



## **PROJECT REPORT**

# **WETTABILITY ALTERATION IN CARBONATE RESERVOIR THROUGH CHEMICAL EOR**

Submitted for partial fulfilment of requirements for the  
Winter Training Programme

**Under**

**The Supervision of**

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## **CERTIFICATE**

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**Akshay K K**

# **ABSTRACT**

Recovery from fractured, oil-wet/mixed-wet, carbonate reservoirs by waterflooding is poor. Dilute surfactant methods are being developed to improve oil recovery from fractured carbonates. This paper investigates the interactions of dilute alkaline anionic surfactant solutions with crude oil on carbonate mineral surfaces. Wettability, phase behavior, interfacial tension and adsorption experiments have been conducted. Anionic surfactants have been identified which can change the wettability of the calcite surface to intermediate/water-wet condition as well or better than the cationic surfactant DTAB with a West Texas crude oil. All the carbonate surfaces (Lithographic Limestone, Marble, Dolomite and Calcite) show similar behavior with respect to wettability alteration with an anionic surfactant. Anionic surfactants, which lower the interfacial tension with the crude oil to very low values, have also been identified. The adsorption of the sulphonate surfactants can be suppressed significantly by the addition of the alkali.

## **Contents**

<b>ABSTRACT .....</b>	<b>4</b>
<b>CHAPTER 1.....</b>	<b>9</b>
<b>ONGC – CAUVERY ASSET .....</b>	<b>9</b>
<b>1.1 INTRODUCTION TO GEOLOGY OF CAUVERY BASIN .....</b>	<b>9</b>
<b>1.2 INTRODUCTION TO CAUVERY ASSET .....</b>	<b>9</b>
<b>1.3 EXPLORATION.....</b>	<b>10</b>
<b>1.4 OUR FIELD EXPOSURES .....</b>	<b>12</b>
<b>1.4.2. CEMENTING SECTION VISIT .....</b>	<b>12</b>
<b>1.4.3. WELL STIMULATION SERVICES.....</b>	<b>12</b>
<b>1.4.4. WELL LOGGING DEPARTMENT .....</b>	<b>13</b>
<b>1.4.5. DRILLING RIG VISIT E760-3.....</b>	<b>13</b>
<b>CHAPTER 2.....</b>	<b>14</b>
<b>2.1 OIL RECOVERY .....</b>	<b>15</b>
<b>2.1.1 PRIMARY RECOVERY .....</b>	<b>15</b>
<b>2.1.2 SECONDARY RECOVERY .....</b>	<b>15</b>
<b>2.1.3 TERTIARY RECOVERY .....</b>	<b>15</b>
<b>2.2 ENHANCED OIL RECOVERY .....</b>	<b>16</b>
<b>2.2.1 IMPROVED OIL RECOVERY (IOR).....</b>	<b>16</b>
<b>2.2.2 ENHANCED OIL RECOVERY (EOR). .....</b>	<b>16</b>
<b>2.3 EOR PROCESSES.....</b>	<b>17</b>
<b>2.3.1 MOBILITY CONTROL.....</b>	<b>17</b>
<b>2.3.2 CHEMICAL PROCESS.....</b>	<b>17</b>
<b>2.3.3 MISCIBLE PROCESS .....</b>	<b>19</b>
<b>2.3.4 THERMAL PROCESSES .....</b>	<b>20</b>
<b>CHAPTER 3.....</b>	<b>22</b>
<b>3.1 ALKALINE FLOODING.....</b>	<b>22</b>
<b>3.1.1 MECHANISMS OF ALKALINE .....</b>	<b>23</b>

3.1.2 IN-SITU SOAP GENERATION .....	23
3.1.3 AQUEOUS REACTIONS .....	24
3.1.4 ION EXCHANGE REACTIONS WITH CLAY .....	24
3.1.5 DISSOLUTION AND PRECIPITATION REACTIONS .....	25
3.2 Surfactant Flooding .....	25
3.2.1 TYPES OF SURFACTANT FLOODING .....	26
3.2.2 SURFACTANTS .....	27
3.2.3 CLASSIFICATION OF SURFACTANTS .....	28
3.2.4 USE OF ANIONIC SURFACTANTS .....	29
3.2.5 USE OF NONIONIC SURFACTANTS .....	30
3.2.6 USE OF CATIONIC SURFACTANTS .....	31
3.3 POLYMER FLOODING .....	31
3.3.1 INTRODUCTION POLYMER FLOODING .....	32
3.3.2 FACTORS OF SELECTING POLYMER FLOODING .....	33
3.3.2.1 BEST TIME FOR POLYMER FLOODING .....	33
3.3.2.2 POLYMER TYPE .....	34
3.3.3 PRE-FLUSH AND POST FLUSH .....	35
3.3.4 ADVANTAGES OF POLYMER FLOODING .....	36
3.3.5 ECONOMICAL POINT OF VIEW .....	36
3.4 ALKALINE-SURFACTANT-POLYMER (ASP) FLOODING .....	37
3.5 CASE STUDY OF ASP FLOODING IN CANADA .....	38
3.6 ASP MECHANISM .....	38
3.6.1 DESIGN .....	40
3.6.2 SCREENING CRITERIA .....	40
3.7 ADVANTAGES OF ASP FLOODING .....	40
3.8 MICELLAR FLOODING .....	41
CHAPTER 4 .....	43
4.1 WETTABILITY .....	43
4.2 CONTACT ANGLE .....	44

<b>4.3 WETTABILITY ALTERATION .....</b>	<b>44</b>
<b>4.4.1 TECHNIQUES TO ALTER WETTABILITY .....</b>	<b>45</b>
<b>4.5 SURFACTANTS .....</b>	<b>46</b>
<b>4.6.1 THE ELECTRICAL DOUBLE LAYER .....</b>	<b>47</b>
<b>4.7 ADSORPTION AT SOLID/LIQUID INTERFACES .....</b>	<b>47</b>
<b>4.8 MICELLE FORMATION AND CRITICAL MICELLE CONCENTRATION (CMC) .....</b>	<b>49</b>
<b>4.9 MICROEMULSIONS .....</b>	<b>49</b>
<b>4.10 MICELLE FORMATION .....</b>	<b>49</b>
<b>4.11 ADSORPTION .....</b>	<b>50</b>
<b>4.12 MICROEMULSION SYSTEMS .....</b>	<b>51</b>
<b>4.13 PHASE BEHAVIOUR .....</b>	<b>52</b>
<b>4.14 EFFECT OF TEMPERATURE AND PRESSURE .....</b>	<b>53</b>
<b>4.15 PHASE EQUILIBRIUM .....</b>	<b>53</b>
<b>CHAPTER 5 .....</b>	<b>55</b>
<b>5.1 CARBONATE RESERVOIRS .....</b>	<b>55</b>
<b>5.2 STRUCTURAL ASPECTS OF CARBONATE RESERVOIRS .....</b>	<b>55</b>
<b>5.2.1 ROCK TYPING .....</b>	<b>56</b>
<b>5.2.2 PERMEABILITY .....</b>	<b>56</b>
<b>5.2.3 MICROPOROSITY .....</b>	<b>56</b>
<b>5.2.4 FRACTURES .....</b>	<b>57</b>
<b>5.3 COMPLEX STRUCTURES .....</b>	<b>57</b>
<b>5.4 WETTABILITY AND ITS EFFECT ON FLUID FLOW .....</b>	<b>58</b>
<b>5.5 CASE STUDY: Evaluating Carbonate Heterogeneity in Abu Dhabi</b>	<b>58</b>
<b>CHAPTER 6 .....</b>	<b>61</b>
<b>6.1 WETTABILITY ALTERATION DURING LOW-SALINITY WATER FLOODING IN CARBONATE RESERVOIR .....</b>	<b>61</b>
<b>6.2 WETTABILITY ALTERATION IN FRACTURED CARBONATE RESERVOIR .....</b>	<b>62</b>
<b>6.2.1 SURFACTANT FLOODING IN CARBONATE RESERVOIR ..</b>	<b>63</b>

6.2.2 IMBIBITION MECHANISM .....	63
6.3 <i>EXPERIMENTAL PROCEDURE</i> : .....	64
6.3.1 PHASE BEHAVIOUR STUDY: .....	64
6.3.2 INTERFACIAL TENSION MEASUREMENT .....	66
6.3.3 WETTABILITY TEST.....	69
6.3.4 SPONTANEOUS IMBIBITION .....	71
6.3.5 ADSORPTION.....	72
6.3.6 ALTERATION IN HIGH TEMPERATURE CARBONATE RESERVOIR .....	73
6.3.7 NONIONIC SURFACTANTS FOR WETTABILITY ALTERATION .....	73
6.3.8 MIXING CHELATING AGENTS IN ANIONIC SURFACTANT FORMULATIONS: .....	75
6.3.9 WETTABILITY ALTERATION BY EDTA.4NA-ANIONIC SURFACTANT FORMULATIONS: .....	76
6.4 WETTABILITY ALTERATION BY NAPA-ANIONIC SURFACTANT FORMULATIONS.....	76
CONCLUSION .....	77
REFERENCES : .....	78



## **CHAPTER 1**

### **ONGC – CAUVERY ASSET**

#### **1.1 INTRODUCTION TO GEOLOGY OF CAUVERY BASIN**

On the east coast of Southern India, in the state Tamil Nadu, of large alluvium covered coastal belt along Coromandel coast including Gulf of Mannar, Palk Bay forms the Cauvery basin (Fig.1). The basin encompasses a total area of around 62,500 sq.km up to a bathymetry of 200m in the Bay of Bengal. The basin is roughly 100 to 150 km wide in E-W direction and 400 km long in N-S direction. The basin evolved as a composite of rifted graben since Late Jurassic and formed a part in the development of East Coast divergent margin of India. Towards eastern margin of the basin few isolated outcrops of Mesozoic and Tertiary sedimentary rocks are seen near Sivaganga, Ariyalur, and Vrudhachalam and Pondicherry areas. The exposed sedimentary rocks along western margin prompted the Geoscientists of ONGC to initiate exploration in 1958 followed by geophysical surveys in 1960.

Twenty years of active exploration has led to the drilling and finding of non-commercial oil strike in 1977 (Karaikal). However, enormous amount of data generated during this period warranted restudy and reinterpretation, a drilling holiday was thus declared between 1977 and 1984. Second phase of drilling commenced in 1984. The next year itself has led to the discovery of two important fields Narimanam and Kovilkalappal. Since then ONGC has never looked back in its exploratory efforts in finding oil and gas fields, across the basin.

#### **1.2 INTRODUCTION TO CAUVERY ASSET**

The Oil and Gas exploration giant ONGC occupies a pride of place among India's Maharatna Companies. Within ONGC, the 'Cauvery Asset', hub of Production and Development activities in the remote Southern most parts of India is one of the success stories in its relentless pursuit of oil and gas. Cauvery Asset is based at Karaikal. ONGC's presence in this region has given a boost to Industrial Development in the districts of Nagapattinam, Karaikal, Tiruvarur, Ramnadu and Cuddalore. The mushrooming of Steel Units, Power Generation Stations, and ceramic industries in these areas bear testimony to this. Private and Public Sector power generation stations operate on gas supplied from ONGC's oil and gas fields. A number of private players apart from TNEB have set up gas-based power projects in this area, using gas from ONGC generating more than 800 MW power. A further feather in the cap for

the Cauvery Asset is the sale of Sour gas from Narimanam and Kovilkalappal fields. The Cauvery Basin covers an area of about 25000 sq.km in the Onshore and extends from Puducherry in the North to Ramnad in the South and Thanjavur in the West to Karaikal in the East. Intense geological processes taking place beneath the sands of this Cauvery Basin have made it the home for the Hydrocarbons. Hydrocarbons in the form of oil and gas are found in reservoir pockets distributed all over this vast basin. The basin is under active exploration and development of oil and gas pools with the deployment of nine drilling rigs and four workover rigs dedicated to the revival of sick wells. The main constraint in this basin is that there are multiple thin layers of Sand hosting the Reservoirs rather than thick Blanket Sands, such as encountered in the Assam Shelf which lend themselves to Reservoir mapping and Interpretation more easily, thus facilitating Development activities. Cauvery Basin has much smaller oil and gas pools.

### **1.3 EXPLORATION**

ONGC's exploration activities in Cauvery Basin started nearly fifty years ago, in 1958 to be precise. The exposed sedimentary rocks along the western fringe of the basin prompted the geoscientists of ONGC to initiate exploration for Hydrocarbons. Drilling began in 1964 and the first taste of success came with the finding of oil in the well 'Karaikal in 1977. Twenty years of active exploration had yielded copious geo-scientific data. Immediately after this, in order to review and reinterpret the findings, a drilling holiday was declared in 1977. After a detailed review of all available data, the second phase of drilling commenced in 1984. Success greeted the dedicated workforce of ONGC, almost immediately, with the discovery of Kovilkalappal and Narimanam fields, in 1985. Cauvery Basin had emerged on the oil map of the country.

This major breakthrough brought the basin into exploratory focus. The rejuvenated exploratory efforts resulted in drilling 618 wells as on 01.02.2012 out of which 144 are oil and 96 are gas wells. This has led to the discovery of 29 oil and gas fields, the milestones of this basin. They are: Karaikal (1977), Kovilkalappal (1988), Adiyakkamangalam (1989), Kamalapuram and Tiruvarur (1990), Mattur, Athikadai, Vadatheru and Vijayapuram (1992), Pallivaramangalam and Kuttanallur (1993), Perungulam (1994), Pundi (1995), Kizhvalur and Kuthalam (1996), Tulsiapatnam, Periyapatnam, Neyveli and Ramanvalasai (1997) and Kali (1998), Kuthalam satellite fields (1999), Kanjirangudi (2000), Palk Bay Shallow-Offshore (2001), Adichapuram (2007), Periyakudi(2010), Madanam & Pandanallur (2012)

<b>Well Status as on 01.12.2018</b>	
<b>Wells Drilled</b>	<b>712</b>
<b>Exploratory</b>	<b>530</b>
<b>Development</b>	<b>182</b>
<b>Flowing</b>	<b>83(Oil) + 87(Gas) = 170</b>
<b>Non-Flowing</b>	<b>82(Oil) + 47(Gas) = 129</b>
<b>Inconclusive</b>	<b>7</b>
<b>Abandoned</b>	<b>391</b>

### **Status of Exploration**

	<b>Offshore</b>	<b>On land</b>
Area (Sq.Km)	25,000	30,000
Prognosticated Resources	430	270
Prospects Drilled	150	34
Oil & Gas bearing	26	3
Success ratio (Prospects)	1:5.76	1:11.33

## **1.4 OUR FIELD EXPOSURES**

### ***1.4.1. EARLY PRODUCTION SYSTEM – NARIMANAM EPS***

Early production system was started by ONGC in 1993 to collect all the hydrocarbons initially from wells located nearby. The first hydrocarbon came from TVR 6 and currently there are 33 wells around the area out of which 20 have current flow. The crude oil which we get will be distributed to CPCL and the gas which we get will be distributed to GAIL through pipelines. GAIL further uses these gases to generate electricity. There we studied about hydrocarbon storage facilities, separators, level control valves, pressure control valves and flare control. 10 wells were high pressure and 5 are low pressure wells. There were 2 separators 1st stage and 2nd stage . 1st stage separators use high pressure to separate oil and gas. The region was divided into Zone 0, Zone1,Zone2 depending upon how flammable or dangerous the area is. The tank capacity is 45 m<sup>3</sup>. The daily production was 90-100 m<sup>3</sup> per day. Studied Christmas tree of well TVR 6 which was currently not under production.

### **1.4.2. CEMENTING SECTION VISIT**

Cementing section plays an important role in drilling . We visited the site and studied what types of cements are used , how cement is stored, and what are the additives used in cementing section. The cement was manufactured by Dalmia cements as well as madras cements. The additives were manufactured by Schlumberger as well as by Halliburton . these additives include accelerators, retarders, flow control etc. Moreover we also saw cement silo which had a very huge capacity and it is used for transportation of cement from site to rig. All the vehicles used were imported from different parts of the world.

### **1.4.3. WELL STIMULATION SERVICES**

The well stimulation department of ONGC Karaikal mainly undergo 4 type of operation ,it include Hot Oil Circulation ,Well Activation ,Compressor Operation and Acidization .There is specific operational unit for HOC and Acidization and another one for compressor unit. The well stimulation department mainly take over the well when the rate of production of the well decreases .When the production rate decrease the well stimulation department will

suggest the remedy to increase the production .The most used methods include acid treatment and gas injection .N<sub>2</sub> is the most commonly used gas .HOC is used to remove the slug formation in the tubing . compressor is used to detect the deformations in the production tubing.

#### **1.4.4. WELL LOGGING DEPARTMENT**

Known to be the eye of the subsurface wing in an oil company which plays a vital role in interpreting the nature of the formation in a reservoir. We gained the knowledge about the logging tools & methods for successful logging which helps in the formation evaluation and reservoir characterization. Experts in well logging interpretation team diligently taught us about how to interpret the logs and understand the subsurface formations. We gained adequate knowledge regarding our project, provided to work with raw data (logging data) of wells and creation of composite logs and correlation of the well data to understand the reservoir.

#### **1.4.5. DRILLING RIG VISIT E760-3**

During the course of our project, we got a chance to visit the rig E760-3. It is a medium level rig, which has drilled about 2600m depth. The officers and crew workers, there explained us about various process during drilling operation, duty of derrick men and mud operation. We also witness working of hoisting system, running of a drillpipe ,mud circulation and BOP system. Hoisting system mainly consists of swivel, kelly, travelling block, crown block and draw works. Drawwork consists of a accelerator and a brake for tripping of drillpipe in and out of the well.it is operated by a derrick men .There is a mud engineer ,which at regular intervals, check the chemical nature of the cuttings and mud taken out of the well. In short,it is a good experience to find about working of a rig.

## **CHAPTER 2**

### **ENHANCE OIL RECOVERY**

#### **INTRODUCTION**

About half of world's known oil reserves are in carbonate reservoirs. Many of these carbonate reservoirs are naturally fractured. Fractured reservoirs are poorly understood and recovery from fractured reservoirs is typically lower than those from unfractured reservoirs. Fractured reservoirs with high matrix porosity and low matrix permeability need a secondary or EOR technique to achieve maximum production, according to a recent review of 100 fractured reservoirs. Recovery factor in these reservoirs depends on matrix permeability, wettability, fracture intensity and fluid properties.

Water-flooding is an effective technique for fractured reservoirs, if the formation is water-wet. The positive capillary force helps in imbibing water into the matrix and expelling the oil out. However, many carbonate reservoirs (about 80%) are mixed-wet or oil-wet.<sup>3</sup> Positive zeta potential on carbonate surfaces at typical pH (~7),<sup>4</sup> presence of sufficient number of negatively charged / asphaltenic molecules in oil,<sup>5</sup> and high capillary pressure during oil migration into the reservoir often render mixed-wettability to the reservoir rocks. Waterflooding does not lead to significant recovery from the matrix porosity because the capillary pressure curve is predominantly negative. Surfactant flooding (or huff-n-puff) is being tested to improve oil recovery from mixed-wet, fractured carbonate formations and is the subject of this study.

By nature crude oil is a limited resource. Nevertheless, the amount of crude oil available has to meet the worldwide demands. From time to time, oil production has been intentionally reduced, and this has resulted in serious oil crises accompanied by a general increase in the oil price. This in turn has forced the oil industry to recover oil from more complicated areas, where the oil is less accessible meaning that recovery techniques are constantly advanced. This has contributed to the development of techniques for enhanced oil recovery, (EOR), which while used today, also constantly undergo further advancement and development. Up to two thirds of the crude oil remains trapped in the reservoirs after primary and secondary recovery in an average oil reservoir. EOR is then required to optimize the depletion, as the remaining oil is trapped in the pore structure inside the reservoir. EOR covers several

different advanced recovery techniques. The mechanisms and procedures of chemical methods will be introduced in this chapter.

## **2.1 OIL RECOVERY**

Oil recovery can be defined in three phases, depending on the producing life of a reservoir:

1. Primary
2. Secondary
3. Tertiary

### **2.1.1 PRIMARY RECOVERY :**

Primary recovery is recovery by natural drive energy initially available in the reservoir. It does not require injection of any external fluids or heat as a driving energy. The natural energy sources include rock and fluid expansion, solution gas, water influx, gas cap, and gravity drainage.

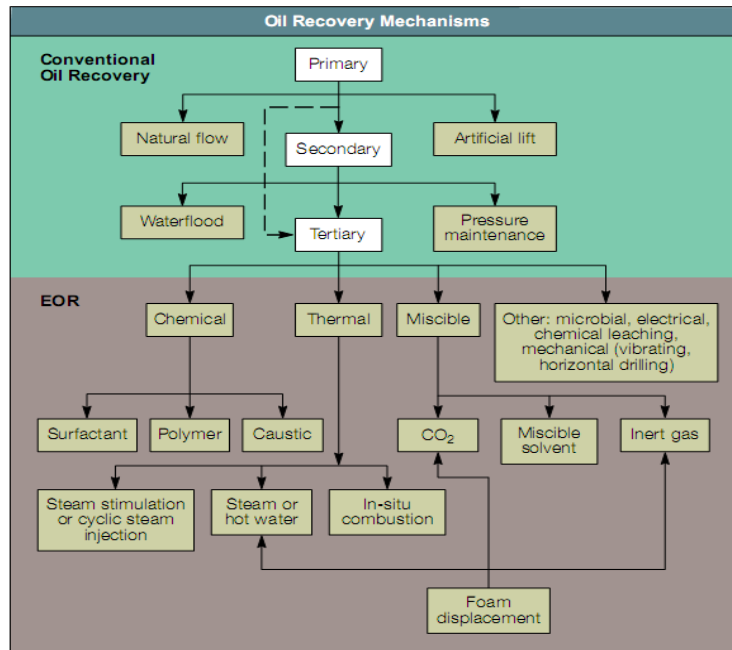
### **2.1.2 SECONDARY RECOVERY :**

Secondary recovery is recovery by injection of external fluids, such as water and/or gas, mainly for the purpose of pressure maintenance and volumetric sweep efficiency.

### **2.1.3 TERTIARY RECOVERY :**

Tertiary recovery refers to the recovery after secondary recovery. It is characterized by injection of special fluids such as chemicals, miscible gases, and/or the injection of thermal energy

Oil recovery mechanisms and their classifications are shown in Figure 2.1



**Figure 2.1 Oil Recovery Mechanisms**

## 2.2 ENHANCED OIL RECOVERY

Several mechanisms contribute to the primary production of oil. Primary production is in general understood as rather inefficient, as it produces less than 20 % of the original oil in place, [Morrow, 1991, p.5]. With the goal of improving oil recovery, EOR is introduced, employing more efficient recovery methods. Another commonly used designation is improved oil recovery (IOR), which covers a broader range of activities. IOR can also include EOR, where IOR and EOR in general are defined as follows:

### 2.2.1 IMPROVED OIL RECOVERY (IOR):

Injection of fluids, which are already present in the reservoir, e.g. water.

### 2.2.2 ENHANCED OIL RECOVERY (EOR): Injection of fluids, which are not normally present in the reservoir, e.g. surfactants.

The concepts of IOR and EOR in practice are often mixed. Nowadays, oil recovery processes are typically classified as primary, secondary and EOR processes. From a fundamental point of view EOR should be understood as methods or techniques whereby extrinsic energy and materials are added to a reservoir to control:

- Wettability
- Interfacial tensions (IFT)
- Fluid properties
- Establish pressure gradients necessary to overcome retaining forces
- Move the remaining crude oil in a controlled manner towards a production well.



One aspect of EOR operations, which in all processes has a considerable influence on the result, is the ability to control the flow of the displacement fluid, so-called mobility control. Since flow pattern prediction is very uncertain, predicting oil recovery becomes difficult. These uncertainties challenge EOR processes. While it is desirable to design the most efficient process in order to increase oil recovery, economic feasibility of the EOR process is more crucial than any other aspect, in order to commercialize the process.

## **2.3 EOR PROCESSES**

Much work has been performed in the area of fluid injection with the objective of improving oil recovery by the natural drive mechanism. The most widely used technique is water flooding, which has been applied for more than 60 years. The oil left in the swept zone after water flooding then becomes the main target for tertiary oil recovery, [Morrow, 1991, p.6-10]. The primary goals in EOR operations are to displace or alter the mobility of the remaining oil in the reservoir. Using conventional water flooding techniques is preferable as long as it is economically feasible. Remaining oil left after primary and secondary recovery operations over long time periods is usually distributed in pores in the reservoir, where the oil is trapped, mainly due to capillary forces and viscous forces. EOR techniques will contribute to a longer lifetime of already existing reservoirs. Unfortunately the application of EOR does not only bring advantages. Using EOR is correlated with higher risks and increases the requirement for additional facilities and investments. The common classifications of different EOR processes are [Green and Willhite, 1998, p.1-10]:

- Mobility-control
- Chemical processes
- Miscible processes
- Thermal Processes
- Other (e.g. microbial EOR)

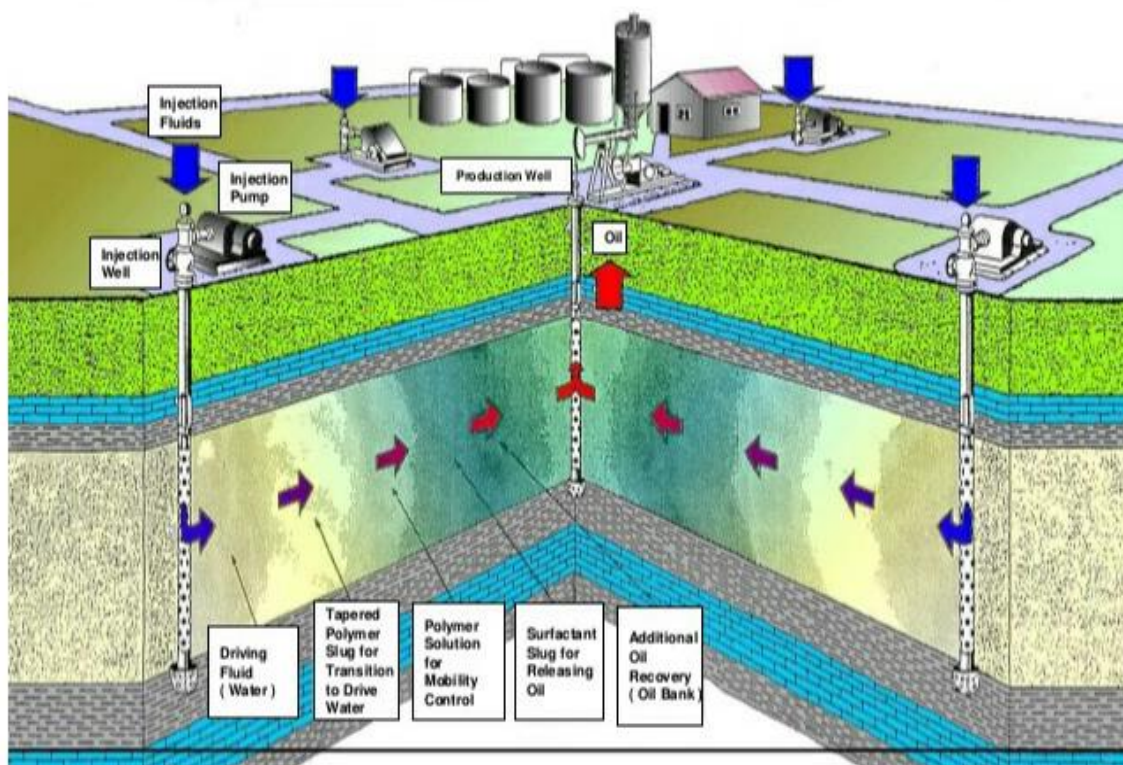
In general the EOR processes involve injection of gas or fluids into the oil reservoir, displacing crude oil from the reservoir towards a production well. The injection processes supplement the natural energy present in the reservoir. The injected fluid also interacts with rock and oil trapped in the reservoir creating advantageous conditions for oil recovery.

### **2.3.1 MOBILITY CONTROL**

Mobility-control is a process based on maintaining favorable mobility ratios between crude oil and water, by increasing water viscosity and decreasing water relative permeability. Can improve sweep efficiency over waterflooding during surfactant processes.

### **2.3.2 CHEMICAL PROCESS**

Chemical processes are injection of a specific liquid chemical that effectively creates desirable phase behavior properties, to improve oil displacement. The principles are illustrated in figure 2.2



**Figure 2.2. Chemical flooding, which is the injection of water and chemicals. Besides the economic point of view, the complexity rises as several additional tasks such as preflush of the reservoir and injection of additional fluids must be applied to accomplish an efficient process.**

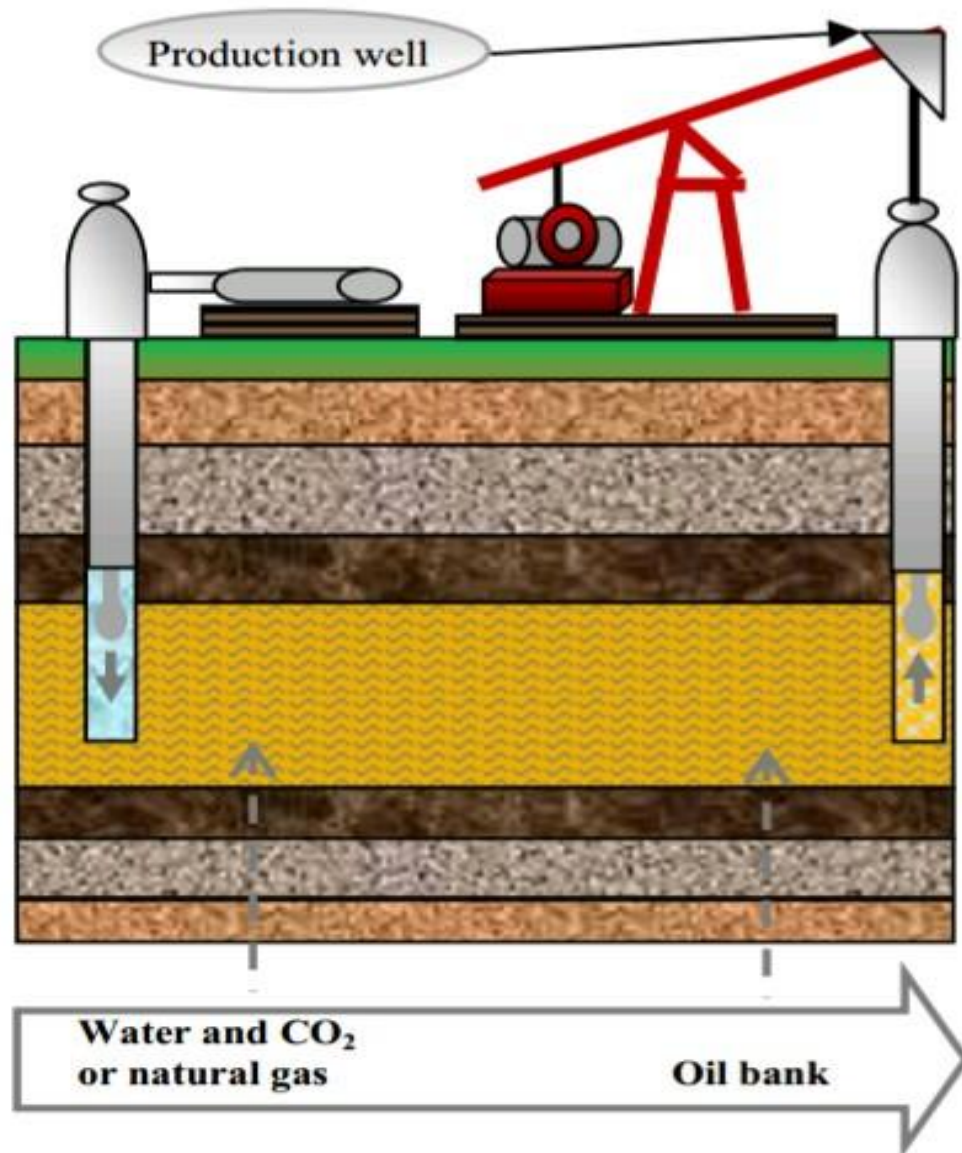
Surfactant flooding is an example of chemical flooding. This is a complex process, where the displacement is immiscible, as water or brine does not mix with oil. However, this condition is changed by the addition of surfactants.

The technique creates low interfacial tension (IFT), where especially an ultra low IFT ( $0.001\text{mN/m}$ ) between the displacing fluid and the oil is a requirement in order to mobilize the residual oil. The liquid surfactant injected into the reservoir is often a complex chemical system, which creates a so-called micelle solution. During surfactant flooding it is essential that the complex system forms microemulsions with the residual oil as this supports the decrease of the IFT and increases the mobility. However, the formation of microemulsions may also be a significant disadvantage, as microemulsions may plug the pores. It is also important to be aware of the high loss of surfactant, occurring as a result of adsorption and phase partitioning inside the reservoir. It is known that surfactant systems are sensitive to high temperatures and high salinity, leading to requirements for developing surfactant systems that can withstand such conditions. Other chemical processes have also been

developed, such as alkaline flooding and various processes where alcohols are introduced. In alkaline flooding, alkaline chemicals are injected into the reservoir, where they react with certain components in the oil to generate surfactants in situ. Alcohol processes have so far only been tested in laboratories and have not yet been applied in the field.

### **2.3.3 MISCIBLE PROCESS**

Miscible processes are based on the injection of a gas or fluid, which is miscible with the crude oil at reservoir conditions, in order to mobilize the crude oil in the reservoir. The process is illustrated in figure 2.3. This process relies on the modification of the components either in the injected phase or in the reservoir oil phase. Modification of either injected fluid or gas or the reservoir oil is achieved through multiple contacts between the injected phase and the oil phase with mass transfer of components between the phases, [Green & Willhite, 1998, p.7]. E.g. injection of CO<sub>2</sub> as a liquid will entail extraction of the heavier hydrocarbons from the reservoir oil, which will allow the displacement front to become miscible, [Holm, 1986].



**Figure: 2.3. Miscible process control, where the injected fluid does mix with oil. In this process the oil is supposed to be mobilized while mixed with either injected gas or fluid.**

### 2.3.4 THERMAL PROCESSES

Thermal processes are typically applied to heavy oils. Thermal recovery processes rely on the use of thermal energy. A hot phase of e.g. steam, hot water or a combustible gas is injected into the reservoir in order to increase the temperature of the trapped oil and gas and thereby reduce oil viscosity, [Green and Willhite, 1998, p.301]. The process is depicted in figure 2.3. The injected hot stream facilitates the flow to the production wells by increasing the pressure and reducing the resistance to flow.

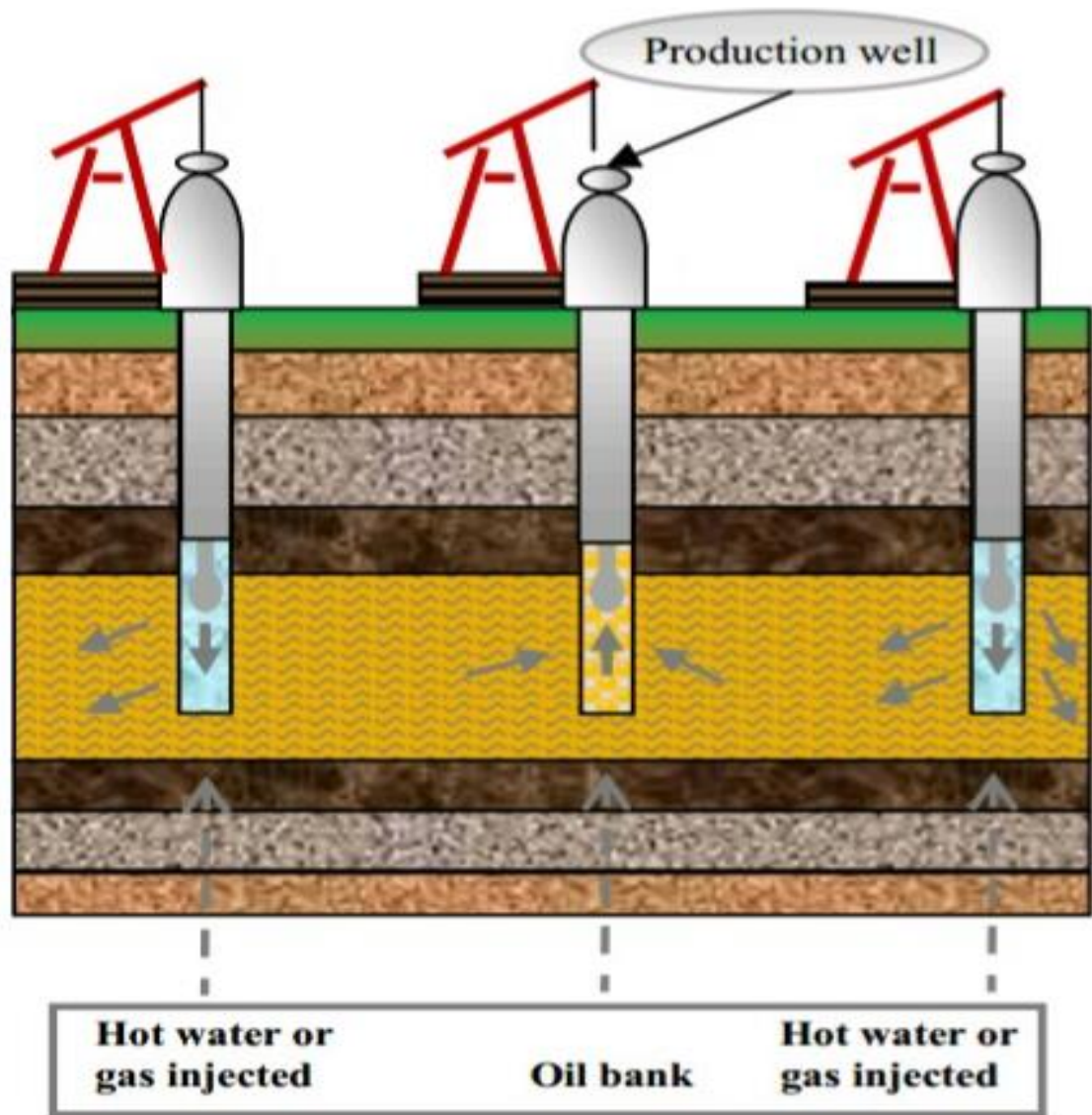


Figure 2.3. Thermal process control. Thermal energy is injected into the reservoir. The injected energy mobilizes the trapped oil and squeezes it away from the capillaries towards the reservoir.



## CHAPTER 3

### CLASSIFICATION OF CHEMICAL FLOODING

#### 3.1 ALKALINE FLOODING

Alkaline flooding is an enhanced oil recovery method in which an alkaline chemical such as sodium hydroxide, sodium orthosilicate or sodium carbonate is added to injected water. The alkaline chemical reacts with certain types of oils and forms surfactants inside the reservoir. Eventually, the surfactants play a big role to increase oil recovery by reducing interfacial tension between oil and water.

The alkaline agents lead to the displacement of crude oil by raising the pH of the flooding water. The reaction between alkaline and acidic components in crude oil forms in situ surfactant at the oil-brine interface. Then the crude oil is mobilized by the mixture and the mixture removes oil from the pore spaces in the reservoir. Normally, alkaline flooding has been used only in reservoirs containing specific types of high-acid crude oils.

The process can be modified by the addition of surfactant and polymer to the alkali which gives an alkaline-surfactant polymer (ASP) enhanced oil recovery method, essentially a less costly form of micellar-polymer flooding.

Chemical EOR is commercially available under limited conditions such as reservoir characteristics, depth, salinity, and pH level. The high cost of chemicals and reservoir characterization studies needs to be reduced to allow expanded use of chemical enhanced oil recovery methods before full implementation can take place. The addition of silicates is an enhancement to alkaline flooding. The silicates have two main functions:

- 1) It is as a buffer, maintaining a stable high pH level to produce a minimum interfacial tension
- 2) It improves surfactant efficiency through the removal of hardness ions from reservoir brines, thus reducing adsorption of surfactants on rock surfaces.

On the other hand, alkaline flooding is not recommended for carbonate reservoirs because of the profusion of calcium and the mixture between the alkaline chemical and the calcium ions can produce hydroxide precipitation that may damage the formation.

The main profits of alkaline are lowering interfacial tension and reducing adsorption of anionic surfactants that decrease costs and make ASP a very smart enhanced oil recovery process provided the consumption is not too large. By numerical simulation process, the alkaline model can be planned and optimized to ensure the proper propagation of alkali, effective soap and surfactant concentrations to promote low interfacial tension and an encouraging salinity gradient.

Alkaline flooding is a complex process where interfacial tension reduction is not always the key mechanism. Depending on the rock and crude properties, emulsification and wettability

alteration can play a major role in oil recovery from mixed-wet naturally fractured carbonates (Liu et al., 2006; Fathi et al., 2008; Zhang et al., 2008).

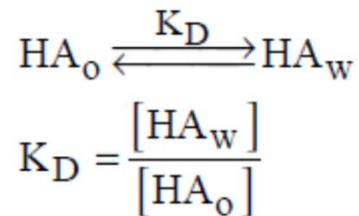
### 3.1.1 MECHANISMS OF ALKALINE

Application of alkaline flooding has four mechanisms

- 1) “Emulsification and Entrainment” in which flowing alkali entrains the crude oil.
- 2) “Wettability Reversal” (Oil-Wet to Water-Wet) in which change of wettability affects change in permeability that makes increase in oil production.
- 3) “Wettability Reversal” (Water-Wet Oil-Wet to) in which we get low residual oil saturation through low interfacial tension.
- 4) “Emulsification and Entrapment” in which movement of emulsified oil improves sweep efficiency. Right alkali is chosen based on some factors such as price and availability at the flooding area, the PH level, the temperature and mineralogy of the reservoir and composition of the mixed water.

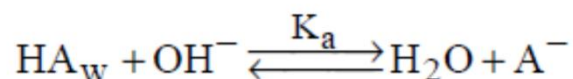
### 3.1.2 IN-SITU SOAP GENERATION

Eventually, soap in situ is generated by reaction of alkali agents such as sodium carbonate with acids in crude oil. Acid number is used as a measure for the possible amount of crude oil to produce soap. The acid number is the quantity of KOH to neutralize the acid in oil expressed in mg KOH/g oil. Fan and Buckley (2006) and Hirasaki (2007) discussed the new protocols for acid number measurements. The making of soap is modeled by the partitioning of acid in the crude oil (HA<sub>o</sub>) to water according to the solubility as:

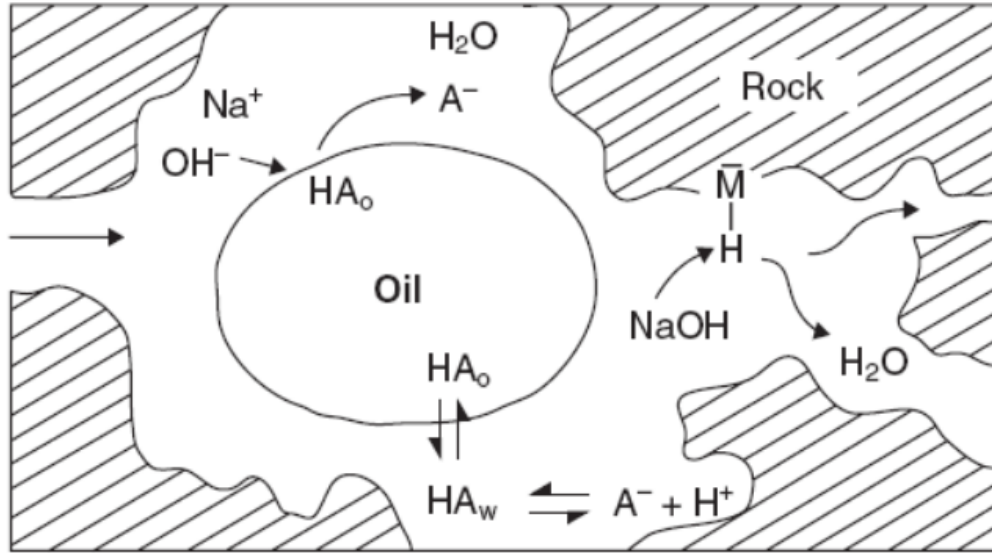
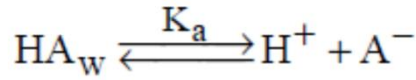


HA<sub>w</sub> - the concentration of acid in water, K<sub>D</sub> - the partition coefficient.

By the time the acid in water will separate in the aqueous phase to generate soluble anionic surfactant (A<sup>-</sup>) referred to as soap according to the expression below:



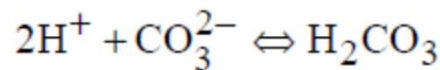
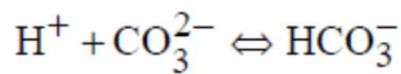
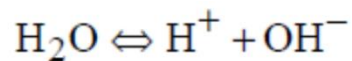
The reaction above is one of the sources of alkaline consumption since the alkali uses hydrogen to generate soap by the following process:



**Figure 3.1: Schematic of alkaline recovery process**

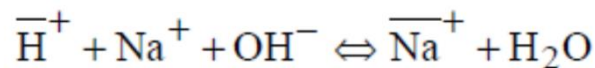
### 3.1.3 AQUEOUS REACTIONS

Buffered reactions can be shown as aqueous reactions. General example of the buffered reactions which are of interest to alkaline flooding process is the carbonate and bicarbonate buffered solutions.



### 3.1.4 ION EXCHANGE REACTIONS WITH CLAY

Ion exchange with clays in the rock causes a postponement in chemical breakthrough time where it has the same effect as adsorption. These reactions are relatively rapid reactions and are reversible. The hydrogen/sodium and sodium/calcium are example of key ion exchange reactions. The hydrogen/sodium ion replace can have a big impact on alkali consumption in

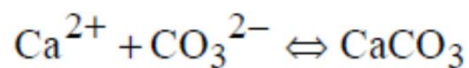




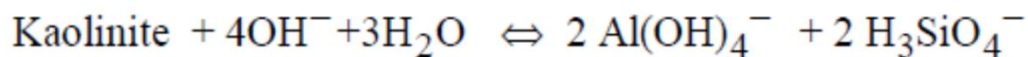
proportion to the cat ion exchange capacity.  
H<sup>+</sup> and Na<sup>+</sup> are the adsorbed ions on the rock.

### 3.1.5 DISSOLUTION AND PRECIPITATION REACTIONS

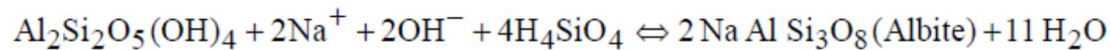
Dissolution and precipitation reactions constitute one of the most important reactions in alkaline flooding. Insoluble salt formation by reaction with hardness ions such as calcium and magnesium as a result of ion exchange from the rock surfaces is example of dissolution and precipitation reactions. These reactions can cause significant loss of alkaline over an extended period of time.



As an example kaolinite, Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>, is found in most sandstone formations. The dissolution of kaolinite at high pH can result in generation of aqueous types such as

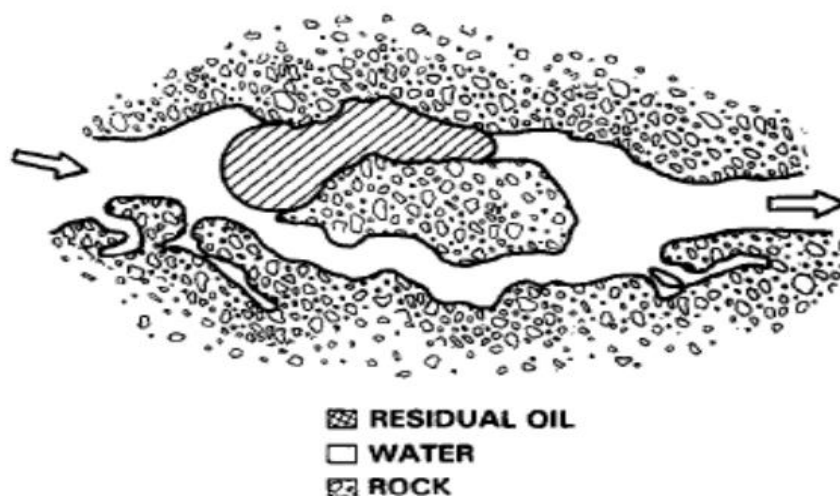


Or dissolution of kaolinite can lead to precipitation of albite or analcime



### 3.2 Surfactant Flooding

Surfactant flooding is injection of one or more liquid chemicals and surfactants. The injection effectively controls the phase behaviour properties in the oil reservoir, thus mobilizing the trapped crude oil by lowering IFT between the injected liquid and the oil. The principle of surfactant flooding is illustrated in fig.3.2



**Figure: 3.2: Principle of flooding, where residual oil is trapped in the reservoir, [O'Brien, 1982]. For the movement of oil through the narrow capillary pores, very low oil/water interfacial tension (IFT) is required; preferably ultra low IFT at 0.001 mN/m is desirable.**

There is a great potential for chemical processes with surfactant flooding, since there is the possibility of designing a process where the overall displacement efficiency can be increased. Nowadays many mature reservoirs under water flood have decreasing production rates despite having 50-75 % of the original oil left inside the reservoir [Flaaten et al., 2008]. In such cases it is likely that surfactant flooding can increase the economic productivity.

Surfactants are added to decrease the IFT between oil and water. Co-surfactants are blended into the liquid surfactant solution in order to improve the properties of the surfactant solution. The cosurfactant either serves as a promoter or as an active agent in the blended surfactant solution to provide optimal conditions with respect to temperature, pressure and salinity. Due to certain physical characteristics of the reservoir, such as adsorption to the rock and trapping of the fluid in the pore structure, considerable losses of the surfactant may occur. The stability of the surfactant system at reservoir conditions is also of great relevance

Polymers are also often added to the injected surfactant solution, to increase viscosity, thus maintaining mobility control. In general there are three types of surfactant flooding for EOR Shown in table 3.1

### 3.2.1 TYPES OF SURFACTANT FLOODING

Type of surfactant flooding	Technique	Note
Micelle/polymer flooding	A micelle slug usually of surfactant, co-surfactant, alcohol, brine and oil is injected into the reservoir	Displacement efficiency close to 100 % (measured in laboratory).

Microemulsion flooding:	Surfactants, cosurfactants, alcohol and brine are injected into the reservoir to form microemulsions to obtain ultra low IFT	Can be designed to perform well in e.g. high temperature or salinity or low permeable areas where polymer and/or alkali cannot work.
Alkaline/surfactant/polymer (ASP) flooding	The addition of alkaline chemicals reduces the IFT at significantly lower surfactant concentrations	Lower concentration of surfactants is involved in this process, which reduces the cost of chemicals.

Surfactant systems usually consist of both surfactants and co-surfactants. However the combination of multiple components in the surfactant solution system does not work well in practice as chromatographic separation occurs in the reservoir. The solution concentration quickly changes from its optimal value as the separation takes place. The optimization criterion in surfactant flooding is to maximize the amount of oil recovered, while minimizing the chemical cost. While it is necessary to reach low IFT for the surfactant system, minimizing only the IFT may not always coincide with optimal oil recovery, as low IFT is not the only essential condition to meet in order to get a successful and efficient oil recovery, [Fathi and Ramirez, 1984]. E.g. attention to the optimal salinity is crucial to include as well.

### 3.2.2 SURFACTANTS

In surfactant flooding, the chemical system contains surface active agents, surfactants, which are polymeric molecules that lower the IFT between the liquid surfactant solution and the residual oil. Surfactants adsorb on a surface or fluid/fluid interface when present at low concentrations. The most common structural form for surfactants is where they contain a nonpolar part, a hydrocarbon 'tail', and a polar or ionic part. The structure is shown in figure;

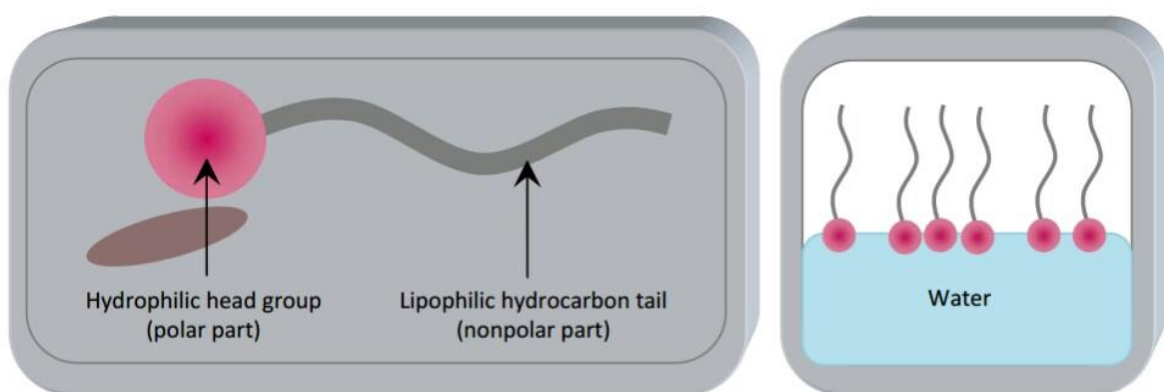


Figure:3.3 Surfactant molecule and surfactant orientation in water. Surfactants are also referred to as amphiphile molecules because they contain a nonpolar 'tail' and a polar 'head'-group within the same molecule,

It is the balance between the hydrophilic and hydrophobic parts of the surfactant that generates the characteristics of the surface active agent. In EOR with surfactant flooding the

hydrophilic head interacts with water molecules and the hydrophobic tail interacts with the residual oil. Thus, surfactants can form water-in-oil or oil-in-water emulsions. Surfactant molecules are amphiphilic, as they have both hydrophilic and hydrophobic moieties. Amphiphiles adsorb effectively to interfaces and typically contribute to significant reductions of the interfacial energy, [Pashley and Karaman, 2004, p. 62].

The primary surfactant is directly involved in the microemulsion formation with regards to the EOR surfactant flooding process.

The co-surfactant, if any, promotes or improves the activities of the primary surfactant, by e.g. changing the surface energy or the viscosity of the liquids. Due to chromatographic separation of surfactant, co-surfactant and any other components, throughout the reservoir, it can be problematic to create a multicomponent surfactant system capable of maintaining optimal properties throughout the flooding process. The predominant disadvantage of separation is that the control of the system deteriorates in the reservoir and therefore it should be avoided if possible. As the co-surfactants prevent gel formation and reduce the equilibration time,

Hydrophilic head group (polar part)

Lipophilic hydrocarbon tail (nonpolar part)

Water they are hard to eliminate from the surfactant systems used for flooding. Oil reservoirs have different characteristics and therefore the structure of added surfactant must be tailored to meet the reservoir conditions to achieve a low IFT. For example the temperature, pressure and rock vary significantly from one reservoir to another.

### 3.2.3 CLASSIFICATION OF SURFACTANTS

Surfactants are frequently classified on the basis of the ionic nature of the head group, as anionic, cationic, nonionic or zwitterionic. Each type possesses certain characteristics depending on how the surfactant molecules ionize in aqueous solutions. In table 1.2 a few commonly used surfactants are shown. Table 3.2. List of common surfactant molecules with different types of charge: anionic, cationic and nonionic.

**Table:3.2 Classification of surfactants**

#### Anionic

**Sodium dodecyl sulfate (SDS)**

**Sodium dodecyl benzene sulfonate**

#### Cationic

**Cetyltrimethylammonium bromide (CTAB)**

**Dodecylamine hydrochloride**

#### Non-ionic

**Polyethylene oxides**

Commonly used surfactants for EOR, are sulfonated hydrocarbons such as alcohol propoxylate sulfate or alcohol propoxylate sulfonate. To achieve an optimal surfactant flood for any given oil reservoir surfactants and polymers are often both included in the flooding. Surfactants are responsible for the reduction of the IFT and the polymer is added to improve the sweep efficiency,[Flaaten et al., 2008]. The demands on surfactants are numerous and it is a great challenge to distinguish which mechanisms are most dominant. Process conditions, such as high temperature and high pressure are often the reality in reservoir environments.

### 3.2.4 USE OF ANIONIC SURFACTANTS

Anionic surfactants are negatively charged. They are commonly used for various industrial applications, such as detergents (alkyl benzene sulfonates), soaps (fatty acids), foaming agents (lauryl sulfate), and wetting agents (di-alkyl sulfosuccinate). Anionic surfactants are also the most commonly used in EOR. They display good surfactant properties, such as lowering the IFT, their ability to create self-assembled structures, are relatively stable, exhibit relatively low adsorption on reservoir rock and can be manufactured economically [Green & Willhite, 1998, p. 241]. Anionic surfactants dissociate in water to form an amphiphilic anion (negatively charged) and a cation(positively charged), which would typically be an alkaline metal such as sodium ( $\text{Na}^+$ ) or potassium( $\text{K}^+$ ). Wu et al. (2005) have investigated a series of branched alcohol propoxylate sulfate surfactants for the application in EOR. Their investigations show that the number of propoxylate groups has a significant influence on the IFT, the optimal salinity and the adsorption. Optimal salinity and adsorption are shown to decrease as the number of propoxy groups is increased. In their work the experiments are conducted at diluted surfactant concentrations, both with and without cosurfactants. Examples from Wu et al. (2005)'s work is shown in figure 3.4, where the results show that the average alkyl chain length has an influence on the performance of the system:

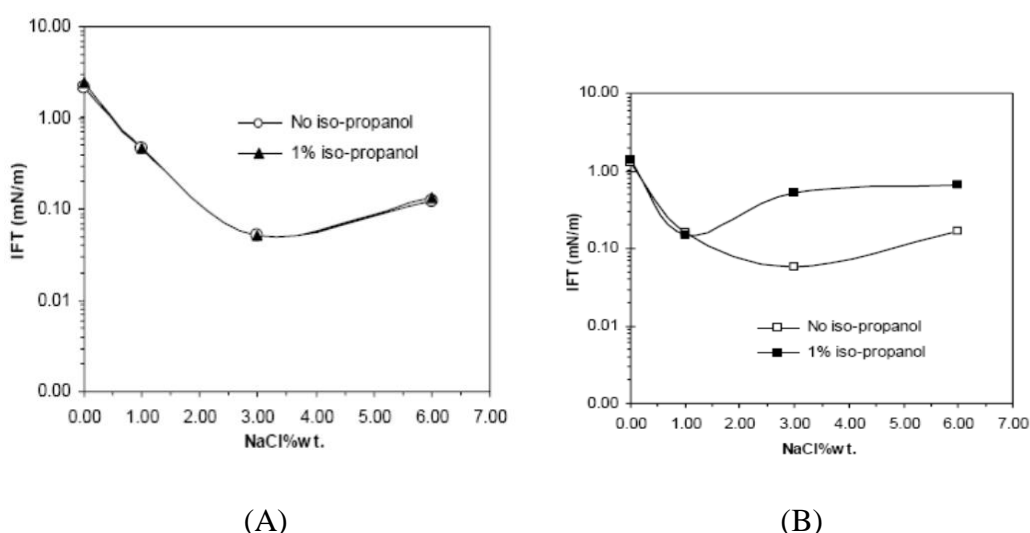


Figure 3.4. IFT versus salinity for two different alcohol propoxylate sulfate surfactant experiments. The surfactant concentration is 2wt. %. In (A): the average number of propoxy groups is 5 and the size of the branched alkyl chain is about C12. In (B): the average number

of propoxy groups is 5 and the branched alkyl chain size is C14. Iso-propanol is added as cosurfactant. [Wu et al., 2005]

In figure 3.4 (A) the IFT values indicate that the optimal salinity is at 3 wt % NaCl with or without the co-surfactant iso-propanol. The effect of co-surfactants, if any, is very small. In figure 3.4(B) the effect of co-surfactant is pronounced at salinities greater than 1 wt %, where it results in a significant increase in IFT which is undesirable.

Barnes et al. investigate families of anionic surfactants, internal olefin sulfonates, (IOS), for use in surfactant flooding at high temperatures, (up to 150 °C), and with varying optimal salinities from 1 % to 13 % depending on the carbon number range. The IOS surfactants show little sensitivity to temperature, which could be an advantage for reservoirs with temperature gradients. Overall the IOS surfactants exhibit promising over a range of reservoir conditions covering moderate to high temperatures and from low to high salinity conditions. Both alcohol propoxylate sulfates and IOS have been studied [Levitt et al., 2006 and Flaaten et al., 2008], where they are identified as promising surfactant candidates for EOR processes. These surfactant candidates are available at low cost and have been tested in different reservoir cores resulting in enhanced oil recovery and low surfactant retention, [Levitt et al., 2006]. It was found in Levitt et al. (2006)'s work that mixing the IOS and the alcohol propoxylate sulfate give the best result. Furthermore Bryan and Kantzas (2007) have conducted an investigation of alkali surfactants for surfactant flooding of heavy oils. Their work showed that alkali surfactant flooding has a great potential for non-thermal heavy oil recovery, as the addition of alkali surfactants reduced the IFT between oil and water by such a magnitude that formation of emulsions was possible.

### 3.2.5 USE OF NONIONIC SURFACTANTS

Nonionic surfactants have no charged head group. They are also identified for use in EOR, [Gupta and Mohanty, 2007], mainly as co-surfactants to promote the surfactant process. Their hydrophilic group is of a non-dissociating type, not ionizing in aqueous solutions. Examples of non-ionic surfactants include alcohols, phenols, ethers, esters or amides.

Curbelo et al. (2007) studied nonionic surfactants with different degree of ethoxylation to investigate the correlation with the adsorption of surfactant in porous media (sandstone). From the experiments the variations in the surface tension with surfactant concentration are shown in figure

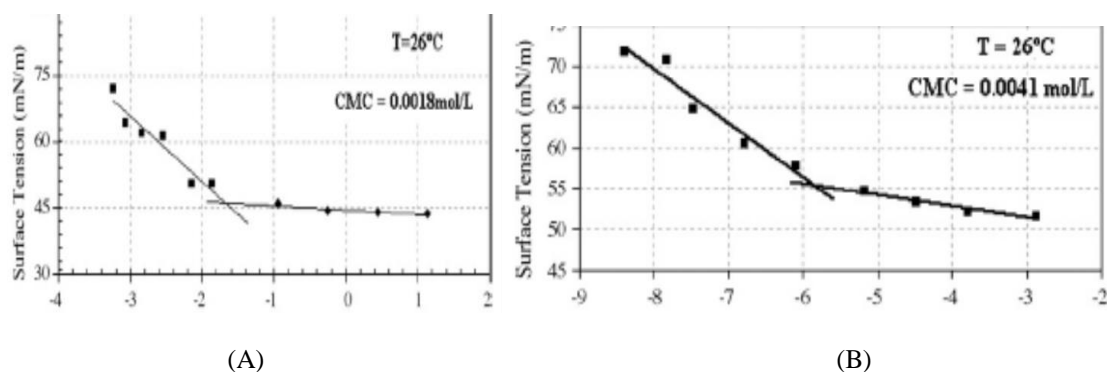


Figure 3.5 Determination of Critical Micelle Concentration (CMC) for two surfactants investigated. (A) is a surfactant with an ethoxylation degree of 9.5 and (B) is a surfactant with an ethoxylation degree of 15.0. The x-axis is the natural logarithm of the surfactant

concentration. The break in both of the curves is where CMC is reached Critical Micelle Concentration (CMC) is reached at a higher surfactant concentration for (B), with ethoxylation degree of 15.0, compared to (A), with ethoxylation degree at 9.5, seen in figure3.6 .With higher ethoxylation degree follows that the surfactant has a larger polar chain and consequently higher solubility towards the aqueous phase. Thus higher concentration of surfactant is required to assure formation of micelles. Curbelo et al. (2007) concluded that the adsorption to the sandstone core is higher in the case of the lower degree of ethoxylation, situation (A), which should be avoided in EOR surfactant flooding.

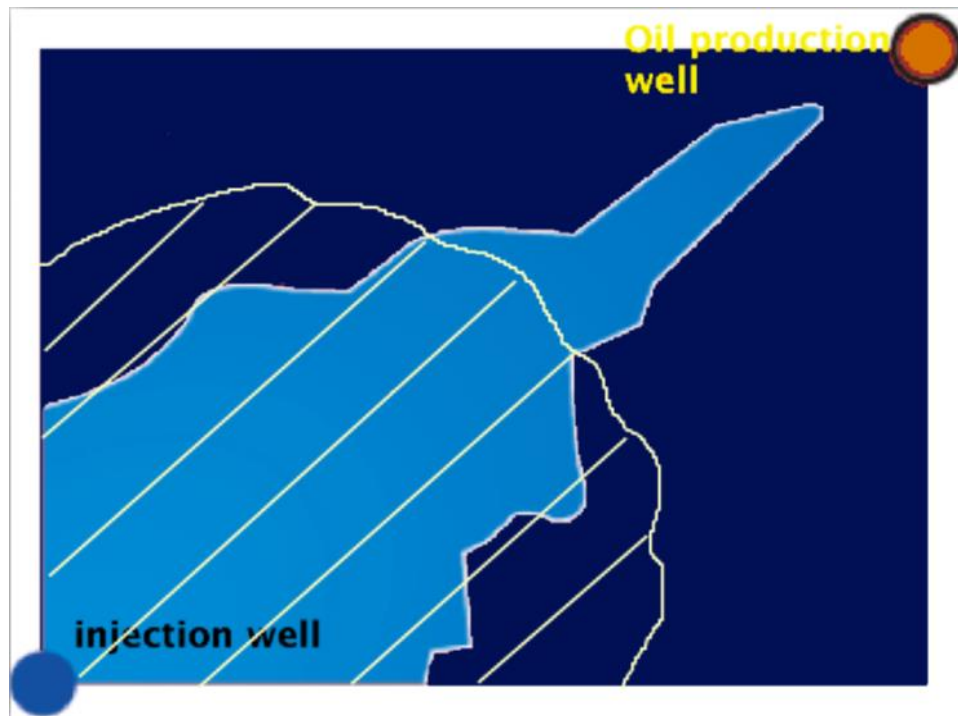
### **3.2.6 USE OF CATIONIC SURFACTANTS**

Cationic surfactants have a positively charged head group. Cationic surfactants dissociate in water, forming an amphiphilic cation and anion, typically a halide (Br-, Cl- etc.). During the synthesis to produce cationic surfactants, they undergo a high pressure hydrogenation reaction, which is in general more expensive compared to anionic surfactants. As a direct consequence cationic surfactants are not as widely used as anionic and nonionic surfactants.

It is, however, reported that cationic surfactants can be used to improve the spontaneous imbibitions rate of water into preferentially oil-wet carbonate. Water containing surfactants of the type alkyltrimethylammonium bromide or chloride was injected [Standnes & Austad, 2002]. The cationic surfactants are most likely dissolved in the oil phase as aggregates between the surfactant and the carboxylates, under creation of ion pairs. In this way the surface becomes more water-wet, thus the aqueous phase can better imbibe by capillary forces.

### **3.3 POLYMER FLOODING**

In conventional oil reservoirs, residual oil after water flooding exists as discontinuous ganglia trapped by capillary forces. This is not the case for water flooding heavy oil reservoirs. The residual oil in the heavy oil reservoirs after water flooding is the result of oil bypassing by water because of high oil viscosity, which causes a poor mobility ratio between displacing and displaced fluids (Mai et al. [2009]). Polymer solution results in increasing volumetric sweep efficiency by improving mobility ratio, and reducing fluid flow through more permeable channels, Figure3.7



**Figure3.7: Mobility control by polymer flooding. Displacement of water flooding and polymer flooding.**

### 3.3.1 INTRODUCTION POLYMER FLOODING

Eighty-five percent of the world's energy demand is provided by fossil fuels, while more than 30% of that is covered by oil and gas. Currently, about 87 million barrels of petroleum per day (32 billion barrels per year) are being produced in the world. In spite of declining oil and gas resources in conventional oil reservoirs, energy demand is raising. Heavy oils have been considered as the most proper and accessible substitute for these resources (sheng [2011]).

Western Canadian oil has the viscosity between 100 to 10,000 cp; so primary oil recovery and water flooding only recover about 10% of OOIP in these heavy oil reservoirs. Water flooding has the low effect on improving oil recovery in Alberta and Western Canadian reservoirs due to its poor sweep efficiency and early viscous fingering. In heavy oil reservoirs water flooding, oil has been produced at very high water/oil ratio; which requires large scale separators. Polymer flooding can be implemented to lowering the water/oil ratio and improving sweep and displacement efficiency in heavy oil reservoirs especially in Western Canada oil reserves

The concept of implementing polymer flooding technique by using polymer solution for improving heavy oil recovery, was introduced by Pye and Sandiford in 1964, and Knight and Rhudy at 1977; and then became one of the most mature EOR techniques. Polymer flooding is considered as a secondary/tertiary oil recovery method, which is a process of injecting long chain polymer molecules with high molecular weights, in order to increase water viscosity to reach the goal of improving mobility ratio, similar to most EOR methods Viscosifying the injected water helps to generate a piston like displacement of heavy oil, which results in



postponing fingering phenomena, and then increases the swept volume (Wang et al. [1993], Alsofi et al. [2011], Knight et al. [1977], Pye [1964], and Sandiford [1964]). There are two goals for every EOR method: Improving the mobility ratio and increasing the capillary number (Maheshwari [2011]).

Polymer flooding will be reached these goals by adding polymer to the injected water due to increasing the viscosity of water and decreasing the permeability of flooding zone; resulting in more oil production. Polymer flooding technique has three potential ways to increasing recovery oil efficiency (Szabo [1975] and Needham et al. [1987]):

1. Effects of polymers on fractional flow;
2. Decreasing the mobility ratio; and
3. Diverting injected water from zones that have been swept to unswept zones.

The following factors should be considered when selecting and operating polymer flooding method as an EOR technique for a given oil reservoir:

### **3.3.2 FACTORS OF SELECTING POLYMER FLOODING**

- Best time for polymer flooding;
- Polymer type;
- Polymer slug size;
- Mobility control;
- Polymer slug concentration;
- Viscosity of polymer slug;
- Density of polymer slug;
- Reservoir's salinity effect;

#### **Pre-flush and post flush;**

Polymer flow behavior in porous media;

- Permeability
- Residual oil saturation effect
- Cross linking effect
- Polymer adsorption
- Resistance factor and residual resistance factor
- Polymer retention
- Inaccessible pore volume
- Polymer rheology
- Polymer degradation
- Advantages of polymer flooding; and
- Economical point of view.

#### **3.3.2.1 BEST TIME FOR POLYMER FLOODING**

The timing for implementing polymer flooding has significant effect on production efficiency. It can improve the recovery factor by two or three times, so it is worthwhile to

know when the best time is for starting polymer solution injection (Sheng [2011]). Using polymer solution injection in secondary floods causes considerably more oil recovery for less polymer usage than tertiary floods. It is always beneficial to start polymer flooding as soon as possible, preferably before any water flooding, because polymer flooding has much greater potential as a secondary process than in post-water flood applications. The amount of polymer used to recover a barrel of oil appears to have been about six times greater in tertiary than in secondary applications. However optimal start for polymer flooding method is at time zero (start of the production) (Needham et al. [1987] and Alsofi et al. [2011]). Using Polymer flood as a secondary oil recovery method and also post water flood oil recovery method had been investigated in this thesis and its effect on increasing oil recovery, injection pressure, and decreasing water cut has been compared.

### 3.3.2.2 POLYMER TYPE

Synthetic polymers (polyacrylamides) and Biopolymers are two general types of polymers, which are used in polymer flooding method (Needham et al [1987]). Polymer molecular weight is a very important parameter in selecting the polymer type. Contradictory points should be considered in polymer selection because of its molecular weight importance (Needham et al. [1987] and Demin et al. [1998]):

1. High polymer molecular weight increases the viscosity of polymer solution,
2. High polymer molecular weight reduces the permeability in high permeability zones,
3. High polymer molecular weight produces higher resistance factor,
4. Very high polymer molecular weight may plug the formation pore spaces,
5. Very high polymer molecular weight has the greater tendency to shear degradation.

The size of polymer molecule should be high enough to increase the viscosity of solution and plug the high permeability channels. Conversely, it should be small enough to let the solution go through the pore spaces. Optimum polymer molecule size is when its gyration radius is five times smaller than average size of pore spaces (Demin et al. [1998]). Polyacrylamide is the most common type of polymer for using in polymer flooding EOR method. The performance of the polyacrylamide in a flooding situation will depend on its molecular weight and its degree of hydrolysis (Needham et al. [1987]). Powder polyacrylamide has the molecular weight equal 10 million Kg/Kg.mole; and its wide use is based on the (Wang et al. [1993] and Shehata et al. [2012]):

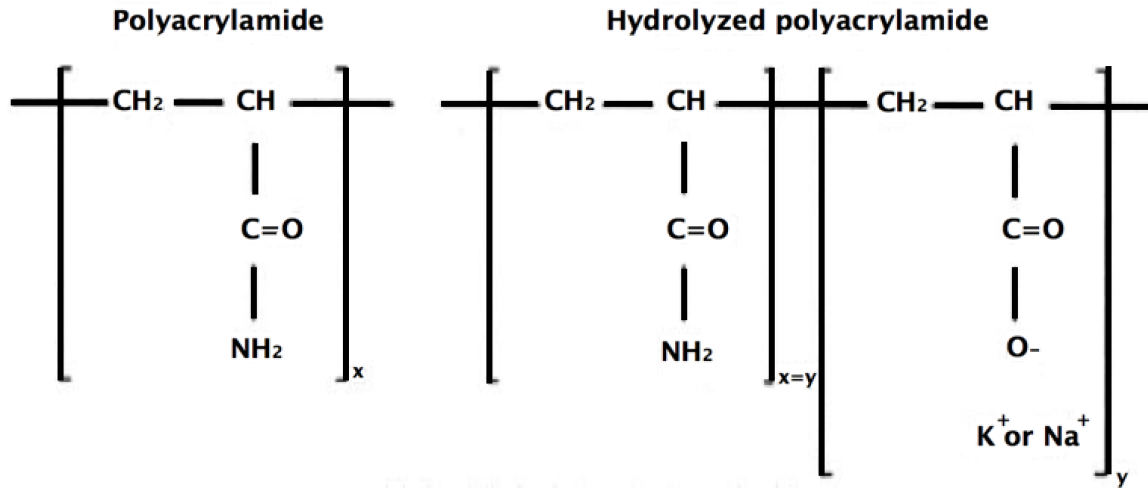
1. Appropriate for the formations with salinity range between 700 to 25000 ppm,
2. Low price compared with other polymer types,
3. Adsorbs on the rock surface to produce a long lasting permeability reduction (the residual resistance effect).

Some polyacrylamides disadvantages are considered as follows (Needham et al. [1987]):

4. Tendency to shear degradation at high flow rates;
5. Poor performance in high salinity water (low viscosity, frequently excess reduction, and high retention level);
6. Precipitate in waters containing too much calcium, at temperature above 170°F (needs high control in salinity of the flooding water).

Partially hydrolyzed polyacrylamide (HPAM) with molecular weight equal to 2500\*10<sup>4</sup> works as the stabilizer (Qingfeng et al. [2012]). In this kind of synthetic polymer,

some of the acrylamide is replaced by, or converted into, acrylic acid. This tends to increase the viscosity of fresh water; but no viscosity reduction in hard waters (Needham et al. [1987])



**Figure :3.8 Polyacrylamide and partially hydrolyzed polyacrylamide (Lake[1989]).**

Biopolymers such as xanthan gums are the other types of polymers with excellent viscosity in high salinity waters and resistance to shear degradation. Biopolymers also have an advantage as they are not retained on rock surfaces, and thus propagate more readily into a formation. This can reduce the amount of polymer required for a flood; but also means that there is no residual resistance effect. A disadvantage is that they thermally degrade too fast at temperatures above 200°F (Needham et al. [1987]). Natural polymers such as guar gum, sodium carboxymethyl cellulose, and hydroxyl ethyl cellulose are less common types of polymers that are used in polymer flooding process (Maheshwari [2011]).

### 3.3.3 PRE-FLUSH AND POST FLUSH

Pre-flush and post flush fresh water slugs, have been performed as a part of a successful model for polymer flooding methods (Needham et al. [1987]). The purpose of injecting these pre and post flushes is to avoid direct contact between polymer and formation saline water. Steady water and oil distribution and decreasing the salinity of the formation water is considered the advantages of pre-flush injection (Wang et al. [1993]). Some pre-flush disadvantages, which can negatively affect on polymer flooding efficiency; can be summarized as follows (Vafaei [2012]):

- Fingering phenomena might occur due to low viscosity of fresh water;
- Long injection time is required for pre-flush to prevent fingering; which can be costly; and
- High water saturation areas in the reservoir will be left after pre-flush.

There are two different ideas about how to operate the pre-flush in order to increase efficiency in polymer flooding method:

1. The effects of polymer flooding will increase by increasing the size of pre-flush water slug (Demin et al. [1998]).
  2. Small slug size of dilute polymer solution with a low degree of hydrolysis due to its less sensitive to salinity, will improve the polymer flooding performance (Vafaei [2012]).
- There is the possibility of breakthrough in polymer flooding by post flush water flooding; thus, a sufficient amount of polymer injected as a mobility control is needed.

### **3.3.4 ADVANTAGES OF POLYMER FLOODING**

Applying polymer flooding enhanced oil recovery method has the following benefits:

- Increased recovery and sweep efficiency;
- Reduce the residual oil saturation through an improvement in microscopic sweep efficiency (Szabo [1975]);
- Improved areal sweep efficiency through improved mobility ratio;
- Increases the displacement result in poor reservoirs with low water cut (Wang et al. [1993]);
- Less water used in Polymer flooding compared to conventional water flooding technology (albertatechfutures website);
- Can be used in thin heavy oil formations with low viscosity where SAGD and VAPEX are not suitable (albertatechfutures website);
- After polymer flooding, fluid breakthrough occurs more uniformly (Wang et al. [1993]);
- Polymer flooding system has a better compatibility with reservoirs (Xue et al. [1999]);
- Polymer flooding has been successfully used in onshore oilfields (Luo et al. [2011]);
- Period of polymer flooding is shorter than that of water flooding at the same injection rate through improved fractional flow characteristic (Wang et al. [1993]);
- Polymer flooding can increase the displacement efficiency both in water wet models and oil wet models (Wang et al. [1993]);
- Polymer flooding can get good results in medium and low permeable formations with multi-sedimentary units, complex sand body geometry and poorer inter-well communication (Demin et al. [1996]); and
- In comparison to the other chemical flooding processes such as caustic emulsion floods or surfactant/polymer processes, straight polymer injection is a relatively uncomplicated process (Wassmuth et al. [2007]).

### **3.3.5 ECONOMICAL POINT OF VIEW**

When screening EOR technologies for possible field application, the basic screening criteria are usually based on economic considerations. It is almost certain that a polymer flood will dramatically improve the oil recovery performance, but it remains to be determined whether or not this can be done in a cost effective manner. Even when dilute (500 to 1500 ppm) solutions of polymers are used, the cost of polymers becomes substantial. The viability of the process depends primarily on the amount of polymer required per incremental barrel of oil produced (Wassmuth et al. [2007]).

The cost of well drilling and basic facility construction is a onetime investment. Cost of polymer flooding increases with the increase of the amount of polymer injected. Income from

accumulative incremental oil production also increases of the amount of polymer injected (Demin et al. [1998]).

Polymer injection initiated at an early stage of water flooding is more efficient than when initiated at an advanced stage (Szabo [1975]). Water flooding, after primary heavy oil recovery, generates an initial high water cut at breakthrough, which decreases when the heavy oil is mobilized after the reservoir is repressurized and a substantial pressure gradient is established between injector and producer (Wassmuth et al. [2007]).

The combination of horizontal wells and polymer technology provides sufficient injectivity to inject the viscous polymer solution and to displace the heavy oil at economic rates. The separation between the horizontal wells is one of the few variables that can be adjusted to dictate the duration of the polymer flood. On a smaller well separation the polymer flood maintains a large pressure gradient between injector and producer, generating higher oil production rates, and decreasing the duration of the polymer flood. The converse is true for larger horizontal well separations to the point where the polymer flood can underperform in comparison to a water flood. When considering a polymer flood application on a heavy oil field, the horizontal well separation is one of the key economic parameters that need to be considered as it impacts the time value of money (Wassmuth et al. [2007]).

### **3.4 ALKALINE-SURFACTANT-POLYMER (ASP) FLOODING**

#### **Definition**

ASP flooding has been recognized to be one of the major EOR techniques that can be successfully used in producing light and medium oils left in the reservoirs after primary and secondary recovery in order to extend reservoir pool life and extract incremental reserves currently inaccessible by conventional techniques such as water flooding (Majidaie et al. [2010], hydrocarbon recovery website, and proven-reserves website). In alkaline flood process, the surfactants are generated in-situ by chemical reaction between the alkali of the aqueous phase and the organic acids of the oil phase. However, for a low acidic oil reservoir, the amount of surfactants generated in-situ is insufficient to produce ultra-low interfacial tension. Nelson et al. (1984) presented the concept of using a chemical surfactant to augment the in-situ surfactant. He found that a properly chosen cosurfactant increases the electrolyte concentration so that a minimum IFT may be achieved. Thus, a co-surfactant can be used to obtain the conditions of “optimum salinity” of an alkaline flood. Schuler et al. (1986) reported the initial laboratory studies demonstrating the benefit of combining alkaline, surfactants and polymers (Ma [2005]). ASP is a new modification to the alkaline process which is the addition of surfactant and polymer to the alkali. ASP has been shown to be an effective, less costly form of Micellar-polymer flooding (netl website). ASP floods have been successfully conducted worldwide in recent years, commonly achieving 20% incremental oil recovery, due to increasing the viscosity of injected fluid, decreasing the oil/water mobility ratio, and enlarging sweeping volume in reservoirs (China national petroleum corporation and proven reserves).

ASP flooding is a potentially viable technique for recovering oil at the conclusion of water flooding (Mai et al. [2009]). Water flooding usually results in a very low secondary heavy oil recovery factor and a high producer water-oil ratio (WOR). This is due to early water breakthrough caused by an extremely high mobility ratio and a high interfacial tension between the injected water and heavy oil. After the point of water breakthrough in water flooding, water channels of low flow resistance were continuous along the reservoir, and the oil production is very inefficient for high rate water flood. In ASP flooding, which is a tertiary recovery method; the surfactant agents act to free oil trapped in the pore spaces of the reservoir and the polymer increases the area of the reservoir sweep. Water flooding resumes after chemical injection to produce oils released by the injected chemicals (Mai et al. [2009] and huskyenergy website). Application of these methods is usually limited by the cost of the chemicals and their adsorption and loss onto the rock of the oil containing formation (hydrocarbon recovery website). The success of ASP flooding method depends on the identification of the proper alkali, identification of the proper surfactant, identification of the proper polymer, and the way they are combined to produce compatible formulation that yields good crude oil emulsion/ mobilization, low chemical losses and good mobility control (Al-Hashim et al. [2004]).

### **3.5 CASE STUDY OF ASP FLOODING IN CANADA**

Western Canada has tremendous heavy oil deposits, which are located in east-central Alberta and extended into western Saskatchewan. Efficient and economical recovery of such heavy oil deposits has gained considerable attention due to an increase in demand for hydrocarbon fuels and decline in production from the conventional light and medium oil resources. The primary oil recovery factor for heavy oil reservoirs is typically as low as 6- 8% of the OOIP, which is mainly attributed to the extremely high oil viscosities and almost immobile conditions of the heavy oils under the actual reservoir conditions.

There have been limited investigations into alkali and ASP flooding in heavy oil reservoirs with varying degrees of success. Most of these works have focused specifically on oil-water IFT reduction as the mechanisms for improved oil recovery. Canada is the world leader in developing EOR techniques for heavy oil production. Huang and Ding (2002) conducted an initial study to assess the suitability of ASP flooding for Southwest Saskatchewan medium oil reservoirs (Ma [2005]). Husky Energy Inc., in Calgary, Alberta, successfully implemented ASP flood technology in Canada to extend the production life of the Taber South Mannville B Pool, in the Warner field, in 2006. The successful implementation of the ASP technique means that a significant number of reservoirs in Alberta may benefit from the knowledge gained from this technology. A similar project at the Crowsnest field near Taber is currently in detailed design phase (huskyenergy website).

### **3.6 ASP MECHANISM**

In the ASP process, a very low concentration of the surfactant is used to achieve ultra low interfacial tension between the trapped oil and formation water. The ultra low interfacial tension also allows the alkali present in the injection fluid to penetrate deeply into the formation and contact the trapped oil globules. Also, addition of a surfactant lowers the interfacial tension between water and oil, which helps to reduce capillary pressure in the reservoir. This allows residual oil to be mobilized and produced from the formation. The alkali then reacts with the acidic components in the crude oil to form additional surfactant in situ, thus, continuously providing ultra low interfacial tension and freeing the trapped oil; and also it can reduce adsorption of surfactants and react with acids in the oil to form soaps. In this process, polymer is used to increase the viscosity of the injection fluid, to minimize channeling, and provide mobility control. The combination of the three chemicals is synergistic; together they are more effective than as individual components (Kazempour et al. [2011], hydrocarbon recovery website, oil-chem website, and huskyenergy website). Displacement mechanisms in ASP method may be summarized as follows (Sheng [2011]):

- Increase capillary number effect to reduce residual oil saturation because of low to ultralow IFT;
- Surfactant adsorption is reduced on both sandstones and carbonates at high pH;
- High pH also improves micro emulsion phase behavior;
- Improved macroscopic sweep efficiency because of the viscous polymer drive;
- Improved microscopic sweep efficiency and displacement efficiency as a result of polymer viscoelastic property; and
- Emulsification, entrainment, and entrapment of oil droplets because of surfactant and alkaline effects.

**The effects of each part of ASP flooding method are summarized as follows:**

**Alkali:**

1. Reacts with acidic components in the crude oil to creating natural soap,
2. Reducing the adsorption of the surfactant on the rock,
3. Alters rock wettability (from oil-wet to water-wet),
4. Adjusts pH,
5. Adjusts salinity,
6. Creates ultra low interfacial tension,
7. Penetrates deeply into the formation and contacts the trapped oil globules, and
8. Releases the trapped oil.

**Surfactants component:**

1. Reducing the interfacial tension between oil and water,
2. Reduce capillary pressure,
3. Releasing the oil from the rock, and
4. Mobilize residual oil.

**Polymer:**

1. Viscosity modifier,
2. Mobilize the oil,
3. Mobility control,
4. Reduce fingering,
5. Reduce the slope of oil recovery decline,
6. Extend the production for a longer period of time,
7. Push solution, and
8. More uniform movement or sweep.

**Driving fluid (water):**

1. Move the chemicals and resulting oil bank towards production wells,
2. Increase the viscosity of the injection fluid,
3. Minimize channeling, and
4. Provide mobility control.

### 3.6.1 DESIGN

The design and formulation for ASP flooding are different for each field and depends on crude oil characteristics, brine characteristics, bottom hole temperature, alkali, surfactant, and polymer type, well history, and treatment design (oil-chem website). Typically, the ASP formulation consists of about 0.5-1% alkali, 1% surfactant, and 0.1% polymer (tiorco website). Ultra-low IFT can be formed by ASP system when the concentration of the alkaline (NaOH) ranges from 0.6-1.2 wt% and the surfactant concentration ranges from 0.1-0.6 wt% (Demin et al. [1999]). Gharbi (2001) looked at ASP design and found optimal polymer concentration to be around 2800 ppm, which is relatively high (Alsofi et al. [2011]). An ASP flood involves injecting a predetermined pore volume of ASP into the reservoir. Often the ASP injection is followed by an additional injection of polymer. Upon completion of the ASP and polymer injection, regular water flooding behind the ASP wall resumes again. The combination of the three chemicals is synergistic. Together they are more effective than as components alone (proven-reserves website). Generally, the reservoir is conditioned by a pre-flush (with water, alkali or polymer depending on rock mineralogy) before the injection of ASP slug into reservoir (tiorco website).

### 3.6.2 SCREENING CRITERIA

Screening criteria have been proposed for all EOR methods. Data from EOR projects around the world has been examined and the optimum reservoir/oil characteristics for successful projects have been noted. Screening criteria for polymer and ASP flooding and other chemical methods have shown in table below

Table 3.2: Summary of oil properties screening criteria for chemical EOR methods

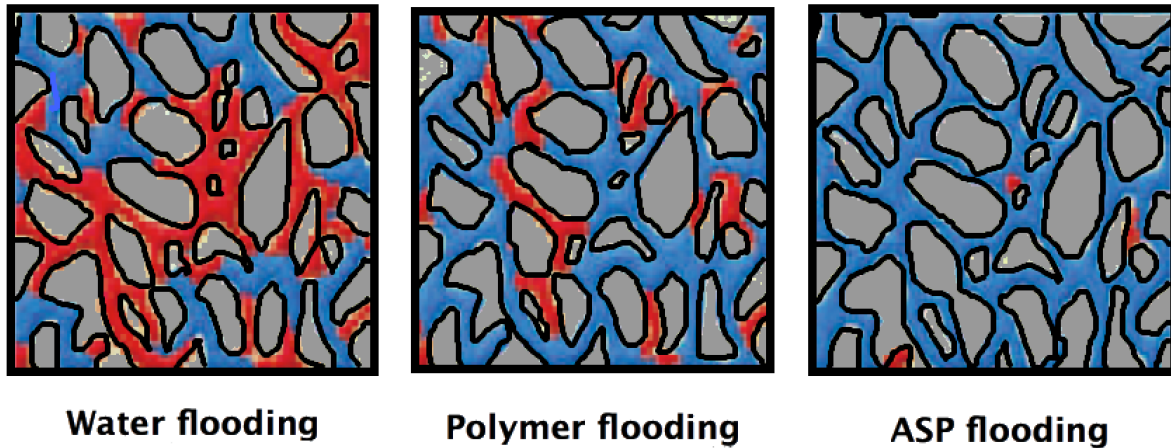
EOR methods	Oil properties		
	API	Viscosity (cp)	Component
Micellar/ Polymer, ASP, and Alkaline flooding	20-35	13-35	Light, intermediate, some organic acids for alkaline floods
Polymer flooding	>15	10-150	NC

### 3.7 ADVANTAGES OF ASP FLOODING

The use of alkali adds many benefits to an ASP flood. The alkali reacts with elements of the oil to form in-situ surfactants. Additionally, it helps make the reservoir rock more water wet,



thus increasing the flood effectiveness. As alkali is inexpensive, this helps to reduce the cost of an ASP flood. The polymer increases the vertical and areal sweep efficiencies of the flood by increasing water viscosity. The increased viscosity decreases the chance of fingering and allows more oil to be contacted on a macroscopic scale.



**Figure:3.9 Residual oil saturation comparison in water, polymer, and ASP flooding (China national petroleum corporation). Picture edited by Author for quality purposes.**

Some advantages of ASP method can be summarized as follows:

- Less surfactant required recovering significantly incremental oil (tiorco website);
- Applicable for more viscous oils;
- Presently has the highest application potential, since they are low risk methods with a well developed application technology (hydrocarbon recovery website);
- Surfactant/polymer flooding is an immature method from an application point of view. It will need substantial research and development to become a technique of any importance compared to ASP (hydrocarbon recovery website);
- The potential and feasibility of ASP flooding continues to grow and offers much potential for increased oil recovery (hydrocarbon recovery website); and
- Achievement of 20% incremental oil recovery.

### 3.8 MICELLAR FLOODING

This EOR method uses the injection of a micellar slug into a reservoir. The slug is a solution usually containing a mixture of a surfactant, co-surfactant, alcohol, brine, and oil that acts to release oil from the pores of the reservoir rock, much as a dishwashing detergent releases grease from dishes so that it can be flushed away by flowing water. As the micellar solution moves through the oil-bearing formation in the reservoir, it releases much of the oil trapped in the rock. To further enhance production, polymer-thickened water for mobility control (as described in the polymer flooding process) is injected behind the micellar slug. Here again, a buffer of fresh water is normally injected following the polymer and ahead of the drive water to prevent contamination of the chemical solutions. This method has one of the highest recovery efficiencies of the current EOR methods, but it is also one of the most costly to implement (netl website).

Micellar flooding is known as microemulsion flooding, micellar-polymer and surfactant-polymer flooding. Generally the basic process consists in injecting a slug of a preflush, followed by the micellar slug proper, followed by a slug of a polymer solution, which is graded into waterflood. Micellar solution can be also defined as a dispersion of a surfactant in an oleic or aqueous solvent that can stabilize large amount of water or oil to form either water in oil or oil in water microemulsions [4]. Although micellar flooding process has some limitations regarding the using of chemicals in its structures, the long term potential for the recovery of residual light oils makes this method one of the most technically applicable methods in the field scale as a tertiary recovery method for low pressure and depleted oil reservoirs. The high cost of this method is due to use of large amount of chemicals in this method, therefore the concentration of the component should be chosen carefully to maximize its effectiveness.

To study the compatibility of the designed slug with the reservoir fluids, it is convenient to refer to the ternary diagram drawn to study the phase behavior of the intended slug with the reservoir crude, connate water, temperature and mobility buffer solution. So for an effective recovery of oil, the multiphase region should be minimal so as to prolong the locally miscible displacement. Also, the interfacial tension should be low for an effective immiscible displacement in the multiphase region.

In order to show each component of the microemulsion (water, oil and surfactant), ternary diagram is used to indicate the phase behavior of the microemulsion as shown in figure 3.10. The model proposed by Winsor explains the simple situation by the presence of three pure components in which the multiphase region is bounded by a continuous bimodal curve.

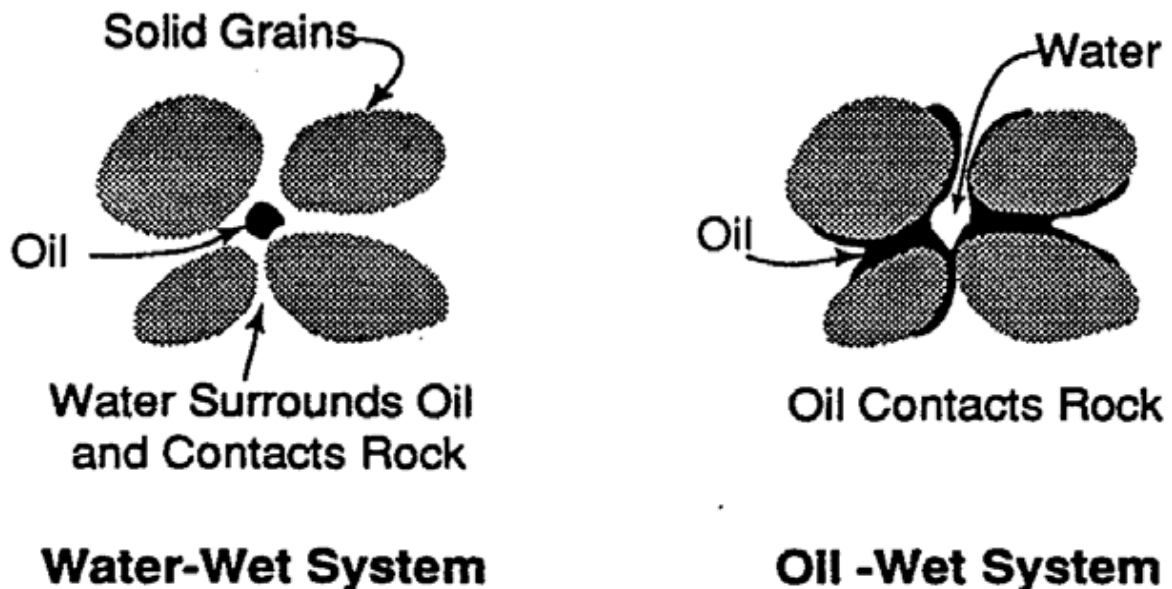
Everywhere above the binodal curve a single phase exist that undergoes transitions among various structural states as the compositional point moves about the diagram. These transitions may be gradual, reflecting an equilibrium in which there is significant coexistence of different micellar configuration.

## CHAPTER 4

### WETTABILITY AND PHASE BEHAVIOUR

#### 4.1 WETTABILITY

Wettability has been defined by Jerauld and Rathmell 9 “as a tendency of one fluid of a fluid pair to coat the surface of a solid spontaneously”. Another important definition is given by Anderson 10 who defines wettability as “the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids”. Therefore, in a fluid/rock system, depending on the preference of the fluid to coat the rock surface, it can be water-wet or oil-wet system (Figure 4.1). In the first case, water has the tendency to adhere to the majority of the rock surface occupying the small pores, whereas in the second case oil is in contact with the majority of the rock surfaces occupying the small pores.

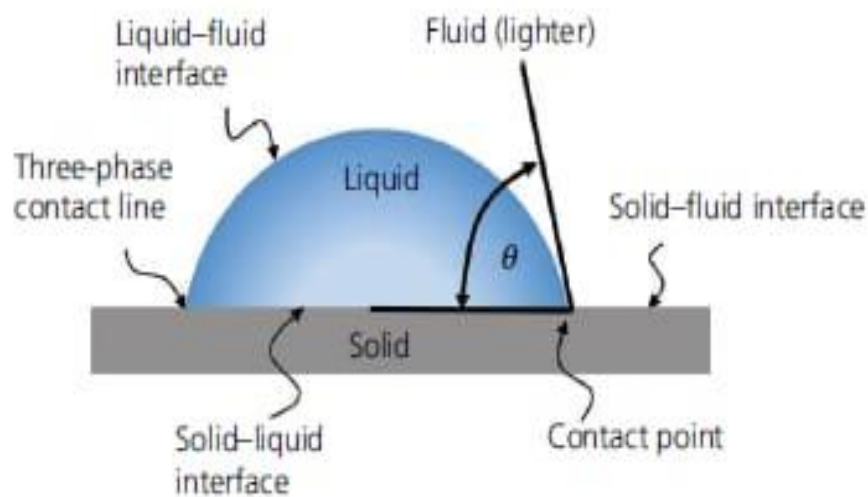


**Figure 4.1 Water-wet vs. Oil-wet systems**

Depending on the interaction between fluids and rock, the systems could be classified as a strongly water-wet or strongly oil-wet. Nevertheless, in some systems, both oil and water tends to adhere to the rock surface which is defined as intermediate (or neutral) wettability. There is also another type of wettability called “fractional” where different areas of the core have different wetting preferences. It occurs where rock surface has variable mineral composition and surface chemistry. A special type of fractional 10 wettability was introduced by Salathiel 11 “mixed-wettability” in which the smaller pores are water-wet and filled with water whereas the larger pores are oil-wet and filled with oil (it forms a continuous path). Salathiel explains this phenomenon: when oil initially invaded originally water–wet reservoir, it displaced water from the larger pores, while the smaller pores remained water-filled because of capillary forces.

## 4.2 CONTACT ANGLE

Contact angle, as a thermodynamic property that characterises the wettability of solid surfaces. A naive view of the contact angle simply considers this thermodynamic property as the observed angle between the tangent to the solid surface and the tangent to the liquid–fluid interface at the contact line between the three phases – An angle experimentally observed on the liquid side (denser liquid side in case that there are two liquids) between the tangent to the solid surface and the tangent to the liquid–fluid interface at the contact line among the three phases (Figure 4.2). The point of intersection between tangent lines is known as the contact point (Figure 4.2)



**Figure:4.2**The contact angle  $\theta$  is shown for a sessile drop. The contact line in this case is the outline of the contact circle between the solid and the liquid (note that the drop is assumed to be axisymmetric with its profile shown)

## 4.3 WETTABILITY ALTERATION

Surfactant adsorption onto solid surface decreases IFT and shifts the wettability of the solid surface making it water-wetting or oil-wetting depending on the orientation between adsorbed surfactant molecules and solid surface. If the orientation of the head groups (hydrophobic) point away from the surface, oil-wetting reduces whereas water-wetting increases. Conversely, if the tail groups (hydrophilic) point away from the surface, oil wetting increases whereas water-wetting decreases.

#### 4.4.1 TECHNIQUES TO ALTER WETTABILITY

There are a lot of methods to alter the wetting properties of mineral surfaces to water and oil. Two methods will be reviewed to alter the wettability of a system from strong water wet system to less water wet as preparation for the initial conditions that will be used in the laboratory.

- I. Silanization
- II. Quilon treatments

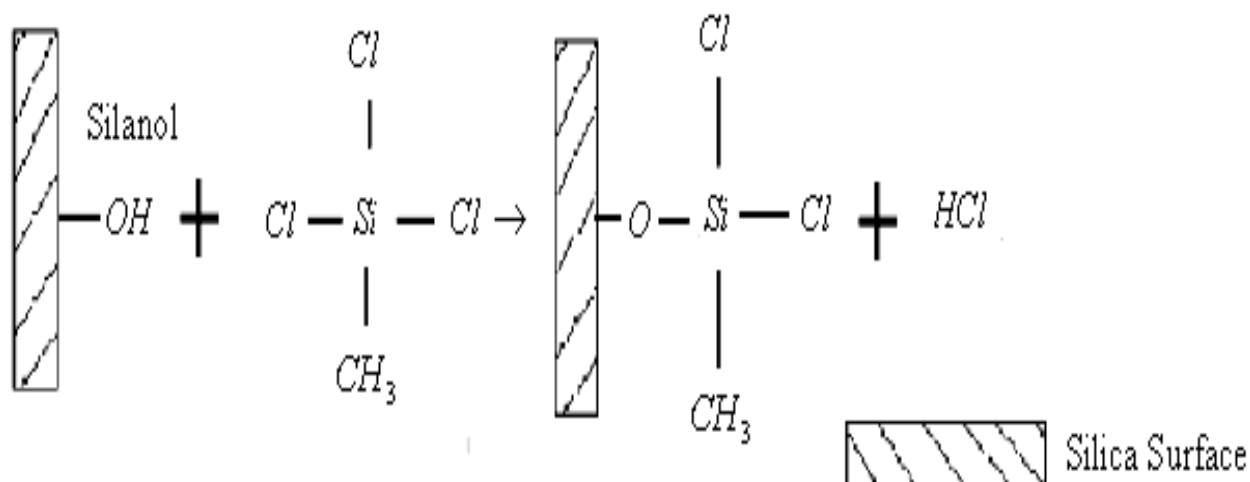
##### I. Silanization

The silanization procedure consists in a chemical reaction where organosilyl group attacks and displaces the hydroxyl group (OH). In this reaction, organochlorosilane compound (silicon molecules with attached chlorines and non-water organic groups, with the formula  $R_nSiCl_{4-n}$ ) react with the hydroxyl group on silicon dioxides surfaces, exposing the organic groups and shifting into a hydrophobic system. In his study, trichloro(methyl)silane reacted with water or hydroxyl groups (silica) to release HCl and form a thin film of methylpolysiloxanes which has low critical surface tension (hydrophobic). The reaction is giving by the following chemical reaction:



The procedure used by Tabrizy in his research to alter the wettability from strong water-wet to strong oil-wet is:

1. Cleaning procedures are applied to the glass beads with an HCl solution (20%) to get a water wet system.
2. Rinse the glass beads with distilled water to remove all residues and then put in an oven for 2 hours at 100 °C.
3. The glass beads are incubated for 15 minutes in a 2% solution of trichloro(methyl)silane and 98% of toluene. A thin film of methylpolysiloxanes covers the grains. It has to be taken into account the HCl formation during this reaction before removing the glass beads from the reaction vessel.
4. Finally, rinse the glass beads with methanol and then dried in the oven. This issue will help to the cross linking reaction and the formation of monolayer silane film.

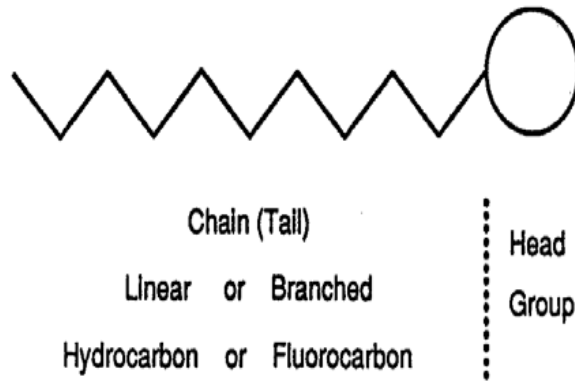


## II. Quilon treatments

Other techniques have been developed to alter the wettability in sandstones cores like Quilon treatments. Maini used Quilon-S whereas Lewis 23 worked with Quilon-C to change the hydrophilic surfaces into hydrophobic (oil-wet). Quilon-C is a chromium complex that contains a fatty acid group (C14-C18). The chromium in Quilon-C reacts with polar groups on charged surfaces (negative) and forms an insoluble layer of polymerized complex which bonds to the rock surface by chromium. The exposing fatty acids groups repel water, thus the rock surface is hydrophobic. Lewis 23 used the following procedure to get a hydrophobic surface: The cores were vacuumed dry for 2 hours, and then saturated with a 20% solution of Quilon-C and reagent grade isopropyl alcohol. After that, the cores were evacuated for 4 hours. The procedure was repeated again, and then the core was flushed with ethanol until effluent was a very slight green color. Finally, the core was heated in an oven at 60 °C for the whole night. This total procedure was repeated again to get a stable treatment.

## 4.5 SURFACTANTS

Rosen 26 defined surfactants as the chemical substances that adsorb on or concentrate at a surface or fluid/fluid interface when present at low concentrations in a system. They consist of a lipophilic portion (hydrocarbon group) and hydrophilic portion (polar group) which are the non-polar (tail) and polar (head) portions respectively as shown in Figure 1.7.



**Figure 4.4 Schematic of surface-active molecule 1**

## *4.6 SURFACTANT ADSORPTION*

Surfactant adsorption occurs when surfactant is in contact with a surface or interface, which may lead to wettability alteration (positive effect) or loss of surfactant from solution (negative effect).

### **4.6.1 THE ELECTRICAL DOUBLE LAYER**

According to Rosen , at any interface the electrical charges are not distributed equally between the two phases. This unequal distribution causes one side of the interface to acquire a net charge of a particular sign and the other side to acquire a net charge of the opposite sign, giving rise to a potential across the interface.

## **4.7 ADSORPTION AT SOLID/LIQUID INTERFACES**

Adsorption of surfactant onto porous media (on the walls of throats or pores, or on fine particles in rock pores) can constitute a loss of valuable surfactant that can determine the feasibility of the oil recovery project.

Static 1 (batch equilibrium tests) and dynamic 1 (core flood measures) experiments are usually used to measure the surfactant adsorption. In the first case, batch equilibrium tests, a specified mass of crushed rock is mixed with a known volume of surfactant solution (at a known concentration) in a sealed container. Fluids samples are withdrawn at intervals and analyzed until the system is at equilibrium (concentration keeps constant with time as shown in Figure 4.5. Material balance is used to calculate adsorption. For the second case, the

dynamic core flood method, surfactant slugs of increasing size are injected into cores until retention reaches a maximum and constant value as shown in Figure 4.6.

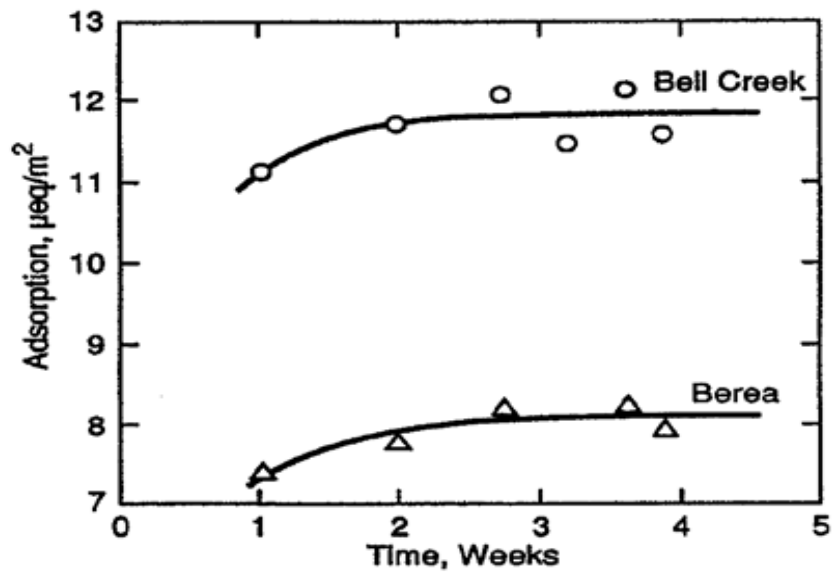


Figure 4.5 Adsorption vs. time

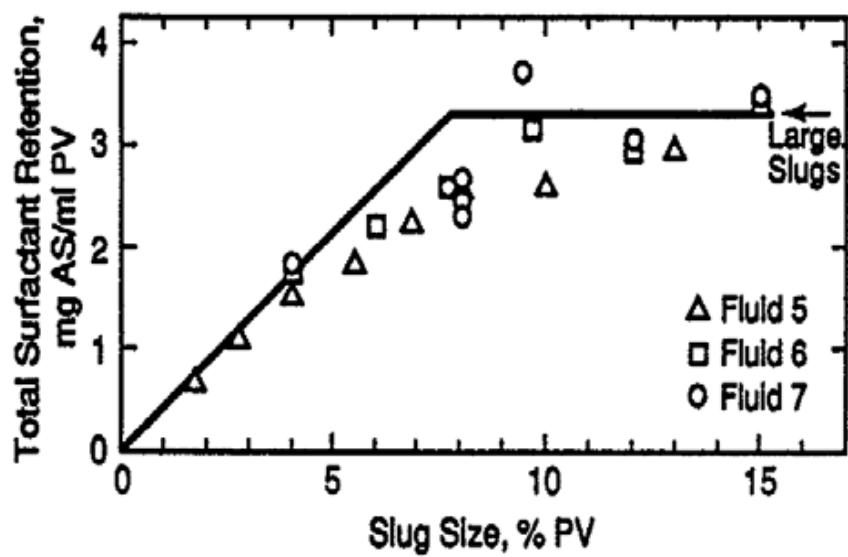


Figure 4.6 Surfactant retention during core flood experiments



The surfactant adsorption onto porous media is affected by surfactant type, concentration and equivalent weight; temperature; brine salinity and hardness; solution pH; rock minerals; wettability; presence of a residual oil phase and the flow rate of the solution.

#### **4.8 MICELLE FORMATION AND CRITICAL MICELLE CONCENTRATION (CMC)**

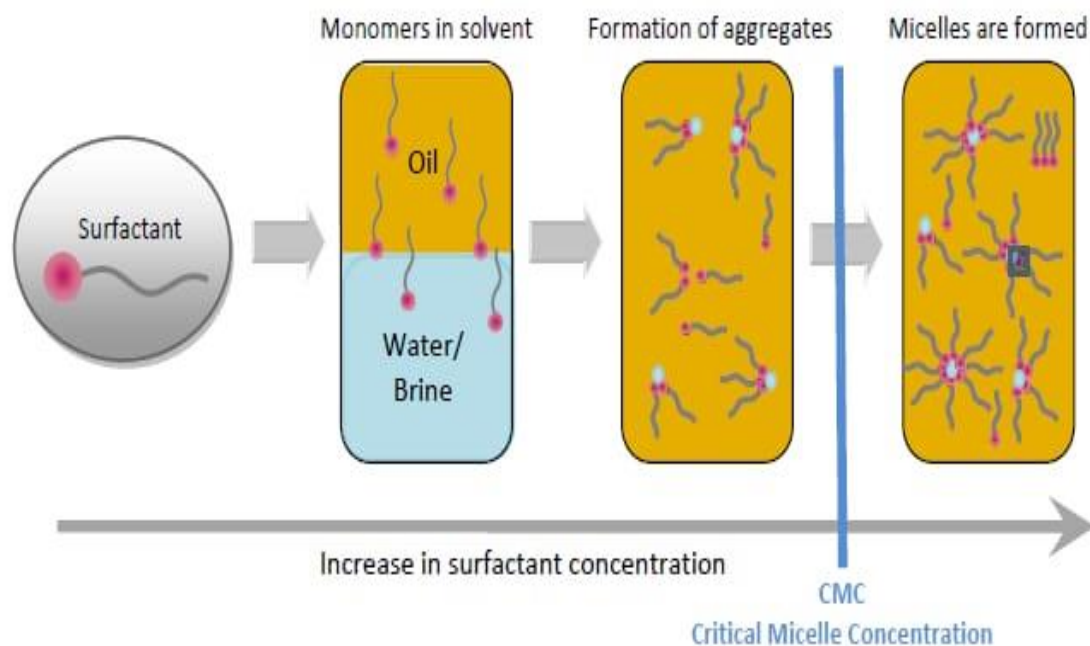
Surfactants also can form micelles (colloidal aggregates in solution) depending on the concentration into a solvent (Figure 4.7). When the surfactant concentration is very low, dissolved surfactants molecules are dispersed as monomers, whereas increasing the concentration, the molecules tend to aggregate until getting the critical micelle concentration (CMC) which is the concentration at which the micelles start to form. For the case of a hydrocarbon solvent, micelles are formed with the head group directed inward and the tail group outward with a continuous hydrocarbon phase. (Figure 4.7 – upper right side). Water is solubilized into the interior of this type of micelle. In contrast, when water is the solvent, the tail group is oriented inward and the head group is outward (Figure 4.7 – lower right side) to form micelles which allow that significant amounts of oil can be solubilized in their interior. This process in which micelles solubilize a phase which is not miscible with the solvent is called micro emulsion.

#### **4.9 MICROEMULSIONS**

Emulsions are colloids which are present in everyday life. Their high stability is both beneficial and challenging in for example the food industry, the production of detergents and in pesticide formulations [Sjöblom, 1996]. It is important to understand the stabilization of emulsions independent of whether they are desirable or undesirable for a process. In surfactant flooding the formation of microemulsions is essential. Water (brine) and crude oil are present as two immiscible phases together with surfactants. In microemulsions the emulsion phase is transparent, creates low IFT and a relatively low viscosity, all of which are crucial parameters in order to mobilize crude oil through the porous media.

#### **4.10 MICELLE FORMATION**

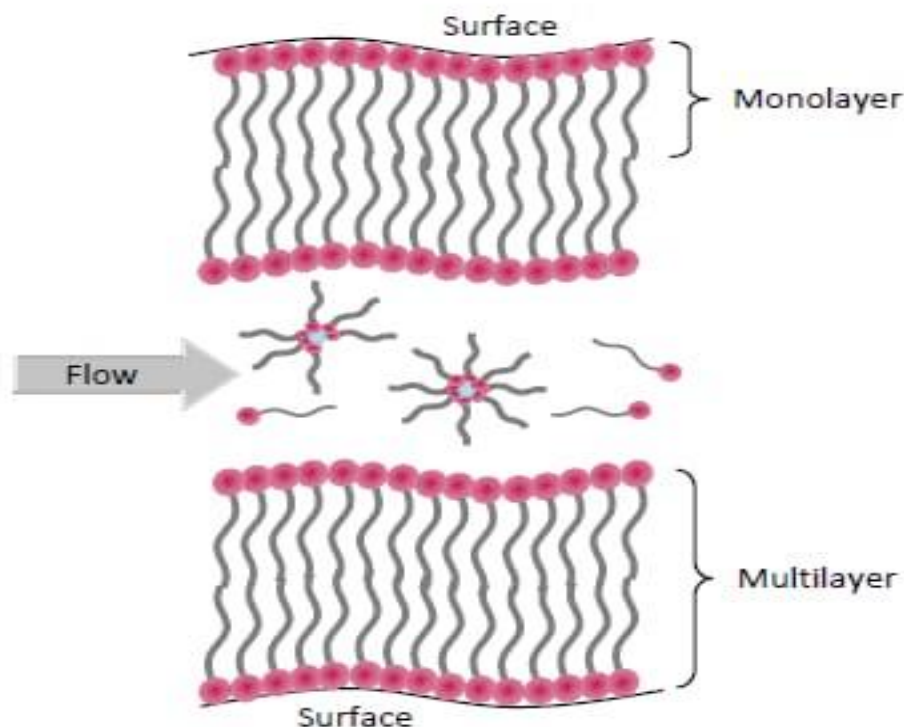
At low concentrations of the dissolved surfactants, molecules are dispersed as monomers. Then as the concentration is increased, (by repeated injections in EOR), the surfactant molecules starts to aggregate and above the critical micelle concentration, (CMC), any further addition of surfactants will form into micelles. The formation from surfactants to aggregates to micelles is illustrated in figure 4.7. When the CMC is reached the concentration of surfactant monomers remains at an approximately constant level, meaning that further addition of surfactant molecules will primarily entail increased formation of micelles, [Green & Willhite, 1998, pp.242].



**Figure 4.7. Micelle formation**

## 4.11 ADSORPTION

Adsorption takes place when surfactant aggregates and micelles form on the surfaces. The surfactant concentration must exceed the CMC value. However, a loss of surfactants will be experienced due to adsorption and retention in the porous media in the reservoir. It is known that the adsorption isotherm is rather dependent on the type of surfactant and cosurfactant, the characteristics of the rock and the type of electrolytes present in the solution [Curbelo et al., 2007]. Adsorption starts with aggregates which are formed at the surface (e.g. rock). A monolayer begins to form and when the equilibrium monolayer adsorption has been reached, the system will form an additional layer. Multilayer adsorption can cause significant surfactant losses, depicted in figure 4.8.



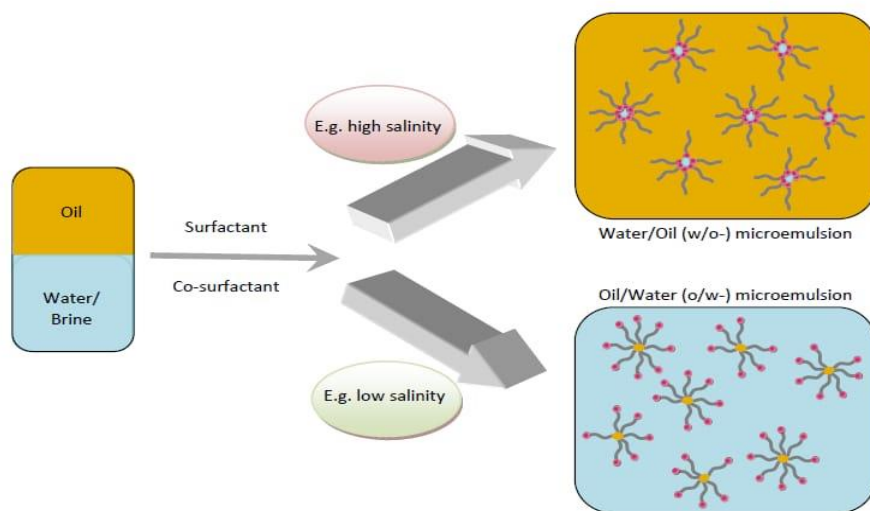
**Figure 4.8 Illustration of multilayer adsorption**

Initially the monolayer adsorption will take place until equilibration is reached. Subsequently the system will start forming an additional layer, thus forming multilayer adsorption. Curbelo et al. (2007) found that the adsorption decreases with the degree of ethoxylation. In their work higher adsorption losses were experienced with surfactant molecules of lower ethoxylation degree.

## 4.12 MICROEMULSION SYSTEMS

Systems with two immiscible phases, such as oil and water, that are made soluble by micelles, are known as microemulsion systems. In contrast to macroemulsions systems, microemulsion systems have much larger particles and are thermodynamically stable, [Green & Willhite, 1998, pp.244]. The mechanisms in microemulsion systems are, however, not well understood and investigations and discussions are ongoing in order to ascertain their precise nature. As oil consists of hydrocarbon molecules, which are nonpolar, they do not interact with the polar water molecules. When trying to mix water and oil it is possible to shake the mixture together to form a droplet emulsion, which will destabilize rather rapidly. Water and oil separate into two phases again, due to the high interfacial energy of the oil-water droplets. By addition of surfactants and co-surfactants the stability of these emulsions can be enhanced, as they reduce the interfacial energy. The addition of emulsifying agents, such as

surface active agents (surfactants), results in either an opaque stable emulsion or a clear microemulsion. The most stable thermodynamic state for an oil-water system is phase separation, which means that oil-water emulsions are only Flow Surface Surface Monolayer Multilayer metastable. In contrast, microemulsion systems may be thermodynamically stable as the interfacial energy tends to zero, [Pashley and Karaman, 2004, pp. 80-81]. Microemulsion systems can be designed, such that they create ultra low IFT values, at about 0.001 mN/m, with either aqueous or hydrocarbon phases, [Green & Willhite, 1998, pp. 245], which is a property that is beneficial to EOR processes. Formation of the low interfacial energy surface is the basis of the stability of all microemulsions and most oil water emulsions, [Pashley and Karaman, 2004, pp.79]. In surfactant systems, salinity should be taken carefully into account, as this has significant influence on the phase behavior of the system. At low salinities the surfactant mixture will preferentially act as water soluble, thus forming an oil/water microemulsion as shown in figure 4.9.



**Figure 4.9. Oil and brine mixed with surfactants and co-surfactants, forming microemulsions.**

An increase in the salinity will lead to different phase behavior as this will induce the surfactant system to form a three phase region at a lower critical endpoint. At the so called optimal salinity, the middle phase microemulsion solubilizes equal volumes of brine and oil. Finally the system will form a water/oil microemulsion at an upper critical endpoint as the surfactant becomes oil soluble when the salinity is high. [Raney and Miller, 1987]

Water/Brine ,Oil, Surfactant, Co-surfactant

E.g. high salinity

E.g. low salinity

Water/Oil (w/o-) microemulsion

Oil/Water (o/w-) microemulsion

## 4.13 PHASE BEHAVIOUR

The phase behavior of surfactant/oil/water mixtures is the single most critical factor determining the success of a chemical flood, [Skauge and Fotland, 1990]. The desired ultra low IFT in surfactant systems is usually measured by examining the phase behavior of the

microemulsion system, where the regions with high solubilization are located. The phase behavior is dependent on the type and concentration of surfactant, the concentration of the co-surfactants, hydrocarbons and brine. Other important parameters are the effect of high temperature and pressure on the microemulsion properties (at typical reservoir conditions). Predictive models, such as equations of state, cannot describe the phase behavior of surfactant systems adequately, due to the presence of both surfactants and salts, which are not included in the available prediction tools. Therefore phase behavior of a particular system has to be measured experimentally.

#### **4.14 EFFECT OF TEMPERATURE AND PRESSURE**

It is in general understood that temperature has an impact on several important parameters for EOR processes, such as the wettability, IFT, the viscosity of the oil and imbibition rates, as well as having a profound influence on the phase behavior of surfactant/oil/water systems. Skauge and Fotland (1990) showed that an increase in temperature results in an increase in the optimal salinity. On the other hand Gupta and Mohanty (2007) showed that for most of the surfactants they tested at higher temperatures, the optimal salinity decreased or remained unchanged. These contradictory examples illustrate the complexity of surfactant systems where the phase behavior will be both component and composition dependent.

Even though the effect of pressure on the phase behavior of microemulsions has been the subject of some studies, there is no clear opinion as to when pressure has a significant effect on the phase behavior or not. Skauge and Fotland (1990) reported that an increase in pressure caused a shift in phase behavior toward a lower phase microemulsion. For experiments on secondary alkane sulfonates, it was observed that an increase in pressure leads to an increase in the optimal salinity. Skauge and Fotland (1990) reported the pressure dependence to be correlated with optimal salinity. Sassen et al. (1989, 1991, 1992) has studied several water/oil/surfactant systems with the goal of experimentally determining the influence of pressure on their phase behavior and to develop a thermodynamic model that can describe this influence. Conclusions from that work are that pressure has a considerable influence on the phase behavior of water/oil/surfactant systems for both nonionic and anionic surfactant systems.

#### **4.15 PHASE EQUILIBRIUM**

In EOR by surfactant flooding the phase behavior and the phase equilibration between the displacing and the displaced fluids very likely will affect the recovery efficiency. Considering the phase behavior of surfactants systems, typically three types of systems are mentioned. They are depicted in figure 4.10. Winsor I systems are systems where the multiphase region has lower-phase microemulsion in equilibrium with excess of oil. The Winsor II systems are upper-phase microemulsions in equilibrium with excess of water or brine. Winsor III systems exhibit a middle phase microemulsion.

Figure 4.10. Ternary diagram types for surfactant/water/oil systems, [Salager et al., 1979]. Winsor type system; Winsor I is multiphase region with lower phase microemulsion in equilibrium with excess of oil, Winsor II, is the multiphase region with upper phase microemulsion in equilibrium with excess of water (or brine) and Winsor III, is the middle

phase microemulsion at which the lowest IFT is observed between oil and water. As showed, optimal salinity is at the Winsor III system, where low or high salinity entails lower or upper phase microemulsions, respectively.

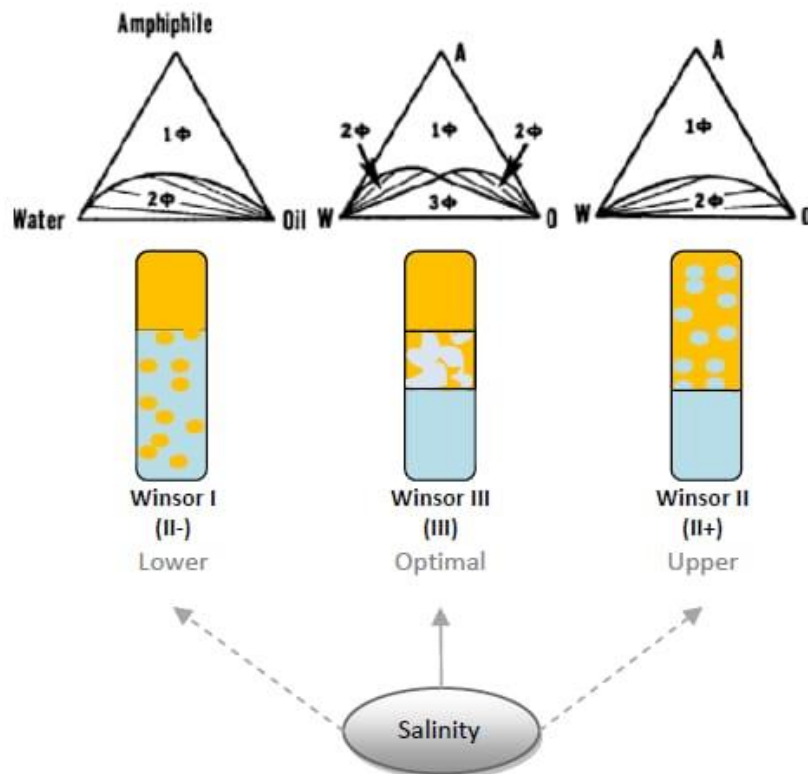


Figure 4.10 shows how a surfactant/water/oil system, in any of the three represented phase environments, can equilibrate as either a single phase or as multiple phases, depending on the overall composition. The Winsor I and II systems have the possibility of a maximum of two equilibrium phases. The Winsor III system has a maximum of three equilibrium phases, where this phase equilibrium system also contains both a type I node and type II node. Salinity.

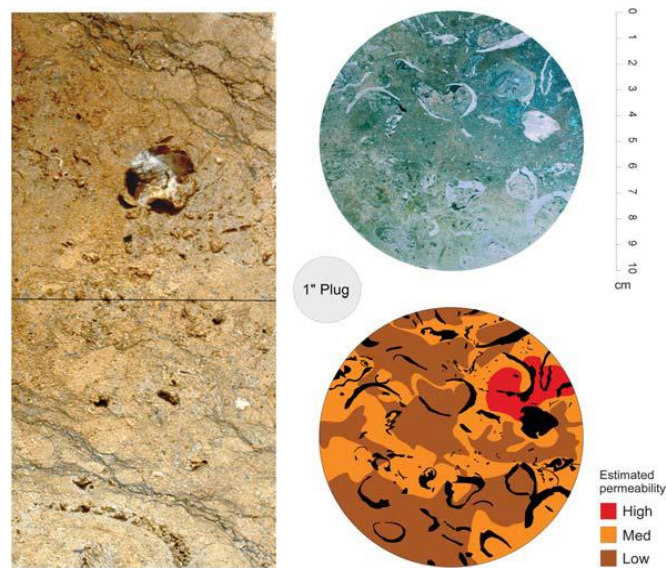
## **CHAPTER 5**

### **5.1 CARBONATE RESERVOIRS**

Carbonates are sedimentary rocks deposited in marine environments with clear, shallow, warm waters and are mostly of biological origin. They are made up by fragments of marine organisms, skeletons, coral, algae and precipitation, and consist mostly of calcium carbonate, which is chemically active compared to the sand which makes sandstones. Another key difference between clastic and carbonate rocks is the distance between the site where the sediment was created and where it was deposited. While sand and silt may travel hundreds of miles down river systems before deposition and lithification, the grains that comprise carbonate sediments are usually deposited very close to the place where they were created. This local deposition contributes significantly to the heterogeneity of carbonate grains. Once carbonate rock is formed, a range of chemical and physical processes begins to alter the rock structure changing fundamental characteristics such as porosity and permeability. This is known as diagenesis. At deposition, carbonate sediments often have very high porosities (35%–75%) but this decreases sharply as the sediment is altered and buried to reservoir depths. As a result, carbonate reservoirs exhibit large and abrupt variations in rock type distribution.

### **5.2 STRUCTURAL ASPECTS OF CARBONATE RESERVOIRS**

A characteristic, although not unique, feature of carbonate reservoirs is that fractures and stylolites are frequently perceived as playing a significant role in reservoir performance. For some of the reasons outlined below, both phenomena undoubtedly occur more commonly in carbonate reservoirs than they do in siliciclastic reservoirs. However, the dynamic impact of both in a carbonate reservoir context is commonly difficult to quantify. Moreover, as in all fractured reservoirs, where the well stock consists largely of vertical wells, dynamically important fractures and faults may not be sampled, increasing the uncertainty as to any fracture permeability component.



**Figure:5.1. A typical vuggy layer within a KharaiB (L. Cretaceous Thamama Group) reservoir from the UAE.**

### 5.2.1 ROCK TYPING

- Predict rock types and permeability in uncored wells
  - Better characterize the pore network and relationship between geological (facies/diagenesis) and petrophysical data
  - New reservoir rock typing workflows/approaches required
  - Effectively use old or low-quality data
  - Upscaling kh/kv – how to get from one rock type definition to reservoir models †
- Numerical models for permeability characterization of heterogeneous rock types

### 5.2.2 PERMEABILITY

- Prediction of reservoir quality in inter-well areas
- Understand processes of permeability improvement/reduction in carbonate rocks
- To determine best permeability values to assign to flow units in reservoir simulators
- To diagenetic processes and properties relate to permeability distribution within carbonate stratigraphic architectures
- Require information on carbonate reservoir body geometries in three dimensions
- and how these relate to stratigraphy

### 5.2.3 MICROPOROSITY

- Role of microporosity in flow and production?



- How to measure fluids in micropores and does the content change?
- Understand relationship between micro and macro pore network
- Require improved understanding of microporosity generation
- Need to determine quantitative relationship between microporosity and SCAL data, that is  $P_c$ ,  $K_r$ , etc.

#### **5.2.4 FRACTURES**

- Need to understand dynamic fracture behaviour in carbonates over time,
  - Distribution with respect to mechanical stratigraphy and rock types
  - Distribution of open fracture networks, microfractures and anisotropy
  - Fracture swarms at subseismic scale and fracture–matrix interactions
  - Understand the role of stylolites (particularly with respect to  $k_v$  or as conduits)
  - Recovery factors and production characteristics from fractured reservoir
- 
- **DOLOMITE**
  - Improve understanding of fault-linked and stratiform dolomite bodies, petrophysical properties and geometry in order to optimize field development
  - What is the lateral extent – how to constrain the dolomite 3D volume in reservoir models?
  - What are the dolomitizing fluid temperature characteristics?
  - What has been the impact on pre-dolomitization porosity distribution?
  - How does dolomitization relate to petroleum systems and hydrogeological control?
  - Need improved seismic detection of dolomite bodies

### **5.3 COMPLEX STRUCTURES**

The porosity of carbonate rocks can be grouped into three types: connected porosity, existing between the carbonate grains; vugs, which are unconnected pores resulting from the dissolution of calcite by water during diagenesis; and fracture porosity which is caused by stresses following deposition. Diagenesis can create stylolite structures which form horizontal flow barriers, sometimes extending over kilometers within the reservoir, having a dramatic effect on field performance. Fractures can be responsible for water breakthrough, gas coning and drilling problems such as heavy mud losses and stuck pipe. Together, these three forms of porosity create a very complex path for fluids and directly affect well productivity.

This heterogeneity also has an impact on the response of logging measurements and therefore on the determination of oil in place.

## 5.4 WETTABILITY AND ITS EFFECT ON FLUID FLOW

In addition to the variations in porosity, wettability is a further heterogeneous characteristic in carbonates. The great majority of sandstone reservoirs are strongly water-wet. However, the aging of carbonate rock containing water and oil turns initially water-wet rocks into mixed-wet or even oil-wet rocks. This means that oil can adhere to the surface of carbonate rock and it is therefore harder to produce. Most carbonate reservoirs are believed to have mixed wettability or to be oil-wet. Simulations show that in reservoirs under-going water flooding only limited amounts of oil can be recovered from oil-wet layers because the water tends to flow mainly through the water-wet layers. In fact, recovery factors can be less than 10%††. Characterizing the distribution of wettability and understanding its effects of on fluid flow within a complex reservoir is crucial in estimating the producible reserves and determining production strategies to maximize recovery.

## 5.5 CASE STUDY: Evaluating Carbonate Heterogeneity in Abu Dhabi

Local operations teams augment the contributionsof formal research efforts to understand carbonate rocks. Scientists and engineers in Abu Dhabi, UAE, have developed new techniques to evaluate heterogeneous carbonate reservoirs by integrating geological, openhole and production-log data. Characterization of the small-scale heterogeneities within reservoir rocks has led to a classification of 17 reservoir rock types (RRT) in the Shuaiba formation. Reservoir rock types are based on lithofacies, wireline log data, core porosity and permeability, capillary pressure and pore-size distributions derived from mercury-injection analyses, and production data.29 RRTs can be used to better correlate zones within reservoirs in the absence of cores. An oil field in Abu Dhabi has been producing from the Lower Cretaceous Shuaiba formation since 1962. Within the field, the Shuaiba formation varies from shallow-water shelf to deepwater slope sediments, with four distinct reservoir facies. RRTs range from nonproductive rocks to those with up to 30% porosity and 20-Darcy permeability.



**RRT 7**



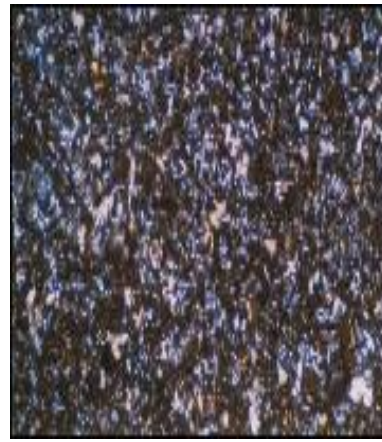
**RRT 8**



**RRT 9**



**RRT 14**



**RRT 15**

**Figure 5.2 Shuaiba heterogeneity. RRTs range from rudists—extinct mollusks similar to oysters—in lime mud (top left) to mixed rudists in a grainy matrix (top center) to diagenetically altered, debris-filled rudstone (top right). A pencil or fingertip in each photograph indicates the scale. RRTs from the northern part of the field comprise rudstone (bottom left photomicrograph) and fine-grained packstone or packstone (bottom right). The field of view of the photomicrographs is 4 mm by 6 mm.**

RRTs range from rudists—extinct mollusks similar to oysters—in lime mud (top left) to mixed rudists in a grainy matrix (top center) to diagenetically altered, debris-filled rudstone (top right). A pencil or fingertip in each photograph indicates the scale. RRTs from the northern part of the field comprise rudstone ( bottom left photomicrograph) and fine-grained packstone or packstone (bottom right). The field of view of the photomicrographs is 4 mm by 6 mm. These significant heterogeneities must be considered when planning well trajectories, well completions and production strategies.

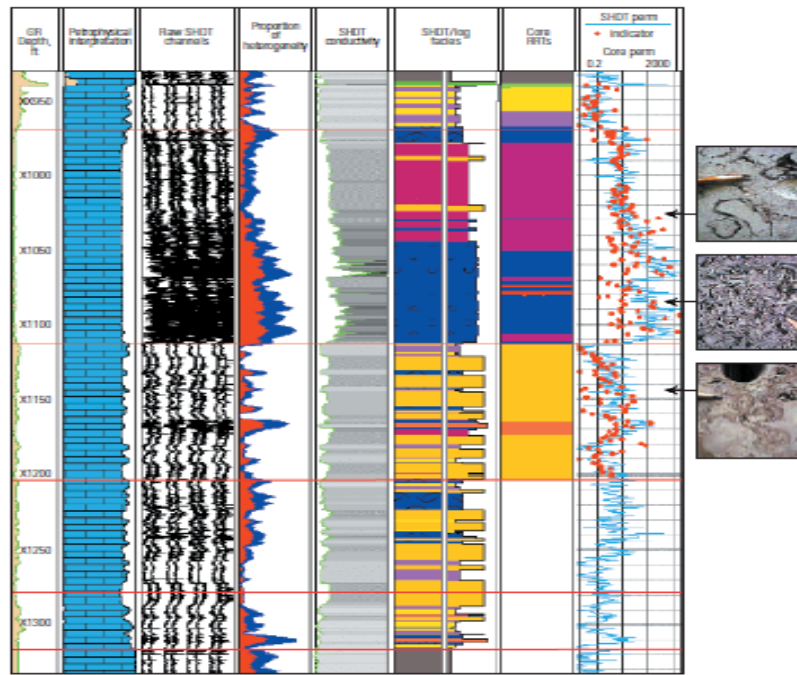


Figure 5.3 Shuaiba RRTs and permeability indicator derived from core and log data. Photographs (far right) in this composite plot from a well in a field in Abu Dhabi show the heterogeneity of three of the distinct RRTs. Permeability characterized by analysis of Stratigraphic High-Resolution Dipmeter Tool (SHDT) data (Track 8) shows close agreement with log and core data.

RRTs are defined on the basis of reservoir quality, distribution and productivity, but are products of their depositional environment and diagenetic history. RRTs observed in cores and logs from two wells in the field have been correlated with logs in uncored wells; this correlation allows more accurate permeability estimation in those wells than with use of log data alone. The RRT study contributes significantly to the field development because the operator, Abu Dhabi Company for Onshore Oil Operations (ADCO), can use realistic permeability estimates and upgraded 3D geological models to optimize field drainage, thereby maintaining and prolonging production. One innovative RRT characterization method relies on careful integration of conventional well logs, such as gamma ray, neutron and density, with high-resolution dipmeter and image logs. Heterogeneities in the form of conductivity variations are quantified using specialized software, including BorTex and RockCell applications, to identify RRTs and generate permeability indicators. In extremely heterogeneous carbonates, permeability derived using this methodology resolves heterogeneity better than 1-in. core plugs or minipermeameter data. The higher resolution and increased borehole coverage of imaging devices provide more accurate differentiation of RRTs than dipmeter logs alone and facilitate identification of flow paths between vugs and large pores. Because dipmeter and image logs are more widely available than core, RRT analysis is a powerful tool for evaluating wells that lack core samples. Another successful technique to evaluate porosity in the Shuaiba formation uses borehole images to map primary and secondary porosity.

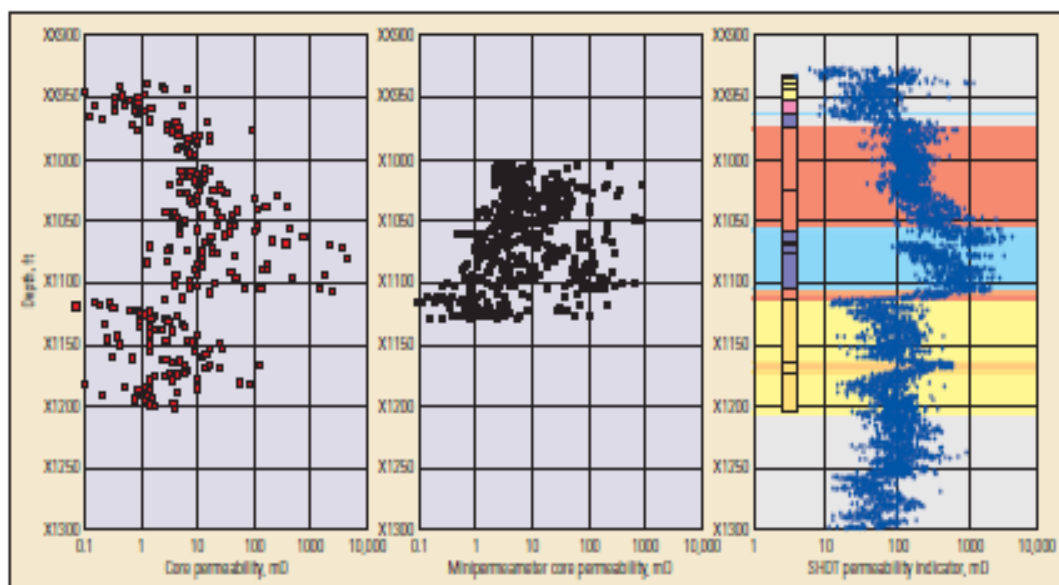


Figure 5.4 Integrated permeability data. Core plugs from 246 one-foot intervals (left) and 586 minipermeameter measurements at 2- to 3-in. intervals (center) from a well in Abu Dhabi show significant scatter because of the extreme small-scale heterogeneity. On the other hand, the SHDT-derived permeability indicator (right) shows a clear trend that closely correlates with RRTs found in cores. Each color in the cored interval represents a distinct RRT of the Shuaiba formation.

## CHAPTER 6

### 6.1 WETTABILITY ALTERATION DURING LOW-SALINITY WATER FLOODING IN CARBONATE RESERVOIR

In carbonate formations, the carbonate rock surface attains a positive charge in presence of formation brine. The positive charge results from carbonate dissolution in brine, which also increases the solution pH (Navratil 2012). In presence of oil, the brine-soluble acidic components of the oil (carboxylate ions,  $R-COO^-$ ) are attracted to the positively charged carbonate rock surface. Some of these acidic oil molecules attach to the positively charged carbonate surface, which makes the surface oil-wet. This is why restoring core wettability is critical factor in any IOR/EOR experiments.

In presence of brine, the positively charged carbonate surface is amenable to anion exchange, which might be the reason for wettability alteration by the seawater in seawater flooding. In

the latter, the sulfate, calcium and magnesium ions ( $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) compete with the carboxylate ( $\text{R-COO}^-$ ) ions to partially alter the rock wettability from oil wet to water wet. Wettability alteration is a complex issue which, in addition to the brine ionic composition, also depends on reservoir temperature. Austad et al. conducted experiments using cores from Ekofisk, Valhall, and Yates fields to improve spontaneous imbibition of water into oil-saturated samples. They observed that the presence of  $\text{SO}_4^{2-}$  improved the spontaneous imbibition regardless of the wetting conditions. Furthermore, studies on low-salinity waterflooding in carbonate reservoirs, with reduced  $\text{Na}^+$ , indicate that  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$  play a major role in the wettability alteration.

## **6.2 WETTABILITY ALTERATION IN FRACTURED CARBONATE RESERVOIR**

Many of carbonate reservoirs are fractured and oil-wet in nature. Enhanced oil recovery field experience in carbonate reservoirs have been reviewed by Manrique. Very few processes work for fractured oil-wet carbonates and many of them have to rely on gravity drainage if the formation is highly fractured. Miscible gas injection, steam injection, and chemical treatment, have been considered to recover oil from highly fractured oil-wet carbonate reservoirs. For example, Christiansan discusses gravity drainage with  $\text{CO}_2$  gas flooding in Yates field. Reduction in oil-gas interfacial tension (IFT) decreases capillary pressure and gravity pushes the oil down. Oil-phase swelling and viscosity reduction also help in improving oil recovery. Shahin et al. studied thermal assisted gas oil gravity drainage for Qurn Alam fractured carbonate reservoir in Oman. Al-Hadhrami et al.<sup>6</sup> have discussed steam injection in fractured carbonates. High temperature can induce wettability alteration, steam can vaporize the light ends, and gravity can drain the oil down. In both the above methods, oil remains the wetting phase with respect to the draining vapor phase which slows the drainage rate. This work looks into the chemical treatment for fractured oil-wet carbonate reservoirs.

Chemical treatment for wettability alteration is one of the techniques to recover oil from such reservoir.<sup>7-14</sup> Work has been done with cationic,<sup>9-11</sup> anionic,<sup>7,8,12,14</sup> and nonionic<sup>13,14</sup> surfactants and just electrolytes<sup>15</sup> to alter wettability of originally oil-wet carbonate rocks. Austad and co-workers<sup>9-11</sup> have shown that cationic surfactants can recover oil from chalk cores by spontaneous counter-current imbibition due to wettability alteration. Tweheyo et al.<sup>15</sup> studied the effect of divalent ions on wettability alteration of carbonates. They found that  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions can change the wettability at 100°C and above without any surfactants in the system. The extent of wettability alteration increases with the increase in temperature. Adibhatla et al.<sup>8</sup> and Gupta et al.<sup>14</sup> have shown that dilute anionic and non-ionic surfactant (concentration <0.1 wt %) solutions can give oil recovery as high as 60 % OOIP from oil-wet carbonate cores. This process is a gravity driven process. The surfactant molecules diffuse/flow from fractures into the matrix and change wettability and IFT. The reduction in IFT decreases the entry capillary pressure. Gravitational forces overcome the entry capillary pressure and water invades the matrix and pushes the oil from the top. The key to recovering oil is the wettability alteration to preferentially water-wet intermediate-wet conditions.

Oil is formed in source rocks and migrates to originally water-wet reservoirs. The polar components of oil collect at the oil-water interface<sup>16</sup> and adsorb on the solid surface if the

water film becomes unstable. Hirasaki,<sup>17</sup> Mohanty et al.<sup>18</sup> and Menezee et al.<sup>19</sup> studied the effect of surface forces on thickness and stability of wetting films and thus on the contact angles. The film thickness depends on the applied capillary pressure and the disjoining pressure, which in turn depends in brine, oil, and mineral compositions. Buckley et al.<sup>20</sup> showed that interactions between polar oil components and solid, surface precipitation of asphaltene type molecules from oil, acid/base and ion binding between ion sites on solid/brine and oil/brine or a combination of them could be responsible for wetting of mineral surfaces by a crude oil. Hamouda et al.<sup>21</sup> worked with a system of n-decane/fatty acid/water on calcite plates at elevated temperature. He showed that the wettability (contact angle) follows the same trend as partition coefficient of fatty acid and IFT which in turn depends on pH and thus on zeta potential of calcite.

### **6.2.1 SURFACTANT FLOODING IN CARBONATE RESERVOIR**

Flooding with cationic surfactants in carbonate reservoir is quite attractive because they bear the same charge as the surface of the carbonate minerals. Austad and coworkers have conducted a series of studies<sup>13-16</sup> on oil recovery from oil-wet chalk cores by use of surfactant solutions. They have shown that cationic surfactants, such as Dodecyl Trimethyl Ammonium Bromide (DTAB), are quite effective (recovery ~70% OOIP) in imbibing water into originally oil-wet cores at concentrations higher than their CMC (~1 wt%).

### **6.2.2 IMBIBITION MECHANISM**

The imbibition mechanism is proposed as:

- (i) The formation of ion-pairs by the interaction between surfactant monomers and adsorbed organic carboxylates from the crude oil,
- (ii) water-wettability of the solid surface due to dissolution of the ion-pairs in the oil phase and micelles,
- (iii) counter-current imbibition of brine due to capillary pressure.

The imbibition rate increases with temperature and decreases with a connate water saturation. The interfacial tension between the surfactant solution and oil were high ( $> 0.1$  mN/m). They found that most of the anionic surfactants tested were not able to desorb adsorbed organic carboxylates. Ethoxylated sulfonates have the ability to displace oil by a spontaneous imbibition of brine. A propo ethoxy sulfate surfactant displaced oil when the buoyancy force exceeded the capillary force caused by low interfacial tension ( $\sim 0.08$  mN/m). But the recovery with the anionic surfactants was slow compared to those with the cationic surfactants. The air-water contact angle on the surfactant adsorbed calcite surface showed low angles ( $12^\circ$ - $28^\circ$ ) for the cationic surfactants, but higher angles ( $39^\circ$ - $63^\circ$ ) for the anionic surfactants. Water-oil contact angles were not measured for these surfactants.

In 2003, Austad and coworkers<sup>17-19</sup> identified several cheap commercial cationic surfactants, C10NH<sub>2</sub> and bioderivatives from the coconut palm termed Arquad and Dodigen (priced at 3 US\$ per kg), which were able to recover 50-90% of oil. The higher cost and the needed concentration (about 1 wt%) of cationic surfactants necessitates evaluating other surfactants.



Chen et al.<sup>20</sup> have performed dilute (~0.35 wt%) surfactant imbibition tests for carbonate cores from the Yates field with a nonionic surfactant and an anionic surfactant. Computerized Tomography (CT) scans indicated that enhanced imbibition is possible due to counter-current flow at the beginning and gravity-driven<sup>21</sup> flow during the later stages. Spinler et al.<sup>22</sup> conducted spontaneous imbibition and adsorption tests with a surfactant which was an ammonium salt of ethoxylated and sulfated alcohols at very low concentrations (~0.05 wt%) and high reservoir temperature (~131 °C). It was found to be effective in improving imbibition in North Sea chalk cores and adsorption was low. Hirasaki and Zhang<sup>23</sup> have evaluated several ethoxylated and propoxylated sulfates in the presence of a low concentration alkali (~0.3 M Na<sub>2</sub>CO<sub>3</sub>). They found that interfacial tension (IFT) can be lowered to ultralow levels (~10<sup>-3</sup> mN/m), wettability can be changed to intermediate wettability, and imbibition can be improved by >35% OOIP by use of very dilute anionic surfactant/alkali solutions.

The key issues for anionic surfactant flooding of fractured carbonates are to achieve wettability alteration and/or IFT reduction at low surfactant concentration, low adsorption of surfactant and mobility control. , we have addressed the first three issues: wettability, IFT and adsorption, for several anionic surfactants

### **6.3 EXPERIMENTAL PROCEDURE:**

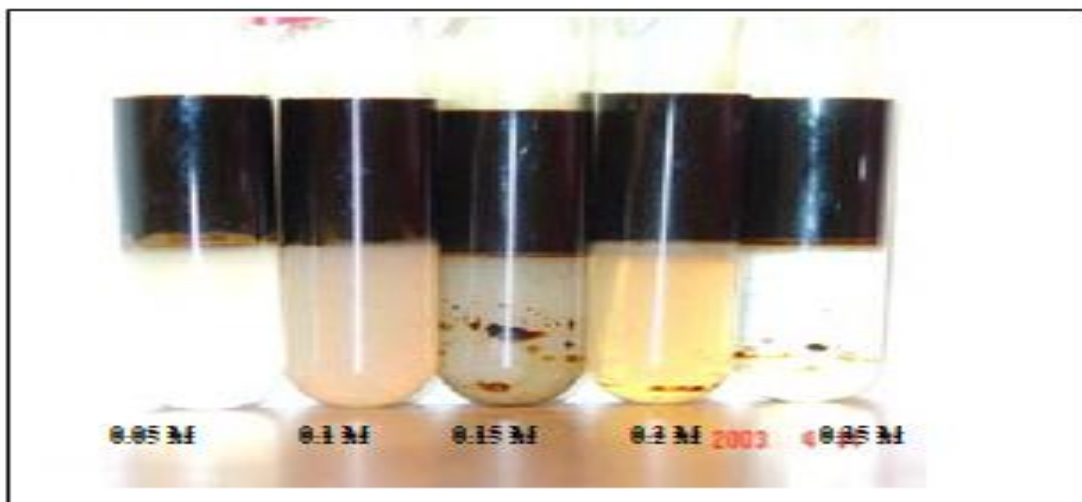
The following experiments were conducted for evaluation of the surfactants: phase behavior study, interfacial tension measurement, wettability test, and adsorption.

#### **6.3.1 PHASE BEHAVIOUR STUDY:**

Dilute solutions of anionic surfactants (0.05 active wt%) were prepared with varying concentrations of sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>). These solutions were equilibrated with equal volumes of oil on a tube shaker for a period of two days. Thereafter the tubes were removed and left to settle for a day. The number of phases and the color of the phases were observed, which indicated the shift from Winsor type II- to type II+ phase behavior with the increase in salinity of the solution.

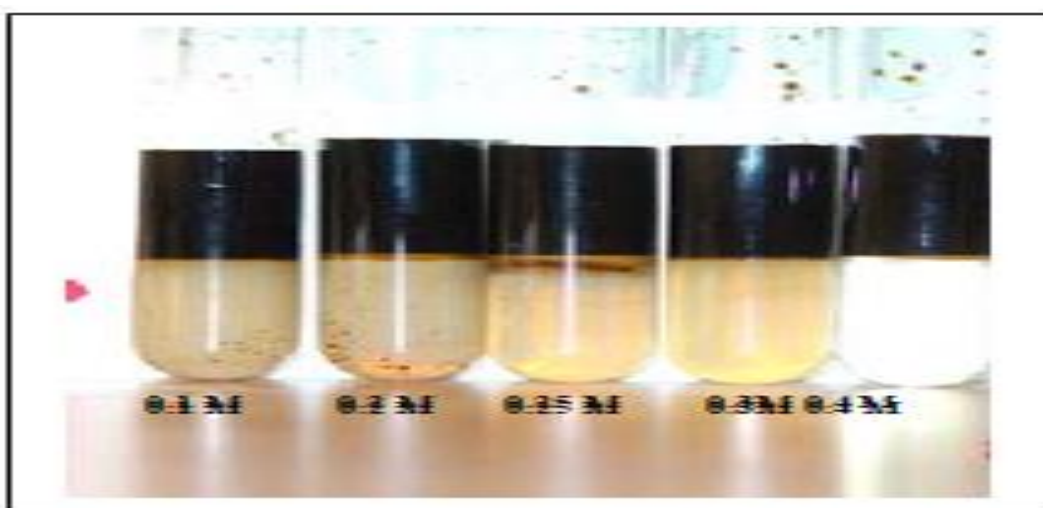
Figure 6.1 (a) shows the phase behavior of crude oil - brine (Na CO ) - surfactant system for three typical cases. Water-oil ratio is kept at 1:1 in all cases shown. Figure 6. 1(a) shows the phase behavior without addition of any synthetic surfactant, i.e., crude oil - Na<sub>2</sub>CO<sub>3</sub> brine. The number underneath each test tube specifies the Na<sub>2</sub>CO<sub>3</sub> concentration in the brine. Two phases (aqueous and oleic) are seen in this case. As the alkali concentration increases, the bottom (aqueous) phase first becomes darker and then clarifies beyond an alkali concentration of 0.15 M. Na<sub>2</sub>CO<sub>3</sub> reacts with some of the naphthenic acid molecules in the crude oil to make in situ surfactants. Some of these surfactants solubilize in the brine and make micelles. These micelles can solubilize some oil into the aqueous phase giving it a darker colour. As Na<sub>2</sub>CO<sub>3</sub> in brine increases, the solubility of the surfactants in brine decreases (because of high salinity); the surfactants partition back to the oleic phase. Thus the aqueous phase clarifies above a certain Na<sub>2</sub>CO<sub>3</sub> concentration.





**Figure: 6.1(a) Phase behavior for varying concentration of  $\text{Na}_2\text{CO}_3$  with no surfactant at  $\text{WOR}=1$**

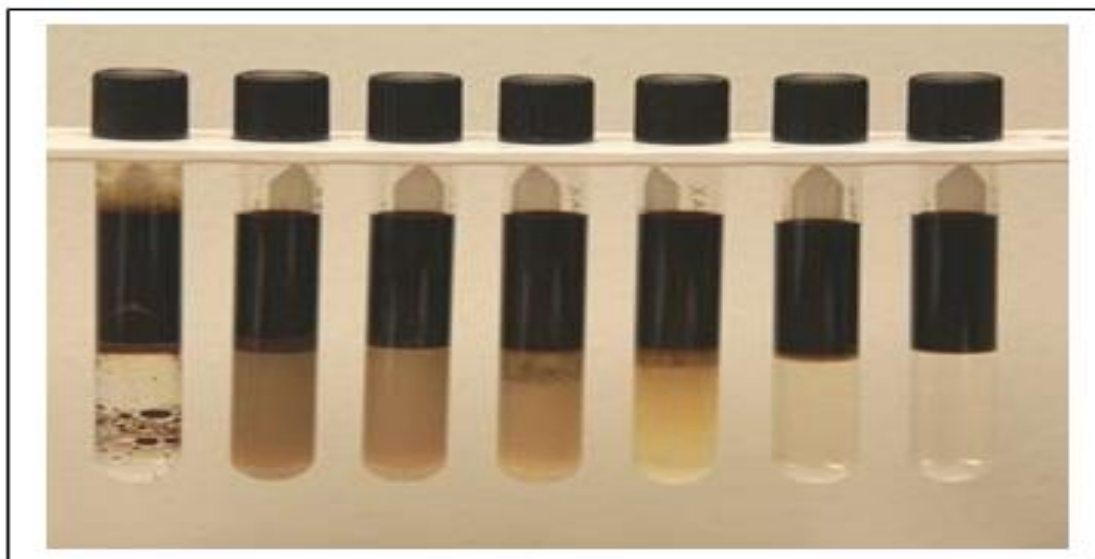
Fig. 6.1(b) shows the phase behavior typical of sulphonate surfactants studied. The concentration of the surfactant 5-166 is kept constant at 0.05 wt% and the  $\text{Na}_2\text{CO}_3$  concentration is increased from 0 to 0.6 M. As the caustic concentration increases, the darkness of the aqueous phase increases, reaches a maximum and then decreases. In this case, the aqueous phase is observed to be the darkest at a  $\text{Na}_2\text{CO}_3$  concentration of 0.2 M. An optimal salinity is defined in the next section on the basis of the lowest water-oil interfacial tension; 0.2 M salinity is close to the optimal. A small, middle phase microemulsion is also observed in the near-optimal region. Since we are operating at a very dilute surfactant concentration (0.05 wt%) the middle-phase microemulsion layer formed is very thin, too small for any analysis. The aqueous phase becomes clear at the  $\text{Na}_2\text{CO}_3$  concentration of 0.4 M indicating Winsor type II+ microemulsion. At this point, the system is in the over-optimum salinity regime.



**Figure: 6.1(b) Phase behavior for 0.05wt% 5-166 surfactant with varying concentration of  $\text{Na}_2\text{CO}_3$  at  $\text{WOR}=1$**

Figure 6.1(c) shows the phase behavior typical of propoxylated sulfate surfactants. The concentration of the surfactant Alforterra-38 is kept constant at 0.05 wt% and the  $\text{Na}_2\text{CO}_3$  concentration is increased from 0 to 0.5 M. Again, as the alkali concentration increases, the

darkness of the aqueous phase increases, reaches a maximum and then decreases. The third phase is more distinct in this case at  $\text{Na}_2\text{CO}_3$  concentrations of 0.25M and 0.3 M.



**Figure: 6.1(c) case behavior for 0.05wt% Alfoterra-38 surfactant with varying concentration of  $\text{Na}_2\text{CO}_3$  at WOR =1**

### **6.3.2 INTERFACIAL TENSION MEASUREMENT**

The IFT between the equilibrated brine and oil phases was measured with help of a spinning drop tensiometer. The equilibrated brine solutions and the equilibrated oil from the phase behavior study were used to determine the interfacial tension between the synthetic brine and oil. This led to the identification of the region of lowest interfacial tension or optimum salinity of the given system. The subsequent wettability experiments were performed at the optimum salinity obtained from these measurements.

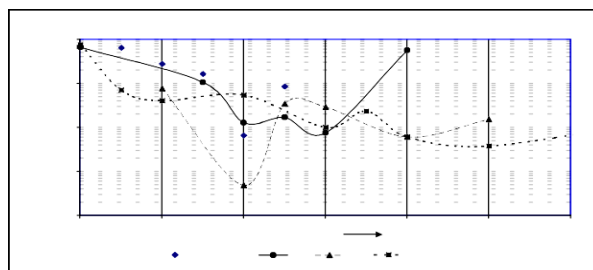
The IFT of the crude oil - brine ( $\text{Na}_2\text{CO}_3$ ) system is shown in Fig. 6.2(a). As the caustic concentration increases, the IFT decreases to slightly below 10-1 mN/m at 0.2 M and then increases. The presence of the in situ surfactants in the aqueous phase is responsible for the decrease in IFT

### Surfactant properties

Trade name	Source	Structural name	Active %	Molecular Wt.	cmc(g/l)
<b>Sulphonates</b>					
4-22	Oil Chem	Alkyl aryl ethoxylated sulphonated phenol	50%	-	0.001
5-166	Oil Chem	Alkyl aryl sulphonate	50%	-	0.001
SS-6566	Oil Chem	Alkyl aryl ethoxylated sulphonate	50%	-	0.002
<b>Propoxylated sulfates, sodium salt</b>					
Alfoterra-33	Sasol	Propoxylated sulfates -3PO	28.1%	485	0.01
Alfoterra-35	Sasol	Propoxylated sulfates -5PO	28.0%	588	0.006
Alfoterra-38	Sasol	Propoxylated sulfates -8PO	26.0%	715	0.005
Alfoterra-63	Sasol	Propoxylated sulfates -3PO	30.0%	467	0.025
Alfoterra-65	Sasol	Propoxylated sulfates- 5PO	31.6%	561	0.018

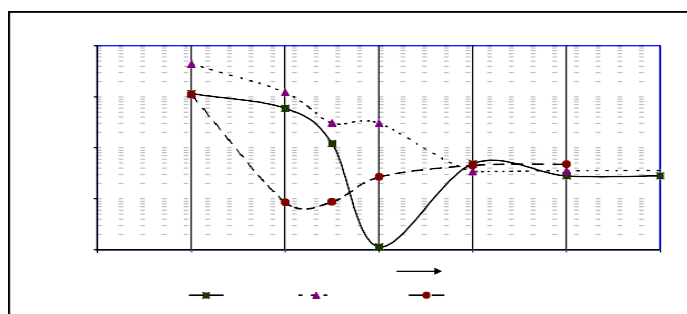
Figure 6.2 (a) shows the interfacial tension (IFT) between the aqueous and the oleic phases as a function of  $\text{Na}_2\text{CO}_3$  concentration in these crude oil - brine ( $\text{Na}_2\text{CO}_3$ ) - surfactant systems. Water-oil ratio is again kept at 1:1 in all cases shown. The anionic surfactant concentration is also kept constant at 0.05 wt% in Fig. 2 (a-c) except for the case with no surfactant.

The IFT of the crude oil - brine ( $\text{Na}_2\text{CO}_3$ ) system is shown in Figure 6.2(a). As the caustic concentration increases, the IFT decreases to slightly below 10-1 mN/m at 0.2 M and then increases. The presence of the in situ surfactants in the aqueous phase is responsible for the decrease in IFT. Optimal salinity is defined as the salinity at the minimum IFT, i.e., 0.2 M in this case. Fig. 6.2(a) also shows IFTs in crude oil - brine - surfactant systems with 0.05 wt% sulphonate surfactants. The ethoxylated sulphonates 4-22 and SS-6566 could lower the IFT of the system to about 10-2 mN/m. However, amongst the obtained with surfactant 5-166, an alkyl aryl sulphonate. The lowest IFT samples corresponded to those with middle phases. Optimal salinity is about 0.2 M  $\text{Na}_2\text{CO}_3$ . IFTs of the order of 10-2 mN/m and lower are capable of mobilizing oil by buoyancy.



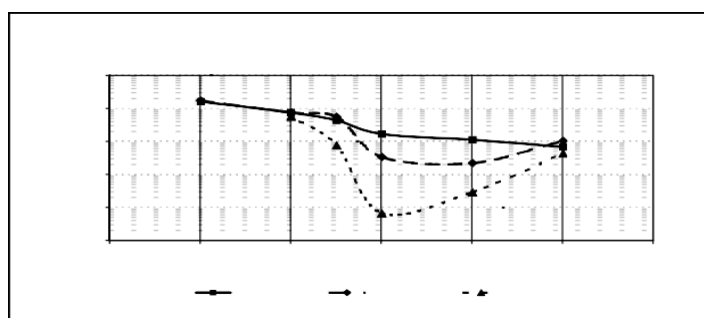
**Figure: 6.2(a) IFT of crude oil with 0.05 wt% sulfonate surfactants and with  $\text{Na}_2\text{CO}_3$  alone**

Fig. 6. 2(b) shows the IFTs for the Alfoterra-3n series of propoxylated sulfate surfactants. The overall trend was similar to that of the other surfactants, i.e., the IFT decreased with increasing  $\text{Na}_2\text{CO}_3$  concentration before reaching a minimum and then increased. The optimal salinity changed from 0.2 to 0.3 M  $\text{Na}_2\text{CO}_3$  for the three surfactants. The minimum IFT was  $10^{-3}$  mN/m for Alfoterra-33,  $3 \times 10^{-2}$  mN/m for Alfoterra- 35, and  $9 \times 10^{-3}$  mN/m for Alfoterra-38. The IFT did not change monotonically with the number of propoxy groups in this series of experiments.



**Figure: 6.2(b) IFT of crude oil with 0.05 wt% Alfoterra-3n series of surfactants**

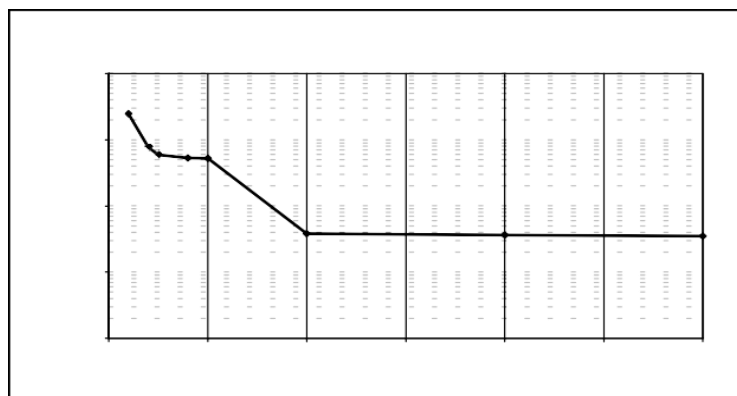
Fig. 6.2(c) shows the IFTs for the Alfoterra-6n series of propoxylated sulfate surfactants. Hydrocarbon chain length is smaller for this series of Alfoterra than the Alfoterra-3n series. The optimal salinity changed from 0.3 to 0.5 M  $\text{Na}_2\text{CO}_3$  for the three surfactants. The minimum IFT was  $10^{-1}$  mN/m for Alfoterra-63,  $2 \times 10^{-2}$  mN/m for Alfoterra-65, and  $7 \times 10^{-4}$  mN/m for Alfoterra-68. The IFT decreased monotonically with the number of propoxy groups in this series of experiments.



**Figure: 6.2(c) IFT of crude oil with 0.05 wt% Alfoterra-6n series of surfactants**

The IFT measurements for the cationic surfactant, DTAB were carried out for varying surfactant concentrations in the field brine at a water-oil ratio of 1:1. The IFT, shown in Fig. 2(d), decreases with the increase of surfactant concentration, but reaches a plateau of about  $4 \times 10^{-2}$  mN/m at a surfactant concentration of 2 wt%. At 1 wt% DTAB (a typical value used by Austad and co-workers), IFT is about 0.5 mN/m. Thus low interfacial tension is not the mechanism for high spontaneous imbibition with 1 wt% DTAB solutions.<sup>15</sup> Among all the surfactants studied here, low IFT ( $< 10$  nN/m) was obtained with surfactants 5-166,

Alfoterra- 33 and Alfoterra-38 and Alfoterra-68. Very low tensions can be generated with anionic surfactants, but not with cationic surfactants, below a concentration of 1 wt%.



**Figure: 6.2(d). IFT of crude oil with DTAB at varying surfactant concentration**

### 6.3.3 WETTABILITY TEST

The wettability tests were done on mineral plates (2 cm x 1 cm x 0.2 cm). The plates were polished on a 600 mesh diamond lap and equilibrated with synthetic brine for a day. The initial wettability state of the plate was determined by measuring the advancing and recently receded contact angle of oil with the plate immersed in brine. The plate was removed from brine and aged with oil at an elevated temperature ( $\sim 80^{\circ}\text{C}$ ) in the oven for about two days to make it oil-wet. The reservoir temperature is close to the room temperature ( $\sim 30^{\circ}\text{C}$ ), but the elevated temperature aging is done to compensate for the short aging time (compared with the geological time). After removing (with oil stuck around it) was contacted with synthetic (sodium carbonate) brine for an hour and the advancing contact angle was measured. The contact angle measurements were made with the help of a Kruss goniometer. Thereafter, the synthetic brine was replaced by the surfactant-brine solution and the evolution of contact angle was studied for a period of two days by imaging the drops attached to the plate. In the cases where the drops were too small ( $< 0.1\text{ mm}$ ), it was difficult to measure an accurate contact angle and a post-wettability test was performed. In the post-wettability test, the plate was washed with brine following the surfactant treatment. This plate was then placed in the brine solution and an oil drop was deposited on the bottom of the surface with the help of an inverted needle (oil drops did not attach to the top of the plate in these cases). The contact angle was then measured. This gave the final wettability state of the plate. Drops were deposited on several parts of the plate and the range of the contact angles was noted. For the cationic surfactant, a similar procedure was followed except that the reformulated field brine replaced the synthetic brine.

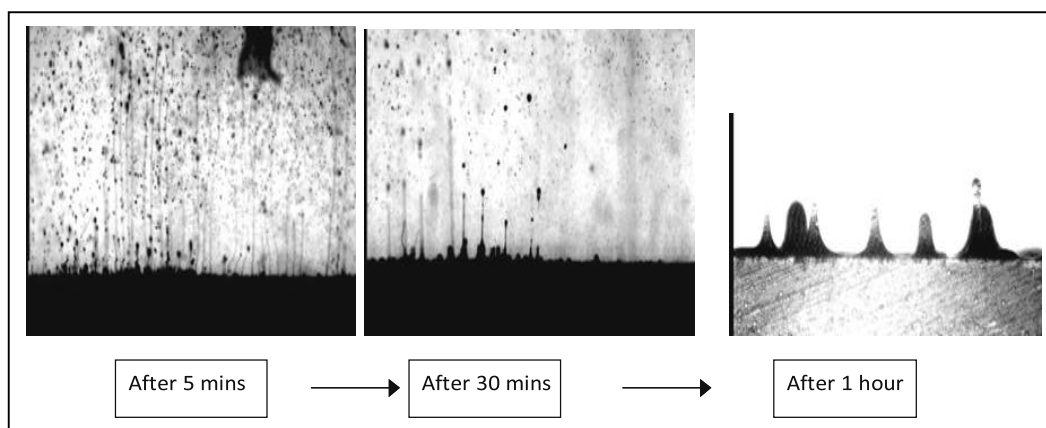
Wettability was evaluated by measuring water- oil contact angles. All the contact angle measurements for the anionic surfactants were made at a surfactant concentration of 0.05 active wt%, at the optimum salinity obtained from the IFT experiments. Fig. 3 shows the contact angles measured at different stages of the wettability experiment for the calcite plate with surfactant SS-6566. 0.3 M  $\text{Na}_2\text{CO}_3$  solution brine was used. Before aging with oil, the mineral plate is found to be intermediate-wet with advancing contact angle greater than  $90^{\circ}$

and receding contact angle less than  $90^\circ$  (the first two points in Fig. 3). After aging the calcite plate with the crude oil at an elevated temperature for 44 hrs, the mineral plate becomes completely oil-wet with an advancing contact angle close to  $160^\circ$  (the 3rd, 4th and 5th points in Fig. 6. 3). The oil-aged plate is immersed in brine and the oil-water contact line on the calcite plate is photographed to obtain this data. The brine is then replaced with a surfactant solution at its optimal salinity. When exposed to the surfactant - brine solution, (much of the oil is released from the plate) the advancing contact angle decreases with time and stabilizes at a value of about  $58^\circ$ - $88^\circ$  depending on the drop size (the last four points in Fig. 6.3).

Wettability tests for the DTAB were conducted with the field brine at 1 and 0.5 wt%. Fig. 7 shows the calcite plate after 48 hours of contact with 1 wt% surfactant. Oil drops attached are bigger than those seen with the Alfoterra surfactants; this is a result of higher IFT. The contact angles of these oil drops are between  $70^\circ$ - $100^\circ$ . For the 0.5 wt% surfactant solution, the contact angles were about  $140^\circ$  (photo not shown). Thus DTAB does not change the wettability, if the concentration is small. At about 1 wt%, wettability changes to intermediate to water-wet.

Fig. 6.4 shows the contact angle at the end of wettability tests (including the post wettability-tests for Alfoterra 35, 38, 63, 65, 68) for all the surfactants studied. Amongst the sulfonates, SS-6566 altered the wettability of the oil-wet carbonate surface to moderately water-wet state. Amongst the propoxylated sulfates, Alfoterra-38 changed the wettability to a near water-wet state. Except for Alfoterra-33, all other propoxylated sulphates resulted in intermediate / water- wet wettability. DTAB at 1 wt% also changed the wettability to intermediate / water- wet state. Lower concentrations of DTAB were not effective in changing wettability. Effect of different carbonate surfaces on wettability alteration was studied with only one anionic surfactant 4-22 (0.05 wt% active). The four different surfaces studied were lithographic limestone, calcite, marble and dolomite. The initial state of all the mineral surfaces except for the limestone, determined after aging the surfaces in synthetic brine, was found to be intermediate-wet. Lithographic limestone was found to be oil-wet. After aging the surfaces at elevated temperature in crude oil for two days all the surfaces exhibited close to oil-wet state. When contacted with the anionic surfactant 4-22, significant amount of oil was seen leaving the surface possibly due to lowered interfacial tension.

**Figure: 6.4 Images of oil drop after the oil-wet calcite plate was contacted with 0.05 wt% 5-166 surfactant solution during the wettability experiment – 5-166 is an example**

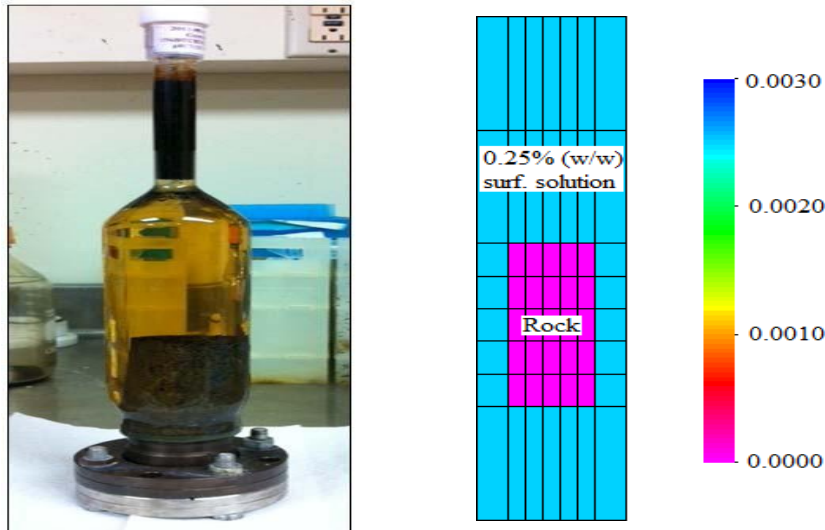


**of a low IFT producing surfactant**

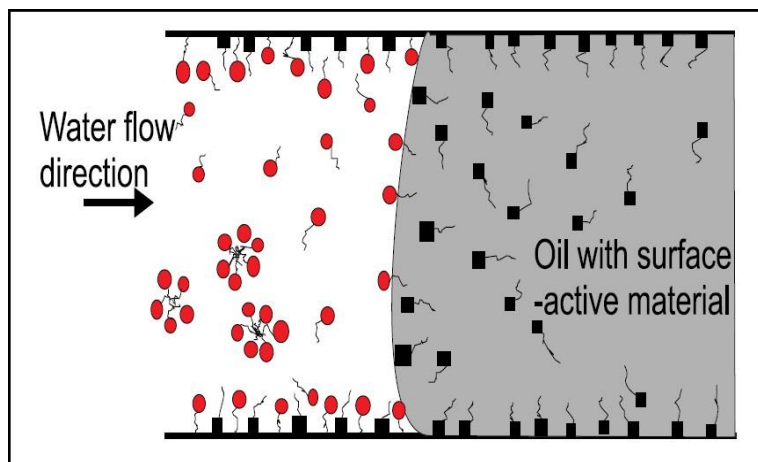


### 6.3.4 SPONTANEOUS IMBIBITION

Cores listed in Table 2 were used for imbibition experiments. Brine saturated cores were injected with 5 pore volumes (PV) of field oil to reach residual water saturation. The oil saturated cores were aged for 60 days at 80°C to make them oil-wet. The aged cores were immersed in a 0.05 active wt % of surfactant solution at its optimal salinity in an imbibition cell. Oil drained from the core floated up and collected at the top of the imbibition cell. The oil recovery was monitored as a function of time. This study was done at 90°C.



**Figure: 6.5 (A) carbonate core inside of an imbibition cell; (B) Imbibition cell test model with all-face open boundary condition.**



**Figure: 6.6 Spontaneous imbibition of anionic surfactant into oil-wet carbonate. Red circles are anionic surfactant head groups, black squares are polar components from the crude oil. (after Standnes and Austad, 2000)**

### 6.3.5 ADSORPTION

Two batches of surfactant solutions were prepared in deionized water, each weighing 10 grams with the surfactant concentration in the range of  $10^{-5}$  M to  $10^{-2}$  M. One of these batches also contained 0.3 M  $\text{Na}_2\text{CO}_3$  in addition. These solutions were then contacted with 10 grams of calcite powder in 50 ml vials. The vials were corked and gently shaken so that the calcite powder comes into contact with the surfactant solution thoroughly. The solutions were allowed to equilibrate with the calcite powder for 48 hours subject to gentle periodic shakings. The slurry was then centrifuged at 1200 rpm for 20 minutes to separate the solid particles from the liquid solution. The supernatant was carefully pipetted out to avoid the solid particles. The supernatant was then centrifuged again for 20 minutes to obtain particle free supernatant. The pH of all the supernatant solutions was measured. UV spectrometry was used to determine the residual surfactant concentration in the supernatant liquid. The adsorbed surfactant concentration was calculated by material balance. Days, while the DF in the same time could get about 30 %. It is interesting to observe that DF could recover a significant amount of oil from the core at  $109^\circ$  contact angle. Surfactants reduce the oil-brine IFT and thus reduce the capillary pressures to a low value. In case of DF, the capillary pressures are low but negative due to the oil-wet nature of the core. At such low IFT, gravitational forces can overcome negative capillary pressure and imbibe brine into the core and push oil out from the top of the core. When wettability is altered to water-wet condition; both capillary forces and gravity forces aid in oil recovery, thus explaining the higher recovery rate in case of Alf-68.

Surfactant loss due to adsorption is one of the important criteria that govern the economics of the dilute surfactant flooding methods for carbonate formations. The adsorption of surfactants on minerals more typical of sandstone reservoirs has been studied extensively. However there is little published literature on the adsorption of surfactants on the carbonate minerals.<sup>25</sup> Figure 9 shows the adsorption isotherm for the anionic surfactants 4-22, 5-166 and SS-6566 in the absence and presence of  $\text{Na}_2\text{CO}_3$ . In the absence of Na, the adsorption is low at low surfactant concentration, increases nonlinearly with the increase in surfactant concentration and then reaches a plateau adsorption value above the CMC of the surfactants. This plateau adsorption value is the highest ( $\sim 3.5$  mg/m<sup>2</sup> of calcite) for 5-166 among the sulphonates studied. For the ethoxylated sulphonates 4-22 and SS-6566, the plateau adsorption values are  $\sim 0.9$  mg/m<sup>2</sup> and  $\sim 1.3$  mg/m<sup>2</sup>, respectively. These adsorption values are similar to those found for SDS on calcite and dolomite surfaces by Tabatabal et al.<sup>25</sup> The pHs of all the surfactant solutions used for the adsorption experiment were found to be between 6 and 7 before contacting the calcite powder. However, after adsorption the pH values of the supernatant were found to be around 8. Some amount of  $\text{CaCO}_3$  from the mineral possibly dissolves in water and the presence of  $\text{CO}_3^{2-}$  ions raises the pH of the supernatant.

Figure 9 also shows the adsorption isotherm for the anionic surfactants in the presence of 0.3 M  $\text{Na}_2\text{CO}_3$ . Surfactant adsorption decreases dramatically in the presence of the  $\text{Na}_2\text{CO}_3$ . In the case of surfactant 5-166, the plateau adsorption is reduced to  $\sim 0.15$  mg/m<sup>2</sup> from  $\sim 3.5$  mg/m<sup>2</sup>. For the other two anionic surfactants, the adsorption was negligible in the presence of  $\text{Na}_2\text{CO}_3$ . The presence of 0.3 M  $\text{Na}_2\text{CO}_3$  raises the pH of the solution to 10.3. This pH is higher than the point of zero charge for the calcite, which was found to be about 8.2 by Somasundaran and Agar.<sup>26</sup> This causes the surface to acquire negative charges and repel the



like charged anionic polar head group of the surfactant. Thus the adsorption of anionic surfactants can be suppressed by the use of the alkali.<sup>12,25</sup>

Imbibition cells, constructed in the University of Texas, work well at high temperatures up to 120°C and pressure buildup. Each aged core was placed on the core stand inside the imbibition cell. The imbibition cell was refilled with the formation brine or a surfactant solution to a desired height. The recovered oil, accumulated on the top part of imbibition cell, was monitored and recorded versus time.

### **6.3.6 ALTERATION IN HIGH TEMPERATURE CARBONATE RESERVOIR**

Oil is formed in source rocks and migrates to originally water-wet reservoirs. The polar components of oil collect at the oil-water interface<sup>16</sup> and adsorb on the solid surface if the water film becomes unstable. Hirasaki,<sup>17</sup> Mohanty et al.<sup>18</sup> and Menezee et al.<sup>19</sup> studied the effect of surface forces on thickness and stability of wetting films and thus on the contact angles. The film thickness depends on the applied capillary pressure and the disjoining pressure, which in turn depends in brine, oil, and mineral compositions. Buckley et al.<sup>20</sup> showed that interactions between polar oil components and solid, surface precipitation of asphaltene type molecules from oil, acid/base and ion binding between ion sites on solid/brine and oil/brine or a combination of them could be responsible for wetting of mineral surfaces by a crude oil. Hamouda et al.<sup>21</sup> worked with a system of n-decane/fatty acid/water on calcite plates at elevated temperature. He showed that the wettability (contact angle) follows the same trend as partition coefficient of fatty acid and IFT which in turn depends on pH and thus on zeta potential of calcite.

*the change in wettability on an initially oil-wet calcite plate by anionic surfactants. We explore possible mechanisms of wettability alteration. We analyze the effect of surfactant concentration, aqueous phase salinity, surfactant type (chain length and number of EO/PO groups) on wettability alteration.*

### **6.3.7 NONIONIC SURFACTANTS FOR WETTABILITY ALTERATION**

Nonionic surfactants show excellent solvency, high chemical stability and high tolerance for hard brine, but their challenge is the low cloud point (Raney, 1991). In addition to a large number of conventional ethoxylate alcohols, glycerol esters and amine oxides have been developed in recent years. In this work, we have studied a family of surfactants called ethoxylated aliphatic amine, trade name Ethomeen® by AkzoNobel. The varying degrees of ethoxylation provide a wide range of properties, allowing for great formulation latitude. At neutral to high pH reservoir environment, Ethomeen® is a triamine with ethoxylate (EO) groups. In acidic brine, it may be protonated and become a cationic surfactant. EO group usually increases the hydrophilicity of surfactant molecules at high temperature.

The structure of Ethomeen® T/25, a tertiary amine ethoxylate containing of tallow alkyl chain (C16-C18), is shown in Figure 3. 1% (w/w) Ethomeen® T/25 surfactant showed very good solubility and thermal stability in hard brine at 100oC, but became cloudy at 120oC. The pH of the 1% Ethomeen® T/25 aqueous solution was ~10. In order to obtain a formulation for temperature at or above 120oC, lauryl-betaine was added to increase the solubility of Ethomeen® T/25 at 120oC. The combination of Lauryl-betaine and Ethomeen® T/25 in 1:1 ratio (w/w) showed clear solutions at 120oC.

	EA-1	EA-2	EA-3	EA-4	EA-5
Enordet® A092	0.25%	0.25%	0.25%	0.25%	0.25%
SASW or SSASW	SASW	SASW	SASW	SASW	SASW
Chelating agents	-	1.0% EDTA	2.5% EDTA	1%NaPA	1%NaPA
pH	7.0/ 10.0	9.5	10.0	9.65	6.88
Aq. Stability @R.T.	Clear	Clear	Clear	Clear	Clear
Aq. Stability @100C	pH7.0, Clear; pH10, <u>Precip</u>	<u>Precip</u>	Clear	Clear	Clear
Wettability Alteration*	Poor (@pH7.0)	N/A**	Intermediate	N/A**	Poor
	EA-6	EA-7	EA-8	EA-9	Test-10
Enordet® A092	0.25%	0.25%	0.25%	0.25%	0.25%
SASW or SSASW	SASW	SASW	SSASW	SSASW	SSASW
Chelating agents	4%NaPA	2.5% <u>Metaborate</u>	-	1.0% Na <sub>2</sub> CO <sub>3</sub>	2.5% EDTA
pH	6.88	10.0	7.0	10.0	10.0
Aq. Stability @R.T.	Clear	<u>Precip</u>	Clear	Clear	Clear
A	Clear	<u>Precip</u>	Clear	Clear	Clear
q. Stability @100C					
Wettability Alteration*	Good	N/A**	Good	Excellent	Excellent

\*Evaluation of wettability alteration based on the performance of contact angle reduction: Excellent ( $\theta < 50^\circ$ ); Good ( $\theta < 75^\circ$ ); Intermediate ( $105^\circ > \theta > 80^\circ$ ); Poor ( $\theta > 105^\circ$ ). \*\*N/A: Experiment was not done yet.

The wettability alteration effect was evaluated by calcite contact angle tests at 100oC. As shown in Fig.6.7, the oil-aged calcite plate was oil-wet in the formation brine. When it was immersed in the 1% Ethomeen® T/25 brine solution, the average contact angle of oil droplets dropped to less than 90o, indicating wettability alteration towards more water-wet. A spontaneous imbibition test with a Silurian dolomite core SD-18 was performed at 100oC. The rock and fluid properties are presented in Table 2. The cumulative oil recovery reached 56% OOIP in 40 days at 100oC (Fig. 6.7). Hence, Ethomeen® T/25 is a very good candidate for wettability alteration under harsh reservoir conditions.

**Table 6.1: Values of parameters used in the calculations of NB-1**

Core #	OOIP%	WetAlter?	$\sigma$ (mN/m)	$\Phi$	k, md	L (cm)	$\Delta\rho$ (kg/m <sup>3</sup> )	$N_B^{-1}$
SD-2	16.87	no	0.05	0.1734	74.6	7.58	133	0.31
SD-15	22.05	no	0.05	0.142	52	7.39	204.25	0.22
SD-6	31.76	intermediate	0.05	0.1697	152.4	5.03	133	0.32
SD-10-2	53.25	strong	0.05	0.219	236	7.07	133	0.17
SD-16	46.67	strong	0.05	0.161	120	7.62	204.25	0.15
SD-18	56.08	strong	0.5	0.161	120	7.7	204.25	1.5

**Table 6.2: History-matching parameters used in the simulations of imbibition tests**

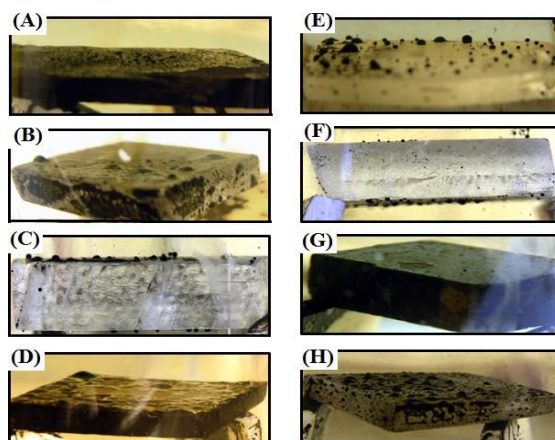
Parameters	Oil-Wet (OW)		Water-Wet (WW)	
	Oil	Water	Oil	Water
Residual Saturation	0.68	0.17	0.352	0.17
Endpoint relative permeability	0.22	0.58	0.48	0.28
Relative permeability exponent	2.5	2.5	6	3
Trapping parameters ( $T_i$ )	1862	15000	5000	2500
Capillary pressure endpoint ( $C_{pc}$ )	-		0.05	
	0.05			
Capillary pressure exponent ( $E_{pc}$ )	2		2	
Wettability Scaling factor ( $\omega$ )	$\omega=0.5$ (Core: SD-10-2)			
	$\omega=0.05$ (Core: SD-6)			
	$\omega=0$ (Core: SD-2)			

### 6.3.8 MIXING CHELATING AGENTS IN ANIONIC SURFACTANT FORMULATIONS:

Divalent cations in hard brine, especially  $Ca^{2+}$  and  $Mg^{2+}$ , can react with anionic surfactants, causing them to work less efficiently or to precipitate out of the bulk solution. In the detergent industry, water softeners (i.e. builders) are added to enhance or maintain cleaning efficiency of the surfactants. Builders remove calcium ions by chelation or precipitation. Typical builders are sodium carbonate, chelating agents, and zeolites. Among these types of builders, sodium carbonate is compatible only with softened brine and precipitates when it reacts with  $Ca^{2+}/Mg^{2+}$ . Zeolites are insoluble in water. Chelating agents can be used in surfactant formulations with hard brines at high temperatures.

### 6.3.9 WETTABILITY ALTERATION BY EDTA.4NA-ANIONIC SURFACTANT FORMULATIONS:

An ultralow tension anionic surfactant formulation (referred to here as UTB) was developed by Lu et al. (2012) for this crude oil. UTB consisted of a Guerbet alkoxy carboxylate and an internal olefin sulfonate (IOS). The optimized solubilization ratio of this formulation was around 16, corresponding to an IFT value of 0.001 dyne/cm estimated by the Huh correlation (1979). The optimum salinity was found to be 57000ppm, corresponding to 100% SASW + 16.5% FB. More details of the phase behavior study can be found in Lu et al. (2012). The wettability alteration capability of this surfactant formulation was evaluated in this work.



**Figure: 6.8. Wettability alteration by UTB and its derivatives: (A) UTB; (B) UTB-1; (C) UTB-2; (D) UTB-3; (E) UTB-4; (F) UTB-5; (G) UTB-6; (H) UTB-7. The compositions for these formulas can be found in Table 4.**

### 6.4 WETTABILITY ALTERATION BY NAPA-ANIONIC SURFACTANT FORMULATIONS

EDTA.4Na chelation might not be an economical; other chelating agents such as sodium polyacrylate, sodium metaborate were explored. Sodium metaborate ( $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ ) has been tested for its compatibility with a thermal stable anionic surfactant Enordet® A092 at the elevated pH environment. The formulation is designated as EA-7 in Table 4. The formulation of EA-7 failed the aqueous stability test because the surfactant precipitated with the addition of 2.5% sodium metaborate in SASW at pH 10.0. The test indicates that divalent ions in SASW,  $\text{Ca}^{2+}$  (480ppm) and  $\text{Mg}^{2+}$  (1342ppm), are above the sequestration capability of sodium metaborate.

As a comparison, sodium polyacrylate (abbr. NaPA), commonly used as scale inhibitor in the oil industry, achieved high performance as a chelating agent. NaPA is a weak base and pH of 1% solution is The pH value of each surfactant solution was adjusted by adding appropriate amounts of NaOH or HCl, as shown in Table 4. Enordet® A092 could stay as clear solution in SASW at 100°C and pH 9.65, when 1% NaPA was added into the surfactant solution,

designated as formulation EA-4. Even lower concentration of NaPA, like 0.2%, did not pass the aqueous stability test. Alkali alone has been considered to alter wettability towards more water-wet in some extent. Formulations EA-1, EA-5 and EA-6, differing in only the amount of NaPA in solution, were tested for their aqueous solubility and wettability at neutral pH environment to exclude the alkali effect. All of these formulations passed the aqueous stability test. However, only EA-6 surfactant formulation, consisted of highest dosage of NaPA (4% w/w), showed strong wettability alteration capability. In EA-5 formulation with 1% NaPA, wettability alteration on calcite was not appreciable. The dosage effect of chelating agent in surfactant solution can be also observed by comparing EA-2 with EA-3 (Table 4). Only with the aid of adequate amount of EDTA.4Na (2.5% w/w), the surfactant solution stayed clear at basic pH and also wettability alteration effect was clearly observed. Enordet® A092 in softened SASW (EA-8) has shown wettability alteration effect, by reducing contact angles of oil droplets to near 90°. This effect was significantly enhanced by adding two types of alkalis 1.0% Na<sub>2</sub>CO<sub>3</sub> (EA-9) or 2.5% EDTA.4Na (EA-10), by which contact angles were dropped to an average of 50°, indicating a strongly water-wet condition.

The effect of NaPA on wettability alteration was further evaluated by performing spontaneous imbibition tests. The core properties and experimental conditions are presented in Table 6.2. In softened brine environment, 0.25% Enordet® A092 with 1% NaPA recovered incremental 20% OOIP compared with oil recovery by surfactant formulation without NaPA. In hard brine SASW, 1% NaPA in surfactant solution was not sufficient to enhance oil recovery, while 4% NaPA resulted in additional 24% OOIP, compared with oil recovery by surfactant only. Combining the wettability alteration results (Table 4) and imbibition test results, it was observed that the amount of NaPA must be sufficient to sequester divalent ions, in order to reactivate the wettability alteration efficiency and enhance oil recovery. The experimental results strongly suggest that hardness ion scavengers, like EDTA and NaPA, are indispensable for anionic surfactant formulation to achieve high performance in the imbibition oil recovery. Lastly, the anionic surfactant achieves wettability alteration only when two essential prerequisites are met: the surfactant itself has the capability and the surfactant is liberated from divalent ions.

The molecular weight of NaPA used in this study is 2100 Dalton, which is in the lower side of low-molecular-weight (LMW) series polymers. Sodium polyacrylate, especially for LMW NaPA, is a weaker metal ion sequestrant than EDTA. The superior performance of NaPA originates from its strong capability of crystal-growth inhibition and dispersion of CaCO<sub>3</sub>(s). The interested reader is referred to the studies of the performance of polymeric additives to surfactant activity by Zini (1995) and Broze (1999).

## CONCLUSION

Anionic surfactants have been identified which can change the wettability of the calcite surface to intermediate/water-wet condition as well or better than the cationic surfactant DTAB. All the carbonate surfaces (Lithographic Limestone, Marble, Dolomite and Calcite) show similar behavior with respect to wettability alteration with surfactant. Anionic surfactants (5-166, Alfoterra-33 and Alfoterra-38 and Alfoterra-68), which lower the interfacial tension with a crude oil to very adsorption of the sulphonate surfactants can be suppressed significantly by the addition of the Na<sub>2</sub>CO<sub>3</sub>. The dilute anionic surfactant formulations look promising for fractured carbonate formations, but core-scale and field-

scale evaluations need to be performed to prove the efficiency of this recovery process . We have investigated the strategies of surfactant formulation development for imbibition into oil-wet rocks for high temperature, high hardness reservoirs. The cloud point for a family of nonionic surfactants is high. 1% Ethomeen T/25 (w/w) in hard brine achieved aqueous stability, high performance in wettability alteration and improved oil recovery from an oil-wet Silurian dolomite core by imbibition (up to 51% OOIP in 20 days) at 100°C. Anionic surfactants, carboxylates and sulfonates, formulated in hard brine achieved thermal stability and low interfacial tension. These anionic formulations in hard brines recover oil mainly by gravity drainage, since no wettability alteration effects were observed without adding chelating agents. Chelating agents, especially EDTA.4Na, sodium polyacrylate (NaPA) and sodium metaborate were investigated for their compatibility and effectiveness in surfactant formulations. It has been identified that with the aid of chelating agents, anionic surfactants achieved high performance in wettability alteration and improved imbibition oil recovery. By sequestering divalent ions in hard brine, chelating agents free anionic surfactants to react at the solid-fluid interface to alter wettability of carbonates from oil-wet towards more water-wet. The chelating agents trigger mineral dissolution, but that does not lead to wettability alteration or contribute to the imbibition oil recovery directly.

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