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Surfactant-Enhanced Oil Recovery Process
For A Fractured, Oil-Wet Carbonate Reservoir

by

Danhua Zhang

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APPROVED, THESIS COMMITTEE:

George J. Hirasaki, A. J. Hartsook
Professor, Chair, Chemical and
Biomolecular Engineering

Clarence A. Miller, Louis Calder
Professor, Chemical and Biomolecular
Engineering

Mason B. Tomson, Professor, Civil and
Environmental Engineering

Mauro Puerto, PhD, Retired Exxon

Houston, Texas
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ABSTRACT

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Oil recovery by water flooding is usually not effective because of capillary forces in fractured, oil-wet carbonate formations. Sodium carbonate/surfactant solution was used to enhance spontaneous imbibition between the fractures and the matrix by both wettability alteration and ultra-low interfacial tensions.

Carbonate formations are usually oil-wet because the mineral-brine and oil-brine interfaces have zeta potentials of opposite sign. The resulting electrostatic attraction destabilizes the water film between the mineral and crude oil. The zeta potential of calcite can be reversed to be negative even at neutral pH, with dilute solutions of sodium carbonate and bicarbonate. Carbonate ion is a potential determining ion for carbonate formations. Thus sodium carbonate can promote water-wetness. Carbonate ion also sequesters calcium from the brine because of the small solubility product. The negative zeta potential and low calcium concentration greatly reduce the adsorption of anionic surfactants on the surface of carbonates.

Another important effect of sodium carbonate is to generate natural soap in situ by saponifying organic acids in the crude oil. Optimal salinity was found to depend only on the soap-to-surfactant ratio. Below optimal salinity, sometimes a thin layer accumulated between the lower-phase microemulsion and excess oil. The IFT of excess
oil with the equilibrated lower-phase microemulsion was high. However, ultra-low interfacial tension was observed when material from the thin layer was dispersed in the lower-phase or added to it. The existence of this thin layer made wide ultra-low interfacial tension possible.

The alteration of wettability is graphically illustrated by observation with a polished marble plate. After aging in crude oil, the plate is strongly oil-wet in brine. When the brine is replaced with a sodium carbonate/surfactant solution, wettability can be altered to water-wetness to intermediate wetness. When sodium carbonate is the only salt, both drop size and contact angle are found to decrease with salinity to an equilibrium value. But when sodium carbonate concentration is fixed at one per cent, and sodium chloride is used to change ionic strength, contact angle is not found to change much with salinity, but drop size goes through a minimum at a salinity corresponding to the optimal salinity at the experimental condition.

Oil in a narrow gap between two parallel plates remains in place when submerged in brine because of capillary forces. However, this oil is displaced by buoyancy when the brine is replaced with a sodium carbonate/surfactant solution. Displacement rate is found to be dependent on electrolyte concentration.

No spontaneous imbibition occurred when a partially oil saturated reservoir core sample was placed in formation brine. Oil was spontaneously displaced when the brine was replaced with a sodium carbonate/surfactant solution. The recovery rate was found to scale with gravity drainage, not capillary imbibition.
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Chapter 1

INTRODUCTION

The oil recovery methods that are commonly used include pressure depletion and waterflooding. On average, water flooding leaves approximately two thirds of the OOIP (original oil in place) as un-swept and residual oil in reservoir for further recovery (Wardlaw, 1996). In fractured oil-wet reservoirs, this number might be higher.

The formation of interest is a fractured and preferentially oil-wet carbonate, where water flooding is not effective because water flows preferentially in the fractures and negative capillary pressure keeps water from entering the matrix, which results in a large amount of residual oil trapped in the matrix below oil-water contact. The average matrix permeability is 100 md, but the fracture permeability is greater than 1,000 md (Chen, 2000). When water invades the reservoir, it flows into fractures instead of matrix, which leads to a high residual oil saturation.

With this background, it is evident that a cost effective enhanced oil recovery method for the targeted reservoir is needed. In the last decade, extensive research on alkaline/surfactant flooding has been carried out worldwide, Bahrain (Zubari and Sivakumar, 2003), Canada (e.g. Tayor and Nasr-El-Din, 1996), China (e.g. Han et al., 1997), France (e.g. Baviere et al., 1995), Saudi Arabia (e.g. Al-Hashim et al., 1996), USA (e.g. Nelson, 1989), to name a few. Alkaline/surfactant flooding combining principal technologies of several traditional chemical methods has great prospect for increasing oil recovery.
Clark et al. (Clark et al., 1988) estimated the ultimate recoveries of water, polymer, alkaline/polymer, and alkaline/surfactant/polymer flooding for West Kiehl field, and alkaline/surfactant/polymer flooding was expected to increase ultimate recovery dramatically.

Olsen et al. (Olsen et al., 1990), too, worked on an oil-wet carbonate reservoir. They compared oil recovery of alkaline/surfactant/polymer flooding with that of alkaline/polymer and polymer flooding, and found alkaline/surfactant/polymer flooding has a much better post-water-flood recovery than the other two. They concluded that a cost effective alkaline/surfactant/polymer flooding could be designed for application in a carbonate reservoir.

Delshad et al. (Delshad et al., 1998) predicted oil recovery of a Chinese oil field by computer simulation. Among water, alkaline, surfactant/polymer, and alkaline/surfactant/polymer flooding, alkaline/surfactant/polymer flooding exhibited the best simulation result.

The goal of this research is to develop an advanced alkaline/surfactant flooding process based on tailoring new high-performance and cost-effective surfactant for the targeted reservoir. The objectives are:

i) Understand the effect of alkali and surfactant on the overall performance,

ii) Understand the effect of surfactant structure on various performance properties and choose a proper surfactant/blend of surfactants,

iii) Understand the mechanisms of the process, and

iv) Combine the process with foam for mobility control.
In this proposal, Chapter 2 is devoted to providing background information. Extensive literature was reviewed. The reason sodium carbonate was chosen as the alkali, the theoretical basis for alkaline/surfactant flooding, and possible recovery mechanisms are elucidated.

Chapter 3 is focused on interfacial properties, such as interfacial tension, zeta potential, and wettability of brine/oil/calcite system. The reasons that carbonate formations are usually preferentially oil-wet and that sodium carbonate promotes water-wetness are discussed. The surface-active constituents (petroleum acids and bases) determine the interfacial properties.

Sodium carbonate/anionic surfactant flooding is covered in the rest of the thesis. Wettability alteration by sodium carbonate/surfactant solution is visualized in Chapter 4. Effect of aging temperature, electrolyte type and concentration, and pre-equilibration solution composition are found to be important to wettability alteration.

In Chapter 5, a method to formulate alkaline/surfactant solution is developed. Phase behavior test is used to determine the active region, followed by interfacial tension measurement with spinning drop method used to determine the optimal composition and the magnitude of the interfacial tension. Both phase behavior and interfacial tension are found to change with time. A protocol to measure reproducible interfacial tension is developed.

The effect of surfactant solution on spontaneous imbibition is tested in Chapter 7. Spontaneous imbibition in a narrow gap visualizes the process. The difference between the spontaneous imbibition in a narrow gap and in porous media is discussed. Oil
recoveries from dolomite cores by spontaneous imbibition, and from limestone cores by centrifuge imbibition with sodium carbonate/surfactant solution are reported.

Surfactant adsorption without or with sodium carbonate is measured in Chapter 8. Sodium carbonate significantly reduces the adsorption of surfactant, with the exception of one surfactant, the reason for which is also discussed.

Finally, Chapter 9 presents conclusions of this thesis, and Chapter 10 finishes with recommendations for future work.
Chapter 2

BACKGROUND

Enhanced oil recovery (EOR) is any oil recovery by the injection of materials that are not part of water flooding or any pressure maintenance operations. To recover additional oil, one must use an enhanced oil recovery method. Waterflooding recovers only 35% of the original oil on the average. Regarding the type of injectants, EOR processes can be classified into three categories (Lake, 1989; Taber et al., 1997): thermal (including steam flooding, hot-water injection, surface mining and extraction, etc.), gas (including CO₂ flooding, nitrogen injection, etc.), and chemical methods (including alkaline flooding, surfactant flooding, alkaline/surfactant/polymer flooding, gel injection, etc.). Based on oil-displacement mechanisms and EOR field project results, Taber etc. (1997) summarized the EOR screening criteria. Among the three methods, thermal and gas account for most of the EOR production. However, some of the chemical methods have great research promise, like alkaline/surfactant flooding.

This research project is devoted to finding a cost-effective alkaline/surfactant/foam recovery method for fractured, oil-wet carbonate reservoirs. It can be used as an alternative where the supply of CO₂ is insufficient or where reservoir conditions such as low pressure rule out the use of CO₂ or make its use unattractive.

In chemical flooding, chemicals are added to achieve one or more of the following effects: interfacial tension reduction, wettability alteration, and mobility control.
**Interfacial tension** (IFT) is the excess free energy or lateral stress at the interface (Miller & Neogi, 1985). Interfacial tension develops due to the imbalanced cohesive forces of like molecules within each fluid and adhesive forces of dissimilar molecules at phase boundaries. Thus the surface area of the resulting interface is minimized. Interfacial tension is commonly expressed in milli-Newtons/meter (mN/m, also dynes/cm). At fixed temperature, IFT can be changed by the addition of surface-active materials, known as surfactants.

**Wettability** is the preference of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids (Craig, 1971). Wettability is the result of interaction between fluid (oil, water, gas) and solid (such as reservoir mineral) phases. Wettability is mainly affected by composition of minerals, composition of fluids, and saturation history. Wettability study is crucial to understand the physical and chemical interactions between individual fluids and reservoir rocks.

Contact angle as a measure of wettability defines which fluid wets the solid surface. It is usually measured through the denser liquid phase. Through force balance analysis, Fig 2.1, equilibrium contact angle is defined by Young’s equation:

\[
\sigma_{ow} \cos \theta = \sigma_{cs} - \sigma_{ws}
\]  

(2.1)

![Fig. 2.1 Force balance at three phase contact line](image)
where $\sigma_{ow}$: interfacial tension between phase oil and water,

$\sigma_{ws}$: surface energy between phase water and substrate,

$\sigma_{os}$: surface energy between phase oil and substrate,

$\theta$: equilibrium contact angle.

In crude oil/water/rock system, according to the value of water advancing contact angle (contact angle measured through water phase when water is the displacing phase), the wettability of a rock is usually defined as preferentially water-wet, intermediate-wet, or preferentially oil-wet (see Fig 2.2, refer to Morrow, 1991). Due to the heterogeneity of porous rocks, there are two other categories of wettability—fractional-wet and mixed-wet. A reservoir is fractional wet if it has local areas that are strongly oil-wet, whereas most of the reservoir is strongly water-wet. It happens when the mineral composition and surface chemistry of a reservoir are variable. Mixed-wettability refers to where smaller pores are water-wet and filled with water, while larger pores are oil-wet and filled with oil. Oil recovery performance is greatly affected by wettability (for their relationship, see Section 2.3).

![Diagram showing different wettability categories](image)

Fig. 2.2 Wettability definition with advancing contact angle (Reference: Yang, 2000)

$\theta_a$: advancing contact angle.
The pressure difference between wetting and non-wetting phases is capillary pressure. Capillary pressure is caused by curved boundaries between different homogeneous fluid phases in a pore (Lake, 1989). Capillary pressure can be related with interfacial tension, wettability (contact angle), and interfacial curvature by Young-Laplace equation:

\[ P_c = 2H \sigma \]  \hspace{1cm} (2.2)

If we assume pores are of cylindrical geometry, then equation 2.2 turns into:

\[ P_c = \frac{2\sigma \cos \theta}{R} \]  \hspace{1cm} (2.3)

where \( P_c \): capillary pressure,

\( \sigma \): interfacial tension between two fluid phases,

\( 2H \): mean curvature of interface,

\( \theta \): contact angle,

\( R \): radius of the curvature.

The pressure head in the non-wetting fluid must exceed the capillary entry pressure to displace the wetting fluid and enter a pore opening. In oil-wet reservoirs, capillary effect is usually the cause for large amount of oil trapped in pores, which cannot be recovered by water flooding. Capillary forces can be overcome by ultra-low interfacial tension (interfacial tension \( \sigma \) of about zero in equation 2.3) or wettability reversal (which changes the sign of \( \cos \theta \)).

Imbibition is a fluid flow process in which the wetting phase saturation increases and the non-wetting phase saturation decreases. In a water-wet reservoir, during waterflood, water will spontaneously imbibe into smaller pores to displace oil, but in an oil-wet reservoir, capillary forces inhibit spontaneous imbibition of water.
**Mobility ratio** is defined as the ratio of mobility behind and ahead of a displacing front (Lake, 1989). At large mobility ratio, displacing fluid tends to bypass oil, which is detrimental to oil recovery. High sweep efficiency is obtained when mobility ratio is smaller than unity, but small mobility ratio means low injection rate. So a practical mobility ratio is a compromise between mobility control and injection rate. Mobility can be controlled by adding polymer and foam.

In order to formulate an effective and low cost alkali/surfactant/foam system, our focus has been concentrated on the effect of surfactant and alkali on interfacial tension reduction and wettability alteration. Since the targeted reservoir is a dolomite formation, the morphology of a real rock sample would result in complex wetting behavior, which hinders the development of understanding of wettability. Therefore, marble, which is capable of being polished, was chosen as the smooth substrate in the experiments.

The following sections will mainly focus on the various facets of experimental and theoretical approach, and the mechanisms behind them. Significant parameters affecting the process have been recognized, and will be discussed below or in the next few chapters.

### 2.1. The Subsurface Characteristics

In considering development of an enhanced oil recovery for fractured oil-wet carbonate reservoirs, one is immediately confronted with the special characteristics of this type of reservoir. The carbonate rocks are originally formed by biological or chemical precipitation. Sedimentology and diagenesis result in the complex pore geometry, and tectonic movements produce fractures (Donaldson et al., 1989). There are
several forms of carbonate minerals, including calcite — CaCO₃, magnesite — MgCO₃, dolomite — CaMg(CO₃)₂, etc. In the experiments of this research project, core samples are of dolomite, while the smooth substrates are of marble, a crystalline CaCO₃.

Contrary to silicate rocks, carbonate minerals have basic surfaces, which attract acidic compounds in crude oils, such as carboxylic acids, and therefore are mainly neutral to oil-wet. The relative wetting tendencies of carbonates are listed in Table 2.1.

<table>
<thead>
<tr>
<th>Wettability, %</th>
<th>Treiber et al.</th>
<th>Chillingarion &amp; Yen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water-wet</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Intermediate-wet</td>
<td>8</td>
<td>12</td>
</tr>
<tr>
<td>Oil-wet</td>
<td>84</td>
<td>80</td>
</tr>
</tbody>
</table>

Table 2.1 Relative wetting tendencies of carbonate reservoirs

(Refer to Tiab and Donaldson, 1996; Treiber et al, 1972; Chilingar and Yen, 1983)

The most probable targets of alkaline/surfactant flooding are reservoirs that have approached their oil production limits by injection of water On average, water flooding

![Fig. 2.3 Fractured, oil-wet carbonate reservoir](image_url)
leaves approximately two thirds of the OOIP as un-swept and residual oil in reservoir for further recovery (Wardlaw, 1996). In fractured oil-wet reservoirs, this number might be higher. In fractured reservoirs, Fig 2.3, when water is invading, the water-oil contact rises in the fracture network, and water partially or completely surrounds the oil-saturated matrix blocks. Because of the density deference between oil and water, gravity tends to move oil upward. If a reservoir is water-wet, capillary forces and gravity both favor an upward displacement of oil; but if a fractured reservoir is oil-wet, capillary forces tends to retain oil in the matrix, and water flooding would be less efficient and water breakthrough would occur earlier.

The height of oil trapped in the matrix h is related to interfacial tension, wettability, and the size of pores by the following equation:

\[ \Delta \rho gh = \frac{-2\sigma \cos \theta}{R} \]  \hspace{1cm} (2.4)

The smaller the pore is, the larger the elevation of oil, Fig 2.4.

In oil-wet systems, since oil is the phase contacting rock surfaces, surface trapping is an important factor retaining oil, especially in rocks with highly irregular
surfaces and large surface areas (Wardlaw, 1996), as shown in Fig 2.5.

![Diagram of oil trapped by surface trapping in oil-wet system](image)

Fig. 2.5 Oil trapped by surface trapping in oil-wet system. (Hirasaki and Zhang, 2003)

2.2. The Alkali

The alkali materials commonly used for oil recovery include sodium hydroxide, carbonate, silicate, phosphate, and ammonium hydroxide.

It has long been recognized that carboxylic acids are constituents of most crude oil, which in the presence of alkali, will be saponified and turned into surface-active soaps (Seifert and Howell, 1969; Seifert et al., 1972; Seifert, 1975; Farmanian et al., 1979). This natural surfactant is capable of reducing interfacial tension (see section 2.4.2); besides, alkali is favorable for wettability alteration (see section 2.4.1), and surfactant retention reduction (see section 2.4.3). Thus addition of alkali helps to improve oil recovery.

The hydrolysis chemistry of the oil and the alkali was proposed in several papers (deZabala et al., 1982, 1986; Chan and Yen, 1982; Ramakrishnan and Wassan, 1983).
The experimental results shown by Borwankar et al. (Borwankar et al., 1985) supported the chemistry proposed by Ramakrishnan and Wassan, whose approach is shown below:

![Diagram showing the mechanism of reaction between oil and alkali solution.](image)

*Fig. 2.6  Mechanism of reaction between oil and alkali solution*  
(Ramakrishnan and Wassan, 1983)

where HA₀ denotes the acid in oil phase, and HA_w the acid in aqueous phase. The deficiency of hydrogen ions in the aqueous phase will promote the generation of A_w⁻. The generated soap A_w⁻ is an anionic surfactant, which can lower interfacial tension and have the general properties of anionic surfactant, which will be described in detail in the next section.

The amount of natural soap that can be generated by the addition of alkali is characterized by the acid number of a crude oil. The acid number is the milligrams of potassium hydroxide (KOH) required to neutralize one gram of crude oil (Lake, 1989).

The most commonly used alkali candidates for enhanced oil recovery include sodium hydroxide, sodium orthophosphate, sodium carbonate, and sodium silicate. Lorenz and Peru summarized the benefits of adding alkalis based on laboratory and field test results (Table 2.2, Lorenz and Peru, 1989).
The deleterious effect of field application involving alkali was excessive alkali loss and plugging due to reaction of alkali with reservoir rocks and hardness ions. Sodium carbonate was found to be advantageous compared with others in terms of reduced consumption and shorter alkali breakthrough times due to its buffering effect (Cheng, 1986). High pH alkalis can react with sandstone, dolomite, limestone, and other formations. Compared with sodium hydroxide and sodium silicate, sodium carbonate is much less corrosive for sandstone (Burk, 1987), and much more compatible with carbonate formations, such as dolomite (Cheng, 1986). When reacting with divalent cations (Ca\(^{2+}\), Mg\(^{2+}\)), sodium carbonate causes less permeability damages compared to hydroxide and silicate (Cheng, 1986).

<table>
<thead>
<tr>
<th>Table 2.2 Alkalis in order of increasing benefits</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Lorenz and Peru, 1989)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>For oil recovery</th>
<th>None &lt; sodium hydroxide &lt; sodium orthophosphate &lt; sodium silicate &lt; (sodium silicate + sodium carbonate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>For interfacial tension lowering</td>
<td>None &lt; sodium silicate &lt; sodium carbonate &lt; sodium hydroxide</td>
</tr>
<tr>
<td>For adsorption reduction</td>
<td>None &lt; sodium hydroxide &lt; sodium carbonate &lt; sodium orthophosphate &lt; sodium silicate</td>
</tr>
</tbody>
</table>

In summary, sodium carbonate was chosen as the alkali of alkali-surfactant flooding for the following reasons:

- Sodium carbonate is inexpensive compared to other alkalis, because it is mined as a sodium carbonate-bicarbonate mineral trona;
• Sodium carbonate reduces the extent of ion exchange and mineral dissolution compared with other alkali;

• Sodium carbonate suppresses calcium concentration;

• Carbonate precipitates less adversely effect permeability compared to hydroxides and silicates.

• Sodium carbonate promotes water-wet conditions (see the next chapter).

Because of the incompatibility of alkalis with divalent ions, soft water should be used for making alkaline solution. Moreover, a preflush is needed to separate the reservoir brine from the alkaline slug if the hardness of the formation water is high.

2.3. The Surfactants

Surfactants, or surface-active materials, possess one or more hydrophilic and one or more hydrophobic group(s) in a single molecule. The polar portion is usually called the head, and the hydrophobic portion (usually hydrocarbon chain) the tail. The structure (e.g. the length of the hydrocarbon chain, being straight or branched) of the tail decides the hydrophilicity of a surfactant. Surfactants exist at the interface of water and an adjacent fluid (such as oil, air) as a monolayer at low concentration. Their unique property is their ability to adsorb strongly at various interfaces and to lower the interfacial surface energy.

According to the ion charge of the head group, surfactants are classified into 4 groups: anionic (such as sodium dodecyl sulfate), cationic (such as dodecyltrimethylammonium bromide), nonionic (such as ethoxylated fatty alcohol), and zwitterionic (such as 3-dimethyldodecylamine propane sulphonate) surfactants.
2.3.1. Micelle and Microemulsion

When a surfactant is added to a solvent at very low concentration, the dissolved surfactant molecules disperse in the solution as monomers. As the surfactant concentration increases, surfactant molecules tend to form aggregates or micelles containing often 50-100 or more monomers each. Above a specific surfactant concentration, called the critical micelle concentration (CMC), addition of surfactant will only result in the increase of micelle concentration and little change in monomer concentration. This is shown in Fig 2.7.

![Image of micelles and monomers](image)

**Fig. 2.7 Schematic definition of the critical micelle concentration**  
(From Lake, 1989)

If the solvent is water, the micelles form with tail portion directed inward and head portion outward. The interior of such micelles is capable of solubilizing organic compounds. For a hydrocarbon solvent, the orientation of the surfactant molecules is reversed, and the interior has the ability to solubilize water. Thus, while oil and water
have very limited solubility for the other phase, the addition of a surfactant at a concentration above its CMC can greatly increase the solubility. This micelle solution of oil and water is called microemulsion.

Microemulsions can be of water-external, oil-external, or bi-continuous depending on which phase is continuous, water, oil or both. The configuration depends on many factors, such as surfactant, salinity, and temperature.

Microemulsion is a term in contrast to macroemulsion. Microemulsion is thermodynamically stable, while macroemulsion is not. The other difference between them is the size of macroemulsion droplets is usually much larger, so that while microemulsion looks translucent, macroemulsion looks opaque.

2.3.2. Phase Behavior of Microemulsion

The phase behavior of microemulsions is very important. The study of it allows determination of ultra-low interfacial tension, which is key to enhancing oil recovery.

The microemulsion phase behavior depends on a number of factors, including the types and concentration of surfactants, cosurfactants, oil, brine, temperature, etc. Generally, increasing brine salinity decreases the solubility of an ionic surfactant in

![Schematic phase behavior of surfactant-brine-oil](image)

Fig. 2.8 Schematic phase behavior of surfactant-brine-oil (Nelson, 1979)
aqueous phase. Thus, brine salinity has a significant effect on phase behavior.

According to salinity, the phase behavior can be divided into three classes (Healy, et al., 1976; Nelson and Pope, 1977; Nelson, 1979), illustrated in Fig 2.8. At low salinity, a surfactant exhibits good aqueous phase solubility. Thus the surfactant stays in the aqueous phase and forms water-external microemulsion, which coexists with excess oil. Since the formed microemulsion is denser than oil, it resides below the oil phase and is called lower phase microemulsion. At high salinity, electrostatic forces dramatically decrease the surfactant’s solubility in aqueous phase, and the surfactant is driven into oil phase to form oil-external microemulsion in coexistence with excess brine. This microemulsion is an upper phase microemulsion. At intermediate salinity, a bicontinuous microemulsion is formed in equilibrium with both excess oil and excess brine, and the microemulsion is called middle phase microemulsion. An example of phase behavior change with salinity is illustrated in Fig 2.9.

System containing a petroleum sulfonate surfactant, a short-chain alcohol, oil and brine

NaCl concentration increases →

Fig. 2.9 Effect of salinity on microemulsion phase behavior
(Miller, 1985)

Several cations were tested as to their effect on phase behavior of anionic surfactants (Martin and Oxley, 1985), and their effect was found in the following order:
\[ \text{K}^+ > \text{Na}^+ \rightarrow \text{NH}_4^+ \]

But anions were found to have little or no effect on the phase behavior studied.

The microemulsion phase behavior can be represented by ternary phase diagrams (Healy, et al., 1976; Nelson, 1979), as shown in Fig 2.10. Since the slope of the tie lines of lower phase microemulsion is negative, this type of phase environment is also called type II (-), or Winsor type I. Similarly, middle phase microemulsion is also called type III/Winsor type III, and upper phase microemulsion is called type II (+)/Winsor type II.

![Ternary representation of microemulsion phase diagram](image)

Fig. 2.10 Ternary representation of microemulsion phase diagram (Healy et al, 1976)

2.3.3. Phase Behavior and Interfacial Tension

Healy and Reed (Healy and Reed, 1974) first correlated microemulsion phase behavior with interfacial tension. The benefit of the combination of the two is: while the phase behavior tests give the active region relatively easily, the quantitative interfacial tension measurement determines the optimal salinity/surfactant concentration, the magnitude of the interfacial tension and quantifies the effectiveness for oil displacement.
Since the microemulsion phase behavior changes progressively with salinity, it is reasonable to deduce that IFT too is a function of salinity, as proved to be true (Healy et al., 1976). Fig 2.11 is a typical plot of IFT between equilibrium phases as a function of salinity.

In the figure, $\sigma_{mo}$ and $\sigma_{mw}$ represent the interfacial tension between the microemulsion/excess oil phase and microemulsion/excess water phase respectively. $\sigma_{mo}$ decreases significantly with increasing salinity as phase behavior changes progressively from II (-) to III, while $\sigma_{mw}$ increases drastically with salinity as phase behavior changes from III to II (+). The salinity where $\sigma_{mo} = \sigma_{mw}$ is called optimal salinity. At optimal salinity, the system interfacial tension in many systems is so small that capillary effect almost disappears, which is one of the main mechanisms for enhanced oil recovery with surfactants.

The reason that interfacial tension is the lowest at optimal salinity can be explained by solubilization parameters (Fig 2.11). Solubilization parameter $Vo/Vs$ is defined as the volumetric ratio of solubilized oil to surfactant, and $Vw/Vs$ is water to
surfactant. \( \text{Vo/Vs} \) increases with salinity while \( \text{Vw/Vs} \) decreases with salinity. At the salinity where they cross each other, equal amount of water and oil is solubilized.

It is noteworthy that in the past a co-solvent (usually an alcohol) was often added to prevent the formation of liquid crystal, which is detrimental to oil recovery. But in recent years, because of the use of branched surfactants, the addition of an alcohol is not necessary. Alcohol is not used in the current research also because it increases interfacial tension and destabilizes foam.

### 2.3.4. Surfactant Retention

For any surfactant-involved EOR process, surfactant loss is a crucial criterion to its economical feasibility. Surfactant may be retained in the reservoir in several ways, the most important ones including adsorption at the solid-liquid interface, precipitation, ion exchange, phase trapping, adsorption at the oil-water interface, and deactivation of surfactant by binding to asphaltenes (Lake, 1988; Mannhardt and Novosad, 1994; Green and Willhite, 1998).

Surfactant adsorption at the oil-water interface depends on the surface excess of surfactant and the amount of interface present. The latter cannot be easily measured. The amount of surfactant deactivated by binding to asphaltenes depends on asphaltene content in a crude oil and the amount of surfactant retained by phase trapping. The mechanisms of surfactant retention by adsorption onto solid surface, precipitation, ion exchange, and phase trapping will be discussed in detail below.
2.3.4.1. Adsorption at the solid-liquid interface

The most important cause of ionic surfactants adsorbing onto a solid is often the electrical interaction between the charged solid surface and surfactant ions (Aveyard, 1984; Wesson and Harwell, 2000). Most reservoir rocks are charged: at neutral pH, sandstone is primarily negatively charged (silica may be negatively charged, calcite and clay edges may be positively charged), and calcite and dolomite are positively charged. Solid surfaces are charged due to different mineralogy and charge imbalance caused by imperfections in the crystal lattice and preferential adsorption of potential determining ions, and the adsorption of surfactants can be explained by electrical double layer theory (Wesson and Harwell, 2000).

Surfactant adsorption is usually presented as the amount of surfactant adsorbed per unit of solid surface area versus equilibrium surfactant concentration. A typical monoisomeric anionic surfactant adsorption isotherm is shown in Fig 2.12.

At low surfactant concentration (Region I), the adsorption of surfactant complies

---

Fig. 2.12 Schematic adsorption isotherm of a monoisomeric anionic surfactant (Wesson and Harwell, 2000)
with Henry’s law. As surfactant concentration increases to Region II, adsorption increases most rapidly, which indicates chain-chain interactions in the adsorbed layer (Aveyard, 1984; Wesson and Harwell, 2000). At higher concentrations (Region III), a decrease in the rate of increase of adsorption with concentration is observed. One explanation is that the tail-tail interaction continues for Region II, but at a different rate (Wesson and Harwell, 2000). In Region IV, little or no adsorption increases with surfactant concentration, because CMC is reached, and there is no increase in monomer concentration.

Surfactant adsorption onto reservoir rock is a function of surfactant type, chain length, and concentration; pH; salinity; rock composition; clay content; temperature, etc. Walker et al. (Walker et al., 1979) found that the addition of salt lowered anionic surfactant adsorption onto silica surface as a result of depression of surfactant CMC. But they also found the addition of salt had a totally opposite effect of surfactant adsorption when the solid surface used was Berea sandstone, as did others (Glover et al., 1978). Summaries of the other effects on adsorption can be found in literature (Green and Willhite, 1998; Wesson and Harwell, 2000).

2.3.4.2. Precipitation

Presence of cations, especially multivalent cations can lead to precipitation of anionic surfactants. Factors influencing precipitation of anionic surfactants include cation valence, salt concentration, surfactant concentration, alcohol concentration, temperature, etc. Multivalent cations reduce the solubility of surfactants. The higher the cation valence, the lower the surfactant solubility (Green and Willhite, 1998). Surfactant
precipitation first increases with surfactant concentration, but after CMC is reached, the precipitate will re-dissolve because of fixation of multivalent ions (Pearson and Lawrence, 1967). Increase of NaCl concentration was proved to have the same effect (Celik et al., 1982). Addition of alcohol increases the solubility of a surfactant when the alcohol/surfactant ratio is sufficiently high (Green and Willhite, 1998).

2.3.4.3. Ion Exchange

Ion exchange happens between electrolytes in solution and those attached to a solid surface. Clays in the reservoir have the capacity to exchange monovalent and divalent cations. By mass action, the controlling equation is:

\[
\frac{[Na^+]_{clay}}{[M^{2+}]_{clay}} = K \frac{[Na^+]_{brine}}{[M^{2+}]_{brine}} \quad \text{(Nelson, 1989)}
\]  

If the sodium to multivalent cation ratio of the injected surfactant solution is larger than that originally in the reservoir, clay will adjust the ratio by releasing multivalent ions into solution and taking sodium ions out, which results in the over-optimum behavior of the surfactant solution.

2.3.4.4. Phase Trapping

When a system is in II (+) phase environment, surfactants exist in the oil phase as upper phase microemulsion. Such a system exhibits relatively high interfacial tension, and oil phase could be trapped as residual oil (Lake, 1988; Green and Willhite, 1998). Multivalent ions were found to lower optimal salinities (Glover et al, 1978, Green and
Willhite, 1998). This effect could cause a type III system change to II (+), and retain surfactant by phase trapping.

Surfactant retention can be significantly reduced by adding some alkaline chemicals (see Section 2.4.3).

2.4. Displacement Mechanism of Alkaline-Anionic Surfactant Flooding

Alkaline/surfactant flooding has long been demonstrated to be a prospective improved oil recovery process (for example, Krumrine et al., 1982; Nelson et al., 1984). Quite a few mechanisms are associated with displacement involving alkali and surfactants, but the main effects alkali-anionic surfactant flooding depends on are wettability alteration, ultra-low interfacial tension, and low surfactant retention (Mayer et al., 1983; Lake, 1989; Green and Willhite, 1998).

Taber (Taber, 1968) found through experiments that no residual oil could be displaced until a critical value of $\frac{\Delta P}{L\sigma}$ was exceeded, where $\Delta P$ is the pressure drop across the distance $L$ and $\sigma$ is the interfacial tension between the oil and water. This $\frac{\Delta P}{L\sigma}$ can translate to an equivalent Capillary Number through Darcy’s law (Melrose and Brandner, 1974):

$$N_{ca}^* = \frac{u\mu_w}{\sigma_{aw}}$$

or

$$N_{ca} = \frac{v\mu_w}{\sigma_{aw}}$$

Where $N_{ca}^* = \phi N_{ca}$, $u$ and $v$ represents the Darcy and interstitial velocity respectively.
Stegemeier (Stegemeier, 1977) correlated $N_{ca}^*$ with residual oil saturation for water-wet system. For $N_{ca}^* < 10^{-5}$, there is no mobilization, while as $N_{ca}^* > 10^{-5}$, the fraction of the residual oil mobilized increases sharply with increasing capillary number. The reduction of interfacial tension will result in the increase of capillary number.

2.4.1 Wettability Alteration

Wettability plays a very important role in oil recovery. For decades, much effort has been made towards understanding the relationship between wettability and oil recovery efficiency. Earlier, oil recovery was reported to decrease with increasing oil wettability with sandstone (Donaldson et al, 1969; Owen and Archer, 1971). But Salathiel (Salathiel, 1973) using sandstone presented evidence of higher residual oil saturation at strongly water-wet conditions compared with that at mixed-wet conditions. Morrow and Jadhunandan (Morrow, 1990; Jadhunandan and Morrow, 1995) with Berea sandstone showed that oil recovery by water flood has a maximum when the wettability is close to neutral wet.

Graue et al. (Graue, et al., 1999) found in their experiments with chalk of wettability ranging from water-wet to neutral-wet that oil recovery by spontaneous imbibition decreased with increasing aging time (which means increasing oil-wetness), but that oil recovery reached an maximum at close to neutral-wet if followed by water-flooding.

McDougall and Sorbie (McDougall and Sorbie, 1995) concluded with their simulation results that oil recovery should be maximum if the network consisted of 50% oil-wet and 50% water-wet pores.
It has long been recognized that addition of alkali results in wettability alteration, which in turn, leads to increase in oil recovery. Wagner, Leach and co-workers (Wagner and Leach, 1959; Leach et al., 1961) found that wettability of sand packs or sandstone cores could be varied by changing pH and salinity of the water phase. Mungan (Mungan, 1966) with alumnum (Al₂O₃) and sandstone cores, Ehrlich et al. (Ehrlich et al., 1974) with sand pack, and Enrich and Wygal (Enrich and Wygal, 1977) with Berea sandstone reported that after flooding with NaOH solution, water relative permeability of core samples was decreased, which gave a more favorable mobility ratio, and wettability was reversed from oil-wet to water-wet, both of which contributed to the increased oil recovery. Emery et al. (Emery, et al., 1970) found that after NaOH flood, sand pack or sandstone cores had become water-wet, which resulted in a great part of the additional recovery. But they also admitted that interfacial tension reduction and breaking of rigid films at oil-water interfaces could also contribute to the additional oil recovery. Cooke et al. (Cooke et al., 1974) claimed that alkali flooding improved oil recovery in sand packs or sandstone cores, with wettability changing from strongly water-wet to preferentially oil-wet. With an alkaline formulation containing 0.5% sodium tripolyphosphate and 2.2% sodium carbonate, Olsen et al. (Olsen et al., 1990) found that the carbonate rock surface was shifted to a less oil-wet condition. Nasr-El-Din et al. (Nasr-El-Din et al., 1992), working with Berea sandstone, investigated the effect of sodium carbonate concentration on alkali/surfactant/polymer flooding, and concluded that at high carbonate concentration (≥ 2%), wettability alteration plays a major role in enhanced oil recovery.
Lake (Lake, 1989) proposed an explanation to the effect of wettability on oil recovery: the change of wettability is more important than the final wettability of the medium. The change of wettability will result in fluid redistribution in pore structure.

2.4.2 Interfacial Tension Reduction

In addition to wettability alteration, interfacial tension reduction has long been recognized as one of the most important factors in enhanced oil recovery (Mungan, 1964). In fact, in most of the research on alkaline/surfactant/polymer flooding conducted in the last decade, people look more into the effect of surfactant solution on interfacial tension reduction, without considering wettability alteration (for example, Arihara, et al., 1999).

Ehrlich et al. (Ehrlich et al., 1974) and Cooke et al. (Cooke et al., 1974) found the addition of alkali could lower interfacial tension between oil and water, but also concluded that low interfacial tension is a necessary but not sufficient condition for obtaining a successful alkali flood.

Jennings and coworkers (Jennings, 1974; Jennings et al., 1974) investigated interfacial tension behavior of a large number of crude oil samples with NaOH solutions of different concentration. They measured interfacial tension with pendant drop method, at about room temperature, and found some oil showed little change in interfacial tension, many showed a very low interfacial tension at only one point, and others displayed very low interfacial tension over a broad range of caustic concentrations. For many systems with low interfacial tension, interfacial tension value was believed to be smaller than
0.001 dyne/cm. They also found multivalent, esp. calcium ion precipitated in contact with caustic solution, and increased interfacial tension.

Krumrine et al. (Krumrine et al., 1982) tested the effect of several alkaline chemicals on dilute surfactant systems. They found, regardless of the alkaline species, low interfacial tension could be achieved with high pH solutions.

Nasr-El-Din et al. (Nasr-El-Din et al., 1992) investigated the effect of sodium carbonate concentration on alkali/surfactant/polymer flooding, and concluded that at low carbonate concentration (≤ 1%), low interfacial tension plays a major role in enhanced oil recovery; whereas at high carbonate concentration, wettability alteration is a more important mechanism.

A large amount of effort has been directed at dynamic interfacial tension study. It was found that interfacial tension minima existed (Rubin and Radke, 1980; Trujillo, 1983; Borwankar and Wasan, 1986) in acidic oil/alkali systems during dynamic tension measurements. Rubin and Radke, and Trujillo (Rubin and Radke, 1980; Trujillo, 1983) attributed these tension minima to the existence of desorption barriers (desorption of the soap from the interface to the aqueous phase). Borwankar and Wasan (Borwankar and Wasan, 1986) concluded that the higher the desorption barrier is relative to the adsorption barrier (dissociative adsorption of the acid), the lower is the minimum interfacial tension. Sharma et al. (Sharma et al., 1989), however, found that at high pH, a maximum in interfacial tension existed, followed by a minimum at a later time. Nasr-El-Din and Taylor (Nasr-El-Din and Taylor, 1992; Taylor and Nasr-El-Din, 1996) examined dynamic interfacial tension of crude oil/alkali/surfactant system. They found that the time
required to reach minimum IFT depended on the alkali/surfactant mass ratio, and the dynamic IFT process was diffusion controlled.

In the last two decades, there has been extensive research on alkaline/surfactant flooding, and ultra-low interfacial tension was recognized to be one of the most important mechanisms in the increase of oil recovery (Nelson et al., 1984; Martin et al., 1985; Shuler, et al., 1989; Olsen et al., 1990; French and Burchfield, 1990; Falls et al., 1992; Baviere et al., 1994 Baviere et al., 1995; Gao et al., 1995; Song et al., 1995; Al-Hashim et al., 1996; French, 1996; Gao et al., 1996; Wang et al., 1997; Wang et al., 1997; Qu et al., 1998; Tong et al., 1998; Wang et al., 1998; Arihara et al., 1999; Wang et al., 1999; Qiao et al., 2000; Vargo et al., 2000; Manrique et al., 2000; Hernandez et al., 2001)

Rudin and Wasan (Rudin and Wasan, 1992) proposed the mechanisms for lowering interfacial tension through their experiments with acidic oil (decane + oleic acid). They suggested that un-ionized acid played a major role in affecting interfacial tension: the un-ionized acid partitioned the synthetic surfactant out of the aqueous phase, and the minimum interfacial tension occurs when the partition coefficient is about unity.

2.4.3 Low Surfactant Adsorption

Alkali as a sacrificial material lowers surfactant adsorption in alkaline/surfactant enhanced recovery process. Many works (Krumrine et al., 1982; Nelson et al., 1984; French and Burchfield, 1990; Baviere et al., 1994; Baviere et al., 1995; Song et al., 1995; Al-Hashim et al., 1996; Wang, 1997; Manrique, 2000; Hernandez et al., 2001) proved this to be the case.
The mechanisms for sodium carbonate reducing surfactant adsorption include the change of charge of the rock surface (see chapter 3), and the reduction of hardness ions (Krumrine et al., 1982).

Alkaline/Surfactant enhanced flooding is a very complicated process, which involves many mechanisms, such as emulsification (Johnson, 1976; Al-Hashim et al., 1996; Tong et al., 1998), bridging etc. (Tong et al., 1998). However, wettability alteration and ultra-low interfacial tension are the most important ones, which determine fluid flow modes in the matrix, which will be discussed in section 2.6.

2.5. Cationic Surfactant Flooding

Aside from anionic surfactants, other types of surfactants have been investigated in their effects in enhanced oil recovery, for example, non-ionic surfactant (Chen et al., 2000), cationic surfactant (Austad and Milter, 1997; Austad et al., 1998; Standnes and Austad, 2000; Standnes et al., 2002, etc.), and blends of cationic and anionic surfactants (Wellington and Richardson, 1995). Since cationic surfactants were proved to be effective in promoting spontaneous imbibition of water into oil-wet cores, the mechanisms associated with this process will be discussed in detail here. Refer to Chapter III for experimental results.
The main effect cationic flooding depends on is wettability alteration (Austad and Milter, 1997; Austad et al., 1998; Standnes and Austad, 2000; Standnes et al., 2002), assisted by low interfacial tension (which is much higher compared with that obtained by alkali-anionic solution, see Chapter III and IV for experimental values) and low surfactant adsorption (Standnes and Austad, 2000).

![Diagram of water flow direction with symbols representing cationic surfactant and anionic surface active organic materials present in oil.](image)

Represents cationic surfactant
Represents anionic surface active organic materials present in oil

Fig. 2.13 Mechanism for the wettability alteration by cationic surfactants in a pore

The proposed mechanism (Fig 2.13) of wettability alteration (Austad and Milter, 1997; Austad et al., 1998; Standnes and Austad, 2000) is the formation of ion-pair between the positively charged surfactant monomer and the negatively charged adsorbed material, mainly carboxylic groups. The desorption makes the rock surface more water-wet, and water will spontaneously imbibe into the matrix due to capillary effect. The desorbed material may exist in the micelles, or in the oil phase in the form of ion-pairs.
2.6. Spontaneous Imbibition

Spontaneous imbibition is the process in which a wetting phase is drawn into the porous medium by capillary forces. In naturally fractured systems with a high degree of interconnection, imbibition forces must be strong for a water or surfactant-enhanced water flood to be effective.

Depending on the ratio of gravity to capillary forces, spontaneous imbibition can occur in either co-current or counter-current modes. Schechter et al. (Schechter et al, 1991, 1994) found that for systems with low permeability and high interfacial tension between the wetting and non-wetting phases, capillary forces dominate and counter-current flow is initiated, whereas for systems with moderately low interfacial tension and high permeability, gravity segregation controls and co-current flow is induced.

Spontaneous imbibition rate is a function of matrix permeability, size, shape, wettability, heterogeneity, and boundary conditions, viscosities of the phases, interfacial tension, etc. (Babadagli, 2001). Imbibition rates with different wettability can be several orders of magnitude slower and displacement efficiencies range from barely measurable to better than very strongly water-wet (Morrow and Mason, 2001).

The primary driving force for spontaneous imbibition in strongly water-wet conditions is capillary forces. If the porous medium is regarded as cylindrical capillaries with an average radius of r, and the flow in all capillaries is assumed to be in the same direction, and co-current, the capillary imbibition rate is given by the Washburn equation:

\[
l^2 = \frac{rt\sigma \cos \theta}{2\mu}
\]

(2.8)

Where l: the length of flow;

\[t: \text{the time of flow;}
\]
\( \sigma \): interfacial tension;

\( \theta \): contact angle;

\( \mu \): fluid viscosity.

Regarding the usually immense length of formation, spontaneous imbibition induced by capillary forces is very slow—proportional to the square of the matrix block length. But gravity dominated flow can substantially increase imbibition rates (Schechter et al., 1991). Gravity dominated flow depends on Gravity Number, which provides a means to compare the importance of gravity forces relative to viscous forces during a displacement of oil by water:

\[
G = \frac{kk_{r_w}AD \rho g \sin \theta}{1.0133 \times 10^6 q_i \mu_w} \quad \text{in Darcy units (Dake, 1978)} \quad (2.9)
\]

Where \( G \): dimensionless gravity number,

\( k \): absolute permeability,

\( k_{r_w} \): end point relative permeability to water,

\( A \): cross section area of the flow channel,

\( \Delta \rho \): density difference between water and oil,

\( \theta \): dip angle of the reservoir,

\( q_i \): total flow rate,

\( \mu_w \): viscosity of water.

For systems that are preferentially oil-wet, spontaneous imbibition of brine would not happen because capillarity retains oil in the matrix. The introduction of alkaline/surfactant solution will enhance oil recovery by both wettability alteration and interfacial tension reduction. Because of the ultra-low interfacial tension, oil will leave
the matrix by buoyancy, and surfactant solution will come in to occupy the place left by oil. Flow will be in the mode of co-current flow (Fig. 2.14).

2.7. Foam for Mobility Control

In surfactant flooding, mobility control has been mainly accomplished by addition of polymer. An alternative is in situ generation of foam. The former is expensive because of the cost of polymer, while the latter is low-cost since surfactants already exist in the system, and the only additional cost is the injection of gas.

The generated foam can reduce the mobility of water and divert at least some of the displacing aqueous phase into the high permeability/unswept region, and recover additional oil. In fractured formations foam is likely to be generated externally and injected into the fracture system.

The thesis does not include work on foam for mobility control, so it will not be further discussed here.

Fig. 2.14 Spontaneous displacement of oil by surfactant solution
Chapter 3

INTERFACIAL PROPERTIES AND WETTABILITY OF CARBONATE SURFACES

3.1. Interfacial Tension of Crude Oil/Brine Interface

It is important to have a representative oil sample when designing an enhanced oil recovery process which is based upon interfacial phenomena, since oil samples could be contaminated with surface-active materials such as emulsion breaker, scale inhibitor, or rust inhibitor. A simple test for contamination is to measure transient interfacial tension at crude oil/brine interface.

Reisberg and Doscher (Reisberg and Doscher, 1956) showed that crude oil/brine interfacial tension can be affected by aging, contraction and expansion of the interface, and the pH of the brine phase. Crude oil/brine interfacial tension decreases with time due to the interfacial deposition of surface-active constituents naturally present in crude oils, which is kinetically controlled by the diffusion and/or adsorption/desorption of the surface-active components from the bulk oil to the interface. Because of the presence of acidic and basic functional groups, the interfacial charge and concentration of the surface-active compounds depend on pH. Therefore, the interfacial tension is a function of pH.

Methods for interfacial tension measurement include capillary rise, maximum bubble pressure, drop weight, Wilhelmy plate, pendant drop, sessile drop, spinning drop, etc (Adamson, 1976; Miller and Neogi, 1985). Pendant drop method is commonly used in measuring relatively high tensions, although there have been numerous efforts in
improving the method to accurately measure ultra-low tensions (Satherley et al., 1990; Lin and Hwang, 1994). This method is relatively easy to carry out, and capable of both static and dynamic tensions. Therefore it was used here to measure crude oil/brine interfacial tensions.

The schematic setup of the pendant drop apparatus is shown in Fig. 3.1. A Ramé-Hart optical bench was used with a Javelin video camera. During a measurement, the optical cell was filled with brine, while the syringe was filled with oil. First an oil drop was expanded slowly and held on the tip of the U-shaped needle which was connected to a micro syringe. The light source directly behind the drop illuminated the drop in the surrounding brine. For best images, a diffuse white-lit background was needed, which is achieved by using a piece of white tissue paper right before the lamp. Through the optical lens, the video camera acquired profiles of the drop, which were digitized by the frame-grabber and acquisition software, then fitted to Young-Laplace equation (see equation 2.2), and transient interfacial tensions were computed.
The pendant drop method can measure the interfacial tension at fluid-fluid interfaces with an accuracy of ± 0.3 mN/m (Anastasiadis et al., 1987; Hansen and Rødsrud, 1991; Lin et al., 1991, Hansen, 1993). The most influential factors on the accuracy of a pendant drop tension measurement include drop size, needle size, and zoom. The size of the drop should be maximized when possible (it is a compromise between the maximum drop size and the required duration of the drop). The zoom should allow the maximum size drop to form. The needle size should be chosen according to capillary constant:

\[
a = \frac{\sigma}{\sqrt{(\Delta \rho) g}} \quad \text{(Adamson, 1976)}
\]  

(3.1)

where \(\sigma\) is the interfacial tension between oil and water, and \(\Delta \rho\) represents the density difference between the two fluids. The closer the needle diameter matches the capillary constant, the more accurately the interfacial tension is computed.

Fig. 3.2 Transient crude oil/brine IFT
Transient interfacial tension of 0.1 M NaCl brine and eight crude oils samples, MY1-8, which came from the same reservoir, but at different times and locations were measured at room temperature (Fig. 3.2). MY1 was aged according to the following procedure: 5 ml of MY1 was mixed with 1 liter 0.1 M NaCl and aged at 80°C for 24 hrs. Then the aged brine was removed, and fresh brine was added. The aging process was repeated twice. It is obvious that interfacial tension of aged MY1, fresh MY1 and MY2 is much lower than that of the other oils and the typical crude oil/brine interfacial tension, which is in the range of 20-30 dyne/cm (private communication with G. J. Hirasaki). This indicates that MY1 and MY2 are probably contaminated with surface-active materials, which slowly diffuse to the interface and reduce the interfacial tension. Samples MY3—MY6 have a much higher initial interfacial tension, and the value does not change significantly with time. All of the rest of the experimental results shown in this thesis were obtained with crude oil samples MY3 and MY4, which came from the same well and have very similar properties.

The other properties of crude oil samples MY1-MY4 are listed in Table 3.1. The higher acid number and viscosity for MY1 compared to the other samples again suggested that it is an outlier, and may be contaminated.

<table>
<thead>
<tr>
<th>Oil ID</th>
<th>* API</th>
<th>RI@20°C</th>
<th>Density@20°C, gm/ml</th>
<th>Visc. @25°C, C. cp.</th>
<th>* Acid #, mg KOH/g oil</th>
<th>** Base #, mg KOH/g oil</th>
<th>B/A</th>
<th>Saturates, %</th>
<th>Aromatics, %</th>
<th>Resins, %</th>
<th>Asphaltenes, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MY1</td>
<td>27.2</td>
<td>1.4979</td>
<td>0.8887</td>
<td>22.6</td>
<td>0.50</td>
<td>1.17</td>
<td>3.2</td>
<td>2.34</td>
<td>64.02</td>
<td>24.59</td>
<td>9.67</td>
</tr>
<tr>
<td>MY2</td>
<td>28.9</td>
<td>1.4941</td>
<td>0.8789</td>
<td>18.1</td>
<td>0.17</td>
<td>1.16</td>
<td>3.7</td>
<td>6.82</td>
<td>62.52</td>
<td>23.72</td>
<td>12.68</td>
</tr>
<tr>
<td>MY3</td>
<td>28.2</td>
<td>1.4955</td>
<td>0.8830</td>
<td>19.1</td>
<td>0.20</td>
<td>1.17</td>
<td>3.3</td>
<td>5.85</td>
<td>61.86</td>
<td>24.83</td>
<td>12.22</td>
</tr>
<tr>
<td>MY4</td>
<td>28.4</td>
<td>1.4943</td>
<td>0.8818</td>
<td>18.8</td>
<td>0.22</td>
<td>1.23</td>
<td>3.4</td>
<td>5.59</td>
<td>65.28</td>
<td>23.69</td>
<td>9.94</td>
</tr>
</tbody>
</table>
* Acid number is defined as the amount of base, expressed in milligrams of potassium hydroxide (KOH) per gram of crude oil, required to titrate the sample in a nonaqueous solvent to a well-defined inflection point.

** Base number is defined as the amount of petroleum base expressed in terms of milligrams of potassium hydroxide (KOH) per gram of crude oil.

### 3.2. Electrostatic Properties at Interfaces

The electrical, or zeta potential of the crude oil/brine interface and of the brine/mineral interfaces is one of the most important factors in the determination of the wettability of crude oil/brine/mineral systems (Buckley et al., 1989; Hirasaki, 1991; Dubey and Doe, 1993). Zeta potential and its measurement will be discussed in this section.

Particles suspended in water and any liquid of high dielectric constant are usually charged, which can happen in several ways, which include the ionization or dissociation of surface groups; and the adsorption of ions from solution onto a previously uncharged surface (Israelachvili, 1991). This net surface charge will be balanced by counter-ions, and an electrical double layer is formed in the region of the particle-liquid interface. When subjected to an electric field, a charged particle experiences a force and moves through the medium. The relative motion between the particle and the medium occur at the shear plane, inside which the solvent moves with the particle. The electrical potential between the shear plane and the bulk solution is called zeta potential.
When a charged particle in solution is subjected to an applied electric field, it accelerates until the viscous force equals the electric force, and a steady velocity is reached. Zeta potential is related to the terminal velocity by Henry equation:

$$
\zeta = \frac{1.5\mu \nu}{E\varepsilon \varepsilon_0 f(\kappa a)}
$$

(3.2)

where $\zeta$: zeta potential,

$\mu$: viscosity of the medium,

$\nu$: terminal velocity,

$E$: electric field strength,

$\varepsilon$: dielectric constant (relative permittivity) of the medium,

$\varepsilon_0$: permittivity of free space,

$f(\kappa a)$: correction factor which takes into account the thickness of the double layer and particle diameter. $\kappa$ is the inverse Debye length – the thickness of the double layer, and $a$ is the particle diameter. For large particles and high electrolyte concentration, or $\kappa a > 100$, $f(\kappa a)$ is 1.5 (Smoluchowski approximation). For small particles in low dielectric constant media, or $\kappa a < 1$, $f(\kappa a)$ becomes 1.0 (Hückel approximation) (Vold and Vold, 1983).

The experiment of setting up a potential gradient in a solution containing charged large particles (such as colloidal particles) and determining their rate of motion is called electrophoresis (Adamson, 1976). The instrument used to make zeta potential measurements in our laboratory utilizes this technology. The device is called DELSA (Doppler Electrophoretic Light Scattering Analyzer) 440 from Coulter Electronics.
In zeta potential measurements, laser beams directed onto particles under electrophoretic motion are scattered as they hit the moving particles. When the scattered light is combined with the unscattered reference beam, the intensity signal fluctuates, the rate of which is proportional to the velocity of the particles. Thus the velocity, and consequently the zeta potential, can be determined.

In addition to electrophoresis, electroosmosis also occurs in the sample chamber due to the charged chamber walls. This leads to a parabolic electroosmotic flow profile (Fig. 3.3). There is a point in the chamber at which the electroosmotic flow is zero. This point is called stationary layer, where velocity and therefore zeta potential can be measured free of electroosmotic error.

![Diagram](image)

Fig. 3.3 Cross-sectional parabolic flow profile in sample chamber channel under electric field (arrows indicate direction and magnitude of electroosmotic flow) (Yang, 2000)

Zeta potentials of crude oil MY1/brine, calcite/brine, and calcite/sodium carbonate and or sodium bicarbonate interfaces are plotted in Fig 3.4 (refer to Appendix A for experimental procedures). At pH 6-8, zeta potential of MY1/brine is negative, and that of calcite/brine (0.02 M NaCl) is positive. The opposite charge between the two interfaces results in an electrostatic attraction between them, which tends to collapse the brine film and bring the oil in direct contact with the mineral surface. Thus, such system
can be expected to be non-water-wet around neutral pH (Morrow et al, 1973; Hansen et al, 2000). This result explains why more than 80% of carbonate formations are preferentially oil-wet (Treiber et al, 1972). However, when 0.02 M NaCl is replaced by 0.1 N Na$_2$CO$_3$/NaHCO$_3$, zeta potential of calcite becomes negative because calcium, carbonate and bicarbonate ions are potential determining ions. The repulsion between the oil and calcite surfaces tends to stabilize a brine film between them. This is one of the reasons sodium carbonate was chosen as the alkali in this project. This result also explains the wettability alteration result to be shown in chapter 6, and surfactant adsorption results in chapter 8.

The isoelectric point (IEP), the pH where the charge at the interface goes from positive to negative, of crude oil MY1 is close to 2.4. Both positively charged and negatively charged groups can be present at an interface simultaneously. The potential of crude oil/brine interface is a combined contribution from surface-active acidic and basic functional groups. At pH lower than IEP, basic groups tend to associate with hydrogen
ions to become positively charged; while at pH higher than IEP, carboxylic acids tend to
dissociate to make the interface negatively charged.

The surface charge of carbonates may develop by the preferential dissolution of
lattice ion/ions (Somasundaran and Agar, 1967; Predali and Cases, 1973; Smani et al.,
1975; Siffert and Fimbel, 1985; Mannhardt and Novosad, 1994, Wesson and Harwell,
2000), re-adsorption of the hydrolysis products of the dissolved lattice ions
(Somasundaran and Agar, 1967), and the adsorption of hydrogen or hydroxide ions
(Wesson and Harwell, 2000). Therefore, there have been discrepancies about what
potential determining ions are in such systems. For example, Ca$^{2+}$, CO$_3^{2-}$, HCO$_3^-$, H$^+$,
OH$^-$, CaOH$^-$, and CaHCO$_3^-$ (Somasundaran and Agar, 1967; Siffert and Fimbel, 1985)
were all claimed to play either major or minor roles in controlling the charge at
calcite/water interface. Thompson and Pownall (Thompson and Pownall, 1989) showed
that only Ca$^{2+}$, CO$_3^{2-}$ are major surface ions, and none of the derived complex species
have significant influence.

The IEP of calcite in the presence of 0.02 M NaCl is close to 8.7, as shown in Fig
3.4. Because of the relatively high solubility of carbonates (as compared to that of quartz
etc.), different species may form in solution by preferential dissolution (Somasundaran
and Agar, 1967), and at the solid-liquid interface by surface precipitation (Thompson and
Pownall, 1989), which results in the high sensitivity of the IEP of carbonates to the origin
of the material, the way samples are prepared, and experimental condition
(Somasundaran and Agar, 1967; Pierre et al, 1990). Therefore, the IEP of carbonates
reported by different investigators is very divergent (Table 3.2). Considering the complex
<table>
<thead>
<tr>
<th>Carbonates</th>
<th>IEP</th>
<th>Aqueous composition</th>
<th>Origin of solid</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>9.5</td>
<td>Water</td>
<td>Iceland Spar</td>
<td>Somasundaran and Agar, 1967</td>
</tr>
<tr>
<td></td>
<td>10.8</td>
<td>Not specified</td>
<td>Iceland Spar</td>
<td>Fuerstenau et al., 1968</td>
</tr>
<tr>
<td></td>
<td>7.0-8.8</td>
<td>Water</td>
<td>Iceland Spar</td>
<td>Kumar et al., 1971</td>
</tr>
<tr>
<td></td>
<td>&lt;6.35</td>
<td>Water, $10^{-2}$ N KCl</td>
<td>Moroccan ore</td>
<td>Smani et al., 1975</td>
</tr>
<tr>
<td></td>
<td>8.2</td>
<td>$2 \times 10^{-3}$ M NaClO$_4$</td>
<td>Broken Hill</td>
<td>Mishra, 1978</td>
</tr>
<tr>
<td></td>
<td>9.5</td>
<td>Water</td>
<td>Labasco Lab</td>
<td>Pugh and Stenius, 1985</td>
</tr>
<tr>
<td></td>
<td>10.5</td>
<td>Water, $2 \times 10^{-3}$ M KNO$_3$</td>
<td>Not specified</td>
<td>Amankonah and Somasundaran, 1985</td>
</tr>
<tr>
<td></td>
<td>&lt;6</td>
<td>Water</td>
<td>Iceland Spar</td>
<td>Smith and Shonnard, 1986</td>
</tr>
<tr>
<td></td>
<td>10.45</td>
<td>$10^{-3}$ M NaCl</td>
<td>Island</td>
<td>Wierer and Dobiáš, 1988</td>
</tr>
<tr>
<td></td>
<td>&lt;7.5</td>
<td>$2 \times 10^{-3}$ M NaClO$_4$</td>
<td>Norvijaur, Sweden</td>
<td>Rao et al., 1989</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>$10^{-2}$ M KCl</td>
<td>Iceland</td>
<td>Oberndorfer and Dobiáš, 1989</td>
</tr>
<tr>
<td></td>
<td>&lt;7.0</td>
<td>$5 \times 10^{-3}$ M NaCl</td>
<td>Synthetic calcite</td>
<td>Thompson and Pownall, 1989</td>
</tr>
<tr>
<td></td>
<td>9.6</td>
<td>Water, $10^{-2}$ M NaCl</td>
<td>Synthetic calcite</td>
<td>Pierre et al., 1990</td>
</tr>
<tr>
<td></td>
<td>9.4</td>
<td>Water, $10^{-3}$ &amp; $10^{-2}$ N NaCl</td>
<td>Natural calcite</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.7</td>
<td>$2 \times 10^{-3}$ M KNO$_3$</td>
<td>Not specified</td>
<td>Somasundaran and Zhang, 1999</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>$10^{-4}$ M NaNO$_3$</td>
<td>San Lois Potosí</td>
<td>Martinez-Luévanos et al., 1999</td>
</tr>
<tr>
<td></td>
<td>9.2</td>
<td>Not specified</td>
<td>Not specified</td>
<td>Wesson and Harwell, 2000</td>
</tr>
<tr>
<td></td>
<td>8.7</td>
<td>$0.02$ M NaCl</td>
<td>Solvay Socal 31</td>
<td>Current study</td>
</tr>
<tr>
<td></td>
<td>8.2</td>
<td>Water</td>
<td>Limestone</td>
<td>Al-Hashim et al., 1988</td>
</tr>
<tr>
<td></td>
<td>&lt;7</td>
<td>Varied</td>
<td>Limestone</td>
<td>Schramm et al., 1991</td>
</tr>
<tr>
<td>Dolomite</td>
<td>&lt;7</td>
<td>Water, $10^{-2}$ &amp; $10^{-2}$ N KCl</td>
<td>Kosice</td>
<td>Predali and Cases, 1973</td>
</tr>
<tr>
<td></td>
<td>&lt;7</td>
<td>Varied</td>
<td>Steetley Resources</td>
<td>Schramm et al., 1991</td>
</tr>
<tr>
<td></td>
<td>9.5</td>
<td>Not specified</td>
<td>Not specified</td>
<td>Yang et al., 1989</td>
</tr>
<tr>
<td></td>
<td>7.4</td>
<td>Not specified</td>
<td>Not specified</td>
<td>Wesson and Harwell, 2000</td>
</tr>
<tr>
<td>Magnesite</td>
<td>&lt;6.5</td>
<td>Water, $10^{-3}$ &amp; $10^{-2}$ N KCl</td>
<td>Kosice</td>
<td>Predali and Cases, 1973</td>
</tr>
</tbody>
</table>
reservoir brine and rock composition, it is difficult to predict the surface charge of carbonates. The table shows that most calcite surfaces are positively charged at neutral pH. However, the same thing cannot be concluded for dolomite and magnesite, due to the divergence and lack of data.

3.3. Wettability of Crude Oils on Carbonate Surfaces

As mentioned in the previous chapter, wettability can be quantified by the measurement of contact angle, which is a thermodynamic quantity unique for any particular system. But it is often found that when an interface advances along a surface, the "advancing" contact angle is usually larger than the "receding" contact angle when the interface recedes (Fig. 3.5). This phenomenon is known as contact angle hysteresis, caused by (Miller and Neogi, 1985) surface roughness, surface heterogeneity, adsorption due to the electrostatic interaction between the solid surface and liquid (for example, the adsorption of amine onto platinum surface), etc. Factors affecting contact angle include the composition of pre-equilibration fluid, the aging time in crude oil, brine pH, etc (Yang, 2000).

The wettability of four crude oils on carbonate surfaces was evaluated by

![Crude oil drop surrounded by brine](image)

Oil drop expanding
Water Receding Contact Angle

![Crude oil drop retrieving](image)

Oil drop retrieving
Water Advancing Contact Angle

Fig. 3.5 Contact angle measurement with crude oil as probe fluid (Yang, 2000)
measuring water advancing contact angle. Since carbonate and silicate surfaces are generally oppositely charged, advancing contact angle was also measured on silicate surface serving as a comparison. Marble and glass plates were used as carbonate and silicate substrates respectively. Glass surfaces were only cleaned by solvents, while the marble plates, after being washed by solvents, were polished on a diamond lap to remove the surface layer. Marble was chosen as experimental carbonate surface because the smooth marble surface offers a well-defined geometrically simple model system for reproducible contact angle measurements (Lowe et al., 1973).

All of the substrates were pre-equilibrated in 0.1 M NaCl brine for 24 hours before being immersed into optical cells filled with 0.1 M NaCl of neutral pH. The microburet was filled with crude oil (Figure 3.5). During each measurement, oil contacted substrates for 5-10 minutes. Results are plotted in Fig. 3.6, which indicate that for 5-10 minutes aging, MY1 is oil-wet on marble plate (see also contact angle dependence of MY1 on pH in Chapter 4), and water-wet on glass; MY2 is intermediate-wet on both carbonate and

![Contact Angle Diagram](image)

**Fig. 3.6** Water advancing contact angle of crude oils on calcite and glass with 5-10 minutes aging time
glass; MY3 and MY4 are water-wet on carbonate and oil-wet on glass. This difference is assumed to be caused by the contamination of MY1 and MY2.

But longer aging time showed different wettability of MY3 on carbonate. Cleaned marble plates were pre-equilibrated in 0.1 M NaCl brine for 24 hours, then aged in crude oil MY3 for 24 hours, either at room temperature or 80 °C (The oil reservoir temperature is close to room temperature, but aging at elevated temperature was to compensate for the short aging time compared to geological time). Then the aged substrates were put in optical cells filled with 0.1 M NaCl brine. After all motion had stopped, the oil drops on the upper calcite surfaces were photographed (Fig. 3.7). Clearly, the water advancing contact angle is close to 180°, which indicates MY3 is oil-wet on carbonate surface either aged at room or elevated temperature. These results demonstrate the importance of aging time on wettability. The oil-wetness of the crude oils on carbonate agrees with zeta potential measurements.

Evidence of oil wetting carbonate cores determined by NMR measurements will be given in Chapter 6.
WETTABILTY ALTERATION WITH SODIUM CARBONATE/SURFACTANT SOLUTION

Sodium carbonate/surfactant solution alters wettability by changing interfacial electrical charge, as stated in section 3.2. This chapter both provides visual observations as evidence of wettability alteration, and discusses important factors, such as pre-equilibration solution composition, aging temperature of the substrates in oil, and alkaline/surfactant composition used for wettability alteration.

Schematic experimental procedure is shown in Fig. 4.1. A cleaned marble plate is first pre-equilibrated in one of the three types of aqueous solutions (sodium chloride brine, sodium carbonate solution, and sodium carbonate/surfactant solution) overnight, then aged in crude oil MY3 for at least 24 hours, either at room temperature or 80 °C. Afterwards, the aged substrate is immersed in an optical cell filled with 0.1 M NaCl brine.

![Diagram of experimental procedure](image)

*Fig. 4.1 Schematic procedure for wettability alteration*

While some oil leaves the plate and rises to the air/water interface due to buoyancy forces, some oil is left on the plate due to capillary forces. The oil left on the upper surface of the plate forms an oil patch. After all motion has stopped, the oil patch is photographed. The
NaCl brine is then replaced with an alkaline/surfactant solution and changes are recorded with a video camera. A Ramé-Hart optical bench as shown in Fig 3.1 was used. Compared with the amount of oil, the amount of aqueous phase in the optical cell was much larger. The water to oil ratio in this experiment was very high.

In Sections 4.1 and 4.2, all the substrates were pre-equilibrated with 0.1 M NaCl.

### 4.1 Effect of Aging Temperature

Fig 4.2(a) and 4.3(a) show oil patches on marble plates surrounded by 0.1 M NaCl. The difference is that the substrate used in Fig 4.2 was aged at room temperature, while the one in Fig 4.3 was aged at 80°C. The two advancing contact angles are both close to 180 degrees, which indicates that marble is oil-wet by with MY3. When NaCl brine was removed, the same 0.05% CS-330/0.5 M Na₂CO₃ was added in both cases. Initially, in both experiments, oil streamed off from the substrates, as shown in Fig 4.2(b).
Fig. 4.3 Wettability alteration of a marble plate with 0.05% CS-330/0.5 M Na₂CO₃ (aged 24hrs at 80°C in MY3). Time: hours: minutes: seconds

and 4.3(b). This phenomenon indicates that interfacial tension was significantly reduced. A detailed discussion on the magnitude of the reduction will be provided later in this section. The oil left on the plate formed oil drops, which were observed with higher magnification. Contact angle was found to decrease with increasing time as shown in (c)-(f) in Fig 4.2 and (c)-(d) and (e)-(f) in Fig 4.3 (two different drops).

While Fig 4.2 shows a complete wettability alteration from strongly oil-wet to preferential water-wet, Fig 4.3 shows only a partial wettability alteration. The contact angle of the small oil drop in (c) and (d) was reduced to below 90 degrees in only an hour, but that of the large oil drop in (e) and (f) was only reduced to approximately 105 degrees. Comparing the two experiments, it can be concluded that wettability of substrates aged at room temperature is easier to alter than those aged at elevated temperature. Although the oil reservoir temperature is close to room temperature, aging at
elevated temperature is necessary to compensate for the short aging time compared to geological time.

4.2 Effect of Electrolyte

A study on the effect of electrolyte type and electrolyte strength was conducted with TC blend surfactant (mixture of equal weight amount of TDA-4PO S and CS-330). All of the substrates were aged at 80°C.

4.2.1 Sodium Carbonate With Sodium Chloride

When sodium carbonate concentration was fixed at 1 wt%, different amounts of sodium chloride were added to adjust the electrolyte strength. Fig 4.4 shows wettability alteration with 0.05% TC blend/1% Na₂CO₃/0.5% NaCl. Streaming off of oil happened in the first few minutes. Later, the oil left on the plate formed 1 mm oil drops. The final contact angles after 66 hours ranged from 80-140 degrees.

Fig. 4.4 Wettability alteration of a marble plate with 0.05% TC blend/1% Na₂CO₃/0.5% NaCl. Time: hours: minutes: seconds
Adding 0.05% TC blend/ 1% Na₂CO₃ / 10% NaCl, Oil kept on leaving the marble plate as shown below:

Fig. 4.5 Wettability alteration of a marble plate with 0.05% TC blend/1% Na₂CO₃/10% NaCl

However, low tension in 0.05% TC blend/1% Na₂CO₃/10% NaCl system (Fig. 4.5) lasted for a much longer time-2-3 hours (tensions were estimated based on the drop size and Eotvos Number in section 4.4). After 52 hours, when no further changes were observed, only a few tiny drops of 0.05 mm were left on the plate. The wettability of the marble plate was altered to intermediate-wet.

Similar observations were made for 0.05% TC blend surfactant at other sodium chloride concentrations. The final maximum drop configurations after 50 hours are illustrated in Fig 4.6, and the measured contact angles and drop sizes are summarized in Fig 4.7. The two figures show that when sodium chloride concentration was increased

Fig. 4.6 Final maximum drop configuration after wettability alteration with 0.05% TC blend/1% Na₂CO₃ and different NaCl concentration. Time : greater than 50 hours.
from 0.5 to 16%, contact angle changed little, but the drop size reached a minimum around 10% NaCl, and is un-measurable at 12%, where at the end of the experiment, no drops could be observed with the maximum magnification. The existence of minimum drop size indicates that at least transient interfacial tension experienced a minimum as sodium chloride concentration was increased.

Fig. 4.7 Contact angle and maximum drop size after wettability alteration with 0.05% TC blend/1% Na₂CO₃/NaCl

0.05% TC blend / 1% Na₂CO₃ / x%NaCl; Time: greater than 50 hours

x = 0.5

Fig. 4.8 Effect of salinity on oil remaining on the marble plate
Similar to drop size, the amount of oil remaining on the substrate in 0.05% TC blend/1% Na₂CO₃/NaCl system also went through a minimum at 10-12% NaCl, when sodium chloride concentration was increased from 0.5-16%, as shown in Fig. 4.8. Therefore, for the wettability alteration experiments, 10-12% NaCl is the optimal salinity. The reason for this will be given in the next chapter.

4.2.2 Sodium Carbonate As The Only Electrolyte

When sodium carbonate was used as the only electrolyte, its concentration was

![Na₂CO₃ increases](image)

**Fig. 4.9** Final maximum drop configuration after wettability alteration with 0.05% TC blend and different Na₂CO₃ concentration. Time: greater than 50 hours.

![Graph](image)

**Fig. 4.10** Contact angle and maximum drop size after wettability alteration with 0.05% TC blend/Na₂CO₃.
adjusted to change the electrolyte strength. Fig 4.9 shows the final maximum drop configuration after wettability alteration with 0.05% TC blend and different amounts of sodium carbonate. The measured contact angles and drop sizes are summarized in Fig 4.10. The error bars on 11 and 15% Na₂CO₃ are not from measurement, but from estimation. Drops left in the two cases were very small and close to spherical shape, which makes the estimation of the contact angles very difficult.

When sodium carbonate concentration was increased from 4.5 to 16%, both contact angle and maximum drop size decreased rapidly until 11%, after which changes were small. The small drop size at high sodium carbonate does not necessarily mean ultra-low tension, because the contact angle is small, as will be discussed in the last section of this chapter.

4.3 Effect of Pre-Equillibration Solution Composition

As stated in Chapter 3, sodium carbonate can change the interfacial charge

- Large contact angle on marble in 0.1M NaCl after aging in 0.1M Na₂CO₃

![Image](image1.png)

- Effect of 0.05% TDA- 4PO S / 0.3 M Na₂CO₃

![Image](image2.png)

Fig. 4.11 Wettability alteration of MY3 on marble plate pre-equilibrated with 0.1 M NaCl by 0.05 % TDA-4PO S /0.3 M Na₂CO₃. Time: hours: minutes: seconds
between calcite and brine. Thus, marble plates pre-equilibrated with sodium carbonate solution are expected to be less oil-wet, and their wettability easier to alter, compared with those pre-equilibrated with sodium chloride. Therefore, three cleaned marble substrates were pre-equilibrated with 0.1 M sodium chloride, 0.3 M sodium carbonate, and 0.05% TDA-4PO S/0.3 M Na₂CO₃ respectively. After being aged in crude oil MY3 at room temperature, they were immersed into optical cells filled with 0.1 M NaCl brine. After all motion stopped, the sodium chloride brine was removed before the same 0.05% TDA-4PO S/0.3 M Na₂CO₃ solution was introduced into the cells. Results are shown in Fig 4.11-13.

- Large contact angle on marble in 0.1M NaCl after aging in 0.3 M Na₂CO₃

Fig. 4.12 Wettability alteration of MY3 on marble plate pre-equilibrated with 0.3M Na₂CO₃ by 0.05% TDA-4PO S/0.3 M Na₂CO₃. Time: hours: minutes: seconds

In all three cases, marble plates were strongly oil-wet in 0.1 M NaCl. Substrates pre-equilibrated with sodium carbonate or sodium carbonate and anionic surfactant were still oil-wet, which might be caused by the adsorption of soap (generated in situ by the
reaction between sodium carbonate and carboxylic acids in the crude oil) and/or synthetic surfactant, despite of the fact that sodium carbonate reduces anionic surfactant adsorption on calcite.

Alveskog et al. (Alveskog et al., 1996) tested the influence of n-(dodecyl) o-xylene sulfonate on the wettability of Berea sandstone. Although the adsorption of the surfactant on Berea sandstone was very low—\(\sim 0.05\) mg/g solid, because sandstone is usually negatively charged at neutral pH, they found that a surfactant concentration as low as 0.006 wt\% (CMC of this surfactant is close to 0.009\%) can change the rock wettability from strongly water-wet to weakly oil-wet. Spinler and Baldwin (Spinler and Baldwin, 2000) suggested that the surfactant adsorption may have created oil-wet pathways.

After adding 0.05\% TDA-4PO S/0.3 M Na\(_2\)CO\(_3\), wettability of plates pre-equilibrated with 0.1 M NaCl and 0.05\% TDA-4PO S/0.3 M Na\(_2\)CO\(_3\) were altered to

- Large contact angle on marble in 0.1M NaCl after aging in 0.05\% TDA-4PO S / 0.3 M Na\(_2\)CO\(_3\)

- Adding 0.05\% TDA-4PO S/0.3M Na\(_2\)CO\(_3\)

Fig. 4.13 Wettability alteration of MY3 on marble plate pre-equilibrated with 0.05 % TDA-4PO S/0.3 M Na\(_2\)CO\(_3\) by 0.05 % TDA-4PO S/0.3 M Na\(_2\)CO\(_3\). Time: hours: minutes: seconds
preferential oil-wet to intermediate-wet, while that pre-equilibrated with 0.3 M Na₂CO₃ was altered to intermediate-wet to preferential water-wet. Comparing the three experiments, it can be concluded that pre-equilibration with sodium carbonate solution made it easier to alter wettability, but pre-equilibration with sodium carbonate/surfactant did not.

### 4.4 Critical Eotvos Number for Gravity Induced Oil Drop Detachment

Phenomena similar to those shown in the previous sections were observed by Chatterjee (Chatterjee, 2001, 2002) with sodium dodecyl benzene sulphonate and a sunflower oil on a stainless steel surface or a ground nut oil on a quartz glass surface. Both wettability alteration and gravity induced emulsification which contributed to most of the oil removal. The maximum size of a pendant drop is determined by Eotvos Number, which is half of the Bond Number.

\[ E = \frac{R^2 \Delta \rho g}{2 \sigma} \]  

(3.1)

where  

- \( R \): radius of curvature at the drop apex,
- \( \Delta \rho \): density difference between the two fluids,
- \( g \): gravitational acceleration,
- \( \sigma \): interfacial tension between the two fluids.

Based on two different expressions of the capillary force- \( 2\pi r \sin \theta \) (Tate’s law, \( r \) is the wetted radius and \( \theta \) the three phase contact angle) or \( 2\pi r \sin \theta + P_c A_w \) (the term added to Tate’s law arising out of the capillary pressure, see Chatterjee, 2002. \( P_c \) is capillary pressure in the drop, and \( A_w \) the wetted area), Eotvos Number can be expressed,
as a function of the three phase contact angle (different from the author, here contact angle is defined as measured through the aqueous phase), in the following two equations:

\[ E_L = \frac{3 \sin^2 \theta}{2 + 3 \cos \theta - \cos^3 \theta} \]  
(3.2)

\[ E_H = \frac{6 \sin^2 \theta}{2 + 3 \cos \theta - \cos^3 \theta} \]  
(3.3)

Eotvos Number is plotted as a function of contact angle in Fig 4.14, above which a drop will be unstable and detach from the surface.

For an oil patch like those shown in Fig. 4.2-4 (a), if contact angle is assumed to be 160°, drop diameter 1 cm, and brine/oil interfacial tension 30 mN/m, Eotvos Number will be 2, which is lower than the lower critical Eotvos Number, 33. Therefore such an oil patch is stable in sodium chloride brine. For such a drop to detach, interfacial tension only needs to drop to the order of 1 mN/cm.

However, when sodium chloride brine is replace by alkaline surfactant solution,
interfacial tension is significantly reduced. Take the system of 0.05% TC blend/1% Na$_2$CO$_3$/NaCl for example. If contact angle at different salinities is assumed to be 120°, interfacial tension is plotted as a function of drop size in Fig. 4.15. A maximum drop size of 0.1mm indicates an interfacial tension of 0.001 mN/m. Experimental interfacial tension measurements and the structure and properties of surfactants mentioned in this chapter will be discussed in the next chapter.
Chapter 5

SODIUM CARBONATE/
ANIONIC SURFACTANT FORMULATION

5.1 Selection of Surfactants

Selection of surfactants is crucial to sodium carbonate/surfactant flooding process. Traditionally, the most commonly used surfactants for alkaline/surfactant flooding are sulfonated hydrocarbons. Their advantages (Salter, 1986) are 1) they are very effective in lowering interfacial tension; 2) they are inexpensive, especially petroleum sulfonates; and 3) they are reported to be chemically stable. But the problem of sulfonates is that they have poor hardness tolerance and salinity tolerance (Green and Willhite, 1998).

Ethoxylated (EO) and propoxylated (PO) sulfates were evaluated (Gale et al., 1981; Osterloh and Jante, 1992; Wellington and Richardson, 1995; Aoudia et al., 1995) because of their known tolerance to divalent ions. Sulfates rather than sulfonates were evaluated in this research due to their greater availability and because the target application is a particular low temperature carbonate reservoir where the sulfate hydrolysis should not be a problem.

Another important property of PO surfactants is that they decrease HLB (Hydrophile-Lipophile Balance) while not compromising solubility. A relatively hydrophobic surfactant is needed due to two reasons: 1) The salinity in the reservoir of interest is low (~10000 ppm); 2) As mentioned in Chapter 2, the alkaline/surfactant flooding process has both natural surfactants and synthetic surfactants. Natural surfactants are mostly very hydrophobic. It is found that the closer the HLB of the added
synthetic surfactants are to the natural soap, the smaller influence Water/Oil Ratio (WOR) has on the process (discussed in the rest of the chapter). The decrease of HLB by increasing hydrocarbon chain length of the surfactant will result in the precipitation of surfactants. The addition of PO groups overcomes this dilemma (Minana-Perez et al., 1995).

In the present study, dozens of anionic surfactants and mixtures, nonionic and cationic surfactants as co-surfactants, and alcohols as cosolvents were considered. Two surfactant formulations that are most promising will be emphasized in this thesis. The involved surfactants are identified in Table 5.1.

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Structural name</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS-330</td>
<td>Sodium dodecyl 3EO sulfate</td>
</tr>
<tr>
<td>TDA-4PO S</td>
<td>Ammonium iso-tridecyl 4PO sulfate</td>
</tr>
<tr>
<td>TC blend</td>
<td>1:1 weight ratio of TDA-4PO S and CS-330</td>
</tr>
<tr>
<td>N67-7PO S</td>
<td>Ammonium C16-17 7PO sulfate</td>
</tr>
<tr>
<td>IOS 1518</td>
<td>Sodium C15-18 internal olefin sulfonate</td>
</tr>
<tr>
<td>NI blend</td>
<td>4:1 weight ratio of N67-7PO S and IOS 1518</td>
</tr>
</tbody>
</table>

Sodium carbonate/surfactant formulation is optimized by two steps: phase behavior tests followed by interfacial tension measurements, which will be discussed in the following sections.
5.2 Phase Behavior Test

Phase behavior test is also known as emulsion screening test, bottle test, etc. The objective of studying phase behavior is to determine the optimal salinity from visual observation of glass tubes containing the mixture of oil and aqueous phases. Depending on which phase the microemulsion resides in, phase behavior is divided into Winsor type I, Winsor type III, and Winsor type II (see Chapter 2).

5.2.1 Materials and Experimental Procedure

5.2.1.1 Materials

Oil: crude oils MY3 and MY4 were both used. Both came from the same well, and have very similar properties (Table 3.1). MY3 was used in most cases, and MY4 was used when MY3 was out of stock.

Water: deionized water, with conductivity of 4-7 μS/cm.

Surfactants: listed in Table 5.1.

Sodium carbonate: purity of 99.8%, with 0.005% calcium, acquired from Fisher, in form of anhydrous powder. A very small amount of precipitate is usually found in its solution of high concentration (e.g., 1M). The precipitate was filtered out with 0.1μm filter.

Two units of sodium carbonate concentration have been used: weight %, and molar (M). Their relationship is: 0.1 M is close to 1%.

Sodium chloride: a Fisher product, certified for biological work.
5.2.1.2. Experimental Procedure

Surfactant solutions and oils were mixed at a specific Water/Oil Ratio (WOR) in glass vials or pipettes. They were first shaken well by hand for 1 minute, then mixed on a rotating shaker for 24 hours. Afterwards, they were put in an upright position and allowed to settle.

It is found that surfactant structure and concentration, ionic strength, WOR are all very important factors affecting phase behavior. WOR is important because at each ratio, there is a different amount of natural soap. In the following sections, phase behavior of several systems will be shown and discussed.

5.2.2 Phase Behavior of Crude Oil and Sodium Carbonate Only

Phase behavior of crude oil MY3 and sodium carbonate at WOR of 1:1 is shown in Fig 5.1. Based on an acid number of 0.2 mg KOH/g oil, a concentration of 0.003M Na₂CO₃ is required to neutralize the acid to soap and NaHCO₃. Sodium carbonate acts here as a salt as well as an alkali. The optimal sodium carbonate concentration is close to 0.1 M, the lower phase color of which is darkest, which indicates that at this concentration, the aqueous phase solublized the most amount of oil.
5.2.3 Phase Behavior of Crude Oil and TC Blend

CS-330 is similar to NEODOL 25-3S used previously by Shell (Nelson et al., 1984), but is too hydrophilic to use by itself (Hirasaki and Zhang, 2004). TDA-4PO S is less hydrophilic, but its solutions at optimal sodium carbonate concentration are turbid and adsorption is anomalously high (Chapter 7). Thus the two surfactants are blended at equal weight ratio, and the resulting surfactant solution is abbreviated as “TC blend”.

5.2.3.1 Surfactant/electrolyte solutions

The appearance of surfactant solutions is very important, because unclear solutions may cause a variety of problems, such as high adsorption (Chapter 7), high viscosity which can occur when gel or liquid crystals are present and result in the prohibition of their application to tertiary oil recovery (Healy and Reed, 1973). The appearance of TC blend/1% Na₂CO₃/NaCl is plotted in Fig 5.2. For this surfactant blend, phase separation happens at a certain salinity-5% NaCl, which is not affected by

![Fig. 5.2 The appearance of TC blend/1% Na₂CO₃/NaCl](image)
surfactant concentration. Solutions in two phase region should not be used because they can result in poor oil recovery as will be shown in Chapter 6. A light beam was applied to solutions in one phase region. If a solution does not scatter light, it is called a “clear” solution. Otherwise, it is labeled “weakly scattering light” or “strongly scattering light” according to the intensity of the scattered light.

5.2.3.2 Soap/Synthetic surfactant ratio

Crude oil and sodium carbonate/surfactant solution were mixed at a variety of surfactant concentrations and WORs. Phase behavior was found to change with both surfactant concentration and WOR. Fig 5.3 illustrates the phase behavior of 0.05% TC blend/1% Na₂CO₃/NaCl at WOR of 1:1 and 3:1. At WOR of 1:1, Fig 5.3 (a), it forms a

0.05% TC blend / 1%Na₂CO₃ / x% NaCl  WOR=1:1, 6 mons settling at 30 °C
x= 0  0.5  1  1.5  2  2.5  3

0.05% TC blend / 1%Na₂CO₃ / x% NaCl  WOR=3:1, 70 days settling at 30 °C
x= 0  1  2  3  4  6

Fig 5.3 Phase behavior is a function of WOR. Arrows indicate optimal sodium chloride concentrations.
lower phase microemulsion at 0.5% NaCl, indicated by the swollen aqueous phase. The creamed middle layer between oil and aqueous phase at 1% NaCl is an oil external emulsion, which indicates that at this salinity, phase behavior is in a Winsor type II region. In a classical oil-water-surfactant system, as salinity increases, phase behavior changes from Winsor type I to type III to type II. But at such a low surfactant concentration-0.05%, the volume of any middle phase, if present, would be small and hard to see. Therefore, phase behavior at low surfactant concentration often appears to change from type I to type II, like that shown in Fig 5.3 (a). The optimal salinity is between the highest under-optimal salinity and the lowest over-optimal salinity. Therefore the optimal sodium chloride concentration of Fig 5.3 (a) is between 0.5-1% NaCl. Similarly, at WOR of 3:1, Fig 5.3 (b), optimal sodium chloride concentration is between 2-3%. Optimal salinities for other WOR values and surfactant concentrations were similarly determined, and are plotted in Fig 5.4.

![Fig. 5.4 Optimal sodium chloride concentration of TC blend as a function of WOR and surfactant concentration (settled for more than 6 months).](image-url)
The dependence of optimal salinity on WOR explains why the drop size in wettability alteration experiments (Chapter 4) depends on electrolyte strength. In a wettability alteration experiment, a small patch of oil is surrounded by a large amount of aqueous solution, so the WOR is very high. When electrolyte concentration is increased, phase behavior gradually changes from under-optimum to optimum to over-optimum. Since IFT is the lowest at optimum, the maximum stable drop size determined by Eotvos number experiences a minimum at optimal salinity.

Dependence of optimal salinity on TC surfactant blend concentration and WOR can be correlated with natural soap/synthetic surfactant mole ratio:

\[
\text{Soap/Synthetic surfactant ratio} = \frac{0.757 \times \text{Acid Number (mg KOH/g oil)}}{C_{\text{surf}} \text{ (weight\%) \times WOR}}
\]

From the acid number-0.2 mg KOH/g oil (Table 3.1), Fig 5.5 can be plotted. Lower soap/synthetic surfactant ratios correspond to the dominance by the synthetic surfactant. The curve plateaus at 12% NaCl, which is close to the optimal salinity of the TC blend.

![Graph](image-url)

Fig. 5.5 Optimal sodium chloride concentration of TC blend as a function of natural soap/synthetic surfactant mole ratio (settled for more than 6 months).
surfactant by itself. The optimal salinity of the soap by itself is about 0-0.5% NaCl.

5.2.4 Phase Behavior of Crude Oil and NI Blend

While the TC blend showed promising recovery results, as will be discussed in the next chapter, it also has some drawbacks, such as high optimal salinity of the synthetic surfactant, optimal salinity decreasing significantly with soap/synthetic surfactant ratio, and the formation of viscous phases. Therefore, a much less hydrophilic surfactant or surfactant blend producing less or no viscous emulsions is needed. A dozen surfactant or surfactant blends were screened, among which the blend of 4:1 weight ratio of N67-7PO sulfate and IOS 1518 was found to be the most promising.

5.2.4.1 N67-7PO S

Phase behavior of 3% N67-7PO S with crude oil MY3 at WOR of 3:1 (soap/synthetic surfactant ratio of 0.03) is shown in Fig 5.6. The optimal salinity at this

![Graph showing phase behavior](image)

**Fig. 5.6** Phase behavior of 3% N67-7PO S/1% Na₂CO₃/NaCl
condition is between 2.2-2.4% NaCl, which indicates that N67-7PO S is a much less hydrophilic surfactant than the TC blend. The photograph also shows that it forms iridescent materials, possible liquid crystals (but not necessarily viscous), close to the optimal condition, 2.2 and 2.4% NaCl.

A classical phase behavior can be obtained by adding alcohol. Fig 5.7 shows the phase behavior of 3% N67-7PO S/8% SBA/1% Na₂CO₃/NaCl at a WOR of 3:1. 0 and 0.5% NaCl systems have colored and larger than the original volume aqueous phases, which indicate they are in the type I region. A middle phase microemulsion formed in each of the 0.6-1% NaCl systems, which indicate they are in the type III region. 1.5% has a clear lower phase and larger than the original volume oil phase, which indicate that it is in the type II region. Although with alcohol, phase behavior is much simpler, because the addition of alcohol increases the cost and often compromises low interfacial tension, it only serves as a comparison, and is not further investigated.

![Phase behavior of 3% N67-7PO S/8% SBA/1% Na₂CO₃/NaCl](image)

Fig. 5.7 Phase behavior of 3% N67-7PO S/8% SBA/1% Na₂CO₃/NaCl
5.2.4.2 N67-7PO S and IOS 1518 blends

Adding a branched surfactant can also improve phase behavior. Abe et al (Abe et al, 1986) found that when a linear surfactant was used alone at room temperature, a large amount of alcohol was needed to get microemulsion free of liquid crystals; but when twin-tailed surfactants were used, less, or even no alcohol was needed, depending on the location of the hydrophilic group on the hydrophobic chain. Based on this finding, IOS 1518, which is a twin-tailed surfactant with the sulfonate group distributed along the hydrocarbon chain, was blended with N67-7PO S.

When N67-7PO S or IOS 1518 was used separately, the salinity of phase separation occurred at 4 and 3% NaCl respectively (after 9 months, N67-7PO S phase separates at 0% NaCl), as shown in Fig 5.8. The phase separation behaviors of the two surfactants were different: IOS 1518 was precipitated out the solution by salt, while N67-

![Diagram showing phase behavior](image)

Fig. 5.8 Salinity of phase separation increases when N67-7PO S and IOS 1518 are blended compared with used alone. * Phase separated after 9 month.
7PO S formed cloudy solutions similar to a nonionic surfactant. However, when they were mixed at 1:1, 4:1, and 9:1 weight ratio, they stayed in the single-phase region over a much wider salinity range. When each of the three surfactant mixtures phase separated, it first formed two transparent phases, which became cloudy as salinity was further increased.

Fig. 5.9 Optimal salinity of 3% total surfactant at different N67-7PO S and IOS 1518 ratio.

Fig. 5.10 Phase behavior of 0.05% NI blend/1% Na₂CO₃/NaCl at soap/synthetic surfactant ratio is of 1.4 (WOR=3:1).
Optimal salinities at 3% total surfactant concentration of N67-7PO S and IOS 1518 mixed at the three different weight ratios mentioned above are summarized in Fig 5.9. The optimal salinity at 1:1 ratio is too high to be acceptable (Fig 5.9), and the emulsion coalescence rate at 9:1 ratio is not acceptable. 4:1 ratio is a compromise between the two. The 4:1 weight ratio blend of N67-7PO S and IOS-1518 shows very good solubilization properties, which will be discussed in Section 5.4. Therefore, this surfactant formulation was further studied. The blend of 4:1 weight ratio of N67-7PO S and IOS 1518 is abbreviated as “NI blend” in the rest of the thesis. The phase behaviors of 0.05, 0.2, 0.5, and 3% NI blend/1% Na₂CO₃/NaCl at WOR of 3:1 are shown in Fig 5.10-13. Viscous emulsions were still found in some systems. However, the solubility ratios were found to be well improved over the N67-7PO S alone.

Fig. 5.11 Phase behavior of 0.2% NI blend/1% Na₂CO₃/NaCl at soap/synthetic surfactant ratio is of 0.35 (WOR=3:1).

Fig. 5.12 Phase behavior of 0.5% NI blend/1% Na₂CO₃/NaCl at soap/synthetic surfactant ratio is of 0.14 (WOR=3:1).
Fig. 5.13 Phase behavior of 3% NI blend/1% Na₂CO₃/NaCl at soap/synthetic surfactant ratio close to 0.02. Viscous emulsions form at 5.8 and 6.0% NaCl.

Fig. 5.14 Soap/Synthetic surfactant mole ratio correlation
The optimal salinity of NI blend was determined the same way as the TC blend. The correlation of optimal salinity of NI blend as a function of soap/synthetic surfactant ratio is shown in Fig 5.14. The optimal salinity of the NI blend is much closer to that of the formation brine than the TC blend. From Fig. 5.8, it can be concluded that the addition of IOS 1518 allows the injection of clear surfactant solutions at or near optimal conditions.

5.3 IFT Measurements by Spinning Drop

![Diagram](image)

Fig. 5.15 Schematic diagram of a spinning drop (Miller and Neogi, 1985)

Liquids from the equilibrated upper, lower, or middle phase in each phase behavior bottles were taken for interfacial tension measurements by spinning drop method. The mechanism of spinning drop method is shown in the above schematic diagram (Fig 5.15). A drop of a less dense fluid (in this case the equilibrated upper phase) is injected into a capillary full of a denser fluid (in this case, the equilibrated lower phase), and the whole system is rotated as shown in Fig 5.15. The configuration of the less dense drop is determined by two types of forces: centrifugal forces, and interfacial tension. As a result of the centrifugal forces, the less dense drop tends to elongate along the axis of rotation, while interfacial tension tends to suppress the elongation due to the increasing interfacial area. An equilibrium configuration, which minimizes system free energy, will be reached after rotating for a period of time. When the drop length is much greater than the radius, interfacial tension can be calculated by the following equation (Miller and Neogi, 1985):
\[ \sigma = \frac{(\rho_b - \rho_A) \omega^2 r^3}{4} \]  

(5.1)

where \( \sigma \): interfacial tension,

\( \rho_A \): density of the less dense fluid,

\( \rho_b \): density of the denser fluid,

\( \omega \): angular velocity of rotation,

\( r \): the radius of the less dense drop.

Spinning drop method was first suggested to be used for measuring surface and interfacial tension by Vonnegut, and developed to the current procedures by Cayias et al (Cayias et al, 1982). The equipment used in the current research is Spinning Drop Interfacial Tensiometer, Model 300. Because the reservoir temperature of the target application is close to room temperature, all the measurements to be presented below were done at room temperature, 22-24°C, and ambient pressure, unless stated otherwise.

Interfacial tension was measured as a function of ionic strength, surfactant composition and concentration, and soap/synthetic surfactant ratio as shown in the following sub-sections.

### 5.3.1 Effect of Synthetic Surfactants

Fig 5.16 shows interfacial tension of MY3 with sodium carbonate by itself, or with both sodium carbonate and a synthetic surfactant of 0.05 wt% at a soap/synthetic surfactant close to 3 (WOR of 1). From the figure, it can be seen that with sodium carbonate alone, the optimal sodium carbonate concentration is close to 0.1M, which is consistent with that determined from the phase behavior test, Fig 5.1. But the addition of sodium carbonate by itself only results in a minimum interfacial tension of close to 0.1
Surfactants identification: C12-3PO S: C12 3PO sulfate ISOFOL 14T-4.1 PO: C14 4PO sulfate. See Table 5.1 for other surfactants identification

Fig 5.16 IFT of MY3 as a function of sodium carbonate concentration, WOR = 1:1, surfactant concentration = 0.05%.

mN/m. The addition of synthetic surfactants along with sodium carbonate, as shown by all the other curves in Fig 5.16, further lowers interfacial tension to the order of $10^{-3}$, and raises sodium carbonate concentration at minimum interfacial tension.

5.3.2 Effect of Surfactant Concentration

IFT of MY3 as a function of TDA-4PO S concentration at WOR of 1:1 is shown in Fig 5.17. For each TDA-4PO S concentration tested, ultra-low interfacial tension is achieved in a certain sodium carbonate concentration region. The optimal concentrations for 0.05%, 0.2%, and 1% TDA-4PO S are 0.3, 0.4, and 1.4M.
Na\textsubscript{2}CO\textsubscript{3} respectively. The optimum increases with surfactant concentration because the soap/surfactant ratio decreases when the synthetic surfactant concentration is increased.

### 5.3.3 Effect of Natural Soap

Fig 5.18 shows the effect of natural soap on interfacial tension for MY3. In the plot, each aqueous composition was held fixed, and only the WOR was changed, which resulted different soap/synthetic surfactant ratios. Interfacial tension is low at high soap/synthetic surfactant ratios near 3 (WOR=1:1), where the alkaline/surfactant systems were optimized. At low soap/synthetic surfactant ratios, IFT of hydrophilic surfactant increases 10-100 times, while that of the less hydrophilic surfactant does not change much with the ratio. It is desirable to keep the IFT below 0.01 dyne/cm over a range of soap/synthetic surfactant ratio as wide as possible.
It is observed that when the samples are not equilibrated, both phase behavior and interfacial tension change with time. But when samples are equilibrated, the small amount of microemulsion at low surfactant concentration makes it difficult to make equilibrium tension measurements. This issue will be discussed in the next section.

5.3.4 Problems and Protocols of Interfacial Tension Measurements

Interfacial tension is usually measured between microemulsion and excess phases (Healy et al., 1976). But because low surfactant concentration results in small amount of microemulsion in the Type III region, measurements are usually either interfacial tension between excess phases (Kang and Wang, 2001; Seethapalli et al, 2004), or non-equilibrium measurements at a low soap/synthetic surfactant ratio (Peru and Lorenz, 1990; Olsen et al, 1990; Nasr-El-Din et al, 1992). The problem of non-equilibrium measurement is as follows. The optimal salinity determined by non-equilibrium measurement is at a very low soap/synthetic surfactant ratio. Interfacial tension at different soap/synthetic surfactant ratio may differ by orders of magnitude, as shown in Fig 5.18. In a non-equilibrium measurement, low tension is often only a transient phenomenon as soap is extracted out of the crude oil, but the equilibrium tension may not be low.

The problem of tension measurements between excess phases is discussed below.

5.3.4.1 Problematic interfacial tension measurements between excess phases

Phase behavior and interfacial tension between excess phases were found to change with settling time, for example, for 0.05% TC blend with sodium carbonate, Fig
5.19. The lower phases of 0.1-0.6 M Na$_2$CO$_3$ were turbid after 19 days' settling, but after 110 days, the lower phase of 0.35-0.6 M cleared up, and there appeared a thin creamed middle layer at the oil-water interface. When interfacial tension of the same system was measured after 19 days of settling, the minimum tension was near $10^{-4}$ mN/m (dyne/cm). However, when the tension was measured again after 110 days of settling, it was found that if the lower phase did not clear up, interfacial tension was close to the measurement after 19 days. But if the lower phase had cleared up, when sampling from the excess phases, tension went up a few orders of magnitude.

5.3.4.2 Cause of change in interfacial tension

Similar phenomena were observed for 0.05% TDA-4PO S/Na$_2$CO$_3$ system, Fig 5.20. Interfacial tension between excess phases was low after 7 days of settling, but went

![Graph showing IFT vs Na$_2$CO$_3$ Concentration](image)

Fig. 5.19 Phase behavior and IFT of 0.05% TC blend/Na$_2$CO$_3$ change with settling time.
up significantly after 9 months. However, when some of the creamed middle layer was sampled along with excess phases, the interfacial tension could be lowered again, especially in the case of 0.3 M Na₂CO₃, where the tension was lowered to a value similar to that measured after 7 days of settling.

This result indicates that the creamed middle layer separated from the lower phase contains at least one active surfactant-rich phase. For short times of settling, this surfactant rich phase is dispersed in the aqueous phase, which results in low tension at the right salinity range. But since this active surfactant rich phase has a lower density than the aqueous phase, it separates from the aqueous phase with time. Therefore, after a long time of settling when all of this active surfactant rich phase leaves the aqueous phase,

![Graph](image)

Fig. 5.20 IFT of 0.05% TDA-4PO/Na₂CO₃ change with settling time. After long time of settling, interfacial tension went up, but the addition of creamed middle layer lowered it again (represented by unfilled spheres and triangles.

Δ: After 9 months settling, added about 0.03 ml of the creamed middle layer in addition to excess aqueous and oil phase
O: After 9 months settling, added different amount of the creamed middle layer to excess aqueous and oil phases. From top to bottom, 0.001, 0.003, 0.02, 0.05, 0.035 ml creamed middle layer was added.)
there is little active surfactant present to lower interfacial tension between excess phases, used in the spinning drop measurement.

This assumption was demonstrated by the 0.2% NI blend/1% Na₂CO₃/2-4% NaCl system. After 1 day’s settling, excess oil and lower phases were sampled. Lower phases were then centrifuged at 6000 RPM for 30 minutes. Interfacial tension was first measured between excess oil and the transparent solutions from the bottom of the centrifuged lower phase. Tensions was found to be higher than 0.01 mN/m, Fig 5.21. Centrifuging accelerates the settling of the creamed middle layer. Therefore, this high tension will be similar to that after a long time settling. But when a little of the topmost layers after centrifuging were added to solutions from the bottom after centrifuging, interfacial tension can be lowered below 0.01 mN/m, Fig 5.21. The topmost layer as the lightest component in the aqueous phase is the oil and surfactant rich phase.

![Graph showing IFT vs NaCl concentration](image)

**Fig. 5.21** IFT of 0.2 % NI blend/1% Na₂CO₃/2-4% NaCl
Fig. 5.22 Phase behavior of 0.2% NI blend/1% Na₂CO₃/x% NaCl, 40 days of settling. Thin creamed middle layers exist at salinity of 2-3.4% NaCl.

This creamed middle layer can be shown in the close-up photograph, Fig 5.22. The figure shows phase behavior of 0.2% NI blend/1% Na₂CO₃/NaCl, at soap/synthetic surfactant ratio of either 1 or 0.35 (WOR of 1:1 and 3:1), after 40 days settling. 2% and 3.4% NaCl are close to the optimal salinities at soap/synthetic surfactant ratio of 1 and 0.35 respectively. At 2-3.4% NaCl, thin creamed middle layers can be observed between excess oil and aqueous phases. Compare the 2% NaCl at soap/synthetic surfactant ratio of 1 with the same salinity-2%. At soap/synthetic surfactant ratio of 0.35, the volume of the creamed middle layer at soap/synthetic surfactant ratio of 1 is larger.
than that at 0.35, Fig 5.22. Therefore, the surfactant in the creamed middle layers could be richer in natural soap.

The creamed middle layer can also be observed during spinning drop interfacial tension measurements. Fig 5.23 shows that during spinning drop tension measurement of 0.2 % NI blend/1% Na₂CO₃/2% NaCl, there clearly existed three phases: creamed middle layer, oil and aqueous phase. As shown in Fig 5.22, the volume of the creamed middle layer is too small to accurately measure the density. In calculation of the interfacial tension, the diameter of the oil phase, and the density difference between oil and the aqueous solution were used.

The system with 3.4% NaCl which has been settled for 23 days and centrifuged with little emulsion left does not have ultralow IFT until over two hours of spinning, Fig

![Graph](image)

**Fig. 5.24** IFT of 0.2 % NI blend/1% Na₂CO₃/3.4% NaCl after 23 days of settling. When aqueous phase sampled in different ways, transient IFT was different but a similar equilibrium IFT was obtained.
5.24. However, if the lower phase is not centrifuged, ultralow IFT is attained in less than an hour. If the creamed layer is added to the centrifuged lower layer, ultralow IFT is attained immediately. Thus this experiment demonstrates that it is the surfactant components in the creamed layer that is responsible for the ultralow IFT.

5.3.4.3 Protocols for interfacial tension measurements

Because the non-reproducible interfacial tension measurement is caused by the settling of surfactant rich phase to the oil/water interface, the most intuitive solution would be to make the tension measurements early enough so that there is still enough of the surfactant-rich phase(s) dispersed in the aqueous phase to lower the interfacial tension.

0.2 % NI blend/1% Na$_2$CO$_3$/2% NaCl solution was mixed with MY4 crude oil at 3:1 volume ratio in several bottles. After being shaken for 24 hours, the samples were allowed to settle for 1, 2, and 4 hours. It was found that although the transient interfacial

![Graph showing change in IFT over time](image)

Fig. 5.25 Transient IFT of 0.2 % NI blend/1% Na$_2$CO$_3$/2% NaCl.
tension was different, the equilibrium interfacial tension was similar, Fig 5.25. Therefore it can be concluded that within a certain period of settling time when there is enough creamed middle layer dispersed in the aqueous phase, interfacial tension is very reproducible.

When the aqueous phase was separated from oil after 1-4 hours settling, and allowed further settling, it was found that there were usually two different water-external emulsions accumulated at the top of the aqueous phase: one was oil-rich while the other water-rich. For the 2 hours settling sample, when the oil-rich emulsion was added to the clear but colored centrifuged bulk aqueous phase, equilibrium interfacial tension reached a similar value as that measured directly after separating from oil, Fig 5.25. This indicates that the oil-rich emulsion is responsible for the ultra-low interfacial tension. This finding provides a fast and reproducible way of measuring interfacial tension.

Interfacial tension measurement made within 4 hours settling time is possible for under-optimum to optimum system. But the oil-continuous phase of the over-optimum system is usually not equilibrated within such a short time. Fig 5.26 shows the phase behavior of 0.2% NI blend/1% Na₂CO₃/2-4% NaCl after 4 hours and 23 days settling. At salinity of 3.6-4% NaCl, after 4 hours settling, the oil phases were all emulsified. However, after 23 days, each system settled into four phases: oil, microemulsion, thin layer of emulsion, and excess aqueous phase.

In over-optimum system within Winson type III region, tension measured between microemulsion and oil is lower than the tension between microemulsion and water (Fig 2.11). Therefore when the three phases are coexistent in an over optimum system, the overall tension is dominated by that between microemulsion and water.
Hence, the interfacial tension in the over-optimum region can be approximated with the tension between microemulsion and water.

![Diagram showing phase behavior](image)

**Fig. 5.26** Phase behavior of 0.2% NI blend/1% Na₂CO₃/2-4% NaCl
Soap/synthetic surfactant ratio of 0.35 (WOR=3:1)

The interfacial tension of 0.2% NI blend/1% Na₂CO₃/2-3.4% NaCl was measured between excess phases after 4 hours of settling. IFT of solutions with 3.6-4.0% NaCl was also measured between excess aqueous and microemulsion phase after 23 days of settling, Fig 5.21. Ultra-low interfacial tension was acquired over a wide range of salinity. It is speculated that lower phase microemulsion usually coexists with at least one other microemulsion phase between 2.0-3.4% NaCl. The latter has a higher soap/synthetic surfactant ratio. Enough of this microemulsion must be present to achieve ultralow IFT. This ultralow IFT can be achieved by making the IFT measurement with the soap-rich microemulsion dispersed in the aqueous phase.
5.4 Correlation between Phase Behavior and IFT

The solubility ratios of 0.2% NI blend/1% Na$_2$CO$_3$/NaCl is calculated from the phase behavior shown in Fig 5.11 and plotted in Fig 5.27. When the lower phase is colored, there often is a thin creamed layer between the oil and lower phase. In calculation of the solubility ratios, the creamed layer volume was counted towards the volume of the lower phase. The error of reading the volumes of oil and aqueous phase was estimated to be 0.01 ml. The error of solubility ratios thus was calculated to be 1.3. The solubility ratios of this system are very high. Even at a low salinity of 2% NaCl, the solubility ratio of oil to surfactant is close to 7.

Interfacial tension can be estimated from Chun-Huh correlation:

\[
\sigma_{ij} = \frac{c}{R_{ij}^2} \quad \text{(Huh, 1979)}
\]  

\( (5.1) \)

Fig. 5.27 Solubility ratios of 0.2% NI blend/1% Na$_2$CO$_3$/NaCl
where $\sigma_{s3}$: interfacial tension between excess oil or aqueous phase and middle phase, $R_{is}$: solubility ratio of oil or water by surfactant, $c$: a constant with a typical value of 0.3.

Interfacial tension of 0.2% NI blend/1% Na$_2$CO$_3$/NaCl estimated from Chun-Huh correlation with $c=0.3$ is plotted in Fig 5.28. At salinity of 2-3.4%, IFT measured by spinning drop method and that estimated from Chun-Huh correlation is very close. But in the over optimal range, the measured IFT is much higher than the correlation. A close match between experiments and correlation requires the constant $c$ take a value close to 10.

The solubility ratios of 0.5% NI blend and IFT estimated from Chun-Huh correlation with $c=0.3$ is plotted in Fig 5.29 and 5.30. Both the solubility ratios and the estimated IFT are very similar to that of the 0.2% in magnitude.

![Graph](image)

Fig. 5.28 Comparison of IFT measured by spinning drop measurements and that estimated by Chun-Huh correlation of 0.2% NI blend/1% Na$_2$CO$_3$/NaCl. $c=0.3$. 
Fig. 5.29 Solubility ratios of 0.5% NI blend/1% Na₂CO₃/NaCl

Fig. 5.30 IFT estimated by Chun-Huh correlation of 0.5% NI blend/1% Na₂CO₃/NaCl. c=0.3.
Chapter 6

SPONTANEOUS IMBIBITION

In a fractured reservoir, the success of surfactant flooding depends on how effectively the surfactant residing in the fracture can penetrate and propagate into the matrix. Thus it is believed that gravity-induced spontaneous imbibition best represents what will happen in a fractured reservoir. As stated in Chapter 2, the introduction of alkaline/surfactant solution overcomes capillarity forces by both wettability alteration and interfacial tension reduction. Oil leaves the matrix by gravity, and surfactant solution comes in to occupy the space left by oil.

In this chapter, three types of gravity dominated spontaneous imbibition experiments are described and discussed.

6.1. Spontaneous Imbibition in a Capillary Gap

The effect of buoyancy displacing oil from a capillary gap between two parallel surfaces was demonstrated with the system shown in Fig 6.1. A marble plate pre-equilibrated with 0.1 M NaCl brine overnight, then aged in crude oil MY3 at 80 °C for 48 hrs, was placed in an optical cell with a plastic film as a spacer to create a 13 μm gap between the plate and the front wall of the cell. A bevel was ground at the bottom of the plate to allow the aqueous phase to be present without flow resistance. The glass of the front of the cell was treated with a dilute solution of hexadecyltrimethylammonium bromide (CTAB) to make it preferentially oil-wet.
Fig. 6.1 Schematic set-up of spontaneous imbibition in a capillary gap. A calcite (marble) plate has two plastic films to create a 13 μm gap between the plate and the front of an optical cell.

Oil in the gap is not displaced when the cell was filled with 0.1 M NaCl brine and left for 20 hrs, Fig 6.2(a). The buoyancy forces could not overcome the capillary entry pressure to displace the oil from the gap. However, when the brine was replaced with 0.05% TC blend/1% Na$_2$CO$_3$/1%NaCl, spontaneous imbibition of the aqueous phase occurred, Fig 6.2(b). The fraction of oil displaced is plotted against dimensionless time for gravity drainage for a range of electrolyte strengths in Fig 6.3.

$$t_{o,s} = \frac{k\Delta \rho gt}{\mu_o L} \quad \text{(Hagoort, 1980)}$$

Here, the flow is assumed to be plane Poiseuille flow between parallel plates. Combining the velocity for Poiseuille flow and Darcy’s law, one can get:

$$k = \frac{h^2}{12}$$

where $k$: permeability,

$\Delta \rho$: density difference between aqueous and oil phases,

$t$: imbibition time,

$\mu_o$: oil phase viscosity,
Fig. 6.2 Displacement of crude oil in a narrow gap: (a) with brine, (b) with 0.05% Blend/1% Na₂CO₃/1% NaCl
$g$: gravitational acceleration,

$L$: height of the narrow gap,

$h$: the gap width between the two parallel plates.

Compared with the analytical solution for gravity drainage of linear relative permeability (n=1) and assuming zero capillary pressure, the displacement rate is about an order of magnitude slower. This can be caused by two reasons: 1) the accumulation of a large amount of oil (compared with that in the gap) in the bevel at the time surfactant solution was added; and 2) the plate surface’s being not perfectly flat, and the gap width being less than that of the spacers.

The system with 4.5% Na$_2$CO$_3$ and 0% NaCl was the system with second best displacement in Fig 6.3. Fig 5.16 shows this to be the system with WOR of 1:1 that had the lowest IFT when measured after 19 days. However, the high WOR observation of a
drop on a plate, Fig 4.9, would suggest that the system with 11% $\text{Na}_2\text{CO}_3$ would have been the optimum.

The systems with 0.05% Blend/1% $\text{Na}_2\text{CO}_3$/NaCl had the maximum oil displacement with 3% NaCl, which is close to the optimal salinity at WOR of 3:1 (Fig 5.3 (b)). At 6% NaCl, the least oil was displaced. It may be because of the phase separation of the surfactant solution (Fig 5.2), after which the denser surfactant rich phase stayed at the bottom of the cell.

The contrast in displacement efficiency between the different systems was not large because the parallel plate geometry has little opportunity for trapping compared to porous media. However, it does illustrate that the optimal salinity for displacement may not be the same as that observed for very large WOR such as the drop on a flat plate, Fig 4.6 and 4.9 Thus the design of an optimal system should consider the multi-component, multi-phase chromatographic displacement in porous media (Hirasaki, 1981).

One qualitative difference between displacement of oil from a gap between parallel surfaces and that from a porous rock is that the gap has 100% oil saturation while in the porous rock, both oil and formation water occupy the pore space. Gravity may

![In narrow gap](image1)

![In porous rock](image2)

**Fig. 6.4** Saturation/concentration profiles in a narrow gap or in a porous rock during displacement of oil by buoyancy
displace the mobilized oil, but may not displace the formation brine unless there is a significant density difference between the alkaline/surfactant solution and the formation brine, which results in the accumulation of a bank of formation brine ahead of the alkaline/surfactant solution. The possible oil and alkaline/surfactant concentration profiles are shown in Fig 6.4 (Hirasaki and Zhang, 2004). Dispersive mixing is necessary for the alkaline/surfactant solution to penetrate the bank of formation brine to contact the trapped oil. Also, the alkaline/surfactant solution must remain active after it mixes with the formation brine.

6.2. Spontaneous Imbibition with Dolomite Cores

6.2.1 Enhanced Oil Recovery by Spontaneous Imbibition

Spontaneous imbibition experiments were conducted with formation brine, stock-tank oil, MY3, and core samples of the dolomite formation of the reservoir of interest. The properties of the dolomite core samples and experimental conditions are listed in Table 6.1. Core preparation procedure and parameter calculation can be found in Appendix B. There was no further extraction or cleaning of the cores. The composition of the formation brine is in Table 6.2.

The initial oil saturation was established by flowing oil with the indicated pressure drop. Some samples were aged 24 hours at 80°C. Oil recovery by spontaneous imbibition was measured by placing the oil-saturated cores in imbibition cells filled with either formation brine or alkaline surfactant solution (Fig 6.5). Not a single drop of oil was recovered by spontaneous imbibition in formation brine during one to two weeks
The formation brine was replaced with alkaline surfactant solution, and the enhanced oil recovery by spontaneous imbibition was measured. Small drops of oil on the top end face of the core could be observed accumulating, detaching, and being collected in the imbibition cell (Fig 6.5(b)). The appearance of oil on the top face rather than the sides of the core suggests that the displacement was dominated by buoyancy rather than countercurrent capillary imbibition.

Table 6.1 Dolomite core properties, spontaneous imbibition experimental conditions and results

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<th>Core A</th>
<th>Core B</th>
<th>Core C</th>
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<td>Diameter, inch</td>
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<td>1.5</td>
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<td>Length, inch</td>
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<td>40</td>
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<tr>
<td>Brine*</td>
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<td>Brine 2</td>
<td>Brine 2</td>
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<td>Crude oil</td>
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<td>Pressure drop (psi)</td>
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<td>82</td>
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<tr>
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<td>Recovery in brine, %OOIP</td>
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<td>0</td>
<td>0</td>
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<td>CS-330+ TDA-4PO</td>
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<td>Residual oil saturation</td>
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* Note: brine composition is given in Table 6.2
Table 6.2 Formation brine compositions

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<th>Brine 2 (g/L)</th>
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<td>CaCl₂·2H₂O</td>
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<td>MgCl₂·6H₂O</td>
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</tr>
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<td>Na₂SO₄</td>
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<td>0.237</td>
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<tr>
<td>Fe(NH₄)₂(SO₄)₂·6H₂O</td>
<td>0.000</td>
<td>0.007</td>
</tr>
</tbody>
</table>

The oil recovery as a function of time is shown in Fig 6.6. Possible factors affecting the difference in oil recovery in the figure include permeability, initial oil saturation, surfactant formulation, and condition of aging. The surfactant formulation and aging conditions are not the dominant parameters because systems with the greatest and least recovery have the same surfactant formulation, and the system aged at 80°C has greater recovery than the system aged at room temperature. The effect of difference in permeability can be evaluated by plotting the oil recovery as a function of dimensionless time for gravity-dominated recovery.

\[
t_{DG} = \frac{k k_{ro} \Delta \rho g t}{(S_{oi} - S_{or}) \phi \mu_o L} \quad \text{(Hagoort, 1980)} \tag{6.3}
\]
where $k_{ro}^0$: endpoint relativity permeability of oil,

$S_{oi}$: initial oil saturation,

$S_{or}$: residual oil saturation,

$\phi$: rock porosity,

$L$: length of the rock sample.

Other variables are defined same as in Equation 6.1.

Fig. 6.6 Oil recovery by spontaneous imbibition.

The fractional recovery is expressed as a fraction of recoverable oil, assuming that the remaining oil saturation at the last measured point in Fig 6.6 is the residual oil saturation. The experimental results are compared to the 1D, gravity-drainage analytical solution (Richardson and Blackwell, 1971; Hagoort, 1980) assuming zero capillary pressure and a relativity permeability exponent of $n = 3$. The analytical solution is as follows:
\[ E_R = \frac{S_{oi} - \overline{S}_o}{S_{oi} - S_{or}} \] ................................. (6.4)

\[ E_R = \begin{cases} t_{Dg}, & t < t_{BT} \\ 1 - \left(1 - \frac{1}{n}\right)^{1/(nt_{Dg})^{n-1}}, & t > t_{BT} \end{cases} \] ................................. (6.5)

\[ t_{Dg, BT} = 1/n \] ................................. (6.6)

where \( E_R \) : recovery efficiency,
\( \overline{S}_o \) : average oil saturation,
\( t_{BT} \) : time of breakthrough.

The fractional recovery is plotted as a function of dimensionless time for gravity drainage and compared with the analytical solution in Fig 6.7. The recovery expressed in this way

\[ t_{D,g} = \frac{k k_r^0 \Delta \rho g t}{(S_{oi} - S_{or}) \phi \mu_o L} \]

\[ E_R = \frac{S_{oi} - \overline{S}_o}{S_{oi} - S_{or}} \]

Fig. 6.7 Oil recovery by spontaneous imbibition as function of dimensionless time for gravity drainage.
accounts for the difference in permeability. The fractional recovery appears to scale as if the rate of recovery of the mobile oil is caused by gravity drainage.

The hypothesis that the recovery was dominated by capillary imbibition was examined by plotting the oil recovery as a function of dimensionless time for recovery by spontaneous capillary imbibition in Fig 6.8.

\[ t_{D,Pc} = \sqrt[\phi \sqrt{\mu_o \mu_w}} \frac{k}{L_c^2} \frac{1}{(Xie, X. and Morrow, 2001)} \] \hspace{1cm} (6.7)

For a cylindrical core sample, \( L_c = \sqrt{\frac{D^2 L_2}{8L_2 + 4D^2}} \), where \( D \) is the diameter of the core.

The IFT in the dimensionless time is a value of \( 10^{-3} \) mN/m, which was a typical value for the three surfactant systems (Fig 5.15 and 5.16) The measured oil recovery occurred faster than that for the very strongly water-wet correlation. This observation implies that either some other mechanism, such as gravity, was contributing to recovery, or capillary

---

**Fig. 6.8** Oil recovery by spontaneous imbibition as function of dimensionless time for capillary imbibition, assuming IFT of 10-3 mN/m.
imbibition was contributing but the IFTs are different from the assumed value.

If the oil recovery is dominated by buoyancy and each matrix block acts independently, the analytical solution, Eq. 6.5, can be used to scale up to different permeability and matrix-block size. The time to a given level of recovery will be proportional to the height of the matrix block, $L$, and inversely proportional to permeability, $k$. However, the assumption that the matrix blocks act independently is challenged by the possibility of capillary contact between matrix blocks. Capillary contact between matrix blocks and re-entry of oil into matrix blocks will lengthen the time for oil recovery.

6.2.2 Wettability Determined with NMR

Freedman et al. (Freedman et al, 2001) evaluated the wettability of Bentheim sandstone, Berea sandstone, and the dolomite formation of the target application. A crude oil from the North Sea was used for the evaluation. Water would spontaneously imbibe into the sandstone cores, but no measurable spontaneous imbibition occurred in the dolomite samples during 24 hours. The relaxation time distributions of the crude oil in the sandstones were identical to that of the bulk oil, indicating that the sandstones were water-wet. However, the relaxation time distribution of the crude oil in the dolomite sample was shortened, indicating surface relaxation of the oil. This occurs because of oil making contact with the pore walls. Thus, this is evidence of oil wetting the pore walls in the dolomite sample.

Cores B and C were analyzed with NMR after brine saturation, oil saturation, and 24 hours’ aging at 80 °C for core B. The measurement procedure and experimental set-up
for aging can be found in Appendix B. The results are compared with the response of bulk oil. If the oil relaxation time $T_2$ in cores is smaller than that of the bulk oil, it indicates that the interaction between the oil and rock surface is stronger, which implies more oil-wetness of the cores. If the oil relaxation time does not change, then the core is still water-wet. Similarly, comparison of the brine response after brine saturation and oil saturation can also provide such information.

**Fig. 6.9** NMR response for bulk MY3

**Fig. 6.10** NMR response for Core B after brine saturation

**Fig. 6.11** NMR response for Core B after oil saturation

**Fig. 6.12** NMR response for Core B after aging in MY3 at 80 °C for 24 hours
Fig 6.9 shows the NMR response of bulk crude oil MY3. The peak of the relaxation time distribution is close to 0.3 s. Fig 6.10 shows the NMR response for Core B after brine saturation. The brine response is wide spread, which indicates that the core has a wide pore size distribution. The peak of its relaxation time distribution is about 0.85 s. After oil saturation, Fig 6.11, the water peak moves to a smaller value, which indicates that the large pores are occupied by oil. The oil relaxation time is 0.15 s, smaller than the bulk oil relaxation time, which indicates partial wetting of oil. After aging at 80 °C, Fig 6.12, the $T_2$ relaxation time of oil is even smaller. Therefore, aging at elevated temperature promotes oil-wetness.

$T_2$ relaxation time is better compared when $T_2$ distributions under different conditions are plotted together. Fig 6.13 shows the $T_2$ distribution of crude oil MY3. $T_2$ relaxation time of the bulk oil is longer than that after brine and oil saturation, which is
longer than that after aging at elevated temperature. This result indicates contact with oil makes the rock surface more oil-wet. The preferential oil-wetness was further promoted by aging in oil at elevated temperature.

6.3 Centrifuge Imbibition with Limestone Cores

Centrifuge imbibition experiments were conducted here instead of spontaneous imbibition experiments because centrifuge imbibition operates at multiple gravitational forces, which makes the process much faster than spontaneous imbibition, and allows multiple experiments – 6 cores can be processed at the same time.

Fig. 6.14 Schematic set-up of centrifuge imbibition with formation brine of surfactant solution.

One inch diameter by one inch length Texas Cream limestone cores were used in the centrifuge imbibition experiments. Each core was first jacketed with heat shrinkable Teflon sleeves to protect core integrity (O'Meara et al, 1992). It was then subjected to vacuum for over 8 hours to remove air. Afterwards, formation brine was added to the vacuum cell till the core was completely immersed. Vacuum was drawn over the whole system for at least 8 hours, then pressure was applied and maintained at 1,000 psi for over 8 hours to insure there was no remaining gas saturation. The brine-saturated core was centrifuged in crude oil to oil saturate the core by primary drainage at 15,000 RPM,
which corresponds to 80 psi pressure drop across the core. At the completion of this process, the core was inverted to displace brine from the opposite end. This is necessary because otherwise the opposite end would still be 100% brine saturated due to the hydrostatic saturation profile (Hirasaki et al., 1995). After the oil saturated core was aged at 80 °C for 48 hours. It was centrifuged at 6,000 RPM, which corresponds to 27 psi, in either formation brine or surfactant solution. The schematic set-up of water or surfactant flood is shown in Fig 6.14. The stainless steel screen was used to allow the aqueous phase to be present at the end of the core and co-current flow allowed to occur.

The duration of a centrifuge experiment should be designed according to experimental conditions. Ideally, an experiment should be run until the residual saturation of the displaced phase is reached. When the displaced phase is the non-wetting phase, time to reach residual saturation is shorter. But if the displaced phase is a wetting phase, its saturation may never reach an equilibrium value. Therefore a realistic time should be used. The equation for the late time response ((Hirasaki et al., 1995) is:

\[
N_p = 1 - \left(1 - \frac{1}{n}\right)(nt_D)^{\frac{1}{n-1}}
\] ................................. (6.8)

\[
t_D = \frac{kk_{vd}^0 \Delta \rho \omega r_0}{\phi(S_{do} - S_{dr})L \mu_d}
\] ................................. (6.9)

where:

- \(n\): Corey exponent,
- \(\omega\): angular velocity,
- \(r_0\): radial distance of a sample from the axis,
- \(S_{do}\): initial saturation of the displaced phase,
\( S_{ro} \): residual saturation of the displaced phase,

\( \mu_d \): viscosity of the displaced phase,

Fig. 6.15 Late time production as a function of time and Corey exponent (Hirasaki et al., 1995)

The last time production response is plotted in Fig 6.15. If the displaced phase is the non-wetting phase with a Corey exponent of 2, it only takes a dimensionless time of 25 to reach 99% of the equilibrium production. However, if the displaced phase is the wetting phase with a Corey exponent of 4, it requires a dimensionless time of \(10^3\) to reach 95% of the equilibrium production, and \(10^5\) to reach 99%.

Alkaline-surfactant solution improves oil recovery by altering wettability and lowering interfacial tension, as shown by the correlation between residual oil saturation and Bond number, Fig 6.16 (Lake, 1989). Bond number can be calculated from the following equation:
\[ N_B = \frac{1.0823 \times 10^{-13} k \text{ (md)} \Delta \rho \text{ (g/cm}^3) r_o \text{ (cm)} \omega^2 \text{ (RPM)}}{\sigma \text{ (mN/m)}} \]

(Hirasaki et al, 1990) \hspace{1cm} (6.10)

Bond number at 6,000 RPM is calculated as a function of IFT for cores with permeability of 6 milidarcy (md), Table 6.3, and marked as dots for water-wet conditions, and diamonds for oil-wet conditions on Fig 6.16. The figure suggests that if IFT can be lowered to \(10^{-3}\) mN/m, ideally, all oil should be recovered for cores of 6 md at RPM of 6000.

0.2% NI blend was used in the centrifuge imbibition with limestone cores. The optimal salinities of 0.2% NI blend/1% Na\textsubscript{2}CO\textsubscript{3}/x% NaCl at WOR of one and three are determined by phase

Table 6.3 Bond number at 6,000 RPM, Perm=6 md

<table>
<thead>
<tr>
<th>IFT, mN/m</th>
<th>(N_B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>(1.6 \times 10^{-4})</td>
</tr>
<tr>
<td>1</td>
<td>(4.7 \times 10^{-5})</td>
</tr>
<tr>
<td>0.1</td>
<td>(4.7 \times 10^{-4})</td>
</tr>
<tr>
<td>0.01</td>
<td>(4.7 \times 10^{-3})</td>
</tr>
<tr>
<td>0.001</td>
<td>(4.7 \times 10^{-2})</td>
</tr>
</tbody>
</table>
behavior to be 1.5 and 3.4 % NaCl (Fig 5.11).

The core properties, experimental conditions, duration of each experiment and results are listed in Table 6.4. The recovery is plotted in Fig 6.17. The oil recovery by formation brine is 67% on average, while the average oil recovery by 0.2% NI Blend/1% Na₂CO₃/NaCl is 84%. The recovery is not as high as expected, possibly caused by the

Table 6.4 Texas Cream limestone core properties, and centrifuge imbibition results

<table>
<thead>
<tr>
<th>Formation brine</th>
<th>NaCl, %</th>
<th>kair, md</th>
<th>φₜ, %</th>
<th>PV, ml</th>
<th>*OOIP, ml</th>
<th>So</th>
<th>t, days</th>
<th>**OR, ml</th>
<th>Sor</th>
<th>N_p, %</th>
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</thead>
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<td>4.93</td>
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<td>2.66</td>
<td>2.11</td>
<td>0.79</td>
<td>4</td>
<td>1.45</td>
<td>0.25</td>
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<tr>
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<td>6.82</td>
<td>22.4</td>
<td></td>
<td>2.90</td>
<td>2.36</td>
<td>0.81</td>
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<td>1.53</td>
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<td>65</td>
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<td>2.97</td>
<td>2.35</td>
<td>0.79</td>
<td>3</td>
<td>1.60</td>
<td>0.25</td>
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<td>3</td>
<td>2.02</td>
<td>0.13</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>4.64</td>
<td>21.8</td>
<td>2.77</td>
<td>2.00</td>
<td>0.72</td>
<td>6</td>
<td>1.64</td>
<td>0.13</td>
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<tr>
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<td>2.69</td>
<td>1.94</td>
<td>0.72</td>
<td>6</td>
<td>1.61</td>
<td>0.12</td>
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<td>3</td>
<td>2.29</td>
<td>0.11</td>
<td>86</td>
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<tr>
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<td>19.8</td>
<td>2.66</td>
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<td>7</td>
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<td>0.11</td>
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<td>22.1</td>
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<td>6</td>
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<td>19.2</td>
<td>2.54</td>
<td>1.90</td>
<td>0.75</td>
<td>7</td>
<td>1.63</td>
<td>0.11</td>
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<tr>
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<td>4.45</td>
<td>20.2</td>
<td>2.70</td>
<td>1.97</td>
<td>0.73</td>
<td>6</td>
<td>1.60</td>
<td>0.14</td>
<td>81</td>
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</tr>
<tr>
<td>2.4</td>
<td>3.70</td>
<td>20.5</td>
<td>2.66</td>
<td>2.08</td>
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<td>7</td>
<td>1.72</td>
<td>0.13</td>
<td>83</td>
<td></td>
</tr>
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<td>2.07</td>
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<td>6</td>
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<td>0.05</td>
<td>93</td>
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<td>2.6</td>
<td>3.95</td>
<td>20.5</td>
<td>2.56</td>
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<td>0.79</td>
<td>7</td>
<td>1.69</td>
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<td>2.7</td>
<td>4.28</td>
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<td>0.71</td>
<td>6</td>
<td>1.76</td>
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<td>87</td>
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<tr>
<td>2.8</td>
<td>3.10</td>
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<td>2.84</td>
<td>2.24</td>
<td>0.79</td>
<td>7</td>
<td>1.82</td>
<td>0.14</td>
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<td>3</td>
<td>5.23</td>
<td>21.6</td>
<td>2.85</td>
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<td>4</td>
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<td>5</td>
<td>9.21</td>
<td>24.4</td>
<td>3.23</td>
<td>2.59</td>
<td>0.8</td>
<td>3</td>
<td>1.96</td>
<td>0.19</td>
<td>76</td>
<td></td>
</tr>
</tbody>
</table>

* OOIP: Original oil in place. ** OR: Oil recovered
mixing with formation brine.

![Graph showing oil recovery vs NaCl concentration](image)

**Fig. 6.17** Oil Recovery by centrifuge imbibition in either formation brine (water flooding) or 0.2% NI Blend/1% Na$_2$CO$_3$/NaCl.
Chapter 7

SURFACTANT CONSUMPTION

The addition of sodium carbonate is expected to reduce anionic surfactant adsorption on calcite. Without adding an alkali, the adsorption of anionic surfactant on calcite is expected to be high, because at neutral pH, the interface of brine/calcite is positively charged (see Chapter 3), which will attract the negatively charged surfactant by electrostatic forces. The adding of sodium carbonate changes the calcite surface to be negatively charged (also see Chapter 3), which will repel surfactant molecules.

Celik et al. (Celik et al, 1988) found that the addition of silicates, as well as n-Butanol, reduced the adsorption of ethoxylated sulfonates on limestone. Sulfonate adsorption also decreased with increased ethoxylation number. Adsorption mechanisms of anionic surfactant on calcite were proposed to be either electrostatic interactions (Al-Hashim et al, 1988; Mannhardt et al, 1992), or chemisorption and surface precipitation (Fuerstenau and Miller, 1967; Somasundaran and Hanna, 1977; Ananthapadmanabhan and Somasundaran, 1985; Andersen et al, 1991; Martínez-Luévanos et al, 1999).

7.1 Sodium Carbonate Reduces Anionic Surfactant Adsorption

Anionic surfactant adsorption without or with sodium carbonate was determined by potentiometric titration with hyamine (see Appendix C for titration procedure). The initial
Fig. 7.1 Adsorption of TC blend.
Solid symbols: without sodium carbonate; open symbols: with sodium carbonate

Surfactant concentration was fixed, while surfactant solution and calcite powder were mixed at varied weight ratios (see Appendix C for sample preparation). The equilibrium surfactant concentration was determined by titration. The calcite powder was acquired from Solvay Performance Chemicals, with a code name of SOCAL31. Its surface area determined by BET adsorption was 17.851 m²/g. Adsorption density was then calculated with the obtained data.

The adsorption of the TC blend without or with sodium carbonate is shown in Fig 7.1. Two initial surfactant concentrations were used: 0.05 and 0.1 wt%. At low surfactant/calcite ratio, the adsorption of surfactant was low. As the ratio increased, the adsorption increased, till an equilibrium adsorption density was reached-2×10⁻³ mmol/m², which corresponds to 83 Å²/molecule. According to Gaudin (Gaudin, 1957), each straight-chain fatty acid molecule occupies approximately 20 Å² in a compact monolayer. Considering
the EO / PO groups on the surfactant molecules, the equilibrium adsorption of TC blend is of the order of close-pack adsorption.

When sodium carbonate was added, the adsorption of TC blend was significantly reduced. Sodium carbonate concentrations ranged from 0.3M (moles/liter) to 0.45M. The adsorption with sodium carbonate was only close to one tenth of that without sodium carbonate.

Similarly, adding sodium carbonate also remarkably reduced the adsorption of the NI blend, as shown in Fig 7.2. The equilibrium adsorption densities at 0.05 and 0.1% NI blend are 2.5 and 3.5 mmol/m² respectively. However, solutions at the same surfactant concentrations but with 1% sodium carbonate have adsorption densities lower than $2 \times 10^{-4}$ mmol/m². The adsorption of CS-330 was also found to be significantly reduced by sodium carbonate.

![Fig. 7.2 Adsorption of NI blend.
Solid symbols: without sodium carbonate; open symbols: with sodium carbonate](image-url)
The low adsorption of CS-330 and TC and NI blends in the presence of sodium carbonate was expected. However, the adsorption of TDA-4PO S was anomalous, which will be discussed in the next section.

### 7.2 Problem with TDA-4PO S

Fig 7.3 shows the adsorption of TDA-4PO S without or with sodium carbonate. Without adding sodium carbonate, the equilibrium adsorption density was close to $4 \times 10^{-3}$ mmol/m$^2$. In the presence of 0.3 M sodium carbonate, the equilibrium adsorption density of 0.05% TDA-4PO S was reduced to half, but that of the 0.1% was even higher than without alkali.

---

**Fig. 7.3 Adsorption of TDA-4PO S**
Solid symbols: without sodium carbonate; open symbols: with sodium carbonate
Table 7.1 Particle size distribution of 0.05 and 0.1 % TDA-4PO S / 0.3M Na₂CO₃

<table>
<thead>
<tr>
<th>Solution</th>
<th>Particle size, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 % TDA-4PO S / 0.3M Na₂CO₃</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>123</td>
</tr>
<tr>
<td></td>
<td>211</td>
</tr>
<tr>
<td>0.1 % TDA-4PO S / 0.3M Na₂CO₃</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>178</td>
</tr>
<tr>
<td></td>
<td>316</td>
</tr>
</tbody>
</table>

The original solutions of 0.05 and 0.1 % TDA-4PO S / 0.3M Na₂CO₃ were visibly turbid. The particle size distributions of the two solutions were analyzed with Digital Light Scattering equipment. Table 7.1 lists the three most significant peaks of each solution. The turbid solutions were filtered with 100 nm filtration papers, but the resulting solutions were still turbid. It was speculated that either the aggregates causing the turbidity were smaller than 100 nm, or that they were larger than 100 nm, but dissociated into smaller aggregates when passing through the filter, and associated again after filtering.

The two original TDA-4PO S solutions were also centrifuged, and the supernatants were titrated to compare with the original surfactant concentration. The surfactant concentration after centrifuging was the same as that before centrifuging. Therefore it can be concluded that the surfactant was not lost during centrifuging by itself. There must be some interaction between the turbid surfactant solution and the calcite powder, which resulted in the loss of surfactant.

This problem can be solved by blending another surfactant to it, which is clear at the desired salinity (see Fig 5.2 for the phase behavior of the TC blend). The
Chapter 8

CONCLUSIONS

In this chapter, the conclusions are presented.

8.1 Interfacial Properties and Wettability of Carbonate

1) Crude oils used for interfacial research should be screened for contamination. One simple way to do this is by measuring crude oil/NaCl brine interfacial tension. If the interfacial tension is between 20-30 mN/m, the oil may be uncontaminated; otherwise, the oil may be contaminated and not representative.

2) Zeta potential is a function of pH. Zeta potential of crude oil/brine interface is positively charged at low pH through the protonation of petroleum base, and negatively charged at high pH through dissociation of petroleum acid.

3) Sodium carbonate and bicarbonate are the potential determining ions for calcite. Calcite/brine interface, which is normally positively charged at neutral pH, can be made negatively charged through the addition of sodium carbonate / bicarbonate.

4) Wettability is a function of oil composition and aging time on the substrate.

5) The system of crude oil MY3, brine and marble plate is strongly oil-wet, which is consistent with zeta potential measurements at interfaces. In sodium chloride brine of neutral pH, the oppositely charged crude oil / brine and carbonate / brine interfaces result in the oil-wetness of the carbonate substrate.
8.2 Wettability Alteration with Sodium Carbonate / Surfactant

1) Wettability can be altered by sodium carbonate/surfactant solution. Advancing contact angle ranged from intermediate-wet to preferentially water-wet.

2) The ease of wettability alteration with alkaline/surfactant solution is a function of pre-equilibration solution composition, aging time and temperature in oil, and alkaline/surfactant solution formulation.

3) Advancing contact angle and drop size of MY3 crude oil on a marble plate are dependent on electrolyte type and concentration. Drop size experiences a minimum with electrolyte strength. Contact angle decreases with increasing sodium carbonate concentration to 11%, where an equilibrium value is reached. When sodium carbonate concentration is fixed at 1%, sodium chloride concentration does not seem to affect wettability alteration.

8.3 Phase Behavior and Interfacial Tension

1) Sodium carbonate can react with petroleum acids to form soap, which acts as anionic surfactant. The natural soap alone is not very effective in reducing interfacial tension. The addition of ethoxylated and / or propoxylated sulfates is effective in both increasing the optimal salinity and lowering interfacial tension.

2) Alkaline / surfactant phase behavior is dependent on salinity, surfactant concentration, and WOR. Dependence of optimal salinity on surfactant concentration and WOR can be correlated with natural soap / surfactant mole ratio.
3) Compared with N67-7PO S by itself, NI surfactant blend has improved phase behavior. NI blend also has high solubility ratios and allows the surfactant solution to be injected at optimal condition as a single phase.

4) Interfacial tension measurements are problematic for alkali/anionic surfactant /crude oil systems. At low surfactant concentration, IFT is measured between excess phases. It changes with settling time because of the separation of surfactant-rich phase from the excess aqueous phase.

5) Interfacial tension of under-optimum to optimum systems should be measured when there is enough surfactant-rich phase dispersed in the aqueous phase. Interfacial tension of over-optimum systems should be measured at equilibrium between microemulsion and excess aqueous phase.

6) Ultra-Low IFT in lower-phase microemulsion region gives wide ultra-low IFT.

7) During a spinning drop measurement, it takes time for surfactant to reach distribution equilibrium even using pre-equilibrated phases. Although during phase behavior test, oil and brine may have been in equilibrium, the redistribution of surfactant but during spinning drop measurements still takes time, which can be a few hours.

8.4 Spontaneous Imbibition

1) After being saturated with oil then aged at elevated temperature, dolomite cores become preferentially oil-wet. In NMR measurements, the T₂ relaxation time of the oil in the dolomite cores is considerably shorter than that of the bulk oil.
2) When such a core is brought into contact with brine, oil is retained in oil-wet pores by capillarity.

3) Oil displacement can occur by buoyancy when such a core is contacted with alkaline / surfactant solution because it lowers interfacial tension and alters wettability to more water-wet conditions. Oil is recovered by spontaneous imbibition.

4) Oil recovery in the narrow gap and in the core is different because only oil is in the narrow gap, while both formation brine and oil are in a porous rock. Dispersive mixing is required for the surfactant to penetrate the accumulated formation brine.

8.5 Surfactant Adsorption

1) The adsorption of anionic surfactants on calcite is a fraction of close-packed monolayer.

2) The presence of sodium carbonate significantly reduces the adsorption of anionic surfactants provided the solution is clear.

3) Turbid surfactant solution can result in high apparent adsorption even in the presence of carbonate.
Chapter 9

FUTURE WORK

9.1 Phase Behavior and Interfacial Tension

1) Follow up on the phase behavior of N67-7PO S aqueous solutions. Investigate the causes of the change in phase behavior.

2) Conduct the phase behavior test at high surfactant concentration (1-3%) and low WOR (for example, 1:9) in long glass pipettes. The difficulties in making reproducible interfacial tension measurements are caused by the low surfactant concentration which results in the small amount of microemulsion. By keeping the soap / synthetic surfactant ratio constant, increasing surfactant concentration and decreasing WOR, middle phases might be produced close to optimal salinity.

3) Conduct the phase behavior test at temperatures higher than the room temperature. Investigate in the effect of temperature on optimal salinity and emulsion coalescence rate.

4) Conduct the phase behavior test and interfacial tension measurements with other crude oils. Investigate the effect of acid number.

5) Extend the interfacial tension measurements of 0.2% NI blend / 1% Na₂CO₃ / 2-4% NaCl to 0-5% NaCl because the reservoir salinity of the target application is low (~1% NaCl), and the optimal salinity of the NI blend is 5%.

6) Use silicate along with carbonate when working with dolomite. Because magnesium carbonate is more soluble than calcium carbonate, silicate will be
needed along with carbonate to suppress magnesium concentration in dolomite formations.

9.2 Spontaneous Imbibition

1) Spontaneous imbibition in dolomite sand packs is needed because dolomite cores are often very different. Sand packs however, can be made of similar properties. A systematic study of the dependence of oil recovery is thus possible.

2) A model of the spontaneous imbibition process is needed to guide the experiment.

3) Forced displacement in dolomite sand columns should be conducted to compare with the spontaneous imbibition.
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NOMENCLATURE

Notations:

A  Area
a  Capillary constant
D  Diameter of a core sample
d  Oil drop or air bubble diameter
E  Applied electric field
E  Eotvos Number
$E_R$  recovery efficiency
G  Gravity number
g  Acceleration of gravity
h  Height of a capillary meniscus above a flat liquid surface
2H  Mean curvature of the interface
k  Absolute permeability
$k_w$  Permeability of water
$k_{rw}$  End point relative permeability of water
L, l  Length of flow
L  length of a core sample
L  Horizontal length of a gap
$Lc$  Characteristic length
n:  Corey exponent
$N_B$  Bond number
\( N_{ca}, N_{ca}^* \)  Capillary number
P  Pressure
P_c  Capillary pressure
\( q_t \)  Total flow rate
R  Radius of curvature
R  Solubility ratio
RI  Refractive index
\( r_m \)  Radius of the less dense drop in spinning drop apparatus
S_o  Oil saturation
S_w  Water saturation
t  Imbibition ime
\( t_{BT} \)  time of breakthrough
\( t_{D,g} \)  Dimensionless time for gravity drainage
\( t_{D,pc} \)  Dimensionless time for capillary imbibition
u  Darcy velocity
\( v \)  Interstitial velocity

**Greek Letter:**
\( \varepsilon \)  Dielectric constant
\( \mu \)  Fluid viscosity
\( \mu_w \)  Viscosity of water phase
\( \theta \)  Equilibrium contact angle
\( \theta \)  Dip angle of the reservoir
\( \theta_a \) Advancing contact angle
\( \theta_r \) Receding contact angle
\( \rho \) Oil drop or air bubble density
\( \rho_i \) Density of phase \( i \)
\( \Delta \rho \) Density difference of two fluid phases
\( \sigma \) Interfacial tension between two fluid phase
\( \sigma_{ij} \) Interfacial tension of interface between phase \( i \) and \( j \)
\( u \) Terminal velocity
\( \omega \) Angular velocity of rotation
\( \zeta \) Zeta potential
\( \Delta \) Increment

**Subscripts:**

\( a \) Advancing
\( A \) Phase A
\( B \) Phase B
\( f \) Medium
\( mo \) Microemulsion/oil interface
\( mw \) Microemulsion/water interface
\( o \) Oil phase
\( os \) Oil/substrate interface
\( ow \) Oil/water interface
\( ws \) Water/substrate interface
List of Accents:

- Vector

[ ] Concentration
Appendix A

ZETA POTENTIAL MEASUREMENT PROCEDURE

A.1. Buffer Preparation for Crude Oil Dispersions

A.1.1 pH 4, 5, and 6

1. Make 250ml 0.2M NaC₂H₃O₂ solution.

2. Make 250ml 0.2M HC₂H₃O₂.

3. Prepare each buffer according to Table A.1, using a 100 ml volumetric flask. Volumes are given in milliliters.

<table>
<thead>
<tr>
<th>pH</th>
<th>0.2M NaC₂H₃O₂</th>
<th>0.2M HC₂H₃O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>18</td>
<td>82</td>
</tr>
<tr>
<td>5</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>94.7</td>
<td>5.3</td>
</tr>
</tbody>
</table>

A.1.2. pH 8 and 10

1. Make 250ml 0.2M Na₂CO₃.

2. Make 250ml 0.2M NaHCO₃.

3. Take 50 ml from the 0.2M NaHCO₃ solution and dilute it to 100ml. This is the pH 8 buffer.

4. Mix 13.2ml Na₂CO₃ with 23.56ml NaHCO₃ and bring the volume to 100ml. This is the pH 10 buffer.
A.2. Sample Preparation Procedure for COULTER DELSA 440

A.2.1. Sample Preparation for Crude Oil/NaCl Brine Zeta Potential

1. Prepare six 50ml 0.02M NaCl brine solution of pH 2-10. pH 4-10 brines are adjusted with a few drops of buffer solutions (A.1), and pH 2-3 brine are adjusted with acetic acid.

2. Mix brine solution with crude oil at a ratio of 5:1, i.e. mix the 50ml brine with 10ml crude oil.

3. Sonicate the brine/oil mixture with the Branson Sonic Probe 450. Place the probe tip about 1/2" into the solution. Set rate to CONSTANT, at setting 6, for 40 seconds.

4. Keep the brine/oil mixture at 25 °C overnight.

5. If the emulsion is cloudy, centrifuge the emulsion at 18000 RPM for 40 minutes.

6. If the emulsion has a lot of particles, a serial filtration needs to be done. Using 1.2μm or 0.45μm filters before using a 0.2μm filter. Filter the samples into a 50ml disposable tri-pour beaker.

7. Add an amount of the original emulsion to the centrifuged emulsion until the sample has the desired particle density. The Delsa runs better on very light particle density compared to a “thick” emulsion, so do not overdo it. One way to check the particle density is to hold the beaker up and look through it, putting a finger behind it. The finger should be blurred but recognizable. If you can not see the finger at all, the emulsion is too dense.
8. Calibrate the Corning 320 pH meter by checking pH 4 and 7. For each emulsion, after sonicating, filtering, and/or centrifuging, record the pH before running the zeta potential measurement.

A.2.2. Sample Preparation for Calcite/NaCl Brine Zeta Potential

1. Prepare five 50ml 0.02M NaCl brine solution of pH 6-11, adjusted with a few drops of 0.1M NaOH or HCl/HNO₃.

2. Mix each brine solution with 1g CaCO₃ powder (Fisher product, 0.824 m²/g by BET).

3. Sonicate the brine/calcite mixture with the Branson Sonic Probe 450. Place the probe tip about 1/2" into the solution. Set rate to CONSTANT, at setting 4, for 1 minute.

4. Let the mixture settle for 20-30 minutes – allow calcite powder to settle a little bit and the temperature to go down.

5. Calibrate the Corning 320 pH meter by checking pH 4 and 7. For each suspension, after sonicating, record the pH before running the zeta potential measurement.

A.2.3. Sample Preparation for Calcite/Na₂CO₃ and/or NaHCO₃ Zeta Potential

1. Prepare 0.02N Na₂CO₃, 0.02N NaHCO₃, and use their blends to reach other pH. (In this proposal, zeta potential measurement with 0.1N Na₂CO₃/ NaHCO₃ was presented, but to compare with the calcite/brine zeta potential, 0.02N would be more proper)
2. Take 50ml Na₂CO₃, 50ml Na₂CO₃/NaHCO₃ mixture, three 50ml NaHCO₃ solution. Mix each of the five samples with 0.5g CaCO₃ powder. In one of the NaHCO₃ sample, add 1N HCl until no bubbles coming out, and in another, add a few drop of HCl to adjust pH to around 8.

Step 3-5 are the same as in A.2.2.

A.3. Experimental Procedures


1. Run Coulter conductivity calibrator (YS 3167), 1000 microsiemens/cm – determine cell constant as described in Chapter 3.15 of the Product Reference Manual.

2. Run mobility standard EMPSL7 (Beckman Coulter PN 8301351) – achieve acceptable results from the specification sheet of the product. If the result is not acceptable, disassemble, clean and reassemble the sample cell, then determine the positions of upper and lower stationary phases of the instrument with the mobility standard. Refer to Chapter 3.16 of the Product Reference Manual or use ADC Method as described in the next section-A.4.

3. Prepare samples as described in A.2.

4. Run mobility and zeta potential of samples at upper and lower stationary phases for at least three times.

5. Average mobility and zeta potential of lower and upper stationary phases respectively.

6. Average mobility and zeta potential of the averaged lower and upper stationary phases.
A.4. ADC Method of Cell Positioning

1. With sample cell in place, determine that detector levels are all less than 10V.

2. Open the Diagnostics menu. Click on “A/D Convertor Test”, select #5, 15 degree detector and select #5: Unused in Conductivity Range.

3. Starting with the laser “in Glass” at the top of the cell insert, move the cell down to bring the detector in line with the top edge of the sample channel. Observe the A/D count as the cell moves. It should vary only a few percent while in or out of the channel, but show a decrease of up to 70 percent as the edge of the channel moves past the detector. Continue to a point a few dial units past the point where you observed a minimum.

4. Reversing direction, jog the cell up one step while watching the ADC count. If the count decreases, shift the micrometer to zero and try another step until the count shows an increase.

5. Continue in the up direction toward the bottom of the channel. After about 100 dial units you will pass a second minima. Reverse direction and go a few dial units back past the minima again.

6. You may position the cell by calculating dial position and approaching that reading from the up direction. For exacting measurements made between different positions in the channel, cell movement should be consistently in one direction (either up or down) to avoid “backlash” errors in positioning.

* Buffer preparation, sample preparation for crude oil/NaCl brine, experimental procedure, and ADC Method of Cell Positioning are adapted from Yang, 2000.
Appendix B

CORE PREPARATION AND PARAMETER CALCULATION

B.1. Core Preparation for Imbibition Experiments

1. Weigh a dry core, and the weight is denoted as $W_{\text{dry}}$.
2. Vacuum the core in a holder by vacuum pump for 8 hours.
3. Saturate the core with formation brine under vacuum for 8 hours.
4. Pressurize the core in formation brine at 1000 psi for 8 hours.
5. Weigh the core again, and the weight is denoted as $W_{\text{brine-saturated}}$.
6. Assemble the core into Hassler core holder.
7. Pass formation brine through the core at different rates. Rates should be measured by graduate cylinder and stopwatch. Record the pressure drop corresponding to each flow rate.
8. Pass 5 PV (pore volume) of crude oil through each end of the core with pump (total 10 PV). Pressure drop should be always lower than the confining pressure. Collect the displaced formation brine in a graduate cylinder.
9. Weigh the core again, and the weight is denoted as $W_{\text{oil-saturated}}$.

B.2. Core Parameter Calculation

1. Permeability Using the experimental results from procedure 7, permeability is calculated according to the following equation:
\[ k_b = \frac{q_b \mu_b L}{-\Delta p_b A} \]  \hspace{1cm} \text{(Willhite, 1986)}  \hspace{1cm} \text{(B.1)}

Where \( k_b \): permeability, \( m^2 \) (1 \( m^2 = 1.01325 \times 10^{12} \) darcy).

\( q_b \): flow rate, \( m^3/s \);

\( \mu_b \): viscosity, \( \text{kg/m·s} (=10 \text{ poise}) \);

\( L \): core length, \( m \);

\( A \): core cross-section area, \( m^2 \);

\( \Delta p_b \): pressure drop, Pa.

2. **Porosity** Porosity is the fraction of pore volume to the total volume. It is calculated by equation (B.2):

\[ \phi = \frac{W_{\text{brine-saturated}} - W_{\text{dry}}}{\rho_{\text{brine}} V_t} \]  \hspace{1cm} \text{(B.2)}

Where \( \Phi \): porosity, \( \% \);

\( W_{\text{dry}} \): weight of the dry core;

\( W_{\text{brine-saturated}} \): weight of the core saturated with formation brine;

\( \rho_{\text{brine}} \): density of the formation brine, \( \text{g/ml} \);

\( V_t \): total volume of the core, \( \text{ml} \).

3. **Saturation** Oil and brine saturations can be calculated in two ways

1) Derived through material balance:

\[ S_w V_r \phi \rho_{\text{brine}} + S_o V_r \phi \rho_{\text{oil}} = W_{\text{oil-saturated}} - W_{\text{dry}} \]  \hspace{1cm} \text{(B.3)}

\[ S_w + S_o = 1 \]  \hspace{1cm} \text{(B.4)}

So,

\[ S_w = \frac{W_{\text{oil-saturated}} - W_{\text{dry}} - V_r \phi \rho_{\text{oil}}}{V_r \phi (\rho_{\text{brine}} - \rho_{\text{oil}})} \times 100 \]  \hspace{1cm} \text{(B.5)}
\[ S_o = \frac{W_{\text{dry}} - W_{\text{oil-saturated}} + V_i \phi \rho_{\text{brine}}}{V_i \phi (\rho_{\text{brine}} - \rho_{\text{oil}})} \times 100 \]  

(B.6)

Where \( S_w \): water saturation, %;

\( S_o \): oil saturation, %;

\( W_{\text{brine-saturated}} \): weight of the core saturated with crude oil after brine-saturated;

\( \rho_{\text{oil}} \): density of the crude oil, g/ml.

The other parameters are as explained before.

2) Calculated through the volume of the displaced brine

\[ S_o = \frac{\text{Volume of displaced brine}}{V_i \phi} \]  

(B.7)

\[ S_w = 1 - S_o \]  

(B.8)

**B.3. Core Preparation for NMR Measurements**

1. After the permeability of a core is measured, wrap the core thoroughly with paraffin film to prevent any evaporation.

2. Mark the direction of the core, then place it in the holder of NMR instrument. Mark the elevation of the holder.

3. Measure the NMR response.

4. After the core is saturated with crude oil, wrap it with heat shrinkable Teflon FEP rollcover.

5. Place the core into the holder of NMR. Note both the direction of the core and the elevation of the holder should be the same as step 2.

7. If the core is aged at 80 °C, after aging, flood the core at high pressure again to get rid of any trapped gas/air. Then repeat step 4-6.

B.4. Method for Core Aging at High Temperature

After a core is saturated with oil, put it in a jar filled with crude oil, as in Fig. B.1. Activated charcoal is used to absorb the evaporated hydrocarbons and H₂S. Put the whole set up in an oven. Adjust the temperature to a desired value.

![Diagram of core aging setup](image)

Fig. B.1 Set up for core aging at high temperature
Appendix C

ANIONIC SURFACTANT ADSORPTION DETERMINATION

C.1. Potentiometric Titration

C.1.1 Equipment and Reagent

1. **Electrode**  The pHoenix Surfactant Combination Electrode, from pHoenix Electrode Co. (Cat. No. SUR1502).

2. **Automatic Titrator**  Metrhom Titrino Model 716, from Brinkman Instruments.

3. **Beaker**  A 100 ml beaker.

4. **Magnetic stirrer**

5. **Balance**  Accurate to at least 10mg.

6. **Titrant**  Benzethonium Chloride (Hyamine 1622), from Gallord-Schlesinger Industries Inc., 0.004 M solution (Cat. No. 192233F), or crystalline solid (250g, Cat. No. 560162Y). For any large number of analyses, the solid materials are much more economical.

7. **Standard Anionic Surfactant Solution (for standardizing the titrant)**  0.01 M sodium lauryl sulfate (sodium dodecyl sulfate), from pHoenix Electrode Co. (Cat. No. SURAS02). (Note: solution will degrade with time.)

8. **Sample Additive (to keeps electrodes clean)**  Diluted Triton X-100, from pHoenix Electrode Co. (Cat. No. SURIS01).

9. **Electrode Filling Solution**  4 M KCl (with Ag⁺), from pHoenix Electrode Co. (Cat. No. R001011).
10. **pH Adjuster Solution** 0.01 M HCl.

11. **Electrode Rinse Solutions** 0.005 M HCl.

### C.1.2 Experimental Procedure

1. Prepare a solution of benzethonium chloride, approximately 0.004 M (If use the standard 0.004 M solution, skip to step 5). This concentration is somewhat arbitrary. A titrant should be dilute enough to yield a measurable titration volume, about half of the burette volume containing the titrant. In our case, we use a 10 ml burette, so the desired titrant volume used is 5 ml. Titrant consumption should not smaller than 1 ml, and not larger than 10 ml, either of which will result in large errors.

2. Weigh about 2 gram standard 0.01M SDS solution into a 100 ml beaker and dilute to approximately 60 ml with deionized water.

3. Immerse the surfactant specific electrode in the solution of analyte. Add one or two drops of a 1% solution of Triton X-100. Commence stirring using a magnetic stirrer. Make sure there is not any air bubble adsorbing to the electrode.

4. Begin adding hyamine solution using the automatic titrator until the maximum rate of voltage change is passed (the automatic titrator will find the point and stop automatically). Calculate the hyamine concentration as follows (assume the density of SDS solution is 1 g/ml):

$$N_t = \frac{C_s \cdot W_s}{V_t} \tag{C.1}$$

Where $N_t$: normality of titrant, M;

$C_s$: concentration of standard SDS solution, 0.01 M;
Ws: weight of standard SDS solution, g;

Vt: volume of titrant consumed, ml.

5. With samples prepared as stated in the next section C.2, weigh enough samples in the 100 ml beaker so that the titrant consumption is about 5 ml.

6. Same as step 3.

7. Same as step 4, but the equation used to calculate sample surfactant concentration is:

\[
Csamp = \frac{Nt \cdot Vt}{Wsamp} \quad (C.2)
\]

Where Csamp: sample concentration, M

Nt: normality of titrant, M;

Vt: volume of titrant consumed, ml.

Wsamp: weight of the sample, g;

Here, the volume of the sample is assumed to the same as its weight. If the sample density deviates far from 1 g/ml, then actual volume of the sample should be used instead of its weight.

C.1.3 Notes on the Method

1. No buffer is recommended.

2. Although the electrode manufacturer, pHoenix Electrode Co., recommends that pH be controlled between 2 and 12, especially, when titrating sulfates and sulfonates, pH should be controlled between 2.5-4.5. It is found that the pH range does not have to be this restrictive. pH does not need to be adjusted even in high pH sodium carbonate solution as long as the titration is performed at slow mode.
Adjusting pH of surfactant solution containing sodium carbonate often causes fluctuating results, possibly caused by the carbon dioxide bubbles generated during neutralization.

3. For surfactant solution containing a considerable amount of salt, the titration rate should be set to slow. For such solution, even at normal speed, the experimental error is usually large, while at slow rate, the error is found to be acceptable.

C.2. Sample Preparation

1. Make surfactant solution of desired concentration (0.05 wt% and 0.1 wt% with/without sodium carbonate). Determine the exact surfactant concentration with potentiometric titration using 4mmol/l Hyamine solution.

2. Add 40g of surfactant solution into each of the centrifuge tubes, then add different amount of calcite powder into each tube to make the weight ratio between surfactant solution and calcite powder to certain value. For surfactant solution without sodium carbonate, the ratio is usually 400, 200, 100, 80, 60, 40, 20, 10, 5, 3, while for surfactant solution in presence of sodium carbonate, the ratio is usually 100, 60, 40, 20, 10, 5, 3 (because at higher weight ratio, the measured equilibrium surfactant concentration is usually very close to the original surfactant concentration).

3. Use Branson Sonifier 450 to sonicate the calcite and solution mixture (set duty cycle at constant, output control at 6) for 1 minute.

4. Put the sonicated samples onto a rotating shaker. Let it mix for at least 24 hours.

5. Centrifuge the mixed samples at 2700rpm for 30 minutes.
6. Take each supernatant and determine the equilibrium surfactant concentration with potentiometric titration.

* Section C.1 refers to:

2. Surfactant Ion Selective Electrodes Reference, pHoenix Electrode Co.