Interfacial Phenomena on the Inorganic Scaling Prevention

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ABSTRACT: Superhydrophobic and lubricated slippery surfaces were tested under high salinity inorganic scaling medium and had their antifouling capacity assessed by optical and electron microscopy. The superhydrophobic surfaces were build up with hierarchically rough electropolymerized polyaniline onto stainless steel substrates and functionalized with low-polarizability thiols. Subsequently, these materials were lubricated with perfluorinated oil to obtain slippery surfaces. Regardless of the large amount of inorganic scale found onto superhydrophobic surfaces after the scaling test, the slippery ones showed to be very efficient as fouling preventers. From crystal quartz microbalance experiments, the wetting regime of the superhydrophobic surfaces was evaluated and shows that the Cassie–Baxter effect was not lost during the entire scaling test. The interfaces energies of the systems were assessed with contact angle experiments and showed that the scaling increases because the interfacial free energy is minimized. These results lead to a better understanding of how superhydrophobic surfaces could induce inorganic scaling instead of preventing it.

INTRODUCTION

Inorganic scaling mitigation plays an important role in many industrial facilities, as boilers of hard water systems and pipes of offshore oil industry. However, it is challenging due to delays in production to repair scaled walls and use of inhibitor agents, which results in elevated costs, loss of productivity, and environment impact. Alternatively, surface modification may be employed to prevent scale formation, but it is important to understand the physical–chemical aspects of the interfaces involved in the scaling processes.

Looking at nature, it is possible to find several ways to prevent adhesion of matter where it is not advantageous, such as leaf surfaces,1–4 wings,3,4 and eyes of insects.5,6 In some of these cases, the low adhesion results in a self-cleaning effect. The most notorious case may be the one called lotus effect,1 which is the ability of some leaves to keep clean due to the low adhesion of water and contaminants over themselves, provided by the combination of hierarchical topography and hydrophobic composition, and is in accordance with the model proposed by Cassie and Baxter7 to explain the contact angle between a liquid droplet and a rough surface.

In the same direction, inspired by a natural effect that can be observed in pitcher plants, Wong et al.8 developed the called slippery liquid-infused porous surfaces (SLIPS), which present omniphobic behavior due to their low polarizability liquid interface.

Both the lotus self-cleaning and the pitcher plants slippery effects are promising options to be mimicked to create materials or coatings that can prevent inorganic scale formation.9–11 In both cases, the direct contact of the surface with the brine is minimized. In the lotus effect, contact is minimized by an air cap that lies between solid and liquid phases, whereas on the slippery surface, the lubricant oil acts like the barrier that prevents the direct contact and adhesion between scale and solid surface.

Barthlott and Neinhuis1 conducted experiments of adhesion of contaminants onto superhydrophobic self-cleaning leaves, like barium sulfate particles, among others, and showed that the lotus effect is efficient to reduce the adhesion of the contaminant with the leaf surface. Nonetheless, the experiments were conducted with crystals particles spread in air and, only after that, washed by water, simulating natural dust and rainy conditions to which leaves are exposed. Literature shows12 that biofouling onto a material is decreased by lowering its surface energy, but biological systems are much more complex than inorganic ones, and not necessarily follow the same fouling mechanisms. Schmäser et al.13 showed the low adhesion of proteins onto superamphiphobic surfaces due to the air cushion formed in their hierarchical structure. Nonetheless, inorganic scaling medium with a high ionic strength, such as found in many industrial processes, are quite different from natural dirtying and washing of leaves as well as from biofouling processes, thus requiring specific experiments to be well understood. Reported works with inorganic scaling nucleated in situ had shown diversity of results in such matter.14–17

Several works demonstrated that electropolymerized polyaniline could achieve hierarchical structure either for

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galvanostatic\textsuperscript{18} or potentiostatic\textsuperscript{19} methods, varying parameters like time of reaction,\textsuperscript{18} current or tension applied,\textsuperscript{20} substrate shape,\textsuperscript{21,22} and electrolyte utilized for electropolymerization.\textsuperscript{23} Furthermore, polyaniline can be easily functionalized by thiol groups,\textsuperscript{22,24} leading to surfaces with different polarity and polarizability, depending on the thiol chain utilized. Despite its mechanical fragility, electropolymerized polyaniline is highly eligible to act as a model to study the effects of the above-mentioned surfaces due to its easy, reproducible, and well-controlled production, which leads to very fashioned structures.

Thereby, the objective of this work is to develop both superhydrophobic Cassie–Baxter surfaces, inspired by the lotus effect, and SLIPS surfaces and test them in high salinity scaling medium, where the inorganic crystals will be nucleated in situ, to assess not only their antiscaling capacity but also the stability of both kinds of effects under such conditions. Thus, electropolymerized polyaniline was used as rough coating over plain stainless steel substrate. Krytox GPL105, a perfluorinated oil, was used as lubricant oil to impregnate the slippery surfaces. Perfluorinated oils are well known for their low polarizability, which implicates in a low surface tension and, so, are commonly used in the lubrication of such surfaces.\textsuperscript{8,9}

\section*{RESULTS AND DISCUSSION}

Polyaniline can be obtained by electropolymerization and results in a rough surface coating, presenting interlaced wire-like structures with interconnect hollows,\textsuperscript{18,20,23,25,26} which are useful for producing both superhydrophobic self-cleaning surfaces\textsuperscript{22,27,28} and lubricated slippery ones.\textsuperscript{9,9} Also, by varying parameters such as time of reaction and current applied, it is possible to change the roughness of the surface.

All samples presented an emerald green color during the electropolymerization and became darker with the progress of reaction. After washing with water and ethanol, they became bluish. Following the deprotonation with ammonium hydroxide, their color resulted in a mixture of violet and blue. As Stejskal et al.\textsuperscript{29} showed, the color of electropolymerized polyaniline varies depending on the protonation degree and oxidation state. According to this statement, there were both emeraldine and pernigraniline oxidation states of polyaniline in the electropolymerized substrates.

The samples electropolymerized onto stainless steel disks, without any functionalization or lubrication, were assessed by field emission scanning electron microscopy (FESEM). The micrographs (Figure 1) showed that, after 600 s of the electropolymerization reaction, the whole stainless steel surface was covered by a thick layer of polyaniline, presenting a hierarchical structure with interconnected microwires covered with nanostructures.

The functionalization of polyaniline with 1\textsubscript{H},1\textsubscript{H},2\textsubscript{H},2\textsubscript{H}-perfluorodecanethiol (PFDT) by thiol group nucleophilic attack\textsuperscript{24} has the objective of changing the surface wettability from hydrophilic to hydrophobic. Compounds with low polarizability, as the PFDT chains, are eligible to add the hydrophobic effect to the polyaniline surfaces, which, combined with a hierarchical structure such as of polyaniline electropolymerized for 600 s, can reach the superhydrophobic self-cleaning behavior.

For the nonfunctionalized samples electropolymerized for 600 s, the contact angle experiment resulted in complete water
absorption, which was expected because polyaniline is a well-known hydrophilic. The spaces between the microstructure of polyaniline are not small enough to prevent water to fill its hollows, and the hydrophilic effect is accentuated by a Wenzel wetting state. So, the roughness allied to the hydrophilic characteristic of polyaniline made these surfaces act like a sponge that absorbs all the liquid.

For samples electropolymerized for 600 s and functionalized with PFDT, the static contact angles were not assessed because the surface showed to be extremely water repellent. The droplet of water does not stick onto the surface and it is not wetted by water because a cap of air remains between the solid and liquid phases (Figure 2). This behavior looks like an extreme Cassie–Baxter type case, with a whole film of air trapped among the hierarchical roughness of the structure. In these cases, hierarchical structure allied to superhydrophobic modification of the surface by the functionalization superably prevents water to fill the hollows. Thus, the superhydrophobic Cassie–Baxter surfaces were obtained by functionalization with PFDT of the rough polyaniline structures.

It was expected that for such pronounced Cassie–Baxter effect, these superhydrophobic surfaces would present no significant scale formation because there is almost no contact between the solution and the surface. However, as shown in Figure 3c, in fact, the surface did not behave so. As polyaniline surface absorbs most of the light incident from optical reflectance microscopy, its surface appears dark in Figure 3, but the salt crystals deposited reflect the incident light and appear bright.

To explain these results, two approaches have been considered, one regarding the contact area of the liquid and the solid surface phases and other regarding its interfacial energy.

It was expected that for a such low contact area between the liquid and the solid surface, due to the Cassie–Baxter regime of wetting, the work of adhesion between the inorganic crystals and the surface should decrease. So, the first hypothesis proposed was that some variable during the scaling process could lead to a transition between the Cassie–Baxter and the Wenzel wetting regime, which would increase the contact area between the phases and thus allow the scaling to take places onto the whole surface.

To test this hypothesis, crystal quartz microbalance experiments were made to evaluate the wetting regime of the surfaces. As can be seen in Figure 4, the results showed that the mass variation per unit of area after the sinking of the surface into water was much greater for nonfunctionalized surfaces than for functionalized ones, which indicates a Wenzel wetting regime for the former and a Cassie–Baxter regime for the last. Besides that, the mass variation did not change significantly between just after the sinking of the surface into water and after 16 h of it, which indicates that there was no transition between the wetting regimes during the period of the experiment. Variables that are present during the scaling process, like ionic strength and nucleated sites onto the surface, were also evaluated and presented also a Cassie–Baxter wetting regime that does not change to Wenzel state during the test period.

With these results, it was possible to attest that the superhydrophobic sample that suffers much more scaling was in the Cassie–Baxter wetting regime during all the scaling process and its low contact area was not enough to prevent it. So, different from the results found in works that test adhesion between already grown large particles and the surface, we conclude that the larger contact area is not decisive for scaling induction when regarding in situ heterogeneous nucleation onto the surface. For nucleation to start, only a seed is required, and it has a minimal size. The sharp structures from the hierarchical topography of the superhydrophobic surface that provides a minimal contact area with the liquid phase when under Cassie–Baxter wetting regime are in large number and work like seeds for heterogeneous nucleation.

The seeds provided by the surface topography under Cassie–Baxter regime can explain why the inorganic scaling
cannot be prevented but cannot explain why it is increased when compared which superhydrophilic Wenzel surface. For that, an energetic study of the interfaces was performed.

The contact between the solid phase of the functionalized and the liquid should present a high energetic interface because the adhesion work of water with perfluorocarbon is much lower than the water cohesion work. To verify that, contact angle experiments were carried out to evaluate the energetic changes at the interface caused by inorganic scale. Contact angle experiments were carried out to evaluate the energetic changes at the interface caused by inorganic scale. Polyaniline electropolymerized over 180 s onto stainless steel 316 was used in these contact angle experiments because the adhesion work of water with perfluorocarbon is much lower than the water cohesion work. To verify that, an energetic study of the interfaces was performed. When compared which superhydrophilic Wenzel surface cannot be prevented but cannot explain why it is increased when compared which superhydrophilic Wenzel surface. For that, an energetic study of the interfaces was performed.

Table 1. Contact Angle Measurements and Their Standard Deviation (θ), Lifshitz–van der Waals Surface Tension Component (γ^LW), Acid Basic Surface Tension Component (γ^AB), Total Surface Tension of the Solid (γ_S), and Interfacial Tension between the Solid and Water (γ_SL)\(^a\)

|               | nonfunctionalized polyaniline | polyaniline functionalized with PFDT | calcite monocrystal |
|---------------|-----------------------------|-------------------------------------|---------------------|
| \(θ_{\text{water}}\) (deg) | 90.8 ± 3.8                  | 176.1 ± 3.0                        | 79.5 ± 4.6          |
| \(θ_{\text{ethanol glycol}}\) (deg) | 216.6 ± 7.3                | 109.6 ± 7.3                        | 74.4 ± 1.7          |
| \(θ_{\text{ZnS}}\) (deg) | 28.7 ± 1.4                  | 119.1 ± 5.3                        | 48.8 ± 2.9          |
| \(γ^LW\) (mJ m\(^{-2}\)) | 44.8                        | 3.4                                | 34.9                |
| \(γ^AB\) (mJ m\(^{-2}\)) | 4.0                         | 1.4                                | 17.2                |
| \(γ_S\) (mJ m\(^{-2}\)) | 48.8                        | 4.8                                | 52.1                |
| \(γ_SL\) (mJ m\(^{-2}\)) | 49.8                        | 77.4                               | 38.9                |

\(^a\)The solid surfaces used were nonfunctionalized polyaniline, polyaniline functionalized with PFDT, and calcite monocrystal. The liquids used in contact angle measurements were water, ethylene glycol, and diiodomethane.

It is possible to observe in the data from Table 1 that the calcite monocrystal has an interfacial tension with water lesser than both polyaniline surfaces, functionalized or not, which justifies the scale formation onto their surfaces. Furthermore, the polyaniline functionalized with the perfluorocarbon chain presents a significantly greater value of interface tension with water than the nonfunctionalized surface. Consequently, the overall system’s energy. For nonfunctionalized samples, the interface with aqueous medium is less energetic than that for the functionalized ones, thus the scale formation onto it is not so prominent.

Therefore, for the electropolymerized polyaniline surfaces used in this work the Cassie–Baxter effect that grants superhydrophobic properties to surfaces cannot prevent inorganic fouling onto them. Moreover, the low interaction of the water molecules with the functionalized groups adsorbed onto the surface, allied to its hierarchical structure, both responsible for the pronounced Cassie–Baxter effect, not only failed to prevent scale formation but also increased it.

Conversely, for polyaniline lubricated surfaces, the functionalization with thiol groups aimed to enhance the wettability of the surface by Krytox. Thus, PFDT, with its perfluorocarbon chain, was used to retain Krytox, which is a perfluorinated polyether, into the hollows of the rough surface. It was expected that the oil would remain impregnated into the rough surfaces even after exposure to the solution due to its much more favorable interaction with the respective thiol chains than with the aqueous solution.

It was expected that the Krytox film formed onto the electropolymerized polyaniline surfaces played a similar role of the air in that extreme Cassie–Baxter effect observed in the superhydrophobic samples, but filling not only the hollows of the hierarchical surface but also covering its outermost surface with a liquid film, preventing the aqueous solution to be in direct contact with the solid surface. Thus, because of the liquid nature of the lubricant phase, even if nucleation of the crystals occurs in the water/oil interface, they cannot adhere to a solid spot and then slide back to the aqueous solution.

Assessing the lubricated samples by optical reflectance microscopy (Figure 6) and comparing them with the nonlubricated surfaces, it is possible to see an effective inorganic scaling prevention by the slippery surfaces. In the micrograph of Figure 6c, it is possible to see some protuberances on the topography shape of the polyaniline surface under the thin layer of oil that remains over it, filling the hollows interconnected through the polyaniline structure. Nonetheless, the amount of oil remaining over the surface after the scaling test was enough to prevent completely the inorganic scaling during the period of test (16 h) as shown in Figure 6.

## CONCLUSIONS

Electropolymerized polyaniline was shown to be a good structure model to test and understand the efficiency and stability of superhydrophobic surfaces and the slippery ones against inorganic scaling medium.
Even though the superhydrophobic surfaces prepared with electropolymerized polyaniline functionalized with thiol groups of low polarizability present a great Cassie–Baxter effect that endures the entire test time and seem nonwettable under contact angle experiments, they did not prevent inorganic scaling. For heterogeneous nucleation to take place, points of minimal contact area are enough to work as nucleation seeds.

Nonetheless, the replacement of the air trapped in the hollows of the superhydrophobic surface by an oil of low polarizability that interacts with the thiol groups leads to a situation where the oil phase lies between the solid surface and the brine. Because it creates a liquid/liquid interface, the inorganic crystals that are formed in it are unable to find adhesion spots and slide back to the aqueous solution. Thus, the solid surface remains protected by the oil layer and inorganic scaling is efficiently prevented during the test period.

Therefore, these results suggest that the development of lubricated slippery surfaces with inorganic antiscaling goal is a more promising alternative than the lotus-like superhydrophobic self-cleaning surfaces.

## EXPERIMENTAL SECTION

### Materials

The salts Na$_2$SO$_4$, NaCl, KCl, CaCl$_2$, MgCl$_2$, BaCl$_2$, SrCl$_2$, NaHCO$_3$, NaBr, and NaCH$_3$COO (all PA-ACS), used to prepare the scaling medium, were purchased from Synth Brazil. Sulfuric acid, isopropyl alcohol, and ethylene glycol (all PA-ACS) were also purchased from Synth Brazil. 1H,1H,2H,2H-Perfluorodecanethiol (PFDT, 97% purity) and diiodomethane (99% purity) were purchased from Sigma-Aldrich Brazil. Krytox GPL105 was purchased from Chemours. Water used was always deionized (Milli-Q Plus Water System, Millipore, 18.2 MΩ).

Stainless steel 316 was used as disks with 12.7 mm diameter and gold exposed to surface, were purchased from Maxtek. Aniline (99% purity) was purchased from Sigma-Aldrich Brazil and distilled twice before use and stocked in the dark under nitrogen atmosphere and in the refrigerator prior to use.

### Preparation of Polyaniline Samples

The electropolymerization of aniline was carried out in a three-electrode cell, in which a platinum plate was used as a counter electrode, Ag/AgCl (6.0726.100 Metrohm) as the reference electrode, and disks made of stainless steel 316 or EQCM Cr/Au as the working electrodes. The galvanostatic method was used to grow the polyaniline onto the metallic surface, with the current set at 1000 μA, using a Metrohm Autolab PGSTAT128N potentiostat/galvanostat, with the time of the electropolymerization reaction of 600 s for scaling test samples and 180 s for contact angle samples.

For stainless steel-316, the meniscus method was employed to guarantee that only desirable surfaces were exposed to be coated by electropolymerized polyaniline. One of the circular faces of the disk was exposed to the solution, which consisted of aniline 4% (v/v) aqueous solution in sulfuric acid for stainless steel 316 working electrode or chloride acid for EQCM Cr/Au, both 1 mol L$^{-1}$, at room temperature.

After the electropolymerization reaction, the samples were rinsed in deionized water, followed by ethanol to remove unbound oligomers, and left sunken in deionized water for 24 h to reach equilibrium between the protonated state of polyaniline and the water, guaranteeing that contact angles could be measured without the influence of protonation/deprotonation reaction of the polyaniline by water contact. Some samples were rinsed in a 1 mol L$^{-1}$ ammonium hydroxide solution for 4 h to assess their doped state.

### Topography Characterization

The morphology of the polyaniline samples surfaces was assessed by field emission scanning electron microscopy (FESEM), carried out in a FEI Quanta FEG 250, using 15 kV of acceleration voltage.

### Functionalization and Lubrication of the Surfaces

Although some samples were left nonfunctionalized and nonlubricated, other samples were functionalized by PFDT, in a 5 mmol L$^{-1}$ solution of the thiol in isopropyl alcohol for 24 h. Some of the samples electropolymerized by 600 s onto stainless steel 316 and functionalized were lubricated with Krytox GPL105 by the deposition of a droplet of the oil onto the sample surface, which was impregnated by capillarity.

### Contact Angle Measurements

Static contact angle measurements between liquid (deionized water, ethylene glycol, or diiodomethane) and the solid surface samples were taken with a Krüss EasyDrop goniometer, using the Drop Shape Analysis 1 software. The volume of the added droplets was 2 μL, at a 150 μL min$^{-1}$ addition rate. Each droplet had its static contact angle measured every 10 s for 60 s. The surface of each sample was tested at three different points. Furthermore, as the major inorganic scale observed in the studied systems are calcite crystals, a calcite monocrystal {104} surface was also assessed by the same methodology.

### Interfacial Tension Evaluation

From contact angle experiments, the surface tensions of the polyaniline electropolymerized for 180 s, both functionalized and nonfunctionalized, and the calcite monocrystal were evaluate using the Van Oss, Chaudhury, and Good method.

Figure 6. Optical micrographs of electropolymerized polyaniline functionalized with PFDT (a) lubricated with Krytox GPL105 before scaling test, (b) nonlubricated after scaling test, and (c) lubricated with Krytox GPL105 after scaling test.
\[ \gamma_L(1 + \cos \theta) = 2\gamma_{LS}^{1/2} + 2\gamma_{S}^{1/2} + 2 \]

where \( \gamma_L \) is the surface tension of the liquid and \( \gamma_S \) is the surface tension of the solid. The LW superscript is the Lifshitz–van der Waals component of the surface tension and \( + \) and \( - \) superscripts are the acid and basic components of the surface tension, respectively. The AB superscript is the total acid basic contribution to the surface tension. The contact angle measured is given by \( \theta \). To evaluate a solid surface tension, one must measure the contacts angles between the solid and three different liquids, and one of them must have a null acid basic component, such as diiodomethane.\(^{35}\)

From surface tensions, the interface tensions between surfaces and water were evaluated by the Young’s equation\(^{36}\)

\[ \gamma_{LS} \cos \theta = \gamma_S - \gamma_{SL} \]  

(4)

where \( \gamma_{SL} \) is the interface tension between solid and liquid.

The values of all liquid surface tension components were obtained from the literature.\(^{35}\)

**Inorganic Scaling Tests.** The inorganic scaling tests were performed in highly saline aqueous medium that simulates the composition of formation water found in oil wells as described by Sousa et al. \(^{37}\) This composition was initially separated into two brines, called brine I and brine II. The composition of each of the brines is shown in Table 2. The mixture of both brines leads to a supersaturated state of calcium carbonate and barium and strontium sulfates that triggers the precipitation process and scale formation.

**Table 2. Composition of Brines Used in Scaling Jar Test, in g L\(^{-1}\)**

| salt        | brine I     | brine II   |
|-------------|-------------|------------|
| NaCl        | 180.8250    | 228.0267   |
| KCl         | 9.4228      |            |
| CaCl\(_2\) 2H\(_2\)O | 84.6521    |            |
| MgCl\(_2\) 6H\(_2\)O | 28.0756    |            |
| BaCl\(_2\) 2H\(_2\)O | 0.5598     |            |
| SrCl\(_2\) 6H\(_2\)O | 16.3241    |            |
| NaHCO\(_3\) | 1.5484      |            |
| NaBr        | 2.6372      |            |
| CH\(_3\)COONa | 0.3068      |            |

The samples were submerged in brine I and then brine II was added in brine I at once in a method named jar test. All tests were done with 60 mL of each brine and, after their conclusion, the samples were carefully washed with deionized water.

All the samples used in inorganic scaling tests were electropolymerized onto stainless steel disks for 600 s and disposed vertically for the jar test. All nonlubricated samples were tested together in the same jar, whereas the lubricated ones were tested together in another jar. All these tests were carried out at room temperature and lasted for 16 h.

All samples were assessed by optical reflectance microscopy, with a Microtornal microscope, after the scaling test. The nonlubricated samples scaling results were also assessed by FESEM.

**Wetting State Assessment.** The wetting state profile of electropolymerized polyaniline was assessed by measurements of mass variation during the sinking of samples into aqueous solutions and was carried out on a QCM200 Crystal Quartz Microbalance, 5 MHz, Stanford Research Systems. For such purpose, polyaniline samples prepared onto EQCM Cr/Au for 600 s of electropolymerization were utilized. The measurements start with the dry sample followed by its instant sinking into 60 mL of liquid. The mass variation was registered at each 10 s for 16 h.

The tests were conducted with nonfunctionalized samples sunken into water and functionalized ones sunken into water or an aqueous solution of NaCl with the ionic strength of 4 mol L\(^{-1}\). The test with water was also conducted with functionalized samples after exposure to the inorganic scaling test. All these tests were carried out at room temperature without stirring.

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