ENHANCEMENT OF OIL RECOVERY UNDER ACTIVE WATER FLOODING USING MODIFIED LIGNIN EXTRACTED FROM COCONUT COIR

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By

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A Dissertation Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science (Chemistry) of the University of Dar es Salaam

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February, 2021

CERTIFICATION

The undersigned certify that they have read and hereby recommend for acceptance by the University of Dar es Salaam a Dissertation titled: "***Enhancement of Oil Recovery under Active Water Flooding using Modified Lignin Extracted from Coconut Coir***", in partial fulfillment of the requirements for the degree of Master of Science (Chemistry) of the University of Dar es Salaam.

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DECLARATION
AND
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I, **Sylvanus Bisaba Ruvubu**, declare that this dissertation is my own original work and that it has notbeen presented and will not be presented to any other University for a similar or any other degree award.

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DEDICATION

To

My Parents

Bisaba William Ruvubu and Fausta Mulalo Ndahaze

My Lovely Wife

Lispa Boniface Msanya, My sons and my Brother

ABSTRACT

The aim of this study was to investigate on the use of modified lignin extracted from coconut coir for active water flooding in Enhanced Oil Recovery (EOR). Three steps of processing coconut coir into sodium lignosulfonate (SLS) werefollowed, which were separation of coir from the outer layer of the coconut fruit, extraction of lignin and sulfonation of lignin to form SLS. Extracted lignin and SLS were characterized by FT-IR and porosimeter analyzer. The TGA was also used to characterize modified lignin while coconut coir was only characterized by FT-IR. SLS was then tested for its use in active water flooding for oil recovery process through simulated geological reservoir. The extraction of lignin wasachieved through acid precipitation method while the modification of lignin was done by sulfonation reaction. In this study, 80.0884 g of coconut coir produced 17.4608 g of lignin. Lignin (8.1112 g) produced 3.4132 g of SLS, which is 42.08% yield by weight. The porosimeter results indicated that modified lignin exhibits large surface area (947.915m^2/g) than unmodified lignin (554.864 m^2/g). The FT-IR results for coconut coir showed peaks at 2250 cm^{-1}, 1595 cm^{-1}, 1464 cm^{-1} and 1019 cm^{-1} which were not observed in spectrum of the extracted lignin. SLS indicated peaks at 1450 cm^{-1} for $—SO_3$, 1037 cm^{-1} for S-O, 1118 cm^{-1} forS=O and 623 cm^{-1} for C-Sas an indicator for successful sulfonation of lignin. Modified lignin showed thermal stability at temperature up to about 200 °C, pertinent to enhanced oil recovery (EOR) processes. Also, during chemical flooding, SLS surfactant solution indicated maximum concentration of 4461.2 ppm and IFT of -3.9096×10^{-5} Nm^{-1}which accounted for the maximum oil recovery of 36% during active water flooding.

LIST OF ABREVIATIONS/ACRONYMS AND SYMBOLS

CMC	Critical Micelle Concentration
EOR	Enhanced Oil Recovery
FT-IR	Fourier Transform Infra-Red Spectroscopy
HLB	Hydrophilic-Lipophilic Balance
IFT	Inter-Facial Tension
PVC	Polyvinyl Chloride
SLS	Sodium Lignosulphonate
TGA	Thermal Gravimetric Analyzer
UDSM	University of Dar es Salaam

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CHAPTER ONE
INTRODUCTION AND LITERATURE REVIEW

1.1 General Introduction

Petroleum remains as the major source of world energy despite the recent energy generation from renewable sources.[1]The over rely on petroleum is fueled by high energy demand following the increase in population, suburbanization and industrial development around the world.[2] Petroleum occurs naturally as liquid, gaseous or solid mixture composed mainly of hydrocarbons that accumulate in the sedimentary rocks under the subsurface.[3]Petroleum fields in most parts of the world are found in sedimentary basins and exploitationsare done either at the off- or on-shore.[4]The offshore exploitation is done underneath the seabed whereas onshore is done under the earth's surface. The underground traps of petroleum are well referred to as reservoirs.

The exploitation of oil is faced with a number of problemswhichare associated with the reservoir rocks and oil properties. Most of the world's hydrocarbon reservoir rocks are heterogeneous and characterized with low porosity, permeability and unfavourable wettability conditionswhich make it hard to produce economic volume of hydrocarbons.[5]Subsequently, the unfavourable mobility ratio between the aqueous and oleic phase exacerbate the problem in hydrocarbon production.[6] These problems together make about 2/3 of the total oil in reservoirs remains trapped.[7]A number of tertiary techniques such aswater, chemical or gas injection are currently exploited to ensure that every drop of hydrocarbon from the reservoir rocks is extracted.[8] This approach is called Enhanced Oil Recovery (EOR). Among the EOR techniques; the chemical flooding is the most pronounced one.[9] However, most of the chemicals used for chemical flooding are synthetic and are reported as being non-environmental friendly and expensive.[10] This limitation triggers a need to search for green techniques.

Application of polysaccharides such as surfactants from agricultural wastes is the promising research area that is still pre mature and needs to be explored at large. Under this research, surfactant from coconut coir was extracted and modified for application in active water flooding as a chemical flooding technique for EOR.

1.1.2 Literature Review

1.1.2.1Enhanced Oil Recovery

Enhanced Oil Recovery (EOR) is a petroleum based technique that aims to recover oil that remains trapped in reservoirs following the failure of primary and secondary techniques.[5] EOR techniques target at lowering the interfacial tension at the oil-water interface and also increasing volumetric sweep by reducing the viscosity (mobility ratio).[8]Lowering of the interfacial tension and mobility ratio are done by injecting suitable surfactants and polymers in the reservoir, respectively.[11,12]Mobility ratio is the ratio between mobility of displacing fluid to the oil (equation (1.1).

$$M = \frac{\lambda_1}{\lambda_2} \qquad (1.1)$$

where,

λ_1 and λ_2 are the mobilities of displacing fluid such as water and oil.

Further, mobility (λ) can also beexpressed as ratio of permeability to viscosity (equation (2)):

$$M = \frac{\lambda_1}{\lambda_2} = \frac{k_w \mu_o}{k_o \mu_o} \qquad (1.2)$$

μ_o is the oil viscosity and μ_w is the water viscosity

k_w is the displacing fluid permeability and k_o is the oil permeability.

Displacing fluids are said to have mobility equal to or lower than the mobility of the oil phase.[5,13] When the water/oil mobility ratio (M) becomes one or slightly less than one, the displacements of the oil by the displacing fluids occur to be a piston-like fashion.[5] In contrast, when M is greater than one, the more mobile water phase will finger through the oil, causing a breakthrough and poor recovery.[8]In order to achieve effective displacement of oil, mobility ratio canbe improved by either lowering the mobility of displacing fluid or increasing the mobility of the displaced fluid (oil). Alternatively, it can be done by increasing the viscosity of the displacing fluid which in turn decreases viscosity of displaced fluid such as oil.[5,14]

EOR techniques can be grouped in different forms depending on the type of flooding agents used.[15,16] The EOR techniques arethereforeclassified into four categories: thermal recovery, miscible displacement, microbial displacement and chemical flooding. Thermal recovery technique uses hot fluids, like steam or hot water. The hot fluids are injected in the reservoirs to reduce the interfacial tension which entraps oil. This method works better for heavy oil reservoirs which are associated with high viscosities.[13]

The miscible displacement method is based on the injection of a gas or fluid. Upon fluid injection in reservoirs oil becomes miscible with the injected gas. Miscible gases tend to displace oil from a depleted oil reservoir by reducing the oil viscosity and the surface forces when injected in reservoirs. This led to oil displacement caused by miscible gases which lowers interfacial tension between the inject fluid and the crude oil.[17] On the other hand, microbial displacement techniqueuses microbes that are capable to ferment hydrocarbons and produce by-products such as biosurfactants and carbon dioxide that help to displace oil.[8]Microbial displacement technique is limited to moderate reservoir temperatures because high temperatures limit microbial life.[8,9]

Chemical flooding is an EOR technique, which involves injection of special chemical liquids namely,polymers, surfactants, alkaline and their combination.[18]Hencechemical flooding technique can be divided into polymer displacement technique (polymer flooding), surfactant displacement technique (surfactant flooding), alkali displacement technique (alkali flooding) and their combination (combined flooding).

1.1.2.2Surfactant Flooding

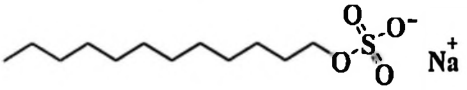
In surfactant flooding, the oil recovery mechanism is based on lowering the interfacial tension (IFT) between water and oil phases.[19,20] Surfactants are amphiphilic compounds which consists of hydrophobic groups (tails) and hydrophilic groups(heads). The amphiphilic structure is responsible for their role as flooding agents that adsorbs onto oil and water interface to reduce interfacial tension.[21,22] The interfacial tension between water and oil decreases with increase in concentration of surfactant molecules.[2,5,11,] The surfactant system used in EOR can be dilute or concentrated. Dilute surfactant system includes active water and micellar solution while the concentrated surfactant system includes micro emulsion. In active water flooding, the concentration of surfactant is lower than the critical micelle concentration (CMC) while for micellar solution flooding, concentration of surfactant is higher than CMC. The CMC is the concentration of the surfactant in a bulk phase above which aggregates of surfactant molecules so called micelles start to form.[22] CMC is an important physical parameter for which most industrial applications of surfactants are always based on. CMC determines the solubilization strength and polarity of surfactant.[23]

1.1.2.3 Classification of surfactants

Surfactants are often organic compounds which are amphiphilic. The amphiphilic property is described by the presence of both hydrophobic groups (tails) and hydrophilic groups (heads) within the surfactant molecule.[5,15,24] The amphiphilic group carries either positive or negative charges. Based on the amphiphilic property, surfactants are classified into four classes namely, anionic, cationic, zwitterionic and nonionic.[5] Anionic surfactant bears a negative charge on the hydrophilic group while the cationic surfactant carries positive charge.[5,25] In case the surfactant consists of both positive and negative charges, the zwitterionic surfactant is formed and if it carries no any charge, the nonionic is resulted.[25]

1.1.2.4 Sources of Surfactants

Applications of surfactants in industries, such as the petroleum and other fields depend on their structures, sources, amphiphilic property and chemical structure.[9] Surfactants are known to be synthetic or non-synthetic.[14] Synthetic surfactants are grouped into four groups based on their amphiphilic property or structures namely, anionic surfactant (1), cationic surfactants (2), non-ionic surfactant (3) andzwitterionic surfactant (4).[6,26]



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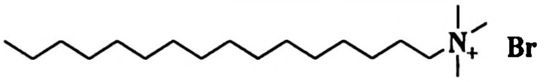

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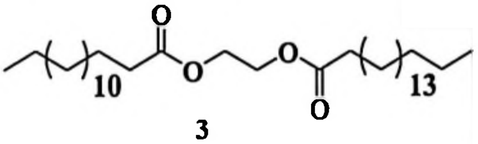

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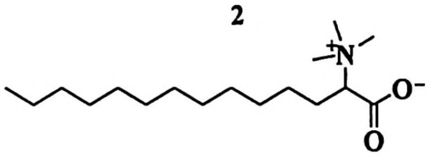

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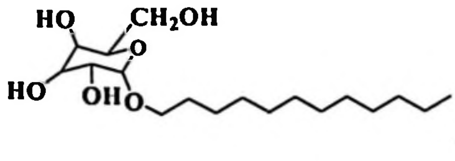
On the otherhand some of non-synthetic surfactants reported for EOR comes from \sugars and amino acids.[27,23]Examples of non –synthetic surfactant reported include alkylglucosides (5), alkylglucamides (6) and sugar esters (7).[23]



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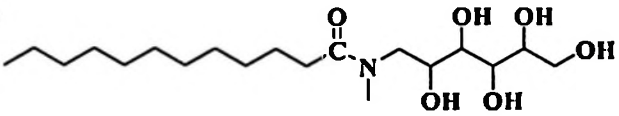

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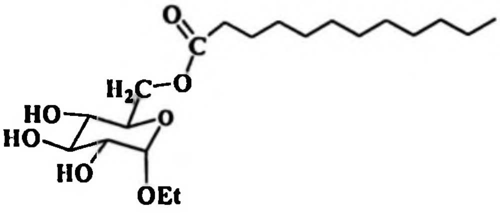

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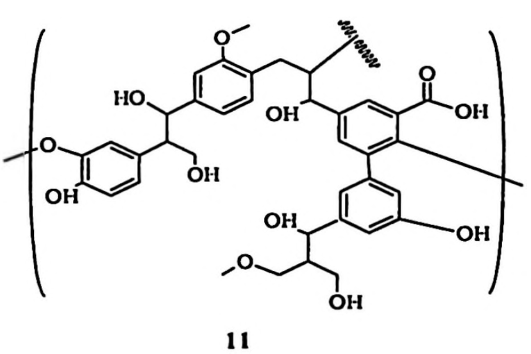
1.1.2.5 Surfactants from Coconut Coir

Coconut coir is extracted from materials that surround the seed of the coconut palm. Coconut coir consists of light weight fibres, which are strong and resistant towards erosion.[28]Coconut coir mostly composes of cellulose (44%), hemi-celluloses (12%), lignin (33%—40%), and extractives (6%), which make these materials interesting feedstock for the production of high value-added chemicals.[29,30,31]Lignin (11) is a polymer that is found in lignocellulosic materials containing cellulose fibers closed into the cell wall structures in a matrix composed of lignin and hemicellulose.[32,33] It consists of functional groups like aliphatic, phenolic, carbonyls and methoxyl groups.



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Lignin is isolated from lignocellulosic materials by chemical reactions. The chemical reactions used are such as kraft pulping methods, organosolv lignin method, soda lignin method, sulfite method; periodate lignin method, Braun's native lignin method,pulping method, and acidic precipitation method.[29,33,34] The acid precipitation method of lignin can be achieved through (reaction 1.3-1.4) as described by Ganie et al.[35].

$$ROH(aq) + NaOH(aq) \rightarrow RONa(aq) + H_2O(l) \qquad (1.3)$$

$$2RONa(aq) + H_2SO_4(aq) \rightarrow 2ROH(s) + Na_2SO_4(aq) \qquad (1.4)$$

whereROH = Lignin

The hydrophobic property, low reactivity, and structural heterogeneityof lignin limit its applications in different industrial fields.[33]Chemical modifications of lignin have been suggested by different researchers so as to broaden its applications in different fields.[4,26,36,37]

1.1.2.6 Application of Gibbs Adsorption Equation in EOR

The Gibbs adsorption equation has been adopted by several researchers[11,38] to determine the interfacial tension (IFT) in oil recovery. IFT is the thermodynamic property of the interface between two immiscible phases.[21]In oil recovery, the IFT may exist between water or the injected flooding solution (displacement agents such as polymers and alkaline solution) and oil which in turn hinder the mobilization of the oil.[11]To overcome the IFT hindrance in oil recovery, surfactants are often injected.[11,39]Application of surfactants in oil displacement is referred to as surfactant flooding. The surfactant flooding can either be dilute(active water flooding) or concentrated. Mathematically, IFT can be expressed as the Gibbs free energy per unit area of the interface at fixed temperature and pressure (equation 1.5).[22]

$$\gamma = \left(\frac{dG}{dA} \right)_{T,P} \qquad (1.5)$$

where,

γ = Interfacial tension (Nm^{-1})

dG = Gibbs free energy change (Joules)

dA = Change in surface area (m^2)

The Gibbs adsorption equation captures the properties of surfactants injected such as the surface activity of a surfactant at air- water or oil-water interface and thus enables the determination of interfacial tension.[18] The derivation of the Gibbs adsorption equation starts from the thermodynamic definition of the surface tension, enthalpy and internal energy based on the Gibbs free energy (equation 1.6).[22]

$$G = H - TS = U + PV - TS \qquad (1.6)$$

where,

G = Gibbs free energy (Joules)

U = Internal energy (Joules)

H = Enthalpy(Joules)

T= Temperature (K)

S = Entropy (JK^{-1})

P = Pressure (Nm^{-1})

V = Volume (m^3)

For an open system $G\ (T, P, n_1, n_2)$, the change in Gibbs free energy is expressed as the changes with respect to pressure, temperature and number of moles. Based on this, equation 1.5 and 1.6 can becombined and expressed as:

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \Sigma_i \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} dn_i = VdP - SdT + \Sigma_i \mu_i dn_i \qquad (1.7)$$

where,

dG = The Gibbs free energy change of the system

V = Volume

dP= Change in pressure

S = Entropy

∂T = Temperature change

μ_i = Chemical potential

∂n_i= Change in amount of components in the system

∂n_j= Change in amount of another component in the system different from i

The change in Gibbs free energy at the surface should also include the effect of surface tension. Thus,equation (1.7) can be written as:

$$dG^{\sigma} = V^{\sigma} \sigma dP - S^{\sigma} \sigma dT + \gamma dA + \Sigma_i \mu_i{}^{\sigma} dn_i{}^{\sigma} \qquad (1.8)$$

where,

dA= Change in surface area of surfactant

Since the surface phase occupies no volume at constant temperature, equation (1.8) can be then expressed as:

$$dG^{\sigma} = \gamma dA + \Sigma_i \mu_i{}^{\sigma} dn_i{}^{\sigma} \qquad (1.9)$$

Using the Euler theorem, the function of Gibbs energy at a surface can be expressed as:

$$G^{\sigma} = \gamma A + \Sigma_i \mu_i{}^{\sigma} dn_i{}^{\sigma} \qquad (1.10)$$

Taking the total differential over the above equation (1.10), equation (1.11) is obtained.

$$dG^{\sigma} = \gamma dA + A d\gamma + \Sigma_i \mu_i dn_i{}^{\sigma} + \Sigma_i n_i{}^{\sigma} d\mu_i \qquad (1.11)$$

Equating the two equations (1.9) and (1.11), equation (1.12) is obtained:

$$dG^{\sigma} = \Sigma_i n_i{}^{\sigma} d\mu_i + A d\gamma = 0 \qquad (1.12)$$

Dividing A under each term andalso considering adsorption as the number of moles per area,equation (1.12)can be written in other equivalent form as:

$$-d\gamma = \Sigma_i \Gamma_i d\mu_i \Rightarrow \Gamma_{i,1} = -\left(\frac{\partial\gamma}{\partial\mu_i}\right)_{T,\,P\mu_{,}\neq 1} \tag{1.13}$$

where,

μ_i = Chemical potential

Γ_i, = Adsorption parameter (surface excess per unit area) in moles/m^2

Equation (1.13) is the Gibbs adsorption (relative) equation for compound $i$with respect to compound 1.[31] For a binary system, if the adsorption of compound 1 (e.g. the solvent) is zero then the relative adsorption of compound 2 (the solute) is given as:

$$\Gamma_2 = -\frac{d\gamma}{d\mu_2} \tag{1.14}$$

When the change in the chemical potential isexpressed as a function of the activities a_2 or as a function of concentration C (for ideal liquid solutions), then the Gibbs equation is written as:

$$\Gamma_2 = \frac{-d\gamma}{R_i T d \ln a_2} = -\frac{a_2\, d\gamma}{R_i T d a_2} \tag{1.15}$$

The new form of equation for component i as surfactant can finally be expressed using concentration of surfactant as related to activity as:

$$\Gamma_i = \frac{C_2}{R_i T}\left(\frac{d\gamma}{dC_2}\right)_T = \frac{-1}{R_i T}\left(\frac{d\gamma}{d\ln C_2}\right)_T \tag{1.16}$$

Γ_i = Surface excess per unit area (moles/m^2)

C_2 = Concentration of surfactant (ppm)

R_i = Universal gas constant (Jmol^{-1}K^{-1})

T = Temperature (K)

$d\gamma$ = Interfacial tension (Nm^{-1})

μ_i = Chemical potential

$\left(\frac{d\gamma}{dlnC_2}\right)$ = Slope

$\left(\frac{d\gamma}{dC_2}\right)$ = Change in interfacial tension per change in concentration

$dlnC_2$ = Change in natural logarithms of surfactant concentration

For any η number adsorbing speciesforwhich there are more than onespecies that adsorb at the interface equation (1.16) is therefore denoted as:

$$\Gamma = \frac{C}{RT\eta}\left(\frac{d\gamma}{dC}\right)_T = \frac{-1}{RT\eta}\left(\frac{d\gamma}{dlnC}\right)_T \qquad (1.17)$$

Equation (1.17) is calledGibbs adsorption equation.

Once the area per molecule of adsorbed surfactant (A) is known, the surface excess per unit area (Γ_i) in equation (1.17) can be calculated.[40] The area per molecule ofadsorbed surfactant canbegiven by equation (1.18) whose derivation is presented on the AppendixA2.

$$A \times 10^{\lambda} = \frac{1}{T_i N_A} \qquad (1.18)$$

Combining equation (1.17) and equation (1.18), the equation (1.19) is obtained and which enables the calculation of interfacial tension.

$$d\gamma = -\frac{RTdlnC}{A \times 10^{\lambda} N_A} \qquad (1.19)$$

where

$d\gamma$ = Change in interfacial tension (Nm^{-1})

R = Universal gas constant whose value is $8.314 Jmol^{-1}K^{-1}$

T = Temperature (K)

$dlnC$ = Change in natural logarithms of the surfactant's concentration

A = The surface area of the surfactant (m^2)

λ =Conversion unit in the surface area (m^2)

N_A = Avogadro's constant (mol^{-1})

1.2 Statement of the Research Problem

The search for effective chemicals that enhance high oil recovery has raised attention in petroleum industry. Most of the available chemicals in use are synthetic in nature and are reported to be expensive, non-environmental friendly, unstable due to high salinity and temperature, corrosive and non-compatiblewith reservoir fluid. Application of non-synthetic chemicals such as lignocellulosic chemicals from agro-wastes to enhance oil recovery has limited information in petroleum industry. Agro-wastes materials are abundantly available and areconsidered as ecological burden to the society. This research therefore utilized coconut coir as a source of ligninfor active water flooding in EOR.

1.3 Research Objectives

The general objective of this study was to investigate on the use of modified lignin extracted from coconut coir for active water flooding in EOR. The specific objectives were:

(i) To improve hydrophilicity of lignin extracted from coconut coir by chemical modification for active water flooding.

(ii) To determine the effectiveness of modified lignin from coconut coir in active water flooding.

1.4 Research Questions

(i) How can hydrophilicity of lignin be improved by chemical modification for suitability in active water flooding?

(ii) How effective is the modified lignin from coconut coir in active water flooding?

1.5 Significance of the Study

Successful findings on application of modified lignin extracted from coconut coir in EOR will contribute to the existing strategies towards recovering trapped oil in reservoirs. In addition, application of modified lignin in EOR will address the problems associated with synthetic surfactants such as high cost, corrosiveness and environmental concerns. Furthermore, the use of coconut coir as source of lignin for

CHAPTER TWO

EXPERIMENTAL PART

2 Introduction

The experimental procedures for the extraction of lignin from coconut coir, modification of lignin by sulfonation and application of modified lignin for oil recovery are described in this chapter.

2.1 Materials

Coconut fruit peels were collected from Luguruni (Dar es Salaam). Lubricant oilwas boughtfrom Ubungo automobile service station. Kaolin clay wassampled from Pugu area in Kisarawe District-Pwani. The chemicals used were purchased from Sigma-Aldrich (SouthAfrica). These chemicals and their assay included sodium hydroxide (99%w/w), sodium bisulphite (58%w/w), sulphuric acid (98% v/v),methanol (99.8%v/v), and sodium chloride (99.99%w/w).Moreover, Whatman filters papers grade no. 3 and distilled water wereobtained from Chemistry Department, University of Dar es Salaam (UDSM).

2.2 Methods

2.2.1 Extraction of Coconut Coir

Coconut fruit peels (Figure 2.1) were washed and dried under sunlight for three weeks.The coir wasseparated from dried coconut fruit peels and cut into small pieces of about 1.5 mm length using a cutting machine available at the Botany Department, UDSM. The resulting pieces were pulverized using a laboratory blender machine and then sieved using a 420 microns sieve, (mesh 38and size 8). The pulverized coir was then dried under sunlight for one week. The dried samples were stored in clean plastic bags prior to the lignin extraction process.

Figure 2.1: A Photograph of Coconut Fruit Peels

2.2.2 Extraction of Lignin

The extraction of lignin from pulverized coir was carried out as described by Ibrahim et al.[41] Coir powder (80.0884 g) wastransferred in an aqueous solution containing 400 mL of 0.5 M NaOH, and was stirred for 2 hours. The resulting black liquor was left undisturbed for 24 hours. The lignin was then precipitated by addition of 300 mL of 1.0 M H_2SO_4 followed by heating under reflux at 80 °C for 4 hours.

2.2.2.1 Modification of Lignin by Sulfonation

Lignin(8.1112 g) was dissolved in a 300 mL of 0.4 M $NaHSO_3$ and stirred at 80 °C for 4 hours. The resulting mixture was filtered to remove unreacted materials using suction filtration; with Whatman filters papers grade no. 3. The obtained solid substance was then dissolved in 250 mL methanol and stirred for 30 minutes. The resulting solution was filtered using suction filtration with Whatman filters papers grade no. 3 to remove undissolved materials. A brown powderwas collected after evaporation of methanol using a rotory evaporator at 40 °C.

2.2.2.2 Characterization of Coconut Coir, Lignin and Sulfonated Lignin

Coconut coir was characterized by Fourier Transform Infra-Red Spectrophotometry(FT-IR). Thelignin and sulfonated lignin werecharacterized using the former (FT-IR)techniqueand Porosimeter analyzer.In addition, the Thermal Gravimetric Analyzer (TGA) instrumentwasused for the characterization of sulfonated lignin. A Lignin andsulfonated lignin were analysed directly on Fourier Transform Infra-Red (FT-IR) (Alpha ATR FT-IR spectrophotometer, Bruker optic GmbH 2011, USA model).Furthermore, porosimeter Analyzer (NOVA 1200e, PRUS Version 11.03, Quantachrome Corporation, Japan) was used for the determination ofsurface area of lignin and sulfonated lignin through nitrogen physisorption at 77 K. Prior to analysis, the samples were dried in an oven at 100 °C for 1 hour. Thereafter,the weight of two samples of approximate 100 mg was placed into the sample tube for degassing to remove unwanted vapour and gases adsorbed on the sample surface. Then the samples were dipped in liquid nitrogen for analysis. The analysis wasrun by NOVA Win software to measure the surface area.

STA PT-100 LINSEIS TGA instrument wasused for thermogravimetric analysis of sulfonated lignin. Prior to TGA analysis, the sample was dried at 100 °C for 1 hour in an oven. TGA analysis was then carried out such thatthe dried powders (0.6514 g,) was heated at a rate of 10 °C per min at a temperature range of 0 °C to 800 °C.

2.2.2.3 Application of SLS in Oil Recovery

Application of SLS in oil recovery was performed in a simulated geological reservoir made of kaolin clay, limestone cores, and simulated brine (NaCl solution) and heavy oil (oil lubricant).Temperature of 25 °C and pressure of 80 PSI wereempirically selected. Kaolin clay wasused to represent one among the types of clays found in the geological reservoir while limestone represented the reservoir rock. The NaCl solution was used to mimic the salinity of water in the reservoir while oil lubricant was used to mimic the oilwhich is found in heavy crude oil reservoirs. The test matrix in the simulated geological reservoir included 100 mL of 3.5% w/w NaCl solution, 5.3223 g of kaolin, 100 mL of oil lubricant with 150 mPs^{-1} and3 cores of limestone. Furthermore, the SLS concentrations used were 50.9, 120.9, 221.3, 304.3, 511.2, 811.2, 2561, 44612, 64889 and 81112 ppm. The experimental set up for EOR test is shown in Figure 2.2.

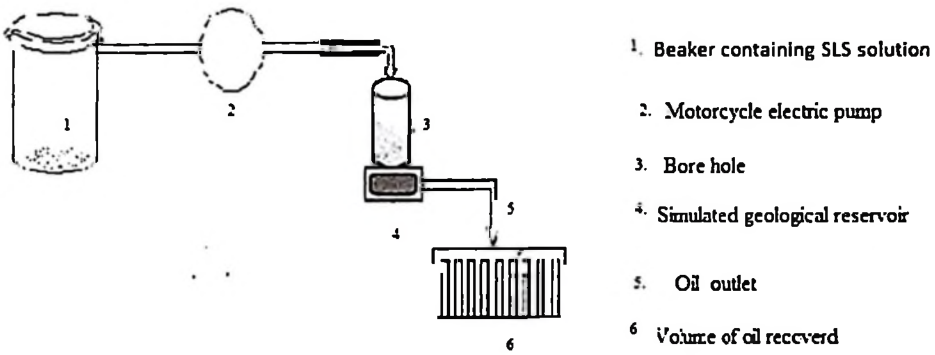

Figure 2.2: A Sketch of the Simulated Geological Reservoir for EOR

A motorcycle electric fuel pump (12 V, DC) connected to an accumulator (lead–acid battery 12 V) was used to pump the SLS solution via the simulated borehole to the simulated reservoir. However, before SLS was injected in the simulated geological reservoir, primary and secondary techniques mimicked by pressure generated from motorcycle electric pump and NaCl solution wereused to recover the heavy oil. Thereafter, the injection test with SLS in the simulated geological reservoir was done in triplicate.

2.2.2.4 Determination of Interfacial Tension (IFT) with Gibbs Adsorption Equation

The IFT was predicted using Gibbs Adsorption equation (1.19) after injection of sulfonated lignin. Furthermore,the CMC with the corresponding IFT were determined.

CHAPTER THREE

RESULTS AND DISCUSSION

3.1 Introduction

In this chapter, the experimental results are presented and discussed. The focus is on extraction of lignin, sulfonation of lignin, characterization of lignin and sulfonated lignin and the application of sodium lignosulfonate (SLS) in oil recovery.

3.2 Extraction of lignin

The obtainedlignin from coconut coir was brown in colour as can be seen in Figure 3.1.

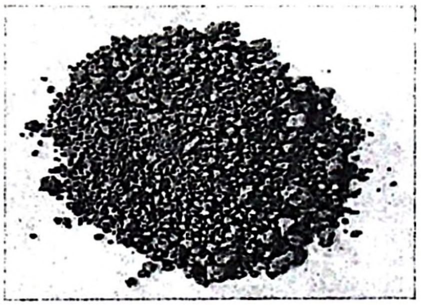

Figure 3.1: A photograph of the Extracted Lignin from Coconut Coir

The method used in this study was able to extract lignin with an average mass of 17.4608 g from 80.0884 g of coconut coir, corresponding to 21.8% yield. These results are relatively in agreement with other studies.[29, 42,41, 43,44]

3.3Characterization

3.3.1Characterization of Coconut Coir and Lignin with FT-IR

The superimposedFT-IR spectra for the extractedlignin and coconut coir are presented in Figure 3.2.

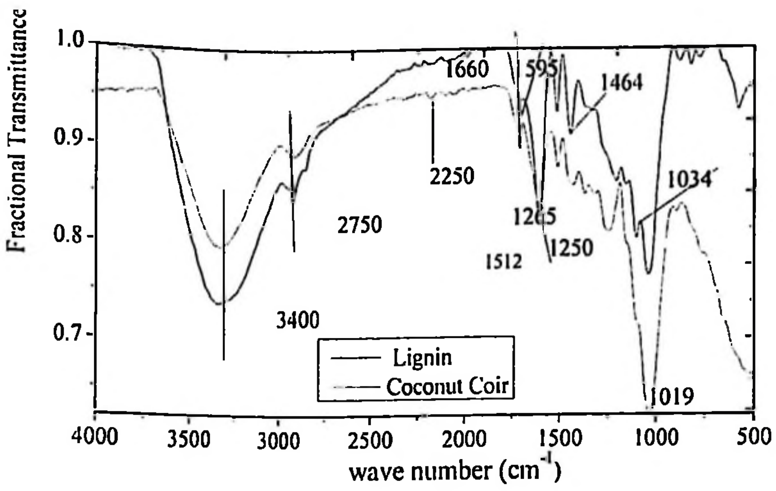

Figure 3.2: The superimposed FT-IR Spectra for Coconut Coir and Lignin

From Figure 3.2, the FT-IR spectra for coconut coir and lignin show some common features. The coconut coir and lignin showed similar and different vibrational bands. The similar bands include those at 3400 cm^{-1} for phenolic group, 2750 cm^{-1} for methoxyl group and 1660 cm^{-1} for C=O stretching. The appearance of new vibrational bands of lignin at 1464 cm^{-1} and 1034 cm^{-1} wasused to differentiate the lignin from coconut coir. These results are in agreement with the findings reported in the literature.[23, 34-37]

3.3.2Characterization of Sulfonated Lignin with FT-IR

In this study, 8.1112 g of lignin produced 3.4132 g of brown powder of SLS, which is equivalent to42.08% yield. Characterization of SLS wasdonewith FT-IR and its spectrum was superimposed with that of lignin for comparison as presented in Figure 3.3.

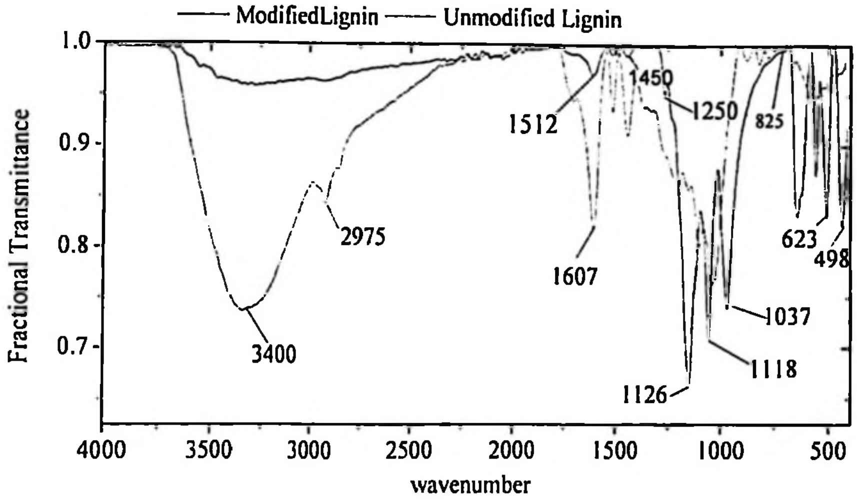

Figure 3.3: Combined FT-IR Spectra for Lignin and SLS

The results presented in Figure 3.3,show some differences in absorption bandsbetween ligninspectrum and that of sulfonated lignin. SLS gave absorption bands at about 1450cm^{-1}, 1118 cm^{-1}, 1037cm^{-1} and 623 cm^{-1}that characterize the presence of —SO_3, S-O, S=O and C-S, respectively. In addition, the FT-IR spectrum for SLS indicated the disappearance of absorption bands at 3400 cm^{-1}and at 2975cm^{-1} present in lignin FT-IR spectrum whicharecharacteristic of aliphatic or aromatic —OH group and —OCH_3, respectively. Similarobservations have been reported by several researchers.[45-47] These findingsindicate the successful conversion of lignin to SLS. The presence of sulfonate group on modified lignin marks an improvement on hydrophilicity of the material because the sulfonate groups are polar in nature.

3.3.3 Characterization of Sulfonated Lignin with TGA

Characterization of sulfonated lignin with TGA is depicted in Figure 3.4. The TGA thermogram shows a steady weight loss starting at about 40 °C up to 100 °C. This weight loss can be associated with a loss of volatile materials such as water and solvents. Furthermore, the thermogram shows a plateau at a region of about 100 °C to 200 °C, indicating an insignificant weight loss as indicate in Figure 3.4.

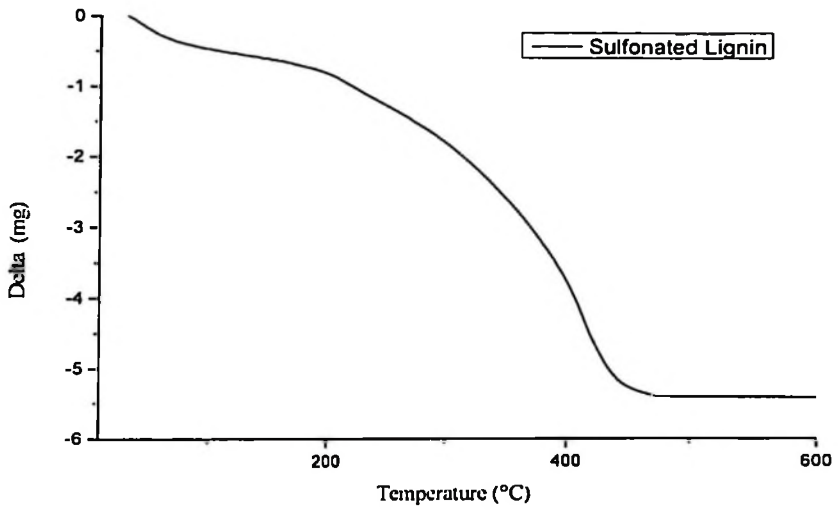

Figure 3.4: TGA Thermogram of the sulfonated lignin

At temperatures between 200 °C up to 450 °C, the thermogram shows a sudden drop,reflecting thermal decomposition of SLS. These results indicate that the obtained SLS is thermally stable up to about 200 °C. Other studies[2,42,48] reported slight difference in decomposition of sulfonated lignin which can be linked to the type of the plant species used for extraction of lignin, and chemical used during extraction and modification. The thermal stability of sulfonated lignin of up to 200 °C signifies that the material can withstand the temperature in sedimentary reservoirs where the temperature ranges from 30-120°C.[26]

3.3.4 Characterization of Lignin and Sulfonated Lignin with Porosimeter

Characterization results of lignin and sulfonated lignin using Porosimeter are summarized in Table 3.1.

Table 3.1 Surface Area Results on Lignin and Modified Lignin

Material	BET Surface Area (m^2/g)
Lignin	554.864
Sulfonated lignin	947.915

BET surface arearesults show that sulfonated lignin has higher surface area than lignin. The large surface area of the sulfonated lignin is linked with the sulfonate group on ligninwhich resulted into increased active pore sites on the surface. The large surface area of sulfonated lignin was a good indication for better adsorption of the material at the rock surface. This property also predicts a decrease in surface excess which is the molar amounts per unit surface[12]. The overall effect on the decrease in surface excess can result to reduction in interfacial tension on the water –oil interface. These properties make sulfonated lignin as the potential candidate material in EOR.[49]

3.4Estimation of Interfacial Tension Using Gibbs Adsorption Equation

The values of interfacial tension wereestimated from the concentration of modified lignin solution and theBET surface Area (m^2/g) using Gibbs adsorption equation (1.19) depicted below:

$$d\gamma = -\frac{RTdlnC}{A \times 10^{A} N_A} \qquad (1.19)$$

For example, with the concentration of 4461.2 ppm, at 25 °C, universal gas constant with a value (R= 8.314 $Jmol^{-1}K^{-1}$), Avogadro Number (N_A)= 6.022 × 1023 mol^{-1}) and BET surface area of 947.91 m^2/g. The interfacial tension wascalculated as:

$$d\gamma = -\frac{RTdInC}{A \times 10^{2} N_A} = -\frac{8.314Jmo^{-1}K^{-1} \times 298KIn446.2}{947.915m^2 \times 10^{-18} \times 6.022 \times 10^{23} mol^{-1}} = -3.9096 \times 10^{-5} Nm^{-1}$$ The interfacial tensions for other concentrations werecalculated using the same approach. Moreover, the plot of IFT as a function of modified lignin concentration is shown in Figure 3.5.

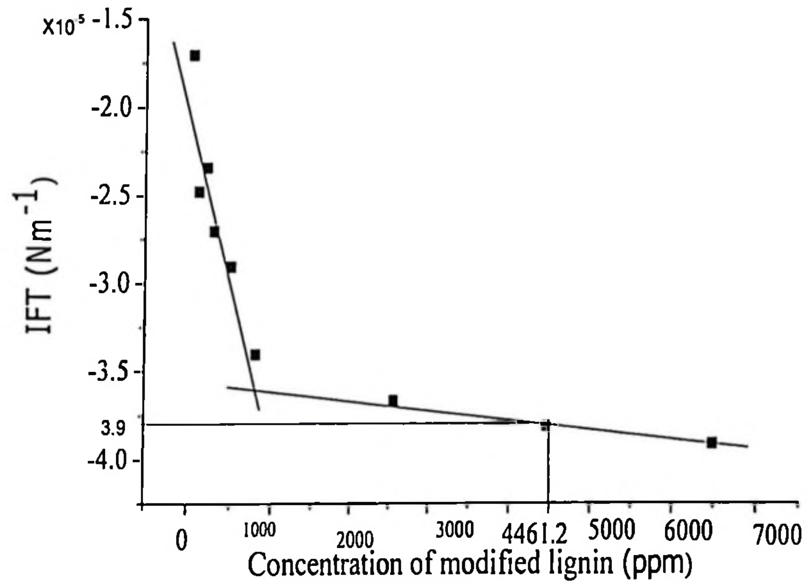

Figure 3.5: Plot of IFT as a function of modified lignin concentration

From Figure 3.5,the CMC value and its corresponding IFT were determinedusing interpolation method on the plot of IFT as a function of modified lignin concentration.From the interpolation method using CMC value of 4461.2 ppm on the plot, the SLS has corresponding IFT of -3.9096× $10^{-5}Nm^{-1}$as indicated on interpolated point on the plot. The 4461.2ppm and -3.9096×$10^{-5}Nm^{-1}$are the maximum CMC and IFT parameters at which the modified lignin surfactant works better under active water flooding. Above the CMC, a sharp transition is exhibited by the modified lignin surfactantwhich implies that there is low adsorption taking place. This observation can be explained by the fact that the surfactant monomers form micelles above CMC.[3,15,50]

Below the CMC, there is no formation of micelles and the sulfonated lignin therefore works better.[15,50]This is the principle behind the active water flooding. Furthermore, the formation of micelle indicates that the hydrophilicity of the modified lignin wasimproved as compared to ligninwhich has poor solubility.

3.5 Amount of Oil Recovered afterSLS Injection

The amounts of oil recovered after SLS injection in the simulated geological reservoir wereplotted against concentrations of the surfactant as indicated in Figure 3.6.The data used to plot Figure 3.6 are indicated on Appendix A1. The plot indicates that oil recovery increases with increase in concentration of modified lignin surfactant solution.

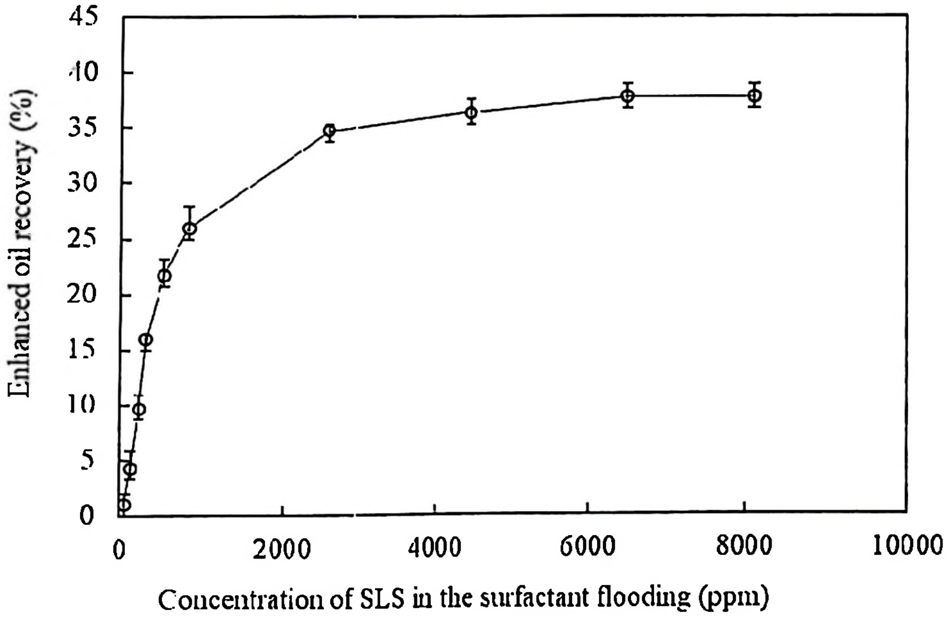

Figure 3.6: A graph of the amount of oil recovered as a function of the concentration of SLS in active water flooding

The optimum oil recovery at CMC with 4461.2 ppm of SLS was 36% which is equivalent to 36 mL out of the 100 mL that were used in the simulated geological reservoir. Above this concentration, no further significant increase in percentage oil recovery was observed. The increase in oil recovery with concentration of SLS is attributed by decrease in interfacial tension.[51]The observation that the oil recovery remained constant at higher SLS concentration was probably due to formation of critical micelle concentrationwhich prevent surfactant molecules to adsorb on the improvised geological oil reservoir.[52]

CHAPTER FOUR

CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions

The work under this dissertation focused on the effectiveness of the modified lignin from coconut coir for active water flooding, an EOR technique. The lignin from coconut coir was isolated by acid precipitation. The lignin was then modified by sulfonation method. Characterization of the coconut coir, lignin and modified lignin was done by using FT-IR. In addition, the TGA and porosimeter wereused to characterize the lignin and modified lignin. The concentrations of modified lignin and the surface area were used to estimate the interfacial intensions (IFT) using Gibbs adsorption equation. The IFTs were plotted against the surfactant concentration so as to determine the CMC and its corresponding IFT.

The findings showed that the amount of lignin isolated was 17.4608 g from 80.0884g of coconut coir while the amount of modified lignin was 3.4132 g. Characterization with FT-IR showed the presence of sulfonate group, which distinguished the modified lignin from lignin and coconut coir. The TGA results showed that the modified lignin was thermally stable up to 200 °C. This physical property signified that the modified lignin can be stable when injected in sedimentary reservoirs, which have temperature in the range of 30 – 120 °C. The surface area for modified lignin and lignin were 947.915 and 554.864 m^2/g, respectively. This large surface area of modified lignin predicts a decrease in surface excess and interfacial tension when the surfactant is injected in the reservoir.

The plot of surfactant concentrations and interfacial tensions showed an inverse proportional relationship. From the plot, the CMC and its corresponding IFT were 4461.2 ppm and $3.9096\times10^{-5}Nm^{-1}$, respectively. Formation of micelle was an indication for improvement on hydrophilicity of modified lignin. At CMC, the surfactant was able to recover amount of oil up to (36 % in volume) while above the CMC there is no further increase in oil recovery. Good oil recovery with surfactants implied good reduction of interfacial tension. This technique of oil recovery with surfactant concentration working better below CMC is called active water flooding. Based on these findings, sulfonated lignin from coconut coir proved to have good hydrophilicity which in turn leads to oil recovery.

4.2 Recommendations

Based on the findings of this study, the following are recommended:

- Modified lignin is thereforerecommended as a suitable candidate to be used in the oil and gas mining industry.
- Further characterization techniques on isolated and modified materials are highly encouragedso asto establish the necessary physical and chemical features necessary for EOR using agro-waste materials such as lignin and modified lignin.
- There is a need to determine other useful parameters of surfactants in EOR such as hydrophilic-lipophilic balance (HLB) and wettability.
- Further researches are highly encouraged to be conducted on the application of bio-surfactants from other agro wasteswhich are currently considered as ecological burden to the society.
- Studies are also encouraged to investigate the variation of intrinsic viscosity with the increase in concentration of modified lignin in oil recoverywhich was not covered in this study due to time limit for measurements.

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3 Appendix A 1 : Oil recovered after SLS injection in the simulated geological reservoir

Initial volume of used oil(mL)	100	100	100	100	100	100	100	100	100	100
Concentration of SLS in surfactant flooding(ppm)	50.9	120.9	221.3	304.3	511.2	811.2	2561	4461.2	6488.9	8111.2
Oil recovery by surfactant flooding(mL)	27	30	35	42	48	52	61	63	63	63
	26	32	37	42	46	50	60	63	65	63
	28	29	35	42	49	54	61	61	63	66
Average oil recovery by surfactant flooding(mL)	27.0±1.0	30.3±1.5	35.7±1.2	42.0±0.0	47.7±1.5	52.0±2.0	60.7±0.6	62.3±1.2	63.7±1.2	63.7±1.2

Appendix A 2: Derivation of the surface excess parameter

Using thermodynamics algebraic expressions, the surface excess parameter of components can be related to surface area as expressed in the equations below.[2]

$$\pi A = n_i R_i T = k_B T \quad \text{(A 1)}$$

where,

π = Osmotic pressure of the surfactant solution

A = Surfacea area of surfactant

n_i = Number of moles of surfactant in a solution

T = Temperature in kelvin

k_B = Boltzmann constant

From Equation (A 1), in above equating the terms, the relation in Equation (A 1) isexpressed as:

$$\pi A = k_B T \quad \text{(A 2)}$$

Expressing n_i in terms of other variables, we obtain Equation (A 3)

$$n_i = \frac{\pi A}{R_i T} \quad \text{(A 3)}$$

where n_i is the number of moles of surfactant solution.

Similarly, with the relation stated in above equations, (A 2) - (A 3), surface excess is also expressed as:

$$\Gamma_i = \frac{n_i}{A} \quad \text{(A 4)}$$

The surface excess of the surfactant adsorbed on the surface can be related as:

where, $n_i = \dfrac{\pi A}{R_i T}$ and $\pi A = k_B T$ (A 5)

Since, the Boltzmann constant k_B is related to the Avogadro's NA and the universal gas constant R_t such that $k_B = \frac{R_t}{N_A}$

to generate equation(A 6), moles, n_t and πA are introduced in the T_t expression as follows.

$$T_t A = \frac{R_t T}{R_t N_A T} \tag{A 6}$$

The Equation (A 6) is finally expressed as:

$$A = \frac{1}{T_t N_A} \tag{A 7}$$

When the surface area per molecule of the surfactant are converted from different units such as nanometer (nm), angstrom(Å) or any unit of area into metre(m) , the expression in above is changed into the general equation expressed as

$$A \times 10^{\lambda} = \frac{1}{T_t N_A} \tag{A 8}$$

where A is the area per molecule of adsorbed surfactant and N_A is the Avogadro constant in molecules per mole) and T_t is the surface excess concentration of the surfactant.