CO_2-Responsive O/W Microemulsions Designed for Treating Oil-Contaminated Drill Cuttings

by

Xiangyu Chen

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Department of Chemical and Materials Engineering
University of Alberta

Abstract

The oil-based drilling fluids are mainly used to explore hydrocarbon resources. During the drilling operation, a significant amount of oil-contaminated drill cuttings, which are crushed rocks, sands and clays mixed with the drilling fluids, are transported to the surface. In order to reduce the residual oil content in the drill cuttings for safe disposal, energy and time-consuming methods such as thermal desorption and land farming have been used to treat the oil-contaminated waste. However, a large amount of energy is used in the high-temperature treatment process and transportation from the drilling platforms to the treatment stations.

In the treatment of the oil-contaminated drill cuttings, it is difficult to reduce the residual oil content (retention of oil on cuttings, ROC) to less than 1 wt% as required by governmental regulations. The objective of this thesis is to investigate and develop an innovative treatment process using CO_2-responsive O/W microemulsions with the prominent capability of solubilizing oil for the purpose of washing the oil-contaminated drill cuttings and reducing the residue oil level for safe disposal.

In the theoretical part of the thesis, a novel CO_2-responsive O/W microemulsion of rapid switching responses was designed based on a CO_2-responsive superamphiphile which had a linear structure and assembled via electrostatic interactions between cationic Jeffamine D-230 and anionic oleic acid at a mole ratio of 1:1. The thermodynamically stable heptane-in-water microemulsions were spontaneously formed by adding the switchable superamphiphile and 1-

butanol as a co-surfactant. After treating this stable microemulsion with CO_2 for 20 seconds, the superamphiphile dissociated into interfacial inactive building blocks, which led to complete phase separation of the microemulsion. Removing the CO_2 from the system by N_2 sparging at 60 ºC for 10 minutes switched the phase-separated system back to a transparent microemulsion as a result of the in-situ formation of the superamphiphile. The O/W microemulsion designed using this novel superamphiphile featured not only unique thermodynamical stability of nano-sized droplets, but also a rapid response to CO_2 to achieve a complete phase separation, and re-microemulsification as desired with N_2 purging. This CO_2-responsive O/W microemulsion can be potentially utilized for the drill cuttings treatment, and many other applications such as soil remediation, enhanced oil recovery and nanomaterial synthesis.

The second half of the thesis mainly focused on the application using such microemulsions. Based on the CO_2-responsive microemulsions, a rapid oil-contaminated drill cuttings treatment process was developed at the ambient temperatures with low energy consumption, which could significantly reduce the ROC from ~15 wt% to below the 1 wt % discharge limit for safe disposal. The treatment process exhibited a fast and deep extraction of residue oil due to the ultra-low interfacial tension and the strong capability of solubilizing oil of the O/W microemulsions. Purging the microemulsions with CO_2 for seconds caused the dissociation of the superamphiphile, leading to a complete phase separation and a concentration of the extracted residue oil at the top. The formed aqueous phase between the oil phase and the clean sediments efficiently prevented the further recontamination of the clean solids.

Compared with other treatment methods from the previous studies, this innovative treatment process using CO_2-responsive microemulsions is easy to operate at the ambient temperatures without any expensive equipment or extreme working conditions, making this microemulsion treatment a promising candidate for commercialization. The results in this thesis can contribute to the feasibility research of using microemulsions to extract the residual oil from the oil-contaminated drill cuttings, and the technical foundation for the scale-up study in the fields to significantly reduce the treatment cost and the associated carbon emission.

Preface

This thesis is composed of introduction, literature review and research papers. Chapters 3 and 4 are research papers which have been published or in preparation.

Chapter 1 Introduction. An original work by Xiangyu Chen.

Chapter 2 Literature review. An original work by Xiangyu Chen, which is undergoing editing for publication as Chen, X.; Xu, Z., "Treatment and disposal methods of oil-contaminated drill cuttings", in preparation. Chen, X was responsible for the literature review, data analysis and the manuscript composition, Xu, Z was the supervisory author and was involved with manuscript composition and edit.

Chapter 3 in this thesis is the theoretical study of the CO_2-responsive O/W microemulsions, which has been published as Chen, X.; Ma, X.; Yan, C.; Sun, D.; Yeung, T.; Xu, Z., "CO_2-responsive O/W microemulsions prepared using a switchable superamphiphile assembled by electrostatic interactions." Journal of Colloid and Interface Science 2019, 534, 595-604. Chen, X was responsible for the concept formation, data collection, analysis and the manuscript composition, Ma, X assisted with the data analysis and the manuscript edits. Yan, C, Sun, D and Yeung, T contributed to the manuscript edits. Xu, Z was the supervisory author and was involved with concept formation and manuscript composition.

Chapter 4 in this thesis is the application study using the CO_2-responsive O/W microemulsions, which is undergoing editing for publication as Chen, X.; Ma, X.; Yeung, T.; Sun, D.; Xu, Z., "Comprehensive treatment of oil-contaminated drill cuttings using CO_2-responsive O/W microemulsions”, in preparation. Chen, X was responsible for the concept formation, data collection, analysis and the manuscript composition, Ma, X, Yeung, T and Sun, D contributed to the manuscript edits. Xu, Z was the supervisory author and was involved with concept formation and manuscript composition and edit.

Chapter 5 Conclusions and recommendations for future work. An original work by Xiangyu Chen.

The appendices at the end of the thesis provide additional figures and tables for chapter 3 and 4.

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List of Abbreviations

96-h LC_{50}	the concentration which causes 50% death of test organisms in 96 hours
AER	Alberta Energy Regulator
CCD	charge coupled device
CMC	critical micelle concentration
DOL	degree of oil liberation
FF-TEM	freeze-fracture transmission electron microscopy
FTIR	fourier-transform infrared spectroscopy
GC	gas chromatograph
ME	microemulsion
MSD	mass selective detector
O/W	oil in water
OBMs	oil-based muds
OSPAR Convention	the Convention for the Protection of the Marine Environment of the North-East Atlantic
PDI	polydispersity index
ROC	fluid retention on drill cuttings
SBMs	synthetic-based muds
SDT	spinning drop tensiometer
TCC	thermo-mechanical cuttings cleaner
t_{EC20}	time leads to 20% of the ultimate oil liberation limit
TGA	thermogravimetric analysis

WBMs	water-based muds
t_0	center index
ΔG	change in Gibbs free energy
A_2	final value
A_1	initial value
t	liberation time
p	power index
W_a	work of adhesion
W_c	work of cohesion

Chapter 1 Introduction

1.1 Introduction to drilling fluids

1.1.1 Circulation of drilling fluids in drilling operations

In petroleum engineering, drilling fluids (muds) are often used in drilling wells for exploration of oil or other hydrocarbon resources [1]. Due to the requirements of difficult drilling projects, the drilling fluids have been developed in the last several decades with better stability and functionalities. However, it also brings negative consequences because drilling waste treatment becomes more difficult and expensive, which increases the overall operation cost.

In a drilling operation, the drilling fluid, which is the “blood” of the drilling operation with pressure as high as 5000 psi, is circulated from the surface, pumped down to the drilling bit and back to the surface via the annulus, as shown in Figure 1-1 [2]. Among all the equipment used in this circulation, the mud pump acts as the heart of the fluid system to drive the drilling fluid. After leaving the mud pump, the fluid goes to the standpipe, then through Kelly hose and down to the drilling bit. Typically, the drilling bit has two or more nozzles which accelerate fluid down to the bottom of well to keep the bit clean and remove cuttings from the formation surface. These cuttings are suspended in the drilling fluid and carried to the surface through the annular space between the wellbore and the pipe [1].

After the cuttings were pumped out of the sloping pipe, the most of the drill cuttings are separated by the shale shaker from this circulating system. The rest drilling fluid goes through the vibration screen and drops into a setting pit where remaining large solids are separated.

Furthermore, the drilling fluid is transported into the stirred pit where gas, sand and silt are removed. In the last step, the drilling fluid is circulated back to the mud pump [1].

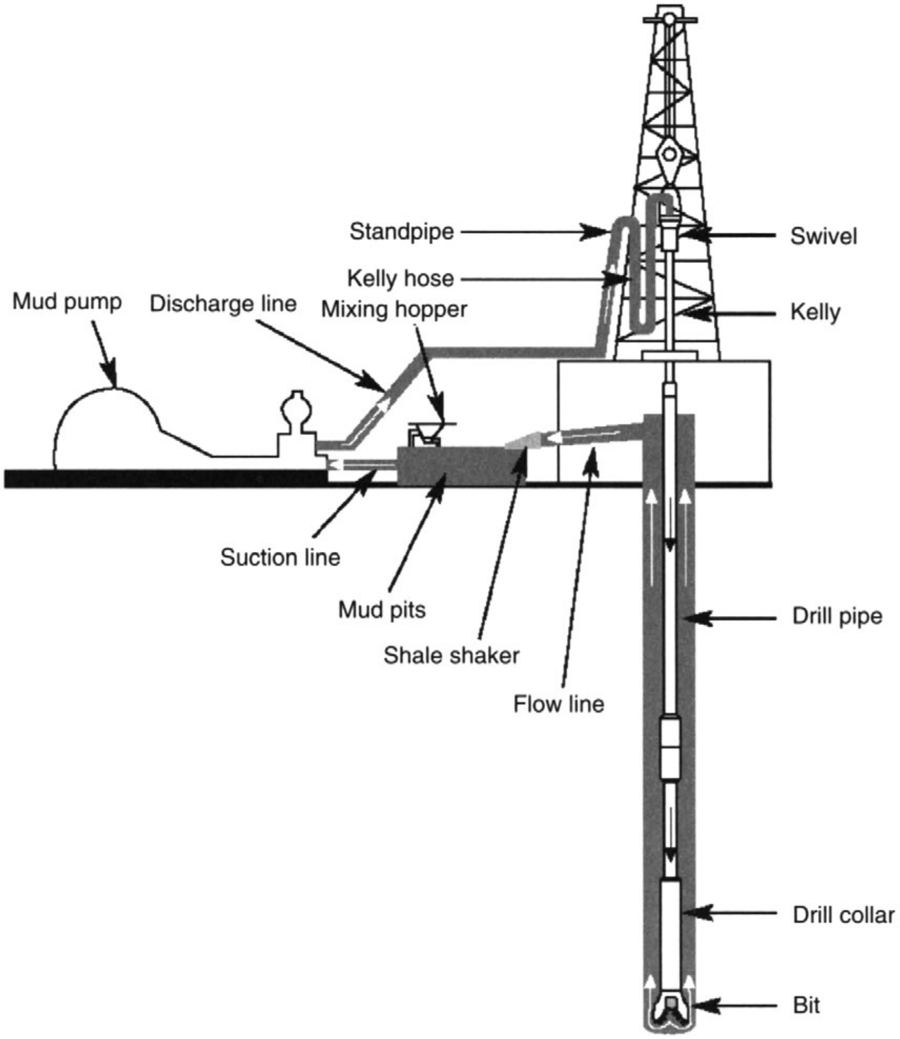


Figure 1-1 The circulating system of the drilling fluid. Reprinted with permission from Ref 2 [2]. Copyright © 2007 PennWell Corp.

1.1.2 Functions of drilling fluids

The objective of drilling activity is to drill, measure and complete a well which produces oil or other hydrocarbon resources. During the operation, the drilling fluids perform essential functions which assist in the drilling activity. To successfully complete the drilling project, the drilling fluids must have the following functions [1, 2]:

1) Remove and suspend the drill cuttings (the drilled solids from the bottom of the well) around the drilling bit.
2) Transmit the hydraulic force to the mechanical force to drive the drilling bit in the deep or horizontal wells.
3) Stabilize the hole by controlling the formation pressure.
4) Seal the permeable formation and prevent fluid loss.
5) Lubricate and support the drilling tools, prevent corrosion.

The most important function of a drilling fluid is to clean the hole by removing the drill cuttings around the bit. In the majority of the drilling projects, an overbalance drilling (a positive differential pressure ranging from 100 to 500 psi across the wellbore wall) is maintained for the safety consideration [2]. However, due to this pressure difference, the drill cuttings are pressed under the drilling bit, which prevent the continuous drilling on new formation surface. For this consideration, a drilling fluid must provide hydraulics to create enough cross flow to sweep out these drill cuttings from the downhole drilling activity. In another word, the drilling fluid should passe through nozzles in the drilling bit, and then move upward with the suspended drill cuttings.

In order to recycle the drilling fluid, cuttings must be effectively separated by the screens and the other treatment equipment at the surface.

1.1.3 Classification of drilling fluids

Drilling fluids can be classified based on the fluid type into three major categories: gaseous, aqueous and nonaqueous, as shown in Figure 1-2. In the gaseous type of drilling fluid, air or nitrogen are used to drill low-pressure formation. Aqueous drilling fluids are usually referred to the water-based muds (WBMs), while nonaqueous drilling fluids generally mean oil-based muds (OBMs) and synthetic-based muds (SBMs). OBMs are made mainly by the distillates from crude oil, such as diesel, mineral oils and paraffins. SBMs, in another name as pseudo-oil-based muds, are made by reaction products of materials like ethylene, for examples, olefins and esters from a serious of chemical reactions, which means they contain a very low concentration of toxic components found in the refined oil such as cyclic or aromatic contents [1].

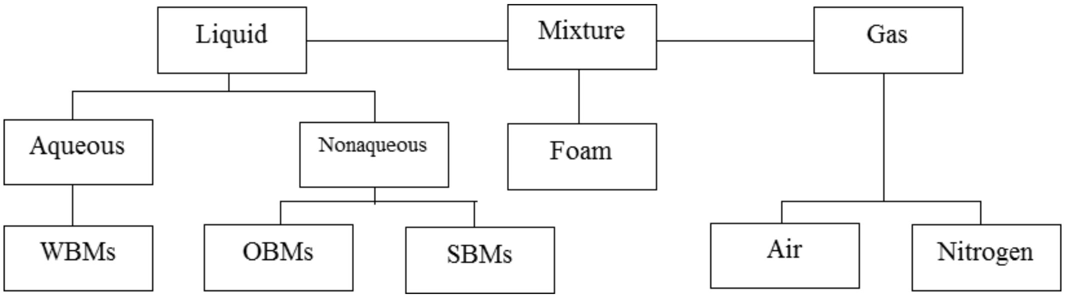


Figure 1-2 Types of drilling fluids. Reprinted with permission from Ref 1 [1]. Copyright © 2005 Elsevier.

The constituents and their proportions may vary for WBMs, OBMs and SBMs depend on the drilling purpose, downhole formation and well depth, etc. In general, WBMs are made of water, bentonite clay and weighing agent barite, as well as other substances to accomplish desired drilling properties, such as lubrication agents, filtration control agents and thinners. A typical example of WBM can be made of 76% water, 15% barite, 7% bentonite and 2% other [3]. A more detailed scheme of substances of WBMs is shown in Figure 1-3 [1].

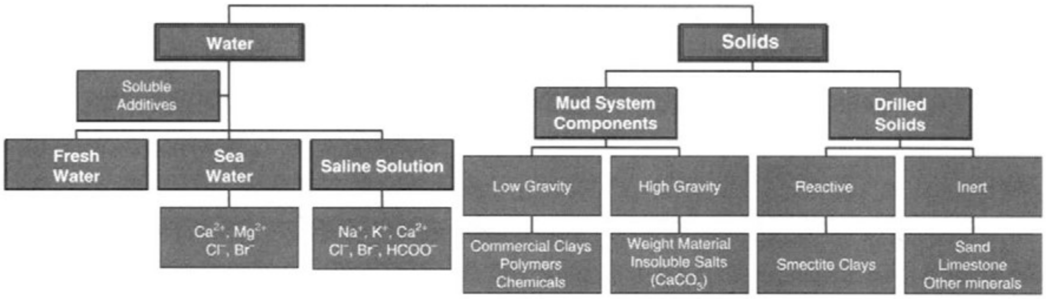


Figure 1-3 Substances of water-based muds. Reprinted with permission from Ref 1 [1]. Copyright © 2005 Elsevier.

On the contrary, OBMs and SBMs are based on non-aqueous materials, sometimes are in the form of invert emulsions. The continuous phase is diesel, crude oil, mineral oil or synthetic oil, and the dispersed phase is water in most cases. Similar to WBMs, other chemicals or substances are added to stabilize the emulsion and achieve the target drilling properties. The barite is again to be used to increase the fluid density, and clay minerals are used to change the viscosity. Different from WBMs, OBMs or SBMs are based on oil which is a good lubrication agent for drilling tools. One example of the composition of this non-aqueous drilling fluid can consist 46% base oil, 33% barite, 18% brine, 2% emulsifiers and 1% other [3]. A detailed scheme of the composition of OBMs and SBMs is shown in Figure 1-4 [1].

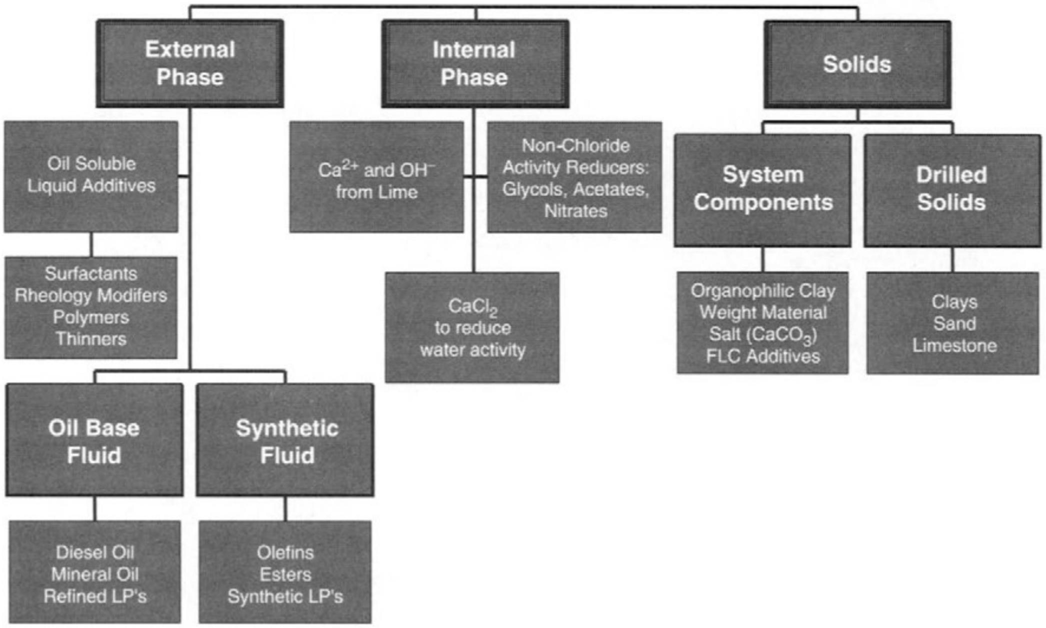


Figure 1-4 Substances of oil-based muds. Reprinted with permission from Ref 1 [1]. Copyright © 2005 Elsevier.

Among many applications, even though harmful to the environment, diesel is chosen to be the oil phase in OBMs with or without water addition, due to its low cost and resistance to the high temperature. Occasionally, crude oil is used to replace diesel, but the safety problem confines its application. As a result, mineral oil and synthetic oil have been widely used nowadays. Among all the oil types, synthetic fluids have the highest operation cost but least toxicity. As the dispersed phase, water in the invert emulsion contains salts such as sodium or calcium chloride.

Surfactants containing calcium are the primary emulsifier in OBMs and SBMs to achieve highly stable emulsions under high temperature and pressure in downhole drilling condition with the existence of contaminants, which are made in the mud system by the reaction of lime and long-chain acids. Secondary emulsifiers are often used to assist to form a stable emulsion system. Moreover, lime can also be used to neutralize acid gases such as H_2S and CO_2 in the shale oil/gas exploration. Amine-treated lignites, gilsonite or asphalt derivatives, wax and polyacrylates can be used as fluid loss control agents. Bentonite, hectorite or attapulgite clays treated with an amine can be dispersed into the oil phase to act as organophilic gellants to increase the viscosity of the mud and control the fluid rheology. Another important component in the drilling fluid is the weighting agent to increase the density of the fluid, which normally include Barite, calcite and hematite [2].

Compared to WBMs, OBMs and SBMs have unique advantages despite their higher cost and potential environmental disposal hazards: (1) Shale stability. OBMs and SBMs are more suitable for drilling water-sensitive formation since the oil-based system does not react with shales. Even though the water phase is dispersed inside of the drilling fluid in some cases, it still has enough salinity to limit water migration into the shale [4]. (2) Drilling rate. OBMs and SBMs allow faster drilling operation compared to WBMs, but still provide outstanding shale stability [5]. (3) High-temperature tolerance. OBMs and SBMs are very suitable to drill formations at the high temperature and high downhole pressure condition [6]. (4) Lubricity. OBMs and SBMs often have a thin filter cake between the drilling pipe and wellbore, and provide better lubricity, which is highly suitable for the drilling of horizontal wells [1]. (5) Corrosion prevention. As the base oil of OBMs and SBMs can coat the drilling tools in the downhole condition, corrosion of metal part of drilling tools is controlled [2]. (6) Recyclable. OBMs and SBMs can be recycled for the next drilling operation and the storage lifetime is longer compared to WBMs [1]. Due to these advantages, OBMs and SBMs are still used in the majority of the drilling projects or the deeper drilling operations, although the development of different WBMs has been carried since the 1930s to reach the same properties as non-aqueous drilling fluids [7]. Therefore, this thesis will mainly focus on the treatment of the cuttings contaminated by the oil-based drilling fluids.

1.2 Introduction to the treatment of drill cuttings

1.2.1 Drill cuttings and treatment methods

The principal purpose of drilling fluids is to suspend and transport drill cuttings to the surface. Drill cuttings are crushed rocks generated by the crushing action of the drilling bit as it cut the sub-surface, which tend to have an angular configuration and can range in size from ~2 μm to over 30 mm [8]. An example of drill cuttings used in this thesis is shown in Figure 1-5. The composition of the cuttings mirrors the geological formation of the sub-surface, as well as other manufactured chemical compounds that had originally added into the drilling fluids. For example, the cuttings from a rig on the Mid-Atlantic shelf contained 21% montmorillonite, 11% of illite, 11% chlorite, and 22% quartz, with a small amount of siderite and dolomite [8]. In the North Sea, cuttings from wells are primarily made of shale and sandstone [9]. Also, abundant quartz and barite were found in the Ekofisk field. The quartz may come from the sandstone in the cuttings and barite is mainly form the weighting agent in the drilling fluid which is adhered to the cuttings [10].

Figure 1-5 Picture of drill cuttings used in this thesis. The drill cuttings were contaminated by the oil-based drilling fluids.

On the drilling platform, the mixture of drilling fluids and cuttings are treated to control solid content. However, as one of the most effective drilling fluids, OBMs are commonly used in many drilling projects. They are removed from cuttings on the rig in most of the operations, but some residue oil still adheres to the cuttings and needs further treatment. As a result, oil-contaminated drill cuttings are glued together and not easy to disperse when discharged. Figure 1-6 shows the schematic flow chart of the general drill cuttings treatment plan [3].

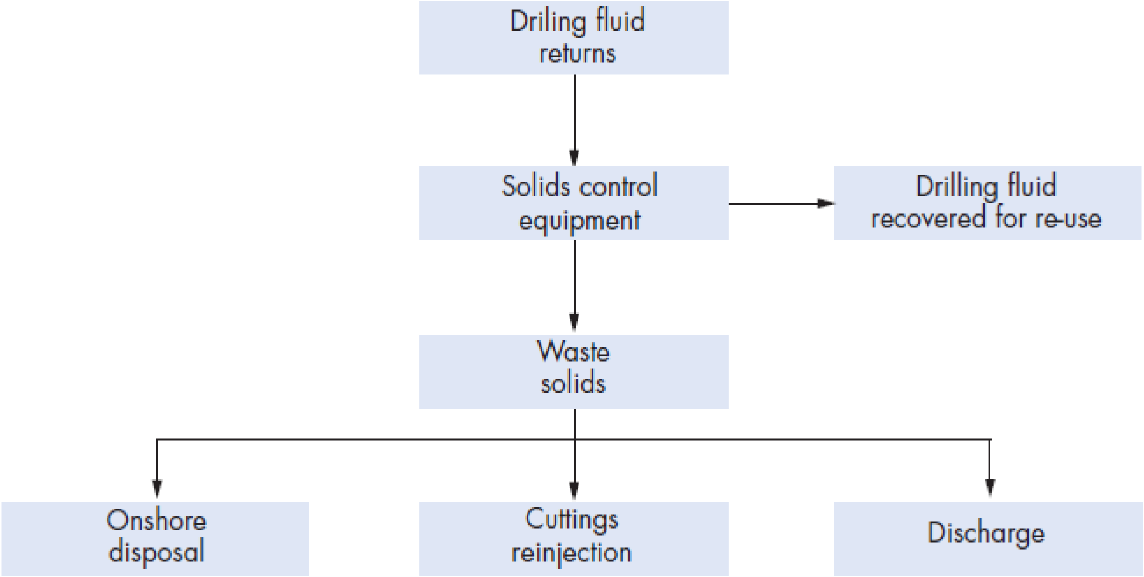


Figure 1-6 Schematic flow chart of the separation of drill cuttings from drilling fluids. Reprinted with permission from Ref 3 [3]. Copyright © 2004 Society of Petroleum Engineers.

The objective of the modern drill cuttings treatment system is to reduce the overall drilling cost by effective removal of clean solids, minimize the loss of drilling fluids and create a safe working condition/desired environmental compliance. In order to introduce the treatment process, this chapter classifies treatment methods into “primary” and “secondary” systems. The primary treatment system is designed on site as the first stage for the solids removal and the drilling fluids recovery, while the secondary treatment system requires additional equipment or methods to increase drilling fluids recovery rate to meet rigorous regulatory requirements for the safe disposal. An overall recycle system for oil-contaminated drill cuttings is shown in Figure 1-7.

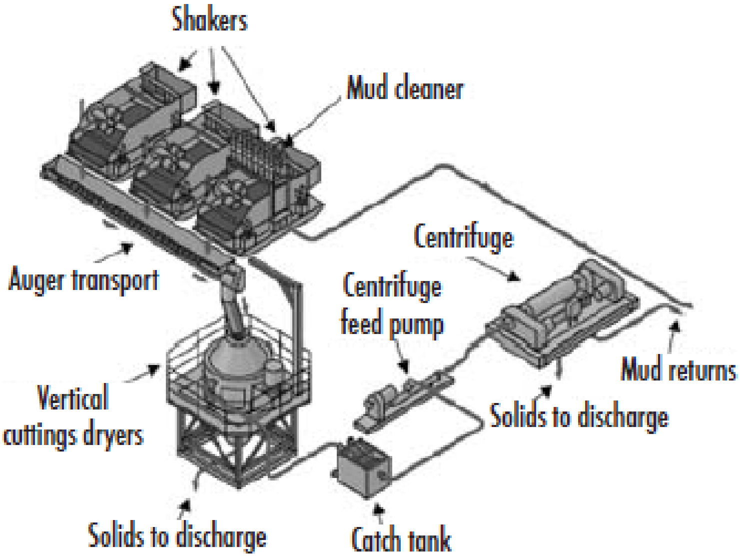


Figure 1-7 Example of a treatment system for SBMs drill cuttings. Reprinted with permission from Ref 3 [3]. Copyright © 2004 Society of Petroleum Engineers.

1.2.2 Primary treatment system

The primary solid-control system is designed based on the type of the drilling fluids, the underground formation and the specific cuttings disposal environmental requirements. The system contains a series of physical separation equipment such as shakers, hydrocyclones and centrifuges to remove coarse to very fine solids, as shown in Figure 1-8 [2]. The components are selected based on field drilling and environmental requirements. As a result, there is no universal treatment process which can be suitable for all primary separation applications. Typically, a well drilling operation can generate ~1000 to 2000 tons of cuttings, and these cuttings normally contain 5-15% drilling fluids after the primary treatment [11].

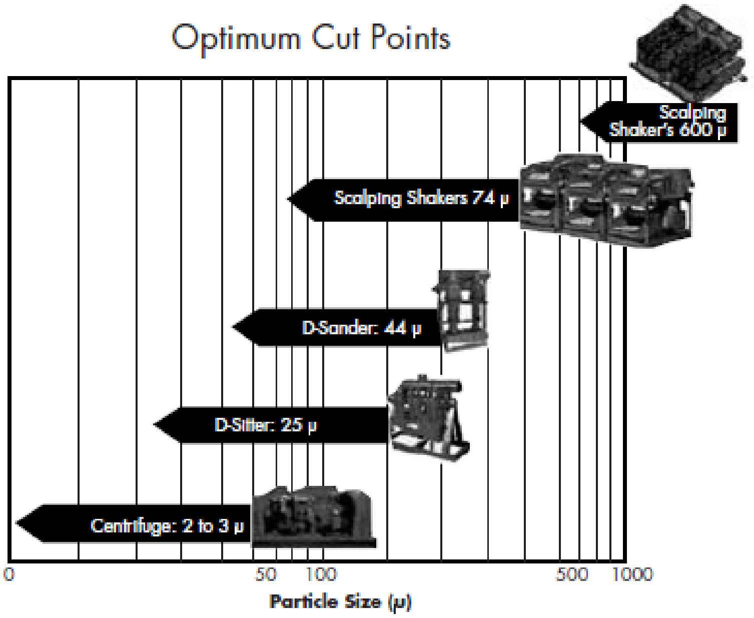


Figure 1-8 Particle size cut points for solids-control equipment. Reprinted with permission from Ref 2 [2]. Copyright © 2007 PennWell Corp.

1.2.2.1 Shale shaker

The shale shaker is a basic solids-control device in the drill cuttings treatment process [3]. The drilling fluids are pumped from the borehole with mixed drill cuttings to the shaker in order to remove coarse-grained cuttings. A series of vibration screens are designed to transport the drill cuttings from the feed to the discharge, where the cuttings are discharged if the environmental requirements are achieved or transported to the next treatment stage. At the same time, the drilling fluids and the small particles can pass through the shaker, then reach the next equipment for further treatment, i.e., centrifuge to separate the fine solids [1]. A typical example of shaker used in the field and its operating mechanism are shown in Figure 1-9.

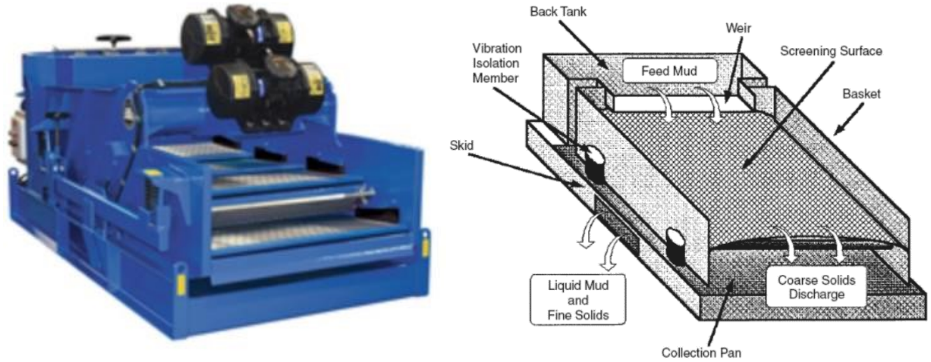


Figure 1-9 Left: A typical shaker used in the field. Right: Screening operation mechanism in shakers. Reprinted with permission from Ref 12 [12]. Copyright © 2019 Engineering 360.

1.2.2.2 Hydrocyclone

The hydrocyclone (Figure 1-10) is usually mounted to the shale shaker. It sucks the drilling fluid from the shaker, separates fine particles in a suspension phase using centrifugal force gravity separation. It is effective to an unweighted drilling fluid system to remove and dry solids but still retain the expensive drilling fluids [1].

Figure 1-10 Desander Hydrocyclone. Reprinted with permission from Ref 13 [13]. Copyright © 2019 NOV.

As shown in Figure 1-11, a hydrocyclone typically has a conical base and a cylindrical top section. The mixture of liquid and solid is fed into the top section where a rotational motion is created to introduce high centrifugal force in order to accelerate gravity separation [1, 2]. The underflow which consists of denser particles is discharged at the bottom. On the contrary, the overflow, which contains lighter drilling fluids and other fine particles, is collected at the top of the equipment and transported to the next treatment process. These hydrocyclones are designed to separate the solids fraction from the suspension. If the shale shaker can effectively remove the sand and slit sized solids, it may not need “desanders” or “desilters” in hydrocyclones to save the overall project cost.

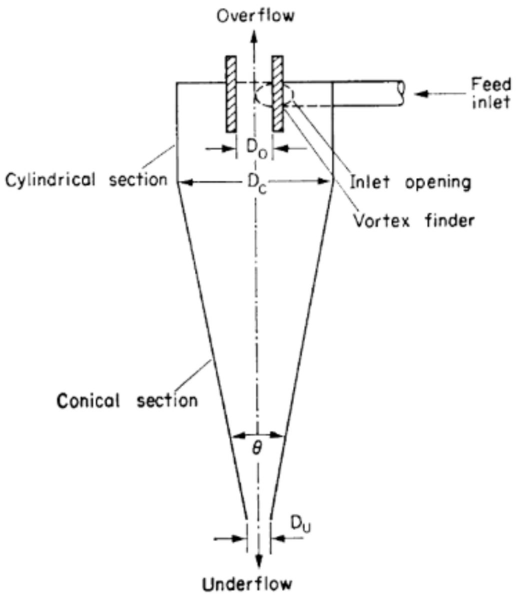


Figure 1-11 Operation scheme of hydrocyclones. Reprinted with permission from Ref 14 [14]. Copyright © 2013 Elsevier.

1.2.2.3 Centrifuge

The centrifuge is used to remove fine solids and recover fluids using very high centrifugal forces up to over 2000 G [1]. An example of the centrifuge is shown in Figure 1-12. As illustrated in Figure 1-13, the feed is input into the unit by the axial port. The solids can be separated in the drying zone and discharged at one end, whereas liquids flow to the poll zone and separated at the other end. For weighted drilling fluids, centrifuges are commonly used to recycle barite [2].

Figure 1-12 Centrifuge used in the field. Reprinted with permission from Ref 15 [15]. Copyright © 2019 M.-I. SWACO.

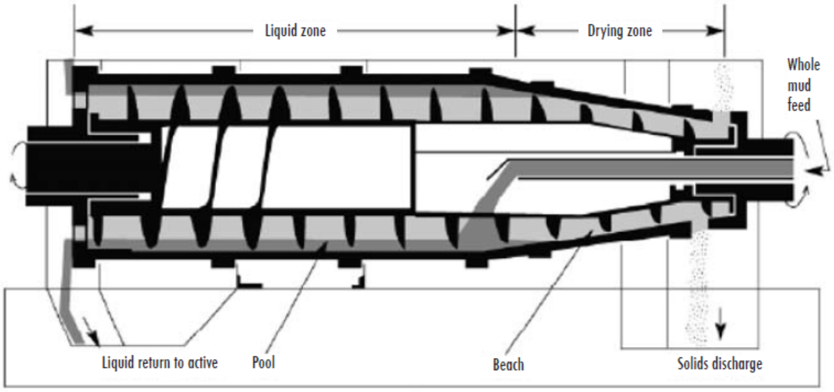


Figure 1-13 Operation scheme of a decanting centrifuge. Reprinted with permission from Ref 3 [3]. Copyright © 2004 Society of Petroleum Engineers.

1.2.3 Secondary treatment system

After the primary treatment, the fluids retention on drill cuttings (ROC) is around 5-15 wt%. To further reduce the ROC, cuttings dryer and thermal desorption station as two most commonly used treatment methods have been commercialized in the secondary treatment stage [1]. Cuttings dryer is mainly used offshore (e.g., in the Gulf of Mexico) to treat SBMs cuttings after the primary treatment. However, it is difficult to achieve the requirement of 1 wt% ROC set by Oslo and Paris Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR Convention). Compared to the cuttings dryer, thermal desorption method can reach the target ROC, but it can be only built on the land with much higher energy consumption [2].

1.2.3.1 Cuttings dryer

A cuttings dryer unit is often mounted with the primary cuttings treatment system, as shown in Figure 1-14. Cuttings from the shakers or centrifuges are sent to the dryer for the secondary treatment. As illustrated in Figure 1-14, the dryer consists of a fine mesh screen, which is mounted on a rotation basket to generate centrifugal forces like a washing machine. The centrifuge can be either vertically or horizontally oriented [16]. The fluids recovered from the unit can be reused, but the recovered fluid with fines inside may need additional dilution using the fresh drilling fluid stream.

Figure 1-14 A vertical cuttings dryer can process drill cuttings up to 60 tons per treatment and achieve ~ 5 wt% ROC. Reprinted with permission from Ref 17 [17]. Copyright © 2019 M.-I. SWACO.

However, only cuttings dryers are not enough to achieve desired ROC as 1wt %. In a study of 23 wells using MI-SWACO vertical cuttings dryers, ROC was reduced from 11.5 wt% to 4.0 wt% [16]. Another report from Johnston et al. indicated that the ROC was reduced to 4.4 wt% for 72 wells drilled using SBMs in the Gulf of Mexico [18].

1.2.3.2 Thermal desorption method

For onshore drilling projects, drill cuttings after the primary treatment are often gathered and shipped to a thermal desorption station, where cuttings are heated to the distillation temperature of the base oil used in the OBMs or SBMs. The temperature is quickly ramped and maintained until most of the oil is separated by vaporization [19]. Screw type and rotary kiln type stations were first successfully commercialized. The screw type unit uses a hollow screw with a heating jacket to vaporize the base oil, while the rotary kiln type unit has a rotating drum which is heated. The temperature ranges typically from 250 ℃ to 350 ℃, and up to 520 ℃ in some conditions to reach the desired ROC if high molecular weight base oil is used [3].

When introduced into drill cuttings treatment industry, thermal desorption station requires large and stationary facilities due to space and energy requirements, which limits their offshore application, as shown in Figure 1-15 [20, 21]. Compared to the onshore waste treatment method, cuttings from the offshore are mainly boxed and transported to the thermal desorption facilities on land. However, this activity may face a significant high shipment cost and the potential risk of leaking during transportation [22].

Figure 1-15 Pictures of typical thermal desorption stations for the oil-contaminated drill cuttings treatment. Reprinted with permission from Ref 21 [21]. Copyright © 2002 Society of Petroleum Engineers.

In order to solve the difficulty during the transportation, an onsite thermo-mechanical cuttings cleaner (TCC) equipment, which is developed by Thermtech AS in Norway, has been introduced both onshore and offshore. This equipment is based on friction technique as it consists of a series of arms which are linked to a high spinning speed central rotational drive, as shown in Figure 1-16. When the cuttings are transported through the chamber, the friction from the arms generates heat to evaporate the water and/or the base oil in the cuttings. The operation temperature of the TCC unit is between 240 °C to 260 °C, in which the composition of the base oil, no matter synthetic or mineral, is less degraded [23]. The water and oil steam are condensed and recovered in the oil condenser. After the treatment from this unit, the solids normally has a ROC < 0.1 wt% [24]. This technique allows a continuous process and a very short retention time for treatment, which is based on the direct mechanical friction to generate heat in order to separate the residue water and oil [24]. Most importantly, the size of this unit is relatively small compared to the onshore thermal desorption station, which allows a feasible treatment process to be built on the offshore platform.

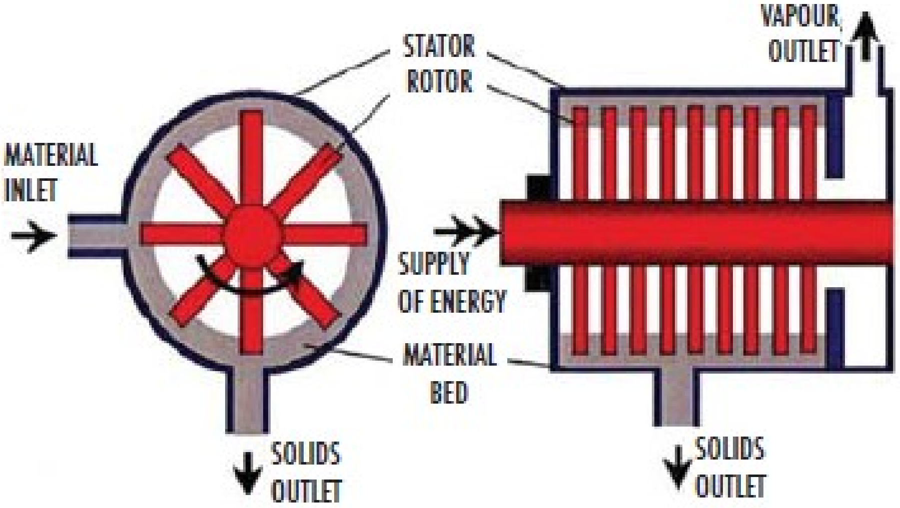


Figure 1-16 Thermo-mechanical cuttings cleaner heat generation mechanics. Reprinted with permission from Ref 24 [24]. Copyright © 2008 Society of Petroleum Engineers.

The TCC method was commercialized in 2003 and already successfully worked at an offshore platform in the U.K. to process more than 30,000 tons of cuttings, even though the other 50,000 tons were still transported elsewhere to process [20]. Another application in Kazakhstan, MI-

SWACO employed this TCC unit to reach a 50,000 tons/year of OBMs cuttings treatment capacity [20]. However, the entire thermal desorption operation must be heated to vaporize the residue water and/or the base oil in the cuttings. Despite the considerable energy consumption and carbon emission, transportation of a significant quantity of drilling waste is another cost consuming factor that needs to be considered.

1.3 Regulations and guidelines

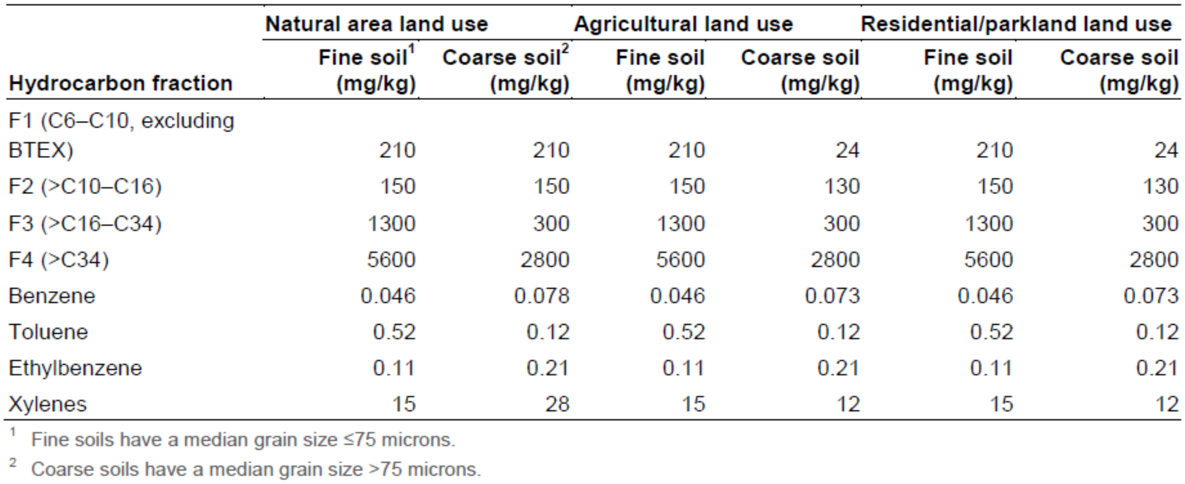
The Protection of the Marine Environment of the North-East Atlantic (OSPAR Convention) specifies that the drilling discharge into the North Sea should have the ROC less than 1 wt% [25]. In the USA, the Environmental Protection Agency (EPA) regulates the ROC to be 0 wt% for offshore drilling using the oil-based drilling fluids. If the synthetic based fluids are used, the ROC should be below 6.9 wt% in the Gulf of Mexico [26].

The treatment and the disposal of drilling waste in Alberta are controlled by the “Directive 050: Drilling Waste Management”, which was published by the Alberta Energy Regulator (AER) [27]. In Directive 050, the drilling waste is defined as the cuttings generated during the wells drilling operation for heavy oils exploration or the pipeline construction. The regulation sets out the hydrocarbon endpoints for the drilling waste. No matter which kind of treatment methods used, the final target has to meet endpoints set by this regulation.

Table 1-1 shows the soil hydrocarbon endpoints for the oil-contaminated drill cuttings in Directive 050. Endpoints are identified for the natural, agricultural and residential areas based on land usage, and coarse or fine grain soils based on the particle size of the drill cuttings. The mixture of soil and waste should be tested within 60 days after disposal, and the hydrocarbon fractions, i.e., toluene, benzene, ethylbenzene and xylenes, should not exceed the endpoints in any conditions [27].

Similar to the OSPAR Convention, Directive 050 also requires the total hydrocarbon in the oil-contaminated drill cuttings to be less than 1 wt% for the safe disposal. Considering the primary and secondary treatment systems consume huge energy, a cost-efficient and environmentally friendly method is highly desired to treat the oil-contaminated drill cuttings and meet the strict safe disposal target.

Table 1-1 Soil hydrocarbon endpoints. Reprinted with permission from Ref 27 [27]. Copyright 2012 Alberta Energy Regulator.



Hydrocarbon fraction	Natural area land use Fine soil[1] (mg/kg)	Natural area land use Coarse soil[2] (mg/kg)	Agricultural land use Fine soil (mg/kg)	Agricultural land use Coarse soil (mg/kg)	Residential/parkland land use Fine soil (mg/kg)	Residential/parkland land use Coarse soil (mg/kg)
F1 (C6–C10, excluding BTEX)	210	210	210	24	210	24
F2 (>C10–C16)	150	150	150	130	150	130
F3 (>C16–C34)	1300	300	1300	300	1300	300
F4 (>C34)	5600	2800	5600	2800	5600	2800
Benzene	0.046	0.078	0.046	0.073	0.046	0.073
Toluene	0.52	0.12	0.52	0.12	0.52	0.12
Ethylbenzene	0.11	0.21	0.11	0.21	0.11	0.21
Xylenes	15	28	15	12	15	12

[1] Fine soils have a median grain size ≤75 microns.

[2] Coarse soils have a median grain size >75 microns.

1.4 Thesis objectives

The main objective of this thesis is to design an innovative CO_2-responsive O/W microemulsion with ultra-low interfacial tension and strong capability of solubilizing oil, and develop a rapid treatment process using such microemulsion for the purpose of cleaning the oil-contaminated drill cuttings and reducing the residue oil level to less than 1 wt% as required by governmental regulations. Moreover, efforts have been devoted to investigate and understand the mechanisms of the microemulsion switching and the residue oil releasing from the drill cuttings during the treatment process. The detailed objectives are:

- Design a novel CO_2-responsive O/W microemulsion of rapid switching responses using a switchable superamphiphile.
- Investigate the switching behavior, the pseudoternary phase diagram, the size distribution, the interfacial tension and the stability of the microemulsion system.

- Understand the switching mechanism during the trigger gas purging at the molecular distribution and thermodynamic aspects.
- Based on the CO_2-responsive O/W microemulsions, design a rapid oil-contaminated drill cuttings treatment process at the room temperature with low energy consumption to reduce the ROC to less than 1 wt%.
- Correlate the droplet size, interfacial tension and capability of solubilizing oil with the ultimate cleaning results, understand the cleaning mechanism using the CO_2-responsive O/W microemulsion in the drill cuttings treatment.
- Optimize the microemulsion composition, select the suitable microemulsion formula to achieve the best treatment performance with the lowest cost.

The major contribution of this thesis to science is providing a new method to design the CO_2-switchable microemulsions by using the superamphiphiles based on the electrostatic interaction to achieve desired phase separation and reconstruction in a very short time. The prepared microemulsion is not only a novel washing medium to clean oil-contaminated drill cuttings or soils, but also a promising substrate for nanomaterial synthesis by creating switchable nanoreactors in the microemulsion polymerization. For the contribution in engineering aspect, this project creates an efficient oil-contaminated drill cuttings treatment process with low cost and energy consumption in the lab scale, which is similar to the surfactant soil washing, but significantly reduces the treatment time and the contaminated oil to the reasonable levels. The study prepares the technical foundation for the scale-up in the fields to treat not only drill cuttings, but also possible contaminated soils and downhole wellbores with unique properties such as efficient treatment result, low treatment cost and decreased carbon emission.

1.5 Structure of the thesis

This thesis is divided into 5 chapters, which are structured as a compilation of introduction, literature review and research papers. Chapters 1 and 2 are restructured in a review paper in manuscript preparation. Chapters 3 and 4 are research papers that have been published or in manuscript preparation.

Chapter 1 provides the introduction of the overall research including the background of drilling fluids, drill cuttings, technical challenges and regulatory requirements. The thesis objectives and outline are also introduced in this chapter.

Chapter 2 presents a comprehensive literature review on the current methods and technologies for the oil-contaminated drill cuttings treatment in the secondary stage. A detailed technical review on the microemulsion is also provided including the thermodynamic calculation, classifications, oil extraction mechanism and switchable property by modification, leading to the technical foundation and guidance for the following chapters. A version of this chapter with partial content of Chapter 1 is undergoing editing for publication. Chen, X.; Xu, Z., "Treatment and disposal methods of oil-contaminated drill cuttings", in preparation.

Chapter 3 illustrates the theoretical study of the CO_2-responsive O/W microemulsions with rapid switching capability based on the novel superamphiphile formed by electrostatic interaction. The microemulsion can be prepared with low-cost, commercially available surfactants, and switches rapidly by purging of CO_2 or N_2. The unique properties of the microemulsion and the specific switching mechanism are investigated and described in this chapter. A version of this chapter has been published as Chen, X.; Ma, X.; Yan, C.; Sun, D.; Yeung, T.; Xu, Z., "CO_2-responsive O/W microemulsions prepared using a switchable superamphiphile assembled by electrostatic interactions." Journal of Colloid and Interface Science 2019, 534, 595-604.

Chapter 4 presents the application study using the CO_2-responsive O/W microemulsions in the oil-contaminated drill cuttings treatment at the room temperature. The ROC can be significantly reduced to below the 1 wt% safe discharge limit by careful optimizing the microemulsion composition. The unique nano-sized droplets, ultralow interfacial tension, strong capability of solubilizing oil are correlated together to investigate the cleaning mechanism using such microemulsion. A version of this chapter is undergoing editing for publication. Chen, X.; Ma, X.; Yeung, T.; Sun, D.; Xu, Z., "Comprehensive treatment of oil-contaminated drill cuttings using CO_2-responsive O/W microemulsions", in preparation.

Chapter 5 summarizes the conclusions of this thesis and the recommendations for future work.

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Chapter 2 Literature review

2.1 Introduction

In the deep or offshore drilling projects, oil-based drilling fluids are mainly used to explore hydrocarbon resources, due to their exceptional properties, such as better lubricity [1], enhanced corrosion protection [2], shale stabilization capability [4] and high temperature and pressure tolerance [6]. During the drilling operation, a considerable amount of oil-contaminated drill cuttings, which are crushed rocks, sands and clays mixed with oil-based drilling fluids, are transported to the surface. In these drilling projects, one of the significant technical challenges is the careful treatment and the safe disposal of the drill cuttings, especially those contaminated with significant amounts of oil-based drilling fluids. Specifically, regulations have been made to regulate the "fluid retention on drill cuttings" (ROC), which is defined as the weight percentage of residue oil in the cuttings, to be less than 1wt % for the safe disposal [25, 27].

Figure 2-1 summarizes a typical schematic circulating system of the oil-based drilling fluid and different treatment methods of the oil-contaminated drill cuttings, which are used to effectively remove drilled solids, minimize the loss of drilling fluids, create a safe working condition and desired environmental compliance. A series of physical separation equipment such as shakers, hydrocyclones and centrifuges are customarily integrated on site with the drilling facility in order to recycle the majority of the expensive drilling fluids from drill cuttings and decrease the oil residue in the disposal solids, which are classified as the primary treatment system [2, 28]. However, after the primary treatment system, the fluids retention on drill cuttings (ROC) is still around 5-15 wt% due to the limitations of the primary treatment technologies [11, 29]. Considering a typical well drilling project usually generates ~1000 to 2000 tons of oil-contaminated drill cuttings, which contain 50 to 300 tons of residue oil-based drilling fluid after the primary treatment, a cost-efficient and environmentally friendly method needs to be developed to treat the oil-contaminated drill cuttings and meet the strict safe disposal target.

To further reduce the ROC, two most commonly used treatment methods, cuttings dryer and thermal desorption station, have been employed in the secondary treatment stage for offshore and onshore applications respectively [1]. As the most commercialized technologies, they still face some practical challenges. In the offshore applications, only cuttings dryers are not enough to achieve the desired ROC [16, 18]. The drilling cuttings with excess residual oil should be boxed and transported to land for further treatment. In the thermal desorption method, the temperature is quickly ramped and maintained at 250 ℃ to 350 ℃, or up to 520 ℃ in some special conditions if the heavy base oil is used [3, 19]. During the entire treatment process, the thermal desorption stations need a high energy consumption and generate a huge carbon emission to maintain this high-temperature process [19, 20, 30].

With the emphasis on sustainability and the development of waste disposal regulations and codes, there is an urgent to develop an environmentally friendly and cost-efficient treatment strategy for the oil-contaminated drill cuttings management. This chapter reviews the currently available technologies for the drill cuttings treatment in the secondary treatment stage, and compares these technologies regarding treatment time, cost and space requirements.

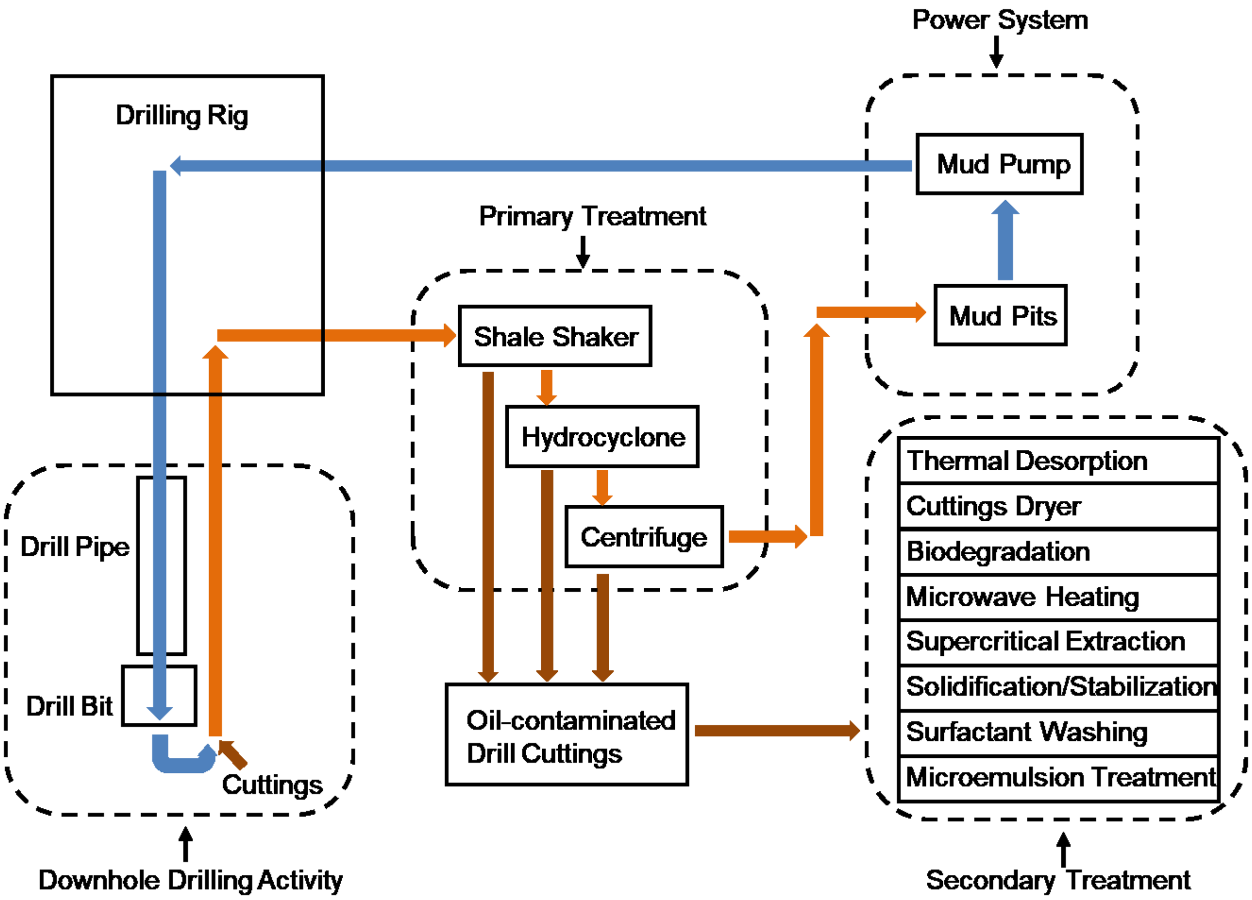

Figure 2-1 Schematic circulating system of the oil-based drilling fluid and the treatment of the oil-contaminated drill cuttings

2.2 Overview of drill cuttings treatment technologies in the secondary treatment stage

In order to achieve desired ROC which is below 1wt %, several alternative methods have been studied in the different stages and introduced into the secondary treatment system to reduce ROC with decreased cost and/or simplified equipment.

2.2.1 Biodegradation

Biodegradation treatment is mainly used onshore for disposal drilling waste [31]. In biodegradation method, recycled cuttings after the primary treatment are mixed with receiving soil, and biodegraded by microorganisms (bacteria, fungi) or enzymes naturally in the land or bioreactors [32, 33]. Similar to the other biological process, the biodegradation rates can be enhanced by improving soil temperature, moisture content and aeration condition. This treatment duration may vary from months to years depending on the ROC and the environmental conditions of the soil.

Among all the biodegradation methods, land farming is the most commonly used, controlled and repeated drill cuttings treatment method. The indigenous microorganisms in the land can break down the contaminated hydrocarbons in the natural attenuation process. Typically, the land farming treatment method only use the soil with a thickness of around 10 - 35 cm for a better aeration condition, which means it needs much more land area compared to the other desorption methods. The biodegradation process is supported by fertilizer and periodic tilling, which is very similar to the agriculture farming [34]. The cuttings can be reapplied to the soil depends on the chemical analysis of the ROC and other indicators of the land. Because higher molecular weight (≥C10) aromatic or aliphatic hydrocarbons are more challenging to be biodegraded, these constituents are often accumulated after the repeated applications [35].

One of the significant challenges in the land farming method is that all the lands used for the drill cuttings treatment are normally uncovered and exposed to all the weather conditions, especially rainfall. This requires the careful controlling and monitoring the land farming areas by the installation of barriers or liners, as to prevent the contaminated hydrocarbons from leaching to the groundwater or surface water, which may add additional cost and potential environmental concerns. Typically, the estimated treatment cost can be at US $ 30-60/ton [30]. Even though the biodegradation method is relatively inexpensive, experience has shown the ROC less than 5 wt% can be very difficult to achieve due to the limitation of this biological process [30].

2.2.2 Microwave heating

Microwave heating method is still based on the thermal desorption mechanism, but utilizes the microwave to generate heating inside of cuttings [36-38]. Compared to the traditional thermal desorption method, the water content in the oil-contaminated drill cuttings no longer wastes the energy to vaporize but acts as the critical heating element under the effect of the electromagnetic field. Robinson et al. proved the feasibility of using the microwave to treat the oil-contaminated cuttings from the North Sea in a laboratory study [36]. Furthermore, they reported an improved microwave treatment method on a pilot scale to continuously process up to 500 kg/h cuttings, as shown in Figure 2-2 [37, 38]. The dry and wet cuttings were first mixed together to reach a desired water content for microwave heating, then the mixture was fed into the microwave cavity. The oil was removed and recycled in the condensation system as similar to the thermal desorption unit. After the treatment, a ROC < 0.1 wt% can be achieved [37, 38]. This processing facility can be built in a compact space and further integrated into the offshore production platforms, which prevents the potential safety hazards during the transportation of large quantities of the oil-contaminated drill cuttings from the offshore rigs to the onshore treatment facilities. Nevertheless, the microwave heating technique still needs high energy consumption.

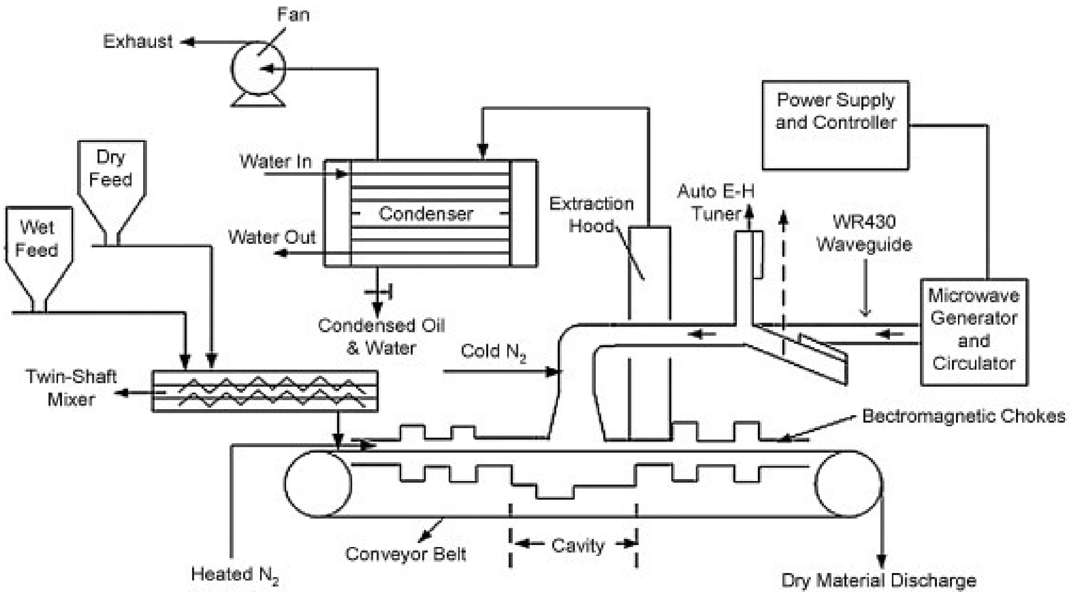

Figure 2-2 Example of a pilot-scale microwave treatment process. Reprinted with permission from Ref 38 [38]. Copyright © 2009 Elsevier.

2.2.3 Supercritical fluid extraction

Above 1070 psi and 35 ℃, carbon dioxide (CO_2) exhibits as the supercritical state and performs as a suitable solvent of hydrocarbons [39-41]. This technique has been commonly used in the extraction process of the pharmaceutical industry to separate active molecules from plants. Saintpera et al. reported the supercritical CO_2 treatment of 6 kg drill cuttings from the North Sea within 5 minutes, the ROC can be as low as 0.2 wt% in the best extraction condition, as shown in Figure 2-3 [41]. Dr. Guigard research group in the University of Alberta reported the process using the supercritical CO_2 to extract SBMs and indicated the structure of extracted hydrocarbons were not altered compared to the original base oil [39]. However, this technique needs very expensive equipment to reach and maintain the high pressure to keep CO_2 in the supercritical state, which limits its application in the oil industry due to the cost and safety considerations [11]. The research is under development to seek an alternative way to keep the supercritical state CO_2 in lab scale.

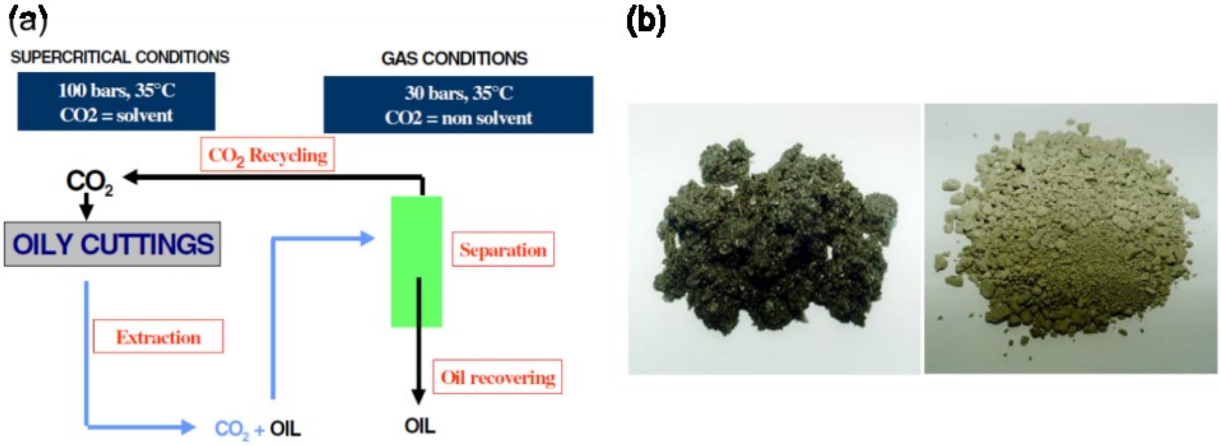

Figure 2-3 (a) Supercritical CO_2 treatment process on oil-contaminated drill cuttings. (b) Drill cuttings before and after the treatment. The ROC was decreased from 13 wt% to less than 1 wt%. Reprinted with permission from Ref 41 [41]. Copyright © 2000 Society of Petroleum Engineers.

Liquefied gas extraction is developed from supercritical CO_2 extraction method, but uses liquefied hydrocarbons such as propane or butane as an extraction medium, as they can be liquefied much easier at lower pressure and ambient temperature compared to CO_2 [11, 42]. As a result, the construction and operation costs can be relatively decreased. Test results in lab scale showed that ROC was reduced to less than 1% for OBMs and SBMs cuttings treatment [11]. The safety investigation is still in process to implement this method for offshore applications.

2.2.4 Solidification/stabilization

Solidification/stabilization is an onshore treatment process which encapsulates the oil-contaminated drill cuttings with binding agents to physically and/or chemically transfer them into less hazardous products [43]. Normally, fly ash, lime, calcium oxide and cement have been used to treat oil-contaminated drill cuttings, where solidification and stabilization processes are combined to ensure the oil-contaminated wastes remaining in the matrix. The chemical reaction immobilizes the pollutant and the cement physically prevents leaching [43, 44]. For example, Vipulanandan et al. used thermosetting polyester to increase the sorption of organic wastes, therefore improved the effectiveness of the overall solidification/stabilization process [45]. Depending on the chemical characteristics of the contaminated drilling oil, the solidification/stabilization process always needs to be changed for a specific application of the treated mixture. After the solidification/stabilization process, the final materials can be used for road/building construction or supporting wetland vegetation [21, 46]. Due to the requirements of using large equipment and space, the solidification/stabilization process can only be used at onshore locations, which is similar to the thermal desorption method that the oil-contaminated drill cuttings have to be transported from the drilling rigs or offshore platform to the facilities. The cost of the process is around US $70-200/ton, not including the landfill expense [30].

2.2.5 Surfactant washing

Surfactants are surface-active amphiphilic molecules, which has the property of adsorbing onto the surface or interface of the system [47]. Typically, the residue oil in the contaminated cuttings is coated on the cuttings surfaces and/or trapped inside of the porous structure [48]. To save the process energy and the equipment cost, the surfactant washing method has been proven to be a good cleaning process for the treatment of the oil-contaminated drill cuttings [49-52]. According to Childs et al. [52], branched C14 to C15 alcohol propoxylate sulfate were highly efficient to remediate oil-contaminated drill cuttings. Na_2SiO_3, as the builder, was added to sequestrate and prevent Ca^{2+} from precipitating the surfactant. The octylsulfobetanie was used as a lime soap dispersing agent to mitigate the high hardness of the cuttings. Then branched alcohol propoxylate sulfate was finally added as the surfactant to reduce the ROC to 2 - 5 wt%.

The oil removal mechanisms using the surfactant washing methods can be summarized and classified into the roll-up mechanism, the snap-off mechanism and the solubilization mechanism [52, 53]. Figure 2-4 (a) shows the roll-up mechanism, which is related to the work of adhesion between the oil and the surface of the solid $W_a = \gamma_{ow}(1+\cos\theta)$. When the surfactant is added into the system, the decreased interfacial tension between oil and water γ_{ow} and the increased contact angle between the oil and the cuttings ($\cos(\theta) \to -1$) yield a negligible work of adhesion W_a. When the surfactant is not efficient to detach the entire droplet from the cuttings surface (contact angle is not close to 180°), the snap-off mechanism domains as the oil breaks in the middle with some residue oil remaining on the surface, as shown in Figure 2-4 (b). Nevertheless, the work of cohesion $W_c = 2\gamma_{ow}$ is also decreased with the reduced interfacial tension between oil and water

γ_{ow}. As the work of adhesion or cohesion becomes small or negligible, the minimal external mechanical force can efficiently facilitate the oil removal from the cuttings. If the surfactant concentration is high, the solubilization mechanism plays a vital role as the oil partitions into the hydrophobic core of formed micelles [54-56].

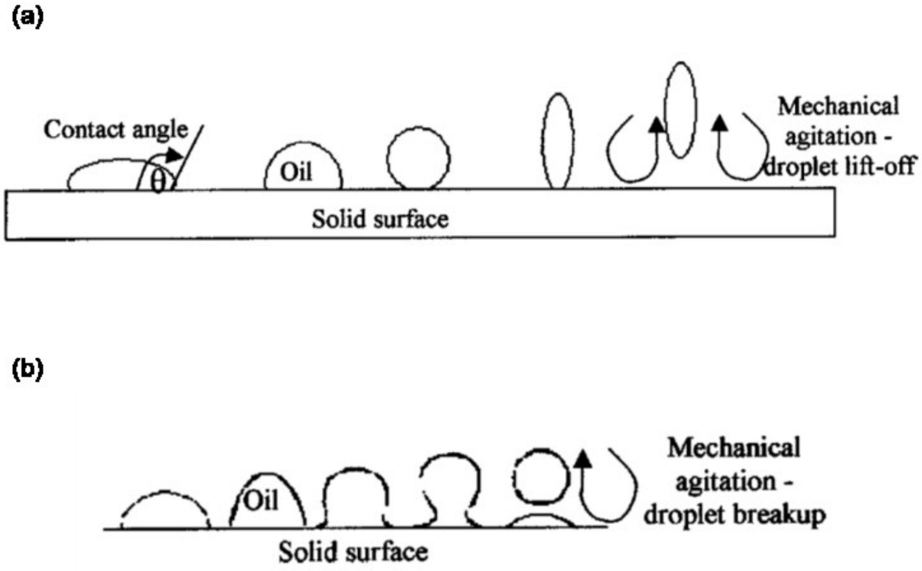

Figure 2-4 Illustration of (a) the roll-up mechanism and (b) the snap-off mechanism. Reprinted with permission from Ref 52 [52]. Copyright © 2004 American Society of Mechanical Engineers.

Since the surfactant washing technology is easy and safe to operate without the requirement of high pressure or temperature container, it has been applied to onshore treatment for the soils contaminated by petroleum products, and will be very promising in offshore applications if a right combination of surfactants can be developed. The processing time can be several hours, and the oil removal capability may be less than other techniques, as the ROC is still 3-10 wt% after the treatments [52, 57, 58]. Additional treatment is recommended before the discharge of cuttings to the environment [59]. During the surfactant washing process, the residue oil from the drill cuttings can also be emulsified into the aqueous phase, which limits the reuse of the surfactant solution. The typical cost of the onshore surfactant washing treatment method is around US $ 30/ton, and up to US $ 200/ton when considering other additives during the offshore treatment process [52].

2.2.6 Improved water-based drilling fluids for replacement of oil-based drilling fluids in the challenging geological drilling

Since the strict environmental requirements and regulations on oil-contaminated drill cuttings disposal have been made, the industries began to research and develop the new generation of water-based drilling fluids that can have the similar properties compared to oil-based drilling fluids, but the corresponding contaminated drill cuttings are easy to process. Several high-performance water-based drilling fluids have been developed, aiming to the applications in the deep and challenging drilling operations [7, 60, 61]. These fluids have been used in the field tests and compared to oil-based fluids, but still not widely used as the performance of these water-based drilling fluids is not constant [7].

2.3 Microemulsion treatment of oil-contaminated drill cuttings

In the commercialized oil-contaminated drill cuttings treatment processes, high energy consumption is used to either distillate residue oil inside of the cuttings, or transport tons of waste from the drilling site to the treatment facility, which result in significant carbon emission, especially at the offshore drilling platform or the mountainous area [19, 20, 30]. In the other new treatment methods during the R&D stage, abundant energy is still needed to generate microwave or maintain the liquid or gas into the supercritical state [36-41]. Even though the surfactant washing method requires less energy consumption, the ROC after the treatment is difficult to meet the strict regulations [52, 57, 58]. Different from the existing treatment methods, the microemulsion extraction process may have the potential advantages such as low temperature or pressure during the operation, less energy consumption and compact space requirement, which can be built onsite to process the drilling waste without transportation. Most importantly, it may further decrease the ROC to the acceptable discharge limit, due to its ultralow interfacial tension and strong capability of solubilizing oil.

2.3.1 Introduction to microemulsion

The microemulsions is an isotropic and thermodynamically stable colloidal dispersion consisting of water, oil and emulsifying chemicals, with the size of the dispersed phase less than 50 nm [62]. Due to the very small dispersed phase, the microemulsion has a number of advantages over the typical emulsion system, such as the excellent stability to aggregation or phase separation [4, 63], the transparent appearance due to the weak light scattering [64], and the exceptional capability of solubilizing the substances encapsulated inside [65-67]. Since first discovered by Hoar and Schulman in 1943 [68], microemulsion has been widely applied in many applications such as pharmaceuticals production, drug delivery, organic synthesis, nanoparticle preparation, ultra cleaning and enhanced oil recovery [47, 69, 70].

In the O/W microemulsion, the surfactants are intended to decrease the interfacial tension, increase the repulsive force and generate the protective layers to stabilize the emulsified system. During the microemulsification process, the system transfers from a phase-separated state to a state in which the oil is microemulsified into droplets of radii a, the change in the Gibbs free energy ΔG can be written as [71]:

$$\Delta G = \gamma_{ow}\Delta A - T\Delta S_{conf} \tag{1}$$

where γ_{ow} is the interfacial tension between the oil phase and the water phase, ΔA is the change in the interfacial area, T is the absolute temperature, and ΔS_{Conf} is the change in the configurational entropy of the system, which can be further expressed as:

$$\Delta S_{Conf} = -nk_B[\ln\phi + \frac{1-\phi}{\phi}\ln(1-\phi)] \tag{2}$$

where n is the number of dispersed phase droplets, k_B is the Boltzmann constant, and ϕ is the volume fraction of the dispersed phase. As one phase dispersed into another, the droplet number increases, thus ΔS_{Conf} is positive, leading to a positive second term in the Gibbs free energy equation. When the interfacial area change ΔA is increased by a factor of 10^4 to 10^5 due to the microemulsification of the oil phase, but the γ_{ow} is small enough with the addition of surfactants, it is possible that the entropic term overtakes the enthalpic term in equation (1), resulting a negative change of the Gibbs free energy, which means a microemulsified mixture of lower energy state compared to the initial phase-separated state. Therefore, the microemulsification process can spontaneously occur and the microemulsion system is thermodynamically stable.

In order to satisfy the condition $\gamma_{ow}\Delta A < T\Delta S_{Conf}$, the interfacial tension in the emulsified system must be less than the critical interfacial tension, which is given by:

$$\gamma_{crit} = -\frac{k_B T}{4\pi a^2}[\ln\phi + \frac{1-\phi}{\phi}\ln(1-\phi)] \qquad (3)$$

The interfacial tension should be in the ultralow level, for example, 10^{-2} mN/m or even lower, which requests the careful selection of surfactants. Some double chain ionic [72] and non-ionic [73] surfactants can produce this low interfacial tension ranging from 10^{-2} to 10^{-4} mN/m. However, most of the single type of surfactants will reach their critical micelle concentration (CMC) before the ultralow interfacial tension is achieved. A possible approach is to use a co-surfactant that has an entirely different chemical nature to further decrease γ_{ow} . The co-surfactant should be absorbed in the interface simultaneously with the primary surfactant, but do not interact with each other [74, 75].

2.3.2 Classifications of microemulsion

Microemulsions can be classified into four types based on the phase equilibrium according to Winsor [76, 77], as showed in Figure 2-5:

- Winsor Type I: O/W microemulsion forms in equilibrium with an excess top oil phase. The surfactants are mainly distributed in the O/W microemulsions while only presented in the form of monomers at a small concentration in the oil phase.

- Winsor Type II: W/O microemulsion forms in equilibrium with an excess bottom water phase. The surfactants are mainly distributed in the W/O microemulsions, but a small concentration in the water phase.

- Winsor Type III: Microemulsion coexists with excess top oil phase and bottom water phase. The surfactants are mainly concentrated in the middle microemulsion, which has nearly equal volumes of oil and water mixing at the nanoscale and result in a bicontinuous mixture.

- Winsor Type IV: An isotropic single-phase swellable micellar solution without coexists with excess oil or water phase. The surfactants and co-surfactant, e.g., medium-chain alcohol, should be selected carefully. The microemulsions of this type can have different microstructures depending on the fractions of the oil/water phase and the hydrophilicity of the surfactant [78]. If the fraction of the oil is relatively low and the surfactant is more hydrophilic, O/W Winsor Type IV microemulsion forms. Similarly, if the water content is low and the surfactant tends to be more lipophilic, W/O Winsor Type IV microemulsion tends to generate. A bicontinuous microemulsion forms when the water and oil contents are nearly equal. In this thesis, the novel CO_2-responsive medium before the CO_2 purging can be classified into the O/W microemulsion of Winsor Type IV.

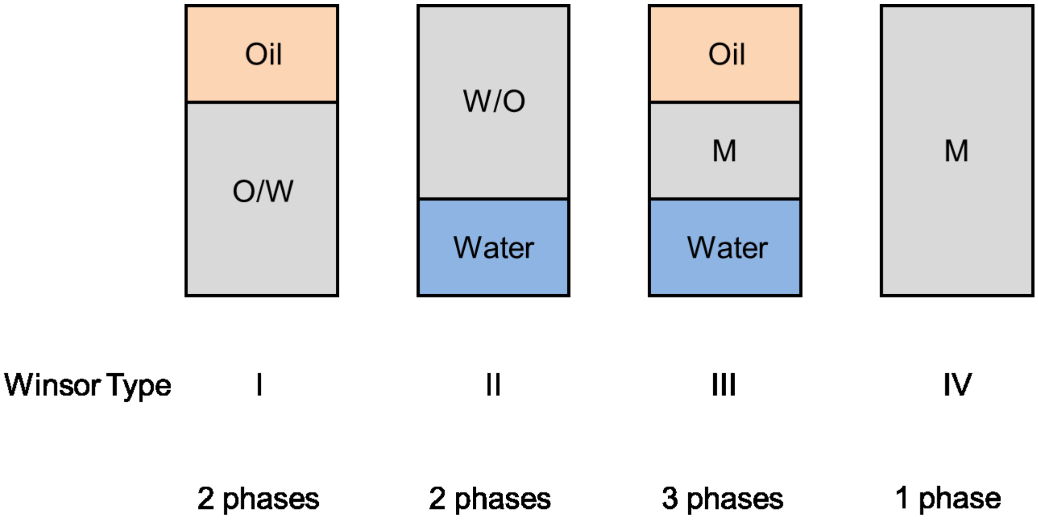

Figure 2-5 Winsor classification of microemulsions. The surfactants are mainly distributed in the gray areas.

Based on the surfactant type, temperature, pressure and salinity, the surfactant arrangement at the interface varies accordingly, leading to the formation of Winsor type I to IV microemulsions. Israelachivili et al. introduced a quantitative evaluation concept to correlate surfactant structure, film curvature and emulsified type, which compared the area of the surfactant head group a_0 and the tail group v/l_c, as shown in Figure 2-6 [79]. When $a_0 > v/l_c$, an O/W microemulsion forms. Similarly, a W/O microemulsion forms if $a_0 < v/l_c$, and a bicontinuous microemulsion generates if $a_0 \approx v/l_c$.

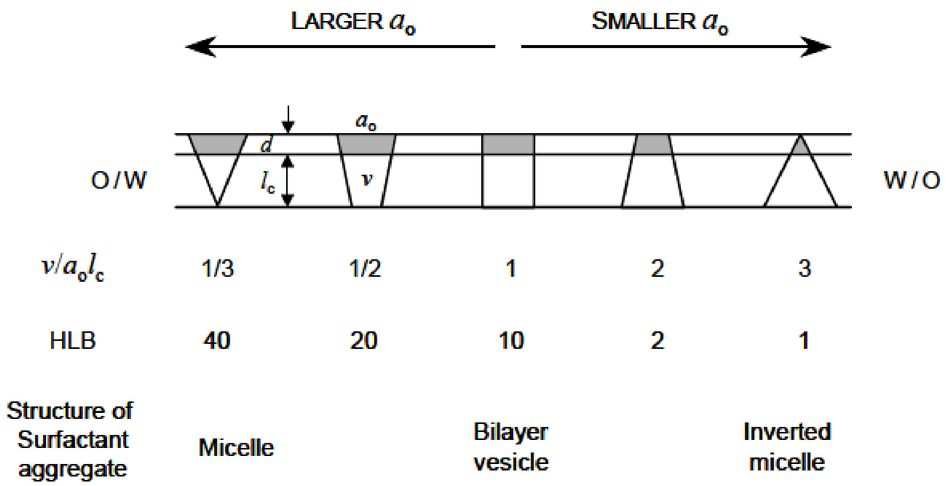

Figure 2-6 Correlation between surfactant structure, packing parameter $v / a_0 l_c$, HLB number and system emulsification. Reprinted with permission from ref 79 [79]. Copyright © 1994 Elsevier.

Alternatively, a Winsor Type I or II microemulsions can be regarded as a Winsor Type IV microemulsion in equilibrium with excess oil or water phase [76]. A Winsor Type III microemulsion can be treated as a Winsor Type IV microemulsion with excess of both oil and water phases [76]. Moreover, the Winsor Type I microemulsion can transit into the Winsor Type IV, and eventually Winsor Type II by increasing the solubilization of the oil phase through (1) add oil-soluble components of hydrogen bonding such as fatty acids, alcohols and amines; (2) increase the lipophilicity of the surfactant; (3) add inorganic salts. Increasing the solubilization of the water phase can also transfer a Winsor Type II microemulsion first to Winsor Type IV, then Winsor Type I by (1) add water-soluble components of hydrogen bonding; (2) reduce the lipophilicity of the surfactant; (3) increase the lipophilicity of the oil phase [76].

2.3.3 Application of microemulsions in oil extraction from oil-contaminated substrates

Compared to the surfactant washing method, the microemulsion has a potential enhanced cleaning capability due to the exceptional capability of solubilizing oil [67, 80, 81]. Although the direct and systematic research of microemulsion on drill cuttings treatment is very limited, many research groups have utilized the microemulsions in cleaning other oil-contaminated substrates. Miller et al. developed a cleaning technology based on O/W microemulsions containing 10 wt% n-Dodecyl tetraethylene glycol ($C_{12}E_4$) and 15 wt% hexadecane, which showed a ~100 % increase in the solubilization of the residue oil from polyester fabric substrate compared to the oil-free surfactant solution [67]. Goual et al. used microemulsions consisting of linear alcohol ethoxylate as the surfactant and d-limonene as the oil phase to displace the oil in the porous media [82]. Because of the ultralow interfacial tension, strong capability of solubilizing oil and wettability alteration, the microemulsions led to a 25 - 35 % oil removal improvement over the surfactant solutions. In the oil sands extraction, a microemulsion containing a light hydrocarbon such as toluene or naphtha also showed a promising performance to recover heavy bitumen from the solids [83].

To better understand the mechanism using microemulsion to treat the oil-contaminated substrates, the molecular dynamics simulation was employed to simulate the oil removal from the substrate under the effect of a microemulsion prepared by ethoxylated linear alcohol [80]. The simulation revealed that the pre-dissolved oil phase of the microemulsions can effectively swell, dissociate and solubilize the adsorbed residue oil, further reduce its Coulomb interaction with the substrates, resulting in an easier removal under a gentle water flow compared to the surfactant solution and water treatments, as shown in Figure 2-7.

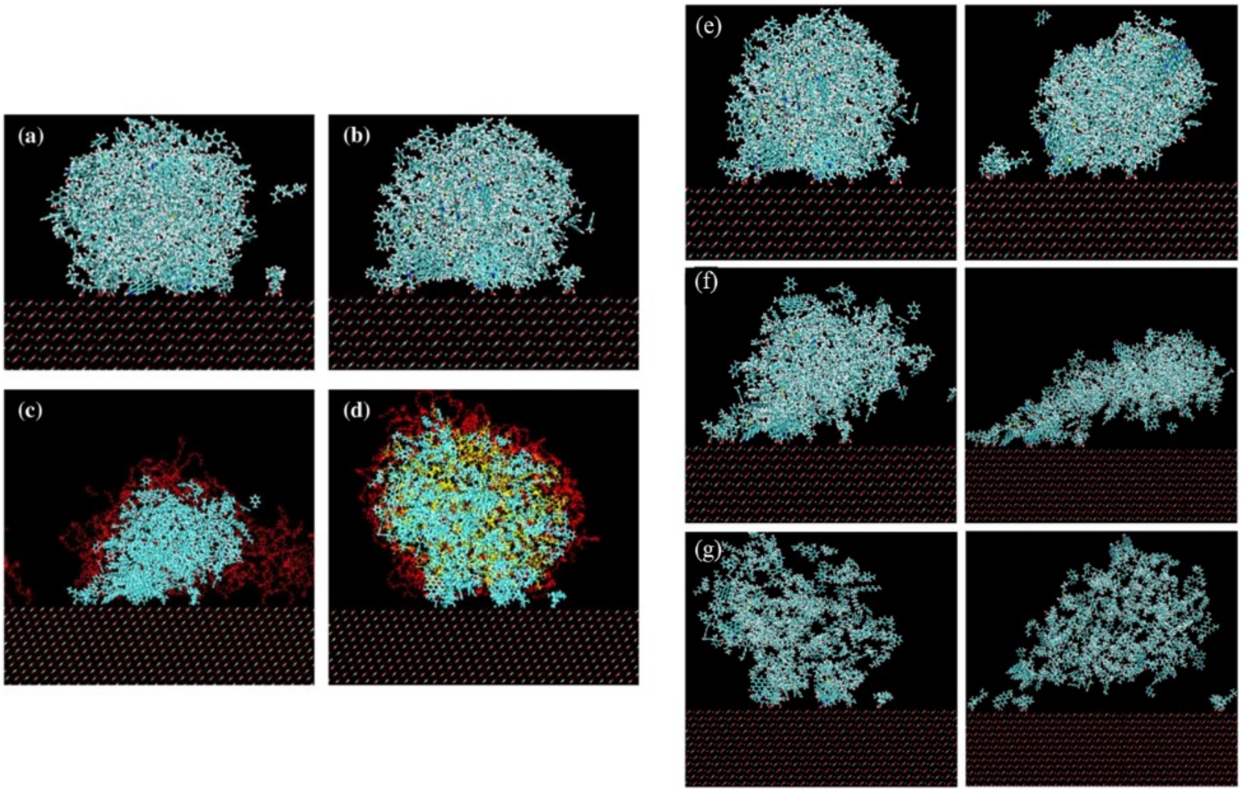

Figure 2-7 Molecular dynamic simulations of residue oil on the substrates at (a) the beginning stage, and at the end of the treatment simulation in (b) water, (c) surfactant solution, (d) microemulsion. The induced flow was then added after the treatment in (e) water, (f) surfactant solution, (g) microemulsion. Surfactants are shown in red and pre-dissolved oil molecules in microemulsion are shown in yellow in (c) and (d). Water and co-surfactants are not shown for clarity. Reprinted with permission from ref 80 [80]. Copyright © 2016 Elsevier.

However, the microemulsion is an isotropic and thermal dynamically stable system, which is only useful in the first few stages of an application. The stability of the microemulsion has to be changed to release the dissolved residue oil for further treatment. In order to destabilize the emulsified systems, chemical demulsifiers are normally added into the mixtures [84-86]. But the addition of the extra chemicals may add additional process cost and yield possible environmental concerns. Therefore, it is highly desired to have a switchable microemulsion by an efficient and rapid switching method to treat the oil-contaminated substrates for practical consideration.

2.3.4 Switchable microemulsions

In the preparation of switchable microemulsions, the phase behavior of the microemulsion can be effectively controlled by using surfactants which can respond to external stimuli and switch their interfacial activities. After the development in the past few decades, switchable surfactants responding to CO_2 [87-97], temperature [98-100], light [101-106], pH [107-114], redox [115-123] and magnetic field [124-128] have been frequently reported. However, switching microemulsion is still challenging and difficult to achieve when compared with thermodynamically unstable emulsion systems, because the phase separation of a microemulsion requires to change the interfacial activity more significantly.

The light-responsive chemicals such as azobenzene or azobenzene-containing molecules were mingled into the AOT-stabilized microemulsions to make switchable systems [129, 130]. When responded to the UV-light at 310 -350 nm, the stability of microemulsions could be shifted by the in-situ transition of azo compounds from trans to cis forms. However, the microemulsion was difficult to achieve complete or near-complete phase separation, and the size of the UV light source limited its practical application. Hatton et al. reported a CO_2-switchable microemulsion prepared with responsive ionic liquids, which could reversibly switch between the transparent and turbid states by adding and removal of CO_2 in the system [131]. Even though the switching process is triggered by nontoxic and affordable CO_2 at the ambient temperatures and pressure, the practical application is still restricted due to the expensive ionic liquid and its uncomplete phase separation.

Focusing on reducing the preparation cost by avoiding the use of expensive chemicals, CO_2-responsive microemulsions were developed by adding amine-containing compounds (such as N, N-dimethyl-N-dodecyl amine or N, N, N', N'-tetramethyl-1,3-propanedi amine) into the hydrocarbon-SDS-butanol-water systems [88, 132]. With the addition/removal of CO_2, the amine compounds can bind with or release from the anionic moiety of SDS at the interface, leading to the SDS redistribution in the system and a near-complete phase separation/regeneration of microemulsions, as shown in Figure 2-8. Among these CO_2-switchable microemulsions, additional amine compounds were added into the pre-stabilized systems where the surfactants were already localized at the interface [88, 132]. The switching efficiency is relatively slow because the protonated amines need to fully bind with SDS, as such that it is required to purge the gas for hours, which needs to be improved for practical applications.

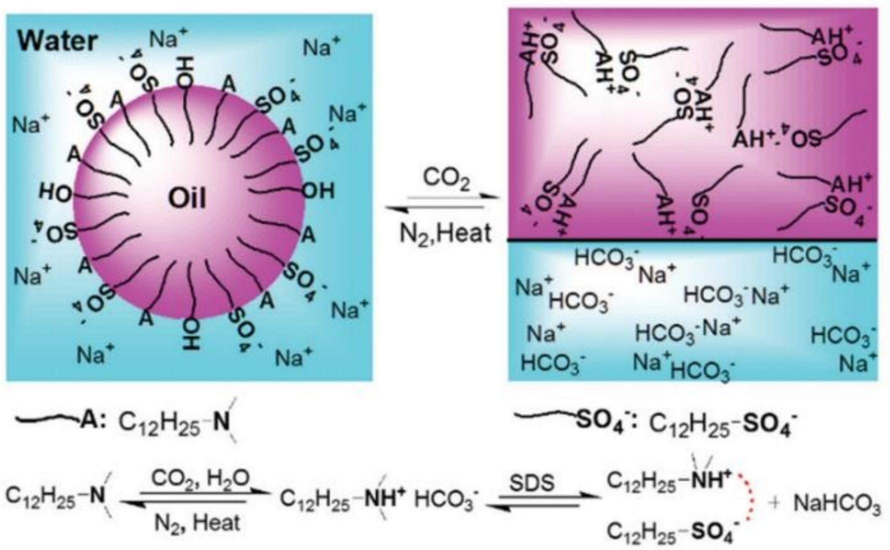

Figure 2-8 Schematic illustration of the mechanism in the CO_2-responsive microemulsion prepared by adding N, N-dimethyl-N-dodecyl amine into the heptane-SDS-butanol-water system. Reprinted with permission from ref 88 [88]. Copyright © 2016 Royal Society of Chemistry.

To improve the switching efficiency, it is urgent to design a "real" switchable surfactant from the molecular level, which can form the microemulsion at the low concentration, significantly switch its interfacial activity under the effect of CO_2, and reconstruct the structure after the removal of the gas. However, the report of this kind of microemulsion is very rare. Recently, Sun et al. developed a series of superamphiphiles [87, 133], which exhibited an efficient and rapid response upon the addition/removal of CO_2 without adding other chemicals. Different from amphiphiles which normally links the hydrophobic and hydrophilic segments by covalent bonds, superamphiphiles are constructed by noncovalent interactions such as electrostatic interaction, host-guest interaction, π−π stacking and hydrogen bond, which have the potential to exhibit a rapid response and a significant interfacial tension change upon an external stimulus [134-136]. Utilizing the unique properties of the superamphiphiles, it is of great interest to develop a rapid CO_2-responsive superamphiphile to form a novel switchable microemulsion with rapid and complete switching characteristic for the purpose of deep drill cuttings cleaning without expensive equipment or additional chemical demulsifiers.

2.4 Conclusions

In the drilling rigs and platforms, a huge amount of oil-contaminated drill cuttings is generated after the primary treatment system with the residue oil content ranging from 5-15 wt%. Such drill wastes have been a serious concern and require effective treatments due to environmental toxicity. As required by more strict regulations, the ROC must be reduced to less than 1 wt% for safe disposal. Current commercial treatment methods such as thermal desorption process and cuttings dryers are commonly employed for the purpose of reducing ROC to the acceptable level. However, they are still facing practical problems, for example, either huge energy consumption or undesired ROC against the regulatory requirement. As a result, advanced technologies have been developed in different stages to fulfill the environmental discharge requirement.

This chapter presented a detailed investigation of the different drill cuttings treatment and remediation methods. A comparison summary including space requirement, treatment time, treatment cost, ROC after the treatment and related notes is shown as Table 2-1. Biodegradation method has been proved to be a low-cost treatment process, but it requires a very long treatment time and large land area. In the solidification/stabilization method, drill cuttings are encapsulated with binding agents, which still requires long-distance transportation and long-term oil leaching monitoring. More advanced technologies such as microwave heating and supercritical gas/fluid extraction have been developed in the research and development stage, which exhibit promising results to reduce the ROC significantly. However, they both have very high capital/treatment cost and relatively long treatment time, making it difficult for the large-scale application. To save the equipment and the process cost, the surfactant washing has been proven to be a good alternative treatment method due to the easy and safe working condition. However, its treatment process is still slow according to the lab scale test results, and the ROC after the surfactant washing is higher than the regulatory requirement.

With the ultralow interfacial tension and strong capability of solubilizing oil, microemulsion treatment of the oil-contaminated drill cuttings is very promising with comparable treatment cost and small land requirements like surfactant washing method, and more unique possibilities such as dramatic reductions of the treatment time and ROC, leading to a fast, deep and efficient treatment method. However, the related research is very rare as such becomes the motivation of this thesis.

Table 2-1 Summary of the oil-contaminated drill cuttings treatment methods and technologies in the secondary stage

Drill cuttings treatment methods in the secondary stage	Space requirement	Treatment time	Treatment cost	ROC after treatment	Note
Cuttings dryer	Compact space of several m^3, can be built on offshore platforms.	~20 - 80 ton/h, depends on the type of cuttings dryer	Relatively low	4 - 5 wt%	Normally mounted with the primary cuttings treatment system. Need additional treatment to reduce the ROC.
Thermal desorption	Relatively large to build the thermal desorption station. Compact space for TCC equipment.	Relatively slow as a batch treatment process, roughly 3 -10 ton/h	$280 - 1000/$m^3$	less than 1 wt%	High-temperature process, consumes considerable energy and releases huge carbon emission.
Biodegradation	Very large land area for land farming treatment.	From months to years, depending on the residue oil type and target ROC	$30 - 60/ton	ROC less than 5 wt% can be very difficult or very time-consuming to achieve	Very slow treatment process using microorganisms to degrade contaminants. Need special care to prevent the contaminated hydrocarbons from leaching to the groundwater.
Microwave heating	Compact space requirement, can be built on the offshore platform.	Relatively slow in a pilot test, up to 0.5 ton/h	TBD, still in the R&D stage	less than 1 wt% when mixed with dielectric components	High energy consumption. Need to blend with dielectric components to reach desired ROC.
Supercritical gas/fluid extraction	Compact space for expensive equipment to maintain the high-pressure condition.	Very slow, need improvement for practical application	Very high considering the gas, fluid and energy consumption	0.2 wt%	Expensive equipment to reach and maintain the high pressure to keep the extraction medium in the supercritical state. Need a safety investigation for practical application.
Solidification/stabilization	Relatively large space and equipment to process the cuttings shipped from drilling rigs.	Slow, 1 - 2 ton/h	$70-200/ton	N/A, oil components are held in the matrix	Need to choose appropriate binding agents to physically and/or chemically stabilize the cuttings. Long-term monitoring of oil leaching is required.
Surfactant washing	Compact space requirement, can be built on offshore platforms.	Currently slow in a lab scale test	Relatively low, $30-200/ton depending on the chemicals applied	2 -10 wt%	Need additional treatment or efficient surfactants to reduce the ROC. Treatment time is relatively slow.
Microemulsion treatment	Similar to the surfactant washing requirement.	TBD, but can be fast due to the ultralow interfacial tension and strong capability of solubilizing oil	Similar or slightly higher than surfactant washing	TBD, target to less than 1 wt%	Due to the ultralow interfacial tension and strong capability of solubilizing oil, the microemulsion treatment of oil-contaminated drill cuttings can be fast, deep and efficient.

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Chapter 3 CO_2-responsive O/W microemulsions prepared using a switchable superamphiphile assembled by electrostatic interactions

3.1 Introduction

Microemulsions are isotropic and thermodynamically stable mixtures consisting of water, oil and emulsifying chemicals, with the dispersed phase in the sizes from 5 to 50 nm [62]. Since its first discovery by Hoar and Schulman in 1943 [68], microemulsion has been broadly used in many important applications ranging from organic synthesis, pharmaceuticals production, drug delivery, ultra cleaning and nanoparticle preparation to enhanced oil recovery, mainly due to its ultrasmall sizes of the dispersed phase and thermodynamical stability [47, 69, 70]. However, the stable microemulsion is only useful in limited stages of an application, and the stability of the microemulsion often needs to be altered for the purpose of components separation, chemical recycle and/or safe disposal of spent wastes. The destabilization of emulsified systems usually requires the use of chemical demulsifiers [84-86]. However, the addition of extra chemicals may increase the process cost and cause potential environmental concerns. Reuse of microemulsions after demulsification, on the other hand, can reduce overall operating cost. Therefore, a rapid switchable microemulsion by an efficient and environmental friendly switching method is highly desirable.

To prepare desirable microemulsions, surfactants are used to reduce the interfacial tension and stabilize the dispersed phase. For the preparation of switchable microemulsions, the stabilization of microemulsion needs to be effectively controlled by using surfactants with switchable interfacial activities in responding to external stimuli. Recently, switchable surfactants which respond to CO_2 [87-93], pH [107-110], temperature [98-100], UV irradiation [101-104], magnetic field [124, 125] and redox [115-117] have been frequently reported. However, destabilizing microemulsion remains a challenging subject when compared with thermodynamically unstable emulsion systems, since the phase separation of a microemulsion requires a more significant variation in interfacial tension, which is difficult to achieve.

AOT-based switchable microemulsions with the addition of light-responsive chemicals such as azobenzene and its derivatives have been reported [129, 130]. The stability of microemulsions can be changed by the transition between trans and cis forms of azo compounds with UV-light radiation or thermal stimulation. However, the azo compounds are potential carcinogens and suffer from the difficulties in storage [137]. Hatton et al. reported a CO_2-responsive microemulsion prepared with ionic liquids, in which the ionic liquid-in-oil microemulsion reversibly switched between clear and turbid states by purging and removal of CO_2 [131]. Focusing on the aspect of green chemistry, Feng et al. developed a CO_2-responsive microemulsion by adding N, N-dimethyl-N-dodecyl amine into the heptane-SDS-butanol-water system [88]. The amine binds with or releases from one anionic moiety of SDS at the interface by the addition/removal of CO_2, leading to a near-complete phase separation/regeneration of microemulsions. In these systems, the switching is slow as such that the prolonged gas purging for hours is required, which is undesirable for certain practical applications.

Recently, a series of superamphiphiles were developed by Sun et al. [87], which exhibited a fast and efficient response upon the addition and removal of CO_2 into and out of the system. Different from amphiphiles which are usually formed by covalent bonds between the hydrophobic and hydrophilic molecular segments, superamphiphiles have the potential to exhibit a rapid response to an external stimulus because they are constructed by noncovalent interactions such as electrostatic interaction, hydrogen bond, $\pi-\pi$ stacking and host-guest interactions [134-136]. However, very few reports have been found on the rapid switching microemulsions using CO_2-responsive superamphiphiles. Based on the early work by Sun et al. [87], we developed a new CO_2-responsive superamphiphile, which was constructed based on noncovalent electrostatic interactions by mixing an anionic fatty acid (oleic acid) and a cationic amine (Jeffamine D-230) at a 1:1 molecular ratio. The responsive superamphiphile formed as such was used as a novel surfactant for creating CO_2-responsive O/W microemulsions. Mixing this superamphiphile with 1-butanol, heptane and water led to the spontaneous formation of desired O/W microemulsions. The stable microemulsions became completely phase-separated upon purging of CO_2 for 20 seconds and re-emulsified to stable microemulsions after removal of CO_2 within 10 minutes, featuring rapid, complete and reversible switching characteristics. As an example of applications, experiments on washing of drill cuttings were conducted at the room temperature using this innovative and cost-effective CO_2-responsive microemulsion. The residual oil in the contaminated solids was found to decrease significantly with such washing. The results indicate that the ultra-low interfacial tension and the rapid switching character of this microemulsion can be very useful for the oil extraction and separation without the addition of additional demulsifiers.

3.2 Materials and methods

3.2.1 Materials

Poly (propylene glycol) bis (2-aminopropyl ether) with an average molecular weight (Mn) of ~230 (known as Jeffamine D-230), oleic acid (technical grade), 1-butanol (ACS grade) and Sudan III (technical grade) were purchased from Aldrich (the USA). Heptane (HPLC grade) was purchased from Fisher Scientific (Canada). Oil-contaminated drill cuttings were obtained from the Lifting Solutions Inc. All the chemicals were used as received. Deionized water was obtained from Milli-Q water purification system (Millipore, the USA) and used throughout this study.

3.2.2 Preparation of CO_2-responsive superamphiphiles

The CO_2-responsive superamphiphile was assembled via electrostatic interactions between the carboxyl groups and the amino groups by simple mixing of oleic acid with Jeffamine D-230 at a molecular ratio of 1:1, as shown in Figure 3-1. At room temperature, the product appeared to be a viscous light yellow liquid [87, 138]. The prepared superamphiphile was characterized by FTIR (Cary 670, Agilent Technologies) and ^1H NMR (Agilent/Varian Mercury two-channel 400 MHz spectrometer, $CDCl_3$).

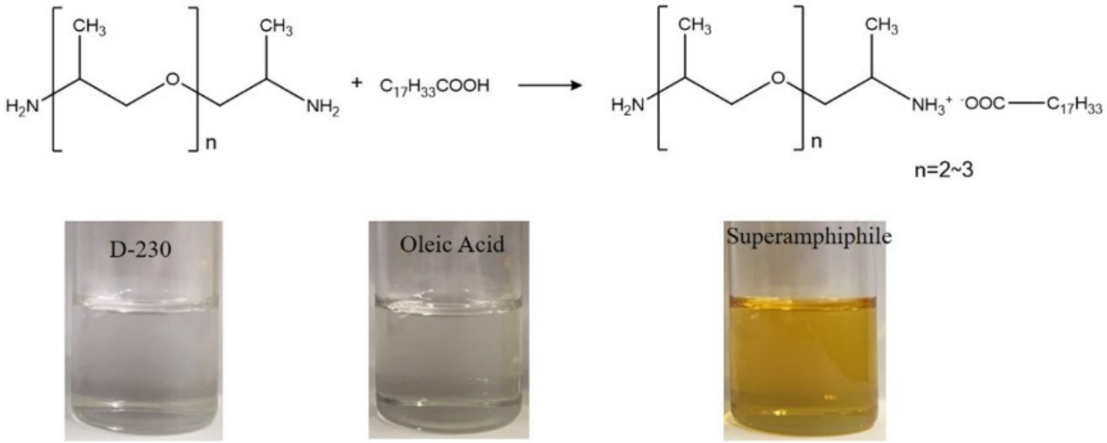

Figure 3-1 Formation and chemical structure of CO_2-responsive superamphiphile.

3.2.3 Pseudoternary phase diagram

A stock solution of superamphiphile was prepared by mixing the superamphiphile with the heptane at 1:2 mass ratio. Pseudoternary phase diagram was created by titrating a mixture of water and superamphiphile-heptane solution at different mass ratios with co-surfactant 1-butanol at the room temperature. Emulsions/microemulsions at different compositions were observed under the Zeiss Axioskop 40 microscope. Based on the pseudoternary phase diagram, the O/W microemulsions which contained 60 wt% water, 20 wt% heptane, 10 wt% superamphiphile and 10 wt% butanol were chosen for further investigation on physicochemical properties and applications of the formed microemulsions throughout this study.

3.2.4 Characterization of the O/W microemulsion

3.2.4.1 Size distribution measurement

The drop size distributions of O/W microemulsions were determined by Zetasizer Nano ZS (Malvern). The reversible switching of microemulsions was accomplished by alternate purging of CO_2 and N_2. Between each switching, ~1 mL samples were taken from the prepared monophasic microemulsion, or from the oil and water phases after phase separation. Samples were analyzed at 20 ºC without any filtration.

3.2.4.2 Freeze-fracture transmission electron microscopy (FF-TEM)

The microemulsion replicas were prepared by Leica EM BAF 060 using the method described elsewhere [139, 140]. A drop (~5 uL) of microemulsion was placed carefully on a thick copper disk, capped by another copper disk to make a sample sandwich. The sample sandwich was immersed quickly into a liquid propane, transferred into a freeze-fracture apparatus for making sample replica. The Pt and C were deposited on the fracture surface of the sample at an angle of 45°. The replica prepared as such was investigated by TEM (JEOL JEM-2100) at 200kV.

3.2.4.3 Interfacial tension measurement

TX500C spinning drop tensiometer (Kino Industry Co, USA) was used to measure the interfacial tension between heptane and aqueous phase containing the desired amount of superamphiphile and butanol. The superamphiphile and butanol premixed at 1:1 mass ratio were added to Milli-Q water to different concentrations. The resulting aqueous phase was used as the heavy phase in the spinning drop tensiometer. A drop of heptane was then injected into the aqueous phase as the light phase in the sample tube. The sample tube was spun at 25ºC for 30 minutes or until the heptane droplet disappeared.

3.2.4.4 Stability measurement of microemulsions

The stability of microemulsions was investigated after storage for a given period of time, centrifugation and repeated heating/cooling cycles. In order to determine the long-term stability, the microemulsion was stored in a glass vial at the room temperature in a cabinet to protect the microemulsions from the exposure to the light. To study the stability of microemulsions under applied external forces, the microemulsion was centrifuged at 4000-g force at 25 ºC for 20 minutes. When investigating the thermal stability, the microemulsion was heated up to 60, 70 and 80 ºC (± 0.3 ºC) in a water bath, and cooled to room temperature. After each treatment, the sample was inspected visually to determine the phase separation as a measure of the emulsion stability.

3.2.5 Switchable behavior of CO_2-responsive O/W microemulsions

At the ambient temperature, 5 g of O/W microemulsion formed spontaneously after simple mixing of all the components in a 20 mL glass vial which was sealed with a gas-tight cap. To destabilize the microemulsion, dry CO_2 gas was purged at 200 mL/min rate into the system at the room temperature for 20 seconds. To switch back to the monophasic O/W microemulsion, dry N_2

gas was bubbled into the system at 300 mL/min for 10 minutes while the sample vial was heated to 60 ± 0.3 ºC using a water-circulating thermal bath. The loss of components, especially heptane, was minimized by the careful seal of the vial. To enhance the visual inspection, one drop of 0.05 wt% Sudan III in heptane solution was used to dye the microemulsion. The pH of the system was measured by a calibrated Oakton pH meter.

3.2.6 Treatment of oil-contaminated drill cuttings using CO_2-responsive O/W microemulsions

Approximately 1 g of the oil-contaminated (spent) drill cuttings and 5 g of the microemulsion were mixed in a 30 mL glass gar and hand-shaken gently for 1 minute. After CO_2 purging at 200 mL/min for 20 seconds, the mixture was centrifuged at 1000 rpm for 15 minutes. The solids were carefully separated and rinsed with 5 g water. After solid-liquid separation, the solids were placed on a Petri dish. After drying in the oven at 102°C for 30 minutes, the solids were analyzed by a thermogravimetric analyzer (TGA, TG 209 F1 Libra®, NETZSCH) to determine the amount of organics remained on solids.

3.3 Results and discussions

3.3.1 Structure characterization of CO_2-responsive superamphiphile

In this work, the novel CO_2-responsive superamphiphile was formed by the electrostatic interactions between the carboxyl group of oleic acid and the amino group of Jeffamine D-230. The linear structure of the assembled superamphiphile (shown in Figure 3-1) was characterized by FTIR and ^{1}H NMR. Figure 3-2 (a) shows the FTIR spectra of the assembled superamphiphile and corresponding precursor components of Jeffamine D-230 and oleic acid. After interacting with the amino group of Jeffamine D-230, the carbonyl peak at 1710 cm^{-1} in oleic acid shifted to 1564 cm^{-1} and 1399 cm^{-1} while the -OH peak at 938 cm^{-1} disappeared, indicating a complete conversion of the neutral acid to its ionized counterpart and the formation of the desirable superamphiphile [87]. For the superamphiphile constructed by mixing oleic acid and Jeffamine D-230 at a 1:1 molecular ratio, one of the -NH$_2$ groups in D-230 is anticipated to receive a proton from -COOH to form -NH$_3^+$, resulting in a new vibrational peak of -NH$_3^+$ at 1626 cm^{-1}. The second amino group is unreacted and left at the other end of the superamphiphile, as shown in the enlarged FTIR spectra in Figure 3-2 (b). The peaks corresponding to -NH$_2$ vibrations disappeared when the molar ratio of D-230 and oleic acid decreased from 1:1 to 1:2, indicating reactions of all -NH$_2$ groups with -COOH groups in oleic acid, as shown in the Figure A - 1 (Appendix A).

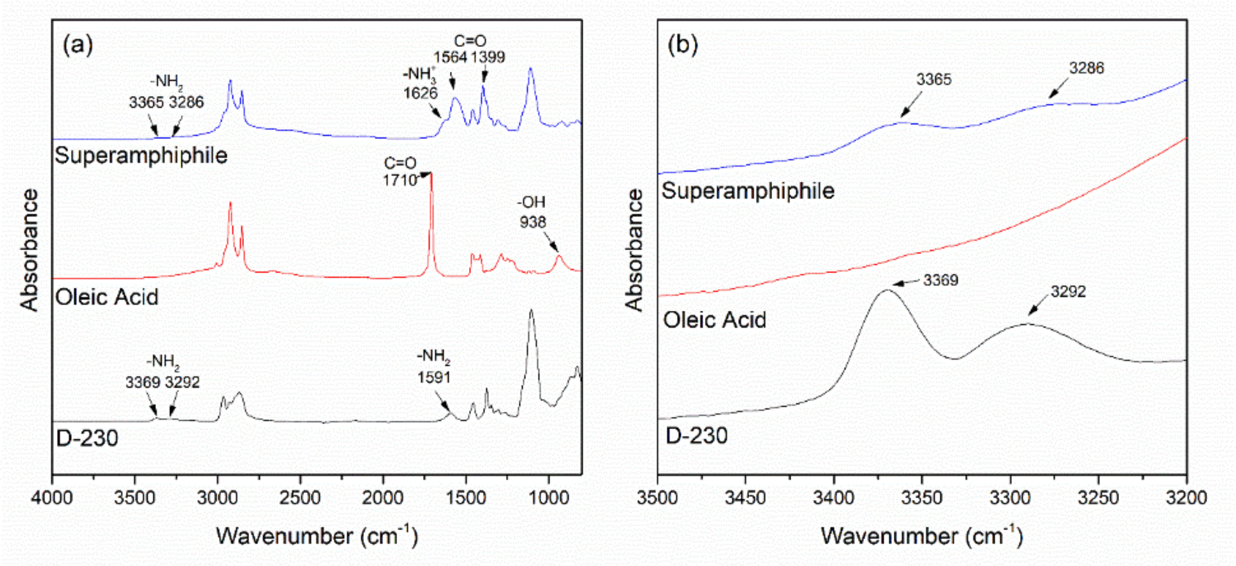

Figure 3-2 (a) FTIR spectra of superamphiphile and precursors of oleic acid and Jeffamine D-230; (b) Enlarged FTIR spectra from 3500 cm^{-1} to 3200 cm^{-1} to show peaks of unreacted -NH_2 groups in the superamphiphile.

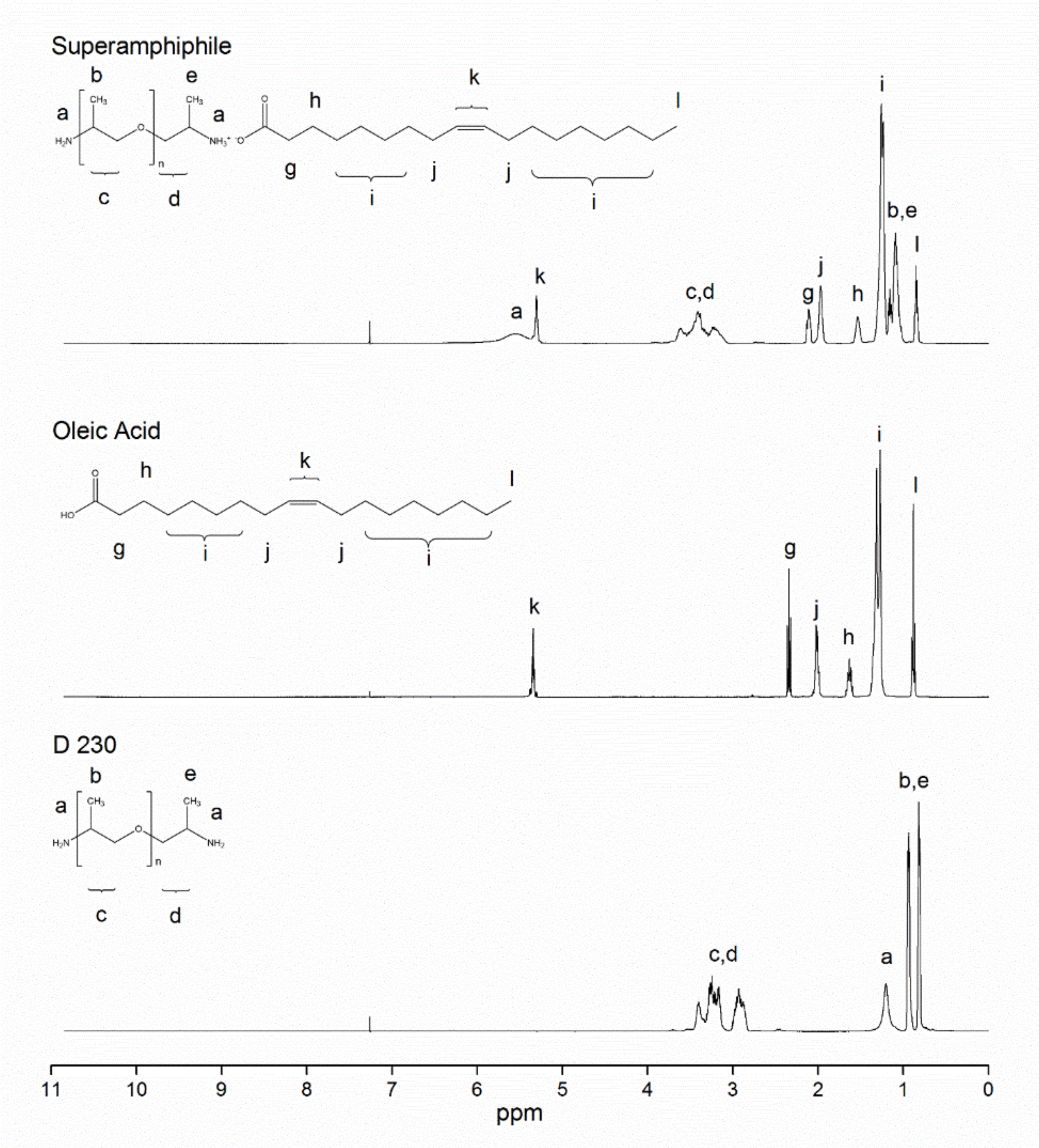

Figure 3-3 ^{1}H NMR spectra of superamphiphile and precursors of oleic acid and Jeffamine D-230 in $CDCl_3$.

The electrostatic binding between the oleic acid and D-230 revealed in FTIR spectra was further confirmed by ^{1}H NMR, as shown in Figure 3-3. When one of the $-NH_2$ groups in D-230 received a proton and transformed into $-NH_3^+$ in the resulting superamphiphile, a new labile proton peak on nitrogen (peak a) appeared at 5.55 ppm, which reflects an averaged chemical shift of the unreacted $-NH_2$ peak at 1.20 ppm and the new $-NH_3^+$ peak in the range of 8 to 10 ppm. This single peak became broader as a result of decreasing the exchange rate of the labile proton in the superamphiphile. Since the quaternary ammonium cation carried a positive charge, which decreased the local electron density, the ^{1}H chemical shifts of the nearby alkyl groups (peak d and e) moved slightly downfield by ~0.25 to 0.50 ppm in the superamphiphile, indicating the protonation of the terminal amine site. On the contrary, the peaks of the methylene groups (peaks g and h) near the carbonyl group in the superamphiphile moved upfield by ~0.10 to 0.23 ppm due to the increased local electron density, reflecting the transfer of the protons from the –COOH. Furthermore, there were no amide peaks being found in the full spectra as anticipated. In summary, the transfer of H^+ from the oleic acid to the D-230 was confirmed, resulting in the transformation of $–COOH$ to $–COO^-$ and one of the amino groups to $–NH_3^+$. The results confirm the formation of the superamphiphile through the electrostatic interaction.

3.3.2 Pseudoternary phase diagram

Figure 3-4 shows the pseudoternary phase diagram obtained using the titration method at the room temperature. The superamphiphile was first dissolved into heptane, then mixed with Milli-Q water at different mass ratios from 1:9, 2:8 … to 8:2, 9:1, and finally titrated with butanol to obtain a single phase. The results showed the formation of single-phase within certain boundaries. The droplet sizes of microemulsions were below the detection limit of the conventional optical microscope, which were determined by DLS/FF-TEM and discussed in section 3.4. In order to minimize the surfactant dosage, an O/W microemulsion formed with 60 wt% water, 20 wt% heptane, 10 wt% superamphiphile and 10 wt% butanol, labeled as point (e) in Figure 3-4, was used for further study.

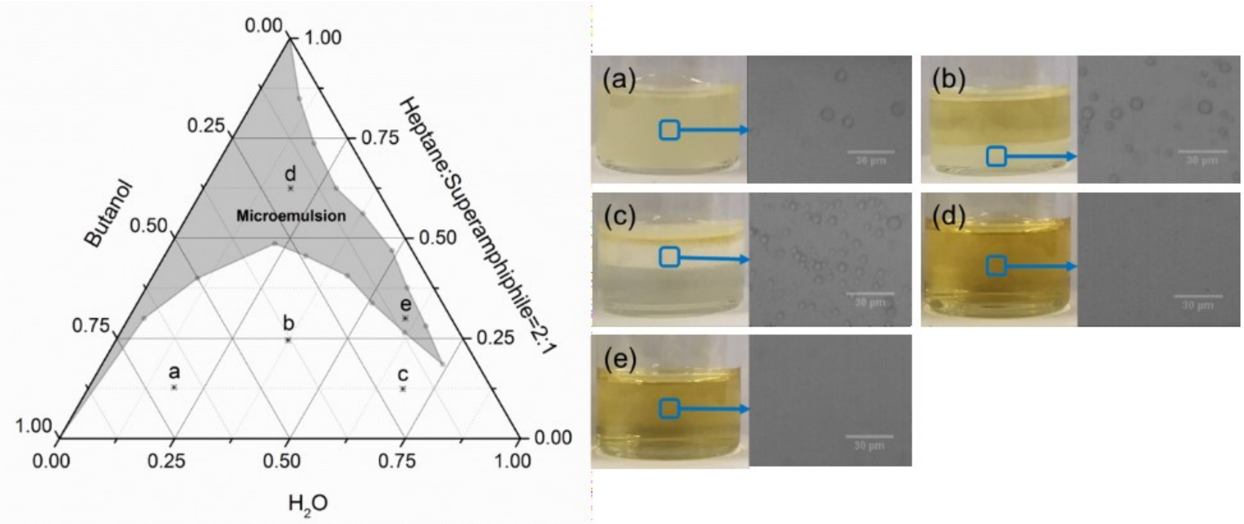

Figure 3-4 Pseudoternary phase diagram drawn in mass fractions for mixtures of water, 1-butanol and superamphiphile in heptane. Points (a) to (e) represent typical emulsions/microemulsions at different compositions. Point (e) is the O/W microemulsion made with 60 wt% water, 20 wt% heptane, 10 wt% superamphiphile and 10 wt% 1-butanol, which is used for further study.

3.3.3 Switchable behavior of CO_2-responsive O/W microemulsions

Before CO_2 was purged, the CO_2-responsive O/W microemulsion formed at the room temperature featured a homogeneous appearance as shown in Figure 3-5. The pH was measured to be 9.98. The hydrophobic dye within the oil core diffused into the whole system and generated a transparent light pink colour. A rapid phase separation occurred during CO_2 bubbling at the room temperature, a clear oil layer formed immediately after removing of the injection needle, and a clear water phase formed after 1.5 hours standing at 40 ± 0.3 ºC in a water-circulating thermal bath. The pH of the water phase was measured to be 8.42. Most of the Sudan III accumulated in the heptane, resulting in a darker colored oil phase, a clear water phase and a distinct oil-water interface. Such a phase separation can be easily reversed by introducing N_2 gas to the biphasic system at 60°C, with a stable O/W microemulsion of pH 9.67 being obtained within 10 minutes of gas purging. The phase transition was repeated by alternating purging of CO_2 and N_2 gas for 3 cycles. No significant effect was found on the CO_2 response, switch speed or stability of the microemulsion, demonstrating a great potential of applications for such switchable microemulsion systems.

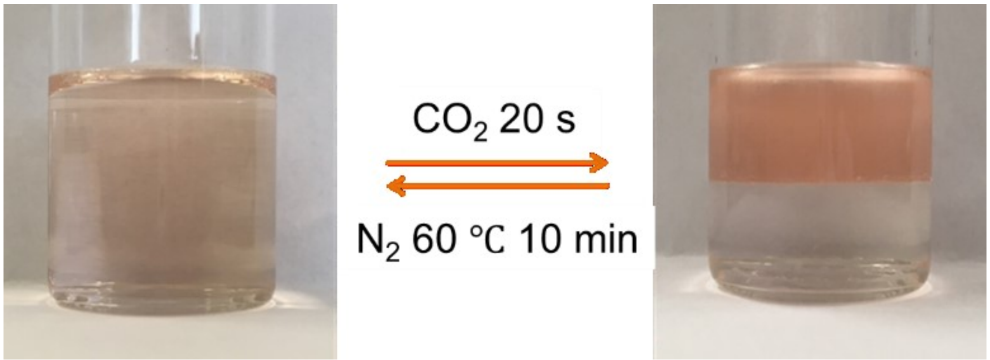

Figure 3-5 Rapid demulsification and re-microemulsification of CO_2-responsive O/W microemulsions. Stable O/W microemulsion switched into oil and water phases by purging of CO_2 at 200 mL/min and room temperature for 20 seconds, and switched back to apparent single phase O/W microemulsion by purging of N_2 at 300 mL/min and at 60 ºC for 10 minutes.

3.3.4 Properties of O/W microemulsions prepared by CO_2-responsive superamphiphile

3.3.4.1 Size distribution of O/W microemulsions

In order to investigate the structure of CO_2-responsive O/W microemulsions, samples were taken from different stages of the switching process and characterized using dynamic light scattering. The droplet size distributions obtained are summarized in Figure 3-6. The O/W microemulsion before the CO_2 purging has a Z-averaged diameter of 10.4 nm and a polydispersity index (PDI) of 0.106, indicating the well-dispersed state of oil droplets in the system. After the phase separation triggered by CO_2, large aggregates with an average diameter of several micrometers were formed in the aqueous phase. Such large aggregates were formed by Jeffamine D-230 which has been reported as an interfacial active chemical [87]. Optical micrographs of these large aggregates are shown in Figure A - 2 (Appendix A). No significant peak was detected in the oil phase since the oleic acid was highly soluble in the oil and did not form aggregates of notable sizes. Once the phase-separated system returned to the transparent O/W microemulsion after the treatment with N_2 at 60ºC, the peak for droplet size of 12.2 nm appeared with a PDI of 0.124, confirming the re-microemulsification of nano-sized oil droplets after the switching process. When further purged with CO_2 and followed with N_2, the system went to another cycle of the phase separation and the recreation of O/W microemulsions. The details on the correlation function and data fitting are given in Figure A - 3 (Appendix A). The results in droplet/aggregate size distribution measurement indicate the formation of a rapid switchable O/W microemulsions system using our novel CO_2-responsive superamphiphile.

The nanostructure of microemulsion droplets was further examined using a freeze-fracture transmission electron microscopy (FF-TEM). As shown in Figure 3-7, the droplets are all spherical and nano-sized. Due to the high concentration of oil content, the droplets are heavily packed. Comparing with the DLS results, the droplets in FF-TEM appear to be larger. The discrepancy may be caused by the expanding of the oil phase during the freezing process and making the replica when the non-wetting Pt is deposited onto the fractured frozen aqueous surface. Similar observations in other microemulsion systems have been reported previously [88, 141]. Furthermore, Egelhaaf et al. found that it is easy to underrepresent small liposomes due to the higher probability of fracturing larger liposomes and the presence of invisibly small cavities and caps from small liposomes, which leads to a larger size observed in FF-TEM images [142].

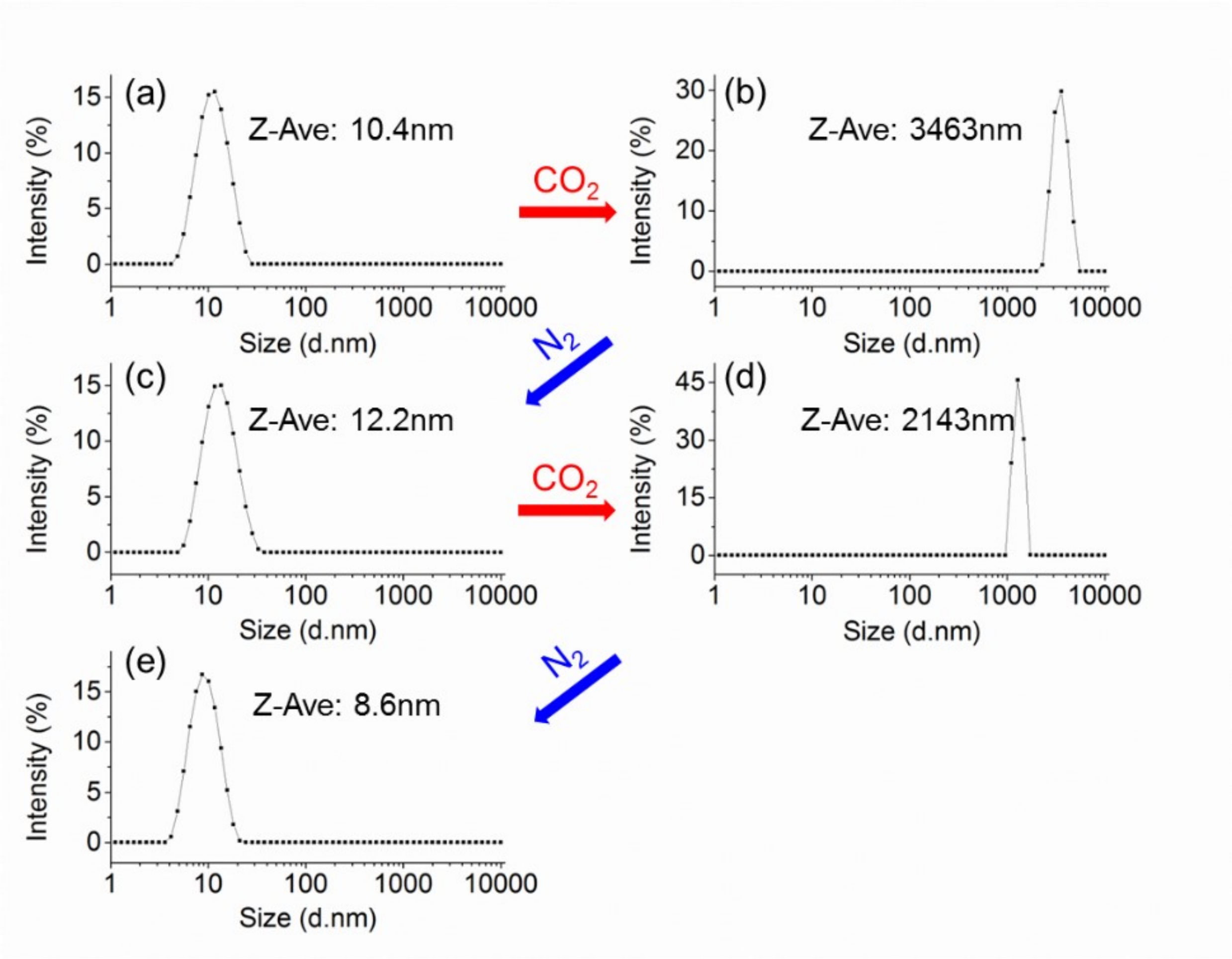

Figure 3-6 Oil droplet size distribution in (a) the original O/W microemulsion; (b) the water phase after first phase separation by CO_2 purging; (c) the O/W microemulsion after switching by removing of CO_2 with N_2 purging; (d) the water phase after CO_2 purging in the second switching cycle; (e) the O/W microemulsion after switching by removing of CO_2 with N_2 purging in the second switching cycle.

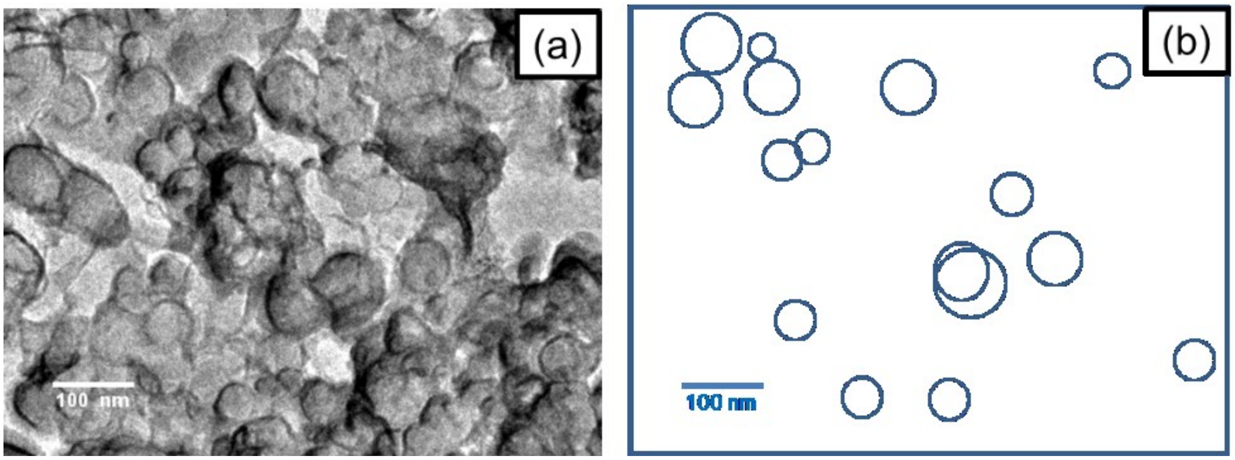

Figure 3-7 (a) FF-TEM images of the CO_2-responsive O/W microemulsion. (b) Schematic representation of spherical and nano-sized oil droplets.

3.3.4.2 Interfacial activity of superamphiphile

Figure 3-8 shows the water/heptane interfacial tension measured by the spinning drop tensiometer as a function of (a) time at different concentrations and (b) surfactant concentration at the last measurable point within 30 minutes, in which the superamphiphile and butanol were premixed at 1:1 mass ratio. At the total surfactant dosage up to 5 wt%, the interfacial tension remained at around 10^{-1} mN·m^{-1} over the test duration, which is shown in Figure 3-8 (a). With more surfactants being introduced into the aqueous phase, the interfacial tension showed a significant decrease with time. When the surfactant concentration reached 10 wt%, the interfacial tension decreased rapidly to 1.15×10^{-2} mN·m^{-1} in 10 minutes at which the oil-water boundary vanished, most likely in the form of microemulsion droplets due to the ultralow interfacial tension. A further increase in the surfactant dosage led to the immediate disappearance of the oil phase once injected into the tube, indicating spontaneous microemulsification at the even lower interfacial tension that could not be measured. Clearly, these results confirm that the superamphiphile and co-surfactant are effective in creating ultralow interfacial tensions and hence capable of emulsifying and stabilizing nano-size microemulsion droplets. The high dosage of the superamphiphile is essential to maintain the high curvature of microemulsified droplets and large interfacial area of the microemulsion.

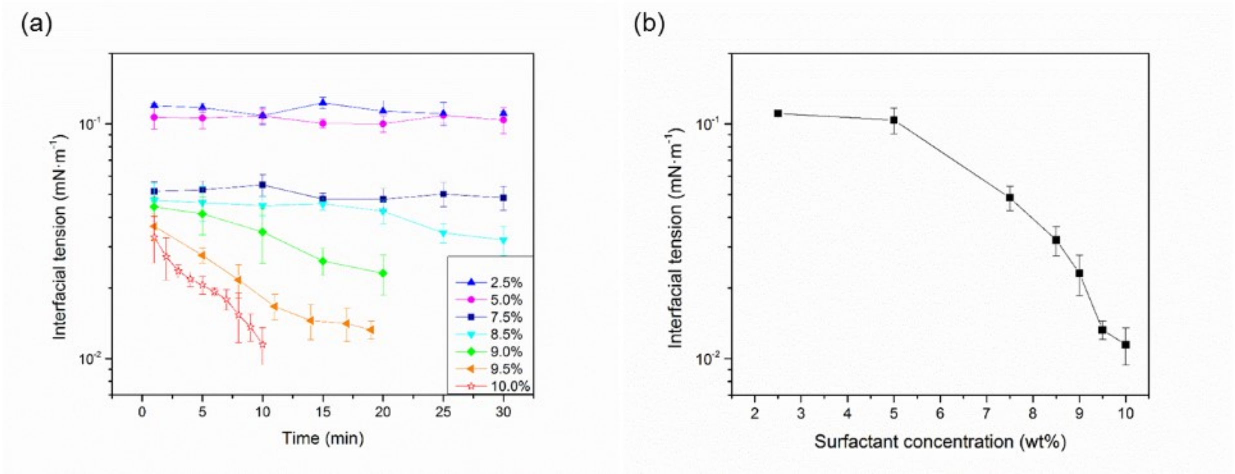

Figure 3-8 Interfacial tension of heptane and aqueous solutions measured at 25 ºC as a function of (a) time at different concentrations; (b) surfactant concentration at the last measurable points within 30 minutes. The surfactant referring to in this figure was a mixture of superamphiphile and butanol at 1:1 mass ratio. Error bars are calculated based on 5 tests at each point.

3.3.4.3 Stability of O/W microemulsion

The stability of O/W microemulsions was investigated against three factors: storage time, centrifugation force, and repeated heating/cooling treatments. Under all conditions, the microemulsions were inspected visually and exhibited excellent stability. After a six-month storage at the room temperature, the O/W microemulsion remained transparent. This microemulsion also remained in a single phase after being centrifuged at 4000-g for 20 minutes or heated up to 70 ºC and cooled down. However, the O/W microemulsion became normal emulsion after being heated to 80 ºC and cooled down to the room temperature, most likely as a result of breaking molecular association of electrostatic interactions between D-230 and oleic acid in the superamphiphile and irreversible evaporation of the heptane and butanol during the heating with the results shown in Figure A - 4 (Appendix A). The exceptional resistance to long time storage, high-speed centrifugation and relatively high temperature makes this CO_2-responsive O/W microemulsion a suitable candidate to be integrated into the industrial processes.

3.3.5 Switching mechanism of O/W microemulsions

Unlike the common emulsions, a microemulsion is thermodynamically stable, i.e., it is at a state of minimal Gibbs free energy G. Consider an oil-water mixture with an oil volume fraction of ϕ. As the system evolves from a phase-separated state to one in which the oil is emulsified into droplets of radii a, the change in Gibbs free energy can be written as [71]:

$$\Delta G = \gamma_{ow} \Delta A - T \Delta S_{conf}$$

where γ_{ow} is the oil-water interfacial tension, ΔA is the change in the oil-water interfacial area, T is the absolute temperature, and ΔS_{Conf} is the change in configurational entropy of the system. The first term in the above expression represents the enthalpic contribution to ΔG, while the second term is entropic in origin. It is clear that as γ_{ow} is lowered (e.g., with the addition of surfactants), the system can reach a point where the entropic contribution overtakes the enthalpic contribution, leading to a lowering of the overall free energy and an emulsified mixture of lower energy state relative to the phase-separated state. The critical interfacial tension at which this occurs is given by:

$$\gamma_{crit} = -\frac{k_B T}{4\pi a^2}[\ln\phi + \frac{1-\phi}{\phi}\ln(1-\phi)]$$

where k_B is the Boltzmann constant. Using parameters obtained previously in this paper for $\phi = 0.2635$, $T = 298\ K$ and $a = 5\ nm$, the result shows γ_{crit} = 2.87×10^{-2} mN·m^{-1}. Such an interfacial tension can be reached easily, as the lowest measurable interfacial tension before the drop disappeared in the section 3.4.2 was 1.15×10^{-2} mN·m^{-1} with only 10 wt% of total surfactant dosage. For the O/W microemulsion with 20 wt% total surfactant, the interfacial tension should be much lower than γ_{crit}, leading to a negative ΔG. This finding indicates that the current system containing CO_2-responsive superamphiphile before CO_2 purging can be emulsified spontaneously and stabilized thermodynamically.

The proposed switching mechanism of the CO_2-responsive O/W microemulsion is based on the association/dissociation of superamphiphile by addition and removing of CO_2, which leads to the changes of the interfacial tension and the Gibbs free energy. As shown in Figure 3-9, the superamphiphile and the co-surfactant were located at the interface. The oleic acid of the superamphiphile was inserted into the oil phase, while the amine was exposed to the water phase. When CO_2 is purged into the O/W microemulsion, the pH of the system decreased from 9.98 to 8.42. As a result, H_2CO_3 forms in the water phase and dissociates into H^+ and HCO_3^-. Then $-COO^-$ in the oleic acid of the superamphiphile is immediately neutralized by H^+, resulting in oil-soluble oleic acid which separates from the interface and dissolves into the heptane. Meanwhile,

–NH_3^+ in the superamphiphile combines with HCO_3^-, forming the water-soluble polyamine bicarbonate which diffuses into the water phase. The detailed explanation based on the molecular state distribution is shown in Figure A - 6 (Appendix A). As a result, the electrostatic interaction in the superamphiphile is eliminated as the corresponding components are separated and moved out of the interface. When the interfacial tension continues to increase and become larger than γ_{crit} (Figure A - 5, Appendix A), the O/W microemulsion loses its special interface activity and cannot maintain the optimized curvature of the nano-sized droplet. Finally, ΔG becomes positive, and the dispersed droplets become unstable and larger through the coalescence, resulting in a rapid response to CO_2 purging and a completed phase separation. Since the electrostatic interaction is no longer effective at the interface of closely packed nanodroplets, the conductivity of the system decreased from 1480±34.64 $\mu S \cdot cm^{-1}$ to 9.29±7.88 $\mu S \cdot cm^{-1}$.

Interestingly, when CO_2 is removed by N_2 purging, the polyamine bicarbonate is gradually converted to its non-ionic state of D-230, as HCO_3^- binds H^+ to form H_2CO_3 which eventually escapes in the form of CO_2 with the help of heating from the system. With the removal of CO_2 by bubbling the N_2, the superamphiphile is reconstructed by D-230 and oleic acid at the oil-water interface through electrostatic interaction. Once the interfacial tension reaches the ultralow level that is lower than the γ_{crit}, the Gibbs free energy change ΔG becomes negative again, making the two separated phases microemulsified spontaneously into the homogeneous and transparent microemulsions. Compared with the rapid demulsification, the speed of re-microemulsification is relatively slow, as the superamphiphile can only be re-assembled when D-230 and oleic acid interact at the interface after diffusing from the separated bulk water and oil phases respectively.

In the demulsification process, on the contrary, CO_2 has a high possibility to interact with the superamphiphile at the interface in the O/W microemulsion. For example, the interfacial area in a 5 g mixture discussed in this paper is increased from 2-3 cm^2 between heptane and water in direct contact to 220 m^2 in the form of the O/W microemulsion. In the previous switchable SDS microemulsion, the SDS is ionized from pH 0 to 14, and can form a very stable microemulsion [88]. The C12A is converted to $C12AH^+$ with a positive charge to bind with one anionic moiety of SDS after CO_2 purging, then move the SDS from the interface into the oil phase. The entire process especially the formation of the C12AH+ SDS and its diffusion into the oil phase takes a relatively long time. On the contrary, the superamphiphiles based on the electrostatic interaction can be quickly dissociated into the amine and acid building blocks upon CO_2 purging. The relatively small amine and acid building blocks (compare with the C12AH+ SDS) can depart from the interface very quickly. The two microemulsion systems are different in the molecular design, thus exhibiting different switching speeds. Most importantly, this novel microemulsion has a distinct rapid CO_2-responsiveness and can switch between a single phase and two separated phases in a very short time.

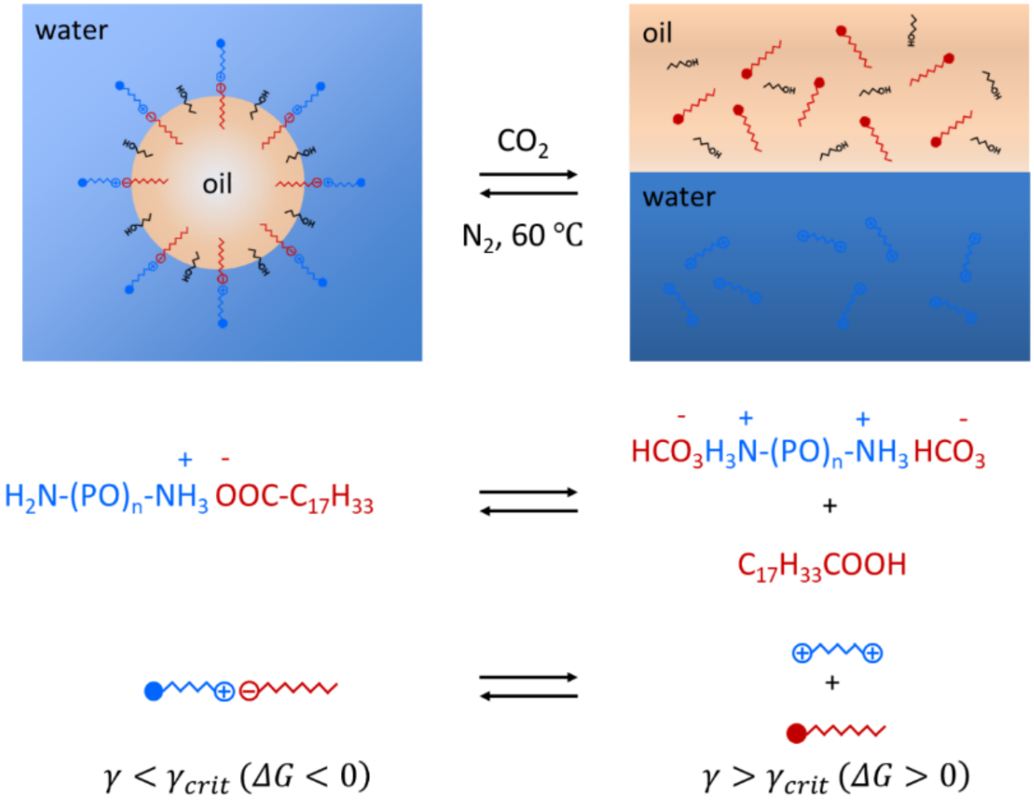

Figure 3-9 Schematic diagram illustrating the switching mechanism of O/W microemulsion prepared using CO_2-responsive superamphiphile.

3.3.6 Application of CO_2-responsive O/W microemulsions to remediation of spent drill cuttings

Using current treatment methods of spent drill cuttings such as offshore cuttings dryers and onshore thermal desorption consume a large quantity of energy to decrease the amount of residual drilling fluid (oil) in the treated cuttings to less than 5 wt%. However, our CO_2-responsive O/W microemulsion can significantly reduce the residual oil in the treated drill cuttings at a very low energy consumption and operating cost. As shown in Figure 3-10 (a), the black spent oil dispersed immediately into the whole microemulsion due to the ultralow interfacial tension while liberating the oil from the contaminated solids. After purging of CO_2 for only 20 seconds and a gentle centrifugation, the ultralow interfacial tension disappeared, resulting in a rapid phase separation as shown in Figure 3-10 (b). The solids in the aqueous phase were then carefully separated and analyzed by TGA, with results shown in Figure 3-10 (c). Clearly, the CO_2-responsive O/W microemulsion decreased significantly the amount of oil in the cuttings to less than 4 wt%, which meets the disposal requirement for drill cuttings remediation. A systematic study on optimization of the treatment process to further minimize the organic content in the treated cuttings will be reported in a separate paper.

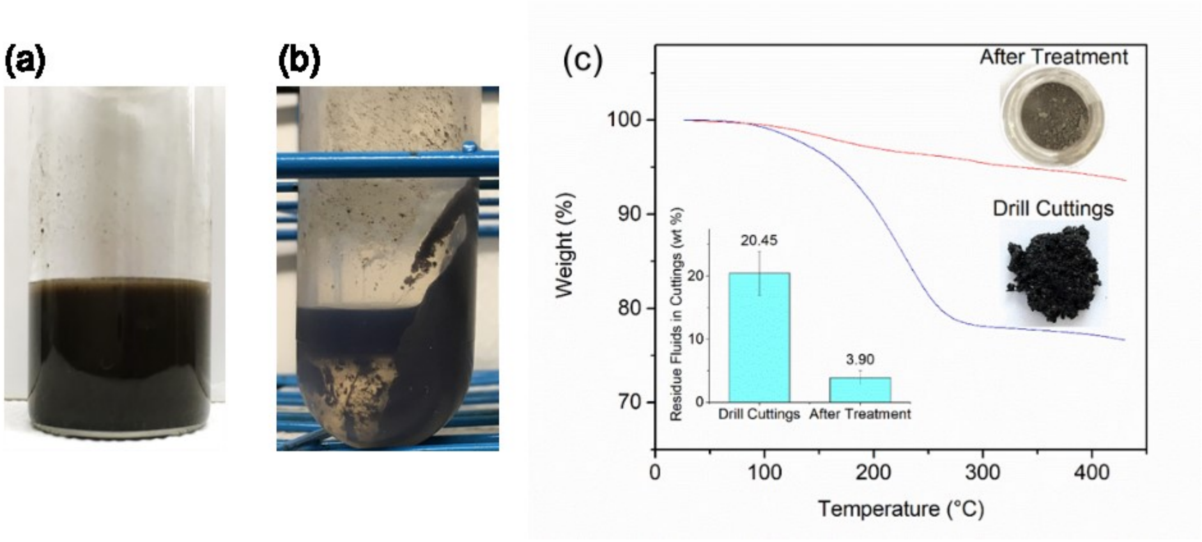

Figure 3-10 (a) Mixture of 1g drill cuttings and 5 g O/W microemulsion; (b) drilling fluid (oil) extracted from the cuttings after CO_2 purging for 20 seconds and centrifugation at 1000 rpm for 15 minutes; (c) TGA results of the drill cuttings before and after the treatment by CO_2-responsive microemulsions.

3.4 Conclusions

We demonstrated a novel O/W microemulsion with a rapid switching speed and a reversible conversion from a monophasic state to the separated oil and water phases by simply addition/removal of CO_2. The pivotal CO_2-responsive superamphiphile used in the microemulsion, which is a linear structure surfactant assembled by oleic acid and Jeffamine D-230 through electrostatic interaction, can greatly change its interfacial activity. Treated by the CO_2 for a few seconds, the microemulsion can be destabilized and separated completely into the oil and water phases as the superamphiphile responses rapidly to CO_2 purging and loses its interfacial activity. Alternatively, after removing of the CO_2 by purging of N_2 at 60 ºC, the superamphiphile can be quickly reconstructed, which reduces the interfacial tension effectively and hence the reformation of transparent O/W microemulsion within 10 minutes.

Compared with the switchable emulsions/microemulsions reported earlier [87-89, 129-131], our O/W microemulsion can be conveniently prepared with low-cost, commercially available surfactants. Most importantly, it switches rapidly by purging of trigger gases (CO_2 and N_2). This switching behavior is also helpful in the rapid treatment of the drill cuttings at the room temperature, where the residue oil in the cuttings can be removed effectively. Such switchable O/W microemulsions of ultralow interfacial tension, nano-sized droplets, rapid CO_2-responsiveness and complete phase separation can have many potential research and industry applications, such as drill cuttings treatment, contaminated soil cleaning, nanoparticles preparation and enhanced oil recovery.

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Chapter 4 Comprehensive treatment of oil-contaminated drill cuttings using CO_2-responsive O/W microemulsions

4.1 Introduction

Drill cuttings are crushed rocks, sands and clays generated by the crushing action of the drilling bit as it cut the sub-surface. The solids in drill cuttings tend to have angular morphology and can range in size from ~2 μm to over 30 mm [8]. In the exploration of hydrocarbon resources, a considerable amount of drill cuttings are transported to the surface, along with the drilling fluids which are either water-based or oil-based, resulting in undesirable environmental concerns [143-145]. In drilling operations, one of the technical challenges is the safe disposal of drill cuttings which are often contaminated with significant amounts of oil-based drilling fluids. These oil-contaminated drill cuttings can have an impact on the local ecosystems by releasing toxic component [146] or forming anoxic conditions in the microbial degradation process [147].

Compared with the water-based drilling fluids, the oil-based drilling fluids have exceptional shale stabilization capability [4], high temperature/pressure tolerance [6], better lubricity [1] and enhanced corrosion protection [2]. These features of oil-based drilling fluids allow a faster drilling operation [5]. Although different water-based fluids have been developed since 1930s, the oil-based drilling fluids are still used in major drilling projects or deep drilling operations due to these excellent advantages [7]. However, the potential environmental hazards of the oil-contaminated drill cuttings are of concern, as the residue hydrocarbon may release and contaminate the groundwater and soil in the long term [44, 148, 149]. In the last two decades, the health impacts of the oil-contaminated drill cuttings have attracted increasing attention. The 96-h LC_{50} which is the concentration that causes 50% death of test organisms in 96 hours, is only 10^4 to 10^5 ug/g in the toxicological study [150]. As a result, both the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR Convention) in North Sea and Alberta Energy Regulator (AER) in Canada required the “fluid retention on drill cuttings” (ROC), defined as the weight percent of residue oil in cuttings, to be less than 1 wt% for safe disposal [25, 27].

Although a thermal treatment station is able to decompose the drill cuttings to a 1 wt% ROC, it consumes a considerable amount of energy and requires costly transportation of drill cuttings from the field/platforms to the stations, generating massive carbon emissions [19, 20, 30]. This activity may also face the potential risk of leaking during long distance transportation [22]. In the land farming method, tons of wood debris are added to dilute the oily cuttings, which needs much more land space and treatment time [31]. With these limitations of commercial treatment technologies, several other methods to reduce ROC of treated drill cuttings have been proposed and studied, but only at the R&D stage. Using supercritical carbon dioxide extraction for example, the ROC of treated drill cuttings can be as low as 0.2 wt%, while the composition of extracted hydrocarbons remains comparable to the drilling base oil [39-41]. The liquefied gas extraction has been developed from the supercritical CO_2 extraction method, where liquefied hydrocarbons such as propane or butane were used as the extraction media. The liquefaction of propane or butane can be achieved at ambient temperatures and lower pressures as compared with the liquefaction of CO_2 [11]. However, these techniques require expensive equipment to reach and maintain the pressure of the extraction medium in the supercritical state, which limits their applications in the oil and gas industry due to the cost and safety considerations. To avoid operations at high-pressure conditions, the microwave heating method has been developed. The microwave treatment is based on the thermal desorption mechanism, but utilizes the microwave to generate the heating inside of the cuttings [36-38, 151]. After the treatment, a ROC less than 1.0 wt% was demonstrated in the lab scale testing [36, 38]. In the microwave treatment, the water acts as the heating element instead of being an energy sinker for its vaporization as encountered in the traditional thermal desorption unit. Nevertheless, the microwave heating technique still needs high energy consumption to heat up drill cutting solids in the treatment process.

To reduce the process energy and the equipment cost, the surfactant washing method has been investigated for treating the oil-contaminated drill cuttings [49-52]. This technology has also been used in treating soils contaminated by petroleum products. The surfactant washing method is easy and safe to operate without the requirement of high pressure or temperature container, but the efficiency of oil removal may be less than other techniques [52, 57, 58, 152-154]. Compared with current surfactant washing methods, washing using O/W microemulsions shows a significant increase in the solubilization of the residue oil [67]. However, microemulsions are isotropic and thermodynamically stable mixtures [62]. The oil once solubilized into the microemulsion may have difficulties to be separated and collected from the microemulsions, generating a secondary waste of oily microemulsions. To solve this problem, the stability of the spent microemulsion needs to be destroyed for effective oil-water separation where the oil is recovered as a byproduct and aqueous phase recycled for regeneration. Chemical demulsifiers are usually added to destabilize the emulsified systems [84-86]. But the addition of extra demulsifiers may add additional cost and other potential environmental concerns. Considering a typical well drilling project generating ~1000 to 2000 tons of cuttings which contain 50 to 300 tons of residue oil with potential environmental impact, a cost-efficient and environmentally friendly method should be developed to treat the oil-contaminated drill cuttings for their safe disposal while recovering the oil as a value-added product.

In this work, we demonstrate an effective treatment process using CO_2-responsive microemulsions for the purpose of cleaning oil-contaminated drill cuttings at ambient temperatures. The CO_2-responsive microemulsions are able to rapidly extract the residue oil from the porous structures in the cuttings due to their ultra-low interfacial tension and strong capability of solubilizing oil, with the oil removed from the cuttings to be phase-separated immediately at the top by responding of novel microemulsions to CO_2 purging. The aqueous phase between the oil phase and the cuttings solids prevents the recontamination of the clean solids. The entire process is shown to reduce the ROC of the treated drill cuttings below the discharge limit of 1 wt % for safe disposal and envisioned to be easy to operate without the need for any expensive equipment, extreme working conditions or additional chemical demulsifiers.

4.2 Materials and methods

4.2.1 Materials

Poly (propylene glycol) bis (2-aminopropyl ether) (known as Jeffamine D-230), oleic acid (technical grade), 1-butanol (ACS grade) and Sudan III (technical grade) were purchased from Aldrich (the USA). Heptane (HPLC grade) was purchased from Fisher Scientific (Canada). Oil-contaminated drill cuttings were obtained from commercial drilling operations in Alberta through Weatherford Canada Ltd. All the chemicals were used as received. Deionized water was obtained from a Milli-Q water purification system (Millipore, the USA) and used throughout this study.

4.2.2 Preparation of CO_2-responsive microemulsions

The novel switchable microemulsions were prepared using a CO_2-responsive superamphiphile, which was a linear surfactant assembled by oleic acid and Jeffamine D-230 through electrostatic interaction at a 1:1 mole ratio. The structure of this CO2 responsive superamphiphile is shown in Figure 4-1. After mixing of heptane, superamphiphile, butanol (co-surfactant) with deionized water at an appropriate concentration, the CO_2-responsive microemulsions were formed spontaneously and used as the washing medium in this work. The composition of the prepared microemulsions is shown in Table 4-1. A surfactant solution was prepared without any heptane and used in the control test. Treated by the CO_2 at 200 mL/min rate for 30 seconds, the superamphiphile lost its special interfacial activity, leading to an immediate and complete phase-separation of microemulsions into the immiscible oil and aqueous phases. The detailed preparations, characterizations and switching mechanism of the prepared microemulsions were described in our previous work [155].

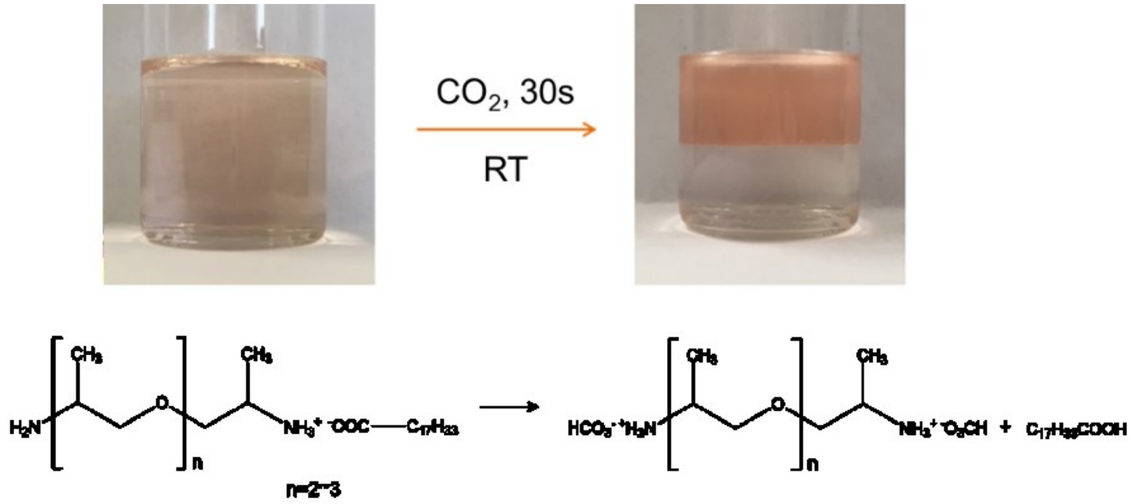

Figure 4-1 Rapid demulsification of O/W microemulsion (top) and the chemical structure of CO_2-responsive superamphiphile (bottom). The picture was taken using ME-1 as an example, one drop of 0.05 wt% Sudan III in heptane solution was added to dye the microemulsion.

Table 4-1 Composition of microemulsions used as washing medium of oil-contaminated drill cuttings

Formulation	Heptane (wt%)	Superamphiphile (wt%)	Butanol (wt%)	Water (wt%)
ME-1	20	10	10	60
ME-2	15	10	10	65
ME-3	10	10	10	70
ME-4	5	10	10	75
Surfactant Solution*	0	10	10	80

*Note: Surfactant solution was used as a control washing medium for comparison.

4.2.3 Characterization of the properties of the O/W microemulsion in the oil-contaminated drill cuttings treatment

4.2.3.1 Size distribution measurement

Zetasizer Nano ZS (Malvern) was used to determine the size distributions of O/W microemulsions. About 1 mL samples were taken from the washing medium listed in Table 4-1, and analyzed at 20 ºC without any filtration.

4.2.3.2 Interfacial tension measurement

Spinning drop tensiometer (SDT, KRÜSS) was used to measure the interfacial tension between the residue oil and washing medium listed in Table 4-1. Each washing medium was used as the heavy phase in the spinning drop tensiometer. A drop of residue oil, which was manually collected from the drill cuttings and filtrated through a 0.45 μm Nylon syringe filter, was then injected into the tube as the light phase. The sample tube was set to spin at 2000 rpm at ambient temperatures. The data was recorded for 20 minutes or until the disappearance of residue oil droplets.

4.2.3.3 Residue oil liberation measurement

The liberation process of residue oil from the drill cuttings was analyzed online using an in-situ liberation visualization cell. Detailed procedures for oil liberation analysis have been described in previous reports [156-158]. For each test, the sample holder was half filled with the oil-contaminated drill cuttings, with the surface being flattened with a small hammer. A coverslip was placed onto the top of the sample holder to prevent the evaporation of the microemulsions, and the washing medium was injected between the cutting surface and the coverslip to fill the ~2 mm gap. The liberation process of the residue oil from the drill cuttings in the washing medium was recorded by a stereo-optical microscope (Olympus SZX 10), which was connected to a charge-coupled device camera (CCD). The images were converted into the grayscale, with the dark areas representing cuttings being covered by the black residue oil. When the residue oil was liberated from the solids by a washing medium, the area became brighter. By carefully analyzing the recorded images, the rate and degree of the residue oil liberation were obtained. An example of oil liberation from the drill cuttings is shown in Figure 4-2.

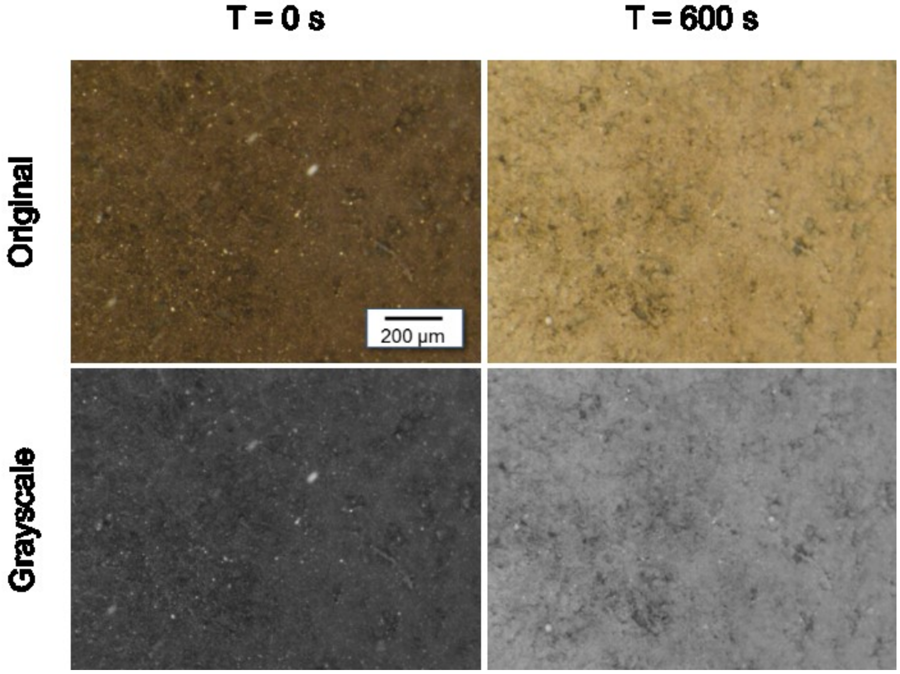

Figure 4-2 An example illustrating the image processing in oil liberation analysis. The degree of oil liberation from the drill cuttings is monitored by the change in the grayscale of cuttings surfaces, which were captured and recorded by an optical microscope.

4.2.4 Preparation of artificially contaminated sands

To verify the feasibility of CO_2-responsive microemulsions treatment, artificially contaminated sands were prepared to simulate the drill cuttings. [57, 58] ~100g of pure sands and ~5g hexadecane were placed into the 400 mL beaker. Then CCl_4 was added to immerse the sands. Several drops of 0.1 wt% Sudan III in CCl_4 solution was added to dye the hexadecane. After mixing all the components, the beaker was placed uncovered in the fume hood for 48 hours to allow the CCl_4 to evaporate. Eventually, the sands were weathered inside the oven at 102°C for another 24 hours. The residue oil level was determined by TGA and discussed in section 4.3.2.

4.2.5 Effective treatment process of oil-contaminated drill cuttings

In order to develop an ambient temperature process to treat oil-contaminated drill cuttings, all the experiments were conducted at room temperatures. As shown in Figure 4-3, approximately 2.0 g of the oil-contaminated drill cuttings and 10.0 g of each washing medium listed in Table 4-1 or water were placed into a 30 mL glass jar with a stirring bar. The jars were capped with polypropylene lids, placed onto magnetic stirrers and mixed at 500 rpm for 30 minutes. The dry CO_2 gas was then purged at 200 mL/min into the glass jar for 30 seconds. After gas purging, the mixture was transferred into a centrifuge tube and centrifuged at 1000 rpm for 15 minutes, where a top dark oil layer, a middle clear aqueous layer and bottom solids were obtained except for water treatment process. The oil and water phases were decanted into a 20 mL glass vial, and another 10.0 g of deionized water was added into the centrifuge tube to rinse the solids. After shaken by hand for 10 seconds, the tube was centrifuged again at 1000 rpm for another 15 minutes in order to settle the solids. The rinse water was decanted into the second 20 mL vial, and the solids were transferred onto a Petri dish and heated in the oven at 102°C for 30 minutes to evaporate the water before the ROC determination.

Figure 4-3 Proposed treatment process of oil-contaminated drill cuttings using CO_2-switchable microemulsions.

4.2.6 ROC determination method

A thermogravimetric analyzer (TGA, TG 209 F1 Libra®, NETZSCH) was used to determine the ROC of washed solids. All the TGA analysis was carried out under the nitrogen protection atmosphere with a flow rate of 25 mL/min. The heating range was set from the room temperature to 500°C with a ramping rate of 10 °C/min. ROC was determined based on the percentage of weight loss at the temperature where the drilling fluids all decomposed. Details on ROC determination and analysis are given in Figure B - 1.

To further identify the organic residue on the solids before and after the treatments, the same TGA was coupled with an Agilent 7890A gas chromatograph (GC) and 5975C inert mass selective detector (MSD). About 10 mg of solids was placed into the Al_2O_3 crucible, and heated inside of the TGA from the room temperature to 900°C at a temperature ramping rate of 10 °C/min under the nitrogen atmosphere. The degradation gas was stored inside a cryotrap which was set at -35°C using liquid CO_2. The cryotrap was then quickly heated to 300°C at 400 °C/min heating rate to transfer the trapped gas to the GC column at 300°C. The electron ionization energy of 70 eV was selected and used for the analysis in MS.

4.3 Results and discussions

4.3.1 Properties of the O/W microemulsions in drill cuttings treatment

4.3.1.1 Droplet size of O/W microemulsions

Unlike common emulsions, the microemulsions appear to be homogeneous and transparent due to small sizes of microemulsified droplets. To investigate the nano-structure of the CO_2-responsive O/W microemulsions, each formulation from Table 4-1 was characterized using dynamic light scattering. The droplet size distributions and corresponding polydispersity index (PDI) obtained are summarized in Table 4-2. Without the CO_2 purging, the O/W microemulsions showed Z-averaged diameters from 11.06 nm to 8.13 nm, as the heptane content decreased from 20 wt% to 5 wt%. The PDI values were all below 0.150, indicating well-dispersed oil droplets in these washing media. These nano-sized droplets enabled the heptane to be delivered into the microporous regions of the cutting solids to extract the residue oil, resulting in deep cleaning of the oil-contaminated drill cuttings [159, 160]. Triggered by the CO_2, the well-dispersed droplets disappeared quickly to form an oil phase on the top of the aqueous phase for easy separation or oil recovery. The detailed size distributions and their correlation functions are given in Figure B-2 (Appendix B).

Table 4-2 Drop size and PDI of microemulsions

Formulation	ME-1	ME-2	ME-3	ME-4
Heptane (wt %)	20	15	10	5
Z-averaged diameter (nm)	11.06±0.09	10.43±0.03	10.02±0.05	8.13±0.08
PDI	0.143±0.008	0.123±0.010	0.139±0.012	0.110±0.003

Note: Error bars are calculated based on 3 tests for each formulation

4.3.1.2 Ultralow interfacial tension of O/W microemulsions

The interfacial tension between the residue oil and washing medium plays a critical role in extracting/cleaning the residue oil from drill cuttings [52, 161]. Without any additives, the interfacial tension between the residue oil and the water was measured using the pendant drop method on a Theta Optical Tensiometer (T200 Biolin Scientific) to be 26.6±0.8 $\mathrm{mN{\cdot}m^{-1}}$. In contrast, the interfacial tension between the residue oil and microemulsions from ME-1 to ME-4 (heptane content from 20 wt% to 5 wt%) was at ultralow levels, as shown in Figure 4-4. The interfacial tension for ME-4 with 5 wt% heptane, for example remained at around 5×10^{-2} $\mathrm{mN{\cdot}m^{-1}}$ over the test duration. Increasing heptane content in the microemulsion led to a significant decrease in residue oil/microemulsion interfacial tension with time, as a result of an increased number of emulsified heptane droplets diffused to the drilling oil/washing medium interface [80, 81]. As the heptane concentration reached 20 wt% in ME-1, the interfacial tension decreased rapidly to 4.3×10^{-3} $\mathrm{mN{\cdot}m^{-1}}$ in only 12 minutes. In such system, the boundary between the residue oil and ME-1 vanished as a result of spontaneous emulsification of the residue oil, as shown in Figure B-3 (Appendix B). Considering the surface thermodynamics of residue oil on the drill cuttings in the washing medium, the work of cohesion (W_c) and the work of adhesion (W_a) in the microscopic scale can be written as:

$$W_c = 2\gamma_{ow} \tag{1}$$

and

$$W_a = \gamma_{ow}(1+\cos\theta) \tag{2}$$

where W_c indicates the tendency of the residue oil to fragment, W_a represents the affinity of the oil to the drill cuttings, γ_{ow} is the interfacial tension between the residue oil and the washing medium, and θ is the contact angle between the residue oil and the drill cuttings. For a system of ultralow interfacial tension, W_c was dramatically decreased, indicating emulsification of the residue oil by only a weak mechanical force such as thermal agitation. Decreasing interfacial tension by adding more heptane in microemulsions also led to a significant reduction in W_a, translating to a detachment of oil droplets from drill cuttings by small mechanical force such as thermal agitation or mechanical shearing. However, a further decrease in the interfacial tension would not necessarily lead to the best overall cleaning efficiency, which was confirmed by the fact that the lowest interfacial tension of the ME-1 did not result in the best ROC after the treatment (section 4.3.3). Even though the ultralow interfacial tension of the microemulsion greatly helps the residue oil extraction, other factors such as the capability of oil solubilization should be considered when determining the ultimate ROC level of the treatment, which is investigated in the next section.

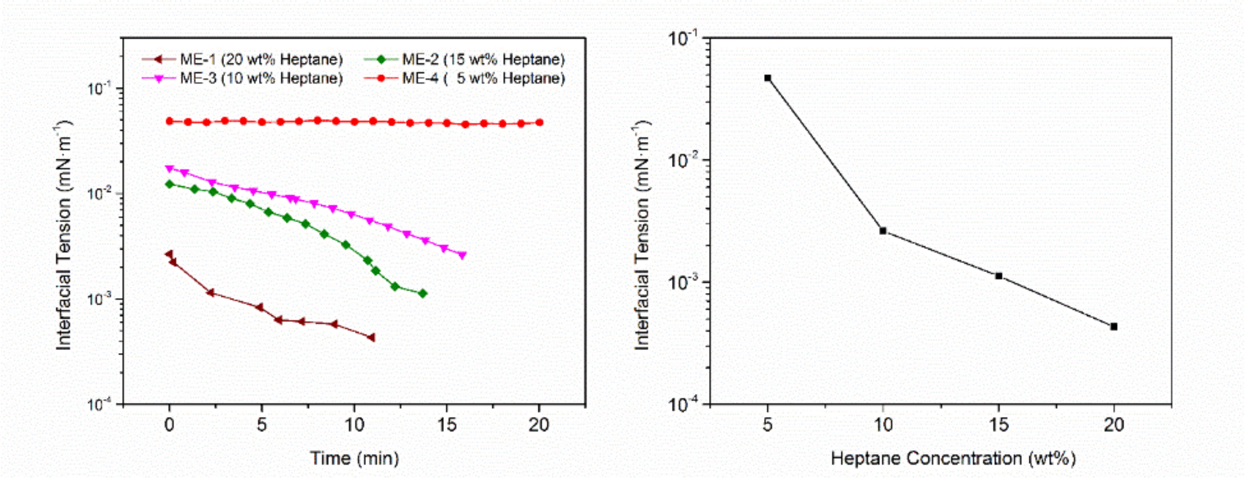

Figure 4-4 Dynamic interfacial tension of residue oil and microemulsions as treatment media measured at 25ºC (a) and interfacial tension at the last measurable points within 20 minutes (b) as a function of heptane concentration. The heptane referred to in this figure was the oil phase in the microemulsions.

4.3.1.3 Effect of oil solubilization by O/W microemulsions on residue oil liberation

To obtain a deep understanding of the role of the microemulsions in the cleaning of drill cuttings, the liberation of residue oil from drill cuttings was studied using different washing media. The liberation kinetics of residue oil was determined using a custom-designed in-situ liberation visualization cell, as described previously [156-158]. Residue oil liberation experiments using microemulsions ME-1 to ME-4 were conducted at the room temperature and the results are compared in Table 4-1 with the case of surfactant solution washing and the water washing as two control tests. The degree of oil liberation (DOL) is plotted in Figure 4-5 as a function of time. A logistic-type empirical function was used to fit the data and evaluate the oil liberation kinetics by different washing media, shown as eq 3:

$$DOL\,(\%) = \frac{A_1 - A_2}{1 + (t / t_0)^p} + A_2 \qquad (3)$$

where t is the liberation time, A_1, A_2, t_0 and p are four fitting parameters which refer to initial value, final value, center and power index, respectively. When $t \to +\infty$, the DOL approaches its upper limit of A_2. Parameter A_2 can therefore be considered to be the ultimate limit of overall oil liberation for a given washing medium. To better compare the oil liberation kinetics, t_{EC20} is introduced to be the time that leads to 20% of the ultimate oil liberation limit. t_{EC20} can therefore be used to evaluate the initial rate of oil liberation from the cuttings. A shorter t_{EC20} represents a faster initial oil liberation rate, thus an enhanced cleaning of residual oil from the oil-contaminated drill cuttings at the initial stage, and vice versa. The characteristic parameters such as R^2, A_2 and corresponding t_{EC20} are summarized in Table 4-3, while the detailed fitting parameters are given in Table B - 2 in the supplementary.

As shown in Figure 4-5 and Table 4-3, the ultimate overall oil liberation A_2 increased significantly from 25.0% in water control test to 99.3% with ME-4 as the washing medium, indicating a significant enhancement in cleaning the residue oil from drill cuttings with a proper heptane concentration in the microemulsion. Such enhancement is a result of a suitable balance between the ultralow interfacial tension and the capability of oil solubilization. A further increase in the heptane content in microemulsions from 5 wt% to 20 wt% decreased significantly the initial oil liberation time t_{EC20} from 26.65 s to 4.31 s, as a result of decreasing the work of cohesion (W_c) and the work of adhesion (W_a) with decreasing the interfacial tension between the residue oil and the microemulsion. However, increasing the heptane dosage in the microemulsion limited its capability of solubilizing residual oil, leading to a drop of the ultimate overall oil liberation A_2 to only 77.9% when ME-1 was used to treat the oil-contaminated drill cuttings. Among all the washing media, the surfactant solution without heptane addition had the highest capability of solubilizing residual oil. Without any heptane droplets to diffuse into the drill cuttings as in the case of surfactant solutions, neither t_{EC20} nor A_2 was comparable with the results from washing using ME-4 microemulsion. In summary, microemulsions with a proper selection of the heptane dosage are clearly shown to benefit the rate and overall degree of the residue oil liberating from the oil-contaminated drill cuttings surfaces.

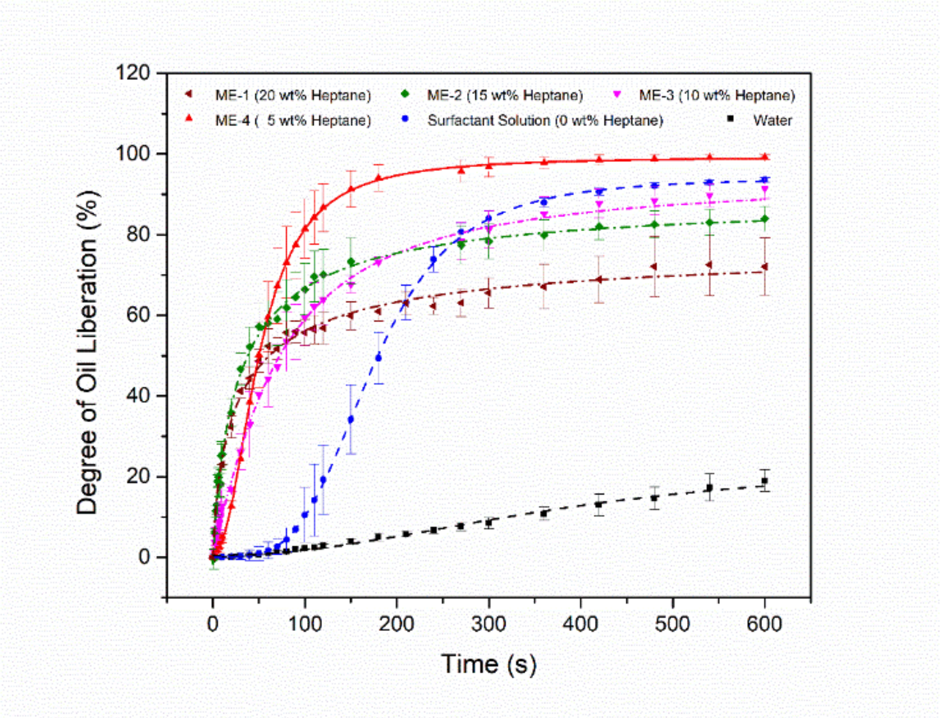

Figure 4-5 Liberation kinetics of the residue oil from the oil-contaminated drill cuttings using microemulsions of different formulations at ambient temperature. Error bars are calculated based on 3 tests at each condition.

Table 4-3 Fitting parameters of logistic function for oil liberation kinetics and t_{EC20} at the room temperature

Formulations		Fitting parameters		
		R^2	A_2	t_{EC20}
Microemulsions	ME-1 (20 wt% heptane)	0.9898	77.9085	4.31
	ME-2 (15 wt% heptane)	0.9964	89.5779	5.45
	ME-3 (10 wt% heptane)	0.9978	94.3275	23.29
	ME-4 (5 wt% heptane)	0.9998	99.3152	26.65
Control Test	Surfactant Solution (0 wt% heptane)	0.9998	94.0897	121.03
	Water	0.9908	25.0179	204.79

4.3.2 Treatment of artificially contaminated sands

In this study, the treatment performance was evaluated based on the residue oil extraction, which was reflected by the residue oil level in the oil-contaminated sands or drill cuttings after the treatment, as required by the regulations to be less than 1 wt% for safe discharge. To demonstrate the feasibility of CO_2-responsive microemulsion treatment process, artificially contaminated sands was selected as the first treatment target, which showed a light pink color after weathering, as shown in Figure 4-6 (a). The CO_2-responsive microemulsion ME-1 was used to verify the feasibility of the microemulsion treatment. Water and surfactant solution were used as two control tests for comparison, in which the surfactant solution has a similar composition with ME-1 but replace the heptane content with excess water (Table 4-1). After mixing with different washing media, the pink hexadecane was extracted rapidly into the ME-1 and surfactant solution. After CO_2 was added for 30 seconds at 200 mL/min and the room temperature, the superamphiphile in the systems dissociated into inactive interfacial components, [155] resulting in an immediate phase separation into a top pink oil phase and a bottom aqueous phase, as shown in Figure 4-6 (b). As a result, the hexadecane was concentrated at the top, and the clean sands in the aqueous phase were carefully separated and analyzed by TGA. In contrast, the hexadecane cannot be extracted and accumulated in the water washing method.

Figure 4-7 shows the TGA results of the residue oil level in the artificially contaminated sands before and after the treatments by ME-1, surfactant solution and water. In Figure 4-7 (a), the artificially contaminated sands kept losing the weight until 150 ºC because of the decomposition of residue hexadecane in TGA. The residual oil level without the treatment was characterized as

3.55 ± 0.46 wt%, as illustrated in Figure 4-7 (b). After the ME-1 and surfactant solution treatments, the mass lost curves became almost flat, and the residual oil levels were significantly reduced by ~10 times to 0.33 wt% and 0.36 wt% respectively, suggesting an enhanced oil extraction during these two treatments. On the other hand, the treatment using water could only slightly decrease the residue oil level, and mainly due to the oil stick to the vials and centrifugation tubes rather than the extraction of the oil from the sands. These results confirmed the feasibility of the CO_2-responsive microemulsion treatment on oil-contaminated substrates at the room temperature. However, due to the low contamination degree of the sands and the ideal properties of the hexadecane, the advantage of using microemulsion over the surfactant solution is not prominent yet, which will be further discussed using the real drill cuttings in the next section.

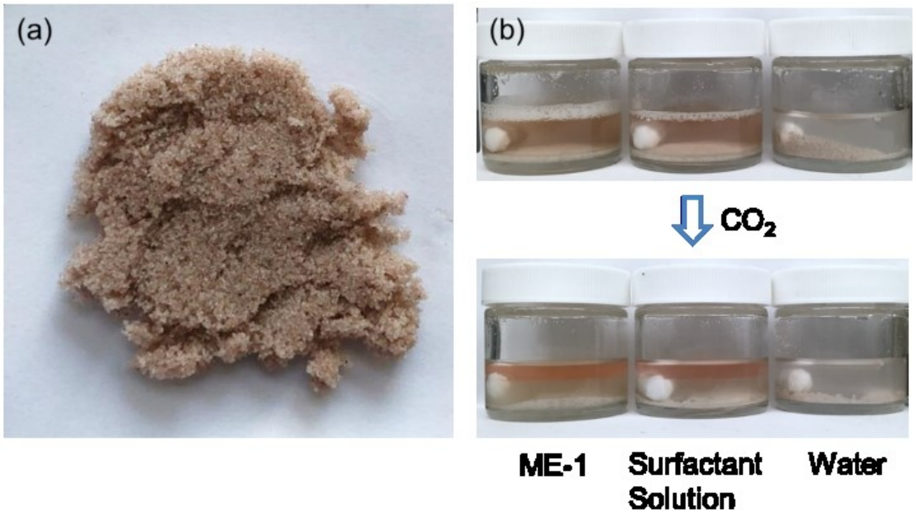

Figure 4-6 Photos of (a) the artificially contaminated sands before the microemulsion treatment and (b) the treatment process, where the dyed hexadecane was extracted rapidly into ME-1 and surfactant solution, then concentrated immediately at the top after CO_2 was added at 200 mL/min

and the room temperature for 30 seconds. In the water washing, the hexadecane cannot be extracted from solids and accumulated at the top.

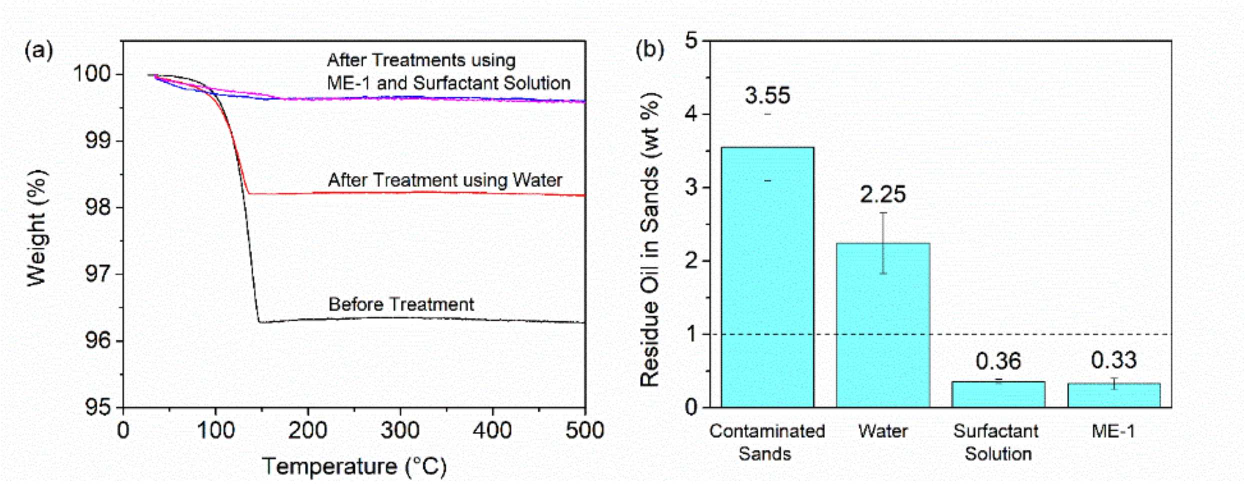

Figure 4-7 TGA results of the artificially contaminated sands before and after the treatments by water, surfactant solution and ME-1: (a) The TGA profile illustrates the complete decomposition of the organic contaminants from the artificially contaminated sands at 150 ºC, and the complete removal of contaminants by ME-1 method; (b) Calculated residue oil in the artificially contaminated sands before and after different treatments. Error bars are calculated based on 3 tests at each treatment.

4.3.3 Treatment of oil-contaminated drill cuttings

The treatment performance was evaluated by analyzing ROC after the treatment. A 1 wt% of ROC is as required by the regulations for safe discharge. Oil-contaminated drill cuttings from Weatherford are shown in Figure 4-8 (a). The oil-based drilling fluids remained inside of the drill cuttings were primarily linear alkanes (data provided by the supplier). The ROC value of 14.43 ± 0.29 wt% determined in the oil-contaminated drill cuttings agrees well with the result shown in Table B-1 (Appendix) from the standard Dean-Stark analysis (ASTM D95). The degree of variability in ROC is due to the heterogeneous nature of the drill cuttings instead of the accuracy of the ROC analysis [162]. It is evident that the amount of residue drilling oil of 14 wt% in the oil-contaminated drill cuttings is much higher than 1 wt% discharge limit. In order to reduce the ROC for safe disposal, an effective treatment method is required.

In this study, the oil-contaminated drill cuttings were cleaned using microemulsions ME-1 to ME-4 listed in Table 4-1. Cleaning tests with surfactant solution and water were also conducted for comparison. After purging of CO_2 for only 30 seconds and gentle centrifugation, rapid phase separation of the microemulsion (ME-4 was shown as an example) occurred as shown in Figure 4-8 (b). The dark residue oil was removed from oil-contaminated drill cuttings and concentrated in the oil phase, with the aqueous phase being sandwiched between the oil phased and sediments to prevent the recontamination of the clean cutting solids. For the washing of oil-contaminated drill cuttings with surfactant solutions, abundant of foam was generated and attached to the centrifugation tube, which could cause additional problems in the industrial operations. The residue oil cannot be removed from the oil-contaminated cuttings by water washing as shown in Figure 4-8 (b).

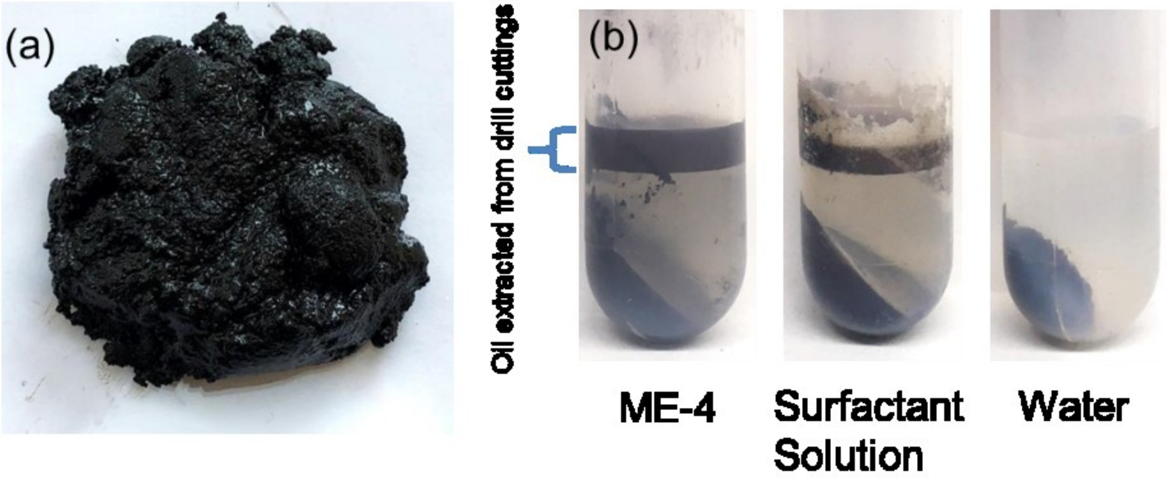

Figure 4-8 Photographs of (a) oil-contaminated drill cuttings before treatment; and (b) drill cuttings after washing with various fluids: left for ME-4 showing an oil layer on top of the phase-separated system with the solids settled to the bottom, middle for surfactant solutions showing limited degree of oil removal from the oil-contaminated drill cuttings and formation of foams, and right for water showing a negligible removal of oil from the oil-contaminated drill cuttings. The photos were taken after CO_2 was added at 200 mL/min and room temperature for 30 seconds for switching followed by gentle centrifugation at 1000 rpm for 15 minutes.

The solid sediments were carefully separated, rinsed by water, dried in an oven and analyzed by TGA. The quantitative results of ROC are shown in Figure 4-9. Without washing, the majority of the organic contaminants in the oil-contaminated drill cuttings were lost before 230°C, as shown in Figure 4-9 (a). The ROC of the original oil-contaminated drill cuttings was determined to be 14.43 wt%, as shown in Figure 4-9 (b). Washing of oil-contaminated drill cuttings with water showed a negligible removal of oil with the ROC remained at around 9 wt%, as anticipated. After washing with microemulsions, the mass loss curves became nearly flat with the ROC being decreased remarkably to < 3 wt%. Decreasing heptane content in the microemulsion to 5 wt% (ME-4) increased its capability of solubilizing oil from drill cuttings, resulting in an enhanced oil removal and a ROC value of 0.76 wt%, which is below the safe disposal limit. Although the surfactant solution has the best capability of solubilizing oil from oil-contaminated drill cuttings, the ROC reached only 1.83 wt% after washing of the drill cuttings with such solution, which was consistent with previous studies [80, 159, 163]. It is evident that the diffusion of microemulsion droplets of heptane play a critical role in the effective removal of oil from the oil-contaminated drill cuttings. These findings collectively suggest that the appropriate formulation of CO_2-responsive microemulsions could reduce the ROC to the safe discharge limit as excessive heptane content in the microemulsion as in the case of ME-1 and ME-2 could limit the overall capability of solubilizing the oil from the drill cuttings.

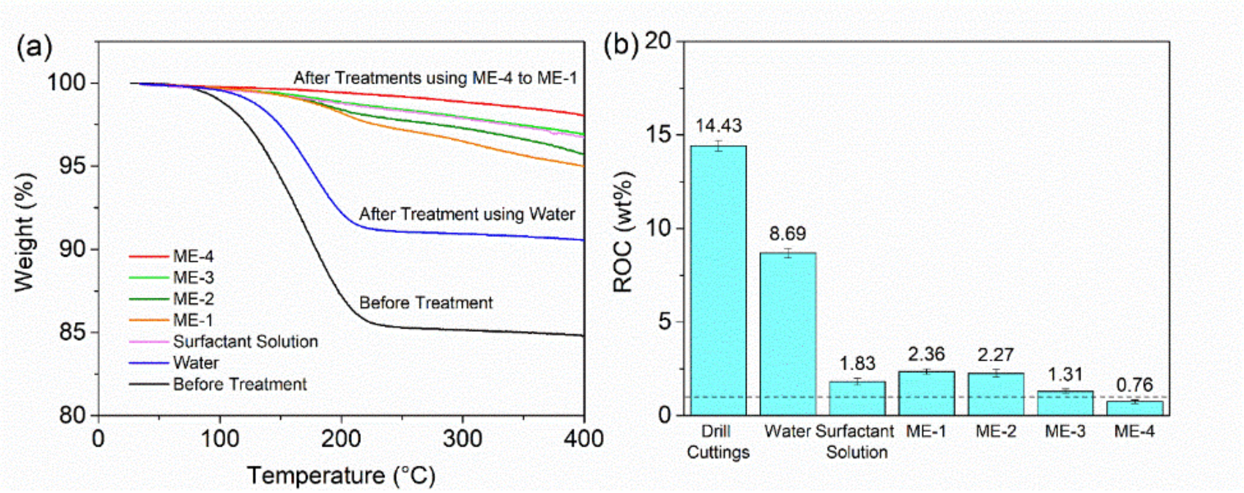

Figure 4-9 TGA results of the oil-contaminated drill cuttings before and after washing by water, surfactant solution and ME-1 to ME-4 microemulsions: (a) TGA profile illustrates the effective removal of the organic contaminants from the oil-contaminated drill cuttings using ME-4, as compared with washing using other microemulsions, surfactant solution and water; (b) Calculated ROC values before and after washing of oil-contaminated drill cuttings by water,

surfactant solution and ME-1 to ME-4 microemulsions. Error bars are calculated based on 3 tests at each treatment.

The oil remained inside the oil-contaminated drill cuttings before and after washing with ME-4 was further characterized by the TGA-GC-MS method. The results are compared in Figure 4-10 with that obtained using solids of a 0.40 wt% ROC after toluene reflux of the oil-contaminated drill cuttings at 220°C using a Dean-Stark apparatus (ASTM D95). Before washing, the original oil-contaminated drill cuttings contained liner alkanes from C13 to C22, which were consistent with the parameters provided by the supplier. After washing of the drill cuttings with ME-4 microemulsion, the ROC decreased significantly. In fact, this ROC value is similar to the results for cuttings after the toluene reflux at a high temperature for 2 hours. Only a small amount of propenamide was observed in the cutting solids after washing with ME-4 microemulsions, which was the thermal decomposition product of superamphiphiles from the microemulsion and contributed to a slightly higher ROC value. In summary, the washing using microemulsion at the ambient temperature could remove effectively the residue oil from the oil-contaminated drill cuttings to meet the stringent discharge requirement. Such superior cleaning efficiency of oil from the drill cutting wastes at ambient temperatures by microemulsion illustrates clearly the benefits of microemulsion technology in reducing energy cost and greenhouse gas emission, as a comparable ROC could only be achieved at a much higher energy intensity in the thermal decomposition method [19, 20, 30], by the supercritical carbon dioxide extraction [39-41] or the microwave treatment [36, 37].

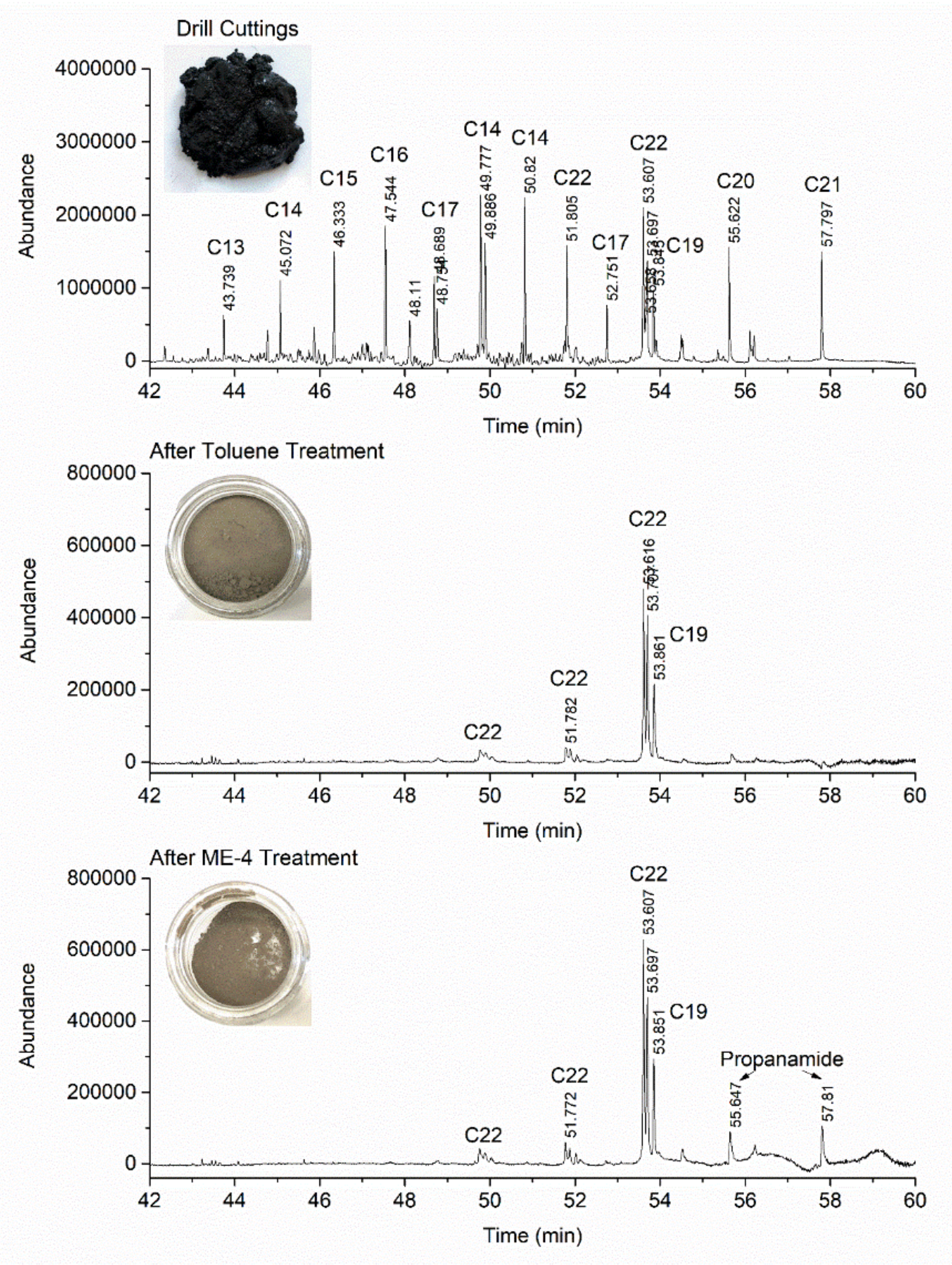

Figure 4-10 TGA-GC-MS results of oil in: (a) the original oil-contaminated drill cuttings showing the presence of linear alkanes, (b) the clean solids washed by toluene reflux at 200 °C

using a Dean-Stark distillation method (ASTM D95), and (c) the solids after washing using ME-4 microemulsion.

4.3.4 Mechanism of the O/W microemulsions in the oil-contaminated drill cuttings treatment

As shown in Figure 4-11, the proposed cleaning mechanism of the CO_2-responsive O/W microemulsion in the drill cuttings treatment can be classified into four stages: (1) contact, (2) solubilization, (3) detachment and (4) phase separation. The first three stages in the oil liberation process are based on the direct contact solubilization mechanism [80, 81, 164, 165]. In the contact stage, the microemulsified heptane droplets diffuse and adsorb onto the surface of the residue oil due to the affinity between the heptane droplets and the residue organic [165]. The nano-sized droplets can even diffuse into the porous structure of the drill cuttings and generate a deep cleaning of the contaminants [159, 160]. During the solubilization stage, the pre-dissolved heptane droplets in the microemulsion swell and dilute the residue oil in the drill cuttings, while the surfactant molecules reside at the interface between oil and water. The decreased W_c, W_a and the diluted oil mixture which has lower viscosity and better mobility enable a significantly reduced initial oil liberation time t_{EC20} compared to the control tests using surfactant solution or water. In the detachment stage, the oil-laden micelles desorb from the drill cuttings, diffuse back into the bulk until all the residue oil is extracted. By careful selection of the heptane content, the microemulsion ME-4 reveals a strong capability of solubilizing oil. In these stages, the superamphiphile actively acts as the main surfactant and reduces the interfacial tension to less than the critical interfacial tension [155], leading to a negative change in the Gibbs free energy ΔG. However, if no CO_2 was added and the final phase separation stage was skipped, the clean solids even after the ME-4 treatment was easily recontaminated by the microemulsified oil mixture or even the superamphiphile itself, resulting in a higher ROC around 2-3 wt% in our preliminary results. These results indicate the necessity to utilize the CO_2-responsive property of the microemulsion to enforce the oil to release out from the micelles during a complete phase separation process in the system.

Finally, in the phase separation stage when CO_2 is added, the superamphiphile in the microemulsion quickly dissociates into the water-soluble polyamine bicarbonate and the oil-soluble oleic acid [87, 155]. Due to the high interaction possibility between CO_2 and the superamphiphile at the large interface area of the O/W microemulsion, this response happens very fast within only 30 seconds. Therefore, the electrostatic interaction in the superamphiphile is eliminated, the interfacial tension is dramatically increased and ΔG becomes positive, resulting in a rapid response to the CO_2 purging and a complete phase separation. The oil accumulates at the top and can be efficiently collected. Moreover, the middle aqueous phase prevents the recontamination of the clean solids by the separated oil, which further enhances the cleaning effect. As a result, the ROC after ME-4 treatment is effectively reduced to less than 1 wt%, which meets the safe discharge requirement.

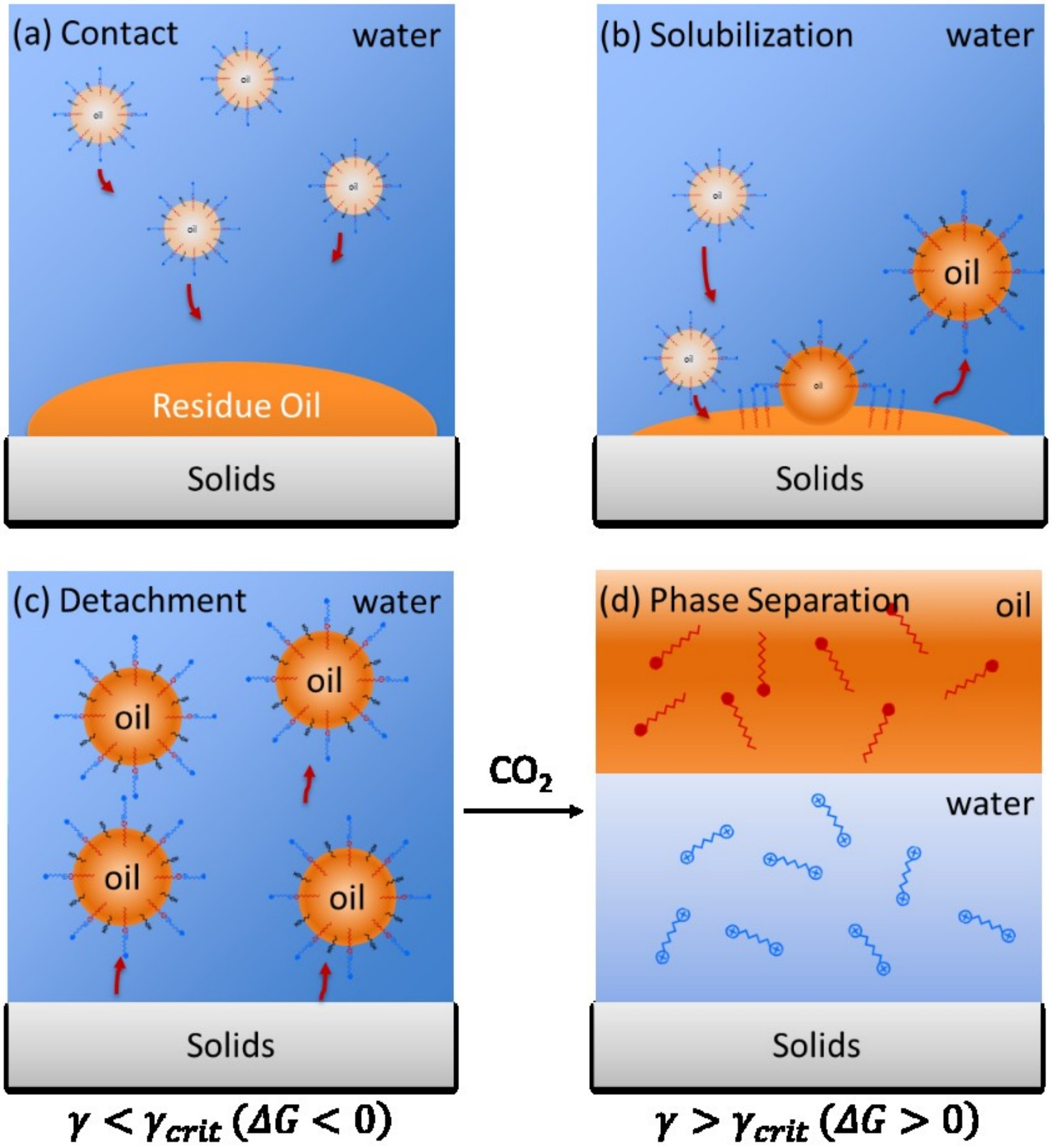

Figure 4-11 Schematic diagram illustrating the oil removal mechanism in the treatment of the oil-contaminated drill cuttings using CO_2-responsive O/W microemulsion.

4.4 Conclusions

A comprehensive treatment of oil-contaminated drill cuttings is demonstrated using a novel CO_2-responsive O/W microemulsion at ambient temperatures, which significantly reduce the ROC to below the 1 wt % environmental discharge limit for safe disposal. The residue oil can be extracted rapidly and completely from the oil-contaminated drill cuttings due to the ultra-low interfacial tension and the strong capability of oil solubilization in the O/W microemulsions. Treated by the CO_2 for only a few seconds, the microemulsion can be separated entirely into the immiscible oil and water phases as the superamphiphile responses rapidly and loses its interfacial activity. The extracted oil is concentrated immediately at the top while the aqueous phase further decreases the possibility of recontaminating the clean solids.

Compared with treatment methods reported earlier [11, 19, 20, 30, 31, 36, 37, 39-41, 49-52, 57, 58, 67], this innovative treatment process of the oil-contaminated drill cuttings using CO_2-responsive microemulsions is easy and safe to operate at ambient temperatures with inexpensive equipment, mild working conditions and low energy cost. Most importantly, it can successfully reduce the residual oil in the cuttings to the acceptable environmental level for safe disposal. Meanwhile, the switching behavior of the microemulsion allows the solubilized oil to be separated easily after the system responds to the CO_2 purging in a very short time, which eliminates the dosage of chemical demulsifiers. The unique nano-sized droplets, ultralow interfacial tension, strong capability of solubilizing oil, fast CO_2 response and complete phase conversion make this CO_2-responsive microemulsion process an energy-efficient and environmentally friendly candidate for the oil-contaminated drill cuttings treatment and possibly other applications such as wellbore cleaning, contaminated soil remediation and enhanced oil sands recovery.

4.5 References

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Chapter 5 Conclusions and recommendations for the future work

Chapter 5 summarizes the major findings on the theoretical study of the CO_2-responsive O/W microemulsions and its related application. The recommendations for the future work are also summarized here.

5.1 Conclusions

(1) The theoretical study of the CO_2-responsive O/W microemulsions

A novel O/W microemulsion was invented based on a CO_2-responsive superamphiphile which was a linear structure surfactant assembled by oleic acid and Jeffamine D-230 through the electrostatic interaction. Treated by the CO_2 for 20 seconds, the superamphiphile rapidly responded to the CO_2 purging and separated into the oil-soluble oleic acid and water-soluble polyamine bicarbonate, as such the electrostatic interaction of the superamphiphile was interrupted. At the same time, the interfacial tension was changed remarkably from the ultralow level (less than γ_{crit}, 2.87×10^{-2} $mN\cdot m^{-1}$) to ~5 $mN\cdot m^{-1}$, and the Gibbs free energy ΔG became positive. As a result, the microemulsion was separated entirely into the top oil phase and bottom water phase. Alternatively, after removing of the CO_2 by purging of N_2 at 60 ºC for 10 minutes, the electrostatic interaction in the superamphiphile was rapidly reconstructed, which effectively reduced the interfacial tension to be less than γ_{crit}, and hence regenerated the transparent O/W microemulsion with the negative ΔG. After two switching cycles, the droplet size was still around 10 nm with a narrow size distribution.

The results provide an in-depth understanding of the electrostatic interaction, the molecular state distribution and the thermodynamic changes during the switching processes of the CO_2-

responsive microemulsions. Different from the switchable emulsions/microemulsions reported earlier, this O/W microemulsion can be conveniently prepared with low-cost, commercially available surfactants. Most importantly, it switches very rapidly when responses to the trigger gases (CO_2 and N_2). Such switchable O/W microemulsions of rapid CO_2-responsiveness, complete phase separation, ultralow interfacial tension and nano-sized droplets can have many potential research and industry applications, such as drill cuttings treatment, enhanced oil recovery and nanoparticles preparation.

(2) The application of the CO_2-responsive O/W microemulsions in the treatment of the oil-contaminated drill cuttings

The novel CO_2-responsive O/W microemulsion was used to treat the oil-contaminated drill cuttings effectively at the room temperature, in order to reduce the residue oil level (ROC) in the cuttings to less than the 1 wt % environmental discharge limit. Due to the strong capability of solubilizing oil of the O/W microemulsions, the residue oil could be extracted rapidly from the oil-contaminated drill cuttings. Treated by the CO_2 at the room temperature for only a few seconds, the extracted oil was concentrated immediately in the top oil phase for recycling, while the formed water phase prevented the recontamination of the clean solids. By careful selection of the heptane content in the microemulsions, the ROC was decreased to 0.76 wt%, which successfully met the safe disposal limit, as confirmed by the TGA-GC-MS and the liberation kinetics results.

Compared with current treatment methods, this innovative rapid treatment of oil-contaminated drill cuttings using CO_2-responsive microemulsions is easy and safe to operate with inexpensive equipment, mild working conditions and a low energy cost. Most importantly, it can successfully reduce the ROC to the acceptable environmental level for safe disposal. After the system responds to the CO_2 purging in a very short time, the solubilized residue oil can be separated easily due to the switching behavior of the microemulsions, which prevents the usage of the chemical demulsifiers. In summary, this CO_2-responsive microemulsion treatment process has unique properties such as the ultralow interfacial tension, prominent capability of solubilizing oil and complete phase conversion, which makes it a cost-efficient and environmentally friendly candidate for the oil-contaminated drill cuttings treatment. It can also be developed to fit other applications such as wellbore cleaning, enhanced oil sands recovery and contaminated soil remediation.

5.2 Recommendations for the future work

Some future work can focus on the points which have been listed below, in order to optimize the switching properties of the CO_2-responsive microemulsions and further decrease the ROC for better treatment performance.

(1) CO_2-responsive O/W microemulsion formula development

Hypothesis 1: Using natural/industrial components could create superamphiphiles and hence microemulsions of desired switching pH. However, the impurity in the natural product may interfere the formation of the superamphiphiles and/or interfacial activity of synthesized superamphiphile, which needs further investigation.

Future work: Design new superamphiphiles using natural/industrial components. Screen the combinations based on the pKa and HLB values; Use longer chain fatty acids in the superamphiphiles to see the effect of switching speed, switching pH and CO_2 dosage, etc.

Future research significance: In Chapter 3, a fast responsive and relatively low surfactant consumption O/W microemulsion was designed based on a CO_2-responsive superamphiphile assembled by oleic acid and Jeffamine D-230. However, total surfactant dosage including the superamphiphile and co-surfactant (butanol) is still high at 20 wt%. It is of great interest to further decrease the total surfactant dosage in the microemulsion system, by careful design of new CO_2-responsive superamphiphile with a different acid and amine combination. However, it should be noted that with low surfactant dosage, the capability of solubilizing oil may decrease, which could probably decrease the overall cleaning performance. As a result, it is necessary to find a balance in the system to consume less total surfactants but maintain or improve cleaning capability.

Hypothesis 2: The switching pH zone is depended on the pKa values of the acid and amine of the superamphiphile. By careful selection of the constituents of superamphiphiles, the switching pH can be changed accordingly.

Future work: Investigate acid and amine of different pKa values to prepare the superamphiphiles; Study the switching pH and speed of the microemulsions.

Future research significance: The modification of the switching pH by changing the acid and amine of the superamphiphile constituents will benefit for different practical applications. It will also provide a deep understanding of the electrostatic interaction and assist to better design the new superamphiphiles.

(2) Recycle of aqueous phase to regenerate microemulsion.

Hypothesis: The aqueous phase after the phase separation in the drill cuttings treatment can be recycled back to regenerate microemulsions with remaining Jaffamine D-230 after addition of oleic acid and heptane and purging of N2.

Future work: Try recycle tests with the aqueous phase after the drill cuttings treatment. Regenerate the microemulsion by adding the missing oleic acid and heptane; Purging the N2 at 60 ºC for 10 minutes to adjust the pH; Measure the impurity concentration in the recycled microemulsion to see the effect of the impurity ions.

Future research significance: In the practical aspect, the overall treatment cost will be significantly reduced if the aqueous phase and the Jeffamine D-230 can be recycled to reproduce the CO2-responsive microemulsion.

(3) Optimize the ratio of microemulsion/drill cuttings to achieve the best removal efficiency.

Hypothesis: Increasing the ratio of microemulsion/cuttings will increase residue oil removal efficiency until the optimized efficiency is reached. However, once the optimized efficiency is obtained, further increasing the ratio of microemulsion/cuttings will no longer reduce the ROC.

Future work: Investigate the residue oil removal efficiency using various ratios of microemulsion/cuttings from 1:1 to 10:1 to investigate the optimized ratio to reach the best removal efficiency.

Future research significance: Exploring the ratio of microemulsion/cuttings will greatly help to optimize the entire treatment process while use minimal microemulsion to reach the maximal removal efficiency. It will also help to calculate the final treatment cost by choosing the best microemulsion/drill cuttings ratio.

(4) Development of oil sands extraction or other treatment process using the CO_2-responsive O/W microemulsion

Hypothesis: The oil composition will affect the extraction of the oil. The pre-dissolved oil droplets should have a good capability to swell and penetrate the residue oil of the target. Replace the heptane with naphtha in the microemulsion will greatly benefit the extraction of the bitumen from the oil sands.

Future work: Naphtha is a good solvent for bitumen, which has been widely used in the naphthenic froth treatment and dilution of bitumen in pipeline transportation. Replace the heptane with naphtha in the microemulsion is hypothesized to greatly benefit the extraction of the bitumen from the oil sands. It is also strongly suggested that to make a new microemulsion phase diagram to find the appropriate oil content of the microemulsion, which will give a relatively large room to solubilize more residue oil.

Future research significance: Utilizing unique properties of the CO_2-responsive microemulsion such as ultralow interfacial tension, the prominent capability of solubilizing oil, rapid CO_2 response and complete phase conversion, it is also possible to develop an oil sands extraction process using the modified CO_2-responsive O/W microemulsion. Once the bitumen is solubilized into the microemulsion, the overall viscosity can be decreased by several orders of magnitudes, which will also be beneficial to pipeline transportation with less solvent diluent consumption.

(5) Molecular dynamics simulation of the oil-contaminated drill cuttings treatment process

Hypothesis: The van der waals force can be reduced when the heptane droplets swell and dilute the residue oil during the microemulsion treatment.

Future work: Employ the molecular simulation to visualize the residue oil liberation process. Study the van der waals force change during the entire process to better understand the effect of using microemulsion to treat oil-contaminated substrates.

Future research significance: It is desired to know the molecular behavior and visualize these four stages using the molecular dynamics simulation, which can provide a systematic comparison between microemulsions with different heptane concentrations or even different microemulsion design. Precise molecular dynamics simulation combined with experimental data are recommended for future work.

(6) Test the CO_2-responsive microemulsion as fracturing fluid candidate.

Hypothesis: The CO_2-responsive microemulsion can be used as a fracturing fluid due to its ability to solubilize oil with low viscosity fluid.

Future work: Investigate the viscosity of the CO_2-responsive microemulsion at different compositions and pH conditions. Test its switching property in the fracturing process.

Future research significance: During the preparation of the phase diagram, it is noticed that the viscosity of the CO_2-responsive microemulsion changed dramatically. It is possible to utilize this property to confirm the right composition of the CO_2-responsive microemulsion with appropriate viscosity and CO_2-switchable property for the purpose of being used as a novel fracturing fluid.

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Appendix A

Additional figures for Chapter 3

1. Enlarged FTIR spectra of chemicals in the microemulsion system

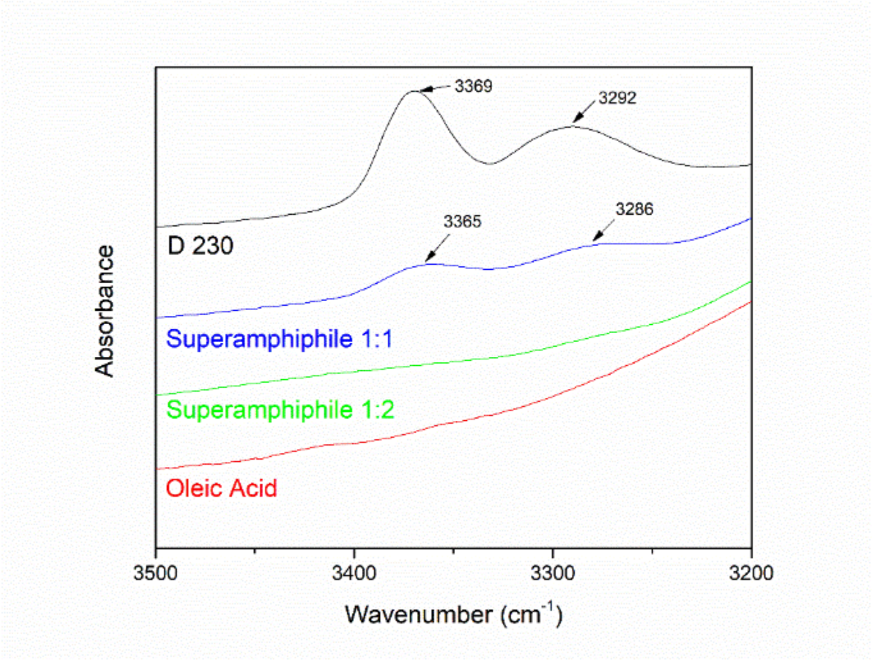

Figure A - 1 Enlarged FTIR spectra of Jeffamine D-230, oleic acid, and superamphiphiles prepared by mixing D-230 and oleic acid at molar ratios of 1:1 and 1:2.

2. Lamellar aggregates in the aqueous phase after the phase separation

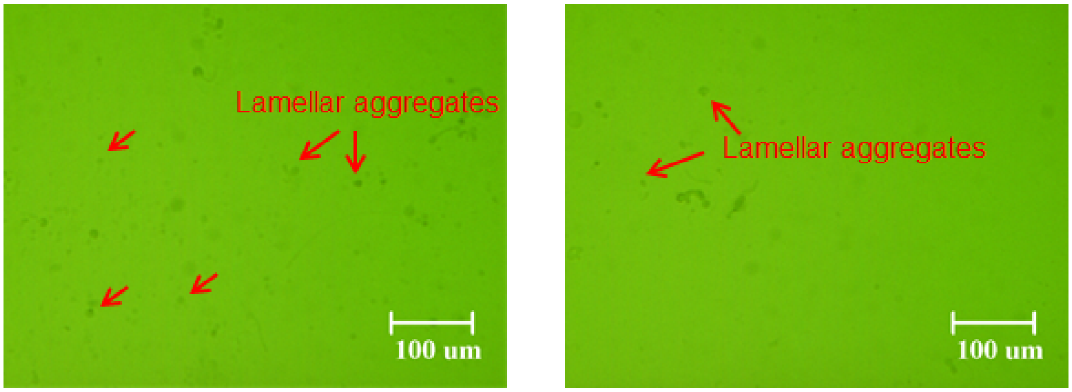

Figure A - 2 Micrographs of the lamellar aggregates in the aqueous phase after CO_2 purging.

3. Correlation functions and data fittings during the size determination using the dynamic light scattering

The corresponding fitting plot is shown below. A proper fitting is still kept after switching twice:

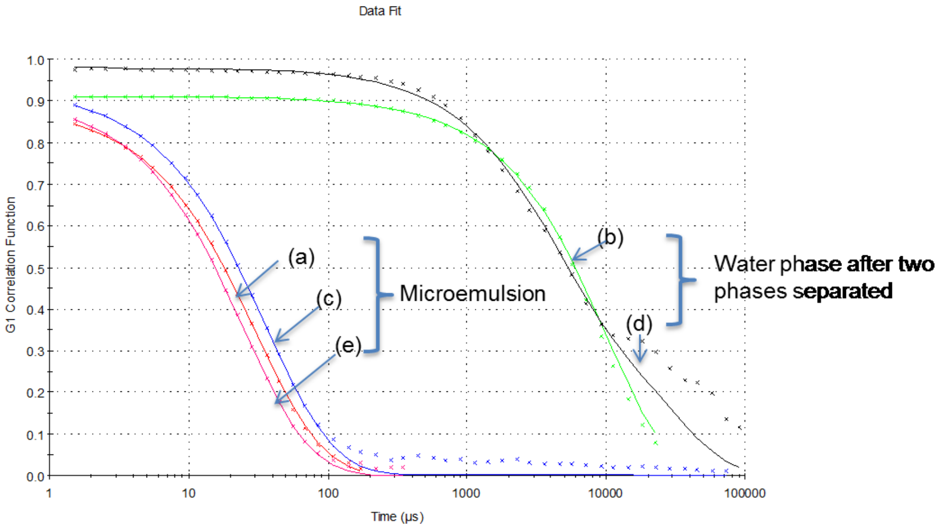

Figure A - 3 Correlation function for oil droplet size in a) the original O/W microemulsion; (b) water phase after first phase separation by CO_2 purging; (c) O/W microemulsion after switching by removing of CO_2 with N_2 purging; (d) water phase after CO_2 purging in the second switching cycle; (e) O/W microemulsion after switching by removing of CO_2 with N_2 purging in the second switching cycle.

4. The stability of the superamphiphile at the elevated temperatures

The superamphiphile used in our work is assembled through electrostatic interactions between the positively charged amine group of D-230 and the negatively charged carboxylate group of oleic acid. Such interactions are relatively weak compared with covalent bonds and therefore could be easily dissociated at elevated temperatures. When the microemulsion was heated to 80 ºC, the molecular association via electrostatic interaction in the superamphiphile could not be maintained, leading to the loss of surface activity of the superamphiphile molecules and hence the phase separation of the microemulsion. Heating continuously at 80 ºC will cause the evaporation of the heptane and butanol, even though the beaker was sealed at our best. The mass loss of the oil phase would shift the composition of the system out of the microemulsion region in the pseudoternary phase diagram. As a result, the microemulsion became normal emulsion after cooled down to room temperature. For practical consideration, 60 ºC was selected to purge N_2 in the re-microemulsification process.

Figure A - 4 Photograph of phase separation after heating at 80 ºC for 1 minute.

5. The dynamic interfacial tension between the heptane and the CO_2 treated aqueous surfactant solutions

The dynamic interfacial tension of heptane and CO_2 treated aqueous surfactant solutions was measured by the Theta Optical Tensiometer (T200 Biolin Scientific) using the pendant drop method. Similar to the spinning drop tensiometer method, the superamphiphile and butanol were premixed at 1:1 mass ratio, then diluted by Milli-Q water to different concentrations. CO_2 was purged into the surfactant solutions at 200 mL/min for 3 minutes to interact completely with the superamphiphile. A drop of a surfactant solution (1.5-3.0 μL) was created at the tip of a needle which was immersed into the cuvette filled with heptane. The shapes of the drop were recorded by a high-speed camera and analyzed by the Laplace equation to obtain the interfacial tension. All the measurements were carried at the room temperature.

As the surfactant concentration increased from 2.5 wt% to 20 wt%, the interfacial tension between heptane and CO_2 treated surfactant solutions decreased from 15.2 $mN\cdot m^{-1}$ to 5.3 $mN\cdot m^{-1}$ due to the surface activity of D230 [87]. However, they are much higher compared to the spinning drop tensiometer results without CO_2 purging. The dramatic interfacial change after the CO_2 purging indicates the separation of the amine and acid parts of the superamphiphile. As the interfacial tension is no longer in the ultralow region, the microemulsions cannot maintain the optimized curvature of the nano-sized droplet, and switches into water and oil phases.

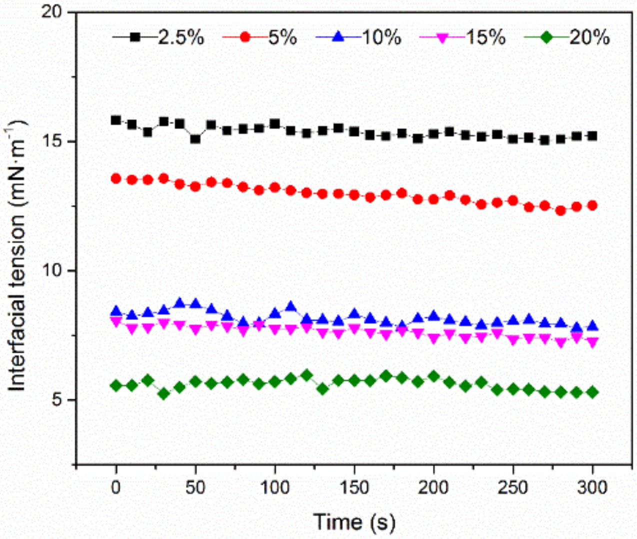

Figure A - 5 Dynamic interfacial tension of heptane and CO_2 treated aqueous surfactant solutions at different concentrations. The surfactant used in this figure was a mixture of superamphiphile and butanol at 1:1 mass ratio.

6. The species distribution of the D-230 and its related protonated products at the different solution pH

According to the ChemAxon pK_a calculation, the $pK_{a,1}$ and $pK_{a,2}$ of the D-230 are 9.4 and 10.0. The species distribution of the D-230 and its related protonated products is shown below. (Please note this is the ideal condition which does not consider the pK_a shift due to the existence of other components in the microemulsion.) When the pH = 9.98 at the original state, more than 65% of D-230 were protonated. When the CO_2 was purged into the system continuously, the pH value decreased gradually and the double protonated D-230 (D-230^{2+}) increased at the same time. At the pH of 8.4, more than 95% of the D-230 were protonated into the D-230^{2+}, which had a very high solubility in water. The microemulsion was destroyed rapidly and switched into two layers as described in section 3.3.3. This also explains the CO_2 responsive behavior of our microemulsion system in the view of the molecular state distributions.

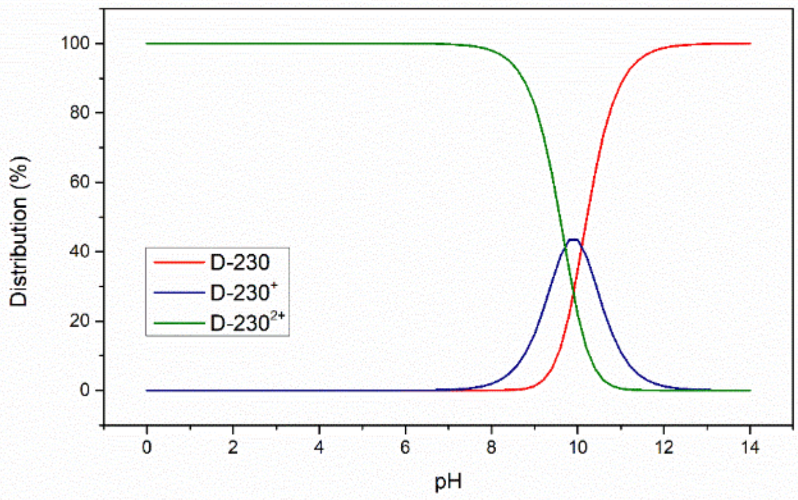

Figure A - 6 Species distribution of D-230 as a function of solution pH.

Reference

[87] P. Xu, Z. Wang, Z. Xu, J. Hao, D. Sun, Highly Effective Emulsification/Demulsification with a Co2-Switchable Superamphiphile, Journal of Colloid and Interface Science 480 (2016) 198-204.

Appendix B

Additional figures for Chapter 4

1. ROC determination method using TGA.

The detailed ROC determination using Weatherford oil-contaminated drill cuttings as an example is shown in Figure B - 1. TGA was used to measure the oil separated from drill cuttings, the original drill cuttings and the drill cuttings after toluene treatment, as described in Section 2.5. To better understand and determine the temperature at which the residue oil evaporates, the residue oil was manually collected from one bottle with an excess amount of drilling oil remaining in the cuttings, filtered by a 0.45 μm Nylon syringe filter, then placed into the Al_2O_3 crucible with a lid and sent for TGA analysis. The TGA result showed this kind of drilling oil has 99.70 wt% loss at 230 °C. To obtain the clean solids, the drill cuttings were washed in the toluene by Dean-Stark standard method (ASTM D95) at a distillation temperature of 220 °C for 2 hours and characterized as 0.4 wt% loss at 230 °C using TGA. To compare with, the drill cutting without any pre-treatment was analyzed by TGA. The TGA showed 14.7 wt% loss at 230 °C, which is consistent with the data obtained by the ASTM D95 method, as shown in Table B - 1.

As showed in Figure B - 1, it can be seen that the majority of the organic content in the drill cuttings evaporated before 230 °C. After 230 °C, the weight loss can be contributed to the solid decomposition at the high temperature. As a result, the ROC of Weatherford drill cuttings before the treatment was determined as the weight loss percentage at 230 °C (14.7 wt%). Moreover, 230

°C was also selected as the cut-off line to determine the ROC of Weatherford drill cuttings after different treatments.

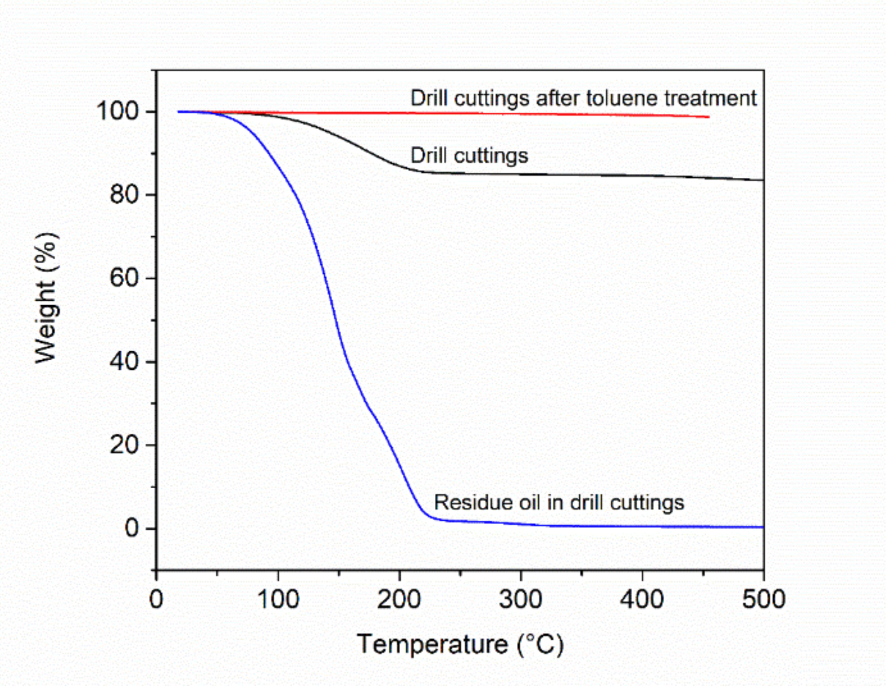

Figure B - 1 TGA analysis of the oil-contaminated drill cuttings without any pre-treatment, the separated residue oil and the cutting solids collected after the toluene distillation treatment method.

2. Determination of the residue oil level in the untreated oil-contaminated drill cuttings by Dean-Stark standard method (ASTM D95)

The residue oil level in the untreated oil-contaminated drill cuttings was also determined by ASTM D95 method, and the result is consistent with our ROC determination method using TGA, as shown in Table B - 1. In order to avoid any confusion, the ROC determinations in our work were all based on TGA as procedure and analysis described in Section 2.5 and supplementary part 1, as it was fast, convenient and accurate. Moreover, the clean cuttings solids after the ASTM D95 method were used to compare with the results after the microemulsion treatments in Section 3.2, which showed that the microemulsion treatment could reach similar ROC as desired with less energy and solvent consumption.

Table B - 1 The residue oil level in the untreated oil-contaminated drill cuttings by ASTM D95 method and the densities of the residue drilling fluids

Sample	Oil (wt %)	Oil Density (g/cm^3)
Weatherford oil-contaminated drill cuttings	14.15±0.30	0.8682

3. Correlation functions and size distributions for oil droplet size of microemulsions from ME-1 to ME-4 before CO_2 purging

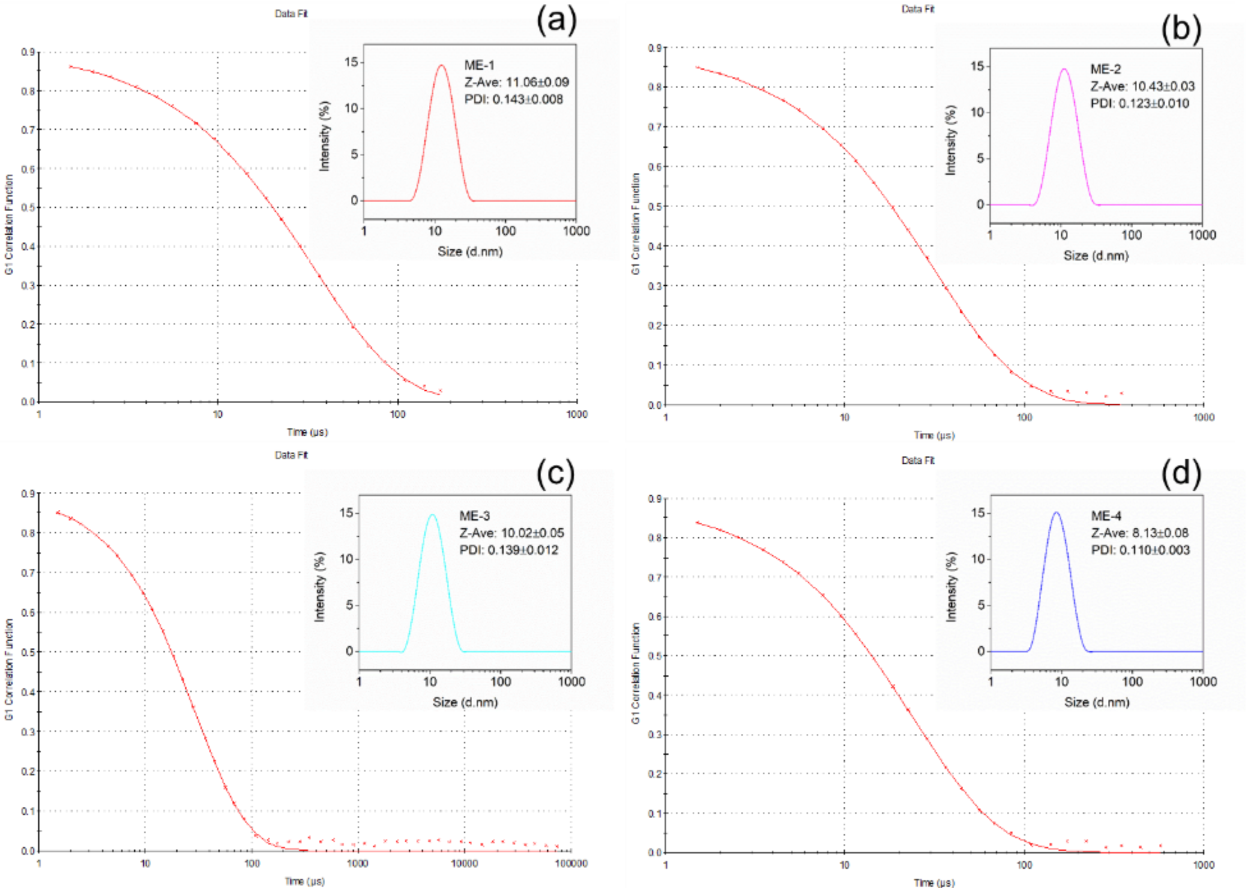

Figure B - 2 Correlation functions and size distributions for oil droplet size in a) ME-1 (20 wt% heptane); (b) ME-2 (15 wt% heptane); (c) ME-3 (10 wt% heptane) and (d) ME-4 (5 wt% heptane). Only one of each three tests is listed for clarity.

4. Boundary vanish between the residue oil and the microemulsions in the spinning drop tensiometer testing tube

During the interfacial tension measurement using the spinning drop tensiometer, the boundary between the residue oil and microemulsions disappeared gradually as the test time increased, especially more evident in microemulsions with higher heptane content. Figure B - 3 showed an example of the fast boundary disappearance between the residue oil (shown as the middle drop) and the ME-1 which had 20 wt% heptane. It can be seen that the dark oil phase quickly fractured into small sections due to the small work of cohesion (W_c) caused by the ultralow interfacial tension. The boundary gradually disappeared and the dark color became lighter as the oil drop was microemulsified into the bulk. No more than 12 minutes, the oil phase disappeared in the spinning tube. These images roughly visualized the oil fragmentation and the microemulsification (solubilization) process in our designed O/W microemulsions, strongly indicated that the ultralow interfacial tension and the strong capability of solubilizing oil could significantly help the residue oil extraction.

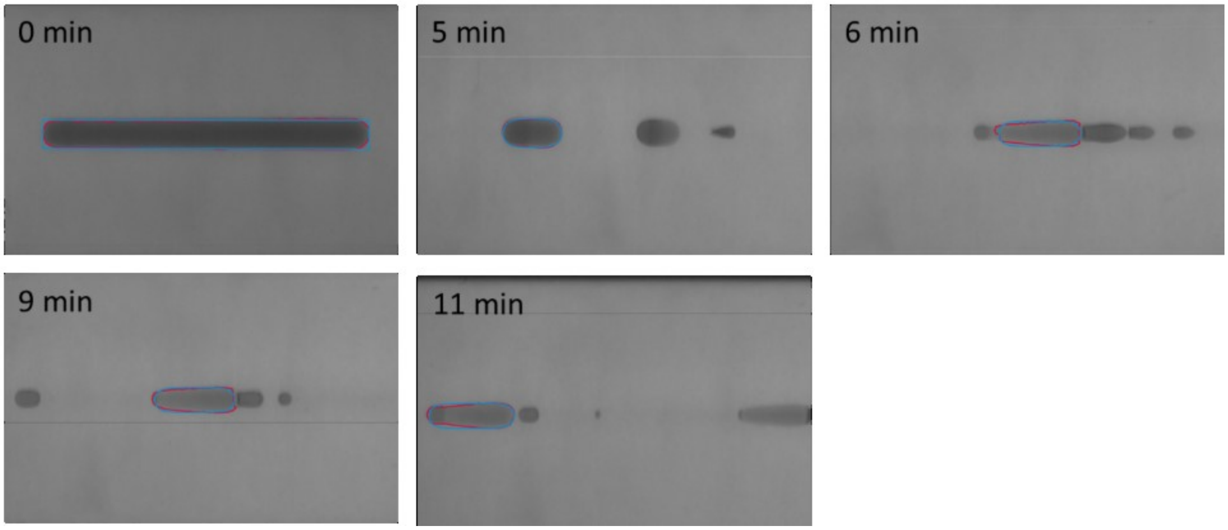

Figure B - 3 Images of residue oil drop in ME-1 at different time during the test using spinning drop tensiometer.

5. Data fittings in oil liberation

Table B - 2 Fitting parameters of logistic function for oil liberation kinetics, and t_{EC20}, t_{EC50} and t_{EC100} for oil-contaminated drill cuttings treatments at the room temperature

Formulation		Fitting Parameter					Result		
		R^2	A_1	A_2	t_0	p	t_{EC20}	t_{EC50}	t_{EC80}
Microemulsions	ME-1 (20 wt% Heptane)	0.9898	-0.3964	77.9085	27.7041	0.7455	4.31	27.70	177.89
	ME-2 (15 wt% Heptane)	0.9964	-1.7179	89.5779	27.5724	0.8550	5.45	27.57	139.51
	ME-3 (10 wt% Heptane)	0.9978	3.2627	94.3275	69.6301	1.2658	23.29	69.63	208.18
	ME-4 (5 wt% Heptane)	0.9998	1.3820	99.3152	50.3721	2.1776	26.65	50.37	95.21
Control Test	Surfactant Solution (0 wt% Heptane)	0.9998	0.1295	94.0897	173.5650	3.8451	121.03	173.57	248.91
	Water	0.9908	0.4839	25.0179	398.0141	2.0862	204.79	398.01	773.56

Appendix C

Standard Operating Procedure in the preparation of CO_2-responsive microemulsions and the treatment of oil-contaminated drill cuttings

1. Preparation of CO_2-responsive microemulsions

The CO_2-responsive microemulsions were prepared based on a pivotal CO_2-responsive superamphiphile, which was a linear structure surfactant assembled by oleic acid and Jeffamine D-230 through electrostatic interaction at a mole ratio of 1:1. After mixing of heptane, superamphiphile, butanol (co-surfactant) and deionized water at the appropriate concentrations (Table C - 1), the CO_2-responsive microemulsions were formed spontaneously and used as the washing media in this work. A surfactant solution was prepared without any heptane and used as a control test. Treated by the CO_2 at 200 mL/min rate for 30 seconds, the microemulsions were separated completely into the immiscible oil and water phases, as the superamphiphile rapid responded and lost its special interfacial activity. The detailed preparations, characterizations and switching mechanism were described in our previous work [155].

Table C - 1 Compositions of washing media

Formulation	Heptane (wt%)	Superamphiphile (wt%)	Butanol (wt%)	Water (wt%)
ME-1	20	10	10	60
ME-2	15	10	10	65
ME-3	10	10	10	70
ME-4	5	10	10	75
Surfactant Solution*	0	10	10	80

*Note: Surfactant solution was used as a control washing medium for comparison.

2. Treatment process of oil-contaminated drill cuttings

In order to develop an energy saving process to reduce ROC in the oil-contaminated drill cuttings, all the treatment tests were conducted at the room temperature. Approximately 2.0 g of the oil-contaminated drill cuttings, 10.0 g of each washing medium listed in Table C - 1 or water were placed into a 30 mL glass jar with a stirring bar. The jars were capped with polypropylene lids, placed onto magnetic stirrers and mixed at 500 rpm for 30 minutes. Then the dry CO_2 gas was purged into the glass jar at a rate of 200 mL/min for 30 seconds. After the gas purging, each mixture was transferred into a centrifuge tube and centrifuged at 1000 rpm for 15 minutes, where a top dark oil layer, a middle clear water layer and bottom solids were obtained except water treatment process. The oil and water phases were decanted into a 20 mL glass vial, and another 10.0 g of deionized water was added into the centrifuge tube to rinse the solids. After shaken by hand for 10 seconds, each tube was centrifuged at 1000 rpm for another 15 minutes in order to settle the solids. The rinse water was decanted into the second 20 mL vial, and the solids were transferred onto a Petri dish and heated in the oven at 102°C for 30 minutes to evaporate the water before the ROC determination.

3. ROC determination method

Thermogravimetric analysis (TGA, TG 209 F1 Libra®, NETZSCH) was used to determine the ROC after the washing treatment. All the thermal characterizations were carried under the nitrogen protection atmosphere with a flow rate of 25 mL/min. The heating range was set from the room temperature to 500 °C with a ramping rate of 10 °C/min. ROC was determined based on the weight loss percentage at the temperature where the drilling fluids (or hexadecane for artificially contaminated sands) all evaporated. A detailed ROC determination and analysis is shown in Figure B - 1.

To further identify the organic residue on the solids before and after the treatments, the same TGA was coupled simultaneously to the Agilent 7890A gas chromatograph (GC) and the Agilent 5975C inert mass selective detector (MSD). ~10 mg of solids was placed into the Al_2O_3 crucible, then heated inside of the TGA from the room temperature to 900 °C with the ramping rate of 10 °C/min under the nitrogen atmosphere. All the degradation gas products were stored inside of a cryotrap which was set at -35 °C using liquid CO_2. Then the cryotrap was quickly heated to 300 °C at 400 °C/min to transfer the trapped products to the GC column, where the column temperature was set at 300 °C. The electron ionization energy of 70 eV was selected and used in MS.

Reference

[155] X. Chen, X. Ma, C. Yan, D. Sun, T. Yeung, Z. Xu, Co2-Responsive O/W Microemulsions Prepared Using a Switchable Superamphiphile Assembled by Electrostatic Interactions, Journal of Colloid and Interface Science 534 (2019) 595-604.