AADE-02-DFWM-HO-24

Invert Emulsion Drilling Fluids: Effect of Emulsifier when Changing Synthetic and Base Oil

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Abstract

The key properties of invert emulsion drilling fluids are strongly influenced by the emulsifier and the type of synthetic base or oil, as well as other formulation variables, such as oil/water ratio, additive chemistry, and additive concentration. A systematic evaluation of emulsifiers, with various base oils (including olefins, paraffin, ester, mineral oil, and diesel oil) was conducted for various oil/water ratios and drilling fluid densities. Results are discussed in terms of effectiveness of the emulsifiers (i.e., emulsion droplet size), high-temperature high-pressure fluid loss (HTHP), electrical stability, rheological properties, and thermal stability of the drilling fluid formulations. The effect of drilling fluid contaminants on emulsion stability and physical properties is discussed for formulations with fluid densities up to 18 lb/gal.

Introduction

Invert emulsions require surfactants for emulsification of brine and as wetting agents for solids incorporation. Most emulsifiers used for invert emulsion drilling fluids are alkanolamides or imidazolines, derived from a variety of starting materials (e.g., fatty acids, amines). Emulsifiers for invert emulsion drilling fluids can be selected using the hydrophile-lipophile balance (HLB) of the emulsifier. A HLB value between four and six is usually adequate for initial testing.[1-3] Other parameters of emulsion formulations (hydrophilic group, length of lipophilic chain, type of oil, mixing temperature, type and concentration of salts),[4] need to be evaluated in terms of downhole conditions. The formulation and composition variables, as well as the mixing process, have a compensating effect on the emulsion.[5]

Wetting agents, used to promote oil-wetting of the normally hydrophilic mineral solids (drilled solids, barite, etc.), are commonly fatty acid sulfonates or polyimides. In some cases, only one surfactant is required in order to achieve good emulsification and oil-wetting of solids. However, in many formulations, two surfactants are necessary, one acting primarily as an emulsifier, and the second acting primarily as a wetting agent.

Proper emulsifier selection and application in drilling fluids has a significant economic impact, in terms of reduction of lost time and potential trouble, and has a direct impact on overall drilling performance and results.This article describes the results of a systematic evaluation of various emulsifiers in invert emulsion formulations, using the following base fluids: olefins, paraffin, ester, mineral oil and diesel. The results indicate that the properties of the invert emulsion drilling fluids are strongly influenced by the type of emulsifier and the base fluid. The differences in observed properties for formulations with various base fluids were more noticeable when the fluids were evaluated under conditions that approached the limits for optimum formulations, such as high temperatures (> 300°F), low temperatures (< 40°F), contamination,and oil/water ratio.

Effect of emulsifier on emulsion droplet size

Invert emulsions prepared with anionic or nonionic surfactants were evaluated in a base formulation with an ester as the base fluid. Emulsifiers that were studied included surfactants having various polar groups, including sulfonates, phosphates, carboxylates, ethoxylated sorbitan ester, ethoxylated fatty acids and glycol ester. The base formulation had an 80/20 base fluid/brine ratio, 4 lb/bbl organophilic clay, and 25% calcium chloride brine. The fluids were mixed and subjected to hot-roll aging for 16 hours at 300°F. The index property for these formulations was the emulsion droplet size distribution and average droplet size, measured immediately after mixing and after aging at 300°F. The emulsion droplet size is a microscopic property that allows fast screening of surfactants used as emulsifiers. Studies made at the Baker Hughes Inteq laboratories reveal no reliable correlation between average droplet size and electrical stability and/or other typical properties for invert emulsions.

Table 1 shows results of average droplet size obtained with various emulsifiers. The results indicate:

- Emulsifiers containing sulfonate groups are very similar in chemical structure and produce emulsions having very small initial droplet sizes. Droplet sizes increase after heat aging, but still remain at a reasonable size for the intended emulsions. In general, anionic surfactants are good emulsifiers for emulsions subject to large temperature changes; however, anionic surfactants are sensitive to ionic contamination. Sulfonated anionic surfactants can overcome this problem when calcium or magnesium is used in the synthesis of the emulsifier.[6]

- Branched phosphate emulsifiers are more lipophilic than linear phosphate emulsifiers, and generate reasonable initial emulsion droplet size. However, both types of phosphate emulsifiers generated large droplet sizes after hot-roll aging at 300°F.
- Emulsions using nonionic emulsifiers were evaluated utilizing various surfactant types, including alkanolamides, sorbitan ester, glycol ester, and imidazolines. For emulsions stabilized with alkanolamides and aged at 300°F, results show that the average droplet size decreases as the lypophilic group (or carbon chain) increases. After hot-roll aging at 300°F, emulsions formulated with sorbitan ester and glycol ester exhibited very low droplet size, which is desirable with regard to long-term stability and rheological properties. Emulsions stabilized with nonionic surfactants are temperature-dependent, since the solubility of non-ionic surfactants varies with temperature.[6] However, blending of nonionic surfactants with anionic surfactants yields a combination that could stabilize the emulsion for temperatures up to 300°F.

Stability of invert emulsions

Droplet size, as a function of time, was measured for selected invert emulsion formulations that showed relatively small droplet sizes immediately following aging for 16 hours at 300 and 350°F. Samples were stored at ambient temperature and droplet size distributions were measured every few days throughout the 30-day test period.

The average droplet size of emulsions based on the formulation containing polyamide emulsifier, isomerized olefin (as base fluid), organophilic clay, and base fluid/water ratio of 85/15 is shown in Figure 1. For the sample aged at 300°F, average droplet sizes increased from 2 to 20 microns after aging, then remained constant for the remainder of the evaluation period. The sample aged at 350°F shows larger droplet sizes after the second day, which then remained stable at approximately 70 microns.

These results indicate that the emulsion hot rolled at 300°F remained stable for a longer period of time than the one hot rolled at 350°F. The emulsion with an average droplet size of 70 microns could eventually show water separation, generated by coalescence of larger droplets at static conditions. However, drilling fluids are subjected to high mixing/shear conditions when pumped through bit nozzles. The mechanical energy of this process regenerates smaller droplet sizes and inhibits coalescence of larger droplets that would eventually lead to water-phase separation.

Exposure to higher temperatures will decrease emulsion stability. Increased temperatures result in greater coalescence rates brought about by accompanying decreases in bulk viscosity, interfacial tension, and surfactant adsorption at the interface. Increased Brownian motion at higher temperatures contributes to decreased emulsion stability.

Invert emulsions formulated with various base fluids and stabilized with alkanolamide emulsifier

A systematic evaluation of invert emulsions with various base fluids, including olefins, paraffin, ester, mineral oil and diesel, stabilized with an alkanolamide emulsifier was performed for 15 lb/gal and 10 lb/gal fluid densities. Fluid compositions are shown in Table 2. Emulsifier effectiveness is discussed as indicated by emulsion droplet size, HTHP fluid loss, electrical stability, and rheological properties for each base fluid.

Properties of 15 lb/gal formulations, after being hot-rolled at 300°F, are shown in Table 3. The results indicate:

- Fluids exhibited similar plastic viscosity (PV) and yield point (YP) values, except for the isomerized olefin formulation which has a relatively high PV and low YP when compared to formulations prepared with the other four base fluids. The low-rpm reading and gel measurements are very similar for all formulations, with the exception of the mineral oil formulation, which shows lower values compared with the other formulations.
- HTHP filtration shows that the best performance was obtained with the isomerized olefin formulation followed by the ester formulation.
- Electrical stability measurements are acceptable, ranging from 1094 volts for the isomerized olefin formulation, to 1500 volts for the diesel formulation.
- Particle size measurements show a very small emulsion droplet size for the diesel oil formulation, followed by the ester and the isomerized olefin fluids. The mineral oil and paraffin formulations show much larger emulsion droplet size. These results reveal no correlation between droplet size and electrical stability, or other typical properties of invert emulsions.

The differences in fluid properties observed in the five base fluid formulations, where the only variable is the type of base fluid, demonstrates the influence of the equivalent alkane carbon number (EACN) of the base fluid on the properties of invert emulsions. EACN is determined from emulsification studies in which the emulsion stability of an "unknown" base fluid is compared with the emulsion stability of base oils of known EACN, using one or more common emulsifiers. The EACN depends on the molecular configuration and number of carbon atoms available in the base fluid chain. Aromatics have a lower EACN than a linear paraffin having the same number of carbon atoms. Diesel has the lowest EACN number, followed by mineral oil, paraffin and olefin base fluids.

Evaluation of 10 lb/gal formulations, described in Table 2, was conducted with fluids that were hot-rolled at 250°F. Rheological properties, HTHP filtration, electrical stabilities, and emulsion droplet sizes are presented in Table 4. The results indicate:

- In general, mineral oil or paraffin fluid exhibited the lowest rheological properties. In contrast, the diesel fluid exhibited the highest rheological properties. Rheological properties varied significantly with the base fluid used in the formulation. Yield point ranged from 7 for the paraffin based fluid, up to 21 for the ester fluid, and 31 for the diesel fluid. Not surprisingly, similar tendencies were observed for the low-rpm readings and gel-strength properties.
- The lowest HTHP fluid loss was obtained with the diesel formulation, followed by isomerized olefin, mineral oil, paraffin, and ester formulations.
- Electrical stability measurements were similar, except for the paraffin formulation that was about 30% lower than the average.
- All formulations performed well, as indicated by emulsion droplet size, with average droplet sizes lower than 3.5 microns after aging at 250°F.

Effect of drilling fluid contaminants on invert emulsions

The effect of contaminants on invert emulsion fluids varies with the type of emulsifier used in the formulation. Drilling contaminants were evaluated in a 14 lb/gal base formulation of isomerized olefin with 80/20 base fluid/water ratio, 5 lb/bbl organophilic clay, and 12 lb/bbl emulsifier. Rheological properties of the fluids were measured at 120°F, after aging the samples at 250°F.

Table 5 contains properties of two base formulations and the same fluids contaminated with 45 lb/bbl Rev-Dust. Except for 10-min gel strength and electrical stability, the measured properties do not show large differences between the two base fluids. However, when the samples were contaminated with Rev-Dust, the formulation with emulsifier 2 shows a considerable increase in some rheological properties and the HTHP fluid loss.

To evaluate the effect of solids contamination at low temperature, similar formulations with reduced organophilic clay concentration (4 lb/bbl) and increased emulsifier treatment (15 lb/bbl), were mixed and hot-rolled at 150°F. The rheological properties were measured at 40°F. Results shown in Table 6 reveal a significant increase in plastic viscosity for the base fluid with emulsifier 2, which is even more noticeable in the sample contaminated with Rev-Dust. These rheological properties are extremely high for field operations.

These results indicate that both emulsifiers 1 and 2 are good surfactants for stabilization of invert emulsions for use between 40 and 250°F. However, emulsifier 2 does not perform well as a wetting agent; therefore, a second surfactant that will act as a wetting agent is required to improve fluid properties after solids contamination. The effects of contaminants, including seawater, solids, and cement were evaluated in a high-density formulation. The base formulation used was an 18 lb/gal isomerized olefin fluid with, 85/15 base fluid/water ratio, 5 lb/bbl of organophilic clay, and 12 lb/bbl emulsifier. The results obtained with emulsifiers 1 and 2 are shown in Figures 1 and 2, respectively.

Rheological properties at 120°F, electrical stability, and HTHP filtration of the samples with emulsifiers 1 and 2 (after 250°F aging), are similar for the base formulation; however, compared with emulsifier 1, lower HTHP fluid loss and higher electrical stability were observed in formulations using emulsifier 2. Formulations contaminated with cement or seawater exhibited no noticeable effects on properties with either emulsifier 1 or 2.

As was observed in the lower density fluid discussed previously, evaluation of emulsifier 2 in the fluid contaminated with Rev-Dust shows the need for a wetting agent in the formulation. The same evaluation with emulsifer 1 does not indicate the need for a wetting agent.

Conclusions

- The properties of invert emulsion fluids depend on the type of base fluid used.
- For the same type of emulsifier, variation of the lipophilic chain generates noticeable differences in fluid properties, when these are exposed to solid contaminants.
- Laboratory tests prove that emulsion droplet size measurement is a quick and useful technique for basic screening of emulsifiers. However, from our studies, there is no apparent correlation between emulsion droplet size and properties such as electrical stability, HTHP filtration, and rheological properties.
- The evaluation of emulsifiers with the same polar group and different lipophilic chain proves that emulsifier HLB affects the emulsification of brine-in-base fluid and wettability of solid contaminants.

Acknowledgements
The authors would like to thank Baker-Hughes Inteq for permission to publish this paper.

Nomenclature
HTHP = High-pressure, high-temperature fluid loss
HLB = Hydrophile-lipophile balance
PV = Plastic viscosity
YP = Yield point
ES = Electrical stability
S/O or O/W = Synthetic/water ratio or Oil/water ratio

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Tables

Table 1 Average droplet sizes of brine-in ester emulsions 10 lb/bbl surfactant

Emulsifier	Type of Surfactant	Initial Droplet Size, microns	Droplet Size after Hot Roll at 300°F, microns
Branched Polyethoxylate Phosphate	anionic	10.1	69.3
Linear Polyethoxylate Phosphate	anionic	37.4	64.9
Linear Calcium Dodecylbenzene Sulfonate	anionic	3.1	30.1
Calcium Phenylsulfonate	anionic	1.2	15.5
Sorbitan Monooleate	nonionic	1.2	5.2
Glycol Stearate	nonionic	7.7	10
Alkanolamide (C_{18} two Double Bonds)	nonionic	11.1	23.1
Alkanolamide (C_{18} one Double Bond)	nonionic	2.2	69.4
Alkanolamide (C_{12})	nonionic	18.8	44.5

Table 2 Invert emulsion formulations for 10 and 15 lb/gal fluids

Additives	Density: 15 lb/gal				
	Isomerized Olefin	n-Paraffin	Ester	Mineral Oil	Diesel
Base fluid, bbl	0.58	0.57	0.59	0.59	0.59
Organophilic clay, lb/bbl	4	4	4	4	4
Emulsifier, lb/bbl	10	10	10	10	10
25% $CaCl_2$, bbl	0.11	0.11	0.11	0.11	0.11
Barite, lb/bbl	411	420	392	403	395
S/W or O/W ratio	85/15	85/15	85/15	85/15	85/15
Additives	**Density: 10 lb/gal**				
	Isomerized Olefin	**n-Paraffin**	**Ester**	**Mineral Oil**	**Diesel**
Base fluid, bbl	0.61	0.61	0.62	0.62	0.62
Organophilic clay, lb/bbl	4	4	4	4	4
Emulsifier, lb/bbl	10	10	10	10	10
25% $CaCl_2$, bbl	0.27	0.27	0.28	0.28	0.28
Barite, lb/bbl	119	129	99	110	102
S/W or O/W ratio	70/30	70/30	70/30	70/30	70/30

Table 3 Properties of 15 lb/gal fluids with various base fluids after hot-rolling at 300°F

Properties Rheology at 120°F	Isomerized Olefin	n-Paraffin	Ester	Mineral Oil	Diesel
Plastic viscosity, cP	27	19	20	24	23
Yield point, lbf/100 ft^2	4	11	15	12	11
3-rpm reading	8	6	8	5	7
10-sec gel, lbf/100 ft^2	8	8	9	7	8
10-min gel, lbf/100 ft^2	8	10	10	8	10
300°F HTHP fluid loss, cm^3/30 min	4	22	8	18	14
Electrical stability, volts	1094	1200	1384	1204	1500
Droplet size, microns	23.1	44.5	22.3	48.9	3.6

Table 4 Properties of 10 lb/gal fluids with various base fluids after hot-rolling at 250°F

Properties Rheology at 120°F	Isomerized Olefin	n-Paraffin	Ester	Mineral oil	Diesel
Plastic viscosity, cP	15	12	14	23	18
Yield point, lbf/100 ft^2	14	9	21	7	31
3-rpm reading	7	4	15	5	15
10-sec gel, lbf/100 ft^2	9	6	13	7	15
10-min gel, lbf/100 ft^2	11	7	13	7	17
250°F HTHP fluid loss, cm^3/30 min	2	6	8	5	1
Electrical stability, volts	902	595	736	828	950
Droplet size, microns	2.4	3.4	2.2	1.6	3.1

Table 5 Properties of 14 lb/gal fluids formulated with isomerized olefin base fluid

Properties Rheology at 120°F	Base Formulation		Base Formulation with Rev-Dust	
	Emulsifier 1	Emulsifier 2	Emulsifier 1	Emulsifier 2
6-rpm reading	8	8	13	19
3-rpm reading	7	7	12	18
10-sec gel, lbf/100 ft^2	8	9	13	29
10-min gel, lbf/100 ft^2	9	15	27	39
PV, cP	22	26	48	40
YP, lbf/100 ft^2	13	10	16	17
ES, volts	1178	865	816	543
250°F HTHP fluid loss, cm^3/30 min	4	5	10	24

Table 6 Properties of 14 lb/gal fluids formulated with isomerized olefin base fluid

Properties at 40°F	Base Formulation		Base Formulation with Rev-Dust	
	Emulsifier 1	Emulsifier 2	Emulsifier 1	Emulsifier 2
6-rpm reading	15	9	17	13
3-rpm reading	13	7	15	11
10-sec gel, lbf/100 ft^2	13	11	14	17
10-min gel, lbf/100 ft^2	14	23	17	41
PV, cP	45	96	74	122
YP, lbf/100 ft^2	31	26	37	28

Figures

Figure 1 Stability of invert emulsion formulated with an alkanolamide surfactant

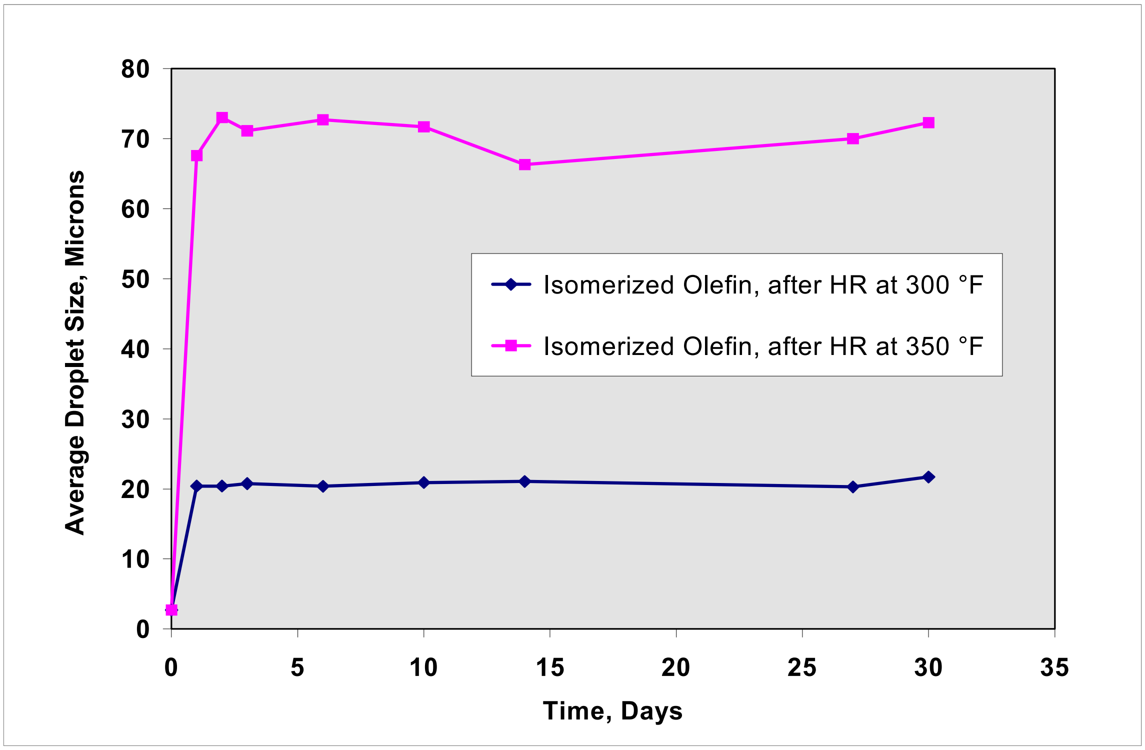

Figure 2 Effect of contaminant in 18 lb/gal fluids stabilized with emulsifier 1

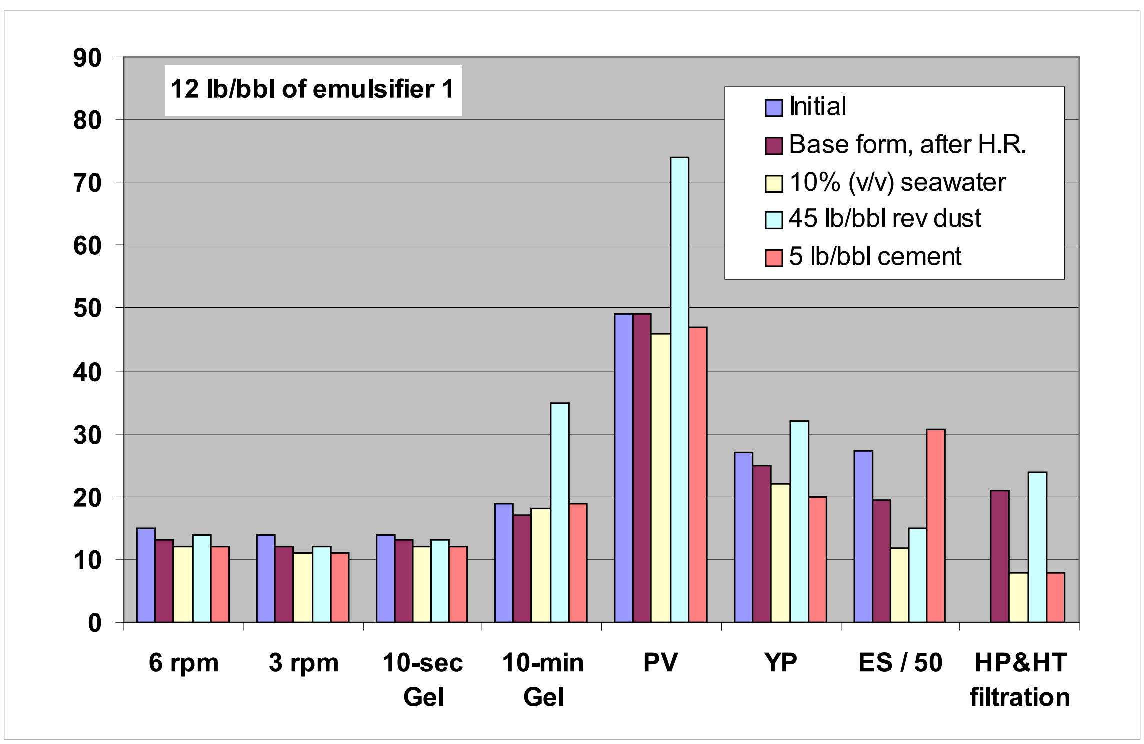

Figure 3 Effect of contaminant in 18 lb/gal fluids stabilized with emulsifier 2