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Microemulsions as Flowback Aids for Enhanced Oil and Gas Recovery after Fracturing, Myth or Reality: A Turnkey Study to Determine the Features and Benefits

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Abstract

Flowback aids have been long reported in the literature as being beneficial to enhance clean-up after stimulation treatments, and in particular hydraulic fracturing. The goal is for the flowback aids to allow the piston like flowback and return of fluids from the reservoir resulting in minimal losses to the formation and no memory effect that hampers back production. Microemulsions have also been reported in the literature and a review (including patent landscape) creates somewhat of a myth around their exact mechanism of performance and benefit to the application.

The present work was concerned with the development of flowback aids based on micro-/nano-emulsion technology for enhanced gas and oil recovery after fracturing application. The goal was to formulate microemulsion concentrates which form nanoemulsions when diluted into fracturing fluids and provide strong surface and interfacial tension reduction to minimize reservoir damage.

Microemulsions have been formulated with various possible surfactants and oil systems. The performance of the different formulations has been evaluated with different test methods, adopted from literature and industry best practice in order to screen for most promising microemulsion systems and compared to their aqueous equivalents to determine the performance benefits offered by emulsified packages. High throughput experimentation and robotic formulation was utilized to screen several thousand formulations from nearly 50 different surfactant packages. This allowed for incredible synergistic properties to be discovered very quickly and efficiently. The development of a new class of microemulsion package that is made up of almost 100% renewable and environmentally friendly components has made a large step change towards the state of the art of this class of flowback aids.

Regain permeability and core flow testing was performed on the best performing microemulsion formulations to determine the effect of field application. The result of this work was that microemulsions do offer some benefits over individual surfactants, not so much in surface tension modification but very much on the non-emulsification of crude oil and water and multiphase flow in porous media – so often seen as the primary damage mechanism in oil well fracturing.

Introduction

Hydraulic fracturing is a technique used to stimulate the production of an oil or gas well. Since Stanolind Oil & Gas Company introduced hydraulic fracturing in 1949 (Clark, 1949), more than 2.5 million fracture treatments have been performed worldwide. Some believe that approximately 60% of all wells drilled today are fractured even before primary production begins. Fracture stimulation not only increases the production rate, but it is credited with adding to reserves which otherwise would have been uneconomical to develop. In addition, through accelerating production, net present value of reserves has increased. Horizontal drilling and hydraulic fracturing have been essential keys in economically producing oil and gas from unconventional resources such as shale gas, shale oil and coal bed methane.

Today, a hydraulic fracturing job often comprises multiple stages including injecting a pre-pad, a pad, a proppant containing frac fluid and finally a treatment with flush fluids. In a typical frac jobs, 2 to 10 million gallons of water is injected downhole in the form of frac fluids. Various chemicals present in frac fluids including: viscosifier, cross-linker, friction reducer, surfactants, scale inhibitors, clay control additives, H_2S scavengers, biocides and corrosion inhibitors, each playing a vital role in success of a frac job. A fractured well does reach its maximum production potential until the frac fluids are completely removed and displaced by formation fluids. Some of this water is lost in the formation, but 25 to 70% of it returns to surface within 1 to 3 months. A challenge in hydraulic fracturing, especially for tight formations, is associated with remediation of formation damage caused by frac fluid invasion into the porous media of the reservoir and formation of oil/water emulsions.

Modification of surface and interfacial properties are keys to a successful remediation of formation damage, enhancing permeability to oil and gas and recovering fluids imbibed into the formation and trapped in propped fractures. Surfactants were introduced early to hydraulic fracturing (Graham *et al*., 1959) to deliver above properties, and extended their application into stimulation by acidizing (Poetket *et al*., 1961). In 1968, Gogarty and Tosch (1968) from Marathon Oil Company introduced a new recovery process for producing oil under both secondary and tertiary conditions that utilizes the unique properties of micellar solutions known as microemulsions. Laboratory and field flooding data proved that the process was technically feasible and that surfactant losses by adsorption on porous media were small. In a paper published by Bae *et al.* in 1974, authors challenged the oil- and water-external microemulsions versus aqueous surfactant systems comprising petroleum sulfonates and co-surfactant. They found that the oil-external microemulsion exhibits both higher retention on reservoir and higher oil-water interfacial tension that other two systems. The oil-external system, however, showed a better tolerance for brine and divalent ions. It was concluded that the aqueous solution would be better choice among the systems tested of surfactant formulations.

During the past decade microemulsions have gained more interests in hydraulic fracturing (e.g. Pursley and Penny, 2004; Paktinat *et al*., 2005). It has been demonstrated that wells treated with fluids containing microemulsion flow back aid additives were more productive than well treated with traditional surfactants. Several commercial microemulsion flow back aids have been introduced to the market, which were defined as complex formulations consisting of surfactant, co-surfactant, mixture of solvents and water. Enhancing the penetration and cleanup of water based frac fluids and allowing higher fluid return and hydrocarbon production are among common attributes to such additives. Even after years of implementation, a fundamental question remains to be answered: is there really a significant advantage for using microemulsion versus aqueous surfactant systems? This paper is an attempt to address some key aspects in evaluating microemulsion formulations and presents a new class of microemulsion package that is made up of almost 100% renewable and environmentally friendly components. The work has made a large step change towards the state of the art of this class of flowback aids.

With development of horizontal drilling and hydraulic fracturing in recent years, there are growing concerns to potential environmental risk for water pollution by frac chemicals. Among pathways for water contamination by hydraulic fracturing, wastewater disposal has been proven to be several orders of magnitude higher risk that the other four pathways. Pressure pumping companies together with chemical specialty companies have taken initiatives to address these concerns by utilizing more environmentally acceptable alternatives in frac fluids. Reducing toxicity and increasing biodegradability to lessen ground water contamination risk are essential in developing new chemical additives for hydraulic fracturing.

Another industry challenge is dealing with use of brine water, produced water and frac flow back water with high salinity (TDS of 200,000 ppm or above) instead of fresh water for frac fluids. There are a number of chemical additives including surfactants that suffer from salinity higher than 50,000 ppm. Multivalent cations such as calcium, magnesium, barium and iron present in flow back water offer even more challenges for traditional chemistries and products. When facing higher downhole temperatures (above 120 °C or 250 °F), a number of common products fail to function. Diversity of reservoir hydrocarbon fluids gives another dimension to the complexity of the above challenges.

Microemulsions

Microemulsions are unique dispersions of oil in water or water in oil, stabilized by a surfactant and co-surfactant. The formation of such a mixture was first reported by Hoar and Schulman in the 1940s when they noticed a mixture of hydrocarbon and surfactant turned milky to clear on the addition of alcohol (Hoar and Schulman, 1943). Schulman and his colleagues introduced the term “microemulsion” in 1959 (Schulman *et al*., 1959)**.** The ability of microemulsions to simultaneously solubilize either aqueous or organic components while remaining isotropically clear and thermodynamically stable attracted much attention, particularly in the 1970s for use in enhanced oil recovery. Microemulsion can be described as system containing water, oil and amphiphile which is a single optically isotropic and thermodynamically stable liquid solution (Danielsson and Lindman, 1991).

Historically, three approaches have been used to explain microemulsion formation and stability. They are as follows:

- Interfacial or mixed film theories
- Solubilization theories
- Thermodynamic treatments

The free energy of microemulsion formation can be considered to depend on the extent to which surfactant lowers the surface tension of the oil water interface and change in entropy of the system such that,

$$\Delta G_f = \gamma \Delta A - T\Delta S$$

Where, ΔG_f = free energy of formation, γ = surface tension of oil water interphase, ΔA = change in interfacial area (A) of microemulsion, T = temperature and ΔS = change in entropy of the system. It should be noted that when a microemulsion is formed, A is very large due to the large number of very small droplets formed. In order for a microemulsion to be formed (transient) a negative value of ΔG_f is required. It is recognized that while value of ΔA is positive at all times, it is very small and is offset by the entropic component. The dominant favorable entropic contribution is very large dispersion entropy arising from the mixing of one phase in the other in the form of large number of small droplets. However, there are also expected to be favorable entropic contributions arising from other dynamic processes such as surfactant diffusion in the interfacial layer and monomer-micelle surfactant exchange. Thus a negative free energy of formation is achieved when large reductions in surface tension are accompanied by significant favorable entropic change. In such cases, microemulsion formation is spontaneous (requiring no physical energy input) and the resulting dispersion is thermodynamically stable.

According to Winsor, there are four types of microemulsion phases exist in equilibria; these phases are referred as Winsor phases:

1. Winsor I: With two phases, the lower (o/w) microemulsion phases in equilibrium with the upper excess oil.
2. Winsor II: With two phases, the upper microemulsion phase (w/o) microemulsion phases in equilibrium with lower excess water.
3. Winsor III: With three phases, middle microemulsion phase (o/w plus w/o, called bicontinous) in equilibrium with upper excess oil and lower excess water.
4. Winsor IV: In single phase, with oil, water and surfactant homogenously mixed.

Microemulsions are dynamic system in which the interface is continuously and spontaneously fluctuating (Gogarty and Tosch, 1968). Structurally, they are divided in to oil in water (o/w), water in oil (w/o) and bi-continuous microemulsions. In w/o microemulsions, water droplets are dispersed in the continuous oil phase while o/w microemulsions are formed when oil droplets are dispersed in the continuous aqueous phase. In systems where the amounts of water and oil are similar, the bi-continuous microemulsions may result (Lam and Schechter, 1987). The mixture oil water and surfactants are able to form a wide variety of structures and phases depending upon the proportions of components (Hellweg, 2002).

The characterization of microemulsions is a difficult task due to their complexity, variety of structures and components involved in these systems, as well as the limitations associated with each technique but such knowledge is essential for their successful commercial exploitation. Phase behavior studies are essential for characterization of surfactant systems and development of phase diagram that provide information on the boundaries of the different phases as a function of composition variables, temperatures, and, more important, structural organization can be also inferred. Phase behavior studies also allow comparison of the efficiency of different surfactants for a given application. In the phase behavior studies, simple measurement and equipment are required. The boundaries of one-phase region can be assessed easily by visual observation of samples of known composition. The main drawback is long equilibrium time required for multiphase region, especially if a liquid crystalline phase is involved.

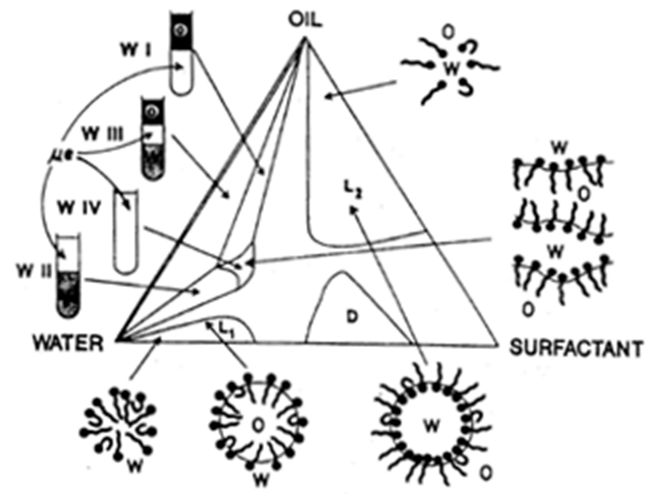

Figure 1. Schematic ternary phase diagram of water–oil–surfactant mixtures representing Winsor classification and probable internal structures. L1, a single phase region of normal micelles or oil-in-water (o/w) microemulsion; L2, reverse micelles or water-in-oil (w/o) microemulsions; D, anisotropic lamellar liquid crystalline phase. The microemulsion is marked by μE, oil by O and water by W (Adapted from Paul and Moulik, 2001)

Experimental

Crude oil

The crude oil used for the formation response and imbibition testing was Bakken crude oil obtained from the Southwest corner of Manitoba. This oil (Bakken 1) is relatively light with an API of 42, and was sweet with a low viscosity. The crude oil contained a notable amount of wax and asphaltene, determined by solvent extraction to be 5 and 6.5% respectively. The Bakken shale in Southwest Manitoba (Bakken 1) is relatively immature, shallow, and thin compared to the Bakken crude oil (Bakken 2) from Saskatchewan. As shown in a comparative GC analysis, the Bakken 1 used for the formation response testing had a relatively lower concentration of C_{10+} alkanes compared to the Bakken 2 that was used for IFT and demulsification studies.

Carbon Profile using High Temperature Gas Chromatography

All measurements were done on a Perkin Elmer Model Clarus-680 Gas Chromatograph with an FID detector and equipped with universal programmable Split-Splitless (PSS) and programmable on-column (POC) injectors design. The instrument was interfaced with a desktop computer running with Total Chrome Workstation software Version 6.3.2 to handle the integration and reports. Separation was achieved on a Elite Series GC capillary column (# 1148134) of 5 m x 0.53 mm size and 0.10 μm film thickness. Crude oil samples were dissolved in carbon disulfide (spectranalyzed grade from Fisher Scientific) and 0.5 μL of this solution was injected into the device. A temperature programing from 50 °C to 430 °C at 10 °C/min was applied. This method can measure % paraffin from C_{10} to C_{100} in crude oil.

Surfactant Flowback Aids

Five commercial products and a new surfactant package optimized for Bakken conditions have been evaluated in this study. A new renewable and environmentally friendly surfactant package was formulated into an aqueous and microemulsion system with identical surfactant contents. A basic description of surfactant formulations used as flowback aids in this work ha beens summarized in Table 1. Products were used at a concentration of 1L per 1000L of frac fluids, also cited as one gallon per thousand gallons of fluid (1gpt), or otherwise stated.

Table 1. Description of surfactant formulations used in this work

Chemical Identifier	Description
SFBA-1	Siloxane Surfactant Blend
SFBA-2	Phenolic Resin / non-ionic Surfactant Blend
SFBA-3	Anionic Surfactant Blend
SFBA-4	New Surfactant Package Optimized for Bakken
MESBA-4	Microemulsion of New Surfactant Package Optimized for Bakken
MESFBA-5	Nanofluid Surfactant Package
MESFBA-6	Nanofluid Surfactant Package

Surface and Interfacial Tension Measurements

All surface tension measurements were done on a Krüss K100C-Mk2 Tensiometer using the Wilhelmy plate method at room temperature. 0.1 gram of each surfactant product was measured and then brought up to 100 gram using DI water, or KCl brines. The solution was allowed to stir for 10 minutes in order to ensure homogeneity. SFBA-2 surfactant solutions had small particles floating in the solution even after being stirred for 15 minutes. Therefore, solutions were filtered off using a 0.45 micron filter before measurement. Interfacial tension measurements were conducted via Drop shape Method using either a TECLIS Tracker H or Krüss DSA100 by fitting the shape of the drop (in a captured video image) to the Young-Laplace equation. Measurements were done in triplicate and an average reported for each surfactant solution.

High Throughput Experimentation and Phase Diagrams

For evaluation of characteristics and phase diagrams of renewable and environmentally friendly surfactants, High Throughput Experimentation (HTE) was utilized to formulate microemulsion with different oils and surfactants. The experiments were carried out on a “Swing Emulsifier” platform provided by Chemspeed. Automated high output solutions enhance efficiency and productivity for experimental workflows and is displayed in Figure 1. As indicated it consistsed of a gravimetric dispenser unit, a four needle head liquid dispenser unit, racks for the formulation flasks (which itself was on a shaking frame used for mixing the formulations), the compound reservoirs and a capper/crimper device.

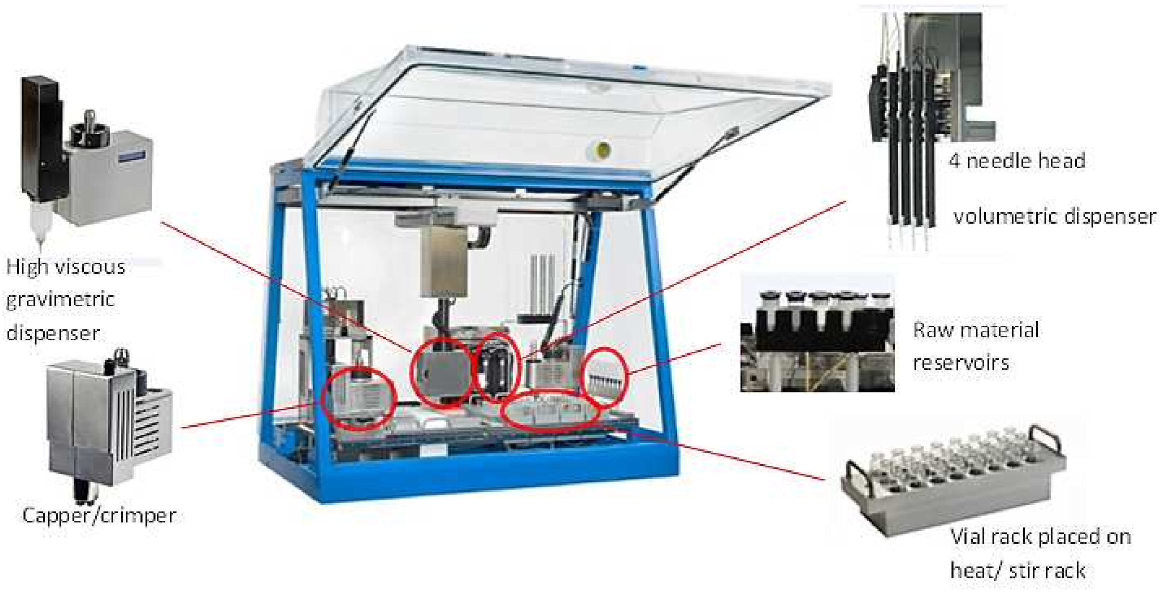

Figure 2. Image of “Swing Emulsifier” platform and robotic tools used for the microemulsion formulations

In order to formulate the many different samples, it was essential to exactly dispense the various compounds with different viscosities. This was achievable due to the high viscosity dispensing unit that could dispense materials ranging from very low viscous liquids to very viscous wax-like pastes. The dispensing parameters had to be optimized for each compound taking into account droplet size and viscosity to be able to achieve fast dispensing with high precision.

Figure 3. Image of a) the used “Swing Emulsifier” platform, b) the dispensing unit, c) close up of the dispensing unit and d) all samples which have been prepared

The exact data for each dispensing step is registered in a log file which can be exported into a excel spread sheet. With the gravimetric dispenser unit the composition of each sample is always known regardless the error compared to the specified amount. Depending on the sample composition, the time for preparing one sample is between 3 and 6 min. For example, for a set of experiments when composition is restricted to about 50% aqueous phase, 17% oil phase, 5% co-solvent and 28% surfactants mixture, the whole pack of 300 samples can be prepared and measured in 36 hours. In this work, high throughput experimentation and robotic formulation were utilized to screen several thousand formulations from nearly 50 different surfactant packages.

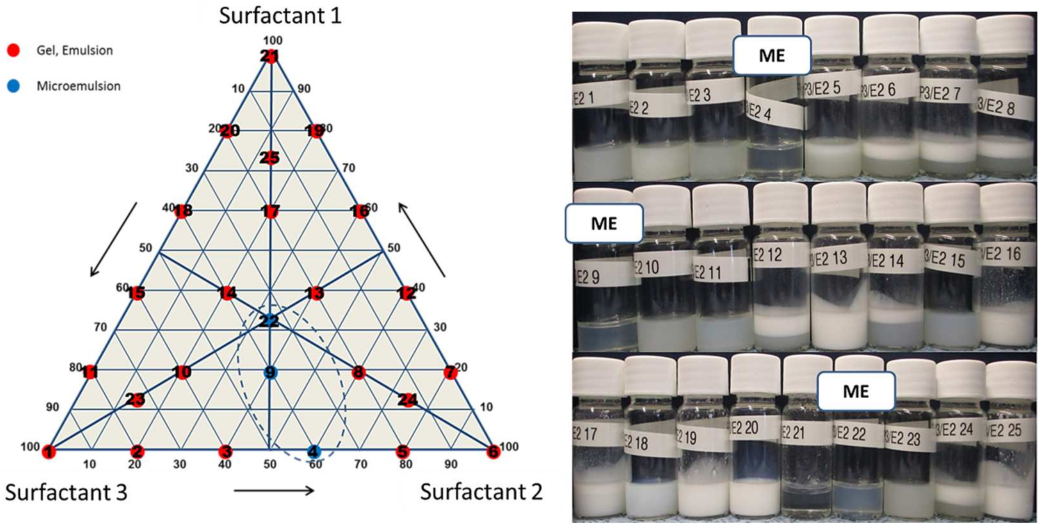

Figure 4. Three components phase diagram and photos of each sample for an HTE run. The samples which give rise to transparent microemulsions (ME) are highlighted

Adsorption Studies of Flowback Aids with QCM-D

Quartz Crystal Microbalance with Dissipation monitoring (QCM-D) is a powerful analytical tool to characterize the formation of thin films (nm). The instrument is based on a sensor that oscillates at a specific frequency when voltage is applied. The frequency of the oscillation changes as the mass on the sensor changes. Turning off the voltage causes the oscillation to decay. The dissipation factor is related to the elasticity and viscosity of the molecular layer on the sensor. Measuring the frequency and dissipation allows the analysis of the state of molecular layers bound to the sensor surface, their mass, thickness and structural (viscoelastic) properties.

All QCM-D measurements were performed on a Q-sense E4 system which has 4 flow modules (Gothenburg, Sweden), where 2 were used. Using the E4 instrument mass and viscoelastic properties of molecular layers which build up at the sensor surface can be determined. All measurements were made at 22°C using silica and alumina sensors. The instrument collected first, third, fifth, seventh, and ninth harmonics of the fundamental resonance frequency.

In order to get a reliable measurement, the following cleaning protocol was adopted. The silica and alumina coated quartz sensors were rinsed with excess deionized water. Then they were place in a suitable holder and placed in a 3 w% Hellmanex III cleaning solution and sonicated in an ultra-sound bath for 30 min. After that the crystals were rinsed with deionized water and dried with pressurized air. Two sensors were connected in parallel and were initially flushed with deionized water pumped at a constant flow rate of 200 μL/min. After a stable reading was obtained using the deionized water, experiments were carried out for two different sample concentrations 0.1 and 0.5 wt% and passed through the sensor at a constant flow rate.

Sand Column Adsorption

A 25 x 1.5 inch chromatography column packed with sand was utilized to compare desorption of an aqueous surfactant versus the same surfactant blended into a stable microemulsion onto the sand surface. The column was filled with 40/70 mesh sand and pre-saturated with 3% KCl brine. The pore volume was measured as the volume of brine that was used to saturate/fill the column. The test solution containing 3% KCl and the surfactant at a loading of 1 gpt was then injected into the column at a rate of 50 ml/min. The effluent was collected over certain pore volume intervals as injection was occurring and retained for surface tension determination.

Measuring the surface tension of the effluent flowing from the pre-saturated sand column during a surfactant treatment injection acts as an indication of the adsorption effect of the surfactant onto the silica. If the surface tension quickly dropped, it would indicate that the surfactant stayed in solution and rapidly propagated through the sand. If the surface tension remained high (surface tension of initial brine), it indicated that adsorption was occurring.

Zeta Potential Measurement

Zeta potential values of fine silica flour and kaolinite was determined by microelectrophoresis on a Malvern Zetasizer Nano ZS. The solids analyzed had a size between 3 and 20 microns. The concentration of silica flour or kaolinite was set at 5 g/L of brine solutions with a pH between 4.0 and 10.0 comparing the effect of the addition of 1 gpt of surfactant.

The Zeta potential is defined by the charge that develops at the interface in the boundary of hydrodynamic shear between solid surfaces as product of the electrostatic repulsion and the attractive forces related to the Van Der Waals Forces. Zeta potential is therefore a function of the surface charge of the particle, any adsorbed layer at the interface, and the nature and composition of the surrounding suspension medium. Zeta potential can be affected by changes in pH, conductivity of the medium (salinity and kind of salt) concentration of particular additives (polymer, surfactants, etc.). Zeta Potential values comprehended (-20 and 20 mV) reflects the effective charge is low enough in the particles that the repulsion between them are lowered to one point where flocculation, coagulation and aggregation could occur (Reed, 1995; Sahimi, 2011).

Amott Cell Imbibition

Amott cells were used for spontaneous imbibition testing, specifically to compare the release of crude oil from a core when exposed to a variety of blends of brine and surfactants. Grey Bandera Sandstone core plugs were utilized for this testing and had an approximate permeability of 1 to 2mD. The clean/dry cores were initially pre-saturated under vacuum with Bakken crude oil. The mass/volume of oil uptake was determined gravimetrically. The saturated core plugs were then placed into Amott cells containing various treatment solutions made up of 3% KCl brine and surfactants at a concentration of 1 gpt. The release of crude oil was then recorded as cumulative volume over time and normalized to the volume of oil that was initially imbibed into the core. The testing was conducted at room temperature and oil release was monitored for a period of 7 days.

Core Flow-Regained Permeability

Core flow testing was performed using a Chandler Engineering Formation Response Tester (FRT). Standard Gray Berea cores (1.5” diameter by 3” length) were used for the testing and had an average initial permeability to kerosene of 100 to 150mD; the mineralogy of Brea core is given in Table 2. The cores were initially vacuum-saturated with 3% KCl brine. A confining stress of 1500 psi was applied and the core holder was heated to 50°C. A back pressure of 100 psi was applied. The core was then further saturated under pressure and temperature with 3% KCl brine at 1, 2, 3, and 4mL/min in the injection direction. Initial permeability to oil was then (kerosene or Bakken crude oil) was established at flow rates ranging from 2 to 4 mL/min in the production direction. Permeability was considered stable when a variation of less than 2.5% was observed over 5 pore volumes during injection. The treatment fluid (3% KCl water plus the surfactant) was then injected (Injection direction) for a total volume of 24 pore volumes using 2 to 4 mL/min. The core was shut in overnight (16 hrs) and then oil was injected in the production direction at the same flow rates that initial permeability was determined to record the regained permeability.

Table 2. Mineralogy of core sample

Mineral Phase	Content
Quartz	86%
Kaolinite	5%
Feldspar	3%
Chlorite	2%
Calcite	2%
Dolomite	1%
Illite	1%

Results and Discussions

Five commercial products and two new surfactant formulations were used in this study as flowback aids for use in hydraulic fracturing applications. The new formulations were made of renewable and environmentally friendly surfactants in the forms of an aqueous blend and an oil-in-water microemulsion. High throughput experimentation and robotic formulation were utilized to screen several thousand formulations from nearly 50 different surfactant packages in developing new flowback aids. Final selection was achieved after comprehensive testing of the top 4 candidates based on key functional properties. The initial goal was to develop products that delivered consistent and robust performance in a wide range of temperature and salinity for hydrocarbon fluids recovery from oil and gas wells. Surface tension of all products tested was measured in DI water and 5% KCl brine. As shown in Table 3, both aqueous and microemulsion forms of new surfactant package (SFBA-4 and MESFBA-4) gave lowest surface tension with no effect from salinity.

Table 3. Surface tension of surfactants used in this study. All measurements are done at 25 °C

Chemical Identifier	**Surface Tension (mN/m)**	
	DI water	**5% KCl**
SFBA-1	35.0	30.2
SFBA-2	29.7	28.6
SFBA-3	35.6	29.0
SFBA-4	27.3	27.6
MESFBA-4	27.2	27.8
MESFBA-5	40.1	38.5
MESFBA-6	34.4	33.5

Two crude oil samples used for the study were from the Bakken obtained from the Southwest corner of Manitoba (Bakken 1) and from Saskatchewan (Bakken 2). Bakken 1 and Bakken 2 contained a notable amount of wax and asphaltene. As shown in a comparative GC analysis (Figure 5), the Bakken 1 used for the formation response testing had a relatively lower concentration of C10+ alkanes compared to the Bakken 2 that was used for IFT and oil/water separation studies. Bakken 2 had a wax appearance temperature (WAT) of 38.7 °C as measured by DSC method, indicating wax and paraffin precipitation can occur at room temperature leaving lighter crude in bulk liquid phase. This is reflected in differences in IFT measurements at 25, 50 and 75 °C. As shown in Table 4, separation of higher molecular weight wax and paraffin at room temperature results in artificially lower IFT for hydrocarbon liquid phase. Therefore, all experiments utilizing Bakken 2 were performed at 50 °C.

Interfacial properties of Bakken 2 were studied in 5% KCl brine comprising all surfactant formulations. As shown in Figure 6, SFBA-3, SFBA-4, MESFBA-4 and MESFBA-5 provided lowest interfacial tension compared to other products. It is noteworthy to mention new surfactant packages delivered equivalent IFT reduction. This was further supported by demulsification tests where SFBA-4 and MESFBA-4 gave best water-oil separation followed by SFBA-3. Photographs of Bakken 2 and brine interfaces are shown in Figure 7.

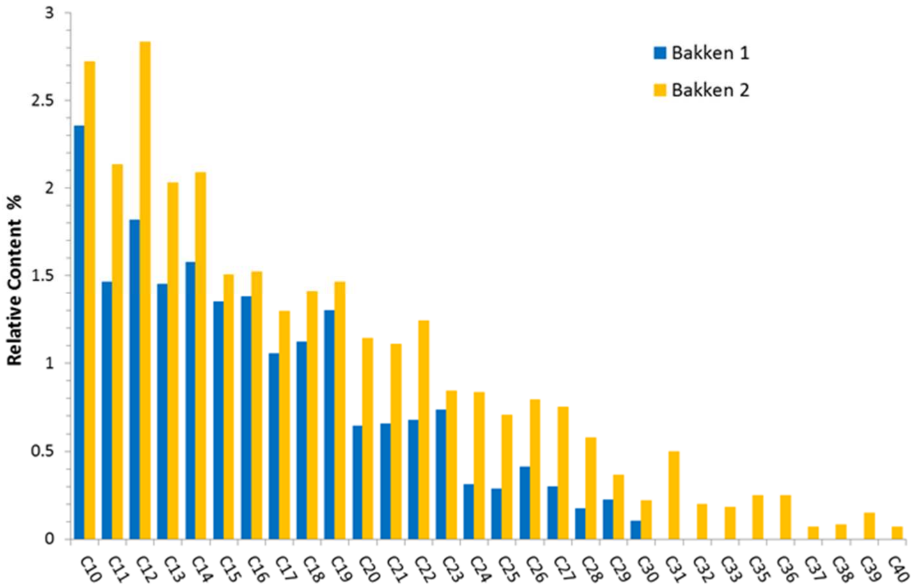

Figure 5. Comparison of carbon distribution of Bakken crude oil samples measured by HTGC analysis

Table 4 – Interfacial tension (mN/m) of Bakken 2 crude oil at 25, 50 and 75 °C as a function of salinity.

Temperature	DI water	5% KCl	10% KCl
25°C	15.16	7.30	5.32
50°C	23.35	18.45	15.30
75°C	23.43	17.78	14.90

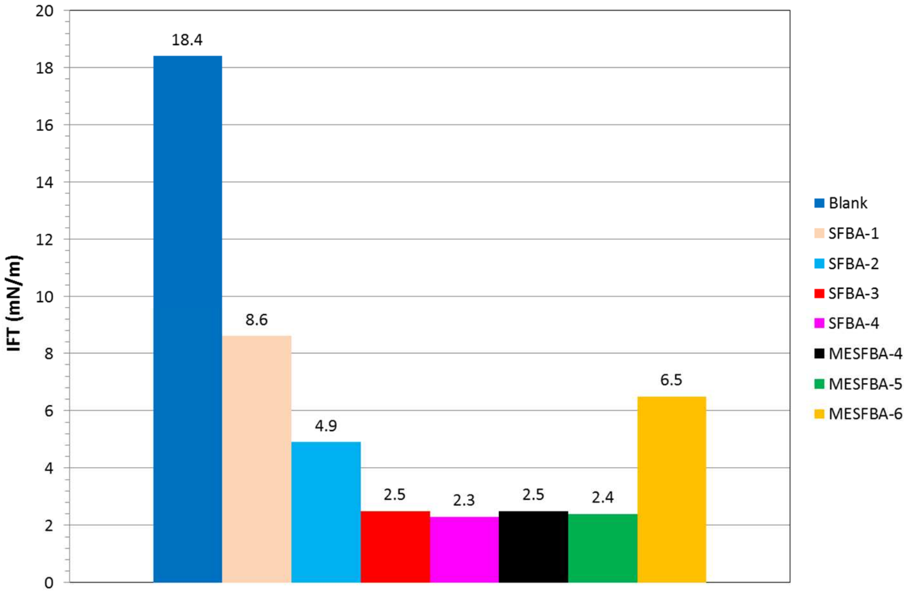

Figure 6: Interfacial tension of Bakken 2 crude oil with 1gpt of surfactant in 5% KCl brine at 50 °C

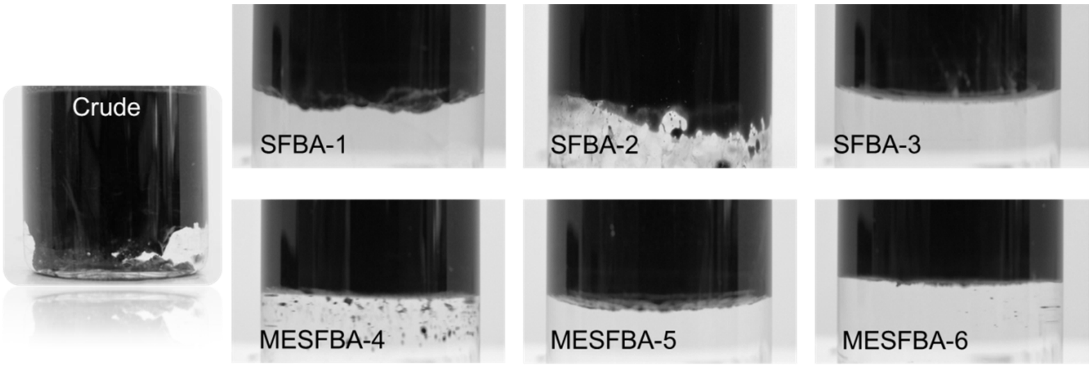

Figure 7. Photographs from oil/water interfaces from demulsification tests using Bakken 2

Amott Cell Imbibition

As shown in Figure 8 when no surfactant was present the release of oil from the core plug was very slow. Further interpretation of results indicated that varying surfactant chemistry obviously affected the release of oil, regardless of whether IFT was low or the demulsification properties were identifcal. When referring to the IFT results in Figure 9, the product that gave the lowest IFT did not result in the best oil production. Of interest is that in the case of the same surfactant chemistry (SFBA-4 vs. MESFBA-4), the micro-emulsified version of the same surfactant improved the oil recovery, and in this data set gave the best result overall. This would lead to the conclusion that putting a surfactant into micro-emulsified state may improve its performance in regards to oil displacement/recovery.

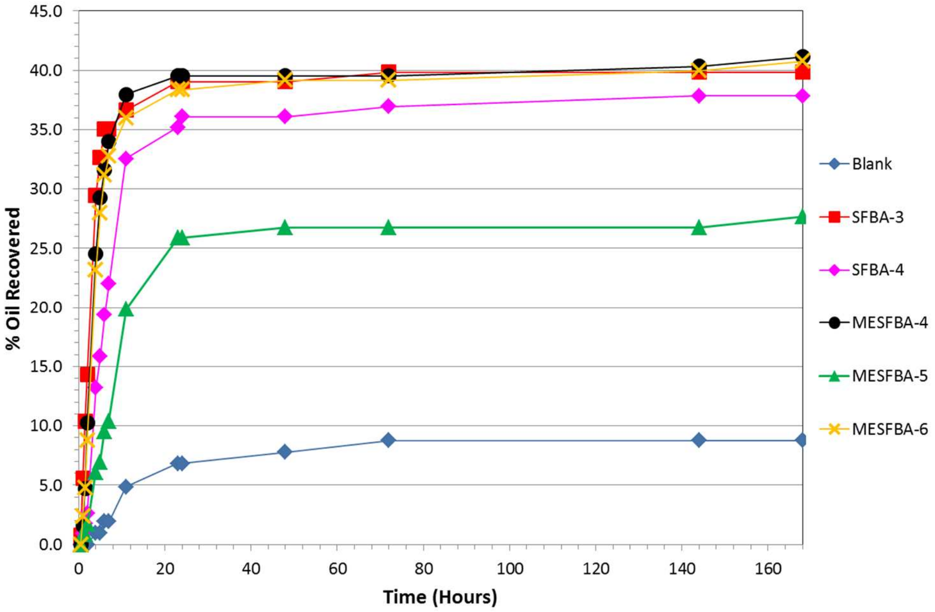

Figure 8. Bakken 1 crude oil desorption over 7 days using surfactants at 1gpt dosage

Also of note was that the top oil recovery results were very close between 2 nano/micro emulsified products (MESFBA-4 and MESFBA-5) and a simple aqueous surfactant, SFBA-3. This could indicate that achieving the best oil recovery may not be related to a micro/nano emulsion formulated surfactant, but more simply the right surfactant chemistry for that test/application.

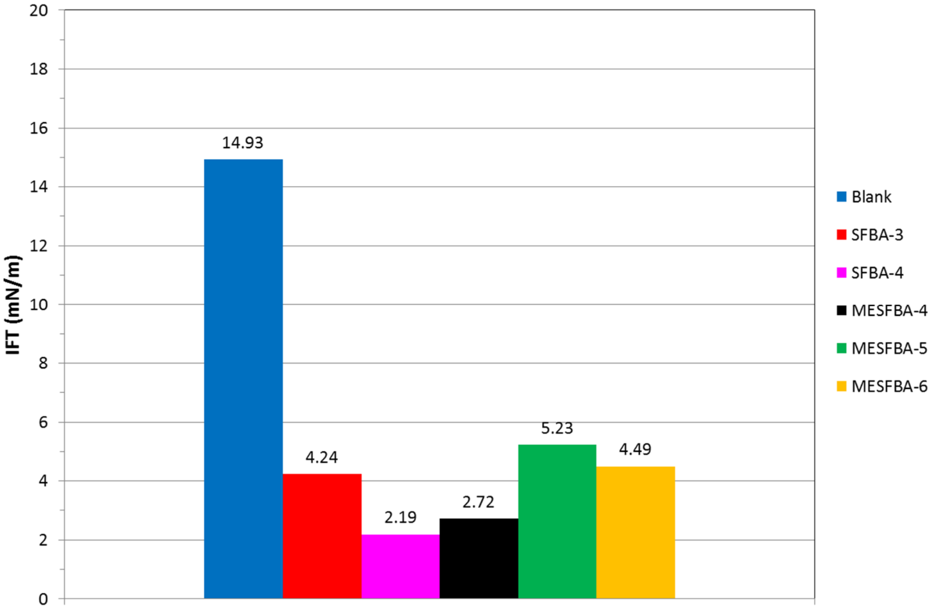

Figure 9. Interfacial tension of Bakken 1 crude oil with 1gpt of surfactant in 3% KCl brine at 25 °C

Core Flow-Regained Permeability Tests

When measuring the regained permeability to kerosene, it was observed that using no surfactant (Blank) would result in some impairment to permeability (76% regained), likely due to oil-water mixing and a slight emulsion tendency. The addition of any of the surfactants used in this study improved the regained permeability. The best performing surfactants actually stimulated the resulting in higher than 100% regained permeability to kerosene. A result of highger than 100% regained permeability would indicate that initial permeability to oil was somewhat hindered by the brine-oil interactions, potentially due to higher interfacial tension or emulsion formation. The addition of the correct surfactant could therefore yield a result that is superior to the initial permeability. The top performing surfactants in this testing included one of the SFBA-3 and the SFBA-4. In this data set, the micro-emulsified form of the same surfactant (MESFBA-4) slightly underperformed compared to its aqueous version (SFBA-4), leading to the conclusion that in the case of regained permeability evaluation by this test procedure, a standard optimized aqueous surfactant may perform as well or better than a micro/nanoemulsified formulations.

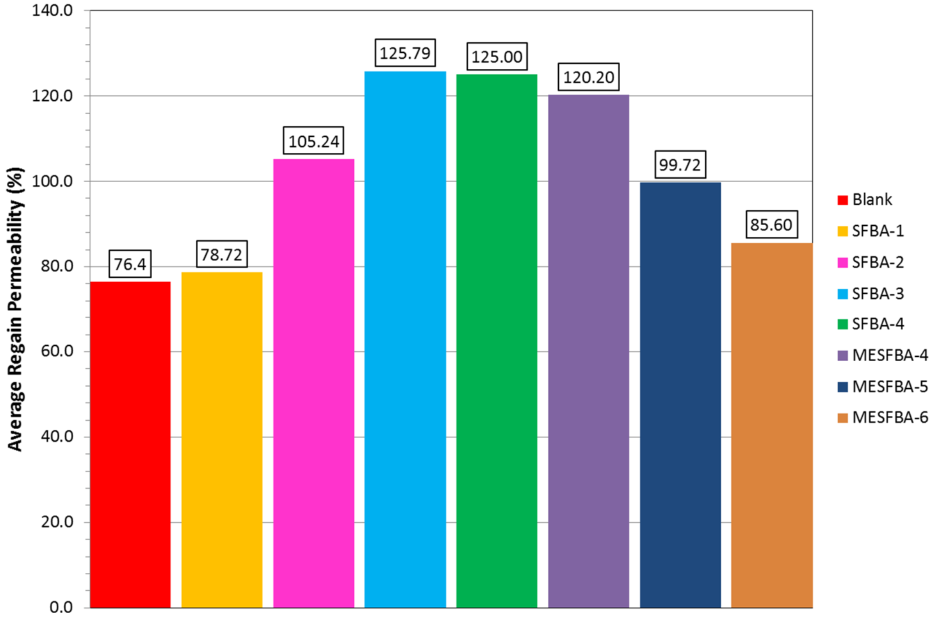

Figure 10. Core flow regained permeability rates using surfactants at 1gpt dosage (Kerosene)

Table 5. Interfacial tension (mN/m) of Kerosene in 5% KCl in the presence of surfactants.

Surfactant	DI water	5% KCl
None	19.5	14.5
SFBA-1	8.1	1.7
SFBA-2	7.2	4.5
SFBA-3	4.1	2.9
SFBA-4	2.1	2.2
MESFBA-4	2.2	2.2
MESFBA-5	3.5	2.1
MESFBA-6	6.5	6.3

Regain permeability testing was repeated using Bakken 1 crude oil but utilized a smaller selection of surfactants that had exhibited the best results in previous IFT, demulsification, and imbibition studies with the Bakken crude. In this testing, it was observed that the SFBA-4, an aqueous surfactant optimized for the Bakken crude oil yielded the best regained permeability with a result of 87% as compared to 56% for a commercial nano-emulsified surfactant. Also observed was that taking the best performing aqueous surfactant and formulating it into a microemulsion (MESFBA-4) did not necessarily hinder performance, but did not appear to improve the performance in regards to regained permeability using these test procedure. Of interest was that the regained permeability data with the Bakken crude oil seems to correlate closely to the IFT's recorded with the same crude oil, where the lower IFT's (Shown in Figure 9) correspond to the higher regained permeabilities.

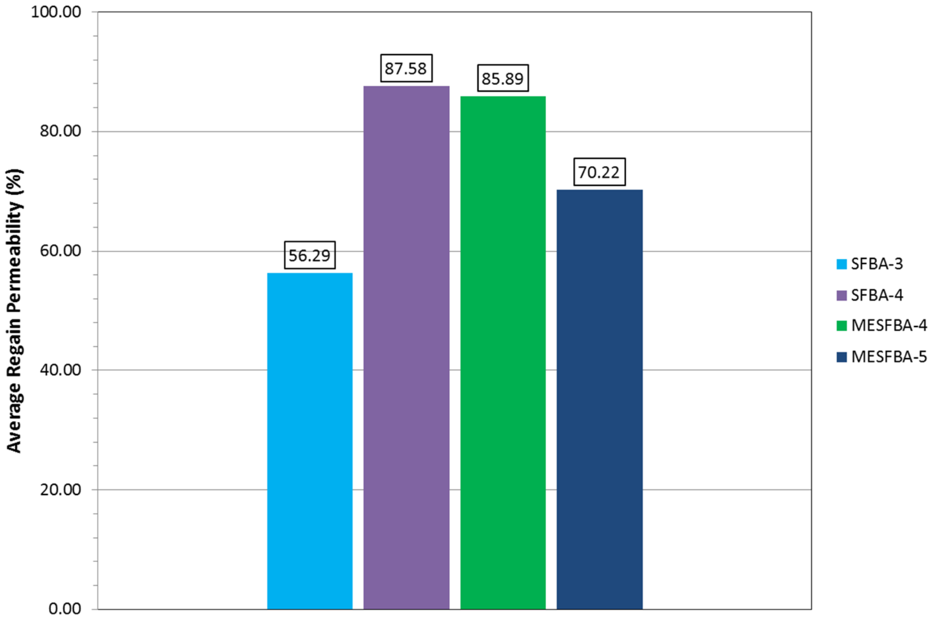

Figure 11. Core flow regained permeability rates using surfactants at 1gpt dosage (Bakken 1)

Zeta Potential Measurements of Fine Silica and Kaolinite

There are several known problems associated with clays and fines in oil and gas activities. It is important to maintain the wellbore stability during drilling and fracturing as well as during production, especially in water-sensitive shale and clay formations. Clay swelling and fine migration, which can occur during a frac job, well remediation or production, can damage formation conductivity. Increase in surface charge of fine solids can increase inter-particle repulsive forces which results in destabilization and fine migration. Zeta potential measurements therefore can be a valuable tool to provide information about the interactions of surfactants with solids and their effects on surface charge activity upon hydraulic fracturing treatments. Clay particles are known to have large surface area which organics can be adsorbed on. Adsorption of surface active molecules onto clays can alter surface charge and thus repulsive force and consequently the double layer gap between the clay particles.

Figures 12 to 15 show the effect of commercial surfactant based flow back additive (SFBA) and microemulsified systems (MESFBA) in the variation of the zeta potential on silica and kaolinite at pH 4.0, 7.0 and 10.0. For silica particles, the use of MESFBA in general showed values less pH sensitive and within range comprehended between -20 and 20 mV observing similar effect when used SFBA-2. In the case of a Kaolinite substrate the trend was similar except when evaluated MESFBA-6. In order to assess the effect of the surfactant formulation, zeta potential values of aqueous (SFBA-4) and microemulsifed (MESFBA-4) forms of the new surfactant package were determined for silica and kaolinite. It was confirmed that the aqueous formulation was slightly more pH sensitive than the microemulsion form (see Figures 16 and 17).

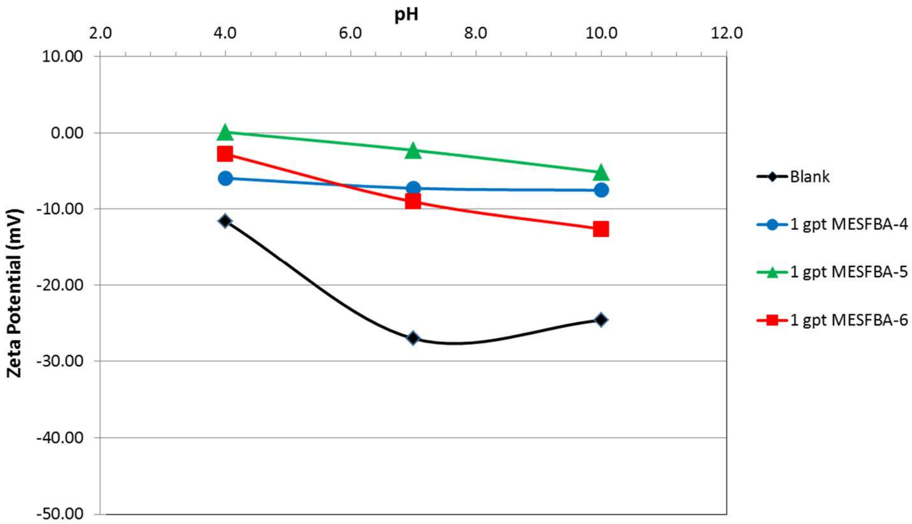

Figure 12. Zeta potential of fine silica in 0.5% NaCl brine with MESFBA products

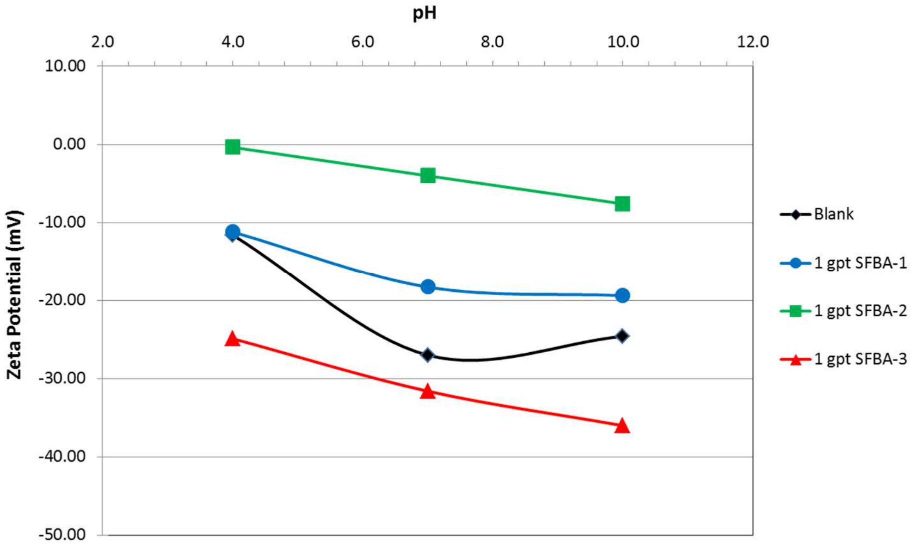

Figure 13. Zeta potential of fine silica in 0.5% NaCl brine with SFBA products

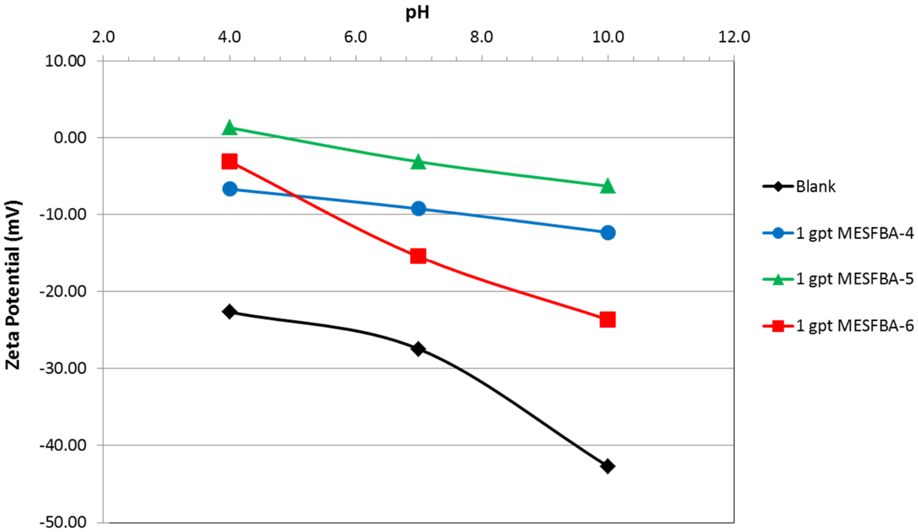

Figure 14. Zeta potential of kaolinite in 0.5% NaCl brine with MESFBA products

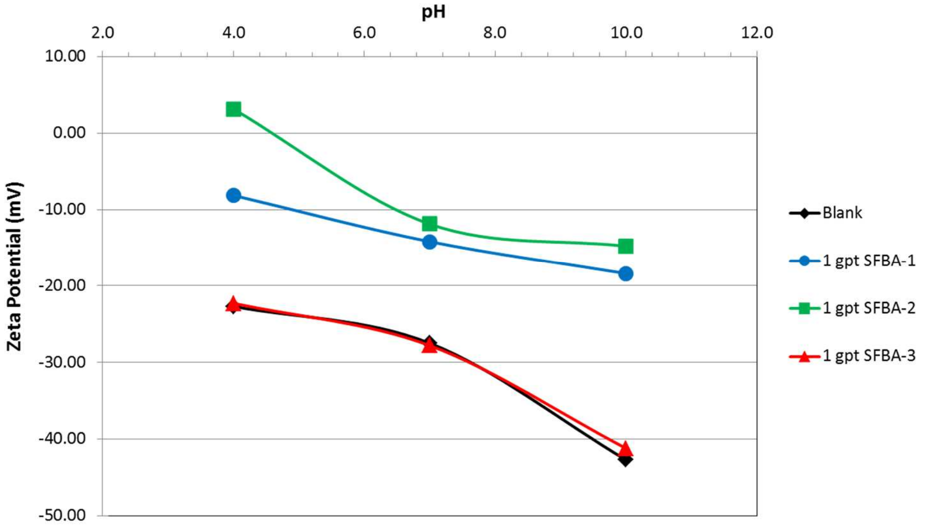

Figure 15. Zeta potential of kaolinite in 0.5% NaCl brine with SFBA products

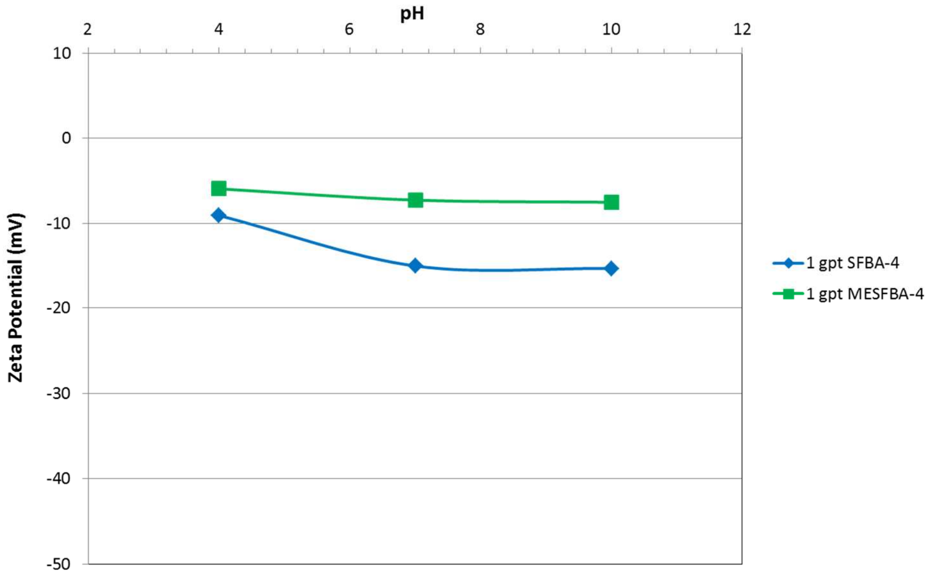

Figure 16. Comparison of zeta potential of fine silica in 0.5% NaCl brine with SFBA-4 and MESFBA-4

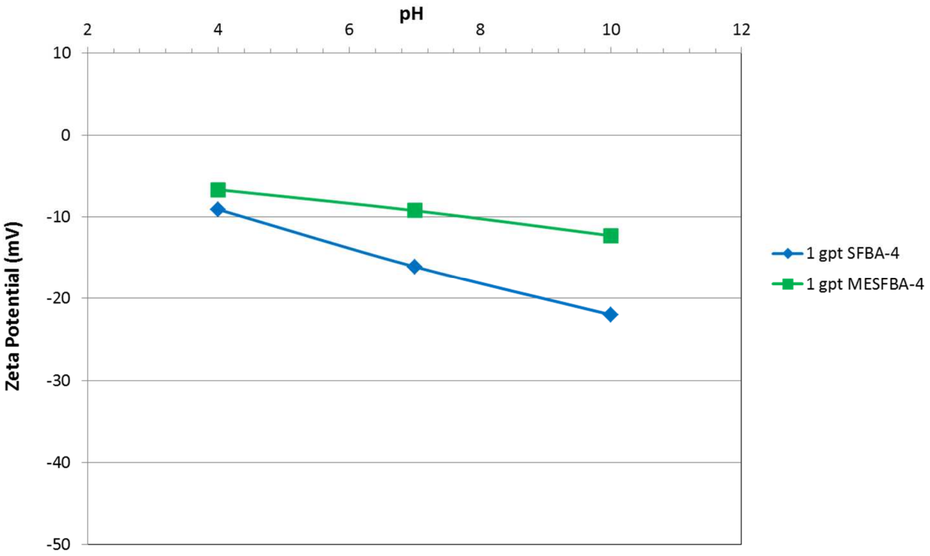

Figure 17. Comparison of zeta potential of kaolinite in 0.5% NaCl brine with SFBA-4 and MESFBA-4

Quartz Crystal Microbalance with Dissipation Data

In this study, the adsorbed mass (ng/cm^2) of new surfactant formulations onto the alumina and silica surfaces were calculated using the frequency change determined from the QCM-D measurements. For all samples two concentrations 0.1 w% and 0.5 w% were measured. Each run consisted of a 2 adsorption / desorption cycles (adsorption of sample followed by washing with deionized water = 1 cycle). The frequency change was converted into the adsorbed mass by the Sauerbrey relationship using QTool software. Adsorption data were not corrected for viscosity of the bulk surfactant solutions, since they were assumed to be close enough not affecting frequency variations in different fluids. Silica and alumina substrate were use to represent surface mineralogy of formation solids.

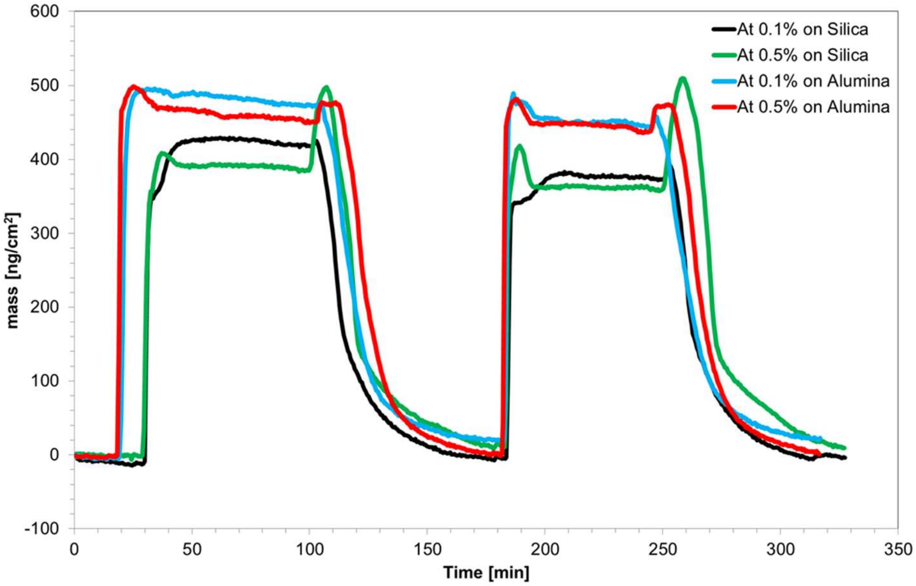

Figure 18. Adsorption/desorption of MESFBA-4 on silica and alumina

From adsorption data, it was found that MESFBA-4 had a high affinity towards both silica and alumina surfaces under conditions test was performed, but adsorption rate did not increase with an increase in dosage applied. The adsorption/desorption profile also indicated that the process was reversible and the surfactants did not permanently retain on minerals surface, minimizing the risk of reservoir damage.

QCM-D is a powerful quantitative technique which was used throughout the development stage to verify:

1) Adsorption/desorption properties of selected surfactant combinations and their microemulsion formulation;
2) Influence of co-surfactant on adsorption/desorption process of surfactants;
3) Influence of oil phase on adsorption/desorption process of surfactants;
4) Influence of co-solvent on adsorption/desorption process of surfactants.

Information obtained from QCM-D studies provided additional insights to the roles of cosurfactant and oil phase in adsorption/desorption characteristics of the final formulations.

Sand Column Adsorption Study

Two surfactant formulations were compared, one was the aqueous form of the surfactant (SFBA-4) and the other was the same chemical but blended into a microemulsion (MESFBA-4). Although the data shown in Figure 19 is somewhat erratic, the trend indicated that the surface tension of the effluent dropped more quickly in the case of the micro-emulsified surfactant compared to the aqueous form. This indicated that placing a surfactant that has a tendency to adsorb onto silica into a oil-in-water microemulsion may reduce the tendency to adsorb and improve penetration when injecting into silica based porous media.

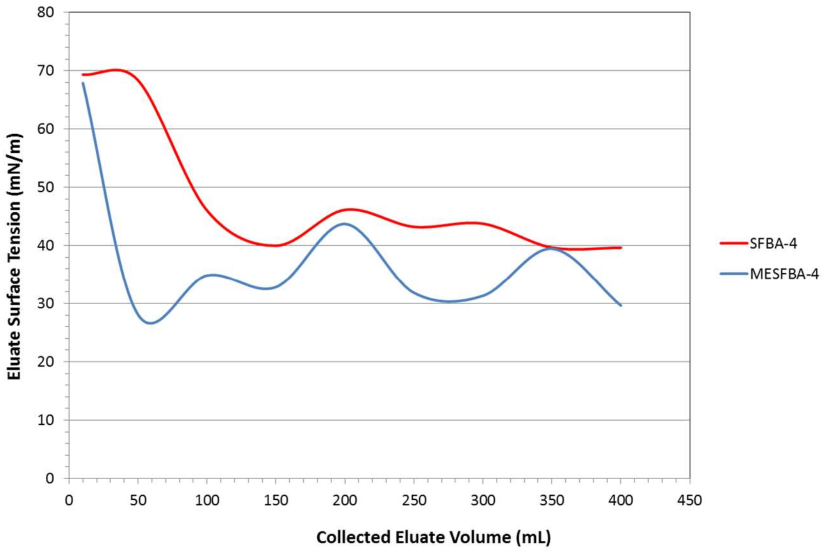

Figure 19. Adsorption of SFBA-4 and MESFBA-4 on sand column. Microemulsion formulation exhibited less retention on sand

Conclusion

Multiphase flow in porous media is complex and governed by several factors including the complex pore structure of the medium and how it affects the distribution, flow, displacement of one or more fluids, or dispersion of one fluid in another. Displacement of one fluid by another can be carried out by many different mechanisms which may involve heat and mass transfer, thermodynamic phase change, and the interplay of various forces such as viscous, buoyancy, and capillary forces (Sahimi, 2011). Under equilibrium condition in reservoir, several solid and liquid phases and interfaces coexist (see Figure 20).

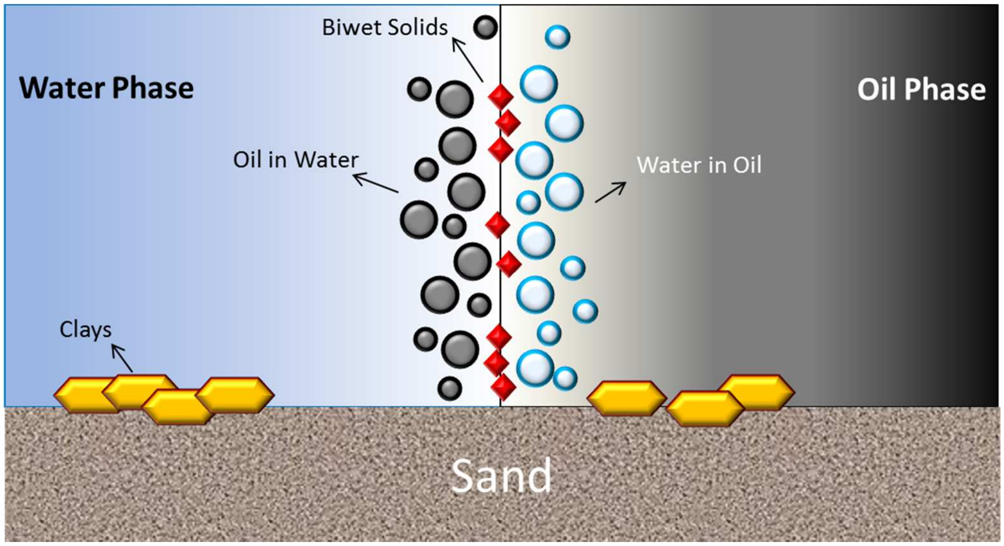

Figure 20. Schematic representation of phases present in equilibrium state under reservoir conditions

Surfactants, regardless of their mode of state: aqueous or microemulsion, can interact with such phases and disturb the equilibrium thus affecting the dynamics of multiphase flow during oil and gas production. In order to achieve higher production, such interactions must cohesively work together and in favor of other. For example, biwet solids (e.g. clays or asphaltene) are known to stabilize crude-water emulsions. Understanding the nature of surfactant interactions with clays or asphaltene aggregates, therefore, could be very important in designing a highly effective frac flowback aid. Lab test methods must be utilized with special care of their scope and with knowledge of their limitations and strength.

The objective of this work was to obtain a valid comparison of microemulsions and aqueous solution for fracturing flowback aids. Results from all experiments performed in this work, clearly indicates the importance of main surfactant chemistry and the nature of its interactions with various phases present in a hydrocarbon reservoir. Once the right chemistry is identified, performance can be fine tuned by addition of co-surfactants and solvents or co-solvents. If an aqueous surfactant fails to function, formulation into microemulsion does not change its characteristics. As shown in the results and discussions, aqueous and micro-emulsified surfactants exhibited similar performance in regain permeability testing and in crude-water separation. Perhaps the advantages of microemulsions are their lower adsorption rate on reservoir rocks and higher stability at elevated pH and salinity when compared to native aqueous surfactant. Microemulsions therefore may be considered as a carrier system which can be used to better deliver surfactant deeper into the reservoir during a frac job.

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