Article

The Influence of Oil Composition, Rock Mineralogy, Aging Time, and Brine Pre-soak on Shale Wettability

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ABSTRACT: Experimental and field studies have indicated that surfactants enhance oil recovery (EOR) in unconventional reservoirs. Rock surface wettability plays an important role in determining the efficacy of this EOR method. In these reservoirs, the initial wettability of the rock surface is especially important due to the extremely low porosity, permeability, and resulting proximity of fluids to the solid surface. This study is designed to investigate the effect of oil components, rock mineralogy, and brine salinity on rock surface wettability in unconventional shale oil/ brine/rock systems. Six crude oils, seven reservoir rocks, and seven reservoir brine samples were studied. These oil samples were obtained from various shale reservoirs (light Eagle Ford, heavy Eagle Ford, Wolfcamp, Middle Bakken, and Three Forks) in the

US. SARA (saturates, aromatics, resins and asphaltenes) analysis was conducted for each of the crude oil samples. Additionally, this study also aims to provide a guideline to standardize the rock sample aging protocol for surfactant-related laboratory experiments on shale reservoir samples. The included shale reservoir systems were all found to be oil-wet. Oil composition and brine salinity showed a greater effect on wettability as compared to rock mineralogy. Oil with a greater amount of aromatic and resin components and higher salinity rendered the surface more oil-wet. Rock samples with a higher quartz content were also observed to increase the oil-wetness. The combination of aromatic/resin and the quartz interaction resulted in an even more oil-wet system. These observations are explained by a mutual solubility/polarity concept. The minimum aging time required to achieve a statistically stable wettability state was 35 days according to Tukey's analysis performed on more than 1100 contact angle measurements. Pre-wetting the surface with its corresponding brine was observed to render the rock surface more oil-wet.
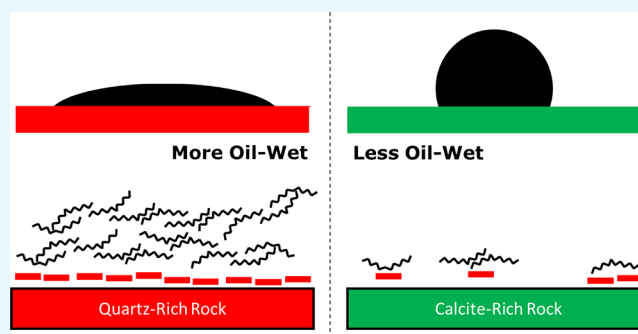
INTRODUCTION

Wettability is defined as the affinity of a solid surface to a certain fluid phase in the presence of another immiscible fluid phase. A shale oil reservoir is a perfect case for wettability investigation because it contains all three phases required for a wettability effect to exist. In this system, interstitial water acts as the polar liquid phase. The water phase always contains salt ions that make it more polar. Crude oil that contains a vast variety of hydrocarbon chains acts as the nonpolar liquid phase. These two liquid phases coexist inside the pore space of a rock, the solid phase. Wettability affects the oil recovery factor, the efficiency of oil production from the reservoir, since it influences the flow pattern of fluids flowing through a reservoir.[1] There has been significant focus in recent years on shale reservoir's wettability, which has been determined to be mostly oil-wet.[2] The oil-wetness is believed to cause a greater effect in a tighter reservoir, i.e., shale oil reservoirs, due to the stronger boundary effect from the pore wall to the pore throat. To solve this problem, several authors have investigated the

application of surfactants as an EOR (enhanced oil recovery) technique by altering the shale wettability from oil-wet to water-wet.[3−12] To design a surfactant system with strong wettability alteration performance, we must first understand the surface oil-wetting mechanism. This is important because minerals commonly found in the reservoir, i.e., quartz, calcite, dolomite, and clay, are actually water-wet after deposition. Additionally, the effect of oil composition, rock mineralogy, and salinity must also be investigated, especially with the heterogeneity of these three parameters observed in shale reservoirs in the US.
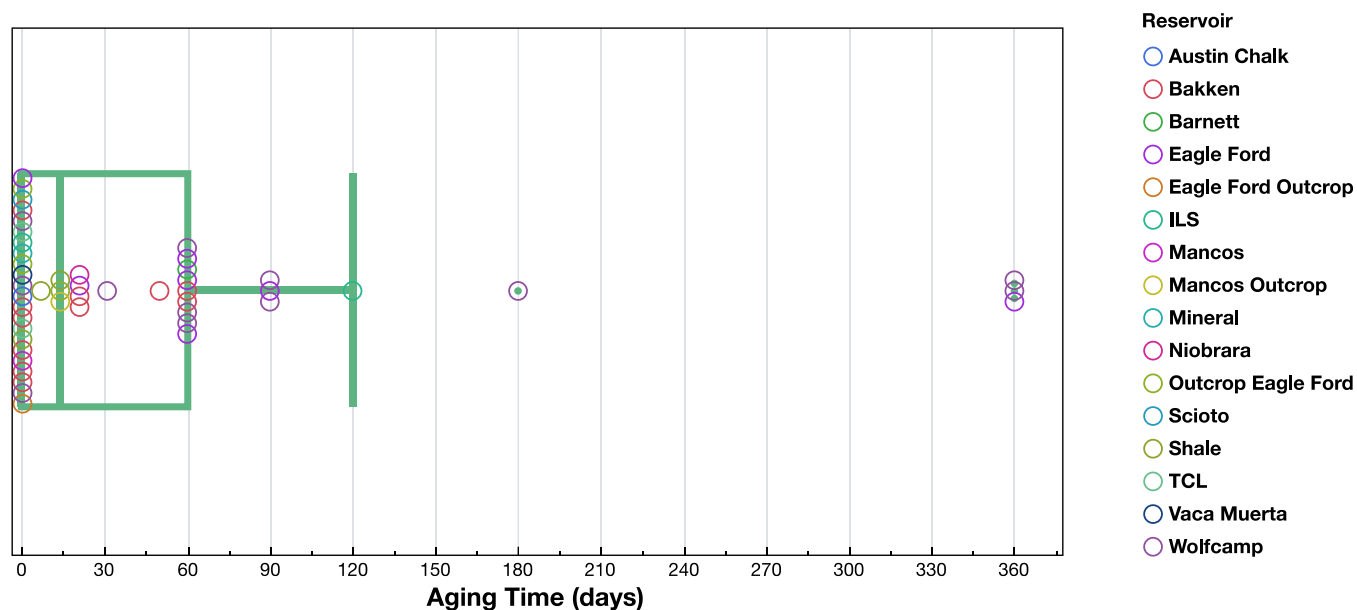
Figure 1. Distribution of aging time from 44 publications of shale EOR involving an aging procedure.

Several authors have investigated the mechanism behind the oil-wetting mechanism of a rock surface. Buckley and Liu proposed four mechanisms for oil-wet surface creation: (1) polar interactions, (2) surface precipitation, (3) acid/base interaction, and (4) ion binding.[13] Polar interaction occurs due to the adsorption of the polar components of crude oil on the rock surface. Zhong et al. supported this mechanism based on their observation of the adsorption of pyridine on a silica surface from a molecular dynamic simulation.[14] Interestingly, other studies have also reported the adsorption of nonpolar saturates of the crude oil on both silica and calcite surfaces.[15,16] However, due to the weak nature of the interaction, it is hypothesized that the rock surface must be free of water molecules during the adsorption process. Surface precipitation occurs when the asphaltene component of the crude oil becomes less soluble. The asphaltene precipitation occurs when the concentration of the lighter components in the crude oil is increased, which results in a stronger oil-wetness observed with a lighter crude oil.[17,18] The acid/base interaction occurs when crude oil has significant acid and/or base contents. The quartz surface is negatively charged, while calcite and dolomite are positively charged. The charge densities of the two carbonate minerals are different with dolomite being more positively charged than calcite.[19] The negatively charged quartz surface will attract the basic components of the crude oil. On the other hand, positively charged carbonates will bond with the acidic crude oil molecules. This interaction is highly dependent on the pH of the system.[20] Temperature has been observed to have a variable impact on oil-wetness caused by the acid/base interaction. An increase in temperature could increase the oil-wetness due to stronger electrostatic bonds.[21–24] In contrast, higher temperatures could also decrease the oil-wetness due to the general onset of desorption and, in the case of calcite surfaces, the reduction of calcium adsorption sites.[17,25,26] The last mechanism, ion binding, occurs due to the presence of salt ions on the rock surface, which bridges the polar components of crude oil to the rock. This mechanism was observed to occur only with divalent ions.[20,27]

Another approach to investigate the mechanism behind the surface oil-wet rendering is through molecular simulation. Atomic-scale simulation provides insights into the different forces that govern the wettability of a rock surface. The initial wettability of a rock surface is a function of oil and rock composition. In the absence of carboxylic acid, van der Waals forces cause oil adsorption on both siliceous and carbonaceous surfaces.[15,16,28] This force is, however, weaker than the electrostatic interaction between the water molecule and the solid surface. Therefore, according to molecular simulation, the creation of a hydrophobic surface with oil can only occur when water is not present in the system. With a carboxylic acid group present in the crude oil, the surface oil-wetting is driven by the electrostatic interaction between the acid to positive calcium ions (calcite-rich surface) and the hydrogen atoms of the hydroxyl group (quartz-rich surface). This interaction was found to be stronger than the interaction between the water molecule and the rock.[14,24,29]

Contamination of reservoir rock samples during the sampling process is inevitable. Before the experiment, reservoir rock samples are often cleaned and conditioned. In the area of wettability or surfactant research, rock samples are aged to restore the reservoir's initial wettability. The aging process consists of submerging rock samples in their corresponding crude oil at high temperature for an extended period of time. A look through the available literature indicates that the duration of the aging process that was employed for surfactant studies in shale varied from zero time up to a year (Figure 1).[3,6,9,10,12,13,30–56] This is worrying because several authors have presented the effect of the aging process on flow behavior. Jia et al.[57] investigated the effect of the aging time on the rock wettability measured on the Amott–Harvey index. They established the required aging time on their specific rock and oil system to be at least 12 days. They also found that higher aging temperatures could decrease the minimum aging time. Drexler et al.[58] reported that 30 days of aging is the minimum requirement to render their sample oil-wet. It is important to note that these two studies were performed mostly using heavy crude with high asphaltene and high acid/base contents. These studies, therefore, might not apply to typical shale crude oil

Table 1. Mineralogy of the Seven Reservoir Rock Samples Included in This Study

	A	B	C	D	E	F	G
calcite	49.63%	0.00%	44.27%	61.90%	81.38%	1.00%	0.00%
dolomite	2.85%	1.97%	2.24%	0.70%	0.65%	34.00%	65.00%
quartz	13.79%	49.49%	29.07%	9.30%	4.88%	35.00%	19.00%
kaolinite	6.63%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
illite	10.46%	24.55%	11.72%	11.30%	7.56%	15.00%	1.00%
pyrite	4.88%	2.53%	1.58%	3.80%	2.90%	1.00%	0.00%
other	11.77%	21.46%	11.12%	13.10%	2.62%	14.00%	15.00%
carbonate:quartz ratio	3.8:1	1:25.1	1.6:1	6.7:1	16.8:1	1:1	3.42:1
reservoir	Eagle Ford	Wolfcamp	Wolfcamp	Eagle Ford	Eagle Ford	Middle Bakken	Three Forks

Table 2. SARA Composition, API Gravity, and Reservoir Source of the Six Crude Oil Samples Included in This Study

	1	2	3	4	5	6
saturates	91%	88%	68%	48%	34%	27%
aromatics	4%	8%	24%	42%	49%	53%
resins	5%	4%	8%	10%	15%	16%
asphaltenes	0%	0%	0%	0%	2%	5%
TAN (mg-KOH/g-oil)	0.02	0.01	0.02	0.02	0.53	
°API	55.75	50.15	43.52	36.84	28.03	24.48
reservoir	Eagle Ford	Eagle Ford	Wolfcamp	Middle Bakken	Eagle Ford	Eagle Ford

characterization because of the lack of asphaltenes. Sample wettability, as affected by the aging protocol, also controls the water imbibition profile. Zhou et al.[59] performed spontaneous imbibition on Berea sandstone samples with various aging periods. Their study showed that although the aging time does not affect the final recovery volume, it reduces the rate of recovery. In another study, Zhou et al.[60] further investigated the effect of aging on waterflood performance. They found a positive correlation between aging time and final recovery. Jadhunandan and Morrow[61] also reported similar results in a separate study. It is important to note that these studies limited their aging time to a maximum of 10 days.

Brine is initially in contact with the sediment that forms reservoir rock. Therefore, during the formation of hydrocarbon in shale rock, water molecules are presumably still present in the reservoir. This hypothesis is often cited as a weakness of the aging procedure. The aging process has been criticized to overestimate the oil-wetness of the shale rock surface as the process is preceded by a solvent (toluene and/or methanol) cleaning procedure. The cleaning process is therefore believed to remove all the water molecules from the rock surface, thereby rendering it unrepresentative of the original reservoir conditions. Additionally, it is believed that the water molecules would "block" the oil from rendering the surface oil-wet, especially with the presence of salt ions in reservoir brine. Studies have shown that monovalent and divalent cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) affect shale's wettability by adsorbing onto the shale surface and providing additional sites for polar interactions on the shale surface.[62,63] To understand the in situ wettability of shale, it is important to understand the conditions in which the reservoir rock is subjected. The effect of the presence of an initial in situ bulk brine phase and the shale hydration effect caused by this aqueous phase on the wettability of complex heterogeneous shale rock are critical in understanding the wettability alteration of shale rock by polar components in the oil.

This study is a continuation of previous work directed toward the effort to understand the polar/nonpolar interaction between various phases in a shale system. In the previous study, we investigated the interaction occurring in a two-phase oil/brine system by interfacial tension (IFT).[64] This paper expands the research by adding the rock variable to the system, making it a three-phase system: oil, brine, and rock. The concept of mutual solubility, which was found to clearly explain the oil and brine interaction, was tested again in the three-phase system. Additionally, this study also aims to investigate the relevance of the surface oil-wetting mechanism available in the literature. Most, if not all, of the literature performed investigations on the crude oil/brine/rock systems of conventional reservoirs. As stated previously, the shale system has a very distinctive feature from conventional reservoirs. That is the absence of asphaltene, acid, and basic contents in the crude oil and the high salinity characteristic of the brine. Last, this study is also intended to develop a standardized aging time protocol for preparing shale rock samples for wettability- or surfactant-related experiments.

■ METHODOLOGY

Rock Characterization. Seven reservoir rock samples were investigated in this study. Rock whole cores or sidewall cores were taken directly from the reservoirs. Then, a block was retrieved from each core. Half of the block was cut into approximately 1 cm × 1 cm-sized chips. While the other half was crushed for mineralogy analysis through an X-ray diffraction (XRD) method. The result of this mineralogy analysis will be described in the next part of this section. Chips were soaked in toluene for 3 days and consequently in methanol for 2 extra days to clean any original or residual oil from the surface. Then, they were vacuum-dried and finally aged for a specific aging time. The procedure followed during the aging process is discussed in the last part of this section.

The mineralogy of the seven rock samples is presented in Table 1. In our previous publications, it was established that US shale crude oils are highly heterogeneous. Likewise, as the data shows, the mineralogy of the investigated shale reservoirs is also widely varied. The calcite mineral content ranges from zero in the Wolfcamp reservoir to 81% in Eagle Ford. Dolomite content ranges from 1% in the Eagle Ford to 65% in

Table 3. TDS and Salt Ion Composition of the Seven Brines Included in This Study

	T	U	V	W	X	Y	Z
TDS	0	1676	20,000	24,610	61,479	109,946	307,213
Na^+	0	497	0	8937	20,939	37,446	98,462
K^+	0	24	10,489	269	287	513	10,814
Ca^{2+}	0	96	0	260	2085	3729	1973
Mg^{2+}	0	9	0	21	342	612	7874
Ba^{2+}	0	0	0	11	0	0	0
Sr^{2+}	0	1	0	201	0	0	0
Cl^-	0	814	9511	14,475	36,807	65,824	188,090
Br^-	0	2	0	104	0	0	0
HCO_3^-	0	0	0	293	683	1221	0
CO_3^{2-}	0	2	0	0	0	0	0
SO_4^{2-}	0	229	0	39	336	601	0

the Three Forks. Quartz ranges from 5% in the Eagle Ford to 50% in the Wolfcamp. Most reservoirs contain both carbonaceous and siliceous material (except for some intervals in Wolfcamp, rock B). The carbonate to quartz content ratio also varies significantly, with values ranging from 1:25.1 to 1:1 to 16.8:1.

Oil Characterization. Six shale crude oil samples were included in this study. The crude oil samples were extracted straight from the wellhead and were centrifuged and vacuumed to remove any impurities. Density measurements were then performed in-house to determine the API gravity, while SARA analysis was performed at a third-party laboratory.

The advantage of using actual reservoir crude oils is the ability to capture the heterogeneity of the oils from different shale reservoirs. As presented in Table 2, the saturate component of the crude oil ranges from 27 to 91%, the aromatic composition ranges from 4 to 53%, and the resin composition ranges from 5 to 16%. Our previous publication established that most crude oil samples contain an insignificant amount of asphaltenes, with the only exception coming from crude oil produced from the shallower section of the Eagle Ford (Oil#5 and Oil#6). Analogously, the oils investigated in this study follow the same trend. Similarly, these shale crude oil samples also have virtually zero acid content as presented, except for crude oil number 5. The API gravity of the six crude oil samples in this study ranges from 55.75 to 28.03° API.

Brine Characterization. Seven brines were included in this study (Table 3). All brines except brines T (Type I DI water) and V (2 wt % KCl) were created based on the brine composition of actual produced water. The TDS ranged from 1676 to 307,213 ppm. In brines W, X, Y, and Z, sodium chloride is the predominant salt, and it accounted for more than 93% of the entire salt content. This observation aligns with our previous oil/water IFT publication where it was determined that most, if not all, shale produced brine is composed mainly of sodium chloride salt.

Test Matrix, Aging Process, and Brine Pre-soak Procedure. As mentioned before, seven reservoir rock samples, six crude oil samples, and seven brine compositions were included in this study. Full factorial Design of Experiment was not implemented to avoid wettability measurement on 294 different oil/water/rock systems. At the core, three rock samples (A, B, and C) and four crude oil samples (1, 3, 4, and 5) were tested in full factorial fashion in brine T. To include actual produced brine, additional oil/water/rock pairings were added based on the reservoirs, for example, rock F, brine Z, and oil 4, which all came from the Middle Bakken reservoir.

The complete lists of the oil/water/rock system tested in this study are presented in Table 4.

Table 4. Rock, Brine, and Oil Combination Measured in This Study

rock	brine	oil	nomenclature	rock	brine	oil	nomenclature
A	T	3	A_T_3	C	T	1	C_T_1
A	T	4	A_T_4	D	W	2	D_W_2
A	T	5	A_T_5	D	U	2	D_U_2
A	T	1	A_T_1	E	T	5	E_T_5
B	T	3	B_T_3	E	X	6	E_X_6
B	T	4	B_T_4	E	X	5	E_X_5
B	T	5	B_T_5	E	Y	5	E_Y_5
B	T	1	B_T_1	E	V	5	E_V_5
C	T	3	C_T_3	F	Z	4	F_Z_4
C	T	4	C_T_4	G	Z	4	G_Z_4
C	T	5	C_T_5				

Standard Aging and Brine Pre-soak Aging Procedures. This study employs two aging methodologies, the standard aging procedure and the brine pre-soak aging procedure. In the standard procedure, cleaned rock chips were submerged in their corresponding oil (according to Table 4) at reservoir temperature for a range of time from zero up to 56 days. After the determined aging time has been reached, the chip was removed from the oil, the excess oil was removed, and contact angle was measured using the captive bubble method (explained in the next section). In this aging procedure, the rock chip was in contact with the aqueous phase only after it was aged in oil, during the contact angle measurement.

The second aging methodology, the brine pre-soak aging procedure, was developed to answer the ongoing debate on the effect of irreducible water saturation on the aging process. It is believed that if water molecules are present during the aging-in-oil process, they will hinder the transformation of the rock surface wettability into an oil-wet condition. With the previous methodology, the rock is completely free of water molecules at the start and during the aging process. In this brine pre-soak procedure, after it was cleaned, the rock chip was first aged in their corresponding brine (according to Table 4) at reservoir temperature. After 2 weeks, it was removed from the brine and then submerged in their corresponding oil at reservoir temperature for a range of time from zero up to 56 days. After the desired aging time has been reached, the chip was removed from the oil, the excess oil was removed, and contact angle data was acquired using the captive bubble method. In

contrast with the first procedure, the rock chip was in contact with the aqueous phase before the start of the aging process. This was performed to establish an irreducible water saturation on the rock surface before the rock was aged in their corresponding oil.

Most of the data provided in this study was from the samples that underwent the standard aging procedure, with the only exception in the last section of the Results and Discussion where the effect of brine pre-soak aging procedures is presented. It is also important to note that in this study, each rock chip was not returned to the aging cell after the measurement to prevent cross-contamination.

Captive Bubble Method. Wettability was determined through contact angle measurements using the captive bubble method. This method was performed on the aforementioned rock chip that was cut from reservoir core samples. These rock chips were cut from close proximity of the rock part used for the XRD analysis to ensure the consistency of the rock mineralogy. To measure the contact angle, a rock chip was removed from their aging vial. The excess oil was removed from the rock chip, and the rock chip was placed inside their respective brine. The brine was preheated to 170 °F before the rock chip was placed. Then, a drop of oil was placed at the bottom of the rock chip. The angle formed by the drop with the rock surface was measured and recorded as the system's contact angle. A detailed schematic containing the configuration of oil, rock, and brine is presented in Figure 2. Additionally, examples of both a water-wet and oil-wet rock surface condition are presented.
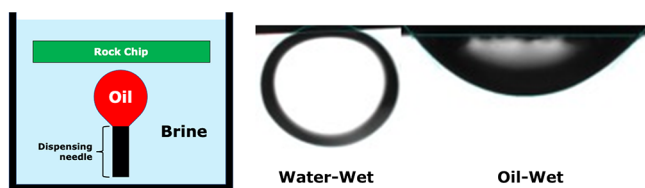

Figure 2. Schematic of the captive bubble method (left) (the picture is not to scale). Examples of a water-wet system (middle) and an oil-wet system (right).

■ RESULTS AND DISCUSSION

More than 1100 contact angle data were acquired. In the following section, the data is dissected by the five control variables: aging time, rock composition, oil composition, brine composition, and the brine pre-soak process. The experimental variables are the magnitude of the wettability, represented by the contact angle, and the rate to reach a stable wettability, referred to as the stable aging time. It was hypothesized that the experimental variables are also influenced by interactions between the five control variables, which complicates the analysis. Therefore, the contact angle is often presented in the graph with multiple control variables presented at once. The stable aging time is determined through Tukey's analysis.

This section starts with the determination of optimum aging time to reach a stable wettability condition. Then, the effects of rock mineralogy, oil composition, and brine salinity are discussed in separate parts. Finally, the effect of the brine pre-soak process on the rock wettability is presented.

Optimum Aging Time. The aging process was observed to render the rock surface oil-wet. In this part of the study, the optimum aging time to achieve a stable wettability condition

was investigated. The stable aging time was first established by averaging the contact angle data based on the aging time. Multiple rock, oil, and brine were included in the mean contact angle average value of each aging time. Then, Tukey's analysis, which is an ANOVA test designed to perform more statistically accurate comparisons for more than one pair of datasets, was conducted on these average means. This method is useful to determine the minimum aging time as nine aging times were compared. The result of the analysis is presented in Table 5 with the graphical representation presented in Figure 3.

Table 5. Tukey's Analysis to Determine the Minimum Aging Time for a Stable Wettability Condition (CI = 95%)

aging time (days)						mean
49	A					137.96974
42	A					136.35000
35	A					135.05300
56	A	B	C	D		119.20000
28		B				117.69361
21		B	C			116.80078
14			C	D		109.07929
7				D		105.04490
0					E	24.10370

In this analysis, 775 contact angle datapoints were included. This dataset includes all seven rock samples, all six crude oil samples, and all seven brine samples. The aging times are presented in rows. Aging times connected by the same letter (A, B, C, D, or E) are those aging times with wettabilities that are not significantly different one to another, i.e., the mean difference is not significantly larger than the combined variance of the two datasets. Zero days of aging resulted in a water-wet rock surface (mean contact angle of 24°, presented on the last row of Table 5), and aging the surface rendered it oil-wet. Aging the rock surface for a week already resulted in an oil-wet surface (contact angle of 105°, the second-to-last row of Table 5). However, the oil-wetness was still developing as aging the surface to 7, 14, 21, 28, and 35 days resulted in a stronger oil-wetness with mean contact angles of 105, 109, 116, 117, and 135°, respectively. When the rock surface was aged for longer than 35 days, all of the mean data for an aging time longer than and equal to 35 days were connected, meaning that there was no statistically significant difference between the mean data of 35, 42, 49, and 56 days of aging. From this, it can be concluded that a stable wettability condition is achieved after 35 days. This conclusion serves as a general guideline that fits the range of rock, oil, and brine included in this study.

Rock Composition Effect on Wettability. In this section, the effect of the rock composition on the surface wettability is investigated. The contact angle data were grouped by their mineral compositions and averaged. This grouping and averaging method meant that measurements from multiple crude oil samples were included in one datapoint. The result from all measurements performed with brine sample T (DI water) is presented in Figure 4. The figure is constructed using 380 datapoints, consisting of three rock samples (A, B, and C) and four crude oil samples (1, 3, 4, and 5). The contact angle is presented as the y-axis. The x-axis represents the composition of four different rock minerals, represented in four columns: quartz, calcite, dolomite, and clay (left-to-right). The contact angle data were also grouped by
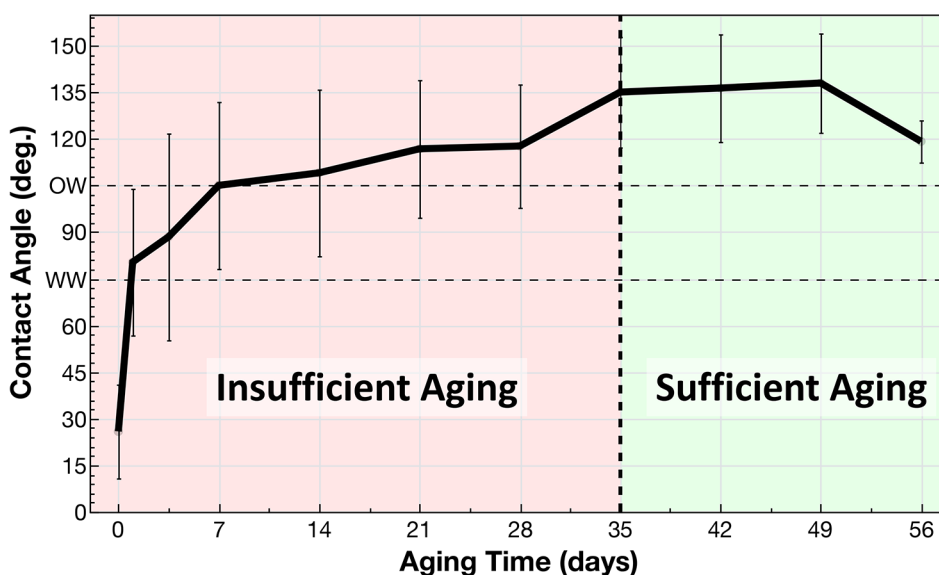
Figure 3. Wettability evaluation throughout 0−56 days of aging for all six crude oil samples and seven rock samples.
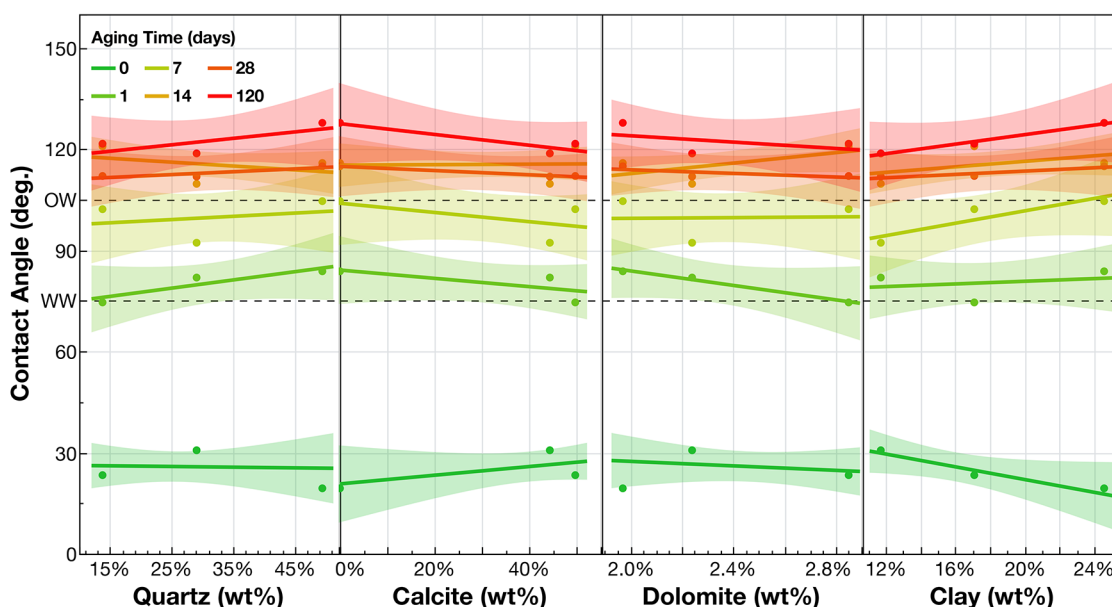

Figure 4. Effect of quartz, calcite, dolomite, and clay contents on the surface wettability after a duration of aging for samples measured in brine T (DI water). Colors represent the length of the aging duration, green-to-red: zero to 120 days of aging.

their aging time, and the groupings are presented based on colors with the aging time increasing from green to red.

The creation of oil-wetness due to the aging process is observed from the graph with the position of the red datapoints significantly higher than the green ones. Before aging, there was no significant relationship observed between the contact angle and the quartz. On the other hand, a positive trend was observed on the calcite content, and a negative correlation was observed on the dolomite and clay composition in the rock. After the rock was aged, a positive correlation was observed between the contact angle and the quartz and the clay content. In comparison, both calcite and dolomite composition exhibited a negative trend. These observations are contrary to the established understanding that carbonates are more oil-wet than quartz. These results were not skewed by the oil composition since each datapoint

presented in Figure 4 was an average value from the four different crude oil samples.

It is hypothesized that the positive relationship between the oil-wetness and the carbonate composition available in the literature is driven by the asphaltene content and the acid number of the crude oil used in the study.[13,18,26] Organic acids found in heavier conventional reservoir crude oil samples are known to easily bond to the free calcium atom on the surface of carbonate rock. The adsorbed organic acid then provides an anchor for the other crude oil component to bond to the surface, creating an oil-wet surface. It has been established in our previous publication and Table 2 that shale crude oil samples have virtually zero asphaltene content and zero acid number. The absence of these important components of the conventional crude oil-carbonate interaction resulted in the
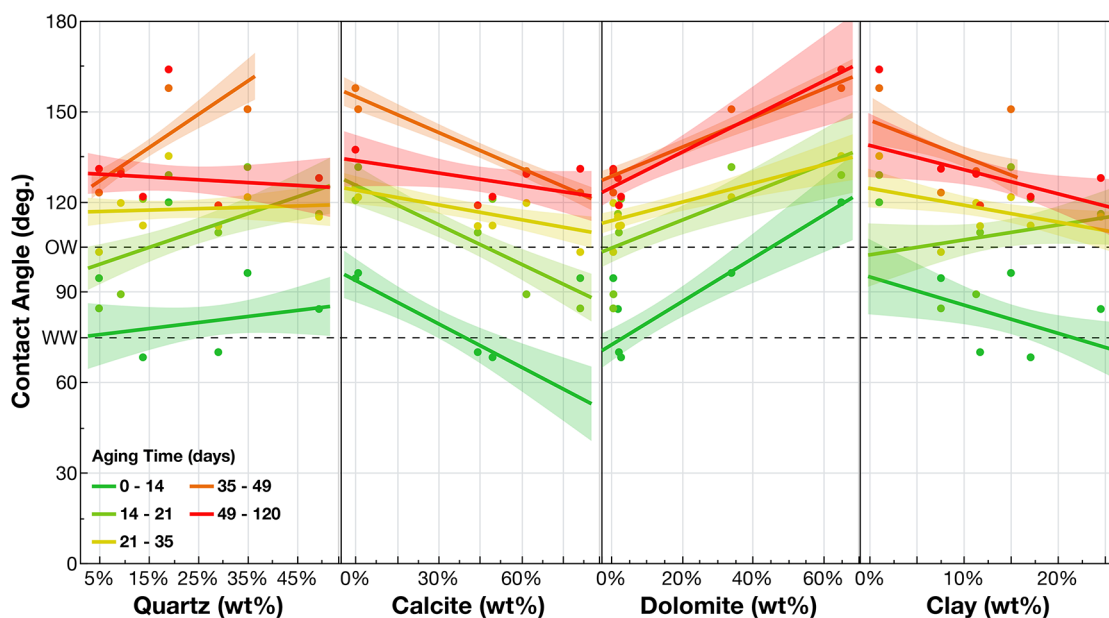
Figure 5. Effect of quartz, calcite, dolomite, and clay contents on the surface wettability after a duration of aging. Colors represent the length of the aging duration, green-to-red: zero to 120 days of aging.
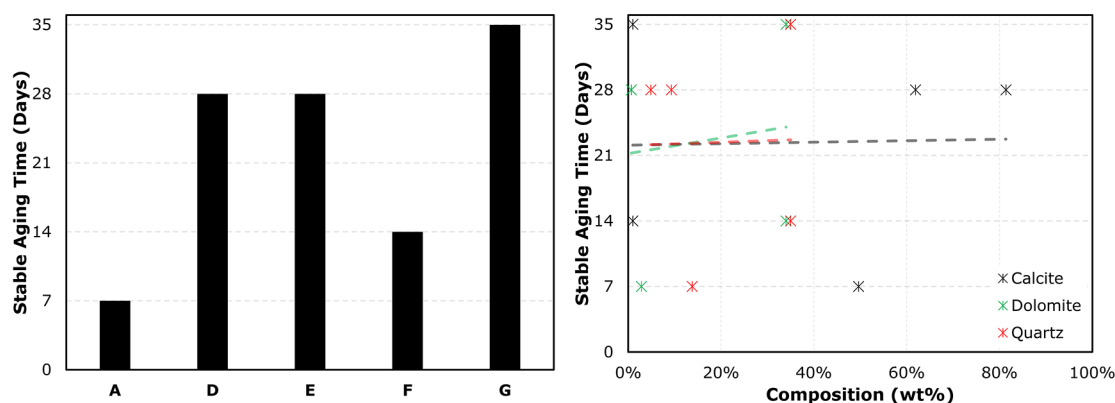

Figure 6. Aging time required to establish stable and consistent wettability for the six reservoir rock samples (left). Values were obtained from Tukey's analysis with contact angle data grouped by rocks. The stable aging time is plotted against the calcite, dolomite, and quartz content (right).

absence of a positive trend between the surface oil-wetness and the carbonate composition.

In our previous publication, it was established that aromatics and resins, in the absence of asphaltene, act as a bridge between the nonpolar saturates component to the water molecule. It is hypothesized that a similar explanation can be used to explain the behavior observed in this study. In the case of surface wetness, the aromatics and resins are bridging the nonpolar components of the crude oil to the rock surface. The polarity of the rock surface is controlled by its mineralogy. Rock samples with a higher concentration of carbonates will become more polar due to the free calcium atom on its surface, while a higher quartz composition results in a surface with less polarity. Carbonate rocks that are highly polar would result in the inability of the aromatics and resins to bond to its surface, resulting in the failure to create an oil-wet surface, hence the observed negative trend between the carbonate content and oil-wetness. Quartz and clay, on the other hand, have less polarity than carbonates and allows for a better bond of aromatics and resins to its surface. This results in a more oil-

wet surface, as observed on the positive relationship between the quartz content and the oil-wetness.

The rest of the oil/water/rock systems in Table 4 were added to Figure 4 and are presented in Figure 5. This figure is constructed with 775 contact angle datapoints that include all seven rock samples, all six crude oil samples, and all seven brine samples. It is important to note that some degree of skewness is observed due to the partial factorial test matrix. For example, rock samples with dolomite contents (rocks F and G) were only measured in combination with oil 4 (the third heaviest oil) and brine Z (the brine with the highest TDS). The positive relationship between the surface oil-wetness and the quartz content was enhanced in this dataset. Similarly, the negative relationship to the calcite content was also observed to increase. On the other hand, the dolomite content exhibited a positive trend, while the clay composition presented a negative trend.

In general, the trends observed in Figure 4 were repeated in Figure 5 except for dolomite and clay. The trends of contact angle to calcite and quartz composition in Figure 5 are accentuated but still follows the same inclination. It is
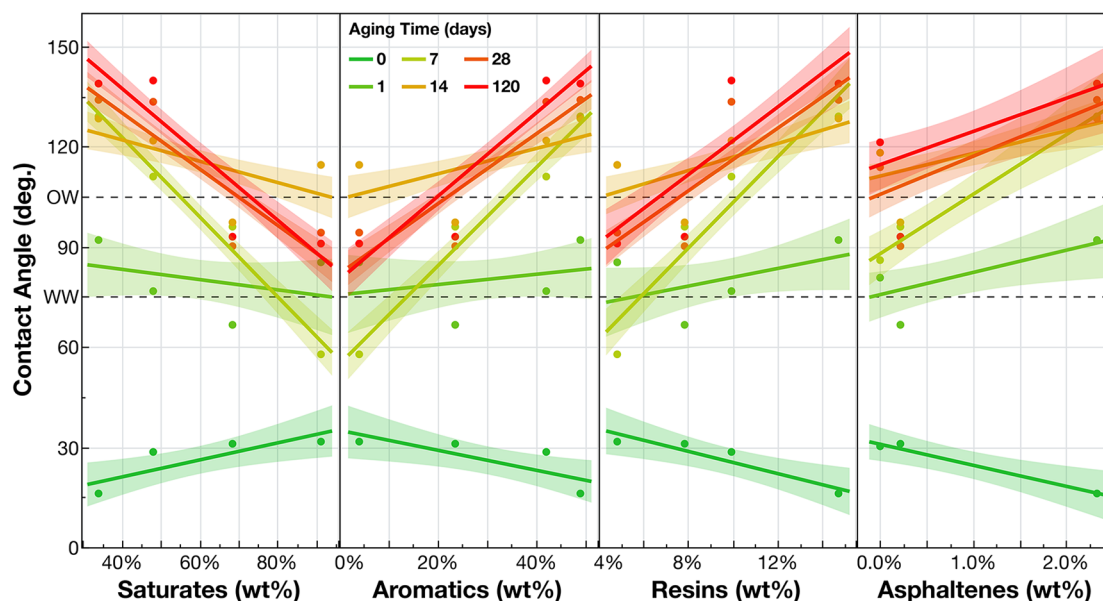
Figure 7. Effect of saturate, aromatic, resin, and asphaltene contents on the surface wettability after a duration of aging for samples measured in brine T (DI water). Colors represent the length of the aging duration, green-to-red: zero to 120 days of aging.

hypothesized that the reversal in results for dolomite was caused by the oil and the salinity. High dolomite contents were observed only on rocks F and G. These rocks were only measured with brine Z (32% TDS brine) and oil 4, which had high aromatic and resin contents. These oil and brine combinations resulted in a strong oil-wetness and skewed the dolomite results to be more oil-wet, especially with the stronger positive charge of a dolomite surface, which promotes more adsorption of crude oil components. However, the difference between Figures 4 and 5 highlighted an important observation. In the range distribution of oil, rock, and brine properties included in this study, which represents the distribution of Lower 48 shale oil/brine/rock properties, the rock composition has a diminutive effect on the surface wettability compared to the effect of crude oil composition and brine salinity.

Also, the optimum aging time for stable wettability for each rock sample was also analyzed. Tukey's analysis was performed after the results were grouped by rock samples. The summary of the optimum aging time is presented in the left graph of Figure 6. The optimum aging data was then plotted against the calcite, dolomite, and quartz content on the x-axis, the right graph of Figure 6. From the right graph, it can be concluded that there was no significant trend observed between the rock composition to the optimum aging time. The independence of optimum aging time to rock mineralogy enforced the idea that in shale oil/water/rock systems, the rock mineralogy plays a minimum role in determining the rock surface wettability.

Oil Composition Effect on Wettability. The effect of saturate, aromatic, resin, and asphaltene contents on the rock surface wettability was investigated. Contact angle data for all measurements performed with brine T (DI water) were grouped by their oil composition. The data are plotted against the saturate, aromatic, resin, and asphaltene composition on the x-axis in Figure 7. The dataset for this figure's 380 datapoints is from three rock samples (A, B, and C) and four crude oil samples (1, 3, 4, and 5). Similar to the previous figures, the datapoints were also grouped by their aging time, with the grouping presented in different colors. Increasing

aging time is presented by the shift from green to red. In comparison to the analysis on the effect of rock mineralogy (presented in Figure 4), the trends observed in Figure 7 were significantly stronger; the gradients of the trendlines were larger than those in Figure 4. At the zero day aging time, a higher saturate content resulted in a more oil-wet surface. On the other hand, a higher aromatic, resin, and asphaltene composition in the crude oil rendered the surface to be less oil-wet. After the rock surface was aged, the trend reversed when the saturate content decreased the oil-wetness of the rock surface while increasing aromatic, resin, and asphaltene contents improved the oil-wetness of the surface.

It was previously hypothesized that the rock composition does not play a significant role in determining the rock surface wettability. The fact that the trendline gradients in Figure 7 were larger than those in Figure 4 confirmed the hypothesis that in the shale oil/brine/rock system, the oil composition is the dominant factor in the surface wettability.

The trend of datapoints at zero day aging time was observed to be the inverse of the aged rock sample data. It was believed that this behavior was caused by the measurement artifact. Due to the water-wetness of the surface, a larger drop volume was needed to detach the drop from the needle and attach it to the surface. The minimum drop volume required for the detachment is a function of density; a lower oil density implies a smaller drop volume and vice versa. A heterogeneous drop volume skewed the contact angle reading with a larger volume creating a smaller contact angle or less oil-wet. This measurement artifact did not exist on aged rock samples as aged rocks had an affinity to the oil, which allowed for easier oil drop placement on the surface.

The trend observed between the contact angle and the four oil components confirmed the applicability of a mutual solubility theory to explain the wetting behavior on shale oil/water/rock systems. Higher aromatic, resin, and asphaltene contents resulted in more crude oil components being initially adsorbed on the rock surface. The initial layer of adsorbed crude oil components then provided additional adsorption sites for the remainder of the oil components, i.e., the nonpolar
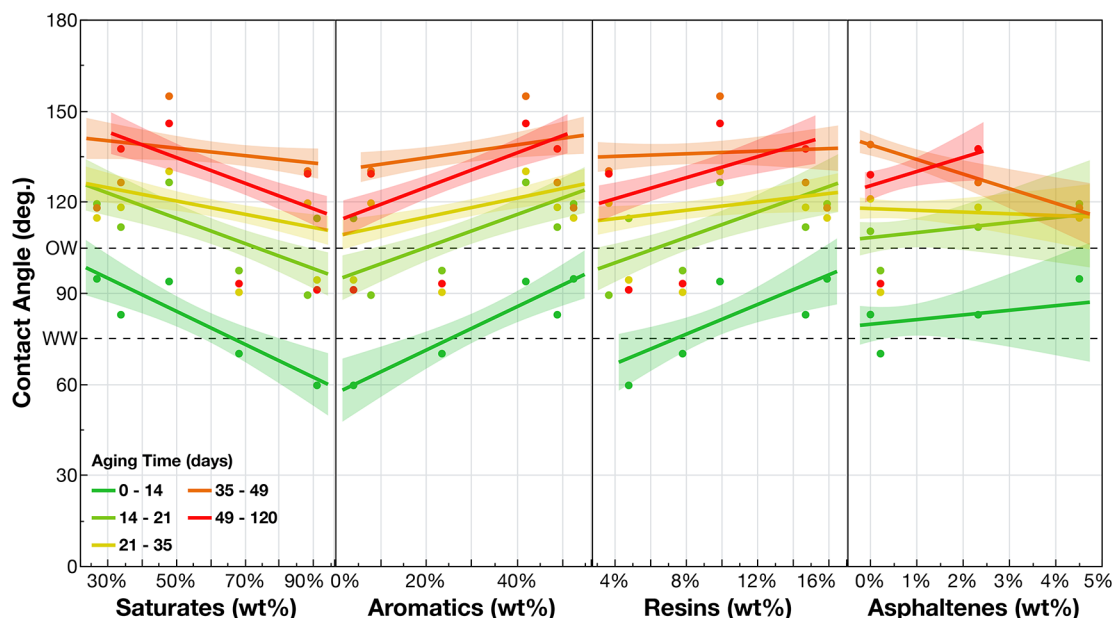
Figure 8. Effect of saturate, aromatic, resin, and asphaltene contents on the surface wettability after a duration of aging. Colors represent the length of the aging duration, green-to-red: zero to 120 days of aging.
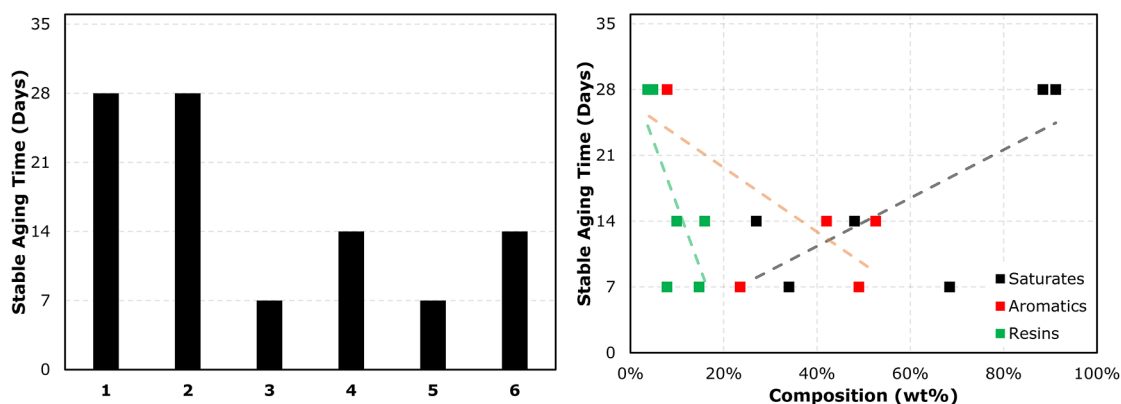

Figure 9. Aging time required to establish stable and consistent wettability for the six crude oil samples (left). Values were obtained from Tukey's analysis with contact angle data grouped by crude oil. The stable aging time is plotted against the saturate, aromatic, and resin content (right).

saturates. Crude oil with lower aromatic, resin, and asphaltene and higher saturate composition lacked the essential initial oil adsorption on the rock surface. Hence, the more water-wet surface is created on these crude oil samples. It is important to note that these high-saturate crude oils still possess the capability to render the surface oil-wet, only to a lesser degree.

Additionally, a significant change in trend gradient was observed at different aging times. At the longer aging time, it was observed that the relationship between the oil composition and the oil-wetness became stronger; steeper trendlines were observed on all four columns in Figure 7 when the aging time was increased. This behavior implied that the adsorption process of the aromatics and resins is strongly influenced by the aging time. Therefore, it is essential to give enough time for the aging process (aging the rock until equal to or more than the optimum aging time) before any further wettability-related experiments. A prematurely aged rock surface would result in a misleading water-wet surface that would strongly affect wettability-related or surfactant studies.

Like the previous part, the rest of the oil/water/rock combinations were added to Figure 7 and are presented in

Figure 8. This figure contains 775 contact angle datapoints from all seven rock samples, all six crude oil samples, and all seven brine samples. The trendlines between the contact angle and saturates, aromatics, resins, and asphaltenes observed in Figure 7 were maintained, unlike the trend reversal observed when investigating the effect of rock mineralogy in Figure 4 and Figure 5. This observation confirmed the dominant effect of the oil composition over the rock mineralogy on the wettability. However, some degree of gradient change from the trendline was still observed. This change was believed to be driven by the brine salinity, which will be discussed in the next part.

The effect of oil composition on the optimum aging time was also investigated. Multiple Tukey's analyses were performed on the contact angle datapoints, which were grouped by their crude oil components beforehand. The summary of the optimum aging time for each of the six crude oil samples is presented in the left graph of Figure 9. The data then were plotted against the content of saturates, aromatics, and resins, the right graph of Figure 9. In comparison to the effect of rock composition on the optimum aging time
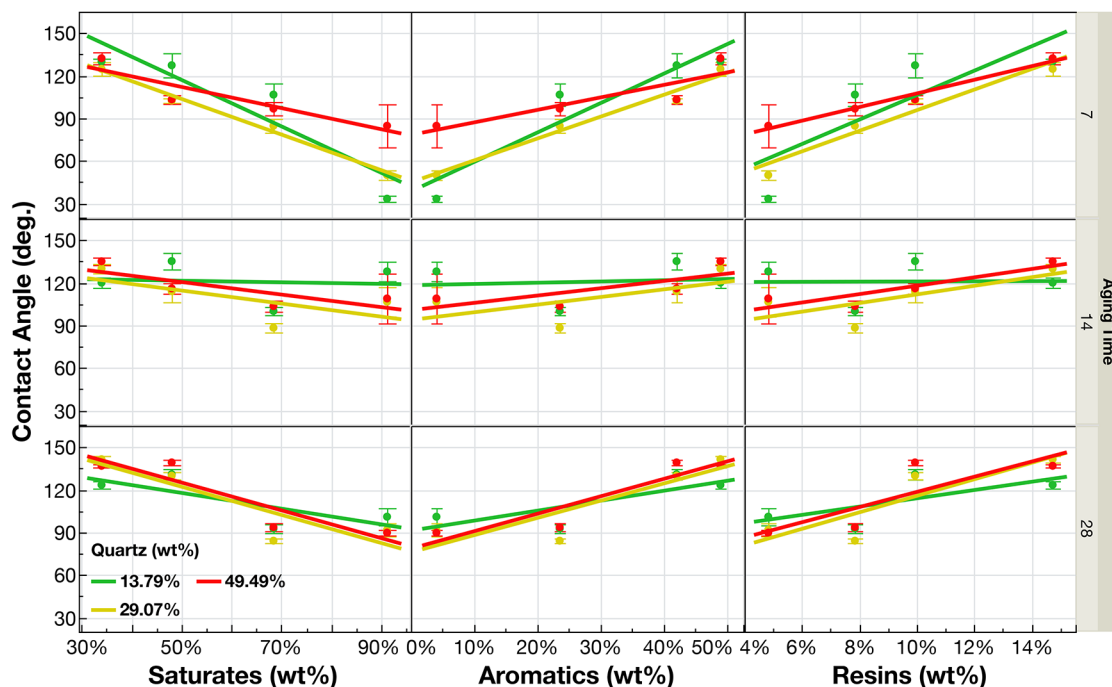
Figure 10. Effect of saturate, aromatic, and resin composition at various quartz contents on the contact angle. This figure was constructed to investigate the interaction between the oil composition and the rock mineralogy to the rock surface wettability.
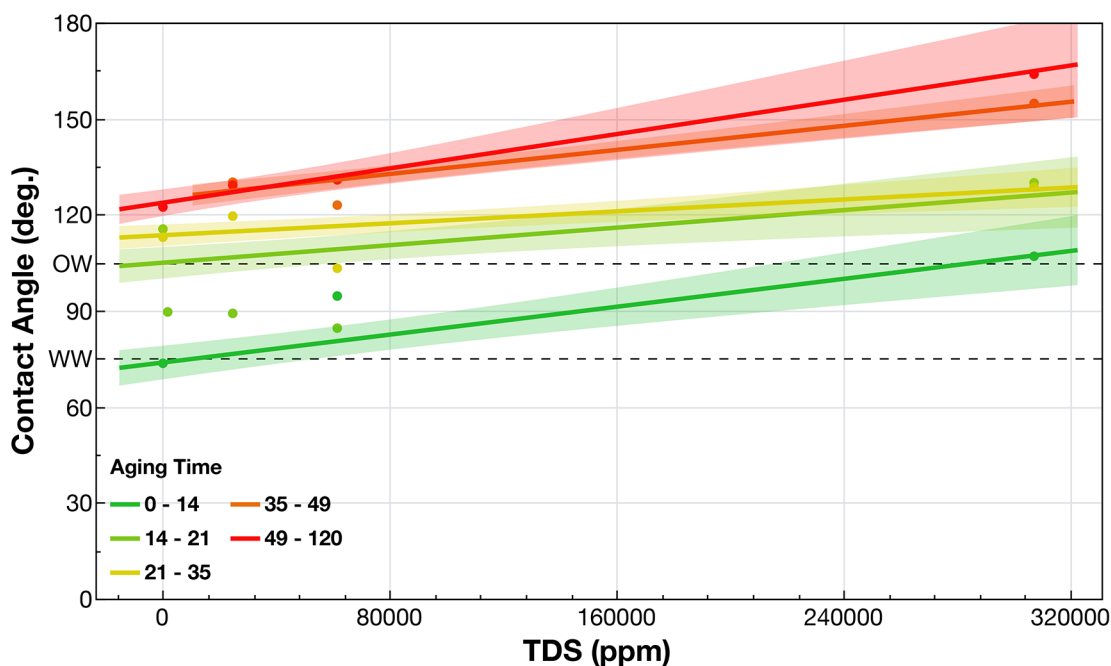

Figure 11. Effect of brine salinity on the surface wettability. Colors represent the length of the aging duration, green-to-red: zero to 120 days of aging.

presented in the right graph of Figure 6, the trend in the right graph of Figure 9 was more dominant. This observation served as another evidence of the hypothesis that the surface wettability is a greater function of the oil composition than rock composition in a shale oil/water/rock system. A larger saturate content increased the required aging time to reach a stable wettability condition, while the presence of more aromatics and resins reduced the time for aging. It was also observed that resins reduced the optimum aging time more

than aromatics, which was indicated by the steeper trendline on resins when compared to aromatics.

The relationship between the crude oil components and the optimum aging time allowed for an insight into the kinetics of the adsorption that renders oil-wetness on the rock surface. A higher concentration of aromatics and resins in the crude oil allows for faster oil adsorption on the rock surface, hence the shorter time needed to reach stable wettability conditions. Additionally, higher Resins composition shortens the optimum
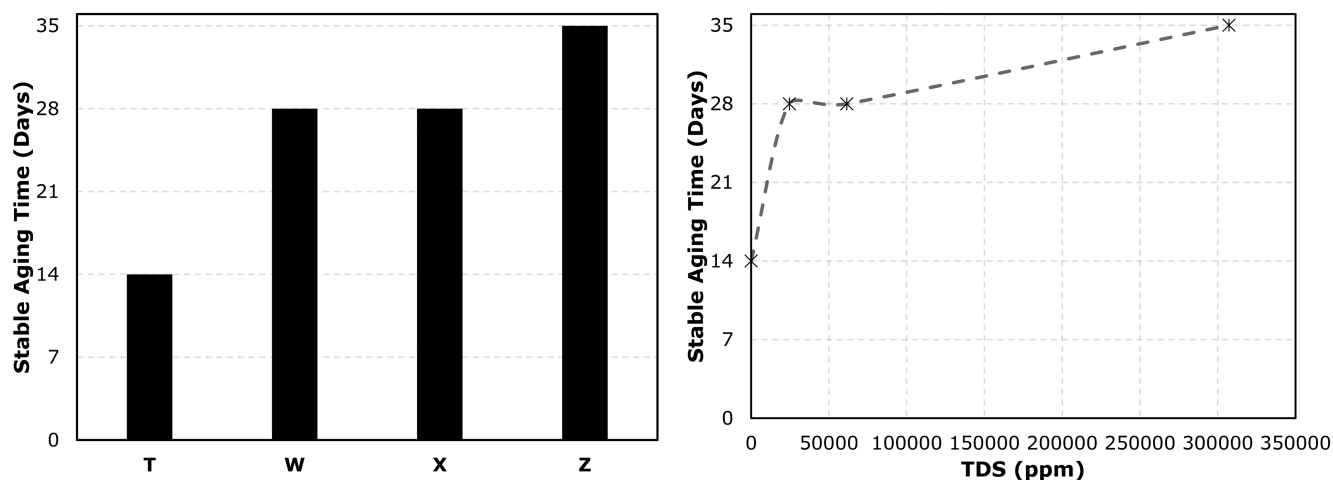
Figure 12. Aging time required to establish stable and consistent wettability for the four brines (left). Values were obtained from Tukey's analysis with contact angle data grouped by brine. The stable aging time is plotted against the TDS (right).

aging time more than the aromatics, which implies that resins in the crude oil cause the greatest oil-wet tendency of a rock surface.

Combined Rock Mineralogy and Oil Composition Effect on Rock Wettability. The effect of both rock mineralogy and oil composition on the rock surface wettability was investigated. To evaluate this, the contact angle data with 7, 14, and 28 days of aging are plotted in Figure 10 against the saturate, aromatic, and resin composition. However, instead of their aging time, the different colors represent the quartz composition as described in the legend. This figure contains 400 datapoints with data from three rock samples (A, B, and C), four crude oil samples (1, 3, 4, and 5), and brine T. Generally, the trends between the contact angle and the three crude oil components were improved at a higher quartz content. The gradient of the positive trend to the composition of aromatics and resins was observed to be larger at a higher quartz content. Similarly, the negative gradient on the saturate content was also observed to be stronger at a higher quartz composition.

In the previous section, a hypothesis of aromatic/resin interaction with the quartz mineral was presented as the main mechanism behind the rendering of surface oil-wetness on shale oil/brine/rock systems. From Figure 10, when both aromatic/resin concentration in the crude oil and the quartz content in the rock were increased, the surface became more oil-wet. Additionally, the individual effect of aromatic/resin concentration on surface oil-wetness was also enhanced when the rock contained more quartz as described earlier. These observations indicated that the aromatic/resin components had a higher affinity to the quartz mineral. The aromatics and resins were adsorbed on the quartz mineral of the surface and created the oil-wet surface, which reaffirmed the hypothesis.

Crude oil sample 5 contains a measurable amount of asphaltene and acid. It is well-established that crude oil with this composition has a higher affinity to the calcite-rich surface, rendering it more oil-wet. A mechanism of quartz-dominated oil-wetness for the shale system was proposed in the paragraph above. However, it was also observed that for crude oil 5, the oil-wetness is driven by the calcite content of the rock. This behavior was only observed with this sample. Additionally, this finding also enforces the statement that crude oil is the

dominant factor in determining the oil-wetness of the shale system.

Salinity Effect on Rock Wettability. The effect of salinity on the surface wettability was investigated. The contact angle data was plotted against the brine salinity (TDS in ppm) (Figure 11). In this figure, 775 datapoints were included, containing all rock, oil, and brine samples presented in the Methodology section. A positive trend between the surface oil-wetness to the brine salinity was observed. Similar to previous graphs, the datapoints were grouped by their aging time, which is presented in colors. Unlike the surface oil-wetness vs oil composition trend in Figures 7 and 8, the trendline gradient in Figure 11 for all aging time was similar. This observation indicated the absence of interaction between the brine salinity and the aging time.

The presence of salt in the aqueous phase increased the polarity of the water when compared to DI water. In an oil/water system, this polarity increment increased oil/water IFT, as has been shown in our previous publication. Subsequent to the aging process, the initially polar surface of the rock is transformed into a nonpolar surface due to the adsorption of polarizable hydrocarbon molecules. On this aged nonpolar surface, increasing the salinity of the aqueous phase causes the increase in the surface free energy of the aged surface in the presence of the aqueous phase since the nonpolar surface repels the increasingly polar brine. On the other hand, the surface free energy in the presence of the hydrocarbon phases remains unchanged. As a result, the surface is more wetting to the nonpolar phase when the brine salinity is increased as presented in Figure 11.

Brine salinity was also observed to alter the optimum aging time. The result from Tukey's analysis on the comparison of aging time under different brine salinities is presented in Figure 12. A longer aging time required to achieve stable wettability conditions was observed in a higher brine TDS. With brine T (DI water), the optimum aging time was 14 days. While when using brine Z, which has more than 300,000 ppm TDS, the optimum aging time was more than doubled to 35 days.

In this study, the aged rock was not in contact with the brine until during the contact angle measurement. This means that at a higher salinity, reassembling of the adsorbed oil layer still occurs at a longer aging time. In our previous work on the interaction of the oil components and the brine salt ions, it was
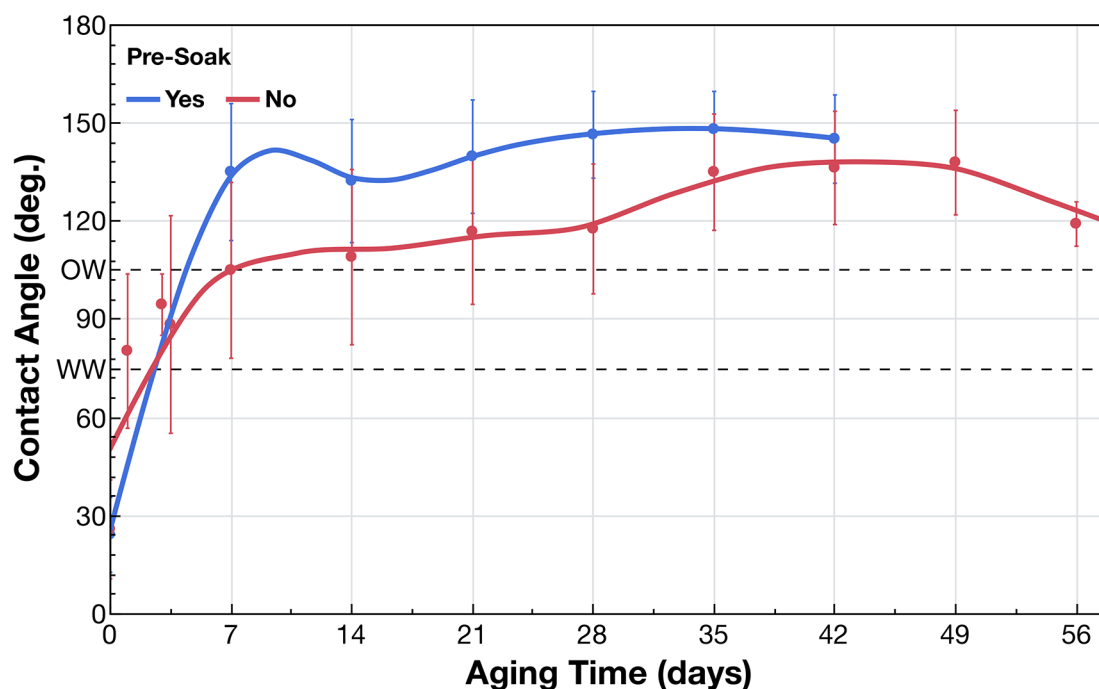
Figure 13. Evolution of the wettability throughout the aging duration for samples with (blue) and without (red) pre-soak.

discovered that the increase in the brine salinity reduced the polarity of the aromatic and the resin components; at a higher brine salinity, these two components lose their ability to reduce the oil/water IFT rendered by the saturates. In the earlier section of this work, it was also established that crude oils with a higher nonpolar saturate content required a longer aging time to reach stable wettability conditions. Based on these two observations, it was hypothesized that the reassembling process of the adsorbed oil layer observed in this section occurred due to the reduction of the polarity of the aromatics and resins in the presence of the brine. As a result, additional adsorption of both components on the rock occurred as they were repelled from the oil/water interface due to the high salinity level. This process kept occurring through-out the earlier aging time, which caused the contact angle to continue increasing. At the later aging time, the amount of aromatics and resins adsorbed on the rock surface hit the maximum. This resulted in the consistent contact angle reading even when the rock was aged longer, or in other words, a stable wettability condition was achieved.

Simulating Reservoir Deposition Process: Brine Pre-soak. The results from the rock samples that were subjected to the brine pre-soak process are presented next. The first analysis performed was to investigate whether the additional step changes the rock wettability. Figure 13 presents the contact angle data evolution from zero to 56 days of aging for both samples with (blue) and without (red) the pre-soak. All 1100+ contact angle data are included in this graph. Before aging in oil, samples that were pre-soaked were more oil-wet; datapoints at zero days of aging show the blue line below the red line. Surprisingly, throughout aging, rock samples with pre-soak were more oil-wet. Student's t-test was also performed comparing the two groups of samples and showed that rock samples with pre-soak were more oil-wet with a significance level of 95%.

Further investigation into the results presented in Figure 13 indicated that the pre-soak process amplifies the trends of the contact angle due to the oil components in Figure 7 and rock mineralogy reported in Figure 4. For example, a higher aromatic and resin content resulted in a more oil-wet surface, as presented in the previous section. However, increasing the aromatic and resin content to the same extent on the pre-soaked rock surface resulted in a larger increase in oil-wetness. It is hypothesized that the ions present in the brine allowed for more adsorption sites for the crude oil components to adsorb. However, further investigation by varying the salt ion content in the brine must be performed to prove this hypothesis. Nevertheless, this result showed that even though the rock surface was pre-wetted or pre-soaked in its respective brine, the rock surface remained oil-wet after the aging process. The rock surface was even more oil-wet when it was pre-soaked before the aging process.

Tukey's analysis to determine the optimum aging time was performed on the pre-soaked data. The optimum aging time was reduced from 35 days for samples without pre-soak to 21 days, as shown in Table 6. However, upon further investigation, under some range of rock mineralogy, crude oil composition, and brine TDS, the optimum aging time for

Table 6. Tukey's Analysis to Determine a Minimum Aging Time for Stable Wettability for Samples with Pre-soak (CI = 95%)

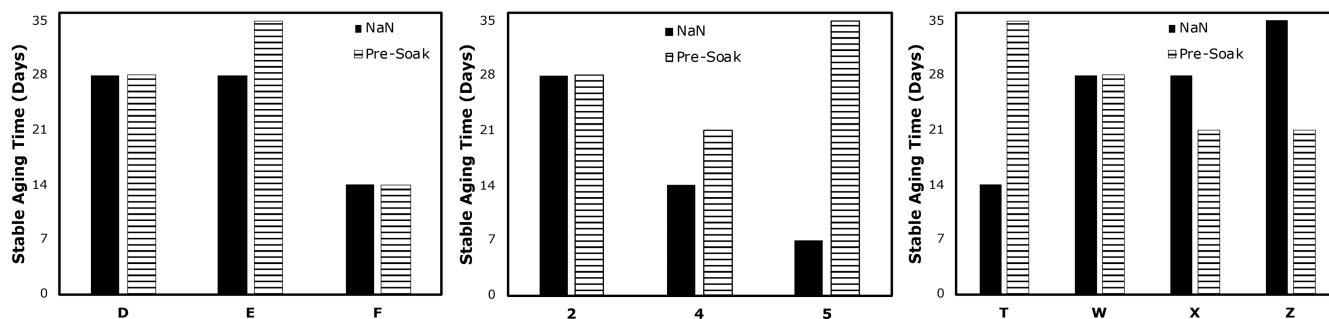| aging time (days)				mean
35	A			148.12429
28	A			146.48980
42	A	B		145.17727
21	A	B	C	139.81111
7		B	C	135.08649
14			C	132.34554
0				D 24.21915

Figure 14. Comparisons of aging time required to reach stable wettability for samples without and with pre-soak. The left graph was generated by averaging on the reservoir rock samples. The middle graph was generated by averaging on the crude oil samples. The right graph was generated by averaging on the brine.
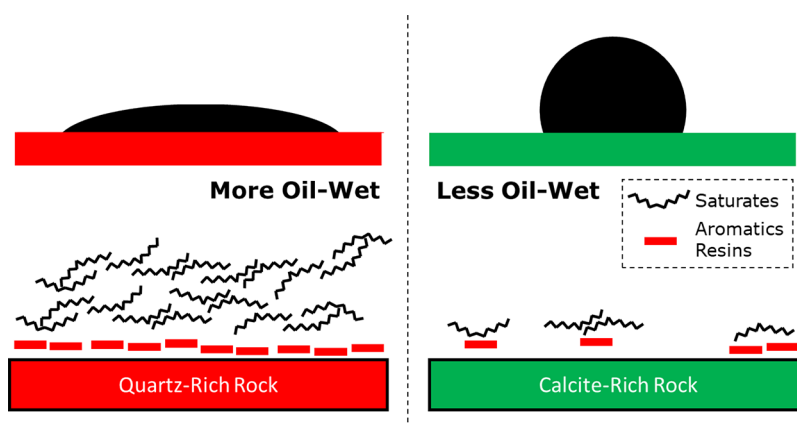

Figure 15. Oil-wetting mechanism for shale oil reservoir oil/brine/rock systems.

samples with pre-soak was longer than those without. Rocks with higher carbonates-to-quartz ratios were observed to lead to a longer optimum aging time when pre-soaked (left figure of Figure 14). Crude oil with a higher aromatic and resin content was also observed to require an extended optimum aging time when the rock samples were pre-soaked (middle figure of Figure 14). A higher brine salinity, on the other hand, was observed to reduce the optimum aging time for pre-soaked samples (right figure of Figure 14).

SUMMARY

In this study, the surface wettability of shale oil/brine/rock systems was investigated by analyzing two experimental variables: the final wettability and the aging time required to reach stable wettability. The first variable determined the magnitude of the wettability and the second one determined the kinetics. Five control variables were included to have a better understanding of the mechanism behind oil-wetness: aging time, rock mineralogy, oil composition, brine TDS, and brine pre-soak.

In this study, shale systems from both the deeper and the shallower section of the Eagle Ford, Wolfcamp (carbonate-rich and silica-rich facies), and Bakken were tested. All shale oil/brine/rock systems investigated in the course of this work are oil-wet. The contact angle measured through the water phase averages above 110° after sufficient aging time.

It was observed that rock mineralogy played a minimal role in determining surface wettability. To some extent, a higher quartz content resulted in a stronger oil-wetness, whereas a higher carbonate content rendered the surface less oil-wet.

This behavior is the opposite of what previous studies have shown. It is hypothesized that the absence of asphaltene and organic acid in the shale crude oil was the reason behind this observation; most wettability studies in the literature were performed on conventional reservoir systems with high asphaltene and organic acid contents.

The oil composition strongly determined the level of oil-wetness of a shale oil/brine/rock system. Higher aromatic and resin contents rendered the surface more oil-wet, while higher saturates resulted in a less oil-wet surface. These crude oil components are more polarizable when compared to the saturate component of the crude oil, resulting in more adsorption on the more polar clean rock surface as observed. It is hypothesized that, once adsorbed, the aromatic and resin components of the crude oil act as adsorption sites for the more nonpolar component of the crude oil, i.e., the saturates, allowing for more crude oil to be adsorbed on the rock. In conjunction with the more oil-wet surface observed on the quartz-rich rock, this strongly implies that the aromatics and resins have a greater affinity to quartz compared to carbonates.

The proposed mechanism behind the oil-wetting of a shale system is encapsulated in Figure 15. The cartoon shows that the aromatics and resins of the crude oil are adsorbed more on the quartz-rich surface. The adsorbed aromatics and resins then serve as adsorption sites for the saturate components of the crude oil. As a result, more oil is adsorbed on the quartz-rich surface, rendering the surface more oil-wet. On the other hand, a carbonate-rich surface has a significant polarity contrast to the shale crude oil due to the absence of asphaltenes and

organic acids in shale crude oil. Therefore, less adsorption of oil occurs, and a less oil-wet surface is created.

A higher brine salinity renders the rock surface more oil-wet. It is hypothesized that the increasing polarity of the aqueous phase forces the aromatics and resins away from the oil/water interface, increasing their adsorption on the rock surface. This results in a more oil-wet surface as was observed for all contact angle experiments.

Generally, a minimum aging time of 35 days was required to achieve a stable surface wettability where the contact angle no longer changes. This number was derived by performing Tukey's analysis on various aging times and this analysis allows determination of the earliest aging time for which there was no significant change observed in contact angle with a significance level of 95%. Under certain conditions, the 35 day rule could be reduced, i.e., when the crude oil contains more aromatics and resins, thereby forcing these components to partition to the surface faster. At a higher TDS, the reassembling process of the adsorbed layer at the rock surface occurs whereas when the brine TDS is low, it does not occur, thus requiring a lower amount of time to reach a stable wetting condition.

The final observation relates to pre-soaking the sample in brine before aging in crude oil. A rock surface that was pre-soaked in its respective brine maintained its oil-wetness after aging in its corresponding oil. This result is important as it showed that the shale surface maintains its oil-wetness even when it is pre-wetted with brine.

CONCLUSIONS

In this study, we investigated the wettability of oil/brine/rock systems that encompasses the property distribution of Lower 48 shale. Shale oil/brine/rock systems in all reservoirs and even the multiple facies in each reservoir investigated (Wolfcamp, Eagle Ford, Three Forks and Middle Bakken) were observed to be oil-wet with contact angles averaging above 110° after sufficient aging time. Samples were aged to recover the initial wettability of the reservoir. We have established that an optimum aging time of 35 days was required to achieve a stable wettability condition on the shale oil/brine/rock systems. We aim to use this as a guideline as the aging time of shale samples in the literature is extremely heterogeneous, from none to up to 365 days. Additionally, the effect of pre-wetting the rock surface with the aqueous phase to the surface wettability was also explored. We found that pre-soaking the samples with brine actually expedites the rate of oil wetting and increases the ultimate degree of oil wettability as determined by contact angle measurements.

The effects of rock mineralogy, oil composition, and brine salinity to the surface wettability were also investigated. The rock with a higher quartz content (50%) created a more oil-wet surface with no effect on the optimum aging time. Oil with a higher concentration of aromatics and resins rendered the surface more oil-wet and reduced the optimum aging time. These two crude oil components were major drivers of the creation of an oil-wet surface on the shale oil/brine/rock systems investigated. Brine with a higher salinity resulted in a stronger oil-wetness and increased the time required to achieve stable aging. A higher brine salinity resulted in an aqueous phase with a stronger polarity, which forces the aromatic and resin components of the crude oil to be more adsorbed on the rock surface. In this study, oil composition and brine TDS affected the surface wettability to a greater degree compared to the rock mineralogy.

Based on the data compiled in this study, a mechanism behind the oil-wetting properties of shale systems was proposed. The aromatic and resin components of the crude oil were observed to form stronger bonds with the quartz minerals associated with the rock (Figure 10), which resulted in more oil-wetness. The new mechanism will be used to optimize surfactants for wettability alteration purposes of the shale reservoir in our future work.

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Notes

The authors declare no competing financial interest.

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