2. (a) SEM micrograph (×100 magnification) of the deposited CaCO₃-Pt sensors with an applied potential difference of −0.7 V. (b) SEM micrograph obtained in the backscatter electron image mode. Elemental mapping of (c) calcium, (d) carbon, and (e) oxygen, where the lighter shade indicates a higher presence of the atom.

Figure 3. QCM frequency (a) and dissipation (b) monitoring of a commercial CaCO₃ sensor in the presence of 0.15 wt % AAS and 100 mM CaCl₂, pH = 9.5, and T = 23 °C. The black arrows indicate the moment of the addition of the AAS or CaCl₂ solution. (c) Real-time observed frequency shift upon varying the CaCl₂ concentrations. For clarity, the start of the curves was set to F₃ = 0 Hz and t = 0 min. (d) Observed maximum frequency shifts as a function of CaCl₂ concentration.
on the central area. These images were mapped onto a binary black and white format using a self-written Python script. The black regions of the image are the CaCO₃ deposition spots, and the white parts are considered as the uncovered Pt sensor surface. Then, the calculated relative occurrence of the black and white pixels was taken as a measure for the sensor coverage (Figure S2). The described method to determine the coverage of the deposited CaCO₃-metal sensors resulted in a good estimate of the actual coverage of the sensors, equalizing to 40 and 35% for CaCO₃-Au and CaCO₃-Pt sensors, respectively. Because the electrocrystallization conditions of CaCO₃ were optimized, these values were almost twice as much when compared to our previous study.²¹

The electrochemically formed model mineral rock deposits of CaCO₃ were characterized using SEM and EDX to study its morphology and elemental composition (Figure 2). From the SEM micrographs, it is observed that mostly cubic-like and rhombic-like CaCO₃ crystals were formed with the crystal sizes of around 20–40 μm. This suggests that the deposit was predominantly the mineral calcite rather than the thin needle-shaped aragonite (additional SEM micrographs can be found in Figure S3). The thermodynamically most stable calcite is described by a two-step process, as deduced from the complete adsorption data can be found in Figure S4. The adsorption to the CaCO₃ are given in Figure 3c. This plot can be attributed to the deposition and drying processes, leading to some dissolution and recrystallization of calcium carbonate.

3.2. Effect of CaCl₂ Concentration on the Adsorption of AAS on a Smooth Commercial CaCO₃ Sensor. The adsorption of AAS on the smooth commercial CaCO₃ surface was monitored when contacted with an aqueous AAS solution [0.15 wt % corresponds to 2.1 mM, which is well above its critical micellar concentration (CMC) in Milli-Q] at pH = 9.5 and room temperature (23 ± 0.1 °C). The solution was applied via a flow system, as described in section 2.5, to the QCM-D sensor. A typical example of frequency and dissipation changes for different overtones with time is shown in Figure 3a and 3b, respectively, for 100 mM CaCl₂. This measurement started from a stable baseline frequency of the salt solution (t = 0 to 10 min). Then, an AAS-containing solution was injected into the flow module at the point indicated with the black arrow (see Figure 3a). A large frequency shift drop was observed, which is interpreted as an increased AAS adsorption on the CaCO₃ surface. The observed frequency shifts were negative because of the increase in the adsorbed mass, whereas the positive dissipation shifts were found because of the bound surfactant layer (soft adsorbed layers are known to enhance the energy dissipation of the sensor freely oscillating at its resonance frequency). For different overtones, the observed frequency and dissipation shifts were similar. From the sharp decrease in the frequency shift, it was concluded that the adsorption process was fast. The dip at t = 11 min likely resulted from a temporarily formed bilayer or multilayer, followed by a fast desorption of the outer, more loosely bound surfactant layer. The surface is considered to be saturated with the adsorbed AAS when the frequency shift is stable. At t = 20 min, surfactant desorption was initiated by switching the flow solution from AAS to a solution containing only 100 mM CaCl₂.

Desorption was found to be a slower process compared to adsorption, which was in agreement with the strong affinity of the AAS surfactants to the CaCO₃ surface. Desorption is characterized by a two-step process, as deduced from the observed resonance frequency shift patterns depicted in Figure 3a: (i) a sharp increase in the resonance frequency indicates a relatively fast desorption process which we attribute to the loosely bound AAS to the surface, followed by (ii) a somewhat slower and more gradual decrease toward the final stable baseline. The slow process (t = 25 to 35 min) is suggested to be related to the desorption of strongly adsorbed surfactants that are directly bound to the CaCO₃ surface. It is speculated that more than one monolayer of AAS is formed. From the dissipation curves (Figure 3b), the dissipation shifts exhibited a conversed behavior to the desorption process (Figure 3a). At t = 20 to 22 min, a large drop in the dissipation shift was observed, which was consistent with the desorption process of a relatively small change in the resonance frequency. At t = 25 to 35 min, there was a small dissipation shift but a large change in the resonance frequency, suggesting a relatively rigid behavior of strongly bound surfactants. Therefore, it can be concluded that the weakly bound AAS played the main role in the contribution to the dissipation shifts.

Similar to the experiment performed when the sensors were flushed with 100 mM CaCl₂ solution, a series of measurements were subsequently repeated with lower salt concentrations until the final salt concentration of 1 mM CaCl₂ was reached. The complete adsorption data can be found in Figure S4. The corresponding resonance frequency changes for the initial AAS adsorption to the CaCO₃ are given in Figure S4c. This plot was calibrated by adjusting the initial resonance frequency shift (Fₒ) and the experimental times to zero. In general, a decreasing trend can be observed in the surfactant adsorption upon flowing from high to low salt concentrations. An explanation for this observation is that when flushing with higher CaCl₂ concentrations, the surface of the negatively charged CaCO₃ was occupied by relatively more Ca²⁺ ions. Because Ca²⁺ is an important potential determining ion for the carbonate surface, its zeta potential increases with increasing CaCl₂ concentration, and the surface becomes less negative.²¹,²² In other words, this provides more positively charged adsorption sites for the AAS surfactant molecules to bind to. Regardless of the CaCl₂ concentration, adsorption was always fast and reached saturation in approximately 2 min. Figure 3d depicts the absolute frequency shift for the investigated salt concentrations. The shape of this curve was observed to flatten when increasing from lower to higher salt concentrations. This suggests that beyond a certain salt concentration, the change in the adsorption of AAS on the studied commercial CaCO₃ sensor becomes negligible. An explanation for this could be that beyond a certain salt concentration, the surface of the CaCO₃ sensor was already fully occupied by the Ca²⁺ ions, and upon further increase, the salt concentration had no additional effect on the AAS surfactant adsorption. Considering 1 mM CaCl₂, the AAS adsorption-induced frequency shift was as high as 15 Hz. This value was different compared to the previously observed negligible adsorption on clay and silica surfaces at the
same low CaCl₂ concentrations.²⁰,⁵² From these comparisons, it brings us to the conclusion that the Ca²⁺ ions at the calcite surface itself likely play a dominant role in AAS adsorption in the absence of the added Ca²⁺ ions. With an increasing CaCl₂ concentration (1–20 mM), the degree of the increased frequency shift was much smaller than the change in the CaCl₂ concentration. It was interpreted that no accompanying change in the adsorption sites for AAS (cation bridging) and the increased electrical double layer repulsion effect also likely contributed to the adsorption. Moreover, the change in CaCl₂ from 1 to 20 mM resulted in the much higher frequency change as compared to the remaining studied concentrations, that is, from 20 to 100 mM.

The adsorbed AAS surfactant layer is described quantitatively (the adsorbed mass, thickness, and the number of adsorbed AAS layers (N_layers)) and are summarized in Table 3.

Table 3. Mass, Thickness, and Numbers of the Adsorbed AAS Layers on a Commercial CaCO₃ Sensor for Varying CaCl₂ Concentrations

<table>
<thead>
<tr>
<th>[CaCl₂] (mM)</th>
<th>Δm (ng/cm²)</th>
<th>thickness (nm)</th>
<th>N_layers</th>
<th>N_layers,th</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>310 ± 3</td>
<td>2.8 ± 0.1</td>
<td>0.80 ± 0.03</td>
<td>0.84 ± 0.01</td>
</tr>
<tr>
<td>2</td>
<td>345 ± 3</td>
<td>3.1 ± 0.1</td>
<td>0.89 ± 0.03</td>
<td>0.93 ± 0.01</td>
</tr>
<tr>
<td>5</td>
<td>381 ± 2</td>
<td>3.5 ± 0.1</td>
<td>1.00 ± 0.03</td>
<td>1.03 ± 0.01</td>
</tr>
<tr>
<td>10</td>
<td>390 ± 2</td>
<td>3.5 ± 0.1</td>
<td>1.00 ± 0.03</td>
<td>1.05 ± 0.01</td>
</tr>
<tr>
<td>20</td>
<td>444 ± 3</td>
<td>3.5 ± 0.1</td>
<td>1.14 ± 0.03</td>
<td>1.20 ± 0.01</td>
</tr>
<tr>
<td>50</td>
<td>465 ± 2</td>
<td>4.2 ± 0.1</td>
<td>1.20 ± 0.03</td>
<td>1.26 ± 0.01</td>
</tr>
<tr>
<td>100</td>
<td>511 ± 3</td>
<td>4.7 ± 0.2</td>
<td>1.34 ± 0.05</td>
<td>1.38 ± 0.01</td>
</tr>
</tbody>
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As calculated with the “thickness” method (N_layers,th) and “mass and headgroup” method (N_layers,th).²⁰

For our system, the density of the adsorbed AAS layer was set at 1200 g L⁻¹, which was determined by weighing a known volumetric amount of an AAS solution (dissolved in Milli-Q) on a weight scale and converting it to a density. These results are based on the Sauerbrey model (see section 2.4) because Δf was much less than Δf and the Δf/Δf was ∼6 × 10⁻⁴ Hz⁻¹. The 3rd, 5th, and 7th overtones were chosen, and the obtained results were averaged. From Table 3, an increasing trend can be observed for the adsorbed mass and thickness of the formed AAS layer as the CaCl₂ concentration increased. As explained earlier, a reason for this increase is the high number of the positively charged adsorption sites existing at the surface of CaCO₃ eventually becoming saturated with the Ca²⁺ ions. It would be interesting to further characterize the formed layer by considering the properties of the surfactant and the type of the formed layer. The determined AAS layer thickness varied from 2.8 to 4.7 nm for CaCl₂ concentrations between 1 to 100 mM. Moreover, we also tested the Voigt model by choosing the 3rd to 13th overtones to derive the adsorbed mass and layer thickness at 100 mM CaCl₂. The chi-square (χ²) was about 0.01, indicating a perfect fit with the Voigt model. The calculated mass and thickness were 554 ± 6 ng/cm² and 4.6 ± 0.05 nm, respectively, which also matched well with the interpretation obtained using the Sauerbrey model (Table 3). Therefore, the used models and calculations are considered as reasonable to approximate the structure and characteristics of the formed AAS layer.

To estimate the amount of adsorbed AAS layers (mono- vs bilayers) at the CaCO₃ surface, the calculated thickness can be divided by the chain length of an AAS molecule. In the literature, the length of an AAS surfactant molecule was estimated to be between 3 and 4 nm,³⁰ and in our calculations, an average length of 3.5 nm was taken. This is referred to as the “thickness” method, and the number of adsorbed layers calculated with this method can be found under the N_layers column in Table 3. Another method to determine the amount of adsorbed AAS layers is derived from the calculated adsorbed mass and the surface area occupied by a surfactant head group. In Table 3, we refer to it as the “mass and headgroup” method. The head group of an AAS molecule consists of a sulfate group. For our calculations, we assumed that this head group is a perfect sphere with the radius given by the length of an S=O bond equal to 143 pm.⁵³ With this in mind, we found that a single AAS molecule adsorbed on a CaCO₃ surface occupies an

Figure 4. Schematic illustration of the structure of an adsorbed AAS layer in the presence of (a) low (1–2 mM) Ca²⁺ concentrations when N_layers < 1 and (b) high (20–100 mM) Ca²⁺ concentrations when N_layers > 1.
area of 31.4 Å². Our findings are in good accordance with the reported values between 20 and 40 Å² molecule⁻¹.20,54 The cross-sectional area of an alkyl chain is ∼20 Å²,55 which is less than the estimated cross-sectional area of the sulfate head group. Therefore, the tilting of the alkyl chain with respect to the surface is likely in order to fill the available space. Based on the surface area occupied by a single AAS surfactant molecule in a tightly packed monolayer, we can easily calculate its theoretical surface density that equals to 3.18 × 10¹⁴ molecules cm⁻². The adsorbed mass of an AAS surfactant at a CaCO₃ surface derived from the QCM-D experiment can be easily converted into the surface density (molecular weight of the anionic surfactant is 700 g mol⁻¹), and for 100 mM CaCl₂, the adsorbed mass equals to 4.4 × 10¹⁴ molecules cm⁻². When we divide this value by the expected and theoretical surface density for a complete monolayer, we obtain a factor of 1.38, indicating that for the concerned CaCl₂ concentration, the CaCO₃ surface is decorated with more than one surfactant monolayer. The number of adsorbed layers calculated with the proposed methods varies between 0.8 and 1.38 when increasing from low to high CaCl₂ concentrations.

For low CaCl₂ concentrations (1–2 mM), the calculated values for Nlayers are less than 1, which suggests that the adsorbed AAS layer is less dense and tends to approach to a tightly packed monolayer. For high CaCl₂ concentrations (20–100 mM), the calculated values for Nlayers are higher than 1, and this indicates a layer structure where the CaCO₃ surface is occupied by a monolayer configuration with areas where bilayers are formed. A schematic illustration of the discussed types of formed layers for low (1–2 mM) and high (20–100 mM) CaCl₂ concentrations are shown in Figure 4a and 4b, respectively. It should be noted that the used models and calculations are based on approximations and may not accurately reflect the actual structure of the adsorbed AAS layer. To the best of our knowledge, it is the first time that the structure and characteristics of the formed AAS layers are quantitatively described, and the presented models can be used as a good starting point for further modeling.

3.3. Effect of CaCl₂ Concentration on the Adsorption of AAS on CaCO₃ Sensors Prepared by Electrocrystallization. The coverage of the deposited CaCO₃-Au and CaCO₃-Pt sensors was determined to be 40 and 35%, respectively (section 3.1). These sensors were used for AAS adsorption with a concentration of 0.15 wt % (2.1 mM) at pH = 9.5 and at room temperature (23 ± 0.1 °C). During our preliminary measurements, it was often found that we encountered instability issues such as a strong noise on the signal and dissolution of CaCO₃ when starting with the CaCl₂ salt solutions before AAS was injected. Therefore, we have turned around this sequence: first, injection with the AAS surfactant solution, and then, flushing the sensors with a CaCl₂ salt solution. This results in stable signals. Clearly, the AAS adsorbed to the CaCO₃ surface contributes to its stability. Because adsorption is a dynamic process, the sequence of the addition of CaCl₂ and AAS is expected to not affect the adsorption state at equilibrium. The observed frequency shift as a function of time for the initial adsorption on the CaCO₃-Au sensor surface is illustrated in Figure 5a. The recorded patterns show a behavior similar to that observed for the commercial CaCO₃ surfaces (Figure 3c). That is, a fast
adsorption step is always observed (abrupt drop in the resonance frequency), and it is followed by the surface saturation (stable frequency change tends to level off). Based on these observations, the maximal amount of AAS adsorption as a function of CaCl$_2$ concentration is shown in Figure 5b. The shape of this curve was observed to flatten when increasing from low to high salt concentrations. When the CaCl$_2$ concentration was less than 20 mM, the adsorption of AAS on the CaCO$_3$-Au sensor increased with the increasing CaCl$_2$ concentration. When the CaCl$_2$ concentration was higher than 20 mM, the change in the recorded resonance frequency was significantly higher and equal to approximately 175 Hz. As mentioned earlier, discussing the absolute frequency shift of the commercial CaCO$_3$ sensor suggests the existence of the CaCl$_2$ concentration beyond which no additional AAS surfactant (or limited amount) can be adsorbed onto the CaCO$_3$ surface.

On the CaCO$_3$-Pt sensor surfaces, the same injection method was chosen as on CaCO$_3$-Au surfaces in order to obtain stable signals. The results are shown in Figure S5, and the outcome of this investigation is summarized together with the data obtained on the smooth CaCO$_3$ and CaCO$_3$-Au surfaces (Figure 5c). AAS adsorption reached saturation after a certain CaCl$_2$ concentration (~20 mM). An important observation that can be made from Figure S5 is that after the desorption process, the plateau of the baseline frequency shifted to lower frequencies, and similar observation was also made for the previous CaCO$_3$-Au surface. This behavior indicates that not all the adsorbed surfactant molecules could be desorbed from the surface when flushing with the salt solution, which was different from the case of the commercial CaCO$_3$ sensor. If not all the adsorbed surfactant was desorbed between each salt concentration, a smaller amount of mass can be removed, and hence, the baseline of the frequency was lower compared to the baseline frequency of the previous salt concentration. The rough nature of the surface of the used deposited CaCO$_3$-metal sensor may likely be the reason for this observation. We think that the pores and cavities present within the CaCO$_3$ framework, once occupied by the AAS surfactant molecules, are not directly accessible to the Ca$^{2+}$ ions from the flushing solution. Consequently, these regions are expected to be resistant to AAS desorption. Moreover, the adsorption process took increasingly longer for the CaCl$_2$ concentrations of 10 mM and below. An explanation for this may be that there are fewer binding sites available for the surfactant to bind to when the measurement proceeds and lower CaCl$_2$ concentrations are used. In turn, this could result in the observed increasingly longer adsorption time for these lower salt concentrations.

An illustration for the general behavior of surfactant adsorption to CaCO$_3$ in the presence of different CaCl$_2$ concentrations is shown in Figure 5c. A critical CaCl$_2$ concentration above which the change in the surfactant adsorption is negligible is found to be around 20 mM. The maximal observed frequency shifts caused by the adsorption of AAS on the investigated CaCO$_3$-metal sensors are up to 5 to
15 times larger than those observed on the smooth commercial CaCO₃ sensors. The possible explanation for this could be the case that the elaborated surface area of the used CaCO₃-metal sensor is much larger (because of intrinsic roughness) than that of the commercial CaCO₃ sensor. The roughness \( R \) of the used sensors for surfactant adsorption measurements, together with the roughness of a clean Pt sensor, was measured using a surface profilometer, and the results are shown in Figure 5d. The roughness of the electrocrystallized CaCO₃-metal sensors is more than two orders of magnitude larger, as compared with a commercial CaCO₃ sensor. A higher roughness and thus a larger surface area offer more adsorption sites for the surfactant to bind to; hence, it facilitates the adsorption processes. These speculations are fully in line with the observations made with the QCM-D adsorption experiments.

Another phenomenon that may have contributed to the observed much larger frequency shifts observed at the CaCO₃-metal sensors could be due to liquid trapping. Surface roughness is an important parameter that determines how a fluid permeates through a surface. High roughness may result in an increase in the frequency shift due to trapping of the liquid molecules from the flooding solution in interfacial cavities and porous spaces in the coating layer. With the lack of information on the trapped liquid (see section 2.4), it is refrained from accurately making quantitative statements regarding the adsorbed mass on the deposited CaCO₃-metal sensors. Assuming that the cubic CaCO₃ crystals are homogeneously distributed over the CaCO₃-metal sensors and that each side of the crystal is equally available for AAS adsorption, we roughly estimated that the maximal adsorption surface area for AAS is at least 5 times higher as compared with that of the smooth commercial CaCO₃ sensor. This statement is based on the frequency shift differences observed at the rough and smooth surfaces. However, we found that the AAS adsorption-induced frequency shifts on the CaCO₃-Pt sensors were up to 15 times larger than the commercial CaCO₃ sensor. It suggests that the additional frequency shifts likely originated from the liquid trapping effect, which may have played a significant role in the total observed frequency shifts. The essence of liquid trapping originated from the trapped surfactants or their hydrated forms, and it also included trapped water. The difference in roughness between the CaCO₃-Pt and CaCO₃-Au sensors is small. However, they exhibited a largely different AAS adsorption, which also suggested the likely liquid trapping for the observed adsorption difference.

Figure 6 schematically illustrates the binding of the AAS surfactant molecules to the smooth and rough CaCO₃ surfaces before and after flooding with the salt solution. A reason for the observation of larger frequency shifts on the CaCO₃-metal sensors is that a rougher surface has a larger surface area, and more surfactant adsorption is possible. On a smooth surface, only the adsorbed surfactants can be removed easily upon flushing with the salt solution, and this is illustrated in Figure 6a,b. A rough surface also contains interfacial porous spaces where surfactants, once adsorbed, are very difficult to be removed even upon flushing with the salt solution (Figure 6c,d). This “surfactant trapping” effect was not observed during the surfactant adsorption measurement when the commercial CaCO₃ sensor was used because this sensor has a smooth surface, and all the adsorbed surfactant could be removed by flushing with the salt solution. This is evidenced by the fact that after each desorption step, the baseline frequency returned to the plateau value of the previous salt concentration. Most importantly, the observations made in this comparison provide new theoretical insights into the adsorption of a surfactant on rough mineral surfaces.

In our work, we showed that the model mineral surface can be formed using electrochemical control, and we studied further with the help of EQCM-D. Given the complex topological nature of the real rocks, the sensors with a rougher CaCO₃ surface, as prepared by electrocrystallization, closely resemble these rock surfaces compared to the smooth commercial CaCO₃-modified sensors. In the future, we plan to further extend our methodology to increase the chemical complexity of the electrochemically formed crystals decorating the EQCM-D sensors. It would be interesting to study the electrocrystallization of other rock surfaces found in oil reservoirs, such as silica, dolomite, and alumina. Also, oil reservoirs consist of heterogeneous mineral surfaces, and in that regard, the deposition of mixed rock surfaces can also be investigated. Additional effort will be contributed toward providing more accurate calculations and better models, allowing the prediction of surfactant adsorption.

4. CONCLUSIONS

Surface roughness has a considerable effect on surfactant adsorption, both in terms of the total amount of adsorbed species as well as the kinetics of adsorption and desorption. The coupling of electrochemical techniques and QCM-D in one analysis setup opens a new avenue to deposit model CaCO₃ rock surfaces and to investigate these surfaces for surfactant adsorption studies. Using the electrochemically assisted deposition method, uniform and well-covered CaCO₃-metal sensors were obtained. The electrocrystallization process was controlled by the nitrate, water, and/or oxygen electrode reduction reactions in the presence of bicarbonate and calcium ions. The deposited mass and coating thickness of CaCO₃ were calculated, together with the coverages for the CaCO₃-Au and CaCO₃-Pt sensors that are equal to 40 and 35%, respectively. From the SEM micrographs, it is observed that mostly cubic-like and rhombic-like CaCO₃ crystals were formed with the crystal sizes around 20–40 μm. The larger crystals were surrounded by the regions of the Pt surface, partly covered with smaller crystals, suggesting the contribution of Ostwald ripening during crystal growth.

Before the investigation of the electrocrystallized CaCO₃ surfaces, the adsorption of the AAS surfactant was studied on a smooth commercial CaCO₃ surface with varying CaCl₂ concentrations. Fast adsorption was observed, whereas the desorption process was characterized as a two-step process. Increasing the CaCl₂ concentration in the solution showed an increased AAS adsorption until a concentration of ~20 mM was reached. At higher CaCl₂ concentrations, the change in the adsorption of AAS was found to be negligible. This is primarily attributed to the limited number of adsorption sites available at the CaCO₃ surface for AAS binding. Also, it is the first time that the structure and characteristics of the formed AAS layer were quantitatively described, and an incomplete bilayer adsorption model was proposed. Compared to the smooth CaCO₃ surface, a similar trend of surfactant adsorption as a function of CaCl₂ concentration was observed in the rough CaCO₃ sensors. However, an increase in the frequency shift by a factor of 5 to 15 times was observed, further underlining the effect of the surface topology on the adsorption process. This
observation can be mainly attributed to the rougher surfaces that possess more adsorption sites for AAS binding as well as to the liquid trapping effect, resulting in additional frequency shifts. This difference was schematically illustrated, showing that the surfactant adsorption on rough surfaces was very different compared to smooth surfaces. It is suggested that a model mineral sensor with a rougher surface is a better representation of a real rock surface, as compared with the smooth mineral surface. The obtained results provide a better understanding of the adsorption behavior of the surfactants onto the mineral surfaces, and EQCM-D also shows great potential for depositing and studying heterogeneous minerals.

**ASSOCIATED CONTENT**

1. Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.0c03695.

SEM micrographs displayed as a black/white image; SEM micrographs of the deposited CaCO3-Pt sensors at low and high magnifications; Surfactant adsorption with varying CaCl2 concentrations on a smooth commercial CaCO3 sensor and on a rough CaCO3-Pt sensor (PDF).

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Notes

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