

## Improving the Kinetic Stability of Emulsions

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### Abstract

Creating a stable emulsion is important for many different drilling, completion, and drill-in fluids. Emulsion stability is especially critical in drill-in fluids as it helps protect the reservoir from damage. This paper highlights laboratory work performed to create a stable emulsion in low-density aqueous-based drill-in fluid.

An emulsion is a blend of two immiscible liquids that are only kinetically stable, that is, the liquids will separate into two phases with time. It is beneficial to increase the time that the emulsion is stable. Emulsions can exist as oil-in-water (O/W) with water as the continuous phase or water-in-oil (W/O) with oil as the continuous phase. Oppositely charged surfactant-surfactant or surfactant-polymer combinations where one molecule is soluble in oil and the other in water form an emulsified fluid. These molecules electrostatically bond at the oil-water interface forming a complex that is soluble only at said interface. This leads to a significant increase in emulsion stability.

When drilling in depleted reservoirs or in underbalanced conditions, it is often necessary to use fluid with a specific gravity (s.g.) of less than 1.0 (water). In order to reduce the s.g. of the water it is necessary to incorporate a lighter phase into the fluid. This can be achieved by emulsifying a non-aqueous fluid into water in order to reduce the overall fluid density. This allows the continuous phase to contact the reservoir while keeping the dispersed phase from disturbing the wetting of the formation, making an oil-in-water emulsion an attractive drill-in fluid for depleted reservoirs.

### Introduction

Low density drill-in fluids (DIF) are desirable when drilling in mature or depleted reservoirs. These reservoirs generally exhibit reduced formation pressures. The hydrostatic pressure exhibited by a column of water may be well in excess of the formation pressure. In these cases it may be beneficial to use an oil-based completion or drill-in fluid to maintain a lower density. However, oil-based fluids may cause formation damage by changing the wettability of the rock/fluid interface from water-wet to oil-wet. In order to help reduce formation damage it is beneficial to retain water or brine contact with the formation surface.

There have been several different approaches to developing a low density DIF while maintaining water wetting conditions with the formation. The approaches have included surfactant-polymer stabilized micro-bubbles, hollow glass

spheres in water and all-oil systems.<sup>1-3</sup> This paper will describe the use of a low density oil-in-water emulsion as a drill-in fluid. Experimental results will show the long-term kinetic stability of the oil-in-water emulsions using the combination of surfactant and polymer chemistries.

### Drill-in fluid Oil-in-Water Emulsions

Oil-in-water emulsions provide a straightforward solution for developing a low-density DIF. By incorporating a lower density internal phase, the overall density of the fluid will be lowered while maintaining water-wet conditions in the reservoir.

### Emulsions

Emulsions are dispersions of two immiscible liquids with one liquid constituting the dispersed (internal) phase and the other fluid the continuous (external) phase. Emulsions are thermodynamically unstable systems and have to be stabilized by the use of surfactants or surface active solids to remain dispersed for any functionally relevant period of time.

The stability of emulsions is determined by intermolecular interactions and surface forces. In order for an emulsion to form, large amounts of energy must be put into the system in the form of shear. This energy is required due to an increase in conformational entropy and surface area. This requirement is best explained using a thermodynamic framework. 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  $\gamma$  is the interfacial tension at the oil-water interface.

If the free energy is less than zero then the process is spontaneous; if it's greater than zero then energy is required to be input into the system to cause the desired change. When creating an emulsion, 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.

Since the change in Gibbs free energy is positive,

emulsions are only kinetically stable, which means they will phase separate with time. Emulsification failure can occur by several different mechanisms, mainly coalescence and Ostwald ripening. Coalescence occurs when two dispersed droplets contact each other and combine to form a larger droplet. This will cause the droplets to get larger and larger with time, eventually leading to separation into two phases. The other mechanism, Ostwald ripening, is caused by molecular diffusion of the internal phase through the external phase due to its partial solubility in the external phase. Smaller droplets generally lose their mass to larger droplets. This can be explained in terms of Laplace pressure:

$$P = \frac{2\gamma_{ow}}{r}$$

where  $P$  is the pressure inside the droplet and  $r$  is the radius of the droplet. Thus smaller droplets (i.e., smaller  $r$  term) have higher internal pressure and this higher pressure causes the growth of large droplets at the expense of little droplets. Both processes lead to larger and larger droplets and eventually phase separation. There are several approaches to stabilize emulsions from microemulsions to solid stabilized Pickering emulsions.

The addition of surfactant/emulsifier decreases the surface tension, making the droplets more stable. The surfactant can also create a steric and/or electrostatic barrier to slow coalescence. This is how kinetically stabilized emulsions are currently produced.<sup>4</sup> A second option is a microemulsion. A microemulsion will use a mixture of surfactants and/or cosurfactants to create a low density thermodynamically stable versus a kinetically stabilized emulsion. Although a microemulsion will be indefinitely stable, large amounts of surfactants are required to solubilize large volumes of oil-in-water, making the solution less economically feasible. Microemulsions can also be very sensitive to external stimuli, making them difficult to drill with as the primary emulsifier.

Solids can also act as emulsifiers at the oil-water interface, stabilizing emulsions.<sup>5</sup> The energy required to displace a solid particle from the interface is roughly 10-100 times that required to displace a surfactant/emulsifier from the same interface. Thus, solid/surfactant stabilized emulsions will have enhanced stability over just surfactants alone. The weakness of solids-only stabilized emulsion is that the inclusion of drill solids or contaminants can destabilize the emulsion, making them of little value as a drill-in fluid.

It is more economically and operationally appealing to extend the kinetic stability of a traditional emulsion using a new surfactant-polymer technology.<sup>6</sup> This approach combines traditional oil-soluble surfactant emulsifiers and water soluble polyelectrolytes. Oppositely charged surfactant-polymer complexes, where one molecule is soluble in oil and the other in water, form an emulsified fluid. These molecules electrostatically bond at the oil-water interface forming a complex that is soluble only at said interface. This leads to a significant increase in emulsion stability.

### Traditional Emulsifiers

The original formulation for the oil-in-water drill-in fluid focused on traditional emulsifiers. These emulsifiers have been observed to work very effectively when used in conjunction with solids and/or a secondary emulsifier. The drill-in fluid was being designed to be solids-free to minimize formation damage. The effect of being solids-free on the emulsion was examined by testing its stability. The stability testing involves mixing the necessary components together for a set time and then observing their stability over a 24-hour period.

The general fluid formulation called for the emulsification of approximately 20 volume-% internal phase (diesel) in 80 volume-% external phase (freshwater and 3 weight-% KCl). Several different emulsifier packages were examined:

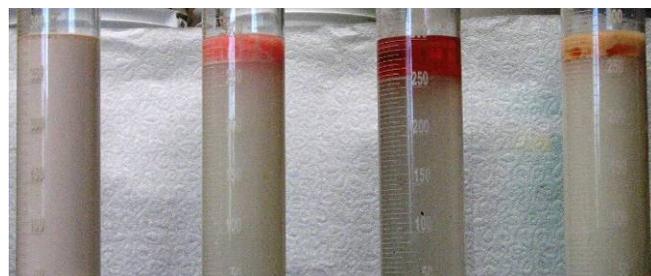
- Emulsifier 1: Non-ionic and anionic surfactant blend
- Emulsifier 2: Non-ionic surfactant blend
- Emulsifier 3: Fatty acid emulsifier blend

**Figure 1** shows Emulsifier 1 and 2 being effective at emulsifying diesel in freshwater and the emulsion remains homogenous after aging 24 hours at room temperature.



**Figure 1: Emulsifier 2 in freshwater (left) and KCl (left, center) and Emulsifier 1 in freshwater (right, center) and KCl (right).**

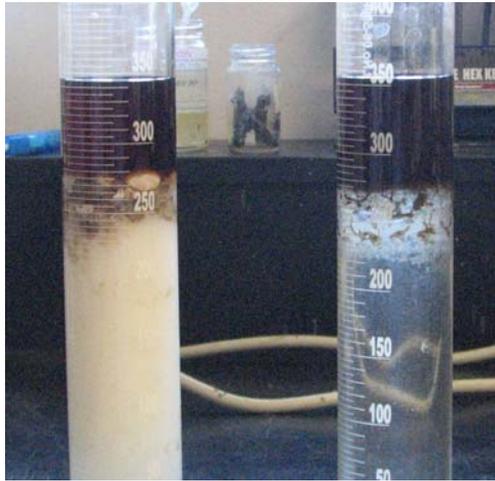
These emulsifiers are ineffective at emulsifying diesel in 3 weight-% KCl. Phase separation occurred in less than 24 hours in the diesel-saltwater emulsions. The samples were then hot-rolled at 230°F for 16 hours and the emulsion was then remixed and allowed to age (**Figure 2**).



**Figure 2: Emulsifier 2 in freshwater (left) and KCl (left, center) and Emulsifier 1 in freshwater (right, center) and KCl (right) after hot-rolling for 16 hours at 230°F.**

Emulsifier 2 was seen to completely fail after hot-rolling in both fresh and salt water, with phase separation of the diesel oil occurring. Emulsifier 1 was still stable in fresh water even after hot-rolling and it failed in the salt water.

Emulsifier 3 was a traditional drilling fluid emulsifier which is used currently for low density drill-in fluid diesel-in-saltwater emulsions. This emulsifier showed little promise for this solids-free application as is evidenced in **Figure 3** below.



**Figure 3: Emulsifier 3 in freshwater (left) and in 3 wt-% KCl (right)**

While fatty acid-based emulsifiers have seen tremendous success in the drilling fluids industry, when used in solids-free formulations they have been observed to have difficulty stabilizing emulsions. This is likely due to their secondary solids wetting capability which allows solids to interact at the oil-water interface, further stabilizing the emulsion. Without solids present, this secondary mechanism of stabilization is no longer present causing the emulsion to rapidly degrade.

The freshwater fluid with Emulsifier 1 was further examined as a possible drill-in fluid by examining the effect of fluid additives on the emulsion stability. Non-ionic biopolymer was added as a viscosifier and cross-linked starch was added as fluid loss agent. The addition of these materials caused the emulsion using Emulsifier 1 to separate after hot rolling at 230°F for 16 hours (**Figure 4**). This fluid had greater than 40% separation.

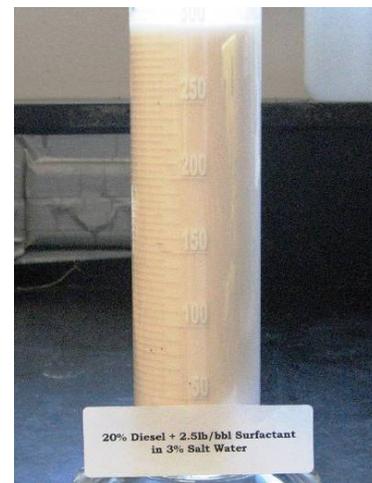


**Figure 4: Emulsifier 1 diesel in saltwater emulsion with viscosifier and fluid loss agent added to the system.**

### **Polymer-Surfactant Emulsions**

Several different formulations were generated that showed extraordinary emulsion stability. Mixtures of oil-soluble surfactants with both water-soluble synthetic polymers and biopolymers were explored. The synthetic polymers allowed the creation of emulsions that were able to withstand elevated temperatures. The use of biopolymers allows the option of removal of polymers retained by the rock, thus remediating any formation damage, by acidizing.

Emulsifier Package 1 (EP1) was formulated with a water-soluble anionic synthetic polymer and an oil-soluble cationic surfactant. The same drill-in fluid was examined as above (20:80 diesel:water ratio, viscosifier, and fluid loss agent) with a total loading of the emulsion package of 2.5 lb/bbl. The emulsion remained intact after hot rolling (**Figure 5**).



**Figure 5: EP1 diesel in saltwater emulsion with viscosifier and fluid loss agent added to the system after hot-rolling 16 hours at 230°F.**

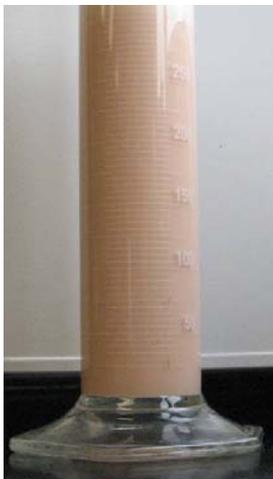
The fluid was then monitored for another 72 hours and no separation of the two phases was seen, suggesting the emulsion remained stable. Since the fluid showed such enhanced stability the fluid was monitored for eight weeks at room temperature. At Week 8 the emulsion still showed no failure, suggesting that the new emulsion stabilization technique was far superior to traditional methods (**Figure 6**).



**Figure 6: EP1 diesel in saltwater emulsion with viscosifier and fluid loss agent added to the system after hot-rolling 16 hours at 230°F.**

The emulsion stabilized by EP1 offered performance similar to a solid/surfactant stabilized emulsion, suggesting that the complex formed at the interface is truly insoluble in either liquid phase.

Many operators prefer to use biopolymers in drill-in fluid as they are easier to remove from the wellbore with acidizing or enzymatic methods. The desire for an easily degradable polymer led to the development of Emulsifier Package 2 (EP2) formulated using a water-soluble anionic biopolymer and an oil-soluble cationic surfactant. The same drill-in fluid was examined as above (20:80 diesel:water ratio, viscosifier, and fluid loss agent) with a total loading of the emulsion package of 2.5 lb/bbl. The results were very similar to those using the synthetic polymer. The emulsion remained stable after hot-rolling for 16 hours at 230°F (**Figure 7**).



**Figure 7: EP2 diesel in saltwater emulsion with viscosifier and fluid loss agent added to the system after hot-rolling 16 hours at 230°F.**

The fluid made using EP 2 was monitored for a total of eight weeks also. The emulsion showed good stability until Week 4 when minor phase separation occurred. The

experiment was stopped at Week 8 when the total amount of phase separation was 10-vol-%. This earlier separation was most likely due to the biopolymer being degraded in the aqueous environment and it also can be attributed to the fluid seeing elevated temperatures.

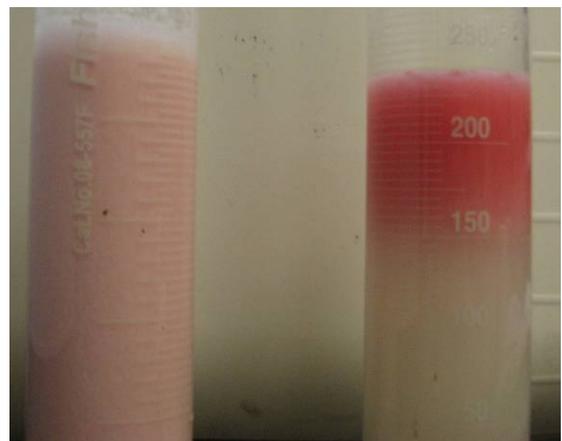
The fluid properties of both EP1 and EP2 were shown to be ideal for a drill-in system. The rheology was similar to the traditional emulsifier stabilized fluids. The pH of the water phase before introducing diesel was >10 for both fluids. Any decrease in pH will actually strengthen the emulsifier package as the components also help to buffer the fluid.

To show the breadth of the emulsion stabilization method, Emulsifier Package 3 was formulated using a water-soluble cationic synthetic polymer and an oil-soluble anionic surfactant. The same drill-in fluid was examined as above (20:80 diesel:water ratio, viscosifier, and fluid loss agent) with a total loading of the emulsion package of 2.5 lb/bbl. The fluid showed excellent emulsion stability, remaining stable for 2+ weeks after hot-rolling (**Figure 8**).



**Figure 7: EP3 diesel in saltwater emulsion with viscosifier and fluid loss agent added to the system after hot-rolling 16 hours at 230°F.**

This fluid had to be buffered between pH 8-10 to be effective. A comparison between buffered and non-buffered fluid is shown below in **Figure 9**.



**Figure 9: Comparison of EP 3 fluid buffered to above pH 8 (left) and at pH 6 (right) after 4 hours.**

The effective pH is ideal for a drill-in fluid and can be easily maintained using traditional pH control methods on the rig site. Figure 9 also demonstrates the stimuli-responsive nature that is possible using this method to stabilize emulsions. Simply by changing the pH of the water external phase, the diesel internal phase can be easily separated from the fluid. The pH 6 fluid was well separated within eight hours (**Figure 10**) and was completely separated within 48 hours.



**Figure 10:** EP3 diesel in saltwater emulsion at pH 6 after 8 hours.

Further work has been performed using:

1. Water-soluble cationic surfactant and an oil-soluble anionic surfactant
2. Water-soluble anionic surfactant and an oil-soluble cationic surfactant

Similar emulsions were created as shown above with stabilities up to two weeks after hot rolling for 16 hours at 230°F. These fluids will offer a polymer-free approach to improved kinetic stabilization of emulsions. This method will be preferred in reservoirs where formation damage by polymer is a concern.

## Conclusions

A novel method of improving the stability of emulsions for drill-in fluids has been found. By using polymer-surfactant interactions, improved kinetic stability of emulsions has been demonstrated. These new emulsions showed much longer stability than current emulsifiers in use and are more tolerant of other components introduced into the fluid than surfactant, solid, or surfactant-solid stabilized emulsions.

Synthetic polymer-surfactant, biopolymer-surfactant, or surfactant-surfactant mixtures have been used to stabilize the various emulsions. The fluids showed stabilities of 2-8 weeks after being hot-rolled at 230°F for 16 hours.

It should be possible by varying the ratios of oppositely charged surfactants and polymers, to stabilize emulsions using a wealth of different molecules. These ideas are also applicable for water-in-oil emulsions, opening up opportunities for improved emulsion stabilization in invert-emulsion drilling fluids.

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## Nomenclature

*DIF* = Drill in fluid  
*KCl* = potassium chloride

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