In-situ observation of reactive wettability alteration using algorithm-improved confocal Raman microscopy

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Hypothesis: The wettability of complex fluids on surfaces usually depends on the adsorption of solutes to any of the constituting interfaces. Controlling such interfacial processes by varying the composition of a phase enables the design of smart responsive systems. Our goal is to demonstrate that 3D Confocal Raman Microscopy (CRM) can reveal the mechanistic details of such processes by allowing to simultaneously monitor the contact angle variation and redistribution of the chemical species involved.

Experiments: Motivated by the enhanced oil recovery process of low salinity water flooding, we studied the response of picolitre oil drops on mineral substrates upon varying the ambient brine salinity. The substrates were pre-coated with thin layers of deuterated-stearic acid (surfactant) that display salinity-dependent stability.

Findings: 3D CRM imaging using a recently proposed faster ‘ai’ (algorithm-improved) mode reveals that the surfactant layer is stable at high salinities, leading to preferential oil wetting. Upon reducing the ambient brine salinity, this layer decomposes and the investigated surfaces of mica and – somewhat less pronounced – silica become more water wet. Eventually, the surfactant is found to partly dissolve in the oil and partly precipitate at the oil-water interface. We anticipate that ai-3D-CRM will prove useful to holistically study similar systems displaying reactive wetting.

1. Introduction

When a surface is reactive to a contacting liquid or responsive to an external stimulus, its wettability is also tuned by the reaction [1]. This behavior can be utilized to design surfaces with smart wettability [2,3], with potential use in self-cleaning surfaces [4–6], microfluidics [7], functional membranes [8,9] and pickering emulsions [10]. The phenomenon of reactive wetting is not only pertinent to artificially tailored smart materials, but it also occurs in geological processes. For example, soils often become very hydrophobic during longer periods of dry weather preventing efficient water absorption and retention upon subsequent rainfall. Organic species on mineral surfaces can adsorb and desorb and...
change their configuration depending on ambient humidity, rendering the initially hydrophilic mineral hydrophobic [11]. Certain parameters like pH and the presence of divalent cations can also affect the soil water repellency persistence [12]. A reactive wettability alteration in the opposite direction has been observed in enhanced oil recovery (EOR), where rock minerals become more hydrophilic after exposure to brines of lower salinity. In low salinity EOR, this change in wettability is believed to be the main cause of the enhanced oil release [13]. However, our understanding of such wettability alterations is often incomplete. This is partly due to a lack of techniques that can address the appropriate range of length scales in one experiment. Microscopic characterization of reactive wettability is therefore of key importance for rational engineering of smart wetting applications.

Wettability characterization is typically performed by taking optical images of a sessile droplet on a substrate and then extracting the contact angles at the three phase contact line (TPCL). However, this method faces two challenges for characterizing reactive wettability alteration: it often limits the characterization to the millimeter scale and lacks any chemical specificity. Many practical applications such as droplet condensation, microfluidics and enhanced oil recovery, involve the wettability of micron-sized droplets. Furthermore, most practical substrates are non-homogenous, causing the wettability to be sensitive to size of the substrate features. The micron-scale wettability could therefore be different from its millimeter-scale counterpart.

To address this problem, various microscopic techniques have been employed, including atomic force microscopy [14], interference microscopy [15], X-ray tomography [16,17], and confocal laser scanning microscopy [18–20], enabling wettability characterization even down to the nano-scale [14]. However, none of these methods provide chemical specificity, which is crucial for revealing the mechanistic details of the wettability alteration. For example, surfactant induced autophobing [21–24] is a complex phenomenon because the dynamics involve multiple chemical components and interfaces. In the absence of detailed information on which materials get redistributed and how, mechanistic interpretations and modelling have to rely on assumptions or ex-situ characterizations. While (fluorescent) dyes can be used to label the different fluid phases and sometimes also the surfactant, these components have a tendency to adsorb at interfaces, thereby affecting the physical chemistry of the system. Similar problems of insufficient information on the (dynamic) presence and chemical nature of compounds, are also prevalent in other systems like emulsions, biological cells, etc. Some of these additionally show heterogeneity at micron length scales, which further aggravates the issue.

Confocal Raman microscopy (CRM), on the contrary, has the potential to address these problems. Its vibrational spectroscopic nature provides unique access to the chemical information of every probed component, and its confocal nature provides three dimensional spatial resolution down to the sub-micron scale. Therefore, it could be used to characterize both the chemical reaction on the substrate and the resultant wettability alteration, giving us an opportunity to study the system more holistically. Until recently, the slowness of confocal Raman mapping was a significant hurdle. Due to the inherently low Raman scattering efficiency, measuring a spectrum from a single laser spot would normally take O(100 ms) of exposure time. Scanning the laser over typical range of O(10 μm) would then require O(1 h) in 2D, and O(1 day) in 3D. Such reaction time scales are often impractical for reactive wettability characterization. This problem can however be mitigated via the recently developed algorithm-improved confocal Raman microscopy (ai-CRM) [25], which is capable of increasing the scanning speed by 1–2 orders of magnitude, by making use of principal component analysis based denoising. The improvement in signal-to-noise ratio (SNR) of the spectral data offered by ai-CRM facilitates fast, simultaneous volumetric mapping of multiple components in-situ at the micron-scale, provided that the number of (spectrally overlapping) components is not too large and the local concentrations are not too low.

In this paper we use ai-CRM to elucidate some mechanistic aspects of a chemically triggered wettability alteration. We consider a system of mica/silica, oil and brine that is often used as a model to represent the low salinity water flooding (LSWF) process in Enhanced Oil Recovery. LSWF is an environmentally friendly and cost-effective EOR technique. In favorable cases (depending on the oil field) a simple dilution of the flooding water can increase the oil recovery efficiency by up to ten percent [26]. However, a wide deployment of LSWF is still hindered by a variability in the outcomes, and debates about the microscopic mechanism.

Many mechanisms have been proposed [13,26–29], including pH-increase [30], fines migration [31,32], double layer expansion [33], and multi-ion exchange (MIE) [34]. The MIE mechanism states that divalent cations in the high-salinity formation brine can adsorb on the negatively charged mineral substrate (typically quartz and clay in sandstone reservoirs), thereby forming a bridge between the substrate and negatively charged surfactants in the crude oil. As a result, the mineral substrate is turned hydrophobic. Injecting low salinity water weakens the cation bridge, supposedly leading to a partial or complete release of the surfactant. As a consequence, the mineral surface becomes more hydrophilic, and oil displacement more efficient.

In recent years, the MIE mechanism has been receiving increasing interest, and several aspects of it have been confirmed for model Crude Oil/Brine/ Rock (COBR) systems. For example, using mica and silica substrates, fatty-acid laden decane, and brines at varying ion content, (ex-situ) AFM studies confirmed the adsorption of divalent cations, as well as the subsequent adsorption of surfactants on the mineral substrate [35]. Contact angle goniometry confirmed the resultant wettability changes on the macroscopic scale [36]. However, to the best of our knowledge, there exists no direct experimental proof in literature which directly links the description of the surfactant to the wettability alteration.

In this paper, we use ai-CRM to provide direct evidence of this reactive wettability alteration in response to lowered ambient salinity. We illustrate this at the microscopic scale, which is the scale relevant to real oil reservoir conditions. Using mica (‘clay’) and glass (‘rock’) as model substrates, we first apply a coating with a surfactant and then immerse them in ambient brine. Subsequent deposition of oil leads to the formation of a microscopic droplet, whose shape is imaged in 3D with the confocal Raman microscope. Using a deuterated surfactant, we simultaneously access the distributions of the separate components: surfactant, oil, water and substrate. Inspecting the changes after lowering the salinity of the ambient brine then allows us to correlate the contact angle change to the redistribution of the surfactant.

2. Materials and methods

2.1. Materials

All chemicals were reagent grade and purchased from Merck, except for mineral oil (mixture of liquid hydrocarbons, density = 0.84 g/ml, BioReagent light oil), which was purchased from Sigma-Aldrich. As substrates, mica sheets (B & M Mica Co., Inc.) and silicon wafers (Okmetic, P type Mica Co., Inc.) and silicon wafers (Okmetic, P type wafers) with 30 nm of thermally grown SiO2 on top were used. Mica substrates were cleaved with Scotch tape right before the dip-coating procedure. 30 nm SiO2/ Si wafers were cleaned by sonicating them in an ethanol and isopropanol 1:1 mixture and then washing with deionized...
water. Then they were dried with a nitrogen gun and put in a UV ozone cleaner (BioForce Nanosciences, Inc.) for 15 min just before dip-coating.

The brine phase for dip coating contained a 10 mM CaCl₂ and 2 mM NaHCO₃ solution in deionized water (Millipore, resistivity 18.2 MΩ cm), similar to their concentrations in seawater. The pH was brought to 8 by adding small amounts of 0.1 N NaOH. The oil phase for the surfactant deposition was prepared by dissolving deuterated-stearic acid (C₁₈D₃₆O₂, d-SA) in n-decane (filtered 5 times through a 5 cm column of aluminum oxide powder prior to adding the d-SA), such that the concentration was 2 mM. The reason for choosing the deuterated variety was to prevent overlap of the C₁₈H₃₆O₂ Raman band with the mineral oil band, both of which show an intense CH₂ stretching mode between 2800 and 3000 cm⁻¹. Deuterating the stearic acid shifts the band to 2000–2300 cm⁻¹. The Raman spectrum of each individual component of the system is shown in Fig. S₁ of the supporting information, which highlights the excellent spectral contrast between the different probed bands used for 3D Raman imaging. Artificial sea water (ASW) was prepared to contain 485 mM of NaCl, 10.3 mM of KCl, 10.8 mM of CaCl₂, 55.5 mM of MgCl₂ and 2 mM of NaHCO₃ in deionized water (DIW) and then adjusting the pH to 8. The ionic strength of ASW is 694.7 mM.

2.2. Methods-Substrate preparation

A cleaned glass vial was filled with 40 ml of the dip coating brine and 20 ml of the 2 mM d-SA solution in decane. After equilibrating for 15 min, the vial was placed in a water bath at 60 °C. The substrate was initially immersed below the brine-oil interface and then pulled out at a velocity of 1 μm/s by clamping it to a motorized long-distance translational stage (Thorlabs). After the dip-coating, the residual n-decane and water on the substrates were blown off with a nitrogen gun. The sample was then dried in a vacuum oven at 40 °C for 3 h. The d-SA multi-layer is expected to be held together and bound to the substrate via calcium cation bridges [34]. Mineral oil was then spin-coated onto the d-SA coated mica/silica substrate. The spin coating parameters were: 30 s at 1000 rpm followed by 60 s at 5000 rpm. The oil film formed on the d-SA coated substrate, breaks up into small droplets when submerged in ambient brine.

2.3. AFM imaging

Atomic Force Microscopy topography imaging (Bruker Dimension Icon) was carried out in air to characterize the thickness of the deposited d-SA layer. The images were made at a resolution of 512 × 512 pixels.

2.4. Confocal Raman imaging

Raman measurements were carried out using a WiTec alpha 300R Raman microscope connected to a 532 nm laser. A 600 g/mm grating was used, which provided a spectral resolution of around 2.3 cm⁻¹. A CCD camera (1600 × 200 pixels, 16 μm pixel size, Andor Newton) was used for detection of the scattered photons. For high spatial as well as depth resolution, a 63x water immersion objective (Zeiss W "N-Achromplan", Numerical Aperture (NA) 0.9, Working Distance 2.4 mm) was chosen. The laser power at the sample was measured using an optical power meter (Thorlabs) and was kept at 18.4 mW under the objective for all scans. Mapping was performed by raster scanning over a 50 × 50 × 30 μm³ volume (resolution: 50 × 50 × 30 pixels) for mica and a 100 × 100 × 20 μm³ volume (resolution: 50 × 50 × 20 pixels) for silica. The integration time used was 0.1 (or 0.05) s/pixel, facilitating a 3D scan in ~2 (or 1) hour(s).

2.5. Fluid exchange and 3D Raman imaging

Initially, the mica/silica + d-SA + oil system is immersed in 15 ml of artificial sea water (ASW) in a petri-dish and allowed to equilibrate with the ambient high salinity brine for an hour. Next, a 3D Raman scan is performed at an appropriate region. The brown cube in Fig. 2a denotes the collected 4D data, where every smaller cube denotes a single pixel raw Raman spectrum. The ASW is then diluted with DI Water, by three times replacing 12 ml of the ASW with an equal volume of DIW. As a consequence, the ionic strength of the ambient brine reduces from 694.7 mM to 5.5 mM. After aging the sample in this low salinity brine for one hour to attain equilibrium, 3D Raman imaging is done at the same location.

2.6. Pre-processing 3D Raman data

Raster scanned Raman imaging is generally a slow process and a typical Raman spectrum can take several hundreds of milliseconds to several seconds per pixel, depending on the material. To improve the SNR of the acquired hyperspectral Raman dataset, ai-CRM is employed. The increase in SNR is achieved via a Principal Component Analysis (PCA) based denoising algorithm. Raman maps are made by integrating the area under the band of interest for every pixel (or voxel): from 55 to 327 cm⁻¹ for silica, 2000–2300 cm⁻¹ for d-SA, 2800–3000 cm⁻¹ for oil, 3000–3550 cm⁻¹ for water and 3560–3700 cm⁻¹ for mica.

3. Results and discussions

Clean mica/silica substrates were coated with a 50–100 nm multi-layer of deuterated stearic acid (d-SA) by dip-coating through an oil-brine interface as shown schematically in Fig. 1a. A detailed study of the hydrophobic stearic acid layers formed under these conditions has been reported elsewhere [37]. After cleaning and drying the d-SA coated substrates (Fig. 1b), mineral oil (henceforth referred to as oil) was spin-coated onto the d-SA coated substrates as shown schematically in Fig. 1c. AFM topographical characterization of the d-SA multi-layer on silica, as shown in Fig. 1d, reveals that the layer is heterogenous and a zoom-in of the visible “flat” regions in Fig. 1d (at cross-hair), depicted in Fig. 1e, suggests the presence of a monolayer of d-SA (~2.6 nm) as the underlying layer in this multi-layer deposit.

Fig. 2a shows the schematic of the fluid exchange protocol for in-situ observation of the surfactant desorption-mediated wettability alteration using ai-CRM. Initially, the mineral + d-SA + oil system is immersed in ambient Artificial Sea Water (ASW) in a petri-dish and allowed to equilibrate for one hour. ASW was chosen as the high salinity brine phase in contact with the oil layer. The oil forms a network of interconnected films as shown in the xy optical image in the inset of Fig. 2a. After this, the ambient ASW is diluted with DI Water, and within a time span of 20–40 min, the film dewets into droplets as shown in the right inset of Fig. 2a. After aging the sample in this low salinity brine for one hour to attain equilibrium of the contact angle, another 3D Raman scan is performed at the same location, to monitor the response of the system to lowered salinity of the ambient brine. Fig. 2b shows an example of a single pixel raw spectrum of the system being investigated and Fig. 2c shows the same spectrum denoised using ai-CRM. Details of the technique and its implementation for 3D Raman data can be found in Fig. S₂ of the supporting information.

Below we demonstrate the capability of ai-CRM for the simultaneous measurement of material redistributions and the corresponding contact angle changes. By applying this to a model system for Low Salinity Water Flooding EOR in sandstone reser-
**Fig. 1.** Schematic of the (a) dip-coating protocol for the deposition of d-SA on a mica/silica substrate, (b) d-SA multi-layer 50–100 nm thick after drying, (c) Spin-coating of mineral oil on the d-SA coated substrate. (d) AFM height map of the deposited d-SA layer on silica, inset: height profile across the white dashed line. (e) AFM height map of a “flat” region at the cross hair shown in (d), showing the presence of a ~2.6 nm layer of d-SA, inset: height profile across the white dashed line.

**Fig. 2.** (a) Fluid exchange protocol for studying the surfactant mediated reactive wettability alteration using ai-CRM. The optical images show the distribution of oil on the substrate in the respective ambient brine condition. Scale bar corresponds to 0.2 mm. (b) An example of a single pixel raw Raman data and (c) same data as (b) after ai-CRM denoising.
voirs, we also gain new insights into the microscopic mechanism underlying the wettability alteration. The quartz and clay fractions of sandstone reservoirs are represented by silica and mica, respectively.

3.1. Reactive wettability alteration on mica

We first consider the wettability alteration on mica. 3D Raman images of mica, oil, water and d-SA were measured for a typical oil droplet, by making xy scans at different z depths and selecting the respective Raman bands. As illustrated in the denoised spectrum in Fig. 2c, even a single pixel Raman spectrum is rich in information and shows good discernibility of the components, facilitating simultaneous imaging. Confocal volumetric scanning using Raman microscopy has the advantage of mapping the local microscopic oil droplet shape as well as the distribution of components in 3 dimensions, which is not possible with standard optical contact angle goniometry. Orthogonal sectioning parallel to the mica plane, at a depth corresponding to the d-SA-oil interface, can be used to visualize the xy component distributions. Fig. 3 shows the reflection mode xy optical and Raman maps of oil, water and d-SA. The large area optical map in Fig. 3a depicts the presence of thin oil patches in (high salinity) artificial seawater (ASW). On reducing the brine salinity (Fig. 3d), these extended oil patches retract and break up into droplets. Fig. 3b shows a representative irregularly shaped oil drop (corresponding to the dashed box in Fig. 3a) in its initial state in ambient ASW. The corresponding Raman map of d-SA shows that the entire solid surface is covered by surfactant (Fig. 3c). Yet, the layer displays substantial heterogeneity, which probably contributes to the irregular shape of the oil drop.

Fig. 3e and f depict the distribution of oil-water and d-SA in response to lowered ambient brine salinity. Over a period of 20–40 min after the fluid exchange, the oil droplet retracts and attains a new equilibrium configuration. As seen in Fig. 3f, the d-SA layer also reorganizes, conforming to the new footprint of the retracted droplet, as evident from the colocalization of the oil droplet and the d-SA distributions. The xy Raman maps clearly suggest a reactive wettability alteration, facilitated by the detachment of the d-SA layer in response to lowered ambient brine salinity. We must mention that we cannot resolve what happens dynamically between the two cases, but it is plausible that the retraction of the oil droplet starts with the release of the d-SA layer, as corroborated by the co-localization of the two distributions.

Orthogonal sectioning of the 3D volumetric Raman data perpendicular to the mica interface enables the visualization of the local contact angle. The xz cross-section Raman maps of the same system, depicted in Fig. 4, provide additional insight into the mechanism of wettability alteration. The xz map was taken at an arbitrary line passing through the center of the xy maps shown in Fig. 3. The cross-section maps clearly show the configuration of the system studied. The mica is coated with a layer of d-SA, atop of which an oil droplet sits in ambient brine. Fig. 4a and b show the distribution of the components with ASW as the ambient, whereas Fig. 4c and 4d show the distribution after the ambient salinity reduction. Two key observations can be made: (1) The droplet retracts its TPCL, thereby increasing its contact angle and (2) the d-SA layer is ‘swept-up’ from the substrate by the retracting TPCL and appears to be now dissolved in the retracted oil droplet after the salinity is reduced. This ‘sweep-up’ mechanism is further illustrated via optical microscopy in Fig. S3b of the supporting information. Previously, ai-CRM has been used to monitor the release of oil droplets from clay due to a flow of lowered salinity brine in a microfluidic channel [38], however that study had to speculate about the role of the surfactant in the wettability alteration. In this work we show, for the first time, the nexus between the reorganization of the surfactant and wettability alteration. It not only

![Fig. 3. Optical and Raman xy maps of oil (yellow), water (blue) and d-SA (red) on a mica substrate. The top row (panels a, b, c) corresponds to an ambient of ASW, while in the bottom row (panels d, e, f) the brine salinity has been reduced. The optical maps (a vs. d) show large area oil films retracting into oil droplets when the salinity is reduced. The dashed box denotes the region where Raman imaging was performed. The before-after comparisons of the Raman maps (b vs. e, c vs. f) clearly reveal that the oil droplet retracts and rearranges the initially conformally covered d-SA layer into its footprint. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
underlines the earlier given mechanistic explanation of wettability alteration via surfactant desorption, but also reveals that the presence of an oil phase provides a crucial pathway for the d-SA adsorbed on the “clay” to reorganize. Without such an oil phase, the dissolution of the d-SA layer in response to lowered salinity is rather modest (refer supporting information, Fig. S4).

### 3.2. Reactive wettability alteration on silica

Silica samples display qualitatively the same behavior as the mica substrates discussed so far. In the initial state, the oil is less widely spread across the substrates and forms drops rather than extended patches in ambient ASW, as seen in Fig. 5a and b. Fig. 5c shows that the d-SA layer is heterogeneous, but can be detected essentially everywhere on the substrate. Upon reducing the salinity, the macroscopic optical images clearly show a retraction of the oil drops, in agreement with the Raman maps of the oil distribution (Fig. 5d and e). Like in the case of mica, preferential removal of d-SA is observed in regions that are not covered by oil drops in the final state, shown in Fig. 5f. This is further corroborated by the xz cross sections shown in Fig. 6, where the coupling between i) the change in substrate wettability and ii) the removal
and dissolution of the d-SA into the oil phase by the retracting contact line are visible. This also means that our mechanistic explanation for low salinity induced wettability alteration on mica applies to silica alike. However, unlike mica, we have repeatedly observed incomplete colocalization on silica, suggesting a stronger adhesion of the surfactant molecules to silica, leading to incomplete removal of d-SA by the retracting oil droplet. The observation that the removal of the layer is more pronounced and homogeneous on mica than on silica is consistent with our earlier observations on wettability alteration as a function of brine composition [35]. Also, the different heterogeneities of the d-SA layers deposited on mica and silica may have played a role: this is shown by AFM height maps in Fig. S5.

3.3. Surfactant redistribution post wettability alteration

After the salinity of the ambient brine was lowered, the oil droplets were aged for an extra hour after the contact angle had stopped changing, see Fig. 7. While the drop shape remained constant – presumably because the contact line was pinned to surface heterogeneities – surfactant redistribution still continued. The partial decomposition of the d-SA layer at the substrate-brine interface remained more pronounced for mica than for silica surfaces. Yet, after the extended waiting time both systems displayed an accumulation of d-SA along the oil-brine interface, as shown in CRM images Fig. 7b and e as well as the spectra at the various interfaces indicated in Fig. 7c and f. These layers were absent in high salinity ambient brines (see insets of Fig. 7b and e).

Based on the relatively weak sensitivity of Raman scattering, we conclude that this layer at the O/W interface has a thickness of at least a few tens of nm. This layer is reminiscent of the interfacial precipitation of Ca-stearate between solutions of stearic acid in decane and Ca-containing aqueous brines reported in ref. [39]. This material formed a stable bulk phase leading to up to micrometer thick solid skins at O/W interfaces. Assuming a similar thermodynamic stability for the interfacial layers observed in the present experiments, it is not surprising that the formation of these layers as well as the concomitant contact angle change are irreversible: increasing the ambient salinity back to the original higher level leaves the contact angle and material distribution unaffected within our experimental resolution, see Fig. S6.

Notably, compared to silica the O/W interfacial accumulation of d-SA is more pronounced for mica, where also the d-SA removal from the substrate is more efficient. These observations are consistent with the idea that the removed d-SA from the solid-liquid interface is the source of the material accumulating at the O/W interface. However, the mechanistic path of the transfer remains unclear, the originally deposited layer might either become transferred directly from the solid substrate to the O/W interface or they might first dissolve in the oil drop and subsequently re-precipitate at the O/W interface as in ref. [39]. Fig. 7c and f, show a small d-SA signal arising from the bulk of the oil, but none from the water phase. The latter is not surprising, as the solubility of d-SA in water should at least be an order of magnitude lower as compared to oil at the same temperature [40,41].

3.4. Substrate dependent contact angle change

The xz cross sections of the Raman maps shown in Fig. 4 and Fig. 6 already demonstrated the qualitative variation of the wettability with salinity. To obtain a quantitative estimate the of contact angle, we fitted a circle through the droplet surface obtained from the Raman cross section using ImageJ (version J2, Fiji) as shown in Fig. 8a. (Obviously, this procedure yields both the contact angle in the oil phase, \( \theta_{\text{oil}} \), and its complement, the water contact angle \( \theta_{\text{water}} \approx 180 - \theta_{\text{oil}} \).) To account for both the known uncertainties in the extraction of surface profiles from the Raman data [42] and for variations in the contact angle caused by the heterogeneity of the substrate, we repeated this procedure for 6 different locations along TPCL and averaged the resulting contact angles. Notwithstanding the uncertainties of the procedure, it is obvious from the results shown in Fig. 8b that a significant reduction of the water contact angle is found for both substrates upon reducing the ambient salinity. Consistent with the qualitative description given above, the contact angle reduction for mica (~55°) is substantially more pronounced than for silica (~25°).

3.5. Wettability alteration mechanism

The experiments discussed above illustrate the unique capability of ai-CRM for gaining microscopic insights into reactive wettability alteration. Drawing cues from the observed contact angle changes and reorganization of the d-SA layer (in response to lowered ambient brine salinity), we propose a mechanism for this reactive wetting, shown schematically in Fig. 9.

Briefly, the initial spin-coated oil film attains an equilibrium in ASW, by breaking up into droplets which sit atop the d-SA multi-
layer. The relatively low contact angle of the oil droplets originates from the hydrophobic tails of d-SA, which are collectively sticking out in the same direction. This self-assembly of the d-SA molecules is facilitated by (probably divalent [43]) cation bridges between the carboxylic acid groups and the mineral substrate. The assembled hydrophobic monolayer either provides a hydrophobic surface directly, or serves as a template for the deposition of additional bilayers, which also have their hydrophobic tails sticking out (see zoom-in, Fig. 9a). On lowering the ambient brine salinity, part of the bridging cations get released into the brine, thereby triggering a partial desorption of d-SA layer. This desorption is assisted by the availability of an oil phase, in which the d-SA molecules can dissolve. We cannot claim that no d-SA layer is left behind on the substrate in the regions of droplet retraction, as the remaining layer could be too thin to be detected within the resolution of the confocal Raman microscope. The ambient brine then seeps into the hydrophylized region, altering the contact angle of the oil droplet as shown schematically in Fig. 9b. Thus, the substrate changes from primarily oil-wet to partially water-wet. Post stabilization of the contact angle, the oil acts as a reservoir and transfer medium for d-SA molecules, allowing the latter to accumulate at the oil–water interface, leading to the formation of a skin which cloaks the oil droplet. This is shown schematically in Fig. 9c.

4. Conclusions

In this work, we demonstrated the utilization of ai-CRM for characterizing reactive wettability alteration mechanisms by...
studying a specific example of the phenomenon occurring in low salinity water flooding EOR. Compared to the conventional techniques of probing the wetting of droplets on substrates [14–20], we show that the benefits of using ai-CRM are twofold: (a) it can be used to spectroscopically monitor changes in multi-component distribution and reorganization triggered by an external stimulus and (b) it can also be used to perform label-free micron-sized droplet visualization enabled by 3D Raman mapping. However, the average time taken per 3D Raman scan using ai-CRM is approximately 1 h. In our case this was insufficient to follow the 3D evolution of the droplet (after reducing ambient salinity), which takes 20–40 min. To actually follow the evolution of the drop shape, one could reduce the scanning to two-dimensional cross sections in the xz or yz directions. While this would speed up data acquisition by approximately 50 times, it would sacrifice the full 3D information, which is not desirable for non-symmetric drops in the present experiments. Specific to the model system studied, we show experimentally for the first time a nexus between reorganization of a surfactant layer and the consequent wettability alteration of the substrate due to change in ambient brine concentration. We also propose a mechanism for understanding the phenomenon in the same system. Although CRM is often considered notorious for being a slow technique, this work shows that by probing the right length and time-scales, ai-CRM can be a powerful technique to image and understand similar systems holistically.

Because of the broad applicability of Raman imaging in general, our analysis method is well-suited to mechanistically examine other wettability alterations, like the recent study on the adaptive wetting of polydimethylsiloxane [44]. A variety of smart materials are designed to be responsive to an external stimulus, and thereby change the wettability of the substrate [2]. A special class of these smart materials is that of polymer brushes, which can change configuration, depending on the pH or ionic strength [45,46]. With ai-CRM, it should be possible to characterize this configurational change by monitoring the low wavenumber (<200 cm$^{-1}$) Raman bands, which originate from skeletal deformation modes or inter-chain interactions (Refer Chapter 9 [47]). Besides that, ai-CRM can also be used for simultaneous micro-contact angle goniometry and spectroscopy in other fields of interfacial science, like two-phase wetting in (Raman transparent) porous media, wetting on composite substrates (e.g. polymer blends) and surface wettability of micron-sized particles and fibers.

CRediT authorship contribution statement

Sachin Nair: Conceptualization, Validation, Formal analysis, Investigation, Data curation, Visualization, Writing - original draft, Writing - review & editing. Jun Gao: Conceptualization, Validation, Investigation, Writing - review & editing. Cees Otto: Data curation, Writing - review & editing, Supervision. Michael H.G. Duits: Data curation, Writing - review & editing, Supervision. Frieder Mugele: Conceptualization, Data curation, Writing - review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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