AADE-11-NTCE-1

Successful Field Applications of Surfactant Nanotechnology to Displace Oil-based Drilling Fluids for Completion Operations

Ryan van Zanten, Larry Deen, and Dodie Ezzat, Halliburton

Abstract

Removing oil-based drilling fluid residue is critical when displacing to clear brine for completion operations. Successful displacement results in a clean low-turbidity/low-solids completion brine, a less reservoir-damaging completion operation and improved production. The development of an effective displacement spacer to remove oil residue is paramount to achieving a successful displacement. Typically mixtures of several different components consisting of solvent and surfactant combinations are run for an effective displacement from oil-based fluid to completion brine. Microemulsion surfactant nanotechnology offers an attractive alternative to the use of these solvent/surfactant combinations. Microemulsion-forming surfactant solutions can solubilize large volumes of oil like a solvent while simultaneously water wetting the casing and formation.

Laboratory testing led to the development of a surfactant-based microemulsion-forming displacement spacer. The microemulsion spacer water wets more effectively than previously used solvent/surfactant spacers and eliminates the use of solvents in the displacement spacer train, allowing for a more environmentally-friendly solution.

Several field applications demonstrating improved displacements have been run in horizontal wells in the Haynesville shale in northeast Louisiana. Operational personnel confirmed that the surfactant package that replaced the use of two displacement spacers, helped lower displacement costs and minimized logistical issues. Initial lab tests were done with field fluid samples to compare cleaning efficiency results. Improved turbidity readings were shown in the wells where the new surfactant package was applied. The application of this new microemulsion surfactant clean up spacer is now the preferred field practice for displacing oil-based drilling fluids with clear completion brines.

Introduction

Oil-based drilling fluid can leave a thin layer of oil on the casing and the formation when displacing to completion brine. This layer of oil can contaminate the completion brine leading to an unacceptable fluid that may cause formation damage due to the dispersed oil in the form of emulsion blockages and particle plugging from the drill solids or polymers. Removing this layer is generally accomplished by running a multiple spacer package ahead of the completion brine. This spacer package usually contains some surfactant or surfactant/solvent as the cleaning and wetting agent. These spacer trains are generally composed of five distinct spacers:

- Thinning spacer (base oil)
- Viscosified, high density push spacer
- Cleaning spacer (solvent)
- Water wetting spacer (surfactant)
- Viscosified brine

In some regions the solvent spacer will be replaced with a second surfactant spacer to remove oil-based residue. Traditional surfactants require high flow rates and are relatively inefficient at solubilizing oil. Synthetic fluids have been found to be particularly difficult to displace to completion brines or to cement.[1]

Using surfactant nanotechnology, it is possible to engineer a surfactant package capable of solubilizing large volumes of oil while aggressively water wetting the casing. By tuning surfactant mixtures, it is possible to form in-situ oil-in-water microemulsions, allowing surfaces to be water wet. This can allow the elimination of toxic solvents and simplifies the surfactant package used. This paper demonstrates the efficacy of surfactant nanotechnology in engineering displacement spacers. The theory and development of the surfactant package is described along with supporting laboratory data. Finally, a brief summary of field applications performed in the northwest Louisiana Haynesville region of the United States is detailed.

Surfactant Theory

Surfactant Self-Assembly

Surfactants are composed of a hydrophilic (water-loving) head and a hydrophobic (oil-loving) tail. Having this amphilic character allows surfactant molecules to self-assemble into a variety of nanostructures from spherical/rodlike micelles to lamellar sheets. The particular form of self-assembled nanostructure is dictated by the geometry of the surfactant. The first level in predicting surfactant self-assembly is the packing parameter, p.[2] This is a simple geometrical relation that can qualitatively predict the structure of surfactant aggregate.

The packing parameter is defined as:

$$p = v/al$$

where v is the surfactant tail volume, l is the length of the surfactant tail, and a is the effective area per molecule at the aggregate surface (also known as the surfactant head group area). It is very important to note that *a* is an equilibrium property of the surfactant and not some set value due to the chemical structure of the head group. This value must be calculated from equilibrium thermodynamic conditions and can be changed by varying the temperature, pH, salinity, etc., of the system.[3]

As oil is added to the system, the micellar or bilayer hydrophobic cores will swell to incorporate it. When more oil is added than the micellar cores can incorporate, separation into two phases will occur. One phase will be oil-swollen micelles in water and the second phase will be the excess oil. The excess oil can be incorporated by vigorous mixing to form an emulsion. For emulsions, the surfactants will self-assemble into a monolayer at the aqueous/non-aqueous interface. This self-assembly of the surfactants at the interface leads to a reduction in surface tension. Emulsions are not equilibrium systems however and the dispersed phase will coalesce or ripen and eventually phase separate back to the original two phases. By using the right blend of surfactants/co-surfactants a microemulsion can be tailored that will efficiently solubilize the oil and will not phase separate with time.

Microemulsions and Wettability

Microemulsions are thermodynamically stable mixtures of oil, water and surfactant, frequently in combination with co-surfactants. In contrast to ordinary emulsions, microemulsions form upon simple mixing of the components and do not require the high shear conditions generally used in the formation of ordinary emulsions. They are thermodynamically stabilized not kinetically stabilized and may consist of one, two or three phases. Microemulsions can consist of oil dispersed in water (O/W) or water dispersed in oil (W/O) emulsions. They are generally described as Windsor type I, II, III or IV emulsions (**Fig. 1**). Microemulsion phases are described as follows:

Windsor I - a two phase system with an O/W micellar dispersion and an excess oil phase

Windsor II - a two phase system with a W/O micellar dispersion and an excess water phase

Windsor III - a three phase system with a bicontinuous sponge-like O/W phase and excess water and oil phases

Windsor IV - a single phase system with swollen micelles dispersed in an aqueous phase

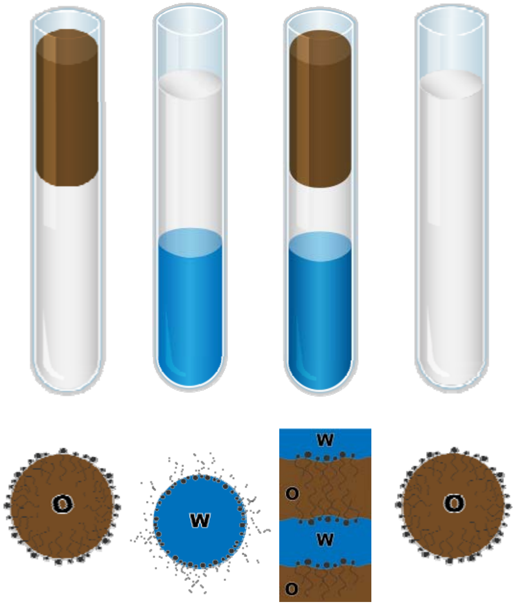

Fig. 1–Windsor I (left), Windsor II (left center), Windsor III (right center) and Windsor IV (right) microemulsions. Blue represents water, brown is oil and the white/clear is a micellar dispersion.

The easy solubilization of oil causes aqueous external phase microemulsions to have organic solvent like properties, allowing for efficiently cleaning and water wetting of oil contaminated surfaces.

In order for an emulsion to form spontaneously there must be a reduction in the free energy of the system. This reduction in free energy is brought about by an increase in conformational entropy, a reduction in surface tension, and a decrease in curvature energy. The free energy change of a system is represented by:

$$\Delta G = \Delta H - T\Delta S$$

or

$$\Delta G = \Delta A \cdot \gamma_{ow} - T\Delta S$$

where G is the Gibbs free energy, T is the temperature, S is the entropy, A is the interfacial area, and γ_{ow} is the interfacial tension at the oil-water interface. The entropy is increased by the creation of several small droplets; however the creation of these droplets also causes a large increase in the oil/water interfacial area. The amount of surface area created is enormous, generating a large energy penalty from contacting oil/water. This energy penalty must be reduced by the addition of surfactants which lower the interfacial tension, thus reducing the amount of energy to form an interface. In a microemulsion, the amount of energy required to create the new interfaces is small (i.e., gentle rolling) compared with the amount of energy that is required to form a traditional emulsion (i.e., vigorous mixing). The extra energy that is input to create a micro/macro emulsion is required due to the interfacial curvature. The energy required to change the interfacial curvature can be represented by:

$$F \propto (\kappa/2)(c_1 + c_2 - 2c_0)^2$$

where κ is the bending modulus, c_1 and c_2 are the radii of curvature, c_0 is the spontaneous curvature. The addition of a co-surfactant to the system reduces the κ term, thus greatly reducing the energy required to produce a curved surfactant film at the oil/water interface. With a lower bending modulus, the monolayer undergoes thermal fluctuations further stabilizing the dispersed oil droplets.

Ideally microemulsions in the Windsor IV region are best for cleaning and water wetting the wellbore. The oil will be fully internalized leaving water as the external phase. This allows the oil to be dispersed and removed from the wellbore leaving the casing and/or formation completely water wet.

Experimental Methods

Surfactant Screening of Oil Solubility

Several different surfactant and surfactant/co-surfactant packages were screened. The process involved mixing of surfactants in several different brines at several different concentrations. A set volume of oil (diesel, mineral, etc.) was then added into each sample and gently mixed by rolling the sample vial. This was continued until the solution went cloudy (i.e., could not efficiently microemulsify any more oil) and the various concentrations were recorded. This allowed for the generation of a very basic phase diagram showing where the various surfactant packages were in the desired Windsor IV region.

Cleaning Efficiency

Two different experimental approaches were used to test cleaning efficiency. First, cleaning efficiency was determined using a glass beaker and/or a metal cup which represents the casing surface. First the clean beaker was weighed. After adding the test mud to the beaker, it was reweighed and the mud weight was ascertained by difference. Care was taken to coat the beaker between the 75 ml and 200 ml marks on the beaker. 175 ml of spacer fluid was added to the beaker containing the mud.

A FANN® 35A rheometer was lowered into the fluid. The rheometer was turned on to the 300 RPM test speed. The test was conducted for a pre-determined time (contact time) of 10 minutes. At the end of the test period, the beaker was removed from the rheometer. The spacer was poured out, and the beaker was gently washed with a wash bottle containing deionized water (between 10 ml and 50 ml to wash out the spacer fluid). After the beaker was rinsed out, it was placed in a vacuum oven set to room temperature and dried out under vacuum for 30 minutes. After drying, the beaker was reweighed to measure retained mud.

The second method involved coating the sleeve of a FANN 35A rheometer by rotating in the test mud. The sleeve was made from a section of drill pipe steel, to ensure an accurate representation of the surface that would be encountered. The sleeve was weighed before rotating in the mud and was then weighed again after five minutes in the mud. The sleeve was then immersed in a beaker containing the cleaning solution, rotated for 10 minutes and removed and then weighed. The cleaning efficiency was then calculated as:

$$efficiency = \frac{W_{mud} - W_{post-cleaning}}{W_{mud} - W_{initial}} \times 100$$

Laboratory Data

Oil Solubility

Several different surfactant packages were found to successfully solubilize significant volumes of oil in brine. The final surfactant package was selected for its ability to solubilize large volumes of oil, robustness and availability. This surfactant package is tolerant of mono-valent (potassium chloride, sodium chloride, sodium bromide, etc.) and multi-valent brines (calcium chloride, calcium bromide, etc.), formation water or seawater. It can solubilize large volumes of multiple base oils while remaining clear with little or no agitation (**Fig. 2-3**).

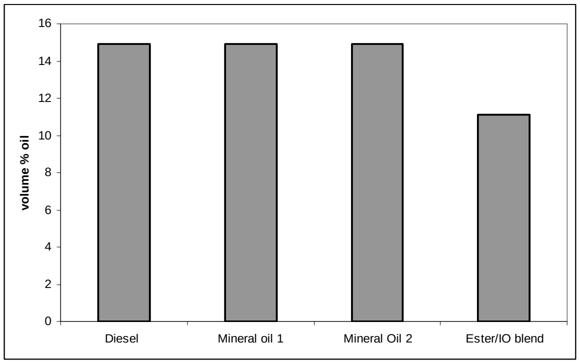

Fig. 2–Volume-% of various oils soluble as clear Windsor IV microemulsions in an 80:20 mixture of brine/surfactant mixture.

Fig. 3–15 volume-% diesel solubilized in an 80:20 mixture of brine/surfactant mixture.

Cleaning Efficiency

The cleaning efficiency of the surfactant package as tested against several different oil-based drilling fluids was also investigated. The cleaning spacer was run as 10 volume-% surfactant mixture and 90 volume-% viscosified weighted pill. Cleaning efficiencies were found to exceed 98% for all invert emulsion oil-based drilling fluids investigated (diesel, mineral oil, internal olefin). The surface of the simulated casing (glass beaker/metal cup) was seen to be cleaned in less than five minutes of contact time (**Fig. 4**).

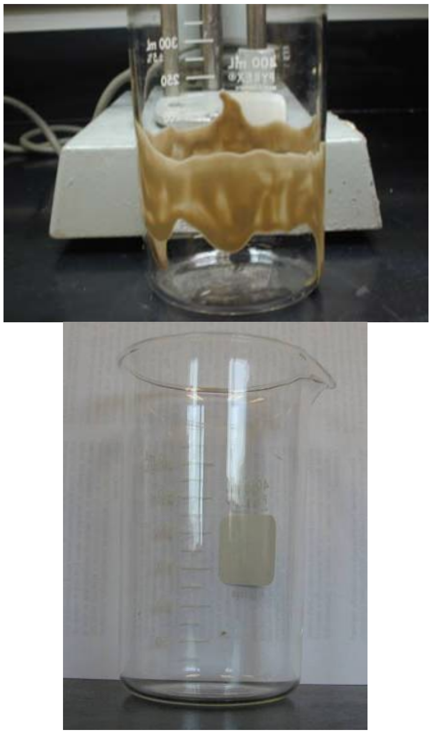

Fig. 4–Cleaning test beaker before (left) and after (right) a 10 minute contact time with the cleaning spacer.

High surfactant loadings were used in this testing as the cleaning spacer was being investigated for use in displacements to completion brines. This requires complete removal of the solids, oil and complete water wetting. Dispersing all the solids consumes a large amount of surfactant coating for all the oil wet surfaces. For fluids with a large loading of hydrophobic fluid loss polymer, a dispersing surfactant was loaded with the microemulsion-forming surfactant to disperse the large (>>1 micron) hydrophobic polymers. This dispersing surfactant was seen to enhance the stability of the microemulsion, allowing for a very effective cleaning spacer.

The spacer also had to approach the cleaning efficiency of solvent-based systems to make it economically viable. Organic solvent-based systems (xylene, terpene, etc.) rapidly solubilize the base oil with little or no shear. These systems then are followed with a water-wetting spacer, which is usually a surfactant in brine at a low loading since there is little organic content to solubilize. Thus, these spacers are very efficient (~100%) at low pumping rates. The microemulsion system has been shown in the testing to approach or match the cleaning efficiencies of the solvent/surfactant system, allowing it to be a viable alternative.

Similar testing was performed using the second screening method for cleaning efficiency. Several different field samples of oil-based drilling fluids were examined and cleaning efficiencies nearing 100% were seen. Before the field trial a 16.0ppg diesel-based invert emulsion drilling fluid field sample was obtained for lab screening. This fluid was representative of the fluid that was to be displaced. Extensive testing was done to ensure that the clean up efficiency would be maximized and near 100%. The surfactant package effectively removed all the oil based drilling fluid present on the sleeve (**Fig. 5**). The fluid showed a cleaning efficiency of 100%, demonstrating that the surfactant package would be successful in the field.

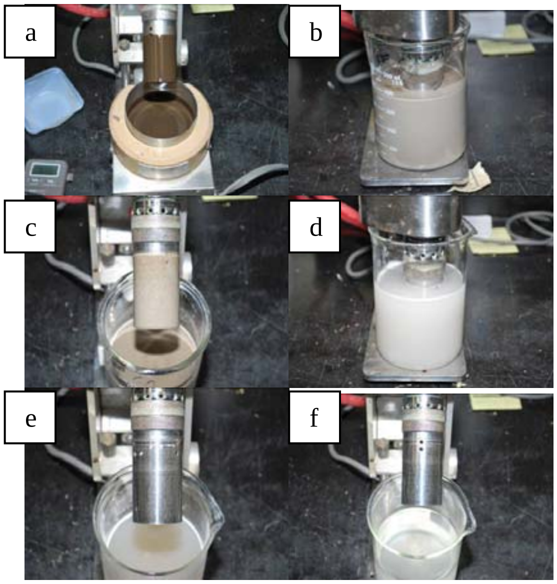

Fig. 5–sleeve coated in oil based drilling fluid (a), sleeve immersed in barite weighted cleaning spacer (b), water wet sleeve with barite on it (c), sleeve immersed in viscosified brine (d), water wet sleeve (e), and sleeve after running in KCl (f).

Field Trials

The field trials were performed in the Haynesville shale region of northwest Louisiana. The operator had drilled the third well of a 10-well discovery phase before launching into full scale development. These wells are drilled with a standard drilling rig and the casing cemented to surface, after which the drilling rig is demobilized and moved to the next drilling site. Coiled tubing is then utilized for the final well clean up and fracture operations. The first two wells were displaced after they were drilled using coiled tubing and conventional solvent/surfactant displacement spacers. The operator used microemulsion surfactant technology for the third well drilled in the Haynesville shale and displaced with coiled tubing as a cost saving measure for future wells.

A solution of 10% microemulsion casing cleaner along with a co-treatment of 10% dispersing surfactant in 10.0 lb/gal NaCl brine was prepared. The microemulsion casing cleaner was pre-mixed and shipped to the well site along with a pre-mixed high viscosity tail sweep.

<u>Microemulsion Casing Cleaner Formulation:</u>
10.0 lb/gal NaCl
20 bbl Microemulsion Casing Cleaner
105 gal Dispersing Surfactant

The well was drilled with a 15.6ppg diesel oil- base mud (OBM), and 11.4ppg $CaCl_2$ was left in the well after bumping the cement plug. A volume of 100 bbl of 3% KCl was used as surface volume to fill the coiled tubing reel. $CaCl_2$ returns were routed to an open top tank and re-circulated. While running in the hole with coiled tubing, a bridge was hit at approximately 15,000 ft and the pump rate was increased to wash through the obstruction. After reaching the toe, spacers were pumped as follows:

Microemulsion Casing Cleaner;	25 bbl Pre-mixed Spacer
High Viscosity Tail Sweep;	10 bbl Pre-mixed Spacer

Spacers were followed with 3% KCl. After 145 bbl of KCl had been pumped, the crew began back washing from toe to heel. Spacers returned on time, and there was no trace of free oil breaking out of the OBM residue left on the casing wall. After the high-viscosity tail sweep returned, 3% KCl returns cleaned up with only a trace of solids and initial well returns of 36 NTU.

The turbidity of the fluid is monitored to determine how well the displacement spacers performed. Relative to the baseline higher turbidity means entrained oil and poor solids removal, lower turbidity means a successful displacement spacer. Final well returns were 11 NTU with 10 NTU fluid being pumped into the wellbore.

Fig. 6–On location images of the field trial performed in the Haynesville shale region of northwest Louisiana.

The use of surfactant nanotechnology in the displacement spacer system resulted in a 35% overall savings in the displacement spacer cost to the operator as compared to a conventional solvent/surfactant displacement. The microemulsion casing cleaner also reduced the number of spacers required for effective cleaning and demonstrated excellent ability to aid in removal of oily residue.

Conclusions

It is possible to harness nanotechnology to effectively engineer a surfactant package for displacements from oil-based or synthetic-based drilling fluids to completion brine. By manipulating the bending elasticity and curvature of a surfactant film it is possible to maximize the water wettability and manipulate the phase behavior to produce organic solvent like properties in an aqueous based fluid. Understanding the nanometer scale phase behavior and thermodynamics of surfactant solutions can lead to highly effective displacement package designs. This can allow one to simplify the amount and variation of surfactants and solvents used and apply a more environmentally friendly solution. This simplification helps to lower operating costs and reduce the chance for human error at the wellsite.

Acknowledgments

The authors would like to thank Halliburton Energy Services, Inc. for their permission to publish this work.

Nomenclature

ppg = *pounds per gallon*
KCl =*potassium chloride*
$CaCl_2$ =*calcium chloride*
NTU = *Nephelometric Turbidity Units*
OBM =*oil based "mud"*

References

1. Patel, A., Wilson J.M., and Longbridges, B.W. 1999. Impact of Synthetic-Based Drilling Fluids on Oilwell Cementing Operations. Paper SPE 50726 presented at the International Symposium on Oilfield Chemistry, Houston, TX, February 16-19.
2. J. Israelachvili. 1992. *Intermolecular and Surface Forces*. Academic Press, London.
3. Nagarajan, R. 2002. *Langmuir. 18,* 31-38.