



Full Length Article

Oil/water/rock wettability: Influencing factors and implications for low salinity water flooding in carbonate reservoirs



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ABSTRACT

Wettability of the oil/brine/rock system is an essential petro-physical parameter which governs subsurface multiphase flow behaviour and the distribution of fluids, thus directly affecting oil recovery. Recent studies [1–3] show that manipulation of injected brine composition can enhance oil recovery by shifting wettability from oil-wet to water-wet. However, what factor(s) control system wettability has not been completely elucidated due to incomplete understanding of the geochemical system. To isolate and identify the key factors at play we used SO_4^{2-} -free solutions to examine the effect of salinity (formation brine/FB, 10 times diluted formation brine/10 dFB, and 100 times diluted formation brine/100 dFB) on the contact angle of oil droplets at the surface of calcite. We then compared contact angle results with predictions of surface complexation by low salinity water using PHREEQC software.

We demonstrate that the conventional dilution approach likely triggers an oil-wet system at low pH, which may explain why the low salinity water EOR-effect is not always observed by injecting low salinity water in carbonated reservoirs. pH plays a fundamental role in the surface chemistry of oil/brine interfaces, and wettability. Our contact angle results show that formation brine triggered a strong water-wet system (35°) at pH 2.55, yet 100 times diluted formation brine led to a strongly oil-wet system (contact angle = 175°) at pH 5.68. Surface complexation modelling correctly predicted the wettability trend with salinity; the bond product sum ($[> \text{CaOH}_2^+][-\text{COO}^-] + [> \text{CO}_3^-][-\text{NH}^+] + [> \text{CO}_3^-][-\text{COOCa}^+]$) increased with decreasing salinity. At pH < 6 dilution likely makes the calcite surface oil-wet, particularly for crude oils with high base number. Yet, dilution probably causes water wetness at pH > 7 for crude oils with high acid number.

1. Introduction

Carbonates rock host most of the world's oil reserves (> 60%) [4], which are composed primarily of the minerals calcite and dolomite together with impurities, e.g., quartz, anhydrite, clay minerals, organic matter, and apatite [5]. However, average recovery typically is lower than 40%. Cost-effective and environmentally friendly techniques to enhance oil recovery from carbonates are therefore of broad scientific interest [6]. One such technique that has gained interest is to modify the injected water chemistry to shift reservoir wettability from oil-wet to water-wet in a process termed low salinity water flooding, which is also called *LoSal* flooding by BP [7,8], *Smart Water* flooding by its originators, Austad and co-workers, at the University of Stavanger, Saudi Aramco [9], and *Designer Water flooding* by Shell [10,11].

Several mechanisms have been proposed to describe how the approach improves oil recovery in sandstones: fines mobilization [12],

limited release of mixed-wet particles [12], increased pH and reduced IFT similar to the alkaline flooding [13], multi-component ion exchange (MIE) [8,14–16], electrical double layer expansion [17–19], salt-in effect [20], salting-out effect [21] and osmotic pressure [22].

The low salinity water effect in carbonate reservoirs is less clear, which limits application of low salinity water in carbonated reservoirs [1]. Previous studies suggest that wettability alteration is the main mechanism for the low salinity water effect in carbonated reservoirs, despite the fact that the specific factors controlling wettability have not been completely elucidated [1–3]. For example, most reports suggest that low salinity water shifts reservoir wettability from oil-wet towards water-wet, lifting oil films off the pore surface, whereas Al-Attar, etc. found the opposite [23], arguing that low salinity water shifted reservoir wettability from water-wet to intermediate wetting, thereby increasing recovery. Sulphate apparently acts as a catalyst by adsorbing at pore surfaces more strongly than oil carboxylate groups, thereby

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changing the rock surface charge locally from positive to negative, and causing repulsion between oil carboxylate groups and pore surfaces [24]. As a consequence, reservoir rock wettability will be shifted from oil-wet to water-wet, thereby increasing oil recovery. However, there is still uncertainty about the nature of wettability change, with some reports suggesting it is double layer expansion [6,25,26], and others suggesting it is mineral dissolution [27] and surface complexation [28,29]. For example, Mahani et al. reported that contact angles were decreased by 5–17° as high salinity formation brine was switched over to sea water after 40 h, which can be interpreted by surface complexation modelling. For example, as pH above 6 at the oil/brine interface, $-\text{COO}^-$ increases and $-\text{COOCa}^+$ decreases in sea water compared to formation brine because of the decrease of the Ca^{2+} , thereby $-\text{COO}^-$ dominates the surface charges at the oil/brine interface. At brine/calcite surface, much more $> \text{CaSO}_4^-$ would be generated in the presence of sea water simply because the concentration of SO_4^{2-} in sea water was 14 times higher than that of in the formation brine (e.g., 234 mg/L in FB, 3384 mg/L in SW). As a consequence, the repulsive force between the oil/brine and brine/calcite increases, shifting the wettability toward more water-wet in the sea water. Note: the pH from Mahani et al.'s test for the fluids before and after the contact angle test did not change (pH for FW = 6.9, and pH for SW = 8.0).

In addition to salinity, pH also affects the interaction of oil/brine/rock system, thus wettability. For example, Austad et al. hypothesized that low salinity likely triggers a substitution of Ca^{2+} by H^+ for compensating the desorption of cations from clay surfaces [30]. This hypothesis explains why low salinity water usually leads to a local pH increase. Low salinity water also likely facilitates the ion exchange between the embedded Na in phyllosilicate and H^+ [31], thus causing a local pH increase. However, quantitative work remains to be made to understand the pH effect on the interaction of oil/brine/rock.

We thus aimed to gain a deeper understanding of the factors governing the wettability of the oil/brine/carbonate system with a combination of approaches (e.g., contact angle test, surface complexation modelling). Given that the conventional dilution approach is widely used in field, to understand the general effect of water chemistries on low salinity effect in carbonate reservoirs, we removed potential determining ion, SO_4^{2-} and explored the effect of pH, salinity as a whole on wettability of the oil/brine/carbonate system.

We examined the effect of salinity level (formation brine/FB with salinity level at 252,244 ppm, 10 times diluted formation brine/10 dFB, and 100 times diluted formation brine/100 dFB), on contact angles of oil droplets at the surface of carbonates. To gain a deeper understanding of the geochemical reactions controlling the contact angle results, we used the geochemical speciation code PHREEQC (Parkhurst et al., 1999) to examine the impacts of calcite dissolution and surface complexation.

2. Rock mineralogy

Rock mineralogy is essential to wettability alteration in carbonated reservoirs. X-ray diffraction (XRD) of rock samples used in the contact angle measurements showed 98.1% calcite, 0.7% quartz, and 1.2% ankerite, but no detectable anhydrite (CaSO_4).

2.1. Brine properties

To specifically focus on the salinity effect on system wettability, we removed SO_4^{2-} from all of the experimental brines. Formation brine (FB) was synthesised based on the composition of produced water from North Rumaila field having a salinity of 286,677 ppm [32]. Formation brine was then diluted by 10 times (10 dFB) and 100 times using deionized water, to obtain low salinity brine (Table 1).

Note that the brines used in this study had low pH values (Table 1) due to the reaction of Iron(II) chloride (FeCl_2) in water, which resulted in formation of ferrous, and chloride ions. This process resulted in the

removal of hydroxyl ions from the solution, leaving hydrogen ions in excess, which made the solution acidic.

2.2. Experimental crude oil

The experimental crude oil was extracted from Stag field located in Commonwealth waters on the North West shelf of Western Australia. To avoid the precipitation and plugging by particulates in the crude oil during injection of crude oil, the crude oil was filtered using 12- μm paper filter. The properties of the crude oil are given in Table 2. Note: the experimental oil had a higher base number (1.02 mg KOH/g) than acid number (0.50 mg KOH/g), suggesting that concentration of $-\text{NH}_2^+$ at oil surface may be two times greater than $-\text{COO}^-$ [29]. This implies that the bond between carbonate and amine group, $[> \text{CO}_3^-][-\text{NH}^+]$, may play an important role in system wettability.

2.3. Contact angle test

To investigate the effect of water chemistry on wettability of carbonate, we tested the contact angle on the rock with crude oil and aqueous ionic solutions using Vinci IFT-700 (Fig. 1). The experimental temperature and pressure was at 60 °C and 2000 psi, respectively. Contact angle tests were conducted using the sessile droplet method. Note: all of the contact angle results were recorded after equilibrium was reached, i.e. the contact angle did not change over 48 h. Also note that while the substrate roughness, contact angle hysteresis, and preparation procedure all may affect the macroscopic contact angle [26], the philosophy of the contact angle test in this study was to highlight the actual trend of the contact angle with salinity rather than the exact initial value of the contact angle.

To obtain representative contact angles, the rock substrates were exposed to air plasma for 10 min to remove organic surface contamination [33]. Note that the aged sample were obtained by putting a clean sample in a beaker with crude oil in an oven at 60 °C for eight weeks to restore wettability. After completing the aging process, samples were dried in the oven and cleaned for 15 min in an air plasma for the second time before measuring the contact angle. Subsequently, the substrates were placed in the HT-HP cell and vacuumed before the cell was filled with brine. Temperature and pressure was set at 60 °C and 2000 psi, respectively. After a state of equilibrium was achieved in the system (constant pressure and temperature), a drop of crude oil (0.04–0.06 ml) was introduced through a 0.6 mm diameter needle at the bottom of the cell into the brine environment. Then the droplet was released from the needle and placed on the substrate to measure the contact angle.

3. Results and discussion

3.1. Effect of water chemistry on contact angle

The contact angle between oil and the carbonate substrate increased with decreasing salinity, implying that dilution shifts the wettability of oil/brine/carbonate towards more oil-wet. This may explain why the dilution approach does not always trigger low salinity water EOR-effect. For example, the contact angle on un-aged carbonate substrate increased from 30 to 81° with decreasing salinity from FB to 100 dFB (Fig. 3). A similar trend was also observed with aged carbonate substrate; the contact angle shifted from 35 to 175° with decreasing the salinity level from FB to 100 dFB.

Although we observed a similar trend in contact angle alteration for both aged and un-aged rock samples, the effect of reduction in salinity on wettability was much more profound on aged substrate compared to un-aged substrate. Our results are in line with Al-Attar et al. [34] who reported that the contact angle increased with the decrease in the salinity level. For example, they observed the contact angle increased from 45° in the presence of FB (197,000 ppm), to 70° when salinity was

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