RESEARCH ARTICLE OPEN ACCESS

Study of the effect of Illite and Kaolinite on low salinity water injection

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Abstract:
Low salinity water flooding as an Enhanced Oil Recovery (EOR) Technique refers to the injection of brine with a lower salt content or ionic strength into an oil reservoir. Although the mechanisms have not yet been verified, the solution and surface chemistry as well as rock/fluid interactions have important roles that can be attributed to reservoir minerals being sensitive to small changes in solution properties.

Among the proposed mechanisms, the clay content of rock and type of clay has been of significant interest in shedding light on the low salinity water flooding process. In this paper, two clay types (illite and kaolinite) have been selected to investigate the individual contribution of each on the rock surface characterization andlow salinity water flooding performance.

The results from contact angle measurement on the oil-wet calcite by low salinity water at room temperature show that the presence of low content of illite in the rock materials, in contrast to the kaolinite, reduces the contact angle significantly. This observation demonstrates that the low salinity water flooding performance depends strongly on the type of clay not on the amount of clay.

I. INTRODUCTION

Due to the low costs as well as less harmful environmental impact, low salinity injection has great potential to improve oil recovery. Jerauld et al. (2008) showed that low salinity injection can increase the water flood performance from 5% to 38%. However, the biggest challenge of low salinity injection is to understand how this process works in the oil production process. It has also been demonstrated that the presence of clay minerals in the sedimentary rocks has an important impact on wettability. As a result of the adsorption of resins and as phaltenic species known as polar components on the rock surfaces, most oil reservoirs andespecially carbonate reservoirs are oil-wet.

Studies have shown that clay minerals such as kaolinite, chlorite, and smectite contribute to the wetting state of reservoir rock for being preferentially oil-wet or water-wet(Skrettingland et al., 2011). Therefore, it is imperative to know how and to what extent these types of clay minerals affect the wettability.

It has been proposed that lowering the concentration of salt ions in the injection brine can increase the oil recovery. This is reflected by the reduction of the contact angle from 48 degrees to 29 degrees for a carbonate rock caused byareduction of salinity from 50,000ppm to 10,000ppm in injection brine (Romanuka et al., 2012).

The change in contact angle is attributed to the cationic exchange process of low salinity water with the clay mineral. In the low salinity water-flooding (LSW) divalent ions such as Ca^{++} and Mg^{++} are adsorbedby the clay minerals; resulting in a modification of the wettability (Dang et al., 2013). Boussour et al (2009) proposed that polar components are attached to the negatives clay minerals in the reservoir by cation exchange; however, when low salinity water is injected, the adsorbed polar components are substituted by the cations present in the low salinity brine and the reservoir will became more water-wet. Berg et al. (2010) proposed that for sandstone rock the cation exchange between the oil and the reservoir is present; however, the double layer expansion is the most important factor which governs the wettabilityalteration.

The objective of this paper is to investigate the individual performance of clay materials (type and content of clay) on the carbonate rock surface wettability alteration by three different brines, from high to low salinity concentration. The clays, which are used in this investigation, are illite and kaolinite.

II. BACKGROUND ON ROCK SURFACE CHARACTERIZATION

Wettability is defined as the preference of a liquid to cover a solid surface. Reservoir's wettability is an important factor used to calculate oil recovery efficiency and residual oil saturation through water injection. Nasralla et al. (2011) suggested that wettability is an imperative aspect affecting water and oil distribution in the reservoir. According to their research, the wetting phase of the rock is determined by the following factors: oil composition, the chemistry of the rock surface and the characteristics of the aqueous phase.

The contribution of otherfactors such as temperature, pressure, as well as injected fluids may result in wettability alteration of rock surfaces.Hjelmeland and Larrondo (1986) proposed that temperature affects the interfacial forces between oil/water; water/rock and oil/rock which in turn results in a wettability alteration. Hamouda and Rezaei Gomari (2006) studied the effect of the temperature on carbonate rock. Their experiments showed that when the temperature increases, the contact angle decreases. The summary of work performed by Hamouda and Rezaei Gomari is presented in Figure 1. As it can be seen from the three presented trend lines, for all three tests the trend-lines were polynomial (second order) and theR-squared values were higher than 0.99 which means that the variation of the contact angle versus the temperature might follow a polynomial function.

In addition to temperature, the ions concentration of the injected water can alter the rock surface wettability significantly. Nasralla et al (2011) have studied the effect of ions using aquifer water at elevated temperatures. Three brine compositions having 10 fold differences in total dissolved salt are examined by the researcher; table 1 shows the ion concentration of the brines. The experiments were developed with a pressure equal to 1000 psi and three different temperatures of 60 ^{0}C, 100 ^{0}C and 121 ^{0}C. Figure 2 shows how the contact angle changed from its original value when aquifer water was injected. Their study showed that the highest reduction in the contact angle was obtained for a system owing highest temperature with lowest salinity, hence the rock wetting state altered towards more water-wet.

Surface potential can be utilized to understand the rock surface characterization. Components in the crude oil adsorb on the reservoir rock; this absorption affects the rock wettability, relative fluid permeability, electrical properties and recovery efficiency (Kakadjian et al 2007). The surface potential between the solid and the fluid interface is discussed by Street and Wang (1966) based on the Cationic Exchange Capacity (CEC)theory.

The concept of zeta potential has been used by Alotaibi et al. (2011) to explain the rock surface charge and zero point charge for kaolinite, illite and chlorite. The experiments were developed to study the influence of seawater, aquifer water and deionized water on different clays and sandstone at 25 ^{0}C. According to the experiments performed by Alotaibi et al., kaolinite, illite and chlorite in all solutions present anegative charge except forchlorite which shows a positive charge in the presence of seawater. The results can be seen in figure 3.

Clay minerals, which are inherently present in the reservoir rock, are studied to determine the reservoir quality, the hydrocarbon emplacement time and the petroleum system (Jiang, 2012).

Kaolinite is the most common mineral in the kaolin group. The chemical composition of the kaolinite is $Al_2\,Si_2\,O_5\,(OH)_4$.Low-defect kaolinite and high-defect kaolinite are the two types of kaolinite; low-defect kaolinite has a low crystal structure defect and high-defect kaolinite has an abundant structural defect (Kogel et al, 2002). In general, kaolinite has a large concentration of hydroxyl groups on its surface. Due to the hydroxyl groups, kaolinite is susceptible to contact with asphaltenes (Bantignies et al. 1997). In oil-saturatedsandstone, the presence of kaolinitein the rock will produce an oil-wet preference for the reservoir (Lebedeva et al, 2010).

Illite is a part of the mica group and it is produced by the smectite dehydration, changing from montmorillonite to beidellite to illite (Galimberti, 2011). The chemical composition of the illiteis M_x $(Si, Al)_8$ $(Al, Fe, Mg)_4$ O_{20} $(OH)_4$ where M is the interlayer cation and x is the layer charge (Sposito, 2008). In oil-saturated sandstone, this type of clay is characteristically preferentially wetted by water. This hydrophilic characteristic of the illite is the result of the presence of cations in the clay surface (Bantignies et al. 1997).

III. METHODOLOGY

Materials: The solids used in this study were: calcium carbonate, two different types of clay (illite and kaolinite), stearic acid and three different brine compositions. Calcium carbonate was supplied by BDH chemical in the form of powder with the purity of 98%. No impuritiesreported with the supplied kaolinite while illite consisted of silicon dioxide, aluminium (III) and calcium oxide. Stearic acid ($C_{18}H_{36}O_2$) which is represented as a dissolved acidic species in the model oil(n-decane); has a molecular weight of 284.48 gr/molwith apurity of 95%. The selected salts utilized to make the synthetic brine are sodium chloride, magnesium chloride and sodium sulphate.

The purity of supplied n-decane ($C_{10}H_{22}$) by Sigma-Aldrich Company was higher than 95%.

Rock sample preparation: Table 2 presents the mixture characteristics of different powder samples (P1 to P6) in this study. A top hot plate stirrer was utilized to blend the distilled water, the calcium carbonate and the illite or the kaolinite. The stirring was developed with medium rotation agitation (45 rpm/min) and the stirring time was approximately 2 hours. The suspension liquid was filtered and then dried at 105 ^{0}C for 24 hoursin the oven. The wettability of dried samples was modified to oil-wet using 0.001 M stearic acid in n-decane. 25g of powderwas added for every 100 ml of acidic oil model.

Brine preparation: Table 3 shows the three synthetic brine compositions used in this work (B1 to B3). B1 represents the main salt components of sea water followed by B2 and B3. The salt content of brine compositions for B1 and B2 was lowered significantly (about 10 and 100 folds respectively) to be able to investigate the low salinity effects on wettability of carbonate rocks in the presence of clay content.

Contact anglemeasurement: The contact angle measurements were executed on the different samples. The method utilized to determine the contact angle was air water and powder surface interface. This method provides a fast way to measure the contact angle. A small amount of powder, around 1 to 2 grams, is placed and squished onto a microscope slide. A droplet of distilled water is placed onto the powder surface. A picture is taken to measure the contact angle on the computer. For each sample, the contact angle was measured three times to ensure reaching the precise value. It is important to point out that the contact angle was calculated from a picture on a computer from each measurement and the result could be affected by the resolution of the picture and also the visual accuracy of the human eye.

IV. RESULTS AND DISCUSSIONS

Clay effect: The presence of clay in the lattice of carbonate rocks and its effect on wettability was studied using contact angle measurements on treated calcite powder. The sample compositions are given in table 2. As it can be seen the amount of clay is investigated individually and clay content is increased systematically from 5% to 15 %.

Results show that the clay concentration, depending on the type of clay, has different effects onthe wetting state of calcium carbonate. Figure 4 shows a comparison between the measured contact angle on the treated calcium carbonate in the presence of different concentrations of illite and kaolinite. In the case of illite, when the percentage of added clay to the calcite increases from 10 % to 30 % the measured contact angle on the treated calcite reduces from 140^0 to 109^{0}respectively. This behavior can be related to the hydrophilic characteristic of the illite. The hydrophilic characteristic of illiteis the result of the presence of cations in the illite surface. The cations make the calcium carbonate less prone to becomingoil-wet within the treatment process using model oil.In fact the ability of $Ca^{2+}$to adsorb carboxylic ions reduces in the presence of received cations from illite.

In the case of kaolinite, as illustrated in Figure 4, insignificant changes in contact angle measurements were observed when increasing the kaolinite concentration. This is an interesting observation since kaolinite consists of hydroxyl groups (R-OH) which could contribute to the wetting state; however, no effect was recorded with the studied concentration. Moreover, the results presented in Figure 4, demonstrate that samples mixed with kaolinite havea higher contact angle than illite. From these observations, it can be concluded that reservoirs with higher concentration of kaolinite are more likely to beoil-wet than reservoirs with low kaolinite. However, reservoirs containing illite may be less disposedtowards being oil-wet. To reach a clear conclusion, these results would require further field testing and analysis.

Low salinity effect in the presence of clay:The effect of water composition on wettability of carbonate rocks in the presence of 10% concentration of clay was studied by measuring the contact angle. The study performed using three brine compositions of high salinity (B1), medium salinity (B2) and low salinity (B3) as presented in Table 3. The total dissolved salt (TDS) for B1, B2 and B3 are 22,716 mg/l, 2,304 mg/l and 230.4 mg/l respectively. The results are shown in Figures 5 and 6.

As it is demonstrated in these figures, suppressing the salt content reduces the measured contact anglesfor both clay types at 10% concentration in the calcium carbonate. The post treating of modified calcite owing10% illite with high salinity brine (B1) reduced the contact angle from 144 to 52 degrees while in thecase of kaolinite, the contact angle drops down from 138 to 66.

These results indicate that the presence of salt modifies the oil-wet calcite surface to water-wet. However, the decrease in contact angle and hence the alterationto water-wetness can be greater if the salinity of the water isdecreased further. This is illustrated in Figure 5 where the measured contact angle on post treated modified calcite surfaces owing 10% illite and 10% kaolinite concentration by B2 (salinity lowered about 10 folds compared to B1) is 37 and 46 degrees, respectively. Further reduction of salinity to about 100 folds compared to B1,reducesthe contact angle to 31 and 32 degrees for post treated samples by B3. The measured contact angles resulting from the low salinity water can be translated intoastrongly water-wet system.

Figure 6, shows the total change in the measured contact angles for the three studied brine compositions. As it can be seen, the highest variation in the contact angle was obtained for the post treated modified calcium carbonate mixed with 10%

kaolinite by B3 which clearly indicates the effect of low salinity in wettability alteration of carbonate rocks.

The comparison between calcium carbonate mixed with 10 % kaolinite and 10% illite from figure 5shows that the presence of 10% kaolinite results in a higher contact angle than the sample with 10% illite. However, figure6shows that the sample with 10% kaolinite has higher variation in the contact angle than the illite when they were treated with lowest salinity water (B3). This illustrates that the kaolinite could be more easily modified by low salinity brine than the illite in a calcium carbonate system.

V. CONCLUSIONS

1. Type of clay and its concentration have a significant effect on wettability alteration of carbonate rocks.
2. The presence of illitein the calcite powder increases the water-wetness of the calcite surface which is attributed to the hydrophilic characteristic of the illite. However, the kaolinite did not produce a significant change in the calcium carbonate wettability when this clay concentration increased.
3. The results showed that lowering salt concentration in the synthetic brine results in a more water-wet system. The strong alteration towards water-wetness reported from modified calcium carbonate mixes with 10% kaolinite treated with the lowest salinity concentration.
4. The higher rate of the contact angle alteration in 10% kaolinite compared to 10% illite suggests that the kaolinite could be more sensitive to be modified by low salinity brine than the illite in a calcium carbonate system.

ACKNOWLEGMENT

The author would like to offer sincere thanksto the laboratory technicians at Teesside University's Chemical Departmentfor theuse of the facilities and the considerable assistance offered during the execution of this project.

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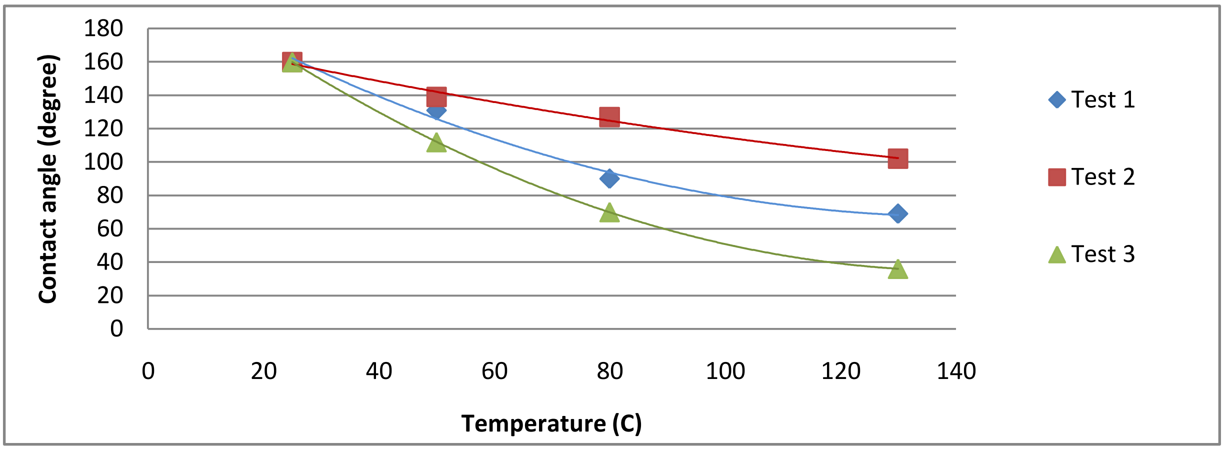

Figure 1: Effect of temperature on contact angle on modified water pre-wet calcite surface aged for 24 hrs in a 0.01M stearic acid in n-decane (Hamouda and RezaeiGomari, 2006).

Table 1: Chemical composition of the seawater (Nasralla and Nasr-El-Din, 2011).

Ions	**Aquifer water (ppm)**	**10% Aquifer Water (ppm)**
Na^+	1,504	150.4
Ca^{2+}	392	39.2
Mg^{2+}	66	6.6
Sr^{2+}	5	0.5
Cl^-	2577	257.7
HCO^{3-}	192	19.2
SO_4^{2-}	700	70.0
Total ppm	**5,436**	**543.6**

Table 2: Samples composition.

Samples elements	**P1**	**P2**	**P3**	**P4**	**P5**	**P6**
Distilled water	200 ml	200 ml	200 ml	200 ml	200 ml	200 ml
Calcium Carbonate	45g	45g	40g	40g	35g	35g
Illite	5g	-	10g	-	15g	-
Kaolinite	-	5g	-	10g	-	15g

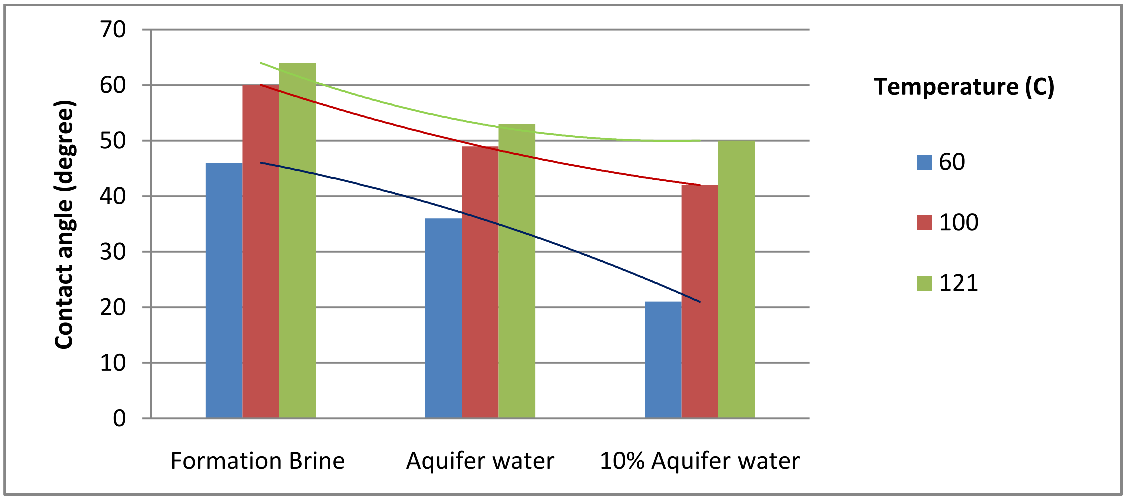

Figure 2: Effect of salinity and temperature on contact angle measurements at 1000 psi (Nasralla and Nasr-El-Din, 2011).

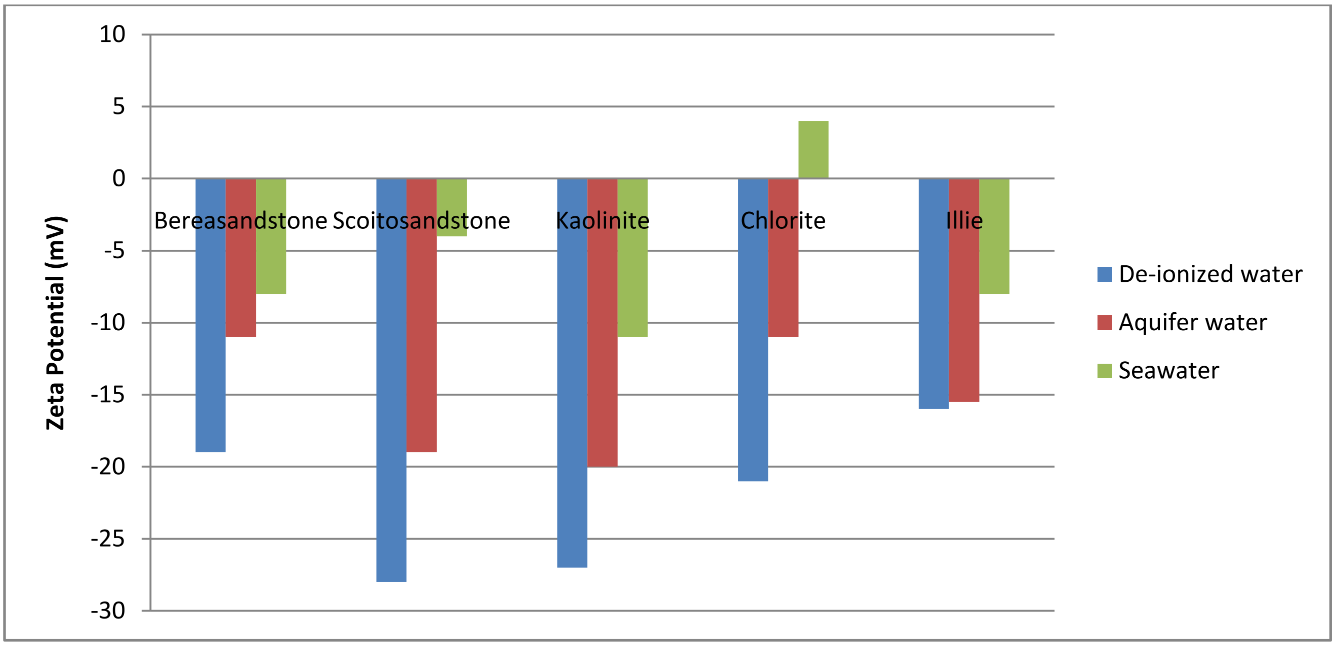

Figure 3: Zeta potential variation for different clays and sandstone (Alotaibi et al. 2011).

Table 3: Composition of studied synthetic brines.

Samples elements	**B1**	**B2**	**B3**
Distilled water	1,000 ml	1,000 ml	1,000 ml
Sodium chloride	16,877 mg	1,504 mg	150.4 mg
Magnesium chloride	2,279 mg	100 mg	10.0 mg
Sodium sulphate	3,560 mg	700 mg	70 mg

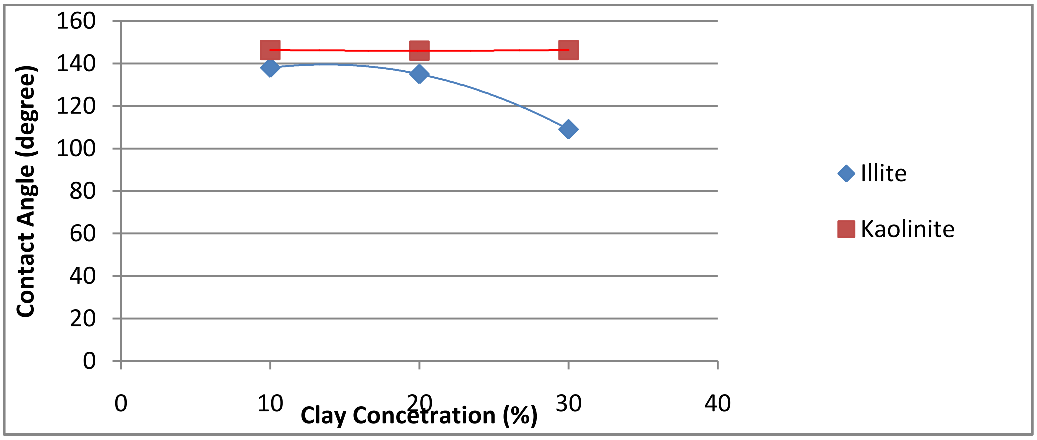

Figure 4: Effect of clay type and its concentration on contact angles for modified calcite surfaces using model oil.

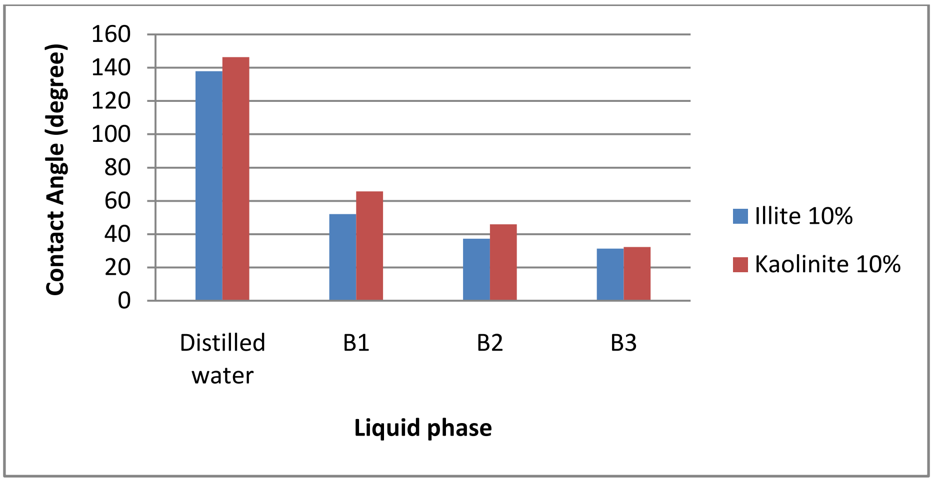

Figure 5: Effect of salinity on contact angle measurements on modified calcite surface in presence of illite and kaolinite.

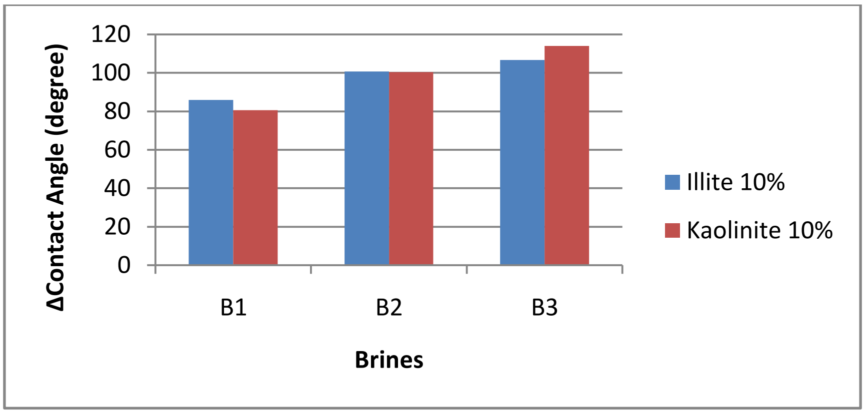

Figure 6:ΔContact angle measurements on calcium carbonate with 10% of illite or kaolinite treated with different synthetic brines. The mixture of calcium carbonate with clay was pre-wetted with model oil.