

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

Final 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

The compositions of drilling fluids for wells drilled in sensitive and harsh environments such as the arctic are dictated by considerations other than what might be optimal with regard to determination of reservoir wettability. Both fluids and cores recovered from such wells are therefore highly likely to be contaminated with a wide variety of components from the drilling mud. Synthetic oil-based muds have many advantages from both drilling and environmental perspectives. Their effects on the wettability of recovered cores, however, can be drastic. In this project we have endeavored to consider the effects of various components of oil-based—especially synthetic oil-based—drilling fluids. Under what circumstances do they most strongly interact with mineral surfaces? Can contaminated crude oil samples be identified? Can cores be cleaned and restored to reservoir wetting conditions?

Several approaches were used in these studies to explore the effects of drilling fluid components on fluid-fluid and fluid-solid interfaces. We expect surfactants to affect the interfacial tension at oil-water interfaces, but interfacial tensions of crude oils have not been well documented. An investigation of the interfacial properties of crude oils with and without surfactant contamination provided fundamental data that can be used to identify contaminated crude oil samples and to predict changes in interfacial tension with changing conditions of the aqueous phase.

Wettability of smooth mineral surfaces was investigated for a wide range of conditions including exposure to filtrates and centrifugates of field samples of synthetic oil-based muds, commercial surfactant solutions, and solutions of surfactants of known structure. The results of surfactant exposure depend on many variables and can be quite

different for initially clean surfaces and those that have been previously exposed to crude oil. In general, the most oil-wet conditions resulted from exposure first to crude oil, then to the oil-soluble surfactants.

Tests of wettability in cores explored many of the same exposure scenarios as those tested on smooth surfaces. In sandstone cores, as on mica surfaces, the greatest effects of surfactant exposure were found for mixed-wet cores that were prepared by exposure to crude oil. These observations suggest that significant changes in wetting should be expected even with low surfactant concentrations in cores from mixed-wet reservoirs. Further wetting alteration associated with destabilization of asphaltenes was demonstrated to result from mixing of asphaltic crude oils with some of the synthetic base oils currently in use to make up synthetic oil-based muds.

Finally we investigated cleaning of contaminated cores. Sequential treatment with a sequence of solvents can effect substantial reversal of wetting changes toward more water-wet conditions, but not without changes in core permeability.

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Executive Summary

The compositions of drilling fluids for wells drilled in sensitive and harsh environments such as the arctic are dictated by considerations such as drilling rate, lubrication, cost, and hole stability. Synthetic oil-based muds have many advantages from both drilling and environmental perspectives. However, fluids and cores recovered from wells drilled with oil-based or synthetic oil-based muds are highly likely to be contaminated with a wide variety of components from the drilling mud, some of which can alter wetting and make evaluation of the original wetting state of the reservoir problematic. In this project we considered the effects of various components of oil-based, especially synthetic oil-based, drilling fluids. For example, under what circumstances do they most strongly interact with mineral surfaces? What specific drilling fluid components are most responsible for wettability alteration? Can contaminated crude oil samples be identified? Can cores be cleaned and restored to reservoir wetting conditions?

Several approaches were used in these studies to try to understand the effects of drilling fluid components on fluid-fluid and fluid-solid interfaces. The main experimental approaches included fluid-fluid interfacial tension (IFT) measurements by static and transient techniques, contact angle measurements and atomic forces microscopy imaging of smooth mineral surfaces, and wettability testing of porous media by measurements of Amott indices and rates of spontaneous imbibition.

Although we expect surfactants to affect IFT at oil-water interfaces, it is difficult to predict the range of their effects since IFTs of crude oils have not previously been well documented. An investigation of the interfacial properties of crude oils with and without surfactant contamination was undertaken to provide fundamental data that can be used to identify contaminated crude oil samples and to predict changes in interfacial tension with changing

conditions of the aqueous phase. Measurements were made by both duNouy ring and pendant drop techniques. In general, the effect of drilling mud surfactants on the IFT of crude oils is to depress oil/water IFT although the actual values depend on identity of the crude oil, brine composition and pH, as well as surfactant identity and concentration. The effect of surfactant is less for crude oil than for comparable concentrations of the same surfactants added to a paraffinic solvent in both relative and absolute terms.

Wettability of smooth mineral surfaces was investigated for a wide range of conditions including exposure to filtrates and centrifugates of field samples of synthetic oil-based muds, commercial surfactant solutions, and solutions of surfactants of known structure. The main techniques used to assess wetting included a variety of contact angle measurements and imaging with an atomic forces microscope. The results of surfactant exposure depend on many variables including surfactant concentrations, treatment duration and temperature, and the order in which treatments occur. Results can be quite different for initially clean surfaces and those that have been previously exposed to crude oil. In general, the most oil-wet conditions resulted from exposure first to crude oil, then to the oil-soluble surfactants, conditions analogous to the alteration of wettability in a reservoir during drilling with oil-based or synthetic oil-based fluids.

Imbibition-based tests of wettability, including Amott-Harvey indices that compare spontaneous and forced displacement and the rate of spontaneous imbibition, were used to judge wetting changes in cores. Exposure sequences were analogous to those tested on smooth surfaces. In sandstone cores, as on mica surfaces, the greatest effects of surfactant exposure were found for mixed-wet conditions that were prepared by exposure to crude oil. These observations suggest that significant changes in wetting should be expected even with low surfactant concentrations in cores from mixed-wet reservoirs. Further wetting alteration

associated with destabilization of asphaltenes was demonstrated to result from mixing of asphaltic crude oils with some of the synthetic base oils currently in use to make up synthetic oil-based muds.

Several cleaning methods were tested on smooth surfaces and in oil- and surfactant-contaminated cores. The most effective were found to be sequential treatments. Treatment with a sequence of solvents can effect substantial reversal of wetting changes toward more water-wet conditions and should be considered for wettability testing of cores obtained during coring with oil-based or synthetic oil-based muds. There are, however, changes in core permeability associated with such extensive cleaning.

1. Introduction

1.1 Surfactants in porous media

The oil industry uses surfactants in a variety of applications. Processes developed and tested for enhanced oil recovery suffered from surfactant loss as the additives intended to reduce interfacial tension or to stabilize foams were adsorbed onto rock surfaces. Similar phenomena can occur when surfactants, included in drilling fluids to serve a wide variety of functions, encounter mineral surfaces in the reservoir, in the pores of cuttings, and in cores recovered during the drilling process. In the reservoir, the concentration of surface active material is likely minimized by filtration through the filter cake; cuttings are exposed to higher concentrations. Cores may experience levels of surfactants between these two extremes; the exact levels of surface-active material that invade cores may be difficult to predict or to duplicate precisely in laboratory studies. An alternative is to examine a range of concentrations spanning the maximum to minimum expected values.

How exposure to surfactants will affect the wetting condition in cores is not obvious. In most cases, existing wetting is mixed, with a pattern of more and less water-wet surfaces that depend on the placement of water and oil in the pore space: more water-wet in corners and in the smallest pores, less water-wet or even oil-wet in larger pores (Salathiel, 1973; Morrow, 1990). Crude oil components are adsorbed or otherwise deposited on mineral surfaces to make those surfaces, in most cases, less water-wet than they would have been originally (Anderson, 1986; Buckley, 2001a; Buckley and Lord, 2003). How tightly they are bound to the surface varies from case to case. The impact of surfactants from the drilling fluid might range from no effect to wettability reversal from water-wet to oil-wet or even wettability reversal from oil-wet to water-wet. The core would become more oil-wet if surfactants adsorbed in the water-wet small pores

and corners. Replacement of weakly bound oil components with more strongly adsorbed surfactants is possible. Specific circumstances where surfactants make surfaces more water-wet, either by removing adsorbed oil components through formation of ion pairs or by adsorbing over oil components, increasing the hydrophilicity of the exposed outer layer of adsorbed material have been demonstrated to occur in chalk (Standnes and Austad, 2000b).

1.2 Components of SBM with potential to affect wettability

Synthetic oil-based muds have been developed mainly to solve environmental problems. The work reported in the literature on their formulation and testing is primarily intended to show that they fulfill all the normal drilling and completion requirements while at the same time reducing adverse environmental impact. Wettability issues are not considered in these evaluations beyond maintaining oil-wet conditions for cuttings transport. The potential for damage to well productivity due to creation of more oil-wet conditions near the wellbore is a problem that has received little attention. The work on OBM wetting effects suggests that wettability problems can be expected in cores recovered with SBM. The extent of damage and potential for wettability restoration in either cores or in the near wellbore region are the focus of this project.

1.2.1 Base oil

The base fluids now in use include a wide variety of synthetic oleic materials (Friedheim and Conn, 1996; Patel, 1998). Aromatic compounds are rigorously excluded because of their biotoxicity. In general, low temperature viscosities are higher for SBM than traditional OBM, but there is also a greater decrease in viscosity with increasing temperature. At reservoir temperatures the new and old formulations are more comparable. Pour points of the SBM base oils are generally lower than those used in traditional OBM formulations—an important

consideration in arctic and sea-floor conditions. Flash points are higher—an important safety consideration. Some of these materials can act as destabilizing agents for asphaltenes, which would have implications for wettability alteration, although no consideration about the potential for asphaltene destabilization appears in published evaluations of SBM base muds.

Some synthetic base oils

Esters have been favored from the standpoint of biodegradation, but the same ester linkage that promotes biological breakdown lacks needed stability, especially at elevated pH and temperature (Patel, 1999) and the byproducts (fatty acids and alcohols) may be more toxic than the original ester. Other oxygenated base oils used are ethers and acetals. Olefins, e.g., linear alpha-olefins (LAO), internal olefins (IO), and poly-alpha-olefins (PAO), are more stable, but still have greater rates of biodegradation and lower viscosities than their saturated analogs.

Asphaltene stability

Asphaltenes are the material in crude oils that is insoluble in low molecular weight paraffins. As oil from the formation mixes with the drilling fluid, the potential exists for asphaltenes to be destabilized. When that happens, the asphaltenes exhibit an increased tendency to adsorb on mineral surfaces and to alter their wetting properties (Al-Maamari and Buckley, 2003). While the stability of asphaltenes as a function of oil composition has been studied for alkanes (Buckley and Wang, 2002), little is known about stability or instability in the synthetic base oils now being used in drilling fluids.

1.2.2 Surfactants

With the development of synthetic base oils have come new surfactants and surfactant mixtures. Fewer chemical details are available about the surfactant packages, as the identity of

the surfactants used is usually considered to be proprietary. However, it is possible to learn generally about the families of compounds in use.

Drilling mud studies inevitably face problems because of the complexity of the whole mud. Filtrate compositions are highly dependent on the filtration process. For systematic studies, representative surfactants at known concentrations are preferable to complex mixtures. For surfactants that form micelles, interactions with surfaces can be quite different above and below the CMC. Mixtures of surfactants introduce additional complexity. Relating the results of systematic studies to more realistic mud conditions is a significant problem.

The surface active materials likely to occur in an SBM formulation include the primary emulsifiers and oil-wetting agents, as well as additives that might be used to modify low-shear rate rheology, and the surfactants used to make fluid loss materials oil-wet.

Fatty acids and alcohols

Whether a fatty acid is classified as an emulsifier or a wetting agent depends on the length of the hydrocarbon chain, which affects the behavior of these and related compounds at interfaces (oil/air, oil/water, oil/solid). The calcium salts of fatty acids are made by mixing the acid with lime (CaO) in the base oil. Oleic acid, an unsaturated fatty acid, has been used to form dimers or trimers to adjust the low-shear viscosity of drilling fluids. Saturated and unsaturated fatty acids are readily available in a range of molecular weights. As acids, the fatty acids themselves should interact most strongly with carbonate minerals. Their impact on clean sandstones should be less than in limestone, dolomite, or chalk cores unless carbonate cements are significant. If cationic crude oil components are adsorbed, however, there is the possibility that fatty acids, especially in their ionized form, might form ion-pairs with the adsorbed species, removing them from the surface.

Derivatives of fatty acid are sometimes added as viscosifiers. These might be related to 12 hydroxystearic acid which can form a gel in mineral or synthetic oil. Either the monomer or polymer might exhibit surface activity.

Alcohols, which can partition between oil and water, have some interfacial activity as well.

Amines and other nitrogen compounds

Amines are likely to adsorb on silicate mineral surfaces, and are used as wetting agents for that reason. Clays are treated with amines to enhance their dispersal in the base oil to increase the oil phase viscosity; some free amine might occur if the clay coating material is removed from the clay, although this is unlikely to be as large a source of surface-active material as the emulsifiers and wetting agents themselves. Primary amine analogs of the fatty acids are available up to about C₁₈, as are a wide variety of secondary and tertiary amines.

Another potential source of amines is the amine-treated lignite used to control fluid loss. Like the clays, this is likely a minor source of amines, compared to the primary and secondary emulsifiers.

In addition to the amines, there are polyamines and amides used as emulsifiers. Derivatives of imidazolines are also used as emulsifiers. Members of this class of compounds are also used as corrosion inhibitors because of their ability to adsorb on and protect steel surfaces. Adsorption on mineral surfaces must also be considered.

Asphalt derivatives

Asphaltic material from the heavy ends of a crude oil is sometimes used as a viscosifier. In crude oils, these are among the materials that adsorb on mineral surfaces and alter wetting, especially near the onset of asphaltene instability. Although they are poorly defined and may

vary significantly from one source to another, they are interfacially active and should be included in the overall consideration of potential effects of drilling mud components on wetting.

1.3 Mixed wettability conditions in reservoir rocks

It is increasingly believed that the wetting conditions of most hydrocarbon reservoirs are mixed-wet (MXW). The MXW state is formed by adsorption of polar crude oil components onto rock surfaces in the presence of initial formation water. MXW cores can be prepared for laboratory study by aging core samples with initial water saturation in crude oil. MXW (film) cores (MXW-F) can be prepared by displacing the crude oil in MXW cores with decalin followed by injection of mineral oil (Tong et al., 2002, 2003a, and 2003b). Displacement tests are then usually run with a refined mineral oil as the probe oil.

2. Experimental Materials and Methods

2.1 Materials

2.1.1 SBM and OBM components

Decane, base oils and mineral oils

Decane (>99.3% purity), used to dissolve oil-soluble surfactants, was purified by passing through a column containing silica (grade 62, 60 – 200 mesh, Aldrich, Milwaukee, WI) and alumina (80 – 200 mesh, Fisher Scientific). Silica was activated in an oven set at 200°C for at least eight hours to remove any sorbed water.

Samples of oleic materials that are used as base oils for synthetic oil-based drilling fluids have been obtained from a number of sources, as shown in Table 2.1.1-1. Experts were consulted to determine which materials would be representative of different classes of base oils that are in widespread use. Also included are decane and paraffinic mineral oils that were used in some core tests. Polar contaminants were removed from mineral oils by passing the oil through columns of alumina and activated silica as described above.

Table 2.1.1-1. SBM base oils and mineral oils (measurements all at 20°C)

Product designation	Density (g/ml)	Viscosity (cP)	RI	Supplied by	Description
Accolade	0.8243	4.9	1.4424	Westport	mixture of internal olefins and esters
Biobase 240 (C-14)	0.7712	2.1	1.4359	ChevronTexaco	linear alpha olefin
Biobase 560 (LP)	0.7596	1.9	1.4278	ChevronTexaco	linear paraffin
Decane	0.7303		1.4112	Fisher Scientific	n-paraffin
EDC 99DW	0.8059	3.0	1.4463	M-I	highly hydrogenated mineral oil
GOM 4 comp blend - IO	0.7845	3.5	1.4436	ChevronTexaco	internal olefins
LVT 200	0.8177	2.9	1.4503	Halliburton	paraffinic mineral oil
Petrofree	0.8581	7.6	1.4420	ChevronTexaco	esters
Petrofree LV	0.8617	3.9	1.4354	ChevronTexaco	esters
Petrofree SF	0.7847	3.6	1.4448	Halliburton	probably olefin
SF Base	0.7852	3.6	1.4445	ChevronTexaco	isomerized olefins
Soltrol 220	0.7833	3.8	1.4371	ChevronPhillips	paraffinic mineral oil
XP-07	0.7617	2.3	1.4286	ChevronTexaco	linear paraffin

Additives

The commercial emulsifier products tested are listed in Table 2.1.1-2.

Table 2.1.1-2. 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%. The concentrations that invade a core might be lower, if surfactant is adsorbed on the filter cake, but in cases where crude oil samples are contaminated by the drilling mud, the exposure to significant amounts of surfactant is likely.

For studies with surfactants of known structure, three liquid surfactants were obtained from Ethox Chemicals, LLC (Greenville, South Carolina): CAM-2, TAM-2, and TAM-5 (Fig. 2.1.1-1). These are similar to surfactants suggested by Patel and Ali (2003) as new emulsifiers with potential application in drilling fluids. CAM-2 is composed of coconut amine (chain length of 12 carbons, C12) plus two ethylene oxides. TAM-2 is composed of tallow amine (chain length of 18 carbons, C18) and 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.

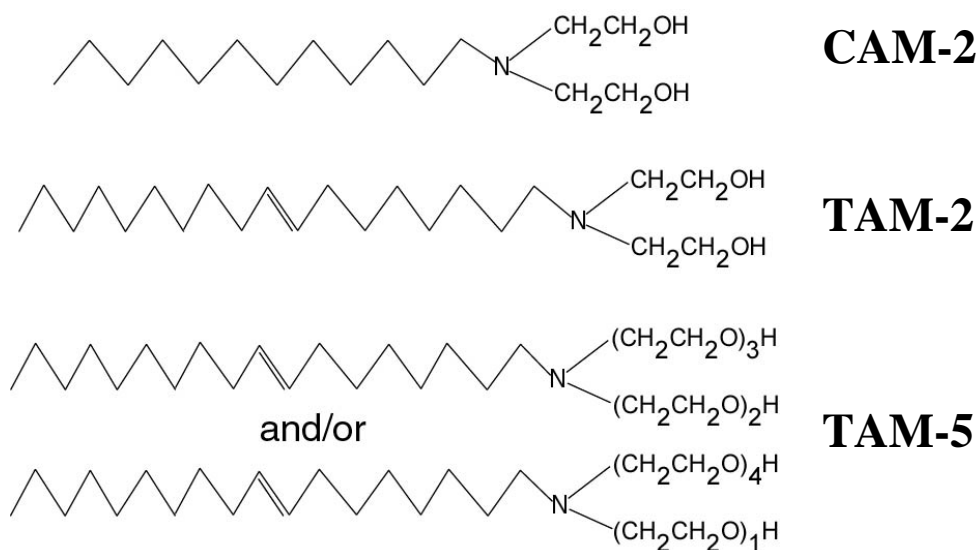


Figure 2.1.1-1. Chemical structures of the surfactants used in this study

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).

Mud fractions

Two samples, obtained from synthetic oil-base drilling muds (SBMs) used in the wells that produced oils C-K-01 and C-L-01, were used in this study. One was a filtered “end of run” sample. The other was the supernatant from a centrifuged sample, referred to as K-f for the filtrate and L-c for the centrifugate, respectively. Note that they are from different sources, not simply from different separation processes.

A disadvantage of using these field samples is that little information was available about the components of the two drilling fluids, nor were there details available regarding how the filtrate and centrifugate were prepared. Nevertheless, the opportunity to test samples of real synthetic drilling fluid fractions outweighed the scientific uncertainties, some of which are addressed in later phases of this project. Additional measurements with fluids and cores from the reservoirs represented by these mud fractions were presented recently (McCaffery *et al.*, 2002).

2.1.2 Crude oils

More than 40 crude oil samples were used in various phases of this project. Details of crude oil properties are summarized in Appendix II.

2.1.3 Brines

Brine recipes were selected to achieve pH buffering, varying levels of ionic strength, and simulation of sea water and various reservoir brines. Brine recipes are given in Appendix III.

2.1.4 Mineral surfaces and surface treatments

Mica

Sheets of Muscovite mica were obtained from S & J Trading Inc. Large stacks of mica were separated into samples a few layers thick. Sheets were cut into samples of about 1 cm by 2 cm for contact angle tests; a disc punch was used to cut circular samples with a diameter of 12.7 mm for AFM tests. Final cleaning was accomplished by pressing adhesive tape to top and bottom layers and pulling apart slowly to expose two fresh surfaces.

2.1.5 Cores

Many oil recovery studies over the past 50 years have been made with a Berea sandstone of about 500 md supplied by Cleveland Quarries. Results for this rock are designated Berea 500 in this report. Recently, rock ordered from this quarry has been in the range of 60 to 120md. Other Berea samples on hand in our laboratory and some blocks supplied by industry provide a wider range of permeability but still show distinct differences in properties to the Berea 500. Properties of sandstones used in this project are summarized in each experimental section. In addition to basic petrophysical properties, clay mineral types from x-ray analysis, BET surface areas, and cation exchange capacities, are being determined for each rock.

2.2 Methods

2.2.1 Interfacial tension (oil/water interfaces)

Interfacial tension (IFT) measurements can be static, transient, or dynamic depending on whether there are mass and surface area changes at the oil/brine interfaces with time (Ball et al.,

1996). Examples of static measurements are du Nouy ring and stationary Wilhelmy plate methods, spinning and pendant drop methods are transient, and drop volume measurements are an example of a dynamic measurement method. Two of these methods, the du Nouy ring and pendant drop, have been used in this work.

du Nouy ring

The duNouy ring method (Adamson and Gast, 1997) was used with a Cahn balance (DCA-312). Care must be taken to avoid contamination of the ring since a zero contact angle between the two fluids at the interface is required for correct interpretation of the results. For oil-soluble surfactant solutions, this means that the ring cannot pass through the oil phase before the measurement, but must be lowered into the aqueous phase before the oil layer is added. Minimum tensions that can be measured by this methods are about 1-2 mN/m.

Pendant drop

The pendant drop method was used to measure IFT between an aqueous phase and oil (crude oil or oil plus oil-soluble surfactants) using an OCA20 pendant drop apparatus with SCA20 analysis software (DataPhysics Instruments GmbH, Germany). In this system, a testing liquid in a gas-tight needle syringe was delivered by electronic control through a connecting tube and calibrated needle with a stepper motor. The liquid dosing system has a delivery range of 0.1-5 μ l/s. An image of the pendant drop formed at the tip of needle can be captured digitally and then analyzed by the SCA 20 software (Dataphysics, 2003) and an interfaced computer. The high speed CCD video camera system can do dynamic tracking analysis at a speed of 1 image/s. The surface tension (SFT) or IFT was calculated by fitting the Laplace equation to the outline of the drop (Adamson and Gast, 1997) using the following equation:

$$\gamma = \Delta\rho * g * z / 2(H_A + H_B) \quad (2.2.1-1)$$

where γ is SFT or IFT (mN/m), $\Delta\rho$ is density difference of two phases, and z , H_A , and H_B are computer fitted image parameters. A thermal plate connected to a circulating water bath and an optical chamber can be set at a desired temperature to an accuracy of $\pm 0.5^\circ\text{C}$. The densities of liquids were measured by a Mettler/PAAR DMA40 digital densitometer. In order to minimize the temperature error, the experiments were conducted at either 20°C or 25°C , close to the usual room temperature. The aqueous phase pH was measured with a combination Corning glass pH electrode with an Orion Model 520A pH meter.

Critical micelle concentration

An important property of surfactants that can form micelles is the concentration at which micelles begin to be the dominant form of surfactant in the solution. This is known as the critical micelle concentration (CMC); below this concentration surfactants mainly exist as monomers, above it they are in aggregates known as micelles. One of the measures of this concentration is a break in the slope of surface tension vs. natural log of the surfactant concentration curves. Below the CMC, IFT decreases with $\ln C$, where C is the surfactant concentration. Above the CMC additional surfactant exists in micellar form and IFT is not further reduced with increasing concentration. For the oil-soluble surfactant solutions, an oil/water equivalent of the CMC was determined based on nominal surfactant concentrations. For a given brine, IFT decreases approximately linearly with the natural log of surfactant concentration until the CMC is reached. At concentrations above the CMC, IFT is roughly constant. The composition of the brine influences IFT, so CMC is defined with respect to a given brine composition.

2.2.2 Contact angles (oil/water/solid interfaces)

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. Contact angles measured for water advancing against decane on clean mica surfaces that were aged for 24 hours in selected brines were all less than 5°, as shown in Table 2.2.2-1.

Table 2.2.2-1. Water-advancing angles on clean mica

Aging temperature	Water/decane advancing contact angles (°) on mica substrates aged in:		
	pH 4, 0.01 M NaCl	pH 8, 1 M NaCl	SSW
ambient (~25°C)	3	1	2
60°C	5	5	5

2.2.3 AFM

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- μ m cantilever, Veeco Instruments, Santa Barbara, CA).

2.2.4 Preparation of MXW-F cores

Sandstone cores are initially very strongly water-wet (VSWW). Upon exposure to crude oil, wettability can be altered to mixed-wet conditions (Morrow, 1990). In the studies presented

in this report, mixed-wet cores were prepared by equilibrating cores first with brine, then with crude oil at an initial brine saturation (S_{wi}). At this stage the wetting state is referred to as mixed-wet (MXW). For the tests in these studies, crude oil was displaced with one of the following: mineral oil, SBM base oil, or decalin followed by mineral oil. At this stage, a film of adsorbed material determines core wetting, which is therefore referred to as MXW-F. Details of core preparation influence the resulting wetting state and are presented in each of the core studies in this report.

2.2.5 Rate of spontaneous imbibition

Results of spontaneous imbibition tests are presented as recovery vs. dimensionless time, calculated using the following equation (Ma, et al., 1995, 1997):

$$t_D = t \sqrt{\frac{k}{\phi}} \frac{\sigma}{\sqrt{\mu_o \mu_w}} \frac{1}{L_c^2} \dots\dots\dots (2.2.5-1)$$

where L_c is a characteristic length that compensates for sample size, shape and boundary conditions; k is absolute permeability (md); σ is the oil/brine interfacial tension (mN/m); μ_o is the viscosity to oil (cp); μ_w is the viscosity to brine (cp); ϕ is the porosity of rock sample and t is the imbibition time (min). Temperature of measurement, T_m , for recovery of mineral oil by spontaneous imbibition was ambient for all tests.

Reference curves for VSWW imbibition

The reference curve designated as Berea 250, $S_{wi} = 0\%$ in Fig. 2.2.5-1 was obtained based on the imbibition test results from two VSWW cores without initial water. The oil recovery associated with this reference curve was calculated using the following equation (Aronofsky et al., 1958):

$$R = R_o (1 - e^{-\alpha t_D}) \dots\dots\dots (2.2.5-2)$$

where $\alpha = 0.01881$ for the adopted experimental conditions and the tested core samples. The other reference curve designated as Berea 250 $S_{wi} = 26\%$ is also presented in Fig. 2.2.5-1 for comparison. An imbibition test was performed on core EV4-1 with an initial water saturation of 26%. The Soltrol 220 /brine/ rock system for EV4-1 gave an Amott wettability index of 1, as expected. Oil recovery reached almost 40% OOIP within 1 hour and increased by only 2% thereafter. Although the wetting conditions associated with both curves shown in this figure correspond to very strongly water-wet condition, compared to Berea 250, $S_{wi} = 0\%$ reference curve, the Berea 250 $S_{wi} = 26\%$ shows a shift toward slightly reduced rate and recovery. The reduction in rate with the presence of initial water saturation is consistent with measurements for Berea 500 reported by Viksund et al (1998).

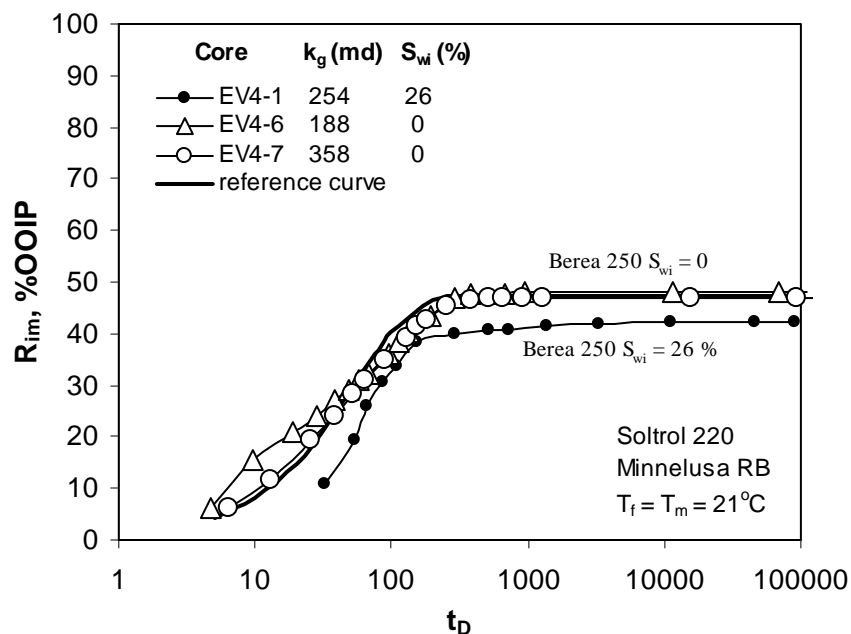


Figure 2.2.5-1. Spontaneous imbibition characteristics for very strongly water-wet cores with 0 % and 26 % initial water saturation.

Figure 2.2.5-2 compares the three reference curves based on the cores with permeability of about 90, 250 and 500 md. These curves are designated as Berea 90, Berea 250 and Berea 500 respectively. The Berea 500 reference curve is well separated from the curves for Berea 90 and Berea 250. However, the Berea 500 result agrees with a wide range of other rock types and synthetic materials (Viksund et al., 1998).

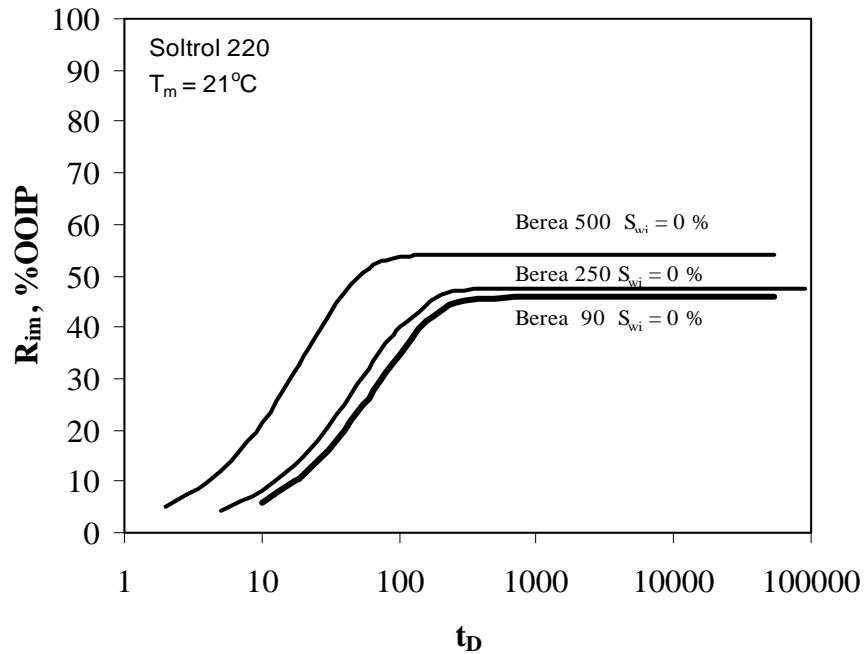


Figure 2.2.5-2. R_{im} vs. t_D for cores with different permeability at $S_{wi} = 0\%$

2.2.6 Amott wettability indices

After spontaneous imbibition the core was set in a core holder and the additional oil recovery was given by forced displacement at 0.5 cc/min. As a check on determining that a robust residual oil had been achieved the flow rate was increased in steps to 1.0cc/min, 2.0cc/min and then 3.0 cc/min. If oil continued to be produced after the flow rate had been increased to 3.00 cc/min, the recovery after injection of 3 PV at this rate was used as the forced imbibition end point. The Amott index to water was calculated using the following equation:

$$I_w = \frac{V_{oi}}{V_{oi} + V_{of}} \dots\dots\dots (2.2.6-1)$$

where V is volume, subscript o is displaced oil, and subscripts i and f refer to displacement first by spontaneous imbibition, then by forced displacement, respectively. Thus V_{oi} is the volume of oil displaced by spontaneous imbibition of water and V_{of} is the additional volume of oil produced by forced displacement after imbibition. The Amott wettability index to oil was measured from spontaneous and forced imbibition of oil and calculated using equation 2.2.6-2.

$$I_o = \frac{V_{wi}}{V_{wf} + V_{wi}} \dots\dots\dots (2.2.6-2)$$

where the volumes are analogous to those defined above except that water is being displaced by oil.

A combined index, called the Amott-Harvey wettability index, I_{A-H} , is $I_w - I_o$ (Boneau and Clampitt, 1977). Cuiec (1990) suggested the classification of wettability from the Amott index shown in Table 2.2.6-1.

Table 2.2.6-1 Interpretation of Wettability Indices

I_{Amott}	-1	-0.3	-0.1	+0.1	+0.3	+1
wettability	oil wet	slightly oil wet	neutral	slightly water wet	water wet	

2.2.7 Asphaltene stability

Evaluation of asphaltene stability is needed to understand the effect that asphaltenes have with regard to wetting and other interfacial phenomena. Microscopic observation of asphaltene flocs is used to detect the onset of asphaltene instability in mixtures of crude oils with solvents.

Solvency is approximated by measurements of mixture refractive index, as described in detail elsewhere (Buckley et al., 1998a; Wang, 2000; Wang and Buckley, 2001).

3. Results and Discussion

3.1 Interfacial tensions (Bryant, Skalli, Fan, and Buckley)

3.1.1 Oil soluble surfactants and buffers

IFTs of oil-soluble surfactant solutions were measured with either the duNouy ring or the pendant drop technique. The lower limit of the ring method for measurements of IFT is in the range of 1-2 dyn/cm. The lower limit of the pendant drop technique depends on needle diameter, but it may be as low as 0.5 dyn/cm. Lower values of IFT should be considered to be estimates and CMC values based on these low IFTs should be considered to be lower limits on the actual CMC values.

Polyethoxylated amines

Figure 3.1.1-1 shows the results of pendant drop measurements of IFT as a function of surfactant concentration. These results were used to determine an oil/water CMC of the three polyethoxylated amine 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.

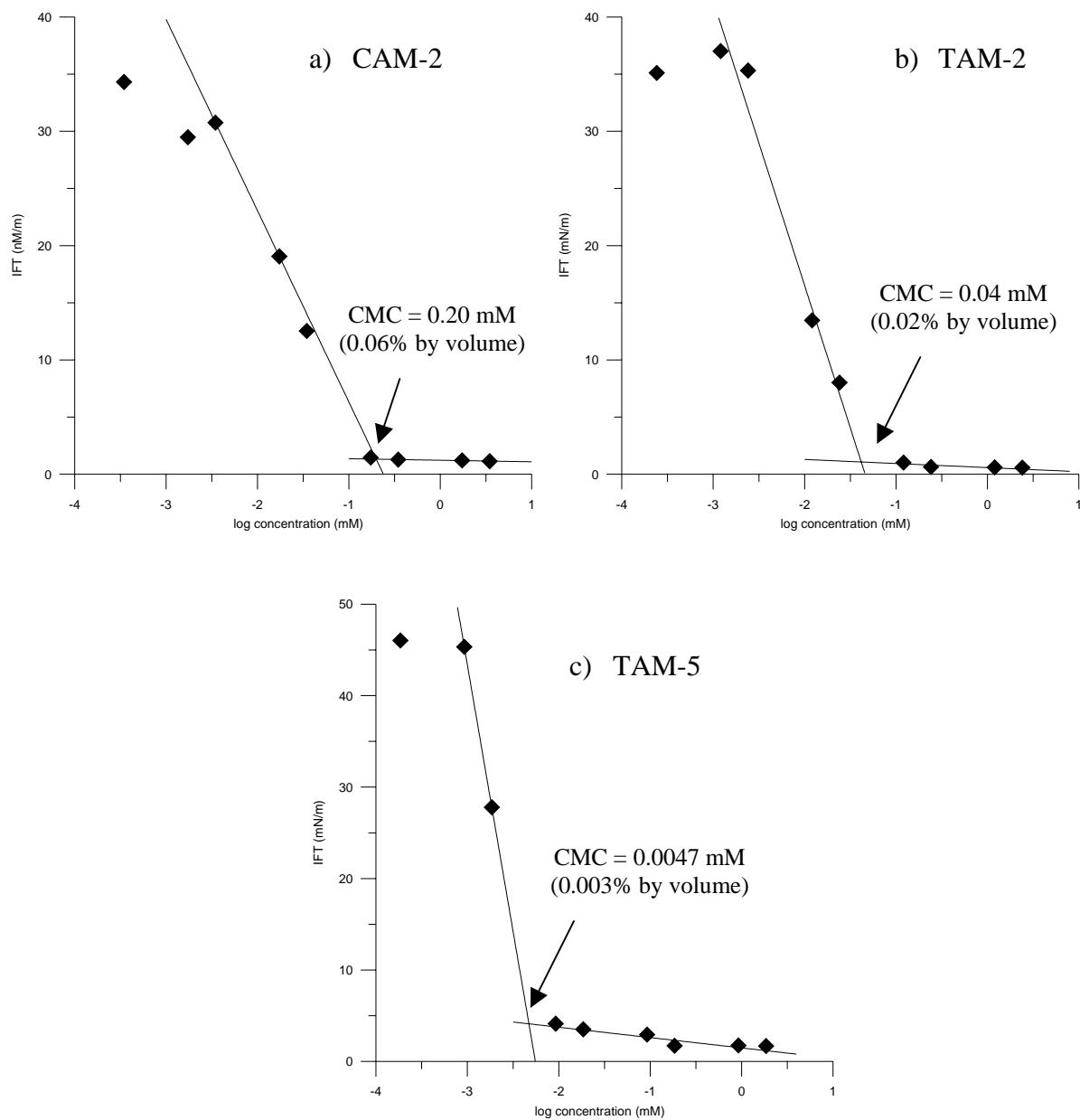


Figure 3.1.1-1. Plots of interfacial tension (IFT) as a function of log concentration were used to determine the CMC for a) CAM-2 b) TAM-2 and c) TAM-5 with pH 4 buffer.

Commercial surfactant mixtures

Mixtures of commercial OBM and SBM surfactants were prepared in decane.

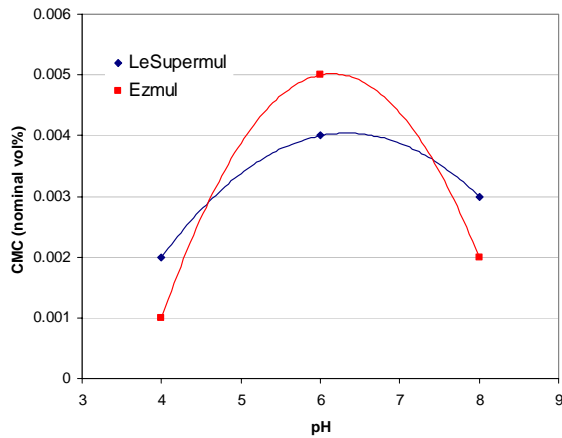
Concentrations are nominal, based on the amount of surfactant product as received. Actual

concentrations may be much different, depending on the product activity. Concentrations may also vary from one sample to another.

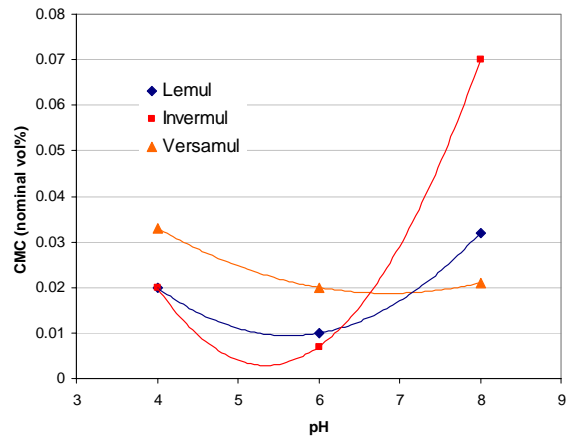
Values of CMC as a function of brine pH, determined from a change in slope of plots of IFT vs $\ln C$ are summarized in Table 3.1.1-1, together with the IFT values at the inflection points. Two different trends were found for the five products tested. In the first group (Fig. 3.1.1-2a) were Le Supermul 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. 3.1.1-2b) 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 minimum. 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 different surfactant structures in the commercial samples we tested. These differences would easily account for the minor differences observed.

Table 3.1.1-1. Effective CMC and IFT at CMC for commercial surfactants—effect of pH

Emulsifier	Brine {4, 0.1}		Brine {6, 0.1}		Brine {8, 0.1}	
	CMC (vol%)	IFT (dyn/cm)	CMC (vol%)	IFT (dyn/cm)	CMC vol%	IFT (dyn/cm)
Le Supermul	0.002	6.064	0.004	3.069	0.003	0.566
Ez Mul	0.001	8.598	0.005	3.201	0.002	0.653
Le Mul	0.02	4.789	0.01	9.607	0.032	1.623
Invermul	0.02	7.827	0.007	9.918	0.07	0.856
Versamul	0.033	0.850	0.02	5.222	0.021	3.237



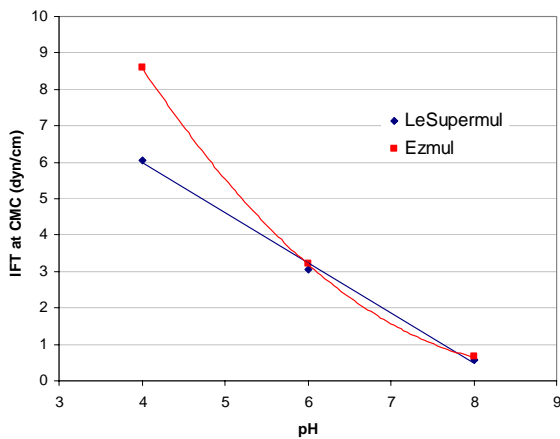
(a) Group 1 emulsifiers



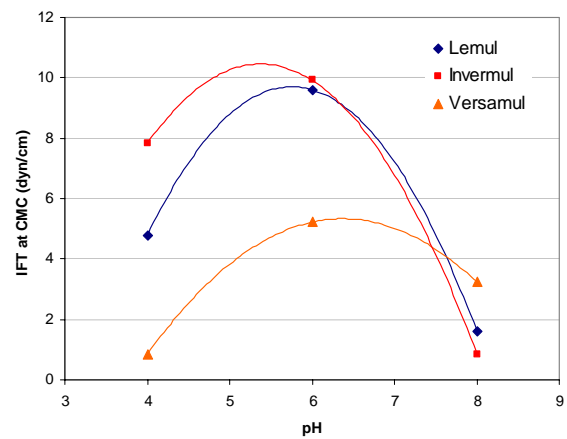
(b) Group 2 emulsifiers

Figure 3.1.1-2. Effective values of CMC for five commercial surfactant products as a function of pH. The products fall into two distinct groups, as shown.

It is also of interest to compare the IFT values measured at these CMC conditions for each of these products. These are shown as a function of pH in Fig. 3.1.1-3. Again the data fall into the same two groups. For Group 1 (Fig. 3.1.1-3a), IFT at CMC is a monotonically decreasing function of pH. Results for the two surfactant packages are very similar when the CMC mixtures are compared. The Group 2 surfactants have lower IFT values at the CMC concentrations at high and low pH and higher values at neutral pH (Fig. 3.1.1-3b).



(a) IFT at CMC – Group 1



(b) IFT at CMC – Group 2

Figure 3.1.1-3. For Group 1 surfactants, IFT at the CMC concentration decreases monotonically with pH. Group 2 surfactants go through a maximum in the value of IFT at CMC at about pH 6.

The two groups of surfactants show different behavior when IFT is plotted as a function of concentration (Fig. 3.1.1-4), using the data plotted in Figs. 3.1.1-2 and 3.1.1-3 above. For Group 2 (Fig. 3.1.1-4b), IFT appears to be generally a function of concentration whereas for Group 1 (Fig. 3.1.1-4a), there appears to be a tendency toward lower IFT at pH 8, regardless of concentration.

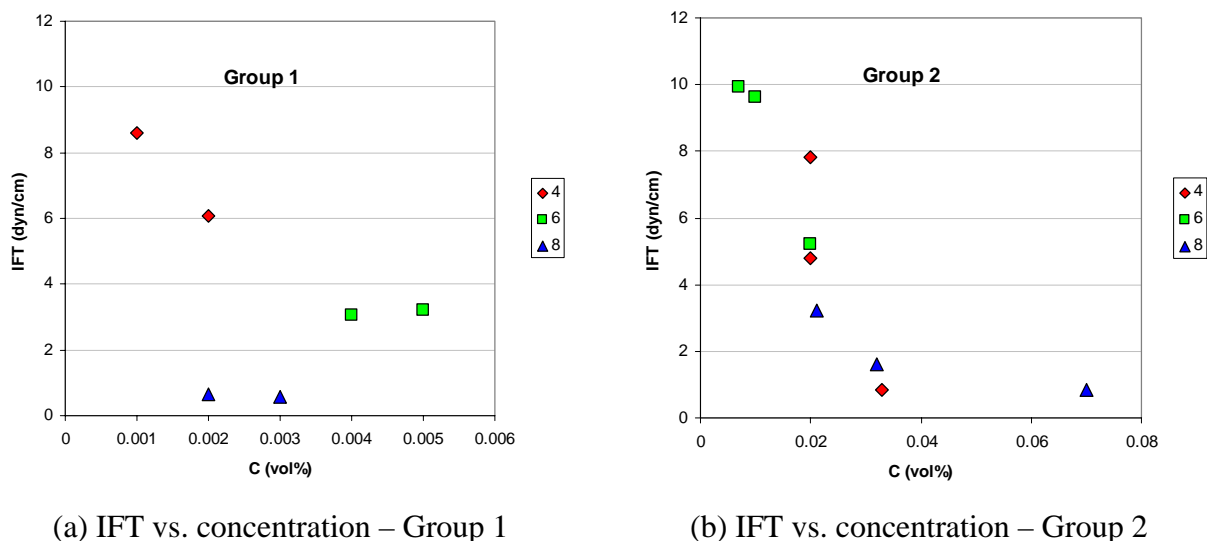
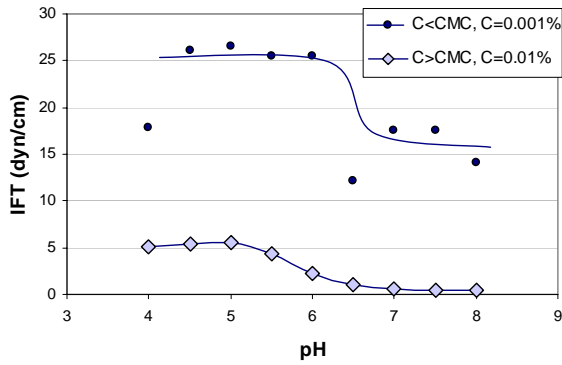
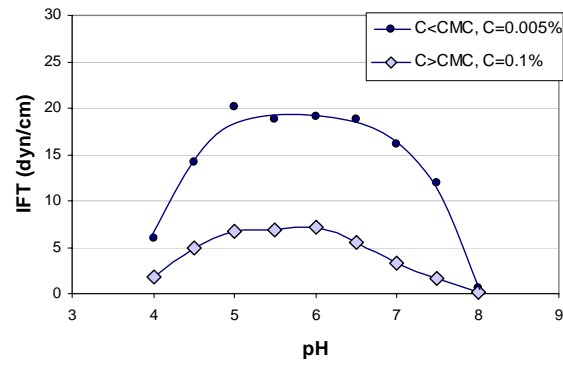


Figure 3.1.1-4. For Group 2 surfactants, the main control over IFT at CMC is concentration; Group 1 surfactants have the lowest values of IFT at CMC when the pH is 8, regardless of concentration.

Finally, 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. 3.1.1-5). The Group 1 surfactant, Le Supermul, was tested at 0.001 and 0.01 vol% (Fig. 3.1.1-5a). 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, 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. 3.1.1-5b).



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



(b) IFT vs. pH – Group 2 (Invermul)

Figure 3.1.1-5. IFT decreases at over the range pH 5-7 for Group 1 mixtures 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” emulsions, whereas those in Group 1 are suggested for conditions where more “relaxed” emulsions are desirable. Both are intended for use in high pH environments where lime is added in substantial amounts. (c.f., Baroid, 2003). Differences between these two groups of surfactants were also noted by Menezes et al. (1989). Figure 3.1.1-6 shows 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. 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.

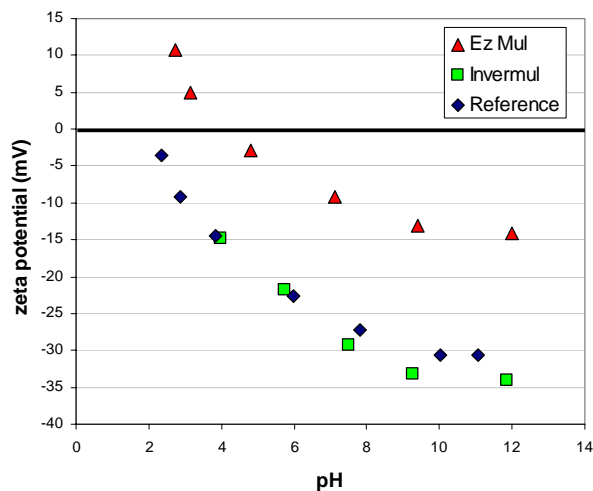


Figure 3.1.1-6. Zeta potentials of silica flour before and after exposure to surfactants, as a function of pH (data from Menezes et al., 1989).

3.1.2 Parametric study of crude oil/brine IFTs

Crude oils are complex mixtures of many thousands of components. Some of these components are interfacially active, slowly accumulating and rearranging at oil/water interfaces so that IFT can change as a function of interface age. Changes in IFT can also be caused by mass transfer between oleic and aqueous phases and chemical reactions of the acidic and basic functional groups in oil with the aqueous phase, which can produce additional surface active materials. Before we can consider the combined effects of crude oil and commercial surfactants, it is necessary to evaluate the parameters that influence crude oil/brine IFT. We have collected oils from around the world and assembled information about their physical, chemical, and surface properties in our Crude Oil-Wettability (CO-Wet) database (Buckley, 2001b; Buckley and Wang, 2002). The information stored in the database and the oil samples themselves represent a valuable resource that are used in this study to investigate the dependence of IFT on oil and aqueous phase compositions as well as measurement parameters that include drop size, drop formation rate, and interface age.

Fluids

Three aqueous phase compositions were selected for study: double-distilled water (DDW), 0.1M NaCl, or synthetic sea-water (SSW). The pH of DDW and 0.1M NaCl solutions were adjusted by addition of small amounts of HCl or NaOH. Two recipes were used for synthetic seawater, differing only in the presence or absence of sodium bicarbonate.

A wide range of crude oil samples have been collected and characterized in previous studies of the effects on reservoir wetting of crude oils and their asphaltene components (Buckley, 2001b, Buckley and Wang, 2002). Most previous studies of crude oil interfacial tensions focus on one or at most a few crude oil samples (e.g., Reisberg and Doscher, 1956; Freer et al. 2003). Given the complexity of crude oil composition, physically meaningful correlations to crude oil properties cannot be expected on the basis of studies of only a few samples.

Drop formation time

Since IFT is expected to change with time, the effect of drop formation time was considered. Figure 3.1.2-1 shows the effect of varying drop formation time on the initial and final IFT measurements (designated $IFT(0)$ and $IFT(eq)$, respectively) for a drop of SQ-95 oil in 0.1M NaCl. Data recording began about 0.1 s after the drop reached a volume of 10 μl . When the formation time was less than 3 s, $IFT(0)$ was nearly constant at a value of 22.5 mN/m; however longer drop formation times resulted in lower initial estimates of IFT. $IFT(eq)$ is the IFT measured after 2000 s (about one-half hour). This value increased slightly with increasing drop formation time, from about 12 to 13 mN/m.

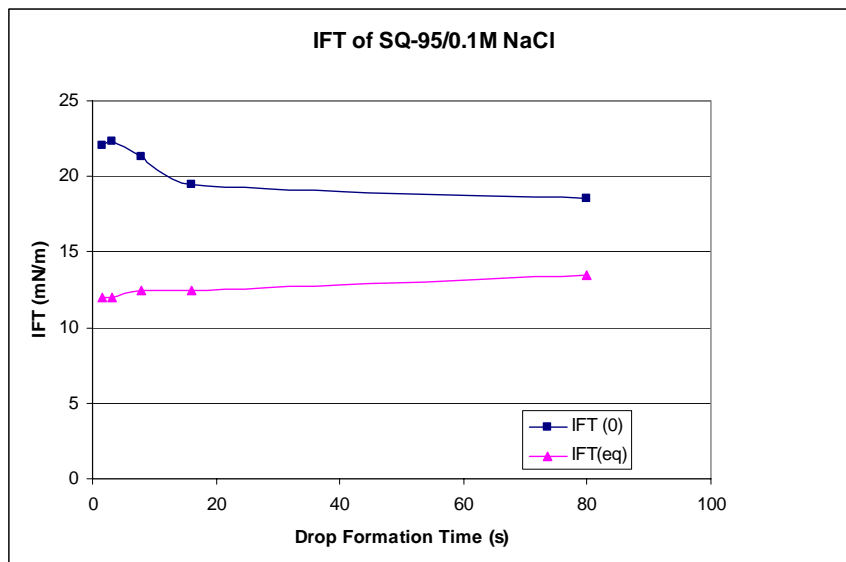


Figure 3.1.2-1 Impact of drop formation time on IFT.

Measurement protocol and fits of IFT vs. time

For the following studies of crude oil IFT, a needle with OD of 0.7 mm was used to form a 10 µl drop. Drop formation time was 2 s. Data recording began immediately after drop volume reached 10 µl and continued for 2000 seconds.

A model equation for IFT vs. time of asphaltene solutions was proposed by Jeribi et al. (2002), based on similar phenomena of rapid diffusion to an interface, followed by slow rearrangement reported for proteins. The data were fit to an equation of the form:

$$\gamma = \gamma_{eq} + (\gamma_o - \gamma_{eq}) * e^{-t/\tau} \tag{3.1.2-1}$$

where γ is interfacial tension (mN/m) with subscripts eq=equilibrium, and o=zero time or initial, t is time, τ is a characteristic time constant with the same units as time, t.

Equation 3.1.2-1 gives reasonable fits to data for a wide range of results. In many cases, however, the first IFT measurement, recorded within one or two seconds of drop formation was

not well captured by fits to the rest of the interfacial tension vs. time data. In order to capture all of the observations, data records include the first measured IFT value as well as the initial and final (or equilibrium) values and τ from the best fits. Data are summarized in Appendix IV.

Low tension limit

The pendant drop method of IFT measurement requires that a stable drop be formed. At tensions less than about 1 mN/m, oil streams continuously out of the drop-forming needle as shown in Fig. 3.1.2-2. Accurate measurements can be made by other methods, such as the spinning drop technique (Adamson and Gast, 1997), but such observations were beyond the scope of the present study.



Figure 3.1.2-2. C-F2-00 streaming upwards when emerging from needle into pH = 10.9 0.1M NaCl.

An overview of IFT measurements for all crude oils and brines

Linear multivariate statistical analysis of all of the final or equilibrium IFT data in Appendix IV produces the correlation shown in Fig. 3.1.2-3. Many crude oil properties accumulated in the CO-Wet database were examined. Density, refractive index, amounts of saturates, aromatics, and resins, and iso-electric point showed no significant correlation with IFT.

The pH of the brine influences IFT, as expected from earlier work (Buckley, 1996) and reports in the literature (e.g., Reisberg and Doscher, 1956). In addition, the amount of n-C₇ asphaltene, acid and base numbers, and viscosity all appear to be correlated with IFT. Oil viscosity at 20°C was a significant variable only in combination with acid number. If acid number was omitted, viscosity no longer contributed to the correlation. Tests of oil property correlations among 139 oil samples in the CO-Wet database show that the log of viscosity at 20°C is highly correlated to a group of properties that include base number, amount of n-C₇ asphaltene, API gravity (or density) and average molecular weight. No relationship between acid number (or any of the other variables in the database) and viscosity could be discerned.

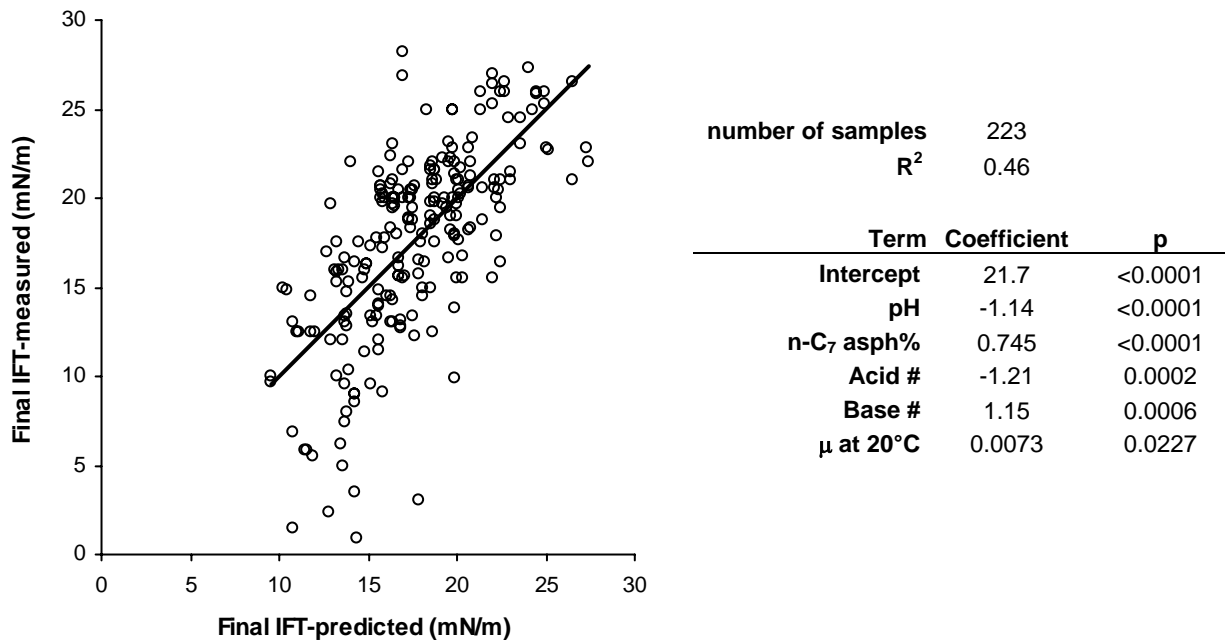


Figure 3.1.2-3. Equilibrium IFT values correlate with pH of the aqueous phase, the amount of n-C₇ asphaltenes, acid number, base number, and viscosity of each oil. The p values represent the probability that a given variable is not correlated with IFT; values of p less than 0.05 indicate significant correlation.

There is too much scatter for such a relationship to be used to predict IFT from oil properties, but it is instructive with regard to differentiating the oil properties that influence the equilibrium values of dynamic IFT at oil/water interfaces. The probability (p) of even the least

significant variable (viscosity) not being correlated with IFT is less than 0.023, showing that all the variables listed are significant. Increasing amount of n-C₇ asphaltene, higher base number and higher viscosity correspond to higher IFT with brine of a given pH. The correlation with pH is negative because large decreases in IFT can occur at the highest pHs tested in this study. IFT can also decrease at low pH, but over the range studied, this effect was much smaller. Increasing acid number contributed to a decrease in IFT. There is some coupling between the significance of viscosity and acid number; if acid number was omitted from the parameter set, viscosity was not correlated significantly with IFT, although the reverse was not true. As might be expected, correlation coefficients are low for any one variable with the highest being n-C₇ asphaltene amount ($R^2 = 0.23$) and the acid number the lowest ($R^2 = 0.01$). Better correlations can be obtained by separating the data into different aqueous phase pH and composition ranges and focusing on the effect of oil properties.

Impact of pH on IFT of crude oil

Two groups of seven crude oils each were selected for comparisons of the effect of pH on magnitude of IFT. Oils in the first group have low acid numbers (less than 0.1 mg KOH/g oil) and a typical range of base numbers. The second group contains oils with fairly high base and acid numbers.

The seven crude oils with low acid numbers are listed in Table 3.1.2-1, acid numbers ranged from 0.08 mg KOH/g oil to unmeasurable values (<0.01 mg KOH/g oil). Base numbers range from 0.11 to 2.5. IFT(0) and IFT(eq) are plotted in Fig. 3.1.2-4a-g for DDW and for 0.1 M NaCl with pH adjusted by addition of NaOH or HCl.

Table 3.1.2-1. Properties of oils with low acid number and varying base number

Oil ID	Acid #	Base #	n-C ₇ asphaltene (wt%)	Viscosity (cP) at 20°C
C-R-01	<0.01	0.40	1.30	17.8
Minnelusa-02	0.01	2.01	8.75	58.2
B-1-00	0.04	0.85	0.62	4.7
Cottonwood-03	0.04	1.87	2.51	26.1
C-Lb-01	0.05	2.50	1.60	22.6
P-VE-00	0.05	1.54	3.43	16.9
C-Br-01	0.08	0.11	0.05	1.2

All the low-acid-number oils have fairly constant IFT(0) and IFT(eq) when pH was lower than 6.4. At pH 8.9 for oils C-R-01 and C-Br-01 and at pH 10.8 for the remainder of the oils, the IFT(eq) decreased abruptly.

The seven high-acid number crude oils are listed in Table 3.1.2-2 in order of increasing acid number. Plots of initial and equilibrium IFT as a function of pH in DDW and 0.1 M NaCl are given in Fig. 3.1.2-5a-g.

Table 3.1.2-2. Properties of oils with high acid and base numbers

Oil ID	Acid #	Base #	n-C ₇ asphaltene (wt%)	Viscosity (cP) at 20°C
C-F2-03	0.70	1.32	1.97	28.6
E-1XD-00	1.56	2.98	2.54	137.4
LB-03	1.57	0.59	0.07	13.1
GOM(2)-00	2.02	1.79	8.63	122.3
C-K-01	2.44	5.19	3.46	393.6
E-1XO-00	3.42	2.57	0.76	15.3
Mars-P	3.92	2.30	4.77	481.1

For all oils, the lowest IFT values were obtained with the highest pH brines. Equilibrium IFT values are lower than initial IFTs. At the same pH, the IFT measured with 0.1 M NaCl were equal to or less than the IFT with DDW.

Low-acid-number oils, had high-pH IFT values that were measurable by the pendant drop technique, whereas for six of the seven oils with higher acid numbers, IFTs with the highest pH aqueous solutions, whether DDW or NaCl, were so low that a stable drop could not be formed.

Additional comparisons are shown in Fig. 3.1.2-6 where the equilibrium IFT values for each oil are replotted for low-acid-number (Fig. 9a for DDW and 9b for 0.1 M NaCl) and higher-acid-number (Fig. 3.1.2-6c for DDW and 3.1.2-6d for 0.1 M NaCl) oils. It is difficult to see any clear trends either among the oils in either of these groups or between the two groups. There are oils whose IFT changes little with addition of NaCl in both groups (Minnelusa-02 in Fig. 3.1.2-4b, B-1-00 in Fig. 3.1.2-4c, LB-03 in Fig 3.1.2-5c, E-1XO-00 in Fig. 3.1.2-5f, and Mars-P in Fig. 3.1.2-5g). The maximum and minimum equilibrated values of IFT at near-neutral pH are similar for both groups, as are the differences between initial and equilibrated values of IFT. One difference was observed: the value of $IFT(0) - IFT(eq)$ at acidic conditions was found to be a linear function of the log of viscosity, especially for Group 1 oils, as shown in Fig. 3.1.2-7.

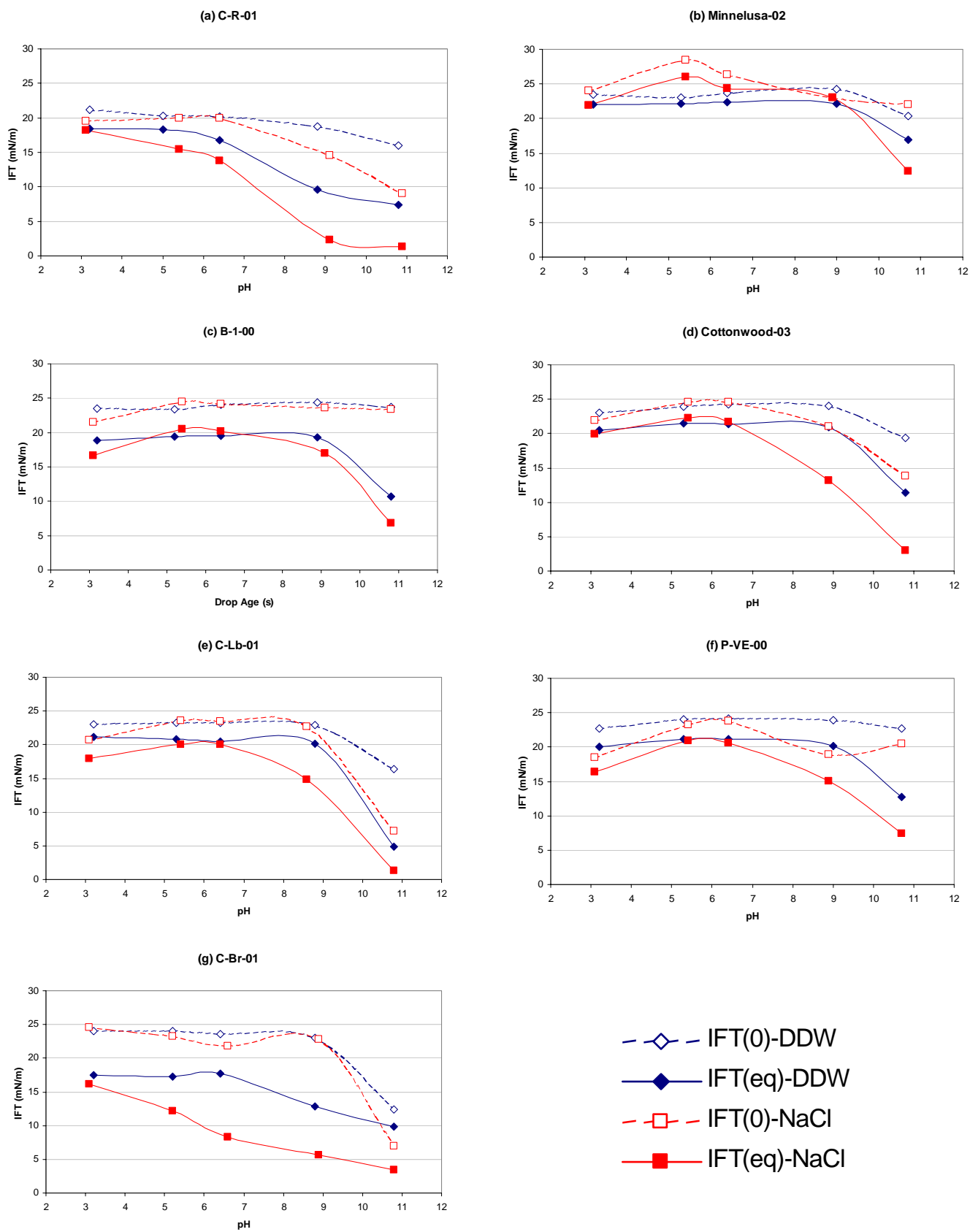


Figure 3.1.2-4. IFT as a function of pH for the low-acid-number crude oils.

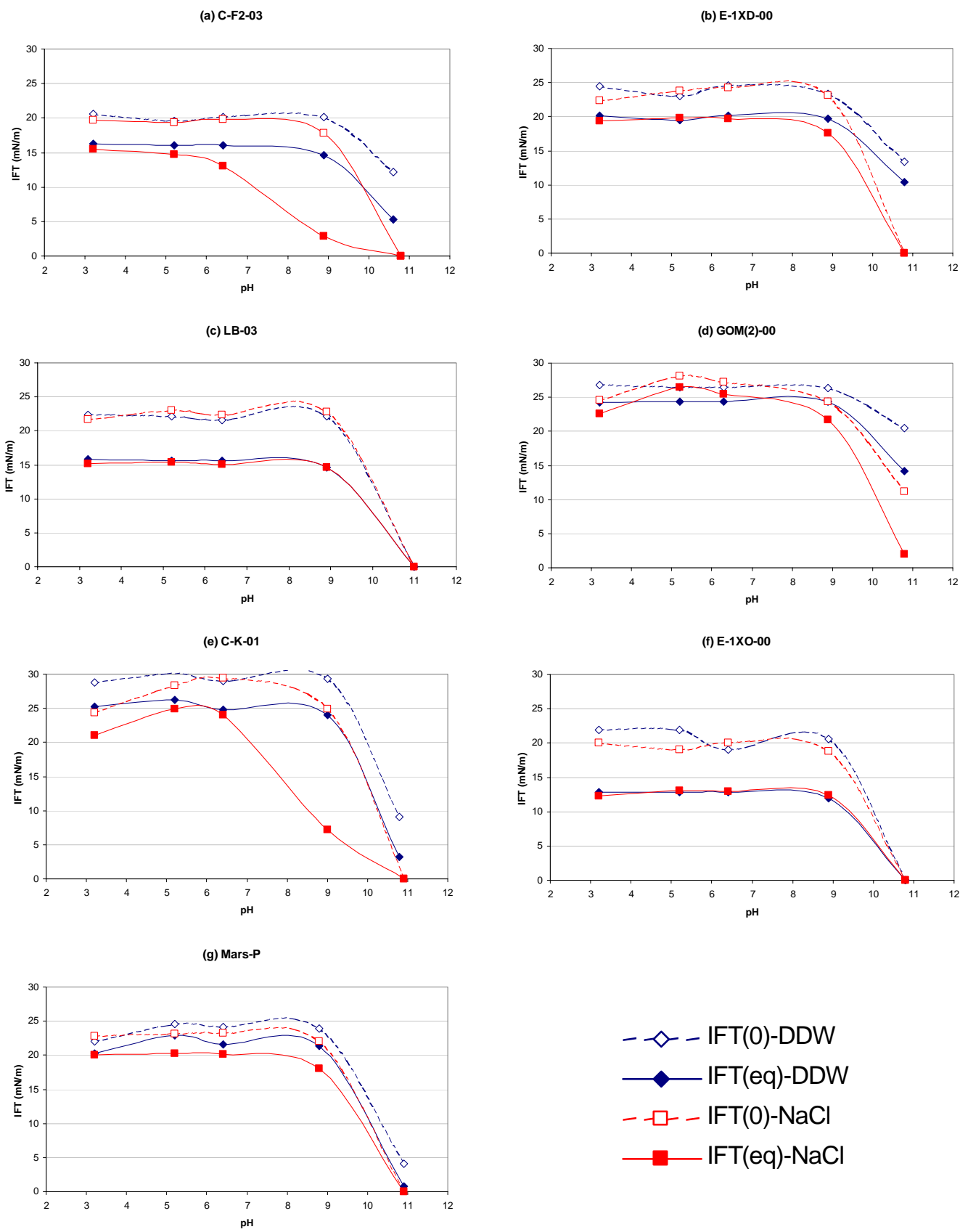


Figure 3.1.2-5. IFT as a function of pH for higher- acid-number crude oils.

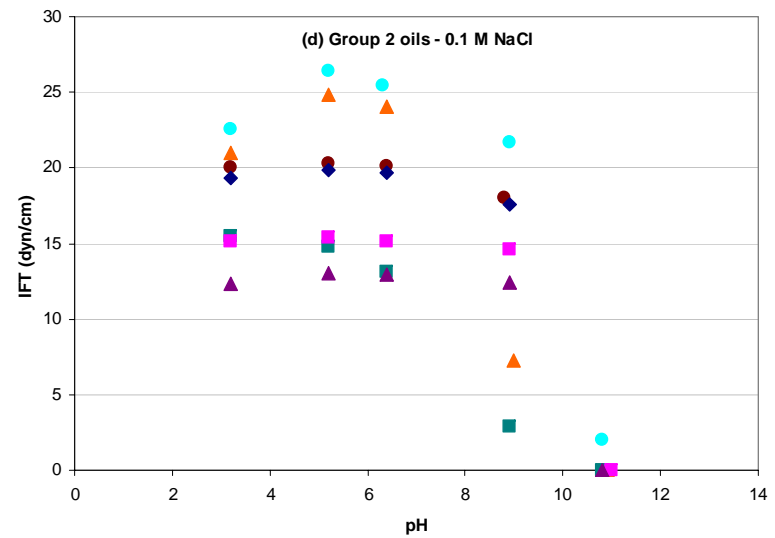
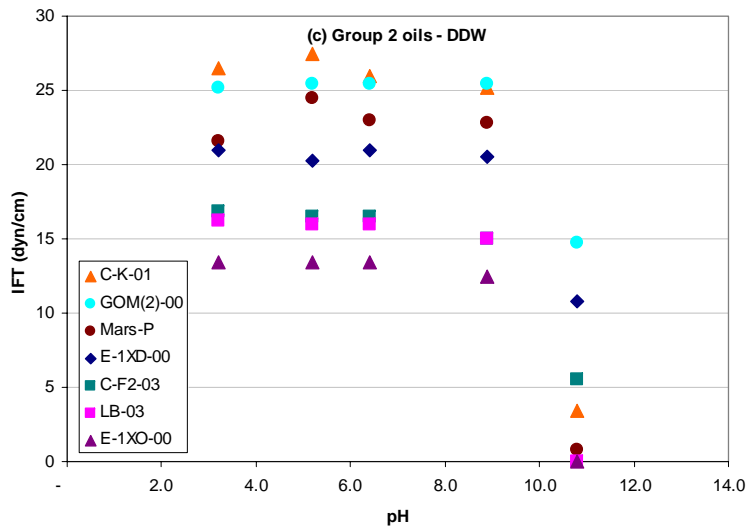
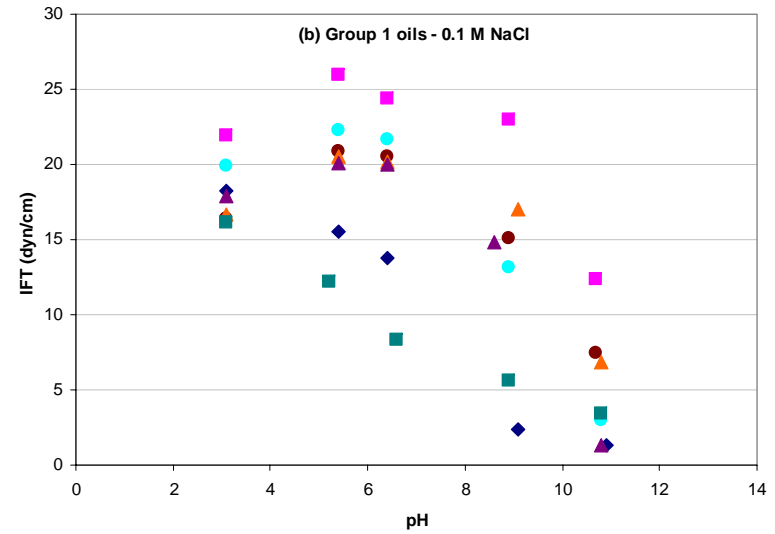
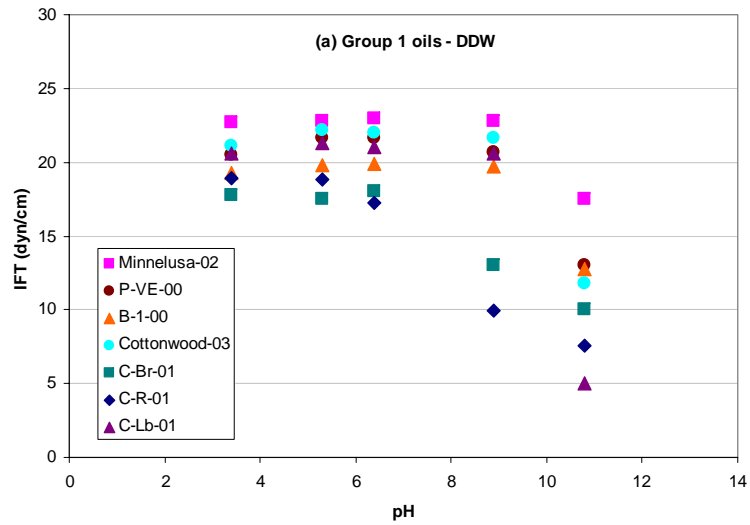
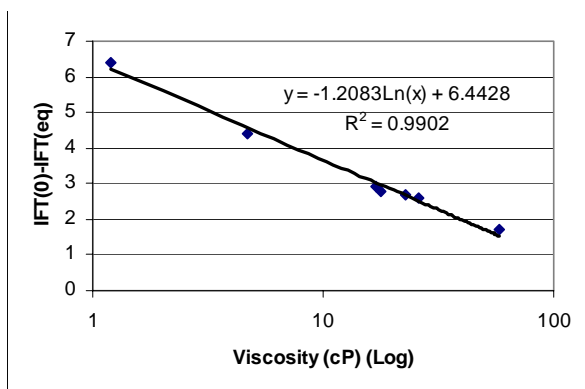
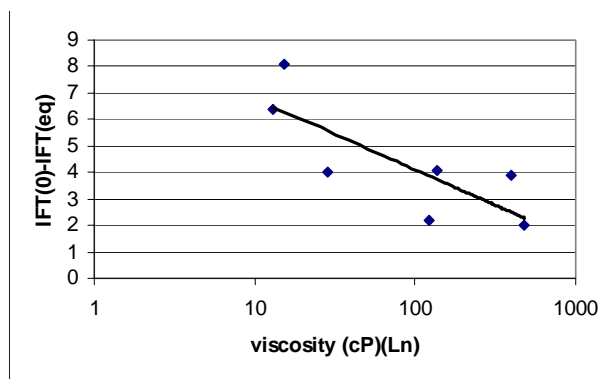


Figure 3.1.2-6. Summary of IFT(eq) data for crude oils measured against pH-adjusted DDW and 0.1M NaCl solutions.



(a) Group 1, low acid number oils



(b) Group 2, higher acid and base number oils

Figure 3.1.2-7. At acidic conditions, the change in IFT with time correlates with log (viscosity).

Comparison of IFT of different crude oils at constant pH

Three pH ranges were selected for examination. Within each range, the data were further subdivided according to the composition of the aqueous phase, which falls into one of the following three categories:

- distilled water to which small amounts of HCl or NaOH were added to adjust pH,
- 0.1M NaCl to which small amounts of HCl or NaOH were added to adjust pH, and
- synthetic sea water (at near-neutral conditions only).

Crude oils tested at each of these conditions are indicated in Table 3.1.2-3. Table 3.1.2-4 summarizes fits to all of the data in each subgroup. For comparison, the same set of variables (n-C₇ asphaltenes, acid number, base number, and viscosity) was used for all of these correlations, although not all four of these variables are significant in every case. Values of p greater than 0.05 that indicate a higher probability of including that variable erroneously are indicated by the shaded boxes. Removing those variables from the group would change the magnitudes of the remaining coefficients somewhat, but in no case were the signs of those coefficients changed.

Table 3.1.2-3. Summary of crude oils tested in each pH and brine composition subgroup

	DDW			0.1M NaCl			SSW
	3	6	9	3	6	9	6
B-1-00	x	x	x	x	x	x	
C-A1-00		x					x
C-AG-03		x					x
C-AL-03		x					x
C-Br-01	x	x	x	x	x	x	
C-F2-03	x	x	x	x	x	x	
C-GC-T1-03		x					x
C-K-01	x	x	x	x	x	x	
C-Lb-01	x	x	x	x	x	x	
C-R-01	x	x	x	x	x	x	
C-T-02		x					x
Cottonwood-03	x	x	x	x	x	x	
E-1XCO-01		x					x
E-1XD-00	x	x	x	x	x	x	x
E-1XFR-01		x					x
E-1XO-00	x	x	x	x	x	x	x
E-2XR-00		x					x
E-8XFR-01		x					x
E-BL-00		x					x
E-S1XCA-01		x					x
E-S1XG-01		x					x
E-S1XL-01		x					x
E-S3XR-01		x					x
GOM(2)-00	x	x	x	x	x	x	
Gulfaks-96		x					
LB-03	x	x	x	x	x	x	x
Mars-P	x	x	x	x	x	x	
Minnelusa-02	x	x	x	x	x	x	
Minnelusa-03		x					x
MY2-02	x	x	x	x	x	x	x
MY3-02	x	x	x	x	x	x	x
MY4-02	x	x	x	x	x	x	x
P-VE-00	x	x	x	x	x	x	
SQ-95	x	x	x				
S-Ven-39		x					x
S-Ven-40		x					x
S-Ven-41		x					x
Tensleep-99	x	x	x				
W-Br-03		x					x
W-Lo-03		x					

Table 3.1.2-4. Summary of pH and brine composition subgroup correlations with standard variables

	pH	n	R ²	Intercept p value	n-C7 asph% p value	Acid # p value	Base # p value	μ at 20°C p value
DDW	3	19	0.54	17.9338	0.4118	-1.7064	0.7572	0.0165
				<0.0001	0.0851	0.0136	0.2298	0.0242
	6	43	0.46	18.2559	0.4609	-1.6492	0.8548	0.0114
				<0.0001	0.0077	0.0009	0.0853	0.0103
	9	23	0.48	13.8502	0.7058	-1.3953	1.5510	0.0138
				<0.0001	0.0450	0.0784	0.0873	0.1206
0.1M NaCl	3	17	0.72	16.8837	0.6018	-1.2887	-0.0738	0.0145
				<0.0001	0.0017	0.0075	0.8584	0.0056
	6	20	0.69	11.5694	1.2503	-0.9129	2.0867	0.0017
				<0.0001	0.0005	0.2543	0.0148	0.8431
	9	15	0.48	6.3557	1.2070	0.6351	2.2863	-0.0037
				0.0227	0.0306	0.6269	0.1820	0.7986
SSW	6	25	0.28	14.7631	0.5721	-2.0157	1.3697	0.0092
				<0.0001	0.1405	0.0995	0.2555	0.3135

The best correlations with the standard group of oil properties were obtained for IFT measured with 0.1M NaCl solutions at all three pH conditions. For synthetic seawater, none of the standard variables were significant. The largest data sets were for measurements with distilled water results. Despite the availability of more data, correlations at all three pH conditions were not as good as those for the 0.1M NaCl solutions. Amount of n-C₇ asphaltene was below the p value threshold of 0.05 in five out of seven cases. In all cases, increasing acid number decreased IFT while increasing base number had the opposite effect. Higher IFT values were also associated with larger amounts of asphaltene and higher viscosities. Which variables were most significant depended on the pH and brine composition. Table 3.1.2-5 summarizes the coefficients calculated for the best fits with no variables included with p values greater than 0.09.

Table 3.1.2-5. Best correlations for pH and brine composition subgroups

pH	brine	R ²	intercept	coefficients		
				n-C ₇ asph wt%	Acid # (mg KOH/g oil)	Base # viscosity at 20°C (cP)
3	DDW	0.52	18.7368	0.4463	-1.6022	0.0199
3	NaCl	0.74	16.8001	0.5983	-1.2971	0.0142
6	DDW	0.46	18.2559	0.4609	-1.6492	0.8548
6	NaCl	0.70	11.5666	1.2425		1.6910
9	DDW	0.42	13.1887	0.8981		1.4604
9	NaCl	0.56	6.3313	1.1645		2.5755

Acidic conditions (pH ~ 3): When the aqueous phase was acidic, amount of n-C₇ asphaltene, acid number, and viscosity were the most significant variables. Base number was not significant with or without added NaCl.

Near-neutral conditions (pH ~ 6): In NaCl solutions, base number and amount of n-C₇ asphaltene were the only oil properties that contributed significantly to IFT. In distilled water at near neutral pH, all the variables were significant at the p<0.1 level. Near-neutral DDW thus seems intermediate between lower and higher pH conditions in that all four variables have some influence. In synthetic seawater, the presence of divalent ions probably increases the importance of specific interactions with the crude oil that are not well correlated with any of the oil properties measured.

Basic conditions (pH ~ 9): In distilled water and NaCl solutions adjusted to pH 9, the amount of n-C₇ asphaltene and base numbers were the significant variables.

Basic conditions (pH 10 and above): Although numerical correlations cannot be made from this study because of the limitation on low IFT measurements by the pendant drop method, it is clear from comparison of Figs. 9b and 9d at high pH that acid numbers above those in Group 1 (i.e., above about 0.1 mg KOH/g oil) must be required to achieve very low tensions.

3.1.3 SBM/OBM surfactants in oil

Crude oil components affect interfacial and surface properties by adsorption on the solid surfaces and accumulation at oil/brine interfaces. Added surfactants have the potential to affect polar components on the surface, replacing or coadsorbing with material from the oil. They might affect the oil/brine interfacial properties since they also accumulate at oil/brine interfaces. Finally, they may interact with polar species in the bulk oil. Clementz and Gerbacia (1977) showed a correlation between an oil's base number and "deactivation" of petroleum sulfonate surfactants. Standnes and Austad (2000a) postulated formation of ion pairs between surfactants and adsorbed crude oil components to explain increased rates of imbibition of water into chalk in the presence of cationic surfactants.

Surfactant in decane

Invermul is a blend of oxidized tall oil and polyaminated fatty acid surfactants that is commonly added to oil-based drilling fluids to promote emulsification of water. Figure 3.1.3-1 shows a comparison of IFT measured against DDW of decane with and without the addition of 0.06 wt% Invermul. Addition of a small amount of Invermul to decane dramatically decreased the both initial and final IFT.

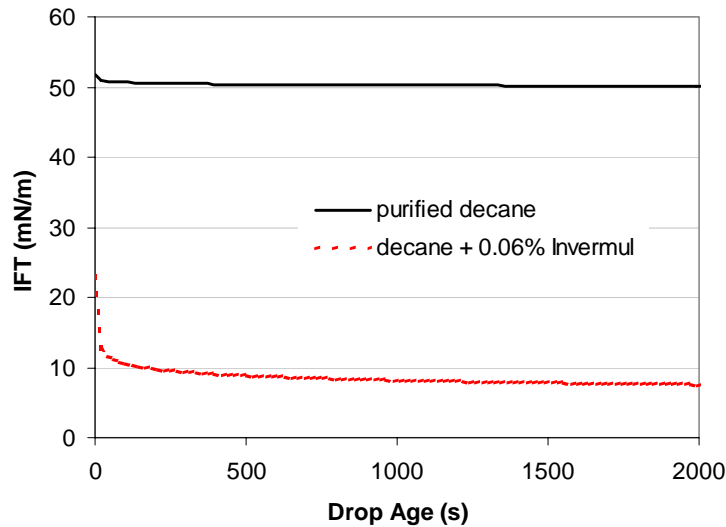


Figure 3.1.3-1. Impact of drilling mud additive on the IFT of decane.

Surfactant in crude oil

The impact of drilling mud additive on IFT of a crude oil was similarly tested by adding 0.06% wt Invermul to C-F-03 crude oil. The IFT of C-F-03 in DDW with and without Invermul is shown in Fig. 3.1.3-2. The IFT(0) were all about the same at 35mN/m for the three measurements. The IFT(eq) for the sample with Invermul was about 3 mN/m lower than that of the crude oil alone. The emulsifier had an impact on IFT but not as much as observed with decane. There appears to be a “deactivation” effect of the polar constituents in the oil that probably varies from one oil to another.

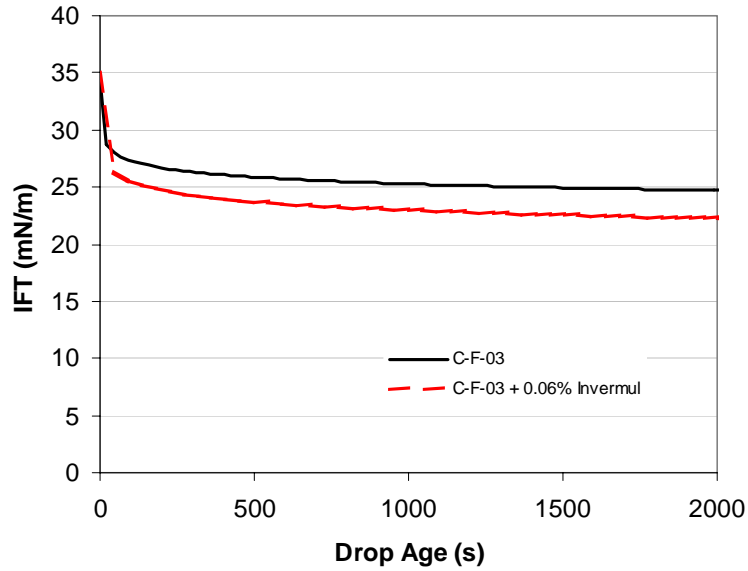


Figure 3.1.3-2 Impact of drilling mud additive on the IFT of C-F-03 oil.

Figure 3.1.3-3 shows additional IFT data for decane and two crude oils in contact with a pH 6 buffer with ionic strength adjusted with NaCl to 0.1M. The initial value of IFT is reported after the first few minutes of equilibration. Also shown are trends of change in IFT over periods up to several hours, during which the drop size was nearly constant. Small amounts of Invermul (0.1%) mixed with decane and the two crude oils were also tested, as was a mixture of C-F-03 with 0.5% of a drilling fluid filtrate (supplied by ChevronTexaco).

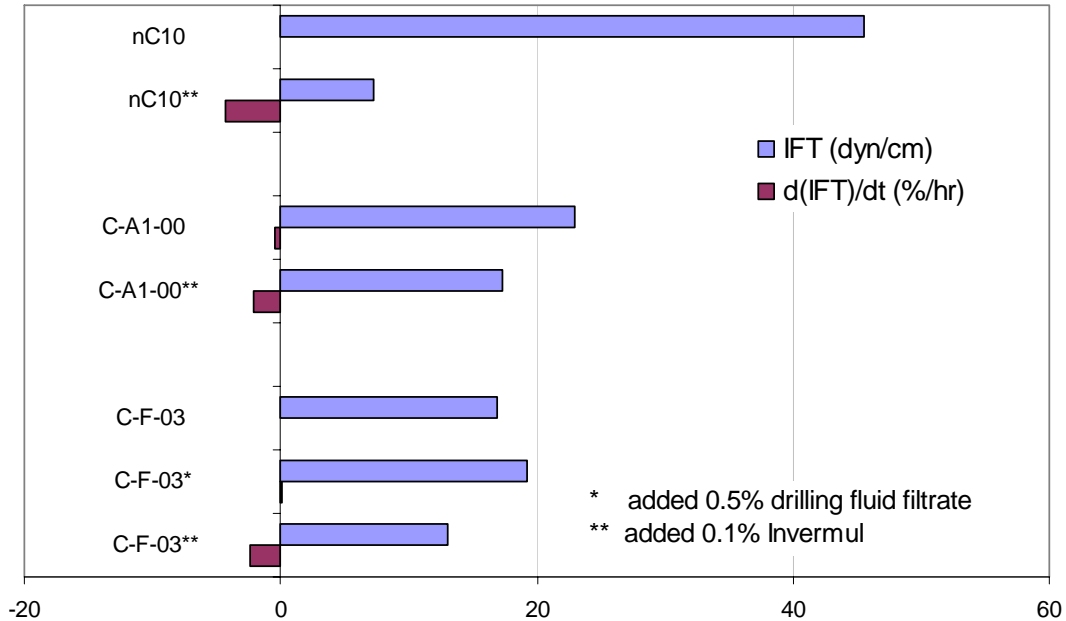


Figure 3.1.3-3. Interfacial tension measured by the pendent drop method and changes in IFT with time. IFT is reported for drops that are more than 1 min, but less than 5 min old. Changes in tension were observed over 4-9 hours.

A pendant drop of decane had an interfacial tension of 45.5 mN/m. That value was reduced to 7.2 mN/m by addition of 0.1% Invermul. The effect of a similar amount of Invermul added to the crude oils was much less dramatic. In both cases the IFT was reduced by 23-24% of the original crude oil IFT (compared to an 84% decrease for decane) and the lowest initial IFT observed was 13 mN/m for C-F-03 plus Invermul. Pendant drops were allowed to equilibrate at ambient temperature for periods from 4 to 9 hrs. Decane and crude oil tensions change little, if at all, as long as drop size was constant. IFT of the mixtures with Invermul decreased significantly over long periods of time, as shown in Fig. 3.1.3-2.

Contaminated crude oil

IFT measurements vs. pH are shown for four additional oil samples, all from the same reservoir: MY1-02, MY2-02, MY3-02, and MY4-02 (Fig. 3.1.3-4). IFTs were reported for these oil samples by Hiirasaki and Zhang (2003) measured in carbonate formation brine with a high

concentration of bicarbonate (35mmole/L). The IFT values reported after 30 min for these four oil samples were about 8, 14, 27, and 27 mN/m, respectively. Based on these results, MY1-02 and MY2-02 were judged to be contaminated because of the low IFT values. Figure 3.1.3-4 shows the effect of varying pH on each of these oil samples measured with pH adjusted distilled water and 0.1M NaCl. The decrease in equilibrium IFT of MY1-02 with increasing pH in 0.1M NaCl, even at near-neutral conditions, is quite different from the behavior of the other three samples. MY1-02 was an outlier in nearly all correlations, as shown in Fig. 3.1.3-5 for measurements with near-neutral, 0.1M NaCl solutions. MY2-02 is much closer to the correlation lines, suggesting that its IFT may have been lower than others in the Hirasaki and Zhang study because of the sensitivity of IFT to high pH, whereas our data tend to support the conclusion that MY1-02 contains surface-active contaminants. MY1-02 has therefore been excluded from all the correlations reported here (except that in Fig. 3.1.3-5). If MY1-02 was removed from the data set, the value of R^2 increased to 0.7.

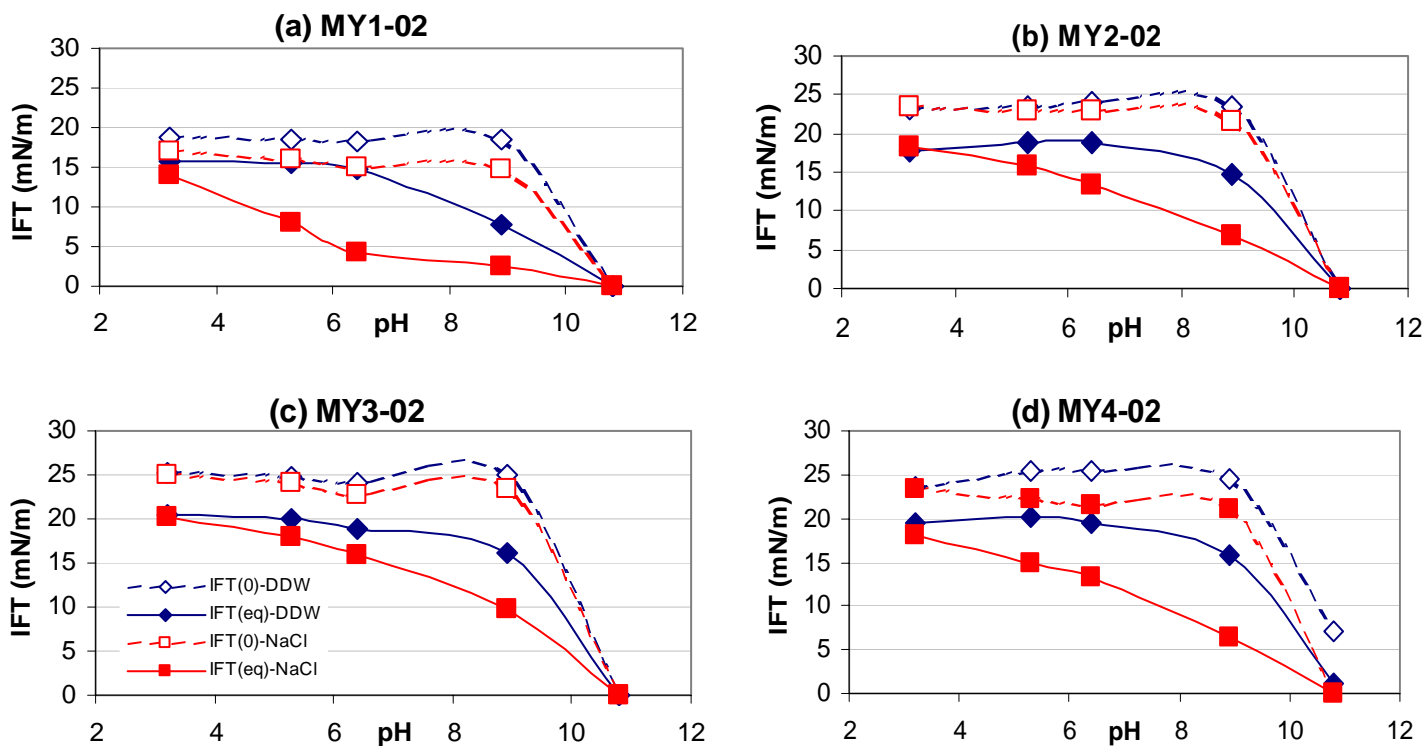


Figure 3.1.3-4. IFT of MY oils supplied by Rice University as a function of brine composition and pH.

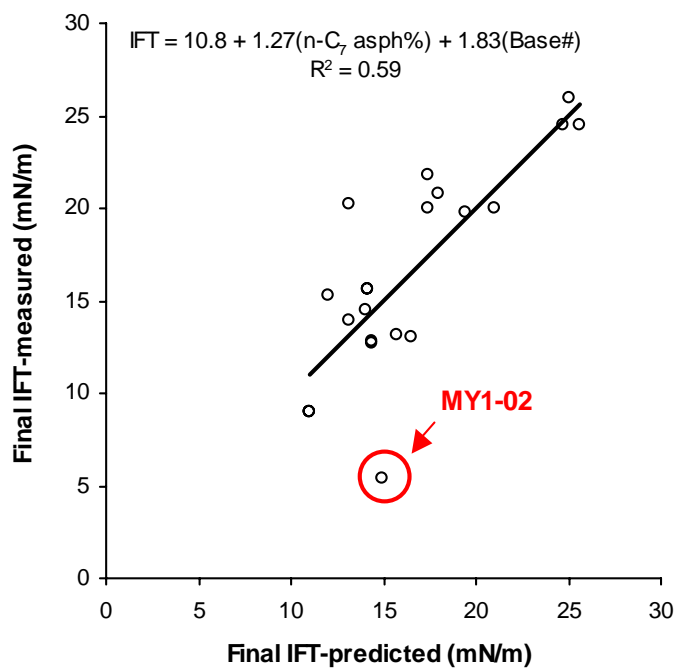


Figure 3.1.3-5. pH6, 0.1M NaCl correlation showing that MY1-02 is an outlier.

3.1.4 Summary of IFT results

- Plots of IFT vs $\ln(\text{surfactant concentration})$ are analogous to similar plots for surface tensions and aqueous phase surfactants. There appears to be a critical micelle concentration that varies with surfactant type, aqueous phase pH and ionic composition.
- IFT of crude oils varies predictably with pH and composition of the aqueous phase.
- Key oil properties that correlate with IFTs measured with pH-adjusted distilled water and 0.1M NaCl solutions are the amount of n-C₇ asphaltenes, acid number, base number, and viscosity. Different combinations of these variables dominate in acidic, near-neutral, weakly basic, and high pH ranges.
- Amount of asphaltenes, as measured by precipitation with n-heptane, is an important parameter at all conditions. IFT increases with increasing amount of asphaltene.
- Acid number and viscosity mainly affect IFT at acidic conditions. IFT decreases with higher acid number and increases with higher viscosity.
- Base number affects IFT at near-neutral and weakly basic conditions. IFT increases with increasing base number.
- Acid number is important in the very basic range above pH 10. Ultralow tensions are achieved only if acid numbers exceed 0.1 mg KOH/g oil.
- Addition of surface-active contaminants reduces the IFT of both decane and crude oil, but the effect is much more dramatic for decane.
- Judging by IFT vs pH trends and by multivariate statistical correlations, oil MY1-02 probably is contaminated with materials that affect its IFT.

3.2 Surface wetting effects of field samples of SBM fluids (Lekkala and Buckley)

3.2.1 Treatment and testing protocol

Clean mica surfaces were treated using the protocol developed in previous work on wettability alteration by crude oils (e.g., Liu and Buckley, 1997, 1999), with the addition of steps in which the samples were exposed to the mud fractions and to various cleaning agents. Unless otherwise specified, mica was first equilibrated with brine for a period of one day. The samples were then drained, but not dried, and exposed to crude oil for at least three weeks at room temperature. To examine the surface, bulk crude oil was removed by rinsing the sample with a small amount of toluene. Toluene is a good asphaltene solvent and thus does not cause asphaltene precipitation from the bulk oil. Following the removal of bulk oil, the samples were submerged in decane, a poor asphaltene solvent that minimizes further changes in the material deposited on the mica surface. Samples treated by this sequence of brine and oil are termed COBR samples since they mimic the sequence of crude oil/brine/rock interactions that occur in an oil reservoir. Decane and water were used as probe fluids to examine the extent of wetting alteration. An outline of this study is given in Fig. 3.2.1-1.

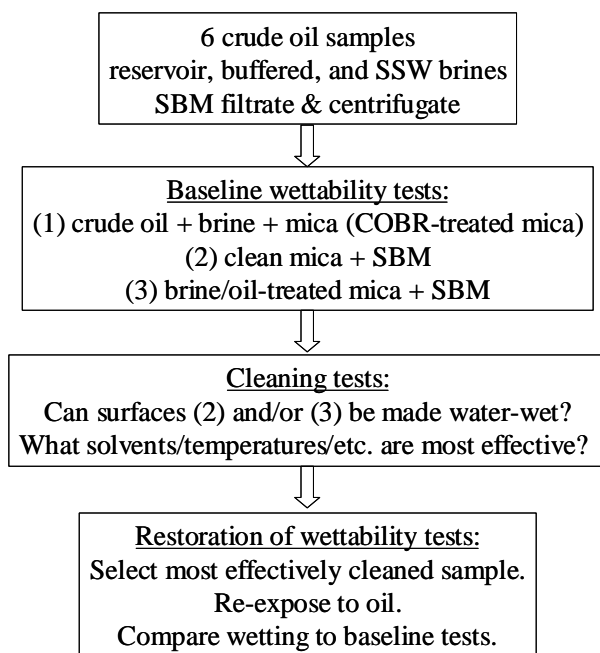


Figure 3.2.1-1. Outline of the test plan for SBM-fraction study.

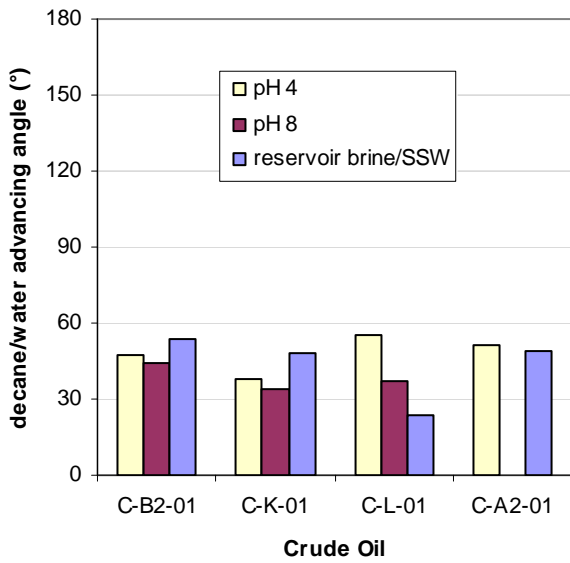
3.2.2 COBR interactions with six crude oils

Six crude oils, listed across the top of Table 3.2.2-1, were selected for this study.

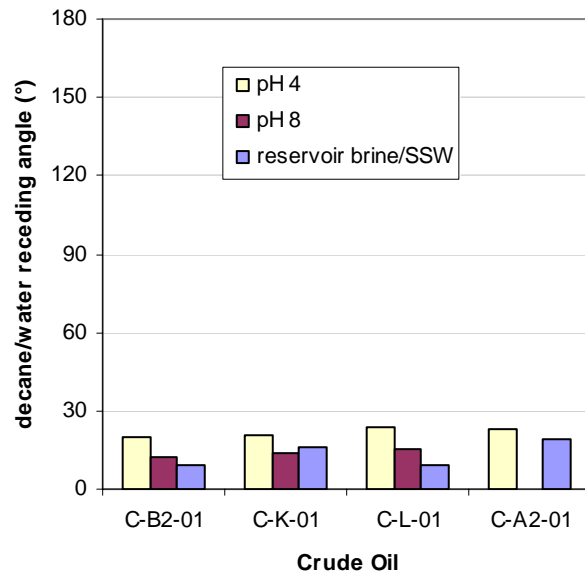
Properties of these oils can be found in Appendix II. Interactions between the selected crude oils and wet mica samples were examined in order to establish a baseline against which the effects of mud contamination could be judged (Table 3.2.2-1). Figure 3.2.1-1 summarizes advancing (Fig. 3.2.1-1a) and receding (Fig. 3.2.2-1b) contact angles between decane and water for four of the six oils. Contact angles depended, to some extent, on the composition of the pre-equilibrating brine, but in none of these cases did the water-advancing angles exceed 60° . This group of oils is therefore designated as the water-wet or WW group. Results of similar tests for the remaining two oils are shown in Fig. 3.2.2-2. More oil-wet conditions were produced by these two oils, forming the OW group.

Table 3.2.2-1. Contact Angles on COBR-Treated Mica Surfaces

		C-A2-00	C-B2-01	C-K-01	C-L-01	E-1XC0-01	S-Ven-41
Brine		Decane – Water Contact Angles (°)					
pH 4, I=0.01M	θ_A	51 ± 4	44 ± 3	30 ± 5	54 ± 4	136 ± 5	128 ± 5
	θ_R	23 ± 4	8 ± 3	16 ± 1	24 ± 3	61 ± 3	55 ± 3
pH 8, I=1.0M	θ_A		43 ± 3	32 ± 5	35 ± 5		
	θ_R		12 ± 1	14 ± 2	15 ± 2		
RB	θ_A		54 ± 5	48 ± 3	24 ± 3		
	θ_R		9 ± 2	16 ± 2	9 ± 1		
SSW	θ_A	49 ± 3				143 ± 6	133 ± 5
	θ_R	19 ± 2				55 ± 6	61 ± 3

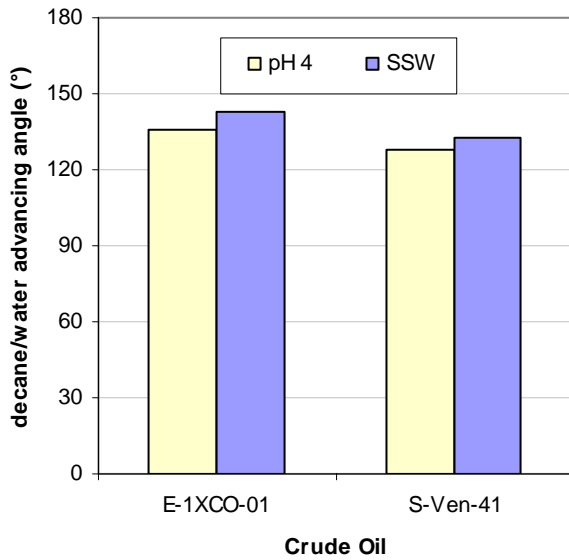


(a) water-advancing angles

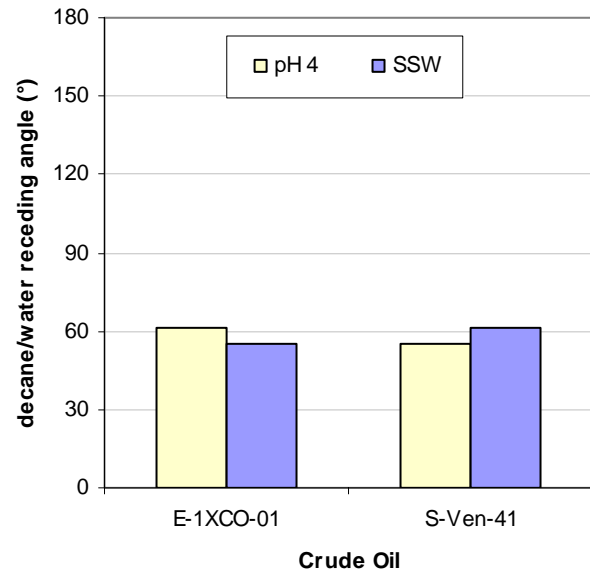


(b) water-receding angles

Figure 3.2.2-1. Results of standard COBR treatments with the WW oils.



(a) water-advancing angles



(b) water-receding angles

Figure 3.2.2-2. Results of standard COBR treatments with the OW oils.

3.2.3 Clean mica exposed to mud fractions

Mica exposed to a pure hydrocarbon, even for an extended period of time, would remain water-wet. That is not what happens when mica is aged in either K-f or L-c fractions of synthetic oil-based drilling fluids, as summarized in Table 3.2.3-1 and shown in Fig. 3.2.3-1. The legend indicates the mud fraction used in these treatments and, in parentheses, the probe oil used to measure the water advancing angles reported. Use of crude oil as the probe oil necessitated drying the rinsed surfaces prior to their submersion in water. A drop of crude oil was formed against the mica surface under water. These angles tended to be somewhat larger (more oil-wet) than those measured with decane as the probe oil. One week of aging appeared to be sufficient to produce the maximum wettability alteration effect with both K-f and L-c fractions.

Table 3.2.3-1. Contact Angles for Dry Mica Samples Aged in Mud Fractions

		K-f filtrate	L-c centrifugate
Aging time	Decane – Water Contact Angles (°) <i>oil drop in water</i> or water drop in oil		
	θ_A	65 ± 4	108 ± 4
1 day	θ_R	15 ± 2	24 ± 2
	θ_A	121 ± 8	131 ± 2
7 days	θ_R	32 ± 2	30 ± 2
	θ_A	117 ± 6	106 ± 4
21 days	θ_R	29 ± 2	27 ± 3
	Crude Oil – Water Contact Angles (°) <i>oil drop in water</i>		
1 day	θ_A		136 ± 2
	θ_R		31 ± 2
7 days	θ_A	126 ± 5	135 ± 10
	θ_R	36 ± 3	30 ± 2
21 days	θ_A	139 ± 9	155 ± 6
	θ_R	31 ± 3	33 ± 2

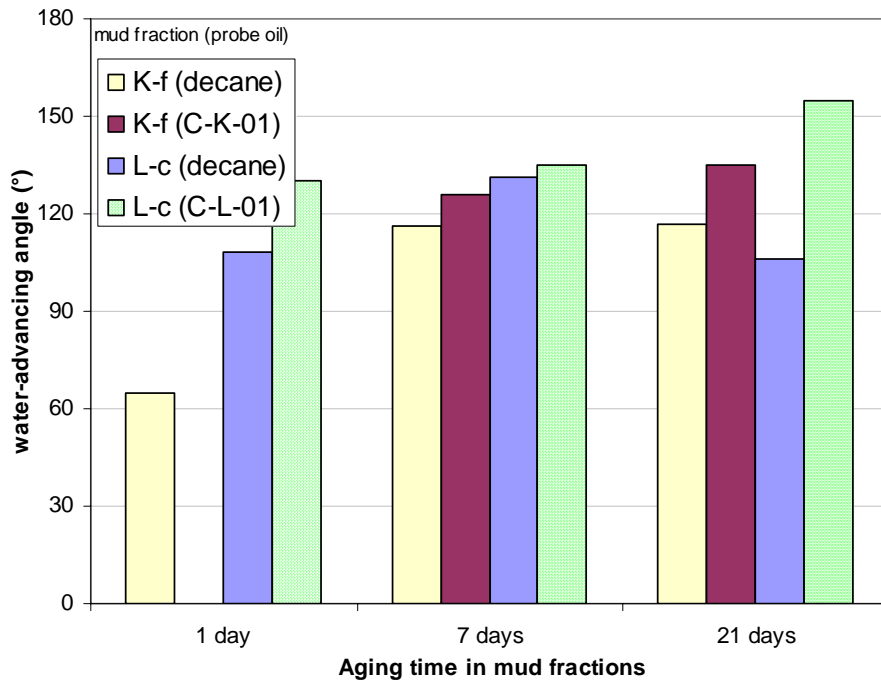


Figure 3.2.3-1. Water advancing contact angles on mica surfaces exposed to synthetic oil-based mud fractions for 1 day, 7 days, and 21 days.

The high advancing angles measured after exposure of clean, dry mica to the two mud fractions confirm that they contain surface active materials, despite the fact that they have both been used in the field where surfactants would have adsorbed on cuttings and other solid surfaces and in spite of further removal of surfactants during filtration of the K-f sample or removal of adsorbed material with the solids separated in the centrifugation of the L-c sample. The results in Fig. 3.2.3-1 also show that rinsing with toluene does not remove the adsorbed material.

Some of the surface-active material can be removed by further washing, as summarized in Table 3.2.3-2 and shown in Fig. 3.2.3-2. Methanol was the most effective solvent of the three organic compounds investigated and cleaning of the mica treated with K-f was more efficient than cleaning of the L-c-treated mica. These results are consistent with the likely removal of the most active surfactant materials remaining in the end-of-run mud during the filtration process. In the centrifugate, surfactants in excess of those adsorbed on the solids existing in the mud, could remain in the supernatant. Thus stronger interactions might be expected with the L-c mud fraction than with K-f. There may also, however, be differences in original formulation and in the changes that occurred during drilling that contribute to differences between these two mud fractions.

Table 3.2.3-2. Contact Angles on Initially Dry Mica Aged in Mud Fractions and Washed with Solvents

Solvents used for washing	Mica aged in K-f filtrate		Mica aged in L-c centrifugate	
	θ_A (deg)	θ_R (deg)	θ_A (deg)	θ_R (deg)
Methylene chloride	40 ± 2	12 ± 1	99 ± 14	34 ± 6
1- Propanol	29 ± 2	10 ± 2	64 ± 2	25 ± 1
Methanol	30 ± 1	12 ± 1	50 ± 1	9 ± 1

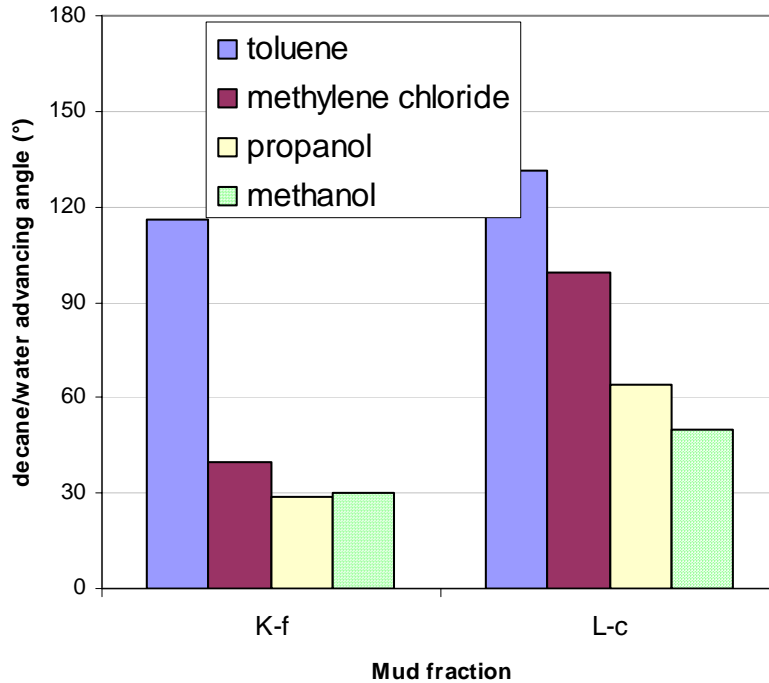


Figure 3.2.3-2. Dry mica samples treated with drilling mud fractions were cleaned by washing with organic solvents.

3.2.4 Effect of mud fractions on COBR-treated mica

Rather than mud components contacting clean, dry mica, a somewhat more realistic scenario would be to have mud components contact surfaces that have already been exposed to connate brine. The ability of the mud fractions to alter wetting on wet mica surfaces is shown by the data summarized in Table 3.2.4-1.

Table 3.2.4-1. Contact Angles on Mica Aged in Brine for One Day and in Mud Fractions for Seven Days

Reservoir brine	Mud sample	Advancing angle (°)	Receding angle (°)
RB (C-L-01)	L-c	135 ± 6	53 ± 4
RB (C-B2-01)	K-f	105 ± 5	56 ± 6
RB (C-K-01)	K-f	110 ± 4	55 ± 4

To simulate somewhat more reservoir-like conditions, COBR-treated mica samples, identical to those described above, were used. In cases where reservoir brine compositions were

available, brine and oil from the same reservoir were matched. The results of the COBR treatments and exposure to mud fractions are summarized in Table 3.2.4-2 and shown in Fig. 3.2.4-1 for the WW oils and Figs. 3.2.4-2 and 3.2.4-3 for the OW group of oils for comparison with advancing angles after similarly treated samples were aged for one week or more in either the K-f or L-c mud fractions.

Table 3.2.4-2. Effect of Mud Samples on COBR-Treated Mica

Aging combination			7 days in SBM		27/36 days in SBM	
Brine (day)	Oil (21 days)	SBM fraction	θ_A	θ_R	θ_A	θ_R
RB	C-B2-01	K-f	65 ± 6	20 ± 3	67 ± 4	21 ± 3
RB	C-K-01	L-c	60 ± 5	28 ± 4	60 ± 2	27 ± 1
RB	C-L-01	L-c	66 ± 4	27 ± 3	64 ± 3	25 ± 2
pH 4	E-1XC0-01	K-f	120 ± 8	28 ± 5	129 ± 13	29 ± 3
pH 4	C-A2-00	K-f	58 ± 3	22 ± 2	58 ± 4	22 ± 3
pH 4	S-ven-41	K-f	75 ± 6	23 ± 2	76 ± 6	22 ± 3
pH 4	E-1XC0-01	L-c	64 ± 7	45 ± 7	73 ± 2	40 ± 3
pH 4	C-A2-00	L-c	56 ± 4	23 ± 2	58 ± 3	22 ± 2
pH 4	S-Ven-41	L-c	55 ± 5	24 ± 5	59 ± 4	26 ± 2
SSW	E-1XC0-01	K-f	47 ± 4	21 ± 3		
SSW	C-A2-00	K-f	110 ± 9	29 ± 1		
SSW	S-Ven-41	K-f	68 ± 13	11 ± 1		
SSW	E-1XC0-01	L-c	47 ± 2	33 ± 5	48 ± 2	31 ± 6
SSW	C-A2-00	L-c	64 ± 6	35 ± 5	58 ± 3	22 ± 2
SSW	S-Ven-41	L-c	45 ± 3	34 ± 4		

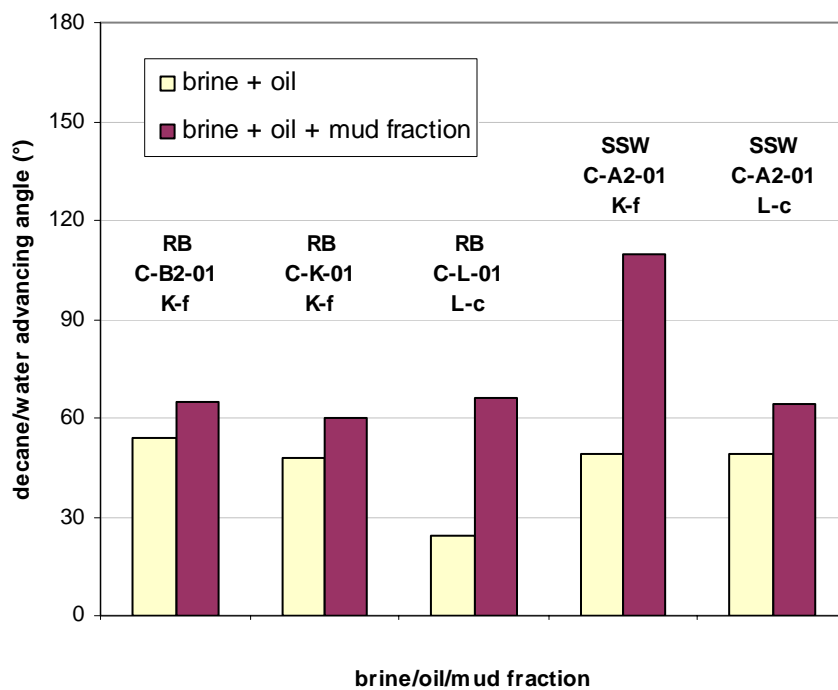


Figure 3.2.4-1. Effect of mud fractions on COBR-treated mica surfaces—WW oils and reservoir brines or synthetic sea water.

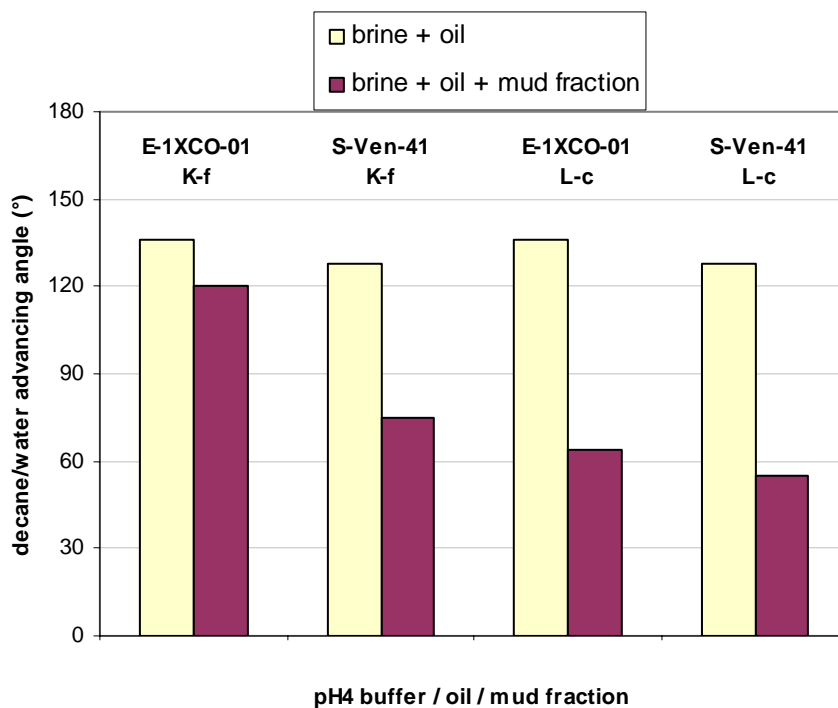


Figure 3.2.4-2. Effect of mud fractions on COBR-treated mica surfaces—OW oils and pH4 buffer.

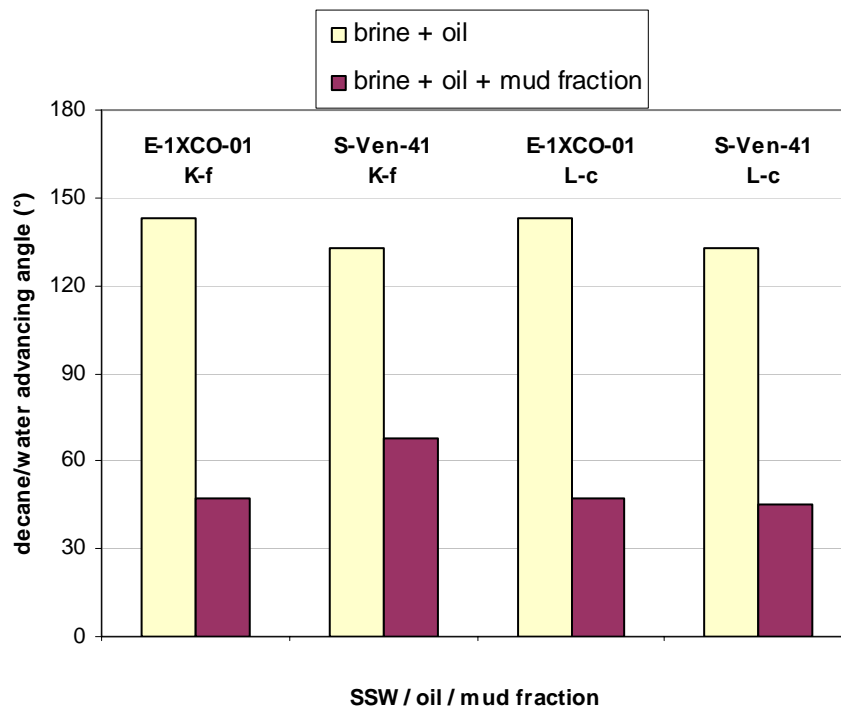
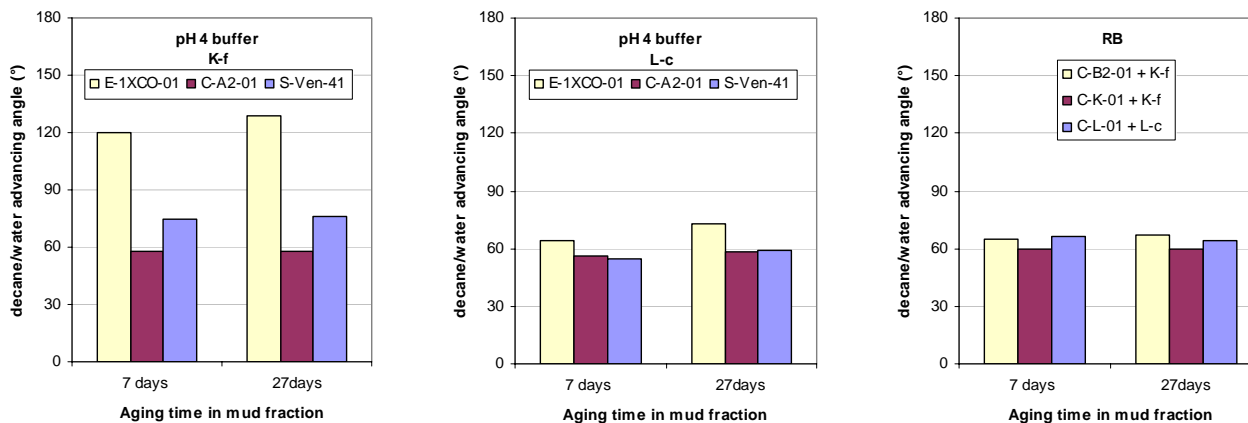


Figure 3.2.4-3. Effect of mud fractions on COBR-treated mica surfaces—OW oils and SSW.

Aging for more than seven days in the mud samples made little difference in the results, as shown in Fig. 3.2.4-4.



(a) pH 4, K-f

(b) pH 4, L-c

(c) RB

Figure 3.2.4-4. Extending the aging time in either mud fraction beyond one week has little further effect on the change in the water-advancing contact angle for a variety of combinations of oil and mud fraction, with or without brine.

In Fig. 3.2.4-5a, effects of K-f and L-c are compared for COBR-treated surfaces produced by three different crude oils with pH 4 buffer. Figure 3.2.4-5b compares the same oil/mud fraction combinations for surfaces initially exposed to SSW. Results in both cases are similar.

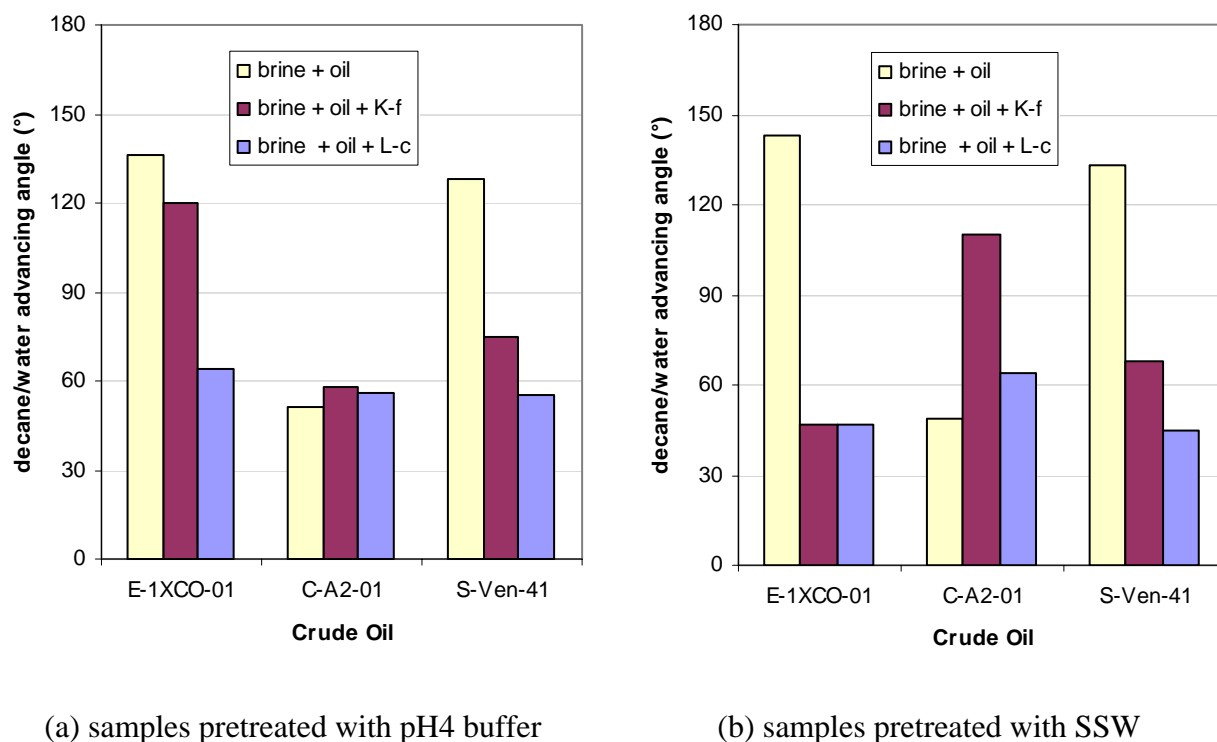


Figure 3.2.4-5. Comparison of the effects of K-f filtrate and L-c centrifugate on COBR-treated mica samples.

The effect of the brine used to pretreat mica during the COBR treatment sequence varies with crude oil composition. For S-Ven-41, there appears to be little effect of brine composition on the subsequent effect of exposure to either of the mud fractions. The changes in samples after exposure to the mud samples were similar, regardless of the composition of the original brine. For crude oil E-1XCO-01, the reduction in contact angles was greater for the surface treated first with SSW, whereas for C-A2-00, the opposite trend was observed.

It is possible that these differences are related to the primary mechanisms of wetting alteration (Buckley *et al.*, 1998b), although an interpretation based on the limited amount of data available must be regarded as speculative. S-Ven-41 is the most asphaltic of these three oils and the one with the least stable asphaltenes. If interactions are dominated by surface precipitation, brine composition would only be important if one of the brines produced stable wetting films. In the case of E-1XCO-01, acid/base mechanisms may dominate, since contact angles are reduced most dramatically for the SSW case and less change occurs with the pH4 brine. Finally, since the SSW case is less affected (contact angles are actually higher after mud treatments) perhaps C-A2-00 interacts with the surface through ion-binding mechanisms.

3.2.5 Cleaning

Since core is often exposed to drilling fluid components, it is essential that cleaning methods be established that remove contaminants so that the cleaned surface can interact with brine and crude oil to reproduce accurately the original wetting condition. Results of washing with single organic solvents and with sequences of solvents are given in Tables 3.2.5-1 to 3.2.5-3. The shaded cells indicate results for samples that were rinsed with toluene and submerged in decane, but were not washed with any additional solvents. Table 3.2.5-1 contains results for reservoir brine COBR-treated surfaces, pH 4 buffer COBR samples are in Table 3.2.4-2, and SSW COBR samples are in Table 3.2.5-3. Results are mixed.

Table 3.2.5-1. Advancing Angles (Decane/Water) for Washing Tests (COBR Mica Samples Aged in RB, Oil and Mud Samples, then Washed as Indicated)

Oil, mud sample combinations: Washing solvent(s)	water advancing contact angle, θ_A (°)		
	C-B2-01 K-f filtrate	C-K-01 K-f filtrate	C-L-01 L-c centrifugate
Toluene (T) rinse only	65 ± 6	60 ± 5	66 ± 5
Methylene chloride (CH ₂ Cl ₂)	50 ± 7	48 ± 4	52 ± 3
hot CH ₂ Cl ₂ (37°C)	63 ± 5		
methanol (CH ₃ OH)	42 ± 4	30 ± 2	41 ± 2
chloroform (CHCl ₃), CH ₂ Cl ₂	36 ± 2		
CHCl ₃ , CH ₃ OH	36 ± 1	39 ± 3	39 ± 3
CH ₂ Cl ₂ , CH ₃ OH		50 ± 9	39 ± 3
CH ₃ OH, CH ₂ Cl ₂	44 ± 2	50 ± 3	
CH ₂ Cl ₂ , CHCl ₃ , CH ₃ OH,		37 ± 2	35 ± 3
hot CH ₂ Cl ₂ , CHCl ₃ , CH ₃ OH	63 ± 3	57 ± 5	57 ± 3
Acetic acid (1/10 of glacial)		71 ± 3	

Table 3.2.5-2. Advancing Angles (Decane/Water) for Washing Tests (COBR Mica Samples Aged in pH 4 Buffer, Oil and Mud Samples, then Washed as Indicated)

Oil	Mud fraction	Toluene rinse only	Washed with	
			T + CH ₃ OH	T + C ₂ H ₄ (NH ₂) ₂
		θ_A	θ_A	θ_A
C-A2-00	K-f	58 ± 3		12 ± 1
E-1XC0-01	K-f	120 ± 8		39 ± 6
S-Ven-41	K-f	75 ± 6		20 ± 3
C-A2-00	L-c	56 ± 4	70 ± 2	18 ± 3
E-1XC0-01	L-c	64 ± 7	102 ± 4	25 ± 2
S-Ven-41	L-c	55 ± 5	104 ± 1	24 ± 1

Table 3.2.5-3. Advancing Angles (Decane/Water) for Washing Tests (COBR Mica Samples Aged in SSW, Oil and Mud Samples, then Washed as Indicated)

Oil	Mud fraction	Toluene rinse only	Washed with		
			T + CH ₃ OH	T + C ₂ H ₄ (NH ₂) ₂	T + CH ₂ Cl ₂
		θ_A	θ_A	θ_A	θ_A
C-A2-00	K-f	110 ± 9		33 ± 5	
E-1XC0-01	K-f	47 ± 4	70 ± 9	57 ± 10	
S-Ven-41	K-f	68 ± 13	93 ± 10	49 ± 3	
C-A2-00	L-c	64 ± 6	73 ± 2	32 ± 2	24 ± 2
E-1XC0-01	L-c	47 ± 2	66 ± 3	25 ± 2	
S-Ven-41	L-c	45 ± 3	56 ± 2	46 ± 3	

3.2.6 Restoration of wettability

Probably the most important question is whether the original wettability established by COBR interactions can be reestablished in a cleaned core. The results of surface tests shown in Fig. 3.2.6-1 and summarized in Table 3.2.6-1 are encouraging. Water advancing angles are compared for surfaces treated by the standard COBR sequence (the initial brine and oil indicated for each set of results) with similarly treated surfaces that were subsequently exposed to one of the drilling fluid fractions, washed, and restored by a second exposure to crude oil. In all cases, preferentially water-wet surfaces were returned to water-wet conditions and preferentially oil-wet surfaces to oil-wet conditions. The contact angles after treatment were often somewhat lower than on the original COBR-treated surfaces, but there are exceptions that make it difficult to generalize about the effects of either the K-f or L-c fluids.

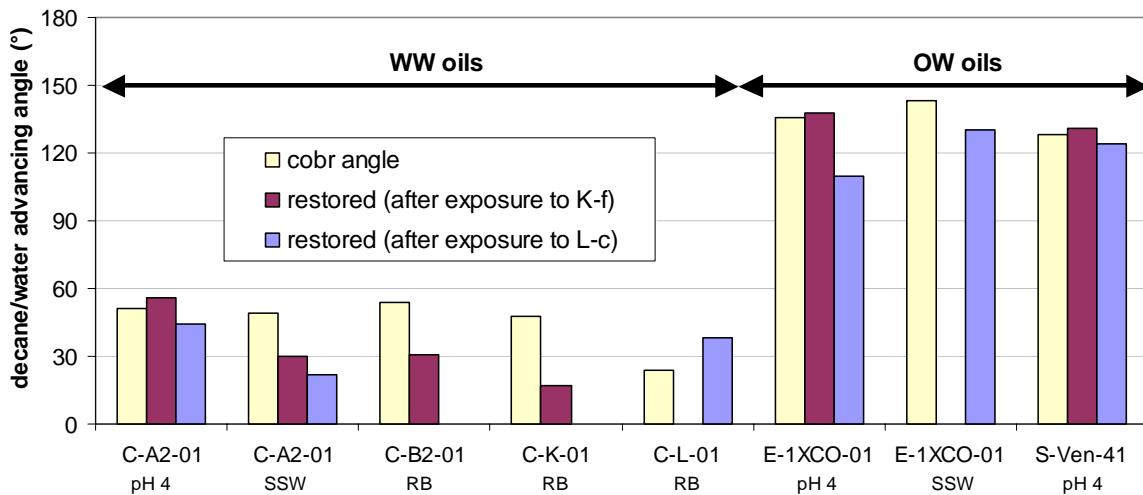


Figure 3.2.6-1. Restoration of wettability by COBR interactions. Water-advancing angles are compared for mica surfaces treated by the standard COBR sequence to those obtained after exposure to drilling fluid fractions, washing, and repeated COBR exposures.

Table 3.2.6-1. Summary of the Decane/Water Contact Angles (Advancing) for Mica Aged in Brine, Oil, Mud Sample, then Washed and Restored

Step 1 Age for 1 day in brine	Step 2 Aged for 21 days in Oil	θ_A after Step 2	Step 3 Age for 7 days in mud fraction	θ_A after Step 3	Step 4 Wash and re age for 21 days in oil	θ_A after Step 4
pH 4	E-1XC0-01	136 ± 5	K-f	120 ± 8	E-1XC0-01	138 ± 3
pH 4	C-A2-00	51 ± 4	K-f	58 ± 3	C-A2-00	56 ± 3
pH 4	S-Ven-41	128 ± 5	K-f	75 ± 6	S-Ven-41	131 ± 3
pH 4	E-1XC0-01	136 ± 5	L-c	64 ± 7	E-1XC0-01	110 ± 4
pH 4	C-A2-00	51 ± 4	L-c	56 ± 4	C-A2-00	44 ± 3
pH 4	S-Ven-41	128 ± 5	L-c	55 ± 5	S-Ven-41	124 ± 4
SSW	E-1XC0-01	143 ± 6	K-f	47 ± 4	E-1XC0-01	*
SSW	C-A2-00	49 ± 3	K-f	110 ± 9	C-A2-00	30 ± 3
SSW	S-Ven-41	133 ± 5	K-f	68 ± 13	S-Ven-41	*
SSW	E-1XC0-01	143 ± 6	L-c	47 ± 4	E-1XC0-01	130 ± 5
SSW	C-A2-00	49 ± 3	L-c	64 ± 6	C-A2-00	22 ± 2
SSW	S-Ven-41	133 ± 5	L-c	45 ± 3	S-Ven-41	*
RB	C-L-01	24 ± 3	L-c	66 ± 4	C-L-01	38 ± 3
RB	C-K-01	48 ± 3	K-f	60 ± 5	C-K-01	17 ± 4
RB	C-B2-01	54 ± 5	K-f	65 ± 6	C-B-01	31 ± 3

* None of the “cleaned” samples were sufficiently water-wet to use in restoration tests.

3.3 Surface wetting effects of polyethoxylated amines (Bryant, Bowman, and Buckley)

3.3.1 An overview of contact angles on mica surfaces exposed to polyethoxylated amines

Tables 3.3.1-1, 3.3.1-2 and Figure 3.3.1-1 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.

Table 3.3.1-1. Summary of contact angle measurements for CAM-2, TAM-2 and TAM-5

Sample	Advancing Angle		Receding Angle	
	Average	Std dev	Average	Std dev
CAM-2				
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
TAM-2				
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
TAM-5				
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

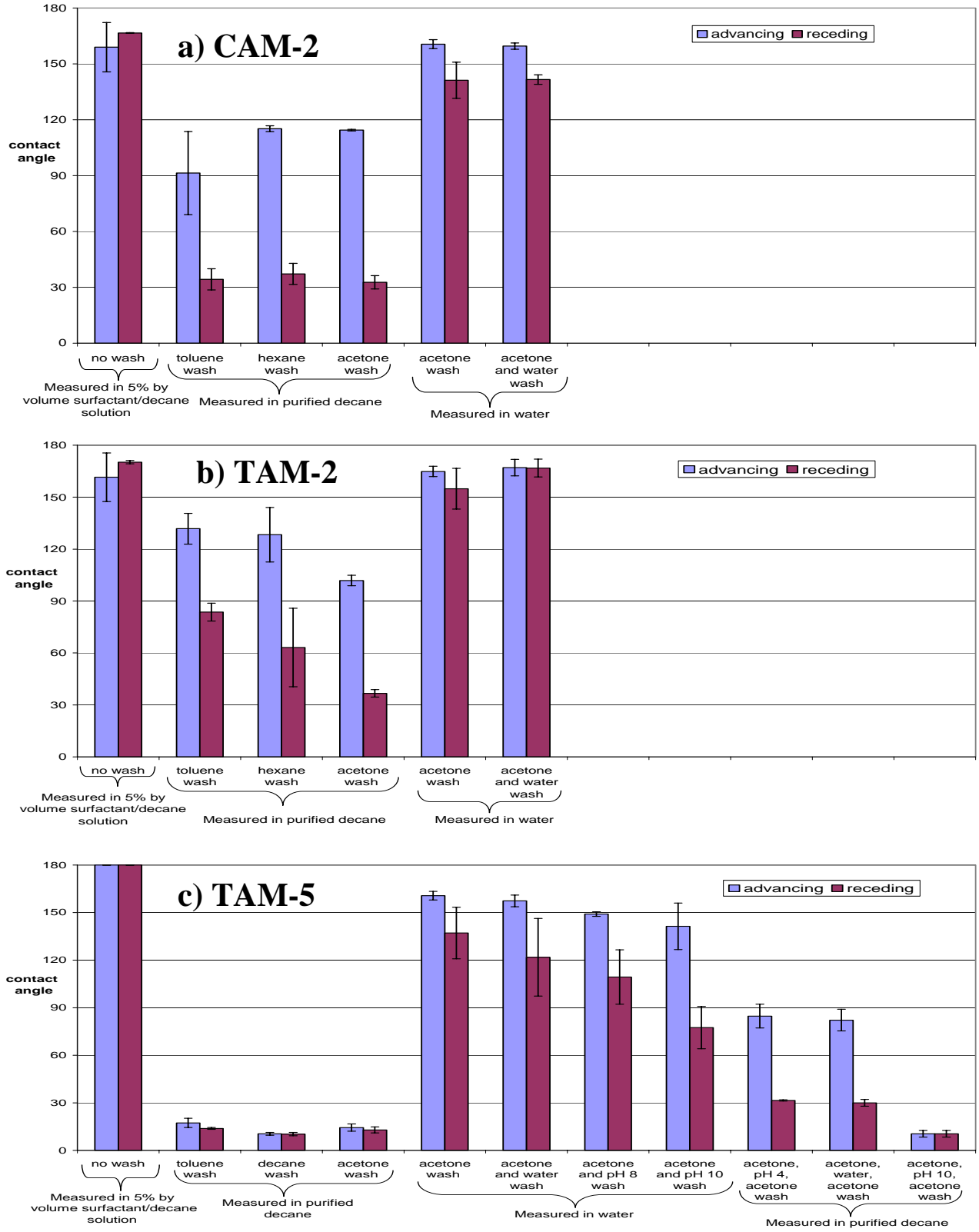


Figure 3.3.1-1. Contact angle results for a) CAM-2 b) TAM-2 and c) TAM-5. Error bars are standard deviations of 18 replicate measurements.

Table 3.3.1-2. Summary of contact angle measurements for TAM-5 solutions that had been pre-equilibrated with pH 8 buffer

Sample	Advancing Angle		Receding Angle	
	Average	Std dev	Average	Std dev
TAM-5 pre-equilibrated with pH 8 brine				
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

3.3.2 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.

The leftmost results in Fig. 3.3.1-1 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 θ_A of approximately 160° (oil-wet) and a θ_R of approximately 170° , while mica treated with TAM-5 had an θ_A and θ_R of approximately 180° (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.

3.3.3 Decane/water contact angles 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 3.3.1-1 and 3.3.1-2 above. 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.

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 3.3.3-2a summarizes the contact angles for pH 4 brine while Figure 3.3.3-1b summarizes 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.

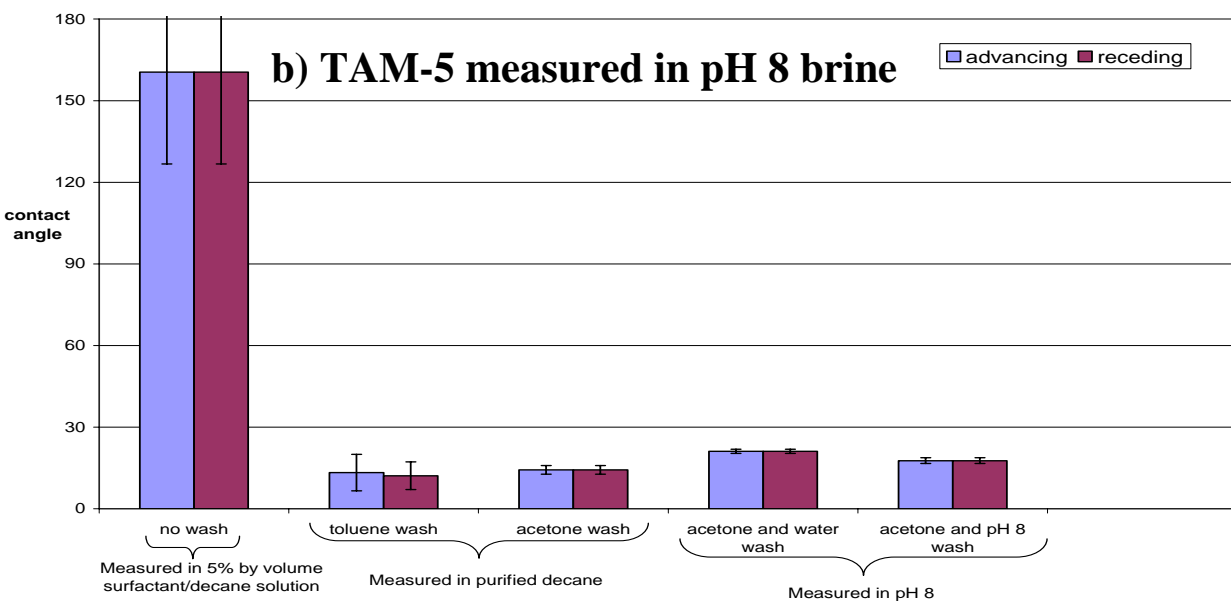
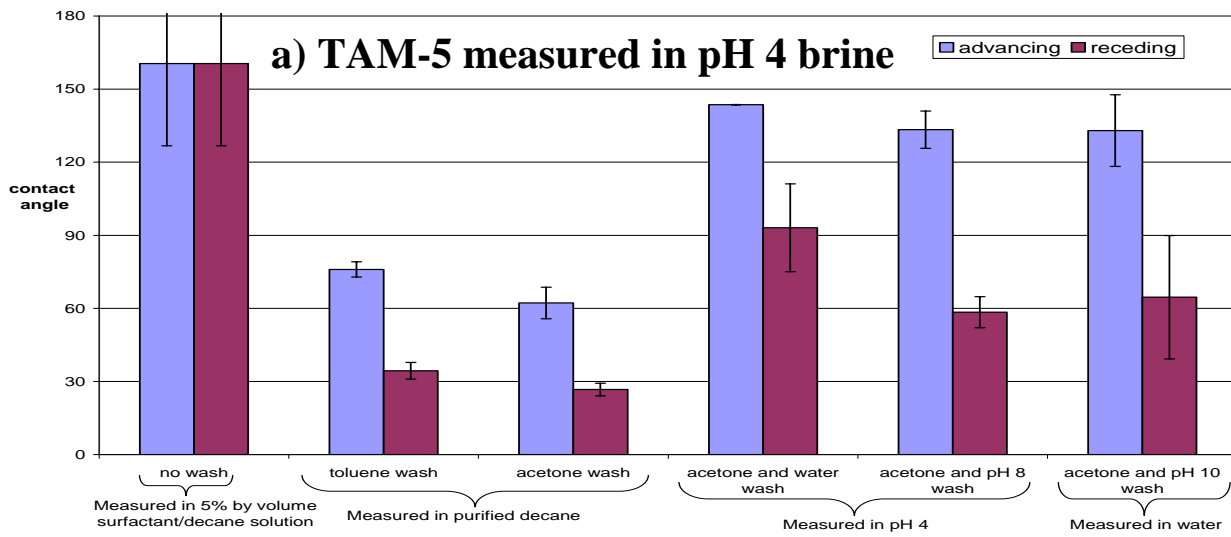


Figure 3.3-1. TAM-5 pre-equilibrated with pH 8 brine measured in a) pH 4 brine and b) pH 8 brine. Error bars are standard deviations of 18 replicate measurements.

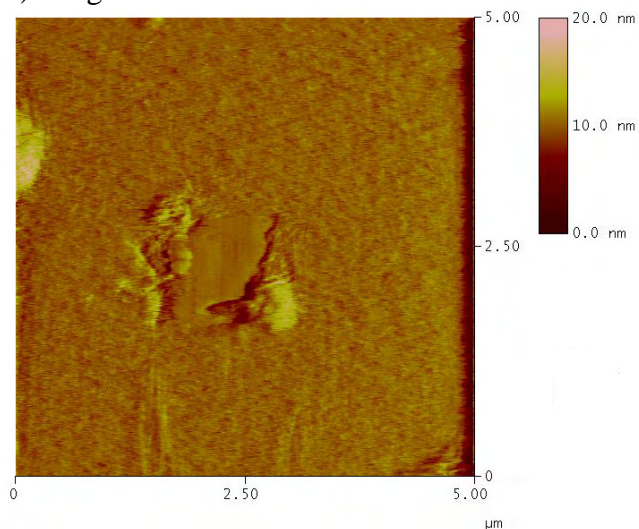
3.3.4 Atomic force microscopy

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

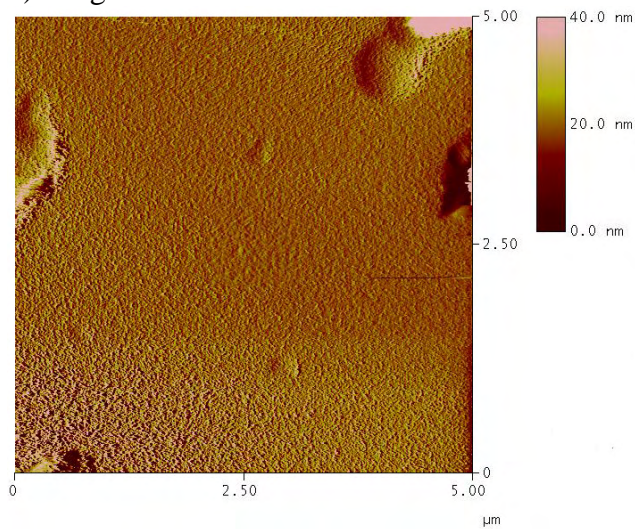
thoroughly in air. The mica was then mounted onto an AFM magnetic puck using a small amount of Super Glue Gel (Ace Hardware, Oak Brook, IL).

Figure 3.3.4-1 shows AFM images of mica treated with TAM-5. All images are of the deflection signal and are 5- μm by 5- μm scans. Figure 3.3.4-1a 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- μm by 1- μm area. Figure 3.3.4-1b was imaged under water. The features on this surface were more stable than under air; a previous 1- μm by 1- μm scan produced no scraping of the surface. Figure 3.3.4-1c 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 3.3.4-1d was imaged under pH 10 brine; this image has the same appearance as clean mica.

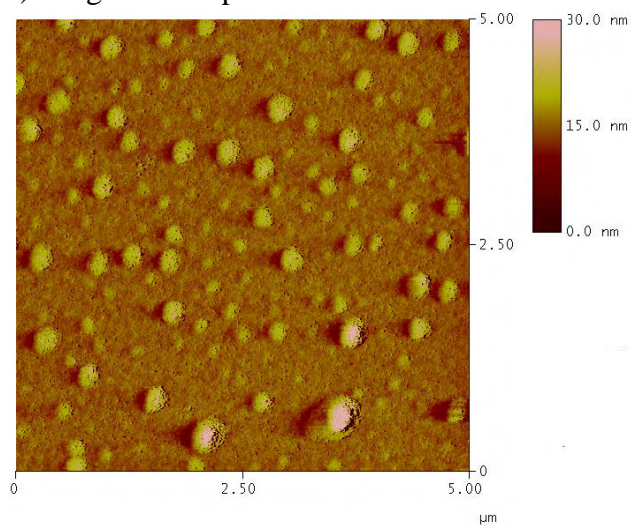
a) imaged under air



b) imaged under water



c) imaged under pH 8 buffer



d) imaged under pH 10 buffer

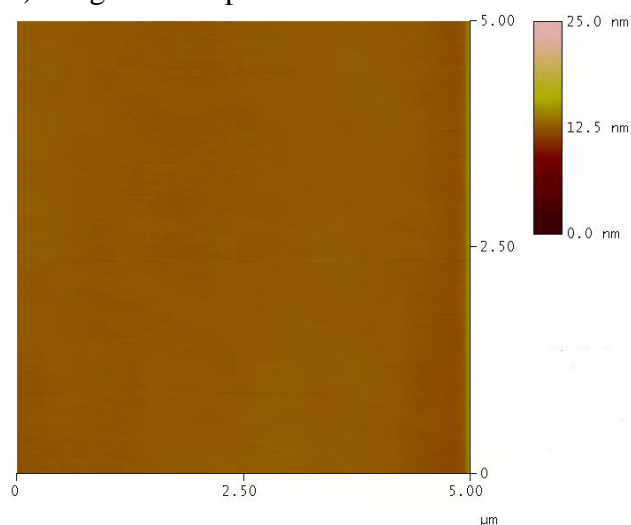


Figure 3.3.4-1. Mica treated with a 5% by volume TAM-5/decane solution imaged under a) air b) water c) pH 8 buffer and d) pH 10 buffer.

3.3.5 Discussion of wetting effects of polyethoxylated amines

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. 3.3.1-1 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.

3.3.6 Summary of wetting effects of polyethoxylated amines

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.

3.4 Surface effects of OBM and SBM surfactant (Skalli and Buckley)

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.

3.4.1 Wetting alteration – surfactant only without crude oil

Conceptual Model

When the surfactant concentration is less than the CMC value, the surfactant exists primarily in the form of monomers (Fig. 3.4.1-1a). Surfactant can accumulate at either the oil/water interface or the oil/mica or both. Each of these interfaces will approach saturation or monolayer coverage as the surfactant concentration increases to values approaching the CMC. Assuming that the hydrophilic heads are oriented toward the mica surface, the surface should appear fairly oil-wet to the approaching drop of water. When concentrations are above the CMC, surfactant accumulation at the oil/brine and oil/mica interfaces should be sufficient to saturate the interfaces, producing monolayer coverage. Excess surfactant exists in micelles, which are in equilibrium with monomers in the bulk phase. Water solubility for the products used in these tests is very low; it is unlikely that micelles can exist in the water phase. At equilibrium, the surfactant distribution should approach the situation illustrated in Fig. 3.4.1-1b. Note that with

more surfactant in the system, a bilayer can form on the solid surface, reducing the contact angle to a drop of water.

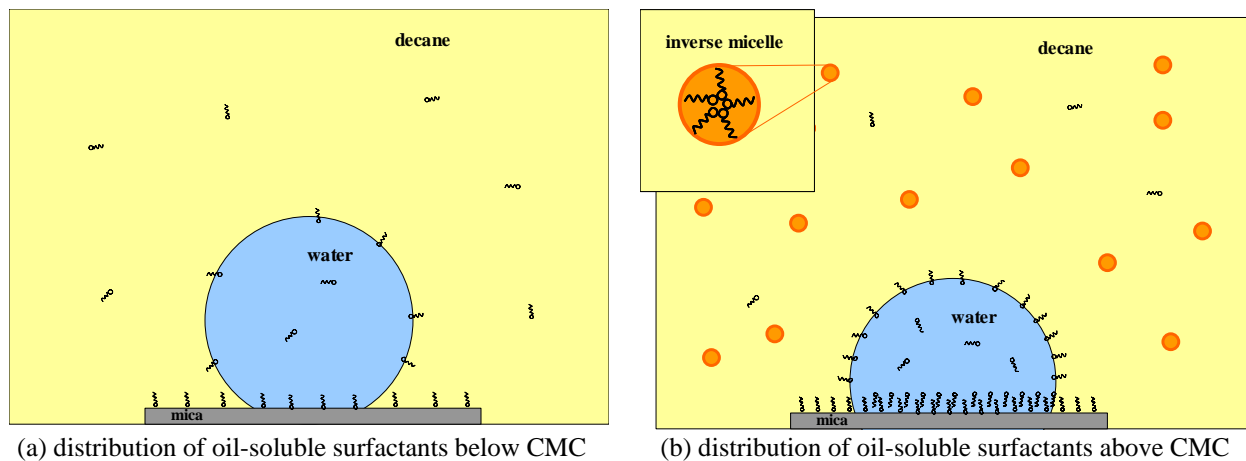


Figure 3.4.1-1. Schematic illustration of surfactant distribution in the oil/water/solid system at surfactant concentrations below and above CMC.

Surfactant concentrations below CMC

Contact angles for water-advancing conditions measured with a drop of {pH 6, 0.1M} buffer under an 0.002 vol% solution of Ez Mul in decane are shown in Fig. 3.4.1-2. Contact time refers to the length of time that the drop of buffer remained in contact with the mica surface before the contact angle was recorded. Wetting conditions are very close to neutral for this low concentration of the Ez Mul product.

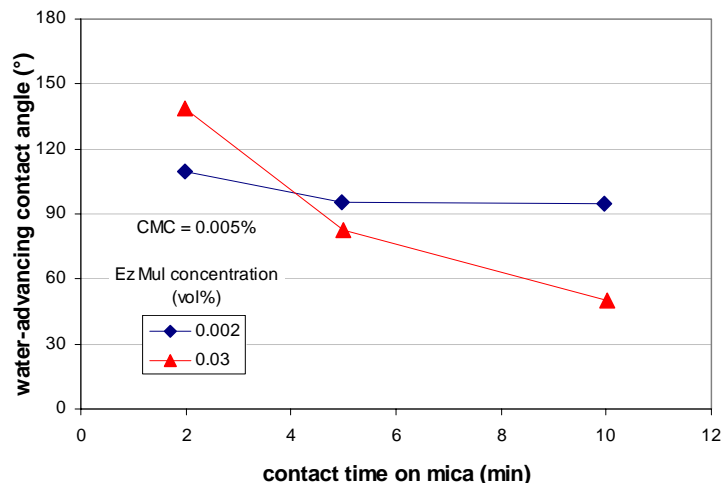


Figure 3.4.1-2. Contact angles as a function of contact time between water drop and mica surface for two concentrations of Ez Mul surfactant mixture in decane, above and below the CMC. The water phase was an unequilibrated drop of {pH 6, 0.1M} buffer.

Surfactant concentrations above CMC

Also shown in Fig. 3.4.1-2 are water-advancing contact angles measured with Ez Mul at a concentration of 0.03vol%, well above the CMC. Unlike the lower concentration, the wetting condition appears to be unstable, with contact angles starting at almost 140° and rapidly decreasing to about 50°.

The effects of all five emulsifiers at a concentration of 0.03 vol% in decane, on wetting of clean mica are shown in Fig. 3.4.1-3. Mica samples were aged for one hour in each emulsifier solution. Contact angles were measured with a drop of the {pH 6, 0.1M} aqueous solution after it had been in contact with the mica surface for 2 min. All of the products promoted neutral to oil-wet conditions, at least initially.

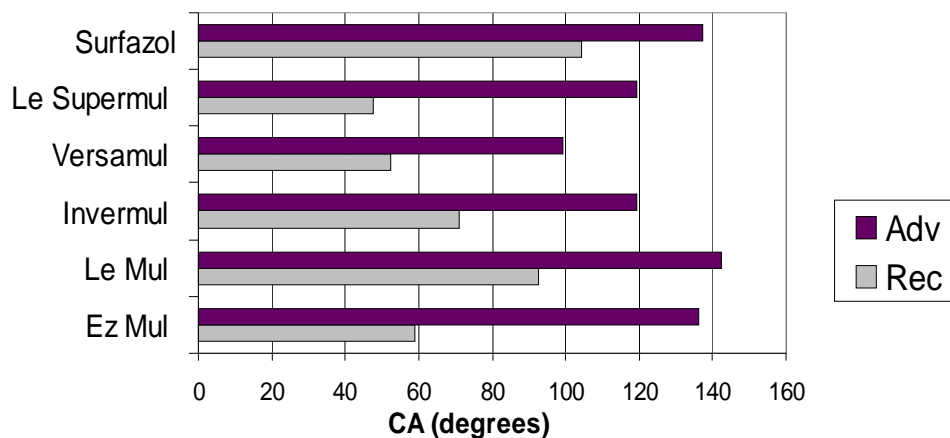


Figure 3.4.1-3. Comparison of the contact angles on clean mica surfaces exposed for 1 hr to emulsifier solutions, 0.03% by volume of product. The probe water drop is {pH 6, 0.1M} buffer. The contact time between the water drop and mica surface is 2 min.

It is not entirely clear, however, given the results in Fig. 3.4.1-2 above, how contact angles should be measured in these systems. The results in Fig. 3.4.1-3 above were measured with mica submerged in the surfactant/decane solution. This raises questions of kinetics of surfactant/surface interactions (the total exposure time is the nominal aging time of 1 hour plus the cumulative time over which measurements are proceeding). There are also questions about the dynamic affects of forming and retracting a drop. In the measurements in Fig. 3.4.1-3, each aqueous drop was formed and immediately contacted with the mica surface where it was allowed to rest for two minutes. Fig. 3.4.1-4 shows changes in advancing contact angles that occur if the drop is allowed to remain stationary on the surface for 5 or 10 minutes. For the Group 1 emulsifiers, substantial decreases in θ_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. 3.4.1-4.

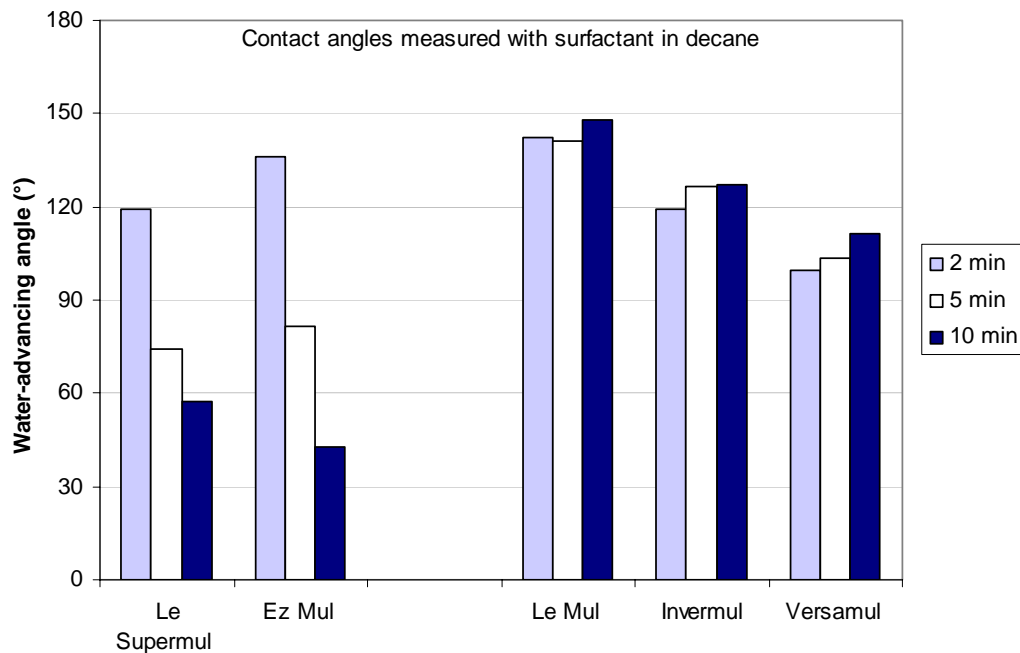


Figure 3.4.1-4. Water-advancing contact angles on mica exposed to surfactant solutions for 1 hr. Contact angles were measured with a drop of {pH 6, 0.1M} buffer in decane solutions of each surfactant (0.03 vol%). Results are shown for contact times of 2, 5, and 10 minutes, during which the advanced aqueous drop remained stationary on the mica surface are shown.

Another question is the persistence of these wetting changes. Surfactant-exposed mica surfaces, analogous to the samples in Fig. 3.4.1-4 above, were transferred to fresh decane where the contact angles were measured with no surfactant except that which remains adsorbed to the mica surface (Fig. 3.4.1-5). Figure 3.4.1-6 compares the initial (2 min) and final (10 min) water-advancing contact angles in surfactant solution (SS) and in decane. Group 1 contact angles start high, but after 10 min are comparable to the measurements in decane. These changes are not due to desorption, since surfactant is present in the decane phase. Desorption might account for the differences observed with the Group 2 surfactants, all of which are stable in surfactant solution and substantially lower in decane.

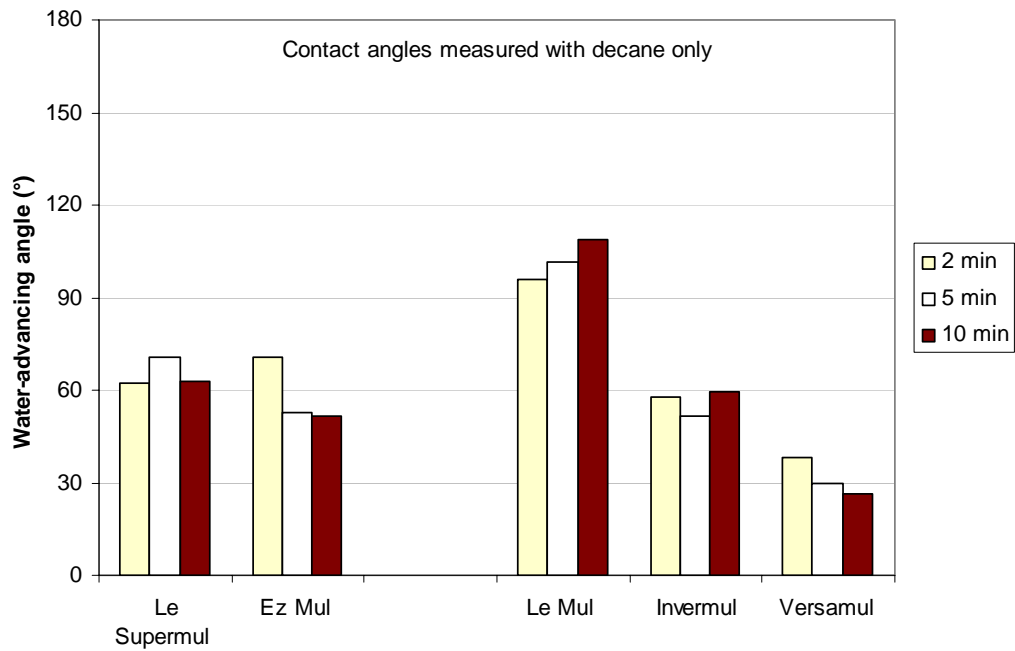


Figure 3.4.1-5. Mica samples treated as in Fig. 10 above. After one hour, mica was removed from the surfactant solutions and submerged in decane for the contact angle measurements with {pH 6, 0.1M} buffer. Contact times between the water drop and mica surface were 2, 5, and 10 minutes.

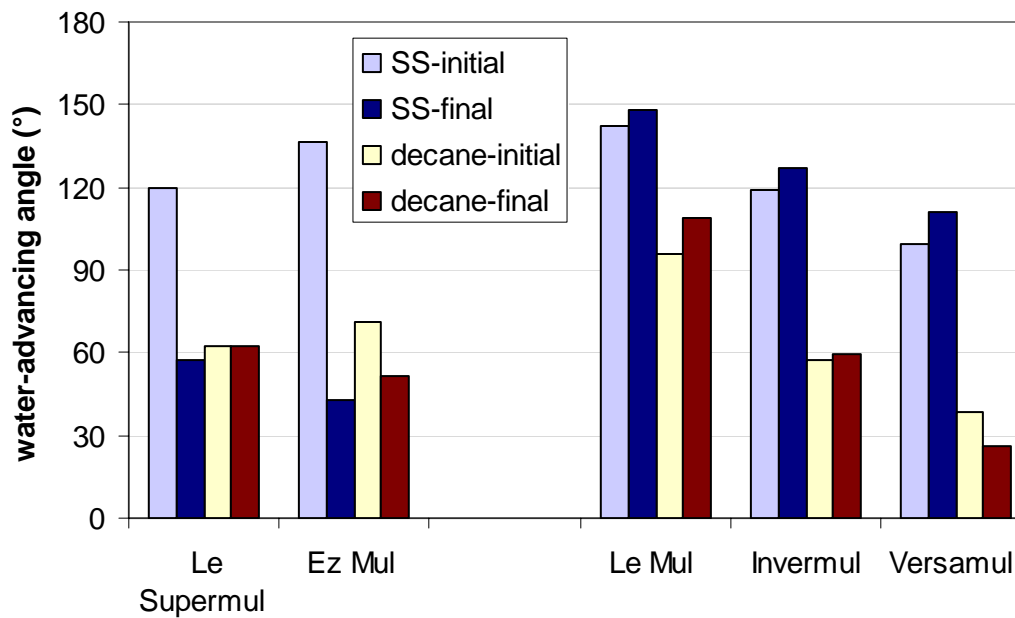


Figure 3.4.1-6. Comparison of initial (2 min) and final (10 min) water-advancing angles for measurements in surfactant solution (SS) and in decane. Data are from Figs. 10 and 11 above.

Much higher contact angles were measured with all of the emulsifiers (except Le Supermul) if a drop of {6, 0.01} brine was formed in the surfactant solution and allowed to equilibrate briefly (up to 10 min) before being brought into contact with the mica surface under the decane solution of surfactants. In most cases 2 min were sufficient to produce oil-wet conditions, as shown in Fig. 3.4.1-7. The changes during the first two minutes after formation of the brine droplet suggest that non-equilibrium effects may be influencing these contact angle measurements. In all cases, measurements were recorded after 5 minutes of contact between the brine drop and mica surface.

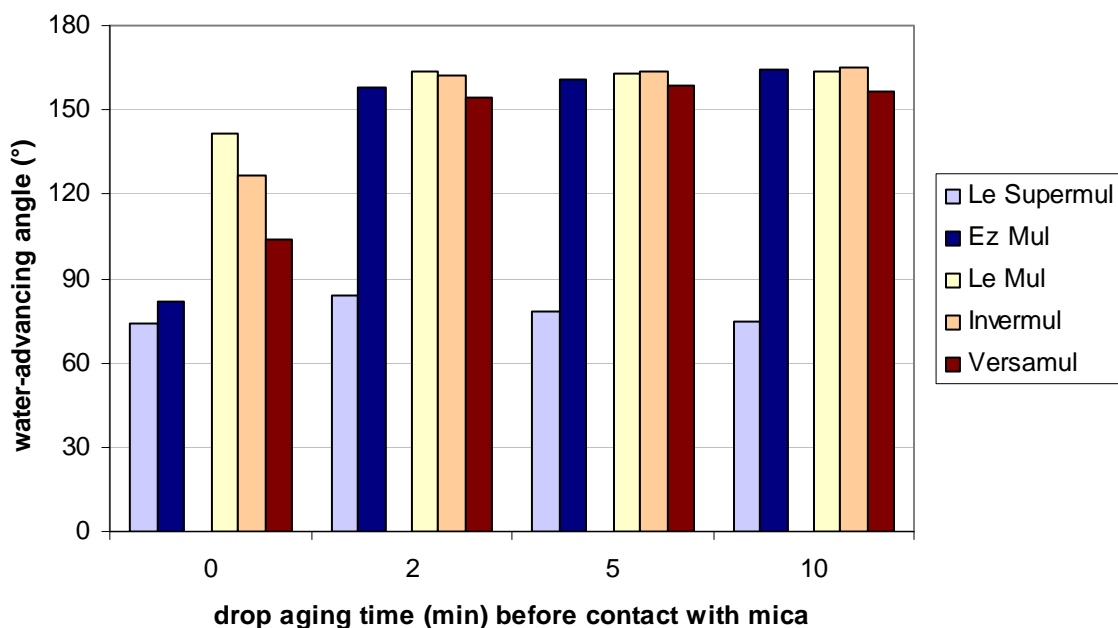


Figure 3.4.1-7. Mica surface aged for 1 hr in an 0.03 vol% solution of surfactant in decane. Contact angles measured in surfactant solution with {pH 6, 0.1M} buffer. Contact time between water drop and mica surface was 5 min. Before contact with mica, the water drop was allowed to equilibrate with the surfactant solution for up to 10 minutes.

We tested the hypothesis that lack of equilibrium caused contact angles to be dependent on details of the test procedure by repeating these measurements using pre-equilibrated brine and surfactant solutions. After equilibration there should be no additional mass transfer when a drop

of the brine is formed in the surfactant solution. Fig. 3.4.1-8 shows that the changes in contact angles were eliminated when the fluids were mixed and allowed to separate for 4-12 days. All measurements were made after 5 min of contact between brine droplet and the solid surface.

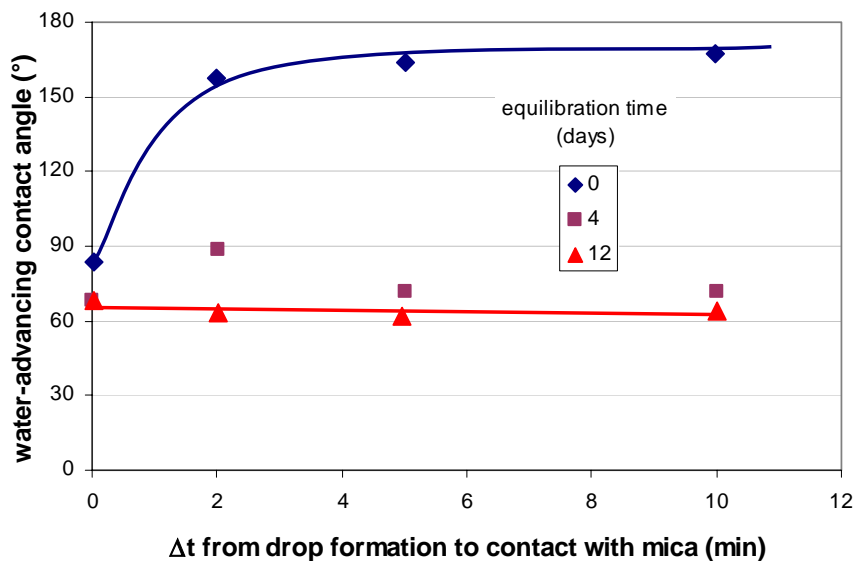


Figure 3.4.1-8. The effect of drop aging time illustrated in Fig. 13 was eliminated if the Ez Mul surfactant solution and aqueous buffer were pre-equilibrated for 4-12 days.

Why the effect of non-equilibrium was so consistently to increase contact angles, making the surface appear more oil-wet, we can only conjecture at this point. During this period, surfactant must be accumulating at the newly formed oil/brine interface. Some surfactant may be transferred into the brine phase although the amount is expected to be small. Since the surfactant concentration is above CMC, the situation is similar to Fig. 3.4.1-1b above, except that the equilibrium conditions of monolayer adsorption at the oil/brine interface have yet to be established. Thus, the distribution of surfactants may resemble the situation illustrated in Fig. 3.4.1-9. Although there is a concentration of monomers, most of the surfactant is in the reverse micelles with the polar heads shielded from contact with the new oil/water interface. In order to satisfy the requirement for additional surfactant at the oil/water interface, some of the micelles

must release surfactant. One way they might do that is to divide into hemi-micelles, exposing polar head groups that partition to the oil/water interface.

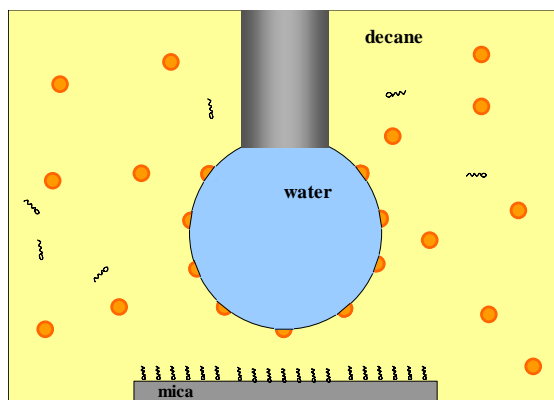


Figure 3.4.1-9. Surfactant distribution in an oil/water/mica system with oil-soluble surfactant concentration greater than CMC, when the brine drop is allowed to equilibrate briefly with the surfactant solution before contact with the mica surface.

This hemi-micelle stage might well be a temporary one, with hemi-micelles replaced by monomers as the surfactants disassociate. During the period when hemi-micelle accumulation dominates, however, excess surfactant might be trapped between water and mica, producing higher-than-equilibrium contact angles. Whether such trapped surfactant could eventually diffuse away from the contact area or would remain trapped has not yet been investigated.

Figure 3.4.1-10 compares contact angles measured with unequilibrated fluids and those measured with fluids that were mixed and allowed to separate for 4 days and for 12 days as a function of contact time between the aqueous phase droplet and the mica surface. Equilibration eliminates the changes that were observed for different contact times, and the angles approach those measured on surfactant-treated mica measured in fresh decane. Ez Mul was used in all of these experiments.

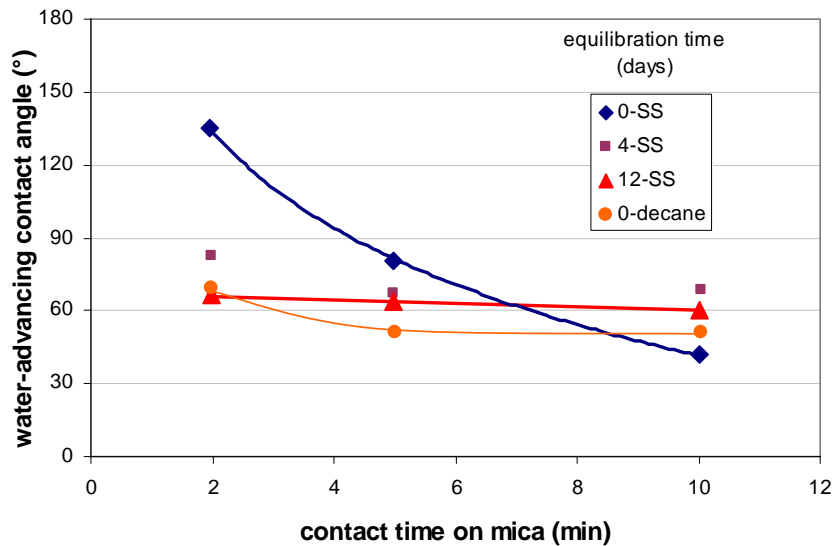


Figure 3.4.1-10. Changes that occur with the time of contact between water drop and mica surface can be eliminated by preequilibration of the oleic and aqueous phases. Contact angles were measured in surfactant solution (SS = 0.03vol% Ez Mul in decane) or in decane alone with {pH 6, 0.1 M} buffer. Contact times between water drop and mica surface were 2, 5, and 10 minutes.

In the interests of reproducibility, preequilibrated fluids should be used for contact angle experiments. However, it is worth considering that non-equilibrium conditions may prevail during the drilling process and that surfaces may, at least temporarily, become quite oil-wet. Whether surfactant can be trapped indefinitely is unclear. Perhaps with time, the excess surfactant would diffuse away from the surface and contact angles would decrease.

We addressed the question of whether enough surfactant could partition into the aqueous phase to alter wetting. Figure 3.4.1-11 shows that very water-wet conditions are produced, comparable to those for clean surfaces with brine and decane, when contact angles are measured using brine that was preequilibrated with a decane solution of surfactant. The differences are within the accuracy of the contact angle measurements.

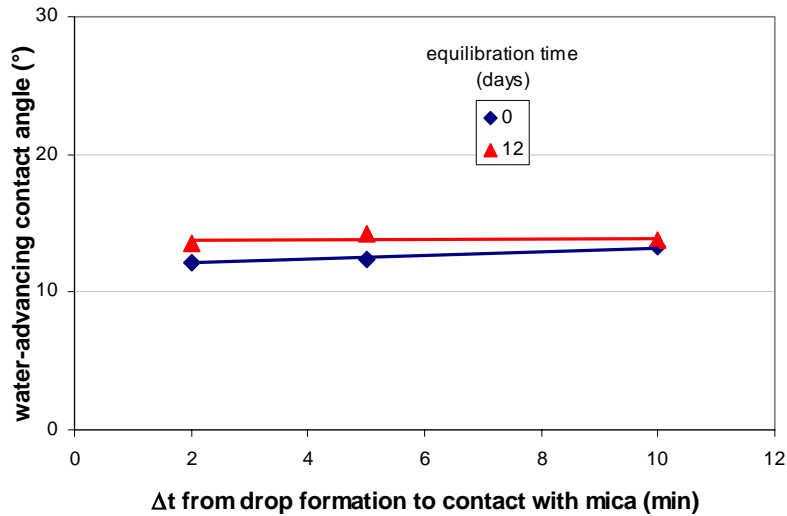


Figure 3.4.1-11. Water advancing contact angles between decane and {pH 6, 0.1M} buffer. The results are indistinguishable regardless of whether the aqueous buffer used had been preequilibrated with surfactant solution (0.03vol% Ez Mul in decane) or not.

3.4.2 Wetting alteration – surfactants and crude oils

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 {pH 4, 0.01M} brine. 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. Three oils were used in this investigation: LB-03, C-AL-03, and Cottonwood-03 (Appendix II). Results are shown in Fig. 3.4.2-1.

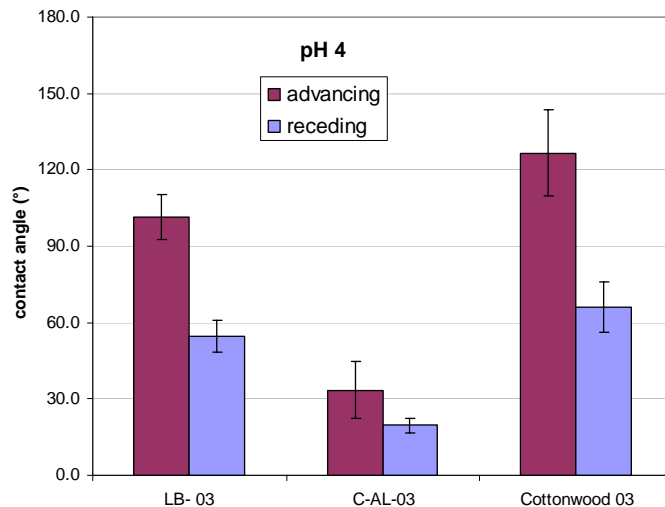


Figure 3.4.2-1. Decane/buffer contact angles for mica exposed to {pH 4, 0.01 M} buffer for 24 hrs, then to one of three crude oils for 21 days at ambient temperature. Crude oil was removed by rinsing with toluene.

Subtle changes in wetting were found when varying amounts of Ez Mul (0.005 – 1 vol%) were added to the LB-03 crude oil, as shown in Fig. 3.4.2-2. Only the intermediate concentrations (0.0025 – 0.01) gave contact angles that were distinctly different than the oil with no added emulsifier and the differences were small (from a water advancing angle of 102° to a maximum of 128° for the 0.0025% mixture). Above 0.01%, the contact angles were lower than the maximum value and indistinguishable from the oil with no added Ez Mul.

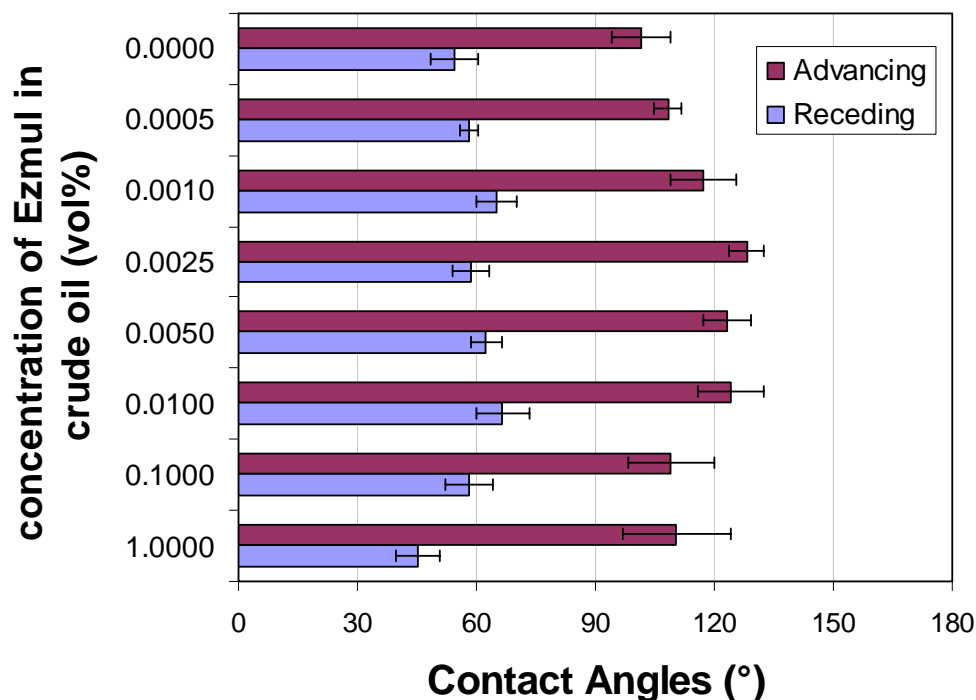
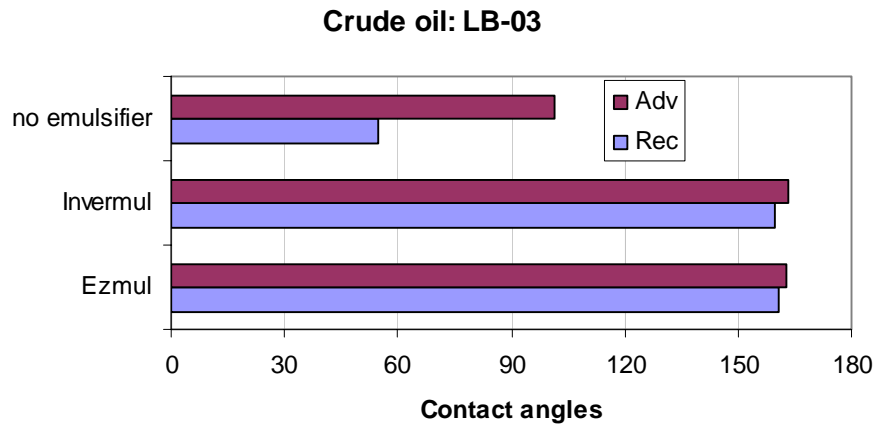


Figure 3.4.2-2. Contact angles for mica surfaces aged in LB-03 crude oil to which varying amounts of Ez Mul were added. Mica was aged for 24 hrs in {pH 4, 0.01 M} buffer, 21 days in oil plus Ez Mul, rinsed with toluene, and submerged in decane. Contact angles were measured with decane and {pH 6, 0.1M} buffer.

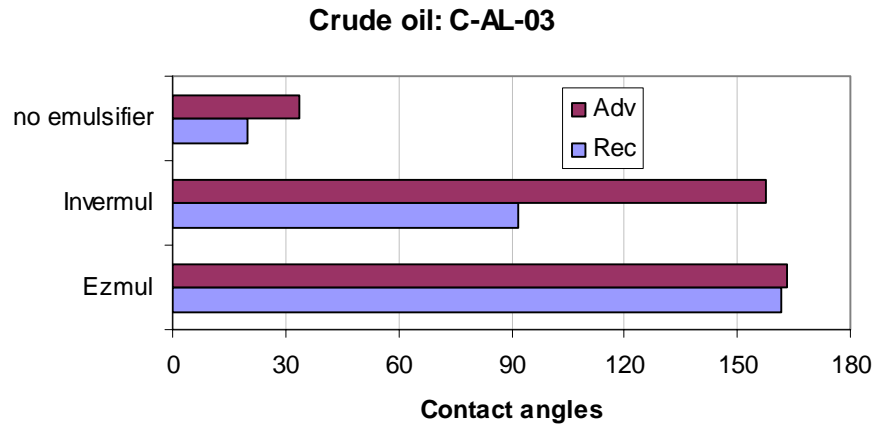
Changes in wetting toward more oil-wet conditions were more dramatic if surfaces were exposed to the emulsifier after they had been treated with crude oil (Fig. 3.4.2-3). All of the mica samples were equilibrated first with {pH 4, 0.01M} buffer for 24 hrs, then with one of the three crude oils for 21 days. Bulk crude oil was removed by rinsing with toluene, then each surface was submerged in one of three decane solutions (Table 3.4.2-1). Contact angles were measured with the aqueous phases shown in Table 3.4.2-1.

Table 3.4.2-1. Test fluids for the contact angle measurements shown in Fig. 3.4.2-3

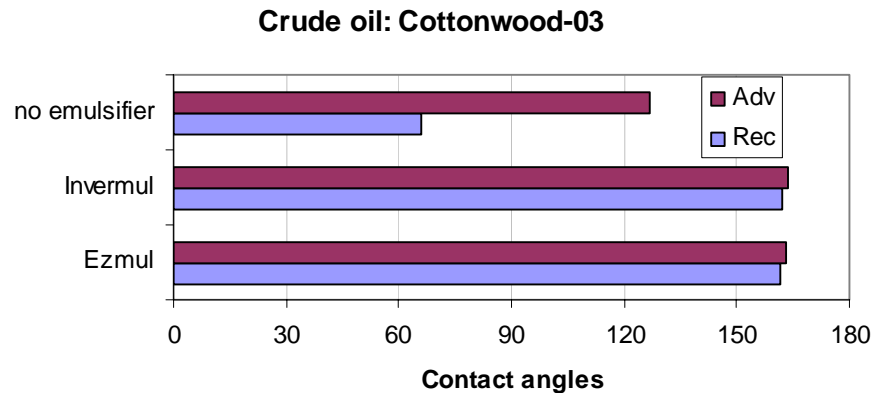
	oleic phase	aqueous phase
no emulsifier	decane	{pH 4, 0.01M}
Invermul	0.03vol% solution in decane	{pH 4, 0.01M} equilibrated with the Invermul solution for 12 days
Ez Mul	0.03vol% solution in decane	{pH 4, 0.01M} equilibrated with the Ez Mul solution for 12 days



(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)

Figure 3.4.2-3. Contact angles (water-advancing and receding) measured on mica surfaces exposed first to buffer, then to crude oil. Contact angles were measured between buffer and decane or decane solutions of emulsifier (0.03vol%).

A suggested mechanism for producing very oil-wet conditions when oil-treated mica surfaces are submerged in surfactant solutions is shown in Fig. 3.4.2-4. Components adsorbed from the crude oil alter the surface properties. Polar head groups of monomers are not likely to adsorb, nor is there any reason why surfactant tails should be adsorbed since that would produce a region of head groups in the non-polar solvent. Instead, reverse micelles could adsorb, making the oil-treated surfaces very oil-wet. Note that the coverage illustrated for the oil components is less than complete, which might produce the weakly-water-wet and intermediate conditions observed for two of the three crude oils (C-AL-03 and LB-03). Only with the added adsorption of reverse micelles of surfactant does the surface become oil-wet in this scenario. A denser coverage with oil components would produce the behavior observed with the Cottonwood oil.

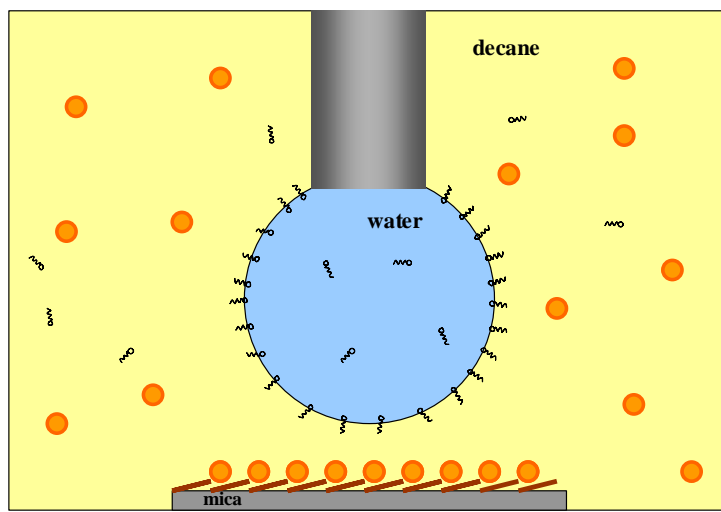


Figure 3.4.2-4. Adsorption of reverse micelles on the oil-treated mica surface would produce very oil-wet conditions.

3.5 Baseline study of MXW and MXW-F cores (Zhang and Morrow)

Crude oils used in this study are designated as Minnelusa'98 (or Minnelusa), Minnelusa'02 (or Minnelusa-02), and Gullfaks (or Gullfaks-96) (see Appendix II for oil properties and Appendix III for brine properties). All of the crude oils were filtered to remove solid particulates. Minnelusa'98 oil was vacuumed at ambient temperature for 1 hour before use to reduce its volatility.

3.5.1 Core treatments

Properties of cores used in this study are summarized in Table 3.5.1-1. Cores from EV4-1 through EV4-5 were first vacuumed and saturated with Minnelusa reservoir brine and aged in the same brine at 75°C for 10 days to reach ionic equilibrium. EV4-1, EV4-4 and EV4-5 were flushed with a 90 cp mineral oil at an injection rate of 0.5 to 3 ml/min at room temperature to achieve the desired S_{wi} 's. The 90 cp mineral oil in EV4-1 was then displaced by Soltrol 220 before running VSWW spontaneous imbibition tests at S_{wi} of 26%. The 90 cp mineral oil in EV4-4 and EV4-5 was displaced with 5 PV of decalin (0.5 ~ 2 ml/min), which was in turn displaced by 5 PV of Gullfaks crude oil. EV4-2 and EV4-3 were flushed with Minnelusa'02 crude oil at 40°C to establish S_{wi} . Initial water saturations for all these cores are about 27 %.

Table 3.5.1-1. Properties of core samples used in spontaneous imbibition tests

Core	k_g md	ϕ %	S_{wi} %	T_f °C	Status	R_{im}^1 %OOIP	R_{wf} %OOIP	I_w	I_o
EV4-1	254	19.5	26	21	Mineral oil	42.1	42.1	1	0
EV4-2	187	18.8	26.8	40	M'02 MXW-F ²	7.7	70.8	0.12	0.12
EV4-3	189	18.9	26.8	40	M'02 MXW	20	i.p. ³		
EV4-4	194	19.1	26.4	21	Gullfaks MXW	40.6	44.5	0.65	0
EV4-5	177	18.7	26.7	21	Gullfaks MXW-F	46	50.3	0.90	0
EV4-6	188	18.9	0	n/a	Soltrol 220	48		1 ⁴	0 ⁴
EV4-7	357	20	0	n/a	Soltrol 220	46.9		1 ⁴	0 ⁴
5B19	81	17.6	25.4	45	Gullfaks MXW	37.1			
5B22	90	18.3	25.9	45	Gullfaks MXW	33.5			
5B23	81	17.7	25.8	45	Gullfaks MXW-F	36.6			
5B25	106	18.6	26.2	45	Gullfaks MXW-F	39.7			
5B2	93	17.9	24.6	50	M'98 MXW	32			
5B8	104	18.5	24.6	50	M'98 MXW	35.5			
5B3	98	18	25	50	M'98 MXW-F	12.5			
5B7	105	18.3	24.6	50	M'98 MXW-F	14.2			
3B14a	106	18.7	27.1	50	M'02 MXW-F	20			
2BV3	149	18.9	25	50	M'02 MXW-F	20			
3B5	94	18.2	26.1	50	M'98 MXW-F	14			

1 The oil recoveries correspond to dimensionless time of 20,000.

2 M stands for Minnelusa.

3 Imbibition test is still in progress.

4 Assumed values.

The cores EV4-2 - EV4-5 containing crude oil were aged for 10 days in sealed stainless steel cells at 75°C. The MXW cores, EV4-3 and EV4-5, were allowed to cool for about 5 hours and then placed in graduated glass imbibition cells filled with Minnelusa reservoir brine. MXW-F cores were prepared by displacing the crude oil in cores EV4-2 and EV4-5 with 5 PV of decalin (C₁₀H₁₈, decahydronaphthalene, perhydronaphthalene) at a flow rate of 0.5 ~ 2cc/min. The decalin was displaced by 5 PV of Soltrol 220 at room temperature.

For all other cores, brine was displaced either with Minnelusa crude at 50°C or Gullfaks crude at 40°C at a flow rate of 0.2 m/min to 5.0 ml/min to establish S_{wi} . After 10 days' aging at T_a 7(5°C), crude oil was displaced by 5 PV of decalin at 3 ft/day (about 0.72 PV/hr). The decalin flush temperature, T_f , was 50°C for Minnelusa treated cores and 40°C for Gullfaks treated cores.

Decalin was then displaced with 5 PV of mineral oil of selected viscosity at ambient temperature (21°C).

3.5.2 Gullfaks oil

Imbibition rates for the Gullfaks core were initially slower than for the Berea 250, $S_{wi} = 0\%$, reference curve and for the Berea 250, $S_{wi} = 26\%$ curve (see Fig. 3.5.2-1). At the late stage of imbibition, recovery from the MXW-F core was higher than for the VSWW cores. The small wettability change observed for the Gullfaks oil is consistent with previous observations (Tong et al., 2002b).

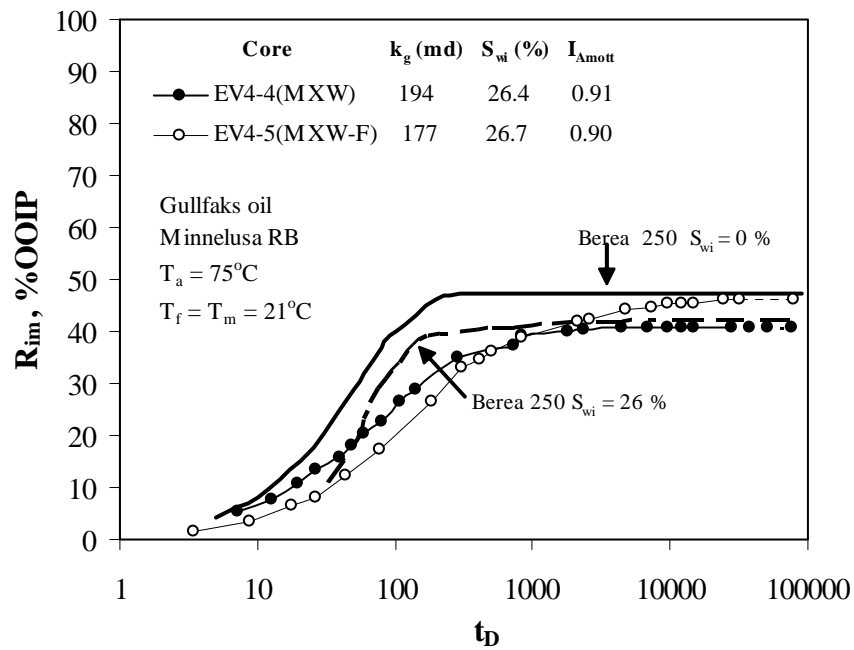


Figure 3.5.2-1. Comparison of spontaneous imbibition characteristics between Gullfaks MXW and MXW-F Berea 250 cores.

Figure 3.5.2-2 shows the imbibition characteristics for duplicate tests of Gullfaks MXW and MXW-F cores. The two curves for either MXW or MXW-F cores show good reproducibility.

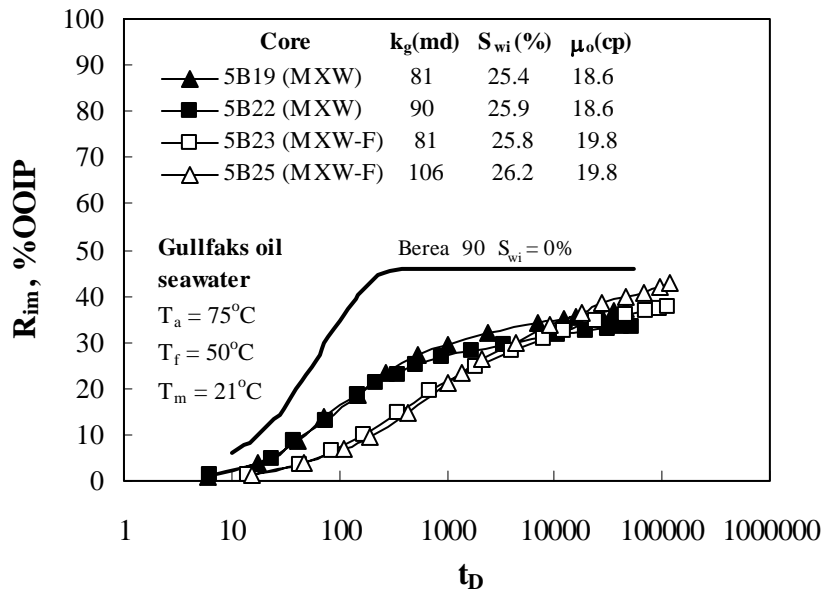


Figure 3.5.2-2. Comparison between Gullfaks MXW and MXW-F Berea 90 cores.

The scaled imbibition curves in Fig. 3.5.2-2 are comparable to those shown in Fig. 3.5.2-1. Both sets of tests show a crossover between the imbibition curves for MXW-F and MXW cores at the late stage of imbibition. After about 8 days' imbibition, the cores EV4-4 and EV4-5 (see Fig. 3.5.2-1) showed cessation of oil production, but the cores presented in Fig. 3.5.2-2 showed slow continued production of oil.

3.5.3 Minnelusa oil

Imbibition characteristics for cores prepared with Minnelusa '02 are shown in Fig. 3.5.3-1. Imbibition rates for the Minnelusa oil prepared cores were much slower than for the cores treated with Gullfaks oil. The Amott wettability index for EV4-2 is 0.

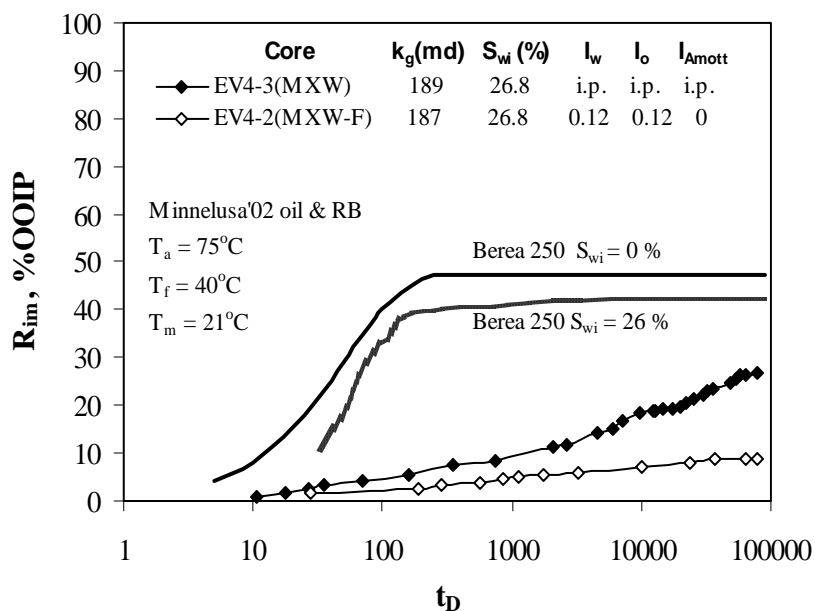


Figure 3.5.3-1. Comparison of imbibition rates between Minnelusa '02 MXW and MXW-F Berea 250 cores.

The cores used to obtain the results shown in Fig. 3.5.3-2 were from a different block of Berea sandstone and treated using Minnelusa'98 oil. The imbibition results give close reproducibility and are qualitatively similar to the comparison of MXW and MXW-F results shown in Fig. 3.5.3-1. Both sets of tests indicate that MXW cores have higher imbibition rate than for MXW-F cores.

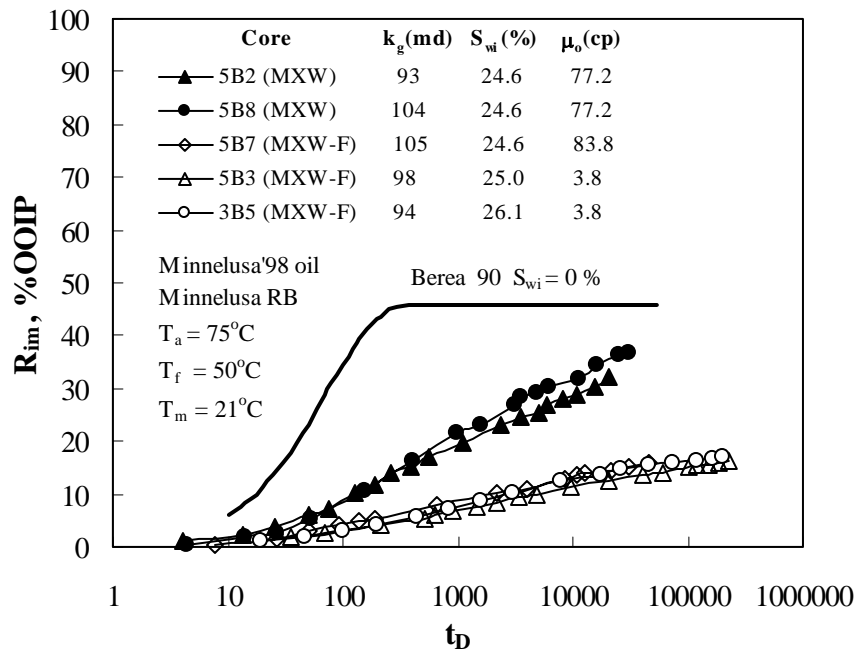


Figure 3.5.3-2. Comparison of imbibition between Minnelusa'98 MXW and MXW-F Berea 90 cores.

Fig. 3.5.3-3 shows a comparison of MXW-F cores for Minnelusa'98 oil and Minnelusa'02 oil. The dotted line is an average result obtained from the three MXW-F curves shown in Fig. 3.5.3-2. The MXW-F cores prepared using Minnelusa'02 oil have a slightly higher imbibition rate than the MXW-F cores prepared with Minnelusa'98 oil.

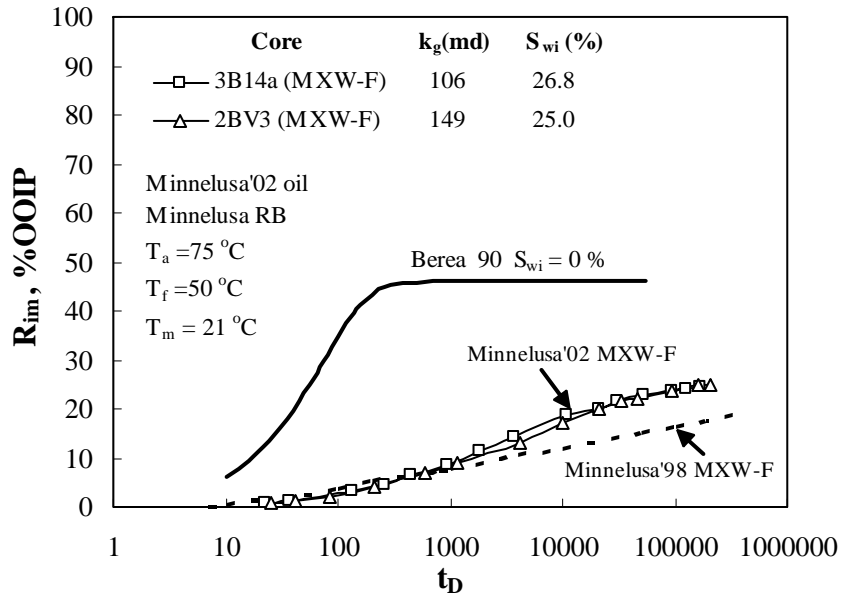


Figure 3.5.3-3. Comparison between Minnelusa'98 and Minnelusa'02 MXW-F Bera 90 cores.

3.5.4 Stability of MXW-F

The stability of the organic film deposited on the on the rock surface was tested for consecutive cycles of imbibition and drainage (Tong et al., 2002b and c). The results are shown in Fig. 3.5.4-1. After the 1st cycle of imbibition, the brine in 5B7 was displaced by mineral oil at room temperature to re-establish initial water saturation. The displacement rate ranged from 0.1 to 6.0 ml/min (about 0.36 to 22.5 PV/hr) based on the viscosity of the mineral oil and the desired S_{wi} . Five cycles of imbibition tests were performed on this core. The imbibition behavior shows good reproducibility indicating that the film on the rock surface is stable.

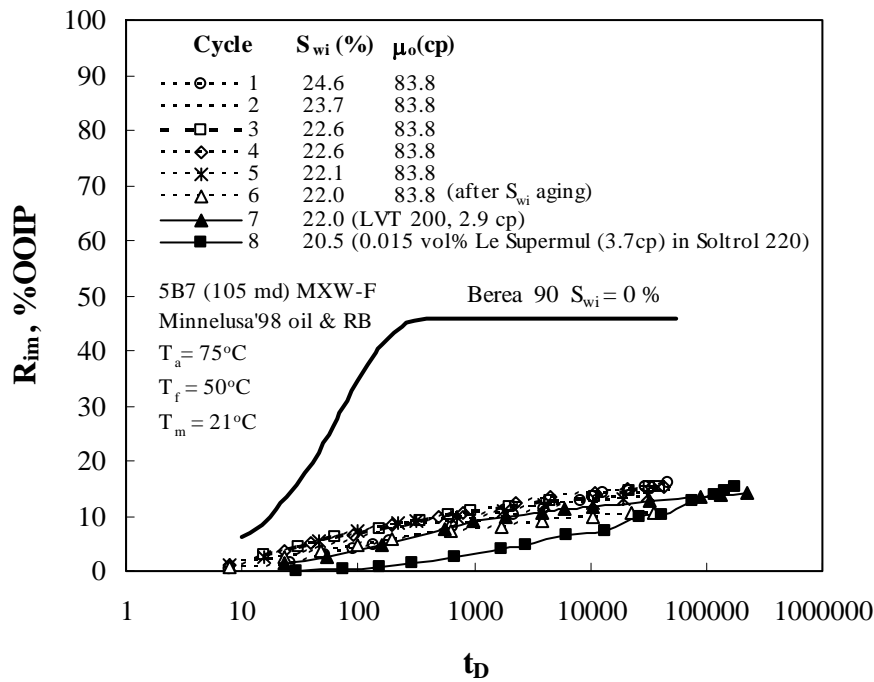


Figure 3.5.4-1. The effect of base oil and addition of emulsifier (LE SUPERMUL) on imbibition for Minnelusa'98 MXW-F Berea 90 core.

The stability of the MXW-F was also tested on another MXW-F core (3B5). Oil recovery versus dimensionless time is presented in Fig. 3.5.4-2. The close agreement in the first three imbibition curves indicated that that wetting conditions for the core did not change significantly during this series of tests.

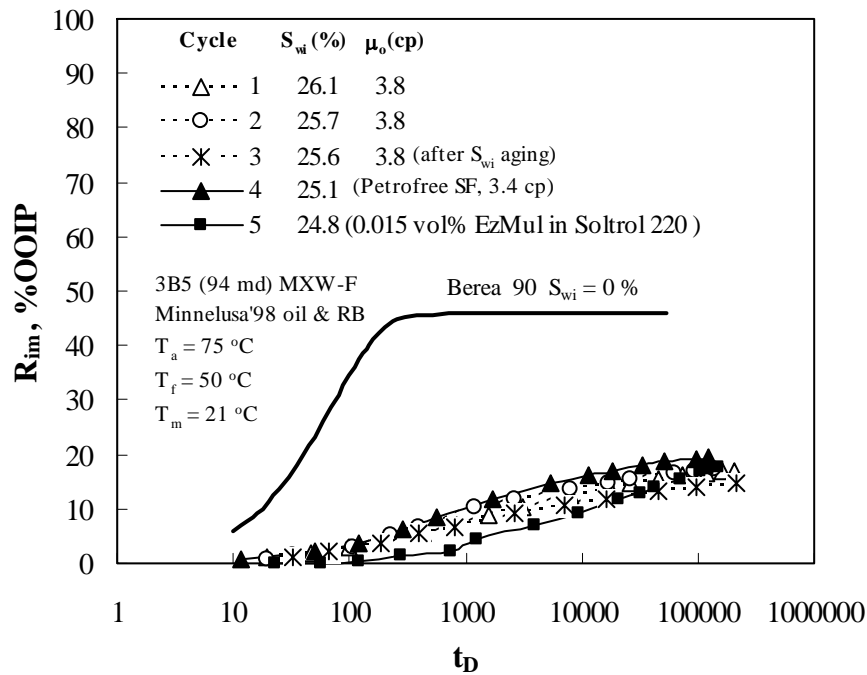


Figure 3.5.4-2. The effect of base oil and addition of emulsifier (EZ MUL[®]NT) on the imbibition of Minnelusa'98 MXW-F Berea 90 core.

3.5.5 Effect of SBM components on MXW-F cores

SBM base oil

After the 5th imbibition into 5B7 and 2nd imbibition into 3B5, S_{wi} was re-established by displacement with viscous mineral oil, which was in turn displaced by oil of selected viscosity (83.8 cp for 5B7 and 3.8 cp for 3B5). Then, the cores were aged for 10 days. The results shown in Figs. 3.5.5-1 and 3.5.5-2 indicate that the re-aging at S_{wi} had minor effect on wettability.

After the 6th imbibition, S_{wi} was re-stored for the 5B7 core by flow of the heavy mineral oil. The heavy oil was displaced with 5 PV of LVT 200 oil. Fig.8 shows that the scaled imbibition behavior of 5B7 treated with LVT 200 oil (viscosity of 2.9 cp) is close to those obtained for the previous six consecutive imbibition measurements made with reference mineral oils.

Another SBM base oil designated as Petrofree[®]SF was also tested. Fig. 3.5.5-2 indicates that this SBM base oil also has no significant effect on the imbibition behavior of the Minnelusa MXW-F core.

SBM emulsifiers

After the 7th imbibition, S_{wi} was restored by flow of heavy mineral oil which was then replaced by injection of 5 PV of Soltrol 220 containing 0.015 vol % of LE SUPERMUL, an emulsifier used in synthetic oil-based mud. The subsequent imbibition test run on this core shows that the early stage imbibition rate was obviously suppressed because of exposure of the core to the emulsifier. A second test was run for SBM emulsifier, EZ MUL[®]NT. After the 4th imbibition cycle, S_{wi} of 3B5 was restored again and then the viscous mineral oil was replaced with 5 PV of Soltrol 220 containing 0.0015 vol % of EZ MUL[®]NT. The curve with respect to the fifth cycle (see Fig. 3.5.5-2) shows significant suppression of spontaneous imbibition.

3.5.6 Summary of baseline core study

- A selection of crude oils rocks and base oils and additives for SBMs have been assembled. Basic characterization of rocks and oils are being obtained.
- Baseline data for VSWW imbibition have been measured for a range of conditions.
- Mixed wettability cores have been prepared by adsorption from two distinctly different types of crude oil. Results could be reproduced and the wetting states were stable with respect to repeated imbibition cycles.
- Base oils for SBM muds had no significant effect on the wettability of MXW-F cores.
- SBM emulsifiers caused a significant reduction in imbibition rate for MXW-F cores.

3.6 Effect of SBM base oils on asphaltene stability and wetting in sandstone cores (Zhang, Morrow, Wang, and Buckley)

3.6.1 Background

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 (SBM) 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.

Asphaltene are implicated in many undesirable phenomena including plugging, fouling, emulsion stabilization, and wettability alteration. The extent to which asphaltene create problems is more closely related to their stability than to their amount in an oil. Asphaltene can be destabilized when oils are depressurized or when oils are mixed with injected or lift gas. Synthetic oil-based drilling muds are a previously unrecognized source of potentially destabilizing fluid.

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.

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, 2001a, 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, 2003a).

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 the oil comes in contact, and the composition of the aqueous phase, if water is present. Buckley et al. (1998b) demonstrated 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. 3.6.1-1 (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 decalin, an intermediate solvent.

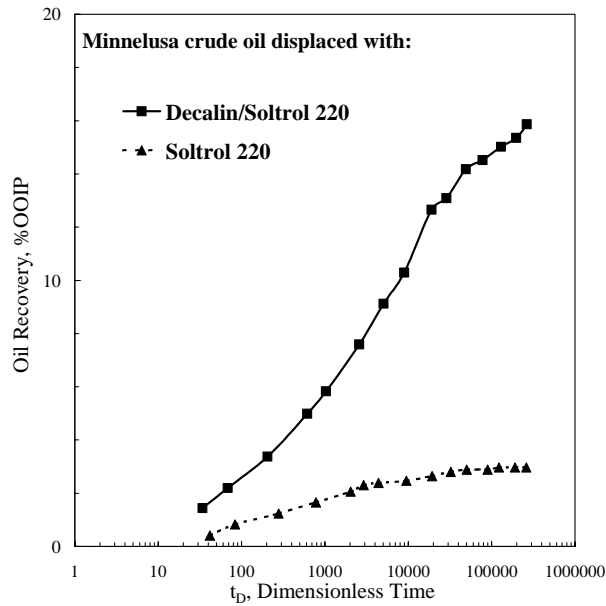


Figure 3.6.1-1. Cores are less water-wet, as indicated by slower imbibition if crude oil is displaced with a paraffinic oil (after Tie et al., 2003). The dimensionless time, t_D , is defined by Eq. 1, below.

Tests of imbibition rates in Berea sandstone cores were 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 from crude oils 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 of asphaltene stability can be used to identify specific crude oil/base oil pairs that precipitate asphaltenes.

3.6.2 Experimental details

Crude oils.

Three crude oils were used in this study: Fuji (or C-F-03) from the Gulf of Mexico, Gullfaks (or Gullfaks-96) from the North Sea, and Minnelusa from Wyoming. Properties of

these oils are summarized in Appendix II. They span a range of asphaltene content from 0.4 to 9%. The tendencies of Gullfaks and Minnelusa to alter the wetting of silicate surfaces has been shown to be quite different (Xie et al., 2002). Strong wetting alteration of a quartz glass surface was shown to be very stable to repeated measurement cycles of water advancing and receding for Minnelusa crude oil, whereas the extent of wetting alteration induced by Gullfaks decreased with each measurement cycle, returning the surface to more water-wet conditions.

Synthetic base oils and *n*-paraffins

Selected synthetic base oils were tested for their tendency to precipitate asphaltenes from Fuji and Minnelusa crude oils. It is difficult to quantify the onset conditions in Gullfaks because there is very little material in the asphaltene fraction (Table 3.6.2-1). Properties of the base oils tested are summarized in Table 2, with density and viscosity data included for oils used in core tests. Soltrol 220, a refined mineral oil composed of C₁₃-C₁₆ iso-alkanes, is not a synthetic base oil, but is included in this study because it is frequently used in laboratory displacement tests, including those shown in Fig. 3.6.1-1. Asphaltene stability was also tested with three *n*-paraffins—*n*-heptane (*n*-C₇), *n*-undecane (*n*-C₁₁), and *n*-pentadecane (*n*-C₁₅), all of which were purchased from Fisher Scientific with greater than 99% purity—for comparison to the synthetic base oils.

Table 3.6.2-1. Properties of base oils and mineral oil

Trade name	Material description	Density at 20°C (g/ml)	Viscosity at 20°C (mPa s)
Accolade	blend of internal olefins and esters		
Biobase 240	linear alpha olefins		
Biobase 560	linear paraffins		
EDC 99DW	highly hydrogenated mineral oil		
GOM 4 blend	internal olefins		
<i>LVT 200</i>	paraffins	0.8177	2.91
Petrofree (original)	fatty acid esters		
Petrofree LV	fatty acid esters	0.8617	3.86
Petrofree SF	internal olefins	0.7847	3.64
SF Base	internal olefins		
Soltrol 220	C ₁₃ -C ₁₆ isoalkanes	0.7833	3.80
XP-07	linear paraffins		

Cores

Berea sandstone core samples, 3.8 cm in diameter and 7.5 cm in length, were cut from two blocks, identified as C4 and C5, with similar petrophysical properties. Their average air permeability (k_g) was about 80md and porosity was about 17%. Initially water-wet cores were exposed first to synthetic seawater (containing 28,000 ppm NaCl, 935 ppm KCl, 5,365 ppm MgCl₂, 1,190 ppm CaCl₂, and 100 ppm of NaN₃ as biocide, with a total dissolved solids content of 35,490 ppm), 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.

3.6.3 Results and discussion

Asphaltene stability

Asphaltenes were destabilized by most of the synthetic base oils tested. Figure 3.6.3-1 summarizes asphaltene onset tests with Fuji crude oil at 20°C. The RI of each base oil is shown next to the RI of the mixture at onset conditions (P_{RI}). The onset conditions observed with mixtures of Fuji and two *n*-paraffins, *n*-heptane and *n*-pentadecane, are included for comparison. The P_{RI} for Accolade was similar to that for *n*-heptane; for other base oils, P_{RI} was closer to that for *n*-pentadecane. No asphaltene onset was found with either Petrofree (original) or Petrofree LV.

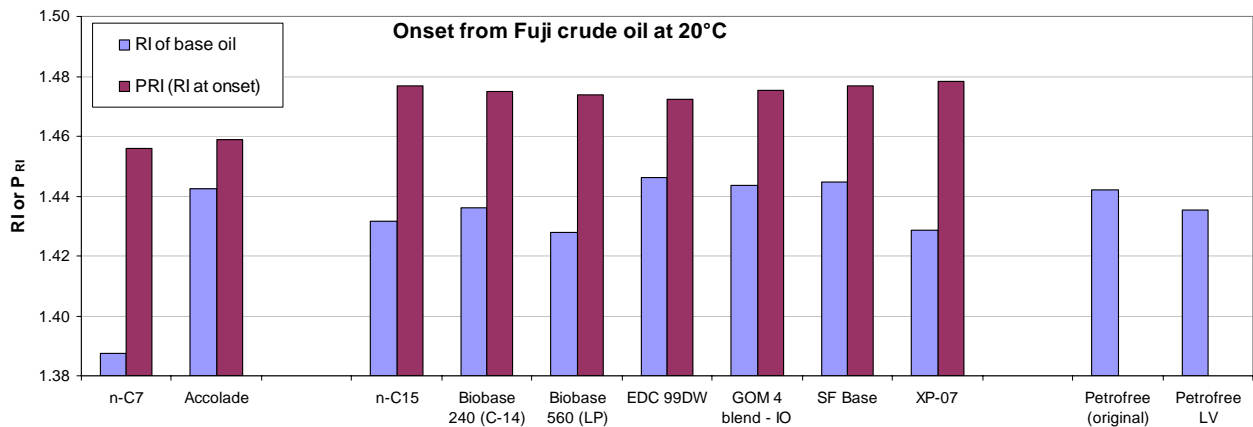


Figure 3.6.3-1. RI and P_{RI} for the onset of asphaltene precipitation from Fuji crude oil at 20°C.

Minnelusa crude oil was tested at 60°C to avoid problems with existing asphaltene aggregates in the stock tank oil. The results are summarized in Fig. 3.6.3-2. LVT 200 precipitates asphaltenes at solubility conditions that are intermediate between *n*-C₇ and *n*-C₁₁; Soltrol 220 and Petrofree SF produce asphaltene aggregates at solubility conditions that are closer to the *n*-C₁₅ onset. No precipitation was observed in mixtures of Petrofree LV with Minnelusa in any proportions.

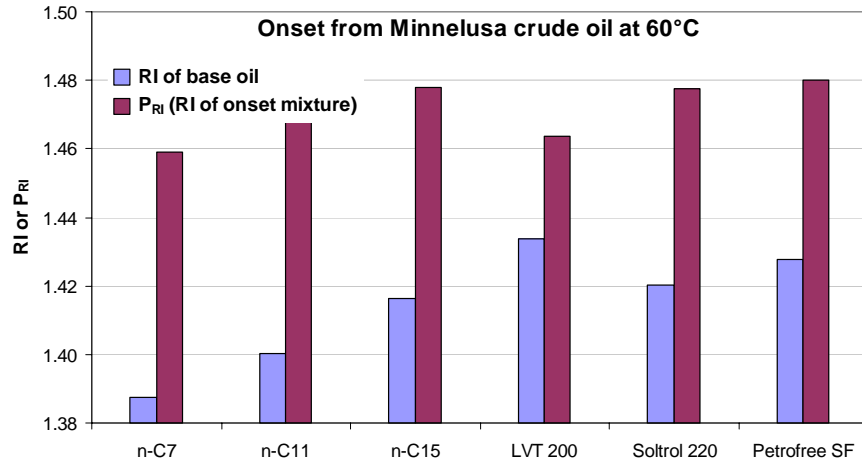


Figure 3.6.3-2. RI and P_{RI} for the onset of asphaltene precipitation from Minnelusa crude oil at 60°C.

Alteration of wetting in cores

A reference curve for very strongly water-wet recovery of refined oil is included in Figs. 3.6.3-3, -4, and -5. Results for Minnelusa crude oil are shown in Fig. 3.6.3-3. Aging in Minnelusa (MXW) resulted in significant change from the very strongly water-wet reference curve. Displacement of the Minnelusa crude oil by any of the synthetic base oils resulted in reduced rate of imbibition. Cores treated with Gullfaks (Fig. 3.6.3-4) are more water-wet, but depressed rates were observed when oil was displaced by either the Petrofree SF (internal olefin) or the LVT 200 (paraffinic oil). Similar results are shown for Fuji crude oil in Fig. 3.6.3-5.

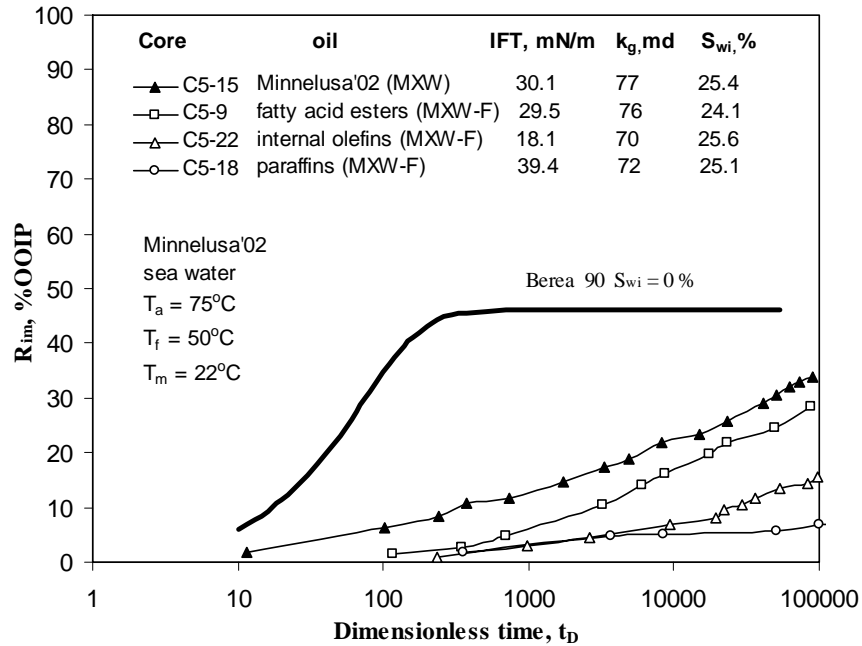


Figure 3.6.3-3. Wetting conditions in Berea core after aging in Minnelusa crude oil are shown by the line labeled MXW. (Numbers beginning C5- identify specific cores; IFT is interfacial tension; T_a , T_f , and T_m are the aging, flushing, and measurement temperatures.) The other three curves show sea water imbibition rates after the crude oil was displaced by the products indicated.

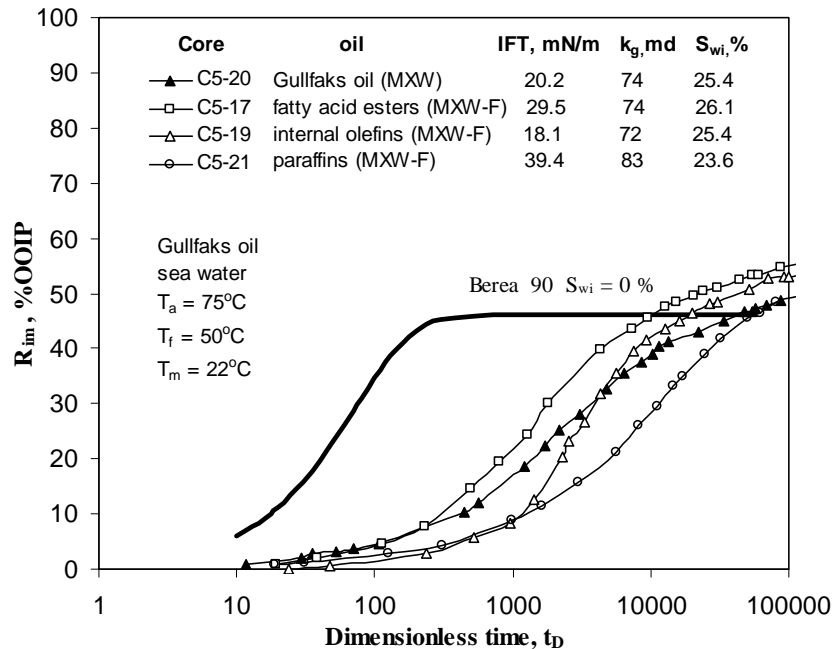


Figure 3.6.3-4. Wetting conditions in Berea core after aging in Gullfaks crude oil are shown by the line labeled MXW. The other three curves show sea water imbibition rates after the crude oil was displaced by the products indicated.

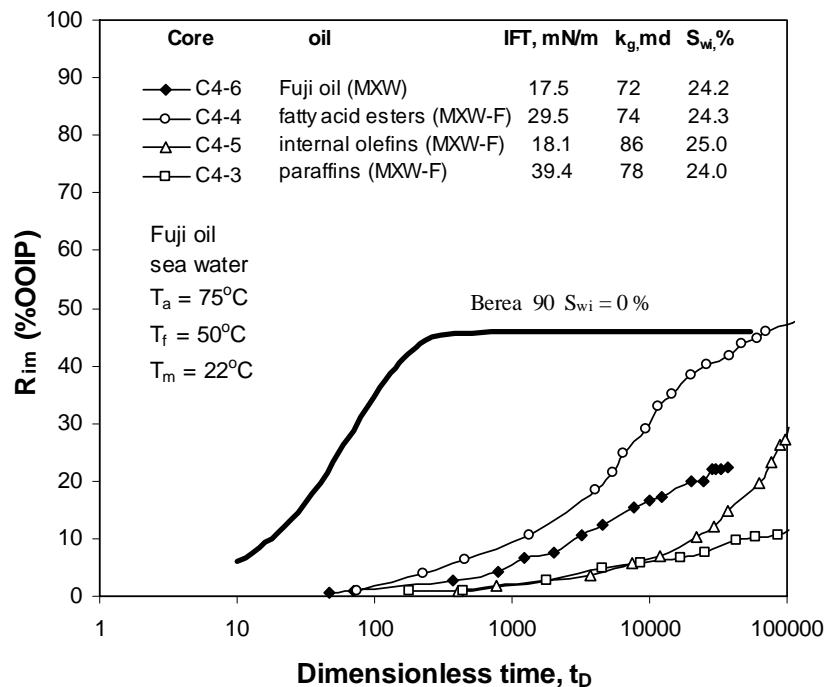


Figure 3.6.3-5. Wetting conditions in Berea core after aging in Fuji crude oil are shown by the line labeled MXW. The other three curves show sea water imbibition rates after the crude oil was displaced by the products indicated.

The internal olefin base oils (Petrofree SF) and the paraffinic LVT 200 consistently suppress the initial rate of imbibition, indicating less water-wet conditions are obtained when any of these three crude oils is displaced with these synthetic base oils. 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. For the fatty acid esters (Petrofree LV), there was no drastic reduction in water wetness. In one case imbibition was somewhat slower and in the other two cases faster than imbibition into the MXW core.

3.6.4 Summary

- 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.

3.7 Alteration of wetting in cores with SBM/OBM surfactants (Zhang and Morrow)

3.7.1 Spontaneous imbibition with and without added surfactants

A small amount of surfactant can significantly affect the rate of imbibition into Berea sandstone cores, as shown in Fig. 3.7.1-1 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 3.7.1-2 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.

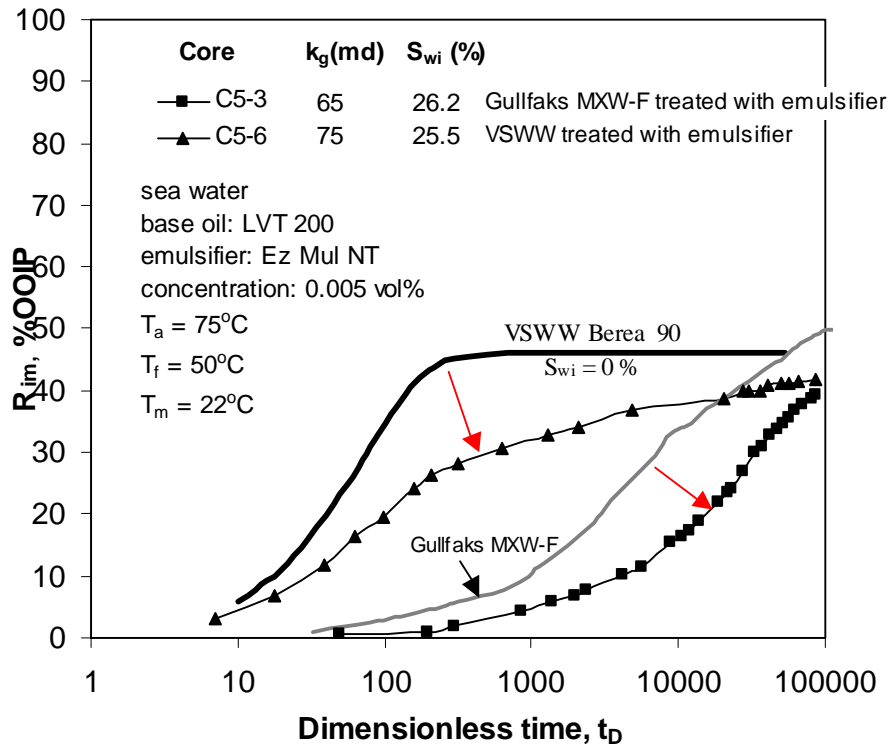


Figure 3.7.1-1. Effect of 0.005 vol% EzMul on wetting of Berea sandstone, with and without exposure of the core to Gullfaks-96 crude oil.

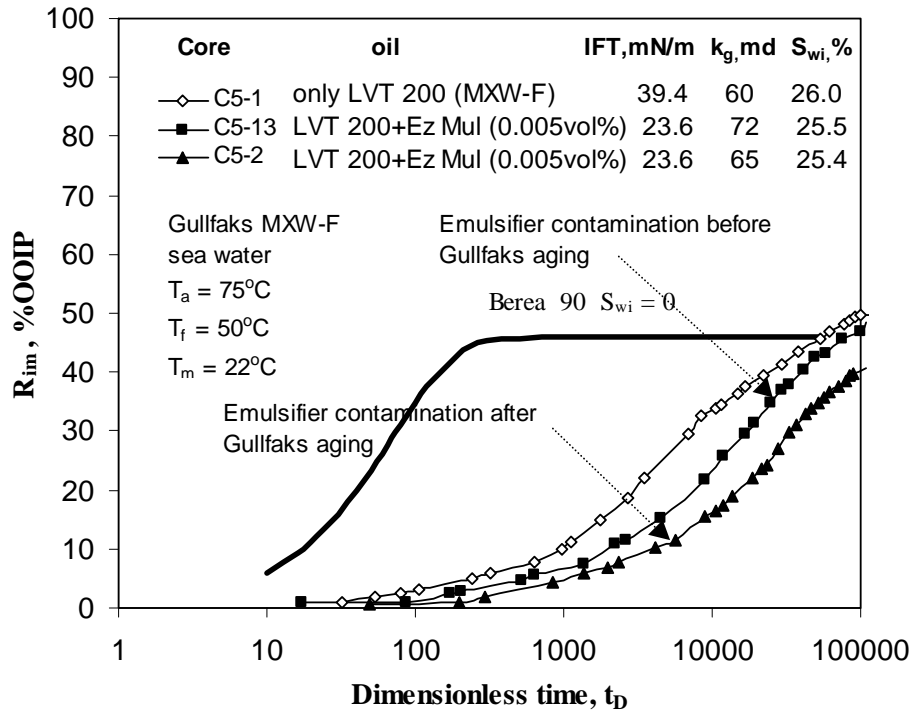


Figure 3.7.1-2. Greater change in wetting is observed when the core is exposed to EzMul after treatment with crude oil to create MXW-F wetting conditions.

Figure 3.7.1-3 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.

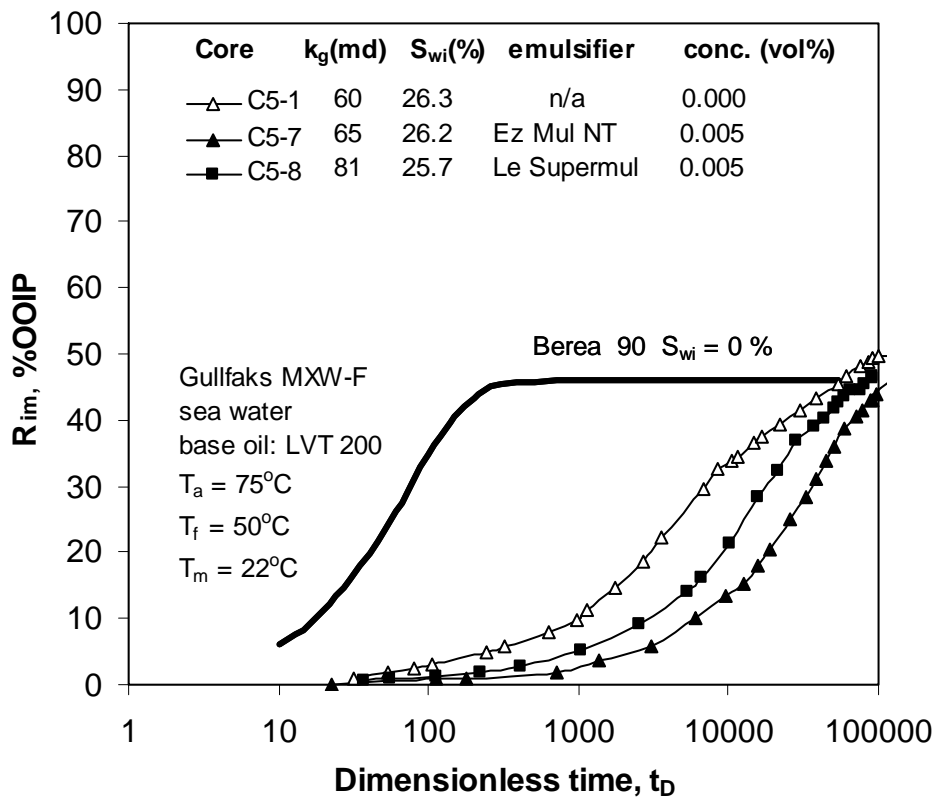
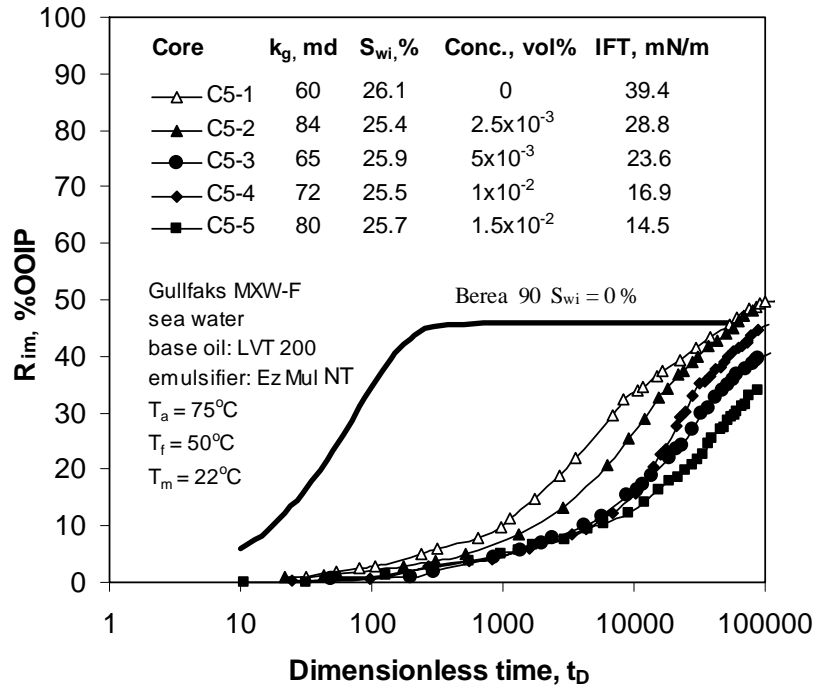
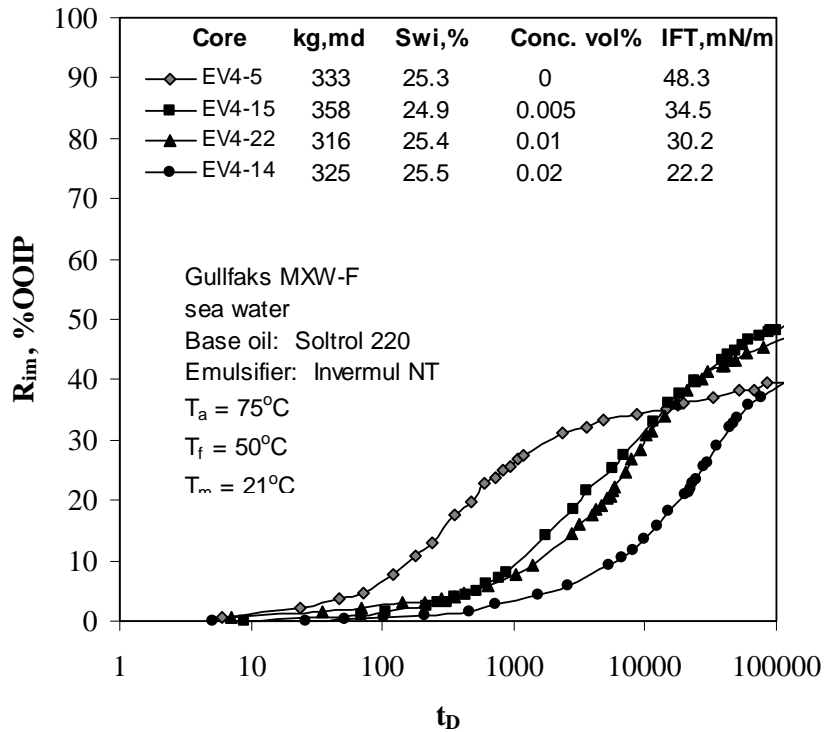


Figure 3.7.1-3. Comparison of the effects of two Group 1 surfactants: EzMul used in traditional oil-based muds and LeSupermul used in synthetic oil-based muds.

Figure 3.7.1-4 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 3.7.1-4. Increasing concentrations of EzMul and Invermul both suppress the rate of imbibition of water.

3.7.2 Summary

- Surfactants used in synthetic oil-based drilling fluids, like those in traditional oil-based muds, cause sandstone surfaces to become less water-wet.
- Increasing concentration of surfactant produced decreasing rates of water imbibition.
- For the products and oils tested, wettability alteration was greatest in cores that have been exposed previously to a crude oil.

3.8 Cleaning Cores after Contamination with Synthetic Oil-based Mud Components

(Zhang, Bell, Morrow, Buckley, and Chen)

3.8.1 Introduction

Drilling muds are used to lubricate drill bit and drill string, maintain formation pressure to prevent blowouts, and transport drilled cuttings from borehole to the surface. A great number of drilling muds have been developed to meet different drilling conditions. These drilling muds can be classified into three categories: water-based muds (WBM), oil-based muds (OBMs) that often used diesel as a base oil, and synthetic oil-based muds in which diesel is replaced by a variety of base oils that meet environmental regulations. OBMs are usually employed to replace WBMs when water sensitive shale formations are being drilled. SBMs are frequently used for drilling in environmentally sensitive areas such as the Gulf of Mexico, the North Sea and Arctic regions where use of OBMs may pose serious environmental issues. While removal of aromatic compounds decreases toxicity of the drilling mud, it can create asphaltene stability problems that do not occur with diesel-based fluids.

During the drilling process, hydrostatic pressure in the borehole often exceeds that in the penetrated formation, so that drilling fluid invades some of the pore space of recovered core. Previous investigation (Sections 3.6 and 3.7) indicated that displacement of crude oils with SBM base oils such as olefins tended to decrease the water-wet character of the tested cores even in the absence of added emulsifiers and oil-wetting surfactants. This wetting alteration was ascribed to surface precipitation of asphaltenes.

When drilling mud emulsifiers are involved, the emulsifiers can adsorb on the rock surface and further increase the oil-wetness of the tested cores. Measurements of imbibition rate as a function of emulsifier concentration showed that cores became less water-wet with increase

in emulsifier concentration (Section 3.7). The wetting change may be further aggravated when the core is brought to the surface because of the loss of light ends or the deposition and oxidation of heavy ends (Wendel et al., 1985).

Change in wettability of the recovered reservoir cores affects special core analysis including capillary pressure, relative permeability, and waterflood recovery (Anderson, 1986, Morrow, 1990), leading to unreliable reservoir evaluation and prediction of waterflood performance. One approach to using SBM contaminated cores is to clean the cores and restore to the original reservoir wetting conditions by re-exposure to reservoir fluids. The efficacy of cleaning processes has been studied for WBM and OBM-contaminated cores (e.g., Anderson, 1986; Cuiec, 1989), but studies of cleaning SBM-contaminated cores are limited (McCaffery et al., 2002).

Gant and Anderson (1988) tested many common cleaning solvents and combinations of solvents for cleaning cores contaminated with invert emulsion oil-based muds. The best results in both sandstone and carbonate cores were achieved using a Dean-Stark extraction method with either a 1:1 mixture of toluene and methanol or the same 1:1 mixture to which 1% NH_4OH was added. Cleaning was judged by USBM wettability index measurements (Donaldson et al., 1969). The authors speculate that flow-through cleaning would be even more efficient than their extraction process with the same solvents.

Hirasaki et al. (1990) tested flow-through cleaning of reservoir cores with several sequences of solvents and solvent mixtures. Whether the cores were suspected of drilling fluid contamination and what kind of drilling fluid was used in the coring program were not specified. As a result of their tests, they recommended displacing oil with toluene or chloroform, followed

by tetrahydrofuran (THF) to remove adsorbed asphaltenes and waxes. The THF can also adsorb, but is displaced along with water and salts by a final flush with methanol.

In this study, Berea sandstone cores were aged in either Gullfaks or Minnelusa crude oil to generate mixed-wet conditions. Mixed-wet cores were then exposed to a simulated SBM. For the simulated SBM, a base oil consisting of fatty acid esters that does not cause asphaltene precipitation was chosen. To that base oil were added two commercial drilling mud surfactant products, an emulsifier and a wetting agent. Wetting conditions were quantified by measurements of the rate of spontaneous imbibition and by Amott indices relating the amount of each fluid that imbibes spontaneously and the amount that can be moved in a forced displacement. In all cases, the mixed-wet cores became preferentially oil-wet upon contamination. Following SBM contamination, cores were cleaned by several techniques including a newly developed sequential strategy that incorporates strongly alkaline conditions.

3.8.2 Experimental details

Cores

Berea sandstone cores, 3.8 cm in diameter and 7.5 cm long, were used in all tests. Average core porosity was 17% and average air permeability was 75 md.

Crude oils

Two crude oils, Gullfaks (or Gullfaks-96) from the North Sea and Minnelusa-02 from Wyoming, were used to create mixed-wet conditions in the Berea sandstone cores. These two crude oils have much different asphaltene contents (properties of crude oils are summarized in Appendix II).

Brine

The aqueous solution used in the initial saturation of cores was selected to simulate the composition of sea water (SSW-Uwyo in Appendix III).

Drilling mud formulation

The simplified synthetic drilling fluid was prepared by mixing Petrofree LV with 0.37vol% Le Supermul and 0.24vol% Le Mul unless otherwise specified. The emulsifier concentrations were one-tenth of the maximum concentrations recommended for use in drilling industry. Petrofree LV is composed of fatty acid esters.

Contact angle measurements

Water-advancing and water-receding contact angles were measured with decane as the probe oil on mica surfaces after exposure of the clean mica to brine, crude oil, SBM components, and cleaning solvents, using the same fluids as those used in the core tests. Treatment and measurement techniques have been described in detail previously (Liu and Buckley, 1997, 1999).

Preparation of contaminated cores

Core samples at initial water and oil saturations were aged in either Gullfaks oil or Minnelusa oil at 75°C for 10 days. After injection of 5 PV of the synthetic drilling fluid, the cores were left in the fluid overnight at 50°C. The properties of the treated cores including Amott-Harvey wettability indices are listed in Table 3.8.2-1.

Table 3.8.2-1. Properties of the oil and SBM-treated cores

Core	kg, md	Swi, %PV	Aging oil	I _{A-H}
C4-1	63	25.2	Minnelusa	-
C4-10	75	25.8	Gullfaks	-0.33
C4-11	63	25.2	Gullfaks	-0.40
C4-14	69	25.5	Gullfaks	-0.46
C4-15	74	25.8	Minnelusa	-0.61
C4-16	74	24.6	Gullfaks	-0.32
C4-17	75	25.8	Minnelusa	-0.53
C4-19	61	25.7	no crude oil	-0.40
C4-21	75	25.4	no crude oil	-0.44

Cleaning methods

Two methods, flow through and extraction, were tested to compare their cleaning efficiency. In the flow-through method, contaminated cores were mounted in a Hassler cell and flushed at a flow rate of 3 ft/day with 10 PV of each solvent at 50°C. The direction of flow was reversed midway through the flushing process for each solvent.

In cleaning tests by the second method, a Soxhlet extraction apparatus was used to flush the cores for 24 hours with 300 ml of each solvent. Cores were inverted after 12 hours to facilitate contact of solvent throughout the length of each core. If the extracting toluene became very dark, indicating that a significant amount of material was removed by toluene, this step was repeated with fresh toluene before introducing other solvents. After cleaning, the core was allowed to dry at ambient conditions for about 5 hours, followed by drying in an oven at 110°C for 24 hours.

Sequence of cleaning solvents

For mixed-wet cores, wettability alteration to more oil-wet conditions can occur if connate water is disturbed while crude oil is in the core (Anderson, 1986). If toluene is used to remove crude oil, water is also removed because it has significant solubility in hot toluene.

Refluxing in toluene has an even greater potential for removing water because at the boiling

point of toluene (110.8°C) water is vaporized. The choice of a solvent to remove bulk crude oil is further complicated by the potential for wetting changes if asphaltenes are destabilized. In this work we selected cyclohexane, which in most cases should not precipitate asphaltenes, as the first solvent. Solubility of water is low in cyclohexane, and its boiling temperature (80.7°C) is below the boiling point of water.

Once oil is removed, the subsequent solvents, toluene, isopropanol, and 1% wt/vol NaOH dissolved in isopropanol, were chosen for their ability to dissolve asphaltenes, remove water, and to cause polar material—from either oil or SBM components—to desorb from pore surfaces. Three step treatments used cyclohexane followed by toluene, then by isopropanol. An even more rigorous cleaning was attempted using a five-step or six-step sequence including 1% wt/vol NaOH in isopropanol. Some single-step tests using the mixture recommended by Gant and Anderson (1988) of 49.5% toluene, 49.5% methanol, and 1% wt/vol NH₄OH, were included in the extraction series for comparison to the multi-step processes introduced in this work. The solvent sequence details, identified by the number of steps involved are summarized in Table 3.8.2-2. Note that the toluene step may be repeated in any of the multi-step treatments.

Table 3.8.2-2. Solvents and sequences in which they are applied in single and multi-step cleaning

Number of steps	Solvents and sequence
1	a mixture of 49.5% toluene + 49.5% MeOH + 1% wt/vol NH ₄ OH
3	c-C ₆ → toluene → IPA
5	c-C ₆ → toluene → IPA → 1% wt/vol NaOH in IPA → IPA
6	c-C ₆ → toluene → IPA → 1% NaOH in IPA → 1% wt/vol KCl in H ₂ O → MeOH

3.8.3 Results and discussion

Results of core cleaning by the various techniques described above are summarized in Table 3.8.3-1.

Table 3.8.3-1. Summary of core cleaning results

Core	Cleaning process	change in k_g (md)	I_{AH} after cleaning
C4-1	1	-15	0.66
C4-14	3	-26	-
C4-15	5	-24	0.93
C4-16	3*	-48	0.33
C4-19	1	-25	0.82
C4-21	6	-38	0.89

* Flow-through cleaning (all others were cleaned by extraction)

Three-step treatments with cyclohexane, toluene, and isopropanol

Mixed-wet cores C4-14 and C4-16 were preferentially oil-wet after exposure to SBM. Neither core imbibed any water. Figure 3.8.3-1 shows the results of the three-step cleaning procedures applied with both flow-through and Soxhlet extraction methods. The top curve in this figure is the very strongly water-wet (VSWW) reference curve obtained from a core that was treated only with brine and purified mineral oil with an initial water saturation of about 25 %. After the three-step cleaning sequence, whether applied in flow-through or extraction mode, the cores spontaneously imbibe water, indicating a return to preferentially water-wet conditions. The rate and extent of imbibition, however, are less than the VSWW reference state, suggesting the need for a more aggressive cleaning strategy for cores exposed to these surfactants. Although in this case the two application methods gave similar results, it should be noted that lower permeability cores might not be cleaned as well by extraction as by a flow-through technique.

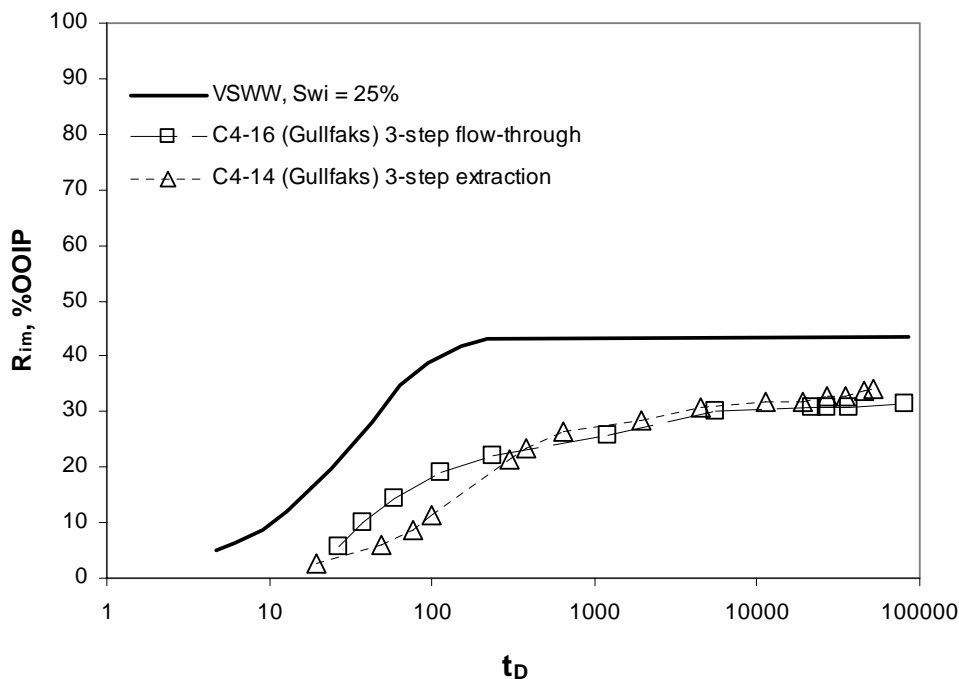


Figure 3.8.3-1. Cores cleaned by three-step solvent sequence of cyclohexane, toluene, and isopropanol are weakly water-wet. There is little difference between flow-through and extraction applications of the solvents.

Five-step treatments with cyclohexane, toluene, isopropanol, 1% NaOH in isopropanol, and isopropanol

A more rigorous cleaning procedure was tested in extraction mode with SBM contaminated core C4-15, for which the Amott index indicated the most oil-wet conditions of any of the contaminated cores. Figure 3.8.3-2 shows the results of the cleaning process both in terms of imbibition rate and Amott number. Initial imbibition of water still trails that of the strongly water-wet core, but the amount imbibed is higher and the Amott index is 0.92. Sodium hydroxide appears to play an important role in removing drilling mud contaminants. It is possible that NaOH might alter the surface chemistry of the core but previous investigation (Pashley, 1978) indicated that the effect would not be significant.

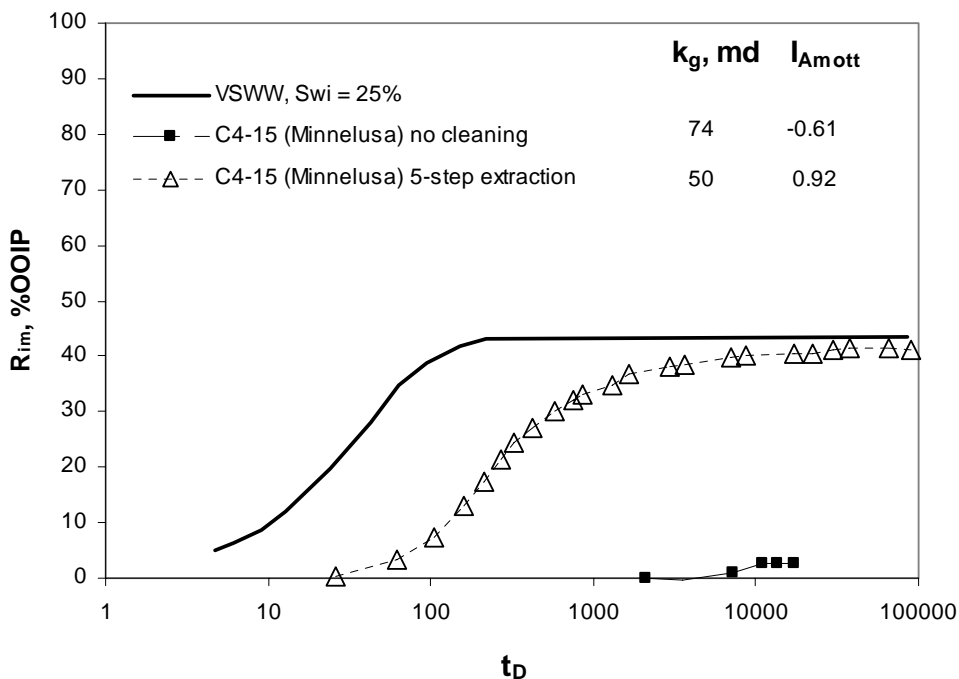


Figure 3.8.3-2. Comparison of imbibition rates before and after cleaning by the five-step extraction process.

A similar solvent sequence was used to clean mica that had been exposed to SSW, Minnelusa crude oil, and the synthetic SBM. Results are summarized in Fig. 3.8.3-3. Mica was exposed first to SSW, then to Minnelusa crude oil either at ambient conditions for 21 days or at 75°C for 10 days. After rinsing briefly with toluene, contact angles were measured with decane and water. Subsequent exposure to synthetic SBM made the wetting of the mica surfaces neutral. Soaking in cyclohexane and toluene at room temperature reduced contact angles only slightly, whereas soaking in a 1% wt/vol NaOH solution in IPA returned the surfaces to a preferentially water-wet condition.

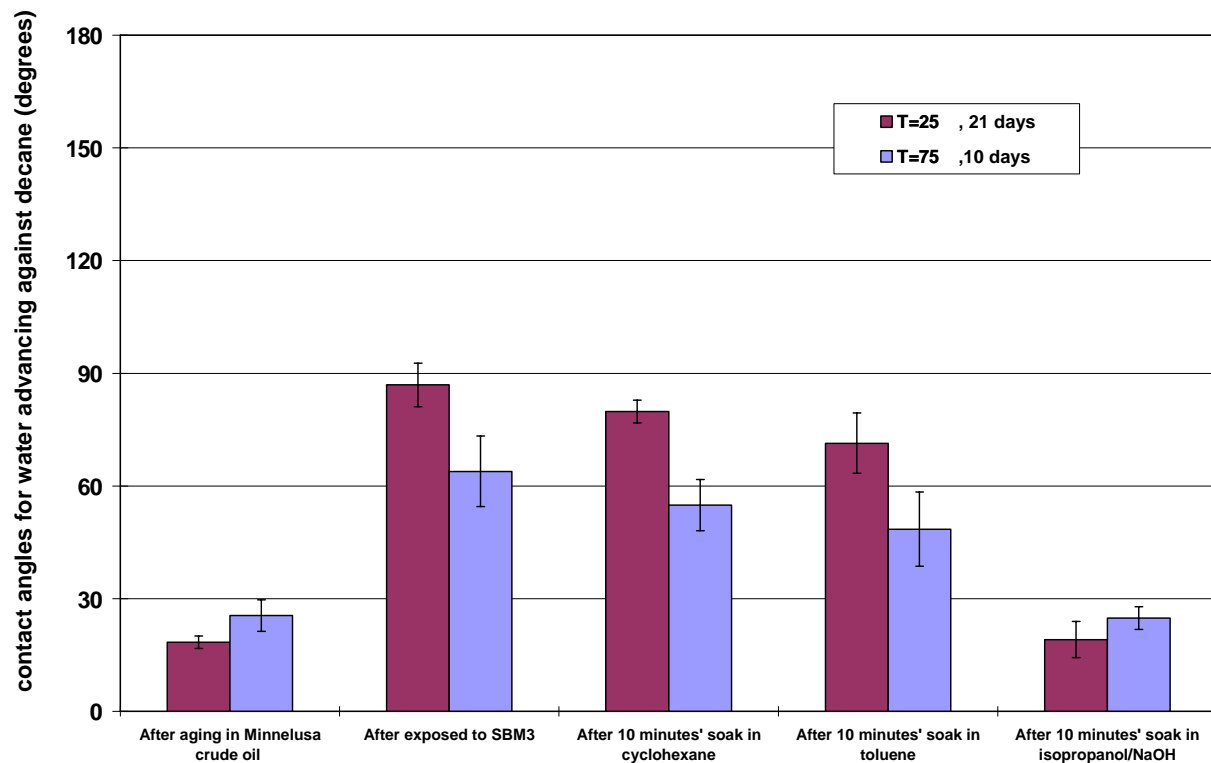


Figure 3.8.3-3. Comparison of imbibition rates before and after cleaning by the five-step extraction process.

Effect of crude oil

Effectiveness of extraction processes that included a high pH step was compared for two cores, one of which was treated with crude oil before exposure to the synthetic SBM. The other core was exposed to SBM only. The extraction processes were adapted for Core 4-21 after the 1% wt/vol NaCl in IPA step to include an aqueous flush followed by methanol because salt crystals were observed. Cleaning was effective for both cores, as indicated by Amott indices of 0.89 and 0.93, but initial rate of imbibition was faster for the core that had not been exposed to crude oil, as shown in Fig. 3.8.3-4.

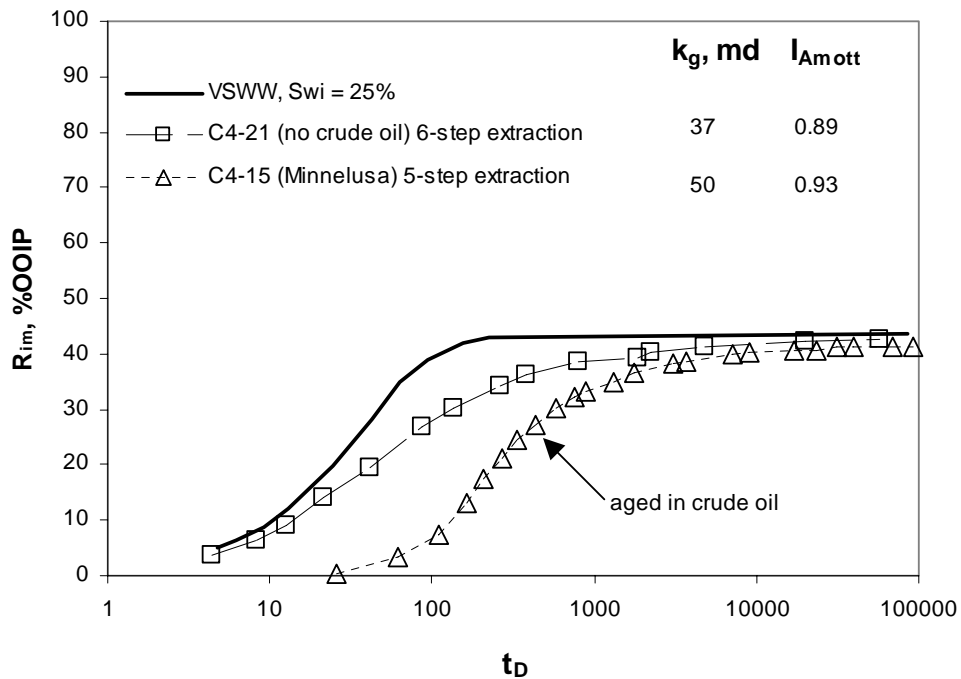


Figure 3.8.3-4. Cleaning of SBM-contaminated cores with a sequential process including a high-pH step is efficient for cores whether they were very strongly water-wet or mixed-wet before exposure to SBM.

Comparisons to single-step extraction

The chemistry of the solvents chosen for this study is similar to those recommended by Gant and Anderson (1998), but there are some significant differences in the specific choices of solvents, in their sequential method of application, and in the cleaning results obtained for SBM-contaminated cores. Figure 3.8.3-5 compares rates of imbibition and Amott indices for cleaning of SBM contaminated cores that had not been exposed to crude oil; Fig. 3.8.3-6 shows similar results for initially mixed-wet cores. In both cases, the multi-step cleaning procedure was significantly more effective than cleaning in a single-step using a mixture of solvents.

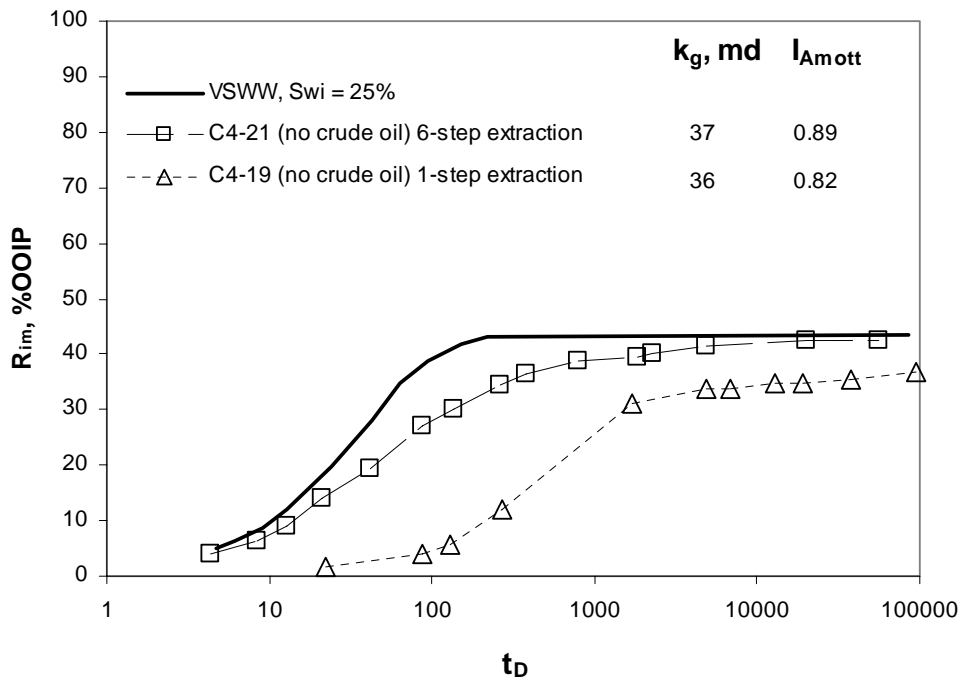


Figure 3.8.3-5. Comparison of cleaning SBM-contaminated cores by single and multi-step processes. Cores were very strongly water-wet before exposure to SBM.

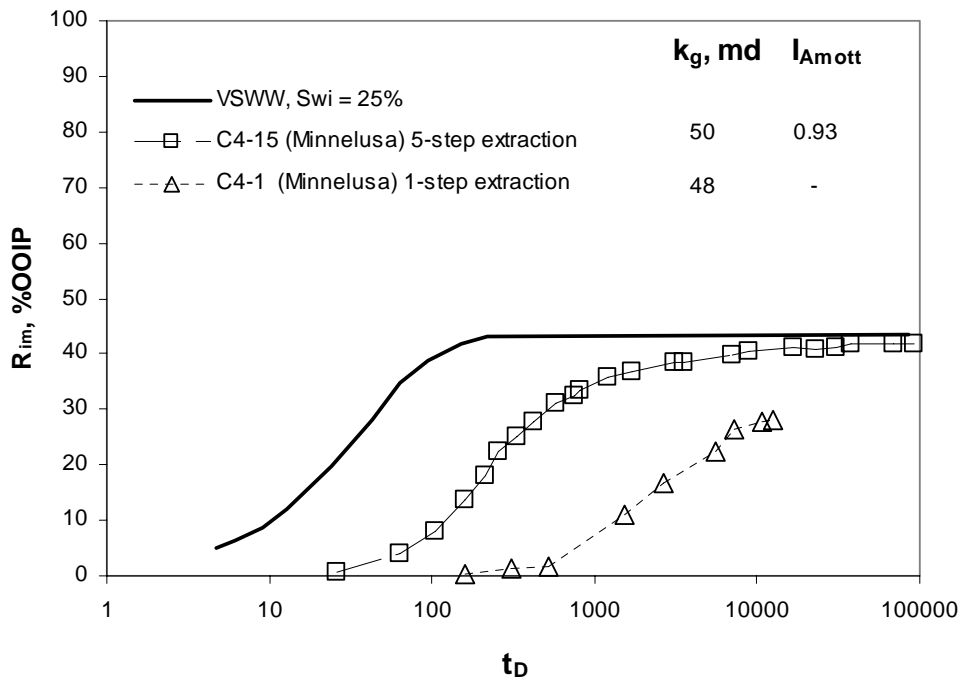


Figure 3.8.3-6. Comparison of cleaning SBM-contaminated cores by single and multi-step processes. Cores were mixed-wet before exposure to SBM.

3.8.4 Summary

- Exposure to synthetic drilling fluid changed the wettability of Berea sandstone cores from their original strongly water-wet condition to oil-wet. Adsorption of emulsifiers and wetting agents added to the synthetic base oil are the major mechanisms for the wettability alteration.
- Little difference was discerned between extractive and flow-through applications of the same solvent sequences.
- In tests with different sequences of solvents, those that included sodium hydroxide were significantly more effective in removing drilling mud contaminants.
- The new sequential core cleaning procedure including a high pH step was more effective in removing the wettability alteration materials from the rock surface than mixtures of similar materials, applied in a single step. The core cleaned with the solvent sequence that included NaOH showed very strong water-wetness, comparable to the uncontaminated cores.

4. Conclusions

In the course of this project, we have investigated a range of components of synthetic oil-based drilling fluids interacting with crude oils, brines, mica surfaces, and sandstone cores. Wetting of COBR, complicated even in undisturbed reservoir conditions, is further complicated by interactions with surface-active SBM components. A less widely recognized cause of altered wetting is asphaltene destabilization that can occur when crude oil mixes with the paraffinic and olefinic base oils that replace diesel in synthetic oil-based drilling fluids to protect sensitive environments. While this study is far from exhaustive, crude oils with a wide range of properties were tested with different emulsifier preparations and base oils so that some general observations and conclusions can be made.

Oil/water interfaces are affected by the presence of surface-active emulsifiers, as expected. However the effects with crude oils are generally less dramatic than they are when the oil-soluble emulsifiers are added to a refined oil. It can be difficult to identify contaminated crude oil samples, but IFT measurements for a range of different aqueous phase compositions have been compared to a database of oil properties. Correlations between oil properties and IFT for a standard, near-neutral brine can highlight oils that deviate from the correlation because of contamination with surface-active materials.

The most significant changes in wetting, both on mica surfaces and in sandstone cores, occurred not when emulsifiers were mixed with crude oil, but when exposure to crude oil and emulsifiers was sequential, a situation that is analogous to exposure around a wellbore. In addition, transient effects were observed in surface tests that make it difficult to design meaningful screening tests and may play a role when reservoir cores are recovered from a well drilled with oil-based fluids.

Changes in wetting occurred even without added surfactants when crude oils were displaced from a core by SBM base oils that can destabilize asphaltenes. The diesel used in older oil-based mud formulation contained aromatic compounds that can have adverse environmental effects. Those same aromatic compounds, however, are asphaltene solvents. Their removal and replacement with paraffins or olefins can destabilize asphaltenes and cause alteration of wetting to less water-wet or oil-wet conditions. Ester-based products that are used less often because of their expense do not appear to be asphaltene precipitants and do not alter wetting in cores by the asphaltene destabilization route.

Since wetting changes appear to be inevitable if cores are recovered with synthetic oil-based muds, effective cleaning methods are essential if the core is to be used for testing at wetting conditions that are relevant to the reservoir before disturbance by drilling. Core and surface tests confirmed the efficacy of sequential treatments with a series of solvents, designed to remove bulk oil before attacking adsorbed and/or deposited organic material from both crude oil and drilling mud. Wettability restoration can therefore be achieved by standard methods, although the uncertainties inherent in restored state core testing—such as whether the reservoir fluids contain the appropriate oil components, how long should cores be aged, and at what water saturation, etc.—remain to be addressed.

Nomenclature

I_w	wettability index to water;
I_o	wettability to oil;
I_{A-H}	Amott-Harvey wettability index ($= I_w - I_o$);
k	air permeability, md;
L_c	characteristic length;
R	calculated oil recovery, fraction;
R_o	final oil recovery, fraction;
S_{wi}	initial water saturation, PV%
t	imbibition time, min;
t_D	dimensionless time;
T_a	aging temperature, °C;
T_f	flooding temperature, °C;
T_m	measurement temperature, °C;
V_{oi}	oil production by spontaneous imbibition, ml;
V_{of}	oil production by forced imbibition, ml;
V_{wi}	water production by spontaneous imbibition, ml;
V_{wf}	water production by forced imbibition, ml;
α	coefficient;
ϕ	porosity, fraction;
μ_o	oil viscosity, cp;
μ_w	water viscosity, cp;
σ or γ	interfacial tension between oil and brine, mN/m;

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Appendix I. Summary of surfactant groups

Use	Class	Example / def	Comment	Typical concentration	Reference
Surfactant	terpene-derived	Barascrub	Flash point: 115 F		
Emulsifiers	fatty acids C16-C18	Omni-Tec Le Mul	HLB = 6 synthetic blend Fatty acid blend in synthetic carrier fluid	Concentration in drilling mud: 9.0-14.0 lbs/bbl-- 25.7-39.9 kg/m3 4-8 lb/bbl 6-10lb/bbl (in SBF)	
	polyaminated fatty acids	Ez Mul NTE Le Supermul Novamul	in ester carrier fluid in synthetic carrier fluid Primary emul/ with solvent blend	6-12 lb/bbl 2-4 lb/bbl 6-10lb/bbl (in SBF)	
	imidazoline	2-phenyl-2-imidazoline	thermal stability		
	amide	R-C(=O)NH ₂	thermal stability		
	polyamide	Omni-Mul	synthetic blend	8-16 lb/bbl	
		Wellguard 1252	invert mud secondary emulsifier		
		Wellguard 1252HF	invert mud secondary emulsifier for drilling fluids that require high flash point components		
		Wellguard 1252HFD	invert mud secondary emulsifier for drilling fluids that require high flash point components		
	modified polyamide	Wellguard 1764A	invert mud secondary emulsifier that can be used without primary emulsifiers		
		Wellguard 4060	invert mud secondary emulsifier for high emulsification and improved oil wettability of drilling solids		
	polyamides and modified fatty acids	Wellguard 1899	invert mud secondary emulsifier that is often used with primary emulsifiers		
		Wellguard 4042	invert mud primary emulsifier for olefin synthetic muds		
	superamides, and dtaa (diethylene triethylene), and amido-amines	alkanolamides with 18-22 C atoms	fatty acid esters (from vegetable triglycerides) transamidified to make alkanolamides with 18-22 C atoms		

Use	Class	Example / def	Comment	Typical concentration	Reference
Emulsifiers (cont.)	poly- α - olefin mud	CH ₃ -(CH ₂) _n -C ((CH ₂) _p -CH ₃) =CH-(CH ₂) _m -CH ₃		5.0 lbs/bbl --14 kgs/m ³	
	polyolefin	Omni-Coat	sulfonate blend, good at high temperature		
	sulfonated amido-amine	EMUL-II	secondary oil mud emul, blended with oil wetting agent	1 to 4ppb	
	phospholipids and amino-amines	Wellguard 4093	all-in-one invert mud emulsifier blend for high-weight muds exposed to high temperatures		
	nonionic phenol ethylene oxide	Surf-Act	liquid, high temperature	active C 60%, 25 to 100 gal of surfa per 100bbl of mud	
	oxidized natural oils	Wellguard 4	invert mud primary emulsifier and wetting agent		
		Wellguard 3088	primary emulsifier that improves oil wettability of drilling solids		
		Wellguard 4057	invert mud primary emulsifier for fluid loss control of ester synthetic muds systems		
	oxidized and modified natural oils	Wellguard 2053	invert mud primary emulsifier for fluid loss control		
	oxidized natural oils and fatty acids, modified amido-amines	Wellguard 3087	invert mud primary emulsifier for a wide range of invert drilling fluids		
oil wetting agents	fatty acids	mostly oleic and linoleic acid			
	Ca salts of ddbsa (dodecylbenzene sulfonic acid)		HLB= 4-5		
	imidazoline	Novawet		1-2 lb/bbl (in SBF)	
oil mud thinner	Fatty acid blend	Novathin		0.5-2 lb/bbl (in SBF)	
	petroleum	alkyl benzene sulfonates			
	lecithin				
	hydrocarbon resins	OFLC-400	used to reduce the filtrate and seepage losses to aid in wellbore stability for oil based invert drilling muds.	2.0 to 10.0 ppb	

Appendix II. Crude oil properties

Section 3.								Oil ID	°API	avg MW g/mole	RI@20°C RI units	P_ri	nC ₇ asph %	ρ @20°C g/ml	μ @20°C cP	Acid# mg KOH/g oil	Base #	Saturates	Aromatics	Resins	n-C ₆ Asph
1	2	4	5	6	7	8	%														
x								B-1-00	37.1	186	1.4697	1.4339	0.62	0.8361	4.7	0.04	0.85	78.8	18.2	2.5	0.5
x								C-A1-00	33.7	197	1.4816	1.4348	1.66	0.8536	10.6	0.34	3.44	68.8	12.2	16.5	2.5
	x							C-A2-00	22.7	306	1.5146	1.4368	4.34	0.9142	127.8	1.28	5.64	58.1	11.9	23.4	6.6
x								C-AG-03	40.3	141	1.4535		0.14	0.8543	1.9	0.08	0.50	82.5	12.5	4.5	0.5
x	x							C-AL-03	18.7	484	1.5288	1.4198	2.40	0.9384	661.0	1.79	4.94	53.8	18.4	25.2	2.7
		x						C-B2-01	36.3	196	1.4732	1.4260	1.31	0.8380	6.5	0.50	2.67	68.5	17.5	12.7	1.3
x								C-Br-01	48.0	148	1.4408		0.05	0.7855	1.2	0.08	0.11	74.8	24.5	0.7	0.1
x							x	C-F-03	29.5	282	1.4973	1.4403	5.96	0.8755	22.1	0.16	1.52	61.7	18.4	13.5	6.5
x								C-F2-03	27.9	335	1.4993	1.4397	1.97	0.8847	28.6	0.70	1.32	63.2	17.9	16.2	2.7
x								C-GC-T1-03	31.1		1.4875		4.56	0.8671	17.0	0.03	1.69				
x	x							C-K-01	18.9	319	1.5287	1.4320	3.46	0.9374	396.0	2.44	5.19	52.8	19.0	24.8	3.3
		x						C-L-01	34.0	216	1.4779	1.4260	1.39	0.8515	19.1	0.21	2.30	66.3	16.7	13.2	3.9
x								C-Lb-01	31.7	241	1.4858		1.60	0.8640	22.6	0.05	2.50	72.0	14.9	10.9	2.2
x	x							Cottonwood-03	26.4	262	1.5044	1.4412	2.51	0.8929	26.1	0.04	1.87	57.9	22.7	16.5	2.9
x								C-R-01	31.1	254	1.4846	1.4446	1.30	0.8674	17.8	< 0.01	0.40	70.6	15.0	12.9	1.6
x								C-T-02	34.2	214	1.4807	1.4211	1.36	0.8511	9.4	0.01	1.30	61.1	22.8	14.6	1.6
x	x							E-1XCO-01	33.8	218	1.4795	1.4163	0.65	0.8532	9.3	0.18	1.93	71.5	18.1	9.7	0.7
x								E-1XD-00	22.3	287	1.5141	1.4336	2.54	0.9165	137.4	1.56	2.98	64.1	18.5	15.3	2.2
x								E-1XFR-01	40.0	179	1.4667	1.4039	0.26	0.8223	3.7	0.16	0.65	70.6	21.5	7.6	0.3
x								E-1XO-00	21.9	264	1.5139	1.4142	0.76	0.9191	15.3	3.42	2.57	57.8	22.1	19.4	0.7
x								E-2XR-00	25.4	235	1.5040	1.4274	1.33	0.8983	47.0	0.91	2.46	65.7	18.4	14.9	1.1
x								E-8XFR-01	38.6	189	1.4676	1.4020	0.30	0.8290	4.7	1.03	0.74	70.9	19.7	9.1	0.4
x								E-BL-00	31.3	213	1.4896	1.4395	3.58	0.8651	23.4	0.17	1.33	66.3	21.2	9.5	3.0
x								E-S1XCA-01	23.2	298	1.5123	1.4626	2.08	0.9115	80.6	0.48	3.42	60.7	19.1	18.3	2.0
x								E-S1XG-01	33.3	237	1.4841	1.4681	0.54	0.8554	9.6	0.14	1.57	68.7	19.8	11.0	0.4
x								E-S1XL-01	33.5	220	1.4800	1.4088	0.42	0.8543	10.3	0.48	1.83	71.5	19.3	8.9	0.3
x								E-S3XR-01	30.0	251	1.4907	1.4238	0.92	0.8732	19.8	0.23	2.03	68.5	16.4	14.5	0.6
x								GOM(2)-00	21.2	287	1.5075	1.4504	8.63	0.9228	122.3	2.02	1.79	55.6	15.4	19.1	9.9

Section 3.								Oil ID	°API	avg MW g/mole	RI@20°C RI units	P_ri	nC ₇ asph %	ρ @20°C g/ml	μ @20°C cP	Acid# mg KOH/g oil	Base #	Saturates	Aromatics	Resins	n-C ₆ Asph
1	2	4	5	6	7	8	%														
x		x	x	x	x	x		Gulfaks-96	27.1	245	1.4930	0.0000	0.40	0.8827	15.8	0.24	1.19	63.3	25.5	10.9	0.2
x		x						LB-03	30.6	244	1.4848	1.4362	0.07	0.8699	13.1	1.57	0.59	70.1	17.6	12.0	0.3
x								Mars-P	16.5	309	1.5384	1.4262	4.77	0.9524	481.0	3.92	2.30	38.4	29.8	25.8	6.0
			x					Minnelusa	24.6	280	1.5143	1.4799	8.98	0.9030	56.0	0.17	2.29	60.1	18.9	11.3	9.7
x		x	x			x		Minnelusa-02	24.3	264	1.5138		8.75	0.9050	60.5	0.01	2.01	58.0	20.2	13.9	7.9
x								Minnelusa-03	24.5	332	1.5201		7.20	0.9039	58.1	0.12	1.71	58.5	19.8	12.7	9.1
x								MY1-02	27.0	256	1.4979		1.59	0.8898	27.7	0.50	1.17	64.0	24.6	9.7	1.7
x								MY2-02	28.8	239	1.4941		0.91	0.8798	18.3	0.17	1.16	62.5	23.7	12.7	1.1
x								MY3-02	28.0	245	1.4955		0.99	0.8842	21.7	0.20	1.17	61.9	24.8	12.2	1.1
x								MY4-02	28.1	244	1.4943		1.03	0.8835	21.6	0.22	1.23	65.3	23.7	9.9	1.1
x								P-VE-00	30.6	242	1.4885	1.4388	3.43	0.8659	16.3	0.05	1.54	66.8	17.2	11.6	4.5
x								SQ-95	37.2	213	1.4769	1.4166	1.30	0.8409	5.8	0.17	0.62	65.2	18.3	13.9	2.6
x								S-Ven-39	28.8	240	1.4976	1.4465	5.79	0.8796	29.8	0.14	1.68	51.1	28.3	14.5	6.1
x								S-Ven-40	30.2	226	1.4922	1.4492	6.08	0.8714	23.7	0.13	1.62	64.8	17.8	11.4	6.1
x	x							S-Ven-41	28.7	243	1.4985	1.4504	7.17	0.8802	33.7	0.43	1.78	60.0	18.3	14.5	7.2
x								Tensleep-99	31.1	270	1.4906	1.4428	4.10	0.8685	18.7	0.10	1.03	64.0	19.8	12.9	3.2
x								W-Br-03	32.7	251	1.4811	1.4108	0.41	0.8589	12.3	0.12	1.56	67.2	18.3	13.8	0.7
x								W-Lo-03	28.1	251	1.4964	1.4217	1.68	0.8836	17.8	0.39	0.94	61.3	20.6	16.2	1.9

Appendix III. Brine compositions

Section 3.				Buffers	Concentration (moles/L)						
1	2	3	4		NaCl	NaHCO ₃	Na Acetate	Glacial Acetic Acid	Na ₂ HPO ₄	NaH ₂ PO ₄	NaOH
	x	x	x	{pH4, 0.01M NaCl}			9.00E-03	4.10E-02			
	x			{pH4, 0.1M NaCl}	6.40E-02		3.60E-02	6.40E-02			
	x			{pH6, 0.1M NaCl}					1.23E-02	8.77E-02	
	x			{pH8, 0.1M NaCl}					4.38E-02	2.65E-03	
		x		{pH8, 1M NaCl}	8.05E-01				9.47E-02	5.30E-03	
			x	{pH10,0.1M NaCl}	6.43E-02	2.50E-02					1.07E-02

Section 3.								Unbuffered solutions	Concentration (moles/L)							
1	2	5	6	7	8	NaCl	KCl		CaCl ₂	MgCl ₂	NaHCO ₃	Na ₂ SO ₄	MgSO ₄	NaN ₃	HCl	NaOH
x								double distilled water (DDW)								varies* varies*
x							1.71E-02	0.1%NaCl								
								Reservoir brines								
	x							RB-C-B2								
	x							RB-C-K								
	x							RB-C-L								
		x					5.10E-01	RB-Minnelusa		1.90E-02		4.16E-02	7.00E-03			
								Synthetic sea water recipes								
x							4.11E-01	SSW		9.98E-03	5.23E-02		2.25E-02			
x	x						4.11E-01	SSW+HCO ₃		9.98E-03	5.23E-02	4.60E-04	2.25E-02			
		x	x	x	x		4.79E-01	SSW-Uwyo	1.25E-02	1.07E-02	5.63E-02				1.54E-03	

* add to achieve desired pH

Appendix IV. IFT measurements and fits to experimental data

oil sample	aqueous phase composition	pH	IFT (mN/m)			τ (s)	r^2
			initial measured	initial fit	final		
B-1-00	0.1M NaCl	3.1	21.5	18.5	16.6	160	0.80
B-1-00	0.1M NaCl	5.6	24.1	22.0	20.5	260	0.87
B-1-00	0.1M NaCl	6.4	24.2	22.5	20.3	160	0.85
B-1-00	0.1M NaCl	9.1	23.6	22.0	17.0	100	0.91
B-1-00	0.1M NaCl	10.8	19.1	13.0	6.9	30	0.84
B-1-00	distilled water	3.2	24.0	22.5	19.4	200	0.89
B-1-00	distilled water	5.0	23.9	22.5	20.0	250	0.88
B-1-00	distilled water	6.3	24.5	23.0	20.0	200	0.88
B-1-00	distilled water	8.9	24.8	22.5	19.7	200	0.91
B-1-00	distilled water	10.8	21.5	19.0	13.0	150	0.91
C-A1-00	distilled water	6.4	24.8	24.0	22.3	180	0.78
C-A1-00	SSW ¹	6.4	23.6	22.2	19.7	330	0.93
C-AG-03	distilled water	6.4	23.2	22.0	16.3	90	0.97
C-AG-03	SSW	6.4	20.6	20.2	16.3	75	0.92
C-AL-03	distilled water	6.4	28.2	28.5	26.0	400	0.69
C-AL-03	SSW	6.4	27.9	28.0	25.8	400	0.67
C-Br-01	0.1M NaCl	3.1	22.0	19.0	16.4	100	0.68
C-Br-01	0.1M NaCl	5.4	20.3	18.0	12.0	180	0.92
C-Br-01 ²	0.1M NaCl	6.6	18.8	16.0	9.0	300	0.97
C-Br-01 ²	0.1M NaCl	6.6	20.6	16.0	9.0	300	0.93
C-Br-01	0.1M NaCl	9.0	21.4	19.0	5.8	220	0.89
C-Br-01	0.1M NaCl	10.8	3.4				
C-Br-01	distilled water	3.2	22.3	21.0	18.0	60	0.85
C-Br-01	distilled water	5.4	22.7	21.0	17.8	100	0.88
C-Br-01	distilled water	6.4	22.8	21.0	17.5	190	0.85
C-Br-01 ²	distilled water	8.7	23.3	20.0	14.5	350	0.94
C-Br-01 ²	distilled water	8.7	22.0	20.0	12.5	600	0.93
C-Br-01 ²	distilled water	10.7	10.0		9.7		
C-Br-01 ²	distilled water	10.7	10.0		10.0		
C-F2-03	0.1M NaCl	3.2	19.2	18.0	15.5	150	0.85
C-F2-03	0.1M NaCl	5.2	19.4	18.0	14.9	130	0.88
C-F2-03	0.1M NaCl	6.3	19.8	17.0	13.2	340	0.95
C-F2-03	0.1M NaCl	9.1	17.6				
C-F2-03	0.1M NaCl	10.9	nm ³				
C-F2-03	distilled water	3.2	20.7	19.0	16.7	200	0.87
C-F2-03	distilled water	5.43	19.6	19.0	16.5	160	0.88
C-F2-03	distilled water	6.35	20.6	19.5	16.6	180	0.90
C-F2-03	distilled water	8.85	20.7	19.5	15.3	190	0.89
C-F2-03	distilled water	10.6	8		5.5		
C-GC-T1-03	distilled water	6.4	28.2	27.0	25.0	300	0.88
C-GC-T1-03	SSW	6.4	25.4	25.4	22.8	210	0.86
C-K-01	0.1M NaCl	3.2	24.4	23.0	21.0	340	0.65

oil sample	aqueous		IFT (mN/m)			τ (s)	r^2
	phase composition	pH	initial	initial	final		
			measured	fit			
C-K-01	0.1M NaCl	5.2	27.7	27.0	25.0	250	0.15
C-K-01	0.1M NaCl	6.3	29.5	28.0	24.5	320	0.51
C-K-01	0.1M NaCl	9.1	21.3				
C-K-01	0.1M NaCl	10.9	nm				
C-K-01	distilled water	3.2	29.5	29.0	26.5	250	0.56
C-K-01	distilled water	5.3	30.6	30.0	27.3	400	0.62
C-K-01	distilled water	6.5	29.8	29.0	26.0	400	0.69
C-K-01	distilled water	9.1	30.5	29.0	25.0	600	0.84
C-K-01	distilled water	10.8	7.7	7.0	3.0	60	0.93
C-Lb-01	0.1M NaCl	3.1	20.7	19.0	17.9	100	0.78
C-Lb-01	0.1M NaCl	5.4	23.6	21.5	20.0	200	0.58
C-Lb-01	0.1M NaCl	6.2	23.5	22.0	20.0	350	0.86
C-Lb-01	0.1M NaCl	8.6	22.7	22.0	14.5	350	0.90
C-Lb-01	0.1M NaCl	10.8	4.3				
C-Lb-01	distilled water	3.2	23.6	22.0	20.6	200	0.78
C-Lb-01	distilled water	5.2	23.9	23.0	21.3	180	0.76
C-Lb-01	distilled water	6.3	23.9	23.0	21.0	120	0.80
C-Lb-01	distilled water	8.9	23.5	22.0	20.5	200	0.79
C-Lb-01	distilled water	10.8	16.8	15.0	5.0	200	0.90
C-R-01	0.1M NaCl	3.1	19.6	19.0	18.2	80	0.59
C-R-01	0.1M NaCl	5.4	19.3	18.0	15.6	80	0.82
C-R-01	0.1M NaCl	6.6	17.7	17.5	13.9	220	0.93
C-R-01	0.1M NaCl	9.1	13.0	10.0	2.4	60	0.96
C-R-01	0.1M NaCl	10.9	8.2	9.0	1.5	9	0.99
C-R-01	distilled water	3.1	20.2	20.0	19.0	40	0.61
C-R-01	distilled water	5.0	20.2	20.0	18.8	40	0.63
C-R-01	distilled water	5.2	20.0	20.0	18.9	40	0.48
C-R-01	distilled water	6.5	19.6	19.0	17.2	150	0.84
C-R-01	distilled water	8.8	19.2	17.0	10.0	100	0.98
C-R-01	distilled water	10.8	12.1				
C-T-02	distilled water	6.4	32.1	31.0	28.2	270	0.85
C-T-02	SSW	6.4	29.4	29.5	26.9	250	0.87
Cottonwood-03	0.1M NaCl	3.1	21.5	21.5	20.0	100	0.89
Cottonwood-03	0.1M NaCl	5.5	23.6	23.5	22.2	100	0.54
Cottonwood-03	0.1M NaCl	6.4	24.6	24.0	21.8	100	0.68
Cottonwood-03 ²	0.1M NaCl	9.0	21.0	20.0	14.0	100	0.77
Cottonwood-03 ²	0.1M NaCl	9.0	21.0	20.0	14.8	60	0.89
Cottonwood-03	0.1M NaCl	10.8	11.9				
Cottonwood-03	distilled water	3.2	23.7	23.0	21.0	220	0.75
Cottonwood-03	distilled water	5.2	24.6	24.0	22.0	240	0.74
Cottonwood-03	distilled water	6.3	25.0	24.0	22.0	200	0.49
Cottonwood-03	distilled water	8.9	24.8	23.5	21.5	400	0.75
Cottonwood-03	distilled water	10.8	20.0	18.0	12.0	150	0.93
Cottonwood-03	RB-Minnelusa	6.4	24.4	23.5	18.5	300	0.95
E-1XCO-01	distilled water	6.4	25.6	25.5	21.6	45	0.87

oil sample	aqueous		IFT (mN/m)			τ (s)	r^2
	phase composition	pH	initial	initial	final		
			measured	fit			
E-1XCO-01	SSW	6.4	22.8	22.7	20.0	140	0.90
E-1XD-00	0.1M NaCl	3.2	22.3	21.5	19.4	60	0.52
E-1XD-00	0.1M NaCl	5.2	23.8	23.0	20.2	100	0.58
E-1XD-00	0.1M NaCl	6.4	24.2	22.5	19.8	180	0.62
E-1XD-00	0.1M NaCl	8.9	23.1	21.5	17.8	200	0.69
E-1XD-00	0.1M NaCl	10.8	nm				
E-1XD-00	distilled water	3.2	25.4	24.5	21.0	150	0.81
E-1XD-00	distilled water	5.3	24.0	22.5	20.5	190	0.75
E-1XD-00 ²	distilled water	6.4	24.3	24.5	21.0	120	0.77
E-1XD-00 ²	distilled water	6.4	24.6	25.0	21.6	130	0.73
E-1XD-00	distilled water	9.1	24.3	23.5	20.7	150	0.75
E-1XD-00	distilled water	10.7	13.5		10.3		
E-1XD-00	SSW	6.4	23.2	22.0	18.8	250	0.89
E-1XFR-01	distilled water	6.4	20.5	20.0	17.3	130	0.78
E-1XFR-01	SSW	6.4	18.3	18.1	9.5	200	0.98
E-1XO-00	0.1M NaCl	3.1	18.5	16.0	12.2	100	0.81
E-1XO-00	0.1M NaCl	5.2	19.1	17.0	13.0	250	0.89
E-1XO-00	0.1M NaCl	6.6	20.1	17.0	13.0	250	0.89
E-1XO-00	0.1M NaCl	8.9	18.1	17.0	12.5	200	0.93
E-1XO-00	0.1M NaCl	10.9	nm				
E-1XO-00	distilled water	3.1	20.0	18.0	13.4	220	0.89
E-1XO-00	distilled water	5.0	19.9	17.0	13.4	250	0.89
E-1XO-00	distilled water	5.2	19.5	17.0	13.4	150	0.85
E-1XO-00	distilled water	6.4	18.6	18.5	14.7	300	0.92
E-1XO-00	distilled water	6.5	19.8	17.0	13.4	250	0.91
E-1XO-00	distilled water	8.0	17.6	16.0	12.5	200	0.87
E-1XO-00	distilled water	8.8	18.8	16.5	12.5	250	0.90
E-1XO-00	distilled water	10.8	nm				
E-1XO-00	SSW	6.4	13.5	16.9	12.8	200	0.89
E-2XR-00	distilled water	6.4	21.8	23.5	20.4	80	0.61
E-2XR-00	SSW	6.4	22.0	21.8	18.3	190	0.91
E-8XFR-01	distilled water	6.4	19.4	18.5	16.4	120	0.82
E-8XFR-01	SSW	6.4	17.4	16.2	8.6	300	0.97
E-BL-00	distilled water	6.4	21.4	21.3	19.8	80	0.47
E-BL-00	SSW	6.4	21.2	20.7	19.0	130	0.73
E-S1XCA-01	distilled water	6.4	20.1	20.5	18.0	200	0.74
E-S1XCA-01	SSW	6.4	17.8	17.5	13.8	100	0.73
E-S1XG-01	distilled water	6.4	27.1	28.0	20.0	270	0.97
E-S1XG-01	SSW	6.4	24.7	24.9	19.6	245	0.95
E-S1XL-01	distilled water	6.4	24.0	23.0	20.8	120	0.69
E-S1XL-01	SSW	6.4	21.2	20.7	18.3	250	0.93
E-S3XR-01	distilled water	6.4	24.0	23.0	20.0	225	0.81
E-S3XR-01	SSW	6.4	22.1	21.6	18.8	120	0.83
GOM(2)-00	0.1M NaCl	3.2	24.6	23.5	22.8	250	0.18
GOM(2)-00	0.1M NaCl	5.2	27.6	27.5	26.5	200	0.03

oil sample	aqueous		IFT (mN/m)			τ (s)	r^2
	phase composition	pH	initial	initial	final		
			measured	fit			
GOM(2)-00	0.1M NaCl	6.3	27.3	26.5	25.9	150	0.00
GOM(2)-00	0.1M NaCl	8.8	24.3	24.0	21.6	150	0.26
GOM(2)-00	0.1M NaCl	10.9	11.2				
GOM(2)-00	distilled water	3.2	27.0	26.5	25.3	100	0.33
GOM(2)-00	distilled water	5.4	27.5	26.5	26.0	250	0.13
GOM(2)-00	distilled water	6.4	27.5	26.5	25.0	1000	0.43
GOM(2)-00	distilled water	9.1	27.1	26.0	25.0	250	0.02
GOM(2)-00	distilled water	10.7	15.0		20.0		
Gulfaks-96	distilled water	6.4	23.4	22.0	19.8	200	0.82
Gulfaks-96	RB-Minnelusa	6.4	21.2	19.4	9.1	230	0.95
Gulfaks-96	SSW-HCO ₃ ⁴	7.8	20.0	18.2	3.5	60	0.96
LB-03	0.1M NaCl	3.2	21.4	19.5	15.5	150	0.90
LB-03	0.1M NaCl	5.2	21.4	19.5	15.5	150	0.93
LB-03	0.1M NaCl	6.4	21.7	19.5	15.3	150	0.93
LB-03	0.1M NaCl	8.9	21.6	19.5	14.8	150	0.94
LB-03	0.1M NaCl	11.0	nm				
LB-03	distilled water	3.4	22.2	19.5	16.2	330	0.94
LB-03	distilled water	5.1	22.0	19.5	16.0	330	0.94
LB-03	distilled water	6.5	21.8	19.5	16.0	300	0.95
LB-03	distilled water	9.1	22.7	19.0	15.0	250	0.95
LB-03	distilled water	10.8					0.00
LB-03	SSW	6.4	21.4	20.7	15.8	150	0.97
Mars-P	0.1M NaCl	3.2	22.1	23.0	21.0	50	0.01
Mars-P	0.1M NaCl	5.2	23.2	23.0	20.7	100	0.27
Mars-P	0.1M NaCl	6.4	19.4	22.0	20.0	250	0.19
Mars-P	0.1M NaCl	8.8	17.5	21.5	18.0	200	0.51
Mars-P	0.1M NaCl	10.9	nm				
Mars-P	distilled water	3.2	22.8	22.5	21.5	300	0.24
Mars-P	distilled water	5.1	26.1	25.0	23.4	300	0.47
Mars-P	distilled water	6.2	25.6	25.0	23.2	150	0.42
Mars-P	distilled water	9.1	24.8	24.5	22.4	300	0.38
Mars-P	distilled water	10.8	4.3	4.5	0.9	25	0.99
Minnelusa-02	0.1M NaCl	3.1	24.0	23.8	22.0	100	0.55
Minnelusa-02	0.1M NaCl	5.2	28.5	28.0	26.0	100	0.16
Minnelusa-02	0.1M NaCl	6.4	25.9	26.0	24.5	100	0.18
Minnelusa-02	0.1M NaCl	8.9	22.5	23.0	22.0	100	0.11
Minnelusa-02	0.1M NaCl	10.7	20.7	20.0	12.5	20	0.83
Minnelusa-02	distilled water	3.2	24.9	24.0	22.8	100	0.37
Minnelusa-02	distilled water	5.0	24.2	23.5	22.7	100	0.36
Minnelusa-02	distilled water	6.4	22.2	24.0	23.0	100	0.09
Minnelusa-02	distilled water	9.0	25.0	24.5	22.8	100	0.54
Minnelusa-02	distilled water	10.7	20.0		17.5		
Minnelusa-03	distilled water	6.4	29.9	29.0	27.0	500	0.87
Minnelusa-03	RB-Minnelusa	6.4	28.5	28.0	26.4	300	0.56
Minnelusa-03	SSW	6.4	27.2	26.7	25.3	500	0.52

oil sample	aqueous		IFT (mN/m)			τ (s)	r^2
	phase composition	pH	initial	initial	final		
			measured	fit			
MY1-02	0.1M NaCl	3.2	16.3	15.1	13.6	110	0.85
MY1-02	0.1M NaCl	5.0	15.0	13.6	8.3	100	0.77
MY1-02	0.1M NaCl	6.0	13.7	11.7	5.4	400	0.97
MY1-02	0.1M NaCl	9.0	13.3	11.7	2.5	100	0.99
MY1-02	0.1M NaCl	10.7	nm				
MY1-02	distilled water	3.2	19.3	18.0	16.2	150	0.87
MY1-02	distilled water	5.4	18.2	17.5	16.0	100	0.73
MY1-02	distilled water	6.4	18.7	17.0	15.1	320	0.90
MY1-02	distilled water	8.8	18.0	16.0	8.0	400	0.96
MY1-02	distilled water	10.8	nm				
MY1-02	SSW	6.4	8.8	7.5	2.4	220	0.97
MY2-02	0.1M NaCl	3.2	21.9	20.9	17.9	350	0.90
MY2-02	0.1M NaCl	5.0	20.9	19.5	15.8	300	0.91
MY2-02	0.1M NaCl	6.4	21.0	20.0	14.5	300	0.91
MY2-02	0.1M NaCl	8.7	19.9	18.5	7.4	500	0.98
MY2-02	0.1M NaCl	10.7	nm				
MY2-02	distilled water	3.2	23.7	22.0	19.0	250	0.85
MY2-02	distilled water	5.4	24.1	23.0	19.4	300	0.88
MY2-02	distilled water	6.4	24.0	22.0	19.4	250	0.86
MY2-02	distilled water	8.8	23.3	22.0	16.0	500	0.96
MY2-02	distilled water	10.8	nm				
MY2-02	SSW	6.4	21.5	20.5	13.0	300	0.94
MY3-02	0.1M NaCl	3.2	23.8	22.4	19.7	190	0.80
MY3-02	0.1M NaCl	5.0	23.4	20.9	17.5	250	0.88
MY3-02 ²	0.1M NaCl	6.1	22.1	20.4	15.6	300	0.91
MY3-02 ²	0.1M NaCl	6.1	22.8	20.0	15.6	400	0.79
MY3-02	0.1M NaCl	8.8	22.7	19.0	9.5	550	0.97
MY3-02	0.1M NaCl	10.7	nm				
MY3-02	distilled water	3.2	25.2	23.5	21.0	300	0.89
MY3-02	distilled water	5.4	24.4	23.5	20.5	200	0.78
MY3-02	distilled water	6.4	24.4	24.5	21.0	130	0.78
MY3-02	distilled water	8.7	24.7	23.0	16.6	500	0.98
MY3-02	distilled water	10.7	nm				
MY3-02	SSW	6.4	21.9	20.5	14.3	350	0.96
MY4-02	0.1M NaCl	3.2	22.6	20.4	17.6	300	0.88
MY4-02	0.1M NaCl	5.0	20.6	19.0	14.5	250	0.92
MY4-02 ²	0.1M NaCl	6.0	20.4	18.5	12.7	450	0.94
MY4-02 ²	0.1M NaCl	6.0	19.8	18.5	12.8	500	0.95
MY4-02	0.1M NaCl	9.0	20.4	17.5	6.2	350	0.99
MY4-02	0.1M NaCl	10.8	nm				
MY4-02	distilled water	3.2	24.4	23.0	20.0	300	0.89
MY4-02	distilled water	5.4	26.7	24.0	20.7	300	0.89
MY4-02 ²	distilled water	6.4	25.4	23.5	20.0	400	0.91
MY4-02 ²	distilled water	6.4	25.9	23.5	20.0	350	0.87
MY4-02	distilled water	9.1	25.2	23.0	16.0	400	0.96

oil sample	aqueous		IFT (mN/m)			τ (s)	r^2
	phase composition	pH	initial	initial	final		
			measured	fit			
MY4-02	distilled water	9.2	25.4	23.0	17.5	350	0.91
MY4-02	distilled water	10.7	nm				
MY4-02	SSW	6.4	21.5	20.0	13.0	300	0.96
P-VE-00	0.1M NaCl	3.1	16.1	17.5	16.4	120	0.79
P-VE-00	0.1M NaCl	5.2	23.3	22.5	21.0	100	0.54
P-VE-00	0.1M NaCl	6.4	23.8	23.0	20.8	150	0.71
P-VE-00	0.1M NaCl	8.9	19.0				
P-VE-00	0.1M NaCl	10.7	20.3	18.0	8.0	50	0.87
P-VE-00	distilled water	3.2	23.2	22.5	20.5	100	0.83
P-VE-00	distilled water	5.1	24.6	23.5	21.7	200	0.83
P-VE-00	distilled water	6.4	24.8	23.5	21.6	320	0.90
P-VE-00	distilled water	9.0	24.5	24.0	20.7	200	0.97
P-VE-00	distilled water	10.7	22.4	20.0	13.5	190	0.90
S-Ven-39	distilled water	6.4	20.8	22.5	20.6	200	0.63
S-Ven-39	SSW	6.4	20.7	20.6	18.2	400	0.87
S-Ven-40	distilled water	6.4	23.4	23.0	21.2	350	0.76
S-Ven-40	SSW	6.4	21.6	22.1	18.3	600	0.92
S-Ven-41	distilled water	6.4	24.6	22.5	20.6	250	0.75
S-Ven-41	SSW	6.4	20.5	21.6	18.8	500	0.79
S-Ven-41	SSW-HCO ₃	7.8	13.3	19.7	9.9	300	0.96
SQ-95	distilled water	3.2	23.8	23.5	22.0	120	0.60
SQ-95	distilled water	5.2	24.4	23.5	22.0	120	0.62
SQ-95	distilled water	6.5	24.3	23.0	20.0	120	0.62
SQ-95	distilled water	8.0	24.6	23.5	22.0	150	0.76
SQ-95	distilled water	9.0	24.0	23.0	12.0	160	0.97
SQ-95	distilled water	10.3	16.4	16.0	5.8	19	0.98
SQ-95	distilled water	10.9	8.0				
Tensleep-99	distilled water	3.5	21.0	19.5	15.5	330	0.98
Tensleep-99	distilled water	5.2	20.3	19.0	15.5	300	0.97
Tensleep-99	distilled water	6.5	20.5	19.0	15.0	280	0.96
Tensleep-99	distilled water	9.0	20.7	18.0	11.5	160	0.96
Tensleep-99	distilled water	11.0	15.5				
W-Br-03	distilled water	6.4	24.3	24.5	23.0	80	0.40
W-Br-03	SSW	6.4	17.6	23.8	20.0	350	0.90
W-Br-03	SSW-HCO ₃	7.8	20.9	22.8	11.4	300	0.98
W-Lo-03	distilled water	6.4	19.8	21.5	19.7	120	0.76

¹ SSW = synthetic sea water (see Table 1)

² duplicate measurements

³ nm = not measureable

⁴ SSW-HCO₃ = synthetic sea water recipe with sodium bicarbonate (see Table 1)