A New Framework to Quantify the Wetting Behaviour of Carbonate Rock Surfaces Based on the Relationship between Zeta Potential and Contact Angle

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Abstract: This study introduces a new framework to quantify the wettability of powdered carbonate rock from existing correlations between zeta potential and contact angle. The new framework has the potential to be faster and cheaper than conventional approaches and could increase confidence in surface wetting quantification, since the results are insensitive to the inherent heterogeneity of rock surfaces. The obtained results from experiments were used to develop a set of equations for determining the carbonate rock contact angle from streaming potential data. The equations were validated for the evaluation of changes in the wettability of carbonate rock using different stearic acid oily solutions. The contact angles calculated from the proposed equations were then compared with measured values on the calcite surface. The results show that the proposed framework was able to quantify the wettability of carbonate rock with an acceptable range of error of about 4%–14%.

Keywords: streaming potential; contact angle; calcite powder; IFT; stearic acid; wettability

1. Introduction

A full understanding of reservoir wettability behaviour will yield an accurate estimation and the optimization of possible oil recovery [1–6]. Rock/fluid interaction is a major factor influencing wettability in hydrocarbon reservoirs, which in turn affects fluid distribution and flow properties. Conventional methods commonly used in the oil industry to quantify the rock wettability are the Amott-Harvey method, the United States Bureau of Mines (USBM) method, and last but not least, different contact angle measurements. However, all of these methods involve limitations in terms of time, cost, and accuracy, especially when applied to carbonate rock with a tight matrix [7–9].

Carbonate minerals are considered to be highly reactive, since they can easily interact with polar components in oil and aqueous phases, which may result in changes to the wetting state of the carbonate rock surface. The extent of such changes depends on the fluid composition within which the oil-rock interaction takes place. It has been shown that there is strong adsorption of the acidic components of petroleum oil to calcite surfaces in both organic and aqueous systems, which leads to the transformation of the natural water-wetness of calcite surfaces to being oil-wet [10–12].

Surface properties such as electrical charge, morphology, and composition are essential in characterizing the wetting behaviour of surfaces. An understanding of the liquid/solid interface charge described by the zeta potential and its relationship to rock surface wettability can reduce

the uncertainty associated with wettability measurement methods [13–20]. The zeta potential is the electro-kinetic potential measured at the slipping plane located in the diffuse layer that separates the charged surface of the electrolyte solution, and it is considered to be a vital parameter in the monitoring of geophysical sub-surfaces, wettability control, and the adsorption of polar components in aquifers and oil reservoirs [19,21–25].

A reservoir's wettability is affected by electrostatic interactions between the oil/water and water/mineral interfaces. A more water-wet condition occurs when the interaction between crude oil and the rock surface is repulsive, because both interfaces possess the same surface polarity. Conversely, an oil-wet condition will occur when the surface/oil charge polarities differ [23,26–28]. Hence, wettability depends on the attractive van der Waals interaction forces and the repulsive electrical double layer [29]. The surface electrical charge and chemical equilibrium govern the dissolution and solubility of the calcite surface [30–33]. In the presence of a water film, calcium ion dissolution occurs, which leads to the surface having a positive charge so that it is prone to adsorbing negative ions available in the water film. Negative ions could originate from dissolved salt ions in the water phase or the deprotonated form of carboxylic acids (carboxylate ions) in the oleic phase. The adsorption of carboxylic acids onto the calcite forms a strongly chemisorbed complex known as calcium carboxylate, which makes the net charge at the calcite surface negative [11,19,34–37]. In this isothermal process, the adsorption and ion exchange phenomena resulting of mass transfer between solid surface and solution bulk are driven by the higher adsorption energy of the carboxylic acid in relation to the adsorption energy of the water molecules [38].

In the present work, zeta potential and contact angle measurements were conducted in order to understand the relationship between wettability and the electrical double layer in the water/solid and water/oil interfaces. The equations derived from this relationship can be used to predict the wettability of carbonate rock, thereby replacing the laborious conventional methods of wettability quantification. It should be noted that the proposed framework is valid only for the mineral used in this study. The contributions of ions from brine, along with reservoir temperature and pressure, were also eliminated to avoid complications in the proposed equations.

2. Materials and Methods

2.1. Materials

Experiments were performed on the solid surfaces of synthetic calcium carbonate. Calcium carbonate in powdered form with a purity of 99.95% was supplied by the Acros Organics Company (Belgium). The oil phase was composed of stearic acid (supplied by BDH Chemicals Ltd., Poole, England) in *n*-decane (VWR, UK), which constituted the model oil. The model oil solution was agitated by a stirrer for 24 h at room temperature before measurement in order to ensure that a completely homogeneous mixture was used. Deionized water with a conductivity of 1 μs was used as the aqueous phase for all of the tests.

2.2. Methods

2.2.1. Calcium Carbonate Surface Modification

Powdered samples of calcium carbonate were aged in the model oil to allow the surface adsorption of the stearic acid onto the solid samples. The ageing process was undertaken to promote an alteration in the wettability of the powder surface from water-wet to oil-wet. A total of 15 mL of stearic acid in *n*-decane and 5 mL of deionized water were added to 5 g of synthetic calcium carbonate. The dispersion was stirred for 24 h at room temperature. After the equilibration period, the dispersion was filtered in a glass conical funnel using 90 mm Fisherbrand filter paper to separate the solid powder from the liquid phase. The filtered solid material was then dried in an oven for 24 h at 70 °C. The ageing of calcium carbonate was performed in three different stearic acid concentrations of 0.001, 0.005, and 0.010 M in

n-decane, and in pure *n*-decane, with an extra four concentrations for the validation of the proposed equations. The latter acid concentrations were considered to represent a blind test to find the error percentage in predicted contact angles.

2.2.2. Rock Surface Preparation and Contact Angle Measurements

Contact angle measurements were performed on prepared pellets of solid disc made from calcium carbonate powder. The solid samples were manually ground and sieved before being used for disc preparation. The discs were prepared by pressing about 1 g of solid sample, which had previously been aged and dried, using powder press equipment (SPECAC, England). A force equivalent of approximately 9 tonnes was applied for 150 s to ensure uniform surface morphology. The uniformity of the pelleted samples was checked by calculating sample porosity using SEM images. Dewinter Material Plus Software was used to analyse the surface in terms of sample porosity on the basis of images taken from SEM. Figure 1 shows a few examples of these images and their corresponding calculated porosities, indicating the consistency of pelleted sample preparation prior to contact angle measurements. It can be seen that the values of porosity calculated for three prepared samples for unmodified and modified calcite are almost the same, with values of 3.9% ± 0.1 and 1.4% ± 0.1 respectively. Contact angles on pelleted samples were then measured using a Kruss DSA 100 goniometer (Germany). Deionized water droplets were put onto the flat surfaces of the solid discs using a syringe with a micrometric screw. Images of the water droplets placed on the disc surfaces were immediately recorded by Kruss data acquisition software, and the contact angle (CA) was automatically determined.
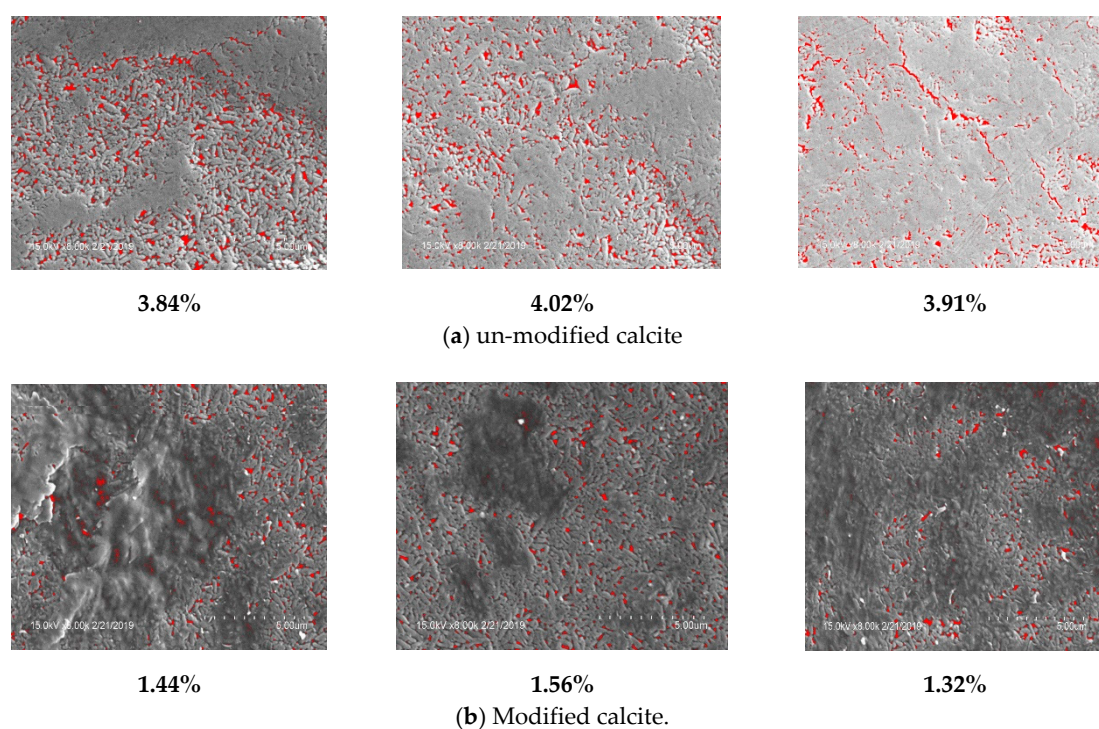

| 3.84% | 4.02% | 3.91% |

(**a**) un-modified calcite

| 1.44% | 1.56% | 1.32% |

(**b**) Modified calcite.

Figure 1. Calculated porosity of two sets of pelleted samples using 0.005 M stearic acid in *n*-decane: (**a**) un-modified samples; (**b**) modified samples.

2.2.3. Zeta Potential Measurements

The zeta potential (ZP) was determined using a Sur Pass electrokinetic analyser (Anton Paar, UK) at room temperature. Measurements of surface potential were performed for the same samples as those used for CA measurements.

2.2.4. Interfacial Tension (IFT) Measurements

The IFT between the model oil with distilled water was measured using a Tensiometer (K9 Kruss GMBH). The aim of the IFT measurements was to find the critical micelle concentration (CMC), at which the two phases experience the lowest forces due to the presence of stearic acid as a surface-active component. In addition, the behaviour of the contact angle at different values of carboxylic acid concentration in the model oil was validated with the interfacial tension data [39].

2.2.5. Scanning Electron Microscopy (SEM)

SEM images were obtained using an FEI Quanta environmental scanning electron microscope (ESEM). Samples were prepared by spreading calcite powder in both modified and unmodified forms on carbon tape mounted on to a metal stub, followed by sputter coating with gold to reduce charging effects under the electron beam. To acquire high-resolution SEM images, a JEOL JSM-7401F (cold-field emission SEM (FESEM)) with an Everhart–Thornley secondary electron detector was used. In this case, samples were placed on a conductive surface but left uncoated.

3. Results and Discussion

The relationship between contact angle and the surface potential of calcium carbonate with different wetting behaviour was first investigated on powdered calcite modified to an oil-wet state using a model oil containing various concentrations of stearic acid. It should be noted that the adsorption of stearic acid onto the calcite surface is significantly affected by the presence of water, as shown in previous research [12,40–43]. In this work, the adsorption of stearic acid was facilitated by the application of two concepts. Firstly, the rock samples used in this study were in powdered form, which significantly increases the surface area and provides a larger available surface for interaction with the stearic acid from the model oil. Secondly, the presence of water promotes the dissolution of calcium carbonate, which in turn enhances the availability of Ca^{2+} to interact with the acid hydrophilic carboxylate group ($RCOO^-$). Figure 2 illustrates the interaction between stearic acid and calcium carbonate in a three-phase system.
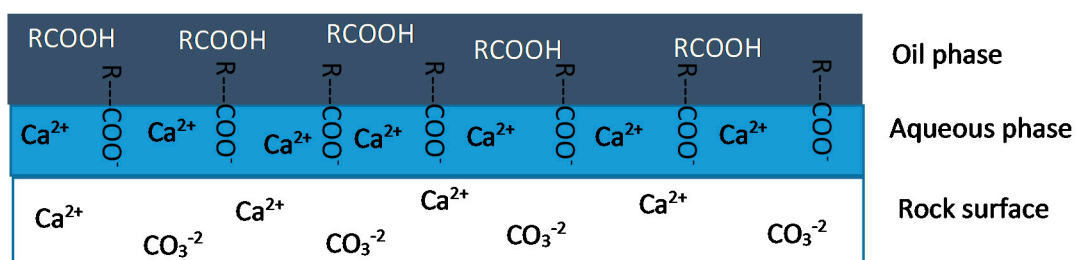

Figure 2. Simple schematic to illustrate the interaction between stearic acid and calcium carbonate in a three-phase system.

3.1. Contact Angle Measurements

After calcite powder was modified with the model oil containing stearic acid, a plate disc was made from the calcite powder in order to perform contact angle measurements. Figure 3 presents the results of contact angle measurement taken on a calcite surface modified by three concentrations of stearic acid. Since the surface of the calcite was prepared using a high-pressure press, an attempt has been made to investigate the impact of droplet relaxation time using the prepared disc. As can be seen for all three cases, the contact angle decreased slightly over time but not to a significant extent, which implies the reliability of the prepared calcite discs for contact angle measurements. The contact angles reported in this paper were taken after approximately 180 s of droplet relaxation and are defined as the average values for the pellets. The reported data for each case are the averages of three droplets placed at three locations on the surface, shown with error bars for each contact angle point versus time.

In this work, a low contact angle represents a more water-wet tendency, whereas high contact angles represent more oil-wet behaviour. The average value of CA for the 0.001 M stearic acid case was found to be 85°, representing a weakly water-wet calcite surface. The results obtained are consistent with previously published data for the same carboxylic acid concentration [40], but on calcite surfaces which were prepared using different approaches. Increasing acid concentration from 0.001 M to 0.005 M and 0.010 M resulted in increases in contact angle by 8° and 22° respectively, representing weakly oil-wet and oil-wet calcite surfaces. As shown in Figure 1, the presence of carboxylic acid in *n*-decane enhances electrostatic attraction at the oil/water interface, which collapses the thin film, and polar components then come into direct contact with the rock surface. A higher concentration of stearic acid therefore results in increased contact angle. Similar arguments about modifications in the wettability of calcite surfaces due to dissolved polar components in oil have been reported elsewhere [12,17,30,44].
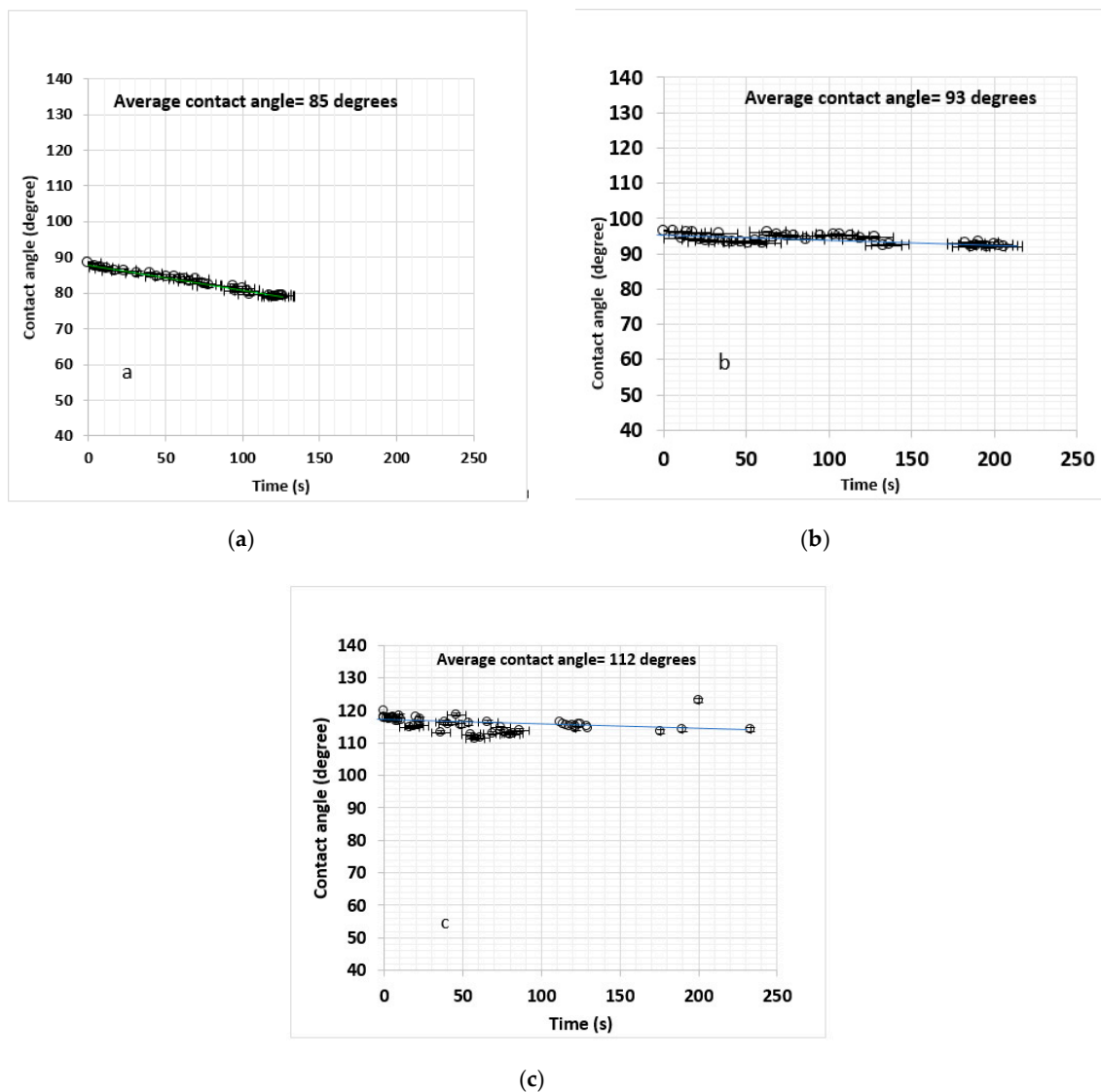

(**a**)

(**b**)

(**c**)

Figure 3. Contact angle of water droplet on calcite, the surface of which was modified by stearic acid in an *n*-decane model oil containing: (**a**) 0.001 M stearic acid; (**b**) 0.005 M stearic acid; and (**c**) 0.010 M stearic acid.

3.2. Scanning Electron Microscopy (SEM) Analysis

In this work, all contact angle measurements were performed on pellets prepared from powdered samples. The adsorption of carboxylate ions onto the calcite surface, and hence the formation of

calcium stearate, is considered to be the main reason for the calcite surface becoming more oil-wet. SEM was used to demonstrate calcium stearate formation on the surface, as illustrated in Figure 4. The SEM micrograph in Figure 4a for calcium carbonate aged in pure *n*-decane without stearic acid shows the absence of deposits on the surface, meaning that pure *n*-decane has a very small or no impact on the calcite surface. On the other hand, Figure 4b shows calcite crystals after treatment with stearic acid at a low concentration of 0.001 M. The presence of stearic acid in the *n*-decane can be seen to result in the formation of small deposits over the surface which are assumed to be calcium stearate.

This is in agreement with the contact angle measurement of 85°, which indicates a change in wettability from water-wet to weakly water-wet calcite surface. Under these conditions, however, the surface is not yet saturated and more Ca^{2+} ions are available to interact with $R-COO^-$ ions from dissociated stearic acid molecules in the water film. Therefore, increasing the stearic acid concentrations to 0.005 and 0.010 M leads to the enhancement of calcium stearate deposition on the surface, making the surface more oil-wet, as shown in Figure 4c,d respectively. It is also noticeable that the morphology of deposits on the calcite crystals in Figure 4b is clearly different from that in Figure 4c,d, which can be attributed to their ability to hold the water and oil in their structure. The latter two images of calcite crystals with stronger affinity for holding oil present a clear coverage of deposited oil with a higher density of calcium stearate.
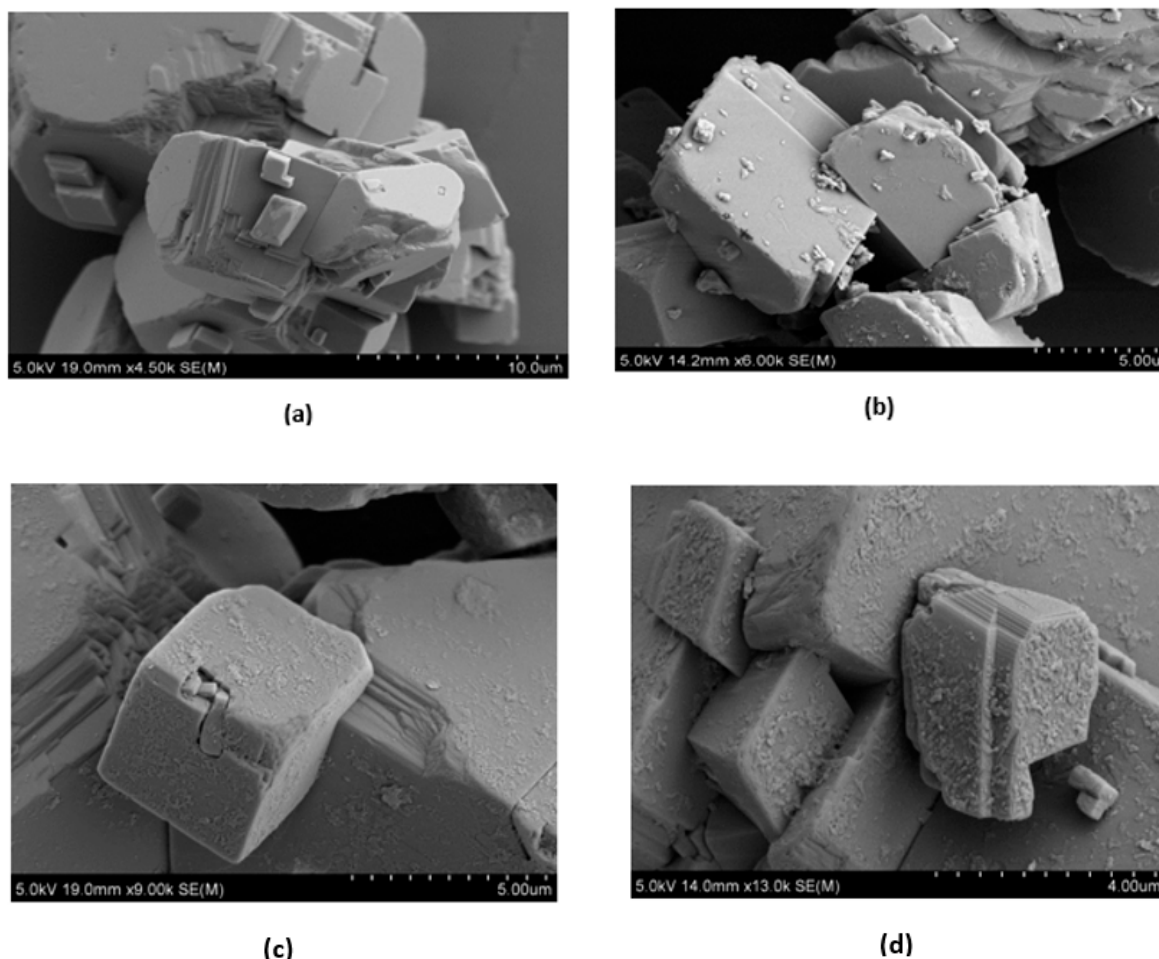

Figure 4. Scanning electron microscopic images of calcium carbonate aged in: (**a**) *n*-decane without stearic acid; (**b**) 0.001 M stearic acid in *n*-decane; (**c**) 0.005 M stearic acid in *n*-decane; (**d**) 0.010 M stearic acid in *n*-decane.

3.3. The Effects of Stearic Acid Concentration on CA and ZP

Figure 5 presents the CA and ZP results for a calcite surface treated with the model oil containing stearic acid at different concentrations in the presence of water. As can be seen in the figure, contact angle correlates well with zeta potential. A contact angle of 0° corresponds to an electric surface charge of +10 mV, while an angle of 112° corresponds to −53 mV. An image of a water droplet on unmodified calcite surface is also included, which was flattened, and measurement was difficult; hence the contact angle was considered to be zero. It is also clear that, as the concentration of stearic acid increased above 0.01 M, no significant change in contact angle was observed. These results correlate well with the zeta potential data. An attempt has been made to derive an equation so that stearic acid concentration and zeta potential data can be used to obtain the contact angle, and hence, the wettability of carbonate rock surfaces can be determined. This would be particularly useful for application to unconsolidated rocks. Equations have been derived previously relating zeta potential with calcium concentration (using pCa, where p is the negative log base 10) [19]. Correlation equations relating pH and temperature have also been created for sandstone rocks where wettability was automatically measured from pore space images based on a Gaussian distribution. However, such methods are somewhat time-consuming [45].
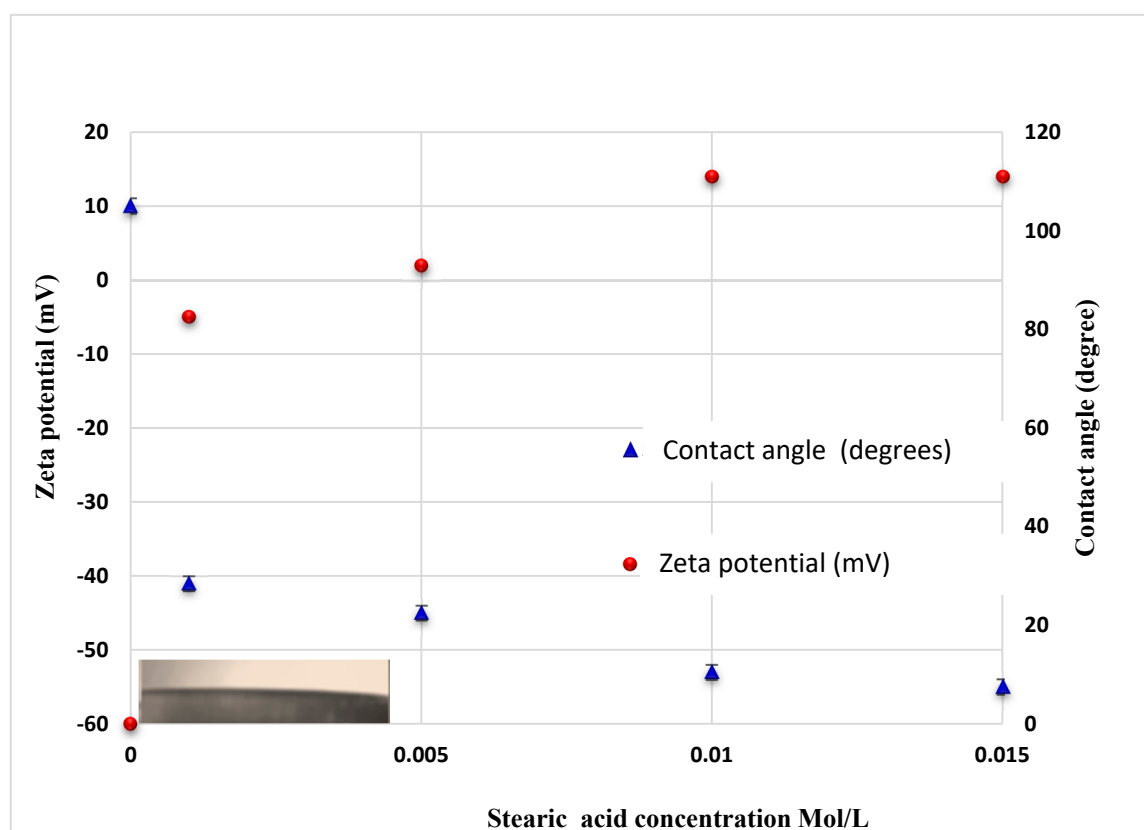

Figure 5. Contact angle and zeta potential as a function of the concentration of stearic acid in *n*-decane in the presence of water. For contact angle of zero, an image of a water droplet on unmodified calcite surface is also presented.

3.4. The Attempt to Derive an Equation for Contact Angle and Zeta Potential against Stearic Acid Concentration

The data for contact angle versus stearic acid concentration and zeta potential versus stearic acid concentration shown in Figure 5 were converted into log-log plots. A non-linear regression analysis was performed on the curve fitting to evaluate the accuracy of the mathematical model. The model

of contact angle versus stearic acid concentration was found to be well-represented by means of a polynomial model, as follows:

$$\text{Log}(\theta) = +0.1482 \times \text{Log}(C_{SA})^2 + 0.8796 \times \text{Log}(C_{SA}) + 3.207. \tag{1}$$

where θ is contact angle and C_{SA} is stearic acid concentration in *n*-decane. Similarly, zeta potential (ZP) versus C_{SA} is described as a polynomial model below:

$$\text{Log}(ZP) = -0.1782 \times \text{Log}(C_{SA})^2 - 1.0026 \times \text{Log}(C_{SA}) - 3.0166 \tag{2}$$

From Equation (2), we can obtain the relationship between $\log(C_{SA})$ and $\log(ZP)$:

$$\text{Log}(C_{SA}) = \frac{\text{Log}(ZP) + 3.0166}{-0.1782 \times \text{Log}(C_{SA}) - 1.0026} \tag{3}$$

Inserting Equation (3) into Equation (1) gives an equation which relates $\log(\theta)$ to $\log(ZP)$. According to the sign of zeta potential, two scenarios can be considered:

(a) For a positive zeta potential, the relationship between contact angle, zeta potential, and stearic acid concentration can be expressed as follows:

$$\text{Log}(\theta) = 0.1482 \times \left[\frac{\text{Log}(ZP) + 3.0166}{-0.1782 \times \text{Log}(C_{SA}) - 1.0026} \right]^2 + 0.8796 \left[\frac{\text{Log}(ZP) + 3.0166}{-0.1782 \times \text{Log}(C_{SA}) - 1.0026} \right] + 3.2078 \tag{4}$$

(b) For a negative zeta potential, the relationship can be expressed as:

$$\text{Log}(\theta) = 0.1482 \times \left[\frac{-\text{Log}/(ZP)/ + 3.0166}{-0.1782 \times \text{Log}(SA) - 1.0026} \right]^2 + 0.8796 \left[\frac{-\text{Log}/(ZP)/ + 3.0166}{-0.1782 \times \text{Log}(SA) - 1.0026} \right] + 3.2078 \tag{5}$$

On the other hand, a direct relationship between zeta potential and contact angle can be extracted from the experimental data as presented in Figure 6 and expressed in Equation (6):

$$\theta = 0.0092 \times ZP^2 - 1.3531\, ZP + 12.599 \tag{6}$$
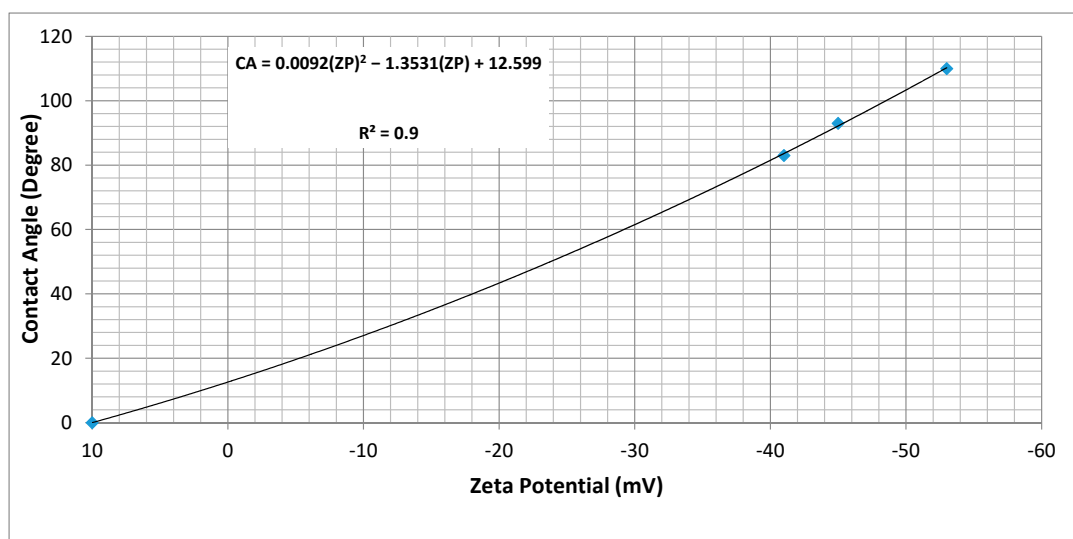

Figure 6. Contact angle as function of zeta potential for calcium carbonate equilibrated with stearic acid in a *n*-decane solution in the presence of water.

It should be noted that the proposed equations are valid only for the calcite minerals used in this study, and for other minerals different equations may apply. Therefore, this framework needs to be tested for other minerals to be able to provide a package for such a relationship between zeta potential and contact angle, and hence, surface wettability. The values of error associated with the contact angles calculated from each equation compared to the measured contact angles are presented in Table 1:

Table 1. The values of error associated with the contact angles calculated from each equation compared to the measured contact angles.

Measured ZP	(Logθ) Equation (5)	θ Equation (5)	θ Equation (6)	θ lab	Error Equation (5)%	Error Equation (6)%
−41	1.9288	79.79	83.54	83	3.86	0.65
−45	1.9685	92.83	92.1	93	0.18	0.95
−53	2.0414	109.8	110.15	110	0.15	0.14

The error and yield equations are given below:

$$Err\% = abs\left(\frac{\theta_{Lab} - \theta_{Eq}}{\theta_{Lab}}\right) \times 100 \tag{7}$$

$$Yield\% = 100 - Err\% \tag{8}$$

As can be seen in Table 1, the values of percentage error for Equations (5) and (6) are less than 4% and 1% respectively, which indicates that the equations are reliable and can be used to calculate contact angle, and hence, to quantify the wettability of calcite minerals used in this study.

3.5. Validation of Proposed Equations

We have conducted several laboratory experiments to validate the proposed equations. For this reason, different solutions of model oil with different concentrations of stearic acid (0.015, 0.020, 0.050, and 0.100 M) were prepared. The experimental results for contact angle versus time on modified calcite using particular stearic acid concentrations are presented in Figure 7. As can be seen, no further change in contact angle was observed in concentrations of stearic acid in *n*-decane above 0.020 M, which indicates that the adsorption of stearic acid reached its maximum saturation level. Usually, at saturation level, all positive calcite sites (Ca^{2+}) are occupied by negative $RCOO^-$ species. Therefore, no further adsorption takes place, and hence, the maximum value for contact angle has been achieved.
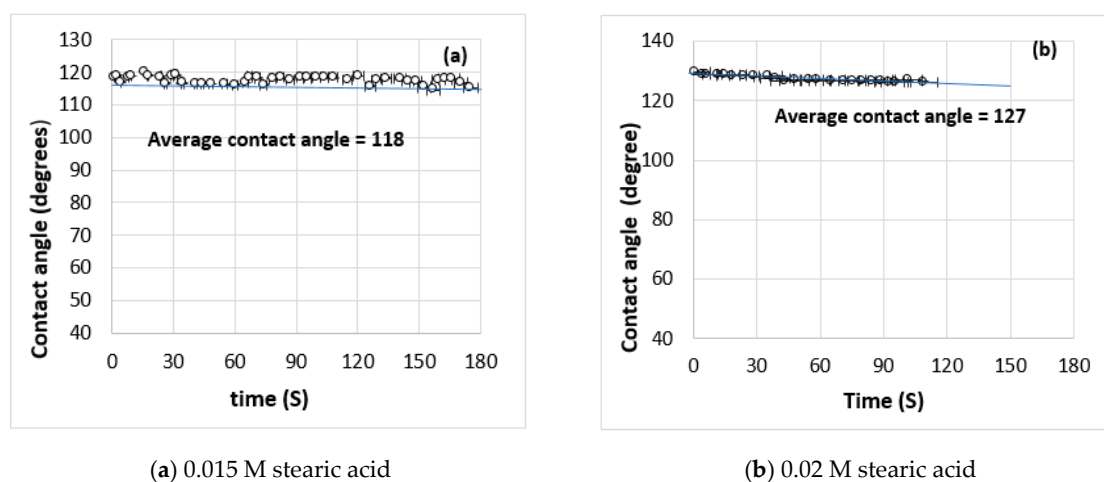

(**a**) 0.015 M stearic acid

(**b**) 0.02 M stearic acid

Figure 7. *Cont.*

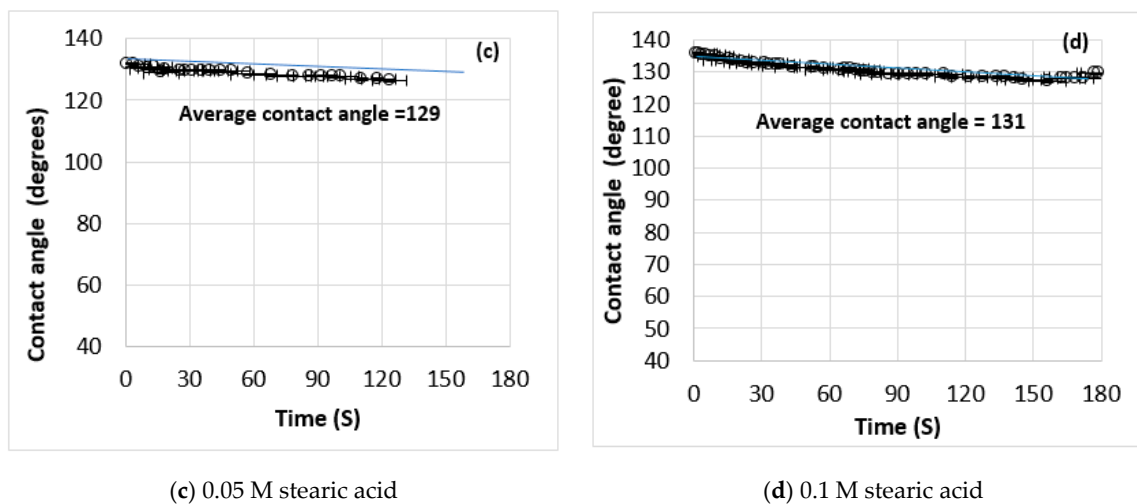(**c**) 0.05 M stearic acid　　　　　　　　　　　　(**d**) 0.1 M stearic acid

Figure 7. Measured contact angle versus time on modified calcium carbonate equilibrated by solutions of stearic acid in *n*-decane in the presence of water at concentrations of: (**a**) 0.015 M, (**b**) 0.020 M, (**c**) 0.050 M, and (**d**) 0.100 M.

Using an approach similar to that employed to generate the results shown in Figure 5, the new zeta potential and contact angle data were plotted against stearic acid concentration, as shown in Figure 8. As can be seen, zeta potential also reached its maximum at the same saturation level as in the contact angle data presented in Figure 7. Table 2 presents a comparison of the contact angle calculated from Equations (5) and (6) and the measured contact angles for calcite treated with selected stearic acid concentrations in *n*-decane. It can be seen that the percentage error between calculated and measured contact angles increases with stearic acid concentration, meaning that the proposed model cannot be used for any concentration above that at which the maximum adsorption occurs. Therefore, it was necessary to define the maximum adsorption level for the proposed numerical programme. In this study, the critical micelle concentration (CMC) for stearic acid in *n*-decane at equilibrium with water obtained from the IFT data was used as the maximum adsorption level. The results are presented in Figure 9, and the CMC value obtained was then used as a cut-off value for the calculation of contact angle from the proposed model.
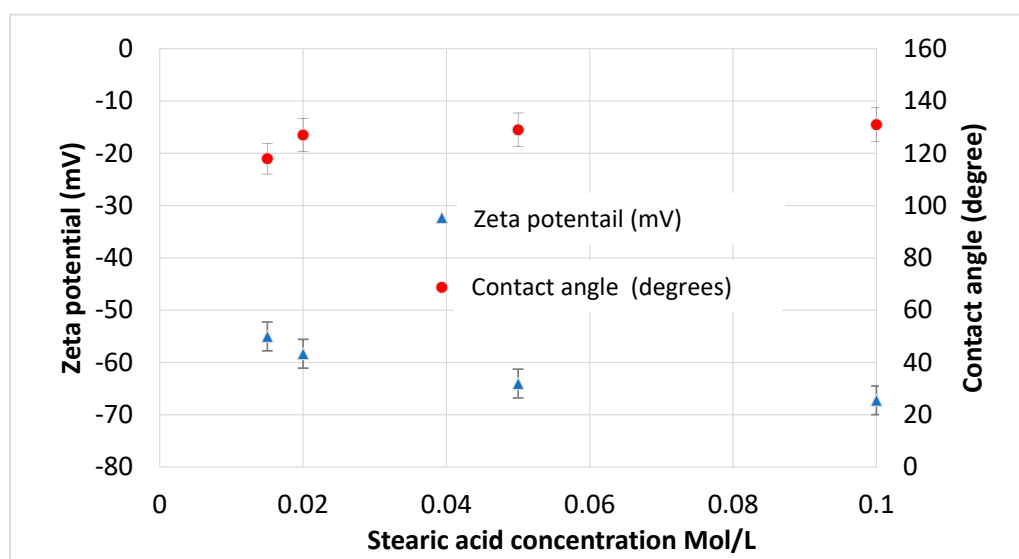

Figure 8. Contact angle and zeta potential as a function of the concentration of stearic acid in *n*-decane in the presence of water for the new set of data used as validation tests for the proposed equations.

Table 2. Comparison of measured contact angle in the lab and calculated contact angle from Equations (5) and (6).

Stearic Acid (M)	θ Lab	θ Equation (5)	θ Equation (6)	Equation (5) Err %	Equation (6) Err %
0.015	118.18	124	128	4.92	8.13
0.02	127	138	145	8.66	14.3
0.03	127.5	162	179.69	27.06	40.94
0.05	129	180	180	39.53	39.53
0.1	131	180	180	37.4	37.4

As is clear in Figure 9a, the calculated contact angle departed from the measured value at a concentration of 0.02 M stearic acid in *n*-decane, which corresponds to the CMC value in the IFT graph (Figure 9b) with a value of IFT at 10 mN/m. In summary, the proposed framework was able to quantify the wettability of carbonate rock with an acceptable range of error of about 4%–14%.

(a)

(b)
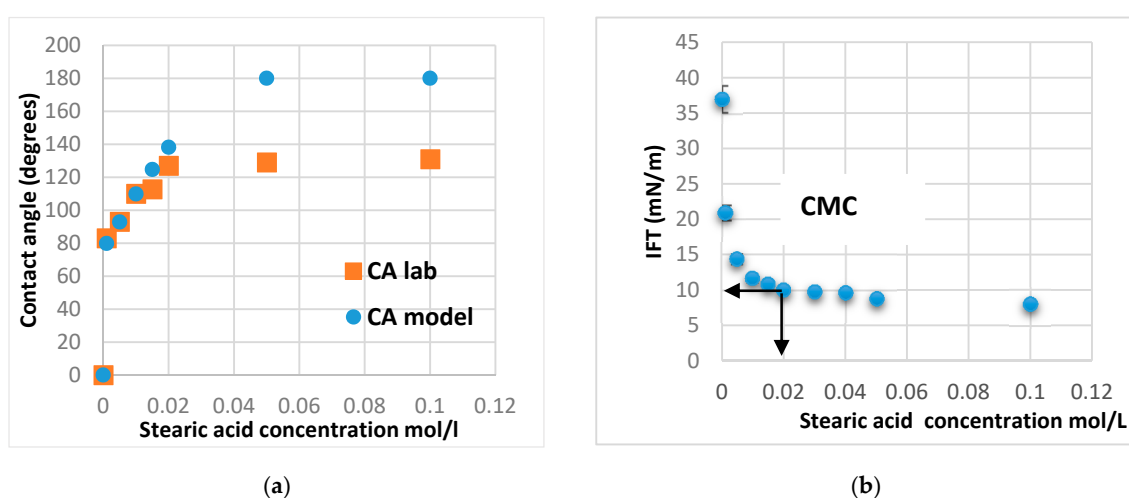
Figure 9. (**a**) Calculated (CA model) and measured (CA lab) contact angle for calcite modified with different stearic acid concentrations. (**b**) IFT between *n*-decane containing stearic acid and deionised water.

Because the proposed equations take into account stearic acid saturation, the error percentages increase at stearic acid concentrations higher than 0.02 M for both calculated contact angle and zeta potential.

4. Conclusions

Currently, oil companies spend significant amounts of time and effort measuring the rock and fluid properties of unconventional resources. Among such parameters, wettability is one of the most challenging to be measured in the laboratory. This is due to the uncertainties associated with wettability measurements using current methods, as it is affected by factors such as oil composition, brine chemistry, rock surface characteristics, pressure, and temperature. Accordingly, all other extracted flow parameters are affected, and to some extent become uncertain. The proposed methodology aims to introduce a new framework to reduce the time and resources required when measuring wettability in challenging reservoirs, and to provide a reliable correlation as an input for emerging techniques such as digital rock analysis methods where surface flow characteristics can be extracted.

A framework for quantifying the wettability of calcite powder from the relationship between the surface zeta potential and contact angle has been proposed. The equations that support this framework were found to be well-established and accurate, allowing the prediction of the wettability of powdered calcium carbonate at different concentrations of stearic acid in the *n*-decane model oil. Taking into account the cut-off value for the proposed equations, we were able to quantify the wettability of carbonate rock with an acceptable range of error of about 4%–14%.

The proposed equations were established based on model oil containing a single polar component. Therefore, it is important to define the equation's limiting factor, such as the value of CMC for the polar component, above which the equations were unable to give an accurate contact angle. To generalise the proposed framework, similar tests would be required using crude oil in the presence of formation water at reservoir conditions. It is also necessary to test the framework for minerals other than the one used in this study, as each may have its own surface characteristics. However, the above framework can be used as a baseline for further investigation.

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