Salinity-Dependent Contact Angle Alteration in Oil/Brine/Silicate Systems: the Critical Role of Divalent Cations

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ABSTRACT: The effectiveness of water flooding oil recovery depends to an important extent on the competitive wetting of oil and water on the solid rock matrix. Here, we use macroscopic contact angle goniometry in highly idealized model systems to evaluate how brine salinity affects the balance of wetting forces and to infer the microscopic origin of the resultant contact angle alteration. We focus, in particular, on two competing mechanisms debated in the literature, namely, double-layer expansion and divalent cation bridging. Our experiments involve aqueous droplets with a variable content of chloride salts of Na+, K+, Ca2+, and Mg2+, wetting surfaces of muscovite and amorphous silica, and an environment of ambient decane containing small amounts of fatty acids to represent polar oil components. By diluting the salt content in various manners, we demonstrate that the water contact angle on muscovite, not on silica, decreases by up to 25° as the divalent cation concentration is reduced from typical concentrations in seawater to zero. Decreasing the ionic strength at a constant divalent ion concentration, however, has a negligible effect on the contact angle. We discuss the consequences for the interpretation of core flooding experiments and the identification of a microscopic mechanism of low salinity water flooding, an increasingly popular, inexpensive, and environment-friendly technique for enhanced oil recovery.

INTRODUCTION

Standard water flooding oil recovery from geological reservoirs is a complex multiscale process with a rather low overall efficiency, typically leaving between half and two-thirds of the oil in the ground by the end of the economic lifetime of a reservoir.1 This poor macroscopic efficiency is caused to an important extent by the microrfluidic two-phase flow processes that arise when oil is displaced by the injected brine on the pore scale. Given the large surface-to-volume ratios on the pore scale and the low capillary numbers typically involved in oil recovery, it is clear that these two-phase flows are controlled to a large extent by the wettability of oil and water on the complex geometry of the porous rock material: the distribution of local contact angles in combination with the pore geometry provide the complex energy landscape, in which the distribution of oil and water typically evolves under quasi-static conditions driven by the externally applied pressure gradient. Numerous experiments, simulations, and theoretical models on different levels of complexity have demonstrated that the resultant final saturation of a porous medium with the displaced phase (i.e., the oil-in-oil recovery) after the invasion of the second immiscible phase (i.e., the injection water) depends very sensitively on the relative wettability of the two phases on the solid matrix.2,3 For instance, a recent study combining experiments with packed beads and numerical simulations consistently demonstrates a substantial increase in the displacement efficiency as the contact angle of the displacing phase is decreased from somewhat above to somewhat below 90°.4 Hence, wettability alteration is a very efficient process to improve the recovery of crude oil in enhanced oil recovery (EOR) processes.

It is important to point, at the outset of any discussion, to an ambiguity in terminology between physical chemists and the petroleum engineering community in this context: in physical chemistry, “wettability” describes a qualitative measure of the contact angle; “wettability alteration” is therefore equivalent to “contact angle alteration”. By contrast, petroleum engineers use the term wettability to express the retention capability of a porous medium in a two-phase flow displacement experiment such as the Amott wettability test; wettability in that sense is therefore a much more complex quantity that is affected by the properties of the aforementioned complex energy landscape and the details of the process parameters such as sample history and flow rates. Throughout this work, we will stick to the generic terminology of physical chemistry, where wettability describes the equilibrium contact angle.

Since the mid to late 1990s, empirical evidence has grown that water flooding oil recovery with brines of reduced salinity gives rise to significant increases in recovery.5−7 Various mechanisms have been proposed throughout the years to
explain the success of this low salinity water flooding (LSWF) process, including the mobilization of fines,\textsuperscript{5,9} mineral dissolution,\textsuperscript{6} emulsification at elevated pH,\textsuperscript{10,11} and wettability alteration.\textsuperscript{12} In fact, in more recent years, wettability alteration from more oil-wet toward more water-wet has become the predominant paradigm in the literature.\textsuperscript{6,7} The microscopic mechanisms causing the wettability alteration, however, are also under debate. Whereas the situation in carbonate reservoirs is particularly complex due to the strong chemical activity of the rock,\textsuperscript{13,14} the discussion for sandstone reservoirs largely focuses on two specific competing mechanisms: double-layer expansion (DLE) upon reducing the salinity,\textsuperscript{8,15,16} and multicomponent ion exchange (MIE)/complex formation.\textsuperscript{17,18} In the MIE mechanism, divalent cations play a prominent role because they are believed to promote the binding of acidic oil components to negatively charged rock surfaces. Empirical correlations of the success of LSWF with the clay content are important for these surface reactions.\textsuperscript{8}

Despite the facts that (i) recovery factors obtained in core flooding experiments are affected by much more complex factors than local contact angles and (ii) local contact angles are not measured in core flooding experiments, it has become customary to discuss the alleged contact angle variation in terms of very specific models based on the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory and its extensions involving specific chemical binding mechanisms. An early overview of the physical ingredients of these models was given by Hirasaki.\textsuperscript{19} Such models provide direct predictions for the variation in the equilibrium contact angle on flat surfaces. One key element of such models is a thin wetting film of brine with a thickness in the nanometer range, which is expected to cover most of the solid surface in a partial wetting situation. The thickness of such a wetting film is governed by a balance of repulsive short-range and/or electrostatic forces and attractive long-range dispersion forces.\textsuperscript{19} In view of the intrinsically hydrophilic character of the rock material, the existence of such a water film is very plausible. However, its existence in experiments is usually only inferred from indirect evidence such as sample history and pretreatment. Direct proof for the existence of these layers has been provided only in very few cases either using neutron reflectivity\textsuperscript{20} or imaging ellipsometry in model systems.\textsuperscript{8}

Experiments aiming to demonstrate the effect of brine composition on wettability with model surfaces, crude oils and brines of variable composition, and at variable temperatures provided mixed evidence.\textsuperscript{22–24} To a certain extent, inconsistencies in macroscopic experiments are not completely surprising given the complexity of both types of surfaces and oils used in different experimental studies. Nevertheless, such inconsistencies raise the question as to whether the basic underlying assumptions regarding the competing candidate mechanisms are justified. This question prompted a series of experiments in our laboratory in recent years to verify one by one the validity of each individual step involved in the competing MIE and DLE mechanisms. On the microscopic scale, we verified the preferential adsorption of divalent cations, as compared with monovalent cations, to mineral surfaces using atomic force microscopy and ellipsometry.\textsuperscript{21,25} On the macroscopic scale, we showed that this adsorption process of divalent cations (Ca\textsuperscript{2+}, Mg\textsuperscript{2+}) induces partial water wetting in idealized decane/brine/muscovite systems.\textsuperscript{26} This transition could be correlated with a reversal of the muscovite/water interfacial charge from negative to positive, leading to attractive electrostatic contribution in the DLVO forces governing the stability of the oil/water film/muscovite system. At the same time, monovalent cations (Na\textsuperscript{+}, K\textsuperscript{+}) always lead to a repulsive electrostatic contribution to the total disjoining pressure and hence to near-zero contact angles. A quantitative DLVO model provided a consistent description of the contact angle alteration with the brine composition-dependent variation of the interfacial charges.

We also performed measurements where small amounts of stearic acid were added to the oil phase, as a model to represent interfacially active acidic oil components.\textsuperscript{26} The combination of stearic acid and divalent cations demonstrated a massive synergistic effect, boosting the range of the observed wettability alteration from approximately 10° to more than 60°. Atomic force microscopy and ellipsometry imaging revealed that this boost in the wettability alteration was caused by the formation of a self-assembled monolayer of stearate rendering the muscovite surface substantially more hydrophobic.\textsuperscript{26,27} These experiments suggested that the divalent cations act indeed as glue, attaching acidic oil components to the mineral surface, as suggested in the MIE model of LSWF.\textsuperscript{17} The fact that the simultaneous presence of the acidic additive and the divalent cations was essential for the formation of these layers is consistent with our earlier observations demonstrating that the stability of Langmuir–Blodgett films of stearic acid under water depends strongly on the presence of divalent cations during the preparation process of these layers.\textsuperscript{27} While supporting the idea of divalent ion-mediated binding of stearate to the surface, the fact that the preparation conditions had an important effect on the ultimate stability of the layers raises questions regarding the kinetics and the equilibration of the adsorption/desorption processes in these systems.

All of these preceding studies thus consistently point to an essential role of divalent cations in increasing the water contact angles by binding the polar oil components. Yet, these studies were mostly carried out with brines containing only a single species of salt. In the present work, we extend the scope of our macroscopic wettability alteration tests by allowing for the simultaneous presence of both monovalent and divalent cations. Therefore, we allow for competition between different cations for complexation both to the surface and to the carboxyate group of the stearate. This extension is important because it allows us to vary independently the concentration of the divalent cations and the overall salinity of the brine. As a consequence, we are able to discriminate between the two proposed mechanisms of DLE and MIE by analyzing the contact angle as we vary either the total ionic strength or the concentration of the divalent cations while keeping the other factor constant. In addition, we established an in situ fluid exchange protocol to vary the salinity of a sessile brine drop while in touch with the solid substrate in ambient oil. This allows us to address important issues regarding the reversibility of the formation of hydrophobizing stearate layers upon reducing the ionic strength or the divalent ion content in the brine drop. Experiments are carried out in parallel on muscovite and silica surfaces to represent the main components of sandstone rock, with large flat muscovite surfaces representing the clay component.

**Experimental Section**

**Materials.** Anhydrous n-decane was used as the oil phase in all experiments. It was passed five times through a 5 cm long column of
aluminum oxide powder to reduce the presence of surface active impurities.\textsuperscript{27} In this oil phase, fatty acids were dissolved to a concentration of 100 \(\mu\)M. In nearly all cases, octadecanoic acid (stearic acid) was used as the fatty acid; the exception was a fluid exchange experiment where a 1:1 molar combination of 12-phenyl-dodecanoic acid and stearic acid was used. For the brine phases, we used purified water (Millipore, resistivity 18.2 M\(\Omega\) cm) in which different combinations of the following salts were dissolved: NaCl, KCl, CaCl\(_2\), 2H\(\text{H}_2\)O, and MgCl\(_2\)·6H\(\text{H}_2\)O. Additionally, small amounts of NaOH were added in case the pH needed to be increased. All chemicals used were purchased from Sigma Aldrich. For the solid substrates, we used muscovite slides (B & M Mica Co., Inc.) and silicon wafers that were coated with a 30 nm amorphous, thermally grown silicon oxide layer (Okmetic Oyj).

Two types of brines were prepared: binary salt solutions and artificial seawater (ASW) variations. Binary salt solutions were prepared from one monovalent and one divalent cation chloride salt in the following combinations: Na\textsuperscript{+} and Ca\textsuperscript{2+}; Na\textsuperscript{+} and Mg\textsuperscript{2+}; and K\textsuperscript{+} and Ca\textsuperscript{2+}. For the ASW variations, we used all four aforementioned salts at their typical concentrations in seawater\textsuperscript{29} to prepare the so-called simplified ASW (Table 1). Three series of ASW variations were investigated. First, a simple dilution (DIL) series, where all salt concentrations are reduced evenly. Second, a series at a constant ionic strength (cIS), where we reduced only the concentration of NaCl and KCl. The concentration ratios of the first ionic species, respectively). Third, a series at a constant divalent cation concentration (cDIV), where we reduced only the concentration of NaCl and KCl. The concentration ratios of Na\textsuperscript{+}:K\textsuperscript{+} and Ca\textsuperscript{2+}:Mg\textsuperscript{2+} are the same for all of these samples.

**Contact Angle Measurements.** Brine droplets with a volume of \(\approx 2\ \mu\)L were deposited on the solid substrate in oil by gently lowering the needle from which they were hanging. After achieving contact with the substrate, lifting the needle was sufficient to release the droplet. Side-view images of droplets were captured using an optical contact angle goniometer (OCA20L) (Figure 1a). The contact angles were measured over 20 measurements consisting of 2 sets of 10 measurements, where each set was performed with freshly prepared brine. Typically, the standard errors of these measurements have values between 2\(^\circ\) and 5\(^\circ\).

**Single Droplet Fluid Exchange.** Muscovite slides were first pretreated to be fully covered by a hydrophobic monolayer of fatty acids. This was achieved by first depositing a 200 \(\mu\)L ASW droplet on a slide submerged in a solution of fatty acid in n-decane. Care was taken to ensure that the droplet covered the entire slide. After a dwell time of 5 min, the brine fluid was extracted using a needle and a syringe pump operated at 50 \(\mu\)L/min. This procedure should result in the deposition of a hydrophobic layer via the receding contact line, as explained in detail in ref. 30. Briefly, after deprotonation of the fatty acid, complexation with a metal cation takes place at the oil/water interface.\textsuperscript{31} The positively charged metal–fatty acid complex gets transferred to the negatively charged solid substrate,\textsuperscript{26} somewhat similar to the Langmuir–Blodgett transfer. The coated substrate was kept in oil.

In the next step of the protocol, a brine droplet of 18.6 ± 1.3 \(\mu\)L was pipetted on the pretreated substrate. The mean and standard deviation of this droplet volume \(V\) were obtained by weighing 20 droplets on an analytical mass balance. Two glass capillaries (100 \(\mu\)m inner and 170 \(\mu\)m outer diameter; VitroCom) were inserted in the deposited droplet after they had been connected to a Legato 270 push/pull syringe pump (KD Scientific), as illustrated in Figure 1b. Connecting the inlet to a reservoir with the brine of interest allowed exchanging the contents of the droplet while maintaining a constant volume. This exchange was carried out at a rate of 10 \(\mu\)L/min.

It turned out that most droplets did not maintain a spherical cap shape when deposited on the pretreated substrate; this was visible as a left–right asymmetry in side-view images and as an irregular, noncircular, contact line in bottom views. These imperfections are ascribed to heterogeneities in the deposited layer; from previous studies of brine droplets under oil with stearic acid\textsuperscript{26} and on exposure of dried Langmuir–Blodgett layers to brine,\textsuperscript{27} it is known that inhomogeneous patterns are formed. To obtain the best representative contact angle, we measured the droplet/muscovite interfacial area using the bottom-view camera. A pixel-counting script was used to measure the area, which was averaged over nine measurements for each condition. The effective contact angle \(\alpha_{\text{eff}}\) was then calculated using the relation between area \(A\), volume \(V\), and contact angle \(\theta\) for a spherical cap

\[
V = \frac{4\sqrt{2}}{3\sqrt{3}} \sin^3 \theta (\cos^3 \theta - 3 \cos \theta + 2)
\]

Measurement of droplet contact angles with the side-view camera, before and after fluid exchange, indicated that the two types of measurements corresponded to each other, within the error margins (before: 58.9 ± 13.7\(^\circ\) for the bottom-view and 69.7 ± 14.5\(^\circ\) for the side-view; after: 27.8 ± 2.6\(^\circ\) for the bottom-view and 30.6 ± 10.7\(^\circ\) for the side-view).

**RESULTS**

**General Behavior.** After deposition on muscovite substrates, most brine droplets showed, after a short phase of rapid spreading, a significant amount of retraction. The latter process was slow enough to measure it via the contact angle. Figure 2a

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Table 1. Brine Compositions and Their Ionic Strengths Used in the Experiments with ASW

| brine name | salt concentration (mM) | NaCl | KCl | CaCl\(_2\) | MgCl\(_2\) | ionic strength (mM) |
|------------|-------------------------|-------|-----|----------|----------|---------------------|
| ASW 100%   | 485                     | 10.3  | 10.8| 55.5     | 694.2     |
| DIL 50%    | 242.5                   | 5.2   | 5.4 | 27.8     | 347.1     |
| DIL 10%    | 48.5                    | 1.0   | 1.1 | 5.6      | 69.4      |
| DIL 0%     | 0                       | 0     | 0   | 0        | 0         |
| cIS 50%    | 582.4                   | 12.4  | 5.4 | 27.8     | 694.2     |
| cIS 10%    | 660.3                   | 14.0  | 1.1 | 5.6      | 69.4      |
| cIS 0%     | 679.8                   | 14.4  | 0   | 0        | 694.2     |
| cDIV 50%   | 242.5                   | 5.2   | 10.8| 55.5     | 446.6     |
| cDIV 10%   | 48.5                    | 1.0   | 10.8| 55.5     | 248.4     |
| cDIV 0%    | 0                       | 0     | 10.8| 55.5     | 198.9     |

**Figure 1.** Schematic of the experimental setups used for contact angle measurements after droplet deposition (a) and during fluid exchange (b).

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shows the kinetics of the relaxation of the contact angle during this phase. This behavior, which has been termed autophobing,\textsuperscript{30} is believed to originate from a metal-stearate transfer from the oil/water interface onto the muscovite.\textsuperscript{26} This hydrophobic monolayer formed at the contact line forces the droplet to a higher contact angle.\textsuperscript{30} The time needed for the droplets to reach a constant contact angle ranged from 10 s to 3 min, depending on the brine composition and pH. Thereafter, the contact angle remained stable for at least 15 min. We will therefore denote it as the final contact angle ($\theta_f$).

Figure 2b illustrates the impact of the valence of the cations in the solution on the contact angle. Raising the concentration of Na$^+$ from 0 to 500 mM increases the contact angle only slightly from approximately 2$^\circ$ to 5$^\circ$. But when Ca$^{2+}$ is used instead of Na$^+$, the contact angle increases to 55$^\circ$. Even 20 mM Ca$^{2+}$ leads to a contact angle of 25$^\circ$. This underlines the relevance of the type of cation for the wetting behavior of solutions of individual species of salts.

**Binary Salt Solutions.** Building on our previous studies with individual salts,\textsuperscript{26} we performed contact angle measurements with droplets containing solutions of binary mixtures of cations on the same type of muscovite surfaces in n-decane in the presence of stearic acid. All experiments were carried out at pH 8 to ensure near-complete stearic acid deprotonation ($pK_a = 4.75$).\textsuperscript{32}

Combinations of NaCl and CaCl$_2$ solutions display an intermediate behavior between pure NaCl and pure CaCl$_2$ solutions with high [Ca$^{2+}$]:[Na$^+$] ratios promoting Ca$^{2+}$-like behavior including autophobing and vice versa (Figure 3). For [Ca$^{2+}$] of 100 mM and higher, $\theta_f$ turned out to be independent of [Na$^+$] up to 0.5 M. At 10 mM Ca$^{2+}$, however, [Na$^+$] of 0.5 M was enough to reduce $\theta_f$ down to $\approx$5$^\circ$, which is the same value as that of a pure NaCl solution (Figure 2b).
To explore the general validity of these observations, we tested different combinations of common cations (Na\(^+\), K\(^+\), Ca\(^{2+}\), and Mg\(^{2+}\)) in seawater. The contact angles of Na\(^+\)/Mg\(^{2+}\) droplets (Figure 4a) display trends very similar to those of Na\(^+\)/Ca\(^{2+}\), except that the contact angles are overall slightly higher for the same concentrations. In particular, even in the presence of 0.5 M Na\(^+\), a finite value of \(\approx 30^\circ\) is observed at 10 mM Mg\(^{2+}\). Surprisingly, even [Mg\(^{2+}\)] as low as 1 mM induces a substantial contact angle of \(\approx 20^\circ\) at high [Na\(^+\)]. Interestingly, at this [Mg\(^{2+}\)], \(\theta_f\) was found to vary in a nonmonotonic manner with increasing [Na\(^+\)].

The K\(^+\)/Ca\(^{2+}\) system (Figure 4b) showed a behavior that is very different from that of Na\(^+\)/Ca\(^{2+}\) (Figure 3b): for all measurements with [K\(^+\)] \(\geq 100\) mM, the droplets reached contact angles of \(\approx 25^\circ\), after an initial phase of spreading and subsequent autophobing. The Ca\(^{2+}\) content affected the contact angle only at the lowest K\(^+\) concentration of 10 mM.

**Modified Artificial Seawater.** Expanding on the experiments with the binary cation combinations, we also studied the effects of the concentrations of the combined mono and divalent cations, as occurring in ASW. Three types of concentration variations were explored (DIL, cIS, and cDIV; Table 1). Here, the DIL series serves as a reference, representing the simplest way to lower salinity. The cIS series keeps the ionic strength constant while the divalent cation concentration is varied. The cDIV series is complementary; here, the divalent cation concentration is kept constant while the ionic strength is varied. Together, these three series offer a way to examine the relative importance of the possible wetting mechanisms; for example, in the case of a dominant DLE, the cIS series should produce invariant contact angles while the cDIV experiments would show a variation. If cation bridging were dominant, then C2MD should produce constant contact angles while cIS would show a variation. To approach the sandstone reservoir surface chemistry, we studied both muscovite and oxidized silicon substrates at a close to neutral pH (6.5).

On muscovite, the DIL contact angles showed a decrease from 25\(^\circ\) to 2\(^\circ\) (Figure 5a). The cIS contact angles superimpose very well on those of DIL, down to a dilution of 10% with respect to ASW. The only significant difference between cIS and DIL was found at 0%. Here, the droplets of cIS 0% had an 8\(^\circ\) contact angle, whereas that of the pure water droplets of DIL 0% was 2\(^\circ\). The cDIV contact angles remained constant at 25\(^\circ\), even though the ionic strength was strongly reduced from 694.2 to 198.9 mM.

On silica, at pH 6.5, no significant wettability alteration was observed in any series, and measurements suffered from a large uncertainty (Figure 5b, inset). Therefore, measurements on silica were also performed at pH 8, where silica had a stronger negative surface charge (Figure 5b).\(^{33}\) Here, a small salinity-induced wettability effect was observed. All three series followed a similar decrease from 19\(^\circ\) to 10–15\(^\circ\), and all contact angles were reached by spreading rather than autophobing.

**Single Droplet Fluid Exchange.** From the trends in \(\theta_f\) reported in the previous sections, it could not be concluded whether these contact angles are truly equilibrium values. If they are, it should be possible to reverse the autophobing process by changing the salt composition of a high \(\theta_f\) droplet to that of a low \(\theta_f\) droplet. We tested this hypothesis using the single droplet fluid exchange setup on ASW droplets of pH 8, which were deposited on a muscovite substrate that was coated with a fatty acid (see Experimental Section). Our aim was to qualitatively reproduce the trends of the DIL, cIS, and cDIV series shown in Figure 5a. In analogy to the LSWF process, we exchanged the droplet content with water, cIS 0% or cDIV 0%.

From the measured brine/muscovite interfacial area (Figure 6a), we calculated the effective contact angle (Figure 6b) using eq 1. For all explored conditions, the observed effective contact angle trends broadly corresponded with the \(\theta_f\) trends of their respective series. ASW droplets that were flushed with water spread over the course of 10 min from an effective contact angle of 60\(^\circ\) to 35\(^\circ\). Droplets flushed with cIS 0% initially spread following a similar trend. But after 10 min, the droplets continued to spread, eventually reaching effective contact angles of around 20\(^\circ\). Droplets flushed with a cDIV solution showed no significant spreading.

In the measurements described above, stearate is the only polar organic compound, whereas in crude oil, many surface active compounds coexist. It is known that stearate monolayers at an air/water interface can be destabilized by additional surface active compounds.\(^{34}\) To ensure that our observations do not rely on a uniform monolayer, we also performed measurements where we used a 1:1 molar combination of 12-phenyl-dodecanoic acid and stearic acid. Both have a similar molecular mass (284 and 276 g/mole, respectively) but differ sterically. Flushing ASW droplets with water on this mixed hydrophobic layer caused them to reach a lower final contact angle (20\(^\circ\)), approximately twice as fast as with stearic acid only.

**DISCUSSION**

**Ion Adsorption-Controlled Wetting.** On a macroscopic scale, the wettability is governed by the balance of interfacial tensions at the three-phase contact line. The present oil/water/
Figure 6. Fluid exchange experiments on pH 8 ASW droplets in n-decane + 100 \( \mu \text{M} \) stearic acid on muscovite pretreated with a stearate layer: (a) experimental setup, (b) stills from side- and bottom-view videos taken during the initial stable conformation (left) and the final video frame after flushing with water (right), and (c) effective contact angles of the spreading droplets. Blue line indicates ASW flushed with water, orange dotted line indicates that with a purely monovalent cation solution at a constant ionic strength, and olive dashed line indicates that with water in an oil phase containing equal parts of stearic acid and 12-phenyl-dodecanoic acid. The shaded areas represent the standard deviation of the datasets.

mineral systems are well-known to fall in the regime of pseudopartial wetting, in which the macroscopic drop is accompanied by a microscopic wetting film covering in equilibrium the entire solid surface (Figure 7). In this case, the presence of surface active stearates in the present experiments increases the complexity even more. In addition to the adsorption of the ions on the solid surface, complexion reactions between the ions and the carboxylate groups of the fatty acid molecules need to be included. More importantly, however, a prediction of the equilibrium contact angle and the equilibrium thickness of the aqueous film would require an explicit model function \( \phi(h) \) for the contribution of the presumed divalent cation bridge between the solid surface and the adjacent fatty acid molecules at the oil/water interface. To understand our knowledge, no analytical expression for this function has ever been proposed. Given the complexity of the problem, a numerical statistical approach based on molecular dynamics simulations, such as the potentials of mean force used, for example, by Horinek et al., in the context of ion adsorption on solid surfaces, may be the only realistic approach to address this problem.

In the present work, we restrain ourselves to a qualitative interpretation of our findings in the context of the extensive literature on the separate interfaces, namely, fatty acid-laden hydrophobic—water interfaces and solid—electrolyte interfaces. In both cases, the interaction of the cations studied here with the relevant surface groups, the carboxylate group, and the surfaces of muscovite and silica have been investigated in great detail. At the near-neutral pH of the present experiments, it is primarily the interaction with the ions, which triggers the deprotonation of the acid group. It is well-known from the extensive literature on Langmuir monolayers of fatty acids, in particular stearic acid, that divalent Mg\(^{2+}\) and Ca\(^{2+}\) interact more strongly with the carboxylic acid group of the stearic acid than Na\(^+\) and K\(^+\). Judging from our binary salt solution experiments, the presence of surface active stearates in the present experiments increases the complexity even more. In addition to the adsorption of the ions on the solid surface, complexion reactions between the ions and the carboxylate groups of the fatty acid molecules need to be included. More importantly, however, a prediction of the equilibrium contact angle and the equilibrium thickness of the aqueous film would require an explicit model function \( \phi(h) \) for the contribution of the presumed divalent cation bridge between the solid surface and the adjacent fatty acid molecules at the oil/water interface. To understand our knowledge, no analytical expression for this function has ever been proposed. Given the complexity of the problem, a numerical statistical approach based on molecular dynamics simulations, such as the potentials of mean force used, for example, by Horinek et al., in the context of ion adsorption on solid surfaces, may be the only realistic approach to address this problem.

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To explain this observation, we should also consider the interactions between the cations and the charged muscovite surfaces of muscovite and silica have been investigated in great detail. At the near-neutral pH of the present experiments, it is primarily the interaction with the ions, which triggers the deprotonation of the acid group. It is well-known from the extensive literature on Langmuir monolayers of fatty acids, in particular stearic acid, that divalent Mg\(^{2+}\) and Ca\(^{2+}\) interact more strongly with the carboxylic acid group of the stearic acid than Na\(^+\) and K\(^+\). But valence is not the only property affecting the binding affinity. Because of the differences in the hydration of cations with identical valence, binding affinities with muscovite and acid groups also vary within the metal groups. The general consensus in the literature is that the binding affinities for these ions with the acid groups follow Ca\(^{2+}\) > Mg\(^{2+}\) > Na\(^+\) > K\(^+\). Judging from our binary salt solution contact angle measurements, shown in Figures 3b and 4, this binding affinity alone cannot explain the wettability trends, particularly in Figure 4b where at equal concentrations, K\(^+\) suppresses Ca\(^{2+}\) in wettability effects.

To explain this observation, we should also consider the interactions between the cations and the charged muscovite surfaces of muscovite and silica have been investigated in great detail. At the near-neutral pH of the present experiments, it is primarily the interaction with the ions, which triggers the deprotonation of the acid group. It is well-known from the extensive literature on Langmuir monolayers of fatty acids, in particular stearic acid, that divalent Mg\(^{2+}\) and Ca\(^{2+}\) interact more strongly with the carboxylic acid group of the stearic acid than Na\(^+\) and K\(^+\). But valence is not the only property affecting the binding affinity. Because of the differences in the hydration of cations with identical valence, binding affinities with muscovite and acid groups also vary within the metal groups. The general consensus in the literature is that the binding affinities for these ions with the acid groups follow Ca\(^{2+}\) > Mg\(^{2+}\) > Na\(^+\) > K\(^+\). Judging from our binary salt solution contact angle measurements, shown in Figures 3b and 4, this binding affinity alone cannot explain the wettability trends, particularly in Figure 4b where at equal concentrations, K\(^+\) suppresses Ca\(^{2+}\) in wettability effects.

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surface. Because of the size and hydration state of K⁺ being ideal to be adsorbed on the muscovite lattice, it is adsorbed more strongly than Na⁺. This could explain why K⁺ is more efficient in suppressing the adsorption of stearic acid on mica as compared with Na⁺ at equal concentrations. However, in our measurements, the autoprophobing effects of Ca²⁺ and Mg²⁺ are not suppressed by Na⁺ at equal concentrations. In a similar mechanism, K⁺ is also known to be more efficient than Na⁺ in inhibiting the adsorption of proteins on muscovite mica. Overall, the binding affinity of cations in our thin-film system is likely to be a collective effect related to the cation valence, the charges of the interacting surfaces, and the hydration of surfaces and ions.

**Relevance for EOR.** As already pointed out, the retention of oil in a porous rock in a core flooding experiment, let alone in an actual oil reservoir, is governed by many more complex factors than the simple variation of the contact angle studied here. These include the complex pore geometry, elevated temperatures and pressures, and the chemical composition of rock, oil, and brine. The present experiments are therefore obviously not suitable to derive quantitative predictions regarding enhanced recovery factors. Nevertheless, the experiments clearly demonstrate a few aspects that should enter into any quantitative description of a low salinity EOR process. First of all, our experiments clearly demonstrate that the salinity of the brine can have a strong influence on the wettability of oil/water/mineral systems in the presence of acidic oil components and that contact angle variations can be as large as 60° upon removal of the divalent cations. This is an enormous effect. If inserted into reservoir simulations or other theoretical models of porous media two-phase flows, such variations have an enormous impact on the predicted recovery, in fact exceeding the observed recovery enhancement by far. In oil reservoirs, the actual contact angle variations are probably very different and most likely much smaller. The abundance of polar components in crude oils will probably reduce the effect of the contact angle variations compared with the idealized situation of a single fatty acid component, as reported by various authors. On the other hand, the increased temperatures in the reservoirs, which tend to promote the adsorption of polar organics, might increase the effect on water wettability again. In any case, according to reservoir simulations, a reduction in the water contact angles of a few degrees is still consistent with the recovery enhancements of several percent, as seen in many core flood experiments.

The difference in the low salinity response between the muscovite basal plane and the amorphous silica surfaces, shown in Figure 5, is rather striking. Although one might have speculated that the adsorption of divalent cations could be even stronger on the amorphous silica surface because of the presence of ionizable silanol groups, the opposite is the case, and the formation of salinity-responsive metal stearate layers is more favorable on the crystalline muscovite surface. Notwithstanding differences between the basal plane of muscovite and other clays typically encountered in oil reservoirs, the strong response on the muscovite surface is nevertheless consistent with the rather widely reported correlation between the clay content and a pronounced low salinity response in core flooding.

Finally, we would like to address the contribution of our results to the ongoing discussion about the relative importance of the electric DLE versus divalent cation bridging in LWSF. Under the conditions of the present simple model system, the results are crystal clear. Reducing the divalent ion content improves the water wettability, whereas reducing the ionic strength at a constant divalent ion content does not. In the literature, the effect of electric double-layer forces is typically discussed in the context of the classical DLVO theory using expressions for the electric part of the disjoining pressure that are obtained from Poisson–Boltzmann theory, sometimes even in the linear Debye–Hückel limit. Although appropriate up to moderate concentrations of monovalent ions and at low concentrations for divalent ones, it is clear that these models fail at concentrations of ASW or higher because they frequently occur in connate brines. For the ionic strengths of the solutions used in this study (see Table 1) and for those in low salinity oil recovery tests, the Debye screening length of electrostatic interactions is typically less than 1 nm; for the undiluted ASW, it even approaches the diameter of a water molecule. Under these conditions, the classical separation of DLVO forces into van der Waals forces and electrostatic forces no longer holds. Short-range chemical forces including hydration effects of both surfaces and the individual ions are of crucial importance in that range, and the thin water film no longer behaves like a continuous bulk water layer. Although the thickness of the Debye layer, according to its formal definition

\[
\lambda_D = \sqrt{\frac{e^2 kT}{2\pi e^2 \lambda B}}
\]

does indeed increase by a factor of 3 upon reducing the ionic strength by a factor of 10 as in many low salinity EOR experiments, it remains in a range where the dominant forces are governed by short-range interactions that are not captured by DLVO theory. Attributing the success of LWSF to the electric DLE is therefore in our view misleading from a conceptual perspective. By contrast, our present experiments directly demonstrate, without need to invoke any model, that the presence or absence of divalent cations has a pronounced effect on water wettability, presumably mediated by a surface bridging and complexation mechanism.

**CONCLUSIONS**

The main aim of this work was to contribute to the ongoing debate about the microscopic mechanism of LWSF for EOR in sandstone reservoirs, focusing in particular on the competing mechanisms of ion exchange versus DLE. Starting from the assumption that contact angle alteration is the macroscopic manifestation of the relevant microscopic processes controlling the efficiency of LWSF, we analyzed the effect of brine composition on the contact angle of a multicomponent brine droplet. To avoid the poorly understood influences of crude oil components, we performed these experiments in ambient decane with fatty acid on muscovite and oxidized silicon wafers. Although some specific cation effects, beyond valence, were observed, the overall effect of diluting and supplementing cation mixtures, resembling those in seawater, turned out to be remarkably simple. Our experimental results in Figure 5 clearly show that for muscovite substrates, reducing the ionic strength while keeping the divalent cation concentration constant has little effect on the wettability. On the contrary, reducing the divalent cation concentration while keeping the ionic strength constant decreases the contact angle of the droplets by tens of degrees. Straightforward dilution of artificial seawater leads essentially to the same behavior as reducing only the divalent cation concentration. By contrast, for silicon oxide surfaces, little effect of dilution on water wettability is only seen. The difference between the two substrate materials is consistent with core flooding experiments that suggest a correlation
between the efficiency of LSWF and the clay content. The in situ fluid exchange measurements reported in Figure 6 demonstrate that these conclusions hold not only for brine droplets of variable composition deposited onto a clean solid surface but also if the composition of a sessile droplet on an already hydrophobized substrate is gradually changed from high salinity to low salinity or low divalent cation condition, in the spirit of EOR by LSWF.

Clearly, these results refer to contact angle measurements in a highly simplified system. As discussed, one should not expect that the presented results translate one-to-one to recovery in an actual oil reservoir, given the different thermodynamic conditions of elevated temperature and pressure, and in particular, the much more complex composition of oils and brines. Nevertheless, regarding the mechanistic details of binding of acidic oil components to mineral surfaces, the present experiments do show that the expansion of the electric double-layer is primarily a collateral effect but not the cause of the wettabili ty (i.e., contact angle) alteration. The latter seems to be driven essentially by the removal of divalent cations. As a general trend, our experiments suggest that the hydration effects of both ions and surfaces play a much more important role than sometimes portrayed in the engineering literature that very often relies purely on electrostatic interactions.

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■ NOMENCLATURE

cIS, constant ionic strength; cDIV, constant divalent cation concentration; DIL, dilution; DLE, double layer expansion; EOR, enhanced oil recovery; LSWF, low salinity water flooding; MIE, multicomponent ion exchange; θp, final contact angle; θeff, effective contact angle; γfp, interfacial tension between phases \( i \) and \( j \)

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