

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

185,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Understanding Wettability through Zeta Potential Measurements

Syed Taqvi and Ghada Bassioni

Abstract

Traditional wettability measurement practices, introduced as early as the late 1950s, are still perceived as reliable industrial methods for characterizing wettability. These techniques, in contrast to the contact angle method, provide indices that can quantitatively describe the degree of wetting state. Nevertheless, these approaches can determine the current state of wettability, subject to limitations. By employing the zeta potential measurements technique, a complete wettability profile is derived. In this chapter, the theory behind this technique is discussed. A case study is presented where the wettability of limestone rock is investigated, as crude oil and asphaltene solutions of varying concentration are added to the limestone-water suspension. Findings of this study are discussed with the possible mechanism in effect when wettability alteration is observed.

Keywords: zeta potential, water-wet, oil-wet interfaces, calcium carbonate, asphaltene

1. Introduction

In the oil and gas industry, wettability studies are extensively carried out on reservoir rocks as it is one of the primary factors that control location, saturation distribution, and flow behavior of reservoir fluids [1]. Consequently, it influences several petrophysical properties such as capillary pressure, relative permeability, waterflood behavior, electrical properties, and enhanced oil recovery (EOR) [1–3].

Traditional methods, devised by researchers over time, have classified wettability of rocks into three main states: (i) oil-wet, (ii) water-wet, and (iii) neutral wet. Oil-wet refers to the state of the reservoir rock when oil, in presence of other fluids, preferentially covers the rock surface. As a consequence, oil forms a thin layer on the surface of the rock, while other fluids remain in the center, as seen in **Figure 1(a)**. For the water-wet scenario, water in the presence of other fluids (i.e., oil) preferentially covers the rock surface. As a result, water forms a thin layer on the surface of the rock, while oil remains in the center, as seen in **Figure 1(b)**. In the case of neutral wetting, the reservoir rock surface does not show any preferential covering for any fluid. It is not necessary that a reservoir rock strongly adheres to either one of these phenomena; rather cases of heterogeneity may exist where many other states of wettability may be defined, such as mixed wettability, fractional wettability, “Dalmatian” wetting, and speckled wetting [3].

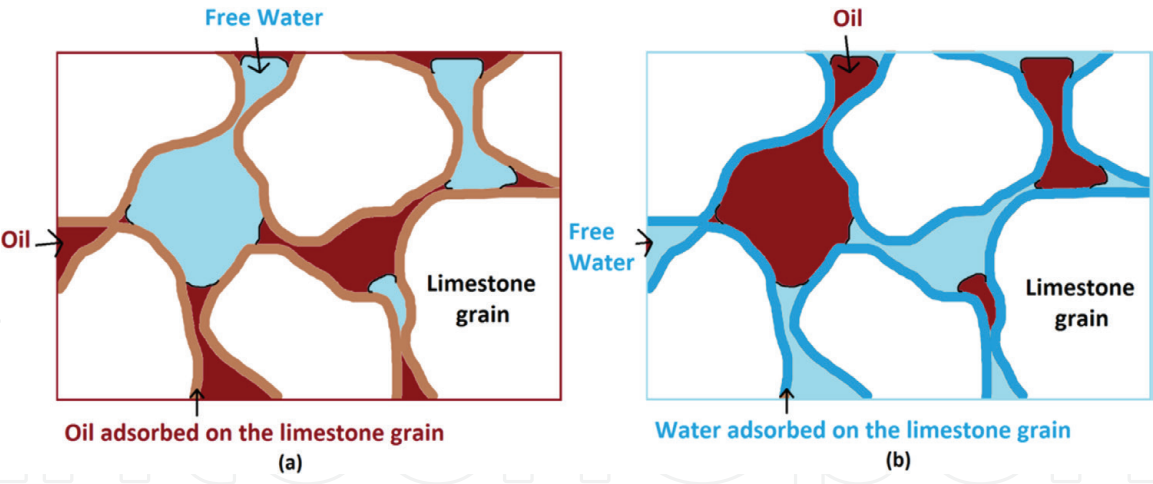


Figure 1.
Schematic diagrams of (a) oil-wet and (b) water-wet states of wettability on a microscopic level.

In the case of mixed wettability, some parts of the rock surface are water-wet, while others are oil-wet [4]. For the fractional wettability scenario, a fraction of the internal rock surface area is wetted by a fluid, either oil or water [5]. “Dalmatian” is a type of nonuniform wettability where oil-wet and water-wet regions, smaller than

		Wettability measurement technique	Advantages	Disadvantages
Quantitative	1	Contact angle	Accurate Simple	Surface heterogeneity can affect reading Cannot provide information regarding organic coatings Impurities can affect reading Liquid drop can form many stable contact angles
	2	Amott/ Amott-Harvey	Reliable	Not very effective to measure neutral wettability No validity as an absolute measurement
	3	United States Bureau of Mines (USBM)	Reliable	No validity as an absolute measurement
Qualitative	4	Imbibition rate	Quick Simple	Not very accurate Imbibition rate does not solely depend on wettability but also other factors
	5	Microscopic examination	In situ wettability alteration can be observed	Based on affinity with no degree of wettability measured
	6	Flotation	Quick	Sensitive to only strongly wetted systems
	7	Nuclear magnetic resonance (NMR)	Ability to study fractional wettability	Requires complex and expensive machinery
	8	Dye adsorption	Quick Simple Cost effective Ability to study fractional wettability	Not very accurate

Table 1.
Summary of wettability measurement techniques.

Index	Oil-wet	Neutral wet	Water-wet
Amott wettability index water ratio (IW)	0	0	>0
Amott wettability index oil ratio (IO)	>0	0	0
Amott wettability index (WIA)	−1.0 to −0.3	−0.3 to 0.3	0.3 to 1.0
United States Bureau of Mines (USBM)	−1	0	1
Contact angle (θ)	>90°	90°	<90°

Table 2.
Index/measurement values depicting different wetting states for different quantitative techniques.

the size of a pore, are mixed randomly [6]. Speckled wetting refers to the situation where oil tends to be trapped in pore throats rather than the pore bodies [7].

All the developed techniques, currently employed, express wettability either quantitatively or qualitatively. A common limitation of all these traditional methods is their inability of in situ measurement of the state of wettability while the wettability alteration process takes place [8, 9]. **Table 1** summarizes the other specific advantages and limitations of wettability measurement practices that are commonly used. For the quantitative wettability techniques, **Table 2** shows the index/measurement values for the corresponding wetting states.

2. Zeta potential approach

Zeta potential is defined as the difference in potential between the particle and its ionic atmosphere surrounding medium, measured in the plane of shear, as depicted in **Figure 2** [10]. In the ideal case, the potential at the Stern layer, Ψ_d , is desired potential. However, due to the non-conductive nature of most minerals, it becomes challenging to measure it [11]. Thus, zeta potential measurements are

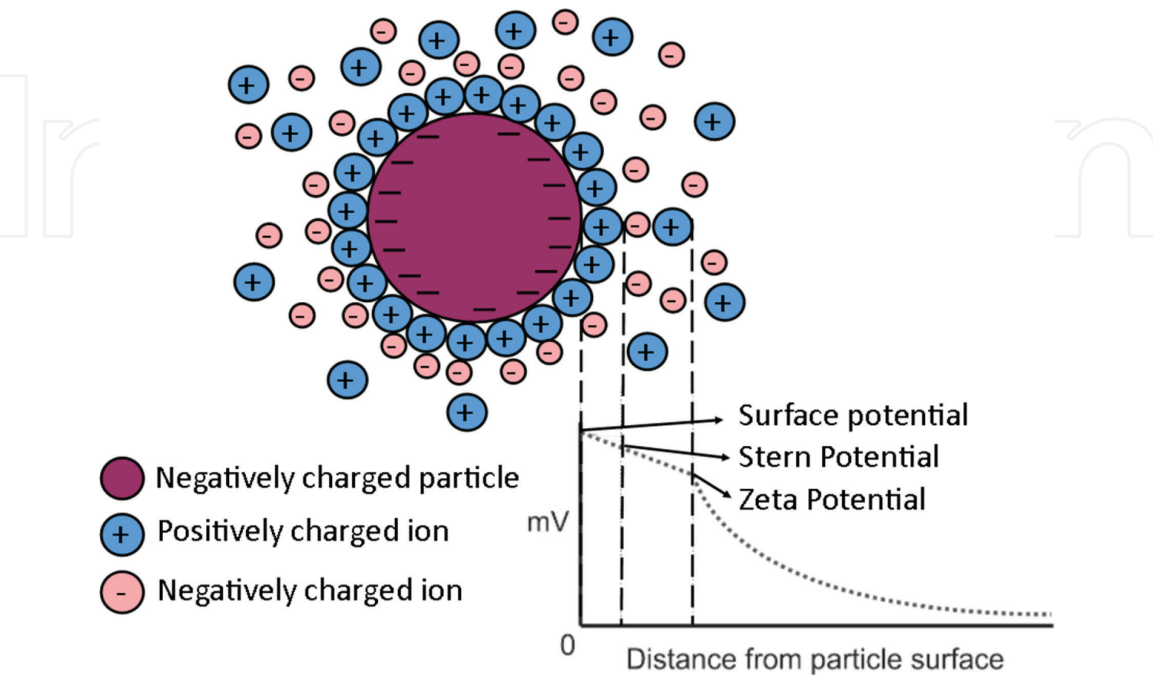


Figure 2.
Diagram illustrating the surface potential, stern potential, and zeta potential as a function of distance of a negatively charged particle in a dispersion medium.

considered that are slightly greater than the Stern potential [10]. Mechanistically speaking, when a solid particle is dissolved in water, the charge on its surface leads to the formation of counterions [12]. For example, in the case of a limestone slurry, the co- and counterions, Ca^{2+} and OH^- , are formed. The charged particles then attract a layer of counterions from the aqueous phase, known as the Stern layer.

Due to ionic radius considerations, the strongly adsorbed anions do not fully offset the surface charge, and hence, a second layer of more loosely held counterions forms, known as the diffuse layer. This diffuse layer is made of free ions which are mobile under the influence of electric attraction and thermal motion. The two layers combined are known as the electric double layer (EDL). At a certain distance away from the charged particle, the surface charge will be fully balanced by the counterions, and beyond this point, a bulk suspension with a balance of positive and negative electrolyte exists [9, 12]. Particles, with a high surface charge, form a large double layer, which prevents particles from getting close to each other because of the electrostatic repulsion between them due to identical charges. However, this behavior aids in stabilizing suspensions [13].

Due to the presence of electric charges in an applied electric field, different phenomena occur in the system, which are collectively known as electrokinetic effects. The zeta potential can be measured based on different phenomena classified as electrokinetic or electroacoustic. Electroacoustic differs from electrokinetic as the former uses ultrasound waves to induce movement of particles in one direction. Unlike the latter, it does not utilize an electric field. However, they are both used to measure the surface charges of stable suspensions composed of small particles of sizes less than 10 μm .

2.1 Electrokinetic measurement

The electrokinetic phenomena are differentiated based on the induced motion of particles [14]. These techniques include:

1. Electrophoresis
2. Electroosmosis
3. Streaming potential
4. Sedimentation potential

2.1.1 Electrophoresis

Electrophoresis is considered to be the most widely used technique in electrokinetics to measure the zeta potential. It considers the movement of a charged particle relative to its liquid medium under the influence of the electric field [14]. It occurs when an electric field is applied across the sample electrolyte and causes the suspended particles to move [14]. However, with an opposing viscous force, equilibrium is achieved. As a result, the particles move with constant velocity. This velocity, or electrophoretic mobility, depends on [14]:

- The strength of the electric field
- The dielectric constant of the liquid

- The medium's viscosity
- The zeta potential

The electrophoretic mobility is measured in a microelectrophoresis system. This system consists of a cell with electrodes at both ends applying a potential across the sample. The suspended particles will move toward the opposite-charged electrode during which the velocity is measured.

2.1.2 Electroosmosis

Electroosmosis, on the other hand, is associated with the movement of the liquid medium relative to a stationary charged surface. The walls of the capillary cell carry a surface charge which causes the liquid adjacent to the wall to flow, once the electric field is applied. This electroosmotic flow superimposes the colloidal particles' electrophoretic mobility [14]. In a closed system, this flow is countered by another reverse flow down the center of the capillary cell. Due to that, there exists a point, known as the stationary layer, in which the two flows cancel each other and result in a zero net electroosmotic flow [14]. At that point, the true electrophoretic velocity is measured [14]. The position of the stationary layer depends on the geometry of the cell.

2.1.3 Streaming potential

Streaming potential phenomenon is associated with the generation of an electric field when a liquid is forced to flow past a stationary charged surface [14]. The potential difference created is known as the streaming potential. This technique is used to measure the zeta potential for large particles in unstable suspensions.

2.1.4 Sedimentation potential

Sedimentation potential, lastly, deals with the generation of an electric field due to the movement of charged particles relative to a stationary medium, in gravitational or sedimentation fields in centrifuges [15]. It is considered to be the opposite of electrophoresis. However, it is rarely used due to its difficulty in measuring the electrophoretic velocity [15].

2.2 Electroacoustic

In electroacoustics, the motion is due to the different densities of particle and medium [16]. This motion disturbs the double layer around the particles and eventually forms a dipole moment. The summation of the dipoles results in an electric field, known as colloidal vibration current (CVI). A two-electrode sensor detects this current and uses it to compute the zeta potential.

The measurement depends on several factors such as zeta potential, density difference between the medium and suspending particles, viscosity, dielectric permittivity of the liquid, and particles' weight fraction. This technique has several advantages over the electrophoresis which are [16]:

- Measurement of high solid content systems, up to 50% volume fraction, with no need for dilution
- Less sensitive to contamination

- Higher precision (± 0.1 mV)
- Low surface charges (down to 0.1 mV)
- Accurate for nonaqueous dispersions

2.3 Significance to the wettability study

Zeta potential measurements are used in nearly all industries that involve colloidal systems. In addition, measuring zeta potential is a reflection of characterizing the surface charge of a suspended particle [17]. Recently, zeta potential measurements have been used extensively to study various biomaterials such as proteins, leukocytes, and DNA [18–20]. Moreover, they have been used to understand the behavior of nanoparticles with human cells, beneficial for applications in the field of medicine [21]. Adhesive properties of various polymers and biomaterial have been investigated using the zeta potential approach [20, 22]. In a study, conducted by Bassioni [23] on environment-friendly construction, zeta potential measurements were used to identify the presence of anionic superplasticizers on cement particles. In addition, Bassioni and Ali [24] performed zeta potential measurements to identify effective dosage of additives to oil-well cement.

In another study, conducted by Bassioni [25], CaCO_3 showed potential to adsorb significant quantities of anions due to its positive surface charge. Moreover, zeta potential measurements were made to determine the surface charge of the calcium carbonate particles in the presence of varying dosages of the adsorbates [25]. Since wettability refers to the adsorption of a fluid, in presence of immiscible fluids, onto a rock surface, zeta potential measurements are a promising way to measure wettability. As compared to all other wettability measurement techniques discussed, the zeta potential approach is significant as it can study the wettability alteration in situ [26]. Wettability studies can be carried out on the reservoir rock in order to determine its tolerance and its interaction with inhibitors, prior to any injections to the reservoir. Predictions can be made to study the effect of reservoir conditions onto the rock wettability.

Several studies have been conducted where researchers have employed the concept of zeta potential for different applications. Elimelech et al. used zeta potential measurements to study reverse osmosis membranes [27]. In another study, zeta potential was used to determine the optimum dosage of additives to cement for hydration [28]. Bousse et al. conducted zeta potential measurements on metallic oxide thin films [29]. In addition, another study carried out zeta potential measurements on some transition metal oxides at high temperature [30].

3. Case study

3.1 Methodology

Several experiments were conducted in order to study wettability on reservoir rocks using zeta potential measurements. These include the wettability study of:

- Crude oil on calcium carbonate in limestone-water mixture
- Water on calcium carbonate in limestone-oil mixture
- Crude oil A on calcium carbonate in limestone-water mixture with inhibitors

- Asphaltenic solutions on calcium carbonate in limestone-water mixture
- Maltenes on calcium carbonate in limestone-water mixture

The experimental setup, as shown in **Figure 3**, mainly comprises of a zeta probe, an electronic stirrer and a mixing cell. Prior to the experiment, the particle size of the powdered reservoir rock (i.e., limestone) was determined using a WJL laser granulometer, as it was suspended in water. For each of the experiment, a colloidal mixture was prepared. For the first study, 200 g of limestone was poured into 200 g of water over a period of 1 minute. The mixture was allowed to sit for 1 minute and then stirred vigorously for 2 minutes before transferring to the mixing cell. In the mixing cells, the mixture is continuously stirred using an electronic stirrer at room conditions. All experiments conducted in this study were carried out using distilled water since wettability effects become very important when brine saturation is lowered [31]. The zeta probe was placed and the zeta potential was measured. After the initial zeta potential value was recorded, the fluid of interest is added mL-wise to the mixture, and successive zeta potential measurements were made.

Model DT-1200 Electroacoustic Spectrometer (Dispersion Technology Inc., New York, USA) was used to measure the zeta potential values of the system. Moreover, the device has a zeta potential measurement accuracy of $\pm 0.1 \text{ mV} + 0.5$, as stated by the manufacturer. Densities of the liquid medium and the suspended solid medium and the suspended solid particle size were the parameter input to the system. The probe was placed in the external cell, and the zeta potential was measured, as illustrated in **Figure 3**. For the proposed zeta potential setup, the zeta probe takes measurements when immersed in a colloidal system. Moreover, the system of solid fluid needs to be smooth so a steady colloidal system exists throughout the analysis. The system works with small particles of sizes less than $10 \mu\text{m}$. If aggregation in the system or deposition on the probe occurs, it may result in inaccurate readings.

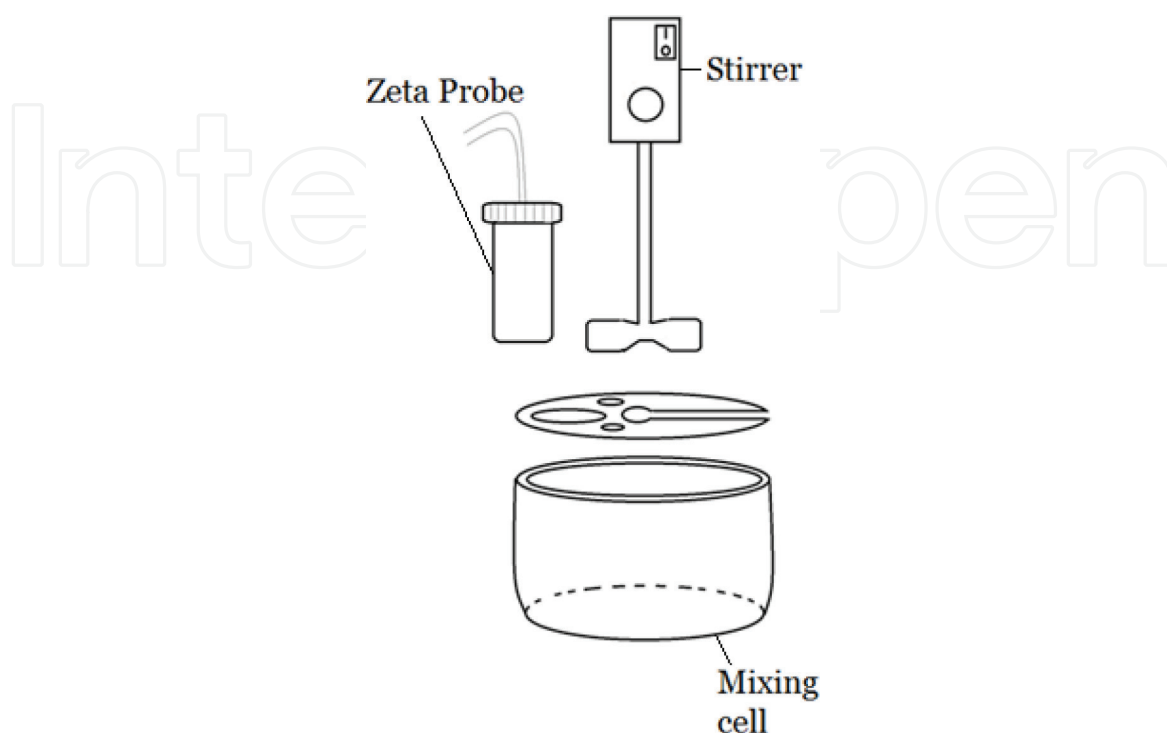


Figure 3.
 Experimental setup [26].

3.2 Results and discussion

This section states the results obtained from each analysis and experiment. In addition, it discusses each observation in detail, with possible explanations for each of the finding.

The D_{50} size of the limestone particle was found to be $7.06 \pm 0.211 \mu\text{m}$ with a surface area of $8.628 \text{ m}^2/\text{g}$ and a density of $2.66 \text{ g}/\text{cm}^3$. On the other hand, the PCD analysis showed that both inhibitors, SD and KT, carry a surface charge of -2097 and -1145 mV , respectively. Additionally, the moisture content in each inhibitor was found to be 96.2 and 71.3% , respectively. The ICP-MS analysis, carried out on the SD inhibitor samples, showed significant concentrations of Rb, Ca, and Mg, in descending order. On the other hand, Ni, Al, and Cr were found in significant concentrations in the KT inhibitor (from highest to lowest, respectively).

Various wettability studies were carried out for different crude oil samples on limestone, in presence and absence of inhibitors, as well as of oil derivatives, such as maltene and asphaltenes. The following sections state the findings of each and discuss the results in detail.

3.2.1 Wettability of calcium carbonate for crude oil in limestone-water mixture

Figure 4 shows the results of the zeta potential measurements of the limestone-water suspension as different crude oils are added to the system.

Initially, the surface charge for aqueous limestone suspension was found to be about $+30 \text{ mV}$. At this stage, the CaCO_3 is completely wetted by water since no crude oil is added yet. Upon addition of crude oil, the zeta potential of the aqueous limestone suspension starts to decrease steadily until a certain limit beyond which a steep fall is observed. This limit differs for each type of oil, as seen from **Figure 4**.

As oil comprises of negatively charged particles [3, 32], oil droplets tend to adsorb to the positively charged CaCO_3 surface as a result of electrostatic interaction, displacing the water particles to the bulk. **Figure 5** depicts this competitive adsorption behavior. Once the entire surface is completely wet with the oil droplets, the wettability curve experiences a steep decrease in the zeta potential value, signifying a complete oil-wet surface. The curve flattens out to indicate the end of the adsorption process.

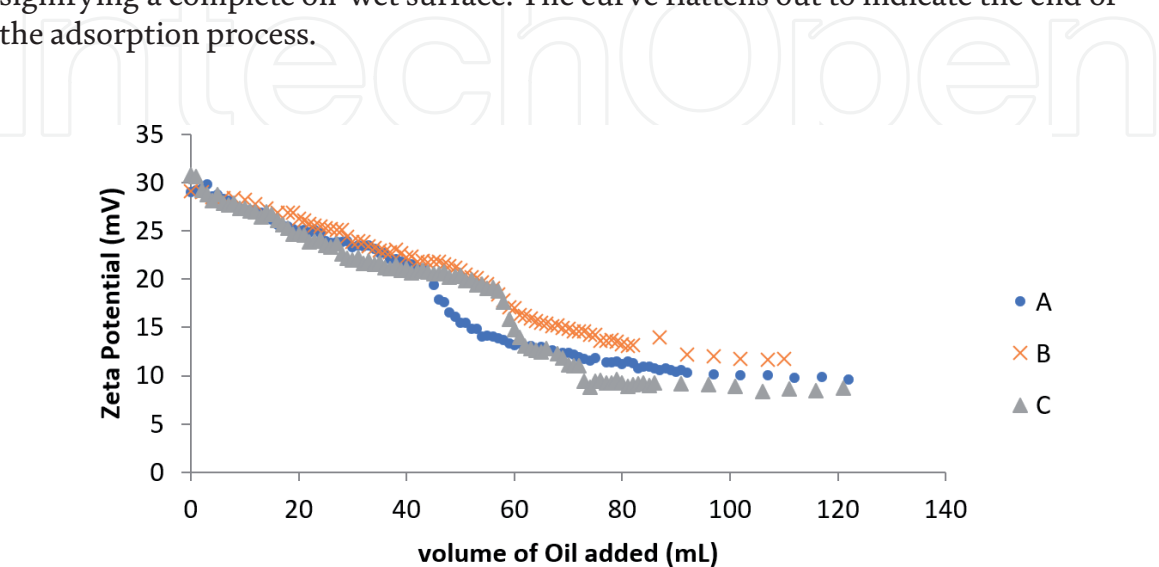


Figure 4. Zeta potential measurements for aqueous limestone suspension with volume of crude oil added [26].

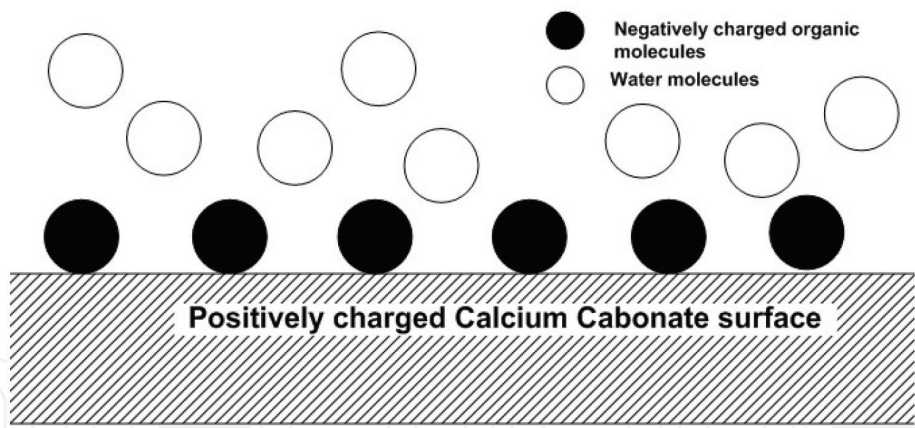


Figure 5.
Negatively charged crude oil particles adsorbing onto positively charged calcium carbonate surface [33].

It can be seen from **Figure 4** that all crude oil samples experience a similar trend upon the addition of crude oil. However, crude oil C tends to have a slightly different trend. This behavior will be explained in the section discussing the wettability alteration due to asphaltene.

As seen from **Figure 4**, it is observed that there exists a general trend in the wettability curve for all crude oil samples. However, the curve appears to be shifted vertically. In accord with our own investigation [26], a previously reported study showed C_7 asphaltene particles, in presence of resins, are negatively charged [34]. Therefore, the more the asphaltene content present, the lower the zeta potential decrease observed. Hence, the vertical shift is observed.

3.2.2 Wettability of calcium carbonate for water in limestone-oil A mixture

Figure 6 shows the zeta potential measurements of the limestone-crude oil mixture as water is added.

The initial zeta potential of the limestone-oil suspension was found to be -15 mV. This signifies that oil carries components with high negative charge, as compared to limestone, lowering the zeta potential value of the limestone suspension to a negative value. Upon addition of water, the zeta potential fluctuates around the average value, as exhibited in **Figure 6**.

Initially, the limestone surface is completely coated by oil (i.e., oil-wet), and the mixture is being stirred smoothly. When water is added to the system, it washes

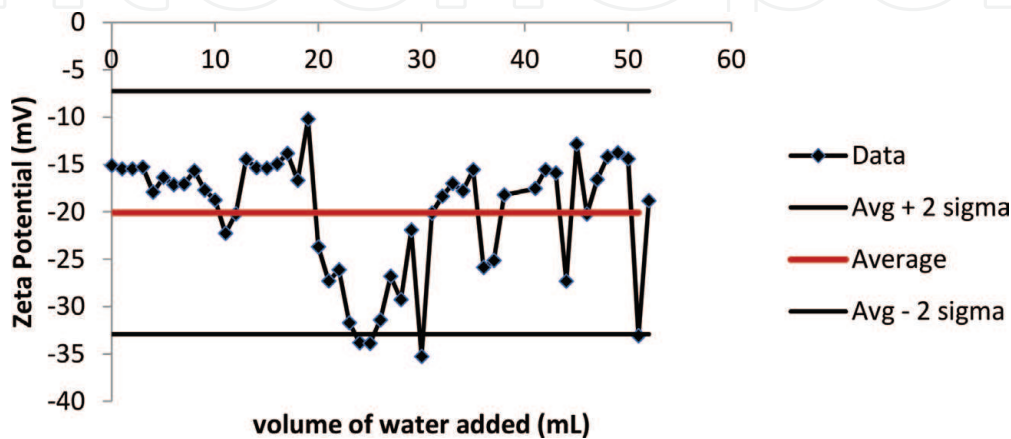


Figure 6.
Zeta potential measurements for limestone-oil A suspension with volume of water added [26].

away the negatively charged adsorbed oil droplets from the surface into the bulk. However, due to electrostatic interactions, these oil droplets tend to return to the limestone surface and adsorb onto it, with time. This continuous behavior results in fluctuations in the zeta potential values. **Figure 7** shows the remainder of the limestone-oil water system when the experiment was halted.

It can be seen in **Figure 7** that deposition of heavy fractions of oil on the limestone surface occurred, forming large chunks of solid matter. The formation of solid chunks became an obstacle for the stirrer in mixing, and the experiment was halted. This situation arose due the addition of water. Water tends to alter the composition of the system, destabilizing the limestone-oil suspension. Due to such disturbance, the heavy fractions aggregate and deposit onto the surface of limestone, as seen from **Figure 7**.

3.2.3 Wettability of calcium carbonate for crude oil A in limestone-water mixture with inhibitors

The wettability experiment was carried out on the aqueous limestone suspension in presence of inhibitors, and the data was compared to the wettability profile of crude oil A in absence of inhibitors, as seen in **Figure 8**.

The initial zeta potential value for the limestone-water inhibitor system for both inhibitors, KT and SD, was 16 mV even though KT has a particle charge of -1145 mV, whereas SD has a particle charge of -2097 mV. The zeta potential decreases with the addition of crude oil to the system. Moreover, both inhibitors decrease the zeta potential of the system to a value of about 4 mV, after 80 mL of crude oil was added. Yet, inhibitor SD experiences an earlier decrease in zeta potential value relative to inhibitor KT.

As compared to the wettability profile of calcium carbonate without inhibitor, it is observed that inhibitor SD decreases the system tolerance to the addition of crude oil, whereas inhibitor KT slightly increases it. In other words, the wettability alteration process, from water-wet to oil-wet, is accelerated by inhibitor SD, while inhibitor KT decreases it. This analysis shows that inhibitor SD is ineffective for crude oil A.

Figure 9 shows an illustration, showing the possible mechanism that the inhibitor particles follow, in the limestone-water inhibitor system, as crude oil is being added.



Figure 7.
Limestone-oil suspension upon addition of 53 mL of water [26].

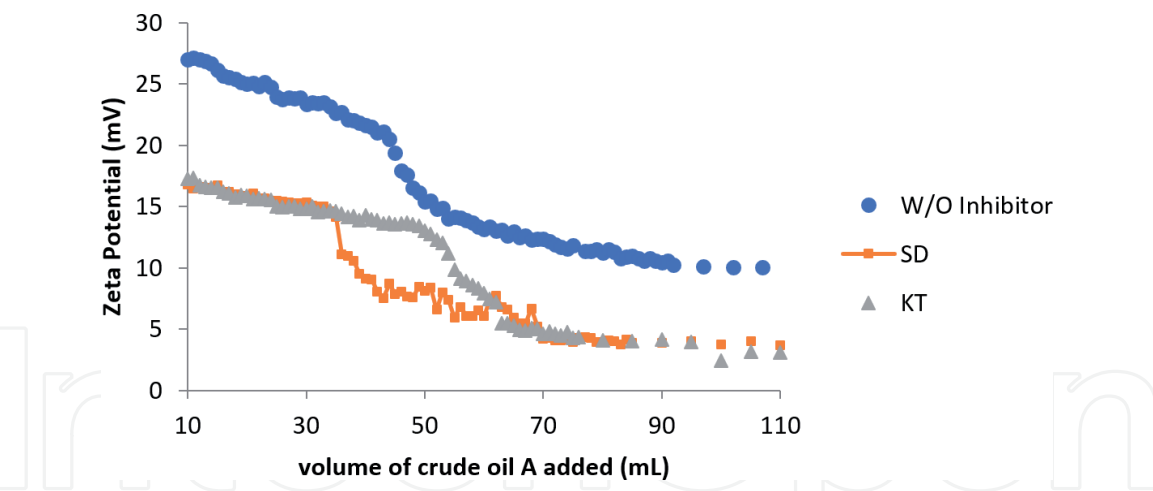


Figure 8.
Zeta potential measurements of aqueous limestone suspension without inhibitor and with inhibitors, KT and SD [26].

In the limestone-water inhibitor system, the inhibitor gets attracted and adsorbed onto the limestone surface due to its high negative particle charge. Since the inhibitor possesses a higher negative charge than the crude oil, upon addition of crude oil, it remains adsorbed on the limestone surface and tends to resist the wettability alteration, keeping the oil particles in the bulk.

The transition is resisted due to the negative charges present on both, crude oil and the inhibitor. These negative charges exert forces of repulsion, preventing the crude oil particles from coming in contact with the limestone surface and keeping them afloat in the oil. By extension, this prevents the deposition of heavy fractions of oil, maintaining the composition of the crude oil. However, it can be seen that in **Figure 7**, the zeta potential value of the suspension decreases to an even lower value upon addition of crude oil. Eventually, the inhibitor particles are forced to desorb due to the increasing concentration of crude oil. Hence, the wettability changes.

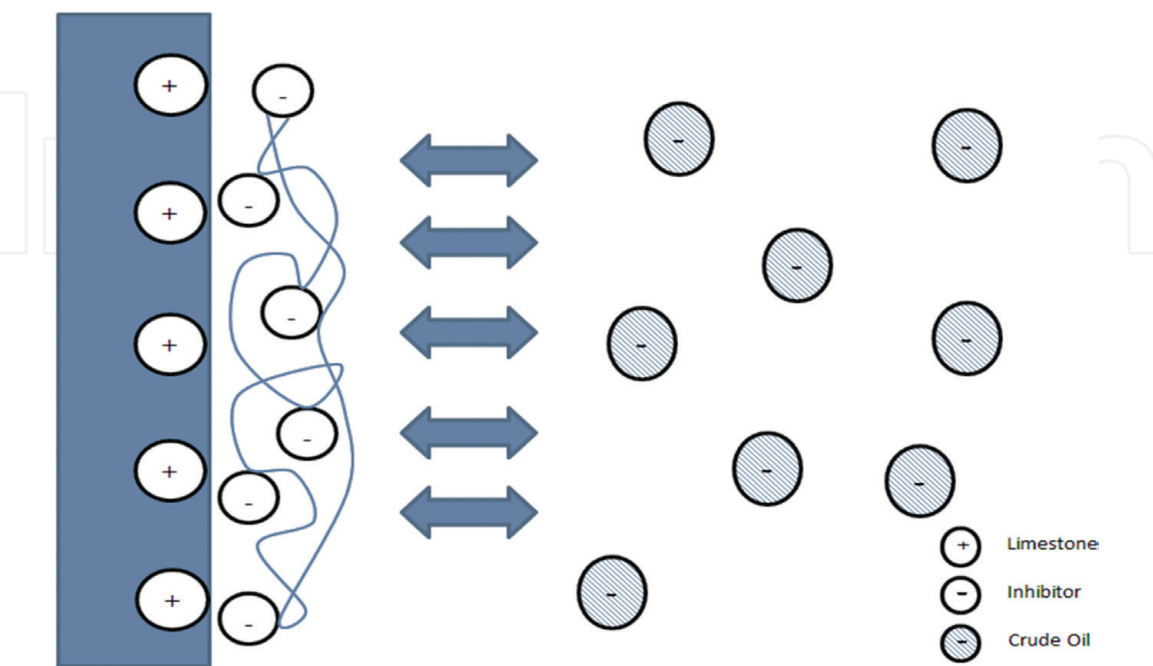


Figure 9.
Mechanism of inhibitor adsorbing on the limestone surface in the presence of crude oil [26].

3.2.4 Wettability of asphaltenic solutions on calcium carbonate in limestone-water mixture

Asphaltene was extracted from crude oil A, and different asphaltene-toluene solutions of varying concentrations were prepared. **Figure 10** shows the wettability curve for each solution.

Initially, the limestone surface in the limestone-water system is completely water-wet. Upon addition of asphaltenic solution, the zeta potential value decreases for all concentrations of asphaltene. This signifies the negative character of the asphaltene molecules in toluene as well as in oil, as supported by Bassioni and Taqvi [26]. As the concentration of the asphaltenic solution increases, the zeta potential tends to fall to a more negative value. All concentrations except 5 wt% follow a similar trend in the decrease of the zeta potential value, upon adding the asphaltenic solution. The reason behind the change in trend in case of 5 wt% asphaltenic solution will be explained in Section 3.3, discussing the wettability alteration due to asphaltene.

Initially, the limestone surface in the limestone-water system is completely water-wet. Upon addition of the asphaltenic solution, asphaltene particles tend to adsorb onto the limestone surface and wet it. The wettability alteration is complete once the wettability curve flattens out, and the plateau, at the end of the wettability curve, marks a completely asphaltene-wet limestone surface.

3.2.5 Wettability of maltenes on calcium carbonate in limestone-water mixture

In addition to the asphaltenes, a wettability study was carried out on the maltenes extracted from crude oil. **Figure 11** shows the wettability curve for maltenes, asphaltenes, and the crude oil.

Initially, the limestone surface in the limestone-water system is completely water-wet. When maltene is added to the system, the zeta potential value decreases until the curve flattens out, as seen in **Figure 11**. Resins, in the maltenes, adsorb onto the surface, and the wettability curve flattens out when the limestone surface is completely maltene-wet.

When compared to the wettability of limestone for crude oil A, the zeta potential values of the maltene wettability curve seem to coincide with it. Moreover, the maltene wettability curve attains a plateau at a zeta potential +20 mV,

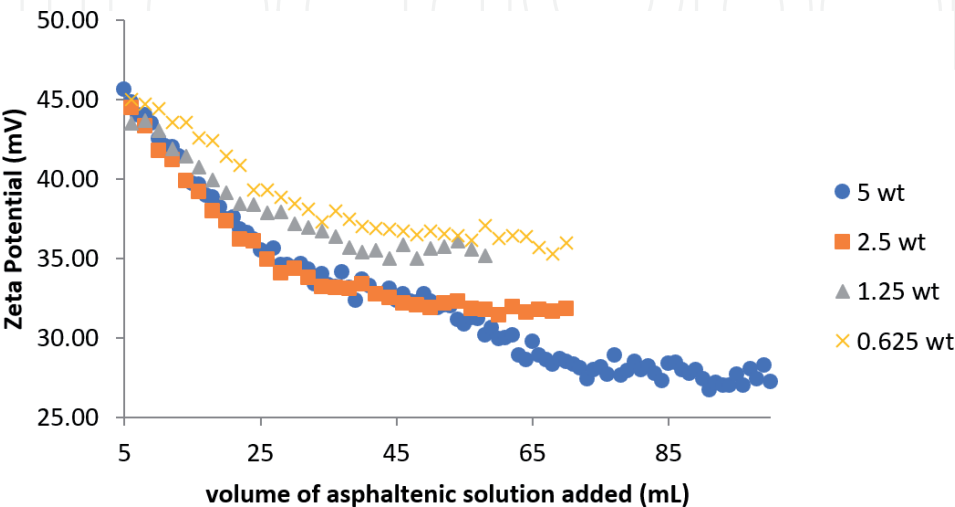


Figure 10. Wettability of aqueous limestone mixture for asphaltenic solutions of varying concentrations of crude oil A [26].

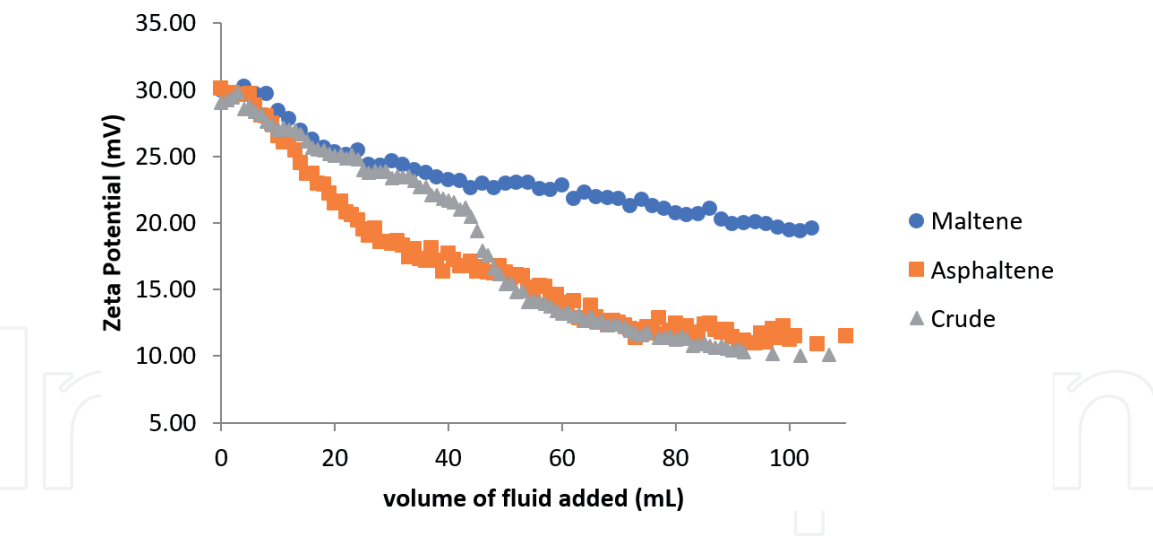


Figure 11.
Wettability profile of limestone for maltene, asphaltene, and crude oil [33].

corresponding to the wettability alteration in the wettability curve of limestone for crude oil. On the other hand, the plateau of the wettability curve for asphaltenic solution coincides with the plateau of the wettability curve for crude oil A. In addition, both wettability curves seem to coincide at a similar value of about +12 mV.

The behavior can be explained such that when crude oil is added to limestone-water mixture, the maltenes, in the crude oil, readily adsorb onto the surface of the limestone particle. After the surface is completely maltene-wet, asphaltenes start adsorbing onto the surface of calcium carbonate. The wettability curve approaches a plateau when the limestone surface is completely asphaltene-wet.

3.2.6 Summary

In contrast to the quantitative techniques discussed in **Table 1**, the zeta potential technique presents an entire wettability profile for the reservoir rock. Wettability measurements are unique for each system. Cases have been presented where different wetting states can be understood from the proposed zeta potential technique. As stated earlier, the quantitative measurement methodologies stated here cannot determine wettability in situ. Thus, if samples of the mixture are drawn at different wetting states, respective values would be observed, as shown in **Table 2**. For the study presented in Section 3.2.1, if a sample from the mixture was obtained anywhere from the beginning of the experiment until where the plateau's first steep drop was observed in **Figure 4** (i.e., ~44 mL of crude oil for oil A), the contact angle method would yield θ values of less than 90° . However, if a sample is drawn from beyond the plateau, the contact angle value would result in greater than 90° .

In all, from the results analyzed above, it was observed that calcium carbonate, in water, is positively charged and has the potential to adsorb particles onto its surface. Oil, on the other hand, consists of negatively charged components which adsorb onto the calcium carbonate surface due to electrostatic interaction.

In a strongly water-wetted calcium carbonate system, upon the addition of crude oil, the zeta potential is observed to decrease until oil particles adsorb onto the rock surface. Effective inhibitors in such systems have been able to increase the surface resistance to adsorb negatively charged oil particles. In a strongly oil-wetted system, the zeta potential fluctuates upon the addition of water and eventually leads to the formation of large chunks of calcium carbonate with asphaltene deposition. Inhibitors have been found to be ineffective in such systems.

As evident from the different wettability studies carried out, crude oil adsorbs onto the limestone surface, initially, with a steady decrease, followed by a steep decrease in the zeta potential value and a plateau. On the other hand, maltenes have been observed to adsorb onto the surface with a steady decrease in the zeta potential value, while asphaltene molecules have been observed to readily adsorb onto the limestone surface, resulting in a steep decrease in the zeta potential value, followed by a plateau. The superimposition of zeta potential values for the wettability profiles shows a strong relationship that will be explained, in detail, in the following section.

3.3 Wettability alteration due to asphaltene

All wettability studies, carried out, indicate the adsorption of oil particles when crude oil or its individual components are added to a limestone-water mixture. However, a detailed explanation is required for such a behavior and the role of asphaltene in the wettability alteration process. **Figure 12** provides a mechanism that the oil components undergo through the wettability alteration process, at a microscopic level.

Initially, the limestone surface in the limestone-water system is completely water-wet. When crude oil is added, the resins, major oil component in the light fraction of oil (i.e., maltene), competitively adsorb onto the limestone surface. Resins are negatively charged in oil with a dipole moment of 2.4–3.2 D, while water has an average dipole moment of 1.85 D [32, 35]. Due to greater forces of electrostatic attraction between the positive limestone surface and negatively charged resins, the resins adsorb onto the limestone surface. At the end of the steady decrease, as indicated in **Figure 12**, a monolayer of resins is formed, pushing the water molecules to the bulk.

Following the steady decrease of zeta potential, the limestone surface experiences a steep decrease in zeta potential value. This is attributed to the competitive adsorption between the resins and the asphaltene molecules. Asphaltene molecules, as reported earlier, have a dipole moment over the range of 3.3–6.9 D [36]. This signifies the ability of asphaltene molecules to carry a greater charge than resins. Therefore, during the wettability alteration process, asphaltenes carry a greater negative charge than resins and competitively adsorb onto the limestone surface,

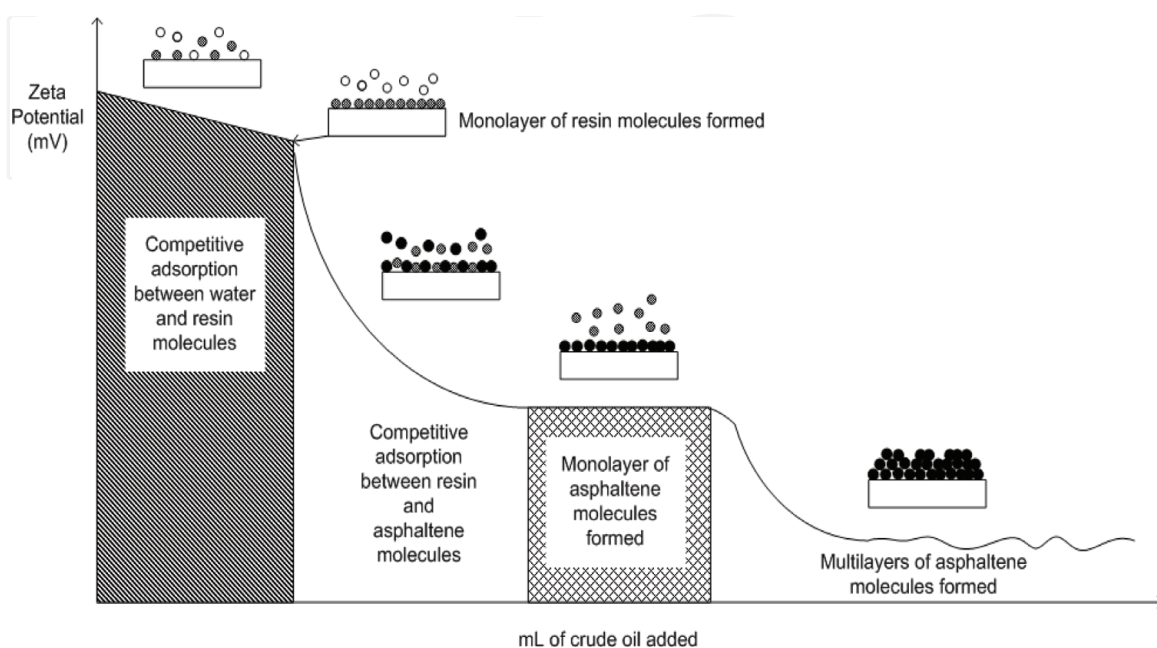


Figure 12.
Mechanism oil particles undergo during a wettability alteration process.

displacing the resin molecules to the bulk. The wettability curve flattens out when the asphaltene molecules form a monolayer on the limestone surface. Wettability studies of limestone for crude oils, A and B, tend to follow this behavior. Moreover, wettability of limestone for all asphaltenic solutions except 5 wt% is believed to follow this mechanism. According to a study conducted by Plank and Bassioni [37], CaCO_3 was found to correspond to a Type II isotherm [38].

According to Gregg et al. [39], the Type II isotherm, observed in physical adsorption, indicates the formation of a monolayer of particles onto the surface near the inflection point in the isotherm. Moreover, it allows for multiple layers to be formed above that monolayer of particles. The additional phenomenon, indicated in **Figure 12**, is believed to be observed in the wettability curve of limestone for crude oil C and is the reason behind the difference between the wettability of limestone for all asphaltenic solutions and 5 wt%. As the concentration of crude oil increases in the limestone-water crude oil system, another steep decrease in the zeta potential value is observed. The curve flattens out, and fluctuations are observed toward the end of the wettability curve. Discussing the mechanism following the monolayer formation of asphaltene molecules on limestone, it is believed that more asphaltene molecules approach the monolayer and adsorb onto it. This results in the formation of multilayers, leading to asphaltene deposition. This behavior can be attributed to the adsorption isotherm IV [38].

As described by Gregg et al. [39], the points of inflection in the adsorption isotherm type IV reflect the completion of monolayer as well as the onset of multilayer adsorption. Moreover, capillary condensation is associated with this isotherm where the adsorbate fills the small pores of the solid. In the case of the wettability alteration by crude oil, the pores can be assumed to be filled by asphaltenes which causes fluctuations. The wettability study, of limestone-oil system with water added, shows fluctuations at a significant level where oil is destabilized by water the system. Significant fluctuations, toward the end of the wettability profiles, are also evident in **Figure 4**, the wettability study of limestone for crude oil C, and evident in **Figure 10**, the wettability study of limestone for 5 wt% asphaltenic solution. When a concentrated liquid coats a porous solid, it tends to permeate through the solid rock and fill its pores. As observed from the wettability study of limestone-oil system with water added, water presence in such a system causes deposition of heavy fractions, leading to instability in the system.

Commonly, physical adsorption gives rise to such an isotherm resulting in multilayer adsorption. Components, comprising of aromatic rings, in the crude oil adsorb onto the monolayer of oil particles adsorbed on the CaCO_3 surface. As multilayers adsorb, the system experiences a steady decrease in the zeta potential value until a plateau is reached. Due to the multilayer adsorption, the thickness is believed to increase causing the CVI to measure a potential value at a distance beyond the electric double layer.

4. Conclusion

Complete wettability profiles of charged surfaces can be generated using zeta potential measurements. Unlike the commonly employed methods, the novel technique is able to study wettability in situ alteration. In the case of calcium carbonate and crude oil, the tolerance of the reservoir rock surface was observed while transitioning from a water-wet to an oil-wet surface. In this chapter, a comprehensive insight for the mechanism of inhibition of asphaltenes by inhibitors was provided. Moreover, a detailed discussion is provided on the role of asphaltene in wettability alteration, by stating the mechanism it follows in order to form multilayer adsorption.

According to literature, factors such as temperature, pressure, and pH have an effect on reservoir rock wettability. Therefore, further research can be carried out in order to study the effect of these factors on the wettability alteration process. Moreover, as the wettability study using zeta potential measurements is a novel technique, various other studies, in which traditional wettability methods were used, can be carried out with this approach. Additionally, a similar analysis can be carried out with different types of reservoir rocks, and wettability profiles can be generated.

Acknowledgements

Figures 3, 5, 11, and 12 have been adapted with permission from Ref. [33].
Copyright 2016 American Chemical Society.

Author details

Syed Taqvi¹ and Ghada Bassioni^{2*}

¹ University of Waterloo, Waterloo, Canada

² Ain Shams University, Cairo, Egypt

*Address all correspondence to: ghada_bassioni@eng.asu.edu.eg

IntechOpen

© 2019 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. 

References

- [1] Bortolotti V, Macini P, Srisuriyachai F. Wettability index of carbonatic reservoirs and EOR: Laboratory study to optimize alkali and surfactant flooding. In: SPE International Oil and Gas Conference and Exhibition in China; 2010. p. 12
- [2] Donaldson EC, Thomas RD, Lorenz PB. Wettability determination and its effect on recovery efficiency. *Society of Petroleum Engineers Journal*. 1969;**9**(1):13-20
- [3] Agbalaka CC, Dandekar AY, Patil SL, Khataniar S, Hemsath J. The effect of wettability on oil recovery: A review. In: SPE Asia Pacific Oil and Gas Conference and Exhibition; SPE; 2008. pp. 1-13
- [4] Glover P. Chapter 07: Wettability, Formation Evaluation M.Sc. Course Notes, Vol. 7, pp. 76-83; 2001
- [5] Fatt I, Klikoff WA. Effect of fractional wettability on multiphase flow through porous media. *Journal of Petroleum Technology*. 1959;**11**(10):71-76
- [6] Mohanty KK, Salter SJ. Multiphase flow in porous media: III oil mobilization, transverse dispersion and wettability. In: SPE 58th Annual Technical Conference and Exhibition; 1983. pp. 1-21
- [7] Lyons WC, Plisga GS, Lorenz MD. Reservoir engineering. In: Lyons WC, Plisga GS, Lorenz MD, editors. *Standard Handbook of Petroleum and Natural Gas Engineering*. 3rd ed. Elsevier; 2016. pp. 5-1-5-291
- [8] Zinszner B, Pellerin FM. *A Geoscientist's Guide to Petrophysics*, TECHNIP. Paris: IFP Publications; 2007
- [9] Taqvi ST, Almansoori A, Bassioni G. Modeling the impact of wettability alterations on calcium carbonate system for crude oil and asphaltenic solutions. *Industrial and Engineering Chemistry Research*. 2014;**53**(12):4773-4777
- [10] Hodne H. Rheological Performance of Cementitious Materials Used in Well Cementing. [Doctoral thesis]. Stavanger: University of Stavanger; 2007
- [11] Han KN. *Fundamentals of Aqueous Metallurgy*. Littleton: Society for Mining, Metallurgy, and Exploration, Inc; 2002
- [12] BTG Instruments GMBH. Product Sheet Mutek PCD-04 Particle Charge Detector. Wessling; 2007
- [13] Talero R, Pedrajas C, Rahhal V. Performance of fresh Portland cement pastes—Determination of some specific rheological parameters. In: Durairaj R, editor. *Rheology: New Concepts, Applications and Methods*. 1st ed. London: IntechOpen; 2013. pp. 57-79
- [14] Malvern Instruments. *Zetasizer Nano Series User Manual*. Worcestershire: Malvern Instruments Ltd.; 2004
- [15] Salopek B, Krasić D, Filipović S. Measurement and application of zeta-potential. *Rudarsko-Geološko-Naftni Zbornik*. 1992;**4**:147-151
- [16] Dukhin AS, Ohshima H, Shilov VN, Goetz PJ. Electroacoustics for concentrated dispersions. *Langmuir*. 1999;**15**(10):3445-3451
- [17] Moulin P, Roques H. Zeta potential measurement of calcium carbonate. *Journal of Colloid and Interface Science*. 2003;**261**(1):115-126
- [18] Patil S, Sandberg A, Heckert E, Self W, Seal S. Protein adsorption and cellular uptake of cerium oxide nanoparticles as a function

of zeta potential. *Biomaterials*. 2007;**28**(31):4600-4607

[19] Schellman JA, Stigter D. Electrical double layer, zeta potential, and electrophoretic charge of double-stranded DNA. *Biopolymers*. 1977;**16**(7):1415-1434

[20] Bangham AD. The adhesiveness of leukocytes with special reference to zeta potential. *Annals of the New York Academy of Sciences*. 1964;**116**:945-949

[21] Zhang Y et al. Zeta potential: A surface electrical characteristic to probe the interaction of nanoparticles with normal and cancer human breast epithelial cells. *Biomedical Microdevices*. 2008;**10**(2):321-328

[22] Weidenhammer P, Jacobasch HJ. Investigation of adhesion properties of polymer materials by atomic force microscopy and zeta potential measurements. *Journal of Colloid and Interface Science*. 1996;**180**(1):232-236

[23] Bassioni G. A study towards 'greener' construction. *Applied Energy*. 2012;**93**:132-137

[24] Bassioni G, Ali MM. Studying the physico-chemical properties of commercially available oil-well cement additives using calorimetry. *Journal of Thermal Analysis and Calorimetry*. 2013;**111**(1):295-303

[25] Bassioni G. Mechanistic aspects on the influence of inorganic anion adsorption on oilfield scale inhibition by citrate. *Journal of Petroleum Science and Engineering*. 2010;**70**(3-4):298-301

[26] Bassioni G, Taha Taqvi S. Wettability studies using zeta potential measurements. *Journal of Chemistry*. 2015;**2015**:1-6

[27] Elimelech M, Chen WH, Waypa JJ. Measuring the zeta (electrokinetic) potential of reverse osmosis membranes

by a streaming potential analyzer. *Desalination*. 1994;**95**(3):269-286

[28] Bassioni G, Ali MM, Almansoori A, Raudaschl-Sieber G, Kühn FE. Rapid determination of complex oil well cement properties using mathematical models. *RSC Advances*. 2017;**7**(9):5148-5157

[29] Bousse L, Mostarshed S, Van Der Shoot B, de Rooij NF, Gimmel P, Göpel W. Zeta potential measurements of Ta₂O₅ and SiO₂ thin films. *Journal of Colloid and Interface Science*. 1991;**147**(1):22-32

[30] Jayaweera P, Hettiarachchi S, Ocken H. Determination of the high temperature zeta potential and pH of zero charge of some transition metal oxides. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 1994;**85**(1):19-27

[31] Anderson WG. Wettability literature survey-part 3: The effects of wettability on the electrical properties of porous media. *Journal of Petroleum Technology*. 1986;**38**(12):1371-1378

[32] Yan J, Plancher H, Morrow NR. Wettability changes induced by adsorption of asphaltenes. *SPE Production & Facilities*. 1997;**12**(4):259-266

[33] Taqvi ST, Almansoori A, Bassioni G. Understanding the role of asphaltene in wettability alteration using ζ potential measurements. *Energy & Fuels*. 2016;**30**(3):1927-1932. DOI: 10.1021/acs.energyfuels.5b02127

[34] Gonzalez G. Surface charge and potential at the asphaltenes-solution interface. In: 8th International Conference on Petroleum Phase Behavior and Fouling; 2007

[35] Clough SA, Beers Y, Klein GP, Rothman LS. Dipole moment of water from Stark measurements of H₂O, HDO,

and D₂O. The Journal of Chemical Physics. 1973;**59**(5):2254-2259

[36] Goual L, Firoozabadi A. Effect of resins and DBSA on asphaltene precipitation from petroleum fluids. AIChE Journal. 2004;**50**(2):470-479

[37] Plank J, Bassioni G. Adsorption of carboxylate anions on a CaCO₃ surface. Zeitschrift für Naturforschung - Section B Journal of Chemical Sciences. 2007;**62**(10):1277-1284

[38] Lowell S, Shields JE, Morral JE. Powder surface area and porosity, 2nd edition. Journal of Engineering Materials and Technology. 1985;**107**(2):180

[39] Gregg SJ, Sing KSW, Salzberg HW. Adsorption surface area and porosity. Journal of the Electrochemical Society. 1967;**114**(11):279C