

# Non-monotonicity of the Contact Angle from NaCl and MgCl<sub>2</sub> Concentrations in Two Petroleum Fluids on Atomistically Smooth Surfaces

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**ABSTRACT:** Wetting and alteration of wetting are among the most important material properties of fluid–fluid–substrate systems in biological and industrial systems. An important industrial application of wetting and wetting alteration is related to displacement of crude oil by water injection in porous media. Water injection in oil reservoirs has been used since the early periods of oil production. Recently, it has been discovered that the salt concentration in the injected water may have a significant effect on the oil recovery. The process is under active research for the need of an improved understanding. In this work, we investigate the governing elements of surface wettability with two different crude oils on two atomistically smooth surfaces (mica and quartz) and one smooth surface (calcite) as a function of the salt concentration (0–3 M) and type (mono- versus divalent). We investigate the change of wettability from NaCl and MgCl<sub>2</sub> salts over a wide concentration for the first time. The measurements are based on long enough aging times and droplet sizes that give equilibrium and size-independent contact angles. Our measurements show a non-monotonic behavior, in that, as NaCl concentration increases, there is a decrease (increase of water-wetting) and then an increase (decrease of water-wetting) of the contact angle in all of the systems that we have studied. MgCl<sub>2</sub> salt shows two trends with an increasing concentration. For mica and quartz, there is first a decrease of the contact angle and then an increase followed by a second sharp decrease at high MgCl<sub>2</sub> concentrations. For calcite substrate, we observe an increase of the contact angle reaching a maximum and then a decrease with an increasing salt concentration. These observations have profound implications on the effect of salts on wettability alteration. The measurements have set the stage for atomistic simulations for a molecular understanding of the salt effect in complex fluids.

## 1. INTRODUCTION

Wetting relates to adsorption of two different fluid molecules on a solid substrate. It is often expressed as the macroscopic contact angle. Wetting and alteration of wetting are among the most important material properties of fluid–fluid–substrate systems in biological and industrial systems. The concentration and type of salts may have profound effects on the wetting state. Waterflooding, injection of water into oil reservoirs, has been employed in improved oil recovery for many decades. As early as the 1960s, researchers started to pay attention to the composition of the injected brine and its effect on waterflood oil recovery.<sup>1</sup> Bernard studied the effect of water salinity on oil recovery in coreflooding.<sup>1</sup> He concluded that fresh water recovers more oil from clay-rich rocks but the high recovery is only achieved with a large pressure gradient. Pressure gradients presented by Bernard were in fact very large, on the order of hundreds of psi/ft; his results were not taken seriously for field applications. It has been recognized that the pressure gradient has a large effect on recovery in mixed-wet rocks, and there is no such effect in strongly water-wet rocks.<sup>2</sup> Jadhunandan and Morrow revisited the effect of brine composition on rock wettability and waterflood oil recovery and concluded that brine composition can affect core wettability.<sup>3</sup> These effects were not as significant as other parameters affecting wettability, such as the initial water saturation and aging temperature, and were not fully investigated. Tang and Morrow re-introduced the idea of low-salinity waterflooding to improve oil recovery and showed that decreasing brine salinity could increase oil

recovery from outcrop cores saturated with dead oil.<sup>4</sup> Their work had a few practical limitations: (1) injected brine and the aging brine were the same (in reservoir conditions, one can only control the injected brine), and (2) a single core was used over and over by resaturating it, the effects of which on core wettability and initial fluid distributions are unclear. Nevertheless, their work sparked a significant interest among researchers to investigate the effect of brine chemistry on waterflood oil recovery and re-introduced low-salinity waterflooding as a potential enhanced oil recovery/increased oil recovery (EOR/IOR) technique. Subsequently, many authors have investigated various rock–fluid systems, on a wide range of pressure and temperature conditions (including high-temperature and high-pressure corefloods), single- and multiple-well field trials,<sup>5–9</sup> and a wide range of mineralogies, including clastics and carbonates.<sup>9,10</sup> Because of its significance, experimental investigation of the effect of the salt concentration has accelerated in the last couple of years.

Some authors show success in low-salinity EOR in field studies,<sup>11–13</sup> and some report no increase in oil recovery.<sup>14,15</sup> The understanding of the underlying mechanisms for low-salinity water injection is the key.<sup>4,16–18</sup> Myint and Firoozabadi have recently provided a review on the proposed mechanisms for improved oil recovery from low-salinity waterflooding.<sup>19</sup>

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The review underlines that most authors single out the wettability alteration as the leading mechanism for low-salinity waterflooding.<sup>19</sup>

Nasralla et al. have employed a contact angle goniometer and  $\zeta$  potential analyzer to examine the wettability alteration of crude oil by low-salinity water.<sup>20</sup> They suggest the wettability alteration to be the primary mechanism of increased oil recovery with low-salinity waterflooding. They have performed contact angle measurements on the mica substrate (muscovite and biotite) after 1 h of aging time and used Berea sandstone cores for waterflooding. They have studied saline water from 0 to 174 g of total dissolved solids (TDS)/L and reported contact angles to decrease in low-salinity water. A decrease in the contact angle (by ca. 15° for muscovite and ca. 40° for biotite surfaces) signifies the surface to become more water-wet at a low salt concentration. They performed  $\zeta$  potential measurements to investigate the effect of water salinity on the electrokinetic charge of rock/brine and oil/brine interfaces. The data showed high-salinity water to have ca. zero charge at the rock/brine and oil/brine interfaces, whereas low-salinity water made the colloids to be highly negative at both interfaces, and the negative charge renders the surface to be more water-wet. On the basis of the measurements, they concluded that improved oil recovery is only due to wettability change. These authors have not considered substrates other than mica and have not assessed the variation in brine composition as one of the key players of wettability alteration.

Yousef et al. were among the first to report on the EOR from low-salinity brine in carbonates.<sup>21</sup> They employed coreflooding and contact angle measurements in carbonate surfaces and reported improved oil recovery by varying brine composition from 100 times diluted seawater (570 ppm) to 213 000 ppm connate water. They showed the highest oil recovery in twice-diluted seawater with ca. 9–10% improved oil recovery. At the highest salt concentration (213 000 ppm), the contact angle on a carbonate rock sample is measured as 90° and it monotonically decreases to ca. 60° at 100 times diluted seawater, rendering the surface more water-wet. They measured the contact angle after 2 days without providing the motivation for aging time. Aging may have a significant effect on wettability, as we will discuss later.

Schultz et al. investigated the surface energy forces and wettability of water on muscovite mica submerged in *n*-alkanes.<sup>22</sup> They present contact angle measurements during the first 30 min of the experiments and conclude that aging may not affect the results in *n*-alkane solutions. Mugele et al. have recently published results on the wettability of water in decane on solid surfaces with 2  $\mu$ L droplets for contact angle measurements.<sup>23</sup> In simple systems, such as *n*-alkenes, the size may not have an effect. Aging may also have a substantial effect in crude oil systems, as we will discuss in this work.

Lashkarbolooki et al. have studied the effect of salinity, asphaltenes, and resins on wettability of an acidic crude oil in carbonate rocks.<sup>24</sup> They have measured interfacial tension and contact angle of the oil–brine–substrate interface at various NaCl, MgCl<sub>2</sub>, and CaCl<sub>2</sub> concentrations (0–45 000 ppm) with 1 and 24 h of aging time; they did not observe a significant change with time and only reported the final reading. They report no change in the contact angle for NaCl and a slight change for divalent salts (by ca. 6° decrease for CaCl<sub>2</sub> and ca. 15° decrease for MgCl<sub>2</sub>), making the surfaces more water-wet when the salt concentration is decreased. Their conclusion is not in line with the work of other authors; they report no

change in the contact angle with a change in the NaCl concentration, while all other studies cited above show change. The acidity of the crude oil or the surface properties of the carbonate rocks may have contributed to their results.

Mahani et al. have investigated the effect of low salinity on wettability alteration in carbonates.<sup>25</sup> They have reported  $\zeta$  potential measurements and contact angle analysis on two different carbonate rocks, limestone and dolomite, from 1800 to 180 000 mg of TDS/L brine concentration. They report up to 40° reduction in the contact angle (more water-wet) when the salt concentration is decreased. They have investigated only carbonate rocks and have not assessed the effect of different salt types.

Alameri et al. have investigated the mechanism of wettability change with low salt by performing contact angle analysis on crude-aged carbonate discs.<sup>26</sup> They have reported ca. 20° reduction in the contact angle when salinity decreased from 50 000 to 1000 ppm. They have used <4  $\mu$ L droplets for all of their contact angle measurements. The size of the droplet may affect the contact angle, as we will discuss later.

A systematic correlation between wettability alteration and brine composition/ionic strength from both experimental and molecular simulations is still lacking, despite much effort and progress. There are a number of recent studies on adsorption of different salt ions on surfaces, such as mica and calcite, by frequency and amplitude modulation atomic force microscopy (AFM) and molecular dynamics (MD) simulations.<sup>27–29</sup> Both MD simulations and AFM measurements show that, on some substrates, there is a layer of ordered ion structures at the solid–liquid interface. There are neither MD simulations on the effect of salts on the contact angle nor systematic measurements on the variation of the contact angle with the salt concentration. A logical step would be to undertake an investigation on the effect of the salt concentration in some simple oils, such as *n*-decane, and an aqueous phase with different salts. We have performed measurements of the contact angle in the *n*-decane–NaCl brine–mica system. The fluid–fluid interface should be part of the investigation. The fluid–fluid interface may exhibit important molecular structure features that may require more complex fluids than *n*-decane. The decane–water interface does not show interface viscoelasticity. The addition of surfactants to the oil may not only change the contact angle but also affect the fluid–fluid molecular structure, leading to important viscoelasticity behavior. Because of important effects from functional molecules in petroleum fluids and important implications from fluid–fluid interface elasticity,<sup>30</sup> this study centers on contact angle measurements of two crude oils that contain natural surfactants

Understanding the interplay of various rock/fluid parameters, such as mineralogy, oil composition, salt concentration, salt valence, and brine composition on wettability is the main objective of our work. In this paper, we investigate wettability changes in a systematic approach for the first time.

## 2. EXPERIMENTAL SECTION

**2.1. Material Used.** Crude oils designated as oils 1 and 2 are from two different reservoirs operated by Chevron. Oil 1 is from a sandstone reservoir, and oil 2 is from a carbonate reservoir. Sodium chloride (NaCl) and magnesium chloride (MgCl<sub>2</sub>) brine solutions (Sigma-Aldrich) were employed to assess the effect of mono- and divalent ions on wettability.

**2.2. Substrates.** Three substrates employed in this study are muscovite mica (V1 highest grade, TedPella), quartz (TedPella), and calcite (from the Chevron Corporation). Quartz is the most abundant component of sandstones, with ca. 70 wt %.<sup>31</sup> Mica represents clays in sandstone reservoirs, which could be up to 20 wt % of the rock.<sup>31</sup> Calcite is used in this study because it is the primary component of carbonates. The size of the substrates for quartz and mica are  $50.8 \times 25.4 \times 1$  mm and  $25 \times 75 \times 0.15$  mm, respectively. Calcite substrates are obtained from the Chevron Corporation in various sizes. To clean mica and quartz substrates, we have developed a protocol. Hellmanex (Sigma-Aldrich), an alkaline solution for surface cleaning, is employed. We have modified the existing smooth surface cleaning protocols, and the best method is assessed as follows:<sup>32</sup> 2 min of toluene power wash + 2 min of 2% Hellmanex power wash + 15 min of suspension in 2% Hellmanex solution + 2 min of deionized (DI) water power wash + 5 min of DI water suspension for 3 consecutive steps. Power wash indicates the washing of substrates with a fluid force applied by a squeeze bottle. We have varied the time and order for each step and found this protocol to more closely match with the untreated substrates. To clean calcite substrates, we have polished the surfaces with the silicon carbide film disks in the following sizes for 2 min each: 30, 15, 5, and 1  $\mu\text{m}$ . The polishing procedure makes the calcite surface very smooth. Our cleaning (mica and quartz) and polishing (calcite) methods lead to reproducible contact angle measurements.

**2.3. Characterization.** A summary of the relevant properties of the two petroleum fluids used in this work is provided in Table 1. The

**Table 1. Characterization of Crude Oils 1 and 2**

	oil 1	oil 2
density (g/mL)	0.926	0.873
API gravity (deg)	21.4	30.6
asphaltene content (wt %)	3.3	2.1
resin content (wt %)	36.8	15.9
TAN (mg of KOH/g of oil)	0.21	0.18
TBN (mg of equiv KOH/g of oil)	5.60	1.14
viscosity at 25 °C (Pa s)	0.449	0.016
viscosity at 37.8 °C (Pa s)	0.233	0.009
viscosity at 60 °C (Pa s)	0.083	0.005

density ( $\rho$ ) is measured with a densitometer from Anton Paar (DMA 5000). The asphaltene content is measured by mixing 1 g of oil with 40 mL of *n*-heptane. Then, the solution is sonicated and filtered through 0.2  $\mu\text{m}$  pore size cellulose nitrate membrane filters (Whatman). The resin content is obtained by the ASTM standard method D2007. The total acid number (TAN) and total base number (TBN) are measured using the ASTM standards D664 and D2896, respectively. Viscosity measurements are conducted using a stress-controlled rheometer with parallel and 2° cone–plate geometry (Anton Paar, MCR 302).

We use a home-built goniometer setup to perform contact angle measurements via the pendant drop technique. A custom-built stainless-steel holder has been used to suspend the substrate in a beaker. Brine solution was poured into the beaker, which contains the substrate. The substrate was held in a horizontal position to ensure reliable and steady contact angle measurements and aged for 1 h before placing the droplets. The 1 h aging is adequate for the establishment of equilibrium. The 100  $\mu\text{L}$  droplets were placed onto the substrate using a bent 1000  $\mu\text{L}$  glass syringe (Hamilton model 1001, threaded plunger syringe). The oil is injected from the tip of the needle, and the droplet rises to the bottom of the substrate surface as a result of the density difference between brine and oil.

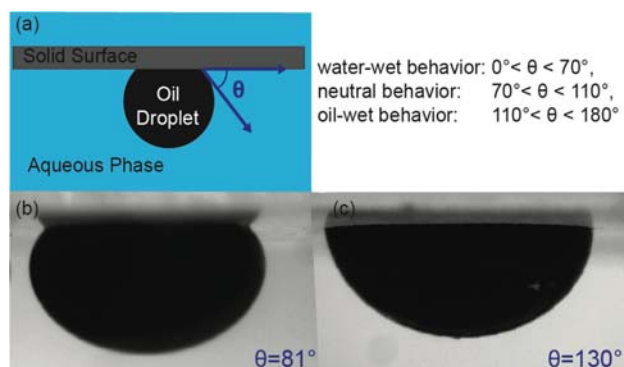
Our contact angle measurements were recorded at various time intervals within the first 72 h. For every concentration of brine on a given surface, five droplets were analyzed and standard deviations are reported. The lines connecting the data points in Figures 2–6 are not fitted; they are placed to aid with visualization of the trends. Images were captured by a 12X ThorLabs camera. Pictures were then analyzed

with an ImageJ program called “DropSnake” designed to measure the contact angle.<sup>53</sup>

### 3. RESULTS AND DISCUSSION

In Table 1, we present a detailed characterization of the two petroleum fluids employed in this study, oils 1 and 2. Oil 1 is from a sandstone reservoir and has a higher viscosity and density than oil 2, with 0.449 Pa s and 0.926 g/mL (at 25 °C), respectively. Oil 2 is light with a density of 0.873 g/mL and viscosity of 0.016 Pa s (at 25 °C). Both petroleum fluids have a relatively low asphaltene content (3.3 and 2.1 wt % for oils 1 and 2, respectively). TAN and TBN measurements reveal that both petroleum fluids are more basic, with oil 1 being more basic than oil 2.

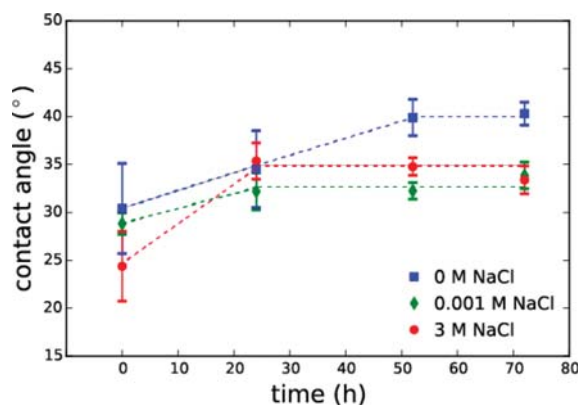
Figure 1 shows two representative oil droplets for which we measure the contact angle and an illustration of how the



**Figure 1.** (a) Contact angle illustration is shown with wettability regimes. Sample images of oil 2 droplets on the calcite substrate in (b) 0 M NaCl and (c) 1 M NaCl, with  $t = 72$  h.

contact angle is determined in the wettability regimes.<sup>34</sup> Figure 1a presents how the contact angle ( $\theta$ ) is measured. It is the angle between solid–liquid and liquid–liquid interfaces. The wettability regime is adopted from dos Santos et al.<sup>34</sup> It considers the contact angle between 0° and 70° as water-wet, from 70° to 110° as neutral, and from 110° to 180° as oil-wet. In Figure 1b, we present the image of oil 2 droplet on calcite in 0 M NaCl at 72 h after the droplet has been placed. The angle for this substrate is 81°, which corresponds to a neutral regime. Figure 1c shows the image of oil 2 droplet on the calcite substrate in 1 M NaCl at 72 h with a contact angle of 130°, which falls in the oil-wet regime. As data suggests, salinity has a strong effect on oil wettability.

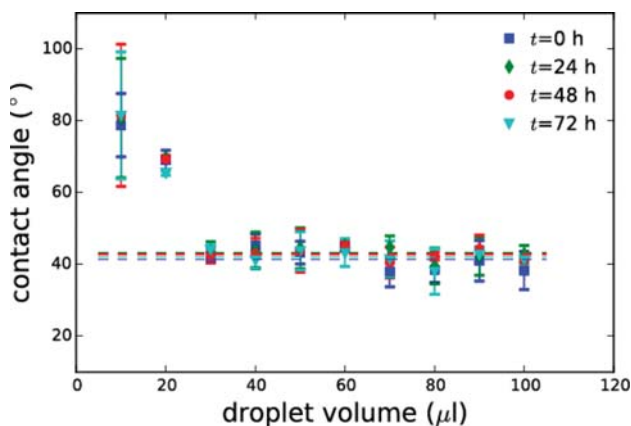
A complete set of contact angle data is presented in Figures 2–6. To determine the effect of aging time, we have performed contact angle measurements of oil 1 on the mica substrate in DI water, 0.001 M NaCl, and 3 M NaCl to 72 h (Figure 2). The obvious finding to emerge from Figure 2 is that aging increases the contact angle and reduces the standard deviation. Contact angle measurements versus time show that, within the first 24 to 52 h, there may be a substantial change in the measurements and then the droplets reach equilibrium and show a plateau. The results indicate that the standard deviation of the contact angle decreases with time, from ca. 5° to 1°. These observations do not suggest that all droplets reach equilibrium after 72 h; however, for feasibility of lab-scale studies, we have determined the adequate time for aging to be 72 h. Some previous studies in petroleum fluids either do not specify the aging employed in the measurements or do not provide the motivation of given



**Figure 2.** Contact angle measurements of oil 1 on the mica substrate in 0, 0.001, and 3 M NaCl versus time with 100  $\mu\text{L}$  droplets. The average contact angle between the five droplets is used as the data point, and standard deviations are reported. The lines connecting the data points are not fitted; they are placed to aid with visualization of the trends.

times.<sup>20,21</sup> A detailed study to report the importance of aging time on the contact angle is provided by Freer et al.<sup>35</sup> They have used brine solution premixed with oil at a 6:1 ratio as the medium and placed two different oil droplets on mica surfaces that are submerged in the medium. They have measured receding and advancing contact angles over a period of 100 h. They report an advancing angle to change drastically with time, by ca. 130°, and a receding angle to change less, by ca. 20°, during the first few hours of the experiment. In that work, the mica is also pretreated with a petroleum fluid, which is different from our work.

In Figure 3, we show the effect of the droplet size on wettability. Droplets of various sizes, from 10 to 100  $\mu\text{L}$ , are



**Figure 3.** Contact angle measurements of oil 1 on mica versus droplet volume in DI water at various times.

placed on a mica substrate in DI water, and contact angle measurements are recorded at various times, from 0 to 72 h. This figure shows the regions where the contact angle measurements are independent of the droplet size at the solid–liquid–liquid interface. The dashed lines in this figure show the average contact angle measured, with all droplet sizes greater than 20  $\mu\text{L}$  at each reporting time.

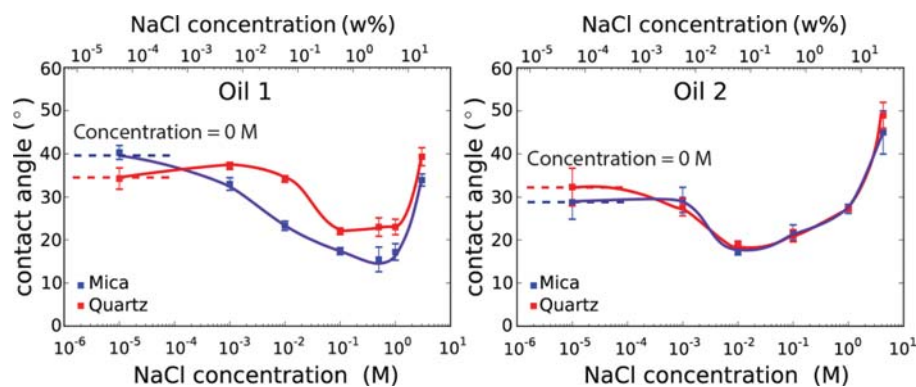
The lines for average pass through all of the data points from 30 to 100  $\mu\text{L}$  within their error bars. Contact angles measured

with droplets smaller than 30  $\mu\text{L}$  do not follow the trend observed in the rest of the data. For the droplets larger than 30  $\mu\text{L}$ , the average of the measured contact angle is 41°, 43°, 43°, and 42° after 0, 24, 48, and 72 h of aging. In this particular case, the effect of aging on the contact angle was not significant as it is in Figure 2 and most other measurements. A number of studies have been carried out on the effect of the droplet volume on the contact angle in the solid–gas–liquid interface,<sup>36–39</sup> but no controlled studies have been reported on the effect of the droplet size on the contact angle in solid–liquid–liquid systems. Drelich and co-workers show that droplet volumes less than 10  $\mu\text{L}$  have a substantial effect on contact angle measurements and the dependency plateaus around 100  $\mu\text{L}$ .<sup>37</sup> Drelich et al. performed the experiments in the solid–liquid–air interface, and our results are recorded in the solid–liquid–liquid interface. The trends seem to be similar. Our results show systematic data on the effect of the droplet size in solid–liquid–liquid systems on smooth surfaces. We have employed high-quality imaging tools and large droplets (100  $\mu\text{L}$ ) in all of our measurements to avoid dependency of the measured contact angle upon the size of droplets.

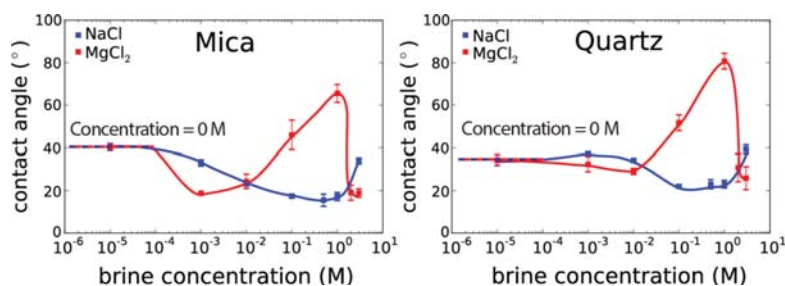
The essence of our measurements is presented in Figures 4–6. Figure 4 shows contact angles of oils 1 and 2 measured on mica and quartz at 72 h of aging as a function of the NaCl concentration. For oil 1, the data for both mica and quartz clearly show a decrease in the contact angle between 0.1 and 1 M, corresponding to 0.6–6 wt %. The measurements show a very systematic decrease from 0 to 0.1 M and an increase after 1 M. At 0 NaCl concentration, contact angles are 40° and 34° for mica and quartz, respectively. These measurements go down to 15° and 22° at 0.5 M NaCl. All contact angles fall in the water-wet regime (between 0° and 70°), but the surfaces become more water-wet at low salt concentrations. For oil 2, both substrates give a minimum contact angle at 0.01 M. It is important to note that the minimum contact angle is observed around the same salt concentration for both surfaces (mica and quartz) with the same type of oil (oils 1 and 2). The type of crude oil affects the wettability behavior. The lowest contact angle measurements are obtained at 0.5 M NaCl for oil 1 and 0.01 M NaCl for oil 2 on sandstone-like surfaces.

To elucidate the effect of mono- and divalent salts on wettability, we assessed the contact angle of oil 1 on quartz and mica substrates at various NaCl and  $\text{MgCl}_2$  concentrations at 72 h (Figure 5). The left panel shows the contact angle for mica, and the right panel shows the contact angle for quartz. It is apparent from this figure that mono- and divalent salts affect wettability differently. Contact angles measured in NaCl show a minimum (at 0.5 M), whereas those measured in  $\text{MgCl}_2$  have a minimum (at 0.001 M) and a maximum (at 1.0 M) for both quartz and mica. Interestingly, the minimum of  $\text{MgCl}_2$  is at a significantly lower concentration than that of NaCl.

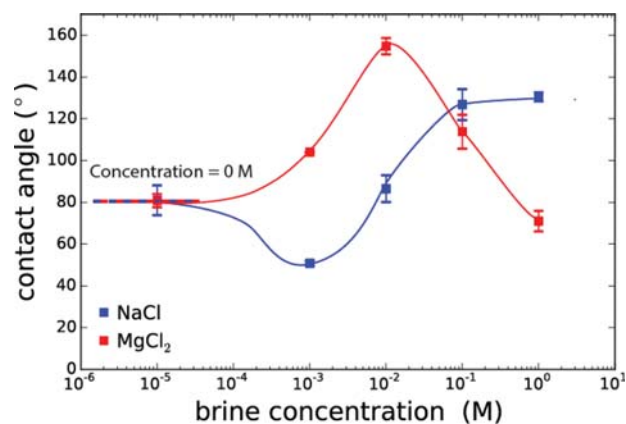
Figure 6 shows the wettability from oil 2 on the calcite substrate in NaCl and  $\text{MgCl}_2$  solutions. As expected, the contact angle for calcite is significantly higher than that for other substrates with the same oil (see the right panel of Figure 4 for contact angles measured on mica and quartz in the same salt and crude oil). For NaCl, the contact angle at 0 M starts around 80° (neutral regime); at 0.001 M NaCl, the wettability shows a minimum with 51° (water-wet regime); and then the contact angle systematically increases to 130° (oil-wet regime) at higher salt concentrations. An interesting finding from NaCl data on calcite is that the minimum contact angle is observed at



**Figure 4.** Contact angle measurements of oils 1 and 2 on mica and quartz substrates versus concentration of brine solution (NaCl) with 100  $\mu\text{L}$  droplets.



**Figure 5.** Contact angle measurements of oil 1 on mica and quartz substrates versus concentration of brine solution (NaCl and  $\text{MgCl}_2$ ) with 100  $\mu\text{L}$  droplets.



**Figure 6.** Contact angle measurements of oil 2 on the calcite substrate versus concentration of brine solution (NaCl and  $\text{MgCl}_2$ ) with 100  $\mu\text{L}$  droplets.

a lower concentration, around 0.001 M, compared to that measured on mica and quartz substrates, around 0.01 M, with the same oil, oil 2 (see the right panel of Figure 4). In previous studies, it has been reported that surface charge and chemical reactivity of sandstone and carbonate rocks are significantly different, which, in turn, affect their wettability behavior.<sup>40,41</sup> Our measurements are in line with the literature: mica and quartz, primary constituents of sandstone, give very similar results; however, calcite, which represents carbonate formations, behaves very differently under the same conditions. The wettability for  $\text{MgCl}_2$  on calcite unlike NaCl shows one maximum. The contact angle starts around  $80^\circ$  at 0 M, shows a steady increase to  $155^\circ$  at 0.01 M, and then decreases to  $71^\circ$  at 1 M  $\text{MgCl}_2$ . In all NaCl experiments, the contact angle

measurements show a very systematic decrease at low-salinity water and then an increase at higher concentrations. The mono- and divalent salts that we employed in this study show very different wettability behaviors. The observed non-monotonicity may be related to the change of ions of salt in the adsorbed layer between the crude oil droplets and the substrates. In NaCl brines, the salt ion concentration in the confined layer may decrease first and then increase as we increase the salt concentration in the bulk. The full understanding of the proposed mechanism will be discussed in our future MD simulation publication.

The pH of all of the ionic solutions employed in this study is  $\sim 6.2$ . We have investigated the effect of pH and  $\zeta$  potential as two governing elements of wettability. Our results show that pH may have a more pronounced effect than the other elements because it renders surfaces from hydrophilic to hydrophobic at various pH regimes. This phenomenon has been discussed before by Drummond and Israelachvili, and our results are in-line with them.<sup>42</sup> We have begun a comprehensive effort in MD simulations of the *n*-decane–brine–mica substrate and a complex oil–brine–mica substrate to develop a molecular understanding of the experimental findings in this work. Results of the MD simulations of *n*-decane–brine–mica show a decreasing trend of the contact angle (more water-wetting), but the complex oil (containing a surfactant) shows a trend similar to measured data in Figure 4. MD simulations provide the composition and structure of the fluid–fluid and fluid–solid interfaces. The work on MD simulations and the effect of pH and interfacial charge will be submitted for publication in the near future.

## 4. CONCLUSION

The main findings of our work are as follows: (1) NaCl shows a minimum in the contact angle. There is a decrease of the contact angle as the salt concentration increases and then an increase of the contact angle with a further salt concentration increase. The trend is the same on quartz, mica, and calcite substrates. (2) MgCl<sub>2</sub> contact angle data show a decrease and then an increase as the salt concentration increases, followed by a decrease with a further increase in the salt concentration on both quartz and mica. (3) MgCl<sub>2</sub> on calcite shows a maximum in the contact angle as the salt concentration increases, then there is a decrease with a further increase in the concentration.

An increase in the contact angle indicates less water-wetting, and a decrease in the contact angle implies more water-wetting. The three observations above, which have not been reported in the literature in the past, have important implications in relation to wettability changes. The molecular simulations of the contact angle and the fluid–fluid structure motivated by the non-monotonic observation of the contact angle from the salt concentration are currently in progress.

In addition to the above, we have systematically studied the wettability of two different crude oils (oils 1 and 2) on three different substrates (mica, quartz, and calcite) with monovalent (NaCl) and divalent (MgCl<sub>2</sub>) brine solutions. Our findings confirm that aging has a considerable effect on wettability, in line with some of the past work.<sup>35</sup> We have found the contact angle to increase and the standard deviation to decrease with time. In this work, we find that an aging time of about 3 days is adequate for equilibrium contact angle measurements on smooth surfaces. Unsmooth surfaces may require more aging time. Pretreatment with a petroleum fluid may also affect aging time. We have studied the effect of the droplet size on the contact angle and found no dependence for droplet volumes between 30 and 100 μL. However, for the systems in this study, drop sizes less than 30 μL affect the contact angle. This investigation shows that the salt concentration plays a significant effect on the contact angle.

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### Notes

The authors declare no competing financial interest.

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