ADSORPTION OF LIGNOSULFONATES ONTO CLAY MINERALS AND THEIR EFFECTIVENESS AS A SACRIFICIAL AGENT

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy

School of Chemical and Energy Engineering
Faculty of Engineering
Universiti Teknologi Malaysia

AUGUST 2020

ACKNOWLEDGEMENT

I would like to express my deepest gratitude to my supervisor, Associate Professor Dr. Muhammad A. Manan, for managing my project timeline, providing me with all required facilities and reviewing my thesis. Besides that, I would like to give thanks to my co supervisor Professor Emeritus Dr. Ahmad Kamal Bin Idris for his continuous support, kindness, inspiration, encouragement and valuable guidance during this PhD journey. Thanks, are also extended to Dr. Zainul Akmal Zakaria for trusted and granted me permission to do my experimental work in his laboratory without any charges. I also wish to express my appreciation to Encik Fairuz Mohamed, Roslan Jas, Encik Zulkifle Nasir and Puan Noorhafiza Mazalan, technical staff at Petroleum department for providing excellent assistance. Thanks to my friend Azad Anugerah and Tengku Amran Tengku Mohd for being there to give mentally support. Finally, the Doctorate support groups which available in facebook shared plenty of tips on how to survive in PhD, writing, viva and so on.

ABSTRACT

Surfactant adsorption on reservoir rock surface is a fundamental issue in surfactant based enhanced oil recovery. Reservoirs contain a significant amount of clays that results in large surface areas, thus causing a large portion of the surfactant to be adsorbed. Sacrificial agent (SA) is meant to be sacrificed, hence serving as a shield that protects the formation of rock by adsorbing into active adsorption site and prevents the subsequent surfactant to be adsorbed onto the surface. Despite the promising initial results, the suitability of numerous available types of lignosulfonate (LS) in the vast market as SA has yet to be investigated. Having that said, the objectives of this study are to determine the readiness of four LS types to adsorb onto clay minerals based on their functional groups, to investigate the adsorption capability and to define the effective method (mixture or pre-treatment), as well as to identify the underlying mechanism responsible for the effectiveness to reduce cetyl trimethyl ammonium bromide (CTAB) adsorption. The most commonly used method to measure adsorption refers to the depletion method, where the concentration before and after adsorption are measured. Adsorption data obtained from the depletion method can be modelled into adsorption model to describe the adsorption process. Four types of LS, which are sodium LS (SLS), ammonium LS (ALS), magnesium LS (MLS), and calcium LS (CLS), were compared in terms of functional group, adsorption capability, and adsorption model to determine their readiness to adsorb onto kaolinite and montmorillonite. Different LS types, concentration, contact time, and model of adsorption were among the parameters tested with different brine salinity and pH. Both mixture and pre-treatment methods were investigated in depth to identify the underlying mechanism responsible to effectively reduce CTAB adsorption. A major finding from this study is that the functional groups in LS, such as (a) hydroxyl group in phenolic and aliphatic, (b) methyl and methylene, (c) aromatic, (d) sulfonic acids and stretching aliphatic, and (e) CH_x bending out plane, were involved in the adsorption process onto kaolinite and montmorillonite. The mechanism appeared to be driven by electrostatic forces. SLS displayed the highest readiness to adsorb onto kaolinite and montmorillonite, which adhered to the following sequence SLS>ALS>CLS>MLS. Higher LS concentration and salinity led to higher adsorption, especially with the change of monovalent salt to divalent salt. Nonetheless, pH had no impact on adsorption. This signifies that pH modification may be ignored when using LS as SA. Equilibrium and kinetic adsorptions adhered to the Freundlich model and the pseudo-second order, respectively. Electrostatic forces, cation-π interaction, hydrophobic interaction, and cation bridging had a crucial role in the adsorption mechanism of LS with kaolinite and montmorillonite. The SLS as SA had successfully reduced CTAB adsorption via pre-treatment method. The effective underlying mechanism revealed in this study is SLS as SA that displayed high adsorption readiness, along with cation bridging assistance from divalent salt and reversed surface charge. As high as 50% CTAB reduction was recorded in the experimental work. As such, this study concludes that SLS is suitable to function as SA to reduce cationic adsorption onto kaolinite and montmorillonite. Pre-treatment is an effective way to reduce CTAB adsorption.

ABSTRAK

Penjerapan surfaktan di permukaan batuan reservoir merupakan salah satu isu asas dalam penggunaan surfaktan bagi perolehan minyak tertingkat. Reservoir yang mengandungi kandungan lempung yang tinggi boleh menghasilkan keluasan permukaan batuan yang lebih besar yang menyebabkan sebahagian besar surfaktan terjerap. Ejen korban (SA) adalah bahan yang dijadikan korban, berpotensi melindungi batuan dengan menjerap ke permukaan aktif penjerapan dan berikutnya menghalang surfaktan dari menjerap ke permukaan batuan. Walaupun hasil kajian awal yang menyakinkan, kesesuaian pelbagai jenis lignosulfonat (LS) yang berada di pasaran sebagai SA masih belum disiasat. Oleh yang demikian, objektif penyelidikan ini adalah untuk menentukan kesediaan empat jenis LS untuk menjerap pada mineral lempung berdasarkan kumpulan fungsinya, untuk menyiasat keupayaan penjerapan dan untuk mengenalpastikan kaedah yang berkesan (campuran atau pra-rawatan) di samping mekanisme yang bertanggungjawab terhadap keberkesanan untuk mengurangkan penjerapan cetil trimetil amonium bromida (CTAB). Kaedah yang paling lazim untuk mengukur penjerapan adalah kaedah susutan di mana kepekatan sebelum dan selepas penjerapan diukur. Data penjerapan yang diperolehi dapat dimodelkan ke dalam model penjerapan yang dapat menjelaskan proses penjerapan. Empat jenis LS iaitu sodium LS (SLS), amonium LS (ALS), magnesium LS (MLS) dan kalsium LS (CLS) dibandingkan dari segi kumpulan fungsi, keupayaan penjerapan dan model penjerapan untuk menentukan kesediaan penjerapan ke atas kaolinit dan montmorilonit. Jenis LS, kepekatan, masa sentuh dan model penjerapan LS adalah parameter yang diuji, di samping kepelbagaian pH dan kemasinan air garam. Kaedah campuran dan pra-campuran diteliti secara mendalam untuk mencari mekanisme yang bertanggungjawab untuk pengurangan penjerapan CTAB. Penemuan utama daripada kajian ini adalah didapati kumpulan fungsi dalam LS seperti (a) kumpulan hidroksil dalam fenolik dan alifatik, (b) metil dan metilena, (c) aromatik, (d) asid sulfonik dan alifatik regangan, dan (e) lenturan CH_x terlibat dalam proses penjerapan kaolinit dan montmorilonit. Mekanisme kelihatan didorong oleh daya elektrostatik. SLS mudah dijerap oleh kaolinit dan montmorilonit dan didapati mengikut urutan SLS>ALS>CLS>MLS. Kepekatan LS dan kemasinan yang lebih tinggi menghasilkan penjerapan yang lebih tinggi terutamanya semasa perubahan dari monovalen kepada divalen, manakala pengaruh pH tidak signifikan. Pengubahsuaian pH dapat diabaikan ketika menggunakan LS sebagai SA. Penjerapan adalah mengikut model Freundlich dan penjerapan kinetik mengikuti urutan pseudo-kedua. Daya elektrostatik, interaksi kation-π, interaksi hidrofobik dan penghubung kation memainkan peranan penting dalam mekanisme penjerapan antara LS dengan kaolinit dan montmorilonit. SLS sebagai SA berjaya mengurangkan penjerapan CTAB dengan menggunakan kaedah pra-rawatan. Mekanisme berkesan yang didedahkan dalam kajian ini adalah SLS sebagai SA yang menunjukkan kesediaan penjerapan yang tinggi, bersama dengan bantuan penghubung kation dari garam divalen dan cas permukaan berbalik. Sebanyak 50% pengurangan CTAB dicatatkan dalam kajian ini. Oleh yang demikian, kajian ini menyimpulkan bahawa SLS sesuai berfungsi sebagai SA untuk mengurangkan penjerapan kationik pada kaolinit dan montmorilonit. Pra-rawatan adalah kaedah yang berkesan untuk mengurangkan penjerapan CTAB.

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LIST OF ABBREVIATIONS

ABS - Absorbance
AES - Alkyl Ethoxy Sulfate
ALS - Ammonium Lignosulfonate
AOS - Alpha Olefin Sulfonate
ASP - Alkaline, Surfactant and Polymer
BCI - Hyamine
CAC - Critical Aggregation Concentration
$CaCl_2$ - Calcium Chloride
CD1045 - Chaser 1045
CEC - Cation Exchange Capacity
CLS - Calcium Lignosulfonate
CMC - Critical Micelle Concentration
CME - Carboxymethylated Ethoxylated
CO_2 - Carbon dioxide
Conc - Concentration
CTAB - Cetyltrimethylammonium Bromide
DTAB - Dodecyl Trimethyl Ammonium bromide
DPC - Dodecylpyridinium Chloride
EDL - Electrical Double Layer
EOR - Enhanced Oil Recovery
Exp - Experiment
FTIR - Fourier Transform Infrared- attenuated total Reflectance
IEP - Isoelectric Point
IFT - Interfacial Tension
IOS - Internal Olefin Sulfonate
LS - Lignosulfonate
m - Weight of solid
MLS - Magnesium Lignosulfonate
mg/g - milligram/gram
ml - millilitre

Na_2CO_3	-	sodium carbonate
$NaBO_2$	-	Sodium Metaborate
NaCl	-	Sodium Chloride
$NaHCO_3$	-	Sodium Bicarbonate
NaOH	-	Sodium Hydroxide
OOIP	-	Original Oil In Place
ORS	-	alkylbenzene sulfonate
PET	-	polyelectrolyte
PSS	-	Polystyrene Sulfonate
ppm	-	part per million
PV	-	Pore Volume
PZC	-	Point of Zero Charge
SA	-	Sacrificial Agent
SAG	-	Surfactant Alternative Gas injection
SDS	-	Sodium Dodecyl Sulfate
SDSH	-	Sodium Dihexylsulfosuccinate
SLS	-	Sodium Lignosulfonate
ST	-	Surface Tension
T	-	Tetrahedral
TX-100	-	Triton 100
UV-VIS	-	Ultraviolet visible
V	-	Volume
XRD	-	X-Ray Diffractometer
XRF	-	X-Ray Fluorescent

LIST OF SYMBOLS

q_e - Amount of surfactant/lignosulfonate solution adsorbed
C_o - Initial concentration
C_e - Equilibrium concentration
q_o - Langmuir constant signify adsorption capability
K_L - Langmuir constant signify energy of adsorption
K_f - Freundlich constant signify to adsorption capability
$1/n$ - Freundlich constant signify adsorption intensity
B - Temkin constant related to distribution of bonding energies
K_t - Temkin constant related to distribution of bonding energies
t - time
q_t - Lignosulfonate adsorbs at time t
K_1 - Constant rate pseudo-first order
K_2 - Constant rate for pseudo-second order
h - Initial adsorption time
$t_{1/2}$ - Half adsorption time
K_i - Constant diffusion ratio

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CHAPTER 1

INTRODUCTION

1.1 Problem Background

Surfactants are applied mainly due to their remarkable ability to influence the properties of surfaces and interfaces. In surfactant-based enhanced oil recovery (EOR) methods, trapped oil can be mobilised by reducing the interfacial tension (IFT) of oil-water interface and by altering the wettability of rock by using the injected surfactant solution (Reed & Healy, 1977). This technique has been proven to recover trapped oil that cannot be recovered via conventional method of water flooding (Hirasaki *et al*., 2011; Sheng, 2015). Surfactant is also used as a foaming agent in CO_2 gas flooding to create stable foam, so as to minimize gas mobility in oil displacement (Bai, 2005; Syahputra *et al*., 2000). Nonetheless, surfactant loss appears to be a major challenge in surfactant flooding (Kovalev *et al*., 2016; Sedaralit *et al*., 2015; Zhu, 2015; Zhu *et al*., 2012).

Surfactant loss in reservoir stems from several mechanisms, including surfactant adsorption, surfactant precipitation, and surfactant entrapment (Somasundaran *et al*., 1984; Novosad, 1984). Surfactant loss due to adsorption on solid surface has been a main issue in surfactant-based EOR (Saxena *et al*., 2019; Wu *et al*., 2016). In pilot field test for chemical flooding, especially in Alkali Surfactant flooding (AS), the role of alkali is to reduce surfactant adsorption. Alkali, such as sodium hydroxide (NaOH/caustic soda), sodium carbonate (Na_2CO_3/soda ash), sodium bicarbonate ($NaHCO_3$), and sodium metaborate ($NaBO_2$), has been applied as chemical agent to decrease the adsorption of anionic surfactants on rocks (Hirasaki *et al*., 2011; Sheng, 2013). Alkali increases the pH and the net negative surface charge, thus reducing the adsorption of anionic surfactants due to electrostatic repulsion (Hirasaki *et al*., 2011). Nevertheless, this is limited to reservoirs with low salinity, as alkali is sensitive to divalent cations, Ca^{2+}, and Mg^{2+}, thus causing alkali to precipitate and become ineffective. In high salinity environment, these multivalent ions can adsorb onto negatively charged rock surfaces and may reverse the sign of the surface charge (Austad *et al*., 1991, Tabatabal *et al*., 1993). Having that said, use of cationic surfactant leads to minimal adsorption due to electrostatic repulsion. Although inclusion of salt can reduce cationic adsorption, adsorption is still bound to happen (Nandwani *et al*., 2019).

Limited laboratory studies have actually attempted to address the cationic surfactant adsorption by introducing new formulations that suit a particular reservoir condition (Ali & Reza, 2013; Barati *et al*., 2015; Cui *et al*., 2014; Iglauer *et al*., 2010; Nandwani *et al*., 2019, Zendehboudi *et al*., 2013). However, it has always been impossible to identify a suitable surfactant for each unique reservoir condition to work as desired. As such, the term “sacrificial agent” (SA) was coined to minimize surfactant adsorption. Nevertheless, studies concerning SA has been in scarcity (Bai *et al*., 2009, ShamsiJazeyi *et al*., 2014, Weston *et al.*, 2014). The SA refers to a substance that can mitigate the adsorption of surfactants into a formation. The SA can adsorb on and occupy sites within the matrix of the formation, thus the ability to eliminate or substantially decrease the tendency for the subsequent injected surfactant in the micellar to adsorb on rock matrix. Additionally, SA is more cost effective than surfactant, easy to access with huge capacity, and environment-friendly. A range of chemicals has been tested as potential SA, including silicates, carbonates, inorganic salts (Falcone *et al*., 1982), water-soluble polyelectrolytes (ShamsiJazeyi *et al*., 2014), ethoxylated sulfonates, carboxylic acids, and lignin-based derivatives (Bonnie, 1989; Novosad, 1984). Although each has its own advantages over the other, some studies have suggested lignin-based derivatives as effective SA due to its renewable and sustainable property, environment-friendly, available commercially, and very affordable (Mu *et al*., 2013; Norgren & Edlund, 2014; Suhas *et al*., 2007; Watkins *et al*., 2015).

The application of lignin as SA to enhance oil recovery has been practiced for less than five decades. Lignin is a natural polymer found in the cell wall of woody tree type and it is usually attained from discharge waste emitted from paper mills. The importance of lignin first drew attention when salt lignosulfonate (LS) as SA was introduced. Novosad (1984) conducted an experiment using Berea sandstone cores to assess the effect of ammonium lignosulfonate (ALS) on oil production during surfactant flooding. The primary objective of the experiment was to prove that LS used as pre-flush could reduce anionic surfactant adsorption and increase oil recovery. However, the study outcomes showed that oil recovery without pre-flush was 79%, which was higher than oil recovery with ALS pre-flush at 68%. This indicated that ALS better served as mixture. Hong *et al.* (1987) evaluated ALS as SA using rock from Glenn Pool reservoir. In a laboratory test, unfortunately, no oil recovery experiment was conducted. The only result from the work was that ALS had successfully reduced anionic surfactant adsorption by 39%. Safarzadeh *et al.* (2011) examined the effect of calcium lignosulfonate (CLS) on surfactant alternative gas injection (SAG) and concluded that CLS added with surfactant can reduce anionic adsorption. Nevertheless, studies that have applied LS as SA to reduce surfactant adsorption are rather limited, thus constraining the discussion on which method and mechanism that dictate the effectiveness of LS as SA. Surfactant involved with the usage of SA is, thus far, constrained to anionic.

Rock type is another crucial factor in determining the successful application of LS as SA. Most rock types in the discussion of LS adsorption are limited to Berea sandstone and carbonate rock. For instance, Grigg and Bai (2004), Bai and Grigg (2005) and Bai *et al.* (2009) conducted static and dynamic experiments to assess the adsorption behaviour of CLS as SA onto Berea sandstone, limestone, and dolomite core. However, surfactant was excluded from the three studies. Furthermore, one cannot dismiss the potential effect of clay minerals on surfactant adsorption, such as the reservoirs in Malaysia (Kovalev *et al.*, 2016) and Sirikit oilfield in northern Thailand (Srisuriyachai *et al.*, 2019). Several core samples from West Malaysia oilfield revealed the presence of clay from 15% to 27% from the total rock mineralogy (Osman *et al.*, 2014), which contained high mineral of kaolinite. Clay minerals in rock can affect the adsorption in many ways, thus making the recovery process uneconomical (Gogoi, 2011). This limitation had led to this investigation.

Reduction of surfactant adsorption using LS as SA had been very much limited to anionic and non-ionic surfactants. Safarzadeh *et al*. (2011) reported on the use of CLS as SA, in which sodium dodecyl sulfate (SDS) (anionic surfactant) adsorption decreased by 22%. In an experiment carried out by Bonnie (1989), which used mixed surfactants of anionic and non-ionic carboxymethylated ethoxylated (CME), a reduction of 69% surfactant adsorption was recorded when using LS as SA. Meanwhile, Hong *et al.* (1987), who used Petrostep 405 and 420 (mixed surfactants of anionic and non-ionic) with ALS as SA, reported reduction of more than 50% surfactant adsorption. The literature depicts that anionic surfactant is still preferred for sandstone reservoir due to the similar charges shared between the surfactant and the rock surface, thus the ability to automatically reduce surfactant adsorption by repulsion forces. Some conventional ways to optimise the surfactant flooding at a successful rate are by matching the charge of surfactant with the charge of rock surface. As such, anionic surfactant is more suitable for sandstones reservoir, while cationic surfactant in carbonate reservoir. To date, no study has used LS as SA to reduce cationic surfactant adsorption. The success of LS as SA in reducing cationic surfactant has a great impact on surfactant selection. More surfactant selection that varies from anionic and cationic can be an option with the presence of LS as SA. The method and the underlying mechanism responsible for the effectiveness of LS as SA can be comprehended for anionic and cationic surfactants.

The LS is the preferred material for SA due to its ability to dissolve in water. However, over the years, LS had been studied separately without any attempt to relate or compare with various LS types in terms of sacrificial use. For instance, Hong *et al*. (1987) examined ALS, Debon *et al*. (1991) studied sodium lignosulfonate (SLS), while Bai *et al*. (2009) and Safarzadeh *et al*. (2011) assessed CLS. In their report, the selection of LS for their research work was not mentioned. These clearly reveal a gap of knowledge, thus presenting an interesting area to explore. It is crucial to compare various LS readiness to adsorb in terms of adsorption ability, functional groups of LS involved in adsorption, and the adsorption mechanism model so that the behaviour of LS can be well studied and understood.

Other factors that can influence the adsorption are the environment and the condition of the reservoir system, such as salinity, temperature, and pH (Hu *et al*., 2017; Li *et al*., 2018; Saxena *et al*., 2019). Grigg *et al*. (2004), for example, examined the effect of CLS adsorption onto Berea sandstone in the mixture of monovalent and divalent (5 wt% of NaCl and 5 wt% of $CaCl_2$), and single divalent (10 wt% of $CaCl_2$) indicated that $CaCl_2$ in CLS solution displayed greater influence on CLS adsorption. Similar finding with the same concentrations (0 wt%, 2 wt%, and 5 wt%) of NaCl and $CaCl_2$ solutions, which revealed that $CaCl_2$ exerted greater influence on CLS adsorption on limestone and dolomite, had been reported by Bai and Grigg (2005) and Bai *et al*. (2009). Nonetheless, no study has examined lower concentration of divalent and higher concentration of monovalent. As for temperature, most of the previous work showed that increased temperature had decreased the adsorption due to exothermic reaction (see Azam *et al*., 2013; Saxena *et al*., 2019; Yekeen *et al*., 2017). Increment in temperature reduced the surface energy of the adsorbent. Therefore, adsorption has always been exothermic, except for non-ionic adsorption that has been reported as endothermic (Belhaj *et al*., 2019; Khazri *et al*., 2017; Tate, 1965). In Bai's work on the effect of temperature on CLS adsorption onto Berea sandstone and limestones, increased temperature from 30°C to 50°C has decreased CLS adsorption. Last but not least, the effect of pH on the adsorption highly depended on the type of surfactant, rock and salinity. Bera *et al*. (2013) reported that the influence of pH greatly relied on surfactant type. Generally, increased pH decreased the adsorption of anionic surfactant, but increased for cationic surfactant. As for non-ionic surfactant, the adsorption decreased up to pH 7 and remained constant at alkaline region. Hence, different types of LS must be examined to determine the role of pH.

For most of the adsorption investigation, depletion method seems reliable to measure the adsorption in both static and dynamic tests. Depletion method measures the concentration of a solution before and after contacted with solid (Salari & Ahmadi, 2016; ShamsiJazeyi *et al*., 2014; Yekeen *et al*., 2017). The results obtained from the depletion method have been discussed in light of adsorption behaviour through adsorption model. Bai *et al*. (2005) concluded that CLS adsorption onto Berea sandstone, limestone, and dolomite core adhered to the Freundlich isotherm, which explained multilayer adsorption on the surface. Qiu *et al*. (2009), on the other hand, found the adsorption isotherms to be Langmuir type for the adsorption of CLS on titanium dioxide (TiO_2) particles. This shows that different solid surfaces generated different adsorption models despite the use of the same solution. Unfortunately, the adsorption model for LS in the literature seems to be limited to Berea sandstone, dolomite, and limestone. Additionally, the adsorption model is limited to CLS. Such limitation has motivated to continue research in this area.

1.2 Problem Statement

The readiness of LS to adsorb has not been investigated before, as there was no attempt to compare various types of LS. The underlying mechanism that is responsible for the effectiveness of LS as SA has not been fully understood. Studies on surfactant involved in LS as SA are limited to anionic and a mixture of anionic and non-ionic.

The LS was assessed previously without comparing with other types of LS, thus limiting the usage of LS as SA. Readiness of LS to adsorb in terms of functional group and adsorption capability was not studied. Both readiness and adsorption capability of LS as SA can provide meaningful insight on how well LS can serve as a shield to protect the rock surface from adsorption of subsequent injected surfactant.

The method of LS as an effective SA is a crucial element for reservoirs in order to determine the success of surfactant aided by flooding, whether by using as mixture or pre-treatment. The underlying mechanism of mixture or pre-treatment that explains how effectively SA works to reduce surfactant adsorption is crucial. However, prior studies related to LS as SA have omitted the aspects of when, why, and how LS can be used effectively as SA to reduce surfactant adsorption. Therefore, there is a pressing need to comprehensively understand the mechanism for LS as SA, as well as to address when and how to effectively use LS as SA.

The issue pertaining to the presence of clay that affects surfactant adsorption is indeed crucial in reservoirs across Malaysia with high clay content. Researchers have concluded that surfactant adsorption results are affected by the presence of clays typically found interbedded in the rock matrix. Previous studies on LS, however, are limited to Berea sandstone and carbonate rock. Past studies on LS as SA are also limited to anionic and a mixture of anionic and non-ionic.

1.3 Research Objectives

This study determined the readiness of LS adsorption onto clay minerals, apart from identifying the method and the underlying mechanism responsible for the effectiveness of LS as SA in reducing Cetyl Trimethyl Ammonium Bromide (CTAB) cationic surfactant adsorption. The objectives of this study are as follows:

1. To determine the readiness of four lignosulfonate types to adsorb onto clay minerals based on their functional groups.

2. To investigate the adsorption capability in the function of lignosulfonates type, concentration, contact time, and model of adsorption onto clay minerals with different brine salinity and pH values.

3. To define the method (mixture or pre-treatment) and the underlying mechanism responsible for the effectiveness of the selected lignosulfonate to reduce CTAB adsorption.

1.4 Scope of the Study

In order to achieve the research objectives, the depletion method was used to measure static adsorption. Depletion method was also employed to determine the concentration of solution before and after the adsorption test. The difference reflects the adsorption density or the adsorption capability in unit mg/g. Adsorption capability refers to the quantity (mg) of adsorbate that can adhere to per gram of the adsorbent material. The higher is the quantity of adsorption capability for LS as SA, the greater is its readiness and efficiency to shield rock surface.

Four types of LS were selected for this study, namely CLS, magnesium LS (MLS), SLS, and ALS, due to their water-soluble characteristic, negative charge, and some of these LS types have been studied in isolation. Although the LS was received in powder form, it was examined in solution form by diluting in aqueous. The LS types and concentration were assessed. However, the size and the molecular weight of LS were dismissed. All LS types are available commercially. The readiness of LS and its adsorption mechanism onto clay minerals had been investigated in this study.

Kaolinite and montmorillonite were the clay minerals assessed in this study due to their high adsorption of CTAB. Kaolinite is found in abundance in Malaysia’s reservoir, while montmorillonite is found the least. These negatively charged clay minerals and the positively charged CTAB can enhance CTAB adsorption onto clay minerals. The selected LS with the highest adsorption capability was mixed with CTAB to evaluate the adsorption of CTAB onto clay minerals. Apart from the mixture approach, the selected LS with the highest adsorption capability was pre-treated with clay minerals prior to CTAB encounter to assess CTAB adsorption.

Cationic CTAB was used as surfactant due to its availability and it is often used in experimental work. The CTAB can further reduce the IFT to low IFT. The advantages of using cationic surfactant over anionic surfactant are that cationic forms stable solutions in brine and wettability alteration. The adsorption of both negatively charged clay mineral and anionic surfactant can spontaneously be reduced by electrostatic repulsion. Studies have proven the success of LS as SA in reducing anionic surfactant. To the best of the author’s knowledge, no study has reported LS as SA to reduce cationic surfactant.

Monovalent (NaCl) and divalent ($CaCl_2$) salts were used to test all adsorption experiments in static condition. The concentration ranged at 1-5 wt% for monovalent salt, while 0.1-1.0 wt% for divalent salt. Lower concentration of divalent salt and higher concentration of monovalent were purposely used to identify the effect of these salts. Acid and alkali regions (1-11) were studied for pH. Temperature was omitted as the universal trend shows that adsorption is reduced upon increment in temperature. All adsorption tests were conducted in aerobic environment.

Static adsorption test was performed to investigate the readiness of LS to adsorb onto clay minerals. Equilibrium and kinetic adsorption models were used to describe LS adsorption. The efficiency of LS as SA to reduce CTAB through mixture or pre-treatment was determined in static adsorption.

1.5 Significance of the Study

The significance of this study is described based on several aspects, such as material, empirical data, conceptual/theoretical, and practicality, as follows:

(a) Material – This study assessed different types of LS and examined the readiness of LS adsorption onto clay. It is the first attempt to compare LS type, functional group, and adsorption capability onto clay minerals with different brine salinity, concentration, and pH values. This study not only evaluated the adsorption behaviour of different LS, but also comprehensively explored the mechanisms responsible for the effectiveness of LS as SA.

(b) Empirical data – This study presents evidence based on experimental work to show the readiness of LS to adsorb onto clay minerals and the best method with effective underlying mechanism to reduce cationic adsorption using SA.

(c) Conceptual/Theoretical – This study tested the compatibility in cationic surfactant that is directly link to other parameters and potentially enhanced the theory of LS as SA, which is limited to anionic surfactant in the past.

(d) Practicality – The success of LS as SA in reducing both anionic and cationic surfactants at sandstone and carbonate reservoir conditions benefits the surfactant selection. Broader variety of surfactants can be selected with less worry on the adsorption.

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