

WETTABILITY AND PREDICTION OF OIL RECOVERY FROM RESERVOIRS  
DEVELOPED WITH MODERN DRILLING AND COMPLETION FLUIDS

Semiannual Report

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## **Project Objectives**

The objectives of this project are:

1. to improve understanding of the wettability alteration of mixed-wet rocks that results from contact with the components of synthetic oil-based drilling and completion fluids formulated to meet the needs of arctic drilling;
2. to investigate cleaning methods to reverse the wettability alteration of mixed-wet cores caused by contact with these SBM components; and
3. to develop new approaches to restoration of wetting that will permit the use of cores drilled with SBM formulations for valid studies of reservoir properties.

## **Abstract**

We report on progress in three areas. In part one, the wetting effects of synthetic base oils are reported. Part two reports progress in understanding the effects of surfactants of known chemical structures, and part three integrates the results from surface and core tests that show the wetting effects of commercial surfactant products used in synthetic and traditional oil-based drilling fluids.

An important difference between synthetic and traditional oil-based muds (SBM and OBM, respectively) is the elimination of aromatics from the base oil to meet environmental regulations. The base oils used include dearomatized mineral oils, linear alpha-olefins, internal olefins, and esters. We show in part one that all of these materials except the esters can, at sufficiently high concentrations, destabilize asphaltenes. The effects of asphaltenes on wetting are in part related to their stability. Although asphaltenes have some tendency to adsorb on solid surfaces from a good solvent, that tendency can be much increased near the onset of asphaltene instability. Tests in Berea sandstone cores demonstrate wetting alteration toward less water-wet conditions that occurs when a crude oil is displaced by paraffinic and olefinic SBM base oils, whereas exposure to the ester products has little effect on wetting properties of the cores.

Microscopic observations with atomic forces microscopy (AFM) and macroscopic contact angle measurements have been used in part 2 to explore the effects on wetting of mica surfaces using oil-soluble polyethoxylated amine surfactants with varying hydrocarbon chain lengths and extent of ethoxylation. In the absence of water, only weak adsorption occurs. Much stronger, pH-dependent adsorption was observed when water was present. Varying hydrocarbon chain length had little or no effect on adsorption, whereas varying extent of ethoxylation had a much more significant impact, reducing contact angles at nearly all conditions tested. Preequilibration of aqueous and oleic phases appeared to have little influence over surfactant interactions with the mica surface; the solubility in water of all three structures appeared to be very limited.

Commercial emulsifiers for both SBM and OBM formulations are blends of tall oil fatty acids and their polyaminated derivatives. In part three of this report, we integrate observations on smooth surfaces with those in Berea sandstone cores to show the effects of low concentrations of these products with and without the added complexity of adsorbed material from crude oils. Unlike the polyethoxylated amines studied in part two, there are significant non-equilibrium effects that can occur when water first contacts oil with dissolved surfactant. Very oil-wet conditions can be produced on first contact. Surfactant dissolved in oil had less effect on wetting alteration for one combination of crude oil and surfactant, although the generality of this observation can only be assessed by additional tests with crude oils of different composition. The wettability-altering effect of surfactants on both mica and Berea sandstone was most significant when they contacted surfaces after adsorption of crude oil components. Tests without crude oil might underestimate the extent of wetting change possible with these SBM and OBM emulsifiers.

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## **Wetting Effects of Synthetic Oil-Based Mud Components**

Synthetic and traditional oil-based muds can alter the wetting of cores with which they come in contact because of the surface active materials added to promote emulsification of water and oil-wetting of cuttings. Synthetic oil-based muds (SBM) have an additional potential for wetting alteration beyond that of traditional oil-based muds (OBM) because of their potential to destabilize asphaltenes in crude oil. In the first part of this report, we focus on the effects of base oils on asphaltene stability and wetting alteration. Parts two and three address the wetting effects of surfactants for materials of known structure and for commercially applied products.

### **1. Effect of Synthetic Drilling Fluid Base Oils on Asphaltene Stability and Wetting in Sandstone Cores**

Yongsheng Zhang, Jianxin Wang, Norman R. Morrow, and Jill S. Buckley

#### **1.0 Abstract**

Tests of imbibition rates in Berea sandstone cores have been used to examine the wettability effects of displacement of crude oils with a number of synthetic base oils. In all cases examined to date, the products that flocculated asphaltenes also caused water-wet sandstone cores to become markedly less water-wet or even oil-wet. Relatively minor effects on wetting were observed with base oils that did not destabilize asphaltenes. A simple diagnostic test can be used to test specific crude oil/base oil pairs so that base oils can be selected for specific drilling projects so as to avoid alteration of core wetting by destabilization of asphaltenes.

#### **1.1 Introduction**

With the increasing use of oil-based drilling fluids, obtaining cores with wettability that is representative of reservoir conditions is becoming more difficult. The surfactants used in oil-based muds have long been suspected of affecting core wettability. They necessitate extensive cleaning and wettability restoration that add to the uncertainty in the results of core studies. The introduction of synthetic oil-based muds has compounded the problem of wettability alteration by raising the prospect of surface precipitation of asphaltenes.

In synthetic oil-based drilling fluids, diesel has been replaced, for environmental reasons, by base oils that are very low in aromatic hydrocarbons. Several types of base oil are now in use. They may be paraffinic or olefinic or they may consist of other organic compounds such as esters. At sufficiently high concentration in mixtures with crude oils (for example in mixing zones associated with displacement of crude oil), the paraffinic base oils are very likely to precipitate asphaltenes. Simple tests of asphaltene onset conditions show that a variety of olefinic base oils can also destabilize asphaltenes whereas ester products do not.

Asphaltenes are implicated in many undesirable phenomena including plugging, fouling, emulsion stabilization, and wettability alteration. The extent to which asphaltenes create

problems is more closely related to their stability than to the amount of asphaltene, by whatever definition, in an oil. Asphaltenes can be destabilized when oils are depressurized or when they are mixed with injected or lift gas. Synthetic oil-based drilling muds (SBM) are a previously unrecognized source of potentially destabilizing fluid.

### **1.1.1 Asphaltene stability.**

Asphaltenes, by definition, are the materials in a crude oil that are soluble in toluene and insoluble in pentane, hexane, or heptane. They represent a range of materials, some of which are insoluble in even higher molecular weight hydrocarbons such as pentadecane and more of which are insoluble in propane, ethane, and methane. The most direct method to assess the potential for any additive to destabilize asphaltenes is to add different amounts of additive to an oil and observe the resulting mixtures after some time has elapsed. (Note that adding oil to additive can result in locally high concentrations of additive and overestimation of the tendency for flocculation to occur.) The amount of time allowed before observations should be determined by the flocculation kinetics, which can sometimes be slow, on the order of days (Mason and Lin, 2003). The appearance of asphaltene aggregates in an initially clear mixture indicates instability. The mixture with the smallest amount of additive in which aggregates appear is designated as the onset mixture.

The solubility parameter of onset mixtures with *n*-paraffins can be estimated from measurements of refractive index (RI) (Buckley et al., 1998a). For the synthetic base oils, there is no simple conversion between RI and solubility parameter. Nevertheless,  $P_{RI}$  (the RI of the mixture at the onset of precipitation) can provide a relative indication of stability.

### **1.1.2 Wettability alteration and assessment.**

Contact with crude oil, bitumen, or their heavy products such as fuel oil, coal tar, or creosote can alter the wetting of initially water-wet minerals through adsorption of polar materials including asphaltenes (Buckley, 2001, and references cited therein). The extent of such wetting changes can be observed on smooth surfaces by measurements of contact angles and in porous media by observing the rate and extent of spontaneous imbibition of water or oil (Morrow, 1990; Morrow and Mason, 2001; Tong, 2003).

### **1.1.3 Surface precipitation.**

The extent to which a particular crude oil alters wetting depends on many factors. These include the nature of the polar fractions of the oil, the mineralogy of surfaces with which it comes in contact, and the composition of the aqueous phase, if water is present. Buckley et al. (1998b) pointed out that adsorption mechanisms in the absence of water can be completely different to those when water is present. In the latter case, there are several potential mechanisms by which oil components adsorb on mineral surfaces including acid/base and ion-binding interactions, and surface precipitation of asphaltenes. The potential for surface precipitation depends on the existence of asphaltene components and on their stability. Al-Maamari and Buckley (2003) demonstrated sharp increases in contact angles, indicating oil-wet conditions, on mica surfaces aged in onset mixtures of crude oils and heptane, compared to mica

aged in the same crude oils without added heptane. It is likely that surface precipitation is responsible for making Berea sandstone cores less water-wet when an asphaltic crude oil is miscibly displaced by a paraffinic mineral oil. A comparison is shown in Fig. 1-1 (using data from Tie et al., 2003) for Minnelusa crude oil, displaced by decalin (5 pore volumes) followed by Soltrol 220 (a paraffinic mineral oil) and the same crude oil displaced directly by the mineral oil. Slow and very limited extent of displacement of oil from Berea sandstone by spontaneous imbibition of water after direct displacement by paraffinic mineral oil indicates that this core is much less water-wet than a similarly treated core in which direct contact between crude and mineral oils is avoided by displacement with an intermediate solvent.

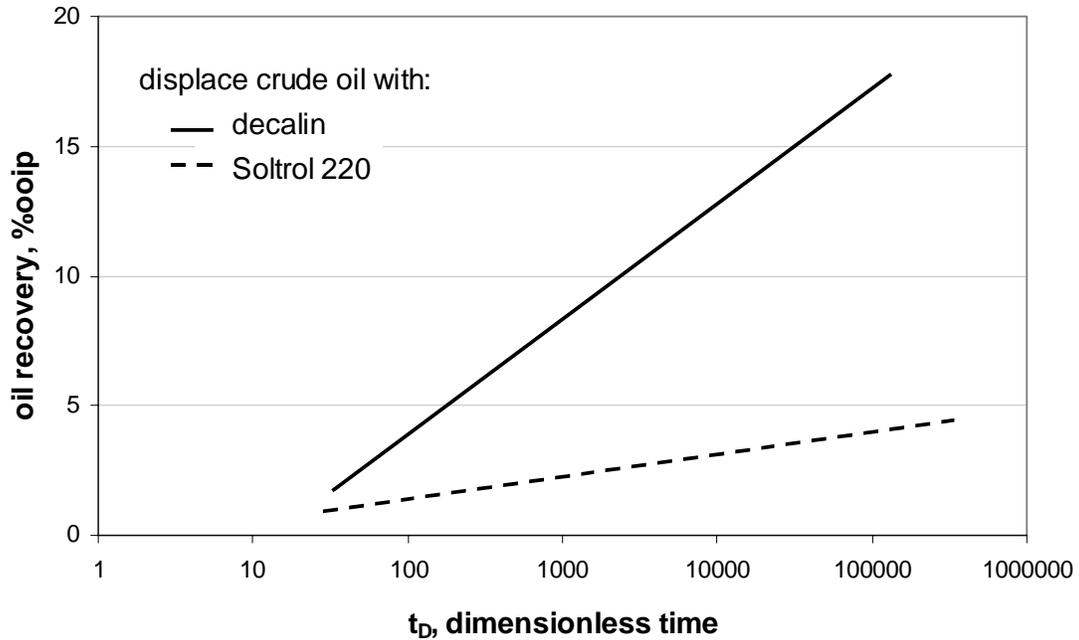


Figure 1-1. Cores are less water-wet, as indicated by slower imbibition if crude oil is displaced with a paraffinic oil (after Tie et al., 2003). Note: see Morrow and Mason (2001) for further explanation of dimensionless time.

## 1.2 Experimental Materials and Methods

### 1.2.1 Crude oils.

Two crude oils were used in this study: Minnelusa from Wyoming and Gullfaks from the North Sea. Selected properties of these oils are summarized in Table 1-1. They are quite different in asphaltene content and in their tendencies to alter the wetting of silicate surfaces (Xie et al., 2002).

Table 1-1. Crude oil properties

Name	°API	RI at 20°C	RI at 60°C	n-C <sub>7</sub> asphaltenes (%)
Gullfaks	27.1	1.4930	1.4761	0.4
Minnelusa	24.6	1.5143	1.4979	9.0

### 1.2.2 Synthetic base oils and n-paraffins.

Selected synthetic base oils were tested for their tendency to precipitate asphaltenes from Minnelusa oil. It is difficult to quantify the onset conditions in Gullfaks because there is very little material in the asphaltene fraction (Table 1-1). Properties of the base oils are summarized in Table 1-2.

**Table 1-2. Base oil properties**

Trade name	Material description	Density (g/ml) at 20°C	Viscosity (cP) at 20°C
LVT 200	paraffins	0.8177	2.91
Soltrol 220	C <sub>13</sub> -C <sub>16</sub> isoalkanes	0.7833	3.80
Petrofree SF	internal olefin	0.7847	3.64
Petrofree LV	fatty acid ester	0.8617	3.86

Asphaltene stability was also tested with three *n*-paraffins—*n*-heptane (*n*-C<sub>7</sub>), *n*-undecane (*n*-C<sub>11</sub>), and *n*-pentadecane (*n*-C<sub>15</sub>), all of which were purchased from Fisher Scientific with greater than 99% purity—for comparison to the synthetic base oils. Soltrol 220 is a refined mineral oil composed of C<sub>13</sub>-C<sub>16</sub> iso-alkanes that is frequently used in laboratory displacement tests, including those shown in Fig. 1-1.

### 1.2.3 Cores.

Berea sandstone core samples, 3.8 cm in diameter and 7.5 cm in length, were cut from a single block. Their average air permeability ( $k_g$ ) was about 80md and porosity was about 17%. Initially water-wet cores are exposed first to water, then flooded with viscous mineral oil to establish an initial water saturation ( $S_{wi}$ ). The mineral oil was displaced by decalin which was in turn displaced by crude oil. Cores were then aged at elevated temperature (75°C) for 10 days. The abbreviation MXW is used to denote mixed-wet cores that contain connate water and crude oil. MXW-F denotes a core from which the crude oil has been miscibly displaced to leave adsorbed films (F) that control the wetting conditions.

### 1.2.4 Onset measurements.

Mixtures with varying volume percentages of crude and synthetic base oils or *n*-alkanes were prepared 24 hours before observation. Temperature was maintained at 60°C during the storage period. The absence or presence of flocculated asphaltenes was determined by microscopic observation, as described in greater detail elsewhere (Buckley and Wang, 2002; Wang, 2000).

### 1.2.5 Rate of imbibition.

The rate of imbibition of water—scaled to account for differences in permeability and porosity, sample geometry, liquid viscosities, and interfacial tension—was determined from the rate of oil recovery versus dimensionless time. The data in Fig. 1-1 are examples of scaled rate of imbibition results for MXW-F cores.

## 1.3 Results and Discussion

### 1.3.1 Asphaltene stability.

Most of the synthetic base oils tested destabilized asphaltenes in Minnelusa crude oil. The refractive indices of mixtures at the onset condition are shown in Fig. 1-2. Also shown are the onset conditions observed with mixtures of the same crude oil and three *n*-paraffins. LVT 200 precipitates asphaltenes at solubility conditions that are intermediate between *n*-C<sub>7</sub> and *n*-C<sub>15</sub>; Soltrol 220 and the internal olefin produce asphaltene aggregates at solubility conditions that are closer to the *n*-C<sub>15</sub> onset. The fatty acid ester base oil is not shown because no precipitation was observed in its mixtures with Minnelusa in any proportions. Note that the volume of precipitant required to initiate precipitation depends on both the P<sub>RI</sub> and the RI of each different product. For a given crude oil, precipitation at higher P<sub>RI</sub> indicates that the asphaltenes are less stable.

### 1.3.2 Alteration of wetting in cores.

Figure 1-3 shows a reduced rate of sea water imbibition for a Berea core after aging in Minnelusa crude oil (MXW), compared to the trend established for strongly water-wet Berea core with no initial water saturation (line labeled Berea 90 S<sub>wi</sub>=0%). Reduced rate of imbibition indicates that the cores are no longer strongly water-wet. Imbibition rates are still lower for sea water displacing any of the synthetic base oils after they in turn have displaced the crude oil. Cores treated with Gullfaks (Fig. 1-4) are more water-wet, but depressed rates are observed when oil was displaced by either the Petrofree SF (internal olefin) or the LVT 200 (paraffinic oil).

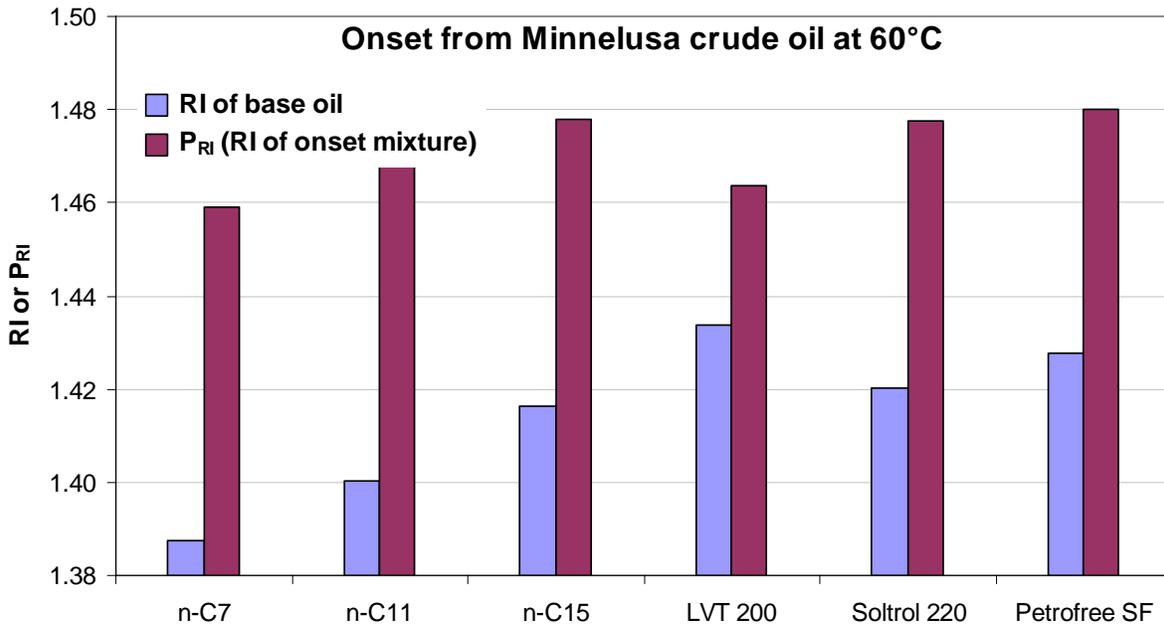


Figure 1-2. RI and P<sub>RI</sub> for the onset of asphaltene precipitation from Minnelusa crude oil at 60°C.

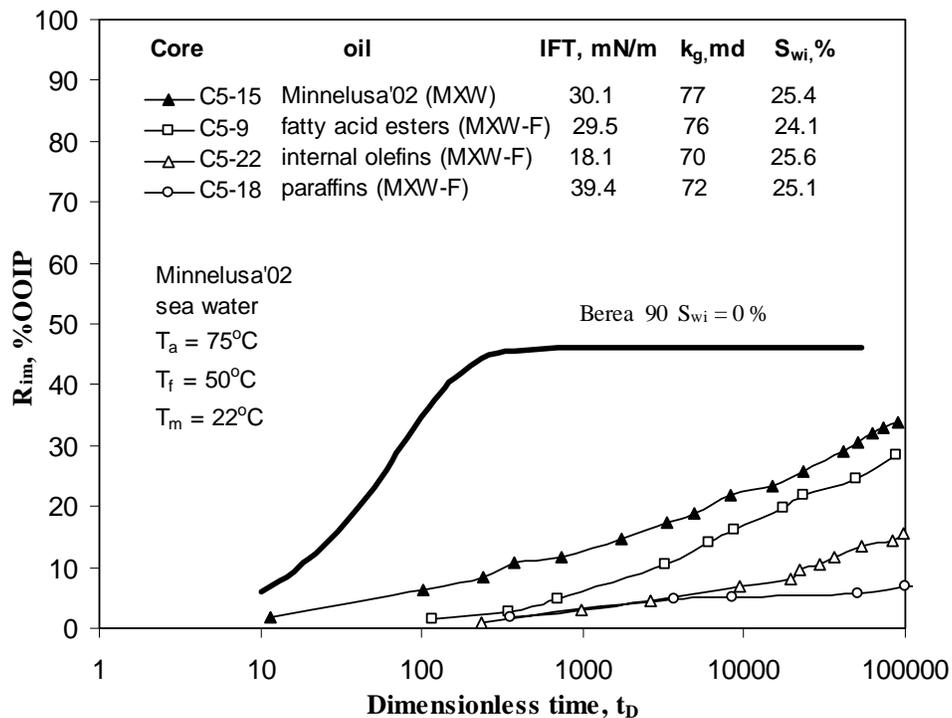


Figure 1-3. Wetting conditions in Berea core after aging in Minnelusa crude oil are shown by the line labeled MXW. (Numbers beginning C5- identify specific cores; IFT is interfacial tension;  $T_a$ ,  $T_f$ , and  $T_m$  are the aging, flushing, and measurement temperatures.) The other three curves show sea water imbibition rates after the crude oil was displaced by the products indicated.

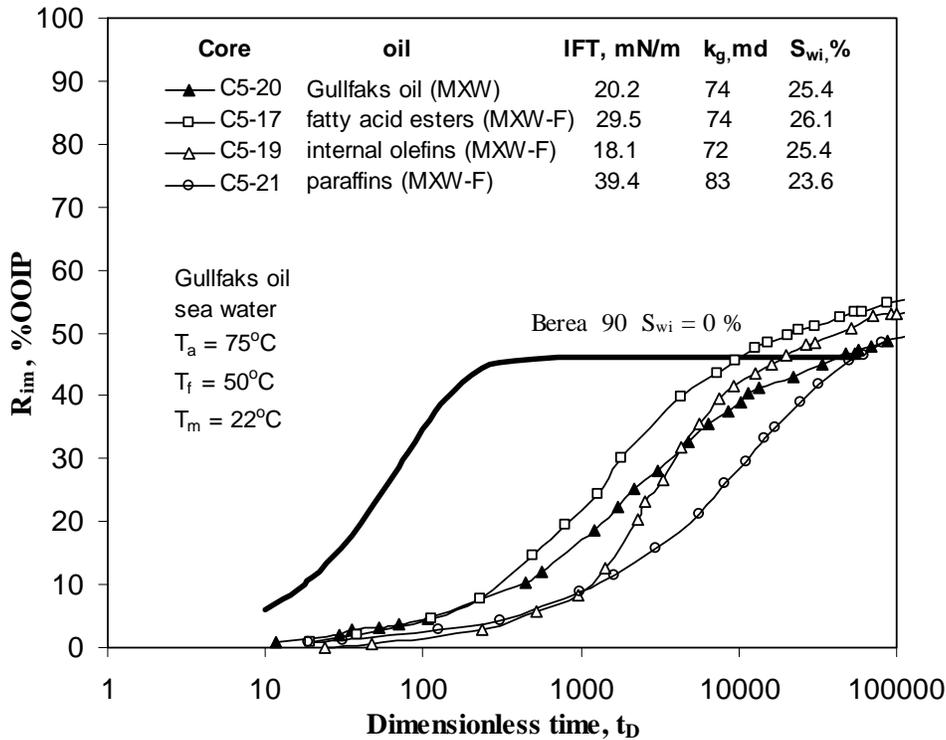


Figure 1-4. Wetting conditions in Berea core after aging in Gullfaks crude oil are shown by the line labeled MXW. The other three curves show sea water imbibition rates after the crude oil was displaced by the products indicated.

The effect of fatty acid esters on wetting is not clear, since in one case imbibition is slower and in the other it is faster than imbibition into the MXW core. The wetting effects of Petrofree SF and LVT 200 are consistent for the two crude oils. The initial rate of imbibition is suppressed about equally for both oils; more of the Petrofree SF is eventually mobilized. Surface precipitation of asphaltenes during the displacement of crude oil by paraffinic or olefinic synthetic base oils must be suspected as a cause of wettability change. The extent of change towards oil wetness will depend on the crude oil/brine/rock combination.

## 1.4 Conclusions

- Paraffinic and olefinic synthetic base oils used in synthetic oil-based muds can destabilize asphaltenes. The solubility conditions at the onset of asphaltene precipitation are comparable to *n*-paraffins in the heptane to pentadecane range.
- Cores in which there was mixing of synthetic base oils with crude oil during displacement became less water-wet, except in the case of exposure to a fatty acid ester. These results are consistent with the surface precipitation mechanism of wetting alteration due to destabilization of asphaltenes.

## 1.5 Acknowledgments

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## 1.6 References

- Al-Maamari, R.S.H. and Buckley, J.S.: "Asphaltene Precipitation and Alteration of Wetting: The Potential for Wettability Changes during Oil Production," *SPE REE* (Aug. 2003) 210-214.
- Buckley, J.S.: "Effective Wettability of Minerals Exposed to Crude Oil," *Current Opinion in Colloid and Interface Sci.* (2001) **6**, 191-196.
- Buckley, J.S., Hirasaki, G.J., Liu, Y., Von Drasek, S., Wang, J.X., and Gill, B.S.: "Asphaltene Precipitation and Solvent Properties of Crude Oils," *Petroleum Science and Technology* (1998a) **16**, No. 3&4, 251-285.
- Buckley, J.S., Liu, Y., and Monsterleet, S.: "Mechanisms of Wetting Alteration by Crude Oils," *SPEJ* (Mar. 1998b) **3**, 54-61.
- Buckley, J.S. and Wang, J.X.: "Crude Oil and Asphaltene Characterization for Prediction of Wetting Alteration," *J. Pet. Sci. Eng.* (2002) **33**, 195-202.
- Mason, T.G. and Lin, M.Y.: "Time-resolved small angle neutron scattering measurements of asphaltene nanoparticle aggregation kinetics in incompatible crude oil mixtures," *J. Chem. Phys.* (2003) **119**, 565-571.
- Morrow, N.R.: "Wettability and Its Effect on Oil Recovery," *JPT* (Dec. 1990) **42**, 1476-1484.
- Morrow, N.R. and Mason, G.: "Recovery of Oil by Spontaneous Imbibition," *Current Opinion in Colloid and Interface Sci.* (2001) **6**, 321-337.
- Tie, H., Tong, Z. and Morrow, N.R.: "The Effect of Different Crude Oil/Brine/Rock Combinations on Wettability through Spontaneous Imbibition," paper SCA 2003-02 presented at the 2003 International Symposium, Pau, 21-24 Sept.
- Tong, Z.X., Xie, X. and Morrow, N.R., "Crude oil composition and the stability of mixed wettability in sandstones" *Petrophysics* (2003) **44**, 233-242.
- Wang, J.: "Predicting Asphaltene Flocculation in Crude Oils," PhD Thesis, NMIMT, 2000.
- Xie, X., Morrow, N.R., and Buckley, J.S.: "Contact Angle Hysteresis and the Stability of Wetting Changes Induced by Adsorption from Crude Oil," *J. Petrol. Sci. Eng.* (2002) **33**, 147-159.

## **2. Wetting Alteration of Mica Surfaces with Polyethoxylated Amine Surfactants**

E. M. Bryant, R.S. Bowman, and J.S. Buckley

### **2.0 Abstract**

Characterization of reservoir wettability is an important part of assessment of potential oil recovery. Oil-based drilling fluids include surfactants, which can alter the wettability of mineral surfaces. Cores exposed to these fluids may not reflect the true wettability of the reservoir materials.

The focus of this study was to observe wettability changes induced by adsorption and removal of surfactants of known structure on mica surfaces using tools that are applicable to studies of wetting alteration by crude oil components. The surfactants used were polyethoxylated coconut and tallow amines with chain lengths of 12 and 18 carbons and head groups consisting of two to five ethoxy groups. Mica was exposed to decane solutions of the surfactants. The treated mica was characterized macroscopically using contact angle measurements and microscopically using atomic force microscopy (AFM).

Upon exposure to the surfactant solutions, the mica became oil-wet ( $\sim 170^\circ$  for both advancing and receding conditions). AFM examination of similarly treated surfaces imaged in air revealed surfactant layers that were easily disrupted or surfaces that showed no surfactant at all. Contact angles were in the intermediate to water-wet range if the mica samples were removed from the surfactant solution, rinsed with non-aqueous solvents, and submerged in decane for measurements of water/decane contact angles. These results suggest only weak surfactant adsorption occurred from non-aqueous solutions. Differences among the structures tested were greater for increased levels of ethoxylation; differences due to hydrocarbon chain length were negligible. Stronger adsorption, higher contact angles, and more stable surfactant layers could be demonstrated when mica was exposed to aqueous solutions after surfactant sorption, depending on the pH of the aqueous phase. Low pH conditions that promote protonation of the surfactants' amine headgroup produced the greatest wetting alteration. Above a pH of 8 or 9, no surfactant remained adsorbed on mica surfaces.

### **2.1 Introduction**

The wettability of an oil reservoir controls how fluids flow and where fluids reside in the reservoir (Anderson, 1986; Morrow, 1990). Thus, it is important to know the wettability of the reservoir in order to recover the maximum amount of oil. Cores are used to characterize properties of an oil reservoir including the wettability. Drilling fluids (muds) can alter the wettability of a core taken during drilling, resulting in improper characterization of reservoir properties. Surface active agents (surfactants) are the primary wettability-altering components of the drilling muds.

Bobek et al. (1958) and Amott (1959) both observed that oil-based muds make cores more oil-wet. Since then numerous studies have focused on the wetting effects of the muds, their

filtrates, or components of oil-based muds (Thomas et al., 1984; Gant and Anderson, 1988; Ballard and Dawe, 1988; Cuiec, 1989; Menezes et al., 1989; Yan et al., 1993; McCaffery et al., 2002; and Skalli, 2003). Menezes et al. (1989) examined the effects of commercial blends of surfactants on the wettability of quartz surfaces. Yan et al. (1993) examined wetting effects in sandstone cores and on quartz surfaces, while Skalli (2003) used mica as a model surface. All found the surfactants used in oil-based muds tended to alter water-wet siliceous surfaces to intermediate-wet or even oil-wet conditions. Since commercial blends of surfactants were used in those studies, the actual chemical structures of the surfactants were not known.

Patel and Ali (2003) suggested the use of ethoxylated amines as emulsifiers in drilling muds because it is possible to change their Hydrophilic-Lipophilic Balance (HLB). Being able to manipulate the HLB value would allow one to alternate between an invert emulsion (water-in-oil) and an emulsion (oil-in-water).

In this study, we used polyethoxylated amines with known structures to gain a better understanding of how the surfactants interact with a siliceous (mica) surface. The ultimate goal of the study was to evaluate wetting changes and possible cleaning techniques designed to regain the original mica wettability after exposure to the surfactants. Mica was treated with a 5% by volume surfactant/decane solution and then washed with various solutions. The surface properties were characterized macroscopically and microscopically before and after washing. Wettability was determined by measuring contact angles using the captive drop method. Microscopically, surficial features were examined using atomic force microscopy (AFM). Macroscopic and microscopic properties were compared to obtain a consistent picture of wetting alteration.

## **2.2 Materials and Methods**

### **2.2.1 Materials**

#### **2.2.1.1 Mica**

Muscovite mica ( $\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$ , S&J Trading, Inc., Glen Oaks, NY) was used as a model surface because mica, a natural mineral, is easily cleaved to produce a clean, molecularly smooth surface. Smooth surfaces are preferred for contact angle measurements and for AFM imaging. The mica was cut into rectangles of approximately 1.5 cm by 2 cm for the contact angle measurements while a disc punch was used to cut circular samples with a diameter of 12.7 mm for AFM tests. All mica was cleaved with adhesive tape to obtain a smooth, clean surface prior to treatment. Care was taken at all times to handle mica samples only by their edges so that the freshly cleaved surfaces were not contaminated.

#### **2.2.1.2 Buffered aqueous solutions**

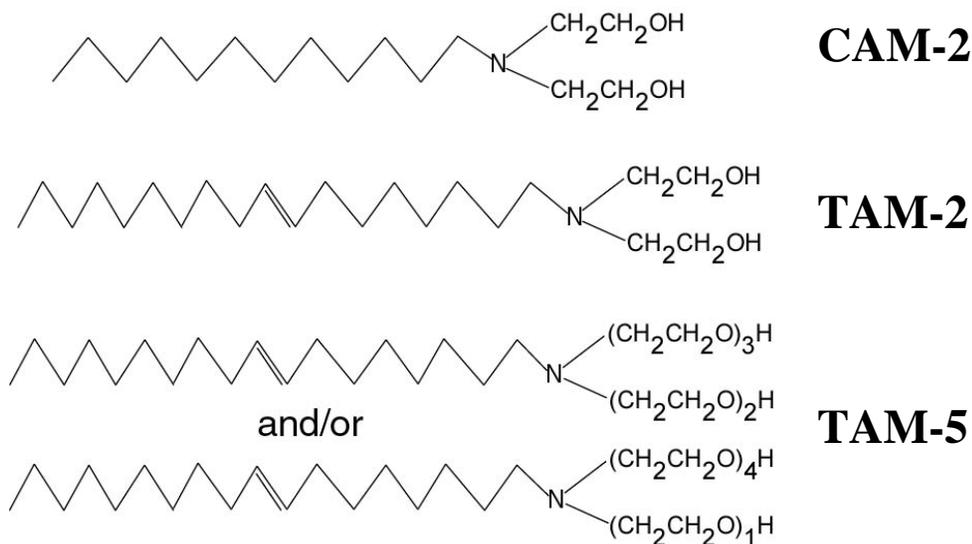
Three buffered brines were used: pH 4, pH 8, and pH 10. NaCl was added as needed to maintain a constant ionic concentration of 0.1 M. The compositions of the buffers are listed in Table 2-1.

**Table 2-1. Buffer compositions**

Buffer:	pH 4, 0.1 M NaCl	pH 8, 0.1 M NaCl	pH 10, 0.1 M NaCl
NaCl (g/L)	3.7402		3.7577
Na Acetate (g/L)	2.9531		
Glacial HAc (mL/L)	3.7		
Na <sub>2</sub> HPO <sub>4</sub> (g/L)		6.2108	
NaH <sub>2</sub> PO <sub>4</sub> (g/L)		0.3179	
NaHCO <sub>3</sub> (g/L)			2.1003
NaOH (g/L)			0.4280

**2.2.1.3 Surfactants**

Three liquid surfactants were obtained from Ethox Chemicals, LLC (Greenville, South Carolina): CAM-2, TAM-2, and TAM-5 (Fig. 2-1). CAM-2 is composed of coconut amine (chain length of 12 carbons, C 12) along with two ethylene oxides. TAM-2 is composed of tallow amine (chain length of 18 carbons, C 18) along with two ethylene oxides, and TAM-5 is composed of tallow amine along with five ethylene oxides. TAM-5 has two possible arrangements of the ethylene oxides on the amine. It is not known whether our sample was one or a mixture of both of these structures. The purity of the surfactants is not known; surfactants were used as received.

**Figure 2-1. Chemical structures of the surfactants used in this study****2.2.1.4 Decane**

All decane (>99.3% purity, Fisher Scientific) used was purified by passing it through a column containing silica (grade 62, 60 – 200 mesh, Aldrich, Milwaukee, WI) and alumina (80 – 200 mesh, Fisher Scientific). Before the silica was used, it was placed into an oven set at 200 °C for at least eight hours to remove any sorbed water.

## **2.2.2 Experimental Methods**

### **2.2.2.1 Surfactant mixtures**

Solutions of 5% by volume surfactant were prepared by diluting 5 mL of surfactant with decane in a 100-mL volumetric flask. Some of the surfactant/decane solutions were pre-equilibrated with buffer solutions. One-hundred milliliters of buffer and 100 mL of 5% surfactant/decane solution were mixed in a separatory funnel. Emulsions formed that required varying amounts of time to separate. After phase separation, the upper phase was used as the surfactant/decane solution and the lower phase as the aqueous buffer. Contact angle measurements using pre-equilibrated fluids were indistinguishable from those with non-equilibrated solutions. Since pre-equilibration does not appear to affect the results of this study, distinction between equilibrated and non-equilibrated fluid results will be omitted in most cases. Complete descriptions of the full suite of experiments are available elsewhere (Bryant, 2004).

### **2.2.2.2 Interfacial tension measurements**

The pendant drop method was used to measure the interfacial tension (IFT) between varying concentrations of surfactant solutions in decane and an aqueous drop of pH 4, pH 8, or double-distilled water using an OCA20+SCA20 (DataPhysics Instruments GmbH, Germany).

The critical micelle concentration (CMC) was determined for the surfactants with pH 4, pH 8, and double-distilled water. A 1% by volume surfactant/decane solution was made for each surfactant and diluted to yield lower concentrations.

### **2.2.2.3 Contact angle measurements**

Clean mica. To test the initial condition of mica, contact angles were measured with a captive drop of double-distilled water on freshly cleaved mica submerged in purified decane. The water-advancing angle ( $\theta_A$ ) and water-receding angle ( $\theta_R$ ) of clean mica were found to be approximately  $10^\circ$ , indicating water-wet conditions.

Contact angles between surfactant solutions and water. Mica was submerged in about 10 mL of 5% by volume surfactant/decane solution and contact angles were measured using the captive drop method with a water drop produced by a Gilmont pipette. The drop was allowed to remain motionless on the surface for 2 minutes before the advancing angle measurements were taken. The receding angles were measured by drawing the water back into the pipette after advancing angles were recorded. All contact angles reported are an average of 6 measurements on three separate pieces of mica for a total of 18 measurements.

Contact angles on surfaces after surfactant sorption. Mica was soaked in the 5% by volume surfactant/decane solution for 40 to 70 min. The treated mica was then washed with one solvent or a sequence of solvents. The solvents tested included toluene, hexane, decane, acetone, water, and pH 4, 8, and 10 buffers. Details of washing sequences are included in Tables 2-2 and 2-3. For each solvent, mica was washed by swirling it in the solvent three times followed by touching the edge of the mica with a Kimwipe to remove excess solution. The washed mica was placed into either decane or water and the contact angles were measured using the captive drop method as described above. If the contact angles were measured in water, the fluid delivered by the pipette (i.e. the drop) was decane.

**Table 2-2. Summary of contact angle measurements for CAM-2, TAM-2 and TAM-5**

Sample	Advancing Angle		Receding Angle	
	Average	Std dev	Average	Std dev
<b>CAM-2</b>				
no wash measured in 5% by volume surfactant/decane solution	159	13	167	0
toluene wash measured in decane	91	22	34	6
hexane wash measured in decane	115	2	37	6
acetone wash measured in decane	114	0	33	4
acetone wash measured in water	161	2	141	10
acetone and water wash measured in water	160	2	142	3
<b>TAM-2</b>				
no wash measured in 5% by volume surfactant/decane solution	162	14	170	1
toluene wash measured in decane	132	9	84	5
hexane wash measured in decane	128	16	63	23
acetone wash measured in decane	102	3	37	2
acetone wash measured in water	165	3	155	12
acetone and water wash measured in water	167	5	167	5
<b>TAM-5</b>				
no wash measured in 5% by volume surfactant/decane solution	180	0	180	0
toluene wash measured in decane	17	3	14	1
decane wash measured in decane	10	1	10	1
acetone wash measured in decane	14	2	13	2
acetone wash measured in water	161	3	137	16
acetone and water wash measured in water	157	4	122	24
acetone and pH 8 wash measured in water	149	1	109	17
acetone and pH 10 wash measured in water	141	15	77	13
acetone, pH 4, acetone wash measured in water	85	8	32	0
acetone, water, acetone wash measured in water	82	7	30	2
acetone, pH 10, acetone wash measured in water	11	2	11	2

**Table 2-3. Summary of contact angle measurements for TAM-5**

(pre-equilibrated with pH 8 buffer)

Sample	Advancing Angle		Receding Angle	
	Average	Std dev	Average	Std dev
<b>TAM-5 pre-equilibrated with pH 8 brine</b>				
no wash measured in 5% by volume surfactant/decane solution	161	34	161	34
toluene wash measured in decane	76	3	34	3
acetone wash measured in decane	62	6	27	3
acetone and water wash measured in pH 4 brine	144	0	93	18
acetone and pH 8 wash measured in pH 4 brine	133	8	58	6
acetone and pH 10 wash measured in water	133	15	65	25
no wash measured in 5% by volume surfactant/decane solution	161	34	161	34
toluene wash measured in decane	13	7	12	5
acetone wash measured in decane	14	2	14	2
acetone and water wash measured in pH 8 brine	21	1	21	1
acetone and pH 8 wash measured in pH 8 brine	18	1	18	1

**2.2.2.4 Atomic forces microscopy**

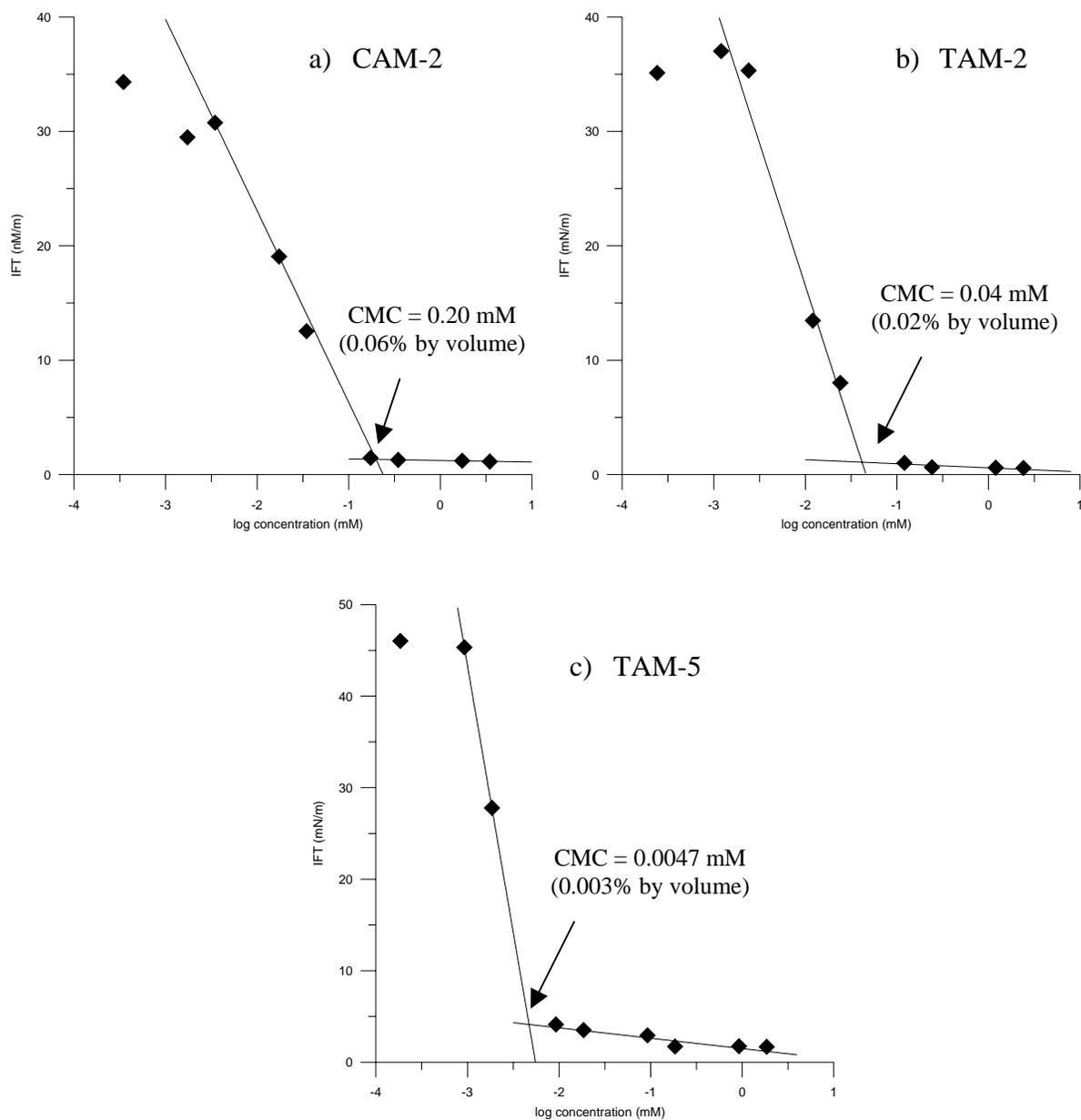
Mica was soaked in a 5% by volume surfactant/decane solution for approximately 45 minutes. Mica samples were removed from the surfactant solution and allowed to dry thoroughly in air. The mica was then mounted onto an AFM magnetic puck using a small amount of Super Glue Gel (Ace Hardware, Oak Brook, IL).

The AFM samples were imaged at ambient temperature in contact mode in air or under a fluid (pH 8 brine, pH 10 brine, or water) using methods described by Lord and Buckley (2002). The AFM used was a NanoScope IIIA (Veeco Instruments, Santa Barbara, CA), and the probes used were Olympus Oxide-Sharpended Silicon Nitride (Model OTR4-35 100- $\mu$ m cantilever, Veeco Instruments, Santa Barbara, CA).

## **2.3 Results**

### **2.3.1 Characterization of the surfactants**

Figure 2-2 shows the results of measurements of IFT as a function of surfactant concentration. These results were used to determine the critical micelle concentration (CMC) of the three surfactants with pH 4 brine. The CMC with pH 4 was 0.20 mM (0.06% by volume) for CAM-2, 0.04 mM (0.02% by volume) for TAM-2, and 0.0047 mM (0.003% by volume) for TAM-5, where the molar concentrations were calculated assuming the surfactants were pure as received. The CMCs for the surfactant/decane solution with pH 8 buffer or double-distilled water were greater than the values reported here for pH 4 buffer (Bryant, 2004). The concentration (5% by volume) of surfactant solution used for treatment of the mica was much greater than the CMCs of the surfactants.



**Figure 2-2. Plots of interfacial tension (IFT) as a function of log concentration were used to determine the CMC for a) CAM-2 b) TAM-2 and c) TAM-5 with pH 4 buffer.**

### **2.3.2 Contact angle measurements**

Table 2-2 and Figure 2-3 summarize the contact angle measurements on mica surfaces during and after exposure to the 5% by volume surfactant/decane solutions for all three surfactants. In general CAM-2 and TAM-2 gave similar results while TAM-5 differed from the other two.

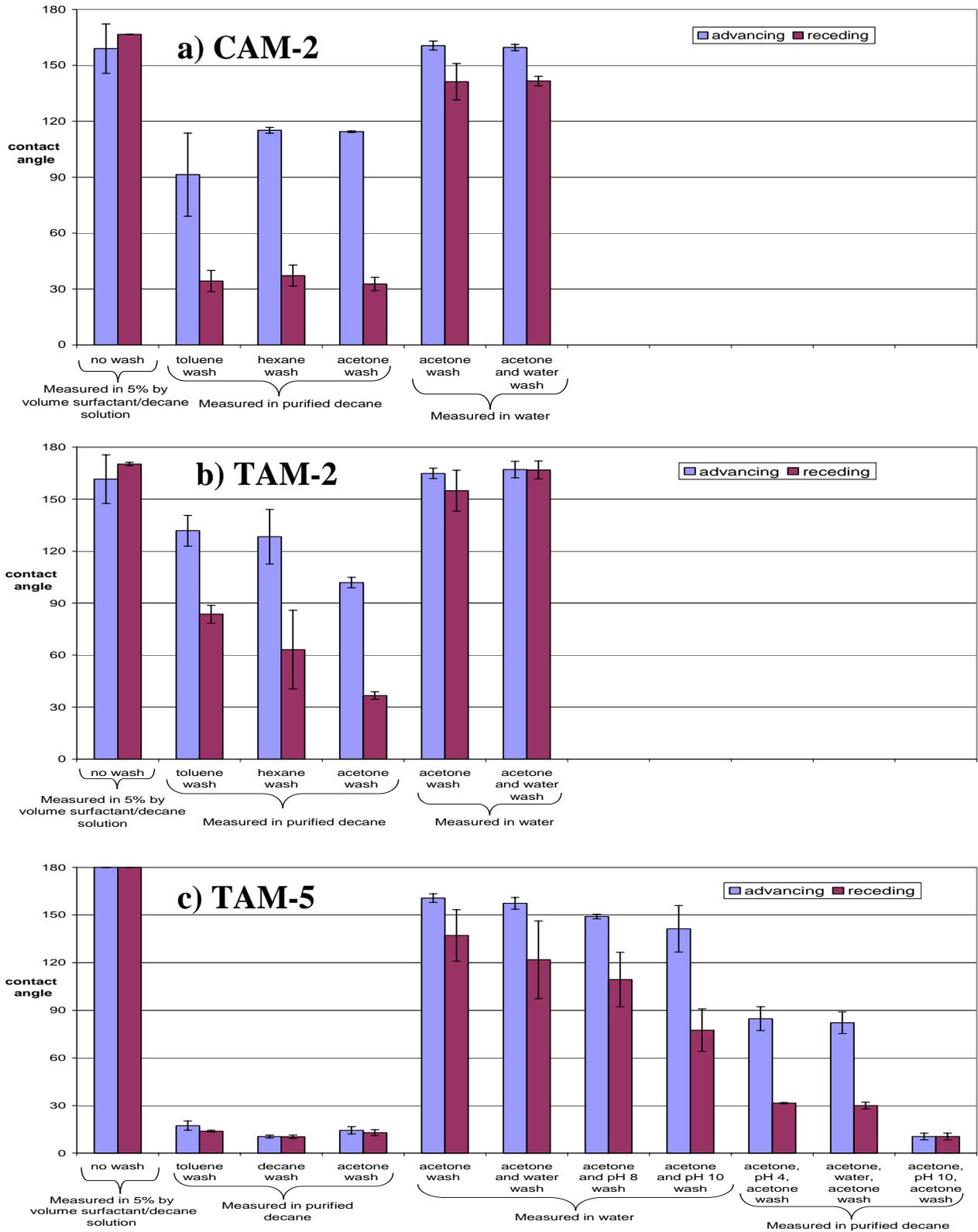


Figure 2-3. Contact angle results for a) CAM-2 b) TAM-2 and c) TAM-5. Error bars are standard deviations of 18 replicate measurements.

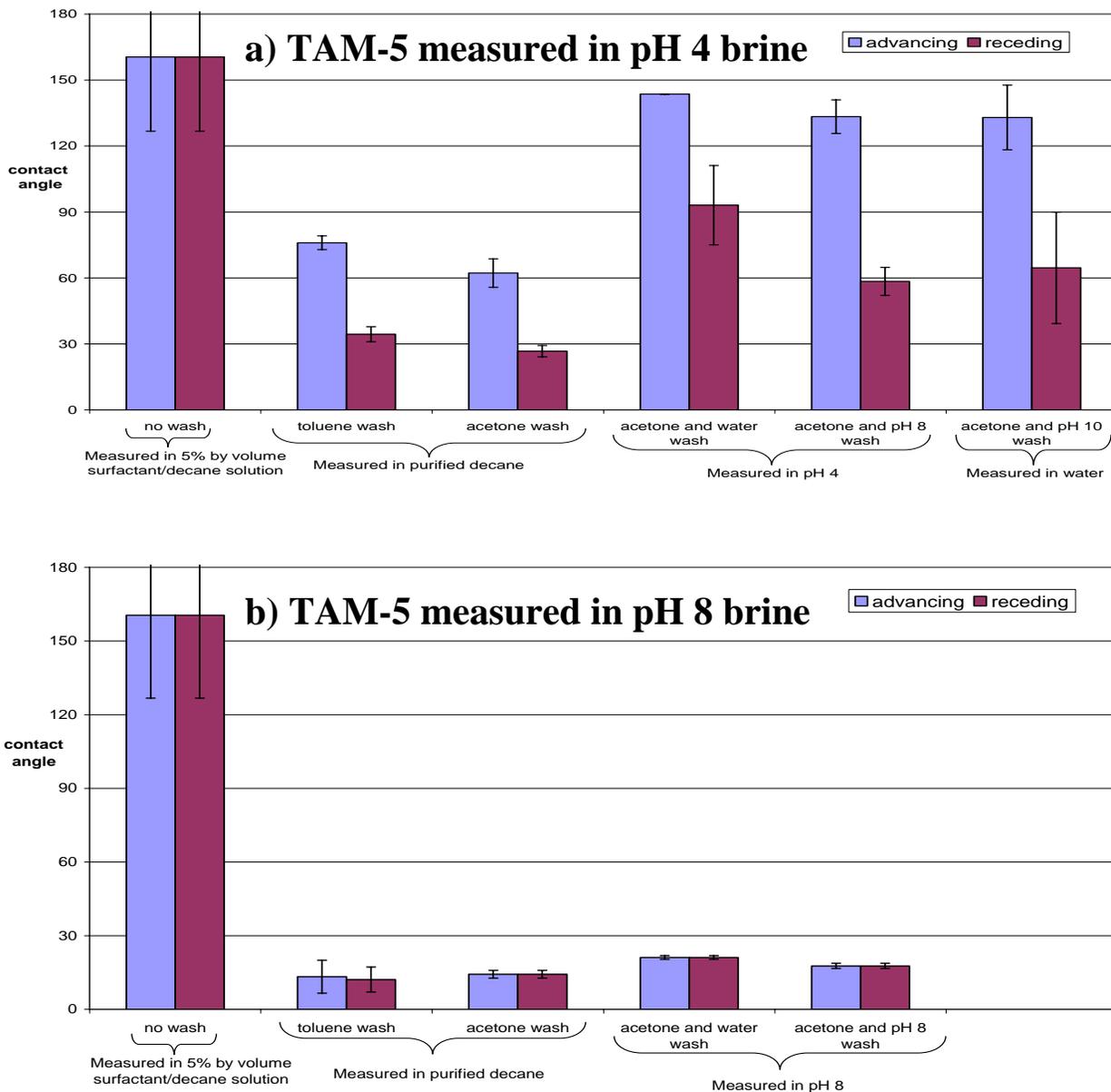
### 2.3.2.1 Contact angles between surfactant solutions and water

The leftmost results in Fig. 2-2 show the contact angles measured with a drop of water on mica that was submerged in surfactant/decane solution. Mica treated with CAM-2 or TAM-2 had a  $\theta_A$  of approximately  $160^\circ$  (oil-wet) and a  $\theta_R$  of approximately  $170^\circ$ , while mica treated with TAM-5 had an  $\theta_A$  and  $\theta_R$  of approximately  $180^\circ$  (oil-wet). An exact contact angle for TAM-5 could not be measured because the IFT was very low for this 5% surfactant/decane solution and water, which caused the water to stream continuously out of the pipette. This caused the water drop to grow continuously; therefore the contact angle was estimated from a moving contact line. Error bars represent the standard deviations of replicate measurements.

### 2.3.2.2 Decane/water contact angles after surfactant sorption

When measured using purified decane, the contact angle of the mica tended to be intermediate (CAM-2 and TAM-2,  $\theta_A \sim 32-83^\circ$ ) to water-wet (TAM-5,  $\theta_A \sim 10-18^\circ$ ) regardless of the washing procedure. When the contact angle was measured in water, surfaces appeared to be more oil-wet ( $\theta_A \sim 141-167^\circ$ ) regardless of which solutions were used to wash the mica.

An additional set of contact angle measurements was made on TAM-5-treated surfaces (using a decane surfactant solution that was pre-equilibrated with pH 8 buffer) with the water phase replaced by pH 8 and pH 4 buffers. Figure 2-4a and Table 2-3 summarize the contact angles for pH 4 brine while Figure 4b and Table 2-3 summarize the results measured with the pH 8 brine. The pH 4 contact angle results were generally less water-wet than comparable measurements with pH 8. The pH 4 measurements are comparable to similar measurements with double-distilled water. With pH 8, the mica surface appeared to be water-wet, while with pH 4, the mica surface was intermediate in wetting.



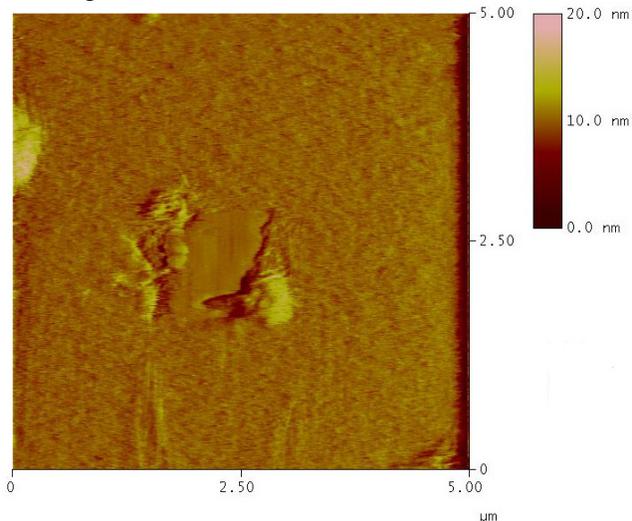
**Figure 2-4. TAM-5 pre-equilibrated with pH 8 brine measured in a) pH 4 brine and b) pH 8 brine. Error bars are standard deviations of 18 replicate measurements.**

### 2.3.3 Atomic Force Microscopy

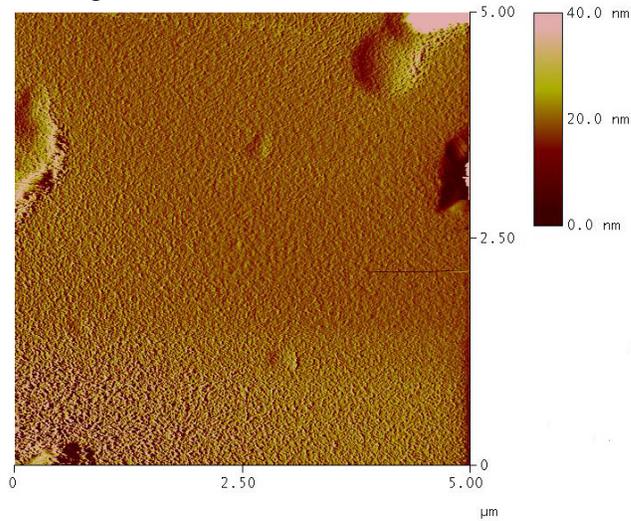
Figure 2-5 shows AFM images of mica treated with TAM-5. All images are of the deflection signal and are 5- $\mu\text{m}$  by 5- $\mu\text{m}$  scans. Figure 2-5a shows the TAM-5-treated mica surface imaged under air. The feature in the middle of the image was scraped by the tip during a previous scan of a 1- $\mu\text{m}$  by 1- $\mu\text{m}$  area. Figure 2-5b was imaged under water. The features on this surface were more stable than under air; a previous 1- $\mu\text{m}$  by 1- $\mu\text{m}$  scan produced no

scraping of the surface. Figure 2-5c was imaged under pH 8 brine. It appeared the pH 8 brine caused some of the features to coalesce into spheres that remained on the surface. Figure 2-5d was imaged under pH 10 brine; this image has the same appearance as clean mica.

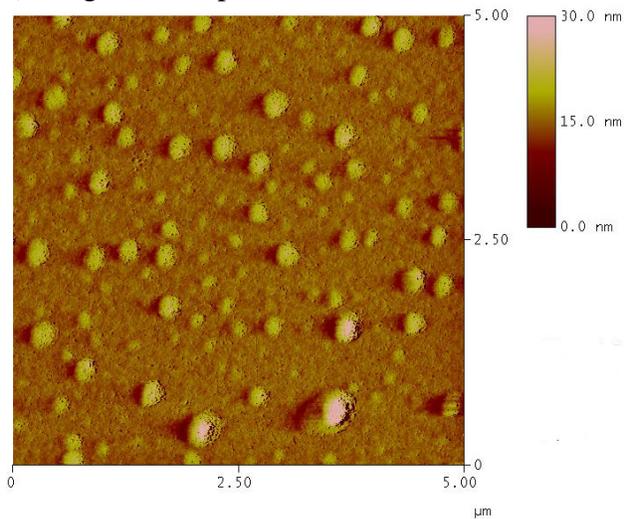
a) imaged under air



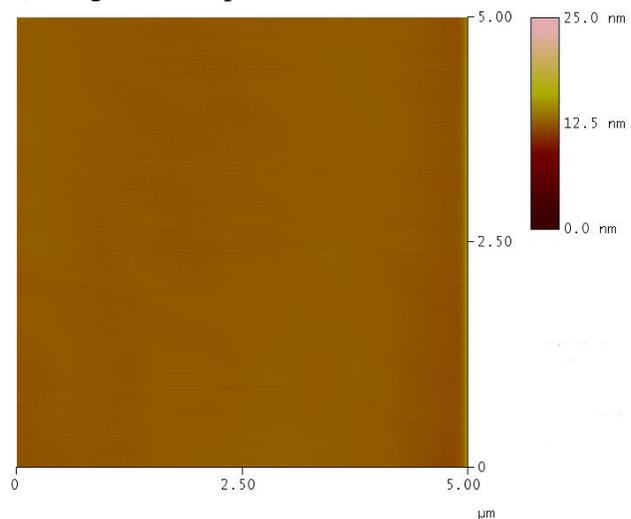
b) imaged under water



c) imaged under pH 8 buffer



d) imaged under pH 10 buffer



**Figure 2-5. Mica treated with a 5% by volume TAM-5/decane solution imaged under a) air b) water c) pH 8 buffer and d) pH 10 buffer.**

## 2.4 Discussion

The difference between CAM-2 and TAM-2 is their respective hydrocarbon chain lengths. Surfaces of mica treated with CAM-2 and TAM-2 had contact angles that were very similar; varying the chain length of the surfactant appeared to have little or no impact on surfactant adsorption on the mica surface. TAM-5, which has the same hydrocarbon chain length as TAM-2 but has five ethylene oxides attached to the nitrogen instead of two, adsorbed

less efficiently on mica. Changing the polar head groups does appear to affect adsorption of polyethoxylated amine surfactants.

Exposure of dry mica to high concentrations these surfactants produced wetting changes that were readily reversed by washing with any of the non-aqueous solvents, if followed by immersion in decane. It appears that any surfactant remaining on the surface after washing can diffuse back into the decane, in which it is quite soluble. Subsequent contact angle measurements indicate water-wet to intermediate-wet surfaces.

If, however, the washed surface is immersed in an aqueous phase, the results can be quite different. This can be seen in Fig. 3 by comparing acetone-washed surfaces immersed in decane with acetone-washed surfaces immersed in water for subsequent contact angle measurements. For all three surfactants, the contact angles measured under water are much higher than those measured under decane. Apparently there is some surfactant remaining on the acetone-washed surfaces. In the presence of water at low or neutral pH, the surfactant nitrogen is protonated and can adsorb much more strongly on the negatively charged mica surface than did the surfactant in a non-polar solution. Diethanol amine, a compound analogous to CAM-2 and TAM-2 without the hydrocarbon chain, has a  $pK_a$  (pH at which the concentrations of protonated and neutral forms are equal) of 8.88 (Dean, 1999); the  $pK_a$ s of the surfactants tested here are likely close to this value. The limited effect of increasing hydrocarbon chain length on the value of  $pK_a$  is demonstrated by a comparison of diethylamine ( $pK_a = 10.8$ ) and didodecylamine ( $pK_a = 10.99$ ) (Dean, 1999). Sorption of the protonated forms of the surfactants produces intermediate to oil-wet conditions. The neutral form of the surfactant that dominates at pH 10 has much less ability to sorb strongly on the mica surface, producing water-wet conditions.

AFM generally confirms the interpretation derived from contact angle measurements. In air, with no water to ionize the surfactant, surfactant is weakly adsorbed and easily moved by the AFM tip. Imaged under water, surfactant adsorption appears much more stable. Imaging under pH 8 starts the process of surfactant removal, while imaging under a pH 10 buffer—where the surfactant is in its neutral form—completes the surfactant removal process.

Since water is present in oil reservoirs, adsorption of surfactants like the polyethoxylated amines in this study is likely to occur in cores obtained with oil-based drilling fluids. The possibility that adsorption of this class of surfactants might be reversible at high pH is encouraging, however, and worthy of additional study.

## 2.5 Conclusions

Polyethoxylated amines adsorb to mica much more strongly in the presence of water (below a pH of about 8 or 9) than in the absence of water. Changing the hydrocarbon chain length from 12 to 18 had little effect on surfactant adsorption, whereas changing the extent of ethoxylation from two to five significantly reduced adsorption. Above pH 10, the presence of water inhibits or even reverses adsorption.

Microscopic AFM images obtained in contact mode on mica surfaces treated with polyethoxylated amine surfactants under air, distilled water, pH 8 and pH 10 buffers were qualitatively consistent with interpretations of macroscopic contact angle measurements.

## 2.6 Acknowledgements

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## 2.7 References

- Amott, E.: "Observations Relating to the Wettability of Porous Rock," *Trans.*, AIME (1959) **216**, 156-162.
- Anderson, W.G.: "Wettability Literature Survey—Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability," *JPT* (Oct. 1986) **38**, No. 11, 1125-1144.
- Ballard, T.J. and Dawe, R.A.: "Wettability Alteration Induced by Oil-Based Drilling Fluid," paper SPE 17160 presented at the 1988 Symposium on Formation Damage Control, Bakersfield, Feb. 8-9.
- Bobek, J.E., Mattax, C.C., and Denekas, M.O.: "Reservoir Rock Wettability—Its Significance and Evaluation," *Trans. AIME* (1958) **213**, 155-160.
- Bryant, E.M.: "Adsorption and Desorption Studies of Some Model Surfactants from Oil-based Drilling Fluids," Unpublished Masters Thesis, New Mexico Institute of Mining and Technology, Socorro, NM (2004).
- Cuiec, L.: "Effect of Drilling Fluids on Rock Surface Properties," *SPE Formation Evaluation* (March 1989) 38-44.
- Dean, J.A.: *Lange's Handbook of Chemistry*, 15th Ed., McGraw-Hill, New York (1999).
- Gant, P. and Anderson, W.G.: "Core Cleaning for Restoration of Native Wettability," *SPE FE* (Mar. 1988) 131-138.
- Lord, D.L., and Buckley, J.S.: "An AFM Study of Morphological Features that Affect Wetting at Crude Oil-Water-Mica Interfaces," *Colloids and Surfaces A* (2002) **206**, 531-546.
- McCaffery, F., Buckley, J.S., Silveira, R., Lekkala, R.K., Goggin, D., and McCarty, A.: "Wettability and Water-Oil Displacement Investigations for Some High Permeability Turbidite Reservoirs," paper 2002-32 presented at the Internat. Symp., Soc. of Core Analysts, Monterey, CA, 23-25 Sept.
- Menezes, J.L., Yan, J., and Sharma, M.M.: "The Mechanism of Wettability Alteration Due to Surfactants in Oil-Based Muds," paper SPE 18460 presented at the 1989 Internat. Symp. on Oilfield Chem., Houston, Feb. 8-10.
- Morrow, N.R.: "Wettability and Its Effect on Oil Recovery," *JPT* (Dec. 1990) **42**, 1476-1484.
- Patel, A. and Ali, S.: "New Opportunities for the Drilling Industry Through Innovative Emulsifier Chemistry," paper SPE 80247 presented at the 2003 SPE International Symposium on Oilfield Chemistry, Houston, TX, 5-7 February.
- Skalli, L.: "The effect of oil-based drilling fluid emulsifiers on wettability of silicate surfaces," MS Thesis, New Mexico Institute of Mining and Technology, Socorro, NM (2003).

Thomas, D.C., Hsing, H., and Menzie, D.E.: "Evaluation of Core Damage Caused by Oil-Based Drilling and Coring Fluids," paper SPE 13097 presented at the 1984 ATCE, Houston, Sept. 16-19.

Yan, J., Menezes, J.L., and Sharma, M.M.: "Wettability Alteration Caused By Oil-Based Muds and Mud Components," *SPEDC* (Mar. 1993) 35.

### **3. Surface and Core Wetting Effects of Surfactants in Oil-Based Drilling Fluids**

L. Skalli, J.S. Buckley, Y. Zhang, and N.R. Morrow

#### **3.0 Abstract**

Surfactants are used in oil-based drilling fluids to emulsify water and to ensure that cuttings are wetted by oil. The products used are based on drilling conditions and are essentially the same for traditional oil-based and synthetic oil-based fluids. Although much of these surface active materials adsorb on cuttings and filter cake, it is still likely that core samples are exposed to significant concentrations. Additional contamination can occur in subsequent core tests if the oil samples used are themselves contaminated with the drilling fluid.

Commercial surfactant packages from several sources have been selected for examination of their effects on the tests normally used to assess the extent of wetting change in crude oil/brine/mineral systems. These products were characterized with respect to their interfacial properties by measurements of interfacial tension as a function of concentration and brine composition. Wetting tests include measurements of contact angles on smooth mineral surfaces and rates of imbibition into porous media. The results show that even very low concentrations of surfactants, much lower than the amounts recommended for use in drilling fluids, can affect the wetting properties of mica surfaces and Berea sandstone cores.

#### **3.1. Introduction**

Although research and field experience have shown that cores recovered using bland water-based fluids and/or low invasion drilling practices are preferred for obtaining cores with wetting properties that are representative of oil reservoirs (Anderson, 1986; Cuiec, 1989; Rathmell, 1990), these options are often not considered for reasons that have to do with hole stability and other drilling concerns. Often the only core available has been captured during oil-based mud drilling projects. The adverse wettability effects of traditional oil-based muds and their components are well established. In environmentally sensitive areas, traditional, diesel-based muds are being replaced by a variety of synthetic oil-based products, but the surfactant packages in use appear to have changed mainly with respect to the oil in which they are dispersed. In this study we compare the interfacial properties of some oil-based and synthetic oil-based mud surfactants. The effects of these surfactants on smooth mica surfaces and in Berea sandstone cores, are examined with and without the added complexity of crude oil.

#### **3.2 Experimental Methods and Materials**

##### **3.2.1 Materials**

###### **3.2.1.1 Mica**

Mica is used as the reference surface to represent silicate minerals. Samples of Muscovite mica were obtained from S&J Trading Inc. in Glen Oaks, NY. Sheets can be cut with

scissors to convenient size samples for various applications. Clean surfaces are prepared by using adhesive tape to remove the upper and lower outermost layers.

### 3.2.1.2 Brines

Brines are buffered using acetic acid/sodium acetate (pH 4) and sodium phosphate/sodium biphosphate (pH 6 and 8). Buffer strength is 0.01 mol/L. NaCl is added to the buffers to increase ionic strength, as required. Synthetic sea water contains about 0.48 M NaCl, 0.0125 M KCl, 0.011 M CaCl<sub>2</sub> and 0.056 M MgCl<sub>2</sub>.

### 3.2.1.3 Crude oil samples

Properties of crude oils used in this project are summarized in Table 3-1.

**Table 3-1. Crude oil properties.**

Oil ID	C-AL-03	Cottonwood-03	Gulfaks-96	LB-03
°API	18.7	26.4	27.1	30.6
MW (g/mol)	484	262	245	244
RI	1.5288	1.5044	1.4930	1.4848
P <sub>RI</sub>	1.4372	1.4412	nm	nm
ρ at 20°C (g/mL)	0.9384	0.8929	0.8827	0.8699
μ at 20°C (cP)	661.5	26.1	15.8	13.1
Acid # (mg KOH/g oil)	1.79	0.04	0.24	1.57
Base # mg KOH/g oil)	4.94	1.87	1.19	0.59
IEP (pH units)	5.2	3.6	3.8	4.2
Sat (%)	53.8	57.9	63.3	70.1
Arom (%)	18.4	22.7	25.5	17.6
Resin (%)	25.2	16.5	10.9	12.0
n-C <sub>6</sub> asph (%)	2.7	2.9	0.2	0.3

nm = not measurable

### 3.2.1.4 Commercial SBM surfactants

Products used in oil-based muds (OBM) and synthetic oil-based muds (SBM) supplied for testing are listed in Table 3-2.

**Table 3-2. Emulsifiers tested.**

Product	Supplier	Recommended use	Chemical description
Le Supermul	Halliburton	SBM emulsifier	a polyaminated fatty acid
Ez Mul	Halliburton	OBM emulsifier	equivalent to Le Supermul
Le Mul	Halliburton	SBM emulsifier	blend of oxidized tall oil and polyaminated fatty acid
Invermul NT	Halliburton	OBM emulsifier	equivalent to Le Mul
Versamul	M-I (from ChevronTexaco)	OBM emulsifier	equivalent to Le Mul

Depending on the application, recommended amounts range from 1 to 20 pounds per barrel, corresponding to percentages on a weight to volume basis of from a little less than 1 to more than 5 %. Adsorption on the filter cake would decrease the surfactant concentration of fluid that invades the reservoir, thus we consider surfactant concentrations that are substantially lower than the recommended amounts in the drilling mud.

### **3.2.1.5 Cores**

Berea sandstone core samples, 3.8 cm in diameter and 7.5 cm in length, were cut from two blocks. The average air permeability ( $k_g$ ) of cores from Block C was about 80md and porosity was about 17%; averages for Block EV were higher, about 350 md and 20%, for permeability and porosity respectively. Initially water-wet cores were exposed first to water, then flooded with viscous mineral oil to establish an initial water saturation ( $S_{wi}$ ). The mineral oil was displaced by decalin which was in turn displaced by crude oil. Cores were then aged at elevated temperature (75°C) for 10 days. The abbreviation MXW is used to denote mixed-wet cores that contain connate water and crude oil. MXW-F denotes a core from which the crude oil has been miscibly displaced with decalin to leave adsorbed films (F) that control the wetting conditions.

## **3.2.2 Methods**

### **3.2.2.1 Interfacial measurements**

Measurements of surface and interfacial tension (IFT) have been made by two standard techniques: duNouy ring and pendant drop (Adamson and Gast, 1997). The duNouy ring was used with a Cahn balance (DCA-312).

### **3.2.2.2 Contact angles**

Contact angles were measured using the captive drop technique, as described previously (Liu and Buckley, 1997, 1999).

### **3.2.2.3 Rate of spontaneous imbibition**

The rate of imbibition of water—scaled to account for differences in permeability and porosity, sample geometry, liquid viscosities, and interfacial tension—was determined from the rate of oil recovery versus dimensionless time (Morrow and Mason, 2001).

## **3.3 Results and Discussion**

The surfactant packages recommended for use in SBM formulations are essentially the same as those used previously in OBM recipes. They consist of acidic materials derived from tall oils with average chain length of about 18 carbons and polyaminated and other products produced from reactions with tall oils. Trade names provide little or no information about the structures of surfactants in these mixtures. Materials for this study were solicited from contacts in oil, chemical, and service companies. Experimental techniques were based on previous experience with drilling mud filtrates (McCaffery et al., 2002).

### **3.3.1 Oil/water interfaces**

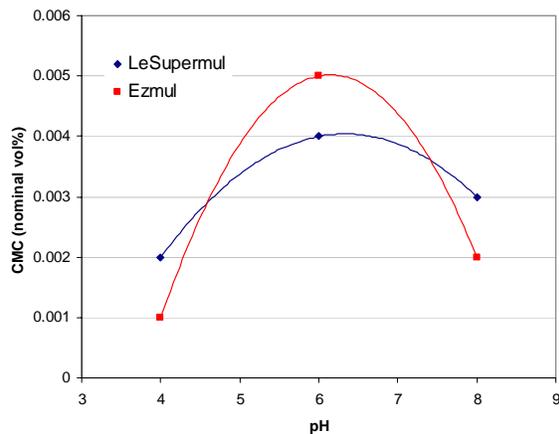
Mixtures of surfactants were prepared in decane. Concentrations are nominal, based upon the amount of surfactant product as received. Actual concentrations may be much different, depending on the product activity. Concentrations may also vary from one sample to another. For this reason and because these are mixtures of surfactants, the CMC is not well defined. Nevertheless, we will refer to this effective value of CMC as the CMC in this report. The lower limit of the ring method for measurements of IFT is in the range of 1-2 dyn/cm.

Lower values of IFT are estimates and CMC values based on these low IFTs should be considered to be lower limits on the actual CMC values.

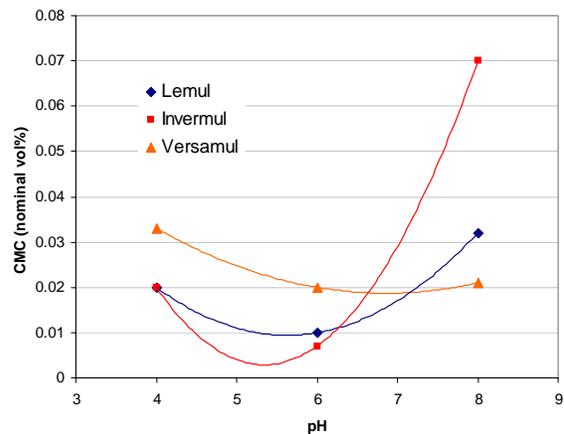
Values of CMC as a function of brine pH, determined from a change in slope of plots of IFT vs  $\ln C$  are summarized in Table 3-3, together with the IFT values at the inflection points. Two different trends were found for the five products tested. In the first group (Fig. 3-1a) were Le Supermul and Ez Mul, both of which are polyaminated fatty acids. Concentrations at the CMC are on the order of 0.001 to 0.005 vol% of product and are highest at neutral pH. In the second group (Fig. 3-1b) were Le Mul, Invermul, and Versamul. CMC concentrations are about 10 times higher than for Group 1 and are either fairly insensitive to pH or go through a maximum. The surfactant packages in this group are mixtures of polyaminated fatty acids and oxidized tall oil. Although the products within each of these two groups are considered to be equivalent according to manuals distributed by M-I, there can be differences in concentration, solvents, and perhaps in the ratios of surfactant structures in the commercial samples we tested that would account for the minor differences in results observed.

**Table 3-3. Effective CMC and IFT at CMC for commercial surfactants—effect of pH**

Emulsifier	{4, 0.1} buffer		{6, 0.1} buffer		{8, 0.1} buffer	
	CMC (vol%)	IFT (dyn/cm)	CMC (vol%)	IFT (dyn/cm)	CMC vol%	IFT (dyn/cm)
Le Supermul	0.002	6.06	0.004	3.07	0.003	0.57
Ez Mul	0.001	8.60	0.005	3.20	0.002	0.65
Le Mul	0.02	4.79	0.01	9.61	0.032	1.62
Invermul	0.02	7.83	0.007	9.92	0.07	0.86
Versamul	0.033	0.85	0.02	5.22	0.021	3.24



(a) Group 1 emulsifiers

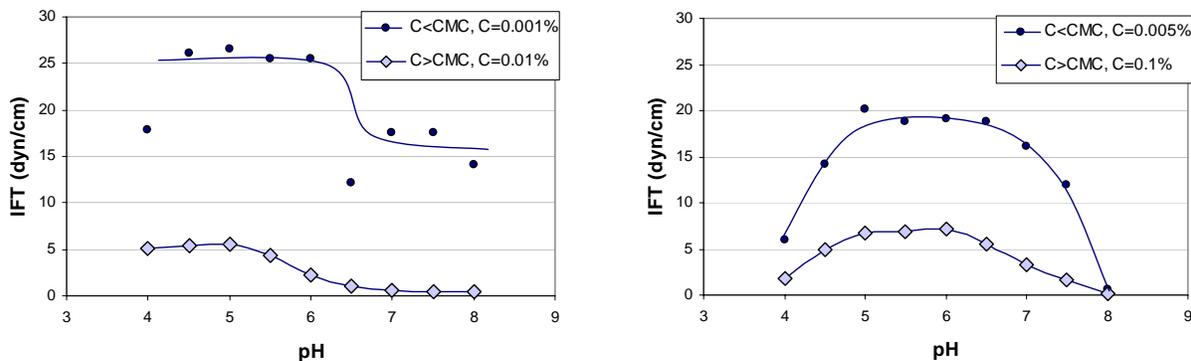


(b) Group 2 emulsifiers

**Figure 3-1. Effective values of CMC for five commercial surfactant products as a function of pH. The products fall into two distinct groups, as shown.**

IFTs of two of the surfactants, one from each group, were measured at constant concentrations above and below CMC as a function of pH (Fig. 3-2). The Group 1 surfactant, Le Supermul, was tested at 0.001 and 0.01 vol% (Fig. 3-2a). At the very low concentration there was considerable scatter in the data, but in general IFT was lower above neutral pH and higher

below. The pattern of the Group 2 surfactant, Invermul (Fig. 3-2b), was clear for both the low concentration (0.005%) and the high one (0.1%); IFT was highest at neutral pH and lower at both low and high pH (Fig. 3-3b).



(a) IFT vs. pH – Group 1 (Le Supermul)

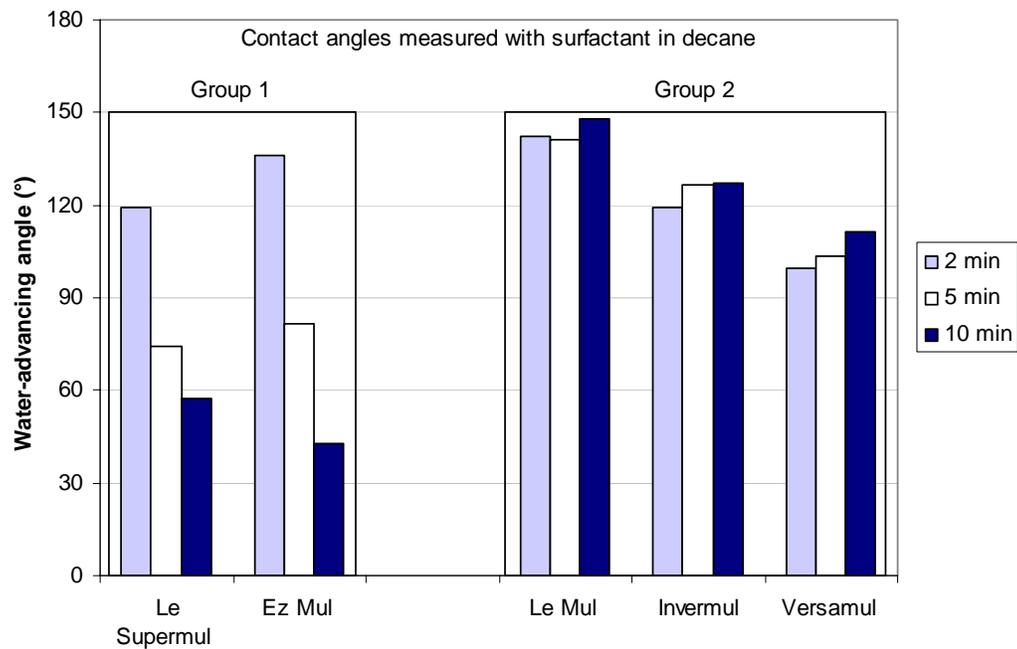
(b) IFT vs. pH – Group 2 (Invermul)

**Figure 3-2. IFT decreases over the range pH 5-7 for Group 1 mixtures at above and below the CMC. Group 2 mixtures have lower values of IFT below pH 5 and above pH 6.5, with a plateau of higher values between these two pH conditions.**

Group 2 surfactant packages are recommended for traditional “tight” or very stable emulsions, whereas those in Group 1 are suggested for conditions where more “relaxed,” less stable emulsions are desirable. Both can be used in high pH environments where lime is added in substantial amounts although high pH is not required for emulsification with Group 1 surfactants. (c.f., Baroid, 2003). Differences between these two groups of surfactants were also noted by Menezes et al. (1989) in their measurements of zeta potentials for silica flour exposed to surfactant solutions in diesel. Ez Mul and similar Group 1 products make the silica surface charge less negative and even reverse the charge to positive at low pH, analogous to the effect of positively charged CTAB (cetyltrimethylammonium bromide). Group 2 products were represented by Invermul, which had little effect on the zeta potential of the silica flour, making it slightly more negative, similar to the effect of an anionic surfactant, sodium dodecyl sulfate.

### **3.3.2 Effect of surfactants on wetting of clean mica**

Fig. 3-3 shows changes in advancing contact angles that occur if the drop is allowed to remain stationary on the surface from two to ten minutes. For the Group 1 emulsifiers, substantial decreases in  $\theta_A$  occur over the ten minute resting time. Much smaller changes in the increasing direction can be seen for the Group 2 emulsifiers in Fig. 3-3. Persistence of wetting changes are shown in Fig. 3-4 for mica surfaces, analogous to the samples in Fig. 3-3 above, that were transferred to fresh decane for contact angles measurements.



**Figure 3-3. Water-advancing contact angles on mica exposed to surfactant solutions for 1 hr. Contact angles were measured with a drop of {pH 6, 0.1M} buffer in decane solutions of each surfactant (0.03 vol%). Results are shown for contact times of 2, 5, and 10 minutes, during which the advanced aqueous drop remained stationary on the mica surface.**

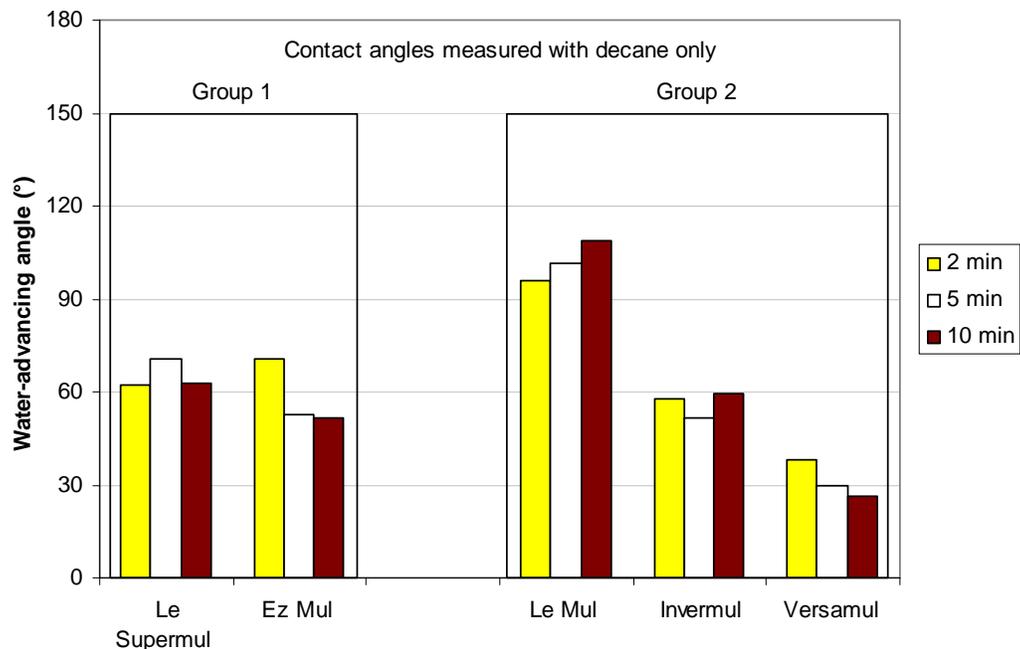


Figure 3-4. Mica samples treated as in Fig. 3-3 above. After one hour, mica was removed from the surfactant solutions and submerged in decane for the contact angle measurements with {pH 6, 0.1M} buffer. Contact times between the water drop and mica surface were 2, 5, and 10 minutes.

Contact angles indicated much more oil-wet conditions if a drop of brine was formed in the surfactant solution and allowed to age for several minutes before being brought into contact with the mica surface. An example is shown in Fig. 3-5 for EzMul. The changes in contact angles (both the decreases in Fig. 3-3 and increases in Fig. 5) were eliminated when the fluids were pre-mixed and allowed to equilibrate for 4-12 days, as shown in Fig. 3-5.

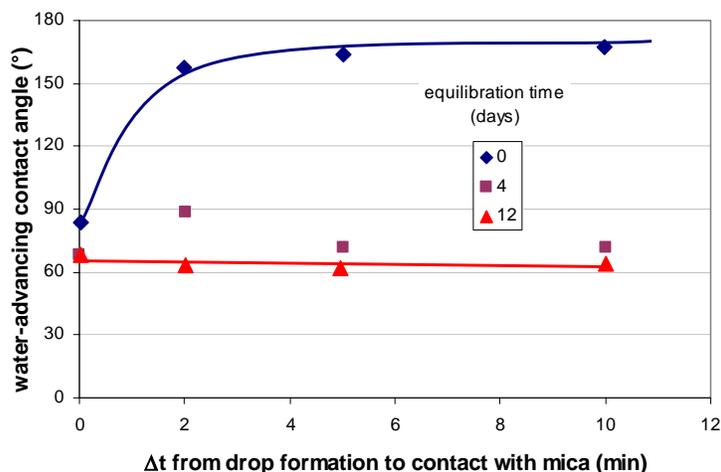
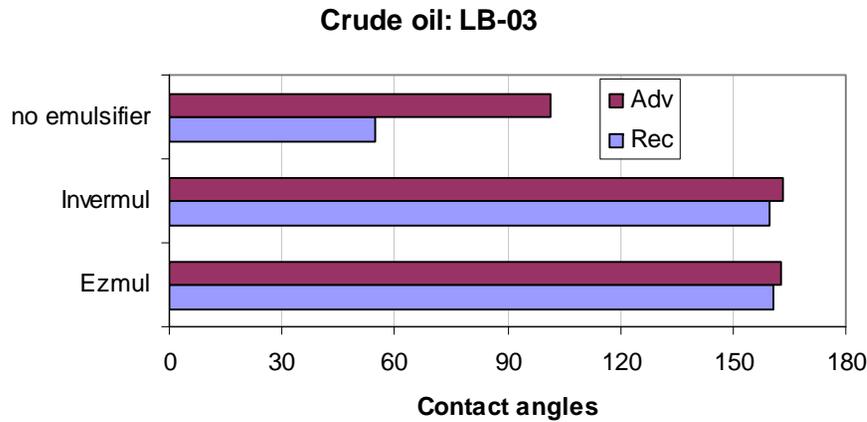


Figure 3-5. The effect of drop aging time illustrated in Fig. 3-3 was eliminated if the EzMul surfactant solution and aqueous buffer were pre-equilibrated for 4-12 days. All measurements were made after 5 min of contact between a brine droplet and the solid surface.

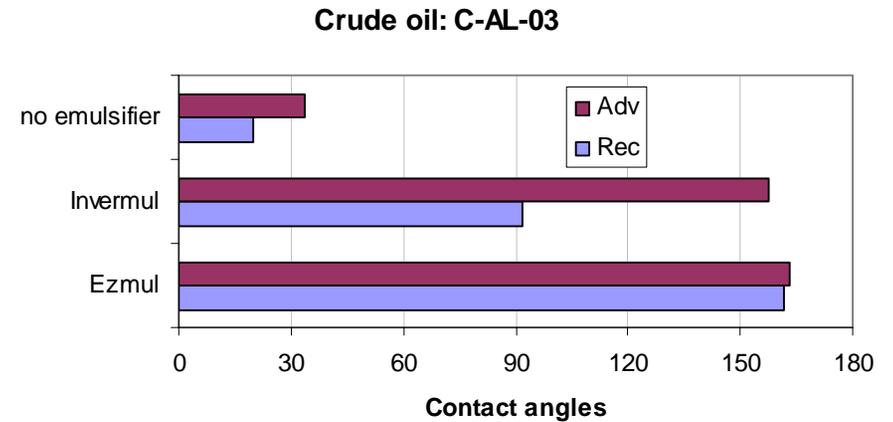
### **3.3.3 Alteration of wetting with crude oils and surfactants**

To study crude oil interactions with mineral surfaces in the presence of an aqueous phase, we used previously established protocols (Liu and Buckley, 1997, 1999). Mica was equilibrated with an aqueous phase for one day. Wet mica was aged in crude oil for 21 days, after which it was rinsed with toluene and submerged in decane for contact angle measurements. Four oils were used in this investigation: C-AL-03, Gullfaks-96, LB-03, and Cottonwood-03 (Table 3-1). These oils were selected to probe a range of wetting conditions from weakly-water wet (C-AL-03 and Gullfaks-96) to intermediate (LB-03) and weakly oil-wet (Cottonwood-03). Gullfaks-96 was paired with synthetic sea water (SSW) to match core tests presented in the next section. The remaining oils were tested with the pH4, 0.1M NaCl buffer.

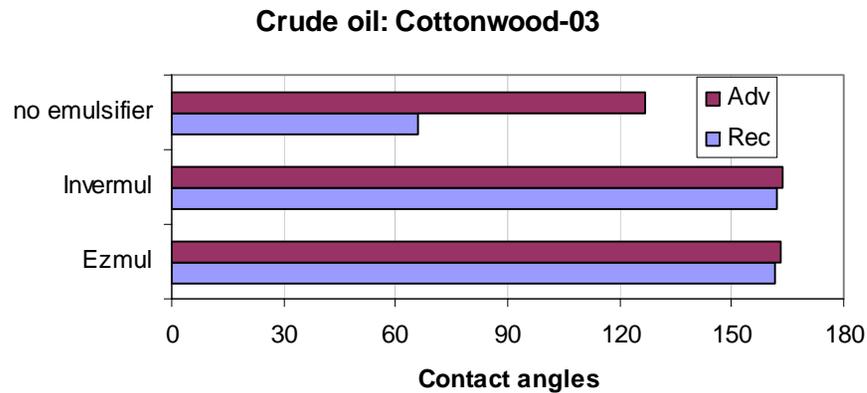
Addition of small amounts of EzMul directly to LB-03 crude oil had a small effect on wetting conditions. Water/decane advancing angles increased from about 100° for the oil with no surfactant to 130° with 0.025 vol% surfactant added to the oil in which mica samples were aged. Increasing surfactant concentration had no additional effect, in fact the water/decane contact angles decreased slightly with surfactant concentrations from 0.05 to 1 vol%. Changes in wetting toward more oil-wet conditions were much more dramatic if surfaces were exposed to the emulsifier after they had been treated with crude oil, as shown in Fig. 3-6. All of the mica samples were equilibrated with an aqueous phase (pH 4 buffer or SSW) for 24 hrs. Wet mica samples were then submerged in one of the four crude oils for 21 days. Bulk crude oil was removed by rinsing with toluene, then each surface was submerged in decane or decane solutions of surfactants. Contact angles were measured under decane with the pH 4 buffer for surfaces that were treated with C-AL-03, LB-03, and Cottonwood-03; surfaces treated with Gullfaks-96 were tested with decane and SSW.



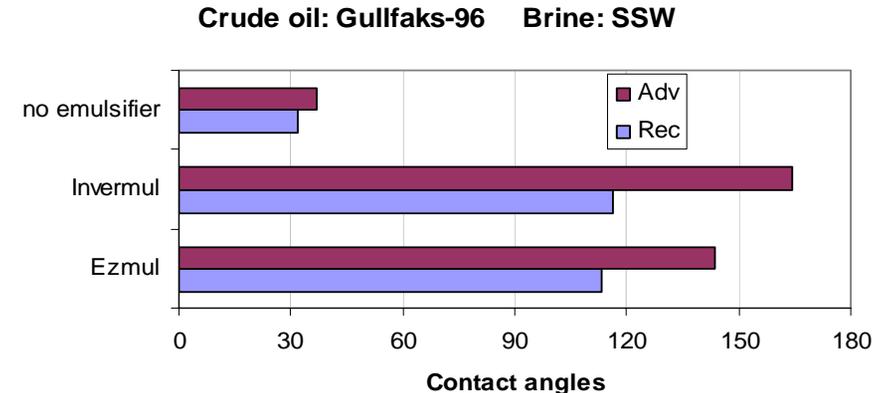
(a) mica treated with {pH 4, 0.01 M} buffer (24 hrs) and LB-03 crude oil (21 days)



(b) mica treated with {pH 4, 0.01 M} buffer (24 hrs) and C-AL-03 crude oil (21 days)



(c) mica treated with {pH 4, 0.01 M} buffer (24 hrs) and Cottonwood-03 crude oil (21 days)



(d) mica treated with synthetic sea water (24 hrs) and Gullfaks-96 crude oil (21 days)

**Figure 3-6. Contact angles (water-advancing and receding) measured on mica surfaces exposed first to brine then to crude oil. Contact angles were measured between brine and decane or decane solutions of emulsifier (0.03vol%).**

### 3.3.4 Alteration of wetting in cores

A small amount of surfactant can significantly affect the rate of imbibition into Berea sandstone cores, as shown in Fig. 3-7 for two cores exposed to an 0.005 vol% solution of EzMul in LVT 200, a paraffinic oil with a density of 0.8177 g/mL and viscosity of 2.9 cP at 20°C. A very strongly water-wet (VSWW) Berea core (core # C5-6) became somewhat less water-wet. A weakly-water wet core that had been aged in Gullfaks-96 crude oil (core # C5-3), flushed with decalin to remove the crude oil, then exposed to the surfactant solution, became even less water-wet, although water still imbibes. These results appear to be in agreement with the contact angles that are highest on oil-treated surfaces. Figure 3-8 compares the effects of the same concentration of surfactant in the same paraffinic oil before and after exposure to crude oil. The greatest effect on wetting occurs when contact with surfactant occurs after exposure to crude oil. This is an interesting observation since it tells us that comparisons of surfactant effects on clean surfaces and in clean cores may underestimate the effects of these surfactants.

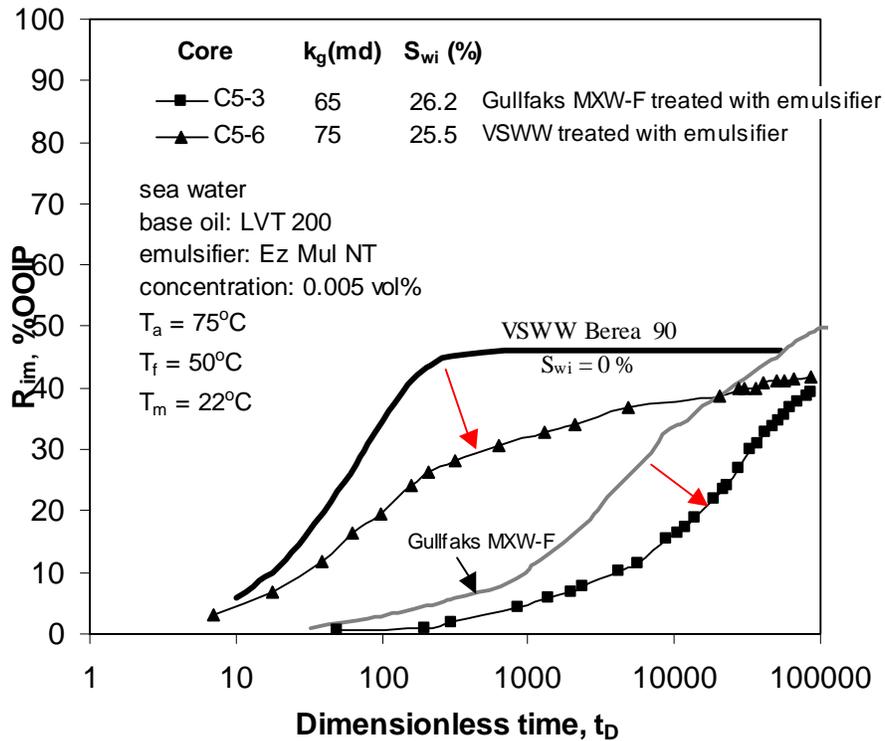


Figure 3-7. Effect of 0.005 vol% EzMul on wetting of Berea sandstone, with and without exposure of the core to Gullfaks-96 crude oil.

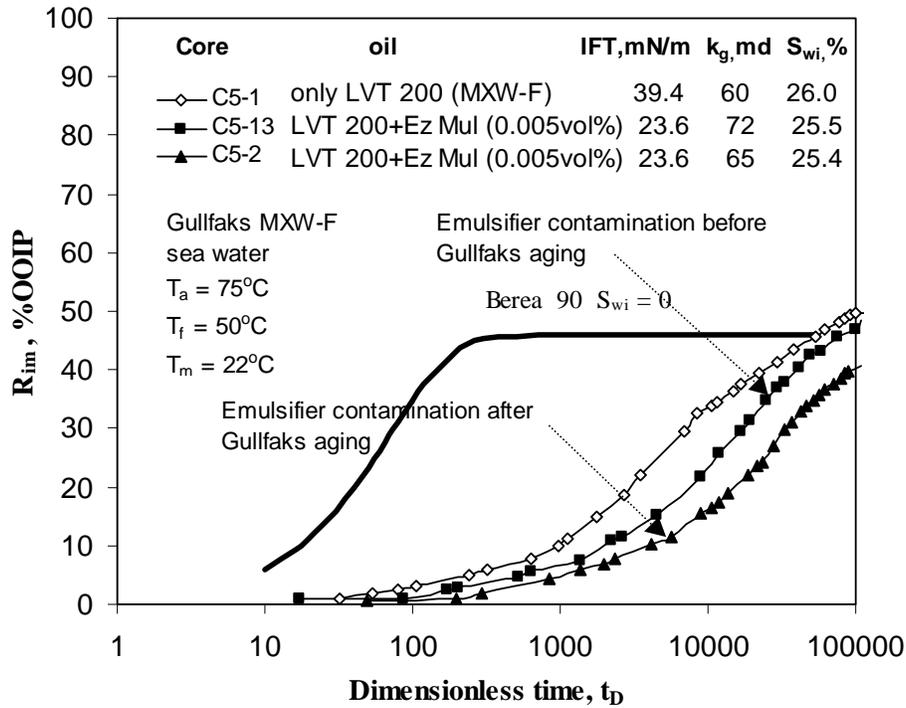


Figure 3-8. Greater change in wetting is observed when the core is exposed to EzMul after treatment with crude oil to create MXW-F wetting conditions.

Figure 3-9 compares two Group 1 surfactants, both of which suppress the rate of water imbibition at a nominal concentration of 0.005 vol%. The greater effect of EzMul suggests that the sample of EzMul used in this test has a greater concentration of active ingredients than does the LeSupermul sample.

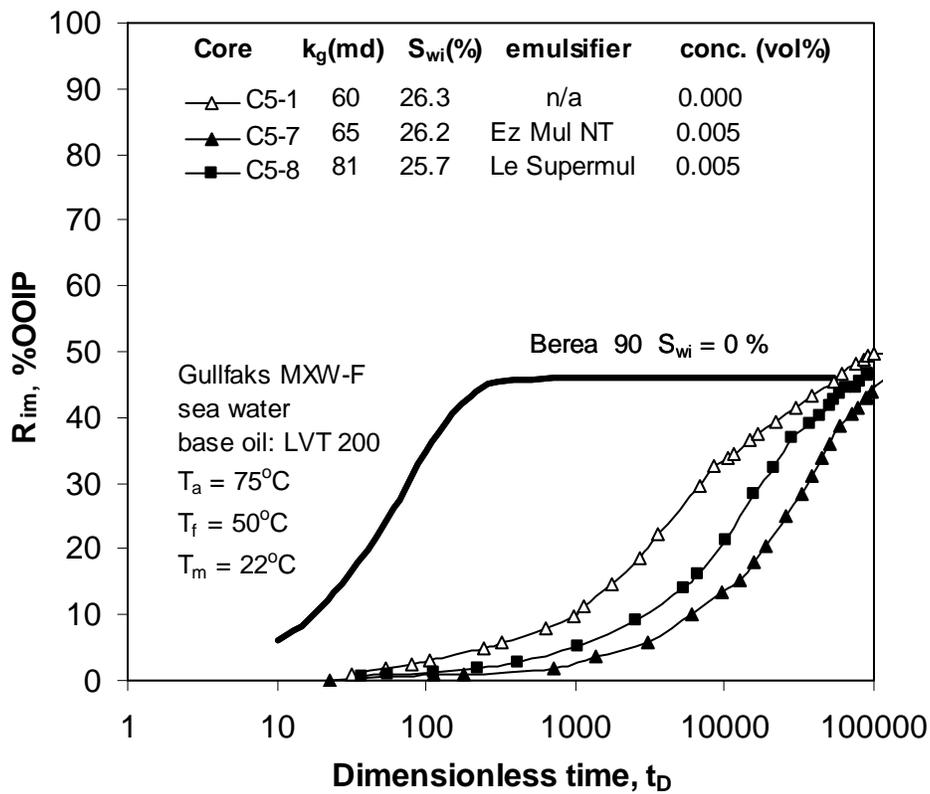
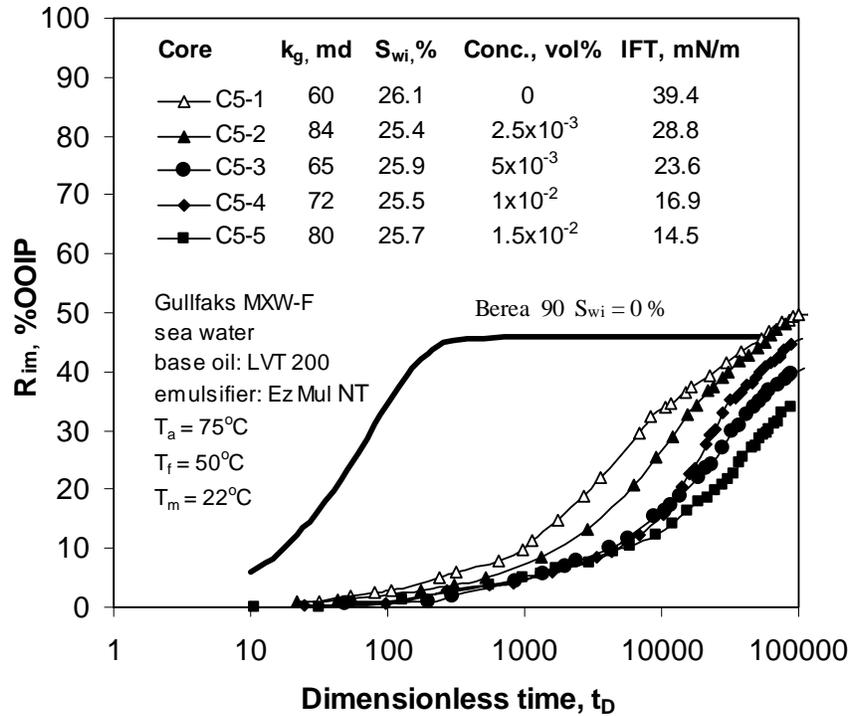
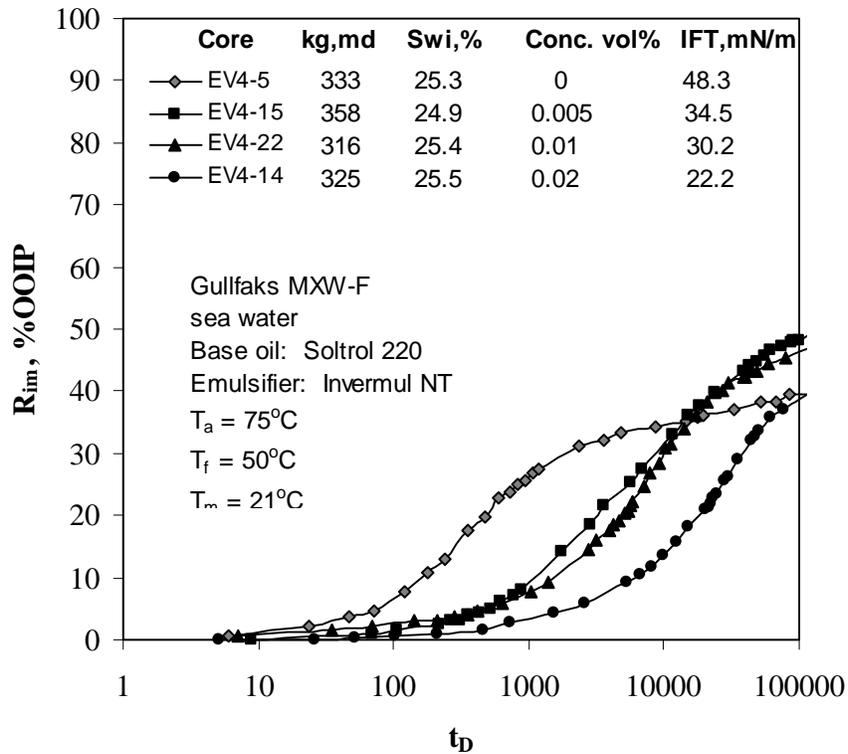


Figure 3-9. Comparison of the effects of two Group 1 surfactants: EzMul used in traditional oil-based muds and LeSupermul used in synthetic oil-based muds.

Figure 3-10 shows the effect of increasing concentrations of EzMul (Group 1) and Invermul (Group 2) surfactants in oil-treated cores. Very low concentrations of surfactant have a significant effect on the rate of imbibition and the rate of imbibition of water is further suppressed with increasing amounts of surfactants.



(a) EzMul in LVT 200 base oil.



(b) Invermul in Soltrol 220.

Figure 3-10. Increasing concentrations of EzMul and Invermul both suppress the rate of imbibition of water.

### 3.4 Conclusions

- Surfactants used in synthetic oil-based drilling fluids, like those in traditional oil-based muds, cause mica and sandstone surfaces to become less water-wet.
- Non-equilibrium effects can make surfaces temporarily appear extremely oil-wet.
- Addition of surfactant to crude oil had less effect than sequential exposure of surfaces first to crude oil, then to surfactant solutions.
- In cores, increasing concentration of surfactant produced decreasing rates of water imbibition.
- For the products and oils tested, wettability alteration was greatest on surfaces and in cores that have been exposed previously to a crude oil.

### 3.5 Acknowledgements

This work was supported by the NPTO office of the US DOE under contract DE-FC26-01BC15164, by the States of New Mexico and Wyoming, by industrial sponsors including BP, ChevronTexaco, and Total. Samples were provided by ChevronTexaco and Halliburton.

### 3.6 References

- Anderson, W.G.: "Wettability Literature Survey—Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability," *JPT* (Oct. 1986) **38**, No. 11, 1125-1144.
- Adamson, A.W. and Gast, A.P.: *Physical Chemistry of Surfaces*, 6<sup>th</sup> ed., John Wiley & Sons, New York (1997) 784 pp.
- Baroid Fluids Handbook & Product Data Sheets (2003) Halliburton.
- Cuiec, L.: "Effect of Drilling Fluids on Rock Surface Properties," *SPE Formation Evaluation* (March 1989) 38-44.
- Liu, L. and Buckley, J.S.: "Alteration of Wetting of Mica Surfaces," *J. Pet. Sci. Eng.* (1999) **24**, 75-83.
- Liu, Y. and Buckley, J.S.: "Evolution of Wetting Alteration by Adsorption from Crude Oil," *SPE FE*, (1997) **12** (1), 5-11.
- McCaffery, F., Buckley, J.S., Silveira, R., Lekkala, R.K., Goggin, D., and McCarty, A.: "Wettability and Water-Oil Displacement Investigations for Some High Permeability Turbidite Reservoirs," paper 2002-32 presented at the Internat. Symp. of the Soc. of Core Analysts, Monterey, CA, 23-25 Sept.
- Menezes, J.L., Yan, J., and Sharma, M.M.: "The Mechanism of Wettability Alteration Due to Surfactants in Oil-Based Mud," paper SPE 18460 presented at the 1989 Internat. Symp. on Oilfield Chem., Houston, Feb. 8-10.
- Morrow, N.R. and Mason, G.: "Recovery of Oil by Spontaneous Imbibition," *Current Opinion in Colloid and Interface Sci.* (2001) **6**, 321-337.

Rathmell, J.J., Tibbitts, G.A., Gremley, R.B., Warner, H.R., Jr., and White, E.K.: "Development of a Method for Partially Uninvaded Coring in High-Permeability Sandstone," paper SPE 20413 presented at the 1990 ATCE, New Orleans, 23-26 Sept.