

**Faculty of Science and Engineering
Department of Petroleum Engineering**

Nanoparticles for Enhanced Oil Recovery Processes

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**This thesis is presented for the Degree of
Doctor of Philosophy
of
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DECLARATION OF ACADEMIC INTEGRITY

To the best of my knowledge and belief, this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

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Date: 5 July 2017

DEDICATION

This work is dedicated to my parents Mr and Mrs Stephen D. Nwidee who are the driving force behind my successes; and my siblings Barizasi, Nate, Kakubari and Praise Nwidee. Thank you for your endless love, prayers and supports. I am forever indebted to you.

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ABSTRACT

With the continuous rise in energy demand and decline in conventional reserves, the oil industry is constantly in search of inventive and novel approaches to optimize hydrocarbon recovery. Unarguably, enhanced oil recovery (EOR) augments additional oil recovery potentials than the primary and secondary methods. However, successful deployment of EOR requires the knowledge of the mechanisms that control efficient fluid displacement and distribution at pore-scale such as wettability. An understanding of wettability is crucial especially in carbonate formation owing to its complex microstructures, highly fractured nature, and hydrophobic character which poses several recovery challenges. When rock surfaces are hydrophobic, any oleic phase present is tightly stored in the rock matrix and produced (hydrocarbon recovery) or cleaned up (soil-decontamination) by standard waterflooding method which is inefficient. It is therefore imperative to conduct wettability quantification of carbonate reservoirs to better understand its wetting propensities as wettability has substantial impact on multi-phase flow in the subsurface and lack of understanding of reservoir wettability can hamper oil recovery efficiency and can also cause formation damage.

Thus, this study systematically investigates the possibility of nanoparticles to be of substantial benefit to EOR, particularly wettability alteration since successful oil recovery from fractured limestone reservoirs show dependency on wettability. As a preliminary step to enhance understanding of processes, an in-depth critical analysis of EOR, wettability, nanoparticles, and their relations thereof was performed. To investigate the effect of wettability on limestone rocks, experimental studies were conducted using two metal oxide nanoparticles (zirconium oxide - ZrO_2 and nickel oxide - NiO) via contact angle measurement and spontaneous imbibition. All experiments were conducted using formulations of complex mixtures of the nanoparticles, brine (sodium chloride), surfactants (cetyltrimethylammonium bromide - cationic; Triton X-100 - nonionic) or deionized water systems. Since the functionality/effectiveness of nanoparticle is influenced by the preparation methods, nanofluid homogeneity, and stability, these factors were duly considered during the fluid preparation and close attention was paid to ensure stable formulations were achieved.

Firstly, the interfacial behaviour of the nanoparticles (NiO and ZrO_2) at solid-liquid

interface was investigated by quantification of the nanoparticles properties and wetting propensities. The structure, morphology, and crystallinity phases of the nanoparticles were analysed through scanning electron microscopy, scanning transmission electron microscopy, atomic force microscopy, and X-ray diffraction. Preliminary wetting test by contact angle was conducted in air using calcite as representative of limestone rock. Prior to the wetting tests, the samples were cleaned and aged to sufficient hydrophobic state. Further surface modification was performed using the formulated ZrO_2 and NiO in blends of NaCl brine. This experiment served as a baseline for all experiments conducted subsequently.

With respect to the qualitative analysis, the study shows that significant potentials for augmenting oil recovery exist through wide ranging enhanced methods. However, nanoparticle as a novel EOR approach offers even more holistic measures, potentials, and opportunities that can stimulate the continuous evolution of EOR processes even at high pressure and high temperature reservoir conditions, thus, offering better benefits over conventional methods. The experimental studies conducted over wide-ranging conditions facilitated the assessment of the technical feasibility of the newly formulated nanofluids as EOR agents. By investigating the nanofluids wetting propensities on hydrophobic limestone rocks, the study identified a prime characteristic of nanoparticle in EOR, which is its ability to improve the property of the dispersal even at very low particle concentrations in the suspensions, and its capacity to significantly alter reservoir rock surface towards favourable water-wet conditions which is crucial for a variety of EOR related processes - better spontaneous oil displacement, enhanced carbon geo-sequestration, and soil decontamination processes.

Publications

A. Book Chapters

Nwidee, L.N., Theophilus, S., Barifcani, A., Sarmadivaleh, M., and Iglauer, S. (2016). EOR processes, opportunities and technological. In *Chemical Enhanced Oil Recovery (cEOR) - A Practical Overview*, InTech Publishing.

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Nomenclature

EOR	-	Enhanced oil recovery
NPs	-	Nanoparticles
θ	-	Contact angle
θ_a	-	Advancing contact angle
θ_r	-	Receding contact angle
NaCl	-	Sodium Chloride
ZrO ₂	-	Zirconium Oxide
NiO	-	Nickel Oxide
Tx-100	-	Triton X-100
C ₁₆ TAB	-	Cetyltrimethylammonium bromide
C ₁₈ H ₄₀ O ₃ Si	-	Dodecyltriethoxysilane
H ₂ O	-	Water
VES	-	Viscoelastic surfactant stimulation
CO ₂	-	Carbondioxide
AMEC	-	Adapted mixed enrichment cultures
CEOR	-	Chemical enhanced oil recovery
CSS	-	Cyclic steam stimulation
GEOR	-	Gas enhanced oil recovery
HPAM	-	Hydrolysed polyacrylamide
HPAM-AMPS	-	Hydrolysed polyacrylamide-acrylamide methyl propane sulfonic acid

ISC	-	In-situ combustion
MEOR	-	Microbial enhanced oil recovery
NGL	-	Natural gas liquids
PAM	-	Polyacrylamide
PWAG	-	Polymer water alternate gas injection
SAGD	-	Steam assisted gravity drainage
SAPc	-	Superabsorbent polymer composite
ST-EOR	-	Solar thermal enhanced oil recovery
SWAG	-	Simultaneous water alternate gas injection
TAGOGD	-	Thermally assisted gas-oil gravity drainage
TEOR	-	Thermal enhanced oil recovery
WAG	-	Water alternate gas injection
HPHT	-	High pressure and high temperature
N_c	-	Capillary number
γ_c	-	Critical surface tension
V	-	Darcy's velocity (m.s^{-1})
σ	-	IFT between the displaced and the displacing fluid (N/m)
E_v	-	Vertical sweep efficiency
E_a	-	Areal sweep efficiency
M	-	Mobility ratio
λ_{ing}	-	Mobility of the displacing fluid

λ_{ed}	-	Mobility of the displaced fluid
k	-	Effective permeability (m ²)
μ	-	Fluid viscosity (Pa. s)
σ_{sg}	-	Solid surface free energy
σ_{sl}	-	IFT between the solid and liquid
σ_{lg}	-	Liquid surface tension
r	-	Roughness ratio
θ_Y	-	Young's contact angle
r_f	-	Wet surface area roughness ratio
f	-	Surface area fractions of solid exposed to a liquid droplet
k_{rw}	-	Water phase relative permeability
k_{rg}	-	Gas phase relative permeability
k_{ro}	-	Oil phase relative permeability
K_{ra}	-	Air phase relative permeability
S_o^*	-	Effective oil saturation
S_w^*	-	Water effective saturation
S_w^-	-	Water saturation
S_o	-	Oil saturation
Q	-	Flow rate,
Δp	-	Pressure difference over a core length
A	-	Cross-sectional area of the core

K	-	Constant of proportionality or characteristic of the rock media (core permeability)
L	-	Core length
μ	-	Fluid viscosity
P_c	-	Capillary pressure (Pa)
P_n	-	Non-wetting pressure (Pa)
P_w	-	Wetting pressure (Pa)
g	-	Acceleration due to gravity (m. s^{-2})
N_w	-	Wetting number
A_I	-	Area under the secondary water drainage curve
A_2	-	Area under the imbibition curve falling below the zero (o) - P_c axis
l_o	-	Displacement by oil ratio
l_w	-	Displacement by water ratio
I_{AH}	-	Amott-Harvey index
f	-	Wetting force
p	-	Perimeter of the line of contact
v	-	Volume of the liquid
γ_{LV}	-	Liquid surface tension
R_1, R_2	-	Radii of curvature
ΔP	-	Pressure difference across the interface
$\Delta\rho$	-	Density difference between the liquid and vapour

h	-	Capillary rise
t	-	Time (minutes)
N	-	Total data points in the measurement
Z_j	-	Vertical deviations measured from the average height of the surface or deviation of j - point with respect to the mean line

Chapter 1 Introduction

1.1 Background

In the past half century, industrial processes in general have experienced a transition in material applications owing to a shift from conventional bulk materials towards nano-scale materials. This has driven innovative applications in wide-ranging areas of science and technology globally, thus yielding a proliferating interest and investment in nanoscience and nanotechnology fields. The increase in possibilities for the manipulation of matter in nanometer-scale have primarily led to this growth with nanomaterials at the leading edge of this fast-developing field. The potentials for direct control of systems at the same scale as nature such as DNA, cells, mitochondria and even reservoir rock pores can yield effective approaches in a wide variety of industrial processes such as the production of chemicals, materials, and energy (Campelo et al., 2009). Although nanostructured materials appear to be a recent development owing to the current growth of research and diverse applications, these materials are not completely new. Nanostructured materials have a rather shocking protracted history. The knowledge of these materials commenced as early as the 1950's by Richard Feynman who proposed that fabrications of materials and devices can be performed at atomic scales. Then in the 1980s, the term nanotechnology became even popular as established by Drexler Eric K. The current applications of these materials are not an exclusive result of modern research or laboratory synthesis, or even restricted to man-made materials. These materials have long been in existence with traceable applications in the old days. For instance, natural asbestos nanofibers and metal nanoparticles were used several decades ago to control the reinforcement of ceramic matrix and as colour pigments in glass and luster technology respectively (Colomban, 2009; Heiligttag and Niederberger, 2013).

Ever since, novel studies of nano-scale fundamentals and principles, design, characterization, production, and application of nanomaterials (Evdokimov et al., 2006; Kamyshny and Magdassi, 2010) have evolved and remained intriguing and ground-breaking. Since 2000, the nanotechnology industry has experienced a rather growing trend and the funding of nanotechnology research has also been on the rise

(Figure 1.1). In 2013, the global market for nanotechnology was estimated at \$22.9 billion. By 2014, the estimate had grown to about \$26 billion with a further projected growth of about \$64.2 billion by 2019 (Nanotek, 2017).

Nanomaterial cut across diverse fields of science and engineering and shows great potentials as effective approach for novel applications with high technological prospects and environmental impact. This technology involves the use of small sized materials which can be considered the nanometer (nm) length scale manipulations of the structure of matter, where, a nanometer represents a billionth of a meter, a distance that is equivalent to 2-20atoms positioned next to one another. Nanomaterials have increasingly gained attention for a variety of processes; electronic cooling and space applications, transportation, biomedicine, cooling of high-power laser diodes and submarines, and heating of buildings and pollution reduction (Jordan et al., 1999; Yu et al., 2008; Ramakoteswaa et al., 2014), with a current drift as novel tools for oil and gas production and process optimization. These materials allow for clear-cut design and manipulation of atoms and molecules and its industrial applications are cost-effective and efficient (Serrano et al., 2009; Khalil et al., 2017) and can be used alone or manipulated for the creation of larger scale materials to facilitate innovative applications.

1.2 Nanomaterial Applications in the Oil and Gas Industry

It is a fact that the period of cheap hydrocarbon recovery is waning as hydrocarbons are currently been explored in remote regions under harsh reservoir conditions of high pressure, temperature, and salinity. This industry is constantly faced with challenges from drilling and completion, exploration and production, to characterization and management of reservoir and other related activities. Thus, more efficient, yet cost-effective, environmentally friendly, and novel alternatives are constantly being searched for the process feasibility in order to meet the current global high-energy demand, as reserve replacement is continuously in decline. Although, advance tools such as sensing technology exist, such tools are limited in operations except seismic. Interestingly, these challenges can be averted through innovative scientific and engineering approaches such as nanotechnology, specifically via the use of nanomaterials. Currently, diverse conventional strategies (waterflooding), and

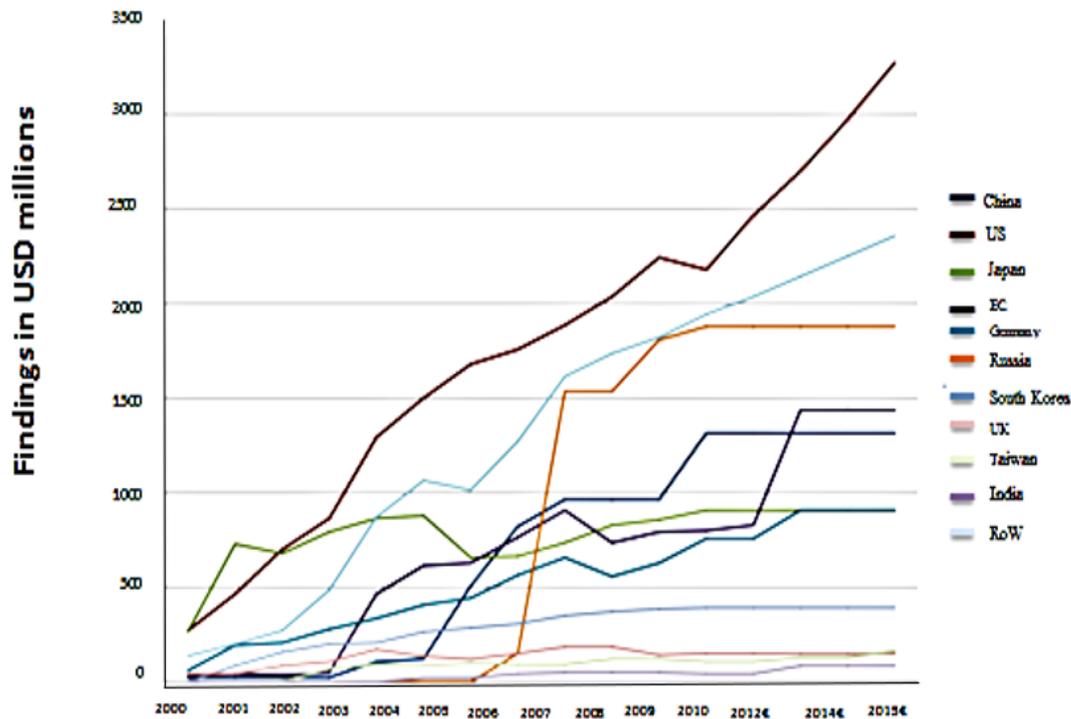


Figure 1.1: Worldwide nanotechnology research and funding by year (Nanotek, 2017).

enhanced methodologies (use of chemicals, gases, and microbes) are being deployed in oil fields. However, nanomaterials have attracted attention for consideration as effective solutions for resolving challenges in the above key aspects of oil and gas engineering. These materials can be in the form of nanoparticles or carbon nanotubes with vast application potentials, however, the choice of specific material type is highly dependent on the application process. The carbon nanotubes (El-Diasty and Ragab, 2013; Khalil et al., 2017) are carbon allotropes with a cylindrical nanostructure in the form of a tube which is classified as single, double, or multiple walled nanotubes. Carbon nanotube materials display better unique properties such as stiffness, strength, and tenacity in comparison to other fiber materials which lack one or more of these characteristics. Also, the thermal and electrical conductivity of carbon nanotubes is higher in comparison to other conductive materials.

Nanoparticles are considered the simplest forms of nanomaterials which are categorized as metallic, metal oxides or magnetic nanoparticles. Unarguably,

nanoparticles effectiveness cut across several industries such as energy, manufacturing, medicine, electronics etcetera, as well as the oil and gas industries. Nanoparticles are of great relevance scientifically, as the material is a bridge between bulk material and their atomic or molecular structure. The molecular or atomic assemblies that form nanoparticles are based on the forces of interaction between the molecules or atoms of the particle. This material exhibits unique physiochemical properties (Strambeanu et al., 2015) that is dependent on discrete molecular or atomic phenomena. Nanoparticle is particularly interesting for oil and gas applications as oil and gas tools are manufactured with nanomaterial functionalities; the inner surfaces of pipelines and production facilities can be coated with nano-based paints; nanoparticle based catalysts are been used in the oil and gas downstream for oil refining and petrochemical activities. Currently, complex reservoir rock heterogeneity and microstructures, and the corresponding effect on multiphase flow, as well as, the reservoir depth information can now be effectively characterized using sensors fabricated with nanoparticle materials. Superparamagnetic nanoparticles can be effectively used for conductive heat generation (Davison et al., 2012). Nanoparticles dispersed in different solvents otherwise called nanofluids are also been used for drilling, exploration, production, and enhanced oil recovery process evaluation (Table 1.1). Despite the relevance of nanoparticles in oil and gas engineering processes, reservoir engineering, specifically enhanced oil recovery (EOR) have attracted the most attention in recent times. However, its understanding is still very limited in EOR especially in wetting evaluations. Harnessing the full potentials of nanoparticle requires an understanding of the material properties as their quality, structure, and composition influences their reactivity and functionality.

1.3 Requisite of Nanoparticles in EOR

With the current decline in conventional reserves (Shihab-Eldin, 2002; Bell, 2004; Amanullah and Yu, 2005; Amanullah and Richard, 2006), the prospects for discovering more hydrocarbon resources are more predominant in offshore deep-water regions than the onshore shallow-water regions. A number of processes and technologies have been used in this regard to upsurge or maintain recovery from existing fields through the use of additives - surfactants, polymers, alkaline, and the

combinations thereof to improve sweep efficiency, interfacial tension reduction, rock surface wetting, and mobility control. These processes facilitate effective displacement of oil towards the producing well, thus, production from matured fields are enhanced as the injected chemicals, gases, or microbes interact with the formation rock and oil systems thereby creating a favourable condition for better recovery. However, the practicality of these mechanisms are hampered owing to the large volume of additives (high particle concentration) and energy requirements which impacts operational cost, material size effect and limited functionalities, chemical incompatibility with the reservoir fluids and conditions, degradation, scale formation, precipitation and susceptibility to high temperature and salinity formations (Muller, 1981; Hong, 1989; Schmidt, 1990; Moan and Omari, 1992; Caulfield et al., 2003; Pu et al., 2016b; Nwidee et al., 2016b). Amidst these challenges is the need for more economically feasible approach (Pereira-Almao, 2012; Amanullah and Al-Tahini, 2009, Hashemi et al., 2014) that will reduce operational cost and improve the quality and amount of recoverable oil to meet the global market demands with less environmental footprints. For feasibility of EOR amid an unremitting increase in energy demand and inaccessible oil reserves, it is imperative that efficient economical and environmentally friendly alternatives are considered.

Nanoparticle though in its early stages is a promising alternative. It is of interest in EOR owing to its properties and transport behaviour. The material can be easily manipulated to perform certain functional tasks and ideal for smart fluid formulations that can address the underlying mechanisms that influence reservoir behaviour. More so, the issue of clogging and increase in pressure drop which are commonly associated with conventional fluids are rather insignificant with nanoparticles owing to the small particle size and volume fraction of nanoparticles. Problems of sedimentations are also greatly reduced owing to the particles large surface area which reduces the non-equilibrium effect between fluid and solid, while increasing the system stability (Das et al., 2003). Since oil is typically recovered from formation rocks with micron-sized pores, nanoparticles are much smaller fine particles with unique size dependent physical and chemical properties that can enhance easy penetration through the reservoir pores, as the particle size is much smaller than the conventional rock pores. Thus, fluid flow through the reservoir pore spaces can be significantly improved with little or no negative impact on the formation permeability, or porous media pore-

plugging or chemical trapping related issues that are commonly associated with conventional EOR processes.

1.4 Characteristics of Nanoparticles

Nanoparticles have an extensive range of unique characteristics for varied functionalities such as surface plasmon resonance, superior catalytic activity, intrinsic reactivity, great adsorption affinity and dispersibility (Perez, 2007; Hashemi et al., 2014). The uniqueness of nanoparticle properties dates to several centuries (9th century AD). The first optical property of nanoparticle was discovered from a lustre technology on a glazed ceramic in Mesopotamia at the time, which later became popular in Egypt, Spain, and Persia. An archeomaterial of this material indicated the optical properties were as a result of the metallic nanoparticles that were dispersed on the outermost layers of the glaze (Sciau et al., 2009). With the advent of time, practicalities of nanoparticle have become even more prevalent owing to their physical and chemical properties. Interestingly, the particles surface functionalities can be engineered (Nassar et al., 2011; Pereira-Almao, 2012) with potentials for subsurface engineering applications.

Comparison of the exceptional properties of nanoparticles to the bulk material counterpart shows that nanoparticles display quite different properties and superior behaviour. Its applications enable the creation of new composites with unique properties that allows for innovative technological advancements. Typically, nanoparticles are characterized by thermal, mechanical, physical, and chemical properties. These properties span through material's grain boundary, particle size, surface area per unit volume, size of the particles, purity, thermal conductivity etc. On basis of their thermal properties, nanoparticle based fluids exhibits high thermal conductivity and high surface area than conventional base-fluids. The thermal conductivity of conventional base liquid can be improved by addition of nanoparticles as heat transfer occurs at the surface of the particles (Lee et al., 1999). The high surface area increases the thermophysical properties and the small particle size enhances their potentials as absorber fluids due to high potential of large surface coverage in heat transfer processes. Choi (1995), Eastman et al., (1996), and Lee et al., (1999) reported that nanoparticle based fluids exhibit higher thermal conductivity with great

dependency on factors such as the material type, size, shape, surface area, particle volume fraction, base fluid material and temperature. The thermal conductivity of ethylene glycol which is a conventional base fluid with thermal conductivity of approximately 0.258 W/m K can be significantly enhanced (20 % increase) upon addition of only about 4 % volume CuO of 35 nm particles. With respect to the mechanical properties, nanoparticle exhibits high ductility, high average hardness, and maximum strain in comparison to other composite materials. Thus, considered suitable for improving fracture toughness. However, the particles geometry can influence the mechanical properties of nanoparticles such as tensile modulus, tensile strength, and fracture toughness (Lim et al., 2010). Zhang and Singh (2004) showed that the addition of 4.5 % volume fraction of well-bonded Al₂O₃ particles to unsaturated polyester led to a 100 % increase in fracture toughness. It has also been reported that nanoparticles are suitable filler materials for improving the mechanical properties of composites. The addition of small amount of rattan nanoparticles (0 - 5 %) to polymer matrix (polypropylene) as fillers enhanced the mechanical performance of the composites (Nikmatin, 2012, 2015).

The physical and chemical properties span through shape, size, structure, quantum confinement, lattice parameter and symmetry, charge, solubility, and surface coating (Cadden, 1987; Rao and Biswas, 2009; Strambeanu et al., 2015). The enhanced physiochemical properties and superior performance of nanoparticles is mainly based on the overriding effect of surface forces from the particles atomic scale size rather than the mass forces. The physical and chemical properties of the bulk materials are typically constant irrespective of the material size and shape, and the number of surface atoms are substantially smaller than atoms in the bulk phase. This is not the case with nanoparticles as they exhibit small particle size, high surface area, and unique transport behaviour that enhance their surface performance. Nanoparticles behave quite differently from bulk materials owing to their size-dependent properties. The particle is small enough to limit the thickness of the common electron layer of metals, such phenomenon generates quantum effects or confinement. Nanoparticles yield applications that are even more extensive with the particle size approaching nanoscale. As the particle size is reduced to near or less than the wavelength of electrons conductivity, the property of the material changes. The particles coalesce into the structure of materials and display strength. The atoms of conventional

materials are in the interior of the particle, whereas, the atoms of nanoparticles are located on the particles surface (Kim et al., 2013; Nwidee et al., 2017a, b; Fakoya and Subhash, 2017). A dramatic change in properties such as thermal resistance, chemical and catalytic activities, melting point, internal pressure, magnetism, and optical behaviour occurs as the atoms at the surface of the material become even more significant which is due to the large surface area to volume ratio. The surface area to volume ratio appears exponentially larger, and the number of surface atoms becomes even more substantial with respect to that in the bulk phase (Lin et al., 2003; Bell, 2003; Kong and Ohadi, 2010; Boysen et al., 2011; Guo et al., 2014; Hashemi et al., 2014; Hashemi-Kiasari et al., 2014; Khalil et al., 2017). Amanullah and Al-Tahini (2009) reported a comparison between the surface area to volume ratio of spherical particles of the same nanomaterial in micrometre, millimeter, and nanometer. Nanoparticle surface area to volume ratio is over a million times higher than the conventional scales and the particle surface area is also higher than the bulk particles - micro and macro materials of the same mother source, which enhances their increased potentials even with a significantly low concentration of the materials in the system. Such high surface area increases the particles surface energy which leads to structural transitioning (Tsuzuki, 2013). This behaviour allows for favourable particle adsorption at the surface boundaries and permits high particles contact tendencies with nearby materials or solvent molecules in suspensions (Nwidee et al., 2017a), and the particles boundaries facilitate their enhanced quantum effects. More so, nanoparticles exhibit strong chemical stability, irrespective of high temperature and pressure conditions of the reservoir (Cao et al., 2015) and great selective adsorption behaviour (Kim et al., 2013; Franco et al., 2015; Nwidee et al., 2017a) which is vital for EOR process optimization.

1.5 Aim and Objectives

The aim of the work is to investigate the effect of selected nanoparticles as an advanced material for wettability enhancement in complex porous medium with particular emphasis on oil-wet limestone reservoir.

The following objectives structure this study to:

- Investigate the influence of nanoparticles on wettability alteration of hydrophobic limestone rocks
- Evaluate the impacts of surfactant on nanoparticle behaviour under different wetting conditions.
- Investigate water-imbibing inclinations of hydrophobic rocks in the presence of nanoparticles by spontaneous imbibition.

1.6 Significance of the Study

Wettability studies in its entirety are not new, several mechanisms have been employed to resolve reservoir wettability challenges, however, this phenomenon has remained vague owing to complexities. More so, the majority of wetting studies have been in sandstone reservoirs with fairly simple pore structures, as oppose to limestone formations with intricate microstructures. Understanding reservoir wettability is by itself complex and controlling wetting mechanisms through surface modification is even more complex. No unambiguous standards exist at laboratory scale or via modelling for its evaluations, as disorder, impurities and roughness play key roles in practical wetting processes which hampers system stability. These complex dynamics is poorly understood in limestone formation, especially for contact lines moving in nanoscale. Conventional waterflooding are inefficient in this formation owing to poor spontaneous water imbibition into its hydrophobic rock capillaries. Ascertaining wettability in limestone is therefore imperative for addressing the wettability issues in this formation that are capable of impeding adequate fluid flow and distribution, which can impact EOR process efficiency. More so, inaccurate assumptions of the reservoir wetting inclinations can lead to possibilities of formation damage, as wetting phenomenon is closely related to the reservoir rock surfaces, as well as, the imbibing fronts. We believe this study will significantly impact the understanding of formation wetting preference, which is crucial for oil recovery process optimization and it will also accelerate the realisation of nanoparticle application for EOR processes at industrial scale.

1.7 Scope of the Study

Although wettability issues impact both sandstone and carbonate formation, this study is focused on carbonate. Carbonate rock is of interest as it holds substantial amount of oil reserves globally and its oil-wet or intermediate wet character and tight matrix blocks disrupt spontaneous water imbibition, which can impede recovery efficiency (Treiber et al., 1972; Chilingar and Yen, 1983; Gonzalez and Moreira, 1991; Yu and Buckley, 1997; Acevedo et al., 1997; Liu, and Monsterleet, 1998). The qualitative part of this study provides an in-depth analysis of EOR, wettability and nanoparticle affiliations. The experimental investigations were conducted using two metal oxide nanoparticles - zirconium oxide (ZrO_2) and nickel oxide (NiO) owing to their superior mechanical, optical, thermal, and chemical properties in comparison to other oxides (Petit and Monot, 2015; Gopalan et al., 2015). Complex mixtures of nanoparticles and cationic ($C_{16}TAB$) and non-ionic TX-100 surfactants, and sodium chloride (NaCl) brine were formulated and their wetting propensities were tested. The synergistic effect of blends of the nanoparticles, brine, and surfactants on solid-liquid interfaces on basis of concentration, time, temperature, rock morphology, particle size and roughness were investigated to simulate subsurface harsh condition. Various systems were systematically measured and analysed under different conditions to address the current issue of limited data on solid-liquid interfaces in complex oil-surfactant-brine-nanoparticle systems. Only the most effective nanoparticle and surfactant type and concentrations were chosen for further wettability evaluation and surface characterization.

1.8 Contributions of this Research Work

After exploring the study objectives, this study has contributed significantly to the existing knowledge on EOR, wettability and nanoparticles through the establishment of diverse correlations for empirical understanding of the wetting inclination of hydrophobic limestone reservoirs. The mechanical property testing, and analysis using scanning electron microscopy, scanning transmission electron microscopy, X-ray diffraction and atomic force microscopy provided fundamental insights into the nanoparticles enhancement potentials. The study demonstrates that nanoparticle as a solid and robust chemical shows great potentials in stabilizing systems and overall

Table 1.1: Nanomaterial applications in the oil and gas industry.

Processes	Material Type	Applications	References
Drilling and completion			
Drilling Bits	Carbon nanomaterial - nano-diamond polycrystalline diamond compact (PDC) Technology	<ul style="list-style-type: none"> • Suitable for functionalization of PDC cutters for drill bits. • Effective for the manufacture of advanced drill bits that has good resistance to abrasion and corrosion upon nano-coating. 	Bialy et al., 2011; Chakraborty et al., 2012; El-Diasty and Ragab, 2013; Ponmani et al., 2013.
Logging while drilling (LWD)	Nanostructured glass-ceramics	<ul style="list-style-type: none"> • Effective neutron detectors - Li-6 scintillation nanostructured glass ceramics shows better efficiency than ordinary Li-6 scintillation materials. 	Nikitin and Korjik, 2012; El-Diasty and Ragab, 2013.
Cementing	Carbon nanotube (CNT)	<ul style="list-style-type: none"> • Suitable as reinforcement materials for cement instead of conventional fibers. 	Rahimirad and Baghbadorani, 2012; El-Diasty and Ragab, 2013.

Continued from the previous page

Processes	Material Type	Applications	References
Drilling fluids	Nanoparticles (NP)	<ul style="list-style-type: none"> • Control of fluid loss and wellbore stability. • Design of drilling fluids suitable for harsh reservoir conditions. • Nanoparticle based drilling fluids can be effective for elimination or reduction of drilling problems such as pipe sticking, equipment wear and tear, rig instability and poor hole cleaning issues. 	Bialy et al., 2011; Hoelscher et al., 2012; El-Diasty and Ragab, 2013.
Exploration			
Geothermal production	NP	<ul style="list-style-type: none"> • Nanoscale metals suitable for delineation of ore deposits during geochemical exploration 	Wang et al., 1997; Kong and Ohadi, 2010; El-Diasty and Ragab, 2013.
Imaging tool	NP	<ul style="list-style-type: none"> • Hyperpolarized silicon NP deliver innovative tools for measurement and imaging oil exploration 	Song and Marcus, 2007; El-Diasty and Ragab, 2013.
Production			
Hydrate Recovery	NP	<ul style="list-style-type: none"> • Nickel-iron NP can be used for dissociation of hydrates 	Bhatia and Chacko, 2009; El-Diasty and Ragab, 2013.
Viscoelastic surfactant stimulation fluid (VES)	NP	<ul style="list-style-type: none"> • NP associates with VES micelles for stabilization of fluid viscosity 	Huang and Crews, 2008; El-Diasty and Ragab, 2013.

Continued from the previous page

Processes	Material Type	Applications	References
Reservoir characterization and management			
EOR	NP	<ul style="list-style-type: none"> Advanced EOR approach - suitable for surface/interfacial modifications. 	Ogolo et al., 2012; Hendraningrat and Torsaeter, 2014; Alomair et al., 2015.
Hydrocarbon detection	NP	<ul style="list-style-type: none"> Suitable for detection of hydrocarbon in formation rocks 	Kanj et al., 2011; El-Diasty and Ragab, 2013; Ponmani et al., 2013.
Oil microbe detection tool	Nano optical fiber	<ul style="list-style-type: none"> Suitable for reservoir penetration and for transmission of laser light which enables the detection of stranded or bypassed oil. 	Jahagirdar, 2008; Ponmani et al., 2013; El-Diasty and Ragab, 2013.
Carbon capture and storage	NP / Nanomembranes	<ul style="list-style-type: none"> Enhances improved gas streams separation and forcontamination removal from oil. 	Kong and Ohadi, 2010; Ponmani et al., 2013; El-Diasty and Ragab, 2013.

process optimization. This is of great relevance as more useful geochemical and wetting analysis are provided, which can further direct understanding of issues relating to wettability and soil contamination restoration in limestone formations.

The study establishes that:

- Understanding of carbonate rock wetting preference is vital for EOR process optimization as poor rock wetting can inhibit efficient fluid distribution through the pore spaces and hydrocarbon flow. Poor rock wettability is mainly due to high hydrophobicity of the reservoir rock surface, poor cleaning, and treatment approaches.
- ZrO_2 and NiO Nanoparticles promote rock wetting inclination, and their prime characteristic in EOR is the ability to improve the property of the dispersals (NaCl brine; $C_{16}TAB$, and TX-100 surfactants) even at very low particle concentrations in the suspensions.
- Nanoparticle based systems ($ZrO_2/NaCl$, $NiO/NaCl$, $ZrO_2/C_{16}TAB$, $NiO/C_{16}TAB$, $ZrO_2/TX-100$, $NiO/TX-100$) act as novel surface-modifiers with better impact in promoting formation wetting. Water contact angle decreased with increase in time, concentration, salinity, surface roughness and temperature in the presence of the formulated nanofluids.
- Carbonate reservoir performance is significantly enhanced when the formation wetting character is substantially hydrophilic than hydrophobic as it facilitates better spontaneous water imbibing potentials especially in the presence of ZrO_2 and NiO nanoparticles. Systems containing blends of surfactant and nanoparticle ($ZrO_2/C_{16}TAB$, $NiO/C_{16}TAB$) exhibited faster water imbibition capabilities and wetting potential than the surfactant system alone.
- The newly formulated systems favourably adsorb on the rock surface thereby facilitating efficient wetting from hydrophobic to hydrophilic conditions. Thus, recommended for EOR project design as potential stabilizer of dispersed systems for production optimization in hydrocarbon recovery, CO_2 geo-storage, and soil de-contamination processes.

- Particle size influences deposition, rock surface homogeneity and particle aggregation tendency thus suitable preparation methods and compatible dispersals should be used to control the particle size.

1.9 Thesis Outline

To achieve the objectives of this study, a systematic approach was adopted based on Figure 1. 2 which shows the thesis structural framework.

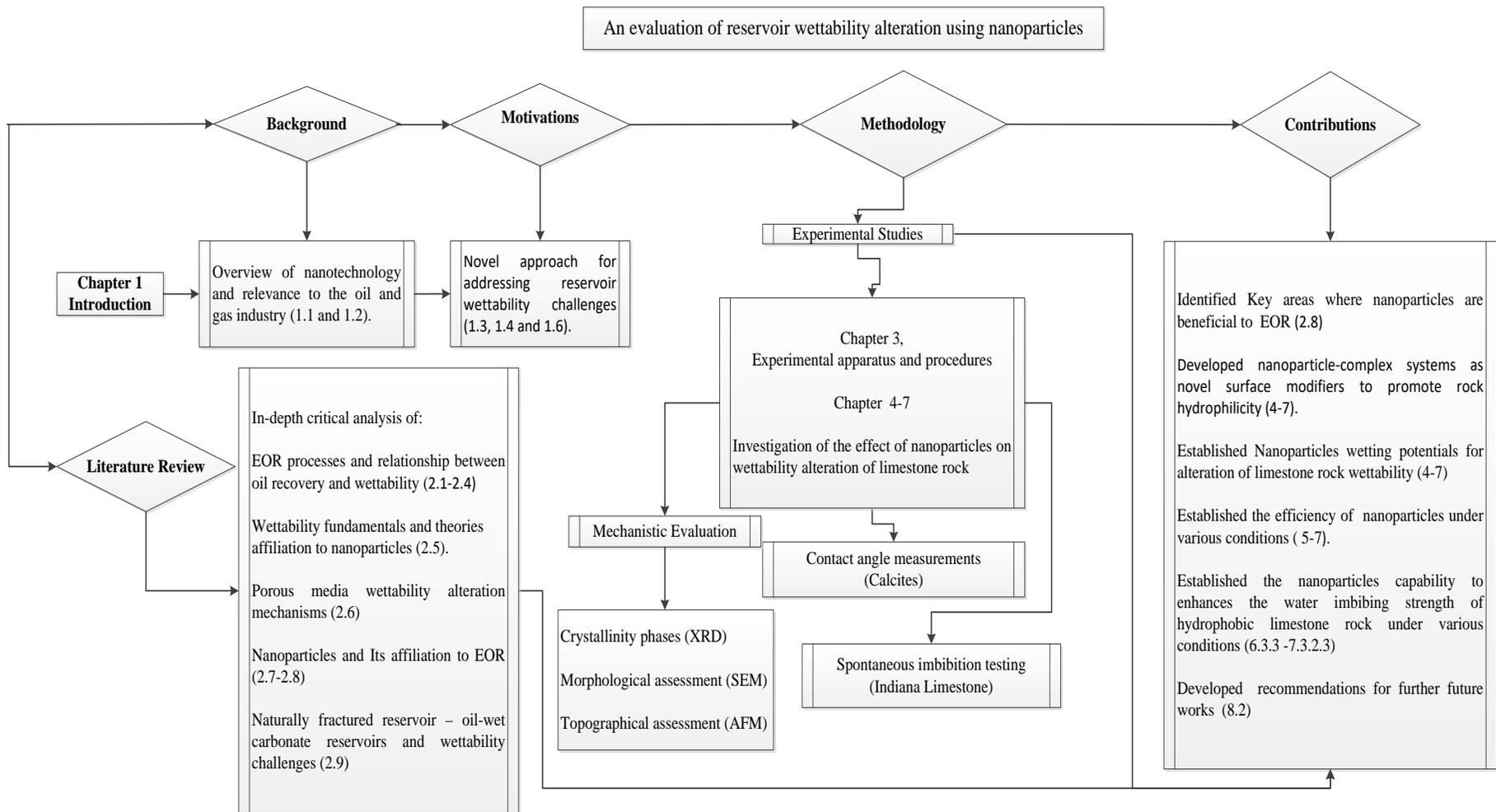


Figure 1.2: Thesis structure

Chapter 2 EOR, Wettability, and Nanoparticles Affiliations

Enhanced oil recovery (EOR) processes are known for increasing oil recovery, however, the selection of the most suitable method to adopt for specific field application is challenging. While it is important to conduct experimental investigations, it is also essential to establish a qualitative knowledge of the underlying mechanisms that influences recovery potentials. An understanding of the relationship between EOR, wettability and nanoparticle - a novel tool for addressing reservoir challenges, is vital for process optimization. Thus, this chapter provides an in-depth critical analysis of EOR methods currently applied in oil fields, the benefits and limitations of the processes and their relation to wettability and nanoparticles to guide decision-making process for optimum productivity.

2.1 Introduction

Globally, the continuous growth in energy demand appears to be predominant amidst feasible renewable energy alternatives. Unarguably, this newer energy sources, such as nuclear, wind, geo-thermal and solar are effective measures that are also currently addressing energy shortage. However, they are yet to be sufficient alternatives for substituting the role of oil in meeting the ever-rising energy demand. To date, these demands are currently being substantiated via hydrocarbon sources especially petroleum, as oil is still the most valuable product with great global economic impact.

The rise in oil demand has continuously been on the increase (Figure 2.1), except for the 1979 and 1983 temporary drop in oil demand. Concurrently, there has been a continuous decline in conventional oil resources. In 2014, an increase in oil consumption by 1.2 million barrels per day (b/d) globally was reported by the U.S. Energy Information Administration, which averaged about 92.4 million b/d (U.S. EIA, 2015). At the end of the year 2015, the oil production rate was approximately 97 million b/d (U.S. IEA, 2015), an increase equivalent to oil consumption rate increase of 1.4 million b/d (U.S. EIA, 2015). Expectations were that the oil consumption rate globally would grow by 1.4 million b/d in 2016 and 1.5 million b/d in 2017 (Figure 2.1). It is also important to mention that since 2014 to present, there is more oil supply

than demand, which is clearly reflected by the drop-in oil price. However, the current excess in the oil supply is as a result of the exploitation of the unconventional oil resources (i.e. tight reservoirs) (Owen et al., 2010). The dramatic increase in oil demand over time has continuously prompted the quest for novel methods to enhance oil production.

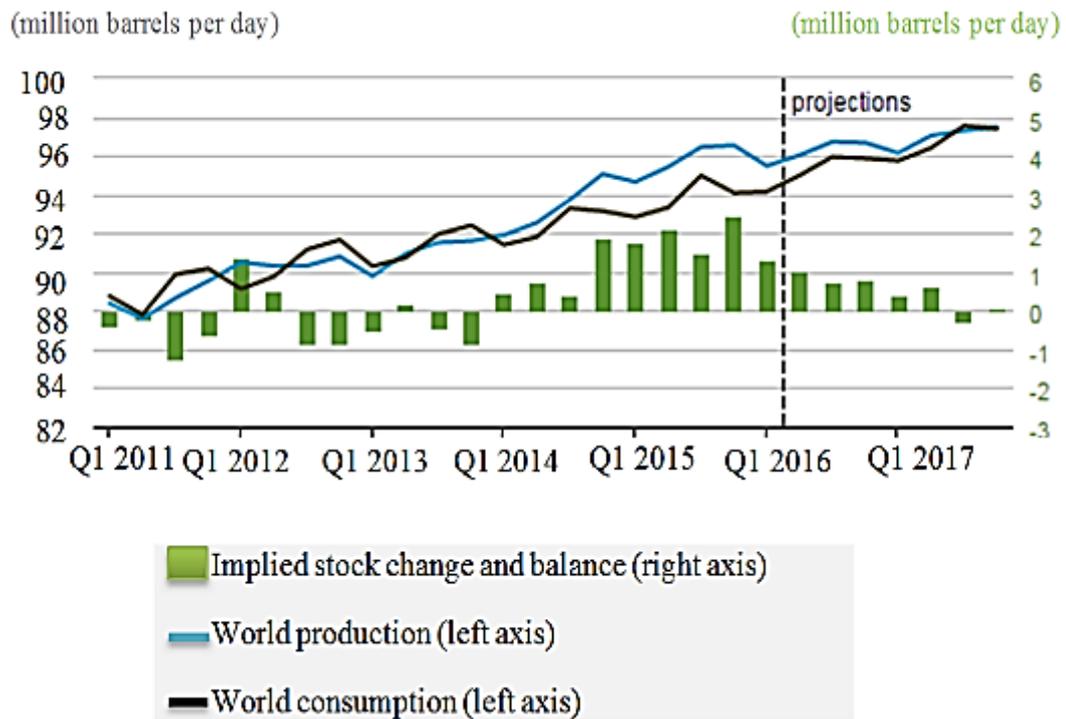


Figure 2.1: Global oil production and consumption (U.S. EIA, 2015).

2.2 EOR Processes

Hydrocarbon recovery goes through three key stages of production - the primary, secondary, and tertiary recoveries. This is often an indication of a sequential reservoir production pattern (Green and Willhite, 1998). The primary recovery mechanisms otherwise known as the natural drive mechanisms involve the initial reservoir production stage, where natural reservoir energy is used without any supplementary energy. Whereas the secondary recovery stage is deployed owing to inadequacy or depletion of the natural drive mechanisms, thus, fluids such as water or natural gas are used instead of the energy in the reservoir to stimulate oil wells and maintain reservoir pressure in the injection wells in order to optimize production. Waterflooding,

although a relatively cheap choice to improve oil recovery (Standnes and Austad, 2000) have been used for hydrocarbon production increase in the last decades, mainly after primary production period. However, the recovery of oil by this technique is relatively low (Anderson, 1986; Buckley et al., 1998; Iglauer et al., 2010, 2011). On average, oil recovery from the primary and secondary production stages is approximately one-third of the original oil-in-place (OOIP) which is considered rather insufficient and leaves behind a large amount of oil during production. The remaining two-thirds of the oil can be partially recovered through the application of tertiary processes also known as enhanced oil recovery (EOR) processes, which are key drivers for incremental oil recovery. EOR is an established approach for reclassifying reserves that have been considered unrecoverable and contingent (Bai, 2011).

EOR is an effective strategy for recovery of inaccessible hydrocarbons as its techniques demonstrate great potentials of recovering stranded oil trapped at the pore scale after the natural drive and secondary mechanisms by capillary pressure-driven snap-off (Kovscek and Radke, 1996, 2003). The key drive for EOR is the possibilities of recovering additional oil economically with its recovery processes and techniques in view (Latil, 1980), and the ability to turn residual cumulative oil into reserves (Veld and Philips, 2010; Tunio et al., 2011; NETL, 2011). This is attained by incapacitating the physical forces that confine hydrocarbons underground (Green and Willhite, 1998; Iglauer et al., 2010). A number of processes and technologies are used in this regard to upsurge or maintain recovery from existing fields. These processes involve the injection of steams (thermal EOR), chemical based fluids (chemical EOR) and gases into a reservoir (gas EOR), and recently microbes (microbial EOR) are also been deployed in oil fields. These processes facilitate effective displacement of oil towards the producing well, thus, production from matured fields are enhanced as the injected fluid, gases, or microbes interact with the formation rock and oil systems, thereby creating a favourable condition for better recovery.

2.2.1 Thermal EOR (TEOR)

Oil recovery using thermal techniques involve the introduction of heat energy into oil reservoirs. Reservoir temperatures are substantially increased to achieve a significant decrease in oil viscosity (Prats, 1986). During the process, usually, a shift in rock

wettability occurs, which enhances the chances for better oil recovery (Kovscek, 2012). Current reports predict that only approximately 30% of the global oil reserves are light oil while the remaining 70% are heavy crude oils (Prats, 1986). Increasing recovery of these heavier crudes can unlock approximately 300 billion bbl (Bbbl) of oil (U.S. DOE/EIA, 2014); thus, TEOR is mainly applicable to heavy and viscous oil formations (Prats, 1986). The TEOR is considered an effective technique for unlocking such heavy oil reservoirs. Several billion barrels of oil have been recovered using TEOR; for instance, more than 4 Bbbls of oil were produced in the USA through steam flooding (SF) from 1980 to 2002 (Moritis, 2002). Despite its effectiveness in heavy oil formations, TEOR can also be deployed in light oil reservoirs (Kovscek, 2012). TEOR is perhaps the best used EOR method for up surging production particularly steam flooding (Moritis, 2010), although the environmental footprint is enormous when compared to conventional oil production (Kovscek, 2012).

TEOR involves in-situ combustion (ISC) and steam injection. Steam injection includes three basic categories: namely, cyclic steam stimulation (CSS; huff and puff), steam flooding and steam-assisted gravity drainage (SAGD).

2.2.1.1 In situ Combustion Mechanisms

In in-situ combustion, air is injected into viscous oil reservoirs to generate heat by burning a portion of the existing oil (Slider, 1983; Sarathi, 1999; Kokal and Al-Kaabi, 2010; Kovscek, 2012). The ISC can be a forward or reverse process, which is mainly dependent on the combustion front. The combustion fronts move in the direction of the injected air (forward combustion) or away from the air/producing well (reverse combustion). In practice, the forward combustion process is generally adopted since the heated zone and oil move towards the producing well and away from the injection well. More so, forward combustion appears to be more economically attractive than the reverse as the heavy ends or unwanted fraction of the oil cokes, used as fuel while clean sand is left behind; the generated heat is used in displacing the oil bank ahead of the combustion zone. Whereas, during the reverse combustion, the process consumes the middle fraction of the oil in place as fuel while unburnt coke is left on the surface of the sand - an indication of inadequate use of the existing energy and can lead to a

permanent upgrading of a tarry crude yielding poor thermal efficiency (Perry et al., 1960).

Typically, oil recovery is achieved using this process through the energy generated by the combustion reaction between the injected air and the oil:

- The oil is ignited, and air is constantly injected to propagate the combustion front away from the well
- Reservoir fluids are displaced at the elevated temperatures (600-700°C) zone.
- The fluids advance towards the production wells and the lighter ends are transported downstream which mixes with the crude oil.
- The heavy ends are burned resulting in the production of large amount of flue gases (Moore et al., 1994; Satter et al., 2008).

Process benefits: ISC efficiently displaces oil in the regions contacted by the hot fluids in the advancing front, oil recovery rates are mostly high, and this process is more cost effective than steam flooding as it uses air. There is a negligible effect of reservoir permeability on the ISC processes, which is effective for oil recovery (Satter et al., 2008) in various formations as follows:

- Deep reservoirs: depths up to 11,000 ft.
- Shallow reservoirs: <1500 ft.
- Light oils: >30° API.
- Heavy oils: 10-20° API.

Process limitations: Compressed air must be used, and the operational variables are complex and difficult to control (i.e. controlling the advancing combustion front) (Green and Willhite, 1998). The ISC process requires very high temperatures, in the order of 700°C and above. The high temperature of this process often damages production tubing and equipment (i.e. failure of pumps, valves, etc.). Furthermore, an adequate knowledge (i.e. rigorous laboratory evaluation) of the ISC dynamics is required for understanding the stability of the combustion front (Ali, 2003; Akkutlu and Yortsos, 2003).

2.2.1.2 Steam Injection Mechanisms

Steam injection entails the injection of steam into shallow, thick, and permeable reservoirs containing high viscosity crude. Steam injection processes include steam flooding, Cyclic Steam Stimulation (CSS) and steam-assisted gravity drainage (SAGD).

In the steam flooding, steam is injected into dedicated injection wells, so that the reservoir fluids are driven towards a separate set of producers (Lake and Walsh, 2008).

Oil recovery is achieved through:

- Constant injection of steam into the formation.
- The injected steam heats the chamber around the injection well.
- The chamber expands in the direction of the production well leading to oil viscosity reduction (Shafiei et al., 2013) and substantial oil displacement.

Process benefits: The introduction of steam into the reservoir efficiently displaces oil (Baibakov and Garushev, 1989) by heating the oil to a temperature at which its viscosity is sufficiently decreased (Nabipour, 2006). Steam flooding is the most applied EOR technique worldwide because it is very effective in rendering high oil recovery ratios. Higher sweep efficiency is achieved with steam flooding than with the application of cyclic steam stimulation (CSS).

Process limitations: Steam flooding is an expensive venture. Significant heat loss (i.e. heating of injection tubing, heating of overburden and under burden rock, etc.) occurs during the extensive steam injection periods (Ali, 2003). Avoidance of sand plugging at the bottom hole, prevention of steam channelling and improvement of steam sweep efficiency are still key challenges of steam flooding operations, especially in super heavy oil formation. Early steam breakthrough at the producing wells decreases the rate of recoverable oil (Lei et al., 2010; Baibakov et al., 2011; Yanbin et al., 2012).

CSS (Chilingarian et al., 1989; Lake and Walsh, 2008) is applied in three stages as follows:

- Steam injection: In this stage, adequate quantities of steam are injected during a pre-established period.
- Soaking stage: After the injection of the required volume of steam, the well is shut-in for several days or weeks to maximise heat transfer and heating of the oil that results in the reduction of oil viscosity.
- Production stage: The well is open to production. Initially, a high oil flow rate is attained; however, it progressively decreases. Oil production might be supported by artificial lifting.

As the reservoir temperature declines, the oil flow rate drops significantly; at this point in time, another cycle of CSS is applied to re-attain the high oil production rates (Chilingarian et al., 1989; Johannes and Han, 2013). CSS applied for several cycles until commercial oil flow rates are obtained.

Process benefits: CSS is effective in reducing the viscosity of the oil due to the cyclic application of steam in the same well with potential for substantial oil recovery, especially in heavy oil reservoirs having thick pay zones (>15 m) (Zhao, Wang, and Gates, 2013). However, the CSS oil recovery factor is low in comparison to steam flooding.

Process limitations: The CSS process is complex. Excessive heat loss occurs, and the radius of the heated zone is insignificant (Liu et al., 2008). Application of CSS in thin heavy oil (<6 m) reservoirs is uneconomical (Zhao et al., 2013).

In steam-assisted gravity drainage (SAGD), steam is constantly injected using two horizontal wells-the upper steam injector well and the lower producer well (collects the heated oil and water). The injector and producer wells counterbalance the effect of high viscosity of the oil through prolonged steam (heat)-oil contact and provide the driving force for the movement of the oil towards the producer well (Hashemi-Kiasari, 2014). SAGD is influenced by the gravity drainage of the heated oil and condensed water (Gates et al., 2008). Fluid mobility predominantly controls the process efficiency. In SAGD, oil recovery is achieved when:

- The upper horizontal well injects steam into a chamber at a temperature that significantly reduces the viscosity of the heavy oil and/or bitumen, which improves oil flows.

- At the edge of the chamber, heat is released through condensation (Gates et al., 2008) and reduction in oil viscosity occurs.
- Then the heated oil drains by gravity through the steam chamber towards the production well (lower horizontal well) (Elliott and Kovscek, 1999).
- The injection of steam and production of oil occurs concurrently and constantly, and the oil production rate is controlled by the expansion of the steam chamber (Hashemi-Kiasari, 2014; Giacchetta et al., 2015).

Process benefits: SAGD is very efficient in recovering bitumen and heavy oil from reservoirs. Oil production increases with the increase in oil pay thickness (>15 m) (Shin and Polikar, 2006), thus production can be considered economical.

Process limitations: Possible loss of injected steam due to poor process control, which can lead to low oil recovery rate. SAGD oil production is considered uneconomical in pay zones with thickness <15 m (Edmunds and Chhina, 2001), due to the high steam-to-oil ratio (SOR) required. This process is susceptible to low mobility control and rapid gravity segregation. The mobility control is considered a limitation as the steam viscosity is much lower than the viscosity of the oil and water. Similarly, the density of steam is much lower than the density of oil and water. Thus, an upward migration of steam to the top of the reservoir often occurs and the steam overrides a larger part of the heavy oil zone. This issue can be partially controlled by heat conduction away from the steam contact. Other limitations of the SAGD process are the significant production of CO₂ emissions during steam generation at surface facilities, heat losses and equipment problems due to the high temperature of the process (Green and Willhite, 1998).

2.2.2 Chemical EOR Techniques (CEOR)

In chemical EOR (CEOR) techniques, oil is recovered through the injection of chemicals (Baviere, 2007; Adasania and Bai, 2011; Wever et al., 2011). CEOR is predominantly suitable for heavily depleted and flooded formations (i.e. mature reservoirs) (Petros Group, 2010). Typical chemicals are polymers, surfactants, alkalis and formulated mixtures thereof (Iglauer et al., 2009; Iglauer, 2010; Adasania and Bai, 2011). The efficiency of such formulations is normally screened in laboratory studies

(Goddard et al., 2004; Iglauer et al., 2004, 2009) and each chemical has different effects on oil production (Schramm, 2000). For example, the application of surfactants or alkali or its mixtures can substantially reduce the interfacial tension between brine and oil (Iglauer et al., 2009; Lake, 2010; Wu et al., 2010); significantly improving the microscopic sweep efficiency at the pore scale (Iglauer et al., 2014; Wei et al., 2014). Mobility ratios can be considerably improved by adding polymers to the injected water (Adasania and Bai, 2011; Iglauer et al., 2011).

The addition of polymer to the injection brine increases the viscosity of the aqueous phase, which leads to an improved macroscopic displacement, as water under-riding is lessened (Chang et al., 2006). The addition of surfactants improves the microscopic displacement efficiency through: (a) the reduction of the oil-water interfacial tension (Schramm, 2000; Curbelo et al., 2007; Zargartalebi et al., 2015) and (b) the production of oil-water emulsions (Adasania and Bai, 2011), which mobilises residual oil. The addition of alkalis induces the in-situ formation of natural surfactants by reacting with the acidic components contained in the crude oil (generally heavy oils). These natural surfactants function in the reservoir in the same fashion as synthetic surfactants (Adasania and Bai, 2011; Trabelsi et al., 2011).

The most common CEOR are polymer, surfactant, alkaline, surfactant-polymer (SP) and alkaline-surfactant-polymer (ASP) flooding.

2.2.2.1 Polymer Flooding Mechanisms

In polymer flooding, polymers (dissolved in water) are injected into the reservoir, followed by a long-term waterflooding, which is performed to drive the slug and the oil bank in the direction of the production wells. The addition of polymer to the injected brine increases the viscosity of the aqueous phase and reduces the effective permeability to water due to polymer retention (adsorption and mechanical trapping) in the formation rock.

The main objective of polymer flooding is to lower the mobility ratio of the waterflooding process. It is well established that the lower the mobility ratio, the more stable the displacing fluid front, and the more efficient the macroscopic displacement process. Therefore, mobility ratio (M) should be controlled to values less than one (M

< 1) to prevent the onset of viscous fingering of the water phase through the oil phase, which will result in unswept regions, where oil is left behind the displacement front (Green and Willhite, 1998; Wei et al., 2014).

The overall mechanisms of oil recovery by polymer flooding are as follows:

- Increasing of the water viscosity.
- Decreasing of the effective permeability to water due to polymer retention.
- Decreasing of the water-oil mobility ratio that improves the macroscopic sweep efficiency

Process benefits: Polymers are effective brine viscosifying agents (Abidina et al., 2012) and can successfully reduce the effective permeability to brine (i.e. polymer retention). Overall, polymer flooding is a cost effective EOR process.

Process limitations: Some of the limitations of polymer flooding are the susceptibility of polymers to thermal (i.e. high temperature reservoirs), chemical (i.e. high salinity and hardness concentration in the injected and formation brine), mechanical and bacterial degradation. Some polymer systems are incompatible with the reservoir fluids and conditions (i.e. temperature). The application of polymer flooding in low permeability rocks may cause problems of injectivity and formation plugging (Abidina et al., 2012).

Common polymers used in the oil fields are of various types with varied functionalities - advantages and disadvantages for a specific formation. Hydrogel polymers have been used for mobility control for several decades. Likewise, polymers in combination with surfactants and alkalis have been applied over the years to improve both the microscopic and macroscopic sweep efficiency (Abidina et al., 2012). In recent times, several new polymers (Table 2.1) have been developed. The most common types (Wever et al., 2011; Sheng, 2011; Abidina et al., 2012) of polymers used for EOR are synthetic and biopolymers (Refer to Table 2):

- synthetic polymers (i.e. polyacrylamide or PAM) (Figure 2),
- hydrolysed polyacrylamide (HPAM).
- biopolymers or biological polysaccharide (i.e. xanthan gum)

- superabsorbent polymer composite (SAPc)

Among these polymers, HPAM (Figure 2.2) remains the most effective and commonly applied polymer for enhanced oil recovery. These polymers are suitable for temperatures up to 99°C and can withstand higher temperatures upon modifications (HPAMAMPS co-polymers - 104°C and sulphonated polyacrylamide - 120°C) (Abidina et al., 2012). HPAM displays fair salt-tolerant than others, good viscosifying properties, ultrahigh molecular weight, and well-known physicochemical characteristics. The effectiveness or advantages of HPAM (Sheng, 2011) relies in the following chemical features: (1) the lack of oxygen single bonds (-O-) in the polymer backbone (carbon chain) provides thermal stability; (2) the presence of non-ionic hydrophilic group (i.e.-CONH₂) promotes chemical stability; and (3) the carboxyl group (-COO-) resulting from the hydrolysis of the amide groups reduces the adsorption tendency of HPAMs onto rock surfaces and increases its viscosity. Other characteristics that make HPAM very attractive for EOR include: (1) fairly easy application with great potential for incremental oil at standard reservoir conditions (i.e.

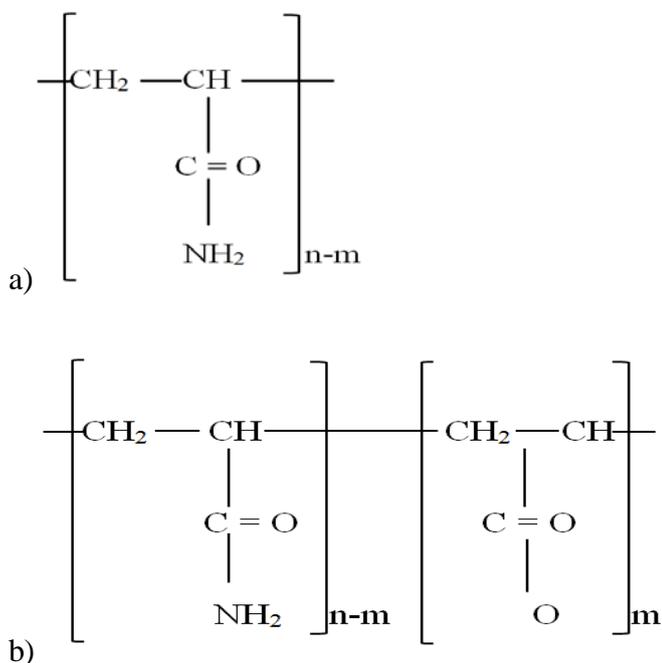


Figure 2.2: Structure of polymers: (a) polyacrylamide (PAM), (b) partially hydrolysed polyacrylamide (HPAM) (refer to Table 2.1).

low temperatures and low salinity and hardness concentration); (2) availability of the polymer in various molecular range (> 20 million Da); (3) the cost of the polymer is relatively low; and (4) its viscosifying and physicochemical characteristics. A key disadvantage of HPAM is its high sensitivity to the brine salinity and hardness which can act as a limitation in HPHT reservoir applications. PAM is the first thickening agent used for aqueous solutions. A major drawback in its applications is that the stability of PAM is also dependent on salinity; at normal salinity - PAM can be stable up to 90°C and at seawater salinity - up to 62°C , thus more limited to on-shore operations as high salinity can dramatically lead to the reduction in its viscosity properties (Abidina et al., 2012). Xanthan gum is a biopolymer also commonly used for EOR applications. The main limitation of this biopolymer is its vulnerability to microbial degradation. Salt compliant microbes (aerobic and anaerobic) have the potential to degrade the xanthan gum chains, which results in viscosity loss (Cadmus et al., 1982; Sutherland, 1982; Hou et al., 1986). Therefore, biocides are injected alongside with xanthan gum to avert microbial degradation. However, xanthan performs remarkably well in brines having high salinity concentrations (Cadmus et al., 1982). Generally, high salinity brines (i.e. 10,000 ppm TDS) polyacrylamide copolymers shows lower viscosities than biopolymers (Sheng, 2011). Nonetheless, HPAMs have better potential for reducing the water relative permeability than xanthan during flow through formation rocks.

2.2.2.2 Surfactant Flooding Mechanisms

Surfactants are organic compounds with polar and non-polar components. The polar parts are hydrophilic in nature and thus, water-soluble (attract water), whereas, the non-polar parts are hydrophobic and thus, oil-soluble (repel water). Surfactants are amphiphilic (hydrophobic and hydrophilic) as these materials have chemical groups that enhance surface activity, thus, normally referred to as surface-active agents (capable of adsorbing at an air/water or oil/water interface, and solids surfaces) and are soluble in water and organic solvents.

Surfactants often accumulate in three-dimensional nano and micro structures (micelles, vesicles, liquid crystalline phases) when they reach sufficient concentration

in solution, with strong capacity to adsorb on surfaces or interfaces (Green and Willhite, 1998; Rosen, 2004; Curbelo et al., 2007; Wu et al., 2011; Skočibušić et al., 2016; Zhou et al., 2016). Typically, if surfactant is dissolved in water or organic solvents, an unfavorable distortion of the liquid structure can occur, which leads to an increase in the total free energy of the system owing to the presence of the hydrophobic group (Myers, 1990). For instance, in an aqueous surfactant solution, the water structure distortion that occurs in the presence of the hydrophobic group reduces the total entropy of the system. The entropy is recuperated upon transport of surfactant molecules to an interface leading to a release of the connected water molecules. Such surfactant, in turn, becomes favourably adsorbed at interfaces or undergoes other processes in order to reduce the system energy, thus, surfactants can effectively reduce the interfacial tension (IFT) of the system. In principle, such phenomenon is due to the fact that the work required to bring surfactant molecules to an interface is much lower than that required for solvent molecules, hence, the surfactant reduces the work required to increase the interfacial area thus yielding IFT decrease.

This amphiphilic structure of surfactant molecules enhances (Myers, 1990) the:

- The inclination of surfactant molecules to adsorb at interfaces.
- Alteration of the parallel interfacial energies.
- The direction of hydrophobic groups away from the bulk solvent phase owing to the favourable orientation of adsorbed molecules, which yields macroscopic effects.

Four basic categories of surfactants exist: anionic, cationic, non-ionic and zwitterionic (Table 2.2). Anionic surfactants are organic substance which creates negatively charged particles when dissolved in water. This is the most commonly used class of surfactants which include wetting agent such as di-alkyl sulfosuccinate, foaming agent - lauryl sulfate, fatty acid; lignosulfonates and alkylbenzene sulfonates. Anionic surfactants are effective for oil recovery and reservoir stimulation applications as they are bio-compatible with reservoir formations, biodegradable and effective wettability agents especially for sandstone reservoirs (Zhu and Rosen, 1984; Jönsson et al., 1991; Walstra, 1993; Tang, et al., 2006; Thampi et al., 2014). Cationic surfactant ionizes in water into the positively charged cations. This class of surfactants are generally costlier than the anionics as its synthesis requires high pressure hydrogenation reaction. They are suitable as positively charged substance that permits adsorption on

negatively charged substrates to produce antistatic effect. Cationic surfactants exhibit strong synergism in their solutions while displaying physicochemical properties that vary distinctly from others owing to their electrostatic interaction between oppositely charged head groups and hydrophobic interaction. For example, the surfactants high surface activity is ideal for emulsification owing to their excellent oil-water IFT reduction effect and also serves as wettability reduction agent (Zhu and Rosen, 1984; Jönsson et al., 1991; Walstra, 1993; Tang et al., 2006). Non-ionic surfactant neither forms cation nor anion in water (no charge groups in its head - net charge). This surfactant does not ionize in aqueous solution owing to its hydrophilic group which is of a non-dissociable type, for example: ether, ester, amide, alcohol or phenol. Its solubility in water is based on the binding of the hydrophilic parts to the water molecules. The presence of a polyethylene glycol chain obtained by the polycondensation of ethylene oxide enhances their hydrophilicity thus referred to as polyethoxylated nonionics (Salager, 2002; Williams, 2007; Beringer and Kurz, 2011; Sheng, 2011; Attwood, 2012; Guo et al., 2015). Zwitterionic or amphoteric surfactant has a head with two oppositely charged groups. The surfactant exhibit both anionic and cationic dissociations depending on the system pH; at low pH some are cationic, at high pH some are anionic with an amphoteric behavior at intermediate pH, and others are insensitive to pH (Salager, 2002; Williams, 2007; Beringer and Kurz, 2011; Sheng, 2011; Attwood, 2012; Guo et al., 2015). This class of surfactants are biodegradable and can form a microemulsion without the assistance of a co-surfactant (Ivanova et al., 2001; Fleancu et al., 2013;) and exhibit relatively low toxicities and are less sensitive to high electrolyte concentrations or multivalent cations or pH changes (Ha et al., 2002; Fanun, 2008; Ahn et al., 2010).

Surfactant flooding has been recognised as an approach that promotes adequate displacement of oil from porous media when used in adequate volumes, especially in depleted formations (Green and Willhite, 1998). Its usage has been widely investigated (Ahmadall et al., 1993; Austad et al., 1998; Chen et al., 2001; Iglauer et al., 2004; dos Santos, et al., 2006; Golabi, 2009; Iglauer et al., 2009, 2010; Jarrahiana et al., 2012; Bera et al., 2012, 2013; Kathel and Mohanty, 2013; Ahmadi et al., 2015; Hou et al., 2015) as active agents for reduction of oil-water interfacial tension (IFT) (Schramm, 2000; Babadagli, 2000; Hirasaki and Zhang, 2004; Iglauer, 2009) and residual oil saturation (Iglauer et al., 2010). Notably, the driving force in surfactant

EOR is IFT reduction, and reservoir wettability alteration which enhances the oil production rate while decreasing the residual oil saturation. During waterflooding, the residual oil saturation is usually approximately 20-30% OOIP upon contacting 100% of a given oil zone. At such saturation rate, the oil is immobile due to the surface tension between the water and oil, and the differential pressure alone is incapable of overcoming the high capillary pressure to move oil out from the pores. The presence of surfactant enables the reduction in the IFT while decreasing the capillary pressure, thus permits water to remove the trapped oil (water bypass). With respect to a typical surfactant flooding process, a dilute aqueous surfactant solution is injected into the reservoir. Mechanistically, the injected surfactant migrates to the oil-water interface, reduces the interfacial tension (IFT) between oil and water and essentially increases the miscibility of these phases. To put this into perspective in a typical waterflooding process, IFT is approximately 30 mN/m; the addition of small concentrations of surfactant (in the range of 0.1-5.0 wt. %) to the injected water can significantly reduce IFT to values of 0.01 mN/m or lower (Shah and Schechter, 1977; Bourrel and Schechter, 1988; Green and Willhite, 1998; Terry, 2001; Thomas, 2008; Iglauer et al., 2010; Wu et al., 2011; Kamari et al., 2015; Negin et al., 2017). With respect to wetting, surfactant play a key role in reservoir wettability alteration (Schramm, 2003; Nwideo et al., 2017b) as it enables detachment of the attached oil film from the reservoir pore walls. Typically, a liquid droplet in contact with a solid surface will form a bead on the surface if it has a weak affinity for the surface - an indication that its surface tension is above the critical surface tension of the solid surface (γ_c - typically between 18-46 mN/m). Thus, it will spread and form a film owing to its strong affinity for the surface which means that its surface tension is less than γ_c . The presence of surfactant can reduce the surface tension of an aqueous solution to values below 40 mN/m which promotes surface wetting.

The critical micelle concentration (CMC), phase behaviour and oil solubilisation ratio are key parameters for the characterisation of the efficiency of the surfactant formulation.

For effective oil displacement:

Table 2.1: Effective polymers for EOR processes.

Polymers	Molecular weight	Polymer Description	EOR Applications	References
Hydrogel	Not given	<ul style="list-style-type: none"> • Water-swollen and cross-linked polymeric network produced via simple reaction of monomer (s). • Capable of retaining a significant fraction of water within its structure without dissolving in water. • Water Absorption capacity is not more than 100% (1 g/g). 	<ul style="list-style-type: none"> • Used mainly for mobility control. • Used in combination with surfactants and alkali for improvement of sweep efficiency 	Omidian et al., 2004; Abidina et al., 2012; Ahmed, 2015.
Polyacrylamide (PAM)	$>1 \times 10^6$ g/mol	<ul style="list-style-type: none"> • PAM is the first synthetic polymer used for thickening aqueous solutions. • The thickening potentials exist in its large molecular weight. 	<ul style="list-style-type: none"> • Efficient viscosity enhancing capability even in low-salinity brines. • High adsorption capacity on mineral or reservoir rock surfaces. 	Sheng, 2011; Wever et al., 2011; Abidina et al., 2012.

Continued from the previous page

Polymers	Molecular weight	Polymer Description	EOR application	References
Hydrolysed polyacrylamide (HPAM)	> 20 million Da	<ul style="list-style-type: none"> • Copolymers of PAM and polyacrylic acid (PAA) or acrylamide and acrylic acid. • PAM is partially hydrolysed to form HPAM. This is achieved by reacting PAM with a base (sodium) to reduce the strong adsorbing behaviour of PAM. • The degree of hydrolysis is usually in the range of 15–35% 	<ul style="list-style-type: none"> • The most commonly used polymer for EOR. • Oil recovery using HPAM is high owing to its viscoelasticity • HPAM displays a better viscosity enhancing capability than PAM. • More effective in low-salinity reservoir brines since it is highly susceptible to degradation owing to temperature and salt sensitivity. 	Sheng, 2011; Wever et al., 2011; Abidina et al., 2012.
Superabsorbent polymer composite (SAPC)	Not given	<ul style="list-style-type: none"> • Crosslinked hydrophilic polymers which have the potential to retain water in swollen form • Ultrahigh water adsorption capacity of 1,000-100,000% (10-1000 g/g). 	<ul style="list-style-type: none"> • Effective for used as plugging agents in EOR processes. 	Omidian et al., 2004; Zu and Luo, 2008; Abidina et al., 2012; Ahmed, 2015.

Continued from the previous page

Polymers	Molecular weight	Polymer Description	EOR	References
Xanthan gum	2 -50 × 10 ⁶ g/mol	<ul style="list-style-type: none"> • A biopolymer produced by microbial (Xanthomonas campestris) action (through glucose or fructose fermentation). • Possess substantial hydrolytic degradation above 70 °C. • Acts like a partially stiff rod with a fair resistivity to mechanical degradation. • Xanthan gum for EOR is often in broth or concentrated form which makes it easy to dilute at suitable concentrations. 	<ul style="list-style-type: none"> • Effective for use in high salinity brine. • Fairly compatibility with surfactants when used for EOR. • Effective as rheological modifier, drilling fluid additive, emulsion stabilizer, and fluid loss controlling agent. 	<p>Leela and Sharma, 2000; Sheng, 2011; Abidina et al., 2012; Ponmani et al., 2014.</p>

- Dilute aqueous surfactant solutions are injected in slugs.
- The injected slugs must attain ultra-low IFT.
- This leads to the mobilisation of the residual oil and creation of oil banks, which allows the continuous phase flow of oil and water.

Process benefit: Effective reduction of the interfacial tension between brine and water that significantly enhances the microscopic sweep efficiency (Green and Willhite, 1998; Iglauer et al., 2010; Sheng, 2013).

Process limitations: The achievement of ultra-low IFT for effective residual oil mobilisation is a complex process. Large amounts of surfactants are required to achieve substantial oil recovery. The viscosity of the surfactant formulation is often lower than that the viscosity of the oil, thus, to augment the viscosity of the surfactant slug, the addition of polymers to the surfactant formulation is required. The high cost of surfactants makes its deployment in the field highly dependent on oil price (Kamari et al., 2015).

2.2.2.3 Alkaline Flooding Mechanisms

Alkaline flooding involves the injection of an aqueous solution of alkaline chemical such as sodium hydroxide, sodium carbonate or sodium orthosilicate in a slug form (Johnson, 1976; Mayer, 1983; Thomas, 2008) (Table 2.3); the most commonly used alkaline chemical is sodium hydroxide (Terry, 2001).

During alkaline flooding, the alkaline solution and organic acids present in the crude oil react to form natural surfactants in situ, which cause the reduction of IFT between the brine and oil. Natural surfactants induce the formation of oil and water emulsions and wettability alteration of the reservoir rock (Froning and Leach, 1967; Terry, 2001; Abu El Ela et al., 2014). All these physicochemical interactions occur at the oil-water rock interfaces, which invariably improve oil recovery.

Process benefit: Alkaline flooding shows potential for heavy oil recovery in thin formations (Huang and Dong, 2004). This process promotes effective IFT reduction

and crude oil emulsification. Overall, alkaline flooding is characterised by low operational costs.

Process limitations: Scale formation is a serious issue during alkaline flooding. Furthermore, the low viscosity of the alkaline solution is associated with the occurrence of unfavourable fingering and poor volumetric sweep efficiency (Nicholas and Jeffrey, 1997).

2.2.2.4 Surfactant-Polymer (SP) Flooding Mechanisms

In surfactant-polymer flooding, separate surfactant and polymer slugs are injected into the reservoir. The alternate injections of surfactant and polymer slugs have the potential to sweep larger reservoir volumes and to increase oil displacement efficiency.

The mobility control is established during SP flooding by injecting the chemical slugs according to the following injection scheme: surfactant slug, polymer slug, polymer buffer (to protect the integrity of the polymer slug) and chase water (Shah, 1981; Rai et al., 2003). Accurate formulation of the surfactant-polymer (SP) mixture can promote capillary number increase (due to the presence of surfactants through IFT reduction) and reduction in mobility ratio. However, an incompatible SP formulation can cause surfactant and polymer phase separation even when oil is not present. Two essential factors for consideration during SP flooding are (a) IFT reduction and (b) viscosity increase (Shah, 1981; Yen, 1990; Rai et al., 2003; Lau, 2014). In addition, the effective permeability to water is reduced due to polymer retention in the formation rock. Therefore, an overall improvement of mobility ratio and sweep efficiency is achieved rendering incremental oil recovery (Needhan and Peter, 1987; Gregersen et al., 2012; Choi et al., 2014).

Process benefits: Accurate SP formulation can achieve ultra-low oil-brine IFT, which promotes effective displacement of residual oil saturation.

Process limitations: The main limitation of the SP flooding process is chemical incompatibility among the additives and brine (injection and formation brine).

2.2.2.5 Alkaline-Surfactant-Polymer (ASP) Flooding Mechanisms

ASP flooding uses alkali-surfactant-polymer cocktails for further improvement of oil recovery efficiency (Gregersen et al., 2012; Panthi et al., 2016). The key reasons for the combination of the three chemicals are IFT reduction and mobility ratio improvement (Thomas, 2008). Alkali decreases surfactant adsorption onto rock surface through an increase of the negative charge density at the rock surface yielding a more water-wet surface (Manrique et al., 2007; Wu et al., 2011). Surfactant decreases the IFT between oil and brine, which promotes oil mobilisation and oil bank formation, whereas polymer offers mobility control (Choi et al., 2014; Alagorni et al., 2015). The amount of chemical consumed per unit volume of oil produced during ASP flooding is usually low when the three chemical slugs (alkaline, surfactant and polymer) are injected in sequence or as a single slug (Froning and Leach, 1967; Thomas, 2008).

Process benefits: ASP is a cost-effective process. The synergistic effects of the ASP mixture make this process attractive for EOR applications.

Process limitations: Some of the limitations of the ASP process are related to issues with chemical separation, emulsions instability and scale formation that could make the process complex (Froning and Leach, 1967; Choi et al., 2014).

2.2.3 Gas injection EOR (GEOR) technique

In EOR gas injection, oil is displaced towards the production wells by injecting gas. Two predominant factors determine the success of this process: (a) the displacement efficiency and (b) the sweep efficiency. The displacement efficiency is the percentage of oil displaced by the injected fluid, whereas, the sweep efficiency accounts for the reservoir volume contacted (swept by) the injected fluids (Donaldson et al., 1989). Gases commonly used for GEOR are carbon dioxide, hydrocarbon gases and nitrogen (Adasania and Bai, 2011). Among these gases, CO₂ is the most frequently applied and it accounts for over 50% of the GEOR production (Baviere, 2007; Parker et al., 2009). For instance, in 2009, Ferguson et al. (2009) reported that 101 GEOR projects in the US produced approximately 250,000 barrels of oil per day. In the United States, CO₂-EOR has been considered the best GEOR method to produce incremental EOR

(Knight, 2011). Nevertheless, GEOR processes are often associated with viscous and density fingering (Green and Willhite, 1998; Sahimi et al., 2006).

The two main gas injection processes involve miscible and immiscible gas flooding.

2.2.3.1 Miscible Flooding Mechanisms

Here the key purpose is to recover residual oil that remains in the gas-swept or water-swept regions of a reservoir, often after secondary recovery through the injection of miscible solvents (CO₂, nitrogen, or hydrocarbon gases) that can achieve miscibility with certain crude oils under reservoir temperature and pressure conditions so as to eliminate the interfacial forces trapping the oil. In miscible gas flooding, gas completely mixes with the crude oil through single or multiple contacts between the gas phase and the crude oil phase. The gas injected reaches miscibility with the crude oil at or above the minimum miscibility pressure (MMP) (Healy et al., 1994; Al-Anazi, 2007). MMP is the minimum pressure at which crude oil becomes miscible with the injected gas at the reservoir temperature. MMP is a determining factor during miscible gas (e.g. CO₂) flooding, as displacement efficiency is highly dependent on it (Fath and Pouranfard, 2014).

CO₂ achieves miscibility with crude oil through multiple contacts between the oil phase and the CO₂ gaseous phase. In this mechanism of multiple contact miscibility, light hydrocarbons (lighter-low carbon, low density) from the crude oil are transferred (vaporised) into the CO₂ phase. Progressively, the gas phase becomes richer in the vaporised light hydrocarbons, which continuously change the composition of the gas phase that eventually becomes heavier and denser. This heavier gas phase condenses into the crude oil zone ahead of the displacement front (i.e. miscible zone) causing the reduction in crude oil viscosity and density. As miscibility occurs between the residual oil and the injected CO₂, the IFT between the gas and the oil phase becomes zero, thus this mixture is displaced as a single phase from the pores of the rock towards the producing well (U.S. DOE, 2009). Very low residual oil saturation is achieved as the

Table 2.2: Effective EOR surfactants (Sheng, 2011; Attwood, 2012; Guo et al., 2015)

Surfactants	Examples	Features	Surface charge	Process Description
Anionic	Sodium dioctylsulphosuccinate, Sodium dodecyl(lauryl)sulphate, Potassium laurate, Hexadecylsulphonic acid	Composed of surface - active specie known as anion.	Negative	<ul style="list-style-type: none"> • Most globally used surfactant for EOR. • Displays low adsorption on reservoir rock surfaces (e.g. Sandstone). • Effective wettability alteration agent. • Effective IFT reduction agent. • Low cost in comparison to Cationic.
Cationic	Dodecylamine hydrochloride, hexadecyl(cetyl)trimethylammonium; dodecylpyridinium chloride	Composed of surface - active specie known as cation.	Positive	<ul style="list-style-type: none"> • Effective for wettability alteration in carbonate rocks than in sandstone. • Considered relatively unsuitable for application in sandstone (negatively charged) reservoirs due to its strong adsorption behaviour onto the rock surface.

Continued from the previous page

Surfactants	Examples	Features	Surface charge	Process Description
Nonionic	Polyoxyethylene monohexadecyl ether; Polyoxyethylene p-tertoctylphenyl ether	Its water-soluble moiety contains hydroxyl groups or a polyoxyethylene chain.	No ionic charge	<ul style="list-style-type: none"> • Mainly function as a copolymer. • Effective for improving phase behaviour of a system. • Tolerant to high salinity and hardness. • Fairly effective IFT reduction agent.
Zwitterionic	N-dodecyl-N, N-dimethyl betaine	Behaves as either anionic, non-ionic or cationic species based on solution pH.	Positive and negative	<ul style="list-style-type: none"> • Effective for IFT reduction. • The effect of electrolytes, pH and temperature changes on zwitterionic is negligible. • Exhibits better temperature resistance and salt tolerance than other surfactant types.

interfacial tension (IFT) in the miscible zone reduces to zero, thus there is no interface between oil and gas anymore (Adasania and Bai, 2011; Sarapardeh et al., 2014).

Process benefits: Miscible gas flooding is usually more cost effective (Sheng, 2013) in comparison to TEOR flooding methods based on operational costs. Miscible gas injection increases the overall displacement efficiency, minimises residual oil saturation, promotes ultra-low (near zero) IFT and increases oil production significantly. E.g., Healy et al. (1994) compared the performance of a miscible flood and waterflood for the Means Lower San Andres reservoir in West Texas via simulation. Recovery by waterflooding accounted for 37% of the original oil in place (OOIP) and sweeps about 80% of the reservoir; with a reduction in the average oil saturation in the water swept regions from 70% (initial value) to 38%. However, the stranded oil (remaining oil) in the region swept by water was trapped as a discontinuous phase within the pore space. The miscible flooding is thus an approach for recovering such trapped residual oil, solvents can displace such oil where there is water slumping, which sweeps the reservoir parts that have already been swept by water, while recovering only a portion of the residual oil. The solvent sweeps approximately 50% of the pattern in comparison to the 80% by water and reduction in oil saturation occurred from 38% to 24%; with a total incremental oil recovery of 11% OOIP for the miscible flood.

Process limitations: Miscible gas injection requires higher (expensive) operational costs (i.e. high gas compression costs). The changes in the crude oil density during the miscibility process can alter the flow path of the oil during the period when the lighter hydrocarbons vaporise into the CO₂ gas phase or when the rich gas phase (CO₂ plus light hydrocarbons) dissolves (condenses) into the oil phase (Han et al., 2016). Failure in miscibility may occur if pressure is not at or above the MMP leading to an unsuccessful miscible displacement process.

2.2.3.2 Immiscible Flooding Mechanisms

Immiscible gas flooding entails the injection of gas below the MMP. Below the MMP, there is no miscibility between CO₂ and oil. Technically, immiscible flooding produces about half of the recovery of miscible gas flooding (Cobb, 2010; EPC, 2012).

During immiscible flooding, incremental oil recovery is mainly achieved through oil swelling, which improves the macroscopic displacement efficiency (Al-Anazi, 2007). At microscopic level, three-phase (oil-gas-water) flow is observed with a complex interplay of the different phases (Oren et al., 1992; Iglauer et al., 2013; Iglauer et al., 2016). Although these microscopic processes are still poorly understood, there is clearly significant potential to further improve oil recovery at the pore level.

Table 2.3: Effective alkaline chemicals for EOR (Sheng, 2011)

Alkaline	Characteristics
Sodium hydroxide NaOH	<ul style="list-style-type: none"> • Most commonly used alkaline for EOR. • Used for IFT reduction. • Corrosion and scale formation issues.
Sodium orthosilicate Na ₄ O ₄ Si	<ul style="list-style-type: none"> • Reduces water hardness through formation of silicates which are less soluble than the hydroxides. • Better IFT reduction potentials than sodium hydroxide in hard water. • Precipitation or scale formation issues.
Sodium carbonate Na ₂ CO ₃	<ul style="list-style-type: none"> • Weaker alkali in comparison to sodium hydroxide and sodium orthosilicate. • Corrosion and scale formation issues.

Notably, constant immiscible gas flooding with gases such as CO₂ is more favourable to light oil than heavy oil reservoirs. To improve recovery in heavy oil formations using CO₂, co-injection or the injection of water alternate gas, known as the WAG process, is performed to somehow control viscous fingering, gas channelling and early gas breakthrough. Upon injection of water and gas into the reservoir, a portion of the injected gas (CO₂) usually dissolves in the oil that leads to oil viscosity reduction. A recent advancement in immiscible flooding is polymer water alternate gas (PWAG) for overcoming viscous fingering and improvement of sweep efficiency (Zhang et al., 2010).

Process benefits: Immiscible gas injection improves oil displacement efficiency. The oil recovery potential from the application of this process is higher from light oil formations (Zhang et al., 2010).

Table 2.4: Effective agents for MEOR (Lazar, 2007; Sen, 2008).

MEOR agents (Microbes)	Functionality
Biosurfactants (i.e. Bacillus, Arthrobacter)	<ul style="list-style-type: none"> • IFT reduction between oil and water. • Promotes oil emulsification owing to reduced IFT. • Improvement of residual oil displacement. • Effective for wettability alteration.
Biopolymers (i.e. Bacillus, Xanthomonas)	<ul style="list-style-type: none"> • Water viscosity can be greatly improved which promotes mobility control. • Effective for selective plugging. • Used for modifying viscosity of the formation water and injectivity profile.
Bacterial consortia (Biogases: Clostridium, Enterobacter; BioSolvents: Clostridium, Zymomonas; Bioacids: Clostridium, Enterobacter)	<ul style="list-style-type: none"> • Produces gases such as N₂, CH₄, CO₂, and H₂ that are effective in promoting oil viscosity reduction, IFT reduction, and oil swelling. • Produces solvents such as alcohols and ketones which dissolve in oil and promotes IFT reduction and oil emulsification. • Produces acids that promote dissolution of clays increasing porosity and permeability.
Biomass (i.e. Bacillus, Xanthomonas)	<ul style="list-style-type: none"> • Effective for selective plugging within the porous media. • Effective for altering rock wettability. • Effective for the partial degradation of crude oil. • Displaces oil through bacterial growth between the oil and the surface of rock and water.

Process limitations: Viscosity ratios of the injected gas (i.e. CO₂) to oil (light or heavy oil) are unfavourable causing the occurrence of gravity override and viscous fingering through permeable zones, early gas breakthrough and poor sweep efficiency (Zhang et al., 2010; Hou and Yue, 2010). This process renders poor oil recovery potentials in heavy crude oil formations in comparison to thermal EOR.

2.2.4 Microbial EOR (MEOR)

In MEOR, indigenous or exogenous bacteria can be activated or injected into the reservoir to generate metabolic chemicals that interact with the crude oil and increase oil production. For these applications, bacteria should be small, spherical and less than 20% of the size of the pore throats in the formation (Brown, 2010). Small cell size (between 0.5 and 5.0 µm) penetrates easily through the reservoir porous medium (Bryant and Burchfield, 1989). Typically, mixed microbial populations are used in combination with metabolic products such as solvents, acids or gases to increase recovery and prolong the life span of the oil wells (McInerney et al., 2005; Ollivier and Magot, 2005; Lazar et al., 2007; Sen, 2008).

These metabolic products are produced by different bacteria (microbes) and exhibit different functionalities in MEOR processes. Solvents such as acetone, butanol and propan-2-diol (produced by *Clostridium*, *Zymomonas* and *Klebsiella*) reduce oil viscosity and thus improve oil mobility (Zobell, 1947; Kalish et al., 1964). *Clostridium*, *Enterobacter* and *Methanobacterium* produce methane and hydrogen, which reduces IFT, oil viscosity (Nazina et al., 2003) and increase oil mobilisation. Among several microbes used for MEOR processes. *Clostridium* microbes are the most applicable owing to their resistant endospores that enable survival at unfavourable conditions (Sarkar et al., 1989). *Bacillus* strains are also effective MEOR agents (Table 2.4) (Van Hamme et al., 2003; Sen, 2008).

2.2.4.1 Mechanisms of MEOR

- **Biosurfactants:** Biosurfactants are biodegradable and more effective in emulsifying aqueous hydrocarbon mixtures than synthetic surfactants (Banat, 1995). Biosurfactants can be produced in bioreactors ex situ and injected as an aqueous

surfactant formulation into the reservoir. As surfactant migrates towards the oil-aqueous interface, IFT is reduced and capillary number increases displacing and recovering residual oil (Banat, 1995; Sen, 2008). The production of in situ biosurfactants takes place by injecting the biosurfactant-producing microbes into the formation ensuring proper propagation of the microbes into the oil reservoir (Bubela, 1985). Selected nutrients are also injected to stimulate the growth of the biosurfactant-producing indigenous microbes in the reservoir (Banat, 1995).

- **Biopolymers:** Biopolymers are mainly used for selective plugging of high permeability thief zones. In this MEOR application, bacteria in aqueous solutions are injected into the formation that preferentially flows through the high-permeability pathways, where the growth of biomass plugs the pore throats, leading to permeability reduction (Sen, 2008). Plugging of high permeability thief zones diverts waterflood towards the lower permeability oil saturated areas.
- **Bacterial consortia:** Bacterial consortia are used for the selective production of biogases (i.e. methane, carbon dioxide and hydrogen), biosolvents (i.e. acetone, ethanol, 1-butanol, butanone, etc.) and bioacids (i.e. acetic, propionic, butyric, etc.). In a pressure-depleted formation, biogases assist in pressure build-up and at high pressures, biogases can dissolve within the oil phase reducing its viscosity. Bioacids are capable of dissolving carbonate rocks leading to porosity and permeability increase in the oil formation (Zobell, 1947; Sen, 2008).

Process benefits: MEOR is environmentally friendly as the MEOR bioproducts are biodegradable low oil production costs, MEOR is not dependent on oil price like the conventional CEOR processes and MEOR consumes less energy than the TEOR processes. MEOR is economically attractive for application in marginally producing oil fields because the injected bacteria and nutrients are low priced (Youssef et al., 2007; Sen, 2008).

Process limitations: The MEOR process is complex because it depends on the reservoir chemistry for bacteria functionality and isolation. MEOR renders low incremental oil recovery (Sen, 2008).

2.3 EOR Global Outlook

EOR has proven to be an effective strategy for recovery enhancement. In 1998, global EOR projects achieved the production of 2.3 million b/d from steam flooding in the Duri field (Indonesia), which was the largest steam-flooding project at the time. A further EOR production of 480,000 b/d was reported for Canada and China with an EOR production of 280,000 and 200,000 b/d respectively (Terry, 2001). In recent times, the EOR global market has experienced an unceasing progression in its growth pattern. In 2012, the global EOR market was 2095 million barrels (Grand View Research, 2015), with a further increase to 2681.6 million barrels by 2013. Globally, EOR contributes about 3.5% of daily oil production (Taber et al., 1997; Abu El Ela et al., 2008), which is approximately 3 million barrels of oil per day (Kokal and Al-Kaabi, 2010). A compound annual growth rate of 29.9% has been projected through 2014-2020; thus, a much higher growth above 16,000 million barrels is expected by 2020 that will amount to about US\$ 283 billion (Grand View Research, 2015). EOR projects appear to be very significant in the recent times, which was not the case decades ago. In the past, EOR projects were stagnated in the mid-1908s, specifically, the gas injection projects; in the 1980s, the thermal and chemical EOR processes experienced a decline.

However, since 2000, GEOR projects have been on the rise due to the growth in the implementation of CO₂-EOR projects (Alvarado and Manrique, 2010). In 2002, gas projects surpassed thermal projects for the first time in three decades although trivial increase in thermal projects has been observed in recent times due to the increase of High Pressure Air Injection (HPAI) projects (Alvarado and Manrique, 2010). Globally, gas (miscible flooding) (GEOR) and thermal EOR (TEOR) techniques have been the most extensively used among the key EOR techniques especially between 2004 and 2014. In 2004, CEOR, MEOR and GEOR (immiscible flooding) had 9,1,15 projects respectively, whereas, TEOR and GEOR (miscible flooding) had 118 and 131 projects, respectively as evident in Figure 2.5 (Abu El Ela et al., 2014). While the global field scale implementation of the chemical EOR (CEOR) method has remained almost stagnant and insignificant since the 1990s with the exception of China (Han et al., 1999, Chang et al., 2006). Only nine CEOR projects were reported in 2004, (Abu El Ela et al., 2014), two projects in 2008 (Alvarado and Manrique, 2010), six, five and

seven projects in 2010, 2012, and 2014 respectively as evident in Figure 2.3 (Abu El Ela et. al., 2014), despite decades of existence in comparison to microbial EOR.

Other recent EOR processes include plasma-pulse enhanced oil recovery and nanoparticles. Plasma-Pulse Technology (PPT) is an easy to use technology, which is still in its patent stage, and it is been considered for enhancing recovery of oil and gas. This method uses a refractory, electro-magnetic pulse, of low power for propagation into reservoir formation. The process is believed to allow efficient oil and gas to the surface for extraction via viscosity reduction, permeability increase and reduction in water cut, without causing hydraulic fracturing, acidization, or any other environmentally harmful processes at reasonable production cost. (Huemoeller-II, 2013; Burgess, 2014).

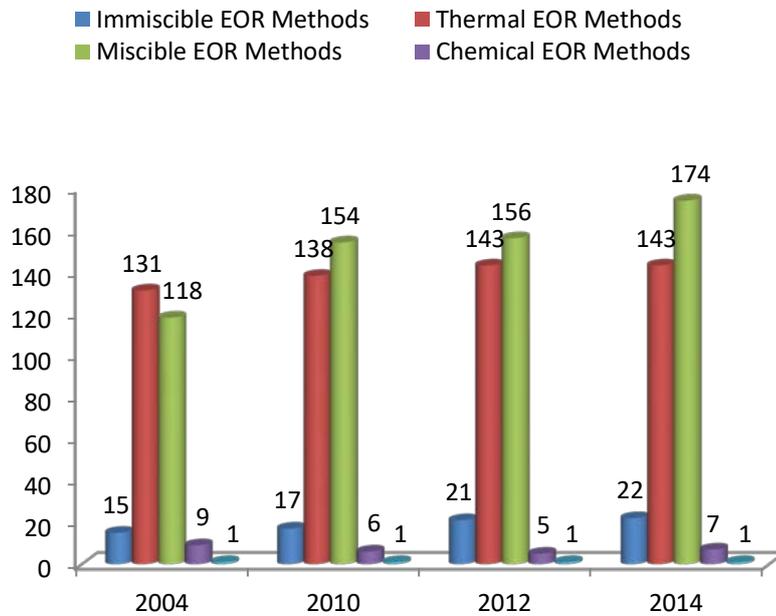


Figure 2.3: Global EOR project status (Abu El Ela et al., 2014).

2.4 Relationship between Oil Recovery and Wettability

In hydrocarbon reservoirs, fluid-rock interactions are predominant occurrences owing to the existence of surface forces between molecules. Fluid displacement in reservoirs, especially, when more than one fluid is involved can contribute to poor oil recovery as the oil gets trapped owing to factors such as IFT between fluids, fluids immiscibility

and rock surface wetting issues. At large scales, wetting or non-wetting plays an essential role during oil recovery (Bertrand et al., 2002).

Wetting processes often involve the interaction of solids such as porous material, suspensions, or fibers; and liquids-water, ink, dye or lubricants. Typical indications of solid-liquid wetting can be illustrated using standard scenarios to correlate the dynamics such as: (1) the interaction between porous soil and water - where the water wets the solid components of the soil; (2) enhanced oil recovery- where the process permeates water into oil-wet porous media. However, the mineral floatation in these processes is often based on the selective wetting characteristics of the mineral particles (de Gennes, 1985).

An understanding of surface chemistry is therefore imperative for evaluating wetting behaviour as porous media wetting are influenced by the rock surface morphology, as well as, the chemical compositions. Surface chemistry modifications of materials facilitate short-ranged chemical interactions. This phenomenon is predominantly governed by the surface and interfacial interactions, which act over the scale of molecules, and electrostatic surface forces that determine the extent to which a fluid can wet a surface (Bonn et al., 2009). Wettability influences particles migration, residual oil saturation distribution, fluids relative permeability, displacement and distribution of reservoir fluids, and the size and direction of capillary forces and the quantity of recoverable oil at the pore scale which can impact on overall project cost and process viability.

The relationship between oil recovery and wettability can be expressed through an understanding of the role of capillary number. Capillary number (N_c) is closely related to oil recovery alongside other variables such as mobility ratio (M) at the macroscopic scale or wettability. Capillary number (Terry, 2001; Thomas, 2008; Sheng, 2011) represents the ratio of viscous forces to interfacial tension (IFT) forces (Equation 2.1) as

$$N_c = V\mu / \sigma \quad 2.1$$

An increase in capillary number leads to a corresponding decrease in residual oil saturation. This effect is mainly due to the increase in Darcy's velocity (V), which is the velocity of the injected fluid and/or viscosity of the displacing fluid (μ) and/or a

reduction in IFT (σ) (Stegemeier, 1977; Hou et al., 2015). Whereas, mobility ratio (M) represents the ratio of the displacing fluid mobility to that of the displaced fluid (Equation 2.2, 2.3) as

$$M = \lambda_{ing} / \lambda_{ed} \quad 2.2$$

and

$$\lambda = k / \mu \quad 2.3$$

The mobility ratio determines the stability of displacement (Thomas, 2008). This is vital for macroscopic displacement efficiency. Favourable mobility ratios occur when the mobility ratio is less or equal to one ($M \leq 1$) which enhances the increase in displacement efficiency (Figure 2.4), whereas, unfavourable mobility ratio occurs when the the mobility ratio is greater than one ($M > 1$), which leads to inefficient displacement of residual oil. Microscopic and macroscopic displacement efficiency, thus, play a vital role in efficient hydrocarbon recovery (Green and Willhite, 1998; Terry, 2001; Lyons and Plisga, 2005).

Generally, microscopic displacement efficiency depicts the extent to which the displacing fluid mobilises the residual oil once in contact with the oil. The microscopic displacement efficiency is predominantly controlled by rock wettability, interfacial tension, capillary pressure, and relative permeability (Thomas, 2008). The increase in microscopic displacement efficiency can, thus, be achieved through a reduction in oil viscosity, capillary pressure, or interfacial tension of the displacing fluid (Satter et al., 2008).

The Macroscopic displacement efficiency also referred to as the volumetric sweep efficiency ascertains the extent to which the displacing fluid is in contact with the oil-bearing parts of the reservoir (Equation 2.4) (Green and Willhite, 1998; Terry, 2001; Lyons and Plisga, 2005; Thomas, 2008; Shrimali, 2015). Macroscopic displacement efficiency is influenced by factors such as the displacing and displaced fluid mobility ratio, the heterogeneity of the formation rock matrix and anisotropy, and the positioning of the injection and production well(s) (Green and Willhite, 1998; Terry, 2001). The overall displacement efficiency is thus, defined as the product of the

microscopic and macroscopic displacement efficiency. The relationship between these factors is established thus (Equation 2.4, 2.5) as

$$E = E_d E_v \tag{2.4}$$

and

$$E_v = E_i E_a \tag{2.5}$$

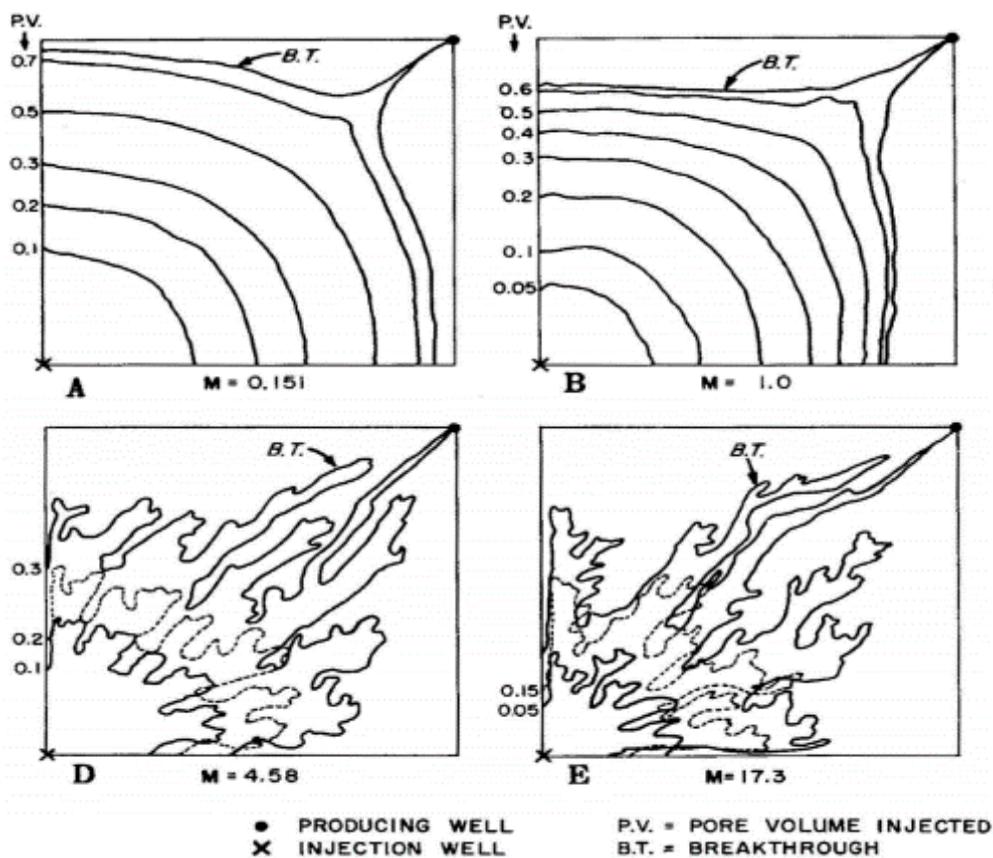


Figure 2.4: Displacement fronts during waterflooding for different mobility ratios and pore volumes injected until breakthrough (Habermann, 1960).

2.4.1 Oil-wet Carbonate Reservoirs and Wettability Challenges

Carbonate rocks are mainly composed of seawater sediments which originate from organic activities. These rocks are more fractured than sandstones, owing to the rock mechanical properties and susceptibility to the post-deposition sediment evolution

(Bourbiaux, 2010). The key differences between the carbonate and sandstone rocks are the locations sediment production site and chemical reactivity. The sediment production locations for carbonates are the autochthonous, whereas, that of sandstone rocks are allochthonous (Ehrenberg and Nadeau, 2005). On basis of chemical reactivity, carbonates are more chemically reactive than sandstone (Choquette and Pray, 1970; Moore, 2001). Chemical reactivity is of great relevance in reservoir evaluation, and diagenesis of the common petroleum reservoirs, which shows that carbonate rocks exhibit wide-ranging lithification and porosity variations in comparison to sandstone, which has a low susceptibility to diagenesis. Typically, these formations display different porosity depths, as well as, porosity and permeability distributions (Lucia, 1999; Moore, 2001; Ehrenberg and Nadeau, 2005, Tucker and Wright, 2009), as such, separate treatment measures are applicable for carbonates and sandstone reservoirs, understanding the variances in these key formation types is vital as it affects hydrocarbon recovery.

Reservoirs were originally strongly water-wet, and the formation traps were initially filled with water, thus the surface of reservoir rocks had high affinity for water in the presence of oil. However, overtime, oil migrated into such formations forming firm adsorbed layers of heavy hydrocarbons that pose several challenges and cannot be altered via gasoline or mere solvent applications which was contrary to the general believe held at the time that connate water will inhibit the formation rock surface from being in contact with the oil. The oil migration and accumulation cause water to be retained in the rock pore spaces due to capillary pressure, while the rock pores surface become covered by oil, and water existed on such surfaces in the form of films. This is due to the rock surface wettability changes owing to the ease of invasion by a wetting fluid, which causes lithological variances. The level of oil migration also determines the formations wetting state. For instance, if the migrated oil is negligible, the possibilities are that the neighbouring formations will be more oil wetting, while the tight regions of the formation would exhibit more water-wet behaviour (Nutting, 1934; Benner and Bartell, 1941; Anderson, 1986; Morrow, 1990; Abdallah et al., 2007). This behaviour is more prevalent in carbonate rocks owing to the oil-wet character of this formation, which is still poorly understood.

Understanding wettability in oil-wet carbonate reservoir is challenging owing to the complex nature of crude oil, and its characterization is even more difficult. Crude oil contains polar compounds which are normally surface-active and capable of altering reservoir rock surfaces when adsorbed (Benner and Bartell, 1941; Yu and Buckley, 1997; Buckley et al., 1998; Tong et al., 2002; Lord and Buckley, 2002). Among such polar compounds, asphaltenes and resins have the most polar oil fractions with high surface-activity. Asphaltenes are known for its propensities to self-associate in solution, with high surface adsorption behaviour. Surface wettability alteration is mainly caused by the asphaltenes through interaction of its polar functional component with the surface polar sites, which leads to operational problems and such interaction poses even more complexities (Gonzalez and Moreira 1991; Acevedo et al., 1997; Kaminsky and Radke, 1997; Buckley et al., 1998; Liu and Buckley, 1999; Standal et al., 1999; Andersen and Christensen, 2000). Since the distribution of the oil in the reservoir is dependent on the degree of the reservoir rock wettability, it is, therefore, imperative to quantify the balance of forces existing at the line of contacts between the rock, oil, and water. Typically, if the oil and water are in contact with the rock surface, either of these fluids will exhibit displacement tendencies of the other or attain equilibrium as the fluids create an angle of contact with the rock. However, such interactions can be affected by factors such as the mineralogy of the rock surface, brine composition, pore roughness and the nature of the oil.

Wetting studies have been conducted with crude oil used to alter originally water-wet surfaces to oil-wet (Standnes and Austad, 2000; Standnes and Austad, 2002; Buckley and Lord, 2003; Standnes and Austad, 2003; Zhang et al., 2006; Seiedi et al., 2010; Bera et al., 2012; Kathel and Mohanty, 2013; Hou et al., 2015). E.g. Standnes and Austad (2000) performed a wettability test on chalk cores and calcite mineral surfaces altered by crude oil to a sufficient oil-wet state using surfactant as the surface-active agents via spontaneous imbibition. The authors reported that the cationic surfactant changed the wettability of the chalk by desorbing the organic carboxylates from the chalk surface leading to an increased oil recovery of about 70% from the chalk. Buckley and Lord (2003) altered mica surface to oil-wet using series of crude oil through atomic force microscopy (AFM) and found that the oils that produce the thickest coatings exhibited the highest water-advancing angles. However, a key limitation with the use of crude oil is its exceedingly complex chemistry, which cannot

be reproducibly simulated in laboratory experiments, thus, refined oils are used as it permits reproducibility and eliminates inconsistencies.

It is well established that limestone as a heterogeneous carbonate rock is more prevalent globally. These formations are predominantly naturally fractured and exhibits diverse wetting conditions; intermediate-wet or oil-wet behaviour with as high as over 80% oil-wetness. The oil-wet nature of limestone formation is due to its surface charges, which tend to attract negatively charged carboxylic acid compounds in crude oils (Treiber et al., 1972; Chilingar and Yen, 1983; Buckley et al., 1998). Ideally, the formations positive surface charges attract the crude oil acidic components. Limestone reservoirs are problematic, as the complex wetting characteristics of this reservoir make the production capacity quite different in comparison to other conventional formations. Typically, an enormous capacity of the original oil in place is left stranded in this formation after primary and secondary oil recovery approaches are employed. Such approaches have been implemented for several decades, however, the fraction of recoverable oil from this reservoir is less than two-thirds (Thomas, 2008).

Fractured reservoir (Dehghani and Ehrlich, 1998; Mollaei and Maini, 2010) with enormous oil resources in its matrix requires advanced approaches for efficient recovery. Although water flooding enhances productivity in this reservoir by imbibing water from the formation fractures into the rock matrix, whilst enhancing oil flow out of the matrix through the fractures to the production well; this is mainly achievable, if the capillary driving force is robust and efficient as it influences recovery efficiency, and the interaction between the matrix and the fracture is required for oil recovery from the formation matrix. Although capillary forces have a significant effect on recovery capacities, its impact is greatly dependent on the nature of the reservoir, whether it is fractured or non-fractured. For non-fractured reservoirs, the presence of strong capillary forces during water flooding traps oil, however, the residual oil saturation becomes relatively high. Hence, the need for a reduction of the oil water interfacial tension forces in order to remobilize residual oil in such formations. Whereas, for fractured reservoirs such as carbonate or limestone, the key driving force for efficient oil displacement in this formation is the spontaneous imbibition of water (Babadagli, 2000; Cheraghian et al., 2013). Capillary effect and wettability are the

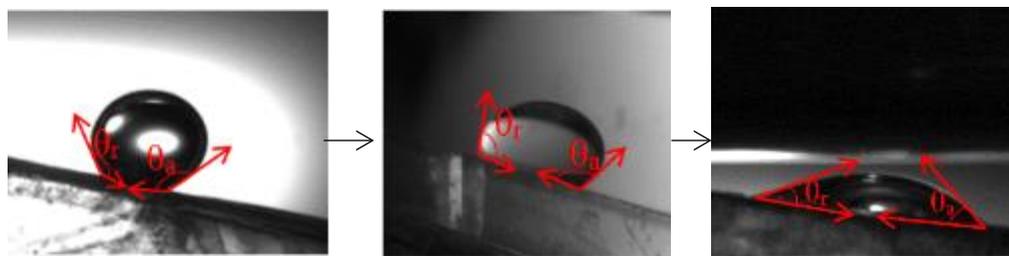
underlying mechanisms in this case. This effect is attainable if the formation rock is hydrophilic (Delshad et al., 2009). Strong capillary effect occurs if the matrix is sufficiently water-wet and the fracture network holds enough water. Ideally, this is not the case with limestone reservoir, as it is characterized by complex microstructures and poor rock wettability (intermediate-wet or oil-wet). This behaviour impedes productivity, hence, harnessing substantial oil from this formation is rather unsatisfactory. Typically, oil recoveries from such fractured reservoirs are usually very poor with average recovery factor of about 10-35% (Babadagli et al., 2000; Jikich, 2012; Nwider et al., 2016b), however, if such oil-wet surface can be rendered water-wet, spontaneous imbibition of water into the matrix pores (where most of the oil resides) massively increases recovery factors to 50-70% (Standnes and Austad, 2000a, b; Standnes et al., 2002; Standnes and Austad, 2003; Seethepalli et al., 2004). Although, water wet media exhibit increased snap-off actions, which lead to increased residual oil saturations after water breakthrough and subsequent poor oil recovery (Alyafei and Blunt, 2016).

2.5 Wettability Fundamentals and Theories

Wetting applies to several practical processes and a variety of industries such as energy, marine, manufacturing and materials. Assuming a system contains only three phases (solid, liquid, and vapor), for any two of these phases to be in contact, a transitional area of molecular dimensions occurs owing to the compositional alteration of the system that leads to phase changes. For instance, if a non-volatile molecular smooth solid is in contact with an inert gas, it is expected that the system will exhibit a transition region thickness of about a molecule, this would cause a change from solid molecules to gas molecules. Whereas, if similar trend occurs on an irregular surface, the transition region would reflect the physical non-uniformity of the surface and a concentration profile of the region would indicate the existence or non-existence of the solid phase. Similar concentration profile phenomenon holds for solid-liquid systems; however, the related specifics are dependent on the solubility of the solid in the liquid or the solubility of the liquid in the solid (Craig, 1971; Myers, 1990).

With respect to petroleum reservoir rocks, wetting is typically ascribed to the measurement of the reservoirs rock affinity for water or oil in a typical rock-fluid-oil

system. An understanding of the wetting preference of rocks is vital as it unveils the mechanisms behind fluid flow in porous media, soil decontamination process evaluations, and ultimately promotes recovery efficiency. Reservoirs exhibit different wetting inclinations: water-wet, oil-wet, or intermediate wet (Figure 2.5). Reservoir rocks considered as water-wet have high affinity for water and water predominantly occupies the tiny rock pores as well as the surface of the formation rock. Whereas, oil-wet reservoir rocks have high affinity for oil and such oil mainly occupies the tiny rock pores and the formation rock surface. In controlled laboratory experiments involving the manipulations of cores or rock samples, the samples are usually cleaned and modified to a preferential wetting state. If such samples have high affinity for



Oil-wet ($105-180^{\circ}$) Intermediate-wet ($75-105^{\circ}$) Water-wet ($0-75^{\circ}$)

Figure 2.5: Rock surface wetting transition from hydrophobic to hydrophilic.

water or were originally water wet, then saturated to a suitable oil-wet state, the rock surface becomes even more oil-wet or hydrophobic upon exposure to oil under efficient and favourable treatment conditions. However, this does not influence the actual wetting affinity of the rock. The actual wetting affinity can be affirmed by exposing such hydrophobic rock to a water imbibition test. The water imbibing potential of the rock can be used to predict its wetting affinity. Ideally, if the rock has high affinity for water then the oil will be displaced from the surface of the rock by water. Whereas a rock with high affinity for oil is saturated with water, and then the rock is placed in an oil-wet environment. The oil will displace the water from the rock surface while efficiently imbibing into the rock pores. In the absence of an actual inclination for water or oil, the formation rock is considered intermediate wetting. Aside from these key-wetting preferences, there also exists fractional wetting where the formation rock exhibit different wetting inclination in different sections of the rock

(Anderson, 1986; Morrow, 1990; Abdallah et al., 2007). Wetting have also been reported via theoretically frameworks such as the Young's equation.

2.5.1 The Young's Equations

Young in 1805 was the first to recognise the relationship between contact angle and surface tension. It was established that contact angle is primarily based on the balance of forces at the contact line between the solid surface and the liquid droplet. The liquid in contact with the solid surface leads to the formation of varied phases, which yields three surface tensions (solid+liquid, liquid+gas, and solid+gas), as such, the wetting state of the fluid can be estimated accordingly if these surface tensions are known. If the solid surface is ideally flat, then, such contact angle is referred to as the Young contact angle (Chau et al., 2009; Linden, 2010; Yuan and Lee, 2013). Young (1805) established that a relationship exists between contact angle, IFT, surface tension, and surface free energy (See Young's Equation - 2.6, Figure 2.6) as

$$\sigma_{sg} = \sigma_{sl} + \sigma_{lg} \cos\theta \quad 2.6$$

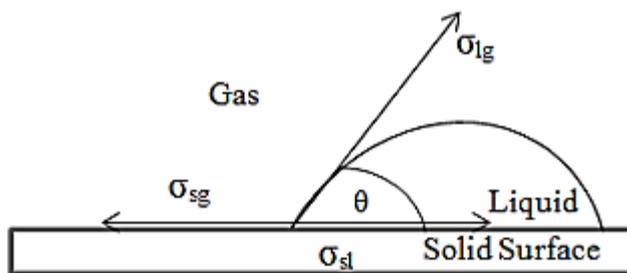


Figure 2.6: Young's equation illustrating a three-phase contact line

However, only two variables are measurable, which are the liquid surface tension and contact angle. Estimation of σ_{sg} and σ_{sl} requires the establishment of an additional relationship between these variables. The key parameters of Young's equations have been well established except for contact angle, which is not fully understood especially

in more complex oil-fluid systems. Bonn et al., (2009) established that three-possible wetting state can exist in a three-phase system based on Young's equation: completely dry, partially wet, and completely wet. In a solid-liquid-vapour system, completely dry is an indication of an intrusion of a macroscopic vapour layer between the solid and the liquid. Partial wetting is due to droplets bounded by microscopic thin film that is adsorbed on the surface of the solid, whereas, complete wetting is due to macroscopic adsorbed thick wetting layer, an indication that a system is in equilibrium as a macroscopic uniform liquid layer covers the whole surface of the solid. The film thickness varies between a fraction to numerous fractions of a molecule. However, the level of thickness is dependent on the affinity of the molecules to the substrate and the corresponding distance to the bulk critical point. The bulk critical point (Cahn 1977; Dietrich, 1988) indicates that a wetting transition occurs when temperature increases towards the critical point ($T \rightarrow T_c$), since temperature is the control parameter that is most commonly used to evaluate wetting transitions. For example; when a system at low temperature is incompletely wet upon contact with a vapour or a near vapour-liquid co-existing point, as the critical temperature (T_c) of the bulk fluid approaches, the system tends to exhibit a completely wet behaviour. E.g., in a diethylene glycolpentylalcohol liquid mixture, the critical point wetting is the partial transition to complete wetting of the interface between lower and upper phases by the middle phase microemulsion as the system approaches the upper or lower critical end point in the H_2O -octane- C_5E_2 (Kahlweit et al., 1993).

Although Young's equation has been a most commonly used model for several decades, the conditions for which it is functional is rather unrealistic for real surfaces especially in complex systems of oil-fluid-rock interactions. Another key limitation (Chau et al., 2009; Seo et al., 2015) with this equation is that it is primarily appropriate for implementation on ideal surface that is typically flat, insoluble, non-reactive, and chemically homogenous surface, without considerations of possible contact angle hysteresis. Young's equations were fundamentally established for ideal surfaces; however, real surfaces are generally not ideal as the real surfaces exhibit chemical heterogeneity, varied surface roughness and rigidity. This deviation of real surfaces from the ideal surface resulted in the term, contact angle hysteresis, which correlates the shift of a contact line due to the liquid droplet expansion or retraction. The hysteresis phenomenon can be further quantified via an estimation of the variations

between the advancing and receding contact angle. Since a liquid droplet in contact with a rough or porous substrate exhibits different wetting states, several models (Gambaryan-Roisman, 2014) have been developed over time for better contact angle description on such surfaces with diverse variables, amongst which are the; (a) Wenzel model, where the liquid wets the rock pores that is directly under the droplet, and; (b) Cassie-Baxter model, where the liquid droplet is partly buoyed by the solid and air without the liquid penetrating into the rock pores.

2.5.2 The Wenzel Model

Wenzel model focuses on homogeneous surface wetting. The key difference between the Wenzel model and the Cassie-Baxter model is that the Wenzel model puts into consideration the chemical homogeneity with a focus on a rough surface. Thus, the model is an indication that contact angle on solid rough surfaces, which is considered real, varies from that of an ideal surface (Wenzel, 1936). With respect to the Wenzel model, the effect of surface roughness on contact angle was described using Equation 2.7 as

$$\cos \theta = r \cos \theta_Y \quad 2.7$$

The apparent contact angle is considered the contact angle at a stable equilibrium condition where the system free energy state is said to be at a minimum. The roughness ratio (r) is described as the ratio of the actual surface area to that of the projected area of the surface, which estimates the extent to which the roughness of the surface influences the solid surface homogeneity. θ_Y is Young's contact angle, which is considered the equilibrium contact angle equivalent to that from Young's equation on an ideal solid surface, which does not put into consideration the roughness of the solid surface.

The Wenzel equation further shows that hydrophobicity of the rock surface leads to increase in contact angle owing to surface roughness. Wenzel emphasized that r was always greater than unity and the solid surface roughness increased the relative contact area of the water-solid (Yang et al., 2010). As such the surface roughness is believed

to amplify surface wetting (Chau et al., 2009; Seo et al., 2015), thus, surfaces that are considered hydrophobic becomes more hydrophobic (> 90) and the hydrophilic surfaces become more hydrophilic (< 90) owing to surface roughness.

2.5.3 The Cassie-Baxter Model

Cassie-Baxter model mainly deals with heterogeneous surface wetting. The primary focus here is on the chemical heterogeneity with respect to flat surfaces (Cassie and Baxter, 1944). Since Wenzel model focuses on surface homogeneity, it was rather considered insufficient for complex surface involving the interactions of various material components. The Cassie-Baxter model for a flat surface with chemical heterogeneity is further described by Equation 2.8 as

$$\cos \theta = r_f f \cos \theta_Y + f - 1 \quad 2.8$$

If $f = 1$, $r_f = r$, which thus results in the Wenzel equation (Marmur, 2003).

It was further established that the solid-liquid contact area was considered a composite surface that is made up of solid-liquid, and gas-liquid surfaces as such droplets on rough surface attained hydrophobicity, owing to the solid-liquid contact area (Yang et al., 2010). The Cassie-Baxter model lays more emphasis on the area fractions under the drop, it is believed that higher contact angle is achieved when the area fraction of air is large (Seo et al., 2015). Both Wenzel and Cassie-Baxter model have been considered valid when the liquid droplet is satisfactorily large in comparison to a typical roughness scale. However, these equations have been thought out to be insufficient for a description of rough surface wetting equilibrium (Marmur, 2003) and several new theories have been developed in this regard (Marmur, 2003; Yang et al., 2010; Seo et al., 2015).

2.6 Porous Media Wettability Alteration Mechanisms

Formation rocks with an interconnected network of pores or voids are porous media characterised by physical and textural properties as well as their porosity, that exhibit

a dependency on their constituents. Wettability has remained a key challenge therein, thus certain mechanisms have been deployed to address this. Qualitatively, the wettability of cores is assessed via relative permeability, capillary pressure/displacement capillary pressure, and imbibition. These methods have been used for several decades, however, the methods are primarily used for water-wet or oil-wet scenarios without consideration for intermediate wet states. Other approaches also used for estimation of wettability, which is considered as quantitative approaches are USBM, Amott method, and contact angle measurements (Donaldson, 1969; Anderson, 1986; Morrow, 1990; White al. et., 2009).

2.6.1 Relative Permeability

Relative permeability is the ratio of the phase permeability to the absolute permeability k . The phase permeability primarily exists as a water, gas, or oil phase as shown in Equation 2.9-2.11 as

$$\text{Water phase relative permeability: } k_{rw} = k_w / k \quad 2.9$$

$$\text{Gas phase relative permeability: } k_{rg} = k_g / k \quad 2.10$$

$$\text{Oil Phase relative permeability: } k_{ro} = k_o / k \quad 2.11$$

Quantification of valid relative permeability curves and wettability is challenging. Stringent time-consuming laboratory test and associated cost are often impediments. Nevertheless, several experiments have been performed in this regard, although most evaluations of relative permeability in relation to wettability have been mainly focused on strongly water-wet or oil-wet cases. Owens and Archer (1971) examined relative permeability at different wetting conditions from strongly water-wet to strongly oil-wet conditions (0° - 180° - Figure 3.4). As the wettability changes from strongly water-wet (0°) to strongly oil-wet (180°) at a specific saturation with respect to the oil-phase, a decrease in the relative permeability to oil occurred upon an increase in oil wetness. Although, no consistent effect on residual oil saturation was reported with the wettability change. This may be due to the water-wetness of the clean core and a low initial water saturation and contact with the oil phase containing bariurn djnonyl naphthalene sulfonate which facilitated a change in the initial distribution of the

simulated connate water saturation and also yielding a change in oil permeability. However, low residual oil saturation was recounted for the strongly water-wet cores (0° and 47°), especially, for the cores with a 0° . For the 138° and 180° oil-wet states, expectations were that the residual oil saturation will be dependent on the water volume and pressure drop, since, oil was the wetting phase. The values of the residual oil saturation were considered insignificant for establishing a definite relationship between residual oil saturation and rock wetting preference. Further assessment was performed in the water phase, in this phase, a decrease in water wettability led to an increase in relative permeability to water at a set specific saturation. The authors emphasized that the change in wettability from water wet to oil wet is an indication of a steady and constant reduction in oil displacement efficiency.

Recently, Falode and Manuel (2014) examined the relationship between wettability and other factors that govern multiphase flow in porous media such as relative permeability, and irreducible saturation. Capillary pressure test via the porous plate method in an air-brine and the air-oil system was conducted. The relative permeability of cores was tested for air-brine and air-oil systems. It was found that the wetting phase of air-brine system exhibited much lower relative permeability than that of the air-oil system. The relative permeability of brine (K_{rw}) was lower than that of air (K_{ra}) at pressures above 5 psia (8-35 psia). The authors further established that the wettability alteration of the core sample from water-wet to oil-wet increases the relative permeability of the wetting phase (Figure 2.7). The wetting phase was easily displaced by the non-wetting phase (air) in the air-brine system, however, for the air-oil system, a lower wetting phase displacement (oil) occurred owing to fractional wettability alteration of the porous rock.

2.6.2 Capillary Pressure / Displacement Capillary Pressure

Capillary pressure is termed the pressure difference between two fluid phases or two continuous immiscible fluids in contact in the rock pore spaces. These phases are classified as wetting and non-wetting (Equation 2.12). This is mainly due to the

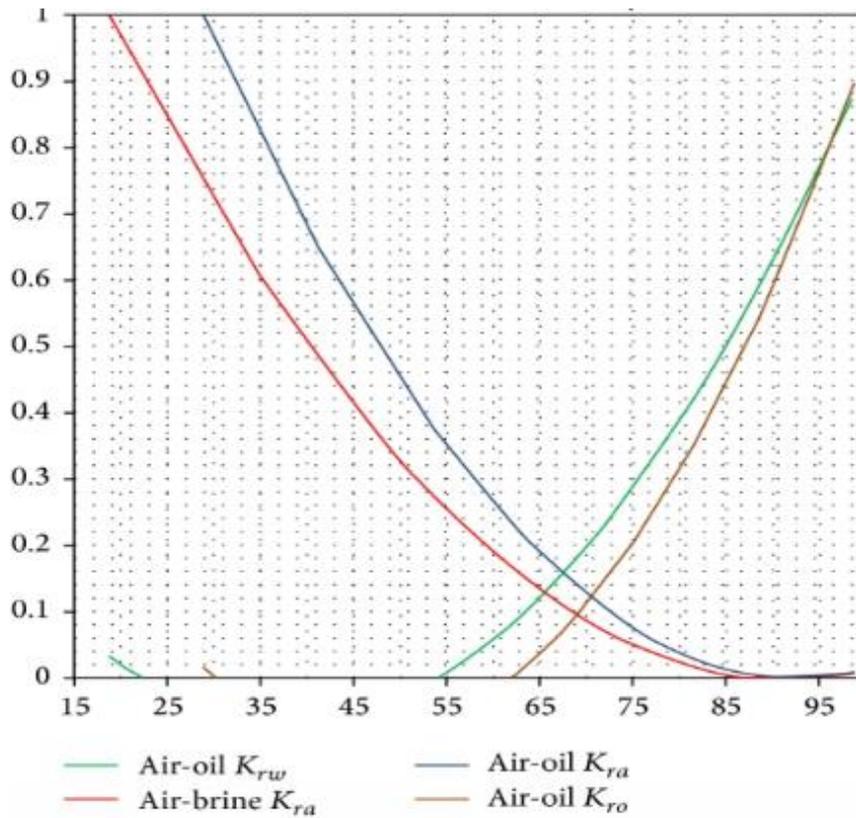


Figure 2.7: Young's equation illustrating a three-phase contact line (Falode and Manuel, 2014).

occurrence of pressure discontinuity across the interface separating the fluids that are in contact. Wetting can exhibit dependency on capillarity especially with respect to the angle of contact and the adsorbed film on the rock surface. At a specific capillary pressure (Dullien and Fleury, 1994; Reeves and Celia, 1996; Falode and Manuel, 2014), if an adsorbed film is at equilibrium with the bulk liquid, the film's thickness will not only rely on the capillary pressure of the bulk liquid but also on the curvature of the solid covered by the film.

$$P_c = P_n - P_w \tag{2.12}$$

Three key approaches are used for capillary pressure measurement; porous plate, mercury injection, and centrifuge methods, of which the porous plate is the most commonly used owing to data reliability, although time has remained the key limitation for this method as it involves time-consuming processes. The mercury

injection method has been perceived as a rather faster approach with possibilities of attaining high capillary pressure, however, the test is destructive, and mercury is a requirement. In the centrifuge method, reservoir fluid is used, and the equilibrium time can be decreased due to the presence of high centrifugal force that is equivalent to a multiple of the gravitational force. With capillary pressure curves (Figure 2.8) parameters such as rock wettability, pore size distribution, residual oil saturation, and irreducible water saturation can be measured (Anderson, 1986; Morrow, 1990; Dullien and Fleury, 1994; Falode and Manuel, 2014). The use of capillary pressure curves for wettability estimation dates as far back as the early 50s (Calhoun, 1951; Gatenby and Marsden, 1957). The knowledge of the relationships between wettability, capillary pressure, and the water and oil distribution in porous media is essential for better understanding of issues relating to wettability. This relationship appears even more complicated in crude-oil-brine-rock systems owing to the complex pore structure, crude oil chemistry, and reservoir rock mineralogy. The crude oil adsorbed organic components also add to these challenges.

The displacement or threshold capillary pressure is one the earliest method for wettability evaluation. It is considered the capillary pressure at which the non-wetting fluid enters a core already saturated with a wetting fluid. Estimation of the apparent contact angle is done via modelling of the rock as a straight, cylindrical capillary tube. The threshold capillary pressure is used for estimation of apparent contact angle, however, its is not a frequently used method owing to pore geometry effects which can influence the measured contact angle and can cause a large deviation in measurement compared to the flat plate method. A key constraint to this technique is that the rock wettability is more achievable for only the largest pores (Anderson, 1986).

2.6.3 Imbibition

Imbibition is one of the most commonly used methods for wettability evaluation. This method simply demonstrates displacement of a non-wetting phase from the rock pore spaces by a wetting fluid. Basically, a saturated core is subjected to an imbibition test, the liquid phase that the core is usually placed is deionized water, brine, or other

imbibing fluids. The pace at which the core imbibes the wetting fluid and the corresponding displaced oil is recorded as a function of time. The core sample is

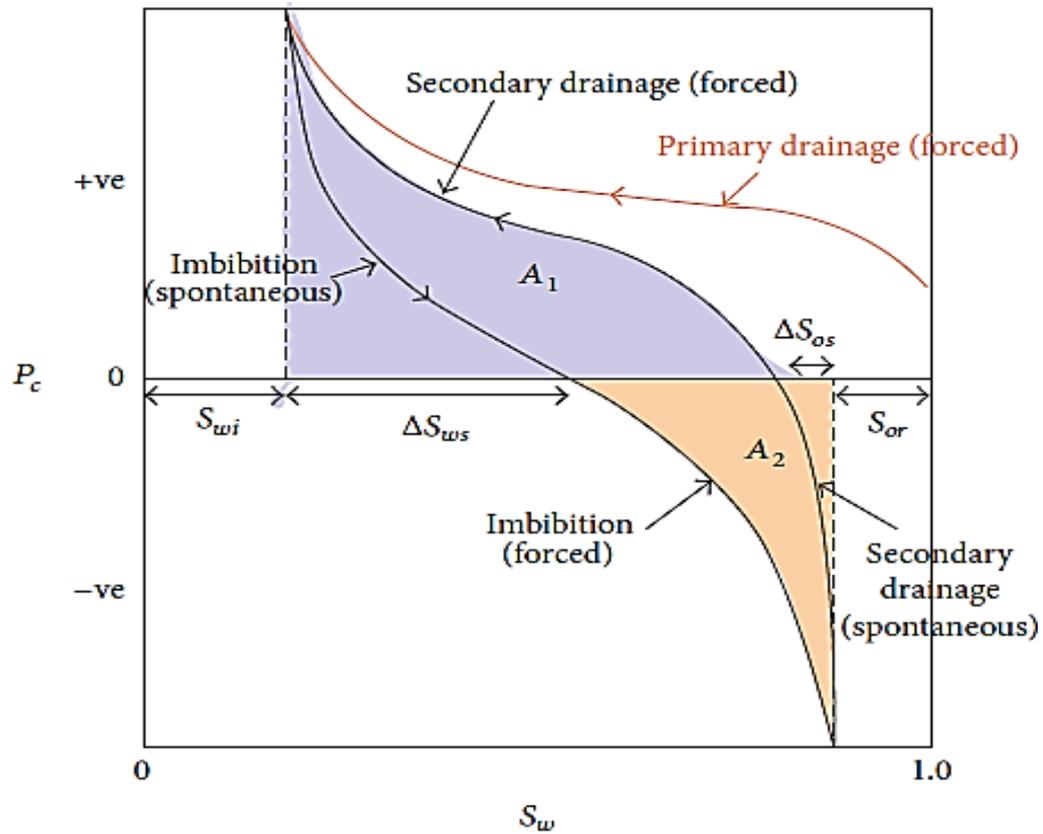


Figure 2.8: Schematics of capillary pressure graph for wettability characterization (Falode and Manuel, 2014).

considered oil-wet or intermediate wet if the imbibing fluid is incapable of penetrating the cores; water-wet if the imbibition process is fast, as the core tends to imbibe the water or brine phase spontaneously. A rather slow imbibing tendency is an indication of prevailing weakly water wet state of the core. Although imbibition is an effective wetting test approach, this process is also dependent on the rock pore structure, fluid viscosity and even relative permeability, aside wettability (Bobek et al., 1958; Anderson, 1986; Morrow, 1990). More so, capillary pressure is the key driving force for the attainment of a spontaneous imbibition process. Several studies have been conducted in this regards with all demonstrating high process efficiency (Geoffrey et al., 2013; Roychaudhuri et al., 2013, Haugen et al., 2014; Tajmiri et al., 2015).

2.6.4 USBM

USBM method and centrifugation are used for estimation of the drainage and imbibition capillary pressures. The focus is mainly on the work required for forced fluid displacement of the wetting or non-wetting phases. The work necessary for each phase can be relatively different. Consider a cell holding a certain amount of water (the wetting phase), and a saturated core (non-wetting phase) is placed in the same cell, in such scenarios, a lesser amount of work will be required for the non-wetting fluid in the core to be displaced by the wetting in comparison to the reverse process due to favourable free-energy change. For instance, a water-wet core will exhibit a much smaller area under the brine-drive capillary pressure curve than a reverse process owing to the spontaneous water imbibition into the core (Anderson, 1986; Morrow, 1990). The wettability number (Equation 2.13) is thus, described as the ratio of the two areas representing the forced imbibition (Figure 2.8):

$$N_w = \log (A_1/A_2) \quad 2.13$$

Where:

The key benefits of the USBM method are the process speed, and the working principles are relatively simple, however, it is not necessarily an absolute approach despite its popularity.

2.6.5 Amott Method

Amott method involves a combination of forced displacement and imbibition. The amount of fluids that imbibe spontaneously and forcibly over time into a saturated (initial water saturation, S_{wi}) core sample placed in a cell filled with a certain amount of liquid (water, brine, etc.) is noted. At the end of the spontaneous imbibition process, usually a change in water saturation (ΔS_{ws}) occurs at this point. For further displacement of oil from the core, a forced displacement approach is implemented. Typically, the core is placed in a cell and water is forced through the core at a high-

pressure gradient or via centrifuge for estimating the average wettability of a rock sample. The wetting fluid spontaneously imbibes into the sample by displacing the non-wetting fluid for additional oil recovery. A reverse process can be performed where the imbibing fluid is oil, not water; irrespective of the type of imbibing fluid the imbibition ends at the point when the interfacial curvature is zero (0). The wettability index for both oil and water cases can be estimated by Equation 2.14 and 2.15 as

$$l_o = \Delta S_{os} / \Delta S_{wi} \quad 2.14$$

$$l_w = \Delta S_{ws} / \Delta S_{wi} \quad 2.15$$

When:

$l_o = 0$; and $l_w = 1$ - the system is considered complete water-wet

$l_o = 1$; and $l_w = 0$ - the system is considered complete oil-wet

There also exists the Amott-Harvey method which involves a change in the way forced displacement is performed. Here, the displacement does not require the use of a centrifuge, an external pressure is applied for achieving the same function using a Hassler core holder. It is considered a modification of the Amott wettability test used for characterization of wettability by a single wetting index with ranges between +1 (complete water-wet state) and -1 (complete oil-wet condition). The index is described as a function of the two ratios (I_w); the displacement by water ratio and displacement by-oil ratio (I_o) (Anderson, 1986; Morrow, 1990; Abdallah et al., 2007; Falode and Manuel, 2014; León-Pabón et al., 2014) as represented in Equation 2.16 as

$$I_{AH} = I_w - I_o \quad 2.16$$

Where:

I_{AH} - Amott-Harvey index

A major benefit of the amott method over the usbm test is that it is more sensitive for neutral wettability as it has positive displacement by water (I_w) and oil (I_o) ratios, which indicates the system is non-uniformly wetted. It is also the best method for unconsolidated samples when forced displacement is performed in a coreholder as centrifuge can damage friable/unconsolidated plugs. This method also allows for measurement of the average wettability of the core while the contact angle measurements is at localised scale. However, there also exist some disadvantages of this method; the results are greatly dependent on duration of the spontaneous imbibition phase. The spontaneous imbibition of brine exhibits great dependency on the amount and distribution of interstitial water present after primary drainage since the surface available for the wettability alteration increases with a decrease in S_{wir} . The maximum pressure applied for the forced stages must be the same for both drainage (+ve PC) and imbibition (-ve PC) (McPhee et al., 2015).

2.6.6 Contact Angle Measurements

Contact angle is considered one of the most common methods for wettability estimation. All the above methods have been well established except for contact angle, especially in complex rock-oil-fluid-nanoparticle systems. Contact angle is presumed to be relatively simple in comparison to other methods. However, this method is not as simple as perceived, as its simplicity can be relatively ambiguous. For instance, most natural or artificial solids such as clays, polymers, pigments, soils etc. that are of great practical interest are normally in powder forms, thus, preparation of a completely flat and smooth surface from such powders can be difficult, as such the direct measurement of contact angle becomes even more complicated and usually unachievable. When contact angle on compressed pellets of the solids are measured, this usually leads to a lot of errors as such pellets are normally rough and porous and yield much smaller contact angles in comparison to similar smooth samples (Chibowski and Perea-Carpio, 2002). More so, contact angle measurement is a complex process, when a liquid wets a solid, the change in wettability can be dramatic even for a slight surface modification of the surface property of the solid. Several methods exist for estimation of contact angle such as the Wilhelmy method, drop profile, drop dimension, Capillary rise at a vertical plate etc

2.6.6.1 Wilhelmy Method

Wilhelmy established this method in 1863, ever since the method has been used as an indirect means of measuring contact angle for thin, smooth, vertical plate. As the plate gets in contact with a liquid, a change in weight can be observed with a balance. The receding or advancing contact angle can be established by the up and down movement of the plate. The wetting force and the total detected force change is estimated by Equation 2.17 and 2.18 respectively.

$$f = p\gamma_{LV} \cos \theta \quad 2.17$$

$$f = P\gamma_{LV} \cos \theta - V\Delta\rho g \quad 2.18$$

The contact angle can be calculated if the surface tension is known. A downward force is said to be exerted if the contact angle is $< 90^\circ$ (Lander et al., 1993; Yuan and Lee, 2013).

The key benefits of this method include the absence of operator variability or error if properly executed. Analysis of the material can be done on large area such that the tiny surface defect does not influence the measured contact angle. The method allows one-dimensional resolution of surface variation, since the motion of the contact line is in one directional. This method is considered an ideal measurement method, especially for contact angle hysteresis estimation. The limitations of this method are that the sample specifications often defy actual or real mineral samples. There is a need for high sensitivity electro-balance which must be used - the samples should have sharp edge corners for minimization of the edge or corner effect. The sample perimeter, composition, and surface morphology must be the same on all sides (the front, back and edges), hence, considered unsuitable for surface modified polymers. Solution swelling and vapour adsorption on the plate surface is unfavourable for Wilhelmy method (Lander et al., 1993; Chau, 2009; Strobel and Lyons, 2011; Yuan and Lee, 2013).

2.6.6.2 Drop Profile

This is a direct means of measuring contact angle and the most widely used method on solid flat surfaces. This method enables the measurement of advancing angles via an increase in the drop size and receding contact angles via a decrease in the drop size. Telescope goniometer is used for viewing and measuring the drop profile as well as its contact profile on a polished solid surface. The droplet image or adhered bubble is projected onto a screen and measurement is done with a protractor, or a photograph is taken. High accuracy of the mechanism is dependent on the quality of the magnifications, thus, high magnifications that allow ample analysis of the intersection of the drop profile and the solid surface is recommended.

The benefits of this method are that the test requires a little amount of liquid for process implementation. Solids with small surfaces can be measured irrespective of size. The limitation is high possibilities for impurity. Heterogeneity or roughness of the surface can lead to a variation of the contact line (Chau, 2009; Yuan and Lee, 2013).

2.6.6.3 Drop Dimension

With respect to drop dimension, contact angle and surface tension are estimated for a sessile drop resting on a surface. The shape of the fluid interfaces is further quantified theoretically via Laplace equation (Equation 2.19).

$$\gamma (1/R_1 + 1/R_2) = \Delta P \quad 2.19$$

In the face of several theoretical advances in these regards, this method is still considered inadequate especially for sessile drops since the drop shape are mainly influenced by gravity. There are also problems of algorithm deficiencies since the error functions are computed via additions of the squares of the horizontal distances between the measured points and calculated curve (Chau, 2009).

2.6.6.4 Capillary Rise at a Vertical Plate

This method enables estimation of capillary rise on a vertical plate. A liquid in contact with a vertical and infinitely wide plate tend to rise. The height of the liquid is estimated by an integration of Laplace equation (Equation 3.20).

The key benefit is that the method allows for temperature related contact angle measurements. The contact angle and surface tension can be estimated at the same time via a combine application of both the capillary rise (Equation 3.20) and Wilhelmy method (2.19) via $\sin^2 \theta + \cos^2 \theta = 1$ (Chau, 2009; Yuan and Lee, 2013). The limitation is that the surface tension (γ_{LV}) of the liquid must be known, which is considered a key constraint as with the Wilhelmy method. It is not appropriate for use in the presence of surface-active agents. High possibilities for alteration in the contact angle and surface tension exist owing to surface adsorption at different interfaces (Chau, 2009; Yuan and Lee, 2013) (see Equation 2.20).

$$\sin \theta = 1 - \Delta\rho gh^2 / 2\gamma_{LV}$$

2.20

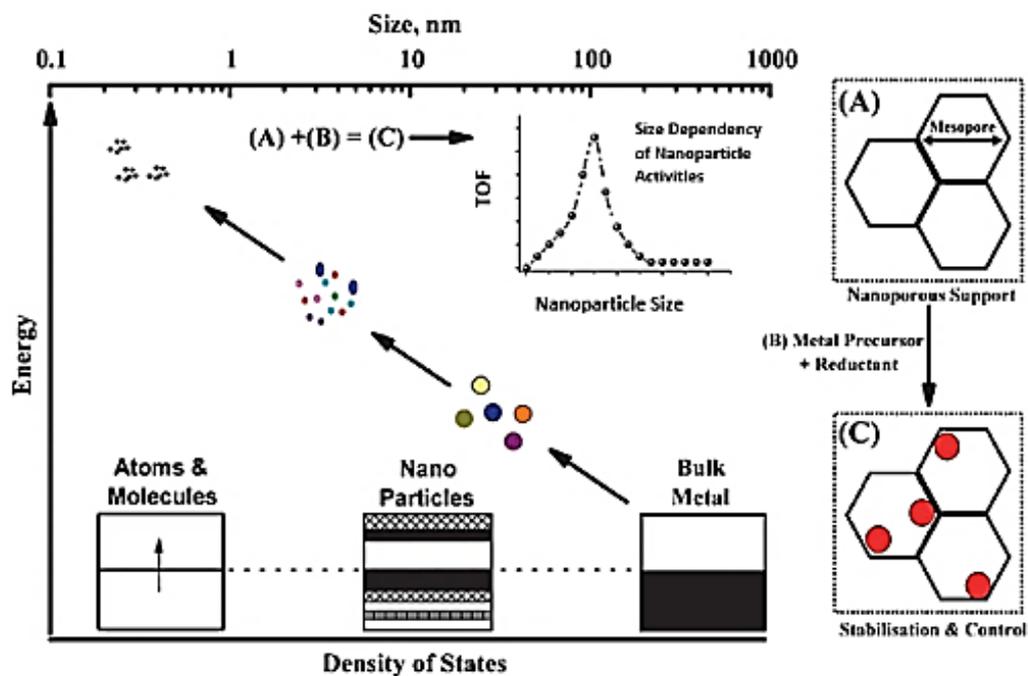


Figure 2.9: Relationship between nanoparticle size, energy, and the principle of the density of states (White et al., 2009).

2.7 Nanoparticles Affiliation to Enhanced Oil Recovery

Nanoparticles are nano-sized structures with at least a phase of one or more dimensions in the nanometer size range (typically 1 - 100 nm). Quantisation of the electronic states of nanoparticles, and the possible state manipulation through shape and size control are the key drivers for research in nanoscience or nanotechnology. At nano-scale, the property changes that occur are based on the nature of the materials and the applied mechanisms. For instance, when metallic nanoparticles transition from the bulk metal to a much smaller metallic particle, the bulk metal energy continuum changes to produce even more discrete energy levels thus an indication that there is a decrease in the density of the electronic states (Figure 2.9) (White et al., 2009; Strambeanu et al., 2015). Nanoparticle cuts across a wide variety of materials such as; (a) materials with surface protrusions spatially separated by distances in the order of nanometers; (b) porous materials with particle sizes in the nanometer range or nanometer sized metallic clusters dispersed within a porous matrix; (c) polycrystalline materials with nanometer sized crystallites (White et al., 2009).

With respect to EOR, nanoparticles applications have emerged a novel EOR pathway for resolving reservoir engineering challenges. The applications of conventional suspensions can be very challenging as opposed to nanoparticle based fluids especially in heat transfer processes. E.g. degradation issues are often associated with a typical polymer based system due to thermal and chemical effects. Polymers when dissolved in solvents are used in oil recovery as they increase the viscosity of the displacing water and improves sweep efficiency, however, polymer systems tend to lose efficiency in prolonged processes. This is primarily due to shear degradation of the polymer which causes viscosity reduction during high shear rates generation by the rotating bit in the well bore. Franck (2004) reported that surfactants added to a high molecular weight polymer promotes high viscosities by formation of complexes that are less sensitive to shear degradation. The surfactant increases the viscosity of the polymer as a result of the bridging of the hydrophobe clusters by surfactant micelles which increases with the number of effective associated junctions. However, with the increase in surfactant concentrations such hydrophobes become solubilized individually, or masked by an excess of spherical micelles which results in a disruption of associations and subsequent decrease in viscosity, and temperature variations results in system instability. Although thermal degradation is usually not a challenge

at relatively low temperatures, however, heat transfer processes involving high temperature applications like district heating and cooling systems are a challenge. For example, polyacrylamide solutions have been shown to be less prone to degradation over a long period of time at approximately 7 °C but highly degradable in only a few hours at 90 °C (Pohorecki et al., 2010). More so, chemical bonds are weaker at high temperatures and an easy breakdown of molecules occurs irreversibly. Whereas, nanoparticle based fluids are functionalized colloids with low solids loading and high thermal properties that exhibits great stability over a wide range of temperature and favourable rheological and flow behaviour (Chen et al., 2007). On basis of their particle size, nanoparticles with large sizes (100 nm) can be considered sub-micron particles rather than nanoparticles, however, the stability of such systems is achievable via the use of a small amount of laurate salt (Xuan and Li, 2000) and the traditional slurries can be eliminated via a reduction of the particles to nanometer dimensions. The typical slurries with suspended particles in the order of micro to millimeters suffer from certain drawbacks: (1) the erosion of components occurs due to the abrasive action of the particles, (2) clogging affects small flow passages (3) pressure drop increases considerably owing to the requirement of momentum transfer (4) fouling issues occurs due to high tendencies of micro/millimeter size particles to settle under gravity. These issues can be resolved via adoption of nanometer dimensions particles (Das et al., 2003). Clearly, nanoparticles display extensive unique characteristics as EOR agents (See chapter 1 - 1.4) over conventional bulk materials. Nanoparticles (Wasan et al., 2011) can form a wetting wedge in form of an ordered structure near the three-phase contact line of a droplet or bubble on rock surfaces as demonstrated in Figure 2.10, which stimulates spreading. These materials exhibit different functionalities via varied mechanisms depending on their types and the applications.

2.7.1 Nanoparticles Types

Nanoparticles are categorized as magnetic (e.g. iron, cobalt etc. and the oxides), metallic (e.g. gold, silver, copper, and Platinum) or metal oxides (e.g. oxides of aluminium, zinc, silicon, magnesium, zirconium, cerium, titanium). Among these categories, the metal oxides are the most commonly used nanoparticles in EOR, as the material offers special unique structures, compositions, and properties. The

effectiveness of this material depends greatly on the preparation methods and subsequent applicability.

1). Magnetic Nanoparticles

Magnetic nanoparticles are particles containing magnetic elements and exhibit high magnetic field strength and unique quantum size properties. Its size-dependent magnetic characteristics make it special for application in diverse processes. These materials are efficient for chemical separation processes owing to the particles versatility and high-performance potentials; and are also able to act as a catalyst that speeds up chemical degradation processes (Jun et al., 2007; Pastrana-Martínez et al., 2015). Efficient manipulation of the surface functionality of magnetic nanoparticles can enhance the particle stability under harsh conditions of high formation salinity and temperature. This material is also efficient for reservoir heterogeneity characterization. Rock surfaces coated with superparamagnetic nanoparticles have high capabilities to flow through micron-size pores across long distances in reservoirs. Interestingly, the retention tendencies of these materials are relatively low and can also change the magnetic permeability of the flooded region in the reservoir. Superparamagnetic nanoparticles have also been identified as having high possibilities

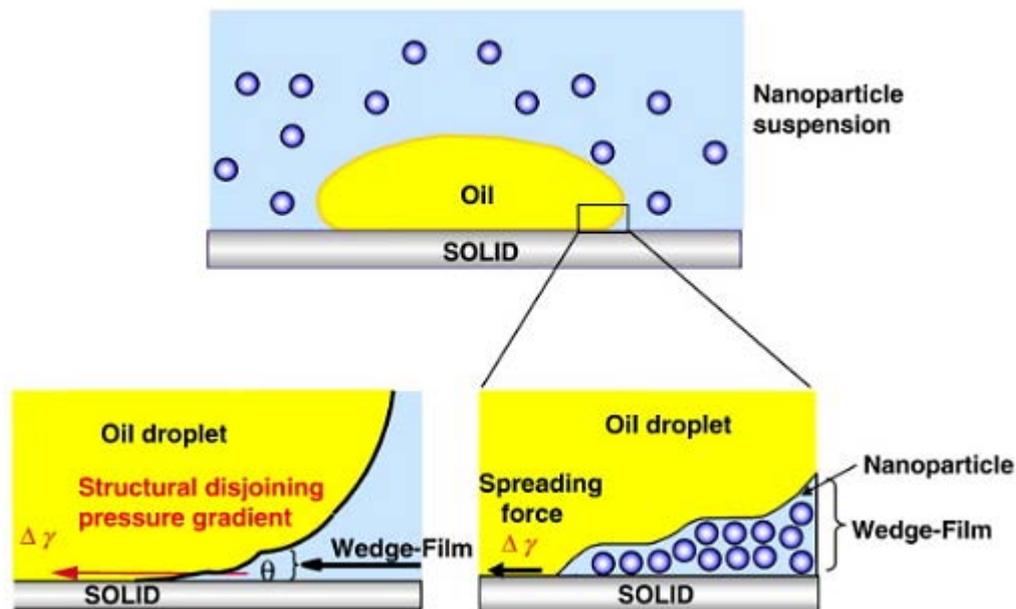


Figure 2.10: Nanoparticles wedge-film, leading to structural disjoining pressure gradient at the wedge vertex (Wasan et al., 2011).

for estimating oil saturation distribution and associated bypassed oils in reservoirs (Avendano et al., 2012; Rahmani et al., 2015). Morrow et al., (2015), also reported the effectiveness of magnetic nanoparticle in shale gas reservoirs as the particle can be used as contrast agents. This material can also be co-injected into wells alongside sweep or fracture fluids, which can be tracked over time by electromagnetic measurements or volume magnetic susceptibility detectors (Avendano et al., 2012; Morrow et al., 2015). Magnetic nanoparticles are also effective for corrosion inhibition. This is achieved via particle adherence to the surface of the carbon steel, which forms a protective layer on the carbon steel surface (Jauhari et al., 2011; Murugesan et al., 2016).

2). Metallic Nanoparticles

This type of nanoparticles has exceptional properties that facilitate extensive usage, which is mainly due to its large surface to volume ratio, high potentials for inhibition of particle aggregation via immobilisation or separation on the heterogeneous supports, and high potentials for enhanced selectivity, size, and shape selective catalysis (White et al., 2009). A key reason for nanoparticles attractiveness in

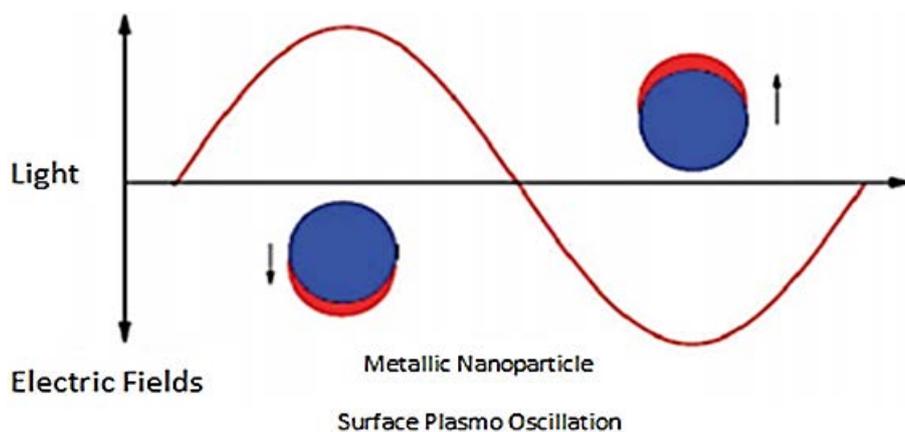


Figure 2.11: Metallic nanoparticle's electron cloud (red) oscillation relative to the metal core (blue) in response to the electromagnetic field; this is the basis for the surface plasmon resonance effect observed in nanoparticles (White et al., 2009).

analytical fields of science and sensors is that analyte adsorbs onto the nanoparticle surface, disrupts resonance oscillation, and generates a change in the electric field that is detectable (Figure 2.11). The oscillation of nanoparticle electron cloud is induced by the electric field part of the incident light. Thus, metallic nanoparticle size and shape has a direct impact on the oscillation, which can impact the electron cloud density (White et al., 2009). In addition, an earlier report by Hyne et al. (1982) established that metals can speed up aquathermolysis of heavy oil leading to improved flow potentials. This is vital for heavy oil recovery processes since high viscosity has remained a major limitation to its recovery. Viscosity reduction is necessary for effective exploitation of heavy oil deposits.

3). Metal Oxide Nanoparticles

Metal oxide nanoparticles are attractive for various processes especially in oil and gas owing to its varied structures, compositions, physical and chemical properties. These materials display high thermal conductivity - the degree to which they conduct electricity. Yu et.al (2008) reported that thermal conductivity can be achieved through heat transfer enhancement in the range of 15-40% in the presence of oxides of nanoparticles in base fluids. Metal oxide nanoparticles also exhibit great stability, however, its stability is dependent on the preparation methods and dispersant. Fedele et al. (2011) reported stability evaluation of this nanoparticle type via a comparison of various preparation methods such as ball milling, sonication, and high-pressure homogenization. The ball milling method produced least stable fluids when compared to sonication which produced better stable fluid. Similarly, Roustaei and Bagherzadeh (2015) also reported sonication as an effective approach. However, the use of high-pressure homogenizers was reported by Yang et al. (2004); Tjong (2007); Fedele et al. (2011) and Mao et al. (2015) as the most efficient approach for nanofluid preparation. Moreso, metal oxides based fluids exhibit great saline-alkaline tolerance and can improve the rheological properties of drilling fluid systems. A micro-model drilling fluid flooding and displacement evaluation of core column, shows that micronano drilling fluid additives are efficient for formation plugging and can significantly improve the pressure bearing capability of formations, and even exhibits great potentials of isolating the interaction between the drilling fluid and the formation fluid, thus vital for borehole stabilization and reservoir protection (Mao et al., 2015). Metal

oxide nanoparticles also exhibit great potentials in hydrocarbon recovery processes via IFT reduction, wettability alteration, oil viscosity reduction etc. (Amanullah and Al-Tahini, 2009; Metin et al., 2012; Ahmadi et al., 2013; Hendraningrat and Torseater, 2015; Salem and Hannora, 2015). Moreso, during oil and gas processes nanoparticles are subjected to conditions of temperature and pressure upon injection into the reservoirs. A major process concern is usually the transport behaviour of this material from the injection point to the targeted region. Recently, metal oxide nanoparticles have been reported as efficient materials that can be easily and favourably transported through limestone and dolomite porous media than quartz sand (Bayat et al., 2015).

2.7.2 Nano-Based Smart Fluids for EOR

Nanoparticle based fluids otherwise called smart fluids for EOR are fluid systems containing nano-additives which exist in the form of suspensions or emulsions. These fluids are considered suitable for EOR processes owing to strong particle surface interaction with solvents, which helps to overcome density differences that make materials float or sink in a system. The nano-based smart fluids can display significantly high functional abilities in different systems while reducing the overall fluid cost, irrespective of the high cost of individual additives. Such suspensions or emulsions are known as nanofluids, nano-catalyst suspensions, or nanoemulsions - more emphasis is laid on nanofluids for the purpose of this study.

1). Nanoemulsions

Nanoemulsions exhibit unique characteristics such as great stability. Nanoemulsions are kinetically stable (Anton et al. 2008; William et al., 2014) irrespective of temperature changes in comparison to other emulsions that are thermodynamically unstable systems with free energy of emulsion formation greater than zero. Such emulsions exhibit poor thermal stability at high temperature and pressure owing to the loss of viscoelastic properties at the interface (Pons et al., 1995; Binks and Rocher, 2009). Since nanoparticles are active emulsifiers of oil and water, preparation of ultra-stable emulsion is attainable by the control of the degree of surface charges (Binks and Lumsdon, 2000; Dickson et al., 2004; Binks and Rodrigues, 2005). The emulsions are not subject to gravity driven separation as the dispersed droplets are relatively small

size, which eliminates separation processes owing to phase density difference (Mandal et al., 2012). The particle dispersals are typically mixtures of water, oil, or surfactant, or brine. It has been reported that nanoemulsions upsurge additional oil recovery (Mandal et al., 2012). Zhang et al. (2010) reported that nanoparticles form stable emulsions, however, the level of stability depends on the oil polarity as the formation of oil-water stable emulsions are more favourable to non-polar oils and water-oil emulsions are preferable with polar oil.

2). Nanocatalysts Suspensions

Another relevant system suitable for EOR processes in porous media is the nano-based catalysts suspensions, which demonstrates high efficiency for heavy oil recovery. The presence of nanocatalyst in porous media has been reported to enhance bitumen conversion to lighter products (Shokrlu and Babadagli, 2011; Pereira-Almao, 2012; Hashemi et al., 2012; Hashemi et al., 2014).

3) Nanofluids

Nanofluids are colloidal suspensions of solid nanoparticles or nanofibers. These solid-liquid composite materials are typically two-phase systems, consisting of a carrier medium and solid phase. The carrier liquids are often water, polymer solution, oil, ethylene glycol and sodium chloride brine. The solid phases are nanoparticles of chemically stable metals and oxides usually within the range of 1-100nm (Choi, 1995; Keblinski et al., 2008; Yu and Xie, 2012; Rudyak, 2013; Nwdee et al., 2016a; Al-anssari et al. 2016, 2017; Nwdee et al., 2017a, b). Nanofluid is continuously attracting great attention owing to its great thermal properties at low volume fractions of less than 1%. To achieve the same functionality with conventional suspensions of well-dispersed particles, high concentrations that are greater than 10% of particles is often a requirement. Such high concentrations increase the issues of rheology and stability which has remained a deterrent to the extensive usage of conventional slurries as heat transfer fluids (Keblinski et al., 2008). The rheology and stability of suspensions exhibit dependency on the volume concentration as there exist interactions between the dispersed particles and its dispersion medium (liquid). If the concentration of the dispersed particle is high, so also is the threshold of the maximally close packing (Π' in, 2011). The solid particles crowd together yielding diverse interactions between them

while forming various structures of which the simplest formed structure in suspensions is a stable surface layer on solid particles, which apparently appear like an increase in the effective volume of a suspended particle. A key advantage of nanofluids over conventional fluids in EOR is that nanoparticles improve the property of its dispersal. The particles in suspension enhance the performance of the carrier fluid during production, owing to high dependency on the unique electrical, rheological, and magnetic properties of the nanoparticles. Since the carrier fluids are normally conventional heat transfer liquids, the particles also enhance the thermal conductivity and convective heat transfer performance of this base liquids as its thermal conductivities are typically an order-of-magnitude higher than that of the base fluids (Yu et al., 2008; Sabet et al., 2016). However, nanofluids may be unstable over time which can lead to formation of aggregates/clusters that can hamper their functionality. Thus, the selection of ideal particle type, size, concentration, dispersals or stabilizers of the nanoparticles in suspension is crucial.

2.7.3 Nanofluid Production and Stability Control Mechanisms

Generally, nanoparticles can be prepared via chemical, biological or physical methods (Saravanan et al., 2008) although the preparation method is mainly based on the nature of the material and the associated chemical reactions, and the applications thereof. The chemical synthesis involves the use of methods such as thermal spraying, chemical vapor deposition, spray pyrolysis, chemical precipitation, or micro-emulsions. Whereas, the physical synthesis involves inert-gas-condensation technique and mechanical grinding approach. The key approaches for the production of nanofluids are the one-step and two-step methods (Yu et al., 2008; Ramakoteswaa et al., 2014).

One-step Method: The one-step method allows a combine production of nanoparticle and dispersion in a fluid in a single process. This method is particularly suitable for nanofluids with high-conductivity metals contents.

Process benefits: The production process impedes particle oxidation; process mechanism is effective as it inhibits particle agglomeration. Offers better nanofluid dispersion characteristics than the two-step technique.

Process limitations: Non-cost-effective approach, production is often done in batches, slows down production time, the rate of production is often low, not ideal for commercial production on large scales.

Two-step Method: In the two-step method, the production process is performed in two separate steps. Firstly, the nanoparticle is produced, subsequently, the produced nanoparticle is dispersed in a fluid.

Process benefits: An effective strategy for commercial use, possibilities for the production of large quantities of nanoparticles, cost effective approach.

Process limitations: Excessive agglomeration rate, high likelihoods for the formation of clusters of the individual particles even before attaining complete dispersion.

In the face of the diverse functionalities of the nanoparticle, a major impediment in the manipulation and application of nanoparticle is the colloidal stability control (Yang et al., 2004; Yu et al., 2008; Koblinski et al., 2008; Wang and Mujumdar, 2008; Paramashivaiah and Rajashekhar, 2016; Khalil et al., 2017). Nanoparticle tends to agglomerate when in suspensions irrespective of its small size. This has remained an issue with the production and utilization of nanoparticle based fluid as this behaviour hampers the overall fluid stability. When particles undergo processing (e.g. sonication), the particles tend to recombine due to the attractive van der Waals forces if the energy supplied by ultrasonication is exhausted. The recombination can be prevented by a decrease in the van der Waals forces through refractive index matching or via an introduction of repulsive forces (e.g. steric, electrostatic, or electrosteric forces). However, if the forces of attraction prevail over the repulsive forces, the particles will aggregate in clusters. Such aggregation can impede fluid flow in porous media as well as in flow based cooling applications. The agglomeration inclination or clustering behaviour of nanoparticles is dependent on the nanoparticles properties, concentrations, production methods, and the dispersants. The nanofluids stability is vital for process efficiency as instability influences the particle functionalities, as such the enhancement of repulsive forces over attractive forces is of great necessity to hamper particle aggregation and ensure stability. The suspension stability can also be significantly improved through the utilization of the appropriate dispersants, suitable fluid production methods, use of surface treated nanoparticles as these particles

display exceptional dispersion in base fluids. Careful consideration should be given to the concentration of the particles, as high particle concentration volume propels high particle agglomeration. Attaining high-performing heat transfer nanofluids require efficient dispersal of the nanoparticle in the base fluid.

2.7.4 Nanoparticles Mechanisms and Synergism

Porous media application of nanoparticles requires an understanding of the nature of the nanoparticles and their interactions with other materials (e.g. surfactants) as well as their synergistic effects on IFT reduction and mobility improvement. In an ideal EOR process in oil reservoirs, the primary role of surfactant is the reduction of the IFT between oil and water via formation of monolayer at the air-water interface to decrease the existing surface tension while increasing oil mobility. Oil displacement is usually more efficient when the drive fluid mobility is significantly lower than the the oil (heavy) mobility. With nanoparticle, its primary role is wettability alteration and IFT reduction. However, wettability is its main mechanism for improving oil recovery since wettability can significantly enhance oil displacement efficiency. Ju et al. (2006) and Ju and Fan (2009) reported that nanoparticles especially hydrophilic particles are efficient modifiers of wettability from a hydrophobic condition towards a hydrophilic state while enhancing oil recovery. Whereas nanoparticles have little or no significant effect on IFT reduction. Hendraningrat and Torsæter (2014) and Al-anssari (2017) reported that IFT reduction by nanoparticle is only but marginal. Understanding of the dynamics of constituent particles in the suspension of nanocolloids and the flow behavior is crucial for characterizing the structure and properties of nanoparticle based fluids and consequently their effect on recovery.

Nanoparticles (Donaldson et al., 2001; Oberdörster et al., 2005) are characterized as particles with diverse sizes, shape, chemical composition, crystallinity, surface area etc. With the decrease in particle dimension comes an exponential increase in the number of surface molecules thus the higher surface area of nanoparticles compared to bulk material (refer to chapter 1 - section 1.4; chapter 4). This material can exhibit hydrophobic or hydrophilic characteristics (Nel et al., 2009) depending on their surface ligands, stabilizers or surfactants used. Dispersion of hydrophobic nanoparticles are challenging with poor stability in fluids other than oil (water and/or

solvent-hating particles) owing to the particle surface charge. When hydrophobic nanoparticles are exposed to surface active agents such as surfactants, depending on the surfactants surface charge (+ ve or -ve), the charge will impact the behaviour of the nanoparticles by changing its characteristics towards hydrophilicity as it dominates the surface area. With the hydrophilic nanoparticles, this can easily disperse in water as they are water-loving and exhibits better stability as opposed to the former that is thermodynamically unstable with high aggregation tendencies. This type of particles does not segregate at the water-air interface (Chandler, 2005; Guzman et al., 2011). Their hydrophilic character can also be modified to hydrophobic depending on the nature the surfactant that they are exposed to. A charged surfactant can readily adsorb on nanoparticle with opposite charge for lowering the hydrophilic/lipophilic balance. For example; nonionic surfactants can adsorb strongly on hydrophilic anionic nanoparticles which in turn raises their hydrophobicity and subsequent adsorption at the oil-water interface (Binks et al., 2007a, b; Gonzenbach et al., 2007; Akartuna et al., 2008).

Nanoparticles interaction with surfactants depend strongly on the individual particle characteristics. Typically, surfactant systems self-assemble to form micelles in aqueous solutions, whereas, for nanoparticle-surfactant complexes, the surfactants tend to remain in the solvent as free micelles, while adsorbing on the nanoparticles (Sharma et al., 2010; Kumar et al., 2014). When nanoparticle and surfactants are in suspension, the surfactants from pre-micelles can dissociate and relocate on nanoparticle surface, creating new surfactant-coated particle. The hydrophobic nanoparticle can intrinsically provide a larger and more hydrophobic core than the pre-micelles for the amphiphilic surfactants, thus, induces higher adsorption inclination. The presence of hydrophobic nanoparticles may not only affect the surfactants in bulk solution, but also the arrangement of monomers at the air-water surface, which will in turn directly impact on the equilibrium surface tension. Such surface tension is typically associated with the quantity of surface active molecules at the air-water surface and its increase are an indication of the loss of the molecules at the interface (Israelachvili et al., 1992; Jiang et al., 2016). With respect to their surface charges, when the nanoparticle and surfactant have opposite charges, there will be a strong interaction between the surfactant micelles and the nanoparticles, however, this can also lead to particle aggregation. With similar charges, the nanoparticles and

surfactant micelles do not interact directly but remain freely in the suspension. E.g. nonionic surfactants adsorb on the nanoparticle surface by micellar or bilayer formation through a weak interaction between the surfactant head groups and nanoparticle surface that is even weaker than the coulomb interaction between an oppositely charged surfactant-surface pair (Ray et al. 2015). Worthen et al. (2014) reported that such weak surfactant and nanoparticle interaction promotes synergism in the formation and stabilization of oil-in-water emulsions as a large fraction of available surfactant molecules can freely adsorb the oil-water interface leading to a reduction in the oil--water IFT which favors small droplet sizes, and the particles can also partition to the aqueous side of the oil/water interface ($\theta_{O/W} < 90^\circ$) (Figure 2.12). However, a non-adsorbing surfactant in a colloidal dispersion affects the colloidal stability of the system. When nanoparticles are dispersed in a solution of non-adsorbing surfactant micelles, a small (tinier than the micelles diameter) gap forms between the nanoparticles while depletion force arises between the particles. The existence of any small gap, will lead to the micelles been expelled from the gap causing an attraction between the nanoparticles owing to entropy increase that decreases the free energy (Asakura and Oosawa, 1958; Méndez-Alcaraz and Klein, 2000; Lekkerkerker and Tuinier, 2011). For example; Ray et al. (2015) investigated the interaction and resultant structure in a mixed system of anionic silica nanoparticles with non-ionic surfactant ($C_{12}E_{10}$) in the presence and absence of electrolyte and found that surfactants micelles adsorb on the nanoparticle surface in the absence of electrolyte as the micelle decorated the nanoparticles core-shell structure (Figure 2.13), thus, providing stability to the nanoparticles in the absence of electrolyte. Whereas, in presence of electrolyte, the micelles are non-adsorbing, thus, induces depletion interaction between the nanoparticles which invariably promoted particle to particle aggregation. Some of such micelles become trapped in the nanoparticle aggregates, precisely in any gaps between the nanoparticles in the aggregates owing to the significant size difference between the nanoparticle and the micelle.

With respect to the synergistic effects of nanoparticle-surfactant complexes on mobility improvement and IFT reduction; during oil recovery reduction in IFT is essential for better fluid mobilization and efficient recovery. In the presence of negative capillary pressure, a favourable reduction in IFT can be achieved owing to a reduction in the resistance forces that impedes efficient oil production. For any two

liquid phases (e.g. gas-water, gas-oil, or oil-water) to be in existence, there is usually an interplay of interfacial tension, which is the force that binds the surfaces of two distinct phases. Sun et al. (2014) investigated nanoparticle-surfactant systems in enhancing oil recovery by using partially hydrophobic modified SiO₂ nanoparticles in

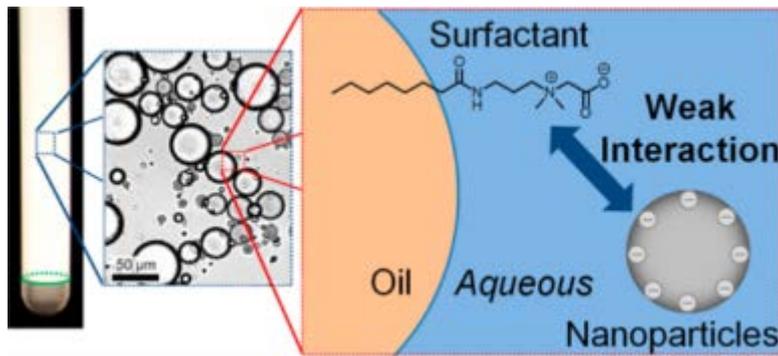


Figure 2.12: Schematic of the weak interaction between surfactant and nanoparticles that promotes synergism in the formation and stabilization of oil-in-water emulsions (Worthen et al. 2014).

combination with anionic surfactant (sodium dodecyl sulfate - SDS). To assess the stability of the system and effect on enhanced oil recovery of the SiO₂ stabilized foam (SiO₂/SDS foam), micromodel flooding and sandpack flooding were adopted. SiO₂/SDS foam displayed better temperature tolerance over the foam stabilized by SDS (SDS foam) owing to the nanoparticles adsorption on the surface of the bubble. The SiO₂/SDS foam also enhanced efficient mobility and displaced more oil than the brine, SDS, and SDS foam flooding alone; the higher viscoelasticity of the SiO₂/SDS foam facilitated the mobility and displacement of more oil on the pore wall and in the dead-end pores. With the enhanced foam stability, gas mobility and channeling were controlled effectively. Nanoparticles in combination with surfactants also exhibit great potentials as IFT reduction agents as the particles display effective adsorption tendencies on the surface of liquids creating separation layers that permits IFT reduction. For example, during emulsification, combination of nanoparticles and surfactant can effectively reduce IFT by reducing the surface tension in favour of the droplet formation while decelerating the emulsion destabilization via mechanisms such as Ostwald ripening, drainage of lamellae, and coalescence (Langevin, 2000; Worthen et al., 2014). This behaviour is mainly governed by the particles surface

adsorption, which is reliant on the phase concentration. Typically, at low concentration, surfactants can decrease surface tension, with increased surfactant concentration comes increase in the number of surfactant molecules in the monolayer until the surface attains saturation leading to the occurrence of micellization in the solution (Holmberg et al., 2002). Monolayers of particles at the interface and partial flocculation of the particles can hamper the coalescence of oil droplets in water (Horozov and Binks, 2006; Dickinson, 2010). However, such coalescence can be reduced through weak flocculation of nanoparticle stabilizers which can improve the system stability (Binks, 2002; Binks et al., 2007; Lan et al., 2007; Horozov, 2008; Hunter et al., 2008).

Surfactants and nanoparticles interaction stimulates competitive adsorption of surfactant on the nanoparticles producing a synergistic effect that is capable of reducing hydrophilic/lipophilic balance (HLB) and IFT (Binks et al., 2007; Lan et al., 2007; Worthen et al., 2014). For example; Lan et al. (2007) investigated the synergistic effects of silica nanoparticles (A200) and cationic surfactants (CTAB) on the emulsion stability on basis of concentration and dispersion ph. It was found that the interfacial adsorption of the silica nanoparticle increased with increasing cationic surfactant concentration, thus, an indication of a clear synergistic effect on interfacial tension (IFT) reduction which was attributed to the emulsion stability. The super-high coalescence stability of emulsions occurred due to the higher elasticity of dense A200 particle layers around the emulsion droplets surface. Whereas the creaming stability was attributed to the viscosity increase induced by the particle aggregates in continuous phase and the networks formed by the particles around the emulsion droplets. Drelich et al. (2010) systematically investigated water in oil (W/O) emulsions prepared with an amphiphilic emulsifier, Span[®]80, or with hydrophobic silica particles, Aerosil[®]R711 as a function of time. Emulsions containing nanoparticles had no significant effect on IFT but provided long-term stability as the particles efficiently stabilize the emulsion droplets by creating a 3D network in the continuous phase with no sign of destabilization for up to 21 days, whereas, for emulsions containing Span[®]80 alone several destabilization processes were detected. However, maintaining system stability is highly dependent on the injected nanoparticle concentration and the synergistic effect of the particles with the surfactants. The presence of nanoparticles could lead to surfactant monomers at the

surface been deprived from the interface, which can possibly participate in the adsorption to the nanoparticles to form surfactant-coated particle. Jiang et al., (2016) reported that even with nanoparticle concentration as high as 1%, the surface tension never returned to 72 mV (the surface tension for the surfactant-free solution), an indication that not all the monomers are deprived from the air-water surface and some surface-active molecules are left behind which leads to the lower surface tension (Jiang et al., 2016). Nanoparticle concentration in the system should be minimized as dispersed nanoparticles can slow film rupture at high particle concentration > 10 vol %. At lower nanoparticle concentrations, the stabilization is influenced by the high surfactant adsorption at the oil-water interface while the NPs contribute to a modest increase in aqueous-phase viscosity thus slowed down the film drainage and droplet approach (Zapryanov et al., 1983; Velikov et al., 1998; Worthen et al., 2014).

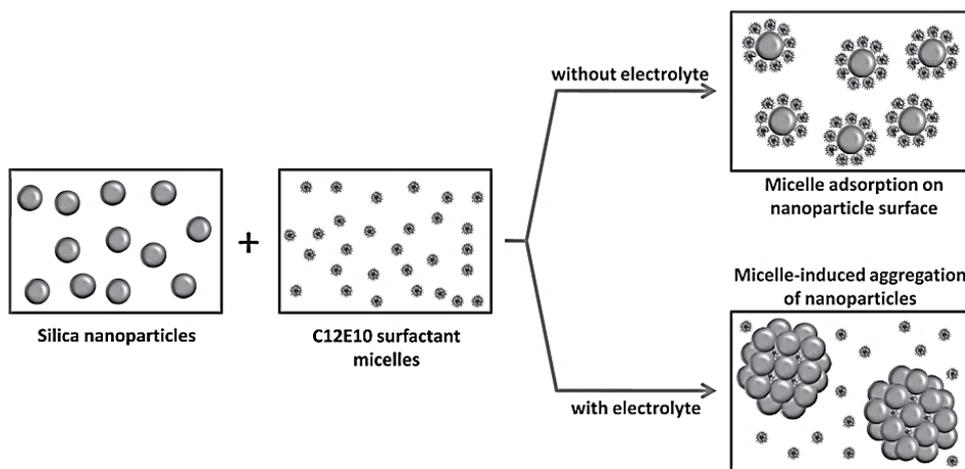


Figure 2.13: Schematic of structures formed in silica nanoparticle-surfactant micelle system in the presence and absence of electrolyte (Ray et al., 2015).

2.7.5 Definite Roles, Mechanisms, and Functionalities of Nanoparticles in EOR

When nanoparticles are injected into reservoir rocks, the system can yield various phenomenal behaviours; adsorption, desorption, transport, and blocking inclinations. The interactions between nanoparticles and the walls of the porous media can lead to adsorption if the force of attraction is higher than the repulsive with the reverse leading

to desorption, however, adsorption and desorption are dynamic balance process that is controlled by the total force existing between the porous media wall and nanoparticle. Blocking can occur if the nanoparticle diameter appears bigger than the size of the pore throat or due to particle to particle aggregation at the pore throat which can inhibit efficient transport of nanoparticle based fluids through the porous media (Mullins and Sheu, 1998; Sjoblom et al., 2003; Syunyaev et al., 2009; Zhang et al., 2010; Pereira-Almao, 2012; Li et al., 2013; Franco et al., 2015; Taborda et al., 2016; Khalil et al., 2017).

The prerequisite for the successful application of nanoparticle in oil reservoirs is an understanding of the transport and fluid flow behaviours in reservoir rocks. Generally, Darcy's law (Equation 2.21) governs how fluids flow through rocks as it demonstrates that the amount of flow between any two points is directly correlated to the pressure difference and distance between the points, and the interconnectivity of the flow pathways in the rock. Such interconnectivity measurement is referred to as permeability; rock permeability plays a key role during fluid flow in reservoirs as it impacts the fluid velocity and can hamper or enhance fluid flow through a series of pore throats or channels. Since oil is typically recovered from formation rocks with micron-sized pores, nanoparticles are much smaller fine particles with unique size dependent physical and chemical properties that enhance easy penetration through the reservoir pores as the particle size is much smaller than the conventional rock pores. As the particle size of is reduced to near or less than the wavelength of electrons conductivity, the property of the material changes (Kim et al., 2013; Nwideo et al., 2017a, b). Thus, fluid flow through the reservoir pore spaces can be significantly improved when nanoparticles are injected with little or no negative impact on the formation permeability, porous media pore-plugging or chemical trapping related issues that are commonly associated with conventional EOR processes. A recent study on nanoparticle adsorption and transport behaviour shows that nanoparticle based fluids can efficiently flow through the porous media without excessive adsorption and retention inclinations with an equilibrium adsorption estimation of 1.27 mg/g for 5000 ppm nanofluid (Yu et al., 2012). Shen et al. (2008) and Zhang et al. (2010) also reported the excellent transport, diffusion, retention, and releasing properties of nanoparticles in porous media. Following equation 2.21, Yu et al. (2015) investigated

$$Q = K \frac{A\Delta p}{\mu L}$$

2.21

the flow enhancement of silica nanoparticles (HNPs-1) to better understand the slip flow of nanoparticle dispersion in microscale reservoir rocks with pore-throat radius between 1.2 and 10 μm . Water exhibited no-slip Darcy flow in all cores and nanoparticle dispersion enhanced fluid flow for approximately 5.7 times higher than water alone, while increasing with the decreasing of pore-throat radius.

Besides, nanoparticles have also shown great efficiency as stabilizers of systems and as conformance control agents in EOR, CO_2 flooding, and sequestration processes thus:

1). Asphaltene Growth Inhibition

Nanoparticles exhibit strong chemical stability, irrespective of harsh reservoir conditions and great selective adsorption behaviour in the presence of heavy components in crude oil such as asphaltenes. Asphaltenes are common petroleum macromolecules which poses challenges such as well bore plugging, adsorption, pipeline deposition, and sedimentation issues. Asphaltenes (Mullins and Sheu, 1998; Sjoblom et al., 2003) exist in forms of solid deposits and usually self-associate with resins in crude oil and are often problematic during production as they can plug wellbore tubing and valves, and contribute to undesirable formation rock surface coating. They exhibit amphiphilic behaviour (contain polar and nonpolar groups) and can form colloidal aggregates and adsorb onto rock surfaces. Such asphaltenes - poly-dispersed (Syunyaev et al., 2009) can exist in the form of colloidal suspensions or micelles which form deposits on mineral surface when the wettability conditions of the reservoirs are altered. For example; when the polar group of the asphaltenes molecular structure (Yan et al., 1997) adsorbs onto the rock surface, the rock wettability changes from water-wet to oil-wet which impacts the final oil recovery properties. This adsorption onto mineral surfaces can cause formation damage in oil reservoirs by reduction in the oil effective permeability (Leontaritis et al., 1994). A study by Franco et al. (2015) on the adsorption behavior of nanoparticles on heavy

components in crude oil such as resins and asphaltenes shows that nanoparticles in contact with crude oil is capable of adsorbing resins and (or) asphaltenes, however, nanoparticles exhibit great selectivity and preferential affinity for adsorption of asphaltenes (n-C₇) compared to resins. This behavior is also confirmed by an earlier report by Franco Nassar et al. (2011), which shows that nanoparticles have great affinity for asphaltenes - where alumina nanoparticles adsorbed asphaltenes more readily than micro porous alumina particles with similar acid content. Taborda et al. (2016) investigated nanoparticles effect on adsorption isotherms of n-C₇ asphaltenes at 298K temperature in complex crude oil systems. The authors compared the performance of different ranges of SiO₂ and Al₂O₃ nanoparticles. The SiO₂A nanoparticles showed better adsorption capacity than others as the adsorption potential to capture n-C₇ asphaltenes is in the order of SiO₂A > SiO₂ > Al₂O₃. The acidic silica exhibited better adsorptive capacity especially at low concentrations owing to increased surface acidity of the nanoparticles as n-C₇ asphaltenes adsorption increases concurrently with increase in surface acidity (Montoya et al., 2014).

Heavy oils are typically known for their high asphaltene content (> 5 wt.%), such asphaltenes (Yudin and Anisimov, 2007; Mullins et al., 2007) forms viscoelastic network of large size nanoaggregate clusters and promote formation damage as a result of self-association, and if sub-saturated oil reservoirs exist at pressures above the bubble point. The asphaltene becomes excluded from the oil matrix and then forms deposits on the reservoir rock. This behaviour causes blockages of the porous media and wettability challenges. Reduction of large asphaltene aggregates using nanoparticles by breaking the attachment points within the viscoelastic network is thus necessary to improve their configuration and distribution in the oil matrix. Taborda et al. (2016) examined the behaviour of n-C₇ asphaltenes in the presence and absence of nanoparticles as a function of time at 298 K temperature. An initial increase in the mean size of asphaltene aggregates (d_{asp}) occurred with time, followed by a decrease in size in the absence of nanoparticles with a notable stabilization of approximately 300 min. This was attributed to the aggregation-fragmentation forces that exist under shear conditions which has a direct growth/reduction effect on d_{asp} . Similar behavior was also observed in the presence of the diverse nanoparticles (Al₂O₃, SiO₂ and SiO₂A) tested, however, a lower d_{asp} and faster stabilization (180 min) was attained in a decreasing order of SiO₂A < SiO₂ < Al₂O₃. Franco et al. (2013) conducted an

asphaltene displacement and adsorption test to inhibit formation damage using nanoparticles at reservoir conditions. The authors reported a significant increase in oil production level owing to the presence of nanoparticles. Increase in oil recovery occurred after the injection of nanoparticle based fluids in damage systems owing to efficient inhibition of the growth of asphaltene aggregates and the swift capture of asphaltene through adsorption.

2). Permeability Improvement

Permeability plays a major role in oil recovery processes as adequate permeability can improve reservoir fluid displacement. High permeable formations permit high fluid displacement alongside other essential factors, such as capillary pressure and formation wettability. Nanoparticles have the potentials of enhancing the reservoirs relative permeability for achieving higher recovery factor. Nanoparticles can efficiently expand the pore radius, enable the reduction of flow resistivity of the water injected into the pores, promote water permeability enrichment, promote reduction in injection pressure and enhance injection volume as well as recovery potentials. Wang et al. (2010) reported that the injection of 0.5 wt. % of SiO₂ nanoparticle concentration led to over 10% increase in oil recovery. The small particle size of this material enabled penetration into the low-permeability layers while averting hydration occurrences from water-rock contact, and promoted injection and subsequent augmentation of oil recovery even in low permeable regions. Guzmán et al. (2017) performed a coreflooding test in bauxite porous media, relative permeability was measured in the presence and absence of fracturing fluid containing nanoparticles. Injection of fracturing fluids into reservoirs can induce formation damage, where the original K_{ro} values appears lower than the base system due to some degree of formation damage. However, with optimized fracturing fluid containing nanoparticles, K_{ro} becomes higher than the base system with mobility range of 0.42 and 0.80. Formation damage reduction from 55 to 16% occurred which was about 71% reduction upon addition of nanoparticles to the optimized fracturing fluid, thus, an indication that the presence of nanoparticles improved the fluids performance and inhibits the associated formation damage which may be due to the porous media wettability alteration as nanoparticle inclusion changes the rock wettability from oil-wet to water-wet.

3). Wettability

Reservoir wettability is a prime factor for determining the microscopic displacement efficiency in the swept regions of a waterflood. Oil recovery exhibits great dependency on the formation wettability as it controls the fluid displacements of the wetting and non-wetting phase at the pore scale. However, wettability is influenced by complex crude oil-brine-rock interactions and the degree to which the crude oil polar components deposits or adsorbs on the mineral rock surface. When nanoparticle is introduced, the presence of nanoparticles promotes surface adsorption, while dramatically changing the formation rock wetting. The wettability change is dependent on the level of contact established between the rock surface and the wetting phase, which impacts the rather immobile fluid on the rock surface while mobilizing such fluids toward the flow lines. Two key mechanisms (Mohammed and Babadagli, 2015) governs wettability alteration of surfaces - cleaning and coating. Cleaning involves the use of surface active agents to desorb surfaces e.g. surfactants induced wettability alteration, where cationic surfactants can desorb the hydrophobic layer on a surface while changing the surface towards hydrophilic condition. Whereas coating involves covering a hydrophobic surface with a hydrophilic material, e.g. hydrophilic zirconium nanoparticle can adsorb on hydrophobic rock surface and form nanotextures capable of coating the hydrophobic surfaces. The later chapters emphasize more on wettability. These phenomena have been reported in several literatures (Binshan et al., 2002; Suleimanov et al., 2005; Lan et al., 2007; Ju and Fan 2009; Loahardjo, 2009; Ismailov and Veliyev, 2011; Ahmadi and Shadizadeh, 2013; Shafie et al., 2014; Zargartalebi et al., 2015; Cao et al., 2015; Hosseini et al., 2015, Al-Anssari et al., 2016, 2017; Nwideo et al., 2016a, 2017a, b). Ju and Fan (2009) tested the wetting inclination of lipophobic and hydrophilic polysilicon nanoparticles in hydrophobic sandstone formation. The authors reported that the presence of nanoparticles caused a change in wettability to hydrophilic state owing to efficient particle adsorption on the surface of the rock. Cao et al. (2015) performed a wetting investigation in the presence of zirconium oxide, and silicon oxide dispersed in surfactant, alkali and brine solutions. The authors reported that the nanofluids displayed great stability even under reservoir conditions of high pressure and high temperature. Wasan and Nikolov (2003) reported the oil displacement from a solid substrate using nanoparticle dispersions by nanoparticle structuring or layering in the wedge film. The formulated systems formed

two-dimensional layered structures in the confines of a three-phase contact region of a wedge film formed between an oily soil and the solid substrate. This led to the formation of a structural disjoining pressure in the wedge film which is higher near the tip of the wedge than in the bulk meniscus yielding an increase in pressure and spreading of the nanofluids over the solid surface, changes the wettability and detaches the oily soil.

4). Pickering Emulsions

The use of conventional emulsions in EOR are promising approach that can promote sweep efficiency improvement, high extraction efficiency, and the systems stability with small molecular emulsifiers and macromolecules (Johnson, 1976; Sarma et al., 1998; Dong et al., 2009; Mandal et al., 2010; Kumar et al., 2012). Microemulsions are considered advantageous over other flooding methods (Pei et al., 2012, 2013; 2014; 2015; Karambeigi et al., 2015; AfzaliTabar et al., 2017; Pei et al., 2017) owing to the unique physicochemical properties (AfzaliTabar et al., 2017; Pei et al., 2017) that promotes ultra-low IFT reduction potentials, great water solubilisation capacity, moderate viscosity, and nano sized droplets. Its droplet size and size distribution provide essential information for reasonable understanding of the governing mechanism of stability and porous media diffusion thus a preferred alternative over alkali, surfactant, or polymer flooding. However, Pickering emulsions are a class of fluids that even shows much higher performance and stability than microemulsions.

Pickering emulsions (Pickering, 1907; Yang et al., 2017) uses solid particle alone as stabilizers instead of organic surfactants. It accumulates at the interface between two immiscible liquids (oil and water phase) and stabilizes droplets against coalescence, thus potential fluids for EOR applications. A comparison of Pickering emulsions stabilized by particles and classical emulsions stabilized by surfactants (Ramsden, 1903; Melle et al., 2015) shows that Pickering emulsions displays better stability over other emulsions. Typically, emulsion types (Binks and Clint, 2002; Bon and Colver, 2007; Leal-Calderon, and Schmitt, 2008; Tang, et al., 2014; Ershadi, et al., 2015) are dependent on the hydrophobic and hydrophilic properties of the particles used as the hydrophobic particles are more efficient for stabilizing water-in-oil emulsions, while hydrophilic particles performs better with oil-in-water emulsions. Since nanoparticles can be partially wettable in oil and water phases, the particles are considered suitable

for emulsification owing to its favourable adsorption behaviour at the oil-water interface. Nanoparticles can be fused with polymer by the inclusion of nanoparticles in the polymeric systems (Maghzi et al., 2013; Maurya and Mandal, 2016) or through grafting or chemical attachment of the polymer on the nanoparticles surface (Balazs et al., 2006; Nguyen et al., 2012). More so, nanoparticles (Ponmani et al., 2014; Williams et al., 2015) have great thermal stability even at high temperature and salinity conditions, thus their presence can further improve the emulsions stability. For example: Maurya and Mandal (2016) performed a rheological investigation of the effect of salt and temperature using silica/polyacrylamide polymer (PAM) suspension in water in comparison to pure PAM solution at different silica/polymer concentrations, shear rates, salt concentrations, and temperatures. The authors reported that the presence of nanoparticle in the PAM solution led to the formation of complex micelle type three-dimensional network structure by irreversible bridging of polymeric chain with nanoparticle. With increase in the silica nanoparticle concentration the network structure of polymeric solution became more strengthened. The polymeric chain adsorbed on the silica nanoparticle surface owing to the formation of hydrogen bonds which promoted apparent viscosity increase of the suspension better than the system containing PAM; and improved salt tolerance and suspension stability against thermal degradation. Kumar et al., 2017 synthesized and characterized surfactant-polymer-nanoparticle based oil-in-water Pickering emulsion using light mineral oil, carboxy methyl cellulose (CMC) and silica nanoparticles (SiO_2) in the presence of anionic surfactant (Sodium Dodecyl Benzene Sulfonate - SDBS). The authors reported that there exists a synergetic effect between SDBS and SiO_2 . A better decrease in IFT with increased system stability occurred in comparison to the surfactant-polymer system and surfactant stabilized emulsions. The emulsions displayed consistent high viscosity even at high pressure and temperature which denotes enhanced stability and better mobility. Zeta potential value of 30 mV - an indication of a stabilized system and an additional oil recovery (> 24 %) was obtained after conventional water flooding and injection of only about 0.5 pore volume of the SPN-3 Pickering emulsion. AfzaliTabar et al., 2017 evaluated Pickering emulsion in comparison to a similar nanohybrids of different carbon structures nanohybrids with SiO_2 nanoparticles. A facile and economical preparation method of the nanoporous graphene/silica nanohybrid was proposed. The results showed that the nanoporous graphene/ SiO_2 nanohybrids Pickering emulsion displayed superior efficiency over the

MWCNT/SiO₂ nanohybrids Pickering emulsion as it exhibits greater stability with salinity and temperature while improving the rheological behaviour of the polymer suspensions, reduced IFT, and decreased reservoir wettability from oil-wet to water-wet condition.

5). Zeta Potential

Zeta potential is a simple, rapid, direct-on-particle approach that permits the characterization of particle modification. This electro kinetic potential allows for estimation of the potential difference in colloidal systems that exist between the dispersion medium and stationary layer of the fluid that attaches to particles.

Understanding the stability of colloidal dispersions requires a knowledge of the key parameter that controls electrostatic interactions in particle dispersions as colloidal dispersions in aqueous media are often associated with electric charge and the development of such charge at the particle surface impacts the distribution of ions in the surrounding interfacial region. Formation of of electrical double layer (liquid layer surrounding the particle - Figure 2.14) can occur due to increased concentration of a counter ions close to the surface. Such electrical double layer is of two forms; (1) diffuse layer, an outer region where the ions are less firmly associated; (2) stern layer, an inner region where the ions are strongly bound. Here, a notional boundary is on the inside where the ions and particles form a stable entity; as the particles move, the present ions within the boundary also moves which is mainly due to electrophoresis. Ions beyond the boundary stay with the bulk dispersant. The potential at this boundary which is the surface of hydrodynamic shear or slipping plane is the zeta potential (Kaszuba et al., 2010). Zeta potential is closely related to the morphology of the particle surface and the suspension stability as the colloidal dispersions stability is dependent on the zeta potential value.

The zeta potential of the rock-water interface and oil-water interface charges can be estimated based on the properties of the particles and suspension conditions (ionic type and strength, pH, and temperature). For example, in carbonate formation (Zhang and Austad, 2006); pH and potential ions that forms a part of the carbonate structure such as Ca₂⁺ and CO₃²⁻ enables the determination of carbonate-water interface via zeta potential. With respect to nanoparticles, zeta potential enables estimation of the

electric potential of particles on the inner boundary of the diffuse layers and surface charge of nanoparticles, since surface charges impact their reactivity, toxicology, and agglomeration behaviors (Thielbeer et al., 2011; Wang et al., 2015). However, the agglomeration inclinations of nanoparticles can promote colloidal instability. Manan et al. (2015) reported that different types of nanoparticles behaves differently owing to their zeta potential. In the study, the zeta potential of four different nanoparticles were compared and reported with varied zeta potential ranges (10 -24 mv); where the zeta potential of Aluminum oxide(Al_2O_3) was 24 mv, Silicon dioxide (SiO_2) - 19 mv, Titanium dioxide (TiO_2) -13 mv, and Copper oxide 10 mv. The higher the zeta potential value whether positive or negative, the higher the stability potentials of the NP suspensions. Low zeta potential of colloidal fluids indicates that the repulsive force is lower than the forces of attraction which promotes precipitation and flocculation. However, such flocculation of nanoparticle based fluids like nano-emulsions can be prevented via steric stabilization owing to their droplet size which is sub-micrometric. Overlapping of interfacial droplet layers causes steric repulsion due to the unfavourable mixing of the stabilizing chain of the adsorbed layer which is dependent on the interfacial layer thickness, density and interactions between the interfacial layer and solvent (Tadros, 1982; Napper, 1983; Tadros et al., 2004; Anton et al., 2008). Theoretically, Derjaguin and Landau (1941) and Overbeek and Verwey (1948) through the DLVO (Derjaguin, Landau, Verwey, and Overbeek) have shown that the stability of colloidal particles in solution is governed by their total energy of interactions (attractive and repulsive) when the particles are near each other.

Nanoparticle as colloidal particle interacts with its carrier fluid or dispersal due to van der Waals attraction or electrostatic repulsion forces, of which the effects of the attraction forces can be higher than the repulsive. A comparative zeta potential tests was conducted by Ahmadi et al. (2013) to examine the interactions between fines and pore surfaces and the change in total energy of the interactions due to colloidal forces of alterations in the presence of nanoparticles. The pore surfaces were coated with MgO (magnesium oxide), aluminium oxide (Al_2O_3) and silicon dioxide (SiO_2). The pore surface changes in potential was tested and the total interaction energy was used to estimate the effects of the nanoparticles on surface properties and fines migration reduction. Upon comparison of the effects of the different nanoparticles, MgO

displayed the highest propensity to attach fines to the surface and significantly reduced fines migration than Al_2O_3 and SiO_2 , thus considered more efficient.

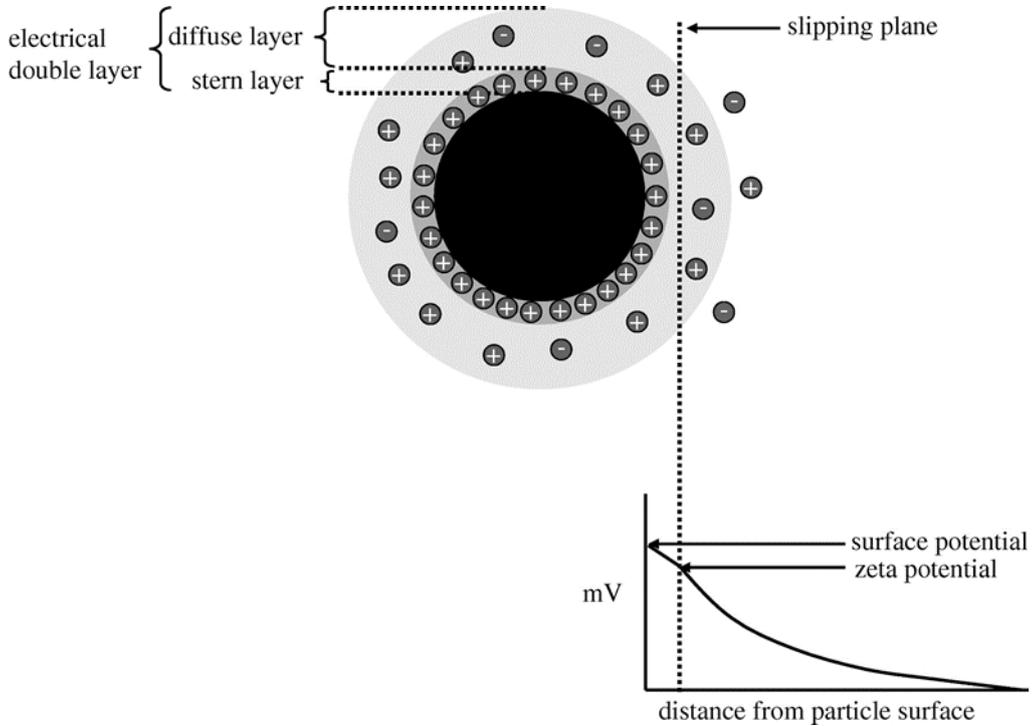


Figure 2.14: Schematic of Zeta Potential showing electrical double layer that surrounds a particle in an aqueous medium (Kaszuba et al. 2017).

6). Interfacial Tension (IFT)

IFT plays a key role in oil recovery enhancement by reducing the resistance forces that hampers efficient fluid flow. Such reduction is greatly enhanced in the present of nanoparticles and several studies have been conducted in this regard (Wasan and Nikolov, 2003; Lin et al., 2003; Chengara et al., 2004; Wasan et al., 2011; Mc. Elfresh et al., 2012; Li et al., 2013; Zargartalebi et al., 2015; Al-anssari et al., 2017; Sharma and Sangwai, 2017). E.g. Sharma and Sangwai (2017) investigated the effect of temperature (30 to 90 °C) on IFT of four paraffin oil (n-decane, n-hexane, n-pentane, n-heptane) using nanoparticle-polymer and nanoparticle-surfactant-polymer. The nanoparticle based fluids decreased IFT with temperature increase for n-decane and n-heptane; whereas n-hexane and n-pentane decreased with subsequent increase after

reaching a minimum value, which was attributed to their low molecular weight that causes volatile losses at high temperature ($> 70\text{ }^{\circ}\text{C}$). Vatanparast et al., (2017) investigated the dynamic IFT of *n*-heptane/water in the presence nanoparticle (SiO_2 concentration - 0-2 wt. %) and surfactants. A sharp reduction in IFT occurred in the absence of nanoparticle and equilibrium was attained in 30 s and from a notable point of about 39 mN/m. For nanoparticle based systems, a rather gradual and steady decrease in IFT occurred over longer time interval (>1500 s). The IFT commenced at about 51 mN/m (close to pure water/heptane IFT) and decreases gradually with increase in the nanoparticle concentration - an indication of the existence of a negligible amount of free surfactant molecules in the system at this point, the nanoparticles did not promote rapid IFT reduction as with the case of the pure surfactant. The exchange of surfactant between the nanoparticle and the interface promoted decrease in IFT as each nanoparticle carries certain amount of surfactant molecules. With the increase in nanoparticle concentration, even more surfactant-nanoparticle complex occurs in the bulk phase which adsorbs to the interface, thus promoting further decrease in IFT at equilibrium condition. A much lower IFT reduction was attained compared to that of surfactant alone. Zargartalebi et al. (2015) and Vashisth et al. (2010) also reported better IFT reduction occurs in the presence of nanoparticles due to the adsorption of nanoparticles at the aqueous suspension/oil interface.

Figure 2.15 (a-e) demonstrates a typical scenario of nanoparticle-surfactant behaviour with increasing nanoparticle concentrations. Prior to the addition of nanoparticles (a), a monolayer of monomers were formed at the air-water surface while others exist as premicelles in the solution. Upon addition of a small amount of nanoparticles (concentration $\leq 0.01\%$ - (b)), the monomers in the premicelles undergoes dissociation, relocates to the nanoparticles surface forming surfactant-coated particles and adsorbs on the surface with the hydrophilic heads outward and hydrophobic tails inward yielding hydrophilicity and dispersity in the solution. This may be due to the presence of enough monomers from the premicelle reservoir to coat the surfactant-coated particles; at this stage most of the surfactants are still on the air-water surface, the monolayer remains intact with little surface coverage change. At nanoparticle concentration $> 0.01\%$, the system appears more complicated as the surfactant-coated particles occupies all the surfactant monomers from premicelles while recruiting

monomers from the air-water surface. With the increase in the nanoparticle concentration (c), the surfactants originally at the air-water surface are slowly removed and shifted to adsorb on the surfactant-coated particles leading to a decrease in the surface coverage, the hydrophobic nanoparticles activate competition for monomers between the particles and the air-water surface. If 80% of the surface are hydrophobized, the nanoparticles would tend to exhibit a stronger attraction for the monomers, hence the monomers would move from the air-water surface to adsorb on the nanoparticle surface. Such loss in monomers yields surface tension increase. However, there exist likelihood that some surfactants may still be left at the air-water surface even at high nanoparticle concentration ($\geq 0.1\%$ - (d) and (e)), here the surfactant-coated particles move to the air-water surface, divulging parts of the bare area to the air and parts of the surfactant coated hydrophilic boundary to the solution, which can cause a release of some monomers back to the air-water surface, hence reducing the surface tension. Such assembly can be seen to as islands of surfactant-coated particles surrounded by surfactant spacers as evident in (d) and (e), as the islands approaches closer, the tendencies for aggregation becomes higher although entropically favourable and can lead to the formation of networks (armed sheath) capable of resisting any surface deformation (Jiang et al., 2016).

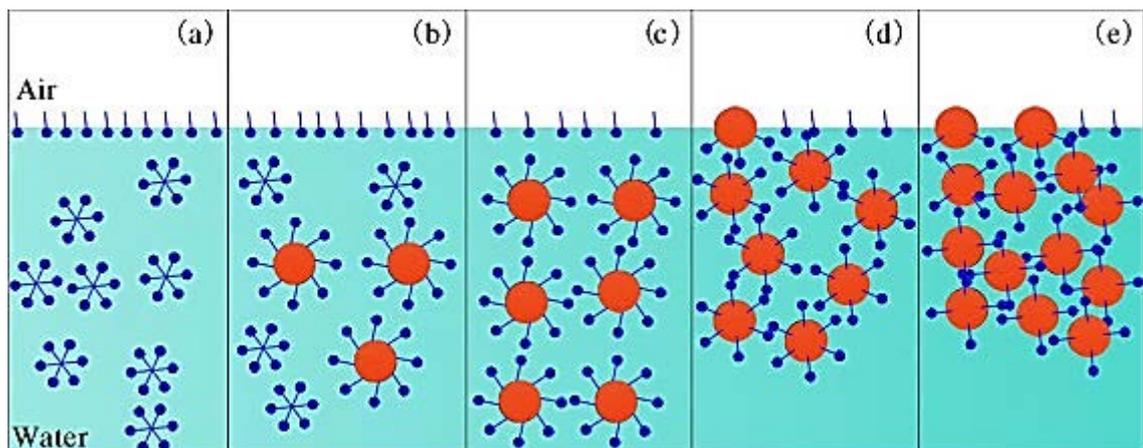


Figure 2.15: Schematic of the underlying mechanisms of ionic surfactants and hydrophobic nanoparticles at the air–water surface as a function of nanoparticle concentration increase: a) without nanoparticles; with nanoparticles: b) low, (c) medium (d) high and (e) extra high (Jiang et al., 2016).

7). Control of Formation Fines Migration

Formation fines migration can be controlled in the presence of nanoparticles to enhance reservoir productivity and oil recovery. In fracture packing operations, nanoparticles coated on proppants exhibit great potentials in holding formation fines in the proppant fractures. The high surface forces of nanoparticles enable the attachment of the particles on the proppant surface during proppant fracturing pumping treatments. Movement of the formation fines to the near-wellbore region is hindered owing to the surface forces of the nanoparticles, which captures the formation fines as it migrates through the nanoparticle treated regions (Huang et al., 2010).

8). Stabilization of Viscoelastic Surfactant (VES) Fluids

Viscoelastic surfactant fluids are fluids that are made up of low molecular weight surfactants that create elongated micelle structures and display viscoelastic behaviour for fluid viscosity increase (Nehmar, 1988; Brown et al., 1996; Samuel et al., 1999). VES fluid has gained vast importance as a fracturing fluid owing to its inherent benefits like low formation damage and ease of preparation (Baruah et al., 2014; 2015). Addition of small amount of nanoparticles to VES solutions leads to a pseudocrosslink between the nanoparticle and the VES micelles owing to charge attraction and surface adsorption, as nanoparticles have high surface area. The nanoparticle stabilizes the VES micelles even at high temperature conditions, while minimizing the VES fluid leakage potential in the porous media (Huang and Crews, 2008).

9) Viscosity and Improvement of Sweep Efficiency in Reservoirs

Improving formation viscosity and sweep efficiency is of great necessity for efficient hydrocarbon flow so as to avoid poor oil, gas or water movement or distribution through the pore spaces. The addition of nanoparticles to injection water can increase contact with more swept zones and upsurge the formations sweep efficiency. Typically, the reservoirs pores are filled with hydrocarbons, the flow of water containing nanoparticles through such pores can control the movement and swelling tendencies of the local clays and other formation fines therein. This will in-turn reduce the accumulation of formation-particles and pore throats plugging in the flow channels which can enhance better water sweep efficiency and subsequent oil recovery (Huang

and Clark, 2015). Maghzi et al., (2013) investigated the effect of nanoparticles on the rheological behaviour of polymer in promoting oil recovery. The authors reported that the presence of low concentration of nanoparticles in the polymer suspension improved the viscosity of the system and the system exhibited better viscosity with much higher oil recovery potential than the polymer system without nanoparticle.

10) Heavy oil Recovery Enhancement

The upgrading of bitumen and heavy crude oil has remained a challenge. The associated high viscosity and density makes handling and transportation processes even more complex. The unique properties of nanoparticle make it effective as adsorbent and catalysts for enhancing heavy oil upgrading. The presence of nanoparticles in reservoirs improves oil recovery through the production of lighter components achieved by catalytic hydrocracking of heavy oil and by altering the rock surface wettability when the porous medium surface is coated with nanoparticles. For instance, Hashemi et al. (2012) tested nanocatalysts suspended in heavy oil matrices containing vacuum gas oil (VGO) in oil sands at high temperature and pressure. This was done to ascertain the transport behaviour of nanoparticles in oil-reservoirs during heavy oil recovery and upgrading. It was found that nanoparticles specifically, UD multimetallic nanoparticles, can be transported through oil sands porous media into heavy oil reservoir as catalysts for heavy oil upgrading (Molina, 2009; Saidur et al., 2011; Shokrlu and Babadagli, 2011; Pereira-Almao, 2012; Hashemi et al., 2014).

11) Thermal Conductivity

The thermal conductivity of a material is an essential characteristic for evaluation of the heat conduction and transmission capacity of a specific material. Nusselt number usually denotes the resistance of a flowing fluid to the heat transfer since it directly considers the thermal conductivity of the fluid and indirectly by the Prandtl number. Interestingly, nanoparticle based fluids exhibits high thermal conductivity and large surface area than conventional base-fluids, although, the physical mechanism that accounts for its potential to enhance thermal conductivity is still not well understood (Eastman et al., 2001; Liu et al., 2006; Timofeeva et al. 2007; Yu et al., 2008; Saidur et al., 2011).

Addition of nanoparticles can significantly improve the thermal conductivity of conventional base liquid. The high surface area increases the thermophysical properties of the fluids and the small particle size enhances their potentials as absorber fluids as it has high potential of large surface coverage in heat transfer processes. An evaluation of thermal conductivity and particle agglomeration of nanofluids was conducted by Timofeeva et al. (2007) where the heat conduction and particle agglomeration effect of Al₂O₃ nanofluids for heat transfer applications was investigated. The authors reported that the key variables that controls the thermal conductivity enhancement in nanofluids are the geometry, agglomeration state, and surface resistance of nanoparticles. Similarly, Choi (1995), Eastman et al., (1996) and Lee et al., (1999) earlier established that nanoparticle based fluids exhibit higher thermal conductivity with great dependency on factors such as the material type, size, shape, surface charge, particle volume fraction, the base fluid containing the particles and temperature. Das et al. (2003) studied the effect of temperature on thermal conductivity enhancement in Al₂O₃ and CuO nanofluids and found that a dramatic increase in the enhancement of conductivity occurred with temperature by a 2- 4fold increase in thermal conductivity enhancement of nanofluids over temperature range of 21°C - 51°C. The small particle size of the nanoparticles in the based fluids also enhanced the fluids conductivity with temperature. Thus, nanofluids were considered more attractive as a cooling fluid for devices with high energy density. Ponmani et al., 2014 investigated the thermal and electrical conductivity with varying nanoparticle loadings zinc oxide (ZnO) and copper oxide (CuO) nanofluid in the presence of xanthan gum (XG). Different concentrations of nanoparticles (0.1 - 0.5 wt.%) were used in a 0.4 wt.% of XG aqueous solution. The authors reported a 25% thermal and 50% electrical conductivity enhancement occurred with increase in concentration of nanoparticles for ZnO and CuO nanofluids respectively. XG also formed a jelly-like structure around the nanoparticles while keeping it suspended in the solution and the system yielded great stability with the CuO based system exhibiting better stability over the ZnO system.

12) CO₂ Foamability, Stabilization and Mobility Control

Surfactants have been used as a common approach for stabilizing CO₂ foams. CO₂-in-water foams permit the reduction of the mobility of CO₂ which upsurges better sweep

efficiency. Despite the process efficiency, the key limitation with this process is that, constant regeneration of surfactant based foams is required for efficient process implementation. Nanoparticle is currently being used to stabilize CO₂ instead of surfactant owing to its unique chemical properties as it offers several advantages over bulk material especially with respect to stability. CO₂ injected with nanoparticle dispersion stabilizes nanoparticle foam, although at a threshold shear rate, since high shear rates are usually connected with preferential flow through high permeability zones in typical field cases. This promotes the tendencies for the creation of self-guiding fluids that selectively reduces the mobility of CO₂ via foam generation in fractured and gravity override regions with rapid CO₂ flow, which normally contains less oil. In the presence of the oil, the foam breaks to facilitate high recovery via contact with the mobile CO₂.

AttarHamed et al. (2014) assessed nanoparticle size effect on foamability and foam stability, and the synergistic effect of surfactant and nanoparticle. To evaluate the foam stability, a glassware test was conducted at ambient temperature and atmospheric pressure using amorphous hydrophilic silica nanoparticle with particle size ranges of 15 nm, 70 nm, and 250 nm (concentration: 0.1 wt.% -1.0 wt.%) and alpha olefin sulphonate - AOS (anionic surfactant). The CO₂ foam behaviour was assessed by injecting CO₂ into 400ml prepared solution in a visual cell at a constant rate of 7.9 mL/min, thereafter, the foam volume and the break time were measured and the normalize foam height estimated using Equation 2.22 and the synergistic effect were also evaluated. The authors reported that the particle size, concentration, and hydrophobicity have significant effect on foam stability. The silica nanoparticles displayed an antagonism effect on foamability with an initial foam height reduction irrespective of their particle sizes - 15 nm, 70 nm, and 200 nm. However, for the synergistic effect on basis of foam stability, only systems containing small size nanoparticles (15 nm) and low particle concentration (0.3 wt.% and 0.5 wt.%) displayed better effect in stabilizing CO₂ in water foams over 70nm and 250 nm particle size and 1 wt.% concentration, and improved CO₂ in water foams stability by 25% at an initial foam volume of 20%. On basis of the particles hydrophobicity, for high stability to be achieved, nanoparticles should be designed with efficient surface coatings for adequate hydrophobicity and formation of CO₂ in water foams.

Normalized foam height = foam height(t)/foam height ($t = 0$)

2.22

Similarly, Singh and Mohanty (2014) reported that nanoparticle-surfactant solutions containing only about 0.3 wt.% nanoparticles significantly modified foam mobility ratio. The increase in nanoparticle concentration (0 - 5 wt.%) increased the mobility reduction factor from 4000 to 8700 and increased foam stability. It has also been experimentally proven that the presence of nanoparticle creates better foam stability than surfactant or VES fluids and even polymer, improves mobility control and efficient for enhancing oil recovery owing to high sweep efficiency and effective viscosity (Salehi et al., 2008; Jikich, 2012; Worthen et al., 2012, 2013; Nguyen et al., 2014; Emrani, and Nasr-El-Din, 2017).

13) CO₂ Storage and Leakage Inhibition

For several decades, the excessive use of fossil fuels has contributed immensely to the increase in the atmospheric concentration of greenhouse gases. Carbon capture and storage (CCS) (Iglauer et al., 2011; 2012; Blunt et al., 2013; Iglauer et al., 2014; 2015a, b; Rahman et al., 2016, Al-Yaseri et al., 2016; Arif et al., 2016; Al-anssari et al., 2017; Iglauer 2017) is considered the most direct carbon management strategy for long-term reduction of such greenhouse gases. However, the capturing and storage process of CO₂ in geological formations such as deep saline aquifers or depleted reservoirs pose potential leakage threats, which has raised several concerns about the feasibility and long-term storage fate of such CO₂. Interestingly, when reservoirs are primed with nanoparticle based fluids, the systems demonstrate potentials of improving storage efficiency and also inhibit CO₂ leakage tendencies thus providing containment security and storage capacity improvement.

Aminzadeh et al. (2013) investigated CO₂ leakage prevention mechanism through nanoparticle application. The study proffers a remediation strategy where injection of nanoparticle dispersion into a leakage pathway after CO₂ escape has been revealed can create a passive barrier against CO₂ leakage whether driven by viscous forces such as pressure, or by buoyancy. Coreflood test was performed to measure the flow pattern and pressure drop in which CO₂ or a CO₂-analogue fluid displaced brine with and without dispersed nanoparticles. The in-situ saturation distribution of the phases was captured in real time for cores positioned horizontally in a modified medical scanner,

and the pressure gradient during displacement was measured using pressure transducers. CT scans were used to evaluate water saturation distribution along the core after injection of 0.1 PV n-octane with and without nanoparticles. Lateral CT scans with brine (2 wt.% salinity) as the initial fluid demonstrates non-uniform displacement front. In comparison, the system containing nanoparticle suspension depicts a more distinct and uniform front with slower displacement front and more uniform CO₂ saturation near the inlet and less gravity override. The authors emphasized that the dispersion of nanoparticles on or above potential CO₂ leakage paths such as faults, abandoned wells or fractures can allow the formation of CO₂/brine foam when CO₂ enters the path, which can avert the possibilities of leakage.

2.8 Conclusions

Mobilizing and recovering of hydrocarbons from geological formations is crucial to meet the unceasing global energy needs. Hydrocarbon can be recovered in three production stages primary, secondary and tertiary processes. However, the conventional recovery methods (primary and secondary) are insufficient. With oil fields development and water breakthrough in oil wells, water wells have become predominant and water injection into such formations is less effective as substantial amount of oil is left behind after recovery thus creating the need for EOR. On average, oil recovery from the primary and secondary production stage (Thomas 2008) is approximately one-third of the original oil in place (OOIP), while the remaining two-thirds can be partially recovered through EOR which are key drivers for incremental oil recovery. However there exist key challenges associated with EOR processes e.g; the thermal EOR processes - high operational cost, and environmentally unfriendliness owing to emissions from surface steam generation; chemical EOR - high chemical cost, possibilities of chemical mismatch, porous media pore-plugging and chemical trapping issues; gas EOR - separation issues, inadequate sources of gas on basis of geographical availability and problems of mobility control; microbial EOR - complex process mechanisms, and poor oil recovery potential (Muller, 1981; Hong, 1989; Schmidt, 1990; Moan and Omari, 1992; Caulfield et al., 2003; Pu et al., 2016b; Nwideo et al., 2016b). Thus, the constant search for new methods to augment additional recovery from porous media. With increasing research on the functionality

and performance of nanoparticle in EOR, one of its key mechanisms is altering reservoir rock surface wetting to a desirable state for oil recovery augmentation. Wettability has remained a crucial factor controlling efficient fluid displacement at pore-scale and optimal oil recovery, however, the mechanism of wettability alteration via nanoparticle in carbonate reservoir is not clearly understood which forms the motivation for this work. Carbonate formations are highly fractured which makes water flooding even more inadequate. Understanding the wetting inclination of limestone reservoir and their solid-liquid interface interaction is crucial as it controls how readily the reservoir oil can be extracted. The goal of this work is to formulate potential systems for altering limestone reservoir rock wetting in EOR applications. The practical applicability of the formulated nanofluids were investigated by systematic testing under various conditions as evident in the subsequent chapters to address the current issue of limited data on solid-liquid interfaces in complex oil-surfactant-brine-nanoparticle systems.

Chapter 3 Experimental Apparatus and Procedure

This chapter presents detailed descriptions of the methods used in achieving the aim and objectives of this study. The study is an experimental base research, which also embodies a qualitative pathway.

3.1 Research Strategy and Justifications

The research strategy adopted in this study was primarily based on the aim and objectives of the study. The qualitative research approach (Figure 3.1) was

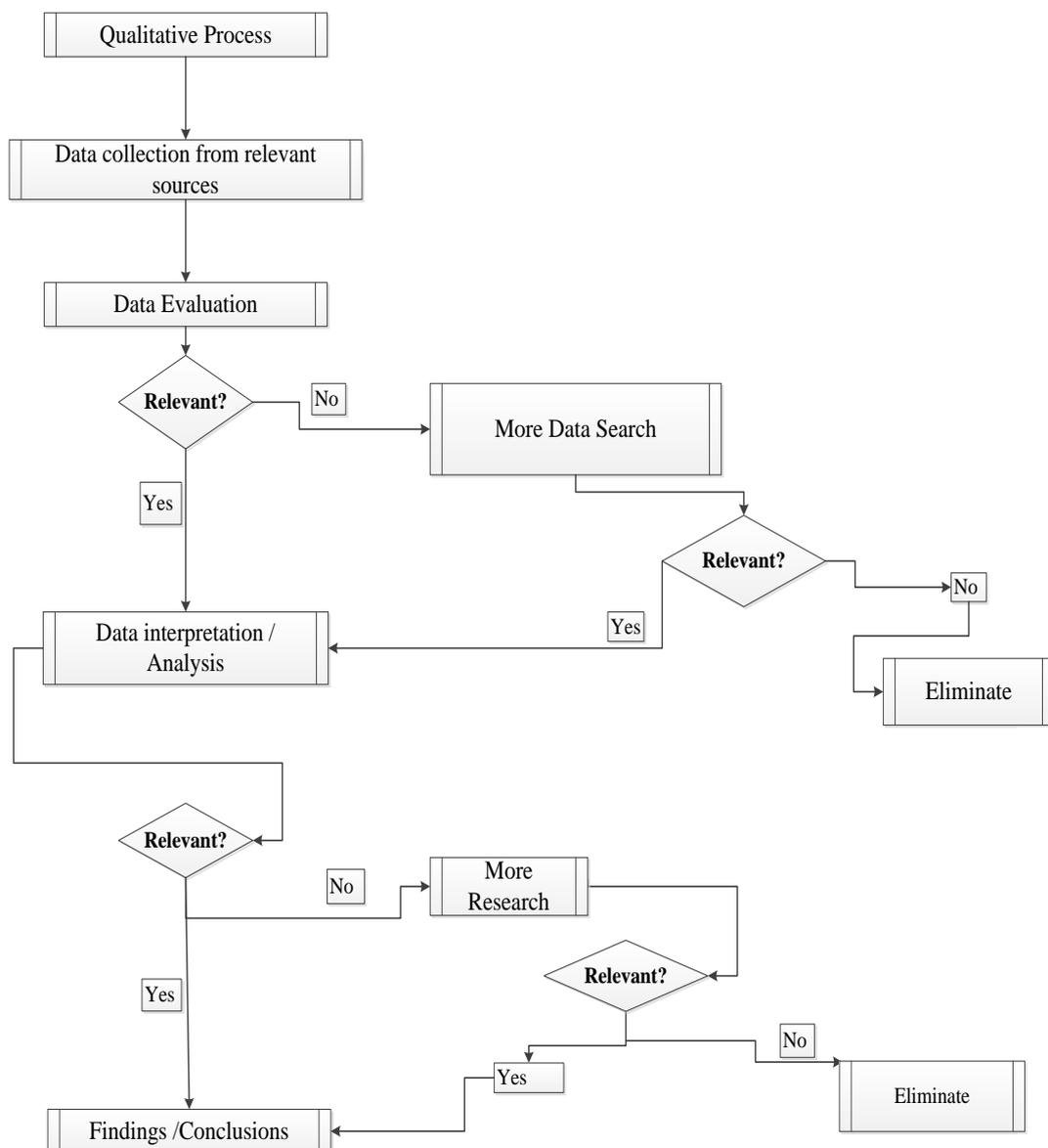


Figure 3.1: Flow Chart of qualitative data process.

specifically adopted for the critical analysis of EOR, wettability, and nanoparticle affiliations, and to identify the existing challenges associated with limestone formation as evident in the previous chapters. The experimental aspect of the study involves laboratory experiments that enabled the attainment of the objectives of the research and makes up for the bulk majority of this work.

3.2 Experimental Task Appraisal

Several experiments were conducted on limestone rock samples at various conditions. The experimental study commenced with the selection of suitable oil for aging limestone samples. At this stage, we ensured an effective modifier is selected that is not only capable of altering the sample surface from its original hydrophilic wetting states to a suitable hydrophobic condition but also able to maintain great stability. After determination of the most stable aging material, sample preparation, oil-wet surface modification, nanofluid formulations and extensive series of wetting tests were conducted.

3.3 Experimental Procedure

3.3.1 Materials

Aqueous Phase: Sodium Chloride (purity ≥ 99.5 mol. %) from Rowe Scientific and ultrapure de-ionised water from David Gray was used. The sodium chloride was dissolved in deionized water to achieve desired concentrations.

Rock Samples: Iceland spar calcite crystals from Ward Science and Indiana limestone cores (Figure 3.2) from Kocurek Industries were used as a representative of limestone formation. The petro-physical properties of the cores were determined; the porosity and permeability were measured with an AP-608 automated porosimeter-permeameter with an accuracy of $\pm 0.1\%$.

Nanoparticles: Zirconium oxide (Purity: 99.5 wt. %; density: 5.89 g/mL at 25°C (lit.)) and nickel oxide (Purity 99.5 wt. %; density: 6.67 g/mL at 25°C) nanoparticles from Sigma Aldrich were used in this study. Table 3.1 shows the properties of the

nanoparticles. This metal oxide nanoparticles were chosen owing to their superior mechanical, optical, thermal, and chemical properties in comparison to other oxides (Kunz, 1981; He et al., 1999; Petit and Monot, 2015; Gopalan et al., 2015).

Table 3.1: Properties of nanoparticles

Sample	Concentration (Wt. %)	Chemical formula	Molecular Weight (g/mol)	Form	Colour	Particle Size (nm)
Zirconium Oxide	(0.004-0.05)	ZrO ₂	123.22	Nano powder	White	< 50
Nickel Oxide	(0.004-0.05)	NiO	74.69	Nano powder	Dark grey	< 50



Figure 3.2: Core plug samples used for measurements.

Surfactants: Non-ionic (triton X-100) and cationic (cetyltrimethylammonium bromide) surfactants were used in this study. Triton X-100 (TX-100 obtained from Sigma Aldrich - purity 99.0 mol.%; molecular weight - 625 g/mol; critical micelle concentration - 0.2 - 0.9 mM) and cetyltrimethylammonium bromide (C₁₆TAB obtained from Sigma Aldrich - Purity 99.0 mol.%; molecular weight - 364.45 g/mol; critical micelle concentration - 0.92 mM) were used as surfactants. The surfactants were dissolved in deionized water to achieve the desired concentrations. Figure 3.3 shows the structure of the surfactants. The surfactants were chosen as stabilizers of the

nanoparticles owing to their electrostatic/repulsive effect that can counterbalance the van der Waals interaction between the surfaces of the nanoparticles against agglomeration (Zhang et al., 2010; Zhang et al., 2013; Chevalier and Bolzinger, 2013; Li and Cathles, 2014; Guo and Aryana, 2016).

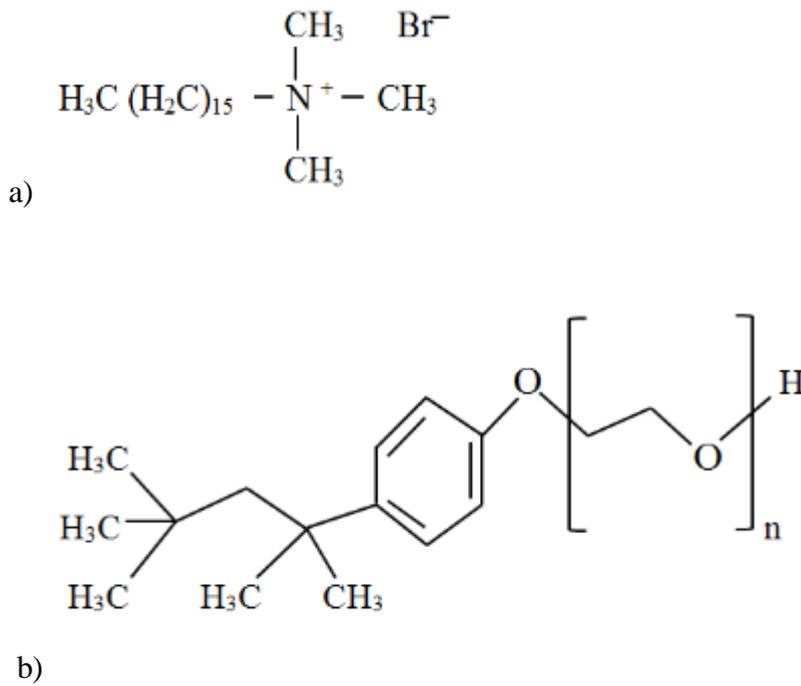


Figure 3.3: Structure of surfactants: a) Cetyltrimethylammonium bromide, b) Triton X-100.

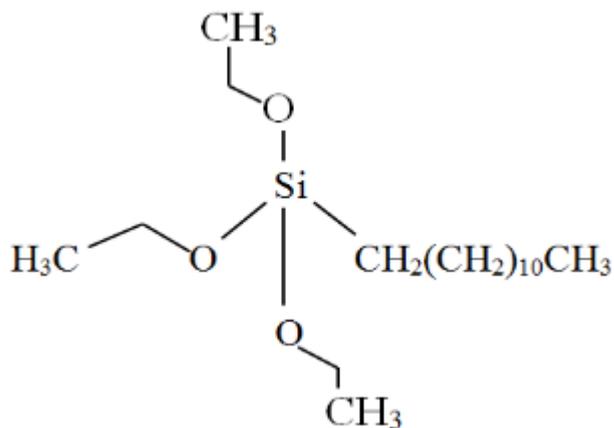


Figure 3.4: Structure of silane – Dodecyltriethoxysilane

Oil Phase: Dodecyltriethoxysilane obtained from Sigma Aldrich ($C_{18}H_{40}O_3Si$ - purity ≥ 99.0 mol. %; boiling point: 538.4k; Density: 875 kg/m^3 - Figure 3.4; 3.5) was used for altering samples to sufficiently stable oil-wet state. Refined oil, toluene (purity 99.9 mol. %) obtained from Sigma Aldrich was used as model oil.

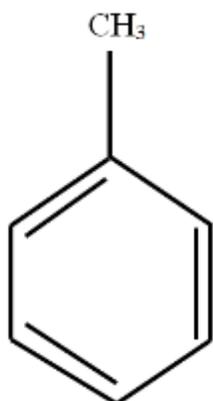


Figure 3.5: Structure of model oil - Toluene.

3.3.2 Sample Preparation

Sample preparation, which accounts for sample treatments and techniques used, is an important requirement in wetting analysis. Proper sample preparation, and adequate sample quality and cleanliness are essential to eliminate any chances of methodical inaccuracies.

3.3.2.1 Rock Cleaning and Aging

Calcite Cleaning: The mineral crystals (calcite) - originally hydrophilic were cleaned with analytical reagent grade acetone and methanol (Rowe Scientific Pty. Ltd), and de-ionised water (David Gray & Co. Ltd). This was done to remove surface fragments and inorganic contaminants. Subsequently, the samples were exposed to air plasma (Figure 3.6) for 15 mins (Love et al., 2005; Iglauer et al., 2014, Sarmadivaleh et al., 2015) to remove any residual organic contaminants.

Aging: Several methods exist for altering wetting preference of rocks towards hydrophobic conditions. Undoubtedly crude oil and refined oils have been used in various ratios. However, the major limitation with the use of crude oil is its exceedingly complex chemistry and the fact that real reservoir coating cannot be reliably and reproducibly simulated in laboratory experiments. Reproducibility is seriously compromised when crude oil is used, and additional effects are prone to happen (E.g. surface-active compounds present in the crude interacting with the mineral surface, etc.), which will overlap with our analysis (effect of nanofluid on wettability and nanofluid-mineral surface interactions), and this can introduce a strong bias. With refined oil (decane, heptane, toluene etc.), a suitable and sufficient strong oil-wet condition cannot be obtained with these oils to simulate the ideal oil-wet states that are required for the limestone rocks. A 100% clearly defined chemical (Figure 3.4) was therefore used for aging samples to a preferentially hydrophobic and stable state, in a highly reproducible way. The clean samples were modified to oil-wet by ageing in the oil phase (dodecyltriethoxysilane) for 12h at 90 °C. To ascertain adequate aging time and temperature, preliminary screening test was performed. Samples were subjected to aging test at varied temperature (22 - 90°C) with time to ascertain sample hydrophobicity. Temperature facilitated the aging process as samples < 80°C and < 10h took a longer time in aging. With temperature increase (90°C), the samples aged faster regardless of time, thus, the aging temperature played major role in determining the wetting conditions. The stability of the salinization process with time had been reported in chapter 7 (subsection 7.3.1.1 - Figure 3.6). Samples were then separated from the oil phase, cleaned with methanol, and deionised water to remove excess silane from the surface of the rock, then dried in air.



Figure 3.7: Plasma for calcite preparation and core sample preparation by soxhlet extraction process.

Core Cleaning and Aging: The Indiana limestone core were cleaned by soxhlet extraction (Figure 3.5) using toluene and methanol for removal of organic contaminants or absorbed material from the core plugs, then dried to constant weight at 60 °C for 24 h. Dried cores were aged in oil at 90 °C under vacuum for 48 h (Anderson, 1986; Rahman, 2016), subsequently, the cores were separated from the oil phase, cleaned with methanol, and deionised water, and dried at 60 °C.

3.3.2.2 Nanofluid Formulation and Stabilization

Nanofluid is typically produced in small quantities at laboratory scale, with high potentials of yielding sufficiently well dispersed, homogenised, and stable fluids. However, homogeneous nanoparticle dispersion is often a challenge owing to agglomerating or clustering tendencies. The functionality or efficiency of nanoparticle-based fluids is primarily influenced by the processing methods, fluid homogeneity and stability. An approach to ensure the stability and homogeneity of nanofluids aside the use of additives or stabilizers is the uniform dispersibility of the particles in the solution. High performance heat transfer nanofluids can be obtained by ensuring an approximately monodispersed or non-agglomerated nanoparticle in liquids during the production of the suspensions, as surface-treated nanoparticles exhibit excellent dispersion characteristics in base fluids and even great thermal properties (Yu et al., 2008). Suitable dispersal and fluid production methods are vital to achieving desirable properties and uniform distribution of the particles in the system which can further prevent issues of agglomeration. Such can also improve the mechanical properties such as strength and ductility of the system (Guo et al., 2014).

To ensure adequate particle dispersal in the base fluid and the fluid uniformity, all fluids were formulated using high frequency ultrasonic homogenizer (Figure 3.7) as also reported (Yang, et al., 2004; Mahdi Jafari et al., 2006; Tjong, 2007; Mao et al. 2015) as an effective strategy for ensuring efficient dispersal of nanoparticles in liquids. The use of magnetic stirrer or ball milling method has been shown to be rather insufficient for stable nanofluid formulation (Mao et al., 2015). A combine use of mechanical dispersion method (ultrasonication) and chemical method of surface functionalization and stabilization (electrostatic/repulsive stabilization via cationic

surfactants C₁₆TAB; nonionic surfactants TX-100) was adopted to improve the particles chemical compatibility with the base fluid which further improved the formulation stability as the systems particle aggregation inclinations is hampered. Thus, the nanofluids (Figure 3.8) were prepared by the following procedures:

- Different minimal concentrations of the ZrO₂ and NiO nanoparticles in powder form were measured using analytical balance.
- Fixed concentration of laboratory scale NaCl brine or surfactants (C₁₆TAB; TX-100) solutions were prepared by addition of desired quantity of NaCl salt or the surfactants to deionised water, and the mixture was stirred magnetically using a 220V/50Hz magnetic stirrer.
- The predetermined amount of nanoparticles were mixed with a fixed amount of dispersals and vigorously stirred over time by ultrasonication.
- To ensure adequate particle dispersal, the nano-suspensions were prepared using a 300VT ultrasonic homogenizer and a titanium micro tip of 9.5 mm diameter to stir particles in solution for a fix time duration of 90minutes. The nanofluid production process ran through 6 periods at 15 minutes intervals, with 5 minutes break between each interval to avoid overheating.
- The formulations were kept in a cool place away from heat and light and the nanosuspensions were subjected to visual monitoring for a fixed period to ensure clear and stable solutions.

On nanoparticle concentration, low nanoparticle concentrations (Table 3.1) were used to obtain optimum particle dispersal and fluid uniformity. With increase in particle concentrations comes increased issues of agglomeration/clustering that can impact the stability of the fluid (Zapryanov et al., 1983; Velikov et al., 1998; Yu et al., 2008; Worthen et al., 2014). Such agglomerate can cause reservoir porosity and permeability impairment/pore rock blockage (ShamsiJazeyi et al., 2014). Cost is another key factor that must be considered alongside process efficiency, it is necessary that economical perspectives are considered since only a minimal amount of additives are typically economically feasible for use in oil extraction on a large scale, thus, we focused on minimal effective concentrations

3.3.3 Wettability Quantification

Contact angle (θ) was used as the deterministic tool for wettability assessments. Atomic force microscope (AFM) and scanning electron microscope (SEM) was also used for mechanistic evaluation of wettability.

3.3.3.1 Contact Angle

Advancing and receding contact angles (Drummond and Israelachvili, 2002) were measured using a tilting stage (Lander et al., 1993) for water contact angle in air and in oil (toluene). A high performance microscopic camera (Basler scA 640-70 fm, pixel size =7.4 μm ; frame rate =71 fps; Fujinon CCTV lens: HF35HA-1B; 1:1.6/35 mm)

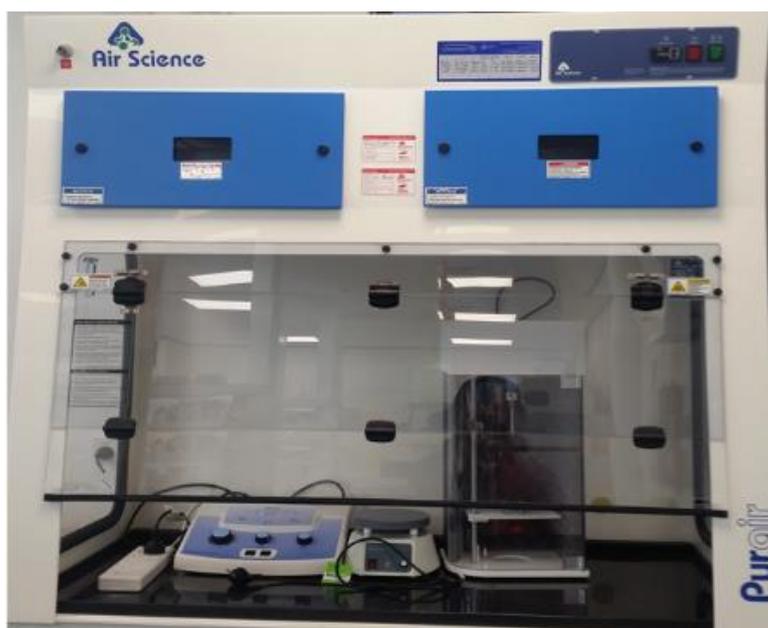


Figure 3.8: Nanofluid processing unit



Figure 3.9: Formulated nanofluids sample containing dispersed ZrO_2 nanoparticle.

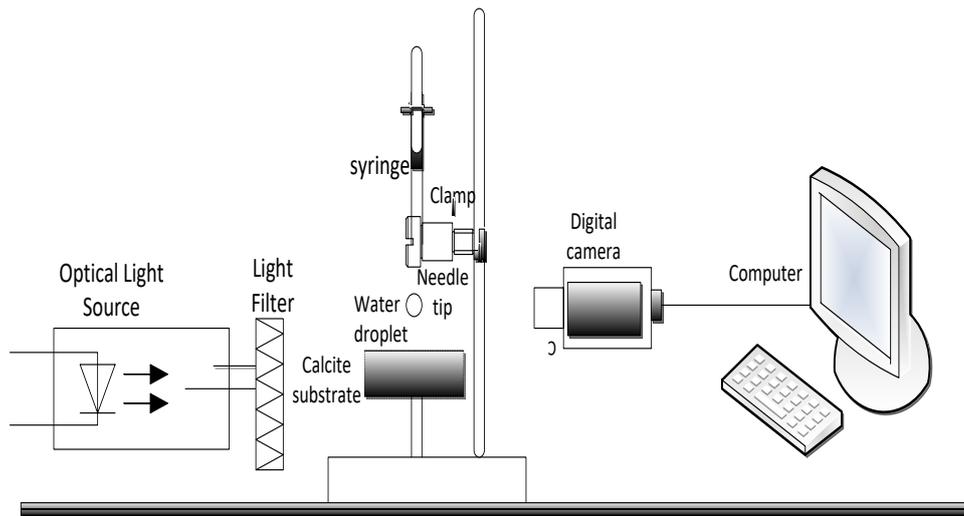


Figure 3.10: Experimental Set-up for Wettability Measurement

was used to capture the water drop dispensing process. The following procedures were used to achieve the contact angle measurements:

- Aged calcite samples were separated from the oil phase, cleaned with methanol, and deionised water to remove excess silane from the surface of the rock, then dried in air
- The samples were exposed to the formulated ZrO_2 and NiO nanofluids or aqueous solutions for a fixed period of one hour (1h) at different temperature conditions ($22-70\text{ }^\circ\text{C} \pm 1\text{ }^\circ\text{C}$).
- The substrates were removed from the aqueous solutions or nanosuspensions and dried in air. Prior to nano-modification of the substrates, reference test was conducted on a clean plate to ascertain their hydrophobic state.
- A water droplet was dispensed on the modified calcite substrate which was placed on a tilted or inclined metal platform and observed microscopically and the receding and advancing water contact angles were measured accordingly.
- Further analysis of the drop was done using Image J software and the standard deviation of the measured data was ± 3 based on replicate measurements.

3.3.3.2 Mechanistic Quantification of Wettability

Mechanistic investigation of samples was achieved by X-ray powder diffraction, atomic force microscope and scanning electron microscope.

X-ray Diffraction: X-ray diffraction (XRD) is a well-known approach for characterizing crystals, as it provides valuable information on the arrangement of atoms in a crystalline material. Crystals are normally periodic in three dimensions designated by the symmetry relations of the atoms within the unit cell, which are considered the smallest box in real space capable of being translated in three dimensions for the creation of the whole structure (Ingham, 2015). Materials suitable for XRD testing are usually fine powders, thin films, and clays. Samples are prepared by placing the fine powders in a sample holder that has been well smeared on a glass slide for measurement. The powdered x-ray diffractometers are mainly composed of the X-ray tube, a sample holder, and an X-ray detector. This device measures the diffraction of x-rays from the planes of atoms within the materials. Diffraction arises through constructive interference due to the illumination of periodic structures of a given spacing with the light of a similar wavelength (Dutrow and Clark, 2017; AMMRF, 2017; Ingham, 2015). The X-ray diffraction patterns of the nanoparticle samples were recorded using powder diffractometer D8 advance (Bruker AXS, Germany), with a copper K alpha radiation source at 40kV and 40mA with a LynxEye detector with an accuracy of $\pm 0.01^\circ$.

Atomic Force Microscope: Atomic force microscopy (AFM) enables imaging of the surface of the samples at extremely high resolutions using a sharp tip for probing the surface features of the samples, through a movement of a cantilever with the probe over the sample's surface. This tool enables micro and nano-scale evaluation of solid surfaces, the topographic changes of such surfaces, and the surface roughness. Substantial data relating to the surface roughness such as mean surface roughness (S_a) and root mean square (RMS) roughness of the solid can be obtained which provides more information on the surface wetting phenomenon. Several wetting studies have been performed by this approach (Buckley and Lord, 2003; Zargari et al., 2010; Jarrahian et al., 2012) with records of effectiveness on diverse rock surfaces. Surface characterization of the modified and unmodified limestone samples was topographically assessed by monitoring of the phase and surfaces changes using AFM

- a Dual Scope TM C-26 Scanning probe and optical microscope with DME software - DSE 95-200. Valuable data of the samples surface roughness and the height distributions were obtained. The surface roughness was quantified through a comparison of the measurement of the vertical deviations of the measured surface with a reference profile. Of the two key parameters; S_a and RMS, S_a is the most commonly used measure. RMS roughness is considered the root-mean-square of the surface average height. However, RMS is highly sensitive to slight changes in the raw profile of the sample and displays a high susceptibility to a large deviation from the mean line, which is not the case with S_a (Marrese et al., 2017). The surface roughness is generally estimated using Equation 3.1 and 3.2 as

$$S_a = \frac{1}{N} \sum_{j=1}^N |Z_j| \quad \text{Equation 3.1}$$

$$RMS = \sqrt{\frac{\sum (Z_j)^2}{N}} \quad \text{Equation 3.2}$$

Scanning Electron Microscope: The scanning electron microscopy (SEM) is an approach for micro-analysis of solid materials with high accuracy. SEM produces high-resolution images for even the smallest structures at nano-scale. SEM has mountable stages and specimen chambers that are sufficiently large enough and suitable for samples. Small specific apparatus can be assembled in the SEM system and operated while the other part is viewed under high magnification. It can display excellent depth of field (Glaeser, 1981). The surface morphology of treated and untreated samples was characterized by scanning electron microscopy - Zeiss Neon 40EsB FIBSEM with an Oxford Instruments x-act Inca SDD x-ray detector and Inca software; and scanning transmission electron microscopy - Tescan Mira3 FESEM instrument. High electron beam was used to scan over the surface of the sample for improved surface characterization. Several researchers have also reported the effectiveness of SEM for morphological evaluations (Nikolov et al., 2010; Winkler et al., 2011; Eshed et al., 2011; Ershadia et al., 2015; Zargartaleb et al., 2015; Son et al., 2015). Further image processing to assess the nanoparticle cluster size distribution was done using Aviso software. Images used were filtered using a non-local means filter

(Buades et al., 2005) and segmentation was done with a watershed algorithm (Schlüter et al., 2014).

3.3.3.3 Spontaneous Imbibition

Here, the whole rock samples were used instead of a substrate. The core plugs were subjected to imbibition testing after surface modifications using the following procedures:

- Core plugs were selected for testing based on the petrophysical properties of cores such as porosity and permeability.
- Cleaning and aging to oil-wet state was done based on the procedure outline in section 3.3.2.1.
- Reference test was conducted for the oil-wet core sample which was used as a bench mark against other surface modified cores.
- Surface modification of core plugs was established by submerging the oil-wet cores vertically in aqueous solution or nanosuspensions to ensure efficient particle adsorption on the rock surface was achieved.
- The cores were aged in the fluids at a temperature of 60 °C for 48h to ensure adequate rock-fluid interaction (to alter the rock wettability), then cores were removed from the nanosuspensions and dried at 50 °C for 24h for imbibition testing.
- Subsequently, the modified dry cores with visible nanofilms evident on the rock samples were suspended in a specific volume of water under an electronic balance.
- The weight gained by the cores was recorded as a function of time until equilibrium was attained.
- Further quantification was done by the estimation of the ratio of the weight of water imbibed at a given time and at equilibrium.

Chapter 4 Nanoparticle Characterization and Its Effect on Solid-Liquid Interface

Based on the wettability issues in limestone formations raised in chapter 2, here, we investigated two specific metal oxide nanoparticle types of interest; zirconium oxide and nickel oxide on basis of their structure, morphology, and crystallinity phases. The wetting efficiencies of the nanoparticles were further tested in air owing to the growing interest in understanding reservoir rock wetting.

4.1 Introduction

Two metal oxide nanoparticles are of interest in this study - nickel oxide and zirconium oxide as oxides of metals that have shown to be of benefit to EOR (see chapter 2).

Nickel oxide (NiO) is a metal oxide nanoparticle in the form of dark grey (Figure 4.1) crystalline solid. This material has good chemical stability, excellent electrical properties, large exciton binding energy, and a stable wide band gap >3 eV (Adler and Feinleib, 1970; Kunz, 1981; Kamal et al., 2004; Choi and Im, 2005; Irwin, 2007). NiO is considered a p-type semiconductor metal oxide particle, thus, a candidate for p-type transparent conducting films (Kunz, 1981; Sato et al., 1993; Bahadur, 2008). This material also exhibits good optical and magnetic properties; anodic electrochromism properties, excellent durability, large spin optical density, and displays strong insulating property (Srinivasan and Weidner, 1997; Kunz, 1981; Liu and Anderson, 1996; He et al., 1999; Chakrabarty and Chatterjee, 2009). On the basis of reactivity, NiO surface that is considered imperfect acts as a useful oxidation catalyst, although, a perfect NiO is weakly reactive. The perfect surface inertness of NiO is in accordance with the non-metallic properties of the material bulk system (Kunz, 1981). NiO is suitable for usage in electrochemical super-capacitors, dye-sensitized photo cathodes applications and smart windows applications (Kunz, 1981; Liu and Anderson, 1996; He et al., 1999; Srinivasan and Weidner, 1997; Chakrabarty and Chatterjee, 2009). Other processes where uniform size well-dispersed NiO nanoparticles are also suitable are in heterogeneous catalytic processes, design of ceramics, magnetic applications, fabrication of gas sensors, films, and cathodes of alkaline batteries (Dooley et al., 1994; Miller and Rocheleau 1997; Yang et al., 1999; Ichiyanagi et al., 2003; Tao and

Wei, 2004; Hotovy et al., 2006; Wu et al., 2007; Thota and Kumar, 2007; Min et al., 2007). Although NiO appears to be suitable for a wide variety of processes, its property and functionality depend on the pore morphology, pore matrix-interface and process application. For instance, a very high specific surface area is required for this material in catalytic applications, whereas a rather dense material is required for cathodic applications (Bahadur et al., 2008).

Zirconium Oxide (ZrO_2) is a metal oxide nanoparticle in the form of white (Figure 4.1 - microscopic image) crystalline solid. ZrO_2 has high refractive index, the high melting point of $2680^\circ C$, wide region of low absorption from the near-UV $> 240nm$ to the mid-IR range $< 8mm$ and high resistance against oxidation (Gao et al., 2000; Venkataraj et al., 2001;). This material is also characterized by high breakdown field, good thermal stability, large band gap $> 5eV$, and high-dielectric constant > 20 (Lopez et al., 2005; Zhang et al., 2009; Petit and Monot, 2015; Balaram et al., 2016), thus, the material has been considered a potential challenger of other nanoparticles. In a recent report, it was established that ZrO_2 exhibits superior chemical and thermal stability than alumina and silica nanoparticles (Petit and Monot, 2015). Similarly, Gopalan et al. (1995) earlier reported that silica nanoparticles exhibit limited chemical and physical stability, as such, ZrO_2 nanoparticle was considered a better alternative and also more chemically stable than γ -alumina or silica. ZrO_2 has an extraordinary high catalytic effect and it is the only metal oxide nanoparticle with four chemical properties on the surface: acidic/basic and reducing/oxidizing properties (Tanabe, 1985). ZrO_2 has attracted attention in a wide variety of processes, as the material displays superior mechanical strength, high temperature resistance, high flexural strength, hardness, and low corrosion potential. As such, it can act as a catalyst, refractory, and insulator in transistors in fuel cells, electronic devices, and oxygen sensors, and also suitable for broadband interference filters, laser mirrors, and ionic conductors (Piconi and Maccauro, 1999; Pareja et al., 2006; Manicone et al., 2007; Muhammad et al., 2012).

With respect to wettability, the recent relevance of nanoparticles in wetting processes is mainly due to the particles excellent range of physical and chemical properties as reported in chapter 1 and 2. The materials surface and interface properties play an essential role in their overall behaviour whether during preparation or applications.

However, there is a lack of understanding of nanoparticles wetting on basis of the solid-liquid interactions, especially, whether strongly hydrophobic surfaces can be

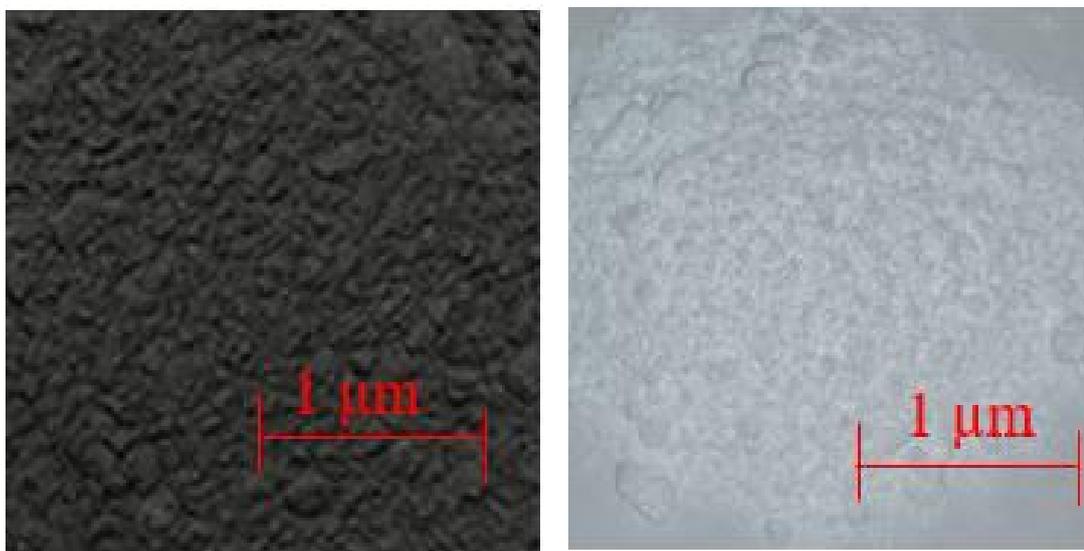


Figure 4.1: Nanoparticles in powder form (NiO-Dark grey green colour; ZrO₂-White colour).

rendered hydrophilic, as this is vital for EOR and carbon geo-sequestration process efficiency. Since successful oil recovery from fractured limestone reservoirs show dependency on wettability (Punternvold et al., 2007), it is, therefore, necessary to establish an understanding of ZrO₂ and NiO nanoparticles properties, specifically, on the key areas that facilitate their process efficiency and subsequent influence on wetting.

4.2 Experimental Procedure

All experiments were performed based on the procedure 3.3 carefully aligned in the previous chapter. The structure, morphology and crystallinity phases of the nanoparticles were characterized by using scanning electron microscopy, scanning transmission electron microscopy, and X-ray diffraction - refer to section 3.3.3.3. The nanofluids were formulated by homogeneously dispersing the nanoparticles (NP) powders in deionized water or NaCl brine and ultrasonicated with high frequency homogenizer (see section 3.3.2.2).

4.3 Results and Discussion

4.3.1 SEM Micrograph of Nanoparticles and Particle Shape

The scanning electron microscope images show the micrograph of ZrO_2 and NiO nanoparticles. Figure 4.2 shows that the ZrO_2 nanoparticle exhibits a distribution of

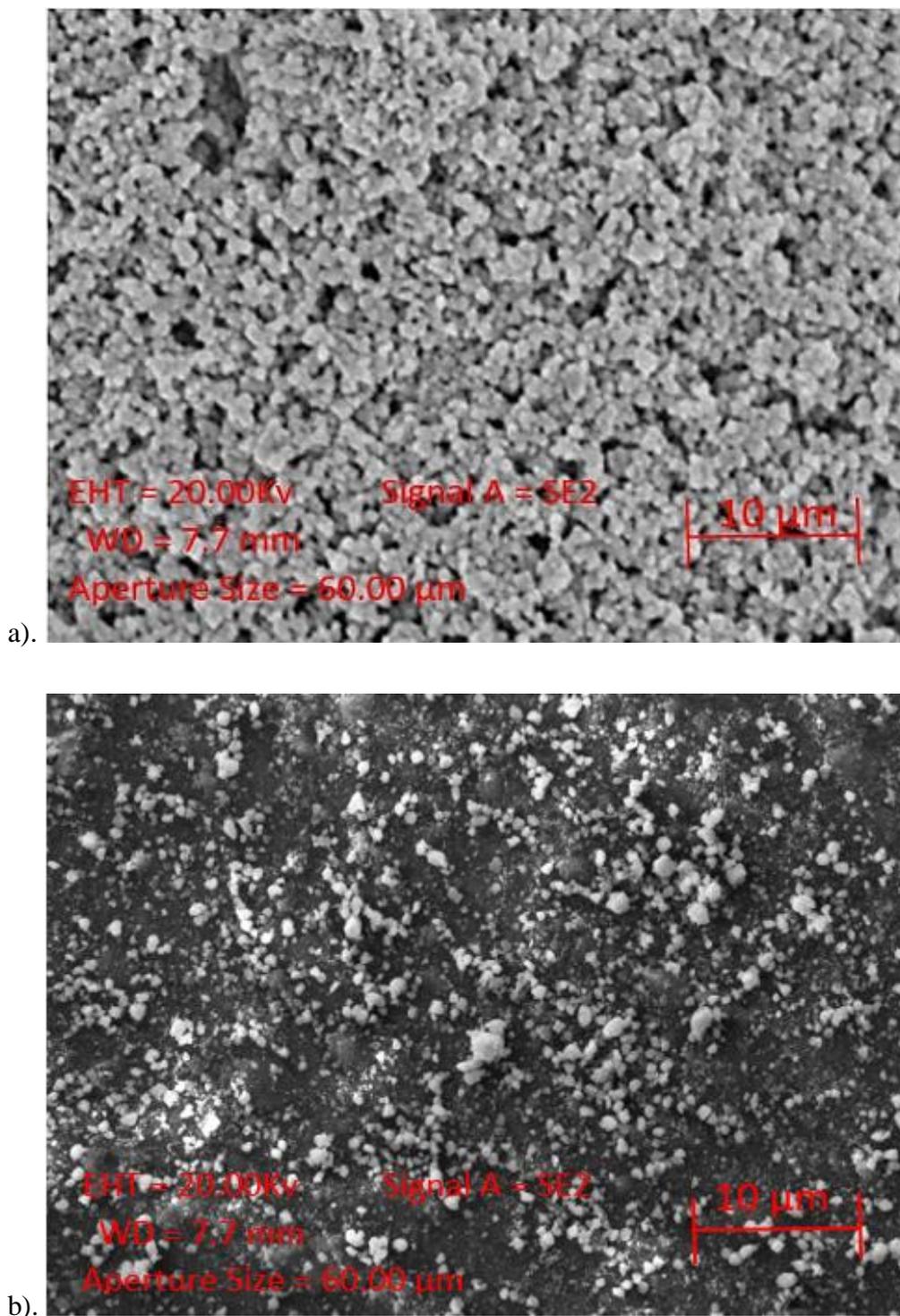


Figure 4.2: SEM images of: (a) ZrO_2 ; (b) NiO nanoparticles.

sphere-like shaped particles and the particle range appears to be < 40 nm, while the NiO nanoparticle displays hexagonal-like shaped particles in the range of < 20 nm. The nanoparticles exhibited approximately uniform size distribution and high trends of finely dispersed particles in the bulk state, thus, an indication of low particle-particle agglomeration inclinations. This behaviour can be attributed to the intrinsic properties of metal oxide (superior stability) and preparation method (homogenization) as reported earlier in section 2.7.13 and 2.8.3.

4.3.2 Particle Size and Surface Area

Particle size plays a vital role in nanoparticle characterization as their physical and chemical properties greatly depend on the size of the particle. The small particle size of nanoparticles yields important features such as surface area. Nanoparticle size and surface area are interrelated; as the nanoparticle size becomes negligible, the particle surface area increases. Bulk materials as opposed to nanoparticle exhibit larger particle sizes (nanoparticle average diameter: < 100 nm; microparticle > 1 μm) with tons of atoms on the inside of the particle and limited atoms at the surface, whereas, with nanoparticles more atoms are predominantly on the outer surface of the particles. Such high surface area enables the bonding of other materials on the particle surface and lead to the generation of even much stronger materials that promote better interaction with neighbouring atoms or ions. Ascertaining the nanoparticles size is therefore essential as it affects particulate materials properties and can act as an approach to determine the quality and performance of materials. The particle size of the ZrO_2 and NiO nanoparticles was thus investigated to obtain more accurate and precise size of the materials. Figure 4.3 - STEM images shows that the ZrO_2 particle size was 21-35 nm and NiO was in the range of 10-12 nm. The average particle diameter for $\text{ZrO}_2 \sim 28$ nm and the average value for NiO was ~ 12 nm.

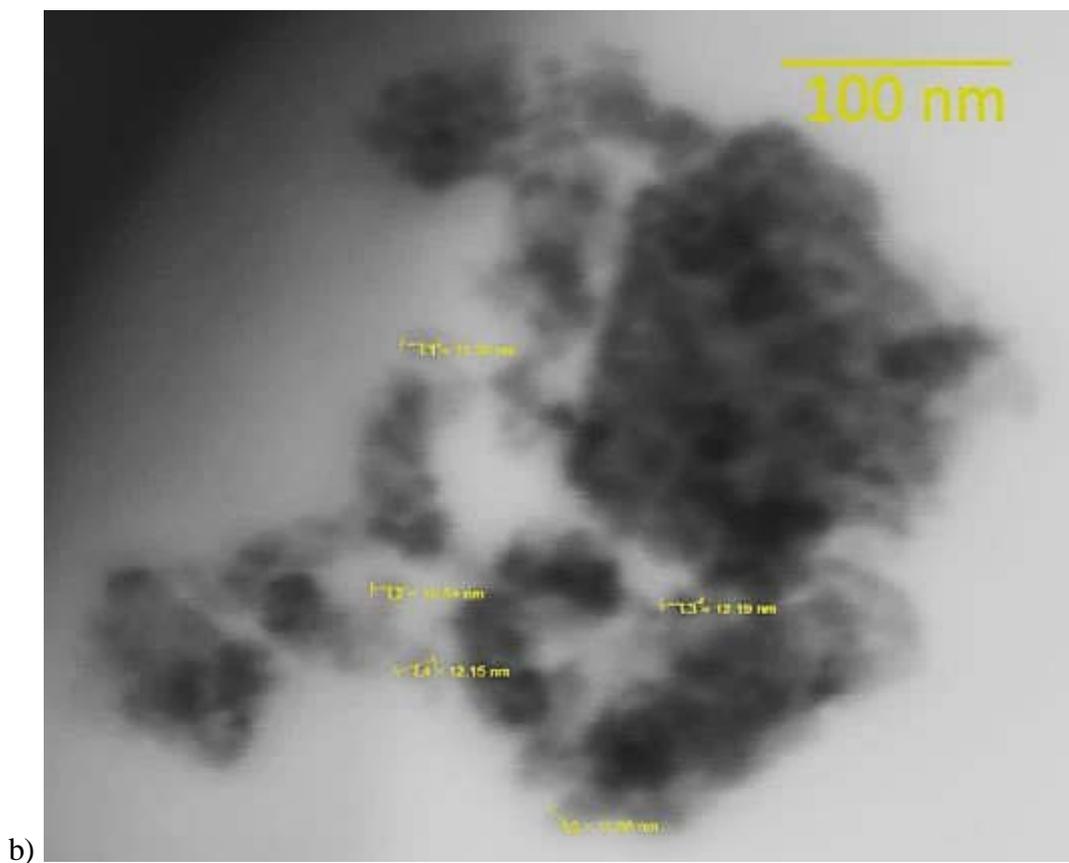
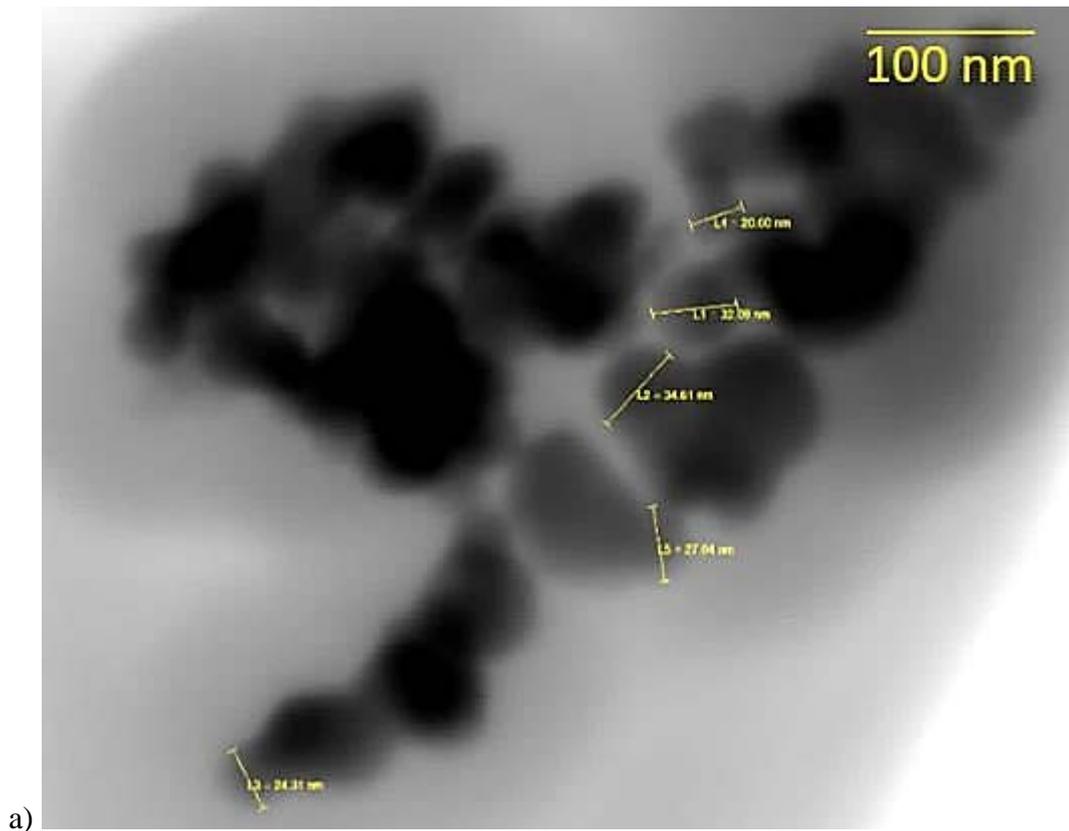


Figure 4.3: Particle size morphology of a) ZrO₂; b) NiO nanoparticles (<50nm).

4.3.3 X-ray Diffraction Analysis

To better understand the crystallographic nature of ZrO_2 and NiO nanoparticles, the materials were further characterized using X-ray Diffraction (XRD). The XRD peaks usually exhibit different patterns and positioning. The pattern of the XRD of a specific sample is mainly dependent on the different arrangements of the atoms. The unit cell dimensions and angles determine the positions of the peaks. Whereas, the types and positions of the atoms within the unit cell determine the intensities of the peaks (Ingham, 2015). Figure 4.4 shows the typical XRD patterns of the ZrO_2 (in red) and NiO (black) nanoparticles. The scan parameters used for phase identification were 2theta scan range (degree): 7.5-90; Step size (degree): 0.015; Time/step: 0.7s and total scan time of approximately 1h. The XRD pattern indicates the crystallographic structure of the nanoparticles. Strong and sharp diffraction peaks at 2θ values were observed in both cases (ZrO_2 - in red; NiO - in black), especially for NiO with precise peaks - 37, 43.5, 63 etc., while the ZrO_2 diffraction peaks value were 28.5, 31.5, 34.5, 50.5 etc. The peaks are indications of the pure phase formation of the ZrO_2 and NiO nanoparticles. The crystallographic phases of the nanoparticles were also identified. Pure ZrO_2 exhibits a tetragonal phase (Figure 4.5a), and the pure NiO exhibits a cubic phase (Figure 4.6) consistent with literature (Kunz, 1981; Mercera et al., 1991).

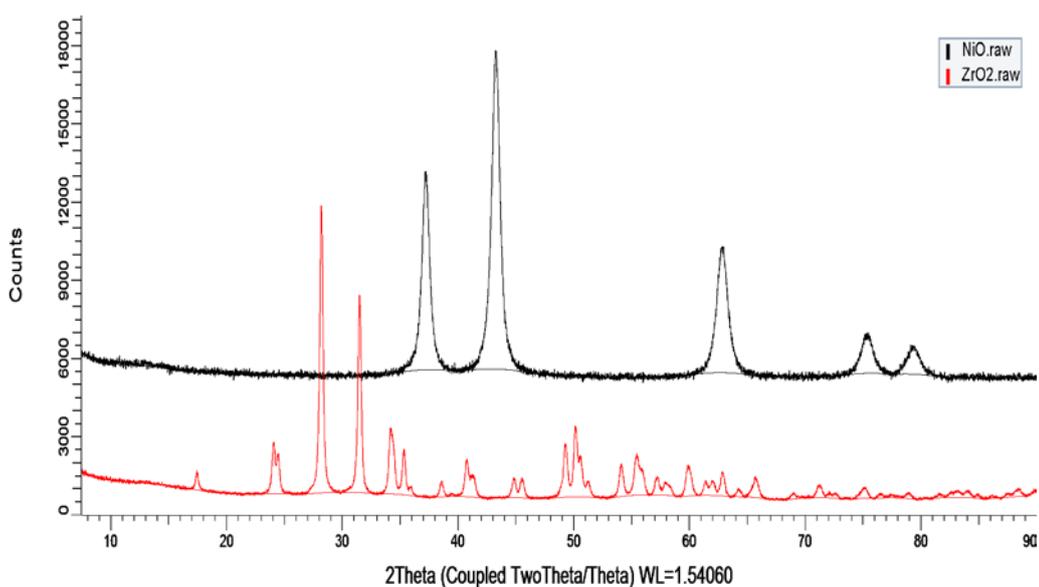


Figure 4.4: XRD patterns of the ZrO_2 and NiO nanoparticles

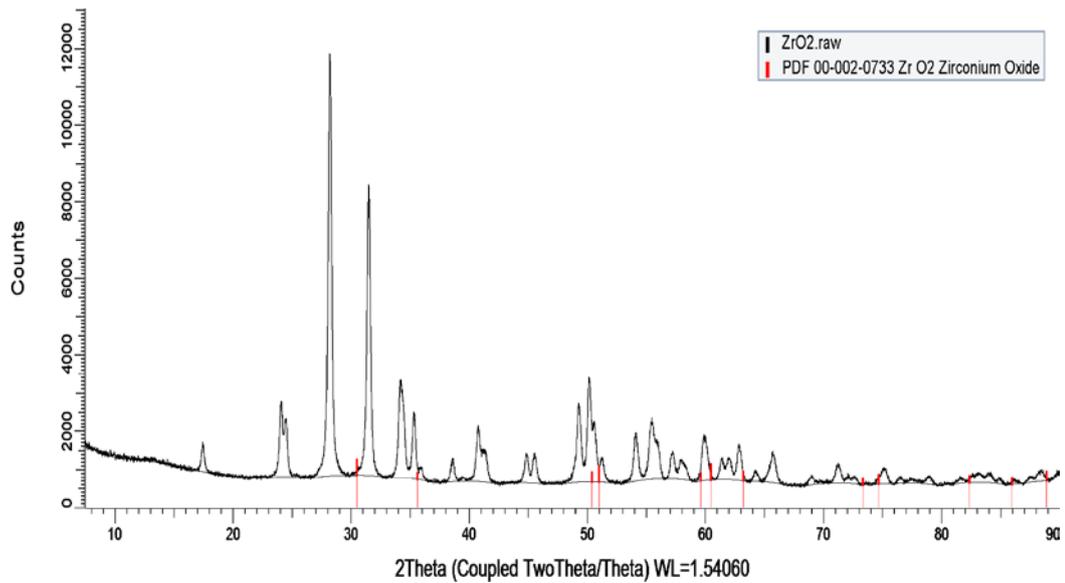


Figure 4.5: Crystallographic phases of the ZrO_2 nanoparticles exhibiting tetragonal phase.

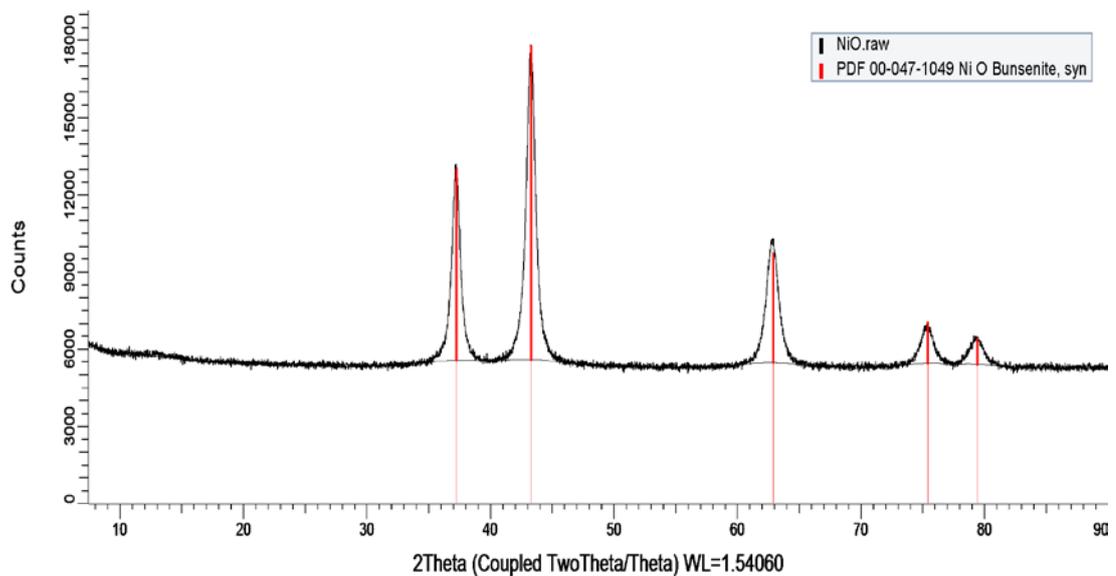


Figure 4.6: Crystallographic phase of the NiO nanoparticles exhibiting cubic phase.

4.3.4 Contact Angle

An understanding of surface chemistry is imperative for evaluating wetting behaviour as porous media wetting are influenced by the rock surface morphology, as well as, the chemical compositions. Since the wettability of a reservoir rock is characterized

by the solid-liquid interface interactions, quantification of wettability of solid surfaces was also performed to ascertain the effects of ZrO₂ and NiO nanoparticle on wettability alteration of the limestone rocks. Contact angle tests were conducted at solid-liquid-air interface at 296 K ± 1 K using calcites substrates to ascertain the wetting variances prior and after nano-modification. Water-advancing and receding contact angles were measured on a tilted platform as it allows for quantification of both advancing and receding contact angles at the same time interval, of which the advancing contact angle better defines wettability since it is relevant to waterflooding (Morrow, 1990). The understanding of contact angle is complex as it exhibits a dependency on the solid-liquid interaction and the structure of the solid or mineralogy of the rock sample, and the surface roughness thereof, as well as temperature. These areas were put into perspective in this study - surface roughness and temperature are discussed in the later chapters. Prior to the contact angle measurement, calcite substrates were cleaned and aged based on procedure 3.3.2.1. The nanofluids were prepared using various nanoparticle concentration (0.005 - 0.05 wt.%) and fixed NaCl brine concentration (7 wt.%) as dispersing agents based on procedure 3.3.2.2. The samples were immersed in the nanofluids and subsequently contact angles were measured (refer to section 3.3.3.1 for the procedure).

Figures 4.7 and 4.8 (SEM) introduces the physics of the process while depicting the surface adsorption behaviour of the systems (nano-modified calcites) as compared to the fresh calcite without any nano-modification and the subsequent effect on rock wetting. The ZrO₂ nanoparticle based system exhibits a spherical-like shape while the NiO exhibits a hexagonal-like shape, and more uniformly adsorbed behaviour on the calcite surface than NiO, which is consistent with the earlier observation in section 4.4.1. Figure 4.11 shows the contact angle as a function of time for ZrO₂ and NiO nanoparticle respectively in air. It is expected that the exposure of the calcite to a different environment would change its surface property.

The calcite upon contact with the ZrO₂ and NiO nanofluids, film-like deposits of the nanofluids were adsorbed on the calcite surface after exposure to air. However, the level of thickness is dependent on the affinity of the molecules to the substrate. Moreover, the nano-films on the rock surface may appear thinner than others, which is dependent on the nanoparticle type, and their optical and electrical properties. ZrO₂

nano-films are relatively thicker than those of other nanoparticles owing to its material properties such as large band gap $> 5\text{eV}$ and high-dielectric constant > 20 (Petit and Monot, 2015). This may have formed better-adsorbed ZrO_2 nano-layers on the oil-wet calcite surface when compared to the NiO nanoparticles.

As the dispensed water droplet comes in contact with the surface of the nano-coated calcite, the contact angle decreases owing to the presence of the adsorbed nano-layers. This behaviour is attributed to the favourable interaction of the nanoparticles with the dispersing fluid (NaCl brine) and high chemical affinity to the calcite. Such solid-liquid interaction at the interface is mainly due to electrostatic interactions. The presence of the nanoparticle increased the surface activity of the brine (NaCl), thereby modifying the calcite surface wetting propensity upon contact. The nanoparticles in suspension act as a coating mechanism by self-structuring into layered NPs and changes the entropy of the system (Nikolov et al. 2010; Wasan et al. 2011; Lim et al. 2016). The particles hydrophilic nature facilitates their adsorption on the rock surface in form of a wedge film which in turn displaces the oil on the surface of the rock, yielding a hydrophilic state.

Ideally, if wettability is preferentially altered to favourable water-wet condition and the IFT is ultralow, the forces that retain oil in a fractured reservoir can be overcome as capillarity is diminished through the ultralow IFTs. Buoyancy often tends to cause a forceful flow of oil upward and out of the matrix into the fracture system, where the injected fluid in the fracture replaces the displaced oil in the matrix, thus, a continuous invasion of the injected fluid into the matrix occurs as long as oil flows out of the matrix (Hirasaki and Zhang, 2004; Ershadi et al., 2015). Figure 4.10 shows image representation of the transition phase towards water-wet in air from $88^\circ \theta_a$ in air to $48^\circ \theta_a$ (NiO/NaCl) and $38^\circ \theta_a$ (ZrO_2 /NaCl). A decrease in contact angle was observed for all the systems tested with an increase in the nanoparticle concentration as shown in Figure 4.11. Calcite substrates coated with ZrO_2 /NaCl fluids demonstrated better wetting propensities than the NiO/NaCl system. The efficiency of the systems is attributed to the efficient surface adsorption of the particles on the pore walls of the rock, which invariably rendered the rock surface sufficiently water wet upon contact.

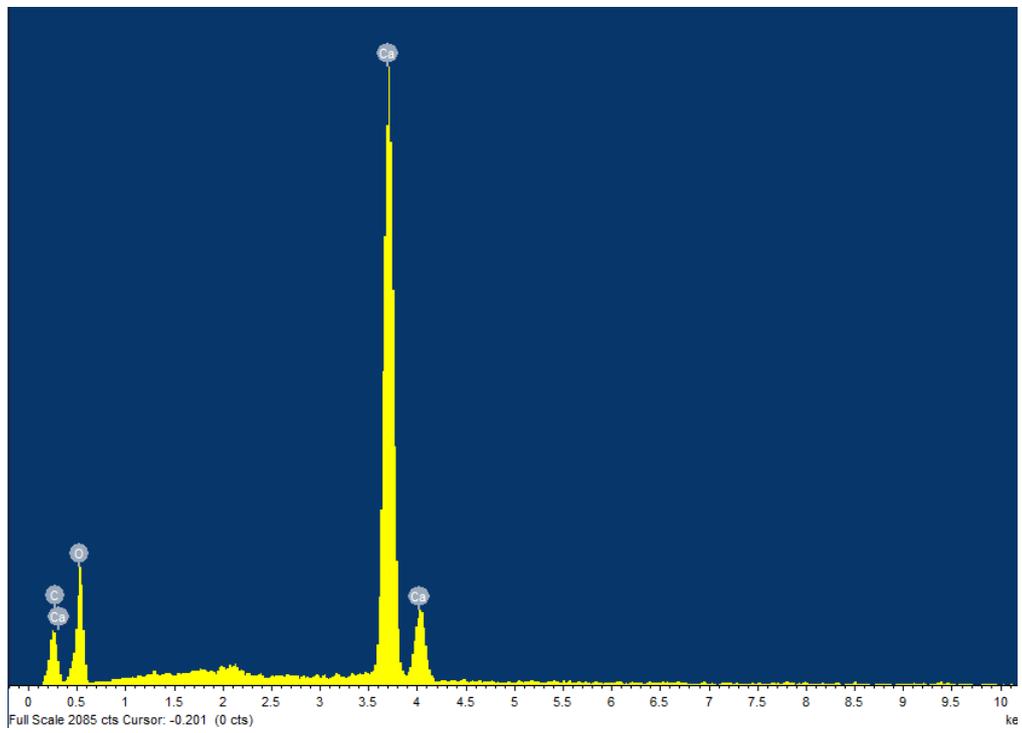
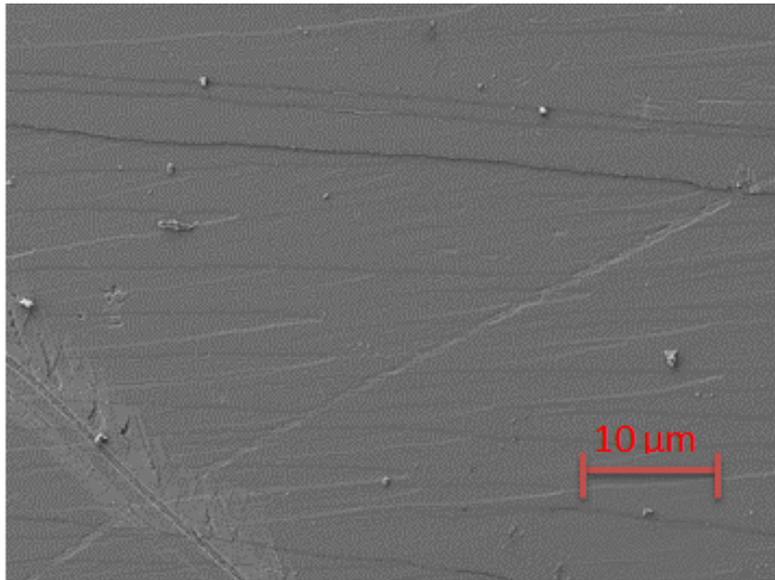


Figure 4.7: SEM image of pure calcite surface: (a) before nano-modification

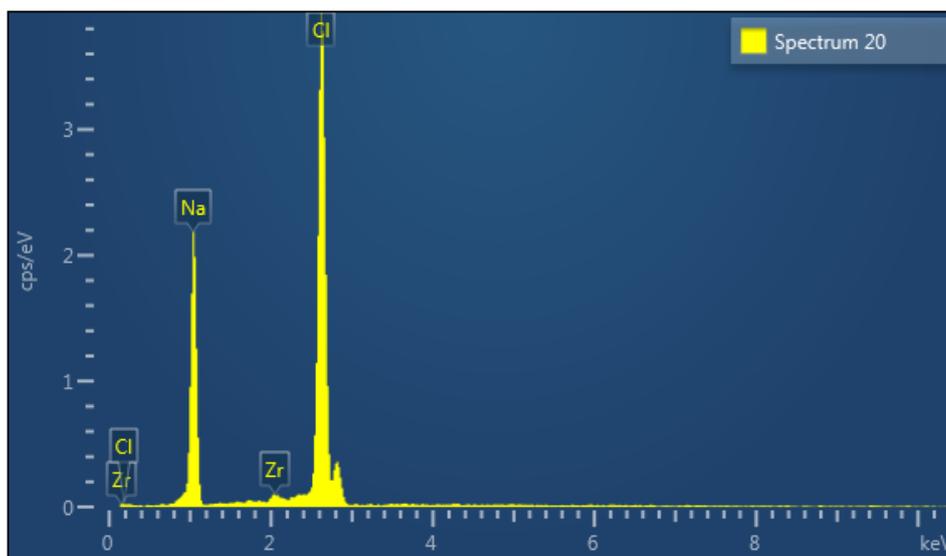
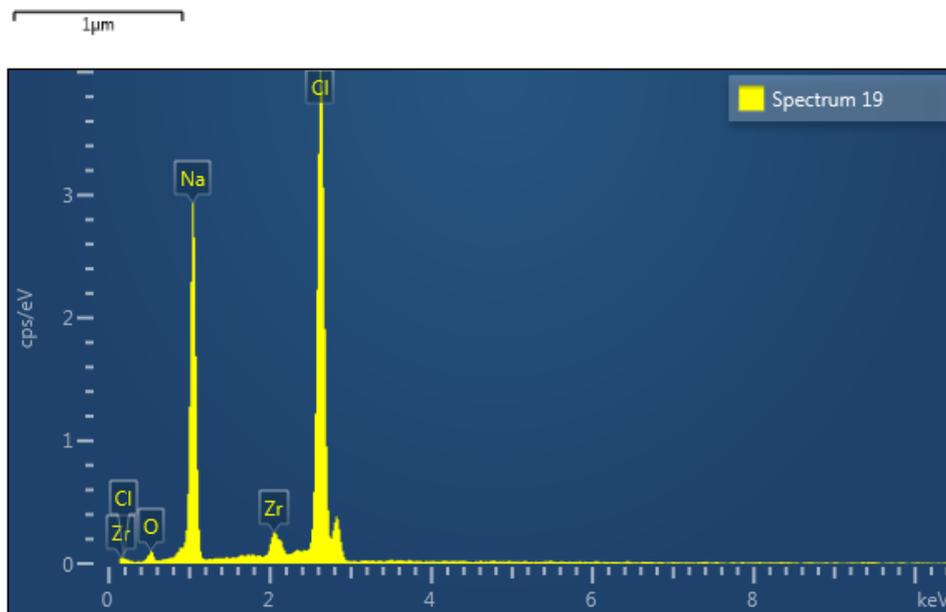
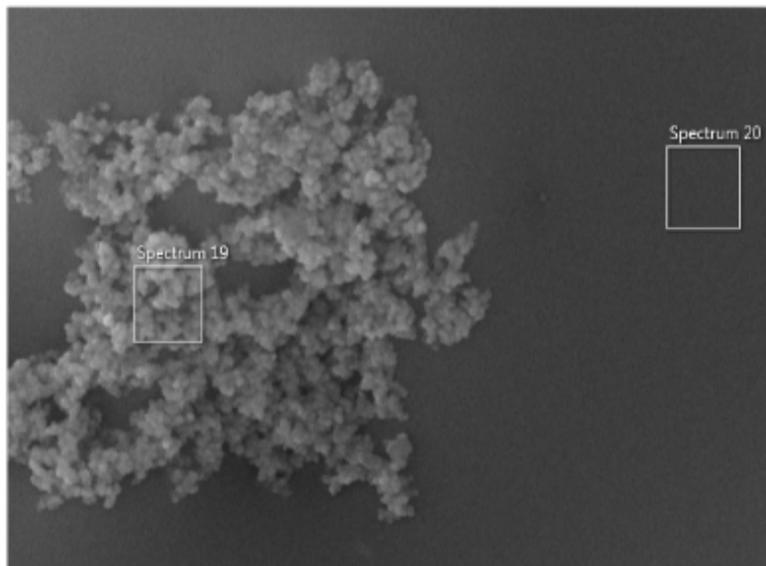


Figure 4.8: SEM image of Calcite surface after ZrO_2 nano-modification

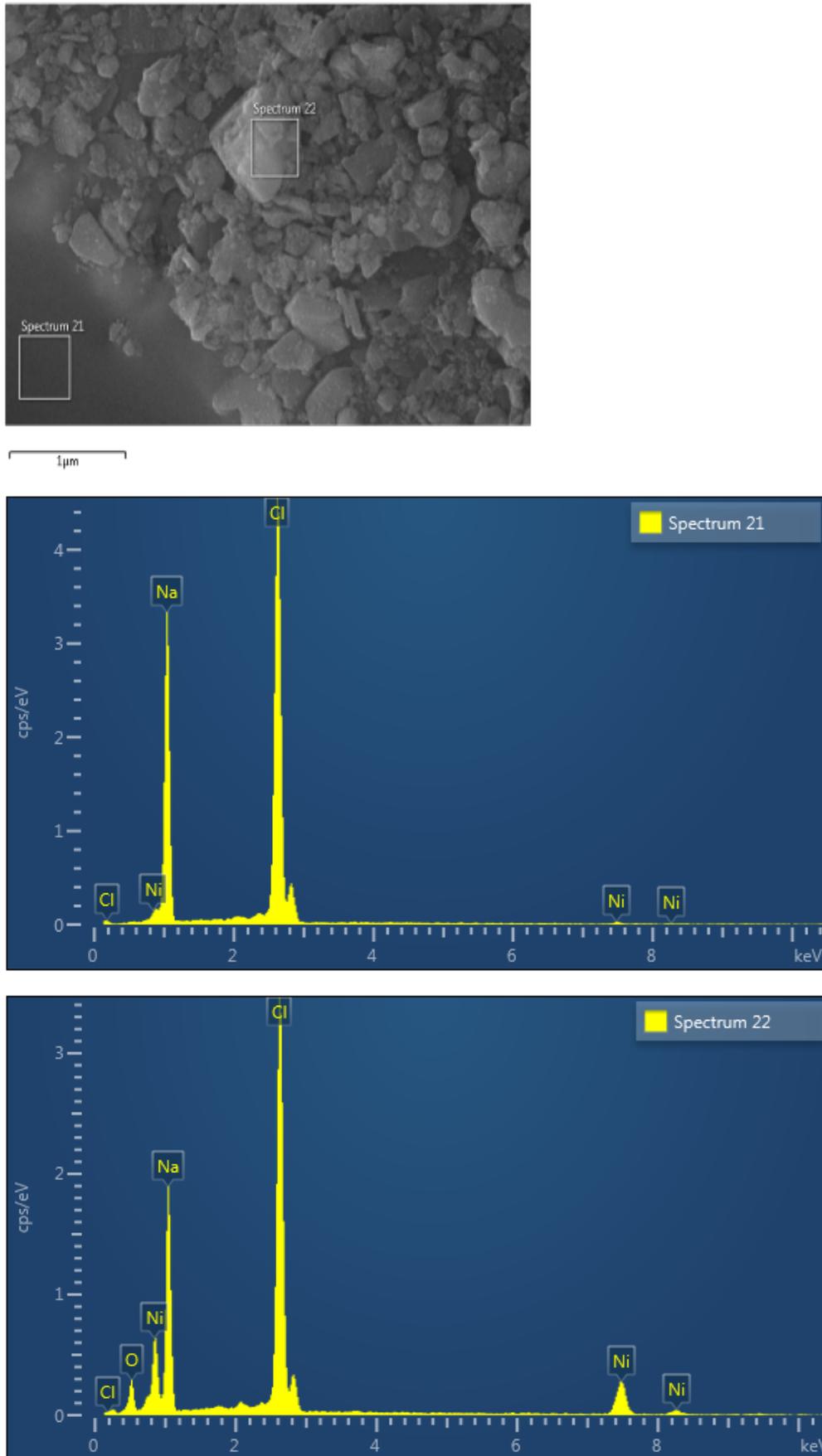


Figure 4.9: SEM image of Calcite surface after NiO nano-modification.

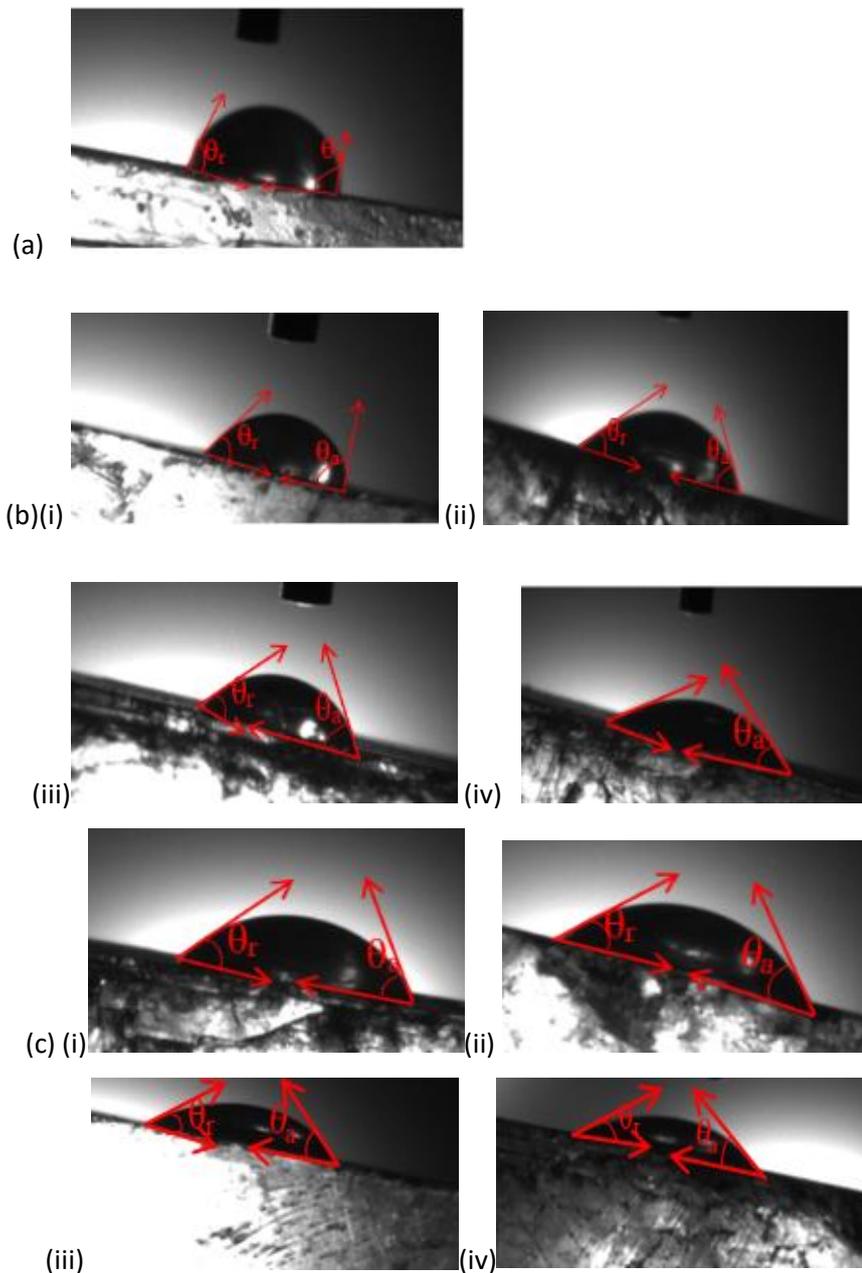
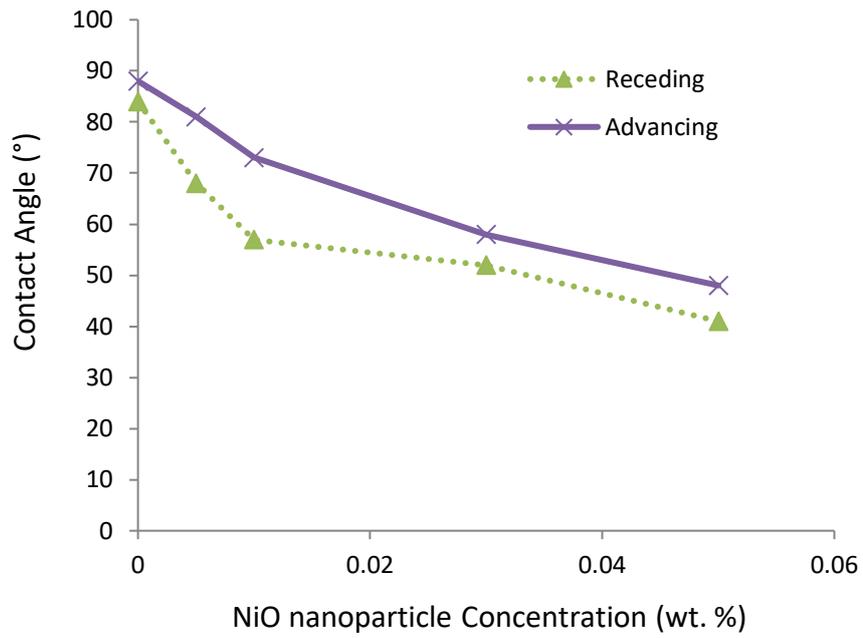
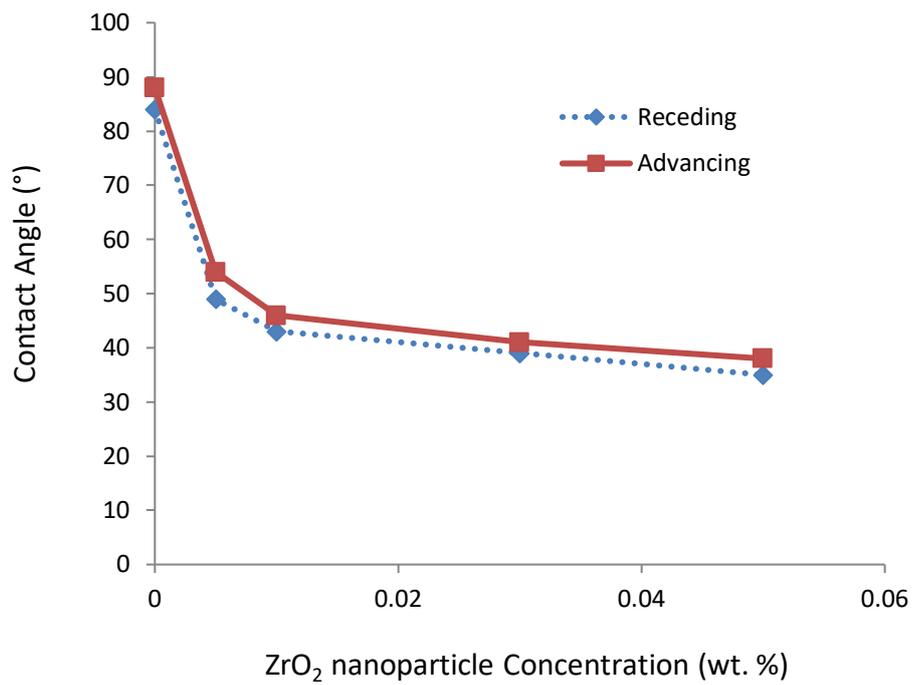


Figure 4.10: Contact angle images showing variation with increase in nanoparticle concentration (A) Non-nano modified (high θ -indicating an intermediate wet-state - $88^\circ \theta_a$); (B) Nano-modified (in the presence of NiO - 0.005- 0.05); (C) Nano-modified (in the presence of ZrO₂ - 0.005-0.05) (B-C indicates low θ which represents strong interaction with the rock surface, and inclination to wet; I - IV); See graphical representation for θ - values.



a)



b)

Figure 4.11: Receding and advancing water contact angles in air (1h exposure time)
 (a) NiO; (b) ZrO₂.

4.4 Conclusions

The interfacial behaviour of nickel oxide and zirconium oxide nanoparticles at solid-liquid interface was studied. The ZrO_2 and NiO nanoparticles exhibited very different structural and morphological features, as well as crystallinity phases. The nanoparticles exhibited particles size in ranges below 50 nm (< 50 nm) and different shape patterns. The ZrO_2 nanoparticles are sphere-like shaped particles while the NiO displayed hexagonal-like shaped particles (Figure 4.2; 4.8 and 4.9). The XRD crystallographic structure and phase identification shows the tetragonal phase of the ZrO_2 , whereas, the NiO nanoparticle has a cubic phase orientation. The nanoparticles also displayed favourable adsorption behaviour on the calcite surface as evident in the SEM images, which facilitated the wetting change quantified by contact angle measurement. The ZrO_2 exhibited more uniform surface distribution and better wetting than NiO .

Chapter 5 Nanoparticles Effect on Wettability Alteration of Hydrophobic Limestone Rocks

This chapter systematically explores the potentials of zirconium oxide (ZrO_2) and nickel oxide (NiO) as metal oxide nanoparticles on wettability alteration of oil-wet limestone rocks. Wettability was assessed through SEM, AFM, and contact angle measurements. The nanoparticle-based systems were evaluated as a function of the particle concentration, exposure time and salinity. The obtained results established the need for further investigations reported in subsequent chapters.

5.1 Introduction

Fractured carbonate formations hold large amounts of global oil reserves - 60% oil and 40% gas (Ahmed, 2010). The oil is often located in the tiny pores of the rock or as a thin film on the surface of the rock thereof (Anderson, 1987). The main mechanism for hydrocarbon recovery, spontaneous imbibition of water into the matrix blocks, is often disrupted due to the oil-wet or intermediate-wet character of the limestone (Thomas et al., 1993; Gomari et al., 2006; Chabert et al., 2010) and associated low (water) suction pressures (Strand et al., 2006). Consequently, poor recovery is typically attained when conventional waterflooding methods are adopted (Anderson, 1986a, b, c; Buckley et al., 1998; Standnes and Austad, 2000; Iglauer et al., 2010) in limestone formations. Capillary pressure (Dawe et al., 2011) mainly controls fluid distribution in such porous media, and the magnitude and direction of the capillary forces are influenced by the formation pore size, fluid saturation, IFT, and wettability. Nanoparticles have been shown to be interfacially active and good rock wettability modifiers (Ju et al., 2006; Ju and Fan, 2009; Hendraningrat et al., 2013; Giraldo et al., 2013; Al-Anssari et al., 2016; Nwidee et al., 2016a) at laboratory scale. Changing wettability towards water-wet has proven very effective in this context. As such nanoparticles have considerable prospect in carbon geo-sequestration as water-wet formations can store more CO_2 than oil-wet formations (Iglauer et al., 2015a, b). Here, the NiO and ZrO_2 nanoparticles potentials as wetting agents were systematically examined on the basis of the particle concentration, exposure time, and salinity.

5.2 Experimental Procedure

All experiments, as well as mechanistic evaluations were performed based on the procedures 3.3 carefully aligned in the previous chapter. The nanofluids were formulated by homogeneously dispersing nanoparticles (NP) in base fluid (NaCl brine). Specifically, ZrO₂ and NiO nanoparticles (concentrations: 0.004 - 0.05 wt.%) and NaCl brine (3-20 wt.%) were sonicated for 90 min using a 300VT Ultrasonic homogenizer. The densities of the nanofluids (ZrO₂, NiO), model oil (Toluene) and brine (NaCl) were also measured at 296 K and atmospheric pressure: (ZrO₂ nanofluid) = 980 kg/m³; (NiO nanofluid) = 950 kg/m³; (toluene = 850 kg/m³; (NaCl brine) = 997 = 997 kg/m³). All tests were conducted at 296 K ± 1 K, using procedure 3.3.3.1 and the standard deviation based on replicate measurements is ± 3°.

5.3 Results and Discussions

5.3.1 Mechanistic Quantification

5.3.1.1 Calcite Surface Characterization

Characterization with scanning electron microscope (SEM) and atomic force microscope (AFM) was conducted on calcite substrates in pure state, oil-wet state and after exposure to nanofluids (Figures 5.1 and 5.2). The nanoparticles were < 50 nm in size since particle size influences nanoparticle transport and retention behaviour in limestone formation. Particle size < 100 nm inhibits direct plugging and bridging in the micro-pore network systems especially in the subsurface (Li and Cathles, 2014) as such can facilitate efficient transport through the formation. In contrast, large particles have high tendencies of poor dispersal into the neighbouring rocks (Serres-Piole et al., 2012) and may sediment and erode the channels therein (Rudyak, 2013).

SEM and AFM are effective tools for morphological and topographical surface wetting evaluation. SEM test shows the morphological structure of the clean calcite sample prior to modification (Figure 5.1a), and after modification with dodecyltriethoxysilane (Figure 5.1b). Upon nanofluid exposure, the adsorbed nanoparticles on the surface of the calcite crystals was clearly visible at higher image resolution (Figure 5.1d, f) which is consistent with Nikolov et al. (2010); Winkler et al. (2011) and Al-Anssari et al. (2016). At lower image resolution, deposits of ZrO₂

(Figure 5.1c) and NiO (Figure 5.1e) nanoparticles were evident with better uniform surface adherence of the nanoparticles apparent on Figure 5.1c (ZrO₂ coated) than Figure 5.1e (NiO coated), thus, indicating better adsorption behaviour. The ZrO₂ particles exhibit more spherical shape particles than the NiO, which exhibits a somewhat irregular shape patterns. AFM was used to evaluate the topography (Buckley and Lord, 2003; Zargari et al., 2010; Jarrahan et al., 2012) of the untreated (Figure 5.2a) and treated (Figure 5.2b-d) samples. The mean roughness and root mean square of the untreated sample was 8.8 and 11 nm respectively. The topography of the sample aged in silane (Figure 5.2b) demonstrates adsorption of the dodecyltriethoxysilane on the calcite surface which explains the change in wettability of the calcite surface from its original water-wet condition to an oil-wet. This is consistent with the SEM tests (Figure 5.2b) and the measured reference advancing contact angle for silane modified surface which indicates a strongly oil wet condition ($\theta=152^\circ$). Figure 5.2 (c and d) also confirms the nanoparticle absorption on the aged calcite surface, consistent with the SEM (Figure 5.1c and e).

5.3.2 Contact Angle Measurements

A comparative study of the influence of ZrO₂ and NiO nanofluids on wettability alteration as a function of nanoparticle concentrations, exposure time and salinity were also evaluated via series of contact angle (θ) measurement. Reference tests for water contact angles (θ) were initially conducted on clean calcite crystals to ensure a completely water-wet state. The water contact angles measured (clean calcite $\theta=0^\circ$) indicate a strongly water wet-state which supports the reports of Karimi et al. (2012) (clean calcite $\theta=32^\circ$) and Al-Anssari et al. (2016) (clean calcite $\theta=0^\circ$) [although Karimi et al. (2012) reported a relatively high θ value of 32° which may have occurred as a result of insufficient cleaning - Iglauer et al., 2014]. Another reference test was performed after establishment of the oil-wet state prior to nanoparticle modification of the calcite surfaces which served as a bench mark. The water advancing contact angle θ in air was 90° , indicating an intermediate-wet state and 152° in toluene, indicating a strongly oil-wet state.

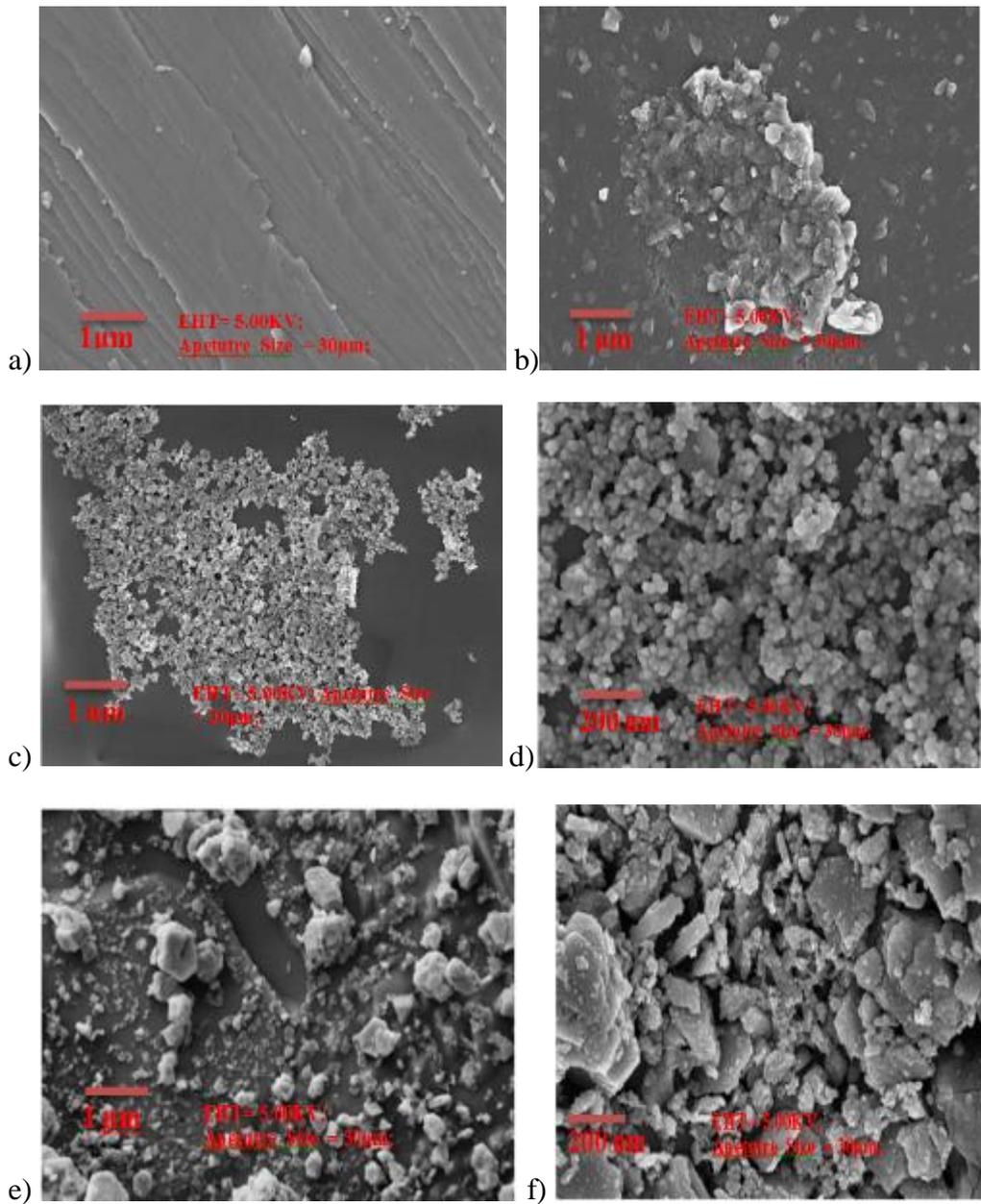
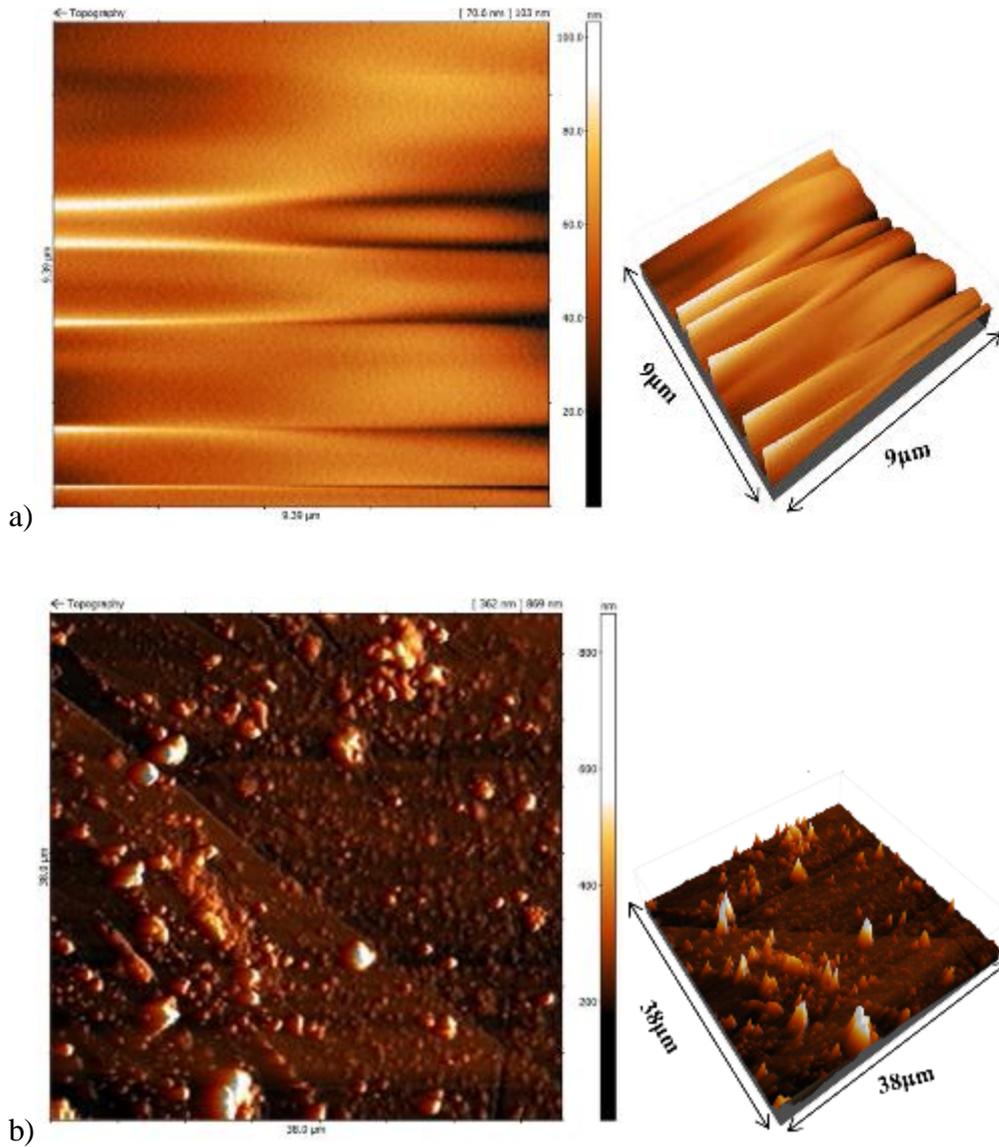


Figure 5.1: SEM images of calcite crystals: (a) before coating - untreated state; (b) after coating with silane; (c) and (d) ZrO_2 adsorption on calcite crystals; (e) and (f) NiO adsorption on calcite crystals at different magnifications.

5.3.2.1 Influence of Nanoparticle - Brine Interaction on Wettability Alteration

Fluid displacements of wetting and non-wetting phase at pore scale are controlled by wettability. However, a shift in the wettability of the porous walls of the oil-wet rock towards water-wet can efficiently enhance fluid flow, as such the effect of nanoparticles concentration on wettability alteration was tested to assess the efficiency

of ZrO_2 and NiO nanoparticles. Low nanoparticle concentrations (0.004–0.05 wt.% ZrO_2 and NiO) were added to fixed concentration of the displacing fluid (7 wt.% NaCl) and stirred ultrasonically over time. The interaction of the nanoparticles with NaCl produced clear and stable solutions. Then the oil-wet calcites were exposed to ZrO_2 and NiO nanofluids at the same specific concentration and a fixed time (3600 s).



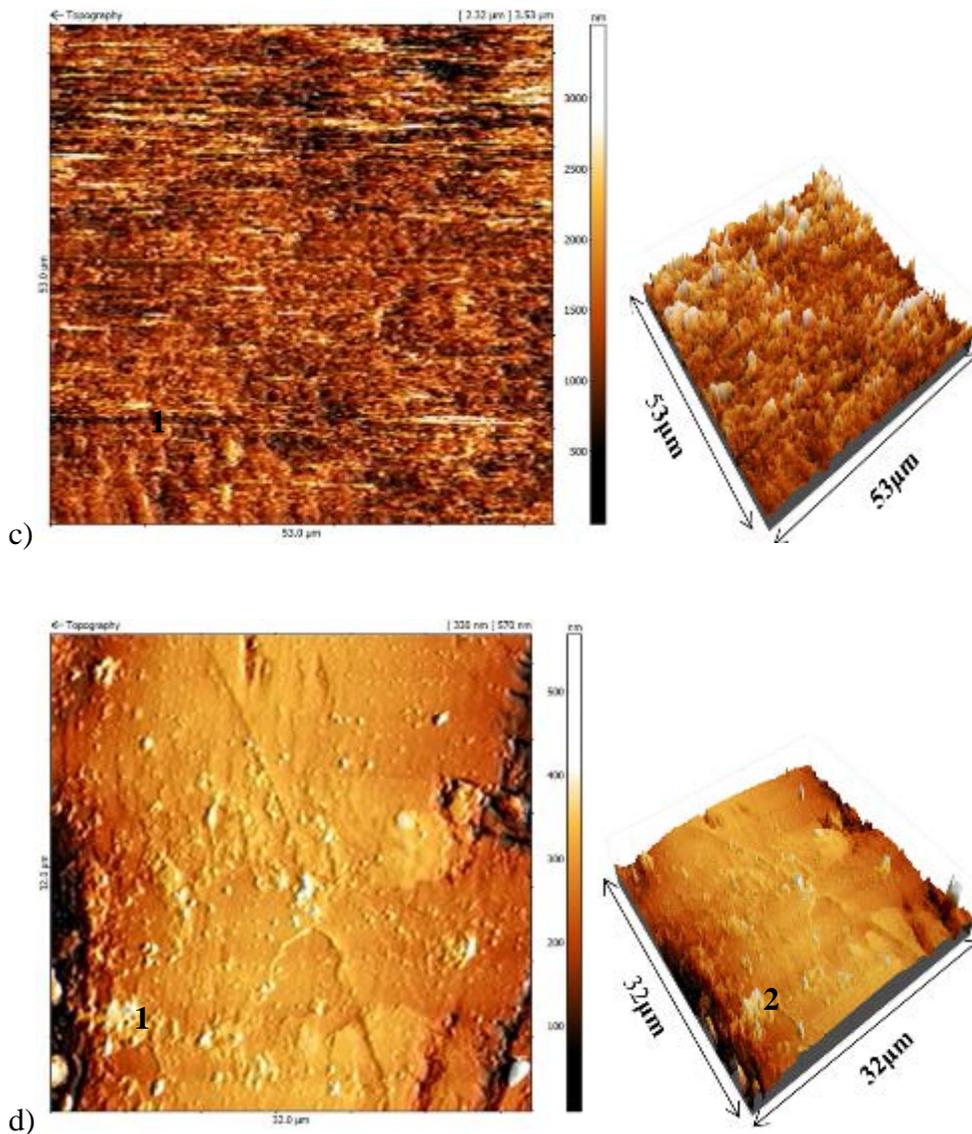


Figure 5.2: AFM height images 2D and 3D of calcite crystals: a) Untreated calcite; b) Silane treated calcite; c) ZrO₂ modified; d) NiO modified. The different colours indicate variation in height of the surface with high Z-values (higher features appearing as white) and low Z-values (lower features appearing as dark shades).

This led to the formation of nanoparticle films or adsorbed layers on the surface of the calcite substrates after exposure to air as evident by the SEM images. Surface energies often dictate the wetting state of the rock, hence the adsorption of the nano-surface active and energetic material on the calcite surface may have led to a significant change in the surface energy. Consequently, water spreads more readily on the calcite substrates, hence, the change in wettability towards water wet. This is evident in the results as ZrO₂ nanofluids (0.004 wt. %) changed the wettability (from 90° in air) to a

water-wet condition (62°) in air and from 152° in toluene to intermediate-wet condition (89°) in toluene, whereas NiO nanofluids changed wettability to intermediate-wet (72°) in air and lowered the contact angle to 126° in toluene (still oil-wet). At subsequent increase in NP concentration (0.05 wt. %), θ decreased to 40° in air and 44° in toluene with ZrO_2 and to 49° and 86° in toluene for NiO (Figures 5.3 and 5.4). ZrO_2 had better adsorbed nano-layers on the oil-wet calcite surface when compared to the NiO. As the dispensed water droplets get in contact with the ZrO_2 nano-coated calcite, the contact angle decreases more readily, thus wettability is efficiently changed towards water-wet at minimal particle concentration. We thus conclude that ZrO_2 is a more efficient wettability modifier than NiO based on exhibited efficacy after an hour exposure time.

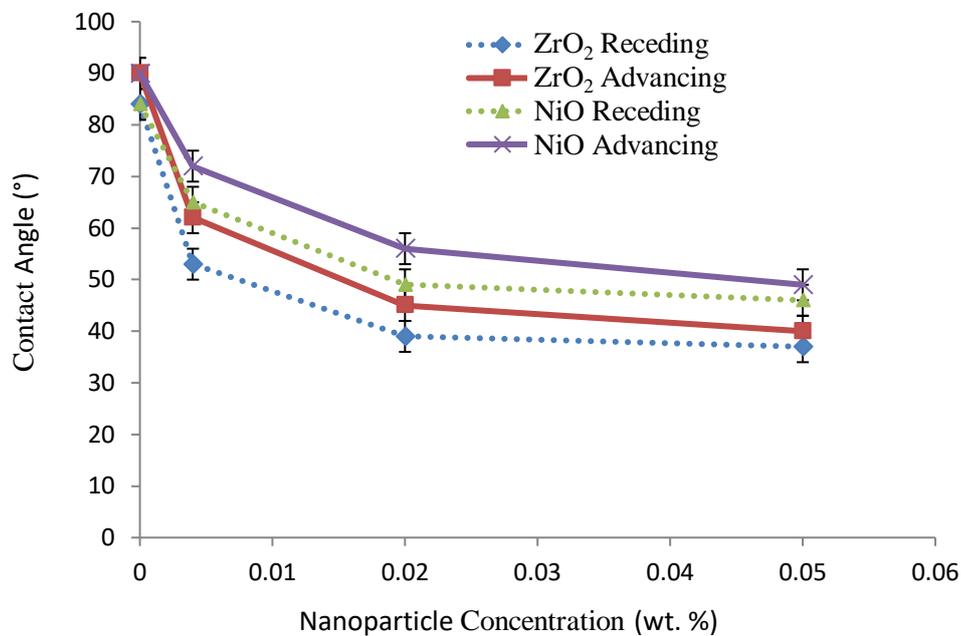


Figure 5.3: Receding and advancing water contact angles (versus air) on initially oil-wet calcite as a function of nanoparticle concentration (60 minutes exposure time).

5.3.2.2 Wettability Alteration as a Function of Time

Nanofluid efficiency is vital as fluid displacement and better oil recovery can be achieved over time when a rock is water-wet than oilwet. Hence, the nanofluid wettability efficiency as a function of time (300-14400 s) was tested. ZrO_2 and NiO

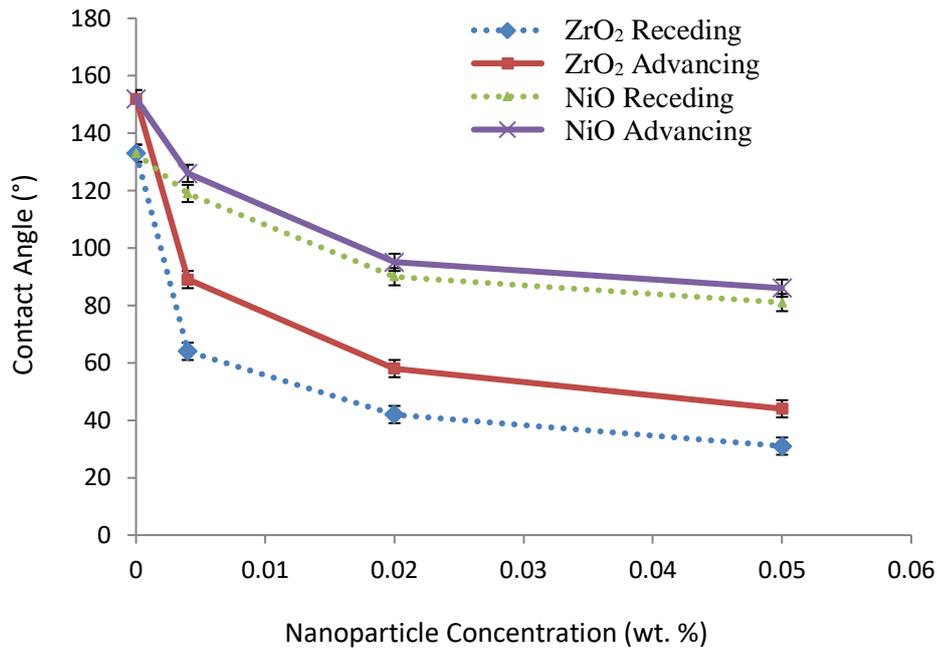


Figure 5.4: Receding and advancing water contact angles (versus toluene) as a function of nanoparticle concentration (60minutes exposure time).

nanoparticles were at the (fixed) optimum nanoparticle concentration (0.05 wt%; chosen due to its effectiveness (see Figures 5.3 and 5.4) and at a fixed 7 wt% NaCl concentration. Both, receding and advancing θ in air and in toluene decreased with time (Figures 5.5 and 5.6); initially rapidly, and after ~ 4000 s in air and ~ 6000 s in toluene the decrease flattened out and only a smaller incremental drop in θ was observed. ZrO₂ displayed a slightly better performance over NiO. After 300 s in air, θ exhibited a small change, θ decreased from 90° to 76° for ZrO₂ nanofluid, and to 82° for NiO nanofluids. However, after 900 s a substantial decrease in θ resulted in a water-wet state ($\theta=60^\circ$ for ZrO₂; $\theta=66^\circ$ for NiO). Overall, the decrease in θ was continuous and smooth. For oil-wet calcite substrates exposed to ZrO₂ and NiO nanofluid in toluene, θ changed from 152° to 123° for ZrO₂ and to 135° for NiO, thus, still denoting an oil-wet state after 300 s. After 900-1200 s exposure time, an intermediate-wet state (89° - 79°) resulted with ZrO₂, and a weakly oil-wet state (118° - 109°) was achieved with NiO. With a further substantial increase in exposure time (7200-14400 s), water-wet conditions were achieved for all substrates (42° and 35° for ZrO₂; 62° and 40° for NiO). The continuous change in θ with respect to time for the systems tested is an indication that the addition of a small fixed fraction of the

nanoparticles to the dispersing fluid significantly impacted the fluid-rock interaction which led to the efficient displacement of oil over time thus the rock surface is rendered more water-wet.

5.3.2.3 Influence of Salinity on Wettability Alteration Efficiency of Nanofluids

The saline nature of oil reservoir influences fluid-rock interaction, consequently, the fluid-rock surface charges change in the presence of ions and this is dependent on the solution chemistry of the aqueous fluid that the rock is exposed to. The mechanism behind this behaviour was reported by Li and Cathles (2014), who also asserted that increase in NaCl concentration influences nanoparticle behaviour. Thus, different NaCl concentration (3-20 wt. %) at the optimum ZrO₂ and NiO nanoparticle concentration (0.05 wt. %) and time interval (3600 s) see above, was tested. Increased salt concentration clearly decreased θ (Figure 5.7 and 5.8) for both, ZrO₂ and NiO nanofluids in air and in toluene. Again, ZrO₂ exhibited good wettability alteration efficiency: θ changed from an intermediate wet-state (90° in air) to water-wet (60°) in 3 wt.% NaCl brine but remained intermediate wet (81°) in the presence of NiO. At 5

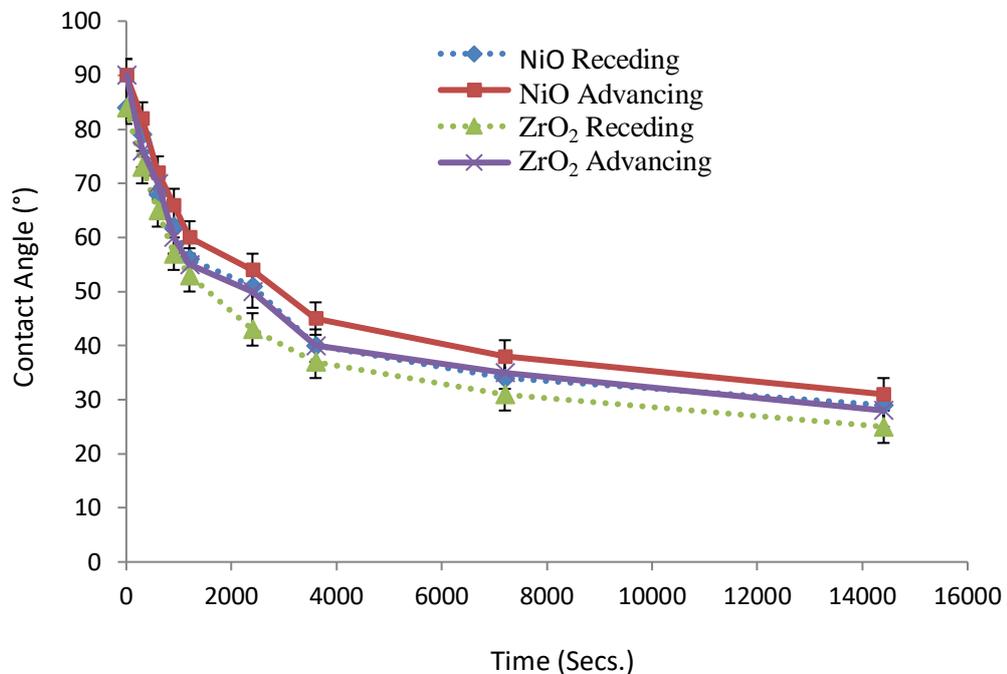


Figure 5.5: Receding and advancing water contact angles (versus air) as a function of time (7 wt. % NaCl brine; 0.05 wt. % nanoparticle concentration).

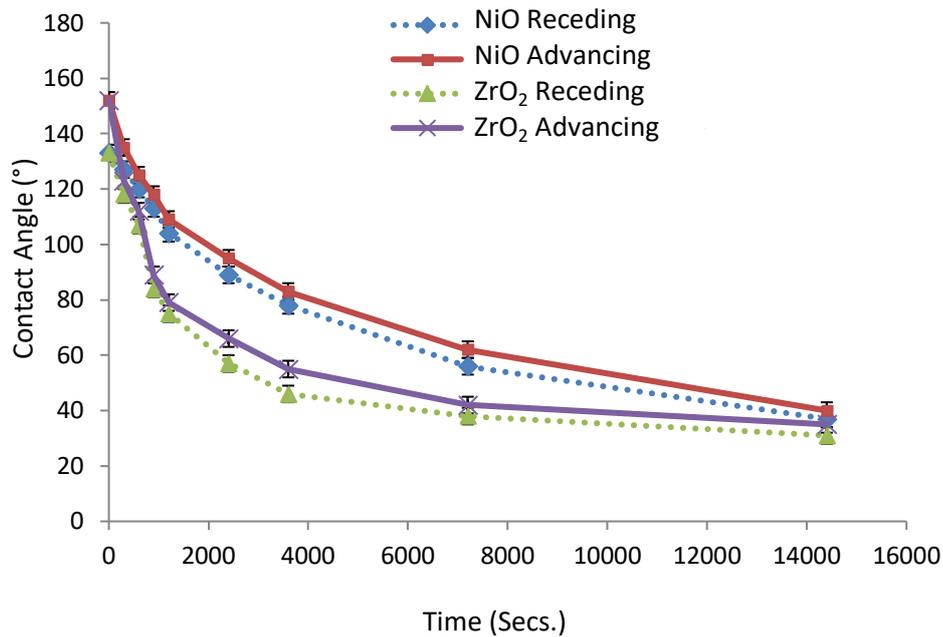


Figure 5.6: Receding and advancing water contact angles (versus toluene) as a function of time (7 wt.% NaCl brine; 0.05 wt.% nanoparticle concentration).

wt.% NaCl concentration, water wetness was achieved in the presence of both nanofluids (49° for ZrO₂ and 68° for NiO in air). A similar scenario, albeit with higher absolute θ values, was observed for toluene: the strongly oil-wet state ($\theta=152^\circ$) changed to intermediate-wet (83°) in ZrO₂ nanofluid and weakly oil-wet (112°) in NiO nanofluid at 3 wt.% NaCl concentration. Highest water-wettability was achieved at the highest salinity of 20 wt.% NaCl, $\theta=19^\circ$ in ZrO₂ nanofluid and 34° in NiO nanofluid. The decrease in θ with increase in salt concentration is consistent with the report of Li and Cathles (2014); Nazari Moghaddam, et al. (2015); Al-Anssari et al., (2016) and Nwidae et al., (2016a). The particle adsorbed on the calcite surface with increase in NaCl concentration which is attributed to the physiochemical interactions or electrostatic forces (Zhang et al., 2013; Li and Cathles, 2014) between the nanofluid and calcite.

Despite the efficiency of the system at high salinity content, the use of low salinity brine (0-10%) is strongly recommended as a more appropriate range as the formation wetting were significantly reduced to a considerable water-wet condition while also

maintaining system stability. More so, lowering the salinity of injected water can increase the repulsive forces between rock surface and the adsorbed organic materials. Extreme salinity can weaken the electrostatic repulsion between the particle and the mineral surface which can lead to high particle adsorption on the rock surface (Bagaria et al., 2013). This can be unfavourable for nanoparticle transport as such low particle adsorption is essential for efficient transport of nanoparticle through the porous media and to achieve low formation damage. Notably, zirconium oxide when compared to other nanoparticles demonstrated better wettability alteration efficiency at a very minimal concentration (0.04-0.05 wt. %). This is much lower than the effective concentrations reported for other nanoparticles in wettability alteration studies such as silica-concentration range: 0.1-0.5wt. % (Ju et al., 2012; Maghzi et al., 2012; Al-Anssari et al., 2016); Alumina concentration range: 0.01-1wt. % (Giraldo et al., 2013) and NiO concentration range: 0.004-0.05 wt. %. We thus conclude that ZrO_2 is a better efficient wettability modifier than SiO_2 , Al_2O_3 and NiO as ZrO_2 base fluid consistently changed water contact angle towards water-wet at minimal particle concentrations,

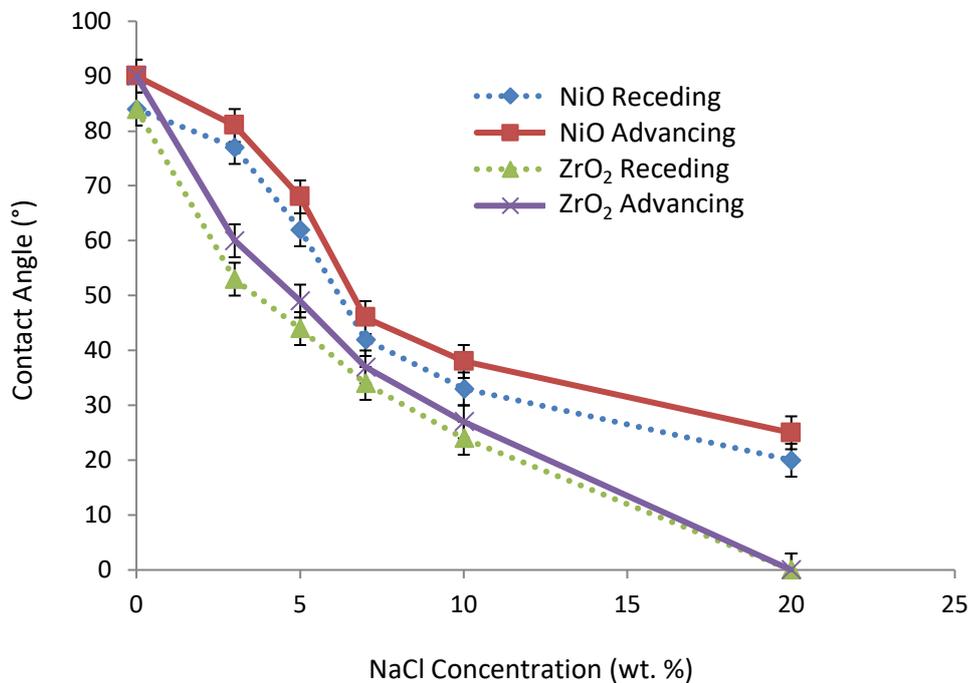


Figure 5.7: Receding and advancing water contact angles (versus air) as a function of NaCl concentration (0.05 wt. % nanoparticle concentration; 60minutes exposure time).

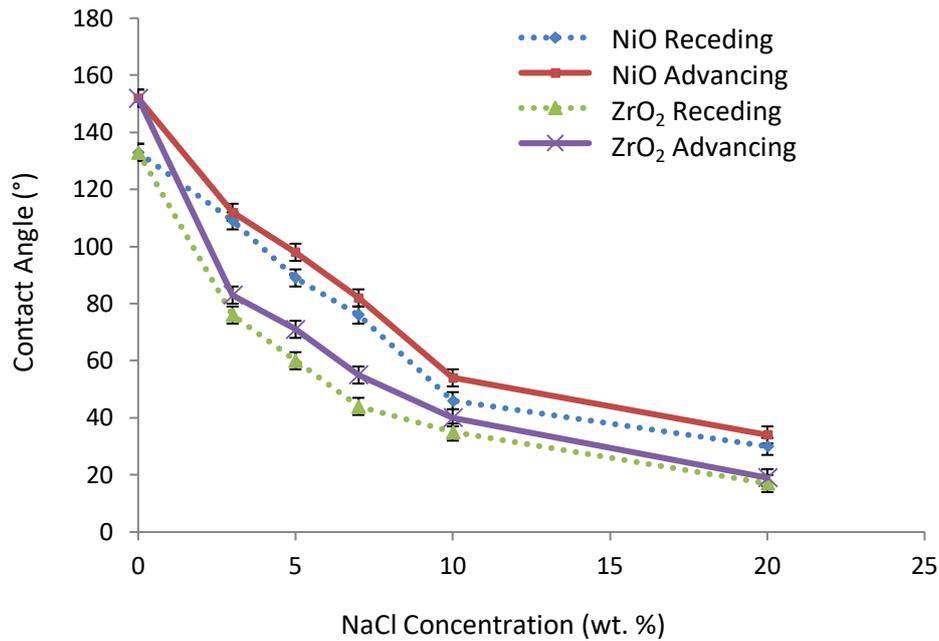


Figure 5.8: Receding and advancing water contact angles (versus toluene) as a function of NaCl concentration (0.05 wt. % nanoparticle concentration; 60mins exposure time.

and over longer exposure time. This behaviour may be attributed to the favourable interaction of ZrO₂ with the dispersing fluid (NaCl brine) and high chemical affinity to the calcite.

5.4 Conclusions

The wetting preference of oil-wet calcite substrates was measured to assess nanofluid wettability alteration efficiency. Results from the extensive contact angle measurements indicate NiO demonstrate potentials in wettability alteration, although NiO is less efficient in comparison to ZrO₂ under the same condition and particle concentration. Poor oil displacement tendencies were observed at minimal particle concentration (0.004 wt.%) and short exposure time (60 min - Figure 5.4). However, oil displacement was attained over longer exposure time at higher particle concentration (0.05 wt.% - Figure 5.6). With ZrO₂ even at minimal nanoparticle concentrations for all conditions tested; a continuous decrease in contact angle with increase in nanoparticle concentration, exposure time and salinity occurred. Mechanistically, the nanoparticles adsorbed on the calcites substrate surfaces as

observed by SEM - Figure 5.1 and AFM -Figure 5.2. Inferring from the study, the following deductions are made:

- ZrO_2 and NiO nanofluids decrease the water contact angle with increase in time, concentration, and salinity in a continuous trend especially at suitable particle concentrations (0.004-0.05 by weight of the solution).
- Nanoparticles adsorbed on the surface of the calcite crystals promoted oil displacement thus contributing to the inevitable change in wettability from oil-wet to water-wet in a very efficient way.
- Application of nanofluids in oil-wet or intermediate-wet formations such as fractured limestone may substantially increase oil recovery efficiency through wettability alteration.

We conclude that NiO and particularly ZrO_2 nanofluids are effective wettability modifiers (changing oil-wet to water-wet conditions), and are thus potentially very efficient EOR agents.

Chapter 6 Surfactants Influence on Nanoparticles Wetting Behaviour

In this chapter, wetting evaluations were further performed under the action of complex interactions between surfactant, nanoparticles, and the limestone rock. The synergistic effect of blends of nanoparticles and surfactants on solid-liquid interfaces to simulate subsurface harsh conditions on the basis of the particle concentration, time, temperature, rock morphology, roughness and topography was investigated. These factors were systematically analysed, while further demonstrating that nanoparticle as a robust chemical shows great potential in stabilizing systems under harsh reservoir conditions. This is vital for improved understanding of enhanced wetting propensities of nanoparticles in limestone formation.

6.1 Introduction

Porous rock wetting and imbibition are complex processes which pose a continual challenge in subsurface reservoir practices. The relevance of wetting and its effect on rock-fluid properties cannot be over emphasized, aside from its importance in subsurface reservoir evaluation, it is of great relevance for characterization and selection of materials. Since water-wet formations display great affinity for water than oil, and oil-wet formations retain the oleic phase much better in the tight pore matrix of the rock; it is however a key question how the wetting state of such formations can be rendered more water-wet to facilitate better hydrocarbon recovery (Morrow, 1990; Standnes and Austad, 2003; Al-Anssari et al., 2016; Nwidae et al., 2017), soil-decontamination, or enhanced carbon geo-sequestration processes (Iglauer et al., 2015; Iglauer, Pentland and Busch, 2015; Arif et al., 2016; Al-Khdheawi et al., 2017). Surfactants are good wettability modifiers for solid-liquid interfaces (Austad et al., 1998; Zhang et al., 2006; Wu et al., 2008), although the kinetics, uniformity and wettability alteration efficiency of surfactants are complex and depend on the properties of the surfactant and the solid surface of the porous medium that the surfactants are in contact with (Bi et al., 2004; Zhang and Somasundaran, 2006). Surfactants main role in EOR is the capacity to adsorb on surfaces or interfaces (Curbelo et al., 2007; Wu et al., 2011; Nwidae et al., 2016b; Zhou, et al., 2016) even

at minimal concentrations. This can lead to surfactant loss due to excessive adsorption on the reservoir rock surface; an effect which needs to be minimized as the efficiency of the EOR process is reduced (Schramm, 2010; Bera et al., 2011; Bera et al., 2013; Zargartalebi et al., 2015; Nwidee et al., 2016). Stable metal oxide nanoparticles (Das et al., 2006; Yu and Xie, 2012; Nwidee et al., 2016a; 2017) have received increased interest as an additive to EOR-surfactant formulations (Sharma et al., 2015; Sharma, et al., 2015) as it displays different and better properties in comparison to the bulk material counterparts. Its great chemical stability makes it particularly interesting for formulations of suspensions or emulsions (Jikich, 2012; Nwidee et al., 2017). Despite the significance of studies on adsorption behaviour and IFT at the liquid-liquid interface (Ahmadi and Shadizadeh 2013; Esmailzadeh et al., 2014; Zargartalebi et al., 2015), the mechanisms and interaction between surfactant augmented nanoparticles on solid-liquid interface is not fully understood and remains a challenge especially for contact lines moving in nanoscale. Such effect has barely been reported in oil-wet limestone reservoir. Hence, we tested the wetting propensity of new nanoparticle-surfactant formulations in strongly hydrophobic limestone. Two different surfactants (cationic and non-ionic) and nanoparticles (zirconium oxide and nickel oxide) were systematically evaluated as a function of surfactant type and concentrations, nanoparticle-surfactant type and concentrations, temperature, and imbibition.

6.2 Experimental Procedure

Fluids formulation, surface cleaning, and modification were performed based on procedures 3.3 of chapter 3. The calcite and limestone core plugs were cleaned and aged based on procedure 3.3.2.1. The core plugs have an average length 5.8 cm and diameter 2.2 cm, average porosity of 19.5% and a wide-range of permeability (Table 6.1). The mineral composition of the rock was evaluated via unique spectrum signature of different elements (Table 6. 2, Figure 6.1) which indicates the calcite fraction of the rock. Procedure 3.3.2.2 was adopted for the nanofluid preparation. Precisely, the surfactant (C₁₆TAB, TX-100: 0.05-0.5 wt. %) solutions were prepared with a 220V/50Hz magnetic stirrer and deionised water as dispersing agent. Nanoparticle-surfactants (ZrO₂/C₁₆TAB; ZrO₂/TX-100, NiO/C₁₆TAB; NiO/TX-100) were

formulated by adding fixed surfactant concentration (C₁₆TAB and TX-100 - 0.5 wt. %) to the nanosuspensions of various concentrations (ZrO₂ and NiO - 0.004 - 0.05 wt. %). The mixture was stirred with a magnetic stirrer (60 min) and sonicated with a 300VT ultrasonic homogenizer (60 min) to create homogeneous fluids.

Table 6.1: Core properties

Cores	Porosity (%)	Permeability (Kair -mD)	Permeability (K-KlinkmD)
Unmodified	20	370	310
C ₁₆ TAB-modified	19	318	264
NiOC ₁₆ TAB-modified	20	262	214
ZrO ₂ C ₁₆ TAB- modified	19	218	175

* C₁₆TAB-modified - cores exposed to cationic surfactants solution

*NiOC₁₆TAB-modified - cores exposed to nanofluids containing blends of nanoparticle (NiO) and -surfactants (C₁₆TAB).

*ZrO₂C₁₆TAB-modified cores are cores exposed to nanofluids containing blends of nanoparticle (ZrO₂) and -surfactants (C₁₆TAB).

Table 6.2: Rock composition.

Element	Symbol	Atomic concentration (%)	Weight concentration (%)
Calcium	Ca	15.67	33.38
Carbon	C	24.15	15.42
Oxygen	O	60.18	51.20

Series of contact angle (θ) measurement and spontaneous imbibition tests were performed to investigate the wetting effect of the nano-suspensions on the hydrophobic rock samples. The contact angle (θ) experiments were conducted over a range of temperatures (22-70 °C \pm 1 °C) and fluid densities (g/ml) were also measured (Toluene-0.848; C₁₆TAB-0.962; TX-100-0.951; ZrO₂/C₁₆TAB-0.977; ZrO₂/TX-100-0.965; NiO/C₁₆TAB-0.947; NiO/TX-100-0.998). Prior to the receding (θ_r) and advancing contact (θ_a) angle measurements, oil-wet calcite samples were exposed to

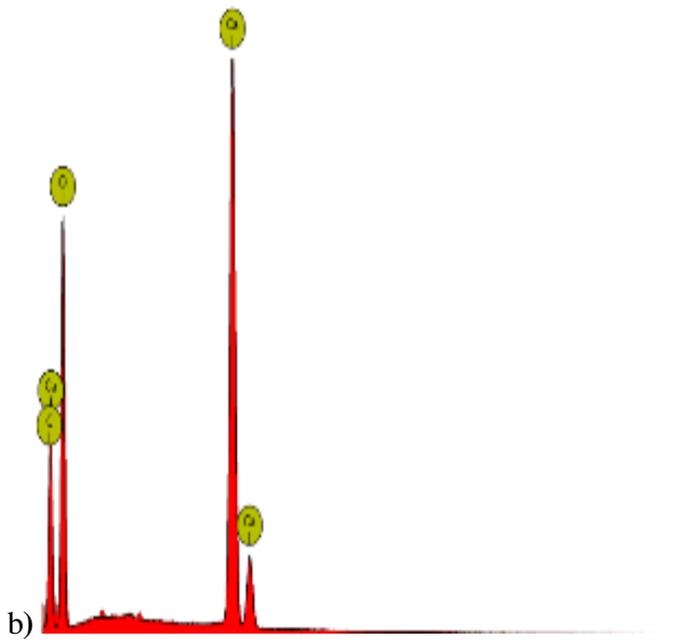
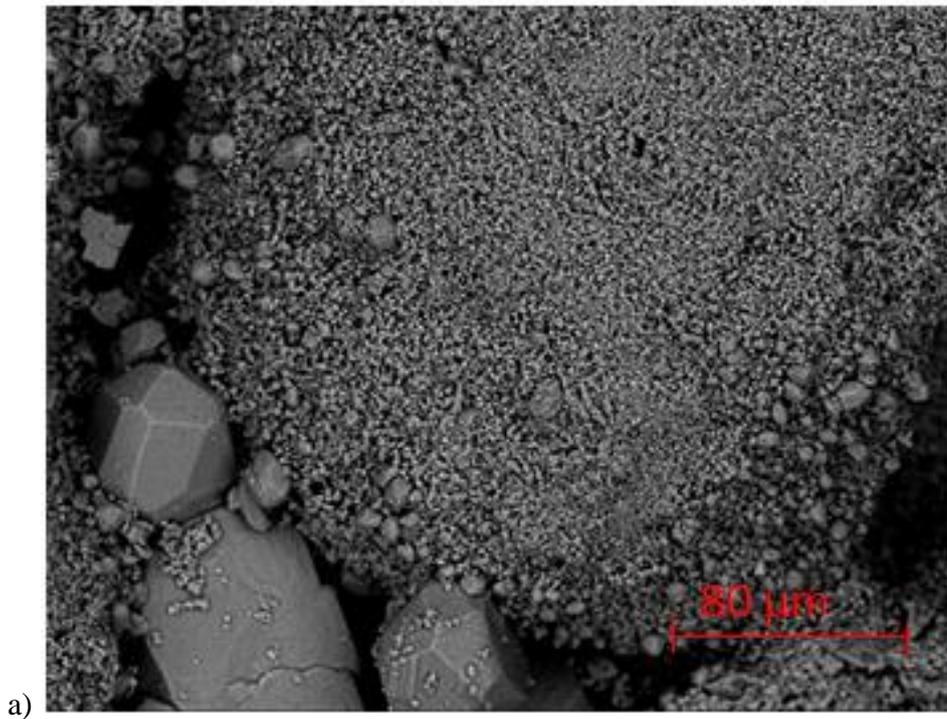


Figure 6.1: Spectrum analysis of calcite fraction of the Indiana rock.

the formulated fluids (surfactants: C₁₆TAB and TX-100; nanoparticle-surfactants systems: ZrO₂/C₁₆TAB, ZrO₂/TX-100, NiO/C₁₆TAB and NiO/TX-100) for a fixed period of one hour at ambient conditions. The contact angle measurement was performed based on procedure 3.3.3.1. With respect to spontaneous imbibition (SI),

wettability was assessed to test the water imbibing potentials of limestone cores using procedure 3.3.3.3.

6.3 Results and Discussions

Improving the wetting and subsequent recovery potentials in limestone formation which is typically intermediate to oil-wet is an essential approach for facilitating fluid displacement at pore scale. As such wettability was evaluated for both nano-modified and unmodified substrates through morphological and topographical assessment, contact angle (θ) measurement and spontaneous imbibition (SI), which are globally accepted approach for quantifying reservoir wettability. Firstly, surfactants wetting propensity as a function of concentration on oil-wet rock in the absence of nanoparticle was investigated, then the nanoparticle-surfactant was tested as a function of nanoparticle concentration and temperature for the preferential selectivity of efficient concentration and suspension type. Only efficient suspension type and the concentrations thereof were used for the spontaneous imbibition evaluation.

6.3.1 Mechanistic Quantification

6.3.1.1 Surface Morphological Evaluation

The morphological layered structure of the nanoparticle and surfactant on the solid-liquid interface was examined via SEM. Figure 6.2(a)-(g) shows the SEM images of the pure calcite and the nanoparticles coated calcites at micrometre scale. Similar structural morphologies are observed in Figure 6.2(d)-(g) which represents the nanoparticle-surfactant coated substrates. ZrO₂ - surfactant blends (Figure 6.2 (f) and (g)) showed more regular particle shape and uniform spreading than NiO (Figure 6.2(d) and (e)). The SEM images depict adsorption of the nanoparticle-surfactants on the surface of the calcite, consistent with previous reports (Winkler et al., 2011; Nikolov, Kondiparty and Wasan, 2010; Ershadia et al., 2015). The adsorption behaviour on the surface of the rock facilitated the wettability change as observed via contact angle measurements for all systems tested (Figures 6.6-6.9).

6.3.1.2 Surface Roughness and Topography

Surface roughness and topography are key parameters that influence rock surface wetting. Although contact angle measurement is considered an effective method for evaluating reservoir rock wettability, key parameters such as surface roughness and the pore rock structures which impact liquid-solid contact lines are often not accounted for during the evaluations. For better understanding of the rock surface behaviour, the topography and surface roughness alteration were assessed here using AFM. Mean surface roughness (S_a) and root mean square (RMS) roughness was used to ascertain roughness variations. The AFM (Buckley and Lord, 2003; Zargari et al., 2010; Jarrahian et al., 2012) tests show the topography of the calcite at nanoscale and the variations in surface roughness for the rock surfaces treated with blends of nanoparticle and surfactant and untreated rock. The untreated calcite (Figure 6.3(a) - reference case) had the lowest peak height of 103 nm (black - 0 nm; white -103 nm) with a corresponding low roughness average (S_a -12 nm) and root mean square roughness (RMS-16 nm - Table 6.3). Different surface roughness variation was observed which impacts wettability as evident via contact angle measurements. The treated calcites showed a significant increase in surface roughness (Table 6.3), as also evident in the SEM images (Figure 6.2) and contact angle measurements (Figures 6.6-6.8) as discussed below. TX-100 nanoparticle system (Figure 6.3(c) and (e); Table 6.3) depicts a relatively less rough surface in comparison to C_{16} TAB (Figure 6.3 (b) and (d); Table 6.3). This surface roughness value is an indication of the presence of layer of adsorbed material on the rock surface, hence, the untreated surface was the smoothest surface.

6.3.2 Contact Angle Measurement

Contact angle (θ) (Hong et al., 2013) measurement is one of the most globally accepted approaches for quantifying reservoir wettability. Typically, θ is generally not unique as it is dependent on whether the liquid droplet on the surface of the substrate is advancing (θ_a) or receding (θ_r). The receding angle (θ_r) measurement is achieved via contraction of the liquid drop, thus, considered the angle at the receding edge of the water droplet or the de-wetting angle. Whereas, the advancing angle (θ_a) measurement is attained via expansion of the liquid drop thus referred to as the angle at the

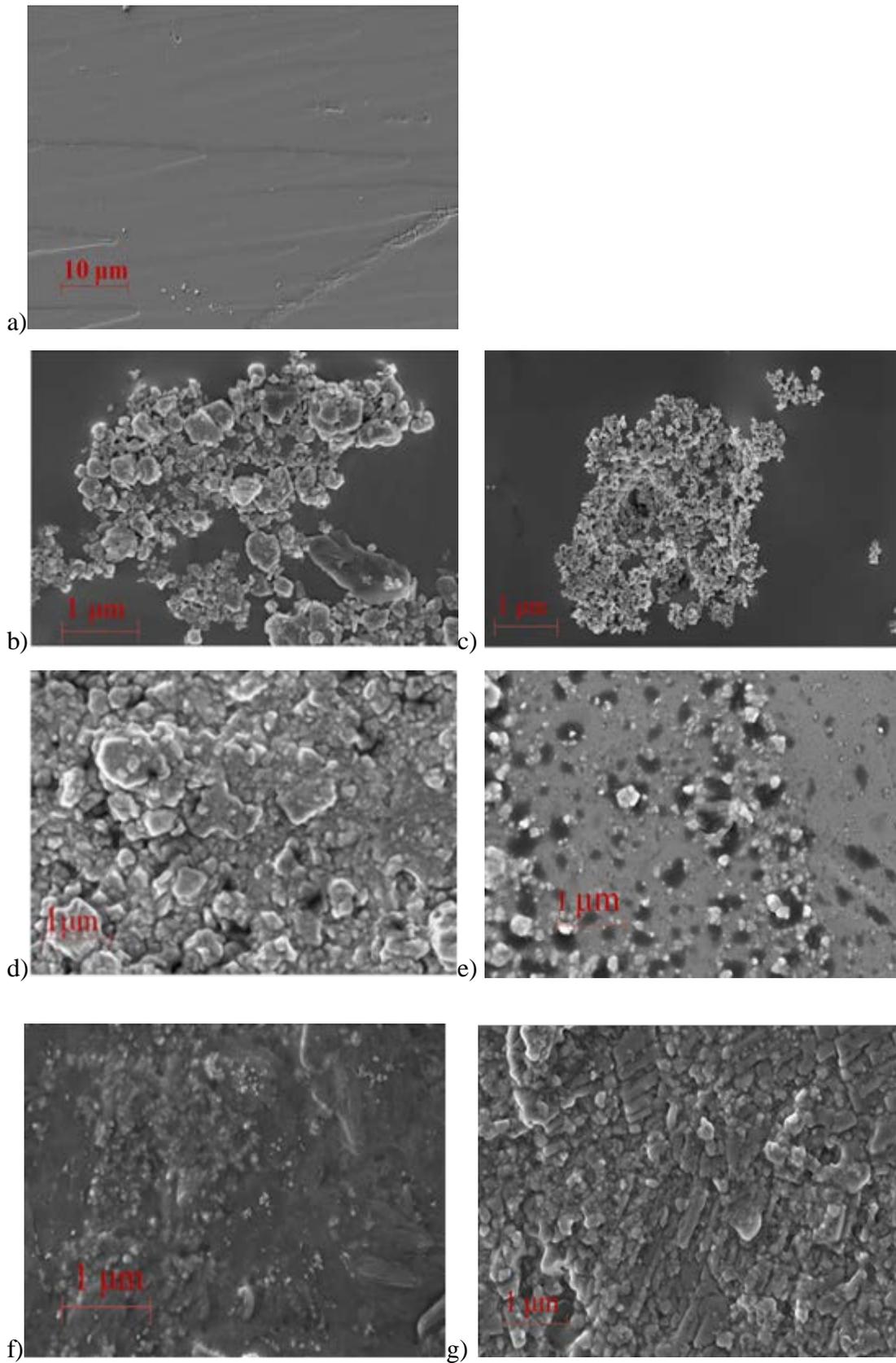


Figure 6.2: SEM images of nanoparticle-surfactant modified surfaces: (a) Untreated calcite (b) NiO, (c) ZrO₂ (d) NiO/C₁₆TAB, (e) NiO/TX-100, (f) ZrO₂/C₁₆TAB (g) ZrO₂/TX-100.

Table 6.3: Surface roughness

Samples	S _a (nm)	RMS (nm)
Untreated	12	16
NiO/C ₁₆ TAB	100	190
NiO/Tx-100	78	180
ZrO ₂ /C ₁₆ TAB	120	200
ZrO ₂ /TX-100	60	83

advancing edge of a water droplet or the wetting angle. The water droplet advancing across the substrate surface exceeds the receding, as such, water-advancing θ is often considered to be of great relevance to reservoir wettability and its imbibing water front. Figure 6.4 shows contact angle measurements on a tilting surface. However, in complex pore space of rocks, variability in surface roughness and mineralogy also influence the contact angle and thus the rock's wettability (Scanziani et al., 2017; Iglauer, 2017).

6.3.2.1 Effect of TX-100 and C₁₆TAB on Wettability

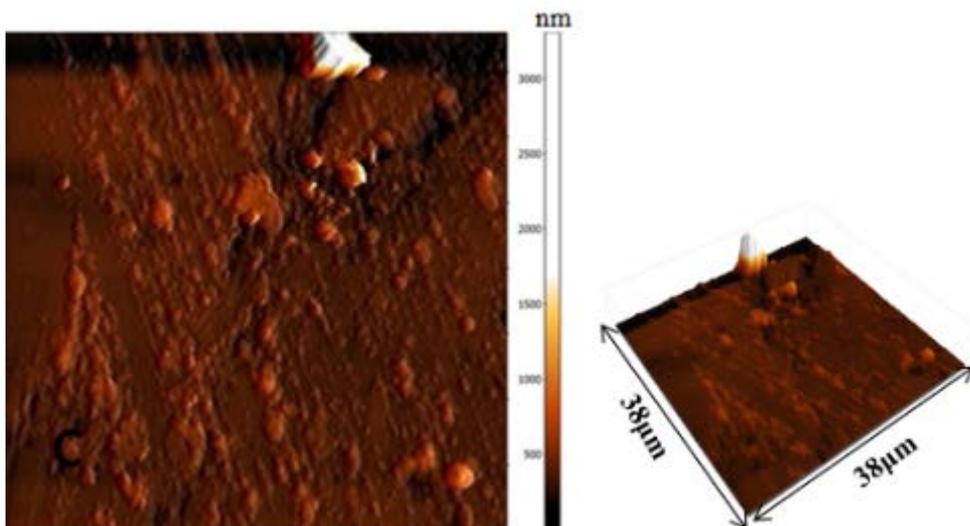
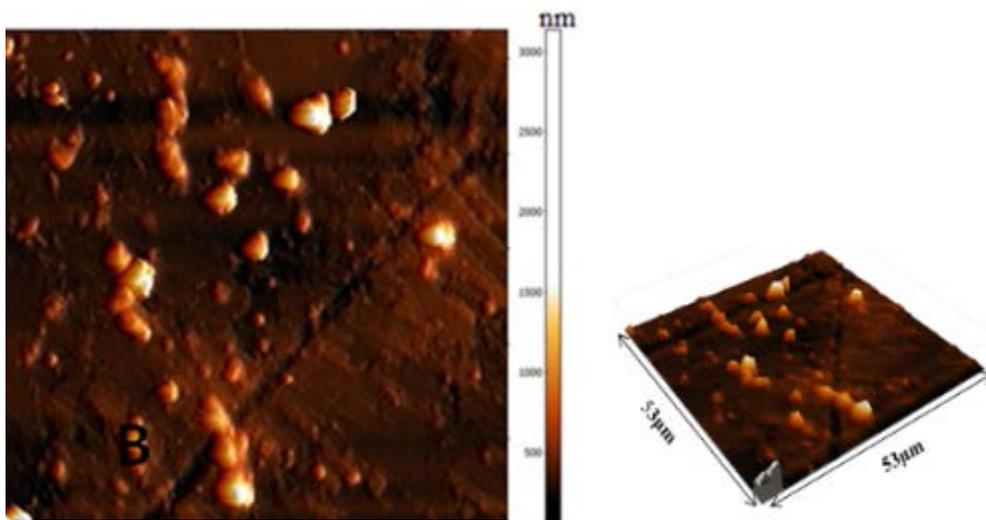
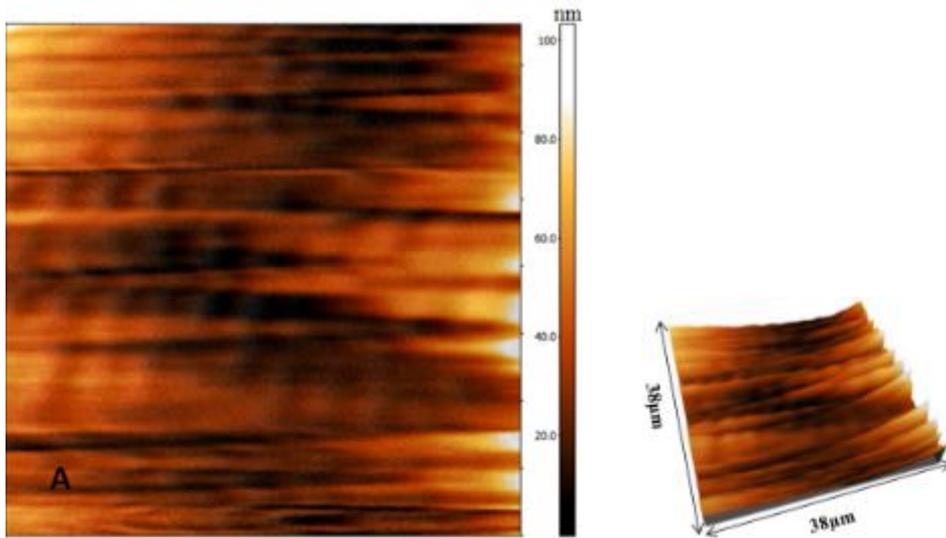
The potentials of the different surfactants formulations as wetting modifiers were tested on the calcite surface. This serves as a preliminary test to ascertain the wetting efficiency of cetyltrimethylammonium bromide (C₁₆TAB-cationic) and triton X-100 (non-ionic) in the absence of nanoparticles. Contact angle (θ) measurements were conducted at different surfactant concentrations (0.005-0.5 wt.%). Low concentrations of surfactant were used to avert excessive free surfactants in the bulk. Figure 6.5 shows a decrease in θ with an increase in TX-100 and C₁₆TAB concentration and an intermediate wetting attained. The surface property of the oil-wet calcites changed upon exposure to the surfactants creating an adsorbed surface with an increase in surfactant concentration.

Although the interaction of the advancing leading edge of the liquid and adsorption on the surface of the solid often lead to a decrease in surfactant concentration near the leading edge (Ananthapadmanabhan et al., 1990). This behaviour can cause an

increase in surfactant loss which is typically influenced by the surface chemistry of the rock, surface roughness, type of fluids that the rocks are aged in and how much of the surface is wetted by the fluid, and the thermo-physical treatment conditions. As such, excessive surface adsorption tendencies of surfactants should be avoided to achieve EOR feasibility (Nwidee et al., 2016b; Zargartalebi et al., 2015; Bera et al., 2012). Overall, C₁₆TAB (θ_a - 86) exhibited better wetting at 0.5 wt.% than TX-100 (θ_a - 97). This is consistent with reports (Austad et al., 1998; Zhang et al., 2006; Standnes and Austad, 2000; Sheng, 2011) that cationic surfactants are better wettability modifiers in carbonate reservoirs, which is due to favourable adsorption behaviour on the surface of the calcite owing to the electrostatic interaction between the rock surface and the cationic surfactant. The higher wetting efficiency displayed by cationic surfactants can also be attributed to their surface charge, as cationic surfactants bear the same surface charge as carbonate minerals (Seethepalli et al., 2004).

6.3.2.2 Effect of Nanoparticle on TX-100 and C₁₆TAB Surfactant Performance

Surfactants have inherent properties as surface active agents, however, the addition of nanoparticles have the potential of enhancing their ability to wet and spread on solid surfaces. To understand the behaviour of nanoparticle-augmented surfactant, the wetting propensity of C₁₆TAB and TX-100 surfactants was further tested at ambient temperature (22 ± 1 °C) in the presence of nanoparticles (ZrO₂ and NiO), thus, changing the property of the wetting fluid. Figures 6.6 and 6.7 show the wetting trends of blends of surfactant (fixed concentration - 0.5 wt.% - owing to efficiency - Figure 6.5) and nanoparticles (ZrO₂/C₁₆TAB, ZrO₂/TX-100, NiO/C₁₆TAB and NiO/TX-100; concentrations - 0.004-0.05 wt.%). The result shows that θ depends on the nanoparticle-surfactant types, concentration, and indeed the surface roughness of the substrate. θ_a and θ_r decreased with increase in nanoparticle concentration in the nanofluid and surface roughness (see AFM - Figure 6.3, Table 6.3). This is in agreement with literature that contact angle is influenced by the fluid-rock interaction and surface roughness of the mineral (Buckley and Lord, 2003; Bera et al., 2012; Al-Yaseri et al., 2016; El-hoshoudy et al., 2016). Although surfactants are active wettability modifiers (Zhang et al., 2006; Bera, et al., 2012; Negin et al., 2017) the higher magnitude of wettability change was achieved in the presence of nanoparticle.



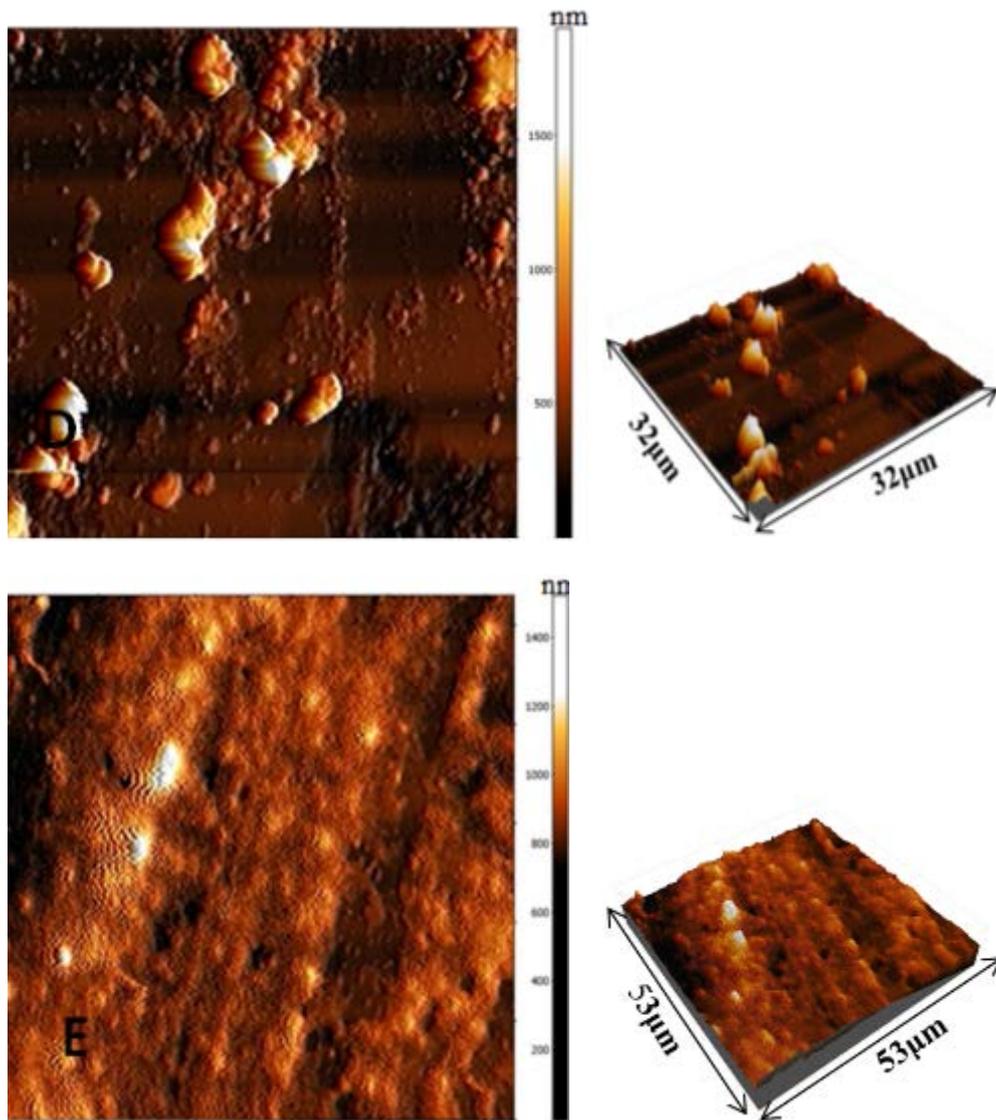


Figure 6.3: AFM images of nanoparticle-surfactant modified surfaces: left: top view, right: 3D view. (a) Untreated; treated with: (b) NiO/C₁₆TAB (c) NiO/TX-100, (d) ZrO₂/C₁₆TAB (e) ZrO₂/TX-100. Low peak heights (low Z-values) depict low surface features (dark shades) and high peak heights (high Z-values) show high surface features (lighter shades).

The presence of the nanoparticles changes the rheological properties of the fluid while increasing the surfactant effect (Hirasaki and Zhang, 2004). The particles attach to the rock surface owing to adsorption as evident via SEM (Figure 6.2) forming nanostructure layers, as the nanoparticle concentration in the fluid is increased, the surfactants at the surface detaches from the interface and adsorbs on the nanoparticles.

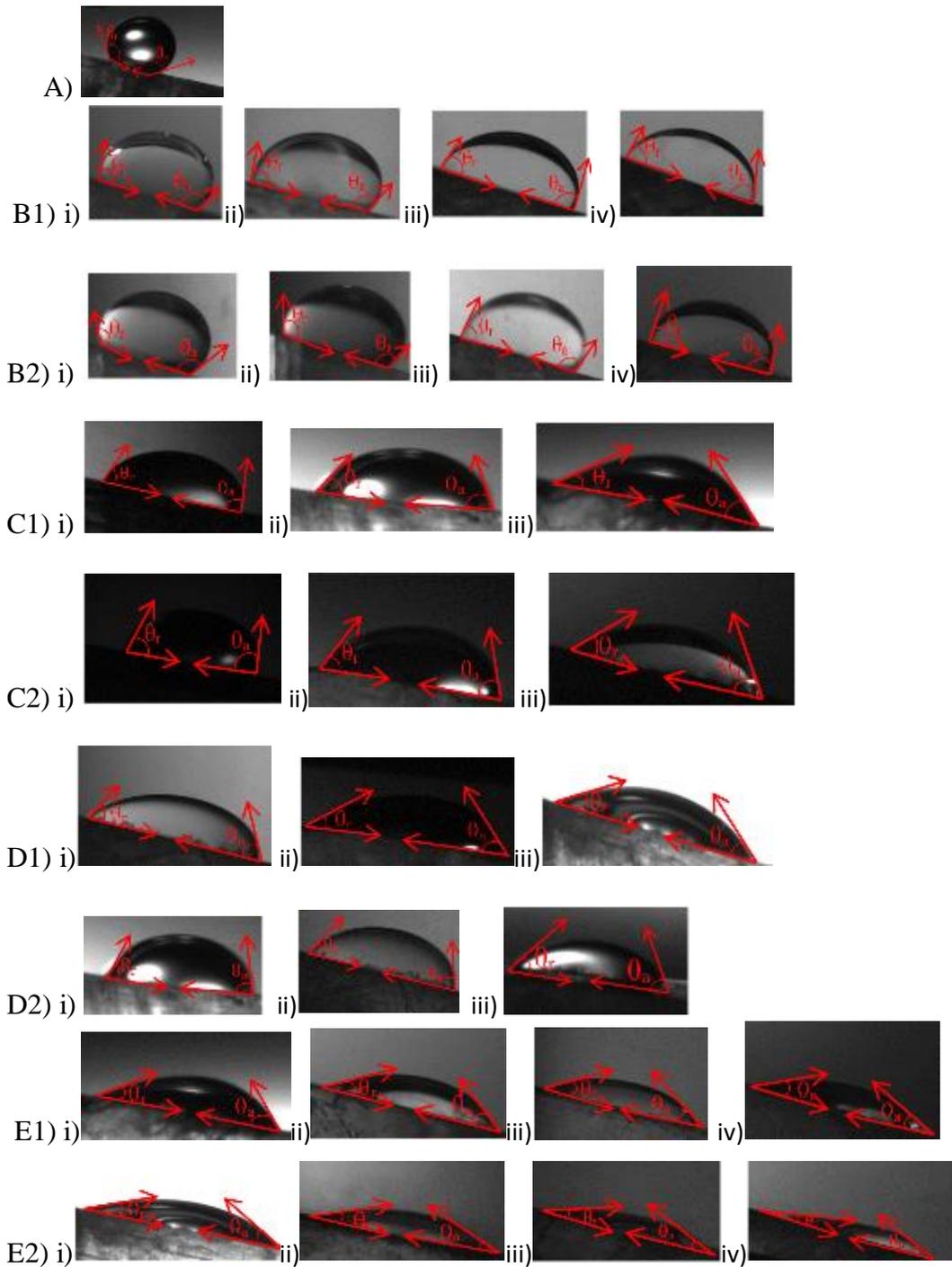


Figure 6.4: Images of contact angle (θ) water droplets on: (A) oil modified rock (high θ - indicates the surface's hydrophobicity - $152^\circ \theta_a$); (B) surfactant modified (Exhibiting intermediate wet characteristics I-IV (B1 - $C_{16}TAB$; B2 - TX-100)); (C) nanoparticle-surfactant modified (C1- $NiOC_{16}TAB$; C2 - $NiOTX100$); (D) nanoparticle-surfactant modified (D1- $ZrO_2C_{16}TAB$; D2- ZrO_2TX100); (E) and nanoparticle-surfactant modified at different temperature (E1- ZrO_2TX100 ; E2 - $ZrO_2C_{16}TAB$); (C-E indicates low θ which represents strong interaction with the rock surface thus exhibiting low surface energies and inclination to wet; I - IV); See graphical representation for θ - values.

The surfactants enhance the physical adsorption on the nanoparticle's surface thus leading to a reduction in surface energy which impedes particle aggregation (Ravera et al., 2006; Muherei and Junin, 2009; Ahmadi and Shadizadeh, 2013; Chevalier and Bolzinger, 2013; Mohajeri et al., 2015; Guo and Aryana, 2016). Typically, surfactant adsorption on solid surfaces is often dependent on the electrostatic binding, like cationic surfactants onto negatively charged sites of the solid. Such adsorptions are influenced by the attraction and repulsion force between the surface and the hydrophilic or hydrophobic group and the lateral interactions between the adsorbed surfactants, which also enhanced θ decrease towards more water-wet conditions. The alteration of formation wettability to preferentially water wet state reduces the forces that binds oil to the rock surface thus causing oil to flow out of the tight formation rock matrix (due to imbibition of water) which facilitate more oil recovery, consistent with literature (Ershadia et al., 2015; El-hoshoudy et al., 2016), contrary to micro-emulsions which changes wettability to intermediate wet conditions (Hussain et al., 1997). Notably, the nanoparticle surfactants system containing TX-100 (non-ionic surfactant) showed better compatibility with NiO (NiO/TX-100 - 55 θ_a - Figure 6.6) than ZrO₂ (ZrO₂/TX-100 - 60 θ_a - Figure 6.7). However, the C₁₆TAB-nano blends (ZrO₂/C₁₆TAB - 35 - Figure 6.6 and NiO/C₁₆TAB - 48 - Figure 6.7) consistently decreased θ than TX-100-nano blend, thus, the C₁₆TAB nano-blends were subjected to further testing.

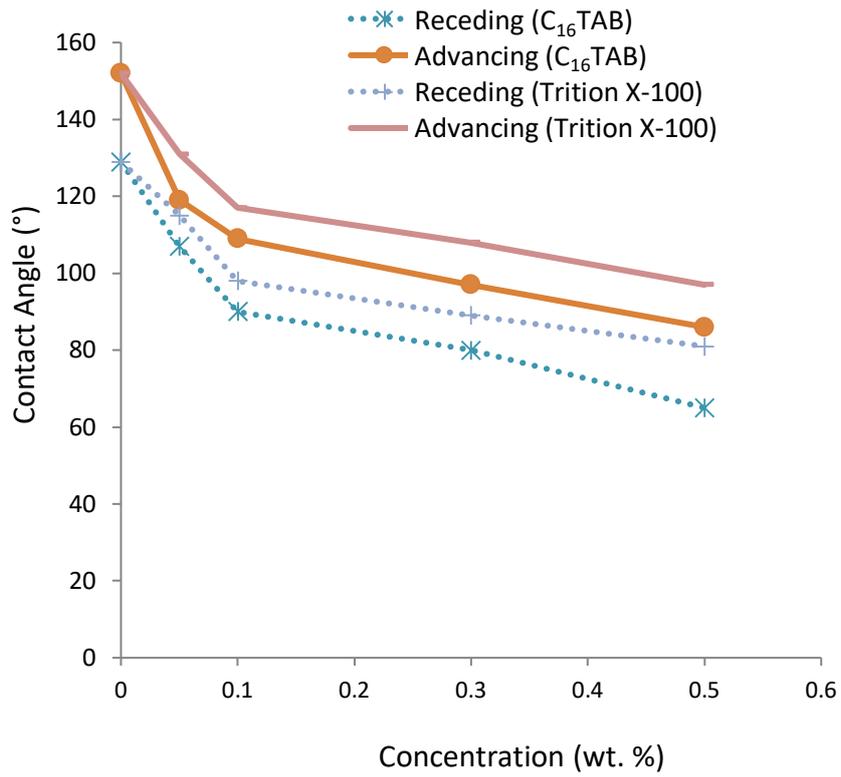
Note that nanoparticles have only a marginal effect on nanofluid-oil interfacial tension in comparison to contact angle (Hendraningrat and Torsæter, 2014, 2015; Al-Anssari et al., 2017). Furthermore, for estimation of the contact angle (and thus wettability), three interfacial tensions are needed (see Young's equation); out of which two (solid-oil and solid-nanofluid) cannot be measured. Hendraningrat et al. (2014, 2015) also emphasized that nanoparticles are more likely to interact with the rock interface than the oil.

6.3.2.3 Effect of Temperature on Nanoparticle-Surfactant Performance

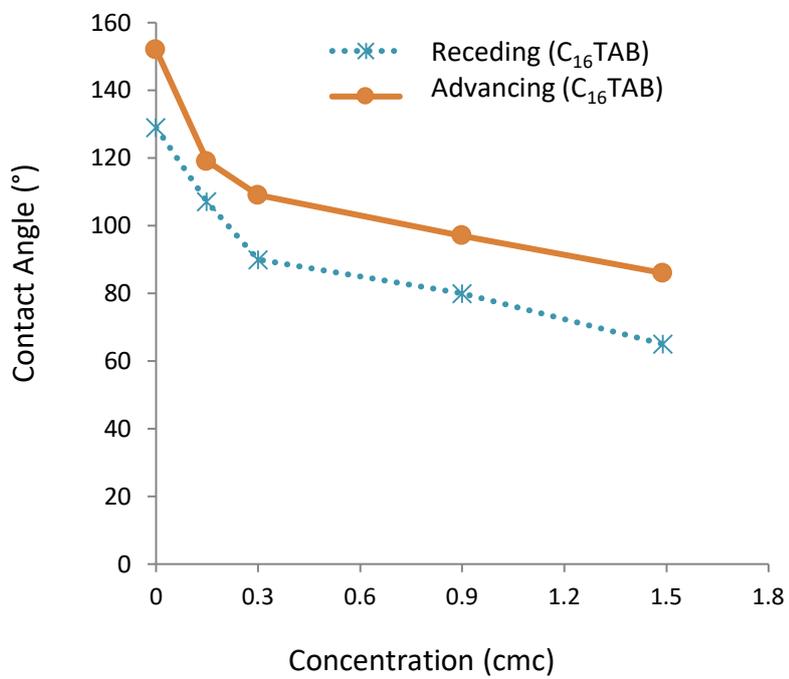
A major challenge with surfactant utilization is temperature sensitivity due to chemical degradation issues. Most surfactant solutions have cloud point temperatures (typical

range: 30-160 °C - dependent on surfactant structure), above which the solution becomes cloudy, and can affect the surfactant performance (Negin et al., 2017). High temperature effect on wettability alteration have been reported in various systems e.g. Hamouda and Gomari (2006) conducted a wettability alteration study on modified hydrophobic calcite with temperature using contact angle, IFT, and Zeta potential measurements. With increase in temperature, the surface of the hydrophobic calcite becomes more hydrophilic. Similar trend was reported for IFT reduction with temperature increase at fluid/fluid interface; the zeta potential of the calcite surface with temperature increase reduced the surface charge to less positive which enhanced the repulsive forces between dissociated acids and calcites surface. The change in surface charge, the adsorption of acids on the surface becomes less effective at high temperatures hence the calcites surface becomes more water-wetting. Gupta and Mohanty (2008) investigated the effect of wettability on oil recovery using divalent ions in oil-wet carbonate under different temperatures (up to 90 °C). High temperature altered the wettability of the carbonate to water-wet. Sulfate ions displayed great efficiency when in combination with magnesium and calcium ions than in the absence. A high concentration of calcium ions alone also altered wettability while wettability was unaltered with magnesium ions alone.

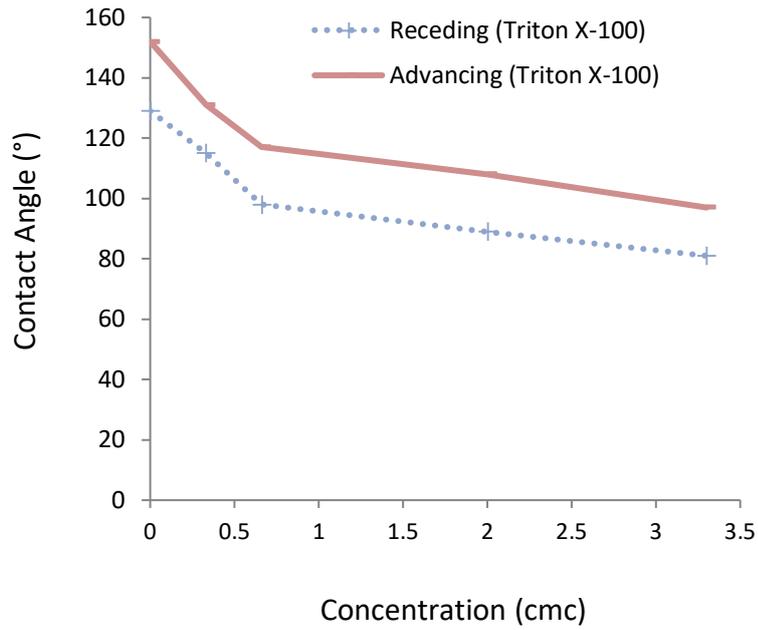
Alternatively, aqueous nanoparticle dispersions can also be used at high temperature. The presence of nanoparticles which are solids and chemically robust has the potential to stabilize systems even under harsh reservoir conditions (Jikich, 2012). As such the effect of the C₁₆TAB nano-blend (0.5 wt.% surfactant; 0.05 wt.% NiO and ZrO₂ nanoparticles concentrations) was further tested over extensive temperature range (22-70 °C), as colloidal stability of nanoparticles and surfactant under high temperature can pose a great challenge to efficient oil displacements from the porous walls of strongly hydrophobic limestone reservoirs. Clearly, θ displays high dependency on temperature (Figure 6.8), the higher the temperature, the higher the decrease in θ_a and θ_r . This trend is in good agreement with literature (Hamouda and Karoussi, 2008; Kvítek et al., 2008; Muherei and Junin, 2009; Mollaei and Maini 2010; Ahmadi and Shadzadeh, 2013; Mohajeri et al., 2015). The temperature increase decreases θ_a and θ_r in the presence of the nanoparticle-surfactant systems owing to increase in surface activity.



a)



bi)



bii)

Figure 6.5: Water θ_R and θ_A as a function of $C_{16}TAB$ and TX-100 concentration in toluene (1-hour exposure time - (a) concentration in weight %; (bi-ii) concentration in cmc).

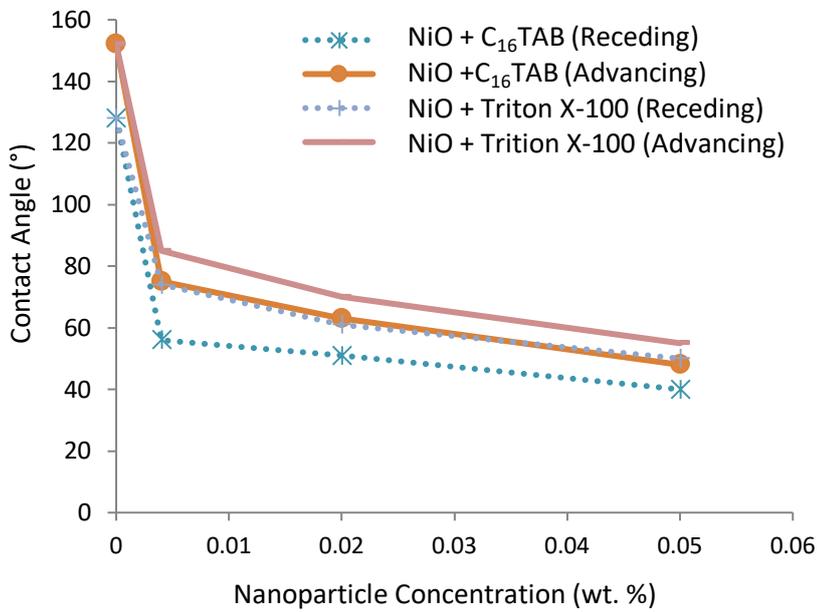


Figure 6.6: Wettability alteration efficiency of NiO - 0.5 wt. % $C_{16}TAB$ and TX-100 in toluene (1-hour Exposure time).

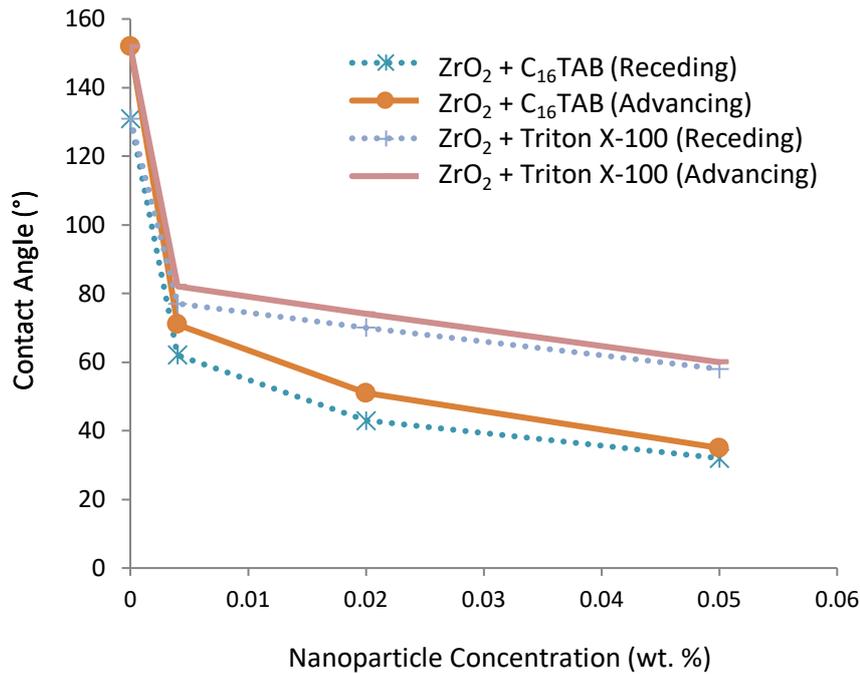


Figure 6.7: Wettability change of ZrO₂ - 0.5 wt. % C₁₆TAB and TX-100 blends in toluene (1-hour Exposure time).

As the surface activity of surfactant is enhanced in the presence of nanoparticle the increase in temperature impacts the oil properties leading to a reduction in the oil viscosity, as such, the actively adsorbed nanofluid on the rock surface desorbs the oil thereof, thereby leading to a more water-wet surface especially the ZrO₂C₁₆TAB formulations. This is also consistent with Muherei and Junin (2009), Bera et al. (2012) and Taborda et al. (2016) reports that oil viscosity reduction enhances oil mobility whilst changing the wettability of the porous medium. Hence, the formulation containing nanoparticles and surfactants enhances emulsion and sedimentation stability via counteracting surface and gravity forces, and formation of swift emulsion as well as, wettability alteration of the porous medium or solid surfaces even at elevated temperature with great potentials for upsurging oil recovery. Thus, an indication that the presence of nanoparticle can enhance the surfactant performance and improve the stability of the emulsion (Mohajeri et al., 2015), this stable behaviour is also similar to microemulsion systems containing surfactant which exhibited great stability with temperature (Hussain et al., 1997). As such nanofluids can be feasible for long-distance migration in the reservoir and have the potential of resolving wettability challenges in limestone formations.

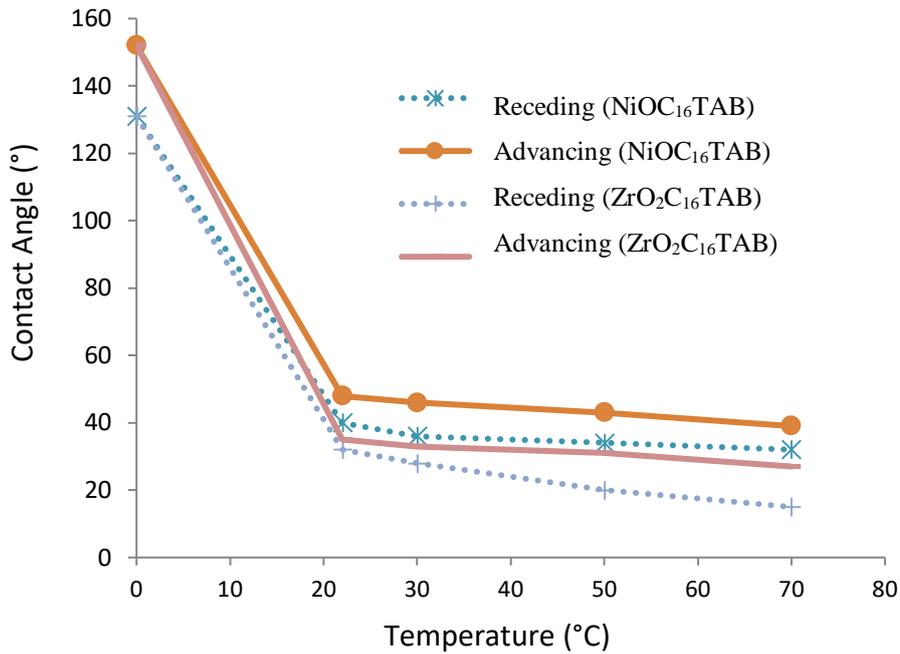


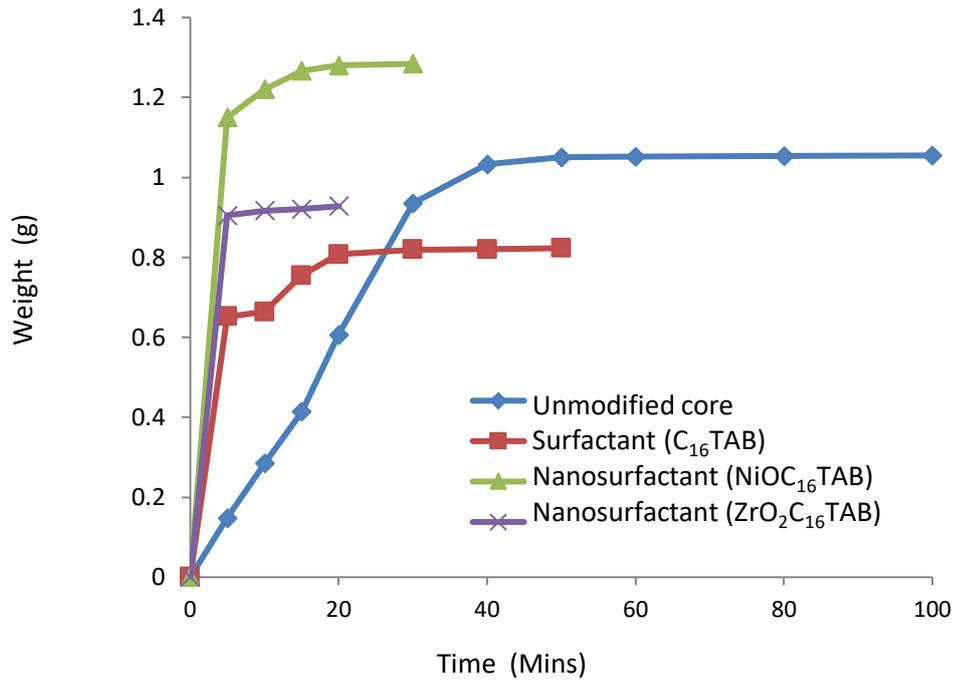
Figure 6.8: θ_R and θ_A depicting wettability change of NiO, ZrO₂ (0.05 wt. %) C₁₆TAB (0.5 wt. %) blends in toluene (1-hour Exposure time) at different temperatures.

6.3.3 Spontaneous Imbibition

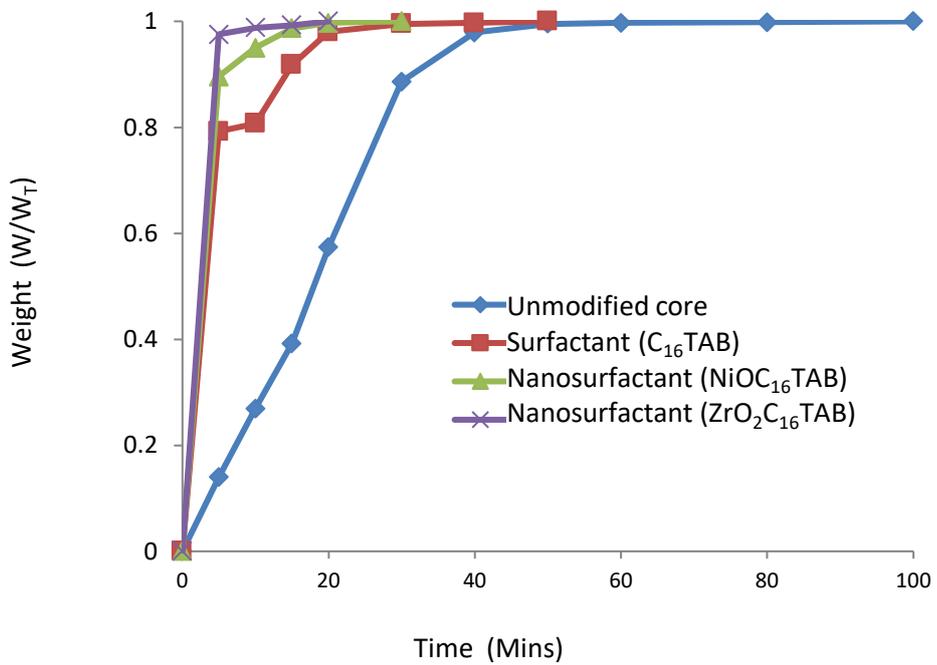
Contact angle is a useful wettability evaluation approach, however, the intricate nature of pore space and surfaces of a real reservoir rock influences the contact angle thus perceived as a limitation. Also, the rock heterogeneity and complex geometry (Anderson, 1986) are often not considered as the measurements are usually conducted on a single mineral crystal while ideal cores contain more challenging pores. Thus, the formulated nanoparticle-surfactants systems were further tested on the potential to enhance water imbibition into the matrix of the limestone rock as the imbibition of a wetting liquid into a porous medium is of great relevance to enhancing reservoir productivity. To avoid repetition, only C₁₆TAB (Concentration - 0.5 wt. %) and the corresponding nanoblends (NiOC₁₆TAB, ZrO₂C₁₆TAB - concentration - 0.05 wt. %) was assessed at different temperature (range: 22-70 °C) as ascertained via the above contact angle test owing to efficiency. The spontaneous imbibition (SI) test was performed using water as the imbibing fluid. The imbibition test was assessed as a function of time and weight as water imbibes into modified and unmodified core plugs.

Comparison of the SI process for core plugs before and after exposure to nanofluids shows similar water imbibing behaviour.

The reference test (prior to surfactant-nanoparticle-modification) showed the slowest imbibition process, water slowly imbibed into the unmodified limestone core (reference test) before attaining equilibrium at 100 min (Figure 6.9). Such slow pace in water penetration into the pores is ascribed to the poor rock wettability, an indication that the surface pore volume is still filled with oil instead of the imbibing liquid (water) as such the pore tends to be less-wetting. The wetting effect of the liquid in contact with the solid surfaces is a key driving force for imbibition. The nanoparticle-surfactant coated (especially $ZrO_2C_{16}TAB$) cores exhibited better water imbibing tendencies as the water-imbibition rate increased (became quicker) than the cores exposed to surfactant alone, which is also in agreement with the contact angle test above. The fast-spontaneous process led to weight gain by the core thus an indication of a more water-wetting condition, consistent with the observation in sandstone cores (Ahmadi and Shadizadeh, 2013). This spontaneous imbibition behaviour by the rock is due to capillary action of the interfaces within the pore spaces, the imbibition occurs via a wetting phase front formed by several interfaces acting in consort. The presence of adsorbed nanoparticles on the porous walls of the rock facilitated the rock wettability change, hence the water imbibing potential of the limestone rock is enhanced, leading to a faster surface wetting and imbibition, as also reported (Ju and Fan, 2009; Maghzi et al., 2012; Mason and Morrow, 2013; Liu et al., 2017). Similarly, Zamani et al., (2010) reported that surface retention of nanoparticles in porous media is mainly due to adsorption, as such the wettability is preferentially changed towards water wet. More so, in real porous media with a complex surface coating by asphaltene, the nanoparticle adsorption is enhanced by the spontaneous adsorption of asphaltene on the nanoparticle surface (Nassar, 2010). Such adsorption effects may even further improve recovery as the asphaltene content in a formation can be stabilized (Franco et al., 2013).



a)



b)

Figure 6.9: Spontaneous water imbibition in limestone rock as a function of weight and time: a) actual weight; b) dimensionless weight.

6.4 Conclusions

Wetting of solid by the liquid is an important phenomenon apparent in most applied and industrial processes. However, there is a lack of understanding in terms of the effect of nanofluids on solid surfaces, particularly; the question of whether strongly hydrophobic surfaces can be rendered water-wet is of great relevance in EOR and carbon geo-sequestration, as it is well known that production from water-wet formations is higher and dramatically lower in oil-wet formations (Morrow 1990; Iglauer, 2015; Iglauer et al., 2015; Nwideo et al., 2017a, b; Al-Khdheawi et al., 2017). Changing the wetting preference of reservoir rock is an essential approach for facilitating fluid displacement at pore-scale especially in limestone reservoirs, which are predominantly oil-wet. Although the use of nanoparticle in combination with surfactant has been previously reported (Ayirala et al., 2006; Ma et al., 2008; Esmaeilzadeh, et al., 2014), the focus has mainly been on IFT at the liquid-liquid interface and adsorption. In this study, the wetting propensity of blends of surfactants and nanoparticles on the solid-liquid interface was systematically evaluated to ascertain the efficiency of the suspension over wide temperature ranges.

New high-performance nanoparticle-surfactant systems were formulated, and the so-called nanoparticle-surfactants (NiO/C₁₆TAB, NiO/TX-100, ZrO₂/C₁₆TAB, ZrO₂/TX-100-nanoparticle-surfactants) showed excellent ability as a new form of EOR agent as the systems clearly enhanced wetting on strongly hydrophobic limestone rock. The presence of nanoparticle had a distinct influence on the behaviour of the surfactants as it changed the rheological properties of the fluid while increasing the surfactant effect (Hirasaki and Zhang, 2004). It is evident that cationic surfactant (C₁₆TAB) and its nano-blends (ZrO₂/C₁₆TAB - $\theta = 35$ and NiO/C₁₆TAB - $\theta = 48$) displayed great affinity over non-ionic surfactant TX-100, consistent with reports for carbonate rocks (Austad et al., 1998; Standnes and Austad, 2000; 2003; Sheng, 2011; ShamsiJazeyi et al., 2014) owing to electrostatic interaction. Albeit, ZrO₂/C₁₆TAB demonstrated better efficiency over NiO/C₁₆TAB for all temperatures tested (0-70 °C).

A highly hydrophilic state was attained as ZrO₂/C₁₆TAB consistently enhanced water spread on the modified oil-wet rock surface with increasing temperature. θ_a and θ_r decreased with increase in nanoparticle concentration in the nanofluid. Taken into account the morphological evaluation, the adsorption effect of the nanoparticle-

surfactants as evident via SEM images (Figure 6.2) facilitated the wettability changes towards hydrophilicity as demonstrated by the contact angle measurements, consistent with previous reports (Zhang et al., 2006; Esmailzadeh et al., 2014; Zargartalebi et al., 2015). The spontaneous water imbibition test also showed faster water-imbibing tendencies for nanoparticle-surfactant coated cores (especially $\text{ZrO}_2/\text{C}_{16}\text{TAB}$) than the surfactant coated cores. The wetting trend clearly showed higher wetting propensity was attained in the presence of the complex nanoparticle-surfactant systems. These newly formulated complex systems are novel surface-modifiers than surfactant solution alone with better impact in enhancing formation wettability.

Chapter 7 Zirconium Oxide Nanoparticle: A Case Evaluation

In this chapter, further investigation of limestone rock was conducted using only zirconium oxide due to its efficiency. Three systems containing $ZrO_2 - ZrO_2/H_2O$, $ZrO_2/NaCl$, $ZrO_2/C_{16}TAB$, were tested on the basis of cluster particle size, shape and surface area, particle concentrations, temperature effects, and spontaneous imbibition. Surface characterization of nano-modified substrates was also performed to stimulate a better understanding of rock-fluid interaction and surface wetting.

7.1 Introduction

The knowledge of wetting and spreading dynamics of formation rock is vital for natural and engineering applications. Wetting of solid by liquid involves several interfaces (solid to liquid, liquid to air and solid to air), of which each of these interactions poses different challenges as wetting proceeds, as the surface energy in each system is different (Wenzel, 1936). Since hydrocarbon distribution and its pore space movements are controlled by wettability, changing the wetting state of formation rocks can enhance the reservoir performance and pore-scale fluid displacement. Nanoparticles have been recognized as novel active measures for improving wetting and spreading tendencies on complex mineral surfaces (Xin et al., 2007; Tsuzuki 2013; Guo et al., 2014). Nanoparticle based fluids often form wedge films on the solid interface, and its structuring characteristics facilitate structural disjoining pressure in the wedge film, which is referred to as the force that is normal to the interface. The force is also considered to be even higher near the tip of the wedge than in the bulk meniscus (Zhang et al., 2014). Nano-sized materials can also be used as adsorbents and catalysts for augmenting heavy oil upgrading and recovery (Hashemi et al., 2014).

Different nanoparticles have been experimentally studied for oil recovery evaluation, especially, silica and alumina (Hendraningrat et al., 2013; Giraldo et al., 2013; Zargartalebi et al., 2015). However, in recent times, there is an increasing interest in the use of other oxides of nanoparticles such as zinc, zirconium, nickel, magnesium and titanium. Cheraghian et al., (2013) examined titanium dioxide and silica

nanoparticles potentials in oil recovery and the influence of both nanoparticles on improving the effectiveness of water-based drilling fluid and found that titanium oxide

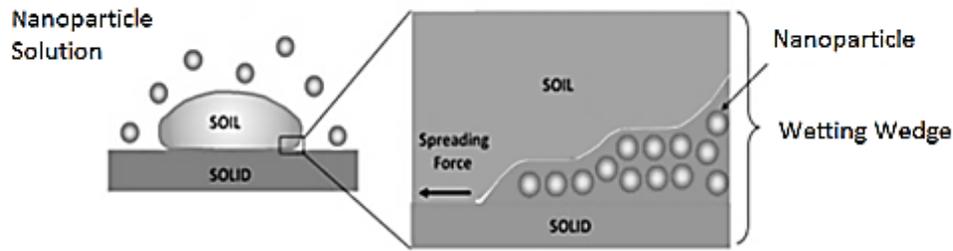


Figure 7.1: Film tension gradient and structural forces that drive oil solid displacement (Zhang et al., 2014).

recovered more oil than silica nanoparticles. Bayat et al., (2015) performed an experimental study on the impact of titanium dioxide, aluminium oxide, and silicon dioxide in limestone media and found that the nanoparticles exhibited varying adsorption capacities on the limestone rock, however, titanium dioxide and aluminium oxide displayed better EOR potentials over silicon dioxide. Here, the focus is on zirconium oxide nanoparticle owing to its superior mechanical, optical, thermal, and chemical properties in comparison to other oxides (Petit and Monot, 2015; Gopalan et al., 2015).

7.2 Experimental Procedure

Three ZrO_2 nanoparticle based fluids were prepared for evaluation using deionized water, sodium chloride brine, and cationic surfactant (ZrO_2/H_2O , $ZrO_2/NaCl$; $ZrO_2/C_{16}TAB$ respectively) at fixed nanoparticle concentration (0.05 wt. %). The NaCl and $C_{16}TAB$ concentrations were 6 wt. % and 0.5 wt. % respectively. All fluid formulations and subsequent tests were performed based on procedures 3.3, alongside specific steps aligned in the experimental procedure section of 5.3 and 6.2 (chapter 5 and 6) for NaCl and surfactant based processes respectively. The deionized H_2O based nanofluids were prepared using a similar approach as procedure 5.3. The fluid densities were also measured 0.847 g/ml (toluene), 0.983 g/ml (ZrO_2 dispersal-water), 0.998 g/ml (ZrO_2 -dispersal-NaCl brine), and 0.979 g/ml (ZrO_2 -dispersal - $C_{16}TAB$).

7.3 Results and Discussion

7.3.1 Contact Angle Measurements

7.3.1.1 Salinization Stability on Hydrophilic Limestone Rock

Generally, system stability is of great relevance as instability can impede efficient process evaluation and impact the system functionality. In principle, the stability of a system can be viewed on the basis of thermodynamics or kinetics. Although thermodynamics facilitate lower energetic states, kinetics can also be a helpful avenue for attaining same tenacity over time. As such, kinetically stable systems can be considered as systems that are thermodynamically unstable but still able to attain stability over extended period of time (Myers, 1990). Owing to the effectiveness of deodocyltriethoxysilane in changing the hydrophilic samples to a suitable hydrophobic state, the stability tenacity of this material was thus tested. Calcite substrate was also used since calcite is the most predominant mineral constituent of limestone rocks, as earlier reported by Lebedev et al. (2014), and also evident in the calcite fraction analysis of Indiana limestone rock in this work. Reference water contact angle (θ) test was initially measured on clean calcite substrate to ensure the samples were originally in a completely water-wet state (clean calcite $\theta=0^\circ$ - strongly water-wet - Figure 7.2i), which was used as a benchmark for subsequent measurements.

During the salinization process, the calcite substrates were fully immersed in a sealable glass bottle containing deodocyltriethoxysilane at 90 °C to achieve adequate surface phase change towards oil-wet. Through the previous chapters, an ideal oil-wet limestone formation has been simulated using this clearly defined oil (silane). The deodocyltriethoxysilane as an organosilane exhibited great efficiency and stable process in changing the hydrophilic samples towards hydrophobicity (Figure 7.2ii; 7.3) even with longer exposure time. This can be attributed to the presence of the alkyl group as deodocyltriethoxysilane is a silane-coupling agent of the alkyl group. Research has also shown that silane containing alkyl groups are particularly effective for changing surfaces towards hydrophobic condition (Mittal, 2009; Plueddemann, 1991; Matisons, 2012), as such several researchers have also generated oil-wet surfaces using silane (Wei et al., 1993; Araujo et al., 1995; Caruana, and Grattoni, 2011; Grate et al., 2012; Al-Anssari et al., 2016; Arif et al., 2016; Dawe, Rahman et

al., 2016). The aging process altered the original hydrophilic calcites (0° - water contact angle) to hydrophobic ($> 90^\circ$ - water contact angle). The silane changed the surface of the calcite via alkylation of the substrate surface, which resulted in high hydrophobicity with great stability with time - an average of $88^\circ \theta_a$ in air and $151^\circ \theta_a$ in oil (Figure 7.2ii).

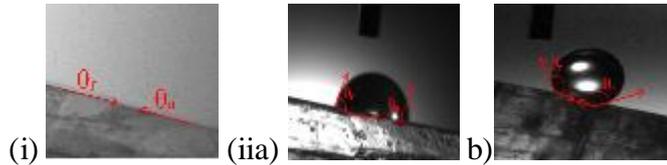


Figure 7.2: Images of contact angle of samples: (i) clean rock substrate (initial surface at hydrophilic condition); (ii) oil-modified rock (a) air; (b) toluene (demonstrating surface hydrophobicity upon exposure to the silane).

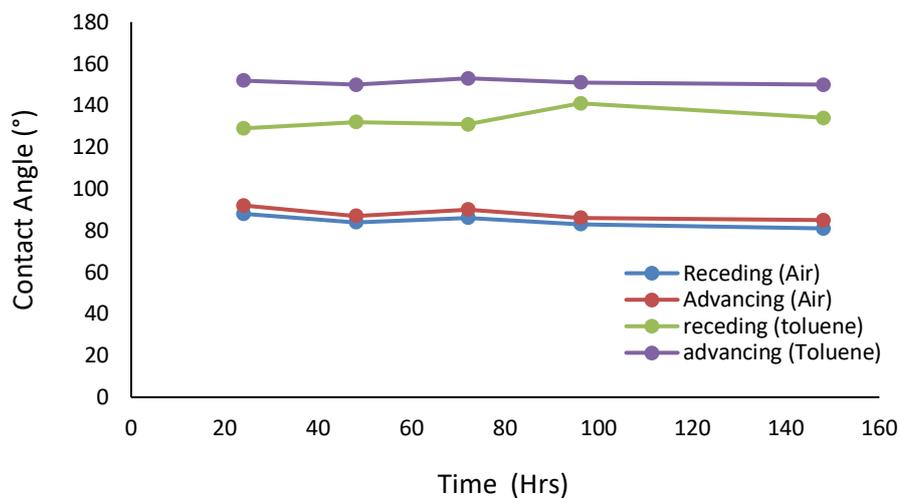


Figure 7.3: θ_a and θ_r for a drop of water on salinized rock surface over time in: a) air; b) oil.

7.3.1.2 Effect of Nanoparticles on Wetting

Although wetting is a thermodynamic process, the pace and extent to which wetting occurs depend on the magnitude of the free energy change. For instance, for a drop of water resting on a solid surface, different specific energy of the solid interface will exist for the wetted regions under the drop and the dry area around the drop. If the

wetted region exhibits a lower specific energy (Wenzel, 1936) a spontaneous spread may occur, however, if equilibrium is yet to be attained then further spreading occurs leading to an increase in the wetted regions under the drop and the free liquid surface over the drop.

The understanding of wetting patterns at micro-scale and nano-scale can be greatly improved by quantifying wettability through contact angle measurements. This can enhance the knowledge of how liquid droplets behave when in contact with surfaces where a chemical micro-scale or nano-scale pattern is imposed. With respect to reservoir rocks, such measurements provide further insights on the formation rocks affinity and how the rocks wetting inclination impacts process efficiency. To ascertain the samples wetting inclinations, the hydrophobic rock substrates were subjected to contact angle tests in various systems - ZrO₂ nanoparticle mix in deionized water (DI-H₂O), brine (NaCl) and surfactant (C₁₆TAB). Fixed ZrO₂ nanoparticle concentrations (0.05 wt.%) was used based on its efficiency evident in the previous chapters; brine-NaCl- 6 wt.%, and surfactant-C₁₆TAB - 0.5 wt.%) were tested at ambient temperature (22 °C ± 1 °C).

The nanoparticles upon contact with the surface of the substrates form wedge films or ordered structures near the contact line. The particles adsorb on the surface of the rock as evident in the morphological evaluation (Figure 7.10; 7.11). The deposited films spread on the calcite surface, and the solutes in the liquid (nanoparticles) enhanced the rock wetting. Similarly, Zhang et al. (2014) reported that nanoparticle based fluids readily spreads over solid surfaces removing the oily soils on the surface of the solid, although efficiency is dependent on the nanoparticle volume fraction, particle size and polydispersity. Figure 7.4 clearly shows a decrease in θ for all three systems in air and oil. The presence of the ZrO₂ nanoparticles in DI-water enhanced the rock wetting potentials, however, the presence of the monovalent ions (NaCl) and cationic surfactant improved the performance of the nanoparticle even much more, thus, better efficiency was attained on application of the formulations (ZrO₂/H₂O - θ_a - 84°; ZrO₂/NaCl - θ_a - 60°; ZrO₂/C₁₆TAB - θ_a - 46°). This influence on nanoparticle behaviour is due to the physiochemical interactions or electrostatic forces between the rock surface and the dispersals (Muherei and Junin, 2009; Li and Cathles, 2014). The

water droplet advancing across the substrate surface exceeds the receding, thus, water-advancing θ is of great relevance to reservoir wetting and the imbibing water front.

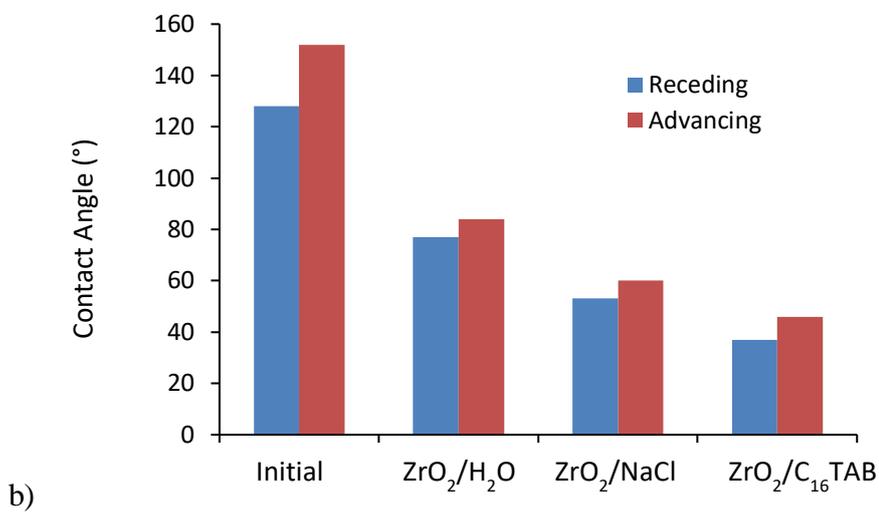
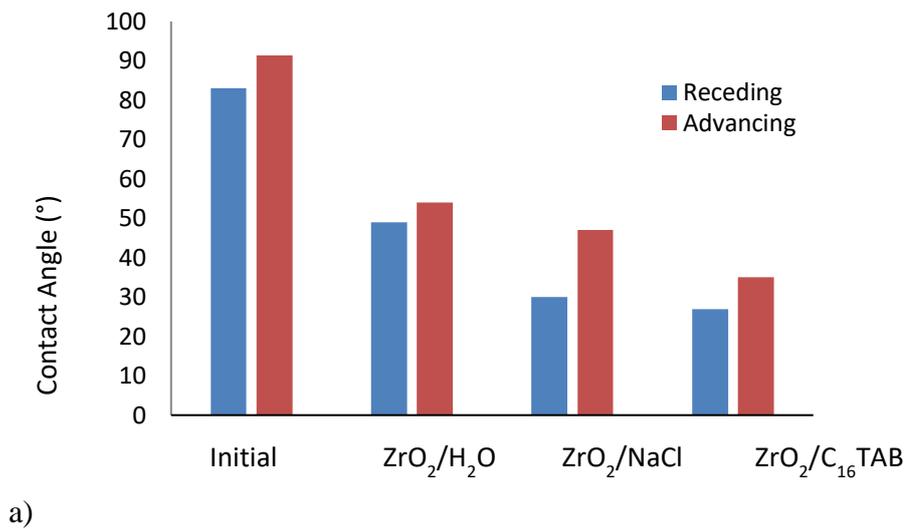
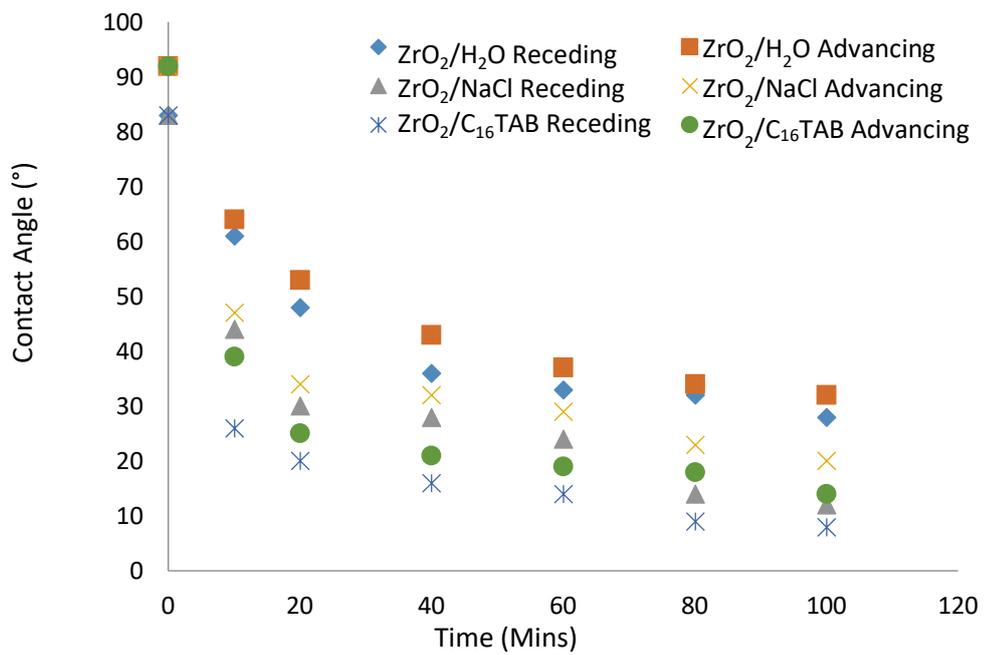


Figure 7.4: θ_a , θ_r for drop of water on calcite substrate at ambient temperature showing initial and modified contact angle measurements in a) air, b) oil.

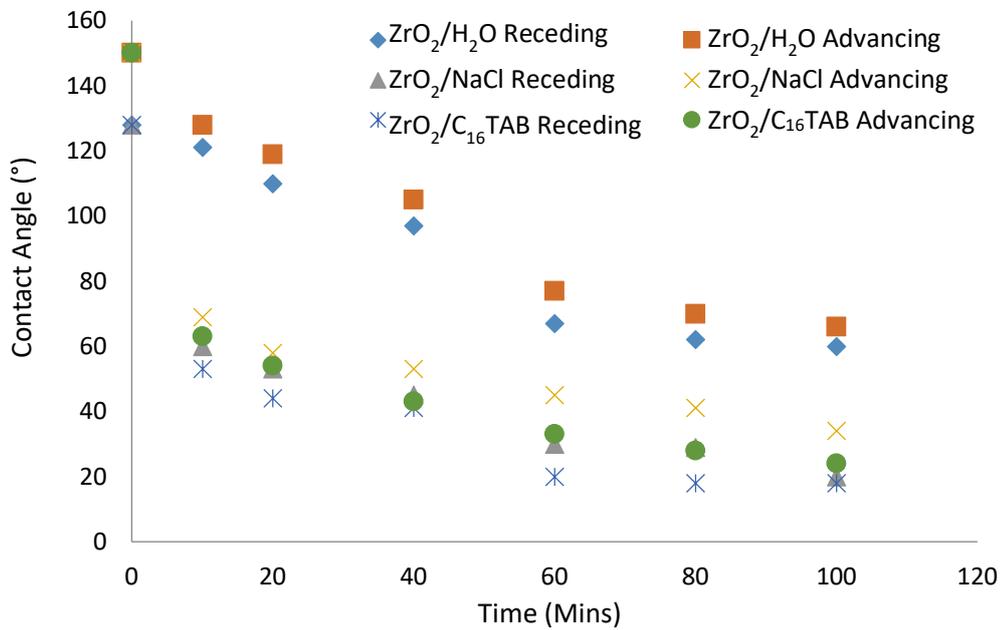
7.3.1.3 Elevated Temperature Effect on Wetting Stability

Stabilization of colloidal based fluid is often challenging, be it an emulsion, a suspension or foam due to their two-phase systems. The forms in which these systems exist depend on the combination of gas, liquid or solid interactions. Emulsion based systems require a combination of liquid-liquid interfaces, while for suspensions or foams, a solid-liquid or gas-liquid interface is required. Nanoparticle based fluids also exist as colloidal two-phase systems and can appear in any of these forms as evident in chapter 2. Although these materials have unique properties that make them superior over conventional bulk materials (chapter 1 and 2), the long-term stability of nanoparticles based fluid is vital for process optimization be it a suspension or an emulsion. Typically for two phases to be in contact, a region through which the properties of the system changes from one phase to another must be in existence, like in the case of the boundary between a solid and a liquid. The stability of such boundaries is, therefore, an indication that an interfacial free energy exists in the system. As such, a boundary between two phases is considered stable if it exhibits a positive free energy at the interface (Myers, 1990; Yuan and Lee, 2013). It is thus necessary to examine nanoparticle-based fluids as a function of time to ascertain the behaviour of these dispersals at elevated temperature, as poor stability can inhibit efficient porous media transportation of nanoparticles under harsh reservoir conditions and overall process efficiency. Such a scenario, with surfactant as dispersal, which is known to be susceptible to, or degradable at high temperatures can become even more complicated in the presence of other chemicals.

The effect of aging stability of the dispersing fluids at fixed elevated temperature above the ambient condition (70°C) was assessed as a function of time. The same ZrO₂ nanoparticle, NaCl brine, and C₁₆TAB surfactant concentrations were used as above (Section 7.3.1.2). The results show that the water contact angle decreased even better in the presence of the nanofluids at high temperature (70 °C) when compared to the ambient temperature condition of 22°C even with the increase in aging time (Figure 7.5). Exposure of the nanoparticle-based fluids (ZrO₂/H₂O, ZrO₂/NaCl, and ZrO₂/C₁₆TAB) to the rock surface increased the reactant concentration near the reactive surface, thus, yielding synergistic effects, which in turn improves the



a)



b)

Figure 7.5: θ_a and θ_r for different systems (ZrO₂/H₂O, ZrO₂/NaCl, ZrO₂/C₁₆TAB) as a function of time at 70 °C temperatures in a) air, b) oil.

formation wetting inclination, consequently, a decrease in θ for all three systems in air and in oil was attained.

This behaviour can also be attributed to the change in the nanofluid chemistry aiding better absorption potentials of the nanoparticles on the surface of the calcite at high temperature. The favourable physico-chemical interactions between the rock surface and the ZrO₂ nanofluids at high temperature enhanced the continuous rock surface change from hydrophobic to hydrophilic state, especially with C₁₆TAB surfactant based system as cationic surfactants generally exhibited strong adsorption inclinations on the solid surfaces. Such characteristics make the C₁₆TAB surfactant ideal for modification of limestone rock surfaces in the presence of nanoparticles at high temperature. This shows similar behavioural trends with earlier reports (Hjelmeland and Larondo, 1986; Saner et al., 1991, Bera et al., 2012), where high temperature enhanced water-wetting tendencies while improving the system stability (Kvítek et al., 2008, Mohajeri et al., 2015; Tajmiri et al., 2015). Mollaei and Maini (2010) also established that high temperature can also enhance the desorption of polar compounds affecting the wetting inclination of the formation rock surfaces in a typical crude oil system.

7.3.2 Spontaneous Imbibition

The contact angle test and spontaneous imbibition test are both targeted at assessing wettability efficiency for all samples tested. However, there exists a remarkable variation in the test methods, which is primarily based on how much of the surface is exposed to the wetting phase or wetted by water.

During the contact angle test, only the outer surface area of the sample was exposed to a drop of water without consideration for the inner surface of the rock, whereas, in the spontaneous imbibition tests, the whole sample is exposed to the wetting phase (Figure 7.6). Thus, the inner surface area of the rock can be accounted for upon displacement of the non-wetting phase (oil) by the wetting phase. For instance, in an oil-wet limestone rock, for oil to be displaced by the wetting phase (water/surfactant/brine solutions etc.), the capillary barriers must be overcome. If the wetting phase penetrates the rock pores, two key possibilities exist; (a) rock wettability change; (b) the presence of a positive capillary due to the wettability change. Such

scenarios can enhance recovery potentials especially if the formation rock is hydrophilic. Figure 7.6b (i-ii) shows a typical case of an oil-wet rock or core sample placed in an imbibition cell containing NaCl brine (the wetting phase). The brine imbibes into the rock or core pores and pushes out the oil in the cores. Such expelled oil sticks on the rock surface while being collected at the top of the cell simultaneously, which can be used for further estimation of the recoverable oil, however, this was not the focus area in this study. Here, we tested the spontaneous water imbibing potentials of the hydrophobic rocks for all three systems (ZrO_2/H_2O , $ZrO_2/NaCl$, $ZrO_2/C_{16}TAB$) under evaluation using procedure 4.3.3.3 and procedure 6.2.

The properties of the limestone rock and the rock compositions are in table 7.1 and 7.2 respectively. Figure 7.7 shows the spectrum analysis of the calcite fraction of the Indiana rock. The ZrO_2 nanoparticle concentration was 0.05 wt. %, brine-NaCl - 6 wt. %, and surfactant - $C_{16}TAB$ - 0.5 wt. %. The oil-wet core plugs were subjected to water imbibition test to further ascertain the wetting efficiencies of the systems. During contact angle measurements, calcite substrates coated with $ZrO_2/C_{16}TAB$ and $ZrO_2/NaCl$ fluids demonstrated better wetting propensities than the ZrO_2/H_2O system. Similarly, the core plugs coated with $ZrO_2/C_{16}TAB$ and $ZrO_2/NaCl$ exhibited more rapid water imbibing propensities than the ZrO_2/H_2O (Figure 7.8). The efficiency of the systems may be due to efficient surface adsorption of the particles on the pore walls of the rock, which invariably rendered the rock surface sufficiently water wet.

When a formation rock exhibits a considerable water-wet condition, the reservoir rock has higher potentials for allowing water into the tight rock matrix pores. Thus, more water-wet rocks allow higher rates in spontaneous imbibition, with possibilities of improving recovery. However, maintaining water wetness of formation rocks depends on the extent to which the water film on the rock surface is stable. The presence of unstable water films can lead to oil migration to the rock surface (like the behaviour observed in Figure 4.5), thus, changing the rock surface wettability. With respect to a typical crude oil system, such behaviour would lead to adsorption of polar compounds on the solid surface which in turn changes the wetting properties of the solid (Morrow, 1990).

7.3.3 Mechanistic Quantification

Here, the rock surface topography, morphology, and cluster size, shape and surface area distribution of the nanoparticle was assessed (See Procedure 3.3.3.2).

7.3.4 Surface Characterization

Quantification of the surface changes of the sample was performed since formation wetting is also controlled by surface morphology and topography. The ZrO_2 nanoparticles were sufficiently diluted to avoid the formation of excessively large aggregates that can impede efficient microscopic investigations.

7.3.4.1 AFM

The topographic evaluation by AFM (Figures 7.9) provides vital insights into the physico-chemical interactions and surface roughness dynamics. The effect of surface roughness on contact angle has been earlier reported by Wenzel (1936 - refer to Equation 2.7- chapter 2) who established that hydrophobicity yields even more hydrophobicity owing to surface roughness (Figure 7.2 shows a typical hydrophobic state - Higher θ -value as evident in Figure 7.3). However, the treatment of hydrophobic solid surfaces (formation rocks) with appropriate surface-active agents can change the



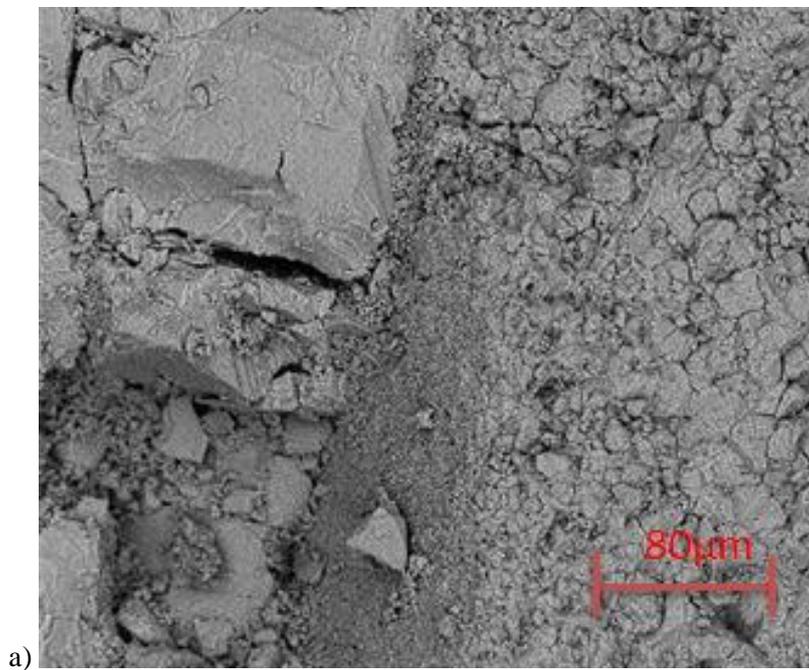
Figure 7.6: Contact angle and spontaneous imbibition (a) contact angle: outer surface area wetted by a drop of water on calcite sample; (b) Imbibition: the whole core sample is wetted by brine (NaCl) in an imbibition cell at different temperature conditions during an imbibition experiment. As the brine imbibes into the cores, the oil is pushed out of the cores to the rock surface and collected at the top of the cell (i) ambient temperature (22 ± 1 °C); (ii) 50 ± 1 °C showing oil droplets that have been pushed out of the cores on the outer surface of the rocks.

Table 7.1: Core properties.

Cores	Length (cm)	Diameter (cm)	Porosity (%)	Permeability (K_{air} - mD)	Permeability (K_{Klin} - mD)
ZrO ₂ /H ₂ O	5.75	2.11	20.09	274.27	224.73
ZrO ₂ /NaCl	5.73	2.13	21.09	295.62	243.87
ZrO ₂ /C ₁₆ TAB	5.72	2.12	19.40	295.35	243.07

Table 7.2: Rock composition.

Element	Symbol	Atomic concentration (%)	Weight concentration (%)
Calcium	Ca	62.76	57.24
Carbon	C	10.78	24.64
Oxygen	O	26.46	18.12



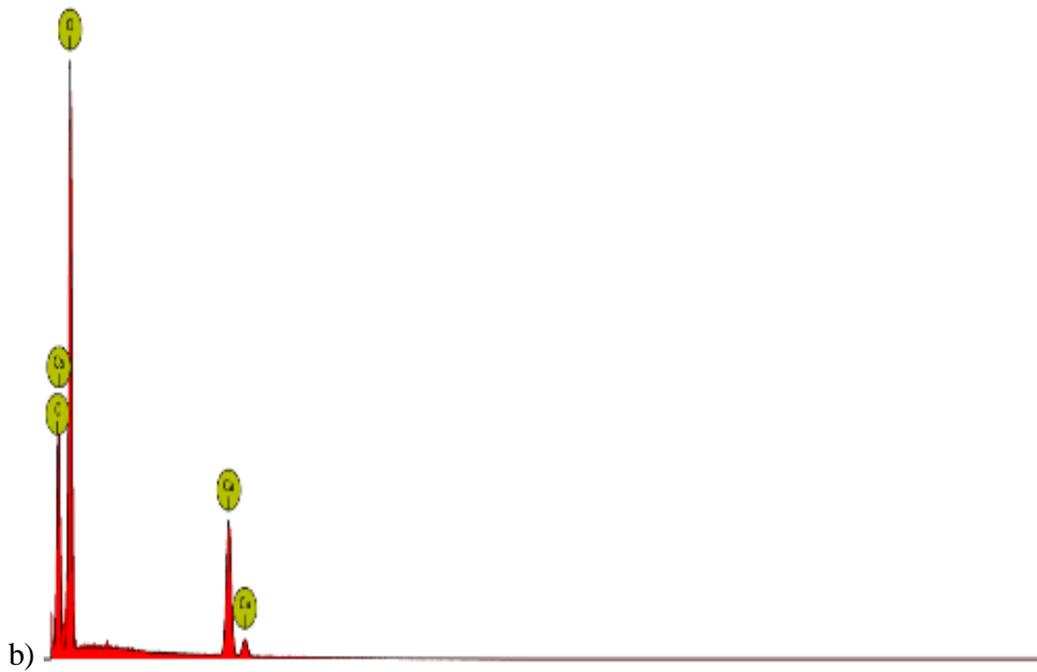


Figure 7.7: Spectrum analysis of the calcite fraction of the Indiana rock.

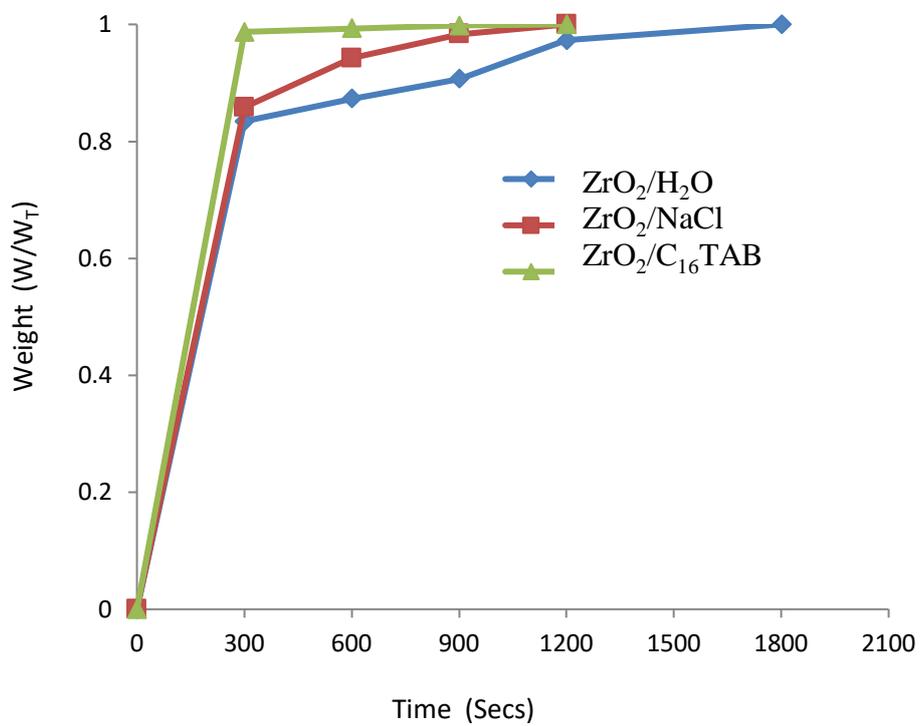


Figure 7.8: Spontaneous water imbibition in limestone rock as a function of weight and time.

surface chemistry of such solids from hydrophobic towards hydrophilic conditions. The exposure of the calcites to the different nanofluids (ZrO_2/H_2O , $ZrO_2/NaCl$, $ZrO_2/C_{16}TAB$) enhanced formation of adsorbed layers on the rock surface (SEM images -7.10) and subsequent reduction in θ (Figure 7.4; 7.5 - contact angle). Figure 7.9 and Table 7.3 show the various topography and surface roughness of the three systems. The ZrO_2/H_2O (Figure 2a) nano-coated samples had the lowest peak height of 250nm (black - 0 nm; white - 250nm) in comparison to the $ZrO_2/NaCl$ and $ZrO_2/C_{16}TAB$ nano-coated calcites and a corresponding low roughness average (S_a - 20 nm) and root mean square roughness (RMS - 27 nm). Systems with higher surface roughness exhibited better decreased θ (θ_a and θ_r - see section 7.4).

7.3.4.2 SEM

The morphological evaluation (Figure 7.10; 7.11) shows the nanoparticle-coated substrate - indicating the nanoparticle adsorption on the surface of the calcite, which facilitated the wettability changes observed via contact angle (Section 7.3). $ZrO_2/C_{16}TAB$ and $ZrO_2/NaCl$ showed more uniform surface particle distribution than ZrO_2/H_2O . However, the presence of surfactant improved the nanoparticle absorption performance yielding a better dispersed systems and efficient decrease in contact angle (Figure 7.3 and 7.4) than the $ZrO_2/NaCl$ and ZrO_2/H_2O systems.

Table 7.3: Surface roughness

Samples	S_a (nm)	RMS (nm)
$ZrO_2/C_{16}TAB$	20	27
$ZrO_2/C_{16}TAB$	20	31
$ZrO_2/C_{16}TAB$	140	190

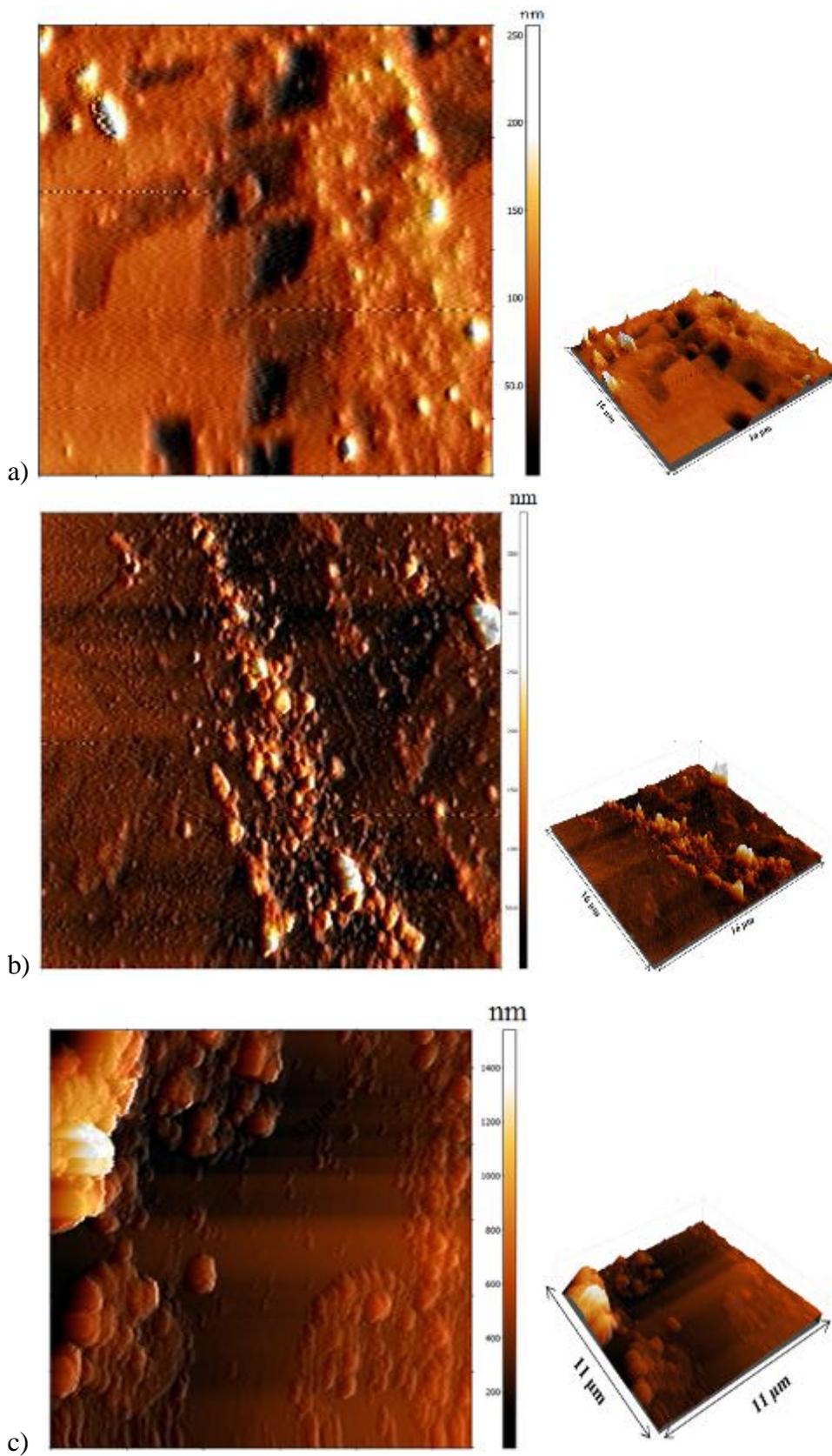


Figure 7.9: AFM images of nano-coated substrates a) $\text{ZrO}_2/\text{H}_2\text{O}$, b) ZrO_2/NaCl , c) $\text{ZrO}_2/\text{C}_{16}\text{TAB}$. The low peak heights depict low surface features (dark shades) and high peak heights show high surface features (lighter shades).

7.3.5 Cluster Particle Size, Shape, and Surface Area

Particle size, shape and surface area are important factors for consideration during nanofluid processing and applications, as these parameters influence colloidal properties. Here the nanoparticle cluster sizes and surface area in distributions for all three systems ($\text{ZrO}_2/\text{H}_2\text{O}$, ZrO_2/NaCl , $\text{ZrO}_2/\text{C}_{16}\text{TAB}$) were measured for a more fundamental understanding of the underlying adsorption and wetting efficiency. The SEM images were filtered and segmented and the nanoparticle cluster sizes were measured (See Procedure 3.3.3.2). Quantification of the particle size for the systems enabled the detection of the variations in the nanoparticles mean size diameter as well as the surface area distribution (Figure 7.12 and Table 7.4).

Figure 7.10 clearly shows the spherical shape morphology of the ZrO_2 , consistent with Eshed et al. (2011); Zargartaleb et.al. (2015) and Son et al. (2015); similar shape morphology was also observed in Figure 7.11(nano-cluster images). With respect to particle size, nanoparticles suitable for nanofluid production are particles with sizes in the range of 1-100nm. Figure 7.12a and Table 7.4 show the cluster size and mean size distribution respectively for over 30 individual nanoparticles in the three systems. Although the cluster size appears large in Figure 7.11 in comparison to Figure 10, the cluster particle sizes in all systems were less than 100 nm (Figure 7.12a). The mean cluster size is in practical agreement with the ZrO_2 particle size reported in the earlier chapter (chapter 4 - ZrO_2 mean particle size - ~ 28 nm) and as also specified by the manufacturer (Sigma Aldrich - ZrO_2 particle size - < 100 nm). This is an indication of well dispersed or less agglomerated systems, as poorly dispersed systems form agglomerated clusters with fractal-like shapes (Ramakoteswaa, Gahane and Ranganayakulu, 2014). A comparison of the differences in interaction of the three systems ($\text{ZrO}_2/\text{H}_2\text{O}$, ZrO_2/NaCl , and $\text{ZrO}_2/\text{C}_{16}\text{TAB}$) shows that the NaCl based particles (ZrO_2/NaCl) exhibit similar particle size and surface area distribution that is almost in the same order as that of the DI water ($\text{ZrO}_2/\text{H}_2\text{O}$). Both systems showed relatively large particle cluster size diameters and surface area distribution (Table 7.4; Figure 12a, b) in comparison to the C_{16}TAB , which may be due to solid particles swelling or expansion effect towards the surface of the particles. Generally, nanoparticles regardless of their small particle sizes are easily susceptible to aggregation in liquid suspensions, which promotes surface adsorption of neighbouring particles or molecules. This behaviour is mainly due to the particles large surface-to-

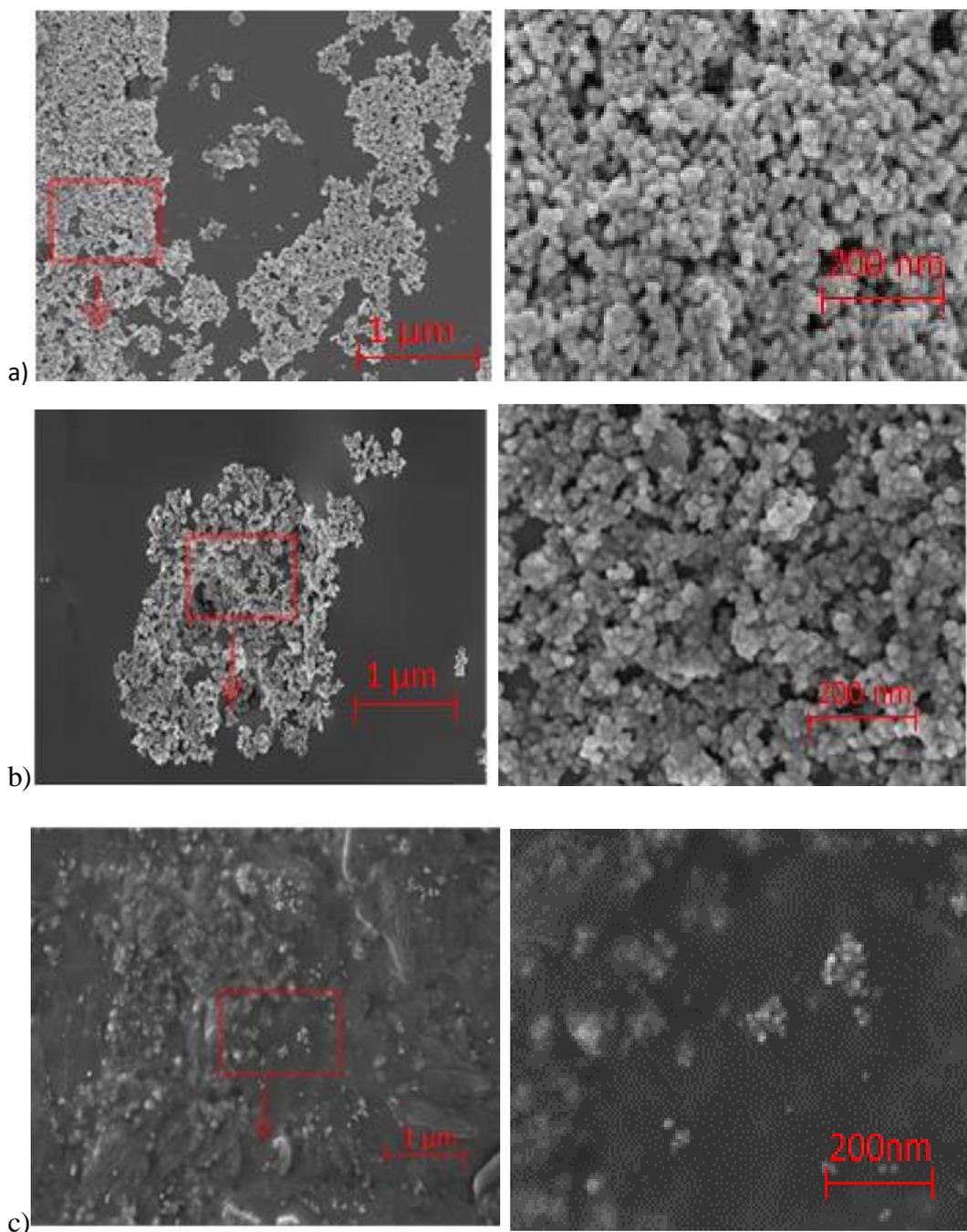


Figure 7.10: SEM images of nano-coated calcite substrate in a) ZrO_2/H_2O , b) $ZrO_2/NaCl$, d) $ZrO_2/C_{16}TAB$.

Table 7.4: Nanoparticle cluster size and surface area

Samples	Size		Surface area	
	Size Distribution Range (nm)	Average Size (nm)	Surface Area Range (m ² /g)	Average Surface Area (m ² /g)
ZrO ₂ /H ₂ O	1-85	33	1-5737	1365
ZrO ₂ /NaCl	1-93	45	1- 6807	1921
ZrO ₂ /C ₁₆ TAB	1-36	8.7	1- 1033	113

volume ratio and poor wettability in the metal matrix (Yang et al., 2004; Yu et al., 2008; Wang and Mujumdar, 2008; Khalil et al., 2017). Also, colloidal particles accumulate surface charge in the presence of water as solid-water interfaces have ionizable sites. This behaviour is even more obvious in the presence of electrolytes. The nature and magnitude of surface charge depends on the compositions of the electrolyte and the concentration thereof. For instance, surface charge can change dramatically upon additions of small amount of salts such as NaCl, which primes the formation of the electrical double layer between the surface charge and the diffuse ion layer surrounding the particle. The thickness of such layer is greatly dependent on the ionic strength of the electrolyte and in the process, electrostatic repulsion occurs if two identical charged surfaces are in contact. However, this behaviour is dependent on the accumulated ions between the particles and the ionic strength of the solute. If the ionic strength is somewhat low, then such double layer thickness will be in the order of the particle size (Evans, 1999; Li and Cathles, 2014). Albeit, the electrolyte weakens the particles electrostatic repulsion forces leading to faster aggregate formation especially at sufficiently high salt concentrations. Such attractive interactions lead to the particle attachment to each other, forming aggregates with an open disordered structure (Evans 1999; Roberts, 1998). Upon close visual observation of Figure 7.10; 7.11, the particles suspended in water and NaCl appears to be somewhat aggregated (low inclinations) than that of the surfactant. This behaviour, even at such low inclination can be attributed to the forces of attraction between the particles that tend to overcome its electrostatic repulsion forces. The presence of water or NaCl salt may have induced a

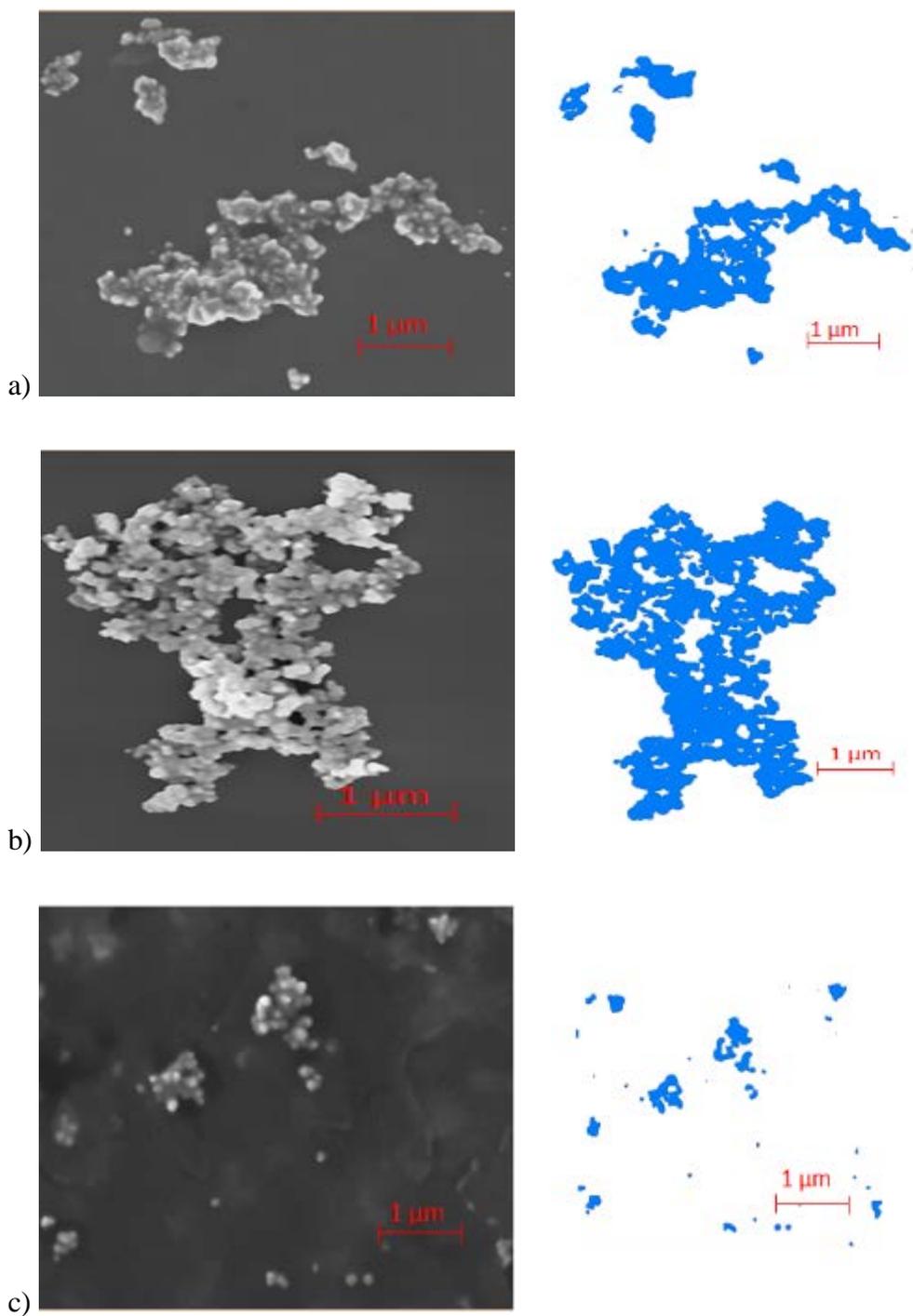
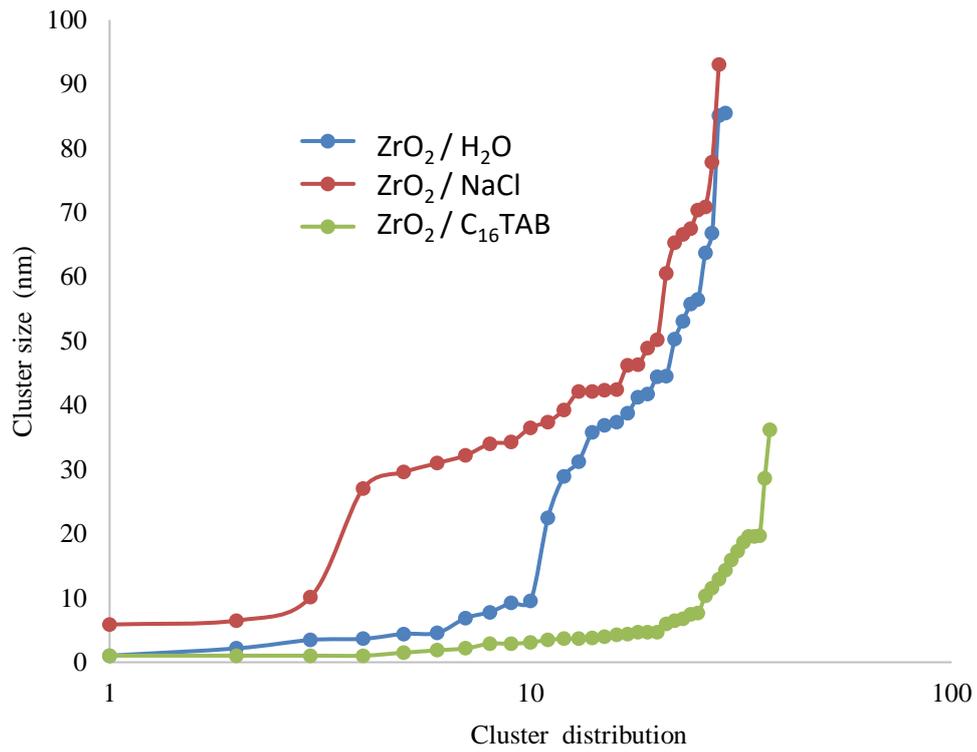
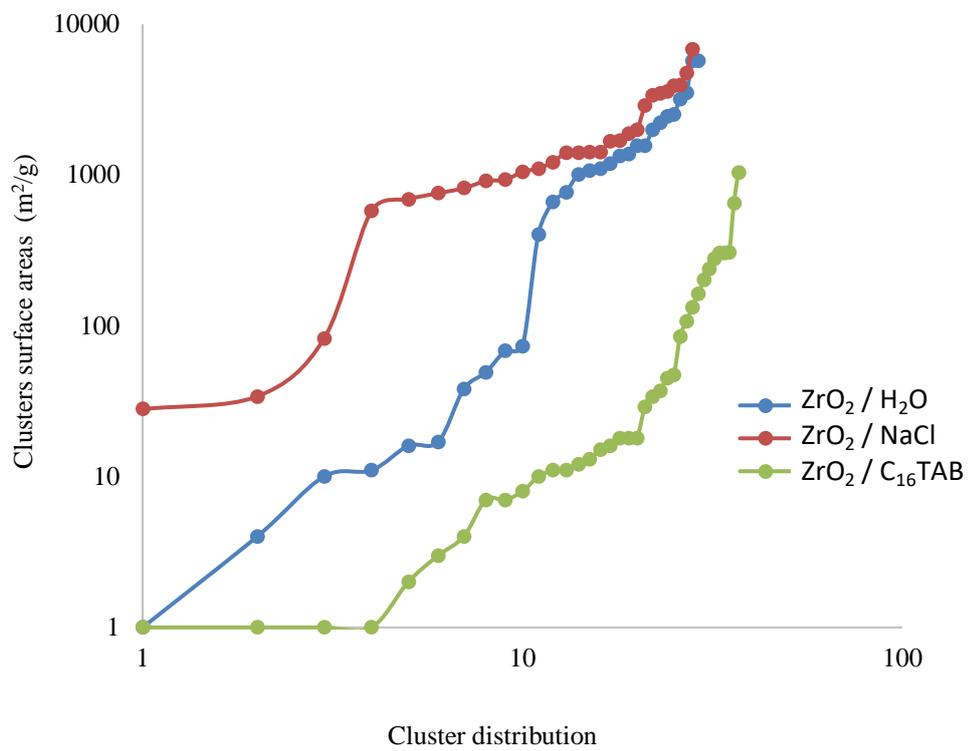


Figure 7.11: Filtered and segmented 2D images of ZrO_2 nano-clusters (a) $\text{ZrO}_2/\text{H}_2\text{O}$; (b) ZrO_2/NaCl (c) $\text{ZrO}_2/\text{C}_{16}\text{TAB}$.



a)



b)

Figure 7.12: ZrO₂ nanoparticle cluster size and area as a function of cluster distribution.

rather rapid aggregating inclination owing to van der Waals potentials. However, in the surfactants based systems, the particles surfaces are enhanced as the surfactants provide efficient coating to induce electrostatic repulsions that counterbalances the van der Waals attractions, which in turn improves the dispersion stability of the system (see the previous chapter). The nanoparticle coated with surfactants become more stable against re-aggregation owing to the presence of repulsion forces between nearby surfactant- coated nanoparticle. Thus, the system yields better adsorption and wetting effects as evident in the contact angle and spontaneous imbibition measurements (section 7.3) as surfactants enhanced adequate dispersion of the nanoparticles. Its efficiency can be attributed to a better stabilized system as system stability impedes particle-to-particle aggregation inclinations.

Since the rock surface wetting is facilitated by well dispersed nanoparticles in based fluids, high possibilities for efficient wettability change exists for uniform or more stable systems than nanofluids with high particle aggregation inclinations. Such will most likely interact with the surface of the agglomerates than the formation rock itself, which can substantially impact the overall fluid efficiency, rock wetting performance, and even impede efficient nanofluid transport through porous media irrespective of the particle size in distribution. It is therefore vital to ensure efficient dispersals of nanoparticles in suspensions to impede agglomeration tendencies which can enhance the nanofluids efficiency.

7.4 Conclusions

It is well established that limestone rock exhibit complex microstructures (Moore, 2001; Tucker and Wright, 2009; Lebedev et al. 2014) that impacts reservoir wetting preference. Thus, wetting tests were conducted at various conditions using Indiana limestone cores and calcite substrates as calcite is a predominant mineral constituent of limestone rock (Lebedev et al. 2014; Nwidee et al., 2017). The oil-phase stability investigation of deodocyltriethoxysilane showed a stable hydrophobic behaviour with time. Exposure of the hydrophobic rocks to the ZrO_2 nanoparticle based systems facilitated a change in wettability. The ZrO_2 based systems were effective in altering the hydrophobic rock substrates to hydrophilic conditions although at varied degrees. The mechanistic quantification provided morphological and topographical evidences

indicating adsorption of the nanoparticle on the rock surface and the corresponding surface roughness. We also found that particle size influences the particle aggregation tendency, deposition, and the rock surface homogeneity, however, particle size in suspension can be substantially controlled through the use of efficient dispersals and the fluid processing methods. The $ZrO_2/C_{16}TAB$ systems consistently displayed better efficiency over ZrO_2/H_2O and $ZrO_2/NaCl$ in both contact angle and spontaneous imbibition tests.

Chapter 8 Conclusions and Recommendations

This chapter consists of the conclusions and recommendations. The conclusions provide highlights from the chapters of this work and recommendations are made for further studies.

8.1 Conclusions

This study evaluated the possibilities of nanoparticles to be of substantial benefit to enhanced oil recovery through wettability alteration. This was achieved by performing qualitative and experimental evaluations. The qualitative studies entail an in-depth critical analysis of EOR methods currently in practice in the oil fields and its relation to wettability and nanoparticles. Series of laboratory experimental studies were conducted to investigate the potentials of ZrO₂ and NiO nanoparticles on wettability alterations of hydrophobic limestone reservoirs. The inferences drawn from this study are below.

8.1.1 Wettability Alteration via Nanoparticle Based Fluids

In most applied and industrial processes, wetting of solid by liquid is a common phenomenon apparent therein. With respect to reservoir rocks, ideally, the formation rocks can exhibit hydrophilic, hydrophobic or a mixed-wet behaviour. The extent to which the formation rock exhibits either of these wetting states is ascertained via evaluation of wettability, which has remained a key underlying factor that controls fluid displacement and hydrocarbon recovery efficiencies.

In this study, the wetting propensities of nanoparticle-based fluids on wettability alteration of hydrophobic limestone rocks was investigated to better understand wetting as it is important for a variety of processes in subsurface reservoir evaluations, and for characterization and selection of materials. Thus, the synergistic effect of blends of two specific metal oxide nanoparticles (zirconium oxide - ZrO₂ and nickel oxide - NiO), brine (sodium chloride), surfactants (cationic - cetyltrimethylammonium bromide and nonionic -Triton X-100), or deionized water systems on solid-liquid

interface was investigated by quantification of wettability through contact angle, spontaneous imbibition, and mechanistic approaches.

The structure, morphology, topography, and crystallinity phases of the nanoparticles were characterized by atomic force microscopy, scanning electron microscopy, scanning transmission electron microscopy, and X-ray diffraction for a better understanding of the nanoparticles properties. These surface characterization and property evaluations are of great relevance to this study as it provides morphological and topographical evidence, on how precisely the nanoparticle-based fluids adsorbed on the solid surface and how that affected surface roughness, particle-to particle agglomeration inclination and subsequent wetting.

The nanoparticles were subjected to wetting tests in air and oil by contact angle measurements on basis of particle concentration, time, salinity, and temperature to simulate subsurface harsh conditions. This is particularly important as numerous applied and industrial practices occur at the line of contact between a liquid and a solid phase. Any liquid droplet in contact with a solid surface exhibits an angle of contact usually measured through the liquid, which can provide fundamental information on rock-fluid interaction. This phenomenon is not yet understood in hydrophobic limestone formation, specifically in complex rock-oil-fluid-nanoparticle systems. In this study, deionized water was considered as the wetting phase for all tests, which signifies phase displacement in a typical reservoir where one phase displaces another. Contact angles were thus estimated via the water phase on a tilted platform, as such tilt allow for quantification of both advancing and receding contact angles at the same time interval. It is also a standard well established technique which gives results widely accepted and (relatively) easily interpreted and analysed. Spontaneous imbibition was also performed to ascertain the water imbibing potential of hydrophobic limestone cores.

The inferences drawn from this study are:

- Changing hydrophobic formation rock towards suitable wetting conditions through efficient method is a key strategy for improving reservoir performance. A typical scenario is the case of capillary pressure, which is more efficient when a system is water-wet than when it is oil-wet. As such, it is vital that formation rocks

are at hydrophilic conditions for favourable capillary pressure effect, as this can improve efficient and spontaneous oil displacement from the porous media.

- A prime characteristic of nanoparticles in EOR is its ability to improve the property of the dispersal even at very low particle concentrations (Chapter 4-7) in the suspensions, and its capacity to significantly alter reservoir rock surfaces
- Favourable adsorption of the nanoparticles (ZrO_2 and NiO) on the limestone rock surfaces enhanced the inevitable change in wettability from oil-wet to water-wet in a very efficient way.
- Nanoparticles functionality or effectiveness is influenced by the processing methods (section 3.3.2.2), nanofluid homogeneity, stability, and the fluid-solid interface interaction. The particles should be uniformly dispersed in the suspensions or emulsions to ensure the stability and homogeneity of nanofluids, aside the use of additives or stabilizers.
- Particle size influences deposition, rock surface homogeneity, and particle aggregation tendency (section 4.2 and 7.3.5) as such, particle size should be controlled by using appropriate preparation methods, and suitable/compatible dispersals. Well-dispersed nanoparticles exhibit low aggregation affinities and impede protonation tendencies or the growth of particle sizes above 100 nm (>100 nm).
- The formulated complex systems are novel surface-modifiers (chapter 4-7), thus, recommended as potential stabilizers of dispersed systems, and ideal for implementation in EOR project design in limestone formations for better process efficiency.

Huge potentials for incremental oil recovery exist through the application of EOR processes; however, the volume of recoverable oil is greatly dependent on the implemented EOR technique. The continuous evolution of EOR processes in the near future should take a synergistic approach from different EOR technologies and the adoption of innovative approaches (nanoparticles) that can substantially address the underlying reservoir issues such as wettability that impedes process efficiency. Adequate knowledge of a formation wetting inclination is essential to avoid poor and un-informed choices, as lack of awareness or understanding of reservoir wetting inclinations can lead to formation damage and impede overall process productivity. We thus conclude that wettability alteration can be optimized through the use of

nanofluids, with possibilities for improved hydrocarbon recovery, and CO₂ geo-storage and soil de-contamination processes can be maximized.

8.2 Recommendations

Further studies should also be conducted using these metal oxide nanoparticles-ZrO₂ and NiO on residual trapping effects, as it will be interesting to examine the role of these materials in CO₂ geo-storage. Another potential area for further investigation of nanoparticles is on hydrate formation potentials.

(1) Investigations on CO₂ Geo-Storage using Nanoparticles

This study has shown that nanoparticles have wide-ranging potentials in oil and gas processes. The literature review shows that nanoparticles are effective in carbondioxide related processes. The effect of residual trapping capacity in water-wet or oil-wet reservoirs in the presence of nanoparticles at typical storage conditions is an area that has not yet been considered. A further investigation of these metal oxide nanoparticles - ZrO₂ and NiO, on their potentials in CO₂ geo-storage for investigation of residual trapping efficiency in water-wet or oil-wet formations through micro-CT (X-ray micro-computed tomograph- μ CT) investigation is recommended, since sequestration can be directly linked to CO₂ EOR.

(2) Gas Hydrate Formation with Nanoparticles

Another interesting area for future study consideration is the use of nanostructured materials for hydrate formation, of which nanoparticle in particular are of interest owing to the unique properties of this material and its based fluids such as high thermal conductivity. This will be of benefit to the oil and gas industry, especially for natural gas transportation and storage processes. A limitation in the transportation of natural gas using hydrate is its slow pace and relatively poor storage capacity. ZrO₂ and NiO metal oxide nanoparticles or any suitable categories of nanoparticles (Magnetic or metallic) as earlier reported in chapter 2 is recommended for investigation on their potentials in natural gas transportation and storage capacity enhancement.

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DH Dale, Evelyn H. <Evelyn.Dale@NETL.DOE.GOV> Wed 9/03/2016 1:10 AM

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Title: Mechanisms of Wetting Alteration by Crude Oils
Author: J.S. Buckley, New Mexico Institute of Mining and Technology; Y. Liu, New Mexico Institute of Mining and Technology; S. Monsterleet, New Mexico Institute of Mining and Technology et al

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Title: Nanoparticle-Stabilized Emulsions for Applications in Enhanced Oil Recovery

Conference Proceedings: SPE Improved Oil Recovery Symposium

Author: Tiantian Zhang, U. of Texas at Austin; Drew Davidson, University of Texas at Austin; Steven Lawrence Bryant, U. of Texas at Austin et al

Publisher: Society of Petroleum Engineers

Date: 2010

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Author: W.W. Owens, Amoco Production Co.; D.L. Archer, Amoco Production Co. et al

Publication: Journal of Petroleum Technology

Publisher: Society of Petroleum Engineers

Date: 1971

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Author: Lei Jiang, Songyan Li, Wenyang Yu, Jiqian Wang, Qian Sun, Zhaomin Li

Publication: Colloids and Surfaces A: Physicochemical and Engineering Aspects

Publisher: Elsevier

Date: 5 January 2016

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Title: Enhanced Oil Recovery (EOR)
Using Nanoparticle Dispersions:
Underlying Mechanism and
Imbibition Experiments

Author: Hua Zhang, Alex Nikolov, Darsh Wasan

Publication: Energy & Fuels

Publisher: American Chemical Society

Date: May 1, 2014

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Title: Supported metal nanoparticles on porous materials. Methods and applications

Author: Robin J. White, Rafael Luque, Vitally L. Budarin, James H. Clark, Duncan J. Macquarrie

Publication: Chemical Society Reviews

Publisher: Royal Society of Chemistry

Date: Dec 18, 2008

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Author: Andrew J. Worthen, Lynn M. Foster, Jiannan Dong, et al

Publication: Langmuir

Publisher: American Chemical Society

Date: Feb 1, 2014

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Title: The wetting and spreading of nanofluids on solids: Role of the structural disjoining pressure

Author: Darsh Wasan,Alex Nikolov,Kirti Kondiparty

Publication: Current Opinion in Colloid & Interface Science

Publisher: Elsevier

Date: August 2011

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Licensed Content Date	Aug 1, 2011
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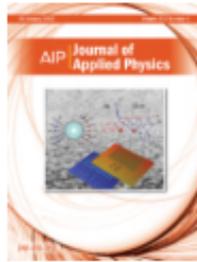


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Title: Micelle-induced depletion interaction and resultant structure in charged colloidal nanoparticle system

Author: D. Ray, V. K. Aswal, J. Kohlbrecher

Publication: Journal of Applied Physics

Volume/Issue: 117/16

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