Investigated Miscible CO$_2$ Flooding for Enhancing Oil Recovery in Wettability Altered Chalk and Sandstone Rocks

by

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PERFACE

This thesis is submitted in partial fulfillment of the requirements for the degree of Ph.D (Doctor of Philosophy) in Petroleum Engineering at University of Stavanger, Norway. The thesis presents the results of the research work conducted at Department of Petroleum Engineering, University of Stavanger (UiS) from June 2009 to May 2012. Part of the research program was performed at CNRS/University de Provence, MADIREL laboratory in France, started March 2010 for 5 months. The outcome of this study is given through 6 papers, which are attached at the end of the thesis.

An overview of the work is given in introduction, followed by the objectives of this work in section two. Materials, used methods and different approaches employed in this study are in section three. The discussion section includes the main results of the study. Conclusions and recommendations are given in the last section. All the cited references are given in section six.
ABSTRACT

The thesis addresses oil recovery by miscible CO₂ flooding from modified sandstone and chalk rocks. Calcite mineral surface is modified with stearic acid (SA) and asphaltene, and the silicate mineral surfaces are modified with N,N-dimethyldodecylamine (NN-DMDA) and asphaltene. The stability of adsorbed polar components in presence of SO₄²⁻ and Mg²⁺ ions is also investigated.

Recovery from sandstone cores is consistently lower than that from chalk cores saturated with the same oil and flooded with CO₂ at all miscible flooding conditions. This may be due to the larger permeability contrasts in sandstone cores, which promote the fingering phenomenon. Miscible CO₂ flooding for chalk and sandstone cores with distilled water, as initial water saturation, shows also lower oil recovery than cores saturated with different ions.

At higher miscible flooding conditions, higher oil recovery is obtained. However, presence of light components (such as C₁ or C₃) in oil reduced the recovery. Oil recovery in presence of methane (C₁) is lower than that in presence of methane and propane (C₁/C₃). A ternary diagram was constructed in order to understand the CO₂ flooding mechanism(s) at the different flooding conditions and in presence of light components.

The side effect of the flooding with CO₂ is the probability for asphaltene deposition. An approach based on solubility parameter in the liquid, is used to assess the risk for asphaltene deposition during CO₂ miscible flooding. The light components (C₁/C₃) and higher flooding conditions enhanced the risk for asphaltene instability. It is also shown higher amount of asphaltene deposition in chalk cores than that in sandstone cores at similar miscibility conditions.
To my lovely parents; my brothers and my sister for all their support and motivation far from home

and

In memory of Dr. Mustafa Chamran Savie
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Stavanger-NORWAY
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NOMENCLATURE

\[ \ce{C} \] initial concentration (mol/l)
\[ N_{\text{VF}} \] viscous fingering number
\[ N_d \] diffusion number
\[ SV_{gr} \] surface area per unit of grain volume (cm\(^{-1}\))
\[ T_c \] critical temperature (K)
\[ P_c \] critical pressure (bar)
\[ WA \] weight percentage of asphaltene precipitated (%)
\[ C \] concentration (mol/l)
\[ d \] diameter (cm)
\[ D \] diffusion coefficient (m\(^2\)/sec)
\[ f \] microcalorimetry conversion factor (mV sec kJ\(^{-1}\))
\[ F \] Archie factor
\[ H \] enthalpy of adsorption (kJ/mol)
\[ I \] mixing zone index
\[ K \] permeability coefficient (m\(^2\)/sec)
\[ K \] permeability of porous media (m\(^2\),mD)
\[ l \] length of capillary tube (cm)
\[ M \] molar mass (g/mol)
\[ N_A \] Avogadro constant \((6.02214 \times 10^{23} \text{ mol}^{-1})\)
\[ n_m \] monolayer capacity
\[ P \] pressure (atm, psia, bar)
\[ P^w \] water vapor saturation pressure (atm)
\[ q \] flow rate (ml min\(^{-1}\))
\[ Q \] heat of adsorption (kJ)
\[ R \] universal ideal gas constant \((8.314 \text{ J mol}^{-1} \text{ K}^{-1})\)
\[ T \] temperature (K, °C)
\[ t \] time (sec)
\[ U \] internal energy (kJ)
\[ v \] darcy velocity (cm/sec)
\[ V \] molar volume (cm\(^3\)/mol)
\[ V \] microcalorimetry signal (mV/sec)
\[ w \] width (cm)
\[ W \] weight (g)
\[ X \] mole fraction
Greeks

\(\pi\)  
surface pressure (mN/m)

\(\gamma\)  
interfacial tension (mN/m)

\(\theta\)  
contact angle (degree)

\(\phi\)  
porosity

\(\delta\)  
Hildebrand solubility parameter (Mpa\(^{1/2}\))

\(\mu\)  
viscosity (cp)

\(\alpha\)  
surface area (m\(^2\)/g)

\(\mu\)  
chemical potential

\(\Gamma\)  
adsorbed amount per unit area (mol/m\(^2\))

\(\zeta\)  
zeta potential

\(\rho\)  
density (g/cc)

\(\sigma\)  
surface coverage (Å\(^2\))

Subscript

a  
advancing

A  
asphaltene

AL  
asphaltene in the liquid

CO\(_2\)  
Carbon dioxide

Liq.  
liquid

m  
modified sample

n  
unmodified sample

o  
oil

r  
receding

sw  
sea water

t  
total

TAL  
total asphaltene in the liquid

TL  
total liquid

Vap.  
vapor

w  
water
Superscript

bl. blank
Exp. experiment
L liquid
S solid surface
s sample
V vapor

Abbreviations

Asph. Asphaltene
ASTM American System of Testing and Materials
BET Braunauer-Emmett-Teller
DVLO Derjaguin, Landau, Verway, Overbeek
DW distilled water
EOR enhanced oil recovery
EOS equation of state
FCM first contact miscibility pressure
GC gas chromatograph
IFT interfacial tension
IOIP initial oil in place
LSW low salinity water
MCM minimum contact miscibility
MFC mass flow controller
MME minimum miscibility enrichment
MMP minimum miscibility Pressure
NN-DMDA N,N-dimethyldodecylamine
PV pore volume
PVT Pressure Volume Temperature
rpm revolution per minute
SA stearic acid
SCF standard cubic feet
SSW synthetic sea water
STB stock tank barrel
TGA Thermo Gravimetric Analysis (TGA)
USBM US Bureau of Mine
WA weight percentage of asphaltene precipitated
WI wettability index
1. INTRODUCTION

CO₂ flooding is one of the most widely used methods for medium and light oil recovery in sandstone and carbonate reservoirs (Moritis, 2006; Alvarado and Manrique, 2010). During the past five decades, extensive laboratory studies, numerical simulations and field applications of CO₂ EOR processes have been reported (Chukwudeme and Hamouda, 2009; Hamouda et al., 2009; Moritis, 2006; Idem and Ibrahim, 2002; Grigg and Schechter, 1997; Burke et al., 1990). In the 1950’s, when the carbon dioxide injection began as an oil recovery method, emphasize was directed to the immiscible process as an alternative recovery scheme for reservoirs in the cases where the water based EOR is inefficient (Jarrel et al., 2002). In recent years, the interest is shifted to more CO₂ injection for better oil recovery (Farouq Ali and Tomas, 1996). CO₂ lowers interfacial tension (IFT) and enhances mobility by reducing oil viscosity and causing oil swelling (Green and Willhite, 1998; Simon et al., 1978).

1.1. Wettability

Wettability affects the distribution of fluids in the rock pore systems. Water is occupying the smallest pores and oil will reside as droplets in the middle of the pores in a uniform water-wet rock. The reverse fluids distribution is occurring in an oil-wet rock (Anderson, 1986a; Anderson, 1986b). The wetting or non-wetting of solid surface by oil and water is better understood by contact angle (Rezaei Gomari et al., 2006c). A schematic illustration is shown in Figure 1.1 to show the contact angles for oil/water/solid system. Carbonate and silicate minerals are naturally water-wet (Craig, 1980; Legens et al., 1998). During primary drainage and oil migration into the reservoir rock, wettability alteration from water-wet to oil-wet is occurring. Initially, the mineral surface is coated by a thick wetting film of water (i.e. interstitial
Introduction

water) preventing the oil from contacting the rock (Basu and Sharma, 1996). Polar components in crude oil may be partitioned into water film, resulting in a direct contact of solid mineral surface and polar components (Kaminsky and Radke, 1997). Adsorption of polar components on rock surfaces alters the wettability towards more oil-wet.

Figure 1.1. Contact angle: a) illustrated by force balance at the oil/water/solid interface and b) Advancing ($\theta_a$) and receding ($\theta_r$) angles (Rezaei Gomari, 2006).

1.1.1. Wettability characterization by surface energy analysis

Wettability characterization of minerals is done using thermogravimetric analysis (TGA), microcalorimetry and water vapor adsorption isotherms (Rezaei Gomari et al., 2006a; Rezaei Gomari et al., 2006b; Hansen et al., 1999; Fuji et al., 1997; Buckton, 1990).
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Thermo gravimetric analysis provides a mean for quantification of the adsorbed components (Thomas and Clouse, 1988). The measurement of the adsorption energy of water molecules with unmodified and modified minerals is carrying out by microcalorimetry (Denoyel et al., 1991). Klier et al. (1973) described a method for classification of hydrophilicity/hydrophobicity of mineral surfaces based on microcalorimetry. In their definition, they set the latent heat of liquefaction for water ($44 \text{kJ/mol}$) as a reference for hydrophilicity/hydrophobicity characteristic of surfaces. Accordingly if the adsorption enthalpy lies above this value the surface is hydrophilic while if it lies below, then the surface is hydrophobic. From the shape of adsorption isotherms; one can also determine the wetting state of a solid (Tadros et al., 1974; Schlangen et al., 1993). For a high energy solid surface, the amount of adsorbed water vapor is infinite at saturation pressure, and the area under the adsorption isotherm is large (Schlangen et al., 1993). For a low energy surface, the area under saturation isotherm is finite and the amount of vapor adsorption is low. This case is defined as partial wetting when a thin film (with the thickness of one or few monolayers) is formed at saturation pressure (Schlangen et al., 1993).

1.1.2. Mineral/fluid interactions

It is well documented that the presence of asphaltene and natural polar components (acids and bases) soluble in the crude oil and their interaction at solid surface are important factors in altering solid surface wettability to more oil-wet (Anderson, 1986b; Morrow et al., 1986; Kaminsky and Radke, 1997). Polar compounds changing the rock wettability are dependent on the type of the minerals. Carbonate minerals are positively charged at basic conditions and are able to adsorb negatively charged acidic groups. Silicate minerals in contact with water form hydroxide functional groups and are negatively
charged at acidic conditions; therefore become more oil-wet after being
exposed to the basic components (Thomas and Clouse, 1989). Different
organic bases such as piperdine, dodcylamine, pyridine and quinoline are
addressed the wettability modification of silicate surfaces from strongly
water-wet to more oil-wet (Zheng, 2001). Silicate based minerals are difficult
to be altered to more oil-wet. At lower pH values (pH<2), basic functional
groups are protonated leading to positively charged at oil/water interface,
resulting to an unlike charge attraction with silicate surface (Zheng, 2001).
The other mechanism to change quartz wettability is to add multivalent ions to
water solution. For example sodium laurate, when added to the aqueous phase
dissociates into a negatively charged laurate ions. Laurate ions can not adsorb
onto the quartz surface since they carry like charges. However, when Ca$^{2+}$ or
Mg$^{2+}$ is added to the system, they promote the adsorption of laurate ions on
the surface (Zheng, 2001). Basic amino acids found in geological
environments such as Lysine (C$_6$H$_{14}$N$_2$O$_2$) is water soluble and have affinity
to adsorb on silicate minerals (Tissot and Welte, 1984). The heavy ends in the
 crude oil (asphaltene and resins) also contain surface active components
which adsorb on quartz and clay minerals and can change the wettability
(Kokal et al., 1994).

Hamouda and colleagues in series of work dealing with calcite, water and oil
revealed that factors affecting the wettability of calcite mineral surfaces are
mainly considered as oil composition, chemical structure of fatty acids, ions
composition, pH, rock surface characteristics and temperature (Rezaei Gomari
et al., 2006b; Rezaei Gomari et al., 2006d; Karoussi and Hamouda, 2007;
Hamouda and Karoussi, 2008; Chukwudeme and Hamouda, 2009). Mg$^{2+}$ and
SO$_4^{2-}$ ions affect the final wetting state of water flooded reservoir rocks
(Petrovich and Hamouda, 1998; Rezaei Gomari et al., 2006b; Rezaei Gomari
et al., 2006c; Karoussi and Hamouda, 2007; Hamouda and Karoussi, 2008; Chukwudeme and Hamouda, 2009). Petrovich and Hamouda (1998) observed an increase of calcium ions and a decrease in the magnesium ion concentrations in produced water as a result of seawater injected into Ekofisk field samples (chalk reservoir). They concluded to the possible adsorption/exchange processes between Mg$^{2+}$ in seawater with Ca$^{2+}$ in calcite, on a field scale. Rezaei Gomari et al. (2006b) showed that alteration of the wettability of modified calcite surface in presence of SO$_4^{2-}$ is not only due to possible reduction of the available active sites on the calcite surfaces but could also be due to a displacement process of various preadsorbed carboxylate ions of the tested fatty acids. This alteration corresponds to the change of the $\zeta$ potential of the calcite particles when adsorption and/or exchange processes occur in the presence of SO$_4^{2-}$ and Mg$^{2+}$ (Rezaei Gomari et al., 2006b). Hirasaki and Zhang obtained also higher oil recovery in their experiments, by addition of inorganic salts (Na$_2$CO$_3$/NaHCO$_3$) (Hirasaki and Zhang, 2004).

1.2. CO$_2$ flooding

Laboratory studies and field reports for CO$_2$ enhanced oil recovery showed that carbon dioxide can recover substantial amount of oil above recovery of water flooding for both light and heavy oils (Rogers and Grigg, 2000; Grigg and Schechter, 1997; Farouq Ali and Tomas, 1996). Grigg and Schechter (1997) reviewed 25 CO$_2$ projects and concluded that understanding CO$_2$/hydrocarbon phase behaviour and reservoir rock characterization are necessary to perform successful EOR process. Oil production by miscible CO$_2$ injection was simulated with a compositional simulator for an oil reservoir in Norwegian continental shelf (Lindeberg and Torleif, 1994). Results indicated
CO₂ injection produced 63 % IOIP while water injection recovered 43 % IOIP (Lindeberg and Torleif, 1994).

1.2.1. Immiscible and miscible CO₂ flooding

In immiscible flooding, the injected CO₂ remains distinct from the oil. In addition, CO₂ can vaporize and extract hydrocarbons and condense to the oil phase, reducing the interfacial tension and developing miscibility under certain conditions of flooding pressure and temperature. When CO₂ contacts oil, several mechanisms promote the mobilization of oil in immiscible and miscible processes (Stright et al., 1977; Klins and Farouq Ali, 1984; Simon et al., 1978; Stalkup, 1990; Shyeh-Yung, 1991):

(1) Dissolution of CO₂ in oil (oil swelling) can increase the oil volume by 10-50% (Klins and Farouq Ali, 1984). The swollen oil forces out the oil from the pore spaces, thereby increasing the oil saturation.

(2) When CO₂ dissolves in oil, viscosity is reduced (Holm and Josendal, 1974). This improves the mobility ratio between the oil and injected CO₂ and gives improved sweep efficiency.

(3) CO₂ dissolves in water to form carbonic acid, which reacts with carbonate rock and forms soluble bicarbonates of calcium and magnesium. This results in increased porosity, and therefore, increased injectivity. Reduction of pH due to carbonic acid stabilizes clay in shaly formation, which also increases the injectivity (Holm and Josendal, 1974).

(4) CO₂ can bring about very low interfacial tension due to vaporization and solubility effects at certain pressures (Simon et al., 1978). Apart from increasing the capillary number, which increases the displacement efficiency,
lower IFT can lead to the formation of water-in-oil emulsions, which improves the mobility ratio (Zick, 1986).

Alavaian and Whitson (2011) and Karimaie and Torsæter (2010) reported a numerical simulation and experimental investigation of miscible CO₂ injection in a chalk core saturated with reservoir synthetic oil consisting of C₁ and n-C₇ at a temperature of 85 °C and pressure of 220 bar. The role of gas/oil diffusion between fracture and matrix on CO₂ enhanced oil recovery was investigated by creating a small space surrounding the core and heating the solid Wood's metal that originally filled this volume before the experiment (Karimaie and Torsæter, 2010). The numerical model and experimental study indicated that the CO₂ recovery mechanism was dominated by viscous force and near-first-contact miscible displacement (Alavaian and Whitson, 2011). Trivedi and Babadagli (2008) studied also first contact miscible displacement in fractured porous media. Solvent injection at lower rate has more time to diffuse into matrix before solvent breakthrough; hence higher recovery is expected (Trivedi and Babadagli, 2008). Mass transfer rate and effective matrix diffusion coefficient are reported linearly dependent on the average fluid velocity in the fracture and the length of porous medium (Trivedi and Babadagli, 2009). Shut down and blow down periods, after continuous CO₂ enhanced oil recovery are examined also in fractured porous media (Trivedi and Babadagli, 2009; Trivedi and Babadagli, 2010).

1.2.2. Viscous instability during immiscible and miscible flooding
Viscous instability is attributed with the processes when the displaced fluid has a higher viscosity than the displacing fluid (Lake, 1998). Finger propagation rate is mainly dependent on presence of permeability heterogeneities, the mobility ratio of the displacing and displaced fluids and
local pressure drop as well as porosity. High mobility ratio and pressure drop promote finger growth, whereas porosity has the opposite effect (Collins, 1976). The other parameters that affect the initiation and growth of viscous fingers are mainly the balance between capillary, gravity and viscous forces (Lake, 1998). It was proposed by Perkins et al. (1965) that the growth of the finger occurs both in length and in width. In length, the finger growth is approximately linear with time. For dispersive type growth, the displacement mixing zone grows with the square root of time (Mahaffey et al., 1966; Blackwell et al., 1959); however transverse dispersion, may cause merging of fingers completely or reduce them, creating a more stable displacement. Chuoke et al. (1959) proposed that instabilities with wavelengths greater than a critical value propagate at displacement velocities greater than a critical velocity. If the wavelengths are less than the critical wavelength, the growth of fingers is inhibited by surface tension. In immiscible displacements, interfacial tension and capillary pressure have an adverse effect on the displacement efficiency. Due to capillary trapping, residual saturation presents after an immiscible displacement. Viscous instability as a result of an unfavorable mobility ratio, contributes to this residual saturation (Gilje, 2008; Peters and Flock, 1981). In first contact miscible displacements, there is no active capillary force; however, dispersion has the same effect as interfacial tension affects immiscible flows (Perkins and Johnston, 1963 and Alkindi et al., 2011). In unstable immiscible displacements with higher injection rate, more numerous and smaller viscous fingers are formed (Peters and Flock, 1981).

1.2.3. Hydrocarbon/CO₂ phase behaviour
The two main categories of miscible flooding mechanisms include (Lake, 1998): (1) First Contact Miscibility (FCM) and (2) Multiple Contact
Miscibility (MCM). In First Contact Miscibility (FCM) process, the solvent and oil are miscible upon first contact in all proportions under flooding pressure and temperature (Lake, 1998). To achieve First Contact Miscibility (FCM), the flooding pressure should be higher than Minimum Miscibility Pressure (MMP). In Multiple Contact Miscibility (MCM), miscibility between reservoir oil and the injected gas is generated through in-situ mass transfer of components, after multiple contacts between the two fluids. There are mainly two types of MCM processes: (1) Condensing gas drive and (2) Vaporizing gas drive. In condensing gas drive mechanism, when the gas contacts the reservoir oil, mass transfer takes place and some of the intermediate components are condensed into the reservoir oil (Danesh, 1998). In condensing gas drive process, the oil composition must lie to the left of the limiting tie-line, and the injected gas composition must lie to the right of the limiting tie-line. In vaporizing gas drive mechanism, when the gas contacts the reservoir oil, mass transfer takes place and extraction of light components (C2-C6) from oil into the gas phase takes place and the gas becomes progressively richer (Danesh, 1998). In vaporizing gas drive, the injected gas composition must lie on the left hand of the limiting tie line and the oil composition must lie on the limiting tie-line or to its right. Schematic of vaporizing gas drive/condensing gas drive mechanism(s) has been shown in Figure 1.3. Menzie and Nielson (1963) showed that condensing/vaporizing mechanisms occur at low temperatures when CO2 is a liquid as well as at temperatures above 88 °F, the critical temperature of CO2. Holm and Josendal (1974) observed that at constant temperature, by increasing the pressure up to the saturation pressure, the relative oil volume increases due to oil swelling (CO2 condensates into the oil) and then decreases at pressures higher than saturation pressure due to extraction (vaporization) of crude oil fractions into CO2 rich phase. When CO2 is injected into the porous medium at pressures
above saturation pressure, the light ends (C1-C4) are vaporized from the oil into a CO2-rich gas phase. CO2 can extract also the C5-C30 fractions from the oil and develops a transition zone. Vaporization of the light ends (C1-C4) from oils of low viscosity (10-12 cp) occurs at high pressures (>2000 psi) and relatively low temperatures (100-200 °F), whereas extraction of C5-C30 fraction from the crude oil can occur at intermediate pressures (1000-2000 psi) and low temperatures (<100 °F). CO2 achieves miscibility with the crude oil after multiple contacts (Holm and Josendal, 1974). Vaporizing gas drive requires considerable amount of C2-C6 components in the reservoir oil, and pressures not less than 5,000 psi for the displacement to be miscible (Jarrell, 2002; Stright et al., 1977). CO2 flooding can develop miscibility with oils that have much less C2-C4 components at considerably lower pressures (Jarrell, 2002). At lower pressures, the transition zone is longer, and at higher pressures, the transition zone contained higher concentration of hydrocarbons (Stalkup, 1983; Zick, 1986; Johns et al., 1994; Johns et al., 2000). This was confirmed by displacement tests, where higher oil recovery and lower residual oil saturation are observed at higher pressures (Holm and Josendal, 1974).
Introduction

Figure 1.2. Schematic of miscible CO$_2$ flooding processes: a) vaporizing gas drive mechanism and b) condensing gas drive mechanisms (Lake, 1998).
Introduction

Zick (1986) showed that condensing/vaporizing mechanism is occurring both at low pressures when CO$_2$ is a gas as well as pressures above 73 bar, the critical pressure of CO$_2$. Figure 1.3 shows a schematic of the CO$_2$ miscible process.

![Figure 1.3. Schematic of miscible CO$_2$ flooding process (Holm and Josendal, 1974).](image)

Miscible solvents injection in multi-component oil could be both vaporizing and condensing drives (Stalkup, 1986). Recently, Johns and colleagues in series of work mathematically showed the combined condensing/vaporizing mechanism (Johns et al., 1993; Johns et al., 1996; Johns et al., 2000). Jaubert and Arras (1998) analyzed live crude oils with an average of 30 components. Mixed condensing/vaporizing mechanism with increasing pressure may turn into a pure VGDM (Vaporizing Gas Drive Mechanism). In another research work reported by Razak et al. (2009), multiple contact miscibility tests were conducted for live reservoir oil to simulate the continuous multiple contact process when the CO$_2$ is injected into the reservoir fluid. They demonstrated the amount of methane in vapor phase had increased significantly, as the number of contacts increases between oil and CO$_2$ while the intermediate fraction became lighter as contact progresses (Razak et al., 2009). Darvish
(2007) reported also series of CO₂ injection experiments, applying a unique technique for saturating the matrix/fracture systems with reservoir live crude oil. These experiments showed at high flooding temperature (130 °C), the produced oil had a variable composition during CO₂ injection, while at the low temperature condition (60 °C), the produced oil initially had a constant composition and then it started to change (Darvish, 2007).

1.2.4. Asphaltene deposition due to miscible CO₂ flooding

Carbon dioxide flooding in EOR processes is encouraging; however it may result to asphaltene deposition which it turns affect reservoir rock and fluid properties (Idem and Ibrahim, 2002; DeBoer et al., 1995; Burke et al., 1990; Simon et al., 1978; Haskett and Tartera, 1965). Different models have been reported in the literature to describe the behaviour of asphaltene deposition using different approaches. Hirschberg (1984) developed a method on the basis of solubility model using the Flory-Huggins approach with a simple thermodynamic model describing the influence of temperature and pressure on asphaltene precipitation. Pan and Firoozabadi (2000) also developed a thermodynamic model based on the micellization process to describe asphaltene precipitation. Nghiem (1999) reported a thermodynamic solid model to determine the dynamic aspect of asphaltene precipitation applying a compositional simulator during CO₂ flooding. Chapman et al. (2004) and Paricaud et al. (2002) applied a simplified statistical association fluid theory (SAFT) description of the thermodynamics of chain molecules used to model the limit of stability of polymer-colloid systems. Verdier et al. (2006) studied the effect of pressure and temperature on asphaltene instability in presence of gas composition. They observed experimentally and verified with the thermodynamic model, the solubility of asphaltene in oil increases with increasing pressure and decreasing temperature. Kirangkrai et al. (2007)
developed an empirical correlation between the onset solubility parameter and the molar volume of precipitants to investigate the effect of dissolved gas on the onset solubility parameter of live oil. They reported solubility parameters of the stock tank oil using equation of state models based on the PVT data of the live oils to predict the asphaltene instability. Gonzalez et al. (2008) demonstrated that CO$_2$ can act as an inhibitor or a promoter of asphaltene precipitation depending on the range of temperature, pressure, and composition studied. They have shown that at fixed pressure, CO$_2$ enhances the asphaltene stability below the crossover temperature, whereas above this point, the asphaltene becomes less stable when the CO$_2$ concentration is increased. Hamouda et al. (2009) developed a modified solubility model to account the effect of CO$_2$ fraction on asphaltene precipitation. The model takes into account the molar volume ratio of CO$_2$ and fluid as a function of the solubility parameter of the fluid. They have demonstrated that below a critical CO$_2$ fraction (mol %) in fluid, asphaltene is stabilized, which otherwise would precipitate based on the predicted and experimental asphaltene solubility behaviour with temperature and pressure.

1.2.5. Minimum Miscible Pressure (MMP)

Minimum miscibility pressure (MMP) is defined as the minimum pressure at which a first contact miscibility drive occurs. Computational models to calculate minimum miscibility pressure include the equation of state (EOS) and the PVT correlations. MMP required to achieve miscibility for CO$_2$ with the reservoir oil is usually lower than that for hydrocarbon miscible fluids or other gases, such as N$_2$ and flue gases (Holm and Josendal, 1974). The minimum miscibility pressures at different temperatures (50 °C, 70 °C and 80 °C) are calculated according to the different empirical correlations (Alston et al. 1998; Yelling and Metcalfe, 1980; Glasø, 1985; Johnson and Pollin, 1980)
Introduction

and SRK EOS using PVTsim version 17. PVTsim data are shown to be in the middle and used in this research (Figure 1.4).

Figure 1.4. MMP for miscible CO₂ flooding using different empirical correlations and PVTsim (Hamouda et al. 2009).
Objectives

2. OBJECTIVES

The main objective of this thesis is to shed light on the effect of CO₂ miscible flooding on the oil recovery from both chalk and sandstone rocks. The work addresses the influence of light gas components (C₁ and C₃) in the oil on the recovery by CO₂. Very little work is reported in literature on the effect of light components on CO₂ miscible flooding. However, it discussed CO₂ flooding of live crude oil, which contains numerous number of components.

The interaction of CO₂ with modified minerals and the effect of ions on CO₂ recovery process are investigated. Asphaltene precipitation associated with miscible CO₂ flooding of oil in presence of light components at different miscibility conditions is addressed.
3. MATERIAL, METHODS AND APPROACHES

In this section, a description of different types of materials and methods used in the experimental works and the applied calculation approaches are presented.

3.1. MATERIAL

3.1.1. Solid powders

Three types of powdered solid were used in this work; quartz, calcite and kaolinite which represent sandstone rock, carbonate rock and clay minerals, respectively. Quartz and kaolinite were supplied by Sigma-Aldrich and their chemical compositions are $\text{SiO}_2$ and $\text{Al}_2\text{O}_3\cdot\text{Si}_2\text{H}_2\text{O}$, respectively. Calcite was provided by Norwegian Talc AS and the chemical composition of calcite powder is given in Table 3.1.

<p>| Table 3.1. Calcite powder chemical analysis |</p>
<table>
<thead>
<tr>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>TiO$_2$</th>
<th>MgO</th>
<th>CaO</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>MnO</th>
<th>P$_2$O$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.09</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.007</td>
<td>0.45</td>
<td>54.74</td>
<td>&lt;0.003</td>
<td>&lt;0.1</td>
<td>&lt;0.002</td>
<td>0.03</td>
</tr>
</tbody>
</table>

3.1.2. Solid crystalline minerals

Crystalline calcite and silicate (quartz) are provided by J. Brommeland AS, Norway and are used for contact angle measurements.

3.1.3. Sandstone and chalk cores

Core flood experiments were conducted using outcrop Stevns klint chalks near Copenhagen and outcrop Benthiemer sandstones. Table 3.2 is the cores detailed description. The outcrop chalks have approximate porosity of 40-48% and absolute permeability of 2.5-6.5 mD. Sandstone cores have lower porosity near 20-25%, and higher permeability range from 600-900 mD.
### Table 3.2. Core characteristics with associated fluids and flooding conditions

<table>
<thead>
<tr>
<th>EXP No.</th>
<th>Core Type</th>
<th>Porosity (%)</th>
<th>L (cm)</th>
<th>K (mD)</th>
<th>$S_w$ (%)</th>
<th>Saturating fluid</th>
<th>Flooding conditions (bar &amp; °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>Chalk</td>
<td>44</td>
<td>6</td>
<td>2.5</td>
<td></td>
<td>Dead oil</td>
<td>90 and 50</td>
</tr>
<tr>
<td>2a</td>
<td>Chalk</td>
<td>46</td>
<td>7</td>
<td>4</td>
<td></td>
<td>Dead oil</td>
<td>120 and 70</td>
</tr>
<tr>
<td>3a</td>
<td>Chalk</td>
<td>48</td>
<td>6.5</td>
<td>6.5</td>
<td></td>
<td>Dead oil</td>
<td>140 and 80</td>
</tr>
<tr>
<td>1b</td>
<td>Sandstone</td>
<td>.25</td>
<td>12</td>
<td>820</td>
<td></td>
<td>Dead oil</td>
<td>90 and 50</td>
</tr>
<tr>
<td>2b</td>
<td>Sandstone</td>
<td>23</td>
<td>13</td>
<td>770</td>
<td></td>
<td>Dead oil</td>
<td>120 and 70</td>
</tr>
<tr>
<td>3b</td>
<td>Sandstone</td>
<td>22</td>
<td>11</td>
<td>650</td>
<td></td>
<td>Dead oil</td>
<td>140 and 80</td>
</tr>
<tr>
<td>1c</td>
<td>Chalk</td>
<td>47</td>
<td>7</td>
<td>5</td>
<td></td>
<td>Live oil A</td>
<td>90 and 50</td>
</tr>
<tr>
<td>2c</td>
<td>Chalk</td>
<td>40</td>
<td>6.5</td>
<td>4</td>
<td></td>
<td>Live oil A</td>
<td>120 and 70</td>
</tr>
<tr>
<td>3c</td>
<td>Chalk</td>
<td>44</td>
<td>6.5</td>
<td>6.5</td>
<td></td>
<td>Live oil A</td>
<td>140 and 80</td>
</tr>
<tr>
<td>1d</td>
<td>Sandstone</td>
<td>22</td>
<td>12</td>
<td>820</td>
<td></td>
<td>Live oil A</td>
<td>90 and 50</td>
</tr>
<tr>
<td>2d</td>
<td>Sandstone</td>
<td>22</td>
<td>13</td>
<td>770</td>
<td></td>
<td>Live oil A</td>
<td>120 and 70</td>
</tr>
<tr>
<td>3d</td>
<td>Sandstone</td>
<td>24</td>
<td>11</td>
<td>650</td>
<td></td>
<td>Live oil A</td>
<td>140 and 80</td>
</tr>
<tr>
<td>1e</td>
<td>Chalk</td>
<td>42</td>
<td>7</td>
<td>4</td>
<td></td>
<td>Live oil B</td>
<td>90 and 50</td>
</tr>
<tr>
<td>2e</td>
<td>Chalk</td>
<td>40</td>
<td>7</td>
<td>2.5</td>
<td></td>
<td>Live oil B</td>
<td>120 and 70</td>
</tr>
<tr>
<td>3e</td>
<td>Chalk</td>
<td>43</td>
<td>6.5</td>
<td>5.5</td>
<td></td>
<td>Live oil B</td>
<td>140 and 80</td>
</tr>
<tr>
<td>1f</td>
<td>Sandstone</td>
<td>20</td>
<td>12</td>
<td>920</td>
<td></td>
<td>Live oil B</td>
<td>90 and 50</td>
</tr>
<tr>
<td>2f</td>
<td>Sandstone</td>
<td>21</td>
<td>13</td>
<td>850</td>
<td></td>
<td>Live oil B</td>
<td>120 and 70</td>
</tr>
<tr>
<td>3f</td>
<td>Sandstone</td>
<td>23</td>
<td>13</td>
<td>700</td>
<td></td>
<td>Live oil B</td>
<td>140 and 80</td>
</tr>
<tr>
<td>1g</td>
<td>Sandstone</td>
<td>23</td>
<td>5.5</td>
<td>770</td>
<td>12</td>
<td>DW/dead oil</td>
<td>90 and 50</td>
</tr>
<tr>
<td>2g</td>
<td>Sandstone</td>
<td>22</td>
<td>6.5</td>
<td>650</td>
<td>13</td>
<td>0.1M SO$_4^{2-}$/dead oil</td>
<td>90 and 50</td>
</tr>
<tr>
<td>3g</td>
<td>Sandstone</td>
<td>24</td>
<td>6</td>
<td>700</td>
<td>12</td>
<td>0.1M Mg$^{2+}$/dead oil</td>
<td>90 and 50</td>
</tr>
<tr>
<td>4g</td>
<td>Sandstone</td>
<td>23</td>
<td>6</td>
<td>850</td>
<td>12</td>
<td>SSW/dead oil</td>
<td>90 and 50</td>
</tr>
<tr>
<td>1h</td>
<td>Chalk</td>
<td>43</td>
<td>5.5</td>
<td>5</td>
<td>.22</td>
<td>DW/dead oil</td>
<td>90 and 50</td>
</tr>
<tr>
<td>2h</td>
<td>Chalk</td>
<td>40</td>
<td>6.5</td>
<td>6.5</td>
<td>23</td>
<td>0.1M SO$_4^{2-}$/dead oil</td>
<td>90 and 50</td>
</tr>
<tr>
<td>3h</td>
<td>Chalk</td>
<td>45</td>
<td>6</td>
<td>3.5</td>
<td>22</td>
<td>0.1M Mg$^{2+}$/dead oil</td>
<td>90 and 50</td>
</tr>
<tr>
<td>4h</td>
<td>Chalk</td>
<td>42</td>
<td>6.5</td>
<td>5</td>
<td>23</td>
<td>SSW/dead oil</td>
<td>90 and 50</td>
</tr>
</tbody>
</table>
Material, Methods and Approaches

3.1.4. Liquids and additives
Normal decane (n-C\textsubscript{10}) and toluene (C\textsubscript{7}H\textsubscript{8}) are used in this study as base solvents for added fatty acid and amine. Both liquids were supplied by Chiron AS in HPLC grade (purity >99 %). The water was purified through Milli-Q Millipore and was used in adsorption isotherm experiments. Stearic acid (SA) and N,N-dimethyldodecylamine (NN-DMDA) were used as oil soluble additives to mimic natural fatty acid and amine in the crude oil. Their structural formula, suppliers and purities are shown in Table 3.3. Asphaltene precipitated from crude oil is used to represent the polar and heavy fraction of crude oil.

<table>
<thead>
<tr>
<th>Components</th>
<th>Supplier and purity</th>
<th>Structural formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stearic acid (SA)</td>
<td>Aldrich ≥ 99 %</td>
<td>CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{16}COOH</td>
</tr>
<tr>
<td>N,N-dimethyldodecylamine (NN-DMDA)</td>
<td>Fulka ≥ 99 %</td>
<td>CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{11}N(CH\textsubscript{3})\textsubscript{2}</td>
</tr>
</tbody>
</table>

3.1.5. Asphaltene
Asphaltene is prepared by precipitation from crude oil in excess of n-heptane (1:40) according to ASTM standard method. The mixture of n-heptane and crude oil is shaken for at least twice a day and then left for 48 hours to equilibrate. The mixture solution was then centrifuged and filtered through a 0.22 micrometer filter (Millipore), and dried for 1 day under vacuum at room temperature. The dried asphaltene was then dissolved in toluene.

3.1.6. Aqueous phase
In all experiments, distilled water (DW) was used in preparation of the different salt solutions and also used as a reference in some experiments.
Material, Methods and Approaches

Na₂SO₄, MgCl₂ and NaCl were dissolved in distilled water to prepare 0.1 M brine solutions in order to investigate their influence on the interaction between organic adsorbates and mineral surfaces and also on oil recovery by CO₂ flooding/imbibition. Some experiments also have been performed for cores initially saturated with synthetic seawater (SSW) and low salinity water (LSW). The composition of synthetic seawater is shown in Table 3.4. Low salinity water is obtained by 1:25 dilution of synthetic seawater with DW.

Table 3.4. Synthetic sea water composition

<table>
<thead>
<tr>
<th>Ions</th>
<th>Concentration (mol/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>0.4</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.01</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.013</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.045</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>0.002</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.024</td>
</tr>
<tr>
<td>TDS</td>
<td>0.494</td>
</tr>
</tbody>
</table>

3.2. METHODS

3.2.1. Water vapor adsorption isotherms

The specific surface areas of the unmodified solid powders were determined by nitrogen and krypton adsorption at 77 K using manometric apparatus, ASAP 2010 from Micromeritics and AUTOSORB-1 from Quantachrome, respectively. Vapor adsorption isotherms were determined gravimetrically at 25 °C using TGA Q 5000 apparatus for both unmodified and modified
samples to estimate the surface areas and characterise surface in terms of hydrophilicity/hydrophobicity.

3.2.2. Thermo Gravimetric Analysis (TGA)
The adsorbed amount of polar components onto the mineral surface was estimated by the weight loss measured by thermogravimetric analysis (TGA). High resolution Thermo Gravimetric Analyzer (TGA Q500 from TA instrument) was used to scan a wide variety of potential adsorbates. The sample was placed in an alumina pan, equilibrated at 30 °C and then heated to 600 °C at the rate of 10°C/min under dried air flow (40 ml/min).

3.2.3. Contact angle measurements
Pieces of calcite and quartz were filed using silicon carbide grinding powders from 120 grits to 4000 grits. The water-wetness of the crystalline pieces was checked by placing a drop of water on the surface before and after filing. After filing, the samples were washed with distilled water and dried for 24 hours under vacuum and the temperature of 120 °C. Contact angle measurements were carried out at 25 °C for two types of mineral surface modifications. In first type, three samples were prewetted in distilled water, 0.1 M concentration of magnesium chloride and 0.1 M sodium sulfate for 30 min. Then, the pieces were immersed in 0.01 M SA dissolved in n-decane (for calcite), 0.01 M NN-DMDA dissolved in n-decane (for quartz) and 0.35 wt% of asphaltene dissolved in toluene (both minerals) for 24 h. The modified minerals pieces were then taken out and washed with n-heptane and dried for 3 h and room temperature. For the second type, the sample is prewetted in 0.01 M Mg²⁺ and 0.01 SO₄²⁻. Then, the sample is aged in dissolved polar component solutions for 24 hours and finally is immersed in 0.1 M solutions of MgCl₂ and Na₂SO₄ or DW over night. After this period of time, the
modified sample is taken out and washed with \( n \)-heptane and then dried under vacuum at room temperature for 3 hours.

3.2.4. **Enthalpy measurements of water vapor adsorption**

Interaction of water vapor on the modified sample with different organic adsorbates can be compared with unmodified sample in term of adsorption enthalpy. The experimental results are interpreted by coupling of heat effects measured by microcalorimetry and the amount of water adsorbed on the sample from adsorption isotherms. To measure the water vapor adsorption isotherm, the sample was introduced inside the calorimetric cell and was dried under nitrogen flow (25 ml/min) until thermal equilibrium was observed. Digital acquisition system was used to record calorimetric signal, water relative humidity inside the calorimetric cell and flow properties.

3.2.5. **Enthalpy measurements of CO\(_2\) adsorption**

Adsorption/interaction of CO\(_2\) with mineral powder surfaces are addressed using microcalorimetric method coupled with gas chromatograph as a detector.

3.2.6. **Adsorption of polar components on mineral surfaces**

Two types of modification were carried out. In the first case, the powder was dried at 150 °C for at least 48 hours under vacuum condition and the liquids (normal decane or toluene) were dried over molecular sieves (0.4 nm) for one night before modification. In the second case the dried solids were first placed in a desiccator in the presence of a saturated solution of K\(_2\)SO\(_4\) for a period of 10 days at 25°C. The saturated solution of a salt provides constant relative humidity and vapor pressure (Wexler and Seinfeld, 1991). For K\(_2\)SO\(_4\) solution, the relative humidity reaches about 97 % at 25 °C which provides sufficient layers of water on the mineral surface to investigate its effect on
subsequent adsorption of organic adsorbates (Rezaei Gomari et al. 2006). For both types of modification, 0.01 M solution of stearic acid (SA) and N,N-dimethyldodecylamine (NN-DMDA) in normal decane were prepared. To investigate the role of asphaltene and co-presence of asphaltene and natural surfactants on wettability alteration of minerals, 0.35 wt% of asphaltene was dissolved in toluene and added to 0.01 M solution of stearic acid and N,N-dimethyldodecylamine (NN-DMDA). Then, two grams of mineral powder were weighted in stopper glass tubes and 20 ml of solution were added. The samples were stirred with a slowly rotating agitator (50 rpm) for 24 h. This period of time was found to be sufficient to reach equilibrium as reported in the literature (Madsen et al., 1996; Kokal et al., 1995; Rezaei Gomari et al., 2006). The suspension was centrifuged for 30 min at 4500 rpm. The solid phase was separated from the liquid, redispersed in toluene for washing, and centrifuged again for 10 min at 4500 rpm. Finally, the solid was dried under vacuum condition at 25 °C.

### 3.2.7. Displacement of polar components by ions from mineral surfaces

In order to determine the interaction of different ions with the pre-adsorbed polar components on the mineral surfaces, modified samples with organic adsorbates were immersed in distilled water, 0.1 M Na₂SO₄ and 0.1 M MgCl₂ solutions. Then the sample was stirred with a slow rotating agitator (50 rpm.) for 24 hours. To separate the solid from liquid phase, the solution was centrifuged for 30 min at 4500 rpm and then dried under vacuum condition and room temperature.

### 3.2.8. Preparation of dead and live oils

The work done here is for synthetic dead oil and two types of live oil, namely live oil A and live oil B. The compositions of dead oil, live oil A and live oil
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B are shown in Table 3.5. The synthetic dead (model) oil is composed of 0.25 g asphaltene dissolved in 22 ml toluene, 0.01M stearic acid (SA) dissolved in n-decane (95% purity) for saturating the chalk cores. 0.01M N,N-dimethylldodecylamine (NN-DMDA) dissolved in n-decane is used for saturating the sandstone cores. Stearic acid (SA) and N,N-dimethylldodecylamine (NN-DMDA) are polar natural fatty acid and amine, respectively. The synthetic live oils are prepared by recombination of gas (C₁ and C₃) to the dead oil at specific gas oil solubility ratio (Rₛ=280 SCF/STB), for detail see Paper V.

Table 3.5. Composition of dead oil, live oil A and live oil B used for CO₂ flooding experiments

<table>
<thead>
<tr>
<th>Components</th>
<th>Dead oil Composition (mole %)</th>
<th>Live oil A Composition (mole %)</th>
<th>Live oil B Composition (mole %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C₁₀</td>
<td>50.88</td>
<td>40.63</td>
<td>39.81</td>
</tr>
<tr>
<td>Stearic acid (or N,N-dimethylldodecylamine)</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Toluene</td>
<td>49.01</td>
<td>39.14</td>
<td>38.34</td>
</tr>
<tr>
<td>Asphaltene</td>
<td>0.06</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>C₁</td>
<td>0.00</td>
<td>20.14</td>
<td>9.87</td>
</tr>
<tr>
<td>C₃</td>
<td>0.00</td>
<td>0.00</td>
<td>11.90</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

3.2.9. CO₂ flooding

Schematic diagram of the experimental setup used for CO₂ flooding experiments is shown in Figure 3.1. The major components of the experimental setup consist of a core holder, pressure regulators, two gas flow meters, pressure manometers, Gilson pump, CO₂ piston cell and graduated gas/oil separator. For data acquisition, lab view version 7.1 is used and
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inlet/outlet pressures, pressure drop and the volume of injected and produced CO₂ are monitored and stored in the computer.

![Figure 3.1. Schematic of CO₂ flooding set up with graduated gas/oil separator.](image)

The CO₂ flooding experiments were done on saturated cores with synthetic dead oil (with and without initial water saturation) and synthetic live oils (without initial water saturation). All cores were aged with dead oil (containing the relevant polar components) for at least two weeks to change the wettability of the cores towards more oil-wet. The CO₂ is injected into the modified and saturated cores with synthetic dead oil. For CO₂ flooding of the saturated cores with live oil, first the dead oil is displaced by live oil with approximately one pore volume with pressure exceeding 20 bar higher than the bubble point pressure. In all experiments, CO₂ injection was carried out at constant pressure and at the miscible mode with pressure equal to MMP. The
flooding conditions are at 90, 120 and 140 ± 0.2 bar with corresponding temperatures of 50, 70 and 80 °C, details are given in Paper V.

3.2.10. Spontaneous imbibition

The cores were initially saturated with different brines (DW, 0.1 M Mg²⁺ and 0.1 M SO₄²⁻) flooded with corresponding model oil and aged at 50 °C. They were then flooded with CO₂ at 50 °C and 90 bar. After CO₂ flooding, the cores were saturated with model oil before carrying out the imbibition tests. The imbibition tests with the different water composition were done at 50, 70 and 90 °C, for the same core to account for the incremental increase due to temperature.

3.3. APPROACHES

3.3.1. Surface energy analysis

Surface pressure at constant temperature is obtained from Eq. (3.1) (Schlangen et al., 1993):

\[
\pi^{SV}(\Gamma) = RT \int_{\Gamma=0}^{\Gamma} \Gamma(\mu) d \ln p
\]

(3.1)

where, \(\pi^{SV}(\Gamma)\) is the surface pressure (mN/m), R is the ideal gas constant (J/K/mol), T is the temperature (K), \(\Gamma\) is the surface excess of vapor on the solid surface (mol/m²) and P is the vapor pressure (Pa).
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The specific surface area of solid powders is calculated based on gas or water vapor isothermal adsorption from the BET monolayer capacity \( (n_m) \) by (Rouquerol et al., 1999):

\[
\alpha(BET) = n_m N_A \sigma
\]  

(3.2)

where, \( N_A \) is the Avogadro constant \( (6.02214 \times 10^{23} \text{ mol}^{-1}) \) and \( \sigma (\text{Å}^2) \) is the average area occupied by each molecule in the completed monolayer (i.e. the molecular cross-sectional area). Brunauer et al. (1983) proposed that the molecular cross-sectional area can be calculated from the density of the liquid adsorbate from the bulk liquid as follows:

\[
\sigma = f \left( \frac{M}{\rho L} \right)^{\frac{2}{3}}
\]  

(3.3)

where, \( f \) is a packing factor, which for hexagonal close-packing becomes 1.091, \( \rho (\text{g} / \text{m}^3) \) is the absolute density of the liquid adsorptive at the operational temperature and \( M (\text{g} / \text{mol}) \) is the molar mass of the adsorptive. The adsorbed monolayer \( (n_m) \) is estimated from the linear plot of BET equation. The linear region of BET equation is expressed as follow:

\[
\frac{P / P^*}{n(1 - P / P^*)} = \frac{1}{n_m C} + \frac{C - 1}{n_m C} \left( \frac{P}{P^*} \right)
\]  

(3.4)

where, \( P / P^* \) is the partial pressure of adsorbing vapor, \( n \) is the amount of adsorbed vapor \( (\text{mol} / \text{g}) \) on the solid powder, \( C \) is constant and \( n_m \) is the monolayer capacity. Thus, the plot of \( \frac{P / P^*}{n(1 - P / P^*)} \) versus \( P / P^* \) should be a straight line with an intersection (i) and slope (s). The monolayer capacity is calculated by:
In the original work of Brunauer et al. (1983), it was found that the type II and III isotherms on various adsorbents give the linear plots over the approximate range of \( P / P^0 \) between 0.05 and 0.35 (Rouquerol et al., 1999).

### 3.3.2. CO\(_2\) adsorption

Areas under the peaks as a function of retention time that are corresponding to CO\(_2\) and N\(_2\) are estimated and related to the corresponding concentrations using:

\[
C_{CO_2}(t) = \frac{A_{CO_2}(t)}{A_{CO_2}^{Max}} \cdot C_{CO_2}^o
\]

In this equation, \( C_{CO_2}(t) \) is the concentration of CO\(_2\) (mol/L) at the corresponding retention time, \( A_{CO_2}(t) \) is the area under CO\(_2\) peak at the specific retention time \( t \), \( A_{CO_2}^{Max} \) is the peak area of CO\(_2\) of the total injected gas without retention and \( C_{CO_2}^o \) is the concentration of the injected CO\(_2\) which is calculated by:

\[
C_{CO_2}^o = \frac{P_{Total} \cdot X_{CO_2}}{RT}
\]

where, \( P_{Total} \) is the total pressure (Pa), \( X_{CO_2} \) is the mole fraction of input injected gas, \( R \) is the ideal gas constant (J/K/mol) and \( T \) is the temperature (K). The adsorbed CO\(_2\) (mol) is then calculated from the breakthrough of the reference (blank) and sample. From the breakthrough curve, the amount of CO\(_2\) reaching the detector is estimated:

\[
n_{CO_2} = \int_0^t C_{CO_2}(\tau)q_{d\tau}
\]
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In this equation, $n_{CO_2}$ is the adsorbed CO$_2$ quantity (mol), $C_{CO_2}(t)$ is CO$_2$ concentration passing through GC (mol/L), $q_i$ is total gas flow (m$^3$/min) and $t$ is the experimental time, which is the time that the heat reaches a plateau. The difference between the calculated amounts of CO$_2$ (mol) from the blank and sample is related to the amount of CO$_2$ adsorbed by the sample:

$$n_{CO_2}^{S} = n_{CO_2}^{Bl} - n_{CO_2}^{Exp}$$

(3.9)

where, $n_{CO_2}^{S}$ is adsorbed CO$_2$ (mol) on the surface, $n_{CO_2}^{Bl}$ is the detected CO$_2$ (mol) from the blank experiment and $n_{CO_2}^{Exp}$ is the detected CO$_2$ (mol) from the experiments.

In addition, CO$_2$ adsorption enthalpies for samples modified by different organic adsorbates are measured at the adjusted relative humidity of 40%. The heat flow due to CO$_2$ is given by:

$$Q = \int_{0}^{t} V dt$$

(3.10)

In this equation, $Q$ (kJ) is the heat flow due to CO$_2$ adsorption, $V$ (mV) is the microcalorimetry signal, $t$ (sec) is time and $f$ (mV sec/kJ) is the microcalorimetry conversion factor. The adsorption enthalpy of adsorbed CO$_2$ on the mineral surface is:

$$H = \frac{Q}{n_{CO_2}^{S}}$$

(3.11)

3.3.3. CO$_2$ Enhanced oil recovery

The relative magnitude of diffusive force to convective dispersion (bulk flow or viscous force) during miscible processes may be expressed as diffusion number according to Eq. (3.12).
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\[ N_d = \frac{D\phi}{\nu_{CO_2} l} \]  \hspace{1cm} (3.12)

In this equation, \( D \) is the diffusivity coefficient according to the Ficks law between \( CO_2 \) and oil, \( \phi \) is the porosity; \( l \) is the length of capillary tube and \( \nu_{CO_2} \) is the linear velocity of the injected \( CO_2 \) through porous medium. The diffusivity coefficient \( (D) \) between \( CO_2 \) and oil can be estimated from the following equation (Renner, 1988):

\[ D = 10^{-9} \mu_{CO_2}^{-0.4562} M_o^{-0.6898} V_{CO_2}^{-1.706} P^{-1.831} T^{4.524} \]  \hspace{1cm} (3.13)

In this equation, \( D \) is the diffusivity coefficient between \( CO_2 \) and oil \((m^2/sec)\), \( \mu_{CO_2} \) is viscosity of \( CO_2 \) \((cp)\), \( M_o \) is the molecular weight of oil \((g/mol)\), \( V_{CO_2} \) is the molar volume of \( CO_2 \) \((cm^3/mol)\), \( P \) \((psia)\) is the pressure of \( CO_2 \) and oil system in equilibrium and \( T \) \((Kelvin)\) is the temperature of \( CO_2 \) and oil system in equilibrium. Both diffusion and convective dispersion have profound influences on miscible processes. At low injection (or production) rate, diffusion tends to dominate and at high injection (or production) rate convective dispersion is more prominent. The diffusivity of \( CO_2 \) in distilled water and seawater could be estimated based on (Al-Rawajfeh, 2004):

\[ \log(D_{CO_2,w}) = -4.1764 + \frac{712.52}{T} - \left( \frac{2.5907 \times 10^{4}}{T^2} \right) \]  \hspace{1cm} (3.14)

\[ \log\left(\frac{D_{CO_2,sw}}{D_{CO_2,w}}\right) = 0.87 \log\left(\frac{\mu_{sw}}{\mu_w}\right) \]  \hspace{1cm} (3.15)

In these equations, \( D_{CO_2,w} \) is the diffusivity of \( CO_2 \) in distilled water \((cm^2/sec)\) and \( D_{CO_2,sw} \) is the diffusivity of \( CO_2 \) in seawater \((cm^2/sec)\). \( \mu_w \) and \( \mu_{sw} \) are the viscosities of distilled water and sea water, respectively. \( T \) is the temperature
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in Kelvin, \( \mu_{sw} \) is viscosity of seawater (cp) and \( \mu_w \) is viscosity of distilled water.

The longitudinal dispersion coefficient (in the direction of gross fluid flow) and transverse dispersion coefficient (transverse to the direction of gross fluid flow) is calculated by the following equations based on the work reviewed of Perkins and Johnston (1963) and Alkindi et al., (2011).

\[
\frac{K_L}{D} = \frac{1}{F \phi} + 0.5 \frac{v d_p}{\phi D} \quad (3.16)
\]

\[
\frac{K_T}{D} = \frac{1}{F \phi} + 0.0157 \frac{v d_p}{\phi D} \quad (3.17)
\]

In these equations, F is Archie resistivity factor, \( v \) is Darcy velocity (m/sec), \( \phi \) is porosity, \( d_p \) is particle diameter (m) and D is diffusivity coefficient (m²/sec). The Archie resistivity factor can be estimated from Eq. (3.18) and Eq. (3.19) for sandstone and carbonate rocks, respectively (Tiab and Donaldson, 2004).

\[
F = \frac{0.62}{\phi^{2.15}} \quad (3.18)
\]

\[
F = \frac{1}{\phi^{5}} \quad (3.19)
\]

For consolidated porous media, the particle diameter \( d_p \) can be estimated from Carman-Kozeny correlation according to Eq. (3.20) and Eq. (3.21) (Tiab and Donaldson, 2004).
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\[ K = \left( \frac{1}{5SV_{gr}} \right) \frac{\phi}{(1-\phi)^2} \] (3.20)

\[ SV_{gr} = \frac{6}{d_p} \] (3.21)

Where in this equation, \( K \) is the permeability of porous media (m\(^2\)), \( SV_{gr} \) is the total area exposed within the pore space per unit of grain volume and \( d_p \) is particle diameter (m).

Perkins and Johnston (1963) and Alkindi et al. (2011) reported that at low velocities \( (0.5v d_p / \phi D < 1) \), the molecular diffusion dominates in longitudinal mixing. For moderate velocities \( (0.1 < 0.5v d_p / \phi D < 4) \) both molecular diffusion and convective mixing are important transport mechanisms and at higher flow rates \( (0.5v d_p / \phi D > 4) \), convective dispersion dominates the mixing process. Similarly in case of transverse dispersion, for values of \( 0.5v d_p / \phi D < 50 \), molecular diffusion dominates in transverse mixing while convective dispersion was found to be the dominant mechanism in transverse mixing when \( 0.5v d_p / \phi D > 300 \).

The development of miscible mixing bank is rapid at first but the rate decreases as the displacement advances. The length of the miscible mixing bank may be defined by the zone within which the concentration of CO\(_2\) varies from 90% to 10% of the injected concentration. The mixing zone length (\( \Delta x \)) depends on CO\(_2\) velocity and the distance (x) traveled by CO\(_2\). This is expressed as follow (Marle, 1981; Collins, 1961):

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The mixing zone index \( I \) can be defined as the fraction of the total distance traveled by CO\(_2\):

\[
I = \frac{\Delta x}{x} = 3.625 \sqrt[3]{\frac{K_L x}{v}}
\]  

(3.23)

In miscible gas flooding processes, the transverse dispersion will tend to cause merging of the formed fingers (Gardner and Ypma, 1984; Stalkup, 1983; Alkindi et al., 2011).

The effect of transverse dispersion on viscous instability may be described by definition of viscous fingering number as follows:

\[
N_{vf} = \frac{K_T L \phi}{\nu w^2}
\]  

(3.24)

Where \( K_T \) is transverse dispersion coefficient (m\(^2\)/sec), \( L \) is displacement length (m), \( \nu \) is Darcy velocity (m/sec), \( \phi \) is porosity and \( w \) is the width over which displacement takes place (m). The number represents the ratio of convective transport time \((1/\nu)\) to dispersive transport time \((w^2/K_T)\).

Larger values of \( N_{vf} \) indicates that the convection time is longer compared to the dispersion time and the displacement is more stable.
4. MAIN RESULTS AND DISCUSSION

The main results are summarized and discussed in this section to address the main project objectives. Detailed results and discussion are presented in the enclosed papers.

In order to achieve the objectives of this thesis, the work is divided into two main parts. The first part concerns with mineral surface modification to more oil-wet. This was a challenging activity especially for silicate minerals which are strongly water-wet, and have higher mineral surface stability, compared to calcite. The modified surfaces are verified using different methods to assess the degree of the modification. The second part addresses oil recovery by miscible CO₂ flooding for both sandstone and chalk rocks. The behaviour of the different minerals in the recovery process, effect of ions (initial water saturation), and influence of CO₂ flooding on asphaltene precipitation are addressed.

4.1. Wettability alteration of calcite, quartz and kaolinite minerals

4.1.1. Isothermal water vapor adsorption isotherm
4.1.2. Contact angle
4.1.3. Stability of adsorbed polar components in presence of ions

4.2. CO₂ Miscible Recovery

4.2.1. CO₂ adsorption on calcite, quartz and kaolinite minerals modified by polar components
4.2.2. Influence of light components on oil recovery from chalk and sandstone
   4.2.2.1. Development of viscous stability/instability during CO₂ flooding
   4.2.2.2. Phase behaviour of CO₂/hydrocarbon system
4.2.3. Effect of different ions on oil recovery by CO₂ flooding and imbibition post flooding
4.2.4. Influence of miscible CO₂ flooding on asphaltene precipitation
4.1. Wettability alteration of calcite, quartz and kaolinite minerals

**Paper II** and **Paper III** address the wettability alteration of carbonate and silicate minerals (calcite, quartz and kaolinite) by different polar components (stearic acid, N,N-dimethyldodecylamine and asphaltene) and the influence of $SO_4^{2-}$ and $Mg^{2+}$ on modified minerals to more oil-wet.

### 4.1.1. Isothermal water vapor adsorption

The isothermal water vapor adsorption on mineral surfaces is done at 25 °C. A comparison between unmodified and modified quartz, calcite and kaolinite minerals are shown in Figure 4.1a and Figure 4.1b, respectively. Adsorption isotherm on quartz surface appears to be type II according to IUPAC classification. The isotherm for kaolinite shows lower affinity to absorb water and appears to be between type II and type III of IUPAC classification. In contrast to quartz and kaolinite, the calcite surface is shown to be of type III and the interaction of water and surface is rather weak. To examine the magnitude of water vapor adsorption on the solid surface in details, the numbers of water layer are addressed in **Paper II** where the relative vapor pressure ($P/P^0$) is equal to 0.15. At this relative vapor pressure, the numbers of adsorbed water layers are estimated to be 1.13, 0.52 and 0.19 for quartz, kaolinite and calcite, respectively. This may be interpreted that quartz surface is more hydrophilic compared to other minerals, which is expected. Surface pressure of quartz is estimated to be 265 (mN/m), which is approximately twice as high as that for kaolinite (140 mN/m) and three times higher than calcite (75 mN/m), are shown in Figure 4.2. The high surface pressure of kaolinite and quartz may be related to the strong hydrogen bond between water and OH groups at the silicate surface.
Figure 4.1. Water vapor adsorption isotherms on: a) unmodified minerals and b) modified minerals.
Main Results and Discussion

![Graph](image)

Figure 4.2. Surface pressure calculated from adsorption isotherms for unmodified minerals.

Figures 4.3, 4.4 and 4.5 show the surface pressure calculated from the area under water vapor adsorption isotherms using Eq. (3.1) for modified quartz, calcite and kaolinite. For unmodified quartz and modified quartz by NN-DMDA, the adsorption is type II while modified quartz by asphaltene and modified quartz by co-presence of NN-DMDA and asphaltene appear to be type III according to IUPAC classification where the amount of water adsorbed is very low near the saturation pressure. As it can be seen from the figure, the amount of vapor adsorbed on the surface and the degree of hydrophilicity may be classified by the following order: unmodified quartz > dried quartz modified with NN-DMDA > dried quartz modified with asphaltene > dried quartz modified by co-presence of NN-DMDA and asphaltene.
Near saturation pressure where several layers of water are present, the surface pressure approaches to a plateau. The plateau may be used to investigate the hydrophilicity/hydrophobicity of the surfaces. In the case of unmodified quartz, the calculated surface pressure is equal to 265 (mN/m), this corresponds to formation of approximately 9 layers of adsorbed water on the surface. For modified quartz by NN-DMDA, asphaltene and co-p resonance of these organic components, the surface pressures are 155 (mN/m) and 41 (mN/m), respectively which corresponds to approximately 7.4 and 3.3 and 2.7 water layers.

This demonstrates the ability of asphaltene and NN-DMDA to alter the wettability of kaolinite towards more oil-wet as the surface pressure of modified kaolinite by NN-DMDA more to be 92 (mN/m) and the surface pressure of modified kaolinite by asphaltene is close to 47 (mN/m). However, modification of calcite with stearic acid and asphaltene is shown to be more hydrophobic compared to the treated quartz and kaolinite with NN-DMDA and asphaltene where the surface pressure of modified calcite by SA and asphaltene are 32 (mN/m) to 8.7 (mN/m), which correspond to 1.56 and 0.66 water layers, respectively. Paper II addresses the approach taken for assessment of modification and the number of adsorbed layers and the effect of surface humidity on the degree of surface wettability alteration.
Main Results and Discussion

Figure 4.3. Isothermal water vapor surface pressure curves for modified quartz minerals.

Figure 4.4. Isothermal water vapor surface pressure curves for modified calcite minerals.
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Figure 4.5. Isothermal water vapor surface pressure curves for modified kaolinite minerals.

4.1.2. Contact angle

Effect of SO$_4^{2-}$ and Mg$^{2+}$ on modified calcite and silicate surfaces, taken DW as a reference, is investigated by contact angle measurements. The measured contact angles are shown in Figures 4.6 and 4.7, for modified calcite with SA and asphaltene and modified quartz with NN-DMDA and asphaltene, respectively. Effects of sulfate and magnesium ions on the wettability consistently reduce the advancing contact angles by about 20 and 41 and about 21 and 49% from that for DW, for calcite and quartz minerals. In other words, SO$_4^{2-}$ and Mg$^{2+}$ ions, made the calcite surface to more water-wet for both SA and asphaltene. Modification of quartz surface with NN-DMDA, shows similar trend as that for calcite, in presence of SO$_4^{2-}$ and Mg$^{2+}$. While the contact angle in case of modifying quartz surface to more oil wet with asphaltene seems to be consistent, where the contact angle is reduced by about
Main Results and Discussion

5% in presence of DW, which is almost same to that in case of NN-DMDA. However, in the case of modification of quartz with asphaltene in presence of magnesium ions, contact angle increased by about 42%. As a condition from this part of verification, contact angle are with the obtained trend from water vapor adsorption isotherm.

Figure 4.6. Comparison of contact angle for unmodified and modified calcite with asphaltene and stearic acid in presence of 0.1 M Mg\(^{2+}\), 0.1 M SO\(_4\)^{2-} and DW.


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4.1.3. Stability of adsorbed polar components in presence of ions

The effect of $\text{SO}_4^{2-}$ and $\text{Mg}^{2+}$ on stability on SA, NN-DMDA and asphaltene on calcite and silicate minerals is investigated. Figure 4.8 shows adsorption isotherms of water on unmodified calcite and modified calcite by stearic acid (SA) and asphaltene (Asph.) in presence of DW, $\text{SO}_4^{2-}$ and $\text{Mg}^{2+}$. As it can be seen from these figures, in terms of hydrophilicity qualitative ranking may be presented as follow: unmodified calcite $>$ modified calcite with SA (or Asph.) in presence of $\text{Mg}^{2+}$ $>$ modified calcite with SA (or Asph.) in presence of $\text{SO}_4^{2-}$ $>$ modified calcite with SA (or Asph.) in presence of DW. In contrast to $\text{SO}_4^{2-}$, which shows a significant effect on adsorption of SA, DW has minor effect. This has been addressed in Paper III which may be explained by the change of the surface charge of the modified calcite in presence of $\text{SO}_4^{2-}$ from positive to a negative charge while such effect is not occurring in presence of DW alone.
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Figure 4.8. Water vapor adsorption isotherms on unmodified and modified calcite in presence of 0.1 M Mg$^{2+}$, 0.1 M SO$_4^{2-}$ and DW: a) modification with SA and b) modification with asphaltene.
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It is observed that Mg$^{2+}$ ions enhance the hydrophilicity of modified calcite surfaces with SA and asphaltene more than that in case of SO$_4^{2-}$ and DW. The exact mechanism(s) by which magnesium ions change the wettability of calcite surface is not fully understood, however it has been shown by Petrovich and Hamouda (1998) that an interaction between Mg$^{2+}$ and calcite surface is taken place. The preferential interaction of calcite with magnesium ions reduces the possible interaction with other competing ions/molecules for the calcite surface.

Adsorption isotherm of water vapor on unmodified and modified quartz surface with NN-DMDA in presence of ion free water (DW), 0.1 M SO$_4^{2-}$ and 0.1 M Mg$^{2+}$ is shown in Figure 4.9a. No significant difference between the modification in presence of DW and SO$_4^{2-}$ is observed. Similar to calcite/SA system, modification in presence of Mg$^{2+}$ shows more hydrophilic surface than that in the case with SO$_4^{2-}$. The effects of ions for treated quartz with asphaltene are shown in Figure 4.9 b. Unlike all the studied cases with modification of the mineral surfaces, the presence of Mg$^{2+}$ makes the modified quartz with asphaltene more hydrophobic. Again, SO$_4^{2-}$ ions show almost similar effect on the quartz surface hydrophilicity to that with DW. Presence of Mg$^{2+}$ in initial water saturation may interlock the negatively charged asphaltene molecules to the negatively charged quartz surface; hence it may act as a bridging ion during wettability alteration process. In case of kaolinite surface modified with NN-DMDA and asphaltene, as shown in Figures 4.10, the adsorption isotherms of water, in presence of SO$_4^{2-}$ and DW are almost the same, while in presence of Mg$^{2+}$ less water vapor adsorbed on the surface compared to the case of DW and SO$_4^{2-}$. 
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Figure 4.9. Water vapor adsorption isotherms on unmodified and modified quartz in presence of 0.1 M Mg²⁺, 0.1 M SO₄²⁻ and DW: a) modification with NN-DMDA and b) modification with asphaltene.

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Figure 4.10. Water vapor adsorption isotherms on unmodified and modified kaolinite in presence of 0.1 M Mg$^{2+}$, 0.1 M SO$_4^{2-}$ and DW: a) modified with NN-DMDA and b) modification with asphaltene.
Main Results and Discussion

This is inline with the explanation, where asphaltene/magnesium bridging may have occurred at the kaolinite surface. The exact mechanism is not fully understood, however, in the previous work (Chukwudeme and Hamouda, 2009) and the work reported by Yan et al. (2009) explained in different experiments, possible bridging as an explanation. In other flooding experiments for enhance heavy oil recovery by alkaline flooding; it was found that oil recovery was greatly affected as wettability alteration of water-wet grains to preferentially oil-wet due to magnesium ion bonding which is observed in micro model tests (Liu, 2007).

To determine the effect of SO\(_4^{2-}\) and Mg\(^{2+}\) on displacing the adsorbed organic materials on the surface of the mineral powders, after modification of humidified mineral surfaces to more hydrophobic, minerals were, then immersed in 0.1 M Na\(_2\)SO\(_4\) and 0.1 M MgCl\(_2\) following the modification procedure. Thermal gravimetric analysis (TGA) was then performed. The surface area coverage per molecule of the adsorbent (i.e., the cross sectional area of adsorbate) from the TGA results are compared. Table 4.1 shows the calculated cross-sectional surface area per molecule of stearic acid, N, N-dimethyldodecylamine and asphaltene. It also, shows the estimated cross-sectional surface area per molecule in presence and absence of Mg\(^{2+}\) and SO\(_4^{2-}\) ions. Accordingly, it may be concluded that SO\(_4^{2-}\) and Mg\(^{2+}\) ions may displace the preadsorbed polar components and/or affect the packing system of adsorbate depending on the characteristics of mineral surface and the type of polar component. This may be explained by the like surface charge of silicate minerals and SO\(_4^{2-}\); hence low interaction. In the case of the modified calcite with stearic acid and asphaltene, the adsorbed organic molecules may be displaced by SO\(_4^{2-}\), due to affinity to ability of SO\(_4^{2-}\) to surface calcium ions.
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The apparent surface coverage of the modified calcite powders changed from about 16.58 and 30.36 Å²/molecule in case of displacement with DW to 23.54 and 40.85 Å²/molecule in case of displacement with 0.01M of Mg²⁺ and to 18.35 and 34.62 Å²/molecule in case of displacement with SO₄²⁻ for SA and asphaltene, respectively. In case of silicate minerals, the effect of SO₄²⁻ displacement on the occupied areas by individual component, i.e. NN-DMDA and asphaltene are almost identical to that case with DW displacement, again in agreement with results obtained by isothermal adsorption of water vapor on modified surfaces.

Table 4.1. Calculated surface area coverage σ (Å²) per molecule of organic adsorbate for different minerals and ions

| Type of modification          | σ (Å²/molecule) | Calcite | Quartz | Kaolinit |e |
|------------------------------|-----------------|---------|--------|----------|
| Modification in DW           |                 |         |        |          |
| SA                           | 16.58           | 18.68   | 16.97  |          |
| N,N-dimethyldodecylamine     |                 |         |        |          |
| Asph.                        | 30.36           | 68.26   | 61.25  |          |
| Modification in 0.01 M Mg²⁺   |                 |         |        |          |
| SA                           | 23.54           | 28.01   | 20.76  |          |
| N,N-dimethyldodecylamine     |                 |         |        |          |
| Asph.                        | 40.85           | 99.01   | 76.33  |          |
| Modification in 0.01 M SO₄²⁻ |                 |         |        |          |
| SA                           | 18.35           | 18.64   | 16.92  |          |
| N,N-dimethyldodecylamine     |                 |         |        |          |
| Asph.                        | 34.62           | 68.01   | 61.03  |          |
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During displacement of adsorbed components on the silicate surface with Mg\(^{2+}\), in the case of quartz, respectively for NN-DMDA and asphaltene, the occupied areas increased from 18.68 to 28.01 and from 68.26 to 99.01 Å\(^2\)/molecule. In the case of kaolinite, the occupied areas by molecules increased from 16.97 to 20.76 and from 61.25 to 76.33 Å\(^2\)/molecule. In summary, it is very interesting to see that the percentage increase of the occupied areas by molecules in case of Mg\(^{2+}\) are about 33\% (±2\%) and 20\% (±2 \%), for quartz and kaolinite minerals, respectively. It may be stated in general that larger effect of Mg\(^{2+}\) on both silicates minerals than that in case of SO\(_4^{2-}\) is observed, which has almost no effect on the adsorbed molecules, NN-DMDA and asphaltene (Paper III).
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4.2. CO₂ Miscible Recovery

In order to understand the CO₂ recovery mechanism(s), this section is divided into four parts dealing with CO₂/rock interaction, influence of light components on oil recovery from chalk and sandstone, effect of different ions (as initial water saturation) on oil recovery by CO₂ and influence of miscible CO₂ flooding on asphaltene precipitation.

4.2.1. CO₂ adsorption on calcite, quartz and kaolinite minerals modified by polar components

Paper IV addresses the interaction of CO₂ with unmodified/modified carbonate and silicate minerals by oil soluble polar components. It is documented that kaolinite has the highest CO₂ adsorbent compared to other tested minerals, followed by calcite and then quartz. However, taken into account the surface area, where kaolinite has the surface area about 15 times higher than quartz and calcite (Paper II), it can be seen in Figure 4.11 for injected gas containing 10 % and 40 % mol of CO₂ that calcite has approximately 10 times higher moles of adsorbed CO₂ per unit area (μmol/m²) than for silicate minerals. The chemical reaction may simply be expressed as:

\[ \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{CO}_3^{2-} + 2\text{H}^+ \quad (4.1) \]

Figure 4.12 compares the adsorption enthalpies of CO₂ on unmodified mineral surfaces, for injected gas containing 10 and 40 % mol of CO₂. As shown, the adsorption enthalpies of CO₂ over calcite are higher than silicate minerals. It can be also seen that, for all minerals, the adsorption enthalpy decreases as the surface coverage increases.
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Figure 4.11. Estimated adsorbed CO\textsubscript{2} mass for unmodified minerals at 25°C and relative water vapor pressure of 0.4.

Figure 4.12. Estimated adsorption enthalpy of CO\textsubscript{2} on unmodified minerals at 25°C and relative water vapor pressure of 0.4.
The modified calcite powder with SA and asphaltene also shows low adsorption of CO$_2$. Figure 4.13 shows the adsorption enthalpies of CO$_2$ over modified minerals, when the injected gas contains 10 % and 40 % mol of CO$_2$. In contrast to adsorption of CO$_2$ on modified surfaces with SA and asphaltene, NN-DMDA shows relatively high heat of adsorption (62 kJ/mol for 40 % mole of injected CO$_2$ and 95 kJ/mol for 10% mole of injected CO$_2$). This is in good agreement with reported values (60-90 kJ/mol) in the literature (Chafee et al., 2007). This may be due to reaction between weak base, resulted from ionization of the amine group in DMDA, and the weak acid (HCO$_3^-$).
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Figure 4.13. Adsorption enthalpy of CO$_2$ on: a) calcite b) quartz c) kaolinite.
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4.2.2. Influence of light components on oil recovery from chalk and sandstone

CO₂ flooding experiments (dead and live oil samples) are carried out at temperatures of 50, 70 and 90 °C and corresponding pressures of 90, 120 and 140 bar, respectively to be within the minimum miscibility conditions. The oil recoveries after about 2 PV of injected CO₂ at different flooding conditions are compared in Figure 4.14 for saturated sandstone and chalk cores with dead and live oils. In general, the higher the miscibility flooding conditions, the higher the oil recovery. Oil recovery from chalk cores is shown to be higher when compared to sandstone at the same miscibility condition. It is also shown that recovery is reduced in presence of light components. With experimental error of about 2 %, it is shown that increasing miscibility condition shows increase of 8 % recovery between the highest and lowest flooding condition of chalk, while for sandstone it is shown about 6 % recovery. Although the differences in both cases are close to the experimental error (2 %), it is a consistent observation at all conditions. The higher recovery from chalk compared to sandstone is addressed later and is based on possible development of flooding front instability/bypassing phenomenon.

Figure 4.15 shows two production samples with different colours that correspond to the CO₂ flooding experiments in chalk at 50 °C and 90 bar and at 80 °C and 140 bar. Lighter colour samples are obtained after the breakthrough. At higher flooding pressure and temperature, the colour shows three distinct colour graduations compared to that for lower flooding pressure and temperature.
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a)

Figure 4.14. Comparison between oil recovery from chalk and sandstone cores saturated with: (a) dead oil and (b) live oils (A and B) as a function of miscible flooding conditions.
Main Results and Discussion

Figure 4.15. Pictures of produced fluids during CO₂ flooding of dead model oil at flooding conditions of: (a) T=50 °C and P=90 bar and (b) T=80 °C and P=140 bar of chalk cores.

Figure 4.16. compares the three miscible flooding conditions for both sandstone and chalk cores, in the case of dead oil. It is observed that, the mixing zone index (I) increases with elevated miscibility conditions. The lighter colour samples were obtained after the breakthrough. In other words, at higher flooding pressure and temperature, more distinct colour gradations are observed compared to that for lower flooding pressure and temperature. This may, qualitatively, demonstrate that the gradual composition is developed in the CO₂ vaporizing/condensing region(s) as it contacts the residual oil, which is behind the original oil. It is also observed that the mixing zone index is
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higher for chalk cores compared to sandstone cores for the same flooding conditions.

![Figure 4.16. Comparison of mixing zone index for chalk and sandstone cores saturated with dead oil as a function of pressure and temperature.](image)

To compare the performance of miscible CO\textsubscript{2} flooding, the oil recoveries as a function of diffusion number (N\textsubscript{d}) for sandstone and chalk cores saturated with dead oil and live oils are compared in Figure 4.17. Higher oil recovery by CO\textsubscript{2} flooding at elevated miscible flooding conditions is shown. This may be attributed to the growth of miscible bank size accompanied by a reduction in interfacial tension, hence better sweep efficiency. The higher oil recovery from chalk cores compared to sandstone cores may be related to a better sweep efficiency for chalk cores caused by homogenous tight rock permeability. Chalk cores have absolute permeability (2.5-6.5 mD) compared to that for sandstone cores having a range of absolute permeability between 600-900 mD. The observation may be explained by two or a combination of
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The two mechanisms. The first mechanism is related to efficient divergence of the CO₂ flow path in low permeable chalk rocks and creation of larger miscible zone size. The second mechanism is related to surface area of the porous media. Chalk cores have smaller pore throat sizes and higher surface areas compared to that for sandstone cores. Calculation based on Kozeny correlation shows that for the tested chalk cores, the surface area varies between 1.1 and 1.7 m²/g while for sandstone cores the surface area varies between 0.02 and 0.04 m²/g. The higher surface area of chalk cores exposed to the flowing CO₂ could enhance the extraction efficiency.

Figure 4.17. Comparison of oil recovery from all the studied cases, as a function of Nd for sandstone and chalk cores saturated with dead and live oils.

The observed trend of lower recovery in presence of light component, (C₁) and (C₁+C₃), is due to the reduction of the mass transfer between CO₂ and oil, hence diffusion and solubility of CO₂ in the oil are reduced, which in turns affect the recovery efficiency.
4.2.2.1. Development of viscous stability/instability during miscible CO$_2$ flooding

In order to explain the difference in oil recovery from chalk versus sandstone, the stability of CO$_2$ front is addressed in this section. To compare the development of viscous fingering during CO$_2$ flooding, the suggested dimensionless number by Alkindi et al. (2011) is used. Figure 4.18 and Figure 4.19, compare the viscous fingering number ($N_{FV}$) as indication of the viscous instability (viscous fingering number) for dead oil and live oil A and B, respectively.

![Figure 4.18. Viscous fingering number ($N_{FV}$) as a function flooding conditions of chalk and sandstone saturated with dead oil indicating viscous instability.](image-url)
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a)

![Graph showing comparison of viscous fingering number (N_{FV}) as a function of flooding conditions for chalk and sandstone cores saturated with live oil type A (with C_{1} as a recombined gas and GOR=280 SCF/STB).]

b)

![Graph showing comparison of viscous fingering number (N_{FV}) as a function of flooding conditions for chalk and sandstone cores saturated with live oil type B (with C_{1} and C_{3} as a recombined gas and GOR=280 SCF/STB).]

Figure 4.19. Comparison of viscous fingering number (N_{FV}) as a function of flooding conditions for a) chalk and sandstone cores saturated with live oil type A (with C_{1} as a recombined gas and GOR=280 SCF/STB) and b) chalk and sandstone cores saturated with live oil type B (with C_{1} and C_{3} as a recombined gas and GOR=280 SCF/STB).
Figure 4.18 shows the effect of CO\textsubscript{2} miscible flooding conditions on the viscous instability of chalk and sandstone cores saturated with dead oil. The figure indicates by the relatively high convective transport time compared to dispersive transport time, that flooding at elevated conditions (140 bar and 80 °C) tends to enhance the viscous stability. It also suggests that sandstone is more likely to develop viscous instability compared to chalk. Figure 4.19 compares N\textsubscript{VF} for the two live oils (A and B). Similar trends are observed as that for the case of dead oil, where the higher the flooding conditions the more stable the flooding. Figure 4.19b shows that introducing heavier gas such as propane (C\textsubscript{3}) reduces the stability of the flooding front as indicated by the calculated N\textsubscript{VF}. Visual observations of cores after CO\textsubscript{2} flooding are shown in Figure 4.20. The figure indicates that the CO\textsubscript{2}/oil front is more stable in chalk core. In contrast, for sandstone core, clear fingers developed and penetrated the core, causing an early breakthrough and lower sweep efficiency than for chalk core.
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Figure 4.20. Pictures of CO$_2$-oil front instability/fingering after miscible flooding of: a) chalk and b) sandstone cores (The interface between swept oil by CO$_2$ and the less swept oil is traced by dots).

a) CO$_2$-oil front stability in CO$_2$ flooding from chalk core

b) CO$_2$-oil front viscous fingering in CO$_2$ flooding from sandstone core
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4.2.2.2. Phase behaviour of CO\textsubscript{2}/hydrocarbon system

Ternary diagrams of CO\textsubscript{2}-hydrocarbon system are generated using PVTi module of Eclipse version 2010.2. The two miscible conditions selected here are the largest flooding conditions, i.e. 80\(^\circ\)C and 140 bar for both live oils (A and B). Figure 4.21 shows the phase behaviour of the two fluid systems (live oil A and live oil B). As it can be seen for live oil B; the two phase region does not exist, while for live oil A, two phase diagram exists. In both cases, the phase diagram indicates that CO\textsubscript{2} flooding at 80 \(^\circ\)C and 140 bar, is in first contact miscibility flooding mode. This may suggest higher oil recovery is to be expected for live oil B, but this is not the case. Again, the flooding pressure and the pressure drop during the experiment were kept constant at 140 bar and 1 bar, respectively. If it is assumed that the pressure drop, during the flooding, had reached 5 bar, at constant temperature (80 \(^\circ\)C), i.e. the pressure would have been 135 bar instead of 140 bar and CO\textsubscript{2} would have contacted live oil A, causing enriched liquid composition and condensation. In contrast, in the case of live oil B, vaporization is the dominant process as shown in Figure 4.22. In Figure 4.22a, CO\textsubscript{2} contacts the reservoir oil and the enriched liquid composition falls at point L\textsubscript{1}. As more CO\textsubscript{2} condenses into the enriched phase (L\textsubscript{1}), the composition moves along the bubble point curve to the point L\textsubscript{2}. Figure 4.22b shows the ternary diagram representing the vaporizing drive mechanism (extraction) of live oil B by CO\textsubscript{2} flooding at T=80 \(^\circ\)C and P= 135 bar. At this condition, the CO\textsubscript{2} mixes with the reservoir fluid and a mixture composition, separates into a gas phase and liquid phase at equilibrium condition. The monitored pressure drop hardly exceeded 2 bars for any of our experiments, which would produce a dominant flooding mechanism similar to that at 135 bar.
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Figure 4.21. Ternary diagrams for CO2 flooding conditions of 80 °C and 140 bar for: a) live oil A /CO2 and b) live oil B/CO2 systems.

a) Live oil A

b) Live oil B
Main Results and Discussion

Figure 4.22. Ternary diagrams for CO\(_2\) flooding conditions of 80 °C and 135 bar for: a) live oil A /CO\(_2\) and b) live oil B/CO\(_2\) systems.

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4.2.3. Effect of different ions on oil recovery by CO₂ flooding and imbibition post flooding

To investigate the effect of initial water saturation on CO₂ oil recovery performance, chalk and sandstone cores were saturated with different brines (DW, 0.1 M Mg²⁺, 0.1 M SO₄²⁻, SSW and LSW), followed by model oil and aged for a minimum of two weeks. Figure 4.23 compares the oil recovery (estimated based on oil volume rather than total pore volume to normalize the effect of water saturation amounts) by CO₂ flooding at 50 °C and 90 bar for cores with and without water saturation. It can be seen that chalk and sandstone cores initially saturated with water, consistently show lower oil recovery compared to cores without initial water saturation. Chalk and sandstone cores initially saturated with SSW (synthetic sea water) shows higher oil recovery compared to that for cores initially saturated with 0.1 M Mg²⁺ and SO₄²⁻. In contrast, chalk and sandstone cores initially saturated with LSW (low salinity sea water) show lower oil recovery compared to that for cores initially saturated with 0.1 M Mg²⁺ and SO₄²⁻. The lowest oil recovery is obtained from chalk and sandstone with DW as initial water saturation compared. This may be caused by the reduction of the available CO₂ for miscible flooding, which is in agreement with the pervious work reported by Hamouda et al. (2009), where they found that chalk core saturated with Mg²⁺ ions has higher oil recovery compared to that for chalk core saturated with SO₄²⁻ ions. Sandstone core saturated with Mg²⁺ ions (more hydrophobic) has lower oil recovery compared to that for sandstone core saturated with SO₄²⁻ ions (Paper III). In other words, for hydrophilic porous media (water-wet), water is not mobilized and wets the pore walls and oil is maintained at the center of pores; hence the more fraction of injected CO₂ may diffusive into the oil and enhances hydrocarbon vaporization/CO₂ condensation mechanisms.
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Figure 4.23. Effect of the initial water saturation on oil recovery by CO₂ flooding at flooding pressure of 90 bar and flooding temperature of 50 °C.

Figure 4.24 shows a schematic illustration of CO₂ enhanced oil recovery in hydrophilic and hydrophobic porous media. In this figure, oil is the brown color; water is shown by blue and CO₂ is represented by white color.

Figure 4.24. Schematic of rock pore in miscible CO₂ enhanced oil recovery for: a) hydrophilic and b) hydrophobic porous medium.

Al-Rawajfeh (2004) showed that presence of seawater ions (such as Mg²⁺ and SO₄²⁻) reduces significantly the diffusivity and solubility of CO₂ in water;

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hence for cores saturated with Mg$^{2+}$ and SO$_4^{2-}$, less fraction of injected CO$_2$ is dissolved in brine and more CO$_2$ is available for oil recovery by miscible flooding. In Figure 4.25, the diffusivity of CO$_2$ in distilled water, seawater and model oil are compared at different temperatures and pressures. The figure indicates that the diffusion of CO$_2$ in distilled water is higher than the diffusion of CO$_2$ in sea water followed by model dead oil.

![Figure 4.25. Comparison between CO$_2$ diffusivity in distilled water, sea water and oil at different temperatures and pressures.](image)

In order to investigate the effect of ions on oil recovery by spontaneous imbibition conducted after CO$_2$ flooding, chalk and sandstone cores are saturated with different brines (DW, 0.1M Mg$^{2+}$, 0.1M SO$_4^{2-}$) flooded by model oil and aged for at least two weeks at 50 °C. Then the cores are flooded by CO$_2$ at 50 °C and 90 bar before starting the imbibition process. The imbibition experiments are carried out at three different temperatures: 50, 70, and 90 °C. The results from spontaneous imbibition from chalk core are
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compared in Figure 4.26. Highest oil recovery is obtained when Mg\(^{2+}\) and SO\(_4^{2-}\) ions are in the initial water saturation and imbibing fluid is DW. Presence of ions such as Mg\(^{2+}\) and SO\(_4^{2-}\) ions enhance the hydrophilicity of modified chalk cores compared to DW (Paper III); hence higher oil recovery by imbibition. In contrast, DW as initial water saturation enhances the adsorption of polar components on calcite surface; hence lower oil recovery is expected.

Hamouda and Rezaei Gomari (2006) reported incremental oil recovery of 8% for core modified with 0.001 M SA in decane and imbibed by DW, when the temperature was increased from 70 to 90\(^\circ\)C. Karoussi and Hamouda (2007), using DLVO theory and experimental observations concluded that fine detachment may be one of the mechanisms that alter the wettability of the rock at elevated temperature. The possible reasons for higher oil recovery in the case of magnesium may be due to combination of mechanisms such as fine detachment and redistribution of adsorbed molecules. In summary, they found three possible mechanisms that may affect the oil recovery. These mechanisms are fine detachment, ionic interaction and the redistribution of the adsorbed molecules on the surface. In addition, lower IFT is obtained in presence of magnesium ions compared to that in presence of sulfate and distilled water (Chukwudeme, 2009). This may partially explain the reason for higher oil recovery in the case of magnesium ion imbibed into chalk cores compared to SO\(_4^{2-}\) and DW. It is worth mentioning that chalk cores are flooded with CO\(_2\) at 50 \(^{\circ}\)C and 90 bar before imbibition experiments, and asphaltenes may have been precipitated in the cores. Presence of water film (DW) enhances the asphaltenes adsorption on calcite minerals (Paper II); the exact mechanism is not clear, however asphaltene have affinity to hydroxyl group; hence chalk cores initially saturated with distilled water and imbibed
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with Mg$^{2+}$ and SO$_4^{2-}$ are more oil-wet compared to other cases; hence lower oil recovery is expected.

![Figure 4.26](image)

Figure 4.26. Comparison of oil recovery by spontaneous imbibition from chalk cores initially saturated with DW, Mg$^{2+}$ or SO$_4^{2-}$ and imbibed by DW, Mg$^{2+}$ or SO$_4^{2-}$. The cores prior to imbibition experiment have been flooded by CO$_2$ at 50 °C and 90 bar.

Figure 4.27 compares the imbibition oil recovery from sandstone cores. In contrast to chalk cores; the highest oil recovery from sandstone cores is obtained when the cores are saturated with DW and imbibed with Mg$^{2+}$ and SO$_4^{2-}$. **Paper III** shows that in the case of modification with asphaltene in presence of Mg$^{2+}$, silicate (quartz and kaolinite) surfaces become more hydrophobic compared to that in presence of DW and SO$_4^{2-}$, that may be caused by formation of network between hydrated magnesium ions and asphaltene; hence sandstone core saturated initially with Mg$^{2+}$ ions is more hydrophobic compared to other cases saturated with DW and SO$_4^{2-}$ ions and lower oil recovery is expected.
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Figure 4.27. Comparison of oil recovery by spontaneous imbibition from sandstone cores initially saturated with DW, Mg\(^{2+}\) or SO\(_4^{2-}\) and imbibed by DW, Mg\(^{2+}\) or SO\(_4^{2-}\). The cores prior to imbibition experiment have been flooded by CO\(_2\) at 50 °C and 90 bar.

4.2.4. Influence of miscible CO\(_2\) flooding on asphaltene precipitation

There are a wide spread definition of the solubility parameter. Verdirer and Anderson (2005) used the definition where the cohesive energy is equal to the residual internal energy represented by the equation below for liquid solubility parameter. This equation is adapted in this work to account for pressure and temperature effects.

\[
\delta_L = \left( \frac{U_{vap}(T, P = 0) - U_{liq}(T, P)}{V_{liq}(T, P)} \right)^{1/2}
\]  

(4.2)

where \(U_{vap}\) and \(U_{Liq}\) are internal energy of vapor and liquid phases respectively and \(V_{Liq}\) denotes the molar volume of the mixture and are obtained from SRK-Peneloux EOS, using PVTsim version 17 (2007). At miscible flooding condition of 90 bar and 50 °C, a comparison of liquid
solubility parameters for dead and live oils is shown in Figure 4.28 for the different mol % of CO\textsubscript{2} in the liquid. At this flooding condition, asphaltene precipitation is probable. The probability increases with the CO\textsubscript{2} content for both dead and live oil. Live oil A shows slightly less difference between $\delta_a$ and $\delta_L$ at all CO\textsubscript{2} contents compared to live oil B, indicating asphaltene instability.

![Figure 4.28. Comparison between liquid solubility parameter and asphaltene solubility parameter for different types of oil at flooding temperature of 50 °C and flooding pressure of 90 bar.](image)

The results obtained for the model oil at 50, 70 and 80 °C and pressures of 90, 120 and 140 bar are shown in Figure 4.29 to Figure 4.31, respectively. For same CO\textsubscript{2} content, it is shown that the higher the pressure, the higher $\delta_L$ is. At CO\textsubscript{2} content less than 10% mole, the asphaltene is stable for the combined miscible conditions of 50 °C and pressures of 140 and 120 bar (Figure 4.29). When the temperature is then increased, for CO\textsubscript{2} content less than 10% mole, to 70 and 80 °C with corresponding pressures 120 and 140 bar, the asphaltene became in the unstable region (Figure 4.30).
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Figure 4.29. Comparison between liquid solubility parameters and asphaltene solubility parameter for model oil at flooding temperature of 50 °C and different flooding pressures.

Figure 4.30. Comparison between liquid solubility parameters and asphaltene solubility parameter for model oil at flooding pressure of 140 bar and different flooding temperatures.
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Asphaltene is shown to be in the unstable region for the combined miscibility conditions of 50 °C /90bar, 70 °C /120bar and 80 °C /140bar (Figure 4.31). It can also be seen that in all cases, increasing pressure increases the asphaltene stability while increasing the temperature reduces the asphaltene stability.

![Figure 4.31](image)

Figure 4.31. Comparison between liquid solubility parameters and asphaltene solubility parameter for model oil at different miscibility conditions (T=50 °C/P=90 bar, T=70 °C/P=120 bar, T=80 °C/P=140 bar).

For the live oil A and B as shown in Figure 4.32a and Figure 4.32b, respectively, at all temperature/ pressure combinations, the oil lay in the unstable region. It is also shown that, in all cases, increasing pressure increases the asphaltene stability while increasing the temperature reduces the asphaltene stability. Asphaltene deposition is estimated using the model developed by Hamouda at al. (2009). Figure 4.33a and Figure 4.33b compare the estimated asphaltene from flooded chalk and sandstone cores, saturated with model oil, live oil A and live oil B, respectively, at miscibility conditions. The experimental results for the different cases are shown in Figure 4.34a and Figure 4.34b, for sandstone and chalk, respectively. Higher
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Asphaltene deposition corresponds to the higher miscible flooding conditions and presence of the light components (C₁ and C₃), for both types of the cores.

Figure 3.32 Comparison of liquid solubility parameter and asphaltene solubility parameter at flooding temperature of 50 °C and different flooding pressures for: a) live oil A and b) live oil B.
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This is in line with the indicated results from the solubility parameter curves, where at the aforementioned conditions and presence of light components, the more the risk for precipitation as the difference between $\delta_A$ and $\delta_L$ increases. It is also shown that the amount of asphaltene deposition is higher in the case of chalk compared to sandstone for the same oil type and flooding conditions. This may be due to the difference in the surface area for the two cores. Chalk cores have smaller pore throat sizes and higher surface areas compared to that for sandstone cores. Calculation based on Kozeny-Carman correlation shows that for the tested chalk cores, the surface area varies between 1.1 and 1.7 m$^2$/g while for sandstone cores, the surface area varies between 0.02 and 0.04 m$^2$/g. It has been shown also in part 4.2.2 that the mixing bank zone increases at elevated miscibility condition and it is higher for chalk cores compared to that for sandstone cores at the same flooding conditions. In other words, surface area and the mixing zone enhance the contact efficiency between the flooding and flooded fluids.
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Figure 4.33. Comparison between predicted amount of asphaltene deposition for different types of oil at different miscibility conditions (T=50 °C/P=90 bar, T=70 °C/P=120 bar, T=80 °C/P=140 bar) in: a) chalk core and b) sandstone core.
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Figure 4.34. Comparison between experimental measured asphaltene deposition for different types of oil at different miscibility conditions (T=50 °C/P=90 bar, T=70 °C/P=120 bar, T=80 °C/P=140 bar) in: a) chalk core and b) sandstone core.
5. CONCLUSIONS AND FUTURE WORKS

In this section, the overall conclusions from this study are addressed. Recommendations for future work are also suggested.

5.1. Conclusions

i. Chalk cores showed higher oil recovery than that from sandstone cores flooded with CO₂ at all miscible flooding conditions. This was explained by the likelihood of developing fingers in sandstone cores due to larger permeability contrast than chalk cores. Visual observation of cores after CO₂ flooding, confirmed finger development and propagation in sandstone cores. The higher surface area of chalk cores compared to that for sandstone cores also may enhance the CO₂ extraction efficiency.

ii. Oil recovery is consistently reduced in presence of light gas components (C₁, C₃) at all CO₂ miscible flooding conditions due to the reduction of the mass transfer between CO₂ and oil.

iii. Pressure reduction within the cores during miscible CO₂ flooding, induced multiple contact miscibility rather than first-contact miscibility. Ternary diagrams indicated that hydrocarbon evaporation dominated the C₁/C₃ system and CO₂ condensation dominated the C₁ system.

iv. Presence of light components (C₁, C₃) in the oil and elevated miscible flooding conditions, induced asphaltene instability. Higher amount of asphaltene deposition in chalk cores was obtained compared to that in sandstone cores, at similar miscibility conditions.

v. Higher recovery is obtained from chalk and sandstone cores with seawater as initial water saturation, compared to that with distilled
Conclusions and Future Works

water/different brines. This may be explained by reduction in diffusivity and solubility of CO₂ in water; hence availability of CO₂ for miscible flooding.

vi. CO₂ interaction with calcite mineral surfaces is higher than that with silicate mineral surfaces. Modification of calcite mineral surfaces with SA and asphaltene reduced the interaction of CO₂ with calcite mineral surfaces, while modification of silicate minerals (quartz and kaolinite) with NN-DMDA enhanced the adsorption of CO₂ over silicate minerals, which may be explained by the interaction of CO₂ with the amine group of NN-DMDA.
Conclusions and Future Works

5.2. Future Works

This research work has given many interesting results that worth looking further into.

i. Mapping saturation profile using CT scanning along cores is a valuable approach which can help on visualizing the development of viscous stability/instability during CO₂ flooding.

ii. It would be interesting to investigate the miscible CO₂ flooding in fractured porous media in presence of light components (C₁ and C₃) to address the diffusion/convective mechanisms in fracture/matrix system.
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