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Initial wetting in sandstone –
Development through time

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ABSTRACT

This thesis is a literature study of initial wettability of sandstone and how the understanding of this phenomenon has developed through history.

Due to the fact that wettability affects several properties to reservoir, such as fluid distribution in porous media, it will have big effect on success rate of a waterflooding. As the initial wetting have such big impact on oil recovery, it is important to get a good understanding how the wettability initially occurs in the reservoir. What affect and determines the degree of wettability to a rock. The chemical interaction between injection water and rock surface. We will research what have been the assumptions and theory regarding this earlier, and how the petroleum industry have led hydrocarbon recovery based on these assumptions, and what recent study concluded with.

There is an agreement that the initial wettability is a product of a complex system in the reservoir and many parameters combined sets the final initial wettability in sandstone. For COBR (crude-oil, brine and rock), parameters such as: wetting components in crude oil, crude oil properties as a solvent, partitioning, interfacial tension, surface roughness, mineral composition etc have been in focus. Also mechanisms such as electrical characterization of the oil/water interface, adsorption, adhesion, spreading and stability of water film, DLVO and electromagnetic force have been discussed. However the main mechanism behind initial wettability is still unknown, due to the fact that in-situ wettability in reservoir cannot be measured.

Over long period of time, it was assumed that all sandstone reservoirs are originally water-wet. Later research has indicated that this is not necessarily true. Some reservoir was found to be mixed- and even oil-wet.

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1 INTRODUCTION

1.1 Introduction

The world population per today is at 7,4 billion and increases with a rate approximately 1,13% per year. This equivalent to a growth at 80 million per year, and results in a higher energy demand(1) . This combined with other factors such as reduction in oil price at the international marked, forces the petroleum industry to become more efficient as to develop improved way for oil recovery at least cost. One of the best way to cope with this issue, is to increase the current oil recovery in the fields that are already in production. The EOR methods plays a key role at this point, as there have been establish that after the primary and secondary stages, one can still recovery a decent amount of hydrocarbon by introducing EOR methods to the reservoir. At this department, there are still room for improvement as there are some processes that are still not fully understood till today.

Recently it have been discovered that by injecting low salinity fluid, also known as smart water, have increased the recovery factor significantly in many sandstone fields. The mechanical process maintain unsolved, but it is believed that the wettability is one of the main factors affecting results. This is great of interest as wettability are linked together and affect several reservoir properties, including capillary pressure, relative permeability, fluid distribution in the porous media, waterflooding behavior etc. To predict the EOR effect and optimize wettability alteration by water-based EOR, it is important to get better understand of the initial wetting in the reservoir.

1.2 Thesis Objective

Till this day, the initial wettability is still not fully understood due to lack of in situ information, and the knowledge of wettability with regard to origin and governing factors is based on laboratory experiments. One of the important goal regarding research on wettability is to establish a foundation of knowledge in order to predict oil reservoir wettability from laboratory experiment.

The main objectives of this thesis are:

1. Discuss initial wetting – The approach was based on understand what parameters that affect wettability and interactions in reservoir that result in the final initial wettability that can be expected.

2. The development of understanding wettability through time. By analyzing papers and reports on wettability through time we can map how the understanding developed.

Important goal of wettability research are to provide rational and consistent explanations of these apparent inconsistencies and to identify optimum conditions for oil recovery.

2. THEORY

2.1 Sedimentology and Mineralogy of Sandstone

2.1.1 Origin

Sediments are loose particles such as sand, silt and the shells of organisms that originate of weathering and erosion. Siliciclastic sediments are made up of physically deposited particles, such as grains of quartz and feldspar derived from weathering granite. These sediments are laid down by running water, wind and ice. As soon as the flowing velocity of the transport medium goes below a grain size dependent threshold, deposition initiates. The grains starts to accumulate.

Sedimentary rock consist of sediments that has been through a lithification process that converts sediments into solid rock. It occurs as compaction and cementation. By compaction, particles are squeezed together due to overlying weight of sediments, forming a denser mass. In cementation, minerals precipitate around deposited particles and bind them together. (2)

2.1.2 Composition

Sandstone is categorized as medium-grained siliciclastic sediment. It is formed by lithified of sand under high pressure, consisting of size particles ranged from 0.062- 2 mm in diameter(2)

The composition depends strongly on the process in geological deposition environment but usually consist mostly of quartz $(\mathrm{SiO_2})$ with fraction of other minerals such as biogenic particles, mica, feldspar, clay etc. Sandstones are often referred as siliciclastic rock, due to its high silica content. Silica is important in EOR as it dissolves in aqueous solution particularly at high temperature and high pH. There is also a minor anion exchange capacity at neutral or elevated pH for the silica minerals. (3)

2.1.3 Mineralogy

Based on mineralogy, sandstone can be divided in 4 major groups:

- Quartz arenites: Consist of mostly quartz, well sorted and rounded. Is a result of extensive weathering before and during transportation which removed everything but quartz that is the most stable silicate mineral

- Arkose: Consist of more than 25% feldspar. More angular and less well sorted. These come from rapidly eroding granitic and metamorphic terrains where chemical weathering is subordinate to physical weathering.

- Lithic sandstone: Mostly fine grains derived from fine-grained rocks such as shale, volcanic rocks and fine-grained metamorphic rocks.

- Graywacke: Strongly heterogeneous mixture of rock fragments and angular grains of quartz and feldspar in which the sand grains are surrounding by a fine-fined clay matrix.

Mineralogical composition of reservoir rock affect the interaction between reservoir minerals and externally added reagent (surfactants/polymers) and their effect on solid-liquid interfacial properties such as surface charge and wettability. Some of the reservoir minerals can be sparingly soluble causing precipitation and change in wettability as well as drastic depletion of surfactants/polymers. (4)

In Anderson wettability literature, he discusses that clean quartz has negative charged surface and tends to adsorb (positively charged) organic bases from solution. The negative charged acids in solution will not adsorb on the surface because they will be repelled by identical charge on quartz surface. Typical reservoir pH for sandstone is around 5, which means under the natural condition the quartz will remain water-wet. However, at the proper pH condition the wettability can be changed and the quartz can be floated by the addition of small amount of many multivalent metallic cations, including $\mathrm{Ca^{2+}, Ba^{2+}, Cu^{2+}, Al^{3+}}$ and $\mathrm{Fe^{3+}}$. (5)

Quartz have tendency to become more oil-wet at higher temperature, but calcite becomes more water-wet.

Without any contamination, most minerals, including quartz, carbonates and sulfates are strongly water-wet. From studies, few minerals have been found to be naturally but weakly water-wet or even oil-wet. This minerals include: sulfur, graphite, talc, coal and many sulfides. Pyrophyllite and other talc-like silicates (silicate with a sheet-like structure) are probably also neutral-wet to oil-wet. (5)

2.2.3.1 Clay

As we study sandstone, mineral clay which always are present in some fraction is of interest. Its properties such as Cation Exchange Capacity and swelling can have big impact on reservoir performance. Clay impact on oil recovery was first presented by Johnston and Beeson in 1945, where their study indicated that permeability of oil sandstone would decrease after contact with fresh water by 70 percent of the 1,200 samples. (6)

The clay minerals usually have microporosity, which is ineffective and isolating pores resulting in low flow of fluid across the pores. Degree of this effect depends both on clay mineral type and position within pore network. The fraction of clay present can diminish significantly the permeability in sandstone. It will also increase the residual water saturation in reservoir zones.

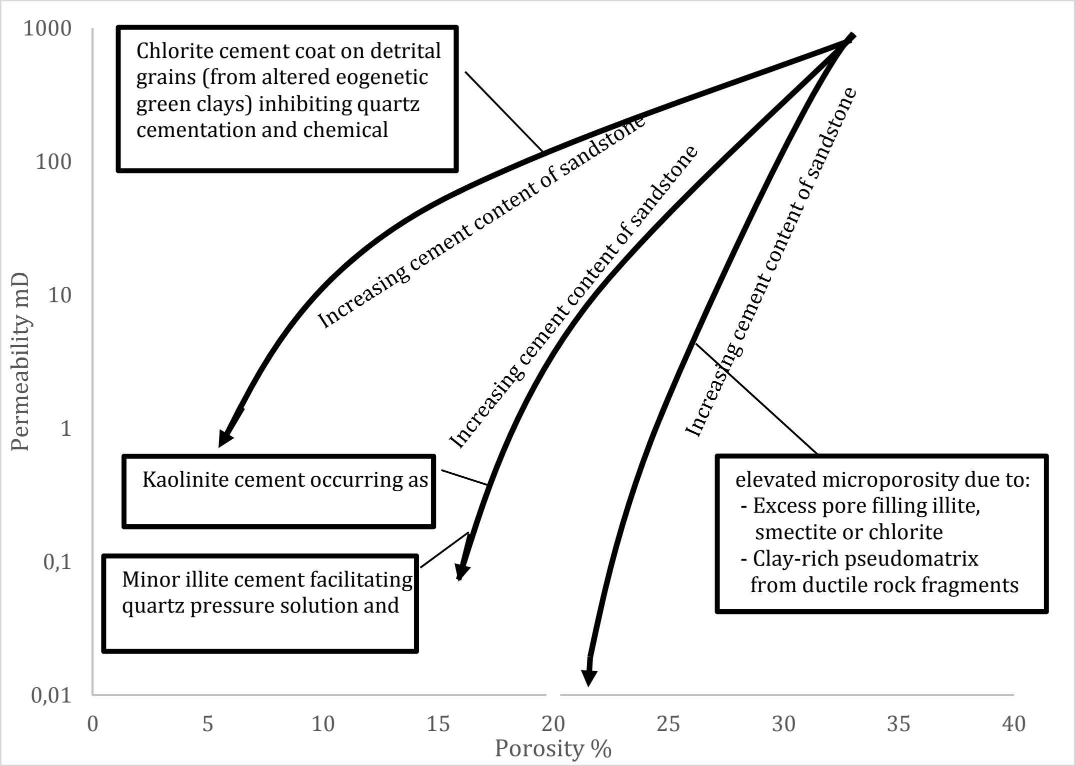


Figure 1: Porosity-permeability diagram shows the effect of the different types of clay and its effect on sandstone properties. Sketch redrawn from source(7).

Clay minerals have sheet-like structure consisting of silicate (Si), alumina (Al), iron (Fe), magnesium (Mg) and can also contain less amount of sodium(Na) and potassium (K). The common clay minerals are kaolin, illite, chlorite and dioctahedral smectite. (7, 8)

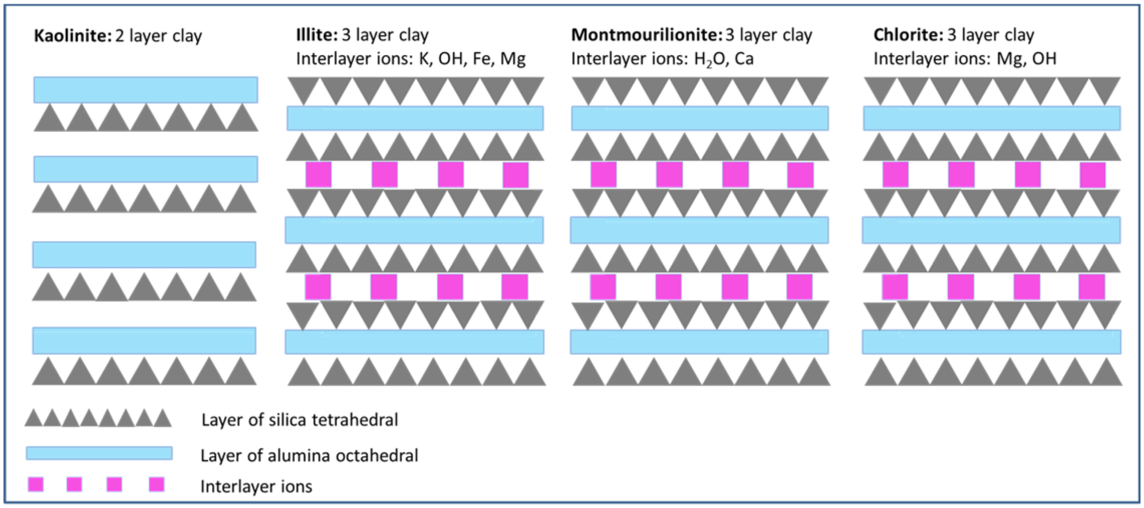


Figure 2: Mineralogy structure of different type of clay.(8)

A characteristic of clay minerals is the presence of negative charge on clay surface which attract and hold positively charged ions from pore-fluid to become neutral in charge(7). This negative charged surface is a result of structure where isomorphous substitution within the structure, from broken bonds at the edge and surface of the clay structure and from the dissociation of accessible hydroxyl group. As the cations are attracted to clay surface, a weak bond are established. This property is measured in CEC (Cation Exchange Capacity), describing quantity a clay can absorb. Unit for this is milliequivalents (mEq) per 100 g of clay or centimoles per kilogram. (7)

As result of the week bond it occurs exchange of cations them between such as K^{+}, Rb^{+} and Sr^{2+}(7). Due to this feature, clay minerals are also referred as cation exchange materials(9).

General order of cation affinity in room temperature:

$$\mathrm{Li}^{+} < \mathrm{Na}^{+} < \mathrm{K}^{+} < \mathrm{Mg}^{2+} < \mathrm{Ca}^{2+} \ll \mathrm{H}^{+}$$

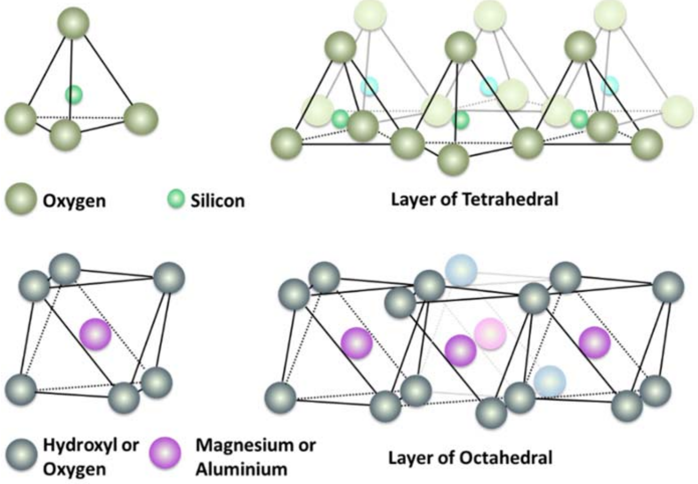


Figure 3: Structure of a tetrahedral and octahedral layer.(8)

There are five dominant group of clay; kaolin, illite, chlorite and dioctahedral. Different clay will have different properties in terms of layer, particle size and CEC:

Table 1: Clay Group Properties. (7, 8)

Properties	**Kaolinite**	**Illite and glauconite**	**Smectite**	**Chlorite**
Layers	1:1	2:1	2:1	2:1:1
Particle Size(micron)	5-0.5	Large sheets to 0.5	2-0.1	5-0.1
CEC (Meq/100g)	3-15	10-40	80-150	10-40

Note that it is not included a column for mixed layer, as within this group there are big variety.

Some of the clay minerals have tendency to swell up as a reaction to the injection brine, leading to reduction in reservoir quality such as permeability and porosity. Based on clay structure and injection fluid, they will swell up at different degree.

In terms of property for different groups, the desirable type are illite and kaolinite due to their CEC value and non-swelling properties.(10)

2.2 Reservoir properties

Sandstone stands for around 60% of all petroleum reservoir. Porosity and permeability is one of the most important parameters, but pore geometry and wetting properties of the mineral surface will also affect the petroleum recovery. Sandstone reservoir properties are function of the primary composition, which is controlled by the texture and mineralogical composition of the depositional environment and of the diagenetic process near the surface and during burial. (11)

2.2.1 Porosity

Porosity is measured of storage capacity of a rock. It is defined as ratio between pore-volume to the total volume:

$$\phi = \frac{V_p}{V_b} \tag{1}$$

ϕ Porosity

V_p Pore volume

V_b Bulk volume

Generally it is distinguished between absolute porosity and effective porosity. Absolute porosity does not consider the conductivity between the pores, while the effective porosity accounts the ratio between the interconnected pore volume and bulk volume. Per definition the effective porosity will always be smaller than the absolute porosity.(12).

Permeability and porosity of a sandstone is related to the primary process under which sandstone was accumulated and the diagenetic process (13). Typical range for porosity is between 7-20 %.(14)

2.2.2 Permeability

In a porous media, permeability is a measure of the capacity and ability of the formation to transmit fluid. This is one of the most important properties to a reservoir as it control the directional movement and flow rate of the reservoir fluids in the formation. Absolute permeability represent the constant property of the porous medium assuming single fluid flows through the porous medium. In cases where there are more than one fluid present, permeability of different phases are known as relative permeability. Relative permeability is affected by the different phase properties such as their saturation, viscosity and capillary pressure between the phases and also rock properties, absolute permeability and reservoir condition. (14)

The porosity and permeability depends on each other and with depth. Nadeu made research with numerous sandstone reservoir to show the relationship with depth and porosity and porosity and permeability. Link between porosity and permeability are shown in figures below.

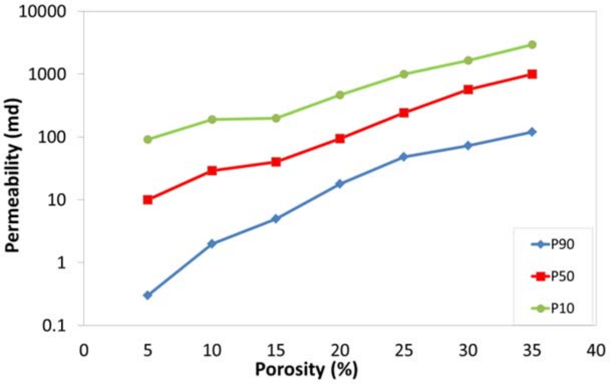


Figure 4: Relationship between permeability and porosity based on sanstone reservoir study around the world(15)

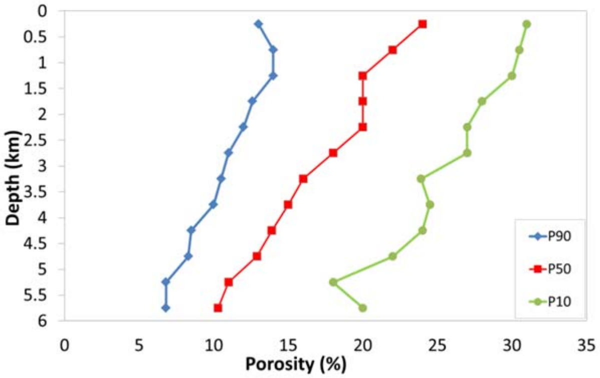


Figure 5: Relationship between porosity and depth based on sandstone reservoir study around the world.(15)

2.2.3 Temperature

Reservoir temperature depends on factor such as depth and the regional temperature gradient. A typical reservoir temperature will thus lie within a temperature range of 14-36°C /km.

There have been extensive analysis temperature distribution in the Gulf Mexico by Enhrenberg (16), where develop a relation between reservoir temperature and depth below sea floor (Fig6**).**

High reservoir temperature, which is located deep with a particularly steep temperature gradient may hinder some type of recovery processes due to sub-optimal condition. Also the wettability of a reservoir is to some degree temperature dependent.

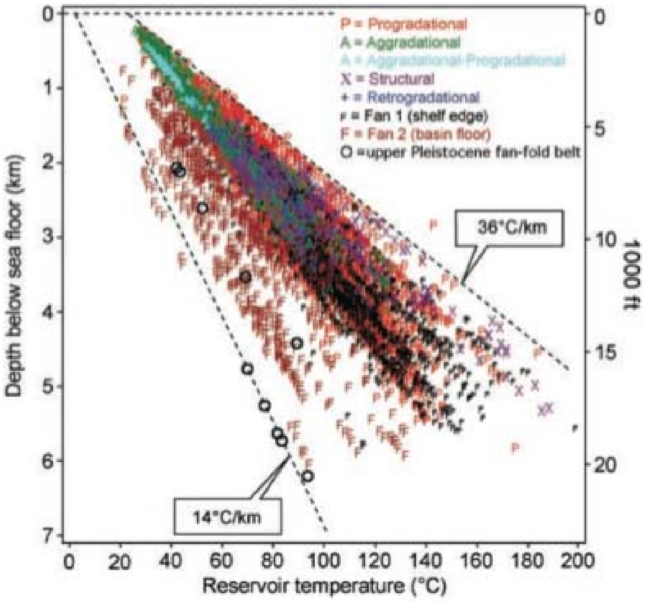


Figure 6: Reservoir temperature vs depth below sea floor.(16)

Rao presented a study regarding wettability effects in thermal recovery operations, where he summarize that the wettability temperature dependent is governed by several factors including the effect of decreasing wetting water film thickness as temperature increases, the influence of brine composition and pH on wetting film stability and the effect of temperature on electro-kinetic properties of hydrocarbons-water and solid-water interface. (17)

2.3 Displacement forces

There are three main types of forces in a reservoir that is behind the driving mechanism of the movement of fluid through the pore network:

- Gravitational Forces
- Viscous Forces
- Capillary forced.

In this section we will briefly overview these different forces.

2.3.1 Gravity-Drainage-Drive Mechanism

The gravity drainage drive mechanism is a result of the density difference in a two or multi-phase reservoir. Segregation of the phases are a result of the gravitational forces acting on them. This is reflected in the reservoir as evidence by the relative position of the fluids, i.e., gas on top, oil underlying the gas and water underlying oil. (12)

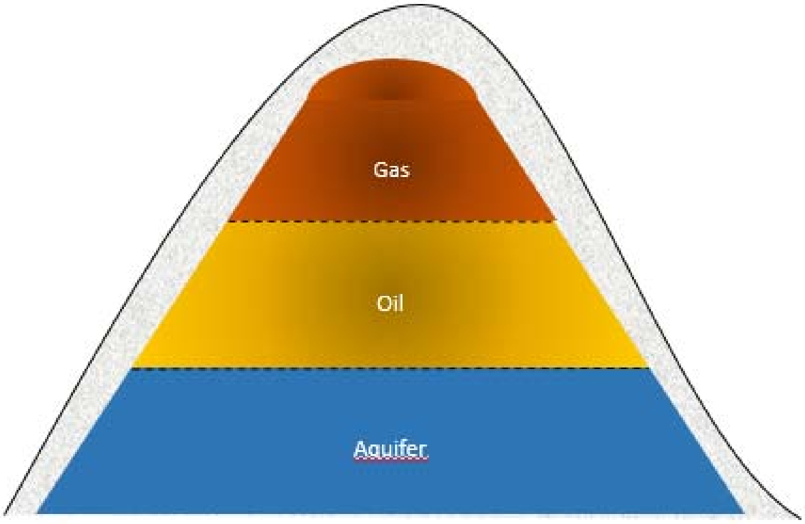


Figure 7: Position of the phases as a result of their density

This is important when there is a large density difference between the phases, as the gravitational forces will dominate of the flow. The buoyancy force is given by following equation:

$$\Delta P_g = \Delta \rho \, g \, h \tag{2}$$

ΔP_g	Pressure difference due to gravity
$\Delta \rho$	Density difference between the phases
g	Acceleration of gravity
h	Height of the hydrostatic column

2.3.2 Viscous Forces

Term viscosity is a measure of the internal fluid friction to flow. In a porous media, the term viscous force are reflected by the lateral differential pressure that force the fluid to move through pore network of reservoir. In order for the oil to be able to flow, the viscous force must be larger than the capillary force. Considering the porous media as a bundle of parallel capillary tubes, the pressure drop across each capillary can be calculated from the Poiseulle`s law(18):

$$\Delta P = \frac{8\,\mu\,L\,\bar{u}}{r^2} \quad (3)$$

ΔP	Pressure difference across capillary tube
μ	Viscosity of the flowing fluid
L	Length of the capillary tube
$\bar{u}$	Average flowing velocity
r	Capillary tube radius.

2.3.3 Capillary Forces

Capillary force is a result of the combined effect of the surface and interfacial tension of the rock and fluids, pore size and geometry, and the wetting characteristics of the system. A curved surface between two immiscible fluids will have a tendency to contract into the smallest possible area per unit volume between two immiscible fluids, or between the non-wetting phase and wetting phase. Capillary pressure can be expressed as:

$$P_c = P_{nw} - P_w \quad (4)$$

P_c	Capillary pressure
P_{nw}	Pressure in the non-wetting phase
P_w	Pressure in the wetting phase

Since the non-wetting phase is usually oil and wetting phase water, this expression can be rewritten as:

$$P_c = P_o - P_w = \frac{2\,\sigma_{ow}\cos\theta}{r} \qquad (5)$$

Where:

P_o	Oil-phase pressure at point just above the oil-water interface
P_w	Water-phase pressure just below the interface
σ_{ow}	Interfacial tension between oil and water
θ	Contact angle measured through the wetting phase (in this case water)
r	Radius of cylindrical pore channel

(12)

From the formula it is observed that the capillary pressure is directly related to the interfacial tension (IFT), relative wettability which is reflected in θ and also pore size r. Capillary pressure might be both positive and negative, where the sign indicate which of the phase pressure is lower, where the wetting phase will always be the lower. By study formula, notice that capillary pressure can be modified by changing oil-water IFT and/or the contact angle (which is a result of the wettability in the reservoir).

Capillary pressure is especially important for the displacement process during imbibition or drainage for a fractured reservoir. Strong capillary pressure will result in an increase of spontaneous imbibition from the fractured channels into the matrix block. This way the microscopic sweep efficiency will increase from low permeability zones. Originally, sandstones aren't usually fractured, which means in these cases low capillary pressure are desirable for favor of causing less oil entrapment.

Capillary-pressure/saturation relationship depends on the interaction of wettability, pore structure, initial saturation and saturation history. Per today, there are no simple relationship exist that relates the capillary pressure to wettability. Therefore to assure most accurate measurement, cores that have native reservoir wettability should be considered. (19)

2.3.4 Displacement Efficiency

The overall displacing efficiency for an EOR process is determined by equation:

$$E = E_D E_V \tag{6}$$

Which indicated that the overall efficiency depends both on the macroscopic and microscopic displacement. Term of microscopic displacement relates to mobilization at pore-scale level where oil has been displaced from the sweep zone at any given time or pore volume injected, and is defined as: (18)

$$E_D = \frac{S_{oi}-S_{or}}{S_{oi}} \tag{7}$$

Based on the formula (7), the microscopic sweep efficiency can be increased by decreasing the oil saturation. To optimize the microscopic sweep efficiency, it is important to understand the displacement forces at pore-scale. Reservoir wettability is an important parameter that affects result of flooding.

The macroscopic efficiency, which depends on the effectiveness of the displacing fluid in contacting the reservoir, both areal and vertically. Term macroscopic efficiency is given as the product of the areal and vertical displacement efficiency.

Equation for the volumetric displacement efficiency(12):

$$E_V = E_A * E_I \tag{8}$$

E	Overall displacement efficiency
E_D	Microscopic displacement efficiency
E_V	Macroscopic displacement efficiency (Volumetric)
E_A	Areal displacement efficiency
E_I	Vertical displacement efficiency
S_{oi}	Initial oil saturation
S_{or}	Residual oil saturation

The areal efficiency is the fraction of area that have been sweep by the injection fluid and is affected by factors such as; fluid mobilities, pattern type, areal heterogeneity and the total volume of fluid injected. Vertical efficiency is the fraction of the vertical section that have been swept, determined by factors such as; vertical heterogeneity, degree of gravitation segregation, fluid mobility and total volume injected(12, 18). Mobility ratio has main impact on macroscopic sweep efficiency, and is defined as the ration of the mobility between displacing fluid and displaced fluid. For waterflooding, mobility ratio is defined as:

$$M = \frac{\lambda_D}{\lambda_d} = \frac{k_{rw}\mu_o}{k_{ro}\mu_w} \tag{9}$$

λ_D	Mobility of displacing fluid
λ_d	Mobility of displaced fluid
k_{rw}	Relative permeability of the water
k_{ro}	Relative permeability of the oil
μ_o	Oil viscosity
μ_w	Water viscosity

If mobility ratio is bigger than 1, it develops unstable displacement process which lead to viscous fingering, that can cause earlier water breakthrough for waterflooding. Mobility ratio less than 1 is desirable, resulting in high macroscopic sweep efficiency.

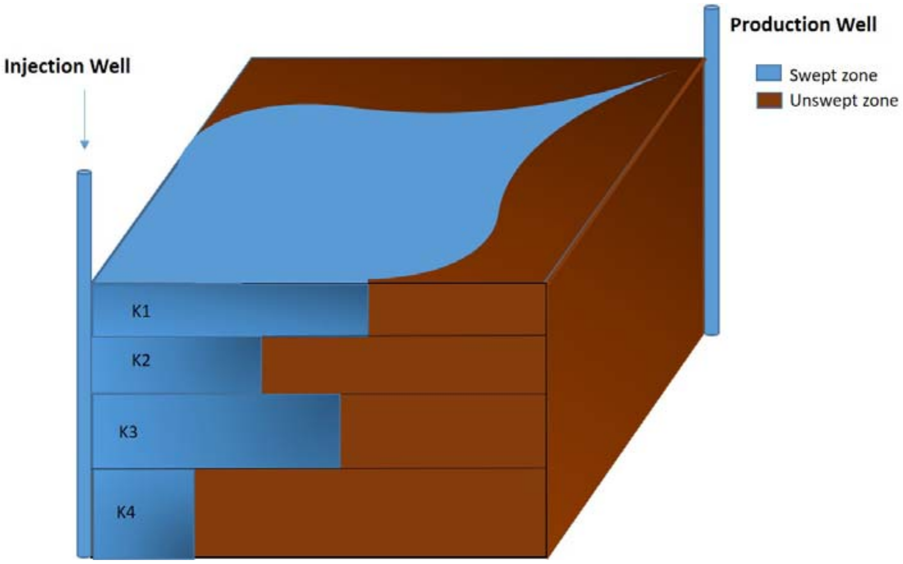


Figure 8 Illustration volumetric/macroscopic sweep efficiency. Note how the vertical sweep efficiency varies as result of different permeability's in different layers.

2.4 Hydrocarbon Recovery Mechanisms

Hydrocarbon recovery production is usually divided in three stages; primary, secondary and tertiary. Primary production period is hydrocarbon production from the displacement energy naturally present in the reservoir. Secondary recovery, usually second stage in production where pressure maintenance by waterflooding or injection of gas. Tertiary oil recovery, also referred as enhanced oil recovery, is recovery of residual oil that has not been produced through the two first stages which may involve use of miscible gases, chemicals, and/or thermal energy. These stages historically describes the production in chronological sense, but in practice is not conducted in specific order. The reservoir and hydrocarbon properties need to be taken in consideration. (18)

2.4.1 Primary recovery

Primary recovery is usually the first stage of reservoir hydrocarbon production. It is also the period where engineers will get a feeling of their reservoir and its properties.

Primary recovery is based on the natural drive from the original reservoir energy, such as (18):

- gasdrive (including gas-cap drive and dissolved gas drive),
- waterdrive
- gravity drainage
- fluids and rock expansion

At the start phase of recovery there is large pressure difference between the bottom hole pressure and the reservoir initial pressure. The pressure depletion force the hydrocarbons out of the reservoir and into wellbore. As the pressure difference is decreased due to hydrocarbon production, the production rate will reduced till it reaches a certain limit where there is no longer cost efficient to produce the hydrocarbon. Before the reservoir reaches this point, one will try to implement secondary stage to uphold the reservoir pressure and production rate(18).

2.4.2 Secondary recovery

As mentioned, due to depletion in reservoir pressure, it is important to stimulate the reservoir to be able to maintain hydrocarbon production at a sustainable rate.
In the secondary recovery period external fluid or gas is injected to maintain the reservoir pressure and production rate. Main goal at this stage is:

- Maintain reservoir pressure
- Displace hydrocarbons towards production well

Gas injection is usually targeted toward the gas cap for upholding reservoir pressure or into oil-column to displace oil immiscibly according to relative permeability and volumetric sweep efficiency consideration. The injection of water or gas is at another well than the production well, called injection well. Per today, secondary recovery is directly associated with waterflooding(18). At this point, primary and secondary recovery, usually results in recovery factor at 15-40% of original oil in place(20).

Waterflooding is one of the most common secondary recovery method. As mentioned this is usually followed after primary recovery, but can also be conducted with the primary recovery. There are several factors affecting how effective a waterflooding process is in a reservoir:

- Reservoir geometry
- Fluid properties
- Reservoir depth
- Lithology and rock properties
- Fluid saturation
- Reservoir uniformity and pay continuity
- Primary reservoir driving mechanism. (14)

In practice, it should be clearly proven that the natural recovery processes are not sufficient before a secondary recovery is undertaken; otherwise there is a risk that the substantial capital investment required for a secondary recovery may not be cost-efficient.

2.4.3 Tertiary recovery/EOR

Tertiary recovery, also known as EOR processes often involves injection of liquid chemicals, gases or thermal energy depending on reservoir and reservoir fluid condition. The injection slugs supplement the natural energy and also interact with the reservoir oil/rock system to create conditions favorable for oil reservoir. The interaction might be such as;

- Lower IFTs
- Oil swelling
- Reduction in oil viscosity
- Wettability modification
- Favorable phase behavior
- Diluted flow/fines migration

The chemical slugs can be expensive and in the field are often injected in slugs followed by another cheaper fluid to make sure the slug will have a good volumetric sweep efficiency. (18)

2.4.3.1 EOR-classification

EOR process can be classified into five categories: Chemical, miscible, thermal, mobility control and other processes, such as microbial EOR. Chemical process are carried out with use of certain chemicals, such as surfactants or alkaline agents or a mixture of these to use a combination of phase behavior and IFT reduction to displace the oil and improveE_D. In cases where the objective is to inject fluids that are directly miscible with oil or that generate miscibility in the reservoir through composition alteration, miscible process is carried out. Thermal process rely in applying thermal energy or in-situ generation of heat to improve oil recovery. Mobility-control are implied when primary goal is to improve E_v factor by maintaining favorable mobility ratio.

It can be tricky to know what kind of EOR process that will give best recovery result, so based on the reservoir characteristics and oil properties it is made a screening table to help to give an idea to engineers on what process would be mostly effective on certain case. These criteria are only approximate and each reservoir situation should be considered individually. (18)

Table 2: Summery of screening criteria for EOR methods(18)

SUMMERY OF SCREENING CRITERIA FOR EOR METHODS									
Oil Properties				Reservoir Characteristics					
EOR method	Gravity ˚API	Viscosity (cp)	Composition	Oil Saturation (%PV)	Formation Type	Net Thickness (ft)	Average Permeability (md)	Depth (ft)	Temperature (˚F)
Gas Injection Methods (Miscible)									
Nitrogen (& Flue Gas)	> 35↗ 48↗[1]	< 0.4↘ 0.2↘	High % of C_1-C_7	> 40↗ 75↗	Sandstone or Carbonate	Thin unless dipping	N.C.[2]	>6,000	N.C.
Hydrocarbon	> 23↗ 41↗	< 3↘ 0.5↘	High % of C_2-C_7	> 30↗ 80↗	Sandstone or Carbonate	Thin unless dipping	N.C.	>4,000	N.C.
Carbon Dioxide	> 22↗ 36↗	< 10↘ 1.5↘	High % ofC_5-C_{12}	> 20↗ 50↗	Sandstone or Carbonate	Thin unless dipping	N.C.	>2,500	N.C.
Chemical									
Micellar/-Polymer, Alkaline/-Polymer (ASP), and Alkaline Flooding	> 20↗ 35↗	< 35↘ 13↘	Light, intermediate. Some organic acids for alkaline floods	> 35↗ 53↗	Sandstone preferred	N.C.	> 10↗ 450↗	< 9,000↘ 3,250	< 200 ↘ 80
Polymer Flooding	>15-< 40	<150, > 10	N.C	> 70↗ 80↗	Sandstone preferred	N.C.	> 10^3↗ 800↗	< 9,000	< 200 ↘ 140
Thermal									
Combustion	> 10↗ 16 →?	< 5,000→ 1,200	Some asphaltic components	> 50↗ 72↗	High porosity sand/ sandstone	> 10	>50[4]	< 11,500↘ 3,500	>100↗135
Steam	> 8-13.5 →?		N.C.	> 40↗ 66↗	High porosity sand/ sandstone	> 20	> 200[5]	< 4,500 ↘ 1,500	N.C.

1. Underlined values represent the epproximate mean or average for current field field projects. ↗ indicates higher value of parameter is better

2. N.C. = not critical

3. <5 md from some carbonate reservoirs.

4. Transmissibility >20 md ft/cp

5. Transmissibility >50 md ft/cp

2.4.3.2 Low Salinity Water

One of EOR which is of high importance is low salinity water, also known as smart water. Initially injection brine composition and ions were believed to have no effect on the recovery efficiency in the waterflooding process, so usually seawater or produced formation water was reinjected as displacement fluid for waterflooding. It wasn't till low salinity water was first introduced by George G. Bernard in 1967 (21).

It has been proved that by decreasing the ionic-strength of injection water, have improved oil recovery significantly. The term low salinity water is brine with lower salt content or ionic strength. The range is typically between 500-3000 part per million of total dissolved solids and no more than 5000 ppm. To put this in perspective, seawater or formation water contains around 30,000 ppm or more.

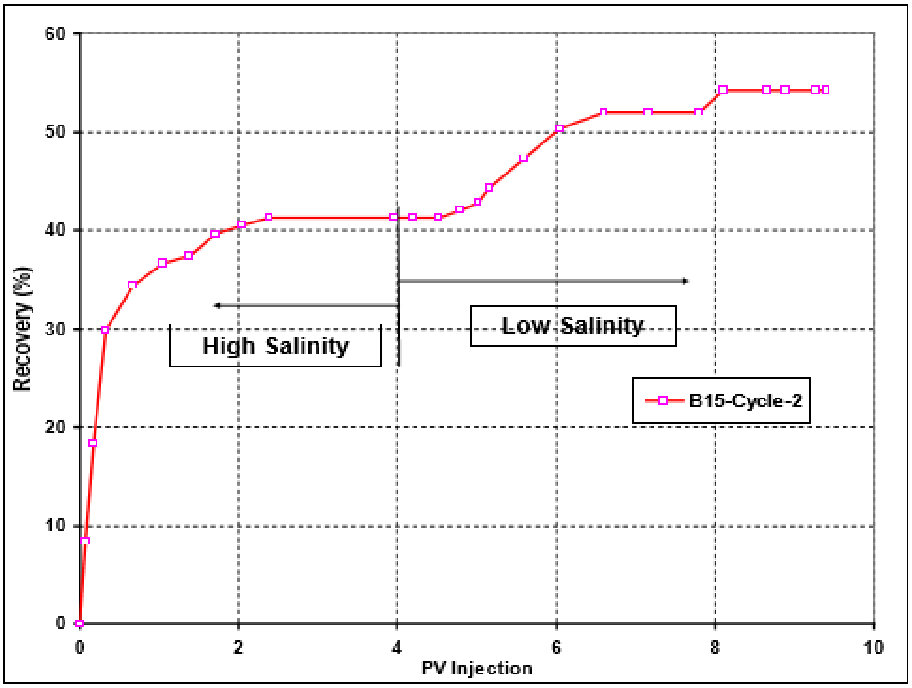


Figure 9: Oil recovery vs pore volume injected with high salinity till 4 PV, and low salinity water injected after 4 PV. In the graph, it is clearly seen a jump in oil recovery as the high salinity water is replaced with low salinity water. (22)

In oil-wet rock, multivalent cations at clay surface will be bonded to polar compounds that are present in the oil phase. This bond will promote oil-wetness in reservoir. Injection of low salinity brines will lead to ion exchange that removes the organic polar compounds and complexes from rock surface and replace with uncomplexed cations. This interaction leads to shift the surface wettability towards more water-wet. (23)

There has been high interest in study of smart water, but yet the mechanism has not yet been emerged. This is due to the high heterogeneity and complexity of the minerals, crude oil and aqueous-phase composition. Some of the factors that are of interest due to its effect on low salinity flooding (LSF) are:

- Polar ionic hydrocarbon molecules that compose the oil
- Mineral composition of the rock
- Dissolved ions and salinity of the formation water
- Water solubility of polar oil components
- Pressure, temperature and initial water saturation of the reservoir
- Capillary pressure(24)

All these factors contributes to confusion about the cause of LSF. The variety of circumstances where LSE might or might not have effect on oil recovery, suggest that more than one mechanism may be in the play. (25)

Some of the theories to describe the mechanism behind LSW are:

- **Fines migration**: During low salinity flooding, study has shown that fine particles of which mainly kaolinite clay were released from the rock surface. This fine mobilization could expose the underlying rock surface which causes the system toward more water-wet condition. This release of clay particles could also divert flow of water toward the unswept area, thus improving the sweep efficiency. (26)

- **Impact of Alkaline Flooding**: This type of flooding will lead to increase in pH. Increase in pH level will allow the reaction to some of the oil compounds of in-situ surfactants. This will lead to increase of oil recovery from the production of surfactant and interfacial tension reduction. (27)

- **Multicomponent Ion Exchange (MIE):** This theory is based on the exchange of ion between clay surface and the low salinity brine. The low salinity injection causes ionic equilibrium disturbance which lead to exchange of ions between rock minerals and fluid. (28)

- **Salting-in Effect:** One of the purposed mechanism was presented in 2009, known as salting-in and salting-out effects. These are term defining change in the solubility of polar organic components in the aqueous phase. Salting-out effect define the decrease in the solubility of organic material in water by adding salt to the solution, vice versa. (29)

- **Expansion of Double-Layer**: Cations will act as bridge between the negative oil components and clay surface. Reduction in multivalent content of a brine will lower the solution Ionic Strength and may contribute to double layer expansion and wettability modification for benefit to increase the oil recovery. (30)

- **pH induced wettability alteration**: Another chemical mechanism that has been proposed is how the low ion concentration of LSE flooding disrupt the equilibrium for COBR and a net desorption of cations, especially Ca^{2+} from the clay leads to pH increase of the water. Lack of calcium amount in the injection brine will lead to ion exchange process between adsorbed cations in the clay surface and protons (H^{+}) in the injected water. Result of this process is an increase of the pH of the water in reservoir. Chemical reaction for this mechanism is following: (31)

  $\mathrm{Clay} - \mathrm{Ca}^{2+} + \mathrm{H_2O} \leftrightharpoons \mathrm{Clay} - \mathrm{H}^{+} + \mathrm{Ca}^{2+} + \mathrm{OH}^{-} + \mathrm{Heat}$

  $\mathrm{Clay} - \mathrm{NHR}_3^{+} + \mathrm{OH}^{-} \leftrightharpoons \mathrm{Clay} + \mathrm{R_3N} + \mathrm{H_2O}$

  $\mathrm{Clay} - \mathrm{RCOOH} + \mathrm{OH}^{-} \leftrightharpoons \mathrm{Clay} + \mathrm{RCOO}^{-} + \mathrm{H_2O}$

3 WETTABILIITY- GENERAL ASPECTS

As described in the book “Enhanced Oil Recovery”(18); the term wettability is defined as the tendency of one fluid to spread on or adhere to a solid surface in the presence of a second immiscible fluid. It describes the balance of surface and interfacial forces(32). The phase that is mostly attracted is called the wetting phase. If the reservoir system is water-wet, the oil will be displaced by water and vice versa. (18) It is important to point out, that what preference a core/rock have don’t depend on what fluid are present.(33)

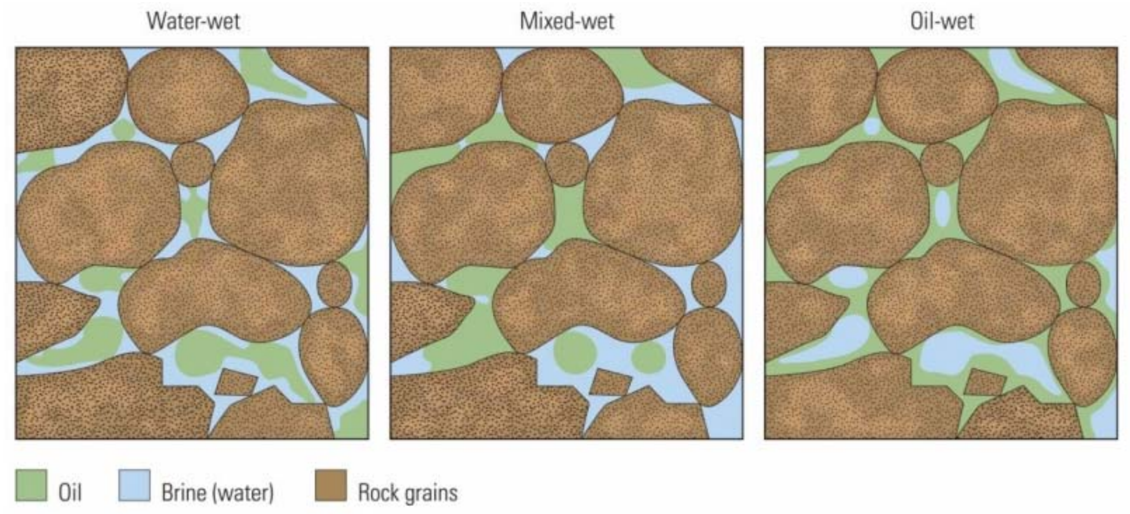


Figure 10: Fluid distribution in different wetting condition. (34)

Reservoir wettability is a key parameter when producing oil as capillary pressure, relative permeability's, fluid distribution and flow direction are dictated by wettability. Wettability have effect on several of reservoir properties such as distribution and mobility of crude oil and brine which again affects the production rates and also oil recovery and oil residual saturation.(35)

Favorable wetting condition for oil recovery will depend on several aspects, such as production rate and time. However, based on study, the most favorable wetting state for a reservoir is mixed-wet. Mixed state behavior, will lead to continuous pathway for both the oil-wet and water-wet surfactants resulting in overall lower residual oil saturation. Strongly water-wet reservoir will lead to trapping of oil and strongly-oil system will lead early breakthrough time, both resulting in much lower residual oil saturation (35). The residual oil will remain as discontinuous droplets, or irregular bodies of oil separated by the capillary forces (36).

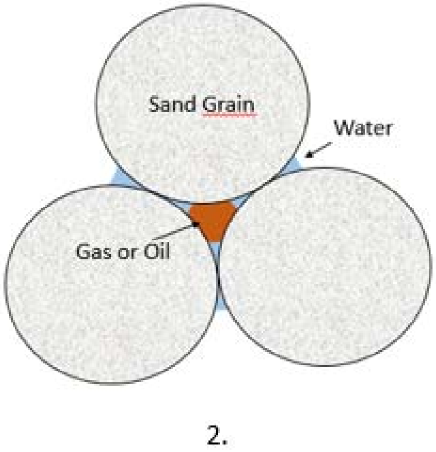
Continuous network of both water-wet and oil-wet pathway can be explained, assuming that wetting is altered by adsorbing molecules that are not able to affect the surface except in the areas of direct contact. Direct contact depends on whether water films are stable, which again depends on the factors such as van der Waals, and other forces such as capillary pressure (37, 38).

Mineralogy may also effect the distribution of wetting, as some may be more active with crude oil than others. The distribution of these reactive minerals lead to a fractional wetting envisioned where there need not be connectivity of oil-wet surfaces. Combination of these and other mechanisms of wetting alterations may lead to complex wettability pattern condition, which has yet only been partly differentiated and described (39).

3.1 Bibliographic overview

In 1940, Leverett presented a study on capillary behavior in porous solid. Under establishment of capillary equilibrium in sand, he discussed the fluid distribution in pore space. He states how Smith, Keen, Versluys and other have pointed out three general types of occurrence of water, or regions of water saturation in porous solids:

1. Saturation region. Complete water saturation
2. Pendular region. Lowest water-saturation range. Water occurs as pendular rings around grain-to-grain contacts. The solid, where not covered by water in the pendular rings, is covered with a very thin film of water if the contact angle is zero or by oil if not.
3. Funicular region. Intermediate water saturation. Addition of water to the pendular rings causes them to grow and soon they become so large that they touch each other and merge.



2. 3.

Figure 11: Nr 2; Pendular saturation ring. Nr 3; Funicular saturation region, water existing as coalesced rings

This study was mainly based on sandstone, and the second type of occurrence of water statement, indicates toward wettability properties of reservoir. Leverett explains that in general it is believed that the contact angle in natural petroleum reservoir is substantially zero, with few exceptions. This view is based on considerable amount of evidence which, if not rigorously conclusive, is strongly presumptive. (40)

Several study by different authors, before 1970, reservoir engineers indicate assumption that all reservoir are water-wet. Such as in 1959 Denekas presented a study on the effects of crude oil components on rock wettability. In this study, he states: “*While most reservoirs are presumably water-wet, they may range in their degree of water-wettability from near-neutral to strongly water-wet.”* He indicates that reservoir that were not strongly water-wet and neutral-wet, where likely induced by adsorption of surface active components from the crude oil on the pore walls of reservoir rock (41).

Morrow (1990) describes how the assumption of all reservoir being water-wet was a result of the discussion and illustrations as if a drained rock surface were still overlaying by a thick film of water. (42)

But as through a reservoir life it became more and more difficult to describe the reservoir behavior, several laboratory investigations were made. The new researched led to discovery where it was proven that some of reservoirs were not water-wet. In 1972, Treiber (43) performed a laboratory evaluation of the wettability of fifty oil-producing reservoir. In the study, he showed that not all sandstone reservoir are water-wet and actually more of the samples were found to be rather strongly oil-wet. During this time, it was also shown that the wettability of a porous medium govern the distribution of fluids in porous media and therefore has considerable influence on the conditions in which oil is recovered. (44).

Jadhunandan and Morrow made a research on the degree of wettability upon oil recovery by using spontaneous imbibition on Berea sandstone. Based on the research, it was found that the most optimal condition for oil recovery was mixed wettability. The maximum in oil recovery at this state, was argued with fact that capillary forced are minimized in this condition. But however, it is the effect of wettability on fluid configurations and interface instabilities that determines oil-displacement rather than the absolute magnitude of capillary force. (45)

Traditional scenario for generation of mixed wettability occurs as the oil is migrating and accumulating into a reservoir, where water is present initially. Water from initially water-wet rock is displaced from the large pores, while capillary forces retain water in small capillaries and at grain contact. This way the large pores are filled with continuous oil, while water is mostly trapped in small pores. This new fluid distribution may also lead to partly oil-wet rock as some of the organic materials from the oil are deposited onto these rock surface that are in direct contact with oil, thus making those surfaces strongly oil-wet by adsorption and deposition. The heterogeneous wettability is affected by factors such as the crude oil kind, concentrations and states of aggregation of surface-active materials present (36).

Another scenario is where the reservoir is also the source rock such that mineral surface is directly in contact with crude oil without presence of water, but most commonly it is assumed a water-film covering rock surface. Wettability may alter due to mechanism such as adsorption and deposition of crude oil components onto the solid surface. There have been several approach to get better understanding of crude oil, brine and rock system, but as this is complex system several experiments have resulted in contradictory and confusing results and lack of consistency. Also the heterogeneity of mineral surface and complexity if crude oil composition makes it even more difficult to develop good models(35).

Mixed-wet systems are distinguished by the existence of a large region of two-phase flow with oil flow continuing down to low oil saturation and spontaneous imbibition of both oil and water. (36)

To establish a direct link between wettability and oil recovery has been plagued by two kinds of logical errors. The mistake of interpolating between results from the extremes of strongly water- and oil-wetted systems to predict flow parameters for mixed-wet condition. From fig. 12, it is clear that oil recovery at weakly water-wet condition is not half-way between strongly water-wet and strongly oil-wet. Also the second problem, when we try to deduce wetting conditions from changes in relative permebilities or residual saturation that can as well be explained by other, perhaps unintended, changes in the system. (39)

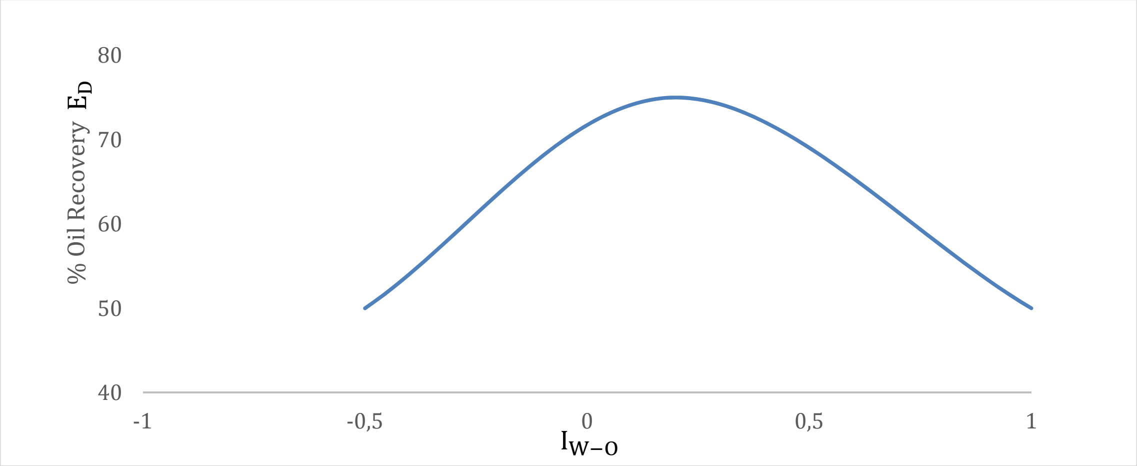


Figure 12: Resketch from source. From fig we can observe that we have optimal recovery at mixed wettability. Oil recovery efficiency first increases, then decreases as Berea sandstone core becomes less water-wet. Data shown are for recoveries after 3 PV. (45)

L. Treiber described in 1972 how research have demonstrated that many crude oil contains natural surface-active agents that are readily adsorbed at solid-liquid interfaces to render the solid surface oil-wet. It was also done several studies to demonstrate the significant effect of rock wetting preference on waterflooding of hydrocarbon. But, in introduction of his study, it is also pointed out that even based on several studies there is still implication in the industry to reject Leveretts and others theory that all reservoir are initially water wet. In his evaluation of wettability fifty oil producing reservoir sandstones he discovered that far more of the sandstones were oil-wet than water-wet.

(43)

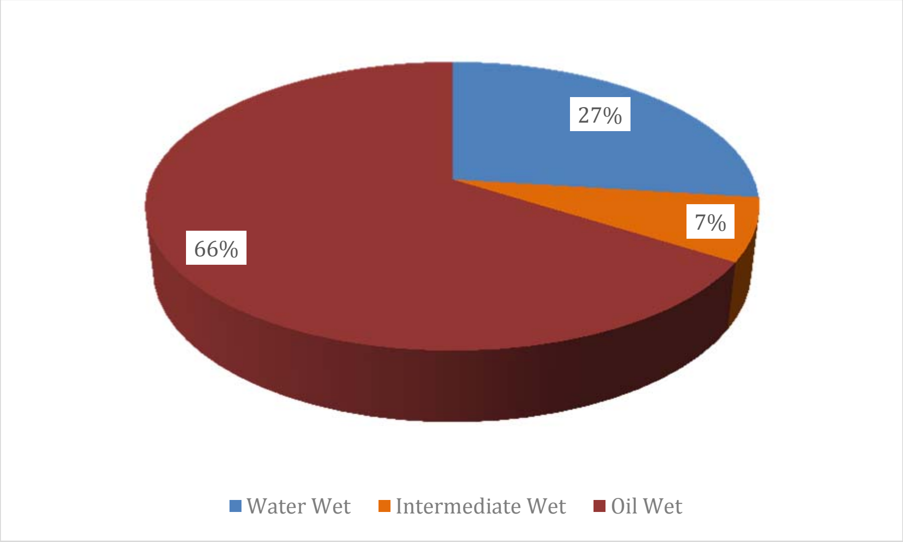


Figure 13: Initial wetting distribution of 55 reservoir. Based on Treiber measurements.

Cuiec wrote in 1984:"It is generally assumed that that the mean wettability of a rock sample of a reservoir is linked to the respective proportions of hydrophilic and hydrophobic surface areas. Theoretically, the hydrophobia of a reservoir rock surface may be due to the nature of the solid, to the presence of adsorb ale compounds in the crude oil, or to the combined effect of both factors." He suggested that the hydrophobic sites exist on the surface of pores before the crude oil has migrated to the rock. (44)

3.2 Wettability Measurements

Several various methods have been developed to measure the wettability of surface. Principal of these techniques include contact angle measurement, two phase separation, bubble pickup, micro-flotation, and vacuum flotation which are based on the fact that water wetting process is essentially an oil displacement phenomenon on the solid surface. (4) For predicting the behavior of the reservoir, it is crucial that the wettability of the core must be the same as the wettability of the undisturbed reservoir rock.

One commonly known method is by measuring the contact angle between the rock surface and non-wetting phase. With this method, it is made assumption and simplification of reservoir consisting of smooth surface, which is not necessarily realistic, as there are high variation both in surface roughness and mineralogy in a reservoir. Different minerals will result in different contact angle. The relation between the three phase system was originally presented by Thomas Young (1855) and is known as Young's equation:

$$\cos\theta = \frac{\gamma_{\mathrm{sw}}+\gamma_{\mathrm{os}}}{\gamma_{\mathrm{ow}}} \tag{10}$$

γ_{SO}	Interfacial tension between solid and oil
γ_{SW}	Interfacial tension between solid and water
γ_{OW}	Interfacial tension between oil and water
θ	Contact angle

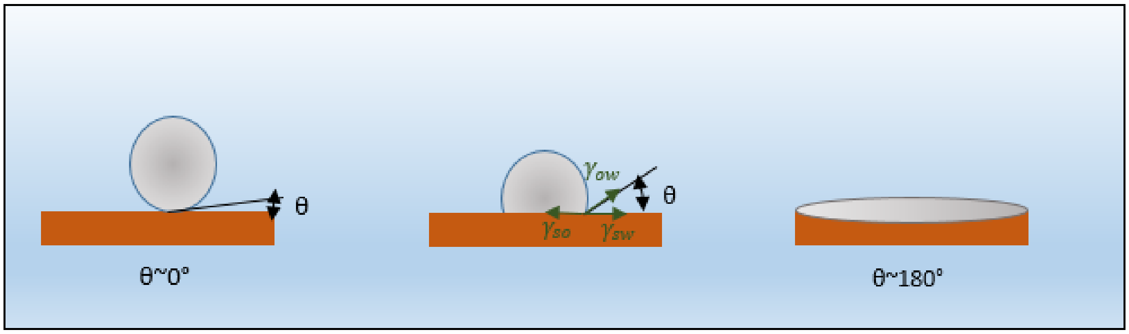


Figure 14: Illustration of oil drop with surrounded water on a water-wet surface. The left case situation with contactangle towards 0, indicating strongly waterwet system. At the center it is Intermediate-wet surface with formula for the force balance in the system as a result of interfacial tension terms. At the right we have contact angle towards 180 degree, where oil drop spreads over the surface, indicating totally oil-wet system. Redrawn from source. (32)

Other known methods are the USBM- and the Amott methods. These two methods are based on measure the displacement if oil or water in presence of both wetting and non-wetting phases on core samples(35). Amott and USB methods measure the average wettability of a core, while the contact angle measures the wettability of a specific surface. (46) This is a more realistic approach to understand wettability properties of a reservoir.

Table 3: Approximate relation between wettability indexes of the contact angle, USBM and Amott methods(35)

Method	Wettability index		
	Water-wet	Neutral-wet	Oil-wet
Contact angle			
Minimum	0 °	60-75 °	105-120 °
Maximum	60-75 °	105-120 °	180°
USBM (index W)	W~1	W~0	W~-1
Amott (index I)	0.3≤ I ≤ 1	-0.3≤ I ≤ 0.3	-1≤ I ≤ -0.3
Water displacement	Positive	None	None
Oil Displacement	none	none	Positive

In petroleum industry, the general methods that are used is a modified form of the sessile drop which was originally described by Leach and Treiber. The sessile drop method involve use of two flat, polished mineral crystals that are mounted parallel to each other on adjustable post. Since sandstone primarily consist of quartz, quartz crystals are used to pore surface of the reservoir rock. Note; the wettability of clay cannot be measured with this method. (46)

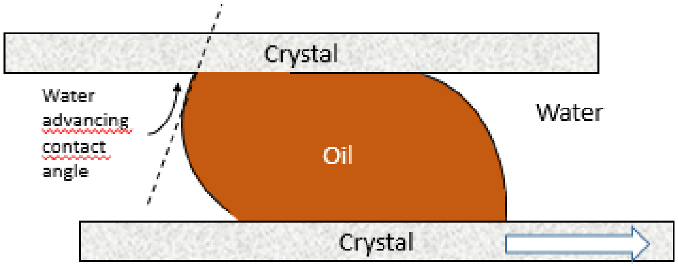


Figure 15: Contact-angle measurement. Redrawn from source.(46)

The minimum contact angle to avoid oil wettability will depend on the mineral and even its history. For hematite or even silica that is aged in water and hence hydrated, the wettability threshold will be higher than 10°, while for pyrite or galena it might be 1° or less. Also the porous nature of the minerals due to possible presence of air micro- and nano-bubbles in the crevices might affect the determent angle.

Degree of wettability is govern by the surface free energy of the substrate and the wetting solution. Reducing the total free energy of the system, the surface that has a higher surface energy tends to be replaced by a liquid that has a lower surface free energy. (4)

3.3 Mechanism of Wetting Alteration

The wetting alteration of a reservoir rock from water-wet to more oil-wet is caused by interaction between the rock surface and organic components in the crude oil. This was first presented by Ciec in 1986 where he reported that oil components might diffuse from the oil and into the water phase, cross water-film and eventually absorbed onto rock surface and causing wetting alteration (44). The same year, Anderson stated the same wetting alteration mechanism in his literature study (33). He also mentions that the degree of alteration is determined by the interaction of the oil constituents, mineral surface and brine chemistry.

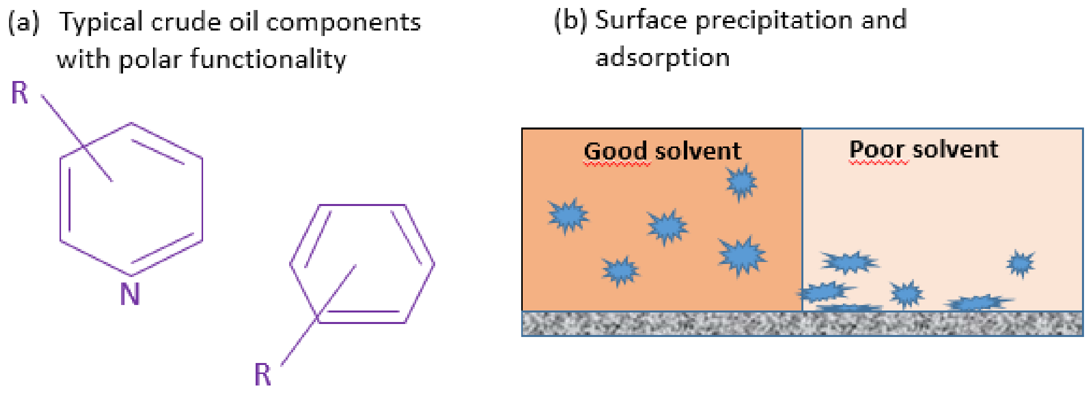
Book "*Clay Mineral Cements in Sandstone"* by Worden and Morad (7) mention that the pH of formation water can indirectly determine the wettability of a reservoir as the surface charge of a mineral is sensitive to pH. Some minerals such as calcite surface is positive at very low pH and negative at high pH. Typical range of pH in reservoir condition is between 4-7. Having positive surface charge will attract molecules in petroleum, and thus the surface will be oil-wet. Usually quartz have negative surface charge till it reaches limit 3 or below. Consequently, this mineral contributes to water-wet condition in typical reservoir condition.

Transition metals that can be found in various type in both formation water and minerals can alter the wettability state of a reservoir. Metals can be in different forms, such as aqueous complexes, organometallic complexes or metallo-porphyrins. Positive transition metals get absorbed to negatively charge mineral surface. Oil-wettability in sandstone reservoir tends to increase as iron oxide quantity increases in bulk volume, and as the proportion of Fe-rich clay increases. Clay with high content of iron tends to typically act as oil-wet. Even a thin fraction coating of Fe in clay can affect its wettability preference toward more oil-wet. The wetting may alter due to this mechanism (7).

However, there have been purposed other opinions regarding the mechanism that may lead to change in wetting behavior. Since the crude oil-brine-rock system is complex it is likely that various mechanisms dominate at different cases. Interplay between each of the three phases and all the influencing factors makes the task of revealing common denominators difficult.(35)

In 1998 Buckley identified a set of interaction mechanism by crude oil/brine/rock which wetting can be altered:

a) Polar interactions that predominate in the absence of a water film between oil and solid
b) Surface precipitation dependent mainly on crude oil solvent properties with respect to the asphaltenes
c) Acid/base interactions that control surface charge at oil/water and solid/water interfaces
d) Ion binding or specific interactions between charged sites and higher valency ions.



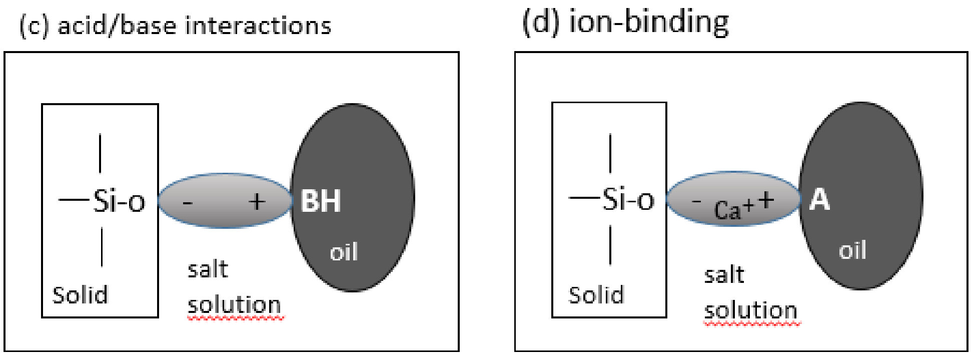


Figure 16: Mechanism of interaction between crude oil components and solid surface (Redrawn from Buckley, 1998)

What can be observed from the redrawn sketch by Buckley, is the lack of polarity characteristics for the crude oil that have not been taken into consideration.

Reservoir wettability is a function of oil composition, mineralogy of the rock, salinity of the brine and presence or absence of any other aqueous phase. The saturation history is also of interest, as it describes what phases have been in contact with rock and may affect the wettability (32). Additionally, pressure and contact time are of interest.

By altering from oil-wet to strongly water-wet system, the oil recovery can be increased significantly from originally oil-wet system reservoir. Chemical agents such as surfactants are known as wettability modifiers in oil-wet system. Effect on wettability by surfactant does not only depend on how much is absorbed, but also on how they adsorb. By manipulating the orientation of the adsorbed layer, a water wetted rock surface can be obtained which is beneficial for displacement of oil. Additional to surfactant, also inorganics such as silicates, phosphates and carbonates and carbonates and polymers such as lignins can be used to control the adsorption and the wettability. (4)

4 Oil-phase, Aqueous phase and the Solid Surface

Hydrocarbon is initially generated in source rock under high pressure. Due to oil density, little by little they are expelled into the water-containing rock layer. After sufficient time, all the crude oil will migrate from source rock into reservoir rock. As the oil enters water-containing rock layer, also known as the reservoir, a new equilibrium will be establishes. In equilibrium a wettability will be formed based on the crude oil, brine and rock (COBR) interactions. Thus it is important to understand what properties of crude oil, brine and rock and what interaction between COBR that effect the final wettability. Also temperature is of interest as it might impact the wettability in reservoir.

4.1 The Oil Phase, - Importance of Crude Oil Composition

Through study, it is found that crude oil is of significant importance for the COBR interactions. By experimental work, it has been presented that introduction of different crude oil under almost identical core condition have effect on wettability. (45)

Crude oil is crucial to wetting alteration in two distinct ways:

1. Organic polar components present in the crude oil
2. The oil itself, the solvent environment that influences partitioning of the surface active components between bulk oil and oil/water or oil/water/solid interface. (33)

Thus, the knowledge about crude oil composition is of significance.

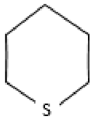
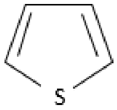
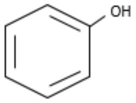
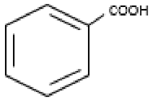
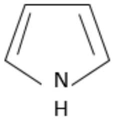
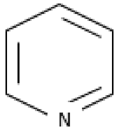
4.1.1 General Crude Oil Composition

Naturally occurring crude oil are complex and contain mixture of hydrocarbons and polar compounds of oxygen, sulphur and nitrogen, as well as metal containing compounds, in particular vanadium, iron, nickel and copper. The overall composition of reservoirs oils depend on the geographical location and geological age of the field. It is also found lateral and vertical variation in composition within the same field.

Throughout the literature study, several authors have stated that it is the non-hydrocarbons NSO (nitrogen, sulphur and oxygen) that play the key role in determining the nature of the crude oil with regard to the process of refining. They are found throughout the whole boiling range, but tends to concentrate in the heavier fraction.

Typical structures of NSO that has been identified in crude oil are given in table below: (47)

Table 4: Typical structures of NSO compounds presented in crude oil. Redrawn fig. and table from Speight 1991

Name of Compound		Molecular structure
Sulphur Compound	Sulphides	R-S-R`
	Cyclic sulphides	
	Tiophenes	
Oxygen Compound	Alcohols	R-OH
	Phenols	
	Carboxylic acids	
Nitrogen Compound	Pyrrols (non-basic)	
	Pyridines (basic)	

Crude oils are generally separated in three or four general fractions based upon solubility or physical and chemical characteristics- asphaltenes, resins and oils (saturates and aromatic). Fractionation of crude oil generally includes precipitation of the asphaltenes with n-alkane (usually n-pentane), and followed by fractionation of the deasphaltened oil using various solvents and/or adsorbent. Main standard procedure known is the SARA method (saturates-aromatics-resins-asphaltenes) (48).

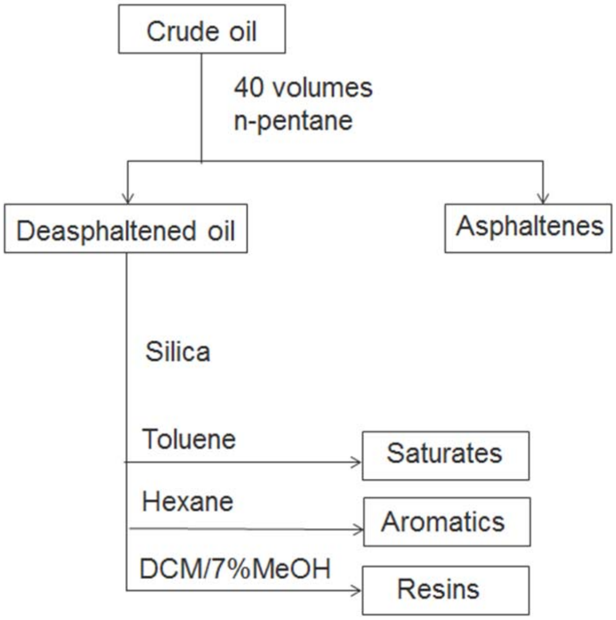


Figure 17: Modified SARA fractionation based upon the standard SARA-fraction of Jewell (1974)(49)

Cuiec (1984) studied the influence of various crude oil fractions on the wettability of porous media and compared it to the crude as a whole. This was to study as the effect of a separate oil fraction alone might have different interactions with a solid surface than in the presence of other crude oil fraction. He discovered that several fractions caused stronger wettability alteration than the crude oil itself. This study of separate fractions may nevertheless support useful information and a basis of comparison (35, 44)

4.1.2 Wetting Component

Already in 1941, Benner and Bartell recognized that the wetting properties of reservoir rock are influenced by the presence of polar compounds in crude oil. This type of adsorption would affect greatly the degree of wetting and the resulting interfacial relationship of the system. Solids that were originally hydrophilic in nature might function as hydrophobic solids as a result of the adsorption (50). It is believed that it is the polar compounds such as carboxylic, phenolic and indolic acid and also bases such as pyridine in the crude oil that is mainly responsible for surface interactions.

Study presented by Denekas (1959) on effect of crude oil components on rock wettability indicate that sandstone wettability may be changed by a complex variety of surfactants varying both in molecular structure and molecular weight. Limestone appears to be particularly sensitive to basic nitrogeneous surfactants (41). The positive charged nitrogen bases are most likely to adsorb to negatively charged silica surfaces. Nitrogen influence on wettability alteration have been emphasized by several authors (33), such as Mitchell in 1990 (51).

Over a period of time, asphaltene has been in focus as the main component for wettability alteration. Bartell (52) reported that it was the asphaltic products responsible for the formation of rigid films are highly absorbable by solids. According to Strassner (53), a crude oil wets the glass the more as it contains asphaltenes. Neumann also points out that the best adsorbed components of the crude oil are asphaltene. In 1997 Kaminsky and Radke researched the transport model for asphaltene diffusion from an oil/water interface through a water film, followed by adsorption of solid/water interface. They concluding that from their results, that the asphaltene adsorption on reservoir rock in the presence of a finite water film is not massive enough to initiate significant wettability alteration. (54)

Others, such as Johansen(55) showed that, in the case of crude oils from Rio Bravo, Tatums and Bartlesville-Dewey, the fraction precipitated by propane contains the product responsible for the oil wettability of a glass surface. Also the role of acid or basic products contained in crude oils has been discussed by many authors, sometimes in contradictory way. Neuman has shown that naphthenic acids become fixed on marble$(\mathrm{CaCO_3})$, but not on sandstone. McCaffery found that stearic acid becomes fixed on calcite but not on quartz, whereas octadecylamine becomes fixed on quartz.(44)

In crude oil there is also present oxygen compounds, which usually present in form of acidic and includes phenols and a large number of different carboxylic acids. Adsorption of acidic species may result in changing wetting properties of mineral surfaces (56, 57). Torsæter demonstrated how the wettability of a Berea sandstone from North Sea was modified from water-wet to neutral-wet, and further to oil-wet by adding small amounts of organic acid or base to the oil-phase (58). It has also been reported a correlation between wettability and elemental sulphur, which is related more or less to the correlation between asphaltenes and wettability. (44)

Polar components have tendency to concentrate in the heavier fractions. Surface-active material in crude oil resembles material in the asphaltene and resin fraction. The individual molecules consist of large polyaromatic and polycyclic condensed ring structures that contain heteroatoms (NSO). The polar functional groups may interact with solid surface. The high molecular polar components and its ability to alter wettability have been emphasized by several authors because of their multifunctional nature. Wettability experiments with resin and asphaltenes on feldspar, calcite and quartz sand showed that the adsorption of asphaltenes was greater than of resins (59).

It can be noted that some of the oil components have tendency to change charge based on pH in the reservoir. The chemical reaction for active components in crude oil: (22)

$$\mathrm{BH^+} \leftrightarrows \mathrm{H^+} + \mathrm{B}$$

$$\mathrm{RCOOH} \leftrightarrows \mathrm{H^+} + \mathrm{RCOO^-}$$

Extensive work have shown that general agreement that polar oil components can affect wetting properties, but mechanism behind wetting alteration are still not fully determined. Concentration of asphaltenes in oil are not necessarily a good predictor of rock/oil interactions. The composition of the remainder of the oil phase is equally important, particularly with regard to its properties as a solvent for some of its largest constituents (60). This is based on experiments, such as by Takamura and Chow where the Athabasca sand was found to be strongly water-wet despite high content of asphaltene.

4.1.3 Crude Oil as Solvent

Solvent quality of the crude oil will also have impact on the COBR interaction. Crude oil properties as a solvent will influence the ability of the oil to alter wetting of a solid surface (61). Solvent quality of the crude oil mixture is a function of composition, temperature and pressure.

Oil density (or gravity) as one measure of the solvency of an oil was presented by Buckley. The refractive indices of oil and their mixture with solvent and precipitants have been used to quantify the solvency of each oil with respect to its asphaltenes. As the asphaltene content increases, the API gravity decreases. Similarly, the crude oil quality as solvent will be affected by precipitation of asphaltene, such as if oil is diluted with higher content of gas. For maintaining mutual solubility of compounds in petroleum crudes, two factors must be considered;

1. Ratio between polar to non-polar species
2. Ratio of high to low molecular weight species. (62)

Sum of these factors mentioned above constitutes the solvent quality of the crude, and may provide some expectations for wettability alteration by precipitation or adsorption of crude oil components to the surface.

4.2 The Aqueous phase, -Oil/Water Interaction

In reservoir, the polar organic compound in crude oil may diffuse from the oil/water interface through a water film followed by adsorption at a solid/water interface (54). The ability of transfer of oil components is thus of interest.

Bobek, Mattax and Denekas describes in the review of reservoir rock wettability in 1958 that laboratory tests have shown that the wettability of reservoir rock may depend on both crude oil composition and the rock type, while fluids such as brine appear not to affect core wettability and may be used when coring to determine reservoir wettability (63). Per today it is accepted that all three factors; crude oil, rock and brine influence the reservoir wettability. This is further under chapter mechanism of wetting alteration in this thesis.

4.2.1 Partitioning

When equilibrium is reached between hydrophobic and aqueous phase, the polar organic components in the hydrophobic will distributed between the two phases. Polarity of the molecules and properties of the hydrophobic solvent as well as pH, salinity and ionic strength of the aqueous phase will affect the degree of distribution. This distribution may be expressed by term K, known as partition coefficient:

$$K = \frac{C_{oil}}{C_{water}} = \frac{[mol/kg]}{[mol/kg]} \tag{11}$$

K	Ratio of components present in both phases
$\mathrm{C_{oil}}$	Total concentration of a compound in oil in equilibrium
$\mathrm{C_{water}}$	Total concentration of a compound in water in equilibrium

The partition coefficient may be defined in several way, but in this thesis it is of interest to determine the polar component on molar basis.

K equal to 1 indicate equal distribution between the phases. Solvent interaction of each phases will affect the partition coefficient. Solubility of polar hydrocarbon compounds in brines of varying salinity has been found to decrease with increasing salinity (35). This will also result in reducing the transfer of polar organic components from oil to water phase, thus increasing partition coefficient. This has been reported as “salting-out” effect by several authors. (64)

Another important variable that influence the partitioning between the two liquid phases is the pH value. For a given acid or base, the relative hydrophilic character is strongly connected to its dissociation constant. A pH variation will hence affect the affinity of the compound for a hydrophilic environment. (35)

4.2.2 Interfacial tension-General Aspects

As discussed, the wettability of a solid surface depends on COBR system and all the three interfaces present: Oil/water, Oil/Solid and water/solid interfacial tension. This can also be observed from Young`s equation. A fundamental understanding of the various interfaces and the influencing factors is needed to clarify the interaction in a COBR system. First it needs to clarify difference between the surface tension and interfacial tension terms. Surface tension is usually applied for cases between a liquid and a vapor or air, while interfacial tension is between two liquids or liquid and a solid.(18)

In a system consisting of two phases, a tension always exists at the interface of fluid phases due to unbalanced molecular attractive and repulsive forces (65). The work to create additional surface area is related to the surface tension (for a given pressure and temperature):

$$W = \sigma dA \qquad (12)$$

W	Work applied to surface
σ	Interfacial tension
dA	New surface area

From equation it can be observed that the work require to create new area is proportional to interfacial tension. Customary units forσ, given in energy per unit area, are $\mathrm{erg/cm^2}$, dynes/cm or mN/m.

IFT depends on the nature and complexity of crude oil, thus σ is a function of the concentration of components at the interface. When the concentration of active components at surface exceeds their concentration in bulk, they have a tendency to reduce the IFT. The surface excess concentration of component i is defined as:

$$\Gamma_i^\sigma \equiv \frac{n_i^\alpha}{A} \qquad (13) \qquad \text{where} \qquad n_i^\alpha \equiv n_i - (n_i^\alpha + n_i^\beta) \qquad (14)$$

A	Cross sectional area of the interface
σ	Interphase
α and β	Bulk phases
n_i^α	Surface excess amount of component i at the interphase

Gibbs adsorption equation describes the change in IFT due to change in the surface excess concentration at constant temperature. Accumulation at the interphase between α and β will cause a reduction in the surface tension:

$$-\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln C_i}\right) = \Gamma_i \qquad (15)$$

C_i	Total bulk concentration of the component i
γ	Surface tension
Γ_i	Surface excess of component i

IFT values between oil solutions of water-insoluble fatty acids and aqueous solutions with increasing pH due to dissociation, are expected to reduce. Also, the dissociation of water-insoluble bases will result in low pH. The IFT is highest at near neutral pH range for an oil/brine interface where both acids and bases are active, but decreases as pH either increases or decreases.

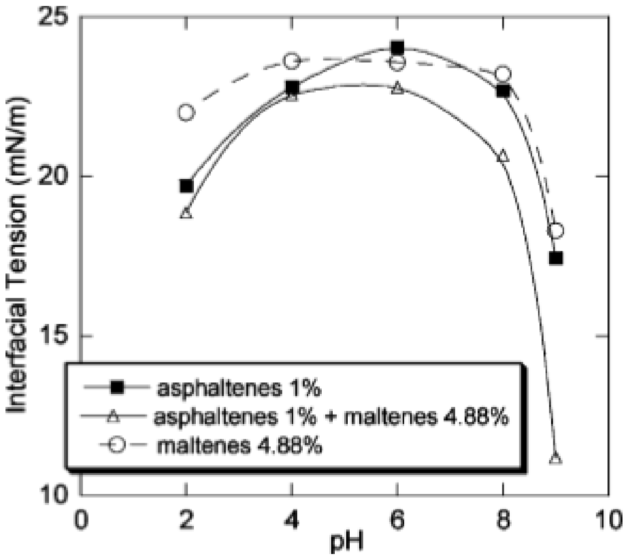


Figure 18: Oil-water interfacial tension measured versus pH for three different asphaltene concentration in toluene.(66)

For a given polar organic compound, the relative hydrophilic character, the affinity for either the hydrophilic or the hydrophobic phase present, is governing its surface or interfacial activity in aqueous solution (67). The surface active components, such as asphaltenes and naphthenic acids compete among themselves at these interfaces. (66)

4.2.3 Electrical Characteristics of the Oil/Water Interface

As mentioned earlier in this thesis, the presence of acids and bases can affect the wettability in a COBR system and thus have received special attention by several authors. Based on this, a review of the electrical characteristics at the oil/water interface is given below.

Cuiec (1975) described how the net charge at the interphase can rise by the adsorption of charged species at the oil/water interphase. Ionized acids and basic sites at the interface will influence the adsorption by which crude oil components may alter wettability. pH, salinity and ionic strength in the aqueous phase are factors that will affect the accumulation of surface-active species at the oil/water interface and the electrostatic force between them. Surface charge at both oil/water and solid/water interface is affected by acid/base interaction. (68)

After experimental research by several authors, it have been reported that crude oil/brine interfacial tensions is a function of pH (37, 69). Figure 19, illustrate an example of a zeta-potential curve of crude oil As discussed in section 4.2.2, the IFT is found highest near the neutral pH range, and decreases as pH is either increased or decreased. Several reports describes how the electrophoresis of emulsified droplets of crude oil in brine have shown that the crude oil/brine interfaces have net positive charge at low pH and net negative charge at high pH. These observations are linked and explains by dissociation of acids and bases (37, 70).

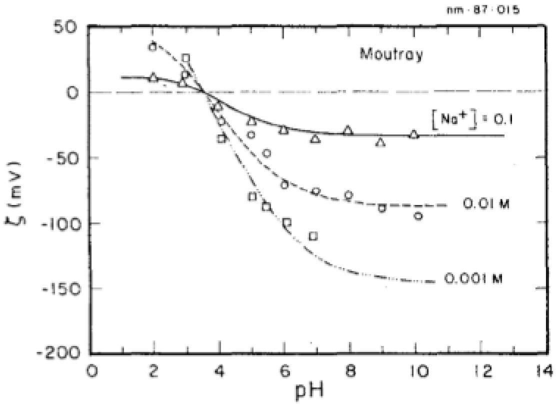


Figure 19: Zeta potential as a function of pH and for$[Na^{+}]$ *Moutray crude oil emulsions.(37)*

The initial pH is a function of dissolved gas in formation water:

$$\mathrm{CO_2 + H_2O \leftrightarrows H_2CO_3}$$

$$\mathrm{H_2CO_3 \rightleftarrows H^+ + HCO_3^+}$$

Based on the chemical reaction it can be observed that the more carbon-dioxide is dissolved, the higher pH will be in the solution. Also mineral present on the solid surface that are in contact with formation water, may affect pH. Feldspar minerals in sandstone will have highest impact on pH as the calcium ions contribute to lowering the pH in the aqueous phase.

Increasing salinity of aqueous phase will generally reduce the interfacial tension between oil and water. As described, the salting-out effect will lead to decreasing the solubility of surface-active compounds in the aqueous phase, and thus increase the amount of surface –active at the interface. Additionally, salt behave as counter ions at the interface resulting in reduction in the electrostatic repulsion between equally charged molecules. Overall, the concentration of surface-active components at the interface increases and the interfacial tension decreases. (39)

To evaluate changes in the charge at the oil/water interface with pH and salinity, usually the ionisable surface-group (ISG) has been applied by several authors. This model has been proven to match experimental data of both zeta-potentials and interfacial tensions as a function of pH. This model is mathematical complicated and thus beyond this thesis. (71, 72)

There is an unequal distribution of anions and cations between oil and aqueous phase when oil is in contact with water containing salt ions. The equilibrium distribution of ions will determine the potential difference between the two liquid phases. A diffuse double layer will develop on both side of the interphase. (73)

4.3 The Solid Surface

Another variable that affect the wetting-behavior of COBR system is the solid surface. The mineralogy of sandstone is important to understand the interaction between crude oil and the solid surface. Sandstone minerology is briefly described in sec. 2.2.3 and 2.2.4. The surface energy of the solid will affect the degree of interaction between a specific crude oil and each mineral.

4.3.1 Surface Roughness and Contact Angle Hysteresis

When studying rocks impact on the wettability, the physical state and structure of the solid surface is important to wettability. The surface of pores which determine wetting behavior within reservoir are generally rough and extremely complex in character because of cementation and other diagenetic effects. This may result in angle hysteresis effects with distinctly different angles for water advancingθ_A, and water receding θ_R conditions (74). Advance contact angle θ_A and receding contact angle θ_R referees to contact angle formed by expanding and contracting the liquid (75). Intrinsic angle θ_E is taken as the basic quantitative measure of system wettability.

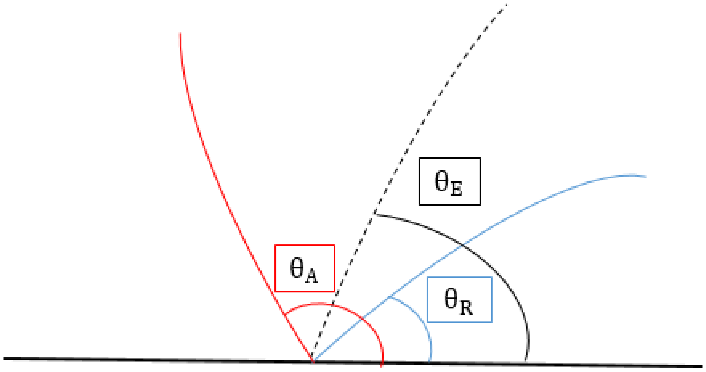


Figure 20: Contact angle hysteresis at a rough surface. Redrawn from source:(76)

These contact angles were measured on rough surfaces and presented later as a function of an intrinsic contact angle θ_E by Morrow. From the fig. 21, it is observed that as wettability of a solid is changed from strongly water-wet to less water-wet (low angle region), high variation will be seen in the advancing angleθ_A, and less variation for the receding conditionθ_R.

In general, surface roughness gives rise to contact angle hysteresis with distinctly different angles θ_R andθ_A. In the oil-wet region (high angles), going from less oil-wet to strongly oil-wet behavior, the variations are opposite. (76)

In 1965, Melrose predicted that the pore structure in typical reservoir rock types of porous solids can lead to hysteresis effects in capillary pressure even if a zero value of the contact angle is maintained. While studying the effect of surface roughness on hysteresis, Morrow found that the difference between advancing and receding angles could be related to the "intrinsic" angle (equilibrium angle) which is a measure in the absence of roughness. In the intermediate wetting range, the difference between advancing and receding angles can exceed 100° which means that there is a very wide range over which the porous medium will not imbibe either water or oil. Together with McCaffery, Morrow studied immiscible displacement over a wide range of wetting condition and found displacement behavior to be systematically related to the contact angle. The greatest difference between drainage and imbibition relative curves was found in the intermediate wetting condition. They found that the relative permeability to the wetting phase increased markedly as the advancing contact angle increased toward and through 90°. Thus, the implication is that water breakthrough occurs earlier in going from water-wet to oil-wet system. (77)

The measurement of water advancing angles by the sessile drop technique requires a transparent model oil in order to observe the water droplet deposited on the surface surrounded by the bulk oil phase. This procedure of measurement might disrupt the equilibrium condition between water, crude oil and solids, as the crude oil needs to be removed after equilibration with the solid. From figure 21, it is observed that a small change in the water receding angle results in significant change in the wettability of the surface of the water-wet region. Even though these angle are less in magnitude than the corresponding advancing condition, this disruption might affect the wettability result. It was in 1994, Skauge and Fosse introduced the measurement of static water receding angles. (78)

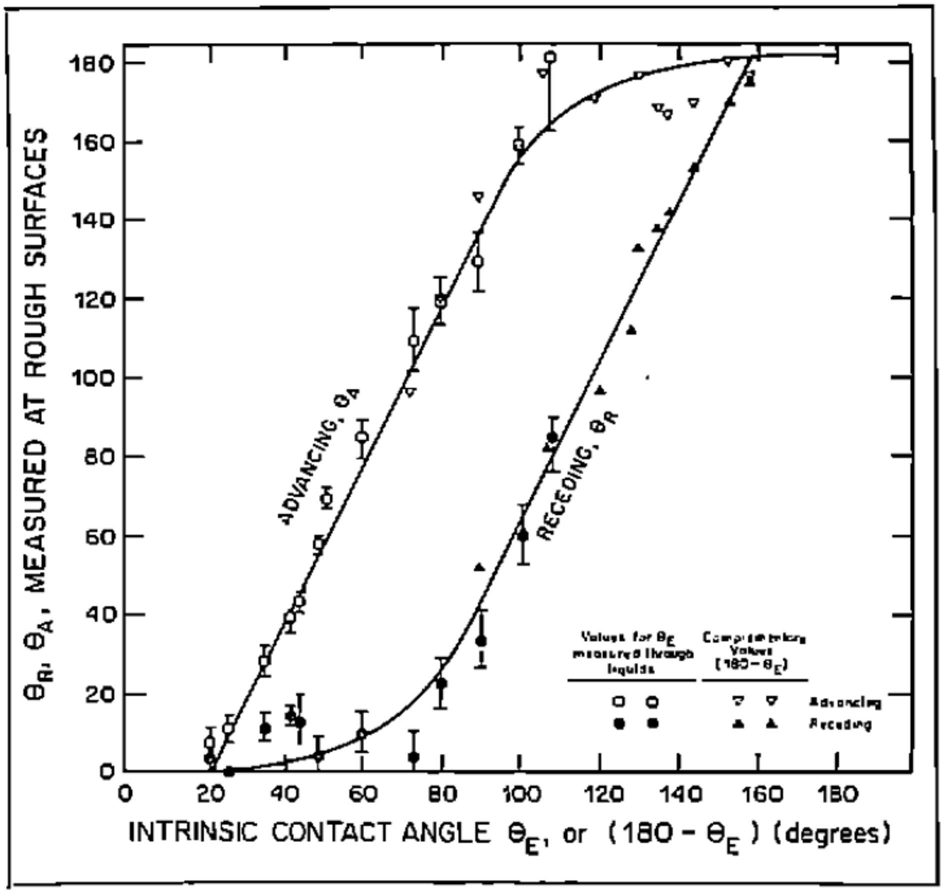


Figure 21: Values of advancing (θ_A) and receding (θ_R) contact angles observed at rough surfaces, versus intrinsic contact angleθ_E. (76)

Stability of water film is affected by heterogeneity in rock morphology. Surface roughness might result in thinning the water-film, and in some cases even rupture water-film. Based on this, some rock surface are more likely to remain water-wet due to the rough structure of the surface. (39)

An ideal smooth and clean quartz surface will have contact angle 0° and be strongly water-wet. This is however a simplification and the deviation are explained by surface roughness and heterogeneities, which might give destabilization of the water-film and consequently increase the contact angle. High surface energy shows tendency to adsorb almost any materials, making it difficult to maintain the surface in a perfectly clean condition (35).

4.3.2 Surface Charge

As briefly discussed, both oil/water and solid/water interfaces have ionisable surface sites. Brine composition have impact on both charging of these sites and the net charge of the interface. At the pH range 2-9, the surface charge of quartz is negative charged.

When surface of many minerals, such as oxides and silicate can become highly hydroxylated, which give rise to silanol groups when exposed to aqueous solution. The solution also becomes saturated with respect to silicic acid.

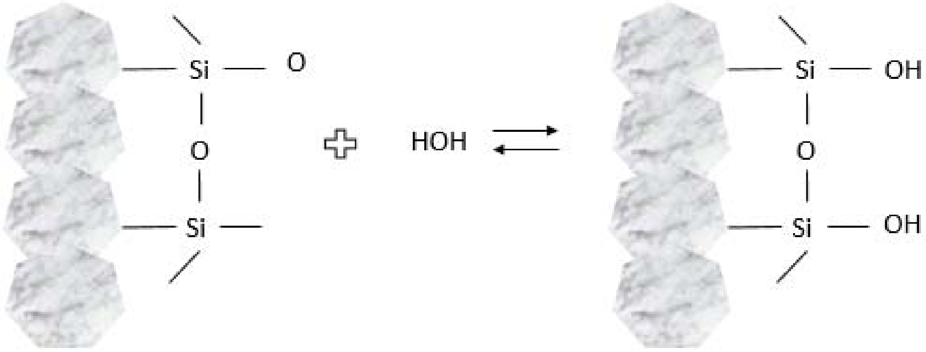


Figure 22: Figure demonstrate reaction between silica surface and H2O. Redrawn from source.

When quartz surface is exposed to water for longer intervals, this surface tends to hydrolyze further to form $= \mathrm{Si(OH)_2}$. (79)

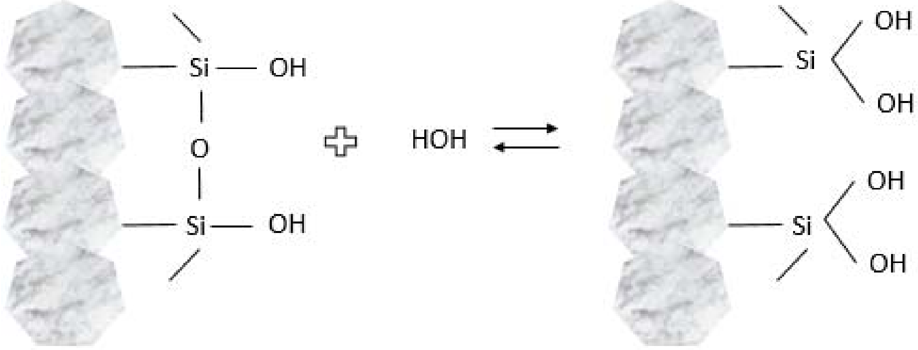


Figure 23: Figure demonstrate further reaction to $= Si(OH)_2$

Formation of more silanol is possible, particularly under low bulk concentration of alkali metals. This way the mineral surface hydrate, i.e. molecular water adsorbs to the hydroxide group and forms further a multilayer of three or more water molecules thick. (79)

The new hydroxide functional groups at the surface may behave as acids or bases, giving ability to ionizing to give a charged surface and further reacting with dissolved ions or molecules in the water phase. Active surface sites in neutral aqueous solution of the mineral are mainly oxides alumina (=AlOH and $= \mathrm{AlOH_2^+}$) and silica ($\equiv \mathrm{SiOH}$ and $\equiv \mathrm{SiO^-}$). Depending on pH of the solution, these groups may act as acids or bases. Reaction can be written as:

$$\text{M-OH} + \mathrm{H^+(aq)} \leftrightarrows \text{M-OH}_2^+ \text{ (as bases)}$$

$$\text{M-OH} \leftrightarrows \text{M-O}^- + \mathrm{H^+}\text{(as acids)}$$

Where M equals either Si or Al. A pH reduction will thus lead to an increase in the positive surface charge. Increasing pH will on the other hand reduce the positive charge and the total surface charge may become negative. (80)

Point of zero charge (PZC) is a concept relating to point at which the amount of positive and negative charges are equal. The net charge of the surface at this point is zero. For the two groups are equal to:

Table 4: pH at PZC for two groups

Group	pH at PZC
Al_2O_3	8.2
SiO_2	2

(81)

From the reaction equation above, it is indicated that at a silica surface the concentration of negatively charged surface sites increases as more silanol groups dissociate, creating negative ions as pH is increased. For silicate groups with increasing pH, this is measured as an increase in the negative zeta-potential (37).

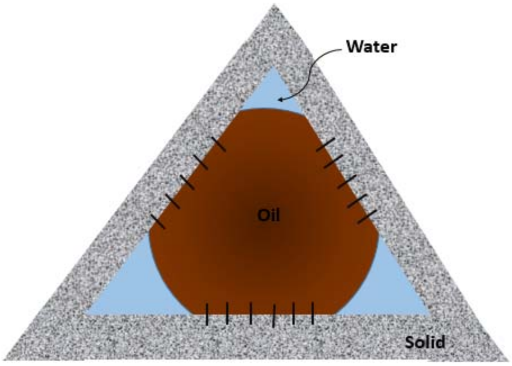
5 Crude Oil/Brine/Rock (COBR) Interactions

The total crude oil/brine/rock system involves complex interactions of fluid-fluid and fluid-solid interfaces. It makes investigation of small compositional variations often difficult to interpret. A minor change in parameters such as pH and ionic strength in the aqueous phase, may cause a severe change with respect to the different interactions acting between molecules, e.g. coulombic forces. The focus in this section will be the mechanism that control COBR wetting.

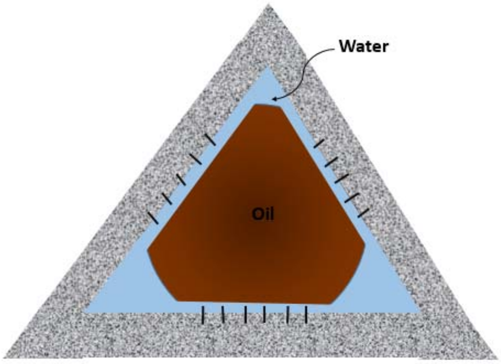
5.1 Adsorption

Reservoir system is complex, where several parameters will affect wettability change and adsorption, such as chemical structure and mix of the surfactants, surface properties of the rock, composition of the oil and the reservoir fluids, nature of the polymers added and solution conditions such as salinity, pH and temperature.(4)

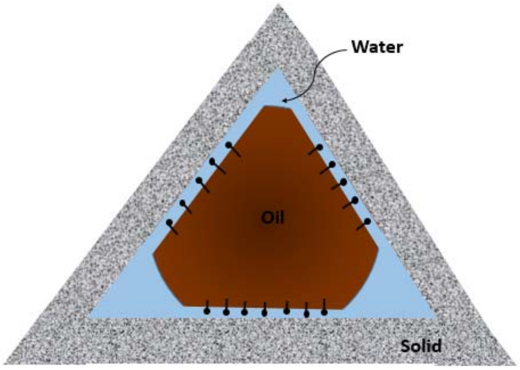
As mentions earlier in thesis, the pore space in most reservoir rock was initially filled with brine. In the process of oil migration into reservoir, oil displaces water during filling of the reservoir. At this point, oil components could then interact with the rock surface, establishing initial wettability. There are several ways for oil component can interact with the rock surface:



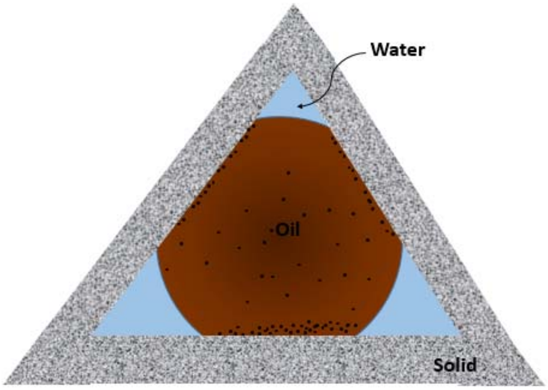
a) Adsorption from the oil phase



b) Adsorption through the water phase



c) Adsorption from the oil/water interface



d) Precipication

a. **Adsorption from the oil phase:** In cases where oil is in direct contact with rock surfaces, surface active material can adsorb on solids from non-aqueous solution to form monolayers, swollen monolayers, or even multiple layers, in complex interactions that can be highly influenced by even small amounts of dissolved water. (82) This is the case where rock surfaces may be oil-wet initially due to specific oil-wet minerals, or also in cases where reservoir is both source and reservoir. By experimental study it has been shown that in cases of direct contact, the asphaltenes will adsorb on mineral surfaces, especially clay. (*Minerals have been discussed in chapter 2.2.3*) Important variables, such as type of clay and its exchangeable cations, nitrogen content of the oil and the solvent in which the polar compounds are dissolved will affect the degree of adsorption.

b. **Adsorption through the water phase:** In presence of water film, oil components may be extracted from the oil into the water phase, which eventually are adsorbed onto rock surface. In 1994, a different mechanism for wetting through a bulk water phase was suggested. It involves precipitation of organo-metallic complexes during oil-migration into the reservoir. Reservoir cores, which could not be cleaned to more water-wet condition with organic solvent, were shown to be cleaned by treatment with complexing agents. (83)

c. **Adsorption from the oil/water interface:** At oil/water interface there can exist acidic and/or basic substituents of large organic molecules. They may then be deposited onto the solid surface by a mechanism analogous to Langmuir-Blodgett deposition of a surfactant film on a solid as it passes through an air/water interface. As result, there are strong ionic interactions-either attractive, repulsive or both. Interfacially adsorbed species can occasionally be seen as a rigid films. (39, 84)

d. **Precipitation:** Alteration of wettability is often suggested as a result of precipitation of asphaltene, but in and of itself has not been demonstrated to contribute to reservoir wettability on a broad scale (85). It has been shown that even cases with extensive organic deposition, have not been firmly linked to wetting alteration. Such case may occur with some crude oils during enhanced recovery with carbon dioxide (86). Overall, it can be demonstrated for wetting alteration mechanism, precipitation of asphaltene can only be a contributing effect for the COBR wetting effect.

5.2 Adhesion and Spreading

Term adhesion $\mathrm{W_{AB}}$, describe the work to the change in energy on separating the two phases, A and B, with an initial common interface, into two liquid-vapor interfaces:

$$\Delta \mathrm{G} = \mathrm{W_{AB}} = \gamma_{\mathrm{final}} - \gamma_{\mathrm{initial}} = \gamma_{\mathrm{A}} + \gamma_{\mathrm{B}} - \gamma_{\mathrm{AB}} \tag{16}$$

where γ_{AB} is the interfacial tension between phases A and B, and γ_{A} and γ_{B} are the surface tensions of A and B, respectively. The corresponding definition for the work of cohesion, $\mathrm{W_{BB}}$ which is a measure of the intermolecular attraction within a liquid given as:

$$\Delta \mathrm{G} = \mathrm{W_{BB}} = 2\gamma_{\mathrm{B}} \tag{17}$$

Should the oil-oil or water-water intermolecular attractions be lower than the oil-water intermolecular attraction, miscibility will occur since the free energy will decrease on mixing. Difference between $\mathrm{W_{AB}}$ and $\mathrm{W_{BB}}$ is also known as the spreading coefficient of phase B on A:

$$\mathrm{S_{B/A}} = \mathrm{W_{AB}} - \mathrm{W_{BB}} \tag{18}$$

A positive spreading coefficient indicates that the A-B interaction is strong enough to promote wetting of phase A by B. Conversely, negative spreading means no spreading. The final shape of the drop that is deposited onto a flat solid surface will depend on the magnitudes of the cohesive molecular forces within drop and the adhesive forces between the liquid and the solid. Contact angle is the index of this effect.

Since the contact angle has high variety due to surface heterogeneities, impurities and other experimental limitations, there have been constructed adhesion maps. The purpose of mapping adhesion is an attempt to reveal interfacial interactions between crude oil, brine and water, a combination of adhesion and contact angle. It can used to identify the brine conditions by which an oil drop rapidly adheres to a solid surface. Stability of an intervening water-film can give rise to adhering, conditional and non-adhering regions. This need to be accounted for when interpreting the results. These regions corresponded to stable, conditional stable and non-stable conditions for the water-film. Stability of the water-film will depend on the disjoining pressure, according to the DLVO theory, and is affected by parameters such as crude oil composition, salinity and pH (35, 39).

5.3 The Stability of Water Films - Disjoining Pressure

Wettability properties of a reservoir is closely connected to the stability of films and film rupture. It is necessary with a preview on a microscopic level with regard to intermolecular forces. The stability of thin wetting aqueous film on rock surface is governed by several variables, including pH, brine and crude oil composition and capillary pressure. A review of the electromagnetic forces is reviewed in the next section.

Kaminsky and Radke (1998), based on their study argue that water-film rupture followed by direct deposition of crude oil onto rock is likely the origin of wettability reversal in reservoir rock. (54)

Stability of the water-film separating the crude oil from the solid depends on the disjoining pressure, Π. Disjoining pressure is the force that tends to disjoin or separate the two interfaces, expressed in Pa. It is a result of intermolecular or interionic forces arising as two interfaces approaching each other. The disjoining pressure was first suggested by Derjaguin in 1987. The contributions to this pressure are:

1. Van der Waals forces
2. Electrostatic forces
3. Structural or solvation forces. (87)

The first two contributions, regarding the stability of colloids were first introduced in 1940. The theory has been named DLVO theory, after Derjaguin, Landau, Verrvey and Overbeek. However, the van der Waals and electrostatic force model does not include the effect of hydrogen bonding and specific ion-water interactions. These interactions have been called, as point three, “solvation”, “hydration” or “structural” effects due to the intermolecular structure of the solvent or water. This effect may be either hydrophilic or hydrophobic (38).

As illustrated in fig 24, each of the forces is a function of the distance that separate the two interfaces. A negative Π means there is an attractive force that result in unstable condition for the intervening water-film, causing water-film rupture. Similarly a positive Π will hinder direct contact between oil and solid due to repulsive forces, resulting in stable condition for the intervening water-film. In the transition zone between the extremes, where the disjoining pressure isotherm may be either positive or negative, the water-film is conditionally stable. Capillary pressure and temperature are variables that influence the stability in this region.

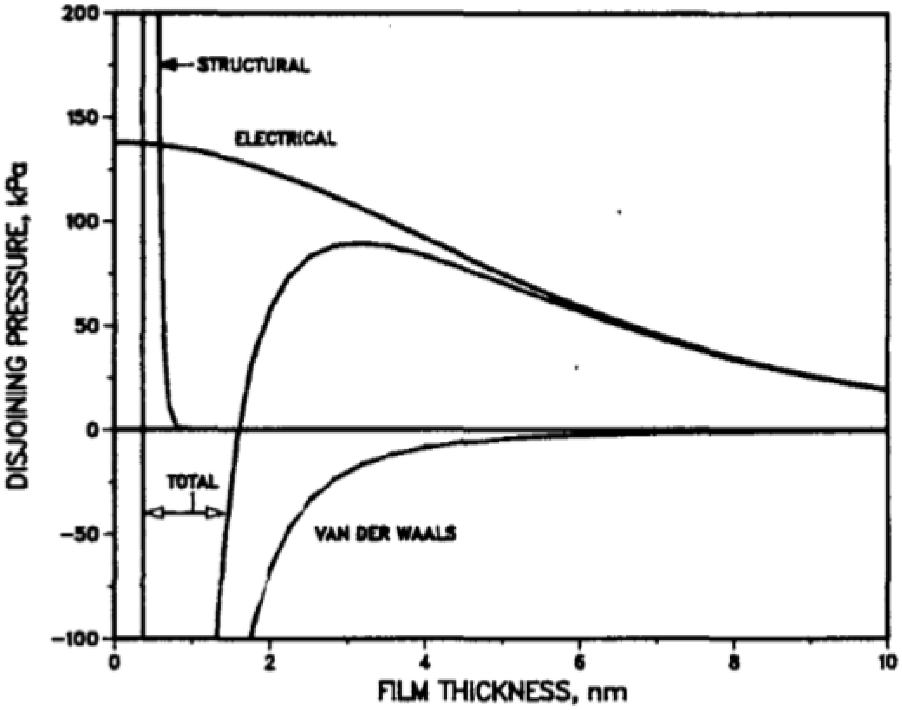


Figure 24: Individual components of disjoining pressure contributing to the force that constitute the disjoining pressure, as a function if distance. (38)

5.4 Electrical Double Layer and DLVO Forces

Electrostatic forces are due to development of the charges between an interacting surface and the liquid bulk media. The charges can be formed either by dissociation of the surface charge or adsorption of the charges onto an uncharged surface. The distribution of electrical charge in the interface region between the two phases is resulting from:

a) Charge transfer between the phases
b) Unequal adsorption of positive and negative ions.
c) Orientations of molecules with permanent dipole moments
d) Distortion (polarization) of electrical charge in molecules. (88)

The distribution of charge is called the electrical double layer, and describes the gradual transition from the electrical potential of one of the bulk phases to the other.

Assumption in working with charge of the solid is that the surface charge is spread uniformly over the surface. Charge in the solution close to the surface is considered to be composed of an equal distribution of point-like ions. Ions nearest to the surface form an inner immobile layer. Following figure represent examples of the change in potential with distance from the solid surface for different types of monolayers.

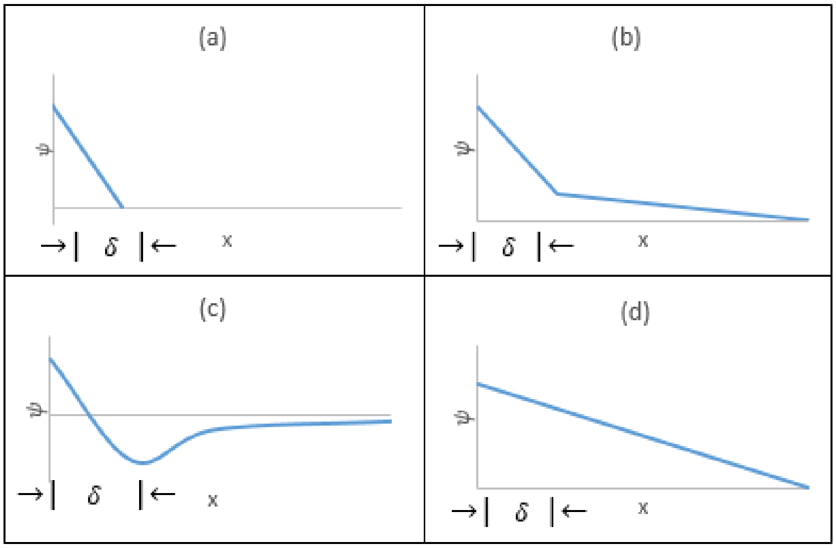


Figure 25: Potential variation in different types of double layers as a function of distance x. Sketch redrawn from source (89).

Further details regarding the structure of the electrical double layer have been described by several authors and are beyond the scope of this thesis.

Surface of shear is an imaginary surface lying close to the solid surface but within stationary fluid. The net charge on the solid particle is given as zeta potential(ζ), which describes the potential of the shear layer. ζ −Potential can be measured by electrophoretic mobility (90). ΔV

The potential drop occurs partly in the oil phase and partly in the water phase and the diffuse double layer develops on both side of the oil-water interface. Ionic strength and degree of adsorption of surface-active species will determine the potential drop at the interface.

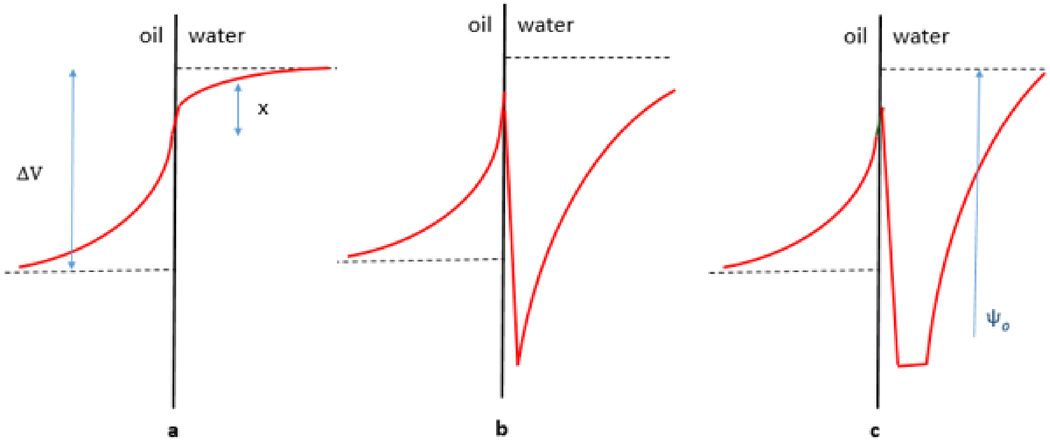


Figure 26: The potential at an oil-water interface.a) in the absence of surface active ions, b) after addition of surface active ions, in solution of very low ionic strength and c) in the presence of surface active ions and high ionic strength. Redrawn sketch from source: (73).

Hirasaki (1991) presented in his study a model of the electrical double layer interaction as two surfaces approach each other in an aqueous medium. In water containing electrolyte ions, when two ions approach each other the overlap of the double layer will cause an energy change in the system. As seen in figure (27), the differential of the energy with respect to thickness of water-film is the electrical contribution to the disjoining pressure.(38)

The electrical double layer will act repulsive. DLVO theory considers the electrostatic forces, Van der Waals forces and the structural forces acting together to model the resulting forces. There are two types of DLVO model, a long-range which is repulsive coulombic interaction and a short-range which is attractive van der Waals interaction. Changes in the coulombic interaction, reflected by the ionic strength will affect the nature in the system. Coulombic interaction will dominate at all distance when the ionic strength is low. Increase in ionic strength may lead to aggregation of the particles as the coulombic interaction no longer “conceal” the attractive part. (91, 92)

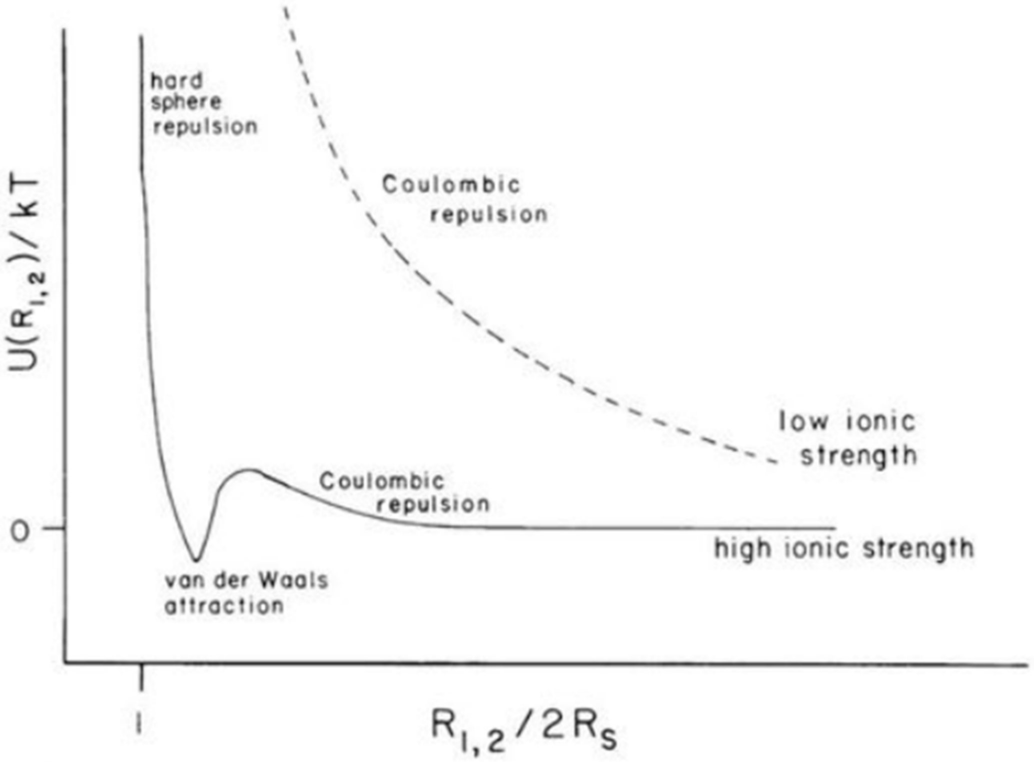


Figure 27: The radial dependence of the DLVO interaction between two charged particles.(92)

Predictions of water film stability is most accurate when salinity is low, limiting application of DLVO in many practical situations. (39)

The weakness of the DLVO theory is that it does not take into consideration the single components in a system, but rather consider it as a homogeneous. Such as in crude oil, there can exist both acids and bases, and this need to be accounted for when evaluating a COBR system.

5.5 Aspects of the Electromagnetic Forces

The long-range forces, the coulombic forces, act between oil and solid through an intervening water-film. Should both the electrostatic forces and van der Waals force be attractive will lead to rupture to the water-film and resulting in a wetting alteration of the solid surface. There have been several studies regarding contact angle on quart, including Brown and Neustadter (1980). They study showed low contact angle at high pH and high contact angles at low pH. This behavior was connected to the net charge of the oil/water and solid/water interfaces as a function of pH. Usually the water/silica surface is negatively charged at almost all pH-range, except at extremely low pH values, due to its low PZC equal to 2. High pH condition at the oil/water interface will give a total net negative charge due to dissociation of acids. This will lead to water-wet surface condition as the two equally charged surfaces will repel each other, thus resulting in low contact angle. The positive oil/water interface at low pH is due to nitrogenous material. Attracted opposite charges at the interface, will cause rupture in the water-film and alter wettability to more oil-wet behavior, giving high contact angle. (93) In intermediate pH range it has been observed more patchy wetting and Brown and Neaustadter (1980) explained this as due to competitive effects between the attractive and repulsive effects, as stated above. The wettability varied depending on the surface charge of the silica.

The study of phenomena electrostatic force has not taken into consideration van der Waals and “structural” phenomena, and is therefore incomplete. However, these statements do provide a qualitative explanation for observation in experiments where wettability behaves as a function of pH. Attractive coulombic force that will result with rupture in water-film, opens for a direct contact between oil and solid, but should the coulombic forces be repulsive does not necessarily means that the water-film is stable as the van der Waals forces may be active. As discussed earlier, the forces are also dependent on the separation distance.

In the research made by Dubey and Doe (1993), they presented an illustration of the electrostatic forces between oil/water and water/silica as a function of pH for a California crude oil. Based on the study, they stated that the state for optimal water-wetness, the repulsive force must be large enough to overcome the van der Waals attraction. (70)

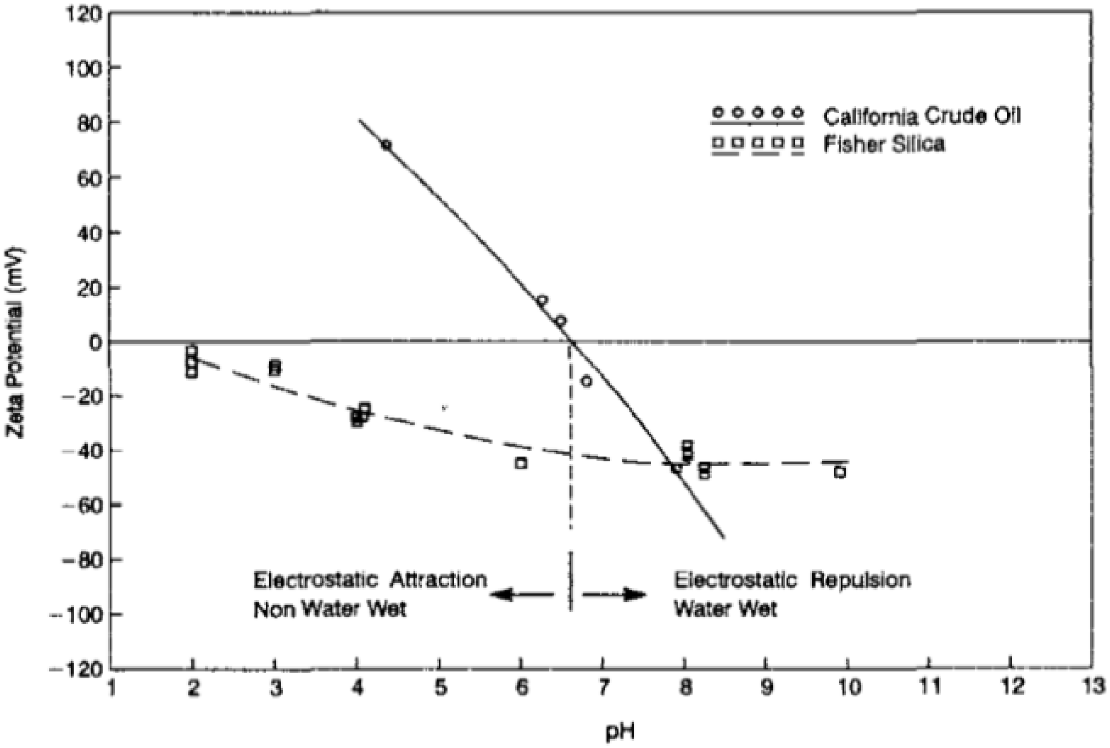


Figure 28: Zeta potentials as a function of pH for California crude oil and silica, illustrating expected relationship to wetting (70)

6 Initial wettability- Overview and discussion

The main objective of this work was to establish a better understanding and a relation between parameters that sets the initial wettability in a reservoir. It is also an attempt to build a timeline, seeing how the research was developed and what has been in focus for understanding wettability. By having a better understanding for initial wettability, it opens up for opportunity to modify and reduce the magnitude of the surface forces which holds the oil back during a displacement process. By optimizing choice of waterflood injection brine composition, temperature of injected fluids and control over reservoir pressure.

It is important to state, by detecting what alters and affect the wettability properties in sediments, can give knowledge for how the wettability in reservoir is established initially. This opens up for a wide range of parameters and mechanism that need to be investigated and studied both separately and in combination.

Over history, there have been made tremendous amount of research for understanding the wettability behavior of reservoir. Significant advances have been made, especially in appreciation of the implications of mixed-wet conditions. These extensive review are in agreement that, despite the large volume of work on COBR wetting phenomena, significant gaps remain in our understanding of both its causes and effects.

Initial wettability in reservoir- Bibliographic Overview

As previewed in this thesis, it can be seen that to understand phenomena wettability some of the parameters that was in focus previously, has been “forgotten” throughout years and focus has been shifted to other aspects that might explain wetting properties of a reservoir. However, now it is seen a trend where old literature studies are taken back in use for explain wettability. Studies from many years back, where parameters such as pH was hot topic are back under consideration for explanation of wettability.

In 1941 Benner and Bartell (51), discussed how originally oil that would migrate and accumulate toward a reservoir, where sediments are completely covered with water. They acknowledge, whether water is entirely or partly replaces by oil, would be a result of either grains are either hydrophilic or hydrophobic. It is stated in the literature paper "*If the complete removal of water from the surface of the sand grain cannot be explained logically, then undoubtedly, as commonly has been assumed, each sand grain in a reservoir must be coated by a tenaciously adhering film of water*". Previously and further in history, it has been assumed a long time that all sandstone reservoirs are water-wet. This statement is also further supported by the statement that since oil and water are immiscible, and water-film was first originally in contact with the solid, it should not be possible for oil to displace the water-film on grain surface. This is due to throughout laboratory test, it has been shown that is it extremely difficult, if not impossible to remove the film of water from silica and glassware under ideal condition in the laboratory. Sum of these arguments has led to the final conclusion of all sandstone reservoirs being initially water-wet. Based on this statement, they also indicate that the oil components may not affect the solid surface due to the immiscible water-film that is cover. However, it is accepted that adsorption of certain substances might affect degree of wetting if there is a direct contact between the oil and solid. Any other wettability behavior other than water-wet for core sample was often ascribed to artifacts related to core recovery and testing procedure.

In 1972, Treiber (43) performed a laboratory evaluation of the wettability of fifthy oil-producing reservoir. In the study, he showed that not all sandstone reservoirs are water-wet and actually more of the samples were found to be rather strongly oil-wet. After the release of this report, it has been slowly accepted that not all sandstone reservoir are water-wet, as first assumed.

As described and shown in this thesis this is not the case. There exist several mixed-wet and even oil-wet state sandstone reservoir. The migration from source rock to reservoir sediment is a slow process and happen over long time, giving the oil time to accumulate and interact with rock and the initial aqueous fluid. All three components, crude oil, brine and rock combined will determine the final wetting state.

COBR-System

Crude oil

As mentioned in chapter 4.1, there are components in the crude oil that can affect the wettability in a reservoir. Benner and Bartell recognized in 1941 that the wetting properties could be affected by the presence of polar compounds in crude oil.

Over long time it was believed that it is the asphaltene that are the main component that have most impact. But later Morrow argues that this is not necessarily true, where their role in wettability alteration was observed and confirmed that deasphalted crude oil no longer exhibited adhesion in the low pH range. To confirm this statement, the Athabasca tar sand is used as example. When a sample of freshly mined Athabasca tar sand is kneaded under water, an abundance of clean sand grains falls from the sample. Thus, even though the tar sand have very high asphaltene contents (about 15%), the sand remains strongly water-wet over geologic time. The stabilization of the water films was explained due to electrical double layer repulsion in the Athabasca tar sand.

There are also present some crude oil components that are soluble in water to some degree, such as soluble acids and possibly even soluble bases. There has been research on these and their effect in carbonates. It is important to remember that carbonates are positively charged while sandstones negatively charged, thus the results is not directly comparable, but it’s likely that it may be a factor and may also affect wetting in sandstone.

It is general accepted that polar components in oil can affect wetting properties, but mechanism behind alteration are still not fully determined. It is believed that polar compound such as carboxylic, phenolic and indolic acid and also bases such as pyridine in the crude oil that is mainly responsible for surface interactions.

Brine

In 1917, Squire proposed adding alkaline materials to floodwater. He showed that dissolved salts such as sodium carbonate and silicates were more effective than water from drainage of oil from rock surface. Later in 1956, Reisberg and Doscher carried out experiment with sodium hydroxide and with strong detergents plus sodium hydroxide to show that the adhering crude oils could be removed very efficient from glass or silica under high pH solution. Although the quantitative aspect of wettability were still uncertain, Wagner and Leah in 1959 with laboratory work showed that drastic change in the pH of the water would change the wettability of rock form predominantly oil-wet to predominantly water-wet, and thereby increase the oil recovery.

When examining the aqueous phase, the partitioning of polar organic molecules between oil and water must be taken into consideration. This will give a better understanding of the transfer of polar organic compounds from the oil phase through the water phase and finally adsorbing on the mineral surface. It has been pointed out that the presence of salt will increase the value of K, which in return corresponds to increasing in concentration of the components in the oil phase. This is explained by the reduction in water solubility of the compounds due to the salting-out effect. This has been previewed in chapter 4.2.1 in this thesis.

pH, salinity and ionic strength in the aqueous phase are factors that will affect the accumulation of surface-active species at the oil/water interface and the electrostatic force between them.

Rock

There are several characterization of the solid surface that will impact the sandstone wettability properties, such as mineralogy and surface roughness. The physical state and structure of the solid surface is important to wettability. The surface of pores which determine wetting behavior are generally rough and extremely complex in character as a result of cementation and other diagenetic effects. This may result in different water advance and receding contact angle.

The surface charge of solid have also been in focus. Minerals such as oxides and silicate can become highly hydroxylated which give rise to silanol groups when exposed to aqueous solution. These new hydroxide functional groups at the surface may behave as acids or bases, giving ability to ionizing to give a charged surface and further reacting with dissolved ions or molecules in the water phase.

Other aspects to wettability

It was also Benner and Bartell who described the reason for advance of water in smaller capillary (water-wet system). Later, in a study by Morrow and McCaffery, they studied immiscible displacement over a wide range of wetting conditions and found displacement behavior to be systematically related to the contact angle. They found the greatest differences between drainage and imbibition relative permeability curve in the intermediate wetting condition.

Usually, when studying wettability, the main effort has been to change wettability with either strong acids or alkali to direct toward making substances more water-wet. Cooke, Williams and Kolodzie on the other hand, described a field trial wherein a water-wet reservoir was actually changed to a system which was more oil-wet with a small increase in recovery resulting from the injection of an alkaline material. To achieve this, it was necessary that the right condition of temperature, pH and especially salt concentration were optimal. In this field trial, an increase oil cut was obtained from 9 to 17%.

Another aspect of wettability properties was studied by Richardson where he compared large number of aged and “fresh” cores taken from the Woodbine Reservoir of the East Texas field. He cleaned the Woodbine cores and re-saturated them with oil to carry out a normal water-flood for residual oil determination, and observed the usual laboratory residual oil values of about 30% of pore volume. However, when the water-flood was conducted on fresh cores, they observed a much lower residual of only 15-18% of pore volume. In certain parts of the reservoir. It was proposed that, on of the significant aspects of wettability information related to oil recovery is the fact that nature may be providing the best possible wettability condition for optimum recovery in some of the reservoirs.

Summary

The objective of this thesis has been to review the initial wetting state in sandstone reservoir and how the understanding of this parameter has been developed through literature history. After reviewed of almost 100 references, following points can be concluded:

- To begin with, it was believed that all sandstone reservoirs are water-wet, but later experimental study has indicated that this is not the case. There exist both mixed- and even oil-wet sandstone reservoir systems.

- The number of combinations of oil components, brine ionic species and surface minerals is very large. This has contributed to the confusion regarding the wettability alteration and mechanism of initial wetting. All relevant mechanism of interaction and parameters in COBR system needs to be considered.

- By identify multiple mechanism and parameters, is the key to understand how the initial wettability in sandstone is obtained. This will provide a link between reservoir properties such as crude oil composition, initial brine and solid etc. and condition like temperature, pH and the initial wetting state.

- It is seen that some factors have higher impact on wettability alteration than others. Polar component, such as acids and bases in crude oil have been shown to alter wettability in reservoir rock. Also asphaltenes in crude oil have been in focus for some time, but several authors have discussed that asphaltene as molecular are rather too big to be able to interact with rock surface in order to modify wettability by itself. It can be a contributor, but not a main factor by itself. Also the crude oil properties as a solvent has been overviewed as how it transfer and transport component. The different minerals will have characteristic wettability behavior, and rock composition should also be of interest. Rock surface charge is important parameter that will determine what polarity it will attract toward surface and what interactions is possible to take place. Brine salinity is another factor, especially in cases where there are present a thin water film, that act as a bridge between crude oil and rock surface. Oil components can be adsorbed into solvent solution and further interact with rock surface. One parameter that are seen frequently in wettability study is pH. It is seen that pH can have more impact on wettability properties of the reservoir than other parameters.

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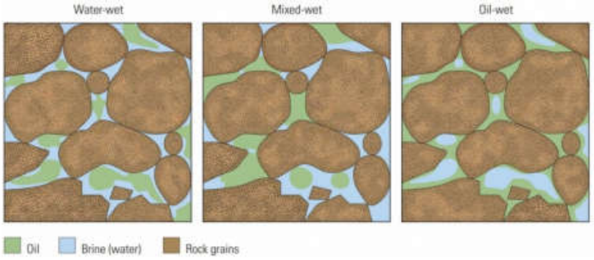
Initial wetting in sandstone

—Development through time

Wettability - General aspect

- Tendency of one fluid to spread on or adhere to a solid surface in presence of a second immiscible fluid.

- Important: Wettability preference to a core/rock have, don't necessarily depends on what fluid are present.



- Wettability is important parameter as capillary pressure, relative permeability, fluid distribution and flow direction are dictated by wettability

- Favorable state: Mixed-wet as this will lead to continuous pathway for both the oil-wet and water-wet surfactants and resulting in overall lower residual oil saturation.

Bibliographic overview

- Over long time it was assumed that all sandstone reservoirs are water-wet.

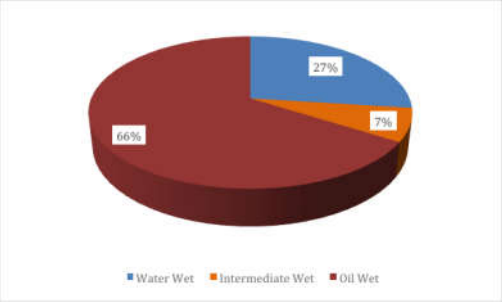
- This was based on statement: Since oil and water are immiscible, and water was originally in contact with the solid, it should not be possible for oil to displace the water-film on grain surface.

- Any other behavior than water-wet was often ascribed to artifacts related to core recovery and testing procedure

- ❖Through a reservoir life, it became more and more difficult to describe the reservoir behavior for some of sandstone reservoir.

- ❖In 1972, Treiber performed a laboratory evaluation of the wettability of fifty oil-producing reservoir. He found that not all sandstone reservoirs are water-wet, but actually most of them were strongly oil-wet (66% of them).

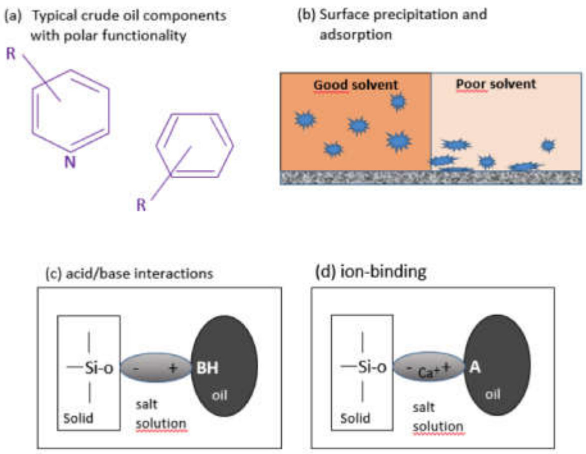
- ❖Slowly, it has been accepted that not all sandstone reservoir are water-wet.



Mechanism of Wetting Alteration

❖In 1998 Buckley identified a set of mechanism of crude oil/brine/rock interaction mechanism which can alter wettability

- ➢Polar interactions that predominate in the absence of a water film between oil and solid
- ➢Surface precipitation dependent mainly on crude oil solvent properties with respect to asphaltenes
- ➢Acid/base interaction that control surface charge at oil/water and solid/water interfaces
- ➢Ion binding or specific interaction



Oil–phase, Aqueous phase and Solid Surface

❖Hydrocarbon is initially generated in source rock and slowly expelled into originally water-containing rock layer (reservoir).

❖A new wettability equilibrium is established in the reservoir, based on the crude oil, brine and rock interaction

❖Thus, for understanding how the initial wettability in a reservoir is established, it is important to look into crude oil, brine and rock properties and the interaction them between.

❖Also temperature is of interest as it might impact the wettability in reservoir.

Oil-Phase

Crude oil is crucial to wetting alteration in two distinct way:

1. Organic polar components present in the crude oil.
2. The oil itself, the solvent environment that influences partitioning of the surface active components between bulk oil and oil/water/solid interface

Oil phase-Wetting components

- In 1941, Benner and Bartell recognized that it is the polar compounds in the crude oil that influence the wetting properties of reservoir rock.
- It is believed that polar compounds such as carboxylic, phenolic and indolic acids and also bases such as pyridine that is mainly responsible for surface interaction
- Denekas (1959) showed that surfactants varying both in molecular structure and weight, can affect sandstone wettability. The positive charged nitrogen bases are most likely to adsorb to negatively charged silica surface.

- Over a period of time, asphaltene has been in focus as the main component for wettability alteration
- Authors such as Bartell, Strassner and Neumann have investigated asphaltinic products, and point out that the best adsorbed components of the crude oil are asphaltene.
- However, in 1997 Kaminsky and Radke researched the transport model for asphaltene diffusion from an oil/water interface through a water film, followed by adsorption at a solid/water interface. They concluded that the asphaltene adsorption on reservoir rock in the presence of finite water film is not massive enough to initiate significant wettability alteration

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- Adsorption of acidic species may result in changing wetting properties of mineral surface
- Torsæter demonstrated how the wettability of a Berea sandstone from North Sea was modified from water-wet to neautral-wet and further to oil-wet by adding small amounts of organic acid or base to the oil-phase.
- General agreement that polar oil components can affect wetting properties, but mechanism behind wetting alteration are not fully determined.
- The composition of the remainder of the oil phase is equally important, particularly with regard to its properties as a solvent for some of its largest constituents.

Oil phase- As solvent

- Crude oil properties as a solvent will influence the ability of oil to alter wetting of a solid surface.

- Solvent quality of the crude oil mixture is a function of composition, temperature and pressure

- For maintaining mutual solubility of compounds in petroleum crudes, two factors much be considered:
  1. Ratio between polar to non-polar species.
  2. Ratio of high to low molecular weight species

Sum of these factors mentioned above constitutes the solvent quality if crude oil, and may provide some expectations for wettability alteration by precipitation or adsorption of components to the surface.

The Aqueous Phase

- In reservoir, the polar organic compound in crude oil may diffuse from the oil/water interface, through a water film followed by adsorption at a solid/water interface.

- In the review by Bobek, Mattax and Denekas in 1958, they describe how fluids such as brine appear not to affect core wettability. Per today we know this is not true, and the aqueous phase will have an effect on wettability properties of a reservoir.

Aqueous phase-Partitioning

- When equilibrium is reached between hydrophobic and aqueous phase, the polar organic components in hydrophobic will distributed between the two phases.

- This distribution is expressed by term K, known as partition coefficient:

$$K=\frac{c_{oil}}{c_{water}} = \frac{[mol/kg]}{[mol/kg]}$$

- The partition coefficient is of interest to determine the polar component on molar basis.

- Polarity of the molecules and properties of the hydrophobic solvent, as well as pH, salinity and ionic strength of the aqueous phase will affect the degree of distribution.

- Solubility of polar hydrocarbon compounds in brine of varying salinity has been found to decrease with increasing salinity

- This will result in reducing transfer if polar organic components from oil to water-phase, thus increasing partition coefficient. This has been reported as ”salting-out” effect by several authors.

- For a given acid or base, the relative hydrophilic character is strongly connected to its dissociation constant. A pH variation will hence affect the affinity of the compound for a hydrophilic environment.

Aqueous phase-Interfacial tension

- As discussed, wettability depends on all three interphases: Oil/water, oil/solid and water/solid interfacial tension.
- IFT depends on the nature and complexity of crude oil, thus the interphase is a function of the concentration of components at the interface.
- When the concentration of active components at the surface exceed their concentration in bulk, they have a tendency to reduce the IFT.
- IFT values between oil solution of water-insoluble fatty acids and aqueous solutions with increasing pH due to dissociation, are expected to reduce

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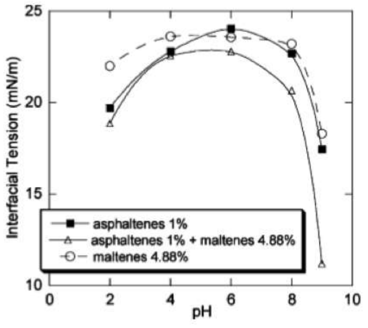
- IFT is highest at near neutral pH for an oil/brine interface where both acids and bases are active, but decreases as pH either increases or decreases:



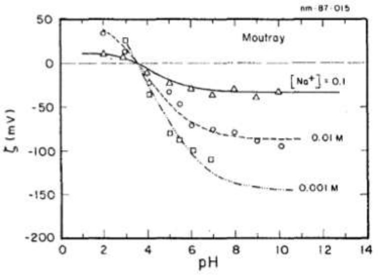
- For a given polar organic compound, the relative hydrophilic character, the affinity for either the hydrophilic or the hydrophobic phase present, is governing its surface or interfacial activity in aqueous solution.

Electrical Characteristics at the Oil/Water Interface

- Cuiec (1975) described how the net charge at the interphase can give rise by the adsorption of charged species at the oil/water interphase.

- pH, salinity and ionic strength in the aqueous phase are factors that will affect the accumulation of surface active species at the oil/water interface and the electrostatic force between them

- After research, several authors have reported that oil/brine interfacial tension is a function of pH.
  The figure illustrate example of a zeta potential curve of crude oil.



- As described, the salting-out effect will lead to decreasing the solubility of surface active compounds in the aqueous phase, and thus increase the amount of surface active at the interface. Resulting in reduction in the electrostatic repulsion between equally charged molecules.

- To evaluate changes in the charge at the oil/water interface with pH and salinity, usually the ionisable surface-groups (ISG) has been applied by several authors.

- There is an unequal distribution of anions and cations between oil and aqueous phase, when oil is on contact with water containing salt ions.

- Equilibrium distribution of ions will determine the potential difference between the two liquid phases. A diffuse double layer will develop on both side of the interphase

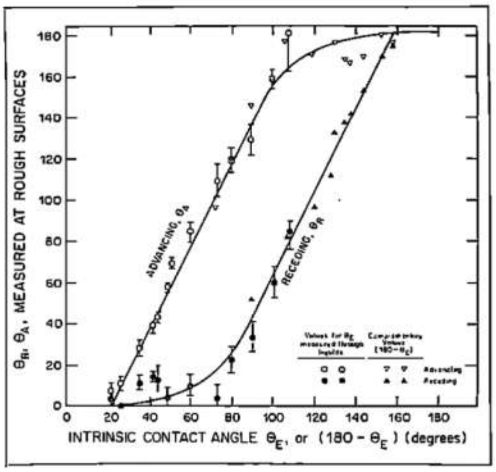
The Solid Surface

- Solid-surface is a part of wetting-behavior of COBR system.
- Mineralogy of sandstone is important to understand the interaction between crude oil and the solid surface.
- Also the surface energy of the solid will affect the degree of interaction between a specific crude oil and each mineral.

Surface Roughness and Contact Angle Hysteresis

- Physical state and structure important, and are generally rough and complex in character due to cementation and diagenetic effects
- This may result in angle hysteresis effect with different angles for water advancing and water receding condition.
- It is observed that as wettability of a solid is changed from strongly water-wet to less water-wet, high variation will be seen in the advancing angle and less variation for the receding condition
- Surface roughness give rise to contact angle hysteresis.

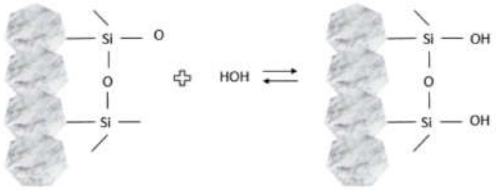
- McCaffery and Morrow found that the the relative permeability to the wetting phase increased markedly as the advancing contact angle increased toward and through 90°
- Thus, the implication is that water breakthrough occurs earlier going from water-wet to oil-wet system.
- From fig, it is observed that a small change in water receding ar result in significant change in wettability of the surface of water-wet region.



- Stability of water film is affected by heterogeneity in rock morphology
- Surface roughness might result in thinning the water-film, or even rupture water-film. Based on this, some rock surface are more likely to remain water-wet.
- Ideal smooth and clean quartz surface will have contact angle 0°, and be strong water-wet.
- High surface energy shows tendency to adsorb almost any materials, making it difficult to maintain surface in a perfectly clean condition.

Surface Charge

- ❖Brine composition have impact on both charging of surface site and the net charge of the interface.
- ❖Surface minerals, such as oxides and silicate can become highly hydroxylated and give rise to silanol groups when exposed to aqueous solution.

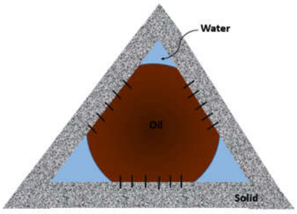


- ❖The solution also becomes saturated with respect to silicic acid.

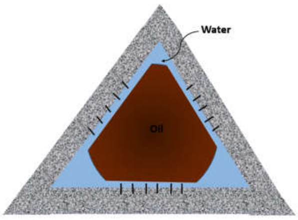
- ❖ Formation of more silanol is possible, particular under low bulk concentration of alkali metals
- ❖ This way the mineral surface hydrate, i.e. molecular water adsorbs to the hydroxide group and forms further a multilayer of three or more water molecules thick
- ❖ The new hydroxide functional groups at the surface may behave as acids or bases, giving ability to ionizing to give a
  charged surface and further reacting with dissolved ions or molecules in the water phase
- ❖ Active surface sites in neutral aqueous solution of the mineral are mainly oxides alumina (=AlOH and $= \mathrm{AlOH}_2^+ = \mathrm{AlOH}_2^+$) and silica ($\equiv \mathrm{SiOH} = \mathrm{AlOH}_2^+$) and silica ($\equiv \mathrm{SiOH}$ and $\equiv \mathrm{SiO}^-$). Depending on pH, may act as acids or bases.

COBR Interactions-Adsorption

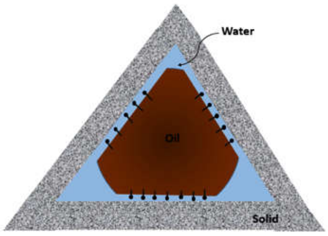
- There are several ways for oil components can interact with rock surface:



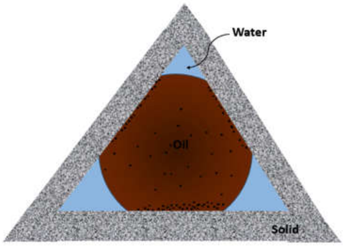
1. **Adsorption from oil phase**. Oil in direct contact with rock. Surface active materials adsorb on solids. Experimental study that in cases of direct contact, asphaltenes will adsorb on mineral surface, specially clay.



2. **Adsorption through water phase.** Oil components may be extracted from the oil into the water phase, which eventually are adsorbed onto rock surface



3. **Adsorption from the oil/water interface**. Acidic and/or basic substituents of large organic molecules be deposited onto the solid surface by a mechanism analogous to Langmuir-Blodgett deposition of a surfactant film on a solid as it passes through an air/water interface.



4. **Precipitation:** Alteration of wettability is often suggested as a result of precipitation of asphaltene, but in and of itself has not been demonstrated to contribute to reservoir wettability on a broad scale

COBR Interaction-Adhesion and Spreading

- Since the contact angle has high variety due to surface heterogeneities, impurities and other experimental limitation, there has been constructed adhesion maps.
- Purpose of mapping adhesion is an attempt to reveal interfacial interaction between crude oil, brine and water, a combination of adhesion and contact angle
- It is used to identify the brine conditions y which an oil drop rapidly adheres to a solid surface

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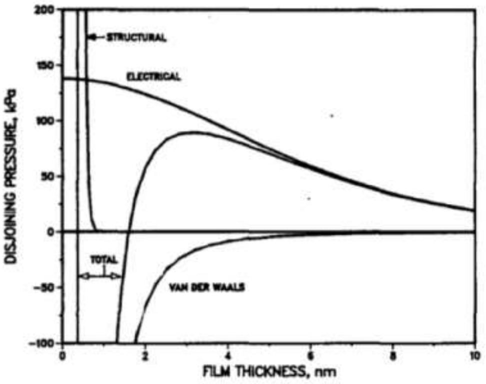
The Stability of Water film- Disjoining Pressure

- Wettability properties of a reservoir is closely connected to the stability of films and film rupture
- Stability of water-film will depend on disjoining pressure, according to DLVO theory and is affected by parameters such as crude oil composition, salinity and pH.
- Disjoining pressure is the force that tends to disjoin or separate the two interface.
- Kaminsky and Radke (1998), based on their study argue that water-film rupture followed by direct deposition of crude oil onto rock is likely the origin of wettability reversal in reservoir rock.

❖ The contribution to disjoining pressure are:
1. Van der Waals forces
2. Electrostatic forces
3. Structural or solvation forces.

❖ Each of the forces is a function of the distance that separate the two interfaces.



Electrical Double Layer and DLVO Forces

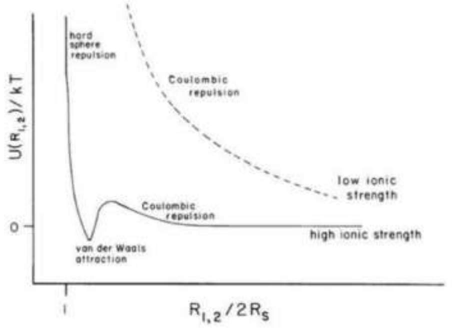
❖Electrostatic force between an interacting surface and the liquid bulk media.

❖Distribution of charge between the two phases is resulting from:

a) Charge transfer between the phases
b) Unequal adsorption of positive and negative ions.
c) Orientation of molecules with permanent dipole moments
d) Distortion (polarization) of electrical charge in molecules

❖Distribution of charge is called the electrical double layer

- In water containing electrolyte ions, when two ions approach each other the overlap of the double later will cause an energy change in the system
- The electrical double layer will act repulsive. DLVO theory considers the electrostatic forces, Van der Waals forces and the structural forces acting together to model the resulting forces.
- There are two types of DLVO model, a long-range which is repulsive coulombic interaction and a short-range which is attractive van der Waals interaction. Changes in the coulombic interaction, reflected by the ionic strength will affect the nature in the system.



Aspects of the Electromagnetic Forces

- Should both the electrostatic forces and van der Waals force be attractive will lead to rupture to the water-film and resulting in a wetting alteration of the solid surface.
- Brown and Neustadter (1980), study showed low contact angle at high pH and high contact angles at low pH. This behavior was connected to the net charge of the oil/water and solid/water interfaces as a function of pH.

❖High pH condition at the oil/water interface will give a total net negative charge due to dissociation of acids. This will lead to water-wet surface condition as the two equally charged surfaces will repel each other, thus resulting in low contact angle

❖The positive oil/water interface at low pH is due to nitrogenous material. Attracted opposite charges at the interface, will cause rupture in the water-film and alter wettability to more oil-wet behavior, giving high contact angle.

❖In intermediate pH range it has been observed more patchy wetting and Brown and Neaustadter (1980) explained this as due to competitive effects between the attractive and repulsive effects

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❖ Based on research by Dubey and Doe (1993), they stated that the state for optimal water-wetness, the repulsive force must be large enough to overcome the van der Waals attraction