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**Influence of Electrostatic Potential to Wettability in Brine-Oil-
Minerals System**

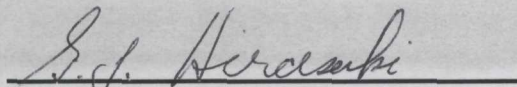
by

Tao Deng

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

Master of Science

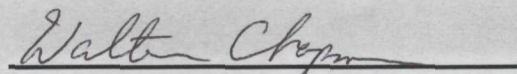
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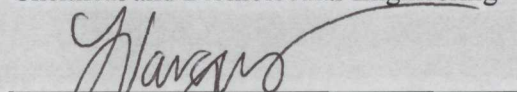
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ABSTRACT

Influence of Electrostatic Potential to Wettability in Brine-Oil-Minerals System

by

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This study improves the microscopic understanding of electrostatic potential to a reservoir's wettability, defined as the tendency of oil-wet or water-wet. Current conclusions about the wettability of oil reservoirs continue to be elusive, relying on some outdated or one-sided physical and chemical knowledge which requires further investigation. Poorly addressed problems on wettability alteration in a reservoir might lead to severe surfactant adsorption and finally reduce the efficiency of Chemical Enhanced Oil Recovery (EOR). By measuring the zeta potential in our Brine-Oil-Minerals (BOM) model system, the effects coming from acid/ basic characteristic of crude oil and operation conditions, such as temperature, salinity and ion composition, are comprehensively evaluated. Combined with the future contact angle measurement, this work aims to demonstrate the influence of electrostatic potential for fluid-fluid and rock-fluid on the wetting state of BOM model system. The micro-mechanisms learned by this study are expected to improve reservoir characterization, reservoir modeling and simulation, thereby optimizing reservoir management, well technology, production methods, and facilities.

Acknowledgments

I would like to express my sincere gratitude to my advisors, Dr. George J. Hirasaki and Dr. Sibani Lisa Biswal, for their guidance, patience and invaluable time spent on discussions in my scientific research at Rice. Their wisdom, insightful ideas, and inspirational encouragement have helped me accomplish this thesis, and will benefit me forever.

I would like to thank several people in the Chemical & Biomolecular Engineering Department. Thanks Dr. Walter Chapman and Dr. Francisco M. Vargas for attending my defense and being my thesis committee members. Thanks Dr. Clarence A. Miller and Ms. Maura C. Puerto for a lot of suggestions and assistance in my research. I thank Dr. Ying Wang for her contribution to the whole research project, as well as the care and help to me.

I am deeply appreciative of my labmates from Hirasaki's and Biswal's labs for their friendship, help and suggestions including Yongchao Zeng, Guoqiang Jian, Pengfei Dong, Leilei Zhang, and many others. I also want to thank several of my good friends in department who studied and played with me in the past two years.

Financial support from the Repsol Oil Company, and Consortium for Processes in Porous Media at Rice is acknowledged.

At the end, I would like to thank my family for their support and encouragement on my way.

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Nomenclature

BOM	Brine-Oil-Minerals system
EOR	Enhance Oil Recovery
USBM	the United States Bureau of Mines
LSW	Low Salinity Waterflooding
AN	Acid Number
BN	Base Number
OOIP	Original Oil in Place
MMP	Minimum Miscibility Pressure
API	American Petroleum Institute Gravity
ASP	Alkaline-Surfactant-Polymer Flooding
IFT	Interfacial Tension
ER	Oil Recovery Efficiency
QELS	Quasi-elastic Light Scattering
PDI	Potential Determining Ions
EDL	Electrical Double Layer
CPC	Cetylpyridinium Chloride
SDS	Sodium Dodecyl Sulfate

Chapter 1

Introduction

Using experimental methods, this thesis focuses on the role of electrostatic potential for quantifying the wettability of oil reservoirs. The primary questions are, 1) how oil components and operation conditions, such as brine composition, pH and salinity, can change the electrostatic potential of rock-brine interfaces and oil-brine interfaces, 2) and how these interactions reflect on wettability change. Measuring the zeta potential and contact angle in the Brine-Oil-Minerals (BOM) model system that I chose for evaluating the wettability change in the reservoir, I am able to answer these two questions and provide a platform to analyze the wettability alteration mechanisms for future research.

1.1. Wettability of Reservoirs

A reservoir consists of rock and void space, which has the ability to accumulate hydrocarbons (oil or gas) (Gluyas and Swarbrick, 2013). Sandstones and carbonates

are two of most common reservoir rocks. The wettability of a reservoir, defined as “the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids”, is determined by the interactions between reservoir rock, brine and crude oil (Craig, 1971). Wettability can significantly affect the capillary pressure, remaining oil saturation and relative permeability in petroleum reservoirs (W. G. Anderson, 1986). Based on these effects, there are two traditional techniques to identify reservoirs’ wetting by measuring capillary pressure-saturation curves: Amott indices measurement (Amott, 1959), and the United States Bureau of Mines (USBM) method (Donaldson et al. 1969).

Extensive studies focus on the mechanism of wettability alteration in reservoirs, but conclusions are still elusive and require further investigation. This is mainly due to a lack of understanding of wettability at the microscopic level, as well as to the complexity of the BOM system (J. S. Buckley and Liu, 1998b; Yu and Buckley, 1997; Collins and Melrose, 1983; W. Anderson, 1986). My work mainly focuses on the fundamental interactions related to wettability in the BOM model system, with an emphasis on electrostatic potential. Some contact angle measurements are planned to conduct for showing the wettability state of rock minerals. Although a complete wettability description of a reservoir requires morphological information about pore space, the wettability does rely on contact angles (Hirasaki, 1991).

1.2. Importance of Wettability to Oil Recovery

Surface forces, including electrostatic, van der Waals or structural, are extremely important to wettability of reservoir systems. An example that shows how these forces work is the phenomenon of capillary rise in cylindrical tubes, as shown in Figure 1-1. The height of rise is determined by the intermolecular forces between the liquid and solid surface. Based on Young-Laplace Equation, the wetting preference of tube surface can translate into the magnitude of water rising by affecting the capillary pressure.

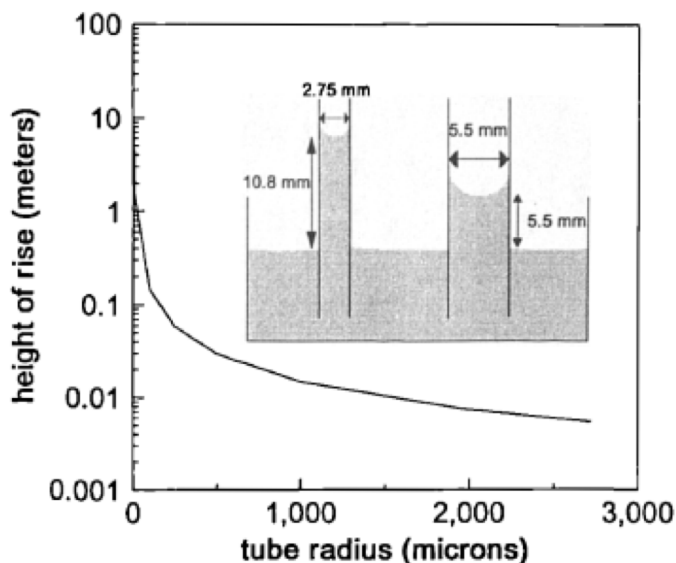


Figure 1-1 Water rises in cylindrical tube by capillary forces

(Jill S. Buckley, 1996)

It has been well known that the oil mixture (gas, oil, and gas) exists within the micron-sized pores of reservoir rocks. Similar to capillary rise, these surface forces in the reservoir are determined by pore structure, fluid properties and wettability state of reservoir rocks. Therefore, new oil recovery techniques should find a balance of

capillary, viscous, and gravitational forces to improve the recovery efficiency (William G. Anderson, 1987).

The wetting state of a reservoir is one of most acknowledged factors that affect oil recovery or oil displacement efficiency. Numerous publications have showed the relationship between rock wettability and oil placement in different multiphase flow problems, ranging from primary production processes to enhanced oil recovery mechanisms. Overall, when the wettability of a reservoir is assumed to be uniform and strongly water-wet, the water wets the surface of rocks and can occupy in the small pores. When injected with brine, some trapped oil drops are induced in large pores. If the reservoir is strongly oil-wet, the oil could wet the rock surface, while

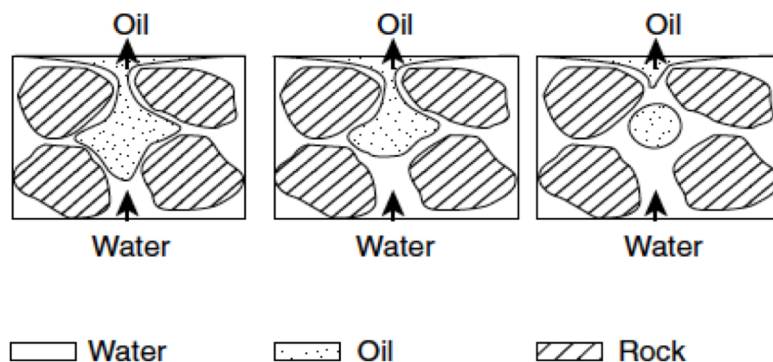


Figure 1-2 Oil displacement by water imbibition process, water-wet sand (Raza, Treiber, and Archer, 1968; William G. Anderson, 1987)

water can be found in some large pores after brine injection (Donaldson and Thomas, 1971). As a result, late breakthrough and little oil production after breakthrough are observed for strongly water-oil reservoirs, while early breakthrough and a relative long period of oil/water production are seen for strongly oil-wet reservoirs. These oil

placement processes are affected by the wetting state of reservoirs and can be shown in Figures 1-2 and 1-3.

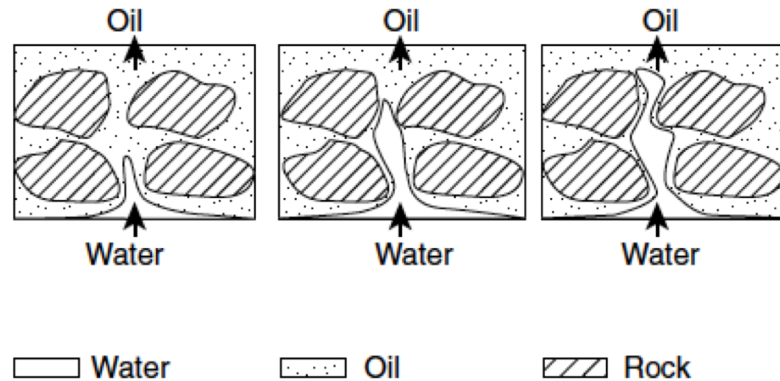


Figure 1-3 Oil displacement by water imbibition process, oil-wet sand (Raza, Treiber, and Archer 1968; William G. Anderson, 1987)

Oil displacement mechanisms dictated by the wettability suggest that oil recovery in strongly water-wet reservoirs by brine injection is more effective compared with oil-wet ones (W. G. Anderson, 1986). At the same time, the residual oil saturation for water flooding in strongly water-wet reservoirs is higher than for intermediate wettability cases but may be less than that for oil-wet cases. As the wettability changes to mixed- or intermediate-wet, the residual oil saturation commonly decreases and oil recovery would reach a maximum at some point, due to mobilization of trapped oil (Morrow, 1987; G.-Q. Tang and Morrow, 1999a; Johannesen and Graue, 2007). Anyway, the influence of wettability on oil recovery is obvious and some further investigations on wettability of reservoir should be continued to help us better understand what happens in oil reservoirs and keep improving oil production efficiency.

1.3. Motivation and Objectives

In this thesis, I propose to use the designed Brine-Oil-Minerals (BOM) model system to systematically study mechanisms governing the wettability of an oil reservoir, in order to improve the efficiency and mitigate uncertainty when applying Chemical EOR Technologies in different types of reservoirs. The learned mechanisms can also help us understand how low salinity waterflooding (LSW) works in a reservoir or even to design “smart water” to increase oil recovery efficiency. Overall, the knowledge of physical and chemical mechanisms in my thesis is helpful to improve reservoir characterization, reservoir modeling and simulation, reservoir management, well technology, production methods, and facilities.

In order to accomplish the objectives of this dissertation, the methods and purposes for each chapter are introduced as follows:

In chapter 2, I give a brief introduction to oil recovery techniques: primary oil recovery, water flooding and enhanced oil recovery (EOR). Then, some important technical background, including interfacial tension, contact angle, capillary pressure, electrostatic potential, and oil displacement mechanism, can help us understand how interfacial potential works in microscopic oil displacement process. Some main theories about how wettability of a reservoir is altered during LSW processes are summarized.

In chapter 3, pure calcite and silica powders, used as model rock samples, were used to study the brine/minerals interactions. The detailed experiment procedures

and methods for zeta potential measurement of rock are presented in this chapter. The zeta potential measuring of silica and calcite under different operation conditions, such as temperature, salinity, pH and ion composition, revealed the sensitivity of electric properties at the interface of rock and brine. Meanwhile, this part also summarizes the mechanisms of zeta potential change for rock-brine interface.

In chapter 4, model oil, mixture of 87% dodecane and 13% toluene, were chosen to model the crude oil in experiments. Acidic and basic chemicals were cyclohexanepentanoic acid and quinoline which are natural compositions of crude oil. Similarly, the procedures and methods to zeta potential measurement of oil are included. The effects coming from base, acid, pH, and ion composition are discussed. Also, it gives a comparison of zeta potential for model oil and silica particle in same brine condition. The aim of this chapter is to understand the brine-oil interactions in terms of the zeta potential.

Finally, the chapter 5 summarizes some mechanisms to explain the wettability change in the BOM system. Some main conclusions from the experimental results, as well as some future work, are introduced to help us understand recent results on wettability alteration in the literature.

Four appendices, at the end, show additional details to help others understand all the results. Appendix A contains glossary terms that were previously used in the introduction and background sections. The acid number (AN) or base number (BN) calculations for modifying model oil compositions are also displayed in Appendix B.

Appendix C will introduce the application of Stokes' Law to predict the settling time for zeta potential measurement. In addition, Appendix D shows all the data for comparing the contact angle change with the zeta potential of silica/ oil droplet in the future.

Chapter 2

General Theory and Literature Review

Global energy demand increases year by year, due to economical growth and rising of population. Statistical review by BP company shows the energy consumption of the world is expected to increase by 34% from 2014 to 2035 (Outlook, 2015). In such situation, hydrocarbons, as the major primary energy, would be always important to meet human's energy need. In order to increase oil production, one option is to search for new petroleum reservoirs, such as deep-sea or arctic reservoirs. However, oil recovery in these reservoir sources is not environmentally friendly or economically affordable under current technology conditions.

Another choice for increasing oil production is to develop new technology that can be used in old petroleum reservoirs. A good example is the application of Enhanced Oil Recovery (EOR), which aims to extract additional crude oil from reservoirs by injecting different fluids. As mentioned in the introduction part, the

wettability of a reservoir has huge impact on the oil displacement efficiency and capability for any types of oil recovery techniques. The wettability study focusing on fluid-fluid or fluid-rock interactions will definitely reduce the uncertainty of EOR applications and help design new oil recovery techniques in the future.

2.1. Overview of Oil Recovery

An oil reservoir is defined as the underground pool with hydrocarbons trapped in porous or fractured rock formations. The conventional reservoir means the crude oil or natural gas is contained by overlying rock formations with low permeability and can be produced at economic flow rates. However, “unconventional reservoirs cannot produce oil commercially without assistance from massive stimulation treatments or special recovery processes” (Etherington and McDonald 2004), including gas sands, gas shales, ultra-low permeability oil systems, and tight heavy oil, etc. The process of extracting oil from oil reservoirs is called oil recovery, and it can be grouped as primary, secondary, and tertiary (enhanced) oil recovery processes.

2.1.1. Primary and Secondary Oil Recovery

Primary oil recovery is the first stage of oil and gas production, in which the oil or gas is extracted by the natural energy drive of oil reservoirs, including gas cap, gravity drainage and water influx. When the hydrocarbons are driven towards the well and to the surface, the driving energy will gradually deplete. Due to the depletion of internal pressure, the primary oil recovery process typically produces 5-15% of

original oil in place (OOIP) (Green and Willhite, 1998).

Considering large amount of oil left in the reservoir after primary oil recovery, people commonly apply secondary recovery techniques by injecting some water or gas to displace oil and drive it to production well. The secondary recovery, sometimes known as water flood or gas flood, results in additional oil production that may account for 20-30 % of OOIP.

2.1.2. Enhanced Oil Recovery

The total produced oil by primary and secondary oil recovery processed generally takes up less than 40% of the original oil in place (OOIP). Since large amount of oil still remains inside the reservoir, Enhanced Oil Recovery (EOR), also known as tertiary oil recovery, is applied to extract more oil that is not economically produced only by water flooding (Donaldson, Chilingarian, and Yen 1989).

Generally speaking, there are several categories of EOR techniques have been successfully applied in oil production, including miscible flooding, thermal flooding, microbial flooding and chemical flooding EOR (Terry, 2001).

- **Miscible Flooding Processes**

The miscible flooding, as its name shows, is a miscible solvent injection process, in which the crude oil is displaced by the flowing solvent (Holm and Csaszar, 1962). The whole displacement process can maintain the reservoir pressure, as well as increase the oil recovery by improving macroscopic sweep efficiency (Shyeh-Yung, 1991). When the mobility ratio is favorable and no viscous fingering occurs, these two

interacting fluids can move like a plug flow as there is no interface. Therefore, miscible flooding improves the overall oil displacement efficiency. Generally, the miscible solvent used in EOR includes condensed hydrocarbons, natural gas, pressurized CO₂ or N₂. The most widely used solvent for miscible EOR is carbon dioxide because it has good miscibility with oil and can be economically used in most area. Since the determination of minimum miscibility pressure (MMP) and asphaltene deposition for CO₂ EOR do rely on the phase behaviors of gas-oil mixtures in the reservoir, factors should be considered are reservoir heterogeneity, temperature, pressure, crude oil composition, etc.

- Thermal Flooding Processes

Thermal flooding is applied to increase reservoir temperature for reducing oil viscosity or vaporize part of crude oil and thus decrease the mobility ratio. The methods to achieve this goal includes steam injection, hot water injection and air injection (combustion) (Willman et al. 1961).

These methods can improve the sweep efficiency and the displacement efficiency of the oil recovery, and be widely used in recovering oil sand or some other heavy oils (API<20). An improved method recently is called solar thermal enhanced oil recovery, which takes use of solar energy to produce steam (Kraemer et al. 2009).

- Microbial Flooding processes

Microbial enhanced oil recovery takes use of some microorganisms, with the ability to degrade heavy oils and produce bio-surfactants, to modify the interfacial properties of oil-water-mineral system and finally facilitate oil production (Banat,

Makkar, and Cameotra 2000). Although the injected or produced chemicals are biodegradable and environmental friendly, microbial EOR is rarely used due to high cost and microbial growth or cultivation problems.

- Chemical Flooding Processes

Chemical flooding EOR refers to the application of alkaline flooding, surfactant flooding, polymer flooding, or any combination of techniques, to improve the oil recovery (Sheng, 2010). The injected alkaline or caustic solutions, like NaOH or Na₂CO₃, can react with some acidic oil component and generate soap to lower the interfacial tension; the injected water-soluble polymers can increase the viscosity of displacing fluid to reduce the mobility ratio; the injected surfactants mobilize the oil by lower the interfacial tension or capillary pressure. For most reservoirs, some common applied chemical EOR techniques are Surfactant-Polymer (SP) flooding, Alkaline-Surfactant-Polymer (ASP) flooding, Alkaline-Polymer (AP) flooding. The choice of these methods need to base on a lot of reservoir parameters, such as heterogeneity, permeability, temperature, chemistry of the rock or crude oil, etc. Some main factors limiting the application of chemical EOR include the high cost of chemicals, adsorption loss, as well as the instability of these chemicals in reservoir conditions with high temperature or high salinity.

As the overview shows, the application of different EOR techniques do rely on the properties of reservoirs, however, it is also strongly affected by economics and crude oil price. The investors' willingness to manage EOR risk or economic exposure is important to the initiation of EOR projects (Alvarado and Manrique, 2010), as

illustrated in Figure 2-1. In the US, the number of chemical and thermal EOR projects keeps declining for a long time, while the EOR gas injection projects exhibits a growing trend after 2000. Two important reasons are: 1) A readily available CO₂ pipeline system; 2) Oil price increases from \$ 20/ bbl. to about \$ 120/ bbl.

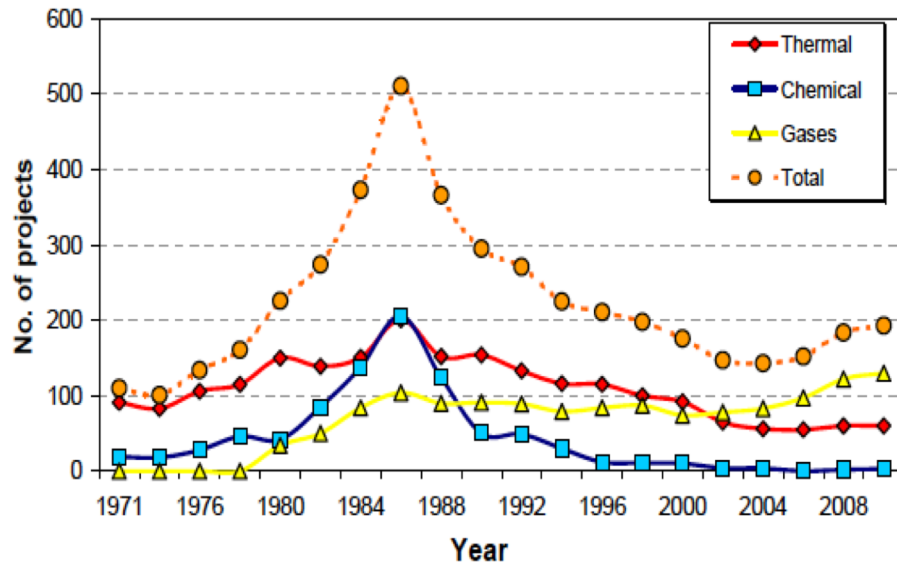


Figure 2-1 Evolution of EOR projects in the United States from Oil & Gas Journal EOR Surveys 1976–2010 (Alvarado and Manrique, 2010)

2.2. Wettability Phenomenon in Oil Recovery

“Wettability is defined as the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids” (Craig, 1971). Since the wettability depends on the interactions among rock, brine and crude oil, a reservoir’s wettability is affected by the chemical or physical properties of the oil and rock, the initial water saturation, the composition of brine, temperature, pressure, etc. It can be simply categorized as oil-wet, water-wet and neutral (or intermediate) wet, which means no strong preference for either oil or water.

2.2.1. Interfacial Tension

Interfacial tension (IFT) is a material property of the interface between two immiscible fluids, caused by intermolecular interactions (Israelachvili, 2011). Surface tension is named if the interface is between liquid and gas. The IFT can be defined as a force per unit length parallel to the interface or the excess free energy per unit area in thermodynamic approach. Both definitions are equivalent, but it is commonly called surface energy, when defined as energy per unit area. The interfacial tension of oil-brine interface is important to oil recovery processes, which can be affected by some reservoir conditions, such as salinity and temperature. For instance, the injected surfactant by chemical EOR can reduce the interfacial tension of oil-brine interface and crude oil viscosity, which finally mobilize the residual oil.

The widely used techniques to measure the interfacial tension include sessile bubble method, spinning drop method or pendant drop method. The Young-Laplace

equation is applied in the calculation, see Equation 2-1.

$$p_A - p_B = -2H\gamma$$

Equation 2-1 Young-Laplace Equation

where p_A is the phase pressure of fluid A, p_B is the phase pressure of fluid B, $2H$ is the mean curvature of interface between fluid A and fluid B, γ is interfacial tension between these two immiscible fluid phases.

2.2.2. Contact Angle

The most common method to quantify the wettability of a reservoir is to measure the contact angle with oil and water on the smooth surface of reservoir rocks. If the rock is strongly oil-wet, the oil (wetting phase) will try to spread over the entire surface; conversely, if it is strongly water-wet, the oil drop (non-wetting phase) will bead up and minimize the contact with the surface (Abdallah et al. 1986).

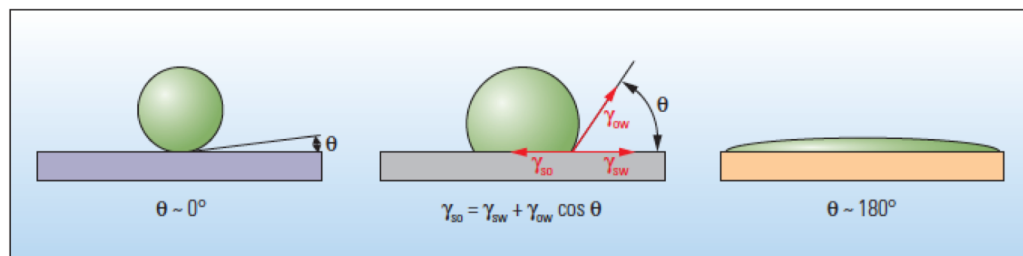


Figure 2-2 Contact angle: force balances at three phase contact line (Abdallah et al. 1986)

However, if the condition is neither strongly oil-wet or water-wet, the balance of interactions in this three-phase system will be established and result in a contact angle θ , as shown in Figure 2-2.

In Figure 2-2, the oil drop (green) is surrounded by water (blue) on the surface of substrate; if the surface is perfectly water-wet (left), the contact angle θ is approximately zero. If the surface is perfectly oil-wet (right), the contact angle should be close to 180° . For intermediate-wet surface (center), the contact angle is affected by the force balance among the interfacial energy terms.

The Young's equation can relate the contact angle θ to the interfacial energy as follows:

$$\gamma_{so} = \gamma_{sw} + \gamma_{ow} \cos\theta$$

Equation 2-2 Young's Equation for contact angle

where, θ represents the contact angle between water and substrate surface (Figure 2-2). γ_{so} is the surface energy between oil and substrate, γ_{sw} is the surface energy between water and substrate, and γ_{ow} is the interfacial tension between oil and water phases.

The Phenomena of contact angle hysteresis is commonly observed in the measurement of contact angle. When the contact line in three-phase system is pinned, the contact angle would be form and keep stable after some time. If keep removing a small amount of oil from the drop, the contact angle θ (in the water phase) would increase and finally reach a maximal one, called water advancing contact angle θ_A . However, if keep adding oil, the contact angle would decrease and the final minimal angle is called water receding contact angle θ_R . The hysteresis of contact angle is normally defined as the difference of advancing and receding contact angles, $\theta_A - \theta_R$. This value is affected by the physical and chemical heterogeneity (Israelachvili 2011).

The adsorption of oil components, like asphaltenes, on the interface would cause big variations to advancing or receding contact angles (Yang et al. 1999; Xie, Morrow, and Buckley, 2002).

2.2.3. Capillary Pressure

Capillary pressure is defined as the pressure difference between two immiscible phases: non-wetting and wetting phases, as the Equation 2-3. The Young-Laplace equation relates this pressure difference with interfacial tension γ , the effective radius R , and the contact angle θ in a circular tube, if assuming a spherical interface, in Equation 2-4. The capillary pressure P_c is affected by the wettability and curvature of interface between two fluids.

$$P_c = P_{nw} - P_w$$

Equation 2-4 Definition of capillary pressure

$$P_c = \frac{2\gamma \cos\theta}{R}$$

Equation 2-3 Young-Laplace Equation for capillary pressure

where, P_c is the capillary pressure between two immiscible fluid phases, P_w is pressure in the wetting phase, P_{nw} is pressure in the non-wetting phase, γ is interfacial tension between two fluid phases, θ is the contact angle, measured in wetting phase, and R is the radius of circular tube.

2.2.4. Oil Recovery Efficiency

The flow through a porous medium can be macroscopically described by

Darcy's equation, which was developed by Henry Darcy in 1856. It shows the superficial flow rate is a function of medium's permeability, fluid viscosity and flow potential. For multi-phase flow problems, effective permeability, relative permeability for each phase, as well as capillary pressure are used.

Based on the overall mass balance in a reservoir, the total oil recovery efficiency (ER) is defined as:

$$ER = \frac{N_p}{N}$$

Equation 2-5 Definition of oil recovery efficiency

where N is the Original Oil in Place (OOIP) for reservoirs, N_p is the cumulative oil recovered by oil recovery processes.

The total efficiency ER consists of macroscopic or volumetric sweep efficiency E_v and the microscopic displacement efficiency E_D , as shown in Equation 2-6.

$$ER = E_D \cdot E_v$$

Equation 2-6 Expression of total recovery efficiency

$$E_v = E_s \cdot E_i$$

Equation 2-7 Macroscopic volumetric sweep efficiency

The macroscopic volumetric sweep efficiency E_v describes the fraction of volumes swept by the displacing fluid to the total volume of reservoirs (Lake L., 1989). In real reservoirs, it can be expressed as the product of areal sweep efficiency E_s and vertical sweep efficiency E_i , shown in Equation 2-7. For any given oil reservoir, the

overall sweep efficiency depends on permeability heterogeneity, reservoir thickness, mobility ratio, density and viscosity difference between fluids, and fractures, etc. Poor sweep efficiency will increase the operation cost and can be solved by mobility control methods, such as foams or polymers.

Microscopic displacement efficiency refers to the ratio of the extractable oil to the original oil in place (OOIP) at the pore level. Some parameters affecting the oil displacement efficiency include capillary pressure, relative permeability, interfacial tensions, and wettability. For oil-wet reservoirs, even if flooding for a long time, some oil would still remain in the pore by forming oil film. For water-wet reservoirs, trapped oil or “oil blobs” would stay in the middle of pore, due to the effect of bypassing and snap-off (Chatzis et al. 1983).

2.3. Electrostatic Potential

The wetting state of reservoir systems is governed by surface intermolecular interactions, and one of the most important interactions is electrostatic force. This force is caused by presence of surface charges on surface. Many different processes, like ions/chemicals adsorption, protonation/deprotonation and external electric field, can affect this charge. For colloidal study, the surface charge is an important surface characteristic because it can determine many properties of suspension or emulsion, such as particle size distribution, stability, etc.

Electrostatic potential measures “the work done in bringing a unit charge from infinity up to the near neighborhood of the charged object” (Hunter, 2013). It depends on the surface charge, distance, and dielectric constant of medium.

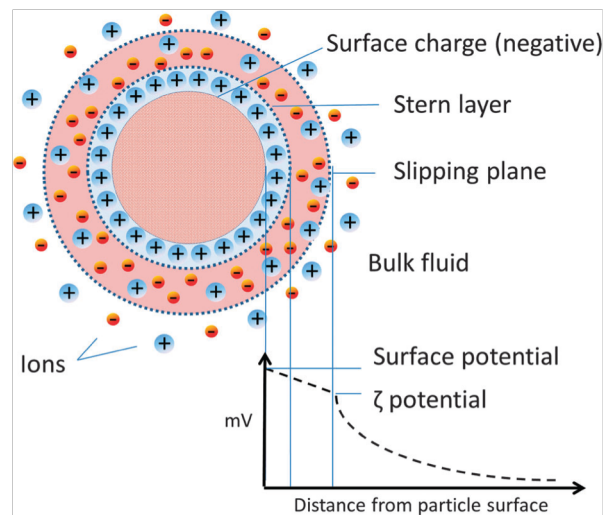


Figure 2-3 The zeta potential of a negatively charged particle (Liese and Hilterhaus, 2013)

2.3.1. Zeta Potential

The zeta potential is the electrical potential in the vicinity of a particle corresponding the “slipping plane” between the fluid that moves with the particle and the bulk fluid (Hunter, 2013), and the position is shown in Figure 2-3. It is a function of the surface charge, which gives a measure of the magnitude for the electrostatic or charge repulsion/attraction between particles. The DLVO theory was developed by Derjaguin, Landau, Verwey and Overbeek in 1940s (Verwey, 1947; Derjaguin and Landau, 1941). Based on DLVO theory, which combines the effects from van der Waals attraction and electrostatic repulsive interaction, zeta potential is an important factor controlling the dispersion stability of suspensions. Therefore, zeta potential measurement can provide us a detailed insight into the causes of dispersion, aggregation or flocculation. It can also be applied to improve the formulation of a dispersed system.

For the wettability of a reservoir, electrical properties (zeta potential) on the interfaces of different fluids are one of important aspects to determine the affinity interaction between the rock and the reservoir fluids. By changing the rock-oil interactions or rock-water interactions, the wetting state of reservoirs may be altered to help improve the oil recovery efficiency. Therefore, electrical surface charge change is one important aspect we should consider when studying wettability alteration mechanisms.

2.3.2. Calculation of Zeta Potential

1) The most common method to measure zeta potential is **electrophoresis**, which is the migration of (macro-) ions in media when applying an electric field. For moderate field strengths, <200 V/cm, the steady-state electrophoretic velocity V_e of the migrating macro-ions is proportional to the applied electric field E . The relationship is shown in Equation 2-8, where μ is the electrophoretic mobility, or velocity per unit electric field.

$$V_e = \mu \cdot E$$

Equation 2-8 Expression of electrophoretic velocity

2) Effective Charge:

If the hydrodynamic radius R_h is known, the effective charge is computed through the following relationship:

$$Ze = 6\pi\eta R_h \mu \frac{1 + \kappa R_h}{f(\kappa R_h)}$$

Equation 2-9 Henry's Equation for zeta potential calculation

where Z is the valence of the macromolecules, e ($\sim 1.6 \times 10^{-19}$ coulombs) is the elementary charge, η is the sample viscosity, κ is the Debye-Hückel parameter, and $f(\kappa R_h)$ is Henry's function. The Henry's function can be simplified as:

$$\lim_{\kappa R_h \rightarrow \infty} f(\kappa R_h) = \frac{3}{2} \qquad \lim_{\kappa R_h \rightarrow 0} f(\kappa R_h) = 1$$

Equation 2-10 Simplification of Henry's Function

Thus, the Henry's Equation can transform into Smoluchowski's Equation or Hückel's Equation.

3) Zeta Potential

Smoluchowski's Equation is the most applied model when the molecular hydrodynamic radius R_h is much larger than the Debye length κ^{-1} , the Smoluchowski's equation can be used as:

$$\zeta = \frac{\eta\mu}{\varepsilon_0\varepsilon_r}$$

Equation 2-11 Smoluchowski's Equation for zeta potential

Where ε_0 ($\sim 8.854 \times 10^{-12}$ F/m) is the permittivity of free space, and ε_r (~ 80 for water at 20 °C) is the solvent dielectric constant.

One of the most widely known usages for zeta potential is in the determination of colloidal stability. If the magnitude of zeta potential increases, the probability of molecules aggregating and flocculating out of the solution would decrease. The accepted criterion for colloidal stability is DLVO theory.

2.4. Zeta Potential and Wettability Alteration

Surface intermolecular forces governing the wetting state of brine-oil-mineral systems can be modelled through the disjoining pressure isotherm (Hirasaki, 1991). In three-phase contact region, disjoining pressure, which combines double layer forces, London-van der Waals forces and structural forces together, can describe the stability of thin water or oil film. The electrostatic component of the disjoining pressure is a function of the charge or electrical potential between two interfaces. As shown in Figure 2-4, because of the large electrostatic potential of interfaces in low salinity brine, the disjoining pressure tends to be positive and cause repulsion of two phases. While at high salinity (larger than 1.0 M), since the magnitude of electrostatic potential on the surface is small, the disjoining pressure is negative and dominant by attractive forces. (Hirasaki, 1991).

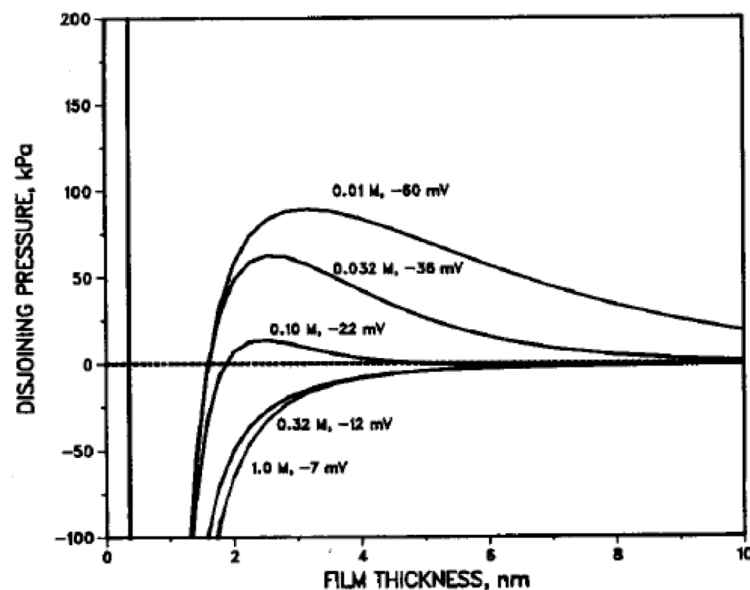


Figure 2-4 Disjoining pressure isotherms under same surface charges but different surface potentials and electrolyte concentration (Hirasaki, 1991)

The electrostatic properties of the oil-brine and mineral-brine interfaces can be characterized by measurement of the zeta potential as a function of operation conditions, such as ion composition, pH, temperature and salinity. If the oil-brine and mineral-brine interfaces has similar charges or zeta potential, the repulsive electrostatic forces can cause a highly positive disjoining pressure, and keep thick water film. In this way, the wetting stating of whole system would be altered to more water-wet (J. S. Buckley et al. 1989; Dubey and Doe, 1993a; Mahani, Keya, Berg, Bartels, et al. 2015).

2.4.1. Zeta Potential of Brine-Minerals interfaces

Sandstones and carbonates are two dominant rock types for reservoirs. The zeta potential close to the surface of minerals do depend on surface charges and

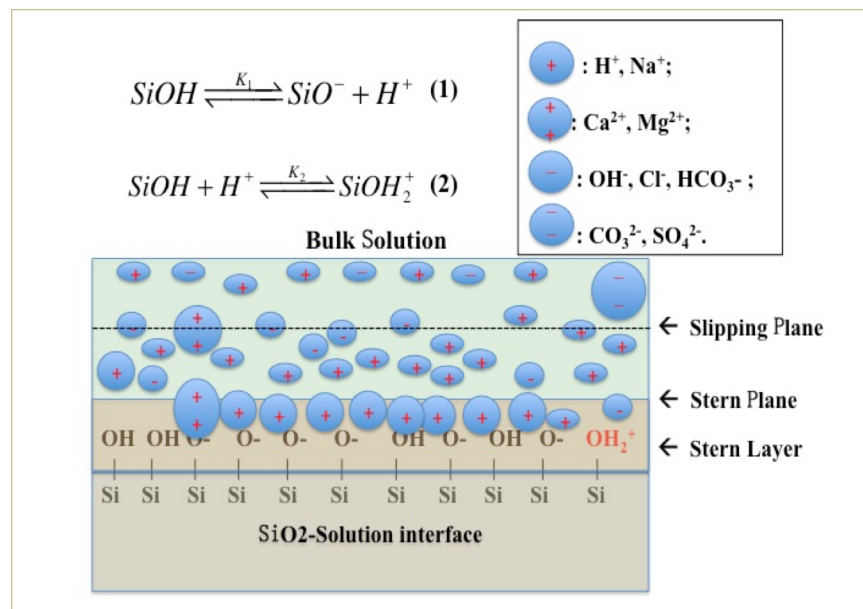


Figure 2-5 Schematic diagram for equilibrium of H^+ protonation/ deprotonation on the surface of silica particle

double layer thickness. In the brine-oil-minerals system, the most important characteristics of brine are pH, salinity, and the concentration of the potential determining ions (PDIs). For sandstones, surface charges of rocks are mainly determined by the pH of brine, based on the degree of H⁺ protonation (Lucassen and Hansen, 1967; Pashley and Kitchener, 1979), shown in Figure 2-5. The zeta potential for quartz is always negative when pH larger than 2. The salinity or ionic strength of brine can reduce the magnitude of zeta potential by compressing the double layer.

For carbonates, the PDIs in brine can significantly change the surface potential. The common PDIs are calcium, magnesium, carbonate, and sulfate ions, which constitute the carbonate minerals. pH still works on the electrostatic potential of carbonates since it can determine the equilibrium of bicarbonate and carbonate ions

Table 2-1 The reactions involved in Calcite-CO₂-H₂O system equilibrium at 25 °C and low ionic strength (activity coefficient=1) (Siffert and Fimbel, 1984; Ma et al. 2013; Cui et al. 2014)

Reaction	Equilibrium Constant	-log ₁₀ (K) at 25 °C
$CaCO_3(s) \leftrightarrow Ca^{2+} + CO_3^{2-}$	$K_{sp} = [Ca^{2+}][CO_3^{2-}]$	8.42
$CO_2(g) + H_2O(l) \leftrightarrow H_2CO_3$	$K_H = \frac{[H_2CO_3]}{P_{CO_2}}$	1.47
$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$	$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$	6.35
$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$	$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$	10.33
$H_2O(l) \leftrightarrow H^+ + OH^-$	$K_w = [H^+][OH^-]$	14.0

in the brine (Somasundaran and Agar, 1967; Thompson and Pownall, 1989; Moulin and Roques, 2003). For the zeta potential measurement of carbonates, such as calcite, the gas-liquid-solid equilibrium is extremely important to get reliable results and the equilibrium can be related to the chemical reactions in Table 2-1. Herberling et al. (2011) reported the isoelectric pH for calcite is a function of partial pressure of CO_2 , based on zeta potential-pH curves under different atmospheric CO_2 pressure, shown in Figure 2-6 (Heberling et al. 2011). Chen et al. (2014) studies the zeta potential of

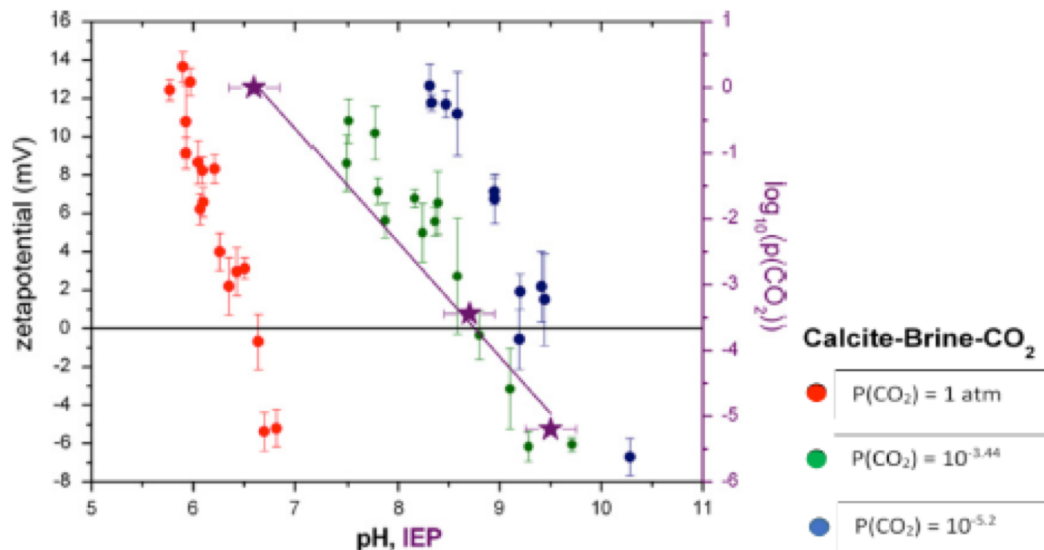


Figure 2-6 Zeta potential of calcite in brine with different CO_2 partial pressure. Purpose line is correlation of isoelectric pH as a function of CO_2 partial pressure. (Heberling et al. 2011)

limestone and found high salinity has dominant effect on the zeta potential, compared with surfactants adsorption (Chen et al. 2014).

The effect of PDIs, such as Mg^{2+} , Ca^{2+} and SO_4^{2-} , to the zeta potential of carbonates (chalk) has been studied by Zhang and Austad (2006). It was observed that the zeta potential can be reduced or even becomes negative if the ratio of sulfate

concentration to calcium concentration decreases (Zhang and Austad, 2006a).

Mahani et al. (2015) explored the effects of salinity and pH on the zeta potential of carbonate rock by surface complexation modeling. The result showed zeta potentials of carbonates at high salinity are positive, while become more negative if diluting to extremely low salinity. The pH dependence (positive slope) of zeta potential at low salinity is stronger than that of high salinity. The study also confirmed that the zeta potentials of carbonates will become more negative if diluting brine or adding sulfate (Mahani, Keya, Berg, and Nasralla 2015).

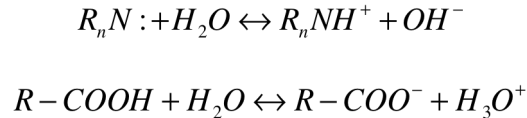
Hirasaki et al. (2004) pointed out the zeta potential of calcite can be negative even at neutral pH condition, when the brine contains excess of CO_3^{2-} and HCO_3^- . If the oil-brine and calcite-brine interfaces are all negative, the electrical repulsion tends to stabilize the brine film between oil and calcite phases and lead to more water-wet (G. Hirasaki and Zhang, 2004).

2.4.2. Zeta Potential of Brine-Oil interfaces

Crude oil contains hundreds of components, some of them even cannot be separated or identified by modern techniques. Based on the physical and chemical properties, these components after SARA separation can be approximately categorized as saturates, aromatics, resins and asphaltenes. Most attention with respect to wettability, has mainly focused on the surface active materials, such as resins and asphaltenes. Generally, they are grouped into acidic, basic or neutral

compounds, which can be expressed as acid number (AN) or base number (BN) to describe the property of crude oil.

Commonly, the acidic materials present in crude oil have long polar tails with carboxylic group, -COOH. The basics contains nitrogen as part of aromatics, RN, which



Equation 2-12 Reactions for base protonation and acid dissociation

can provide reactive pairs of electrons to protonate with H⁺. pH of brine determines the charge state of the acidic or basic crude oil components, as shown in Equation 2-12. With the decrease of pH in brine, the zeta potential measurement shows the brine-oil interfacial charges can change from negative to positive.

The surface charge of brine-oil interfaces is affected by dissociation of acids, protonation of bases, as well as the presence of asphaltenes (J. S. Buckley et al. 1989; Dubey and Doe, 1993b). Nasralla et al. (2011) reported the zeta potential of brine-oil interfaces is highly negative with low salinity water, while almost zero with high salinity water. This highly negative zeta potential in low salinity water can explain the wettability alteration in mica surface, due to the increase of repulsion forces (Nasralla, Bataweel, and Nasr-El-Din 2011).

2.5. Wettability Alteration in Low Salinity Waterflooding

The wettability alteration can occur in any kind of oil recovery processes, ranging from primary oil recovery to enhanced oil recovery techniques. The most important application of wettability alteration is low salinity waterflooding (LSW). By modifying the composition of the injection brine, the water flood processes, also called “smart water”, are able to change the wettability of reservoirs and improve oil recovery (Austad, 2013). Therefore, to illustrate the importance of oil-brine or mineral-brine interactions, the following part will give an introduction on the wettability alteration mechanisms for LSW, including: 1) Fine migration; 2) Multiple ion exchange; 3) Double layer effects; 4) Mineral dissolution; 5) Effect of pH increase and soap generation, etc.

- Fines migration

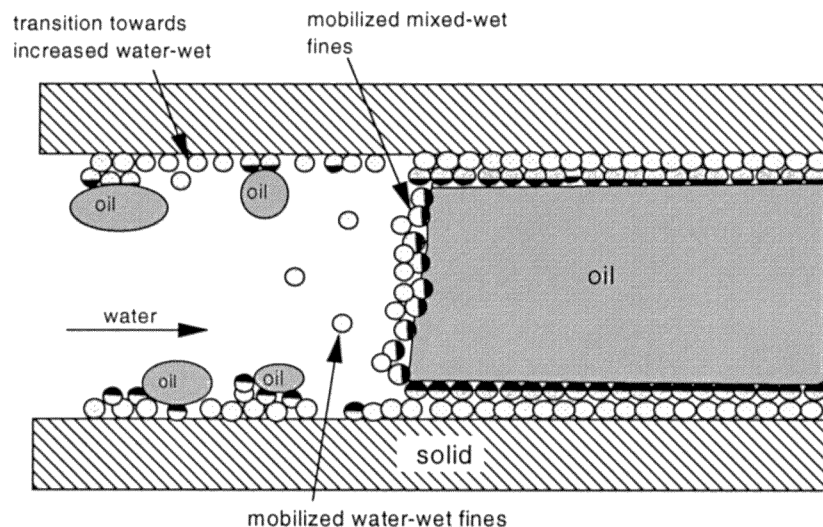


Figure 2-7 The migration of mixed-wet fines in pore during waterflooding (G.-Q. Tang and Morrow, 1999b)

Some polar components of crude oil, such as acid or base, can be adsorbed on the surface of minerals. Since mobile clay fragments or fines also exist in the outer surface of minerals, the mixed-wet fines would be formed due to the adsorption. After changing the brine salinity and composition during waterflooding, the fines would be released from the rock surface, due to the change of disjoining pressure. The polar component adsorbed on fines will also detach and move with fines, which improves the water-wetness and oil recovery (G.-Q. Tang and Morrow, 1999b; G. Tang and Morrow, 2002). Additionally, the movable fine particle can improve the microscopic sweep efficiency by blocking the pore throats and diverting the water flow direction. The performance of fines migration depends on brine-minerals interactions, which can be related with mineralogy, as well as brine salinity and composition.

- Multiple ion exchange

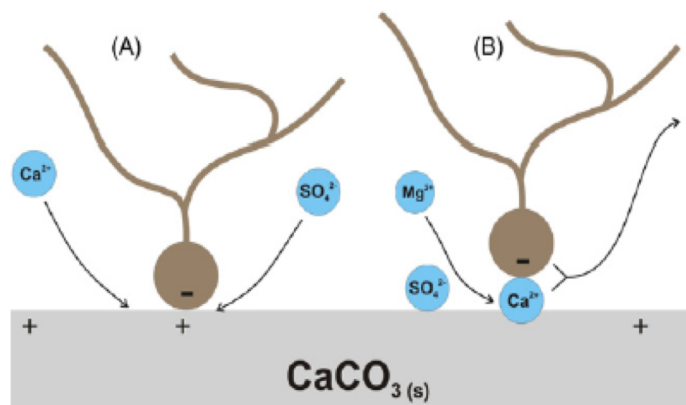


Figure 2-8 Wettability alteration by multiple ion exchange, A) The presence of Ca^{2+} and SO_4^{2-} at lower and high temperature; B) The presence of Mg^{2+} at higher temperature. (Zhang, Tweheyo, and Austad 2007)

Some divalent ions, like Ca^{2+} , Mg^{2+} and SO_4^{2-} , are defined as potential determining ions (PDIs). As shown in Figure 2-8, the wettability modification

happens in water-rock interfaces: the divalent anion, SO_4^{2-} , can compete with acid components of crude oil to adsorb on the positively charged water wet-sites of mineral surface. When the mineral surface becomes less charged, more divalent cations, Ca^{2+} or Mg^{2+} , will also be attracted to the surface and react with adsorbed acids. Therefore, more acid components would be released from the mineral surface and lead to more water-wet condition. At the same time, the Mg^{2+} in brine can also replace the Ca^{2+} in mineral (chalk) lattice or calcium-acid complex at high temperature, which accelerates the release of acids from the surface (Zhang and Austad 2006b; Zhang, Tweheyo, and Austad 2007; Strand, Høgnesen, and Austad 2006).

- Double layer effects

In a reservoir, the polar and ionic components in crude oil can be attracted or absorbed on the surface of minerals. If the surface is negatively charged as silica, some components with positive charges are more likely to adsorb on the surface; while some negatively charged molecules can also be attached to mineral surface by multivalent cation bridging (Lee et al. 2010).

In the low salinity waterflooding process, the diffuse layer around the mineral-oil complex would expand, due to the reduction of salinity and multivalent ion concentrations. The expansion of double layer will result in displacement of multivalent ions and increase the electrostatic repulsion, which help release of oil components from mineral surface and then change the wettability of rock surface (Ligthelm et al. 2009; Nasralla and Nasr-El-Din 2014).

All of these three wettability alteration mechanisms, which explain the improvement of oil recovery efficiency for LSW, are related to the change of oil-brine and minerals-brine interactions in reservoir systems. Apart from these three mechanisms, the dissolution of minerals, especially for the carbonates, can also change the wettability of reservoirs and release polar oil components from the pore surface (Pu et al. 2008). For crude oil with high acid number, the increase of pH in brine can lead to in-situ surfactant generation and removal of multivalent cations; the produced surfactants can also reduce the interfacial tension of crude oil by generating foam, just like in alkaline flooding processes (Jensen and Radke, 1988).

2.6. Reasons for Using Model System

A real oil reservoir contains three phases: crude oil, formation brine, and rock minerals. Its initial of wetting property is established by chemical equilibrium among these three phases under specific reservoir temperature and pressure for a long time. All kinds of components in brine-oil-mineral systems interact with each other, and it is hard to describe the whole equilibrium relationship by involving all the components. Considering this problem, we can use model system to help us describe the wettability of reservoir systems and find the dominant factors for wettability alteration under different operation conditions. The chemical or physical mechanisms gotten by this fundamental study will definitely improve our understanding of enhanced oil recovery processes and help design more efficient oil recover techniques in the future.

Chapter 3

Electrostatic Potential Measurement of Minerals

The interfacial phenomena in the brine-oil-minerals (BOM) system are controlled by the electrical double layer (EDL) forces. The charged species in brine can change the forces by transferring across or accumulating in the double layer. Therefore, in order to know more about wettability, it is necessary identify these charged species and their effects on electrostatic potential. Other factors, such as salinity, temperature and pH, also need to be considered in the study for evaluating the wettability under different reservoir conditions.

This chapter will focus on the electrostatic potential (zeta potential) of calcite and silica, areas studied could be quickly summarized: 1) Stokes' Law, describing spherical objects with low Reynolds number in viscous solution, is used to give a prediction of particle-settling times suitable for zeta potential studies, as introduced in Appendix C. 2) Proper procedures to measure zeta potential of rock sample. 3)

Zeta potential of calcite: systematic study on effects coming from ions (divalent ion adsorption), equilibrium time, salinity and temperature. 4) Zeta potential of silica: systematic study on effects coming from ions (divalent ion adsorption), NaHCO_3 -neutralization, salinity, pH and temperature.

3.1. Summary

The Stokes' Law, describing spherical objects with low Reynolds number in viscous solution, was introduced to give a prediction of the particle-settling times. An acceptable settling time was found so to be sure that there are enough small particles dispersed in solution, which can produce reliable test results with small zeta potential deviation.

Several electrolytes brine solutions with ionic strength of 0.1 M were prepared to explore ions effect on the zeta potential of calcite. Test results indicated that (1) an equilibrium time of 24 hours is enough to get a stable zeta potential for calcite dispersions, except for the case in bicarbonates. (2) The dissolution of calcite in DI water or NaCl brine can make positive zeta potential. (3) Divalent ion adsorption can make a big change to zeta potential of calcite; excess of divalent cations, like Ca^{2+} , Mg^{2+} , makes more positive zeta potential; excess of divalent anions, like CO_3^{2-} , SO_4^{2-} , can even change the zeta potential into negative, compared with the zeta potential in NaCl solution. (4) Large pH, like pH in Na_2CO_3 , NaHCO_3 solution where the dissolution is limited, could also alter its zeta potential. (5) Further results showed a small

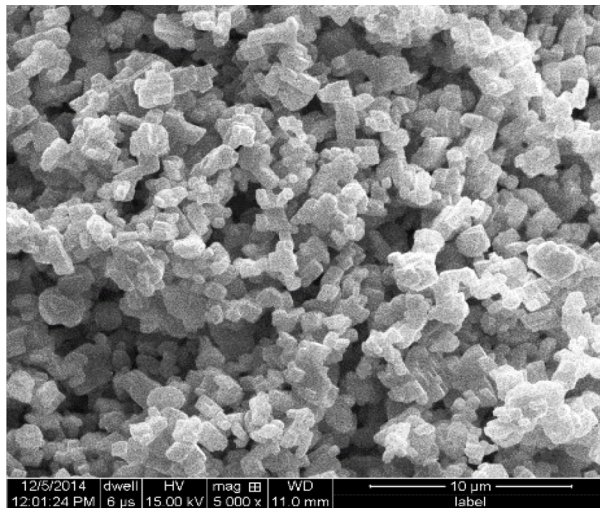
increase of temperature can change the magnitude of zeta potential by reducing the extent of dissolution, while its effect on ion adsorption (Ca^{2+} and SO_4^{2-}) is limited.

Then, same experiments were conducted to study the zeta potential of silica. Test results indicated that (1) divalent cation adsorption, like Ca^{2+} , Mg^{2+} , can significantly reduce the magnitude of negative zeta potential; large pH, like pH in Na_2CO_3 , NaHCO_3 solution, could also make its zeta potential more negative, compared with the zeta potential in NaCl solution. (2) Test showed NaHCO_3 neutralization during sample pretreatment obviously makes the zeta potential more negative, compared with that of silica without neutralization. (3) Further results showed that the zeta potential of silica is sensitive to pH change, and it needs to mention the final pH to have the zeta potential make sense. (4) Salinity is another factor affecting silica's zeta potential, higher salinity makes less negative zeta potential. (5) Tests also showed increasing temperature makes the zeta potential less negative.

3.2. Experimental Studies

3.2.1. Materials

A model for carbonate sample in experimentation is calcite powder. It is provided by Alfa Aesar (USA), with a catalog No. 11403. This sample has a high purity of 99.5%, and its average size is less than 5 microns, which was selected because it can be tolerated by the equipment used for testing, in Figure 3-2. Figure 3-1 shows that the calcite sample is size-uniform. Since experiments showed having enough small particles in supernatant (solution for injecting) is important to get a higher accuracy, the calcite sample is ground for getting a larger size distribution before doing measurement.



**Figure 3-1 SEM picture of calcite powder, Alfa Aesar USA
(Provided by Guoqing Jian)**

The model for quartz/sand in experimentation is silica powder. It is freely provided by US SILICA Company, with a catalog of MIN-US-SIL5. This sample is produced in Berkeley Spring, West Virginia, with a high purity of 99.2%. Its median size is 1.6 μm .

For the silica sample, due to the hardness of quartz, the grinding process will cause a large amount of iron left in the powder sample. The product data sheet shows test sample contains 0.035% of iron (including Al, Mg, Ca, Ni) that can significantly affect the zeta potential of silica. For this reason, there is a pretreat step for iron removal by rinsing the silica sample with HCl solution. The HCl-rinse is followed with several water-rinses; afterwards test sample should also be neutralized with NaHCO_3 for one hour.

3.2.2. Fluids/Solutions

The first step was exploring the effect of different ions on zeta potential of rock-sample where some important parameters should be considered: pH, salinity, temperature, etc. However, based on the equations for calculating zeta potential, the

Table 3-1 Some brines for zeta potential measurement

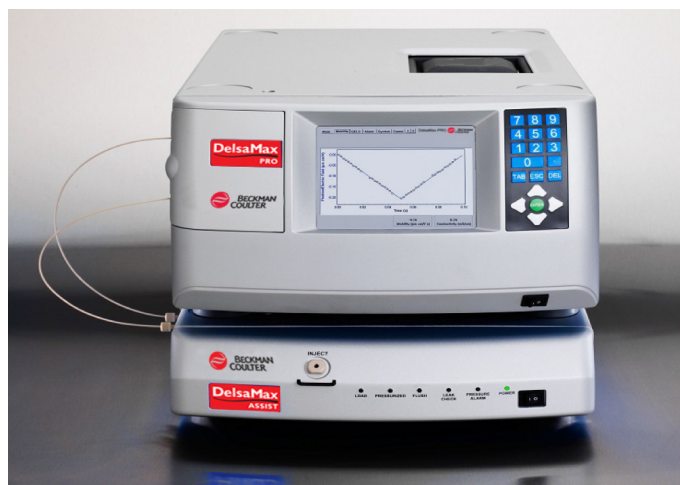
Salt	mol/L	Salinity g/L	pH	Ionic Strength mol/L
NaCl	0.1000	5.844	5.7	0.100
CaCl₂.2H₂O	0.0333	3.699	6.0	0.100
NaHCO₃	0.1000	8.401	8.4	0.100
Na₂CO₃.H₂O	0.0333	3.533	11.5	0.100
Na₂SO₄.10H₂O	0.0333	4.730	5.8	0.100
MgCl₂.6H₂O	0.0333	3.171	5.4	0.100
MgSO₄	0.0250	3.009	5.8	0.100

ionic strength and temperature should be kept constant to get the same Debye Length to all particles, which is the only way to examine how zeta potential is affected by

individual ions. The pH change of solution was recorded for comparison or further usage. Table 3-1 shows some solutions utilized in experimentation. 0.1 N HCl or NaOH solution was used to change the pH of brines if pH regulation was needed.

3.2.3. Experiment Setup

The equipment we use is DelsaMax PRO, produced by Beckman Coulter, see Figure 3-2. It allows simultaneous analysis of both zeta potential and particle size for sample volumes as small as 45 μ l, in less than one second.



**Figure 3-2 DelsaMax Pro for zeta potential measurement
(From user manual)**

This instrument uses a reusable flow-through cell for mobility and Quasi-elastic Light Scattering (QELS or DLS) measurements. The flow-through cell can be plumbed in either flow or batch configuration. However, the flow has to be stopped to make a mobility measurement. Aliquot samples can be introduced by manual injection. The DelsaMax PRO light scattering analyzer also has a temperature control

capability and is able to perform automated temperature measurements, some detailed operating parameters are summarized in Table 3-3.

Table 3-3 Listing of operating parameters for DelsaMax Pro

DelsaMax Pro		Parameters
Size Range	0.4 to 10,000 nm, hydrodynamic diameter	
Minimum Sample Volume	45 μ L	
Minimum Measurement Time	1 s	
Zeta Potential Measurement		
Minimum Sample Volume	170 μ L	
Conductivity Range	0.1 to 50 mS/cm	
Mobility Size Range	2 nm to 15 μ m diameter	
Mobility Sensitivity	1 mg/ μ L Lysozyme	
Minimum Measurement Time	1 s	
Temperature Range	4 to 70 $^{\circ}$ C	

Table 3-2 Listing of parameters for DelsaMax Pro. software setting

Instrument Setting	DLS Acq. Time s	DLS Number	Voltage V	Collection Period s
	5	6	2.5	15
Sample Setting	Temperature $^{\circ}$C	Viscosity cP	Dielectric constant	Refractive Index@589 nm
Solvent 1	25	0.90	80	1.333
Solvent 2	50	0.55	70	1.330

For the analysis software for DelsaMax Pro, there are two major parts for the setting of parameters to get accurate results. All solvents tested have low concentration, their viscosities are all close to that of water under same temperature

and for convenience it is assumed that all solvent have the same viscosity and dielectric constant, shown in Table 3-2.

3.2.4. Measurement Procedures

For the experiments to measure zeta potential of rock sample, the methods are all similar. Below will give an introduction on some important steps for measuring the zeta potential of calcite particle in different electrolyte solutions.

Pretreatment: Since the particle size of calcite powder is large and uniform, we should use a mortar to grind it for making it smaller and having a larger size distribution. Small particles with large size distribution can help get more stable zeta potential results.

Dispersion (0.8 wt. %): Add 0.2 g ground calcite powder to 25 mL solution/DI water with known pH value. Then, mixing the dispersion in a shaker for 24 h at 25 °C to prepare the equilibrated dispersions to be tested. (For experiments to explore the effect of temperature, instruments with temperature control, such as Digital Incubated Shaker and Thermostatic Water Bath, would be used to keep a constant temperature of 50 °C at any time.)

Settling: Help remove large calcite particles and reduce the amount of dispersed particles. Based on the Stokes' Law, we can get a predicted settling time, usually 60-90 minutes. (The detailed application of Stokes' Law is attached in Appendix C.) Then, the supernatant containing some small particles would be for

measurement. A laser is used to test whether the scattering light can form a solid beam.

Measurement: Record pH change after reaching equilibrium; then use DelsaMax Pro to measure zeta potential and size at 25/50 °C. Generally, it is better to measure at least 5 times for each sample for calculating the mean and standard deviation of zeta potential. The procedure of rock experiment can be showed as below, Figure 3-3.

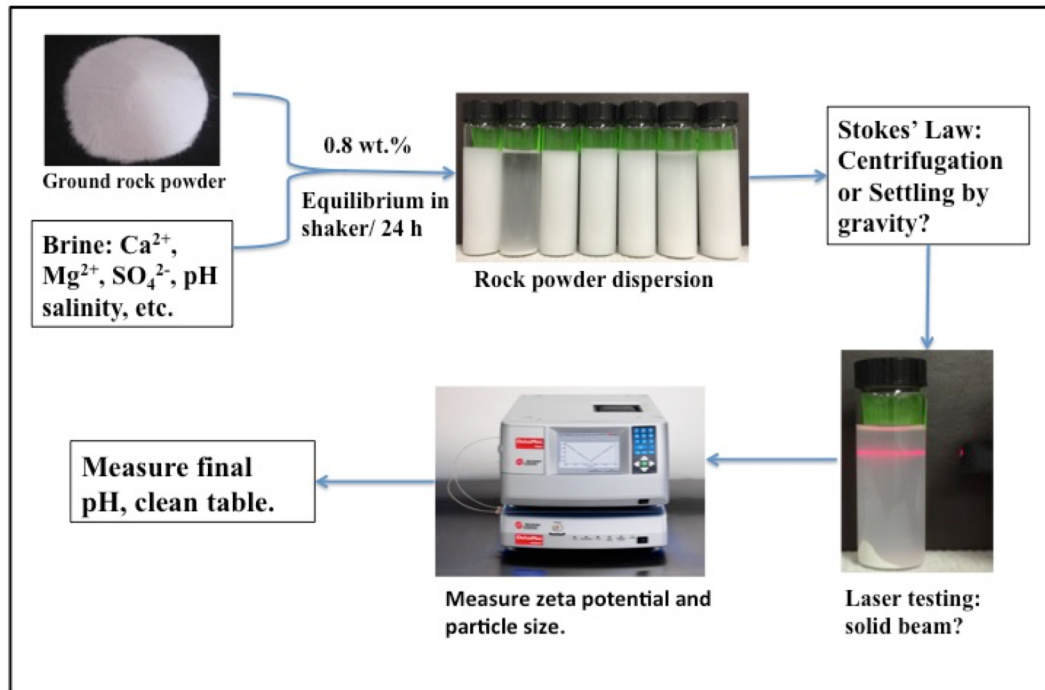


Figure 3-3 The procedure for measuring zeta potential of rock sample

3.3. Results and Discussion

3.3.1. Dispersions of Calcite Sample

According to Stokes' Law, if the particle is falling in the viscous fluid under its own weight due to gravity, then a terminal velocity, also called settling velocity, is reached when the frictional force, buoyant force and gravitational force balance together.

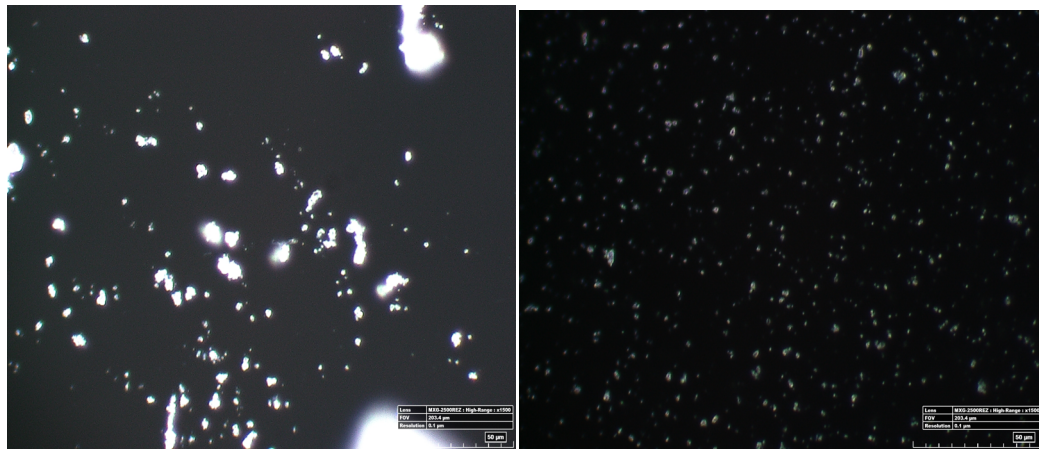


Figure 3-4 The ground calcite powder in Microscope (left), and the ground calcite powder dispersed in DI water and settling for 2 h (right)

Based on the Equation of Stokes' Law, this velocity is proportional to particle size's square, and we can predict this time for settling. A laser is used to test if there are enough particles left in supernatant. A solid beam through the supernatant means the size and amount of dispersed particle in solution is good enough for light scattering, so we can get good results with small deviation.

In Figure 3-4, some small ground calcite particles have aggregated, due to molecular interactions. But it still can be found to have some small particles with size of 1-2 micron. After settling in DI water for 2 h, a lot of small particles can disperse in the supernatant of dispersions, while large particles have been settled down. In these two microscopic pictures, we can tell the particle with size of 0.1 micron.

The amount of calcite sample added to solution can affect the settling way of calcite particle, as Figure 3-5. For the dispersions with a large amount of calcite, the excess of dispersed particles is like a filter, which removes smaller particle left in supernatant (no solid beam), causing large deviation for zeta potential measurement. In order to have enough small particle left in the supernatant, we decided to use 0.8 wt.% as a weight standard for all the mineral experiments.



Weight percent: 4.0% 2.8% 1.6% 0.8% 0.4%

Figure 3-5 Equilibrated calcite dispersions (Na_2CO_3 , $I=0.1$ M), Settling for 60 min, Laser coming from left

3.3.2. Dispersions of Silica Sample

Since the dispersed silica particle is small enough (no aggregation due to large magnitude of zeta potential), it is necessary to centrifuge the sample. The samples, pictured in Figure 3-6, are centrifuged for 2 min with 3000 rpm. The weight percent for all samples is 0.8% (0.20g silica+25 mL electrolytes) and equilibrium time is 24 h under room temperature. Obviously, the particles can settle well in MgCl_2 and CaCl_2 samples, due to larger particle size. The solid beam can be seen in dispersions, except in MgCl_2 and CaCl_2 solution, because there are not enough small particles dispersed in MgCl_2 and CaCl_2 solution after centrifugation.

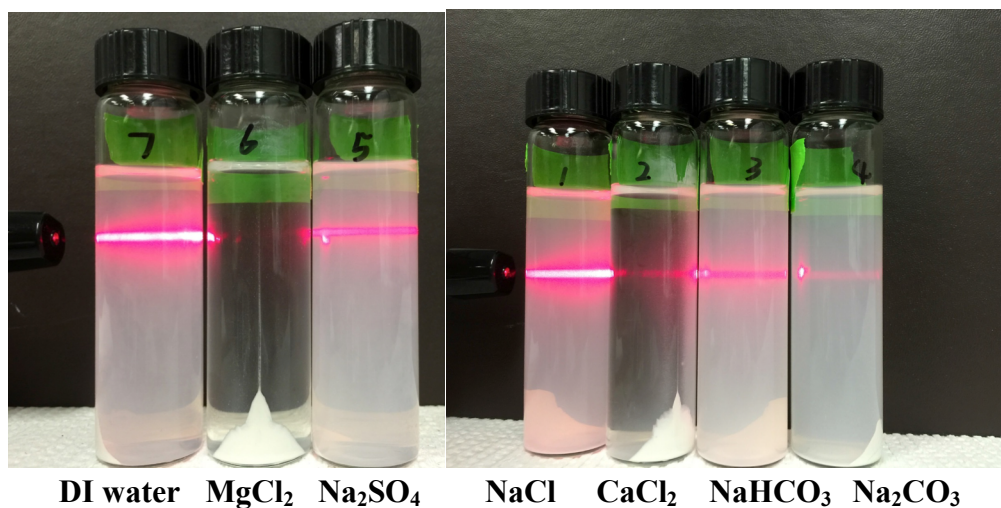


Figure 3-6 Laser beam scatters in centrifuged dispersions

3.3.3. Zeta Potential of Calcite Particle

In order to compare different ions' effect on the zeta potential of calcite, it is necessary to keep ionic strength, temperature and equilibrium time as constants. Also, some preliminary experiments showed the amount or particle size of sample added to dispersions does not change the zeta potential, but affects the settling of particles.

- Effect of Equilibrium Time

A good equilibrium time for CO₂-brine-calcite system is important to get stable results and help others repeat our experiments (Somasundaran and Agar 1967; Heberling et al. 2011). For the calcite experiment, the process of ion adsorption or ion exchange and mineral dissolution determines the equilibrium time. When calcite dispersions reach equilibrium in atmospheric environment, the pH and ion

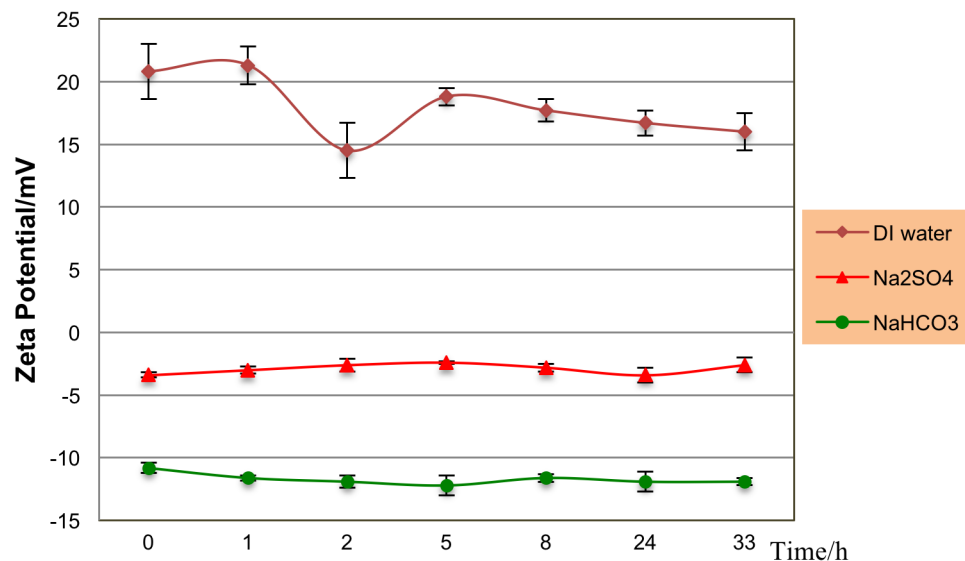


Figure 3-7 Zeta potential of calcite in different time, I=0.1M, 25°C

composition in liquid phase should be fixed and we can get stable zeta potential in this specific environment.

The Figure 3-7 examined the effect of equilibrium time for the calcite powder experiments. This experiment was done in DI water, Na_2SO_4 and NaHCO_3 solutions with ionic strength of 0.1 M at 25 °C. The preliminary conclusion here is: 24 h is enough to get stable results for most calcite dispersions. Also, the deviation of zeta potential was larger when testing with DI water. It is because the conductivity is too small for DI water dispersions; the little change of conductivity can cause a big deviation for zeta potential calculations. On contrast, if the conductivity is too large, breakdown current would occur in the flow cell.

For the DelsaMax Pro, the range of ionic strength is 0.1-50 mS/cm (4 times the conductivity of physiological saline) and the DI water (0% salinity) should not be used.

- Effect of Individual Ion

In Table 3-4 and Figure 3-8, the zeta potential of calcite in DI water is positive; since calcite's zeta potential is affected by both dissolution and presence of

Table 3-4 pH change for calcite dispersions, I=0.1 M, 25 °C/24 h

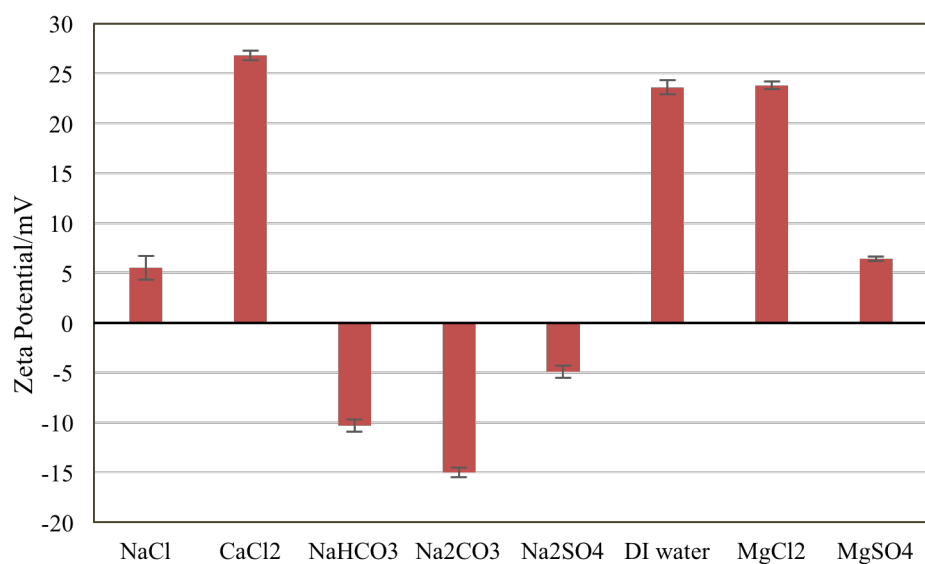
Solution	NaCl	CaCl₂	NaHCO₃	Na₂CO₃	Na₂SO₄	DI water	MgCl₂	MgSO₄
pH0	6.1	7.4	8.3	11.2	6.3	5.9	5.7	5.8
pH1	9.7	8.6	8.3	11.1	9.8	9.7	9.1	9.6

pH0 is the original pH of electrolytes, pH1 is the equilibrated pH after 24 h.

multivalent ions, the pH change showing the effect of mineral dissolution can be connected with the variation of ion species in bulk solution.

Based on the results of pH change, severe mineral dissolution happens in NaCl/ Na₂SO₄/MgCl₂/MgSO₄ solution as well as DI water and the pH ranges from 9 to 10 after reaching equilibrium. The equilibrated pH for calcite dispersions in HCO₃⁻ and CO₃²⁻ does not change much, due to the buffering effect.

For the zeta potential, excess of Ca²⁺ and Mg²⁺, make the zeta potential more positive, while SO₄²⁻ and CO₃²⁻ make the zeta potential negative, compared with the



**Figure 3-8 Zeta potential of calcite for different ions, 0.8 wt%,
I=0.1 M, 24 h/25 °C**

zeta potential of calcite in NaCl solution. We should also notice the large pH in Na₂CO₃ solution, which might also be a reason for more negative zeta potential (Heberling et al. 2011). The zeta potential of calcite in MgSO₄ solution is affected by both Mg²⁺ and SO₄²⁻. The explanation is that mineral dissolution occurs on the surface of calcite can

change the ratio of $\text{Ca}^{2+}/\text{CO}_3^{2-}$ in the bulk solution, which are PDIs for the zeta potential of calcite (Cui, L. 2014). An excess of Ca^{2+} can make the zeta potential more positive, while the excess of CO_3^{2-} reduces the zeta potential or even change it into negative. Also, the relative amount of Mg^{2+} and SO_4^{2-} in solution has same effect as calcium and carbonate ions. The pH can change the zeta potential by altering the ratio of $\text{Ca}^{2+}/\text{CO}_3^{2-}$ in the bulk, due to mineral dissolution. Figure 3-8 tells us the huge impact of different ions on calcite's zeta potential.

- Effect of Temperature

Some reservoirs have much higher temperature, while high temperature means large rate of chemical reaction and change of chemical equilibrium. Our instrument can measure the zeta potential of rock at a maximum temperature of 70 °C, so it's necessary to explore the temperature's effect on zeta potential in different electrolyte solutions.

Some small divalent cations, like Mg^{2+} and Ca^{2+} , are strongly hydrated in solution if the temperature is low. Increasing the temperature, their activity coefficient would increase by dehydration. Thus, the divalent ion can become more easily absorbed on the surface of rock particles and change the zeta potential (Zhang and Austad, 2006b). At the same time, the dehydration of anions (SO_4^{2-} , CO_3^{2-}) causes CaSO_4 and CaCO_3 precipitation, due to the reduction of solubility (Moghadasi et al. 2003). This is to say, high temperature can limit the degree of dissolution and increase divalent ion adsorption.

Table 3-5 shows when temperature is increased to 50°C, nearly all the pH of equilibrated solutions decreases a little bit, except for pH in NaHCO₃ solution; if equilibrium time increases from 24 h to 5 or 6 days, pH nearly stays constant, which means that most of calcite dispersions reach equilibrium within 24 h, except with bicarbonate. For the pH of dispersion with bicarbonate, the loss of CO₂ from bulk solution at high temperature changes the equilibrium of calcite and leads to additional calcite dissolution. Another evidence to prove the calcite dissolution with bicarbonate is the change of conductivity, which changes from 10.6 to 11.3 mS/cm, if equilibrium time increases from 24 h to 6 days at 50 °C. Therefore, for calcite dispersion with bicarbonates at high temperature, pH changes with time even after a long time for equilibrium.

Table 3-5 pH change for calcite dispersions, 0.8 wt.%, I=0.1 M

Solution	NaCl	CaCl₂	NaHCO₃	Na₂CO₃	Na₂SO₄	DI water
pH0	6.1	7.4	8.3	11.2	6.3	5.9
pH1	9.7	8.6	8.3	11.1	9.8	9.7
pH2	9.5	8.4	8.4	11.0	9.6	9.5
pH3	9.7	8.7	8.5	11.2	9.9	9.6
pH4	9.6	8.6	9.6	11.1	9.7	9.5

Here, pH0 is the original pH of electrolytes at 25°C; pH1 is the solution's pH at 25°C /24 h; pH2 is the solution's pH at 50°C/24 h; pH3 is the solution's pH at 25°C/5 days; pH4 is the solution's pH at 50°C/6 days.

Table 3-6 pH change and Ca^{2+} concentration for calcite dispersions, $I=0.1 \text{ M}$ simulated by PHREEQC without gas phase

Solution	NaCl	CaCl ₂	NaHCO ₃	Na ₂ CO ₃	Na ₂ SO ₄	DI water
pH25	9.9	8.8	8.0	11.1	10.0	9.9
Ca²⁺/M 25 °C	2.63E-4	3.34E-2	3.93E-5	6.36E-6	3.15E-4	1.23E-4
pH50	9.6	8.4	7.8	10.6	9.4	9.3
Ca²⁺/M 50 °C	3.27E-4	3.34E-2	3.86E-5	7.89E-6	3.83E-4	1.48E-4

pH25: The final pH simulated by PHREEQC at 25 °C; pH50: The final pH simulated by PHREEQC at 50 °C.

Table 3-6 summarizes the calculated pH and calcium concentration for calcite dispersions with different electrolytes. The pH is simulated by PHREEQC software and

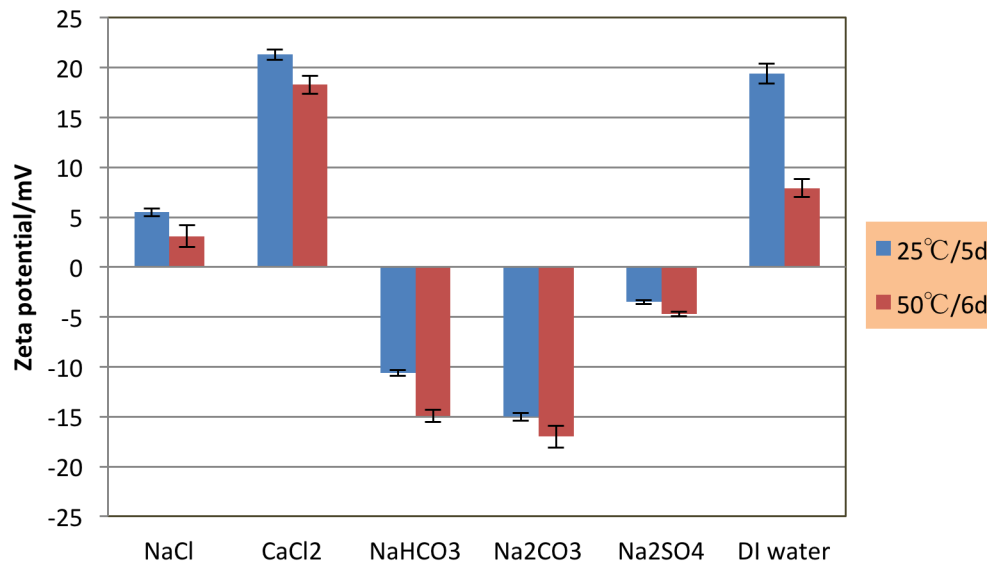


Figure 3-9 Zeta potential of calcite at 25/50°C, $I=0.1 \text{ M}$, 5/6 days

assuming no gas phase. By comparing table 3-5 with table 3-6, we can verify that 24 h is enough for most calcite dispersions to reach equilibrium, except for the dispersion

with 0.1 M NaHCO_3 . In NaHCO_3 solution, calcite needs more time to reach equilibrium with the bulk solution, due to the loss of CO_2 . Also, it appears that at 25 °C the calcite system with bicarbonate is far from equilibrium, and the temperature increase can accelerate the equilibrium process. The concentration of calcium shows the calcite dissolution in carbonate and bicarbonate solution is limited, due to buffering effect.

In Figure 3-11, the big deviation for zeta potential in high temperature is likely due to lack of equilibrium time after 24 hours, and the deviation is much less after 6 days. Also, as temperature increases, the viscosity of solution reduces a lot, which means there might be less particles dispersed in supernatant in the same settling time. This figure shows that increasing temperature can change the magnitude of zeta

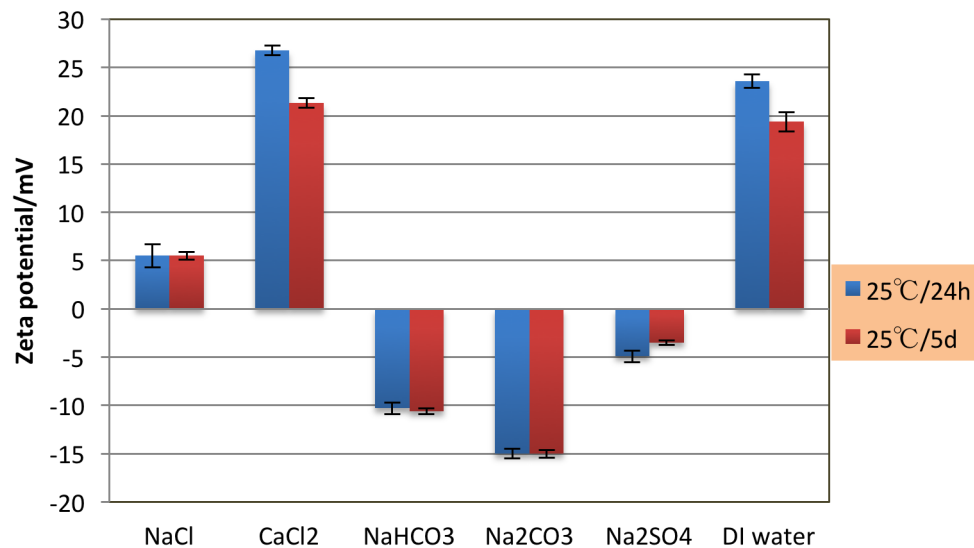


Figure 3-10 Zeta potential of calcite equilibrated for 24 h/5 d, 25 °C, I=0.1 M potential, due to the concentration changes of potential determining ions in different solution. The below figures are made by using same data.

From Figure 3-9~3-12, we can know that the dissolution in DI water or NaCl brine makes the zeta potential of calcite positive and increases the bulk pH to ~ 9.5 . Since temperature increases to $50\text{ }^{\circ}\text{C}$ can reduce the extent of dissolution, the zeta

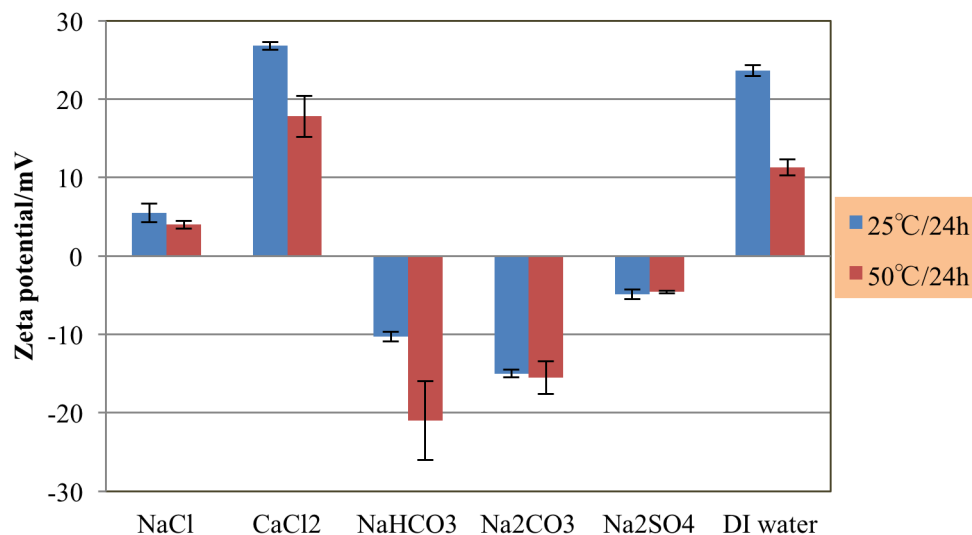


Figure 3-11 Zeta potential of calcite in 25/50°C, I=0.1 M, 24 h

potential of calcite particle in DI water and NaCl decreases by 40-60 %. For CaCl₂ and Na₂CO₃ solution, due to excess of PDIs (Ca²⁺ and CO₃²⁻), temperature increase cannot change the zeta potential of calcite so much. For NaHCO₃ solution, the pH increases with time due to the loss of CO₂ and additional calcite dissolution, so the zeta potential becomes more negative after 6-day equilibrium.

For Na₂SO₄ solution, the zeta potential of calcite almost keeps the same with time or temperature, because the excess of SO₄²⁻ can absorb on the surface of calcite particle and determine the surface potential. Increasing temperature to $50\text{ }^{\circ}\text{C}$ cannot make a big change to adsorption, thus its effect on zeta potential here is limited.

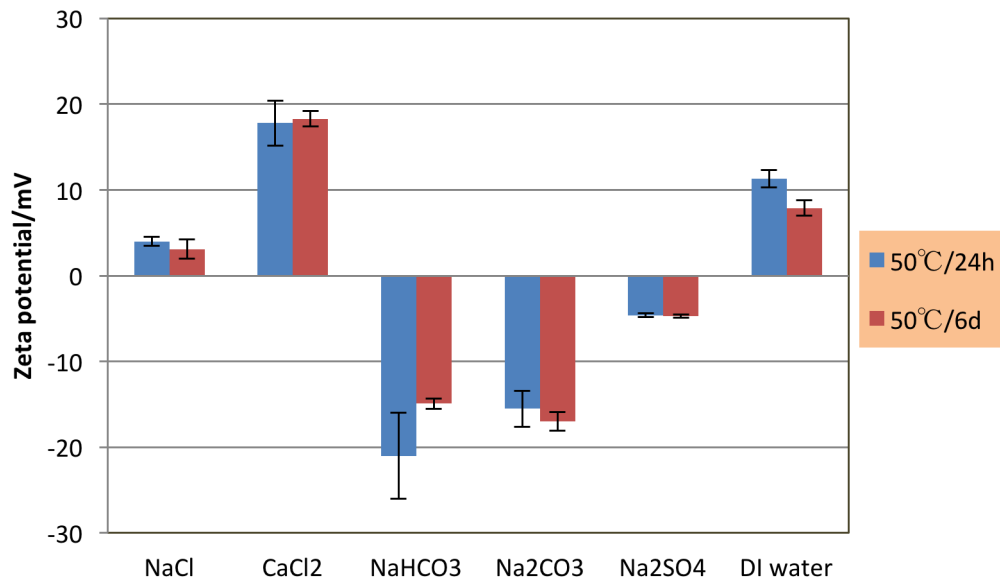


Figure 3-12 Zeta potential of calcite equilibrated for 24 h/ 6 d, 50°C, I=0.1 M

3.3.4. Zeta potential of Silica Particle

- Effect of NaHCO_3 -Neutralization (pH)

**Table 3-7 pH change for different silica dispersions equilibrated for 24 h
I=0.1 M/ 25 °C**

Solution	NaCl	CaCl ₂	NaHCO ₃	Na ₂ CO ₃	Na ₂ SO ₄	MgCl ₂	MgSO ₄
pH1	5.7	6.0	8.4	11.5	5.8	5.4	5.8
pH2	6.2	6.2	8.6	11.1	6.5	6.4	--
pH3	6.5	6.4	8.6	11.1	7.0	7.0	7.2
pH4	7.9	7.8	8.6	11.3	8.2	6.9	7.9

pH1 = pH of original electrolytes solution.
pH2 = pH of equilibrated HCl-cleaned & unneutralized silica dispersion.
pH3 = pH of equilibrated HCl-cleaned & NaHCO₃ neutralized (1 h) silica dispersions.
pH4 = pH of equilibrated HCl-cleaned & NaHCO₃ neutralized (24 h) silica dispersions

In Table 3-7, pH for NaHCO_3^- neutralized silica dispersions appear larger than that of un-neutralized silica dispersions in same solution after 24-h equilibrium time. For most silica dispersions, the longer neutralization time means larger pH after equilibrium. Because the degree of protonation on the surface of a silica particle can affect the equilibrium relationship of H^+ and OH^- in silica dispersions.

The zeta potential of 0.8 wt.% silica in different salt solutions as well as soaking time in NaHCO_3 solution after being acid washed are plotted in Figure 3-13. The equilibrium pH is also showed in figure to help us analyze the effect of pH to silica particle's zeta potential. It is noticeable that 1) the zeta potential is sensitive to pH change. If pH of silica dispersions increases, the zeta potential of silica would become more negative; 2) the zeta potential should be combined with pH to make sense; 3)

effects of neutralization on the zeta potential of silica in some dispersions are small, due to divalent adsorption (Ca^{2+} , Mg^{2+}) and buffering effect (HCO_3^- , CO_3^{2-}).

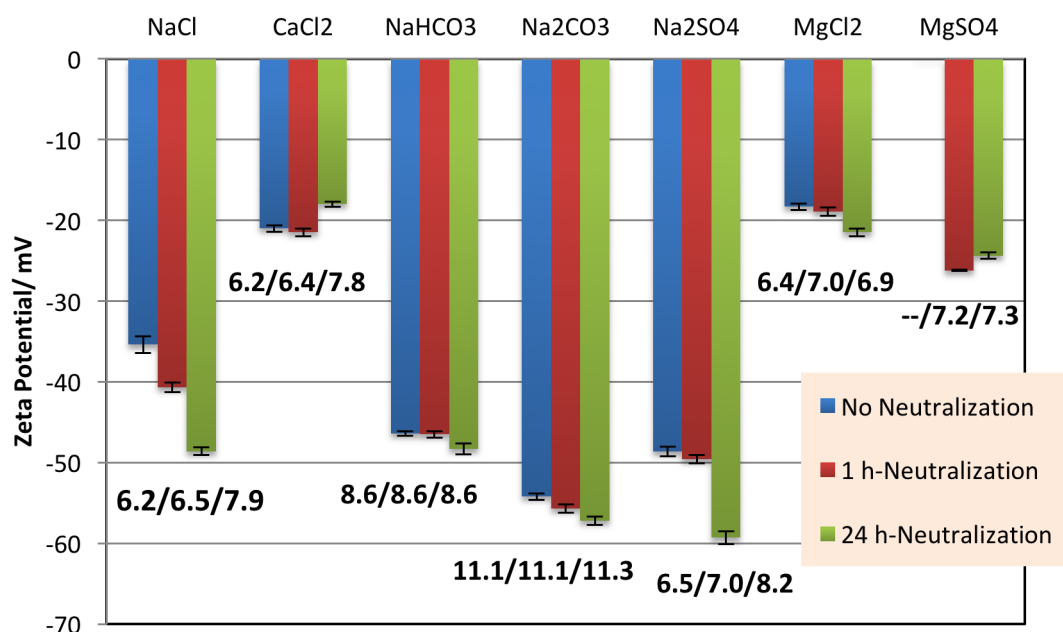


Figure 3-13 Zeta potential of silica with 0 h, 1 h and 24 h-neutralization time in different solutions, 0.8 wt.%, I=0.1 M, 24 h/ 25 °C

When silica sample is neutralized with NaHCO_3 (0.1M, pH=8.5), a new equilibrium will be established when changing the bulk solution. Neutralizing for a longer time can help increase the dissociation on the surface of silica particle, and make the zeta potential more negative. With 24 h neutralization in NaHCO_3 solution, the silica is over-neutralized in the slightly alkaline solution and it raises the pH of the electrolyte solution that is added. Since the neutralization step can change the pH after equilibrium, then followed by zeta potential change, it needs to take the neutralization and neutralization time into consideration to make all the results more convincing.

- Effect of Individual Ions

Table 3-8 Test results for silica experiment equilibrated for 24 h at 25 °C

Solution	NaCl	CaCl ₂	NaHCO ₃	Na ₂ CO ₃	Na ₂ SO ₄	MgCl ₂	MgSO ₄
Conductivity mS/cm	11.28 ±0.04	7.14 ±0.05	7.87 ±0.02	5.86 ±0.02	6.50 ±0.01	6.70 ±0.03	3.31 ±0.01
pH1	5.72	6.01	8.40	11.51	5.80	5.43	5.80
pH2	6.48	6.41	8.62	11.06	6.98	6.99	7.15
Zeta potential mV	-40.7 ±0.6	-21.5 ±0.5	-46.5 ±0.4	-55.7 ±0.5	-49.6 ±0.6	-18.9 ±0.4	-26.3 ±0.1
Diameter nm	185.3 ±2.5	688.7 ±126.0	183.3 ±1.1	173.0 ±1.0	187.4 ±1.3	711.0 ±32.9	209.6 ±1.5
pH1 is the original pH of electrolytes; pH2 is the pH after equilibrating for 24 h. (1 h- Neutralized silica sample)							

The average diameter, in Table 3-8, for dispersed silica particle is close to 200nm in centrifuged dispersions, and they have uniform size (size deviation is small), compared with particle size in CaCl₂ and MgCl₂ solution with no centrifugation. Some testing experiments show that the zeta potential change of silica particle is independent to particle size or aggregation.

Here, zeta potential of silica particle is mainly determined by ion adsorption and pH effect. Divalent cation adsorption, like Ca²⁺ and Mg²⁺, can make the zeta potential less negative, compared with zeta potential in NaCl solution. For NaHCO₃ and Na₂CO₃, the large pH also plays a big role for more negative zeta potential, due to dissociation effect to Si-OH. All the zeta potentials are reasonable, except in DI water, because the reliable zeta potential cannot be determined in solution with low conductivity. The comparison of different ions' effect can be seen in Figure 3-14.

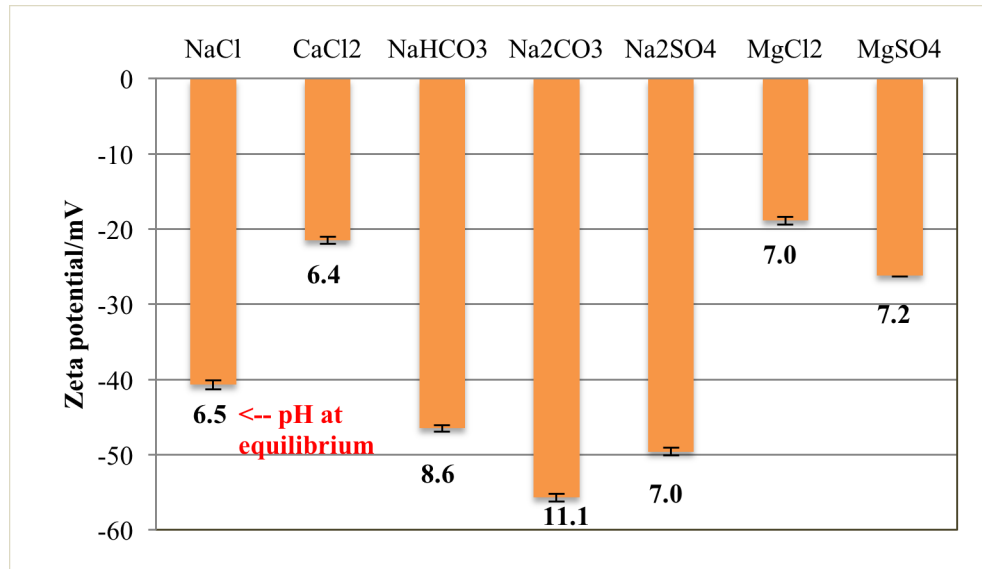


Figure 3-14 Zeta potential of silica in different solution, I=0.1 M, 24 h, 25 °C (1h- Neutralized silica sample)

- Effect of pH

From above sections, we realized the pH is one of main factors determining zeta potential of silica particle. Both the weight percent of silica and neutralization time can finally affect the pH of equilibrated silica dispersions. The zeta potential becomes more negative, if increasing pH in a range. Thus, Figure 3-15 is provided to help correlate zeta potential of silica with different pH. The experiment was conducted in NaCl solutions with a constant ionic strength of 0.1 mol/L. HCl and NaOH solutions with the same concentration of 0.1 M were used to regulate the pH of NaCl solution, so we could neglect the effect of salinity here. At high pH, since the silica surface is fully dissociated, the magnitude of zeta potential cannot increase anymore if we keep increasing pH.

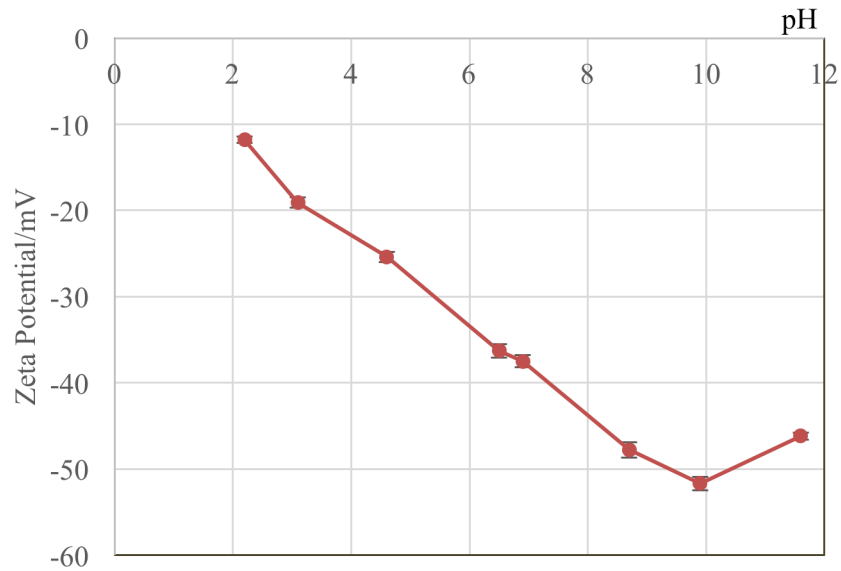


Figure 3-15 Zeta potential of silica with different pH in NaCl solution, 0.8 wt.%, I=0.1 M, 24 h /25 °C (1 h- Neutralized silica sample)

- Effect of salinity (Ionic Strength)

Besides pH, the salinity or ionic strength is another major factor affecting zeta potential of silica. In Figure 3-16, increasing the ionic strength of solution from 0.1 M to 0.5 M, the magnitude of zeta potential decreases by 40-65%. Since the pH difference between relative dispersions is very small, we can conclude: If the salinity is larger, the magnitude of surface potential would be smaller.

Increase of the salinity or ionic strength can reduce the Debye Length, due to the compression of the double layer. The magnitude of electrical potential closed to the surface of silica particle is reduced.

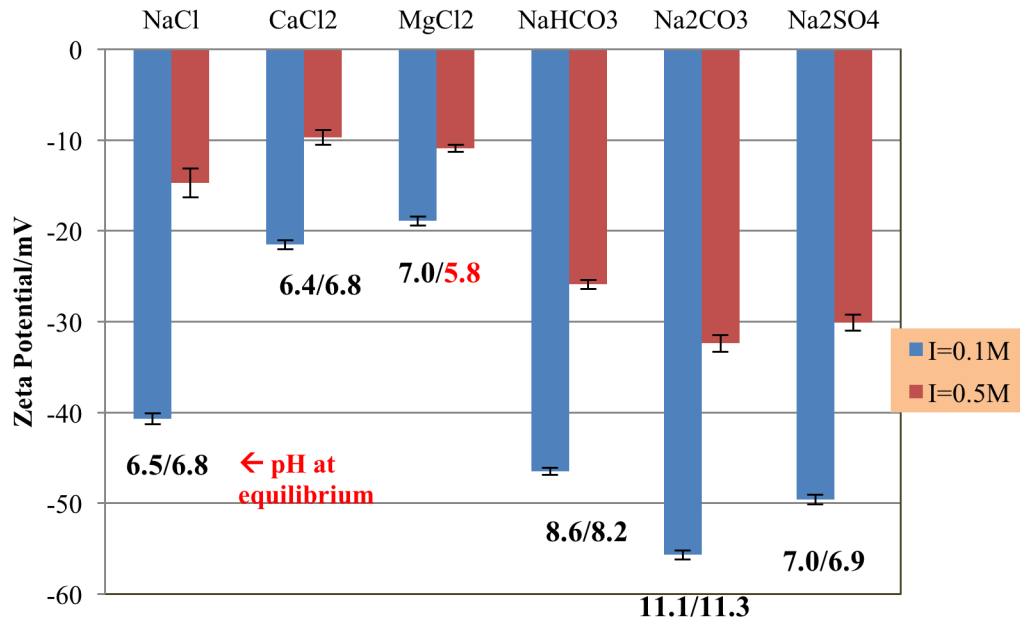


Figure 3-16 Zeta potential of 0.8 wt.% silica in different solutions, I=0.1 M/ 0.5 M, 24 h /25 °C (1 h- Neutralized silica sample)

- Effect of Temperature

All the silica dispersions were equilibrated for 24 h in a shaker with constant temperature of 50 °C, and then settling in a Thermostatic Water Bath. The silica dispersions were centrifuged to help settle larger particles, except in MgCl₂, CaCl₂ and MgSO₄ solution. Because the zeta potential of silica in these solutions is small, and could cause particle aggregation. Large particles are easy to settle under gravitational effect. In Table 3-7, the relationship between zeta potential and particle size can be easily found: silica with more negative zeta potential tends to have smaller particle size, due to the larger repulsive electric forces. The correlation of particle size and zeta potential can be described by DLVO theory.

For the zeta potential of silica, when temperature increases, it is necessary to notice the effects coming from both surface charge and Debye Length change. Figure 2-5 shows that increasing temperature could change the surface equilibrium and make the surface more negative charged. Here, the Debye Length change and divalent cation adsorption for some dispersions also work at the same time. It's possible that the effect of surface charge increase is smaller than other effects. Therefore, the magnitudes of silica zeta potential at 50 °C is a little smaller than those at 25 °C, as shown in Figure 3-17.

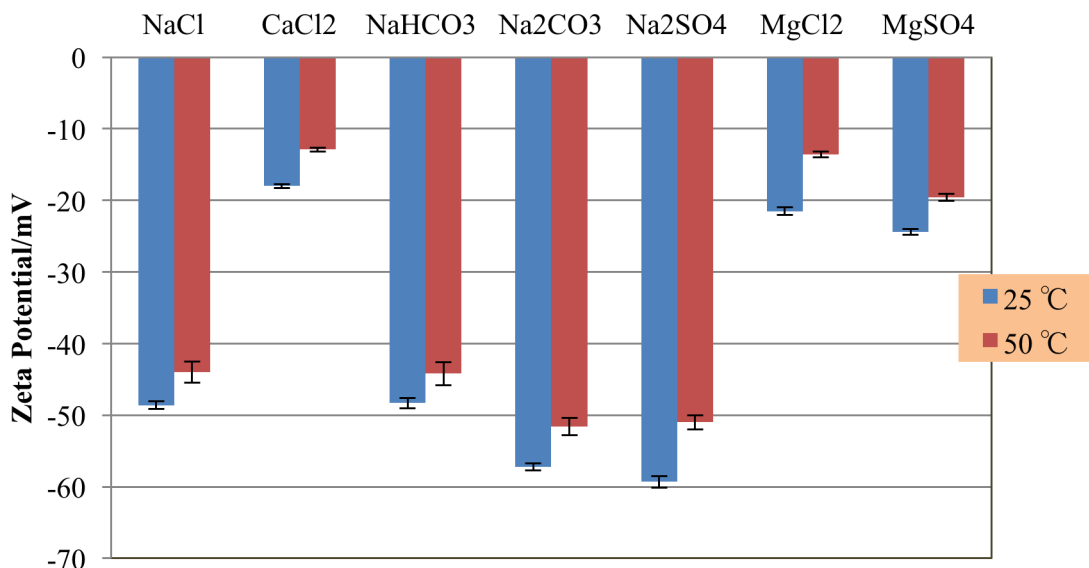


Figure 3-17 Zeta potential of 0.8 wt.% silica dispersions equilibrated for 24 h, I=0.1 M, 25 °C/ 50 °C (2 h- Neutralized silica sample)

3.4. Mechanisms and Conclusions

For the zeta potential of calcite:

Experiments shows an equilibrium time of 24 hours is enough to get a stable zeta potential to calcite, and this time will be set as a standard for the following experiments, except for calcite dispersion with bicarbonate.

The concentration ratio of divalent cations to divalent anions in the solution can determine the zeta potential of calcite. Calcite dissolution tends to make positive zeta potential in DI water and NaCl solution by introducing more Ca^{2+} ; excess of divalent cations, like Ca^{2+} , Mg^{2+} , makes more positive zeta potential; while excess of divalent anions, like CO_3^{2-} , SO_4^{2-} , can even change the zeta potential into negative, compared with the zeta potential in NaCl solution.

Temperature can change the zeta potential of calcite by changing the extent of dissolution, while its effect on ion adsorption (Ca^{2+} and SO_4^{2-}) is limited. HCO_3^- is special, increasing temperature would cause pH to increase, due to increased kinetic-limited calcite dissolution or loss of CO_2 . Therefore, the zeta potential measuring of calcite in NaHCO_3 needs more time to reach equilibrium.

For the zeta potential of silica:

The neutralization or neutralization time can affect the pH of silica dispersions after equilibrium; longer time for neutralization leads to more negative zeta potential. However, effects of neutralization on the zeta potential of silica in some dispersions are small, due to divalent adsorption (Ca^{2+} , Mg^{2+}) and buffering effect (HCO_3^- , CO_3^{2-}).

Unlike the zeta potential of calcite, silica's zeta potential cannot be changed from negative to positive by altering the operation conditions, such as ion composition (not including trivalent ions), salinity or pH. However, these factors do change the magnitude of zeta potential. For different ion species, divalent cation adsorption, like Ca^{2+} and Mg^{2+} , can make the zeta potential less negative, compared with zeta potential in NaCl solution. Also, pH and dissociation of Si-OH should be taken into consideration to explain larger zeta potential in Na_2CO_3 and NaHCO_3 solution.

In summary, pH is an important factor to the change of zeta potential, because H^+ protonation/ deprotonation occurring on the surface of silica particle can change its surface charge, and then change the zeta potential of silica. For this reason, the zeta potential should be combined with pH to make sense.

Increase of the salinity or ionic strength makes silica's zeta potential less negative, due to the compression of double layer. Increasing temperature can increase the negative charges on the surface of silica, while the zeta potential becomes less negative, due to the change of Debye Length and divalent ion adsorption.

Chapter 4

Electrostatic Potential Measurement of Model Oil

The composition of crude oil affects the wetting state of reservoirs, especially for the surface active components. One of mechanisms influencing the wetting is through the base/acid effect on electrostatic interactions with the mineral surface (Dubey and Doe, 1993a). The chapter 3 has studied the electrostatic potential of minerals (rock powder) under different operation conditions, so this chapter focuses on the electrostatic potential of model oil for correlating the wettability behaviors with electrostatic potential in the brine-oil-minerals system.

For the preparation of oil emulsions, the relationship among oil percent, ultrasonic time, salinity and settling time was important to obtain stable zeta potential of oil. Some preliminary tests revealed that (1) high-oil percent and large salinity causes the oil-drop size to increase substantially, if keep constant ultrasonic time. (2) In spite that increasing ultrasonic time can reduce particle size, it can make

the dispersion too opaque, which causes a large deviation to zeta potential. (3) Severe oil aggregation happens with a long settling time, especially in solution with high salinity. Based on these observation, a laser was used to test whether the oil emulsions can form a solid beam and get stable results or not.

The area of study for this chapter includes (1) the zeta potential of model oil under different ion compositions; (2) pH effect on zeta potential of model oil; (3) the base and acid effects on the zeta potential of model oil; (4) a comparison of zeta potentials for model oil and silica particle in same brine condition.

4.1. Summary

Experiment results showed the zeta potential of model oil in different solution behaves like that of silica; divalent cation adsorption, low pH and high salinity all can change the zeta potential.

For the presence of surface active chemicals, 1) the base used in model oil can increase the isoelectric pH, while the used acid has little effect on it. 2) At low pH, the model oil with base tends to have less negative zeta potential due to base protonation, while the base compound has little effect on zeta potential at high pH, compared with those of model oil. 3) At high pH, the model oil with acid tends to have more negative zeta potential, while acid compound has little effect on zeta potential at low pH, compared with those of model oil. 4) A combination of base and acid can significantly increase the magnitude of zeta potential, which means the existence of base can help

the dissociation of carboxylic acid group and/ or increase the surface coverage of acid, as well as the negative surface charges of oil droplet.

4.2. Experimental Studies

4.2.1. Materials

Considering the high molecular complexity of crude oil, simple molecules will be selected to represent the main functionalities of the crude oil (Basic, Acid & Neutral) for trying to understand the interactions in oil/rock/brine interface and thus, aiming to determine the basic principles controlling the mechanism between liquid phases and later between liquids and rocks.

The model molecules selected in this phase to simulate the main crude oil polar functionalities would be the same that could be employed in the interfacial tension and contact angle measurements. These test results will be also validated employing real oil fractions from specific crude oils in the future. Table 4-1 shows compositions of the model oil (87 vol. % Dodecane + 13 vol.% Toluene); and mixtures of the model oil with Quinoline of Base Number (BN) 2 and Cyclopentanehexanoic of

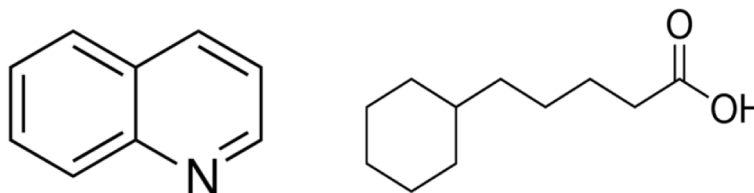


Figure 4-1 Basic and acidic components used in model oil (Left is Quinoline for base; right is Cyclopentanehexanoic Acid for acid.)

Acid Number (AN) 3. The calculation of acid and base number is described in the Appendix B.

Table 4-1 Oil composition in tests

Name	Composition	pH of aqueous phase
Model oil	87 vol.% Dodecane + 13 vol. %Toluene	7.3
Oil with BN2	Model oil + Quinoline (BN=2)	7.3
Oil with AN3	Model oil + Cyclopentanehexanoic Acid (AN=3)	5.1
Oil with AN3 &BN2	Model oil + Cyclopentanehexanoic Acid (AN=3) + Quinoline (BN=2)	5.7

4.2.2. Fluids/Solutions

The central point of this chapter is exploring the effect of pH on zeta potential of oil droplet in NaCl solution. However, based on the equations for calculating zeta potential, the ionic strength and temperature for each sample should be kept constant to get a same Debye Length to all droplets, which is the only way to examine how zeta potential is affected by pH. The brine in this experiment was NaCl solution with an ionic strength of 0.1 M, and HCl or NaOH solution with same concentration (0.1 M) was used to pH regulation for getting some samples with pH variation.

4.2.3. Apparatus and Procedure

Below will give an introduction of some important steps for measuring the zeta potential of oil droplets in different electrolyte solution. The procedures are shown in Figure 4-2.

Preparation: Prepare oil sample and brine solution. (For experiments to check pH effect, the pH of brines would be regulated by 0.1 M HCl or NaOH solution.)

Emulsification: A) Model oil is added to brine solution, oil percent is 5 % (95 mL brine + 5 mL model oil); after shaking, the mixture would be equilibrated for 24 h before emulsification. B) Disperse oil in Sonifier Ultrasonic Homogenizer for 10 min at fixed ultrasonic strength; avoid excessive temperature increase by stopping sonication for every 5 min. C) Laser is used to estimate the amount of dispersed oil. The undispersed model oil can be removed to avoid too opaque solution during ultrasonication.

Stabilization: Equilibrate emulsions for 15~30 min, and let temperature reach room temperature.

Measurement: A) measure zeta potential and oil drop size on DelsaMax Pro at 25 °C. B) Measure at least 6 times for each sample, then calculate the mean and standard deviation of zeta potential or drop size for each oil sample. C) Some emulsions will be centrifuged for 10 min/ 5000 rpm to get rid of oil and be able to accurately measure pH of each emulsion.

Cleaning: Use Isopropanol to clean the tube and leave it overnight to remove all the oil adhering to tube.

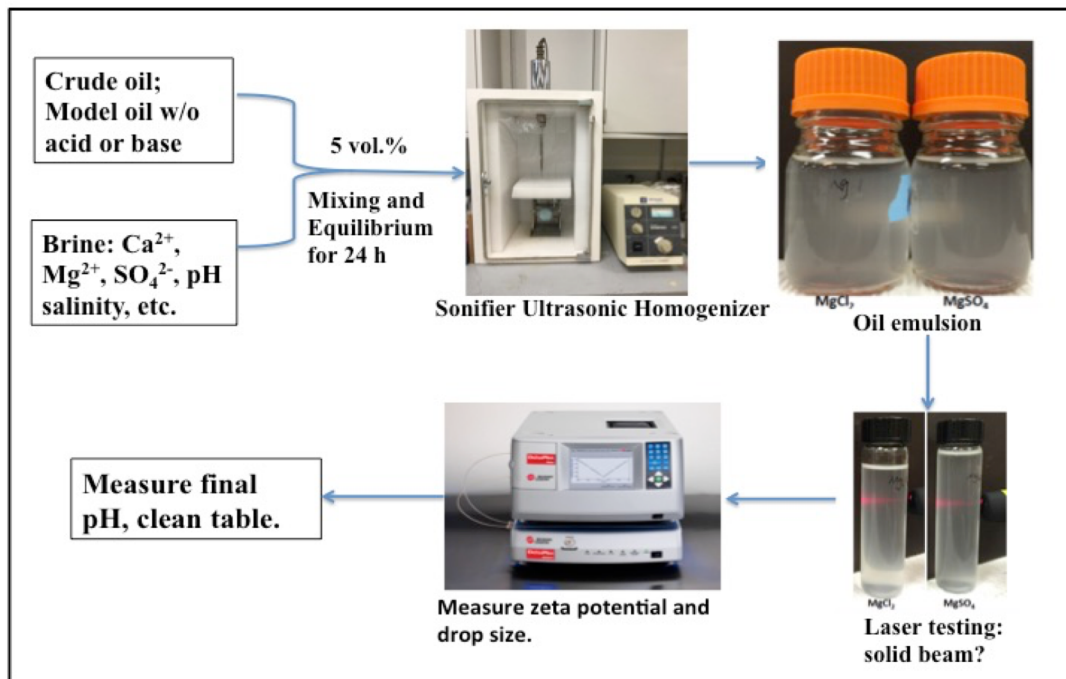


Figure 4-2 The procedure for measuring zeta potential of oil sample

4.3. Results and Discussion

4.3.1. Dispersions of Model Oil

Some preliminary tests showed the oil volume percent, ultra-sonication time and settling time are all important to get good emulsions for zeta potential measurement. In order to make emulsions with small oil drop size but less opaqueness, we need to find a balance among these three parameters. A good testing method is to use laser; if we can see a solid beam through the supernatant, as shown in Figure 4-3, then the emulsion can result in stable results.

Figure 4-3 shows some model oil emulsions for zeta potential measurement. These emulsions with same ionic strength (0.1 M) have a total ultrasonic time of 10 min and settling time of 30 min, which are determined by the result of laser testing; the solid beam through the solution is the guarantee for stable zeta potential results.

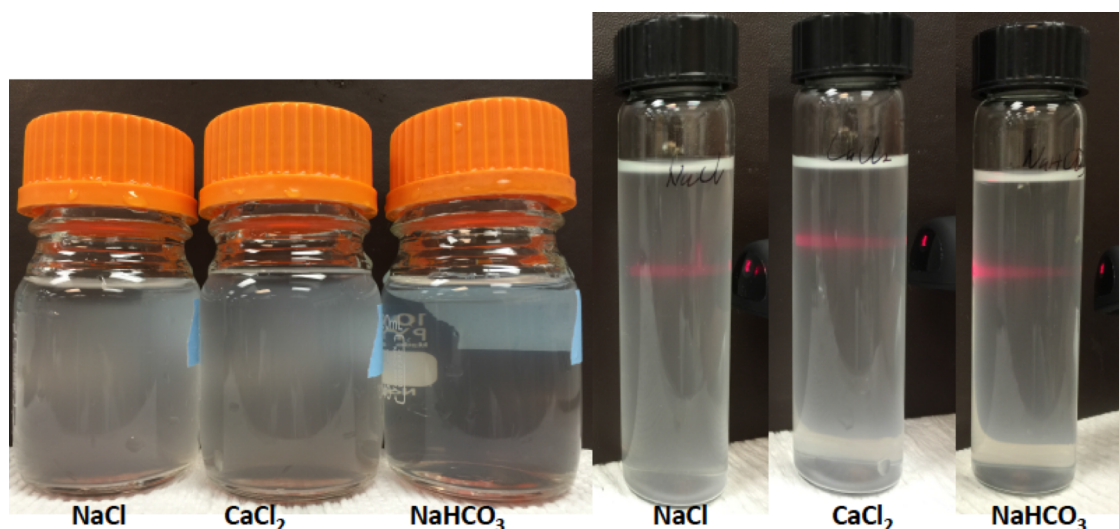


Figure 4-3 5 vol.% model oil emulsions and laser testing results at 25 °C

Based on experimental results, the capability to form emulsion in different solution varies, it is easier to form emulsion in NaCl solution than in other solutions. Factors, such as pH, salinity and oil percent, can also affect such capacity. For the control of experiment, an ultrasonic time of 10 min (fixed ultrasonic strength) plus 24-h equilibrium time is set as a standard for most of oil sample experiments.

4.3.2. Zeta Potential of Model Oil

Figure 4-4 is the zeta potential results in different brines with a same ionic strength of 0.1 M. The ultrasonic time for emulsions is 10 min, and the equilibrium time before emulsification is 24 h under 25 °C. It indicates zeta potential of model oil in different solution behaves like that of silica. Divalent cation adsorption, such as Mg^{2+} and Ca^{2+} , can make the zeta potential less negative; high pH, by comparing the

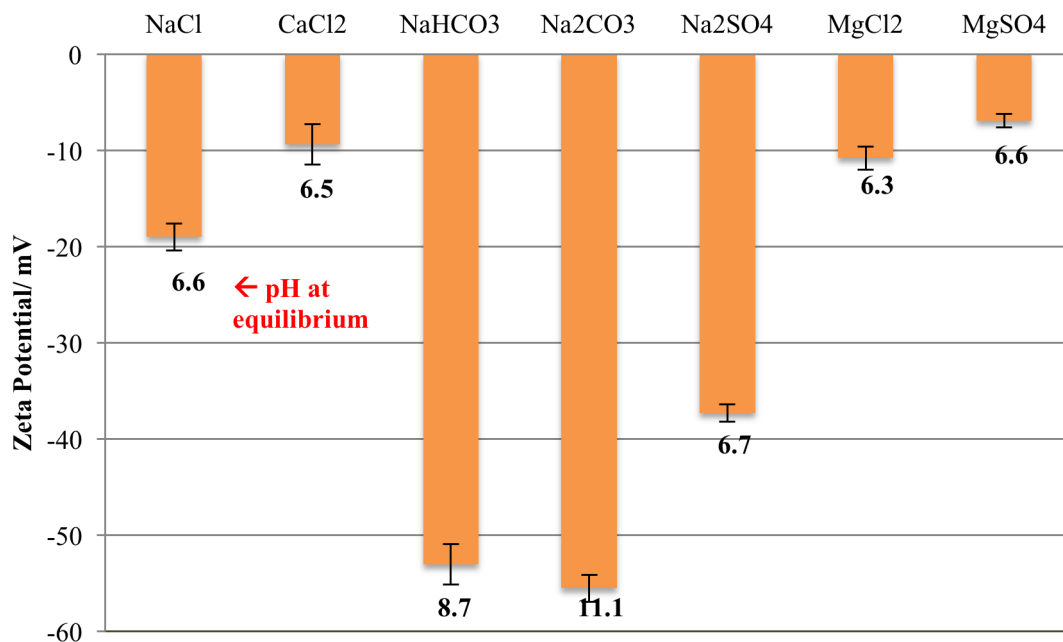


Figure 4-4 Zeta potential of 5 vol.% model oil emulsions in different brines

zeta potential of model oil in Na_2CO_3 and Na_2SO_4 solution (same ionic strength), makes the zeta potential more negative.

Figure 4-5 expresses the relationship between zeta potential of model oil and its drop size in 0.1 M NaCl brines (Ultrasonic time -10 min, Equilibrium time-24 h at $25\text{ }^\circ\text{C}$). Since the magnitude of zeta potential determines the stability of oil emulsion,

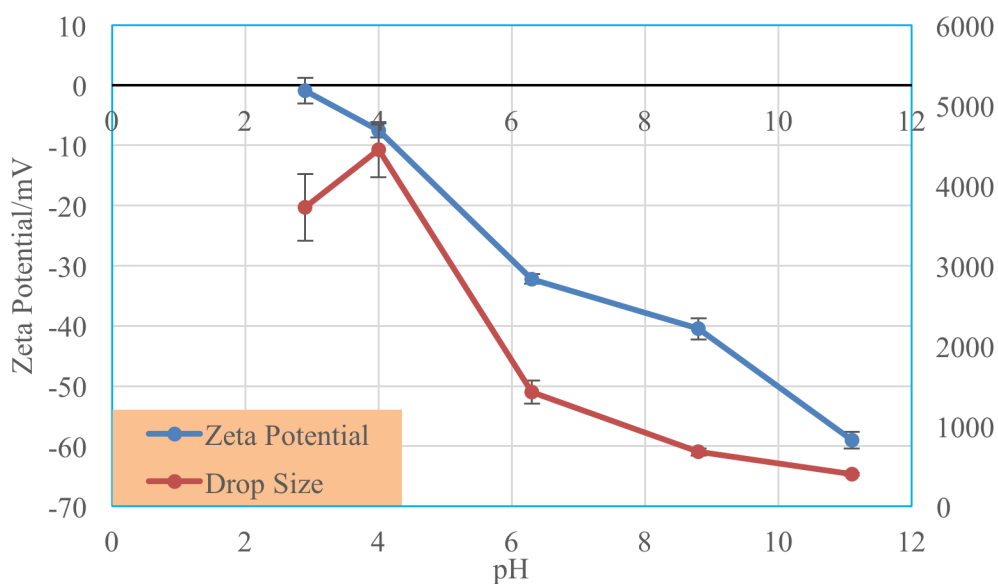


Figure 4-5 Zeta potential and drop size (nm) for 5 vol.% model oil in 0.1 M NaCl brine

oil droplets with small zeta potential magnitude are more likely to aggregate together and form large oil drop under same condition. The figure also tells us the isoelectric pH (the pH when zeta potential is zero) for model oil is about 3.0. The increase of pH from 3 to ~11 causes more negative zeta potential and smaller drop size for model oil.

4.3.3. Zeta potential of Model Oil with Base or Acid

The base components in crude oil can increase the positive charges on the surface of oil drop by H^+ protonation, which means the zeta potential would become less negative or even positive, compared with that of oil without base in the same condition. If the pH is small, the base effect would be more obvious. In Figure 4-6, in

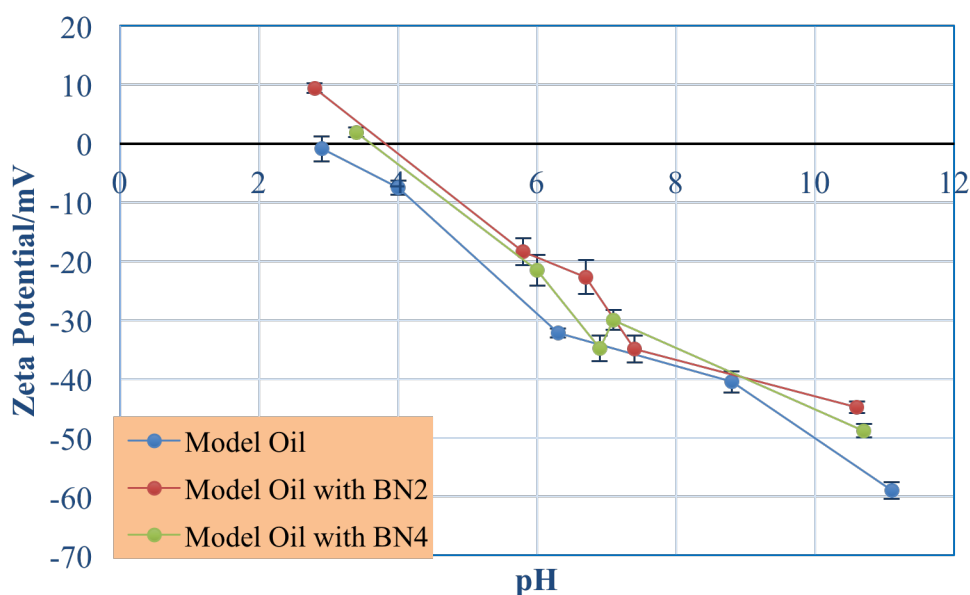


Figure 4-6 Zeta potential for 5 vol.% model oil with base number (0,2,4) emulsions in 0.1 M NaCl brine

order to illustrate the base effect of quinoline, zeta potentials of model oil with or without base are measured under same brine (0.1 M NaCl). The ultrasonic time for emulsions is 10 min, and equilibrium times is 24 h at 25 °C.

The zeta potential-pH curve shows the isoelectric pH for model oil increases from 3 to ~ 4, after adding base (BN2). However, if additional base is added, no further effect is observed. At high pH, the zeta potentials of model oil with or without

base are all close to each other. The possible reason might be: 1) Quinoline is a kind of weak base ($pK_a=4.9$), and positive charges on the surface of oil droplet could not be increased anymore by adding more quinoline. 2) Since the water solubility of quinoline after protonation will increase, a lot of base might have leached to the bulk brine and increase the bulk pH a lot at low pH condition (Carvajal-Figueroa, 1989).

Figure 4-7 is a comparison of zeta potential of model oil with acid or base under difference pH value in 0.1 mol/L NaCl brine. Results show the base compound in model oil can increase the pH of isoelectric point, while the acid has little effect on isoelectric pH.

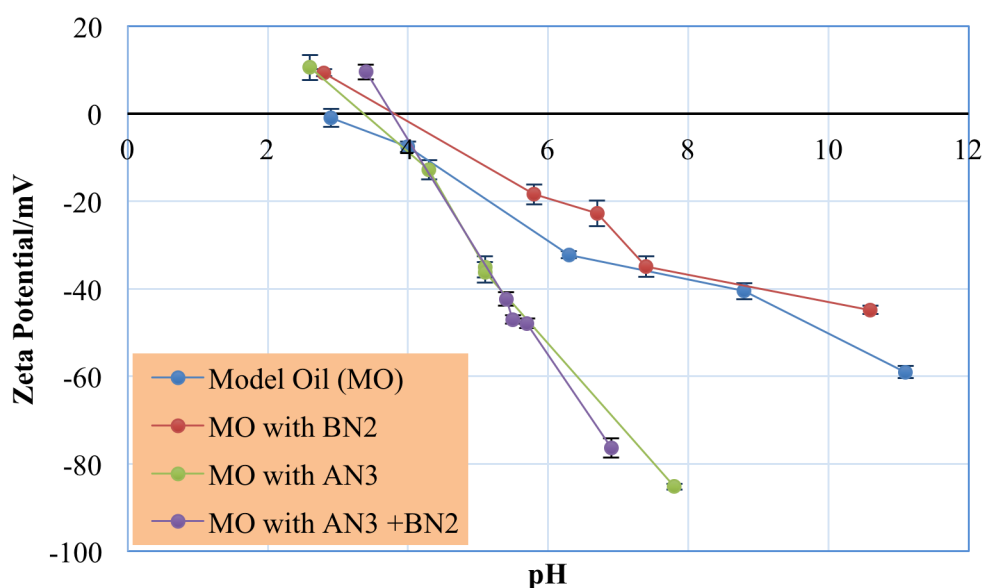


Figure 4-7 Zeta potential for 5 vol.% model oil/ model oil with BN2, AN3 or both in 0.1 M NaCl brine

At low pH, the model oil with base (BN2) tends to have less negative zeta potential due to base protonation, compared with those of model oil. But at high pH,

the base compound has little effect on zeta potential. For model oil with acid (AN3), it tends to have more negative zeta potential at high pH. However, acid compound has little effect on the zeta potential at low pH condition.

The zeta potential of model oil with base (BN2) and acid (AN3) shows a combination of acid and base effects, which means surface active chemicals increase the positive surface charges by H^+ protonation at low pH, while increasing negative surface charges by acid dissociation at high pH.

4.4. Zeta Potential of Model Oil and Silica Particle

In order to illustrate the influence of electrostatic potential on the wettability in the brine-oil-minerals (BOM) system, some more experiments are conducted in several brines 1) 0.2 % NaCl solution; 2) 0.5 % NaCl solution; 3) 3 % NaCl solution; 4) 0.15 % $CaCl_2$ solution; 5) 0.2 % NaCl + 0.15 % $CaCl_2$ solution. The zeta potentials of silica particle and oil droplet can be used to explain the effects of salinity and Ca^{2+} presence on contact angle change in the future. The brine systems used in contact angle measurement should be similar to those in zeta potential measurement.

Electrostatic potentials of brine-oil and brine-mineral interfaces play big roles in determining the disjoining pressure for the three-phase contacted region. The zeta potentials of model oil and neutralized silica for quantifying the electrical potential effect are measured in similar brine conditions. The final pH after 24-h equilibrium time is recorded for showing the leaching, protonation or dissociation effects of acid

and base to the bulk pH, see Figure 4-8 & 4-9. The original data will be summarized in Appendix D.

In Figure 4-8, it is obvious that the magnitude of zeta potential for model oil with BN3&AN2 is the largest, and the second one is model oil with AN3. The zeta potential for model oil with BN2 is close to that of model oil. The Figure 4-9 shows adding base to model oil lead to the increase of final bulk pH, while adding acid to model oil reduces the bulk pH. All the zeta potential and pH results in different brines are consistent with the results before.

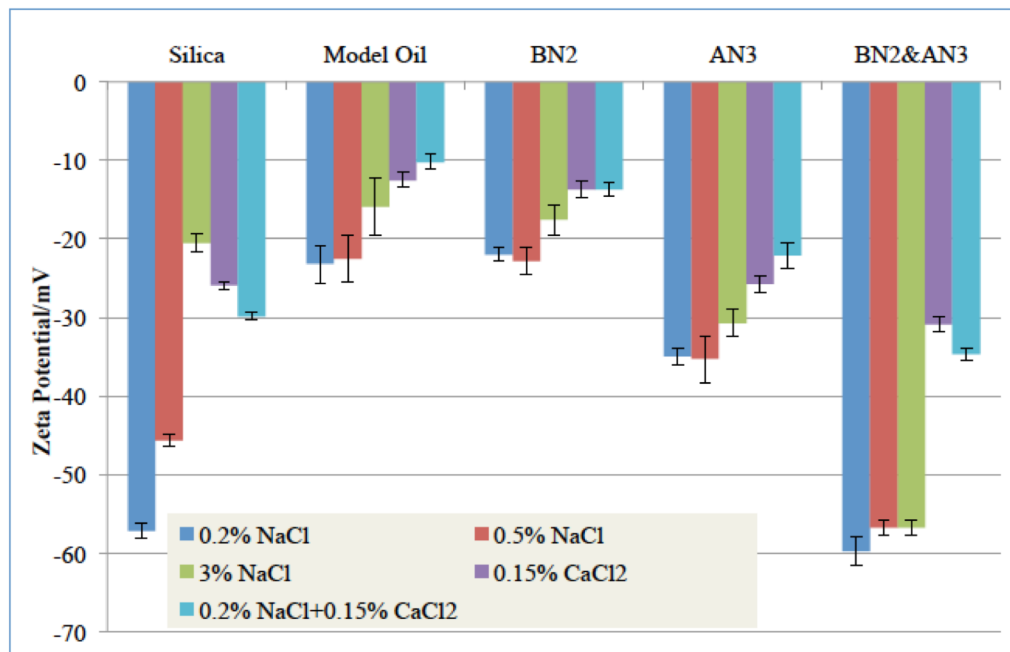


Figure 4-8 A summary of zeta potential results for different sample

The change of equilibrated pH in brine is due to base/acid leaching and base protonation or acid dissociation. In Figure 4-9, the average pH for model oil is about 6.5; for model oil with AN3 is about 5.0; for model oil with BN2 is about 6.7; for model oil with BN2 & AN3 is about 5.5. Apparently, the effect coming from acid dissociation

is dominant to the bulk pH. When comparing the zeta potential with different components (acid/base), we need to take the pH change into consideration.

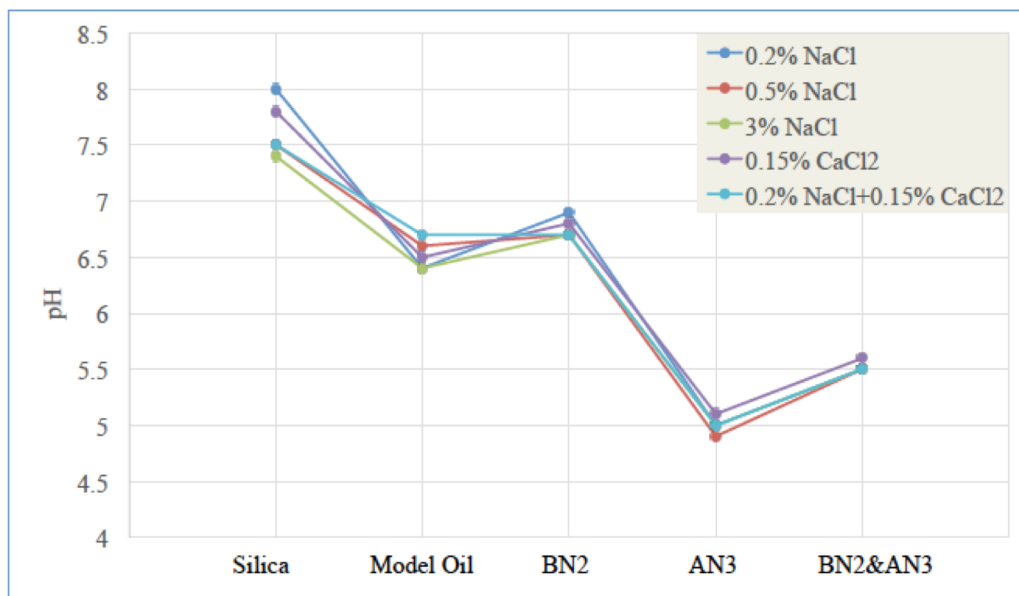


Figure 4-9 A summary of equilibrated pH for different sample

Since the quinoline is weak base, the zeta potentials with base is very close to those of model oil in same brine. The increase of salinity can reduce the magnitude of silica's zeta potential, but its effect is smaller for the zeta potential of oil. However, the presence of divalent ion, Ca^{2+} , can significantly reduce the magnitude of zeta potential for both silica and oil.

A combination of base and acid can greatly increase the magnitude of zeta potential. One explanation for such phenomenon is that the presence of base can help the dissociation of carboxylic acid group and/or increase the surface coverage of acid, as well as the negative surface charges of oil droplet.

The proposed mechanism is: the base can act as H^+ receptor, and increase the degree of acid dissociation. Since the hydrophilic carboxylic group is easier to expose to the surface (more hydrophilic), the negative surface charges increase.

4.5. Mechanisms and Conclusions

The main reason for large deviation in zeta potential of oil-brine interfaces is large-size effect; oil-drop size should be optimized, decreased by increasing ultrasonication time, while avoiding making solution too opaque. Laser beam through oil emulsion can help make sure if the sample can produce stable results.

Zeta potential of model oil in different solution behaves like that of silica particle: increase pH or reduce salinity makes the zeta potential of model oil more negative. Divalent cation adsorption, such as Ca^{2+} , Mg^{2+} , makes the zeta potential less negative, while divalent anion (SO_4^{2-}) leads more negative zeta potential.

The base components used in model oil can increase the pH of isoelectric point while the acid component has little effect on this pH. At low pH, the model oil with base tends to have less negative zeta potential due to base protonation, compared with those of model oil. But at high pH, the base compound has little effect on zeta potential.

At large pH, the model oil with acid tend to have more negative zeta potential, compared with those of model oil. But at low pH, acid compound has little effect to zeta potential.

A combination of base and acid can significantly increase the magnitude of zeta potential, which means the existence of base can help the dissociation of carboxylic acid group and/ or increase the surface coverage of acid. The negative surface charges of oil droplet will increase, due to hydrophilic property of carboxylic acid group.

Chapter 5

Conclusions and Future Directions

5.1. Mechanism Summary

The wetting state of a reservoir is determined by the interactions among brine, crude oil and reservoir rock (clay) in specific temperature and pressure. In this work, the focus is the electrostatic properties (zeta potential) of oil-brine and brine-silica interfaces.

For brine, main mechanisms affecting the zeta potential of silica and model oil are cation adsorption by multivalent ions, double layer compression by high salinity, pH-surface charges, and the adsorption of dissolved oil component, etc. For crude oil, we care about the influence of surface active materials (acid or base) on the zeta potential of model oil. Temperature increase in the whole system can increase the activity coefficient of multivalent ions, but its effect on our experiment is limited, due

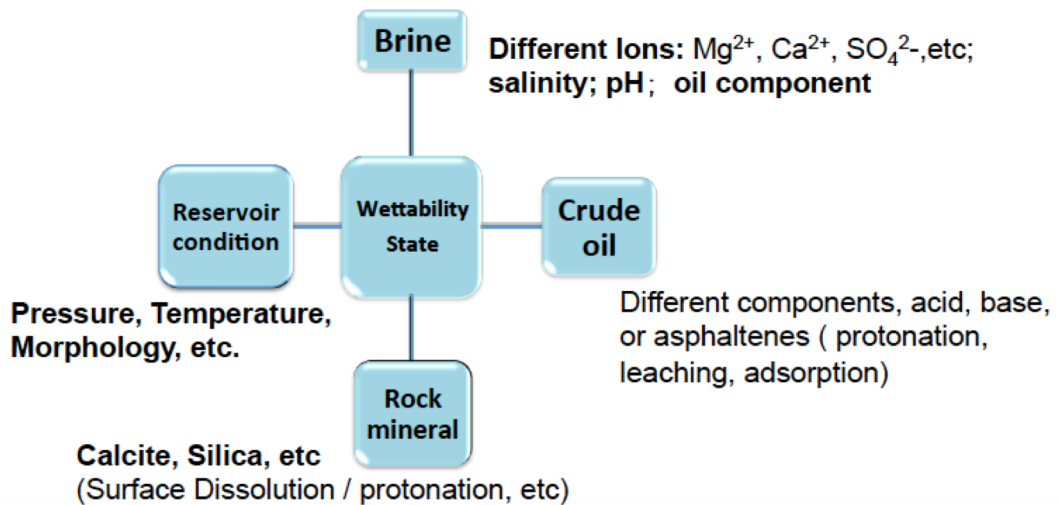


Figure 5-1 The components in reservoir systems

to a small temperature increase (from 25 °C to 50 °C). The whole experiment design is based on the relationship of components in reservoirs as Figure 5-1.

Surface intermolecular forces governing the wetting state of brine-oil-mineral systems can be modelled through the disjoining pressure isotherm (Hirasaki, 1991). In three-phase contact region, the disjoining pressure, which combines double layer forces, London-van der Waals forces and structural forces together, describes the stability of thin film, shown in Figure 5-2. The electrostatic component of the disjoining pressure for our BOM system is a function of the charge or electrical potential between oil-brine interfaces and silica-brine interfaces.

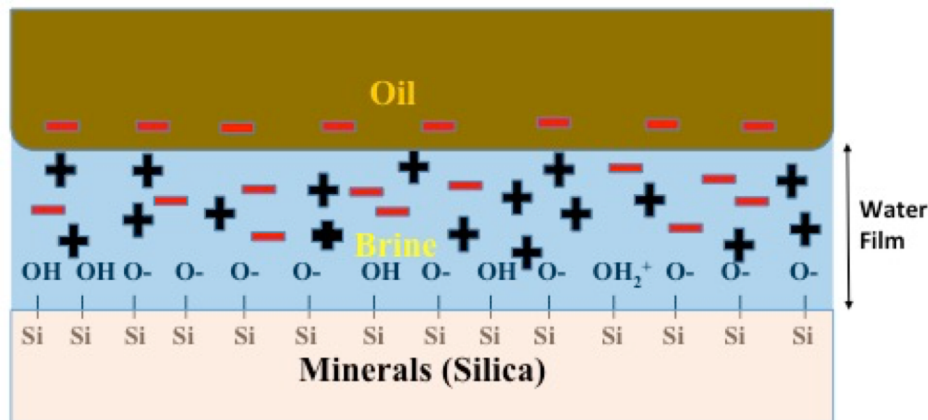


Figure 5-2 The water film in Brine-Oil-Silica Minerals system

A general guideline for the wettability state is whether the oil/brine and brine/mineral interfaces have similar or dissimilar charge density or surface potential (W. G. Anderson 1986; Hirasaki, 1991; Dubey and Doe, 1993a). Surfaces with similar surface charges tends to repel or disjoin the two interfaces. Interfaces

with dissimilar charge tends to attract or co-join the oil/brine and brine/mineral interfaces. Thus the former tends to be water-wet and the latter tends to be oil-wet.

For the brine-oil-mineral system, where oil components (surface active chemicals) may adsorb on the surface of mineral, the mechanisms governing brine-oil-solid interactions include: Polar interaction, surface precipitation, acid-base interaction and ion binding interaction (Jill S. Buckley, 1996; J. S. Buckley et al. 1998; J. S. Buckley and Liu, 1998a), summarized in Figure 5-3.

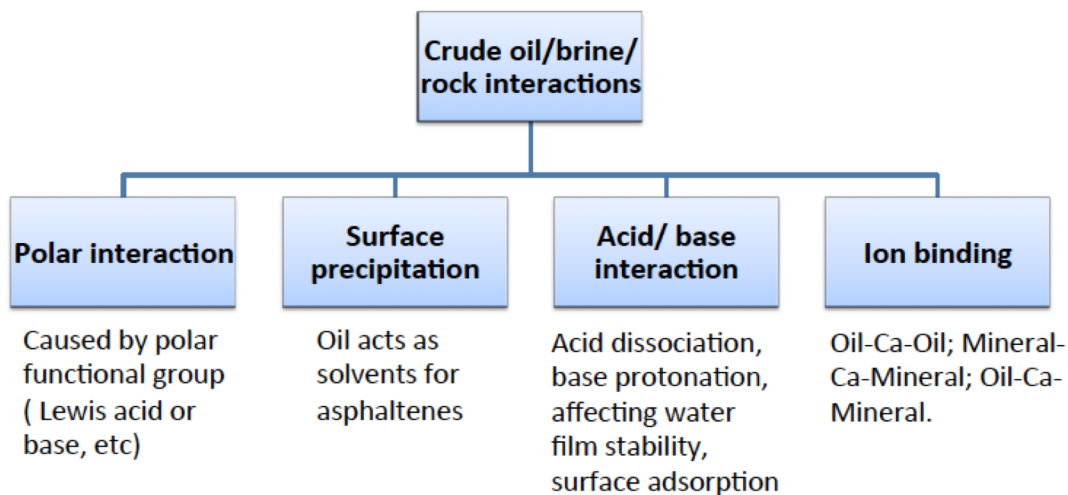


Figure 5-3 A summary of interactions accounting for wettability change (contact angle) in Brine-Oil-Minerals system (J. S. Buckley et al. 1998)

- Polar Interaction

Most of crude oil components have polar groups, and these polar parts can interact with the polar sites on the surface of minerals. The polar interaction would be dominant to the wetting condition of surface if water is absent or thin water film exists. A good example is the interaction between silica and acid or base components

in model oil, shown in Figure 5-2. When the model oil contains acid components, the hydrogen bonding would be formed between Si-OH and carboxylic acid group. Therefore, the contact angle might increase and wetting state tends to more oil-wet.

- Surface Precipitation

The oil component precipitation does depend on the solvent quality, which can be indicated by refractive index or API gravity. Severe surface precipitation would change the electrostatic property of crude oil and even alter the mineral surface from water-wet to oil wet. In oil experiment, the quinoline is weak base and the leached quinoline from model oil might adsorb on silica plate surface and strengthen the polar interaction and base-acid interaction. Therefore, the contact angle might increase and wetting state tends to more oil-wet.

- Acid-Base Interaction

The presence of water can lead to acid dissociation and base protonation, which might change the surface charges of oil-brine interfaces. Some important parameters for brine include pH, ion composition, salinity, etc. Based on the disjoining pressure isotherm, the water film stability, mainly affected by salinity, between mineral and oil is important to the wettability alteration. At the same time, the dissociated acid and protonated base components would easily adsorb on the surface of minerals, which depends on the surface charges of mineral.

- Ion Binding Interaction:

In the experiment, Ca^{2+} ions can mask the purely acid-base interactions by bridging the two negatively charged surfaces. The formations in reservoir might be Oil-Ca-Oil, Mineral-Ca-Mineral or Oil-Ca-Mineral. In this way, some negatively charged molecules can also be attached to negatively charged mineral surface by multivalent cation bridging (Lee et al. 2010).

5.2. Some Important Conclusions

- The Stoke's Law is applied to predict the settling time for zeta potential measurement. An acceptable settling time was found so to be sure that there is enough small particle dispersed in solution, which can produce reliable test results with small zeta potential deviation.
- The ratio of divalent cations (Ca^{2+} , Mg^{2+}) to divalent anions (CO_3^{2-} , SO_4^{2-}) in brine can determine the surface potential of calcite. Some operation conditions, such as pH and ion composition, can even change the calcite's zeta potential from positive to negative by altering this ratio.
- The neutralization or neutralization time can affect the pH of silica dispersions after equilibrium. Unlike the zeta potential of calcite, silica's zeta potential is hard to change from negative to positive by altering the operation conditions, such as ion composition (not including trivalent ions), salinity or pH.
- The base component chosen for experiment can increase the pH of isoelectric point while the acid component has little effect on it.

- At low pH, the model oil with base (quinoline) tends to have less negative zeta potential due to base protonation, compared with those of model oil. But at high pH, the base compound has little effect on zeta potential.
- At high pH, the model oil with acid tend to have more negative zeta potential, compared with those of model oil. But at low pH, acid compound has little effect on zeta potential.
- A combination of base and acid can significantly increase the magnitude of zeta potential, which means the presence of base can help the dissociation of carboxylic acid group and increase the negative surface charges of oil droplet.
- Salinity increase can reduce the magnitude of silica's zeta potential, but its effect to oil sample is smaller. Divalent ion, Ca^{2+} , can significantly reduce the magnitude of zeta potential for both silica particle and oil sample.
- Based on the zeta potential results, the quinoline is too water soluble base, and its effect on zeta potential is limited at low pH (but shifting the isoelectric point pH from 3 to 4.)

5.3. Future Work

5.3.1. Contact Angle Measurement

This thesis mainly focuses on the influence of electrostatic potential for fluid-fluid and fluid-rock interfaces on reservoir wettability. As introduced in chapter 2, contact angle measurement is the common method to quantify the wetting state of reservoir rock. Therefore, the next step is to measure contact angles in the BOM system with the same brines as zeta potential measurement: 1) 0.2 % NaCl solution; 2) 0.5 % NaCl solution; 3) 3 % NaCl solution; 4) 0.15 % CaCl₂ solution; 5) 0.2 % NaCl + 0.15 % CaCl₂ solution.

Based on experimental results, base adding (quinoline) just increased the isoelectric pH from 3 to 4. At the same time, the zeta potentials for oil and silica were all negative in same brine with pH ranging from 5 to 8. In order to improve the understanding on how electrostatic potential of oil affects system's wettability, it is necessary to explore the pH effect to the contact angle (pH<4). At low pH, the magnitude of negative zeta potential for silica would be reduced while the zeta potential of oil might become positive. The wetting of brine-oil-silica system possibly changes from strongly water-wet to neutral wet or even oil-wet in the electrostatic attraction area (Dubey, Doe, 1993b), as shown in Figure 5-5.

5.3.2. Base or Acid Adsorption on Minerals

The protonated base (quinoline) in experiments can easily adsorb on the surface of silica plate, and then alter the wetting or contact angle by improving polar interactions. Therefore, the amount of leached base should be determined to better understand the base effect on the whole experiment system, especially for the electrostatic potential of oil or minerals.

The surface active chemicals existing in crude oil is like the surfactant applied in enhanced oil recovery. Exploring the effect of base or acid adsorption to electrostatic potential of minerals will definitely help us know how surfactant modify the reservoirs' wettability. Ma et al. (2013) studied the adsorption of cationic and anionic surfactants on natural carbonates, and these two surfactants are cetylpyridinium chloride (CPC) and sodium dodecyl sulfate (SDS). He pointed out that the cationic CPC can be absorbed on the negative binding sites (silica or clay) on the carbonate surface, and the CPC adsorption would reduce in presence of 1 atm CO₂; the anionic SDS would precipitate from the solution due to the divalent cation binding (Ma et al. 2013), shown in Figure 5-6.

Obviously, electrostatic potential of rock-fluid interfaces can also affect the adsorption of surfactant or some other surface active chemicals in reservoirs. To prove the adsorption mechanisms and show the influence on electrostatic potential or wettability, some more experiments should be done with the presence of acid or base.

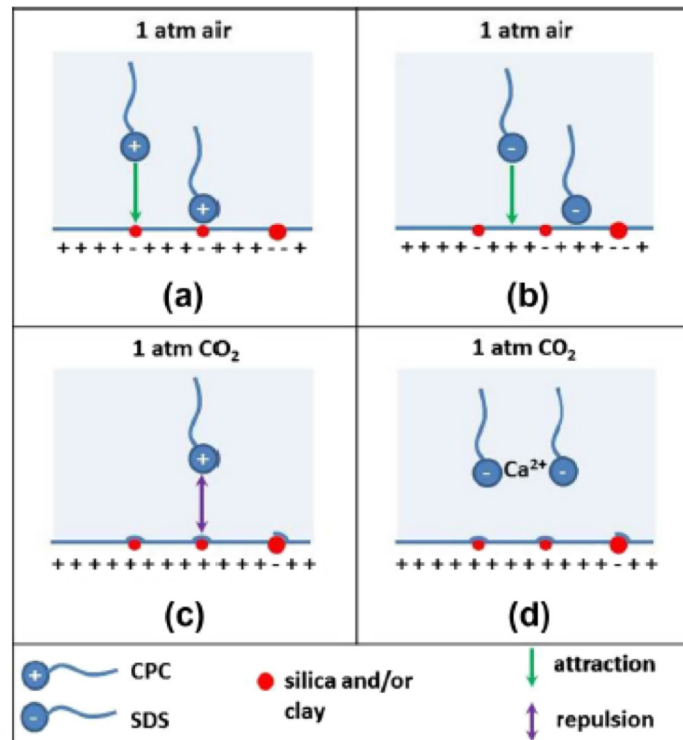


Figure 5-4 Mechanisms for CPC/SDS adsorption on natural carbonates in the presence or absence of CO₂ (Ma et al. 2013)

5.3.3. Zeta Potential of Oil

For the zeta potential measurement of oil, some other components which can significantly increase the isoelectric pH of oil are needed to be used in experiments. Figure 5-5 shows the California crude oil (AN=0.22, BN=4.90) had a high isoelectric pH of ~6.8. The possible mechanisms are 1) the presence of strong base with small water solubility; 2) weak acids in crude oil facilitate the protonation of base, which increases the positive surface charges of oil.

Anyway, some further experiments should be conducted to help recognize how acid or base components affect zeta potential of oil and then change wetting state of reservoir rock.

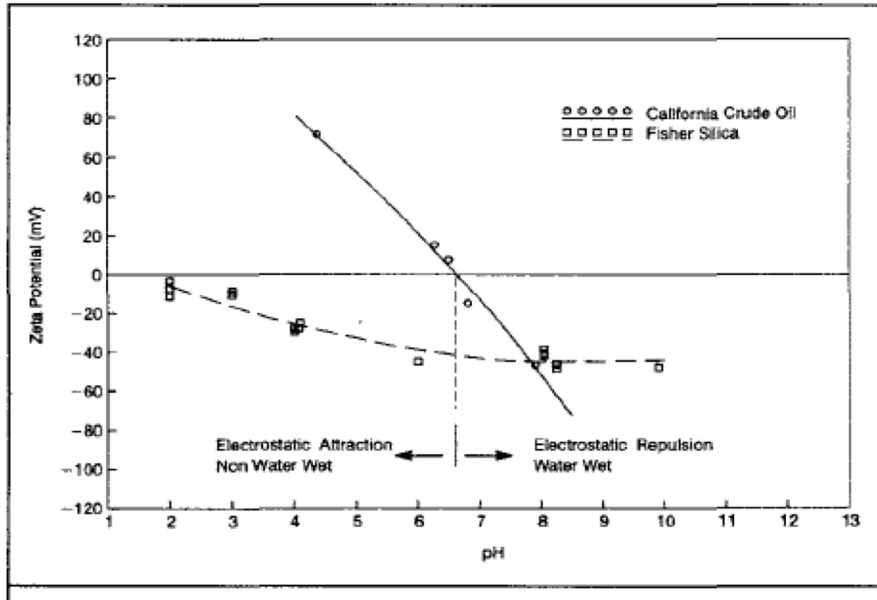


Figure 5-5 Zeta potential VS. pH curves for California crude oil and silica and expected relationship to wetting (Dubey and Doe, 1993b)

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Appendix A

Notations

Glossary of Terms

p_A	Phase pressure of fluid A
p_B	Phase pressure of fluid B
$2H$	Mean curvature of interface between fluid A and fluid B
γ	Interfacial tension between these two immiscible fluid phases
θ	Contact angle between water and substrate surface
γ_{so}	Surface energy between oil and substrate
γ_{sw}	Surface energy between water and substrate
γ_{ow}	Interfacial tension between oil and water phases
θ_A	Water advancing contact angle
θ_R	Water receding contact angle
R	Effective radius
P_c	Capillary pressure between two immiscible fluid phases
P_w	Pressure in the wetting phase
P_{nw}	Pressure in the non-wetting phase
N	Original Oil in Place (OOIP) in oil reservoirs
N_p	Cumulative oil recovered by oil recovery processes

E_v	Macroscopic volumetric sweep efficiency
E_s	Areal sweep efficiency
E_i	Vertical sweep efficiency
V_e	Electrophoretic velocity of particle in electric field
E	Strength of applied electric field
μ	Electrophoretic mobility, or velocity per unit electric field
R_h	Hydrodynamic radius of particles
Z	Valence of the macromolecules
e	Elementary charge ($\sim 1.6 \times 10^{-19}$ coulombs)
η	Viscosity of solution
$\kappa (\kappa^{-1})$	Debye-Hückel parameter (Debye length)
$f(\kappa R_h)$	Henry's function
ϵ_0	Permittivity of free space ($\sim 8.854 \times 10^{-12}$ F/m)
ϵ_r	Solvent dielectric constant (~ 80 for water at 20 °C)

Appendix B

Calculate Acid and Base Number

(1) Acid Number: The acid number is the amount of potassium (KOH) in mg needed to neutralize the acid group in 1 g of crude oil. The acid number was calculated based on equivalent weights of the acid and KOH. The acid used in the experiment is cyclohexane pentatonic acid (CHPA).

Molecular weight of CHPA = 184.28; Molecular weight of KOH = 56.11

For the acid base titration:

1 equivalent of acid = 1 equivalent of base;

1 equivalent of CHPA = 1 equivalent of KOH.

184.28 g of CHPA = 56.11 g of KOH..... **(Eq. 1)**

For a solution with acid number 3 mg KOH / g of crude oil, the grams of CHPA been neutralized by 3 mg of KOH should be calculated.

From **Eq 1,**

56.11 g of KOH neutralizes 184.28 g of CHPA;

Then, 3 mg of KOH neutralizes 9.85 mg of CHPA.

Therefore, 9.85 mg of CHPA is to be dissolved in 1 g of model oil to prepare a solution with acid number 3 mg KOH/ g of crude oil.

To make 20 ml of model oil with AN=3 (acid number 3 mg KOH / g of crude oil):

Weight of 20 ml of model oil = $20 \times 0.755 = 15.1$ g (0.755 g/ml is the density of model oil at room temperature)

For AN=3, 1 g of model oil 9.85 mg of CHPA is to be dissolved,

Then 15.1 g of model oil needs $15.1 \times 9.85 = 148.74$ mg of CHPA is to be dissolved.

Since the density of CHPA=0.96 g/ml, 148.74 mg corresponds to 154.94 μ l of CHPA.

Therefore, 154.94 μ l or 148.74 mg of CHPA is to be dissolved in 20 ml of model oil to prepare a solution with acid number 3.

(2) Base Number: Base number is the amount of potassium hydroxide in mg that is required to neutralize the acid titrant used in the base titration of 1 g of crude oil.

1 equivalent of acid titrant = 1 equivalent of base in crude oil **(Eq. 2)**

1 equivalent of KOH = 1 equivalent of acid titrant..... **(Eq. 3)**

Combining **Eq. 2 and 3**

1 equivalent of KOH = 1 equivalent of base in crude oil;

When use quinoline as the base,

1 equivalent of KOH = 1 equivalent of quinoline;

Molecular weight of quinoline = 129.16; Molecular weight of KOH = 56.11

Therefore, similar calculations as above can be made for quinoline and the solution with required base number are prepared.

Appendix C

Application of Stokes' Law to Predict Settling Time

The Stokes' Law, describing spherical objects with low Reynolds number in viscous solution, can be used to give a precise prediction of the particle-settling times. An acceptable settling time was found important to reduce the amount of dispersed silica (opaqueness) and help settling large-size particles. Only in this way, can we see a solid beam through dispersions, which in turn produces reliable test results with small zeta potential deviation.

$$V = \frac{2(\rho_p - \rho_f)}{9\mu} g R^2$$

Where

V = flow settling velocity (m/s).

Vertically downwards if $\rho_p > \rho_f$,

Upwards if $\rho_p < \rho_f$.

$g = 9.80 \text{ m/s}^2$ gravitational acceleration; ρ_p = mass density of the particles;

ρ_f = mass density of the fluid; μ = dynamic viscosity.

Example of calculation for silica mineral/model oil:

L = Length of glass vial = 10-cm; $2R$ = Mean diameter particle = 1.6-micron;

ρ_p = Mass density of particles (2650 kg/m³ for silica; 2710 kg/m³ for calcite; 750 kg/m³ for model oil);

ρ_f = Mass density of fluid (999.97 kg/m³)

μ =Dynamic viscosity (0.001kg /m*s).

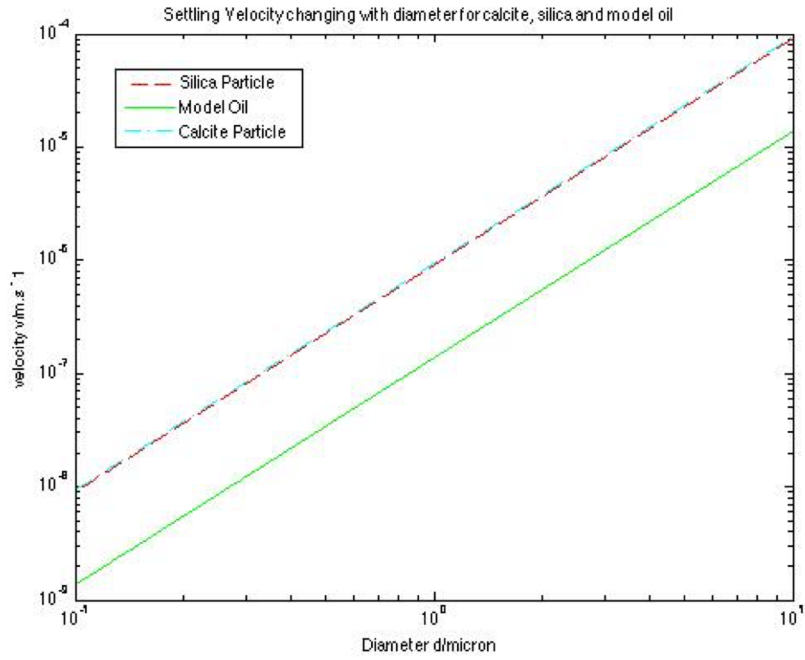
Then,

V = Settling speed of silica particle = 2.30e-6 m/s;

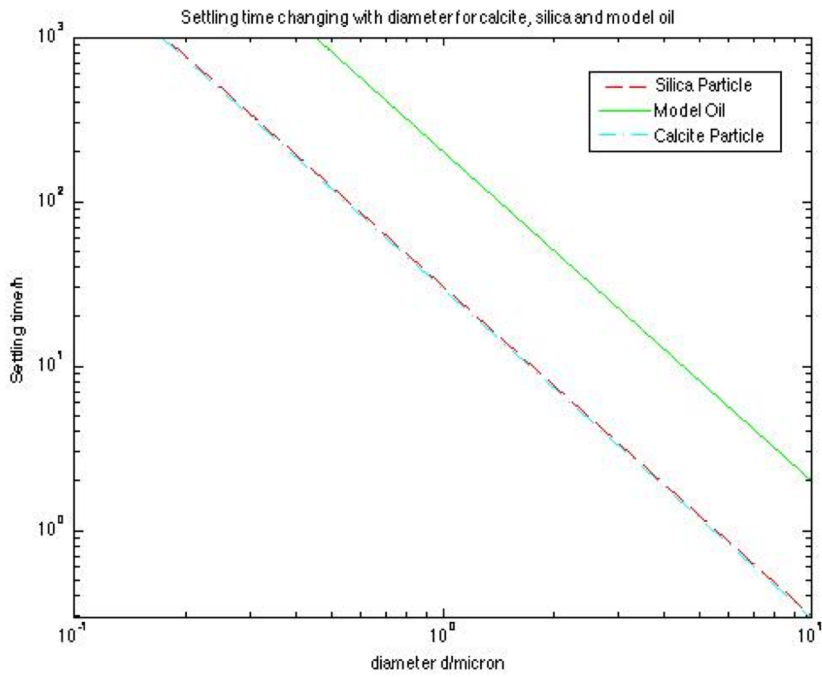
Settling time (all particles with same size settled) =12.08 h.

It is important to (1) let the equilibrated slurry or suspension settle for a while, because some big particle can easily block the tube of the equipment and (2) avoid injecting supernatant with high concentration because it provokes large measurement deviation caused by the weak signal of light scattering. Thus, using **Figure 5 and 6** above, a suitable settling time can be easily predicted for each kind of sample to get stable results. If the time is too long, centrifugation could be chosen for removing most of the particle in slurry.

Stokes' Law gives the settle time for particles with a given size. For oil experiment, the only complication is that the drop size is changing with time since aggregation is occurring.



APP-Figure 1 Settling speed changes with diameter of minerals/model oil



APP-Figure 2 Settling time changes with diameter of minerals and model oil

Appendix D

Zeta Potential for Explaining Contact Angle Change

APP-Table 2 and Table 3 summarized the zeta potential results for explaining the contact angle change. Results show the increase of salinity can reduce the magnitude of silica's zeta potential, but its effect is smaller for the zeta potential of oil. However, the presence of divalent ion, Ca^{2+} , can significantly reduce the magnitude of zeta potential for both silica and oil.

For the pH of equilibrated emulsions, the average pH for model oil is about 6.5; for model oil with AN3 is about 5.0; for model oil with BN2 is about 6.7; for model oil with BN2 & AN3 is about 5.5. Apparently, the effect coming from acid dissociation is dominant to the bulk pH. When comparing the zeta potential with different components (acid/base), we need to take the pH change into consideration.

APP-Table 2 A summary of results for explaining contact angle change

Sample@25 C	Silica		Model oil		Model oil with AN3	
	pH	Zeta potential mV	pH	Zeta potential mV	pH	Zeta potential mV
DI water	8.2	-63.3 +/-6.8	N/A	-62.7+/-3.4	N/A	N/A
0.2% NaCl	8.0	-57.2+/-1.0	6.4	-23.2+/-2.4	5.0	-35.0+/-1.1
0.5% NaCl	7.5	-45.7+/-0.8	6.6	-22.5+/-3.0	4.9	-35.3+/-3.0
1.0% NaCl	7.7	-38.7+/-1.0	6.7	-20.8+/-0.9	N/A	N/A
3.0% NaCl	7.5	-20.5+/-1.1	6.4	-15.9+/-3.6	5.0	-30.7+/-1.8
0.15% CaCl ₂	7.8	-25.9+/-0.3	6.5	-12.5+/-1.0	5.1	-25.8+/-1.1
0.2% NaCl+ 0.15% CaCl ₂	7.5	-29.9+/-0.5	6.6	-10.2+/-1.0	5.0	-22.1+/-1.6
Notice	0.8 wt.% silica dispersion, 2 h-HCl washed & 1 h- NaHCO ₃ Neutralized silica sample, 24 h for equilibrium. 5 vol. % model oil emulsion, 24 h for equilibrium.					

APP-Table 1 A summary of results for explaining contact angle change

Sample@25 C	Silica		Model oil with BN2		Model oil with BN2&AN3	
	pH	Zeta potential mV	pH	Zeta potential mV	pH	Zeta potential mV
DI water	8.2	-63.3 +/-6.8	N/A	N/A	N/A	N/A
0.2% NaCl	8.0	-57.2+/-1.0	6.9	-22.0+/-0.8	5.5	-59.8+/-1.9
0.5% NaCl	7.5	-45.7+/-0.8	6.7	-22.8+/-1.7	5.5	-56.8+/-1.0
1.0% NaCl	7.7	-38.7+/-1.0	N/A	N/A	N/A	N/A
3.0% NaCl	7.5	-20.5+/-1.1	6.7	-17.6+/-1.9	5.5	-44.3+/-1.0
0.15% CaCl ₂	7.8	-25.9+/-0.3	6.8	-13.7+/-1.0	5.6	-30.9+/-1.0
0.2% NaCl+ 0.15% CaCl ₂	7.5	-29.9+/-0.5	6.7	-13.7+/-0.9	5.5	-34.7+/-0.7
Notice	0.8 wt.% silica dispersion, 2 h-HCl washed & 1 h- NaHCO ₃ Neutralized silica sample, 24 h for equilibrium. 5 vol. % model oil emulsion, 24 h for equilibrium.					