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

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Principal Investigator:
Jill S. Buckley PRRC, New Mexico Institute of Mining and Technology
Co-Investigator:
Norman R. Morrow Dept. of Chemical & Petroleum Eng., University of Wyoming

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New Mexico Petroleum Recovery Research Center
New Mexico Institute of Mining and Technology
801 Leroy Place
Socorro NM 87801

Department of Chemical and Petroleum Engineering
University of Wyoming
P.O. Box 3295
Laramie, WY 82071-3295

Disclaimer

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

In this report we focus on surface studies of the wetting effects of SBM components; three areas of research are covered. First we present results of tests of interfacial properties of some commercial emulsifiers that are routinely used in both oil-based and synthetic oil-based drilling fluids. These products fall into two main groups, based on their CMC and IFT trends with changing pH. All can alter the wetting of mica, but measurements vary widely depending on the details of exposure and observation protocols. Non-equilibrium effects appear to be responsible for these variations, with equilibrated fluids generally giving lower contact angles than those observed with fluids that have not been pre-equilibrated. Addition of small amounts of emulsifier can increase the tendency of a crude oil to alter wetting of mica surfaces. The effects of similar amounts of these emulsifiers can be detected in interfacial tension measurements.

Next, we report on the preliminary results of a study of polyethoxylated amines of varying structures on the wetting of mica surfaces. Contact angles have been measured for unequilibrated and pre-equilibrated fluids. Reduction in contact angles was generally observed when the surfaces were washed with toluene after exposure to surfactant solutions. Atomic forces microscopy is also being used to observe the interactions between these surfactants and mica surfaces. Finally, we show the results of a study of asphaltene stability in the presence of synthetic base oils. Most of the base oils in current use are paraffinic or olefinic—the aromatic content is minimized for environmental reasons—and they destabilize asphaltenes. Tests with two crude oils show onset conditions for base oils that are comparable to n-heptane and n-pentadecane in terms of the solubility conditions at the onset. Two ester –based products, Petrofree and Petrofree LV, did not cause asphaltene flocculation in these tests.

A meeting of the research groups from New Mexico Tech and the University of Wyoming, was held in Laramie on the 9th and 10th of October. All the members of the research teams presented updates on their progress and exchanged views on directions for the remainder of the project.

Table of Contents

List of Figures

List of Tables

Update on Surface Tests of Synthetic Oil-Based Mud Components

Jill S. Buckley,[1] Laila Skalli,[1] Elizabeth Bryant,[2] Jianxin Wang,[1] and Rob Bowman[2]

[1]PRRC, New Mexico Tech
[2]Hydrology Program, Earth &Env. Sci. Dept., New Mexico Tech

1. Introduction

A study with filtrates of synthetic oil-based muds indicated that these products affect the wetting of mineral surfaces, as expected. How they change wetting depends on the condition of the surface (wet or dry, clean or exposed to crude oil, etc.) as reported previously (Lekkala and Buckley, 2002).

Synthetic oil-based muds can influence the wetting of mineral surfaces with which they come in contact in at least two different ways. The first is the effect of surfactants that are added to the mud to maintain stability of water-in-oil emulsions and to ensure that cuttings are oil-wet. These surfactants are common to the oil-based muds that have been studied in the past as well as to the newer synthetic fluids. In this report we present results of wetting studies of some commercially-available surfactants that are used in SBMs. We have also selected some oil-soluble polyethoxylated amines of known chemical structures for studies of their effects on the wetting of mica surfaces.

A second effect of some of the synthetic oil-based mud (SBM) products is their influence upon asphaltene stability. Traditional oil-based drilling fluids had base oils such as diesel that include aromatics as well as paraffinic components. For environmental reasons, it has been necessary to eliminate the aromatic compounds from base oils used in environmentally sensitive areas. Instead, SBMs use mineral oils from which aromatics have been removed and synthetic products including olefins and esters. Paraffinic mineral oils are known to be asphaltene precipitants; less is known about the effects of olefins and esters. Asphaltene stability has been tested in the presence of SBM base oils; preliminary results are included in this report.

The results reported here are being used to guide more detailed studies in porous media, which will be the subject of our next report.

2. Experimental Materials and Methods

2.1 Materials

2.1.1 Mica

Mica is used as the reference surface to represent silicate minerals. Samples of Muscovite mica were obtained from S&J Trading Inc. in Glen Oaks, NY. Sheets can be cut with scissors to convenient size samples for various applications. Clean surfaces are prepared by using adhesive tape to remove the upper and lower outermost layers.

2.1.2 Brines

Brines are buffered using acetic acid/sodium acetate (pH 4) and sodium phosphate/sodium biphosphate (pH 6 and 8). Buffer strength is 0.01 mol/L. NaCl is added to the buffers to increase ionic strength, as required.

2.1.3 Base oils

Samples of 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 1. Experts were consulted to determine which materials would be representative of different classes of base oils that are in widespread use.

Table 1. Base oils for synthetic oil-based drilling fluids tested.

Product designation	RI at 20°C	Supplied by	Description (if available)
Accolade	1.4424	Westport	
Biobase 240 (C-14)	1.4359	ChevronTexaco	linear alpha olefin
Biobase 560 (LP)	1.4278	ChevronTexaco	linear paraffin
EDC 99DW	1.4463	M-I	highly hydrogenated mineral oil
GOM 4 comp blend - IO	1.4436	ChevronTexaco	internal olefins
LVT mineral oil	1.4503	Halliburton	mineral oil
Petrofree	1.4420	ChevronTexaco	ester
Petrofree LV	1.4354	ChevronTexaco	ester
Petrofree SF	1.4448	Halliburton	probably olefin
SF Base	1.4445	ChevronTexaco	isomerized olefins
XP-07	1.4286	ChevronTexaco	linear paraffin

2.1.4 Crude oil samples

Properties of crude oils used in this project are summarized in Table 2.

Table 2. Crude oil properties.

Oil ID	°API	MW (g/mol)	RI at 20°C	P_ri	ρ at 20°C	μ at 20°C (cP)	Acid #	Base #	IEP (pH units)	Sat (%)	Arom (%)	Resin (%)	n-C$_6$ asph (%)	n-C$_7$ asph (%)
							(mg KOH/g oil)							
C-AL-03	18.7	484	1.5288	nm	0.9384	661.5	1.79	4.94	5.2	53.80	18.40	25.20	2.70	2.40
C-F-03	29.5	282	1.4973	1.4560	0.8755	22.1	0.16	1.52	3.9	61.67	18.40	13.47	6.47	5.96
Cottonwood-03	26.4	262	1.5044	nm	0.8929	26.1	0.04	1.87	3.6	57.87	22.68	16.54	2.90	nm
LB-03	30.6	244	1.4848	nm	0.8699	13.1	1.57	0.59	4.2	70.13	17.58	12.00	0.29	0.07
Minnelusa-99	24.6	280	1.5143	1.4768	0.9030	56.0	0.17	2.29	4	60.06	18.93	11.27	9.74	8.98

nm = not measured

2.1.5 Commercial SBM surfactants

Product supplied for testing are listed in Table 3.

Table 3. 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
Surfazol 1202A	Lubrizol	W/O emulsifier	polyolefin amide alkeneamine

Depending on the application, recommended amounts range from 1 to 20 pounds per barrel are suggested, 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.

2.1.6 Polyethoxylated amines

Finding pure surfactants of known structure with significant oil solubility is a challenge. Quaternary amines remain water soluble even at high molecular weights because of the fixed positive charge. Other compounds are available only as mixtures. Table 4 lists some of the surfactant structures considered for this project.

Table 4. Surfactants tested.

Name	Formula	Source	MW	Soluble in decane?
Sodium dodecyl sulfate (SDS)	$C_{12}H_{25}SO_4Na$	Fluka	288.4	no
Cetyltrimethylammonium bromide (CTAB)	$CH_3(CH_2)_{15}N(Br)(CH_3)_3$	Aldrich	364.5	no
Docosanoic acid	$CH_3\ (CH_2)_{20}\ COOH$	Aldrich	340.6	yes
CAM-2	see Fig. 1	Ethox	273.5	yes
TAM-2	see Fig. 1	Ethox	355.6	yes
TAM-5	see Fig. 1	Ethox	487.8	yes

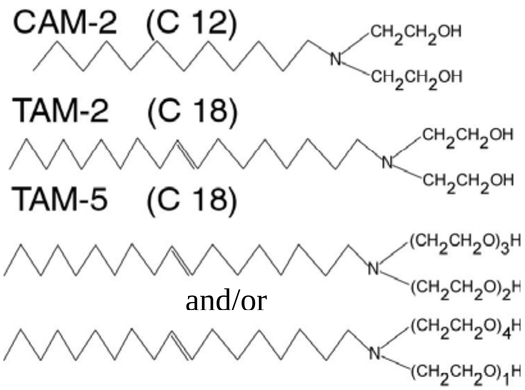


Figure 1. Structures of the polyethoxylated amines.

2.2 Methods

2.2.1 Asphaltene stability

Asphaltene stablility is assessed by titrations with a series of liquid normal alkanes to find the onset of instability for each alkane precipitant. Solubility conditions in the oil and onset mixtures are assessed by measurements of refractive index. Tests of asphaltene stability have been described in detail in PRRC 01-18.

2.2.2 Interfacial measurements

Measurements of surface and interfacial tension (IFT) have been made by two standard techniques: duNouy ring and pendant drop (Adamson and Gast, 1997). The duNouy ring was used with a Cahn balance (DCA-312). The pendant drop technique (DataPhysics OCA20+SCA20) was used to observe changes in IFT over times up to 24 hours.

2.2.3 Contact angles

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

2.2.4 AFM

A Nanoscope 3a from Veeco Metrology was used to obtain tapping and contact mode images of mica surfaces after exposure to surfactant solutions. Details of use of a similar instrument in contact mode have been published previously (Lord and Buckley, 2002).

3. Results and Discussion

3.1 Commercial surfactant packages

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 (PRRC 02-24).

3.1.1 Interfacial tension and CMC

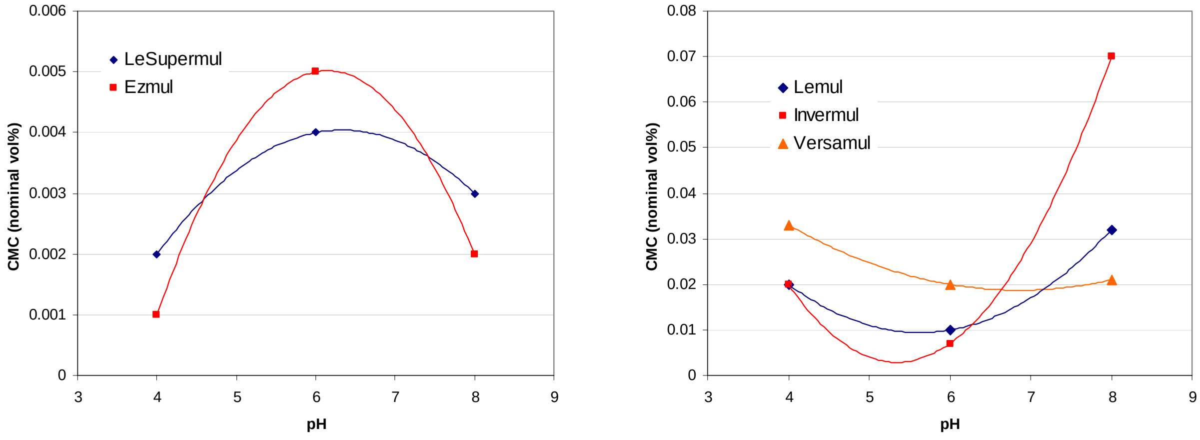
An important property of surfactants that can form micelles is the concentration at which micelles begin to be the dominant form of surfactant in the solution. This is known as the critical micelle concentration or CMC; below this concentration surfactants mainly exist as monomers, above it they are in aggregates known as micelles. One of the measures of this concentration is a break in the slope of interfacial or 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 single-component surfactants, this concentation is well defined. In the case of surfactant mixtures, mixed micelles can form and there may not be a single value of CMC. Nevertheless, it is helpful to measure the interfacial tension as a function of surfactant concentration to determine concentrations at which the slope of the IFT vs ln C curve changes.

Mixtures of 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 percentage of the product that is surface active. Concentrations may also vary from one sample to another. For this reason and because these are mixtures of surfactants, the “CMC” is not well defined. Nevertheless, we will refer to this effective value of CMC as the CMC in this report.

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 5, together with the IFT values at the inflection points. Two different trends were found for the five products tested. In the first group (Fig. 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. 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 maximum. The surfactant packages in this group are mixtures of polyaminated fatty acids and oxidized tall oil. Although these products 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 5. Effective CMC and IFT at CMC for commercial surfactants—effect of pH

	Brine {4, 0.1}		**Brine {6, 0.1}**		**Brine {8, 0.1}**	
Emulsifier	**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
Surfazol 1202A	0.02	0.185	0.02	0.959	0.15	0.838

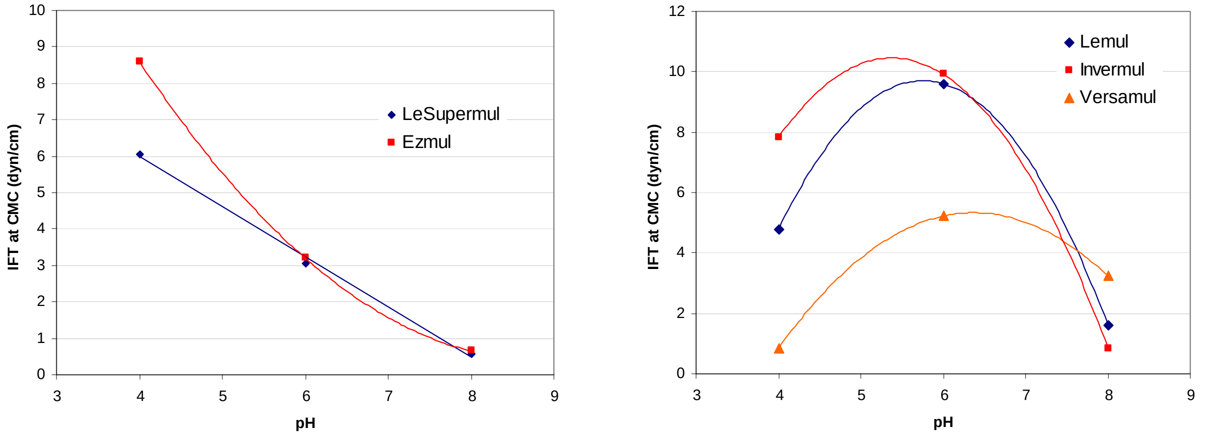


(a) Group 1 emulsifiers

(b) Group 2 emulsifiers

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

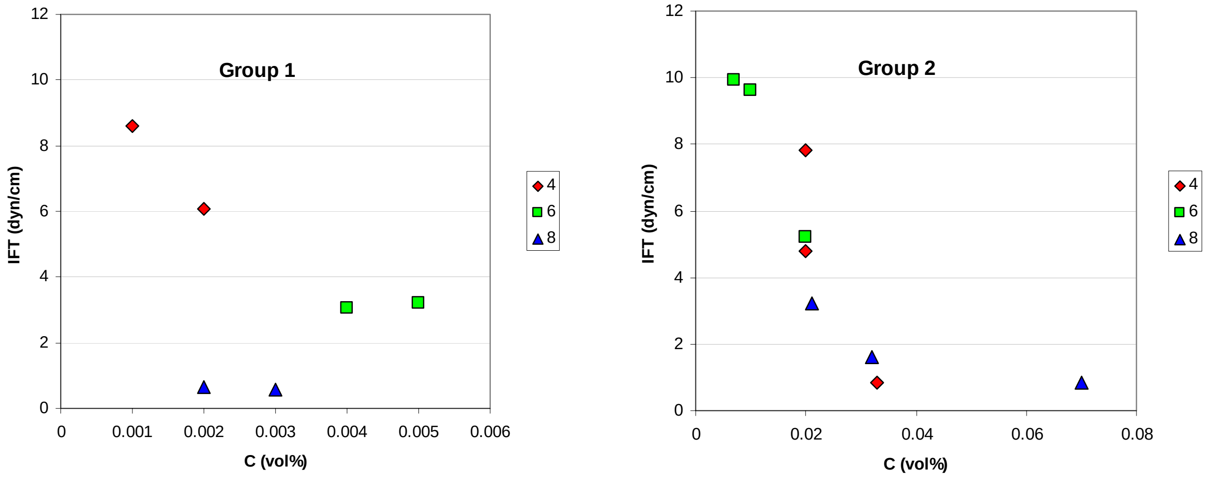
It is also of interest to compare the IFT values measured at these CMC conditions for each of these products. These are shown as a function of pH in Fig. 3. Again the data fall into the same two groups. For Group 1 (Fig. 3a), IFT at CMC is a monotonically decreasing function of pH. Results for the two 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. 3b).



(a) IFT at CMC – Group 1 (b) IFT at CMC – Group 2

Figure 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. 4), using the data plotted in Figs. 2 and 3 above. For Group 2 (Fig. 4b), IFT appears to be generally a function of concentration whereas for Group 1 (Fig. 4a), there appears to be a tendency toward lower IFT at pH 8, regardless of concentration.

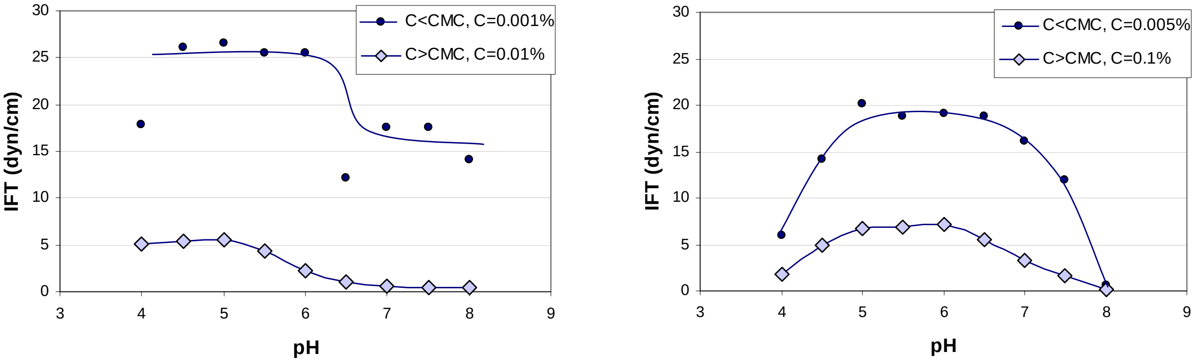


(a) IFT vs. concentration – Group 1 (b) IFT vs. concentration – Group 2

Figure 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. 5). The Group 1 surfactant, Le

Supermul, was tested at 0.001 and 0.01 vol% (Fig. 5a). At the lower 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. 5b).



(a) IFT vs. pH – Group 1 (Le Supermul) (b) IFT vs. pH – Group 2 (Invermul)

Figure 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).

3.1.2 Contact angles – without crude oil

The effects of the emulsifiers at a modest concentration, nominally 0.03 vol% in decane, on wetting of clean mica is shown in Fig. 6. 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. All of the products promoted neutral to oil-wet conditions.

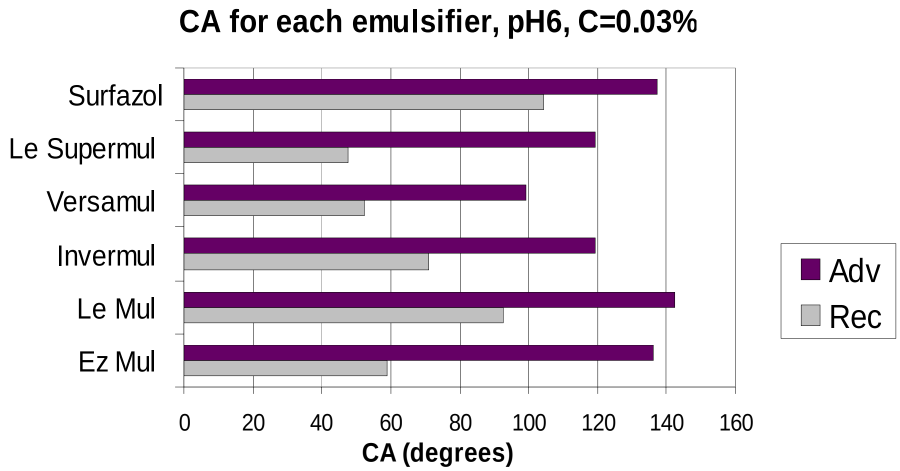


Figure 6. Comparison of the contact angles on clean mica surfaces exposed for 1 hr to emulsifier solutions, 0.03% by volume of product. The probe water drop is {pH 6, 0.1M} buffer. The contact time between the water drop and mica surface is 2 min.

It is not entirely clear how contact angles should be measured in these systems. The results in Fig. 6 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 above, each aqueous drop was formed and immediately contacted with the mica surface where it was allowed to rest for two minutes. Fig. 7 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. 7.

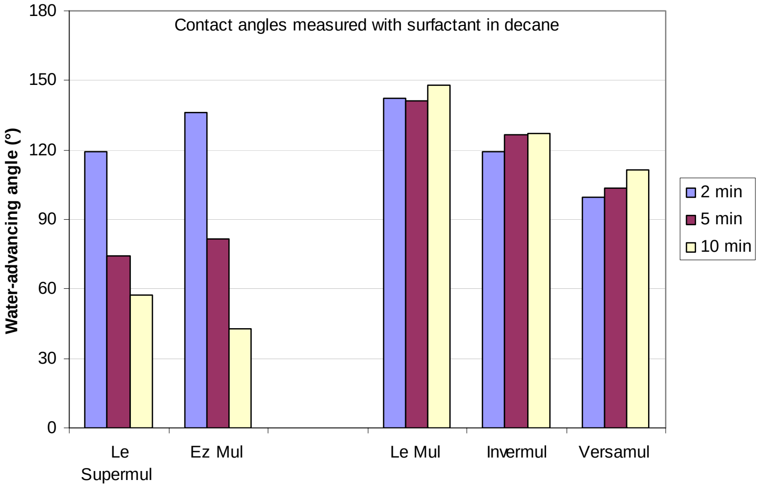


Figure 7. Water-advancing contact angles on mica exposed to surfactant solutions for 1 hr. Contact angles were measured with a drop of {pH 6, 0.1M} buffer in decane solutions of each surfactant (0.03 vol%). Results are shown for contact times of 2, 5, and 10 minutes, during which the advanced aqueous drop remained stationary on the mica surface are shown.

Another question that must be addressed is the persistence of these wetting changes. Surfactant-exposed mica, analogous to the samples in Fig. 7 above, were moved to fresh decane where the contact angles were measured with no surfactant except that which remains adsorbed to the mica surface. Figure 8 shows that water-advancing contact angles are substantially lower under these conditions, ranging from water-wet (about 30°) to neutral wetting (about 100°). In most cases, the contact angles were reduced suggesting that some of the surfactant desorbs into the fresh decane.

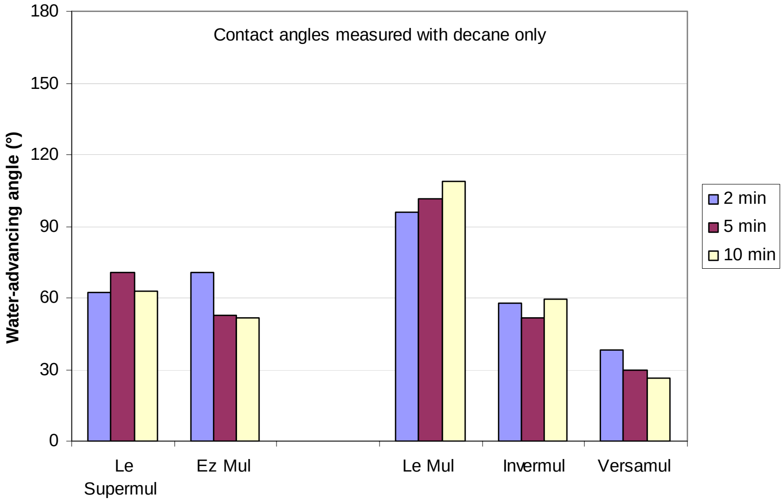


Figure 8. Mica samples treated as in Fig. 7 above. After one hour, mica was removed from the surfactant solutions and submerged in decane for the contact angle measurements with {pH 6, 0.1M} buffer. Contact times between the water drop and mica surface were 2, 5, and 10 minutes.

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 for Ez Mul in Fig. 9. The steep change in both advancing and receding angles during the first two minutes after formation of the brine droplet suggests 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.

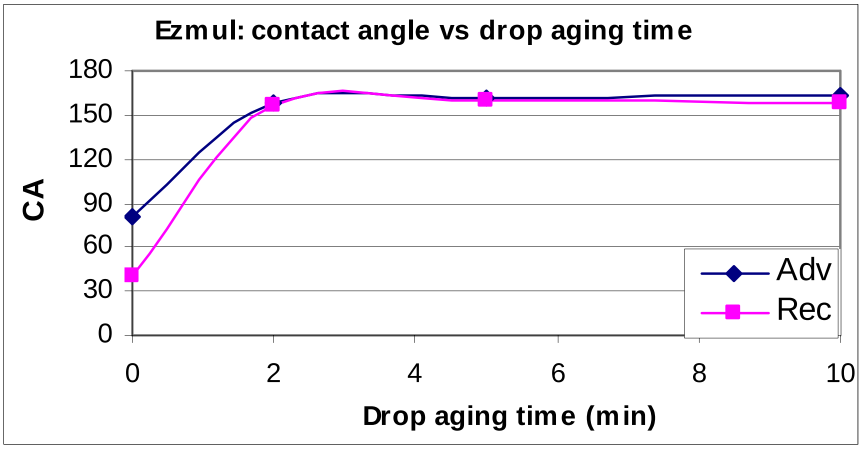


Figure 9. Mica surface aged for 1 hr in an 0.03 vol% solution of Ez Mul in decane. Contact angles measured in surfactant solution with {pH 6, 0.1M} buffer. Contact time between water drop and mica surface was 5 min. Before contact with mica, the water drop was allowed to equilibrate with the surfactant solution for up to 10 minutes.

We tested the hypothesis regarding lack of equilibrium by preequilibrating 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. 10 shows that the changes in contact angles were eliminated when the fluids were premixed and allowed to separate for 4-12 days. All measurements were made after 5 min of contact between brine droplet and the solid surface. Why the effect of nonequilibrium was so consistently to increase contact angles, making the surface appear more oil-wet, we can only conjecture at this point. Possibly the transfer of surfactant from decane to brine increases the interfacial concentration of surfactant during equilibration. When the drop is contacted with the surface, that excess surfactant creates a layer of adsorbed or trapped surfactant that shields water from contact with the surface, making the surface appear more oil-wet than it would with monolayer coverage due to adsorption.

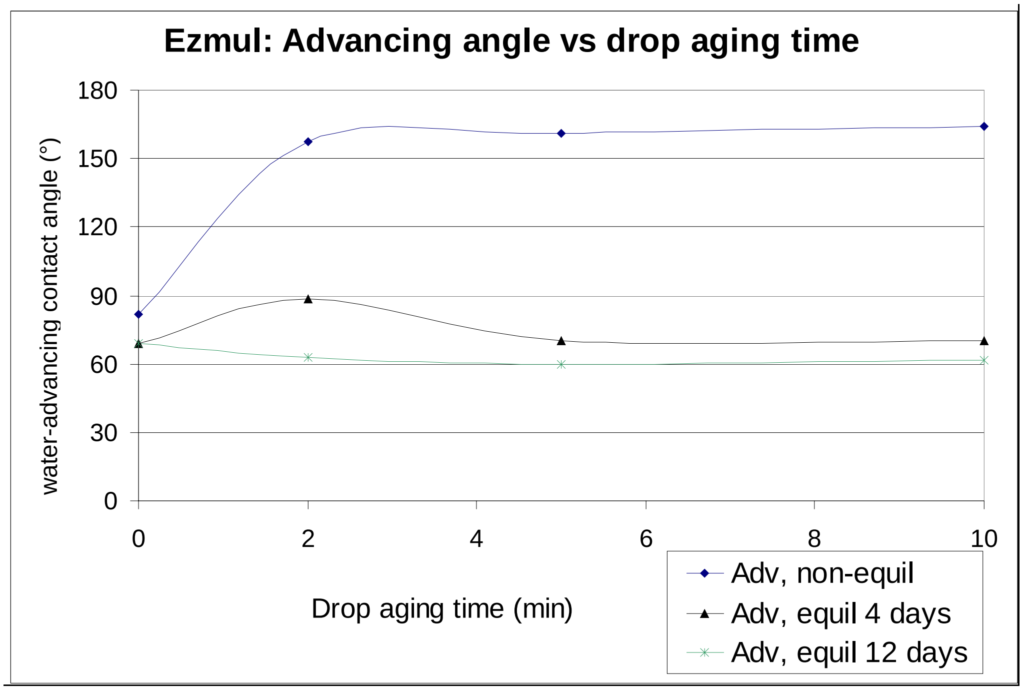


Figure 10. The effect of drop aging time illustrated in Fig. 9 was eliminated if the surfactant solution and aqueous buffer were preequilibrated for 4-12 days.

Figure 11 also 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.

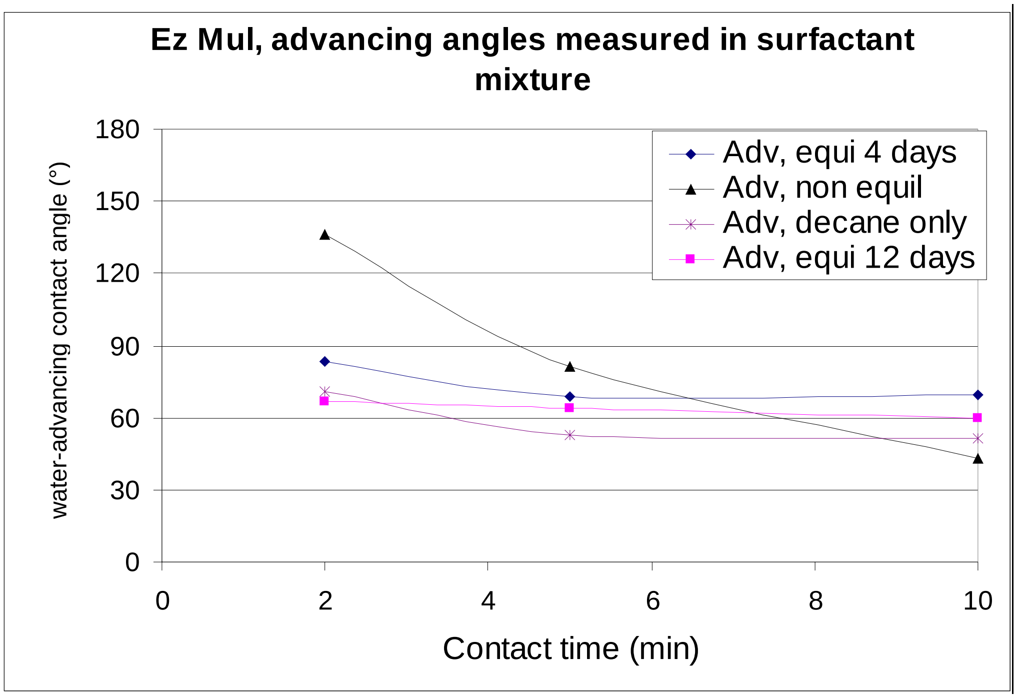


Figure 11. **Changes that occur with the time of contact between water drop and mica surface can be eliminated by preequilibration of the oleic and aqueous phases. Contact angles were measured in surfactant solution (0.03vol% Ez Mul in decane) or in decane alone with {pH 6, 0.1 M} buffer. Contact times 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 12 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.

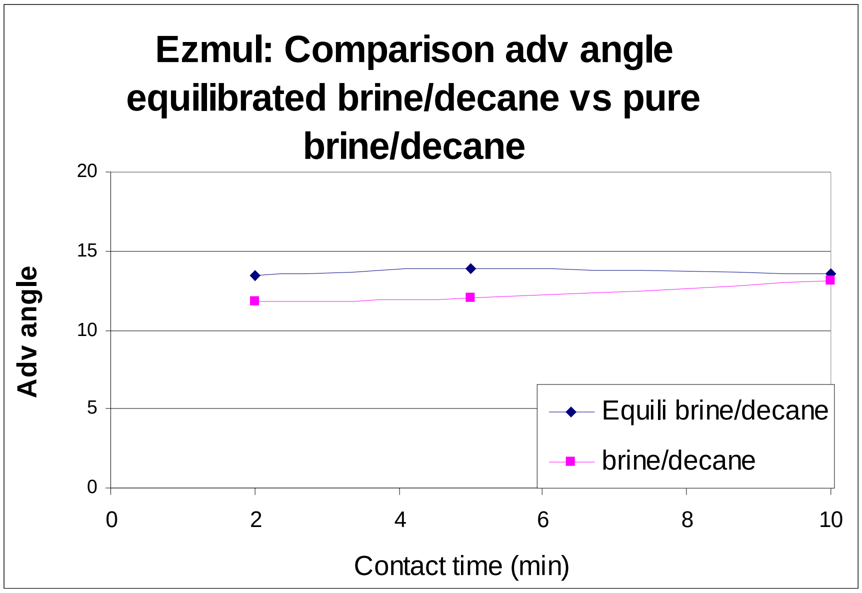


Figure 12. Water advancing contact angles between decane and {pH 6, 0.1M} buffer. The results are indistinguishable regardless of whether the aqueous buffer used had been preequilibrated with surfactant solution (0.03vol% Ez Mul in decane) or not.

3.1.3 IFT and contact angle experiments – with crude oil

Crude oils contain polar components that alter reservoir wetting. How those components might interact with surfactants is not obvious. Crude oil components affect interfacial and surface properties by adsorption on the solid surface 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 (2000) 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.

Figure 13 shows IFT measured at ambient temperature by the pendant drop technique 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).

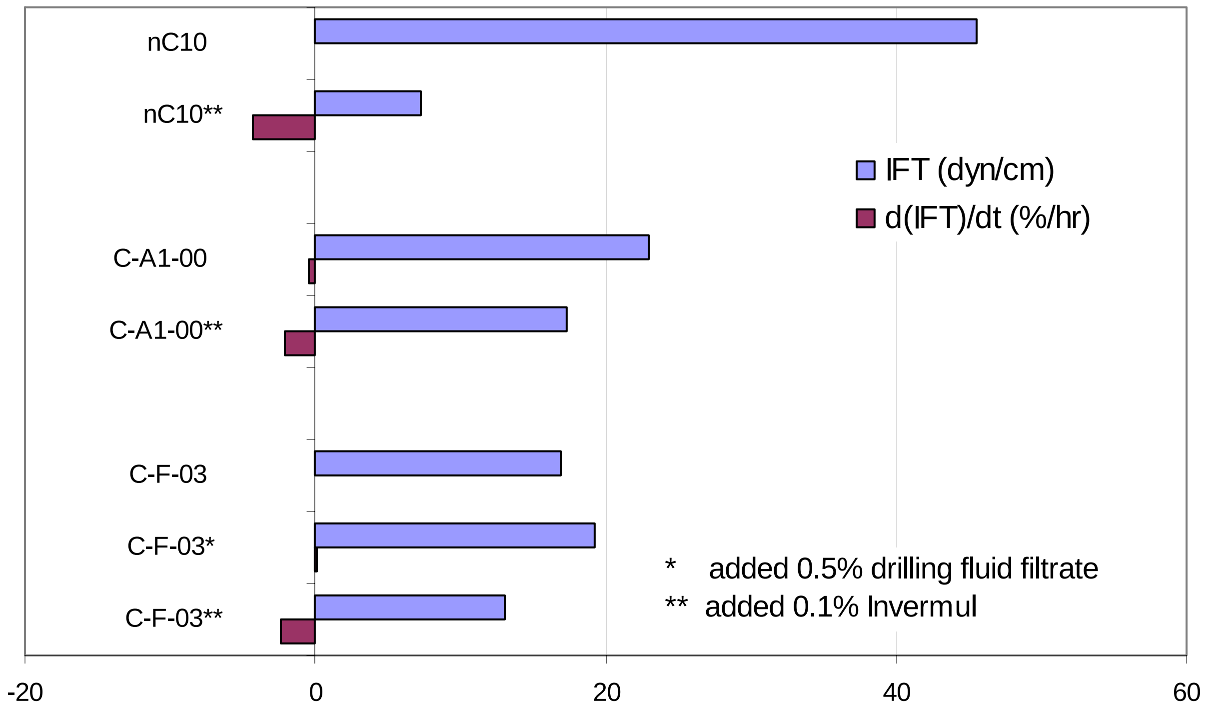


Figure 13. Interfacial tension measured by the pendent drop method and changes in IFT with time. IFT is reported for drops that are more than 1 min, but less than 5 min old. Changes in tension were observed over 4-9 hours.

A pendant drop of decane had an interfacial tension of 45.5 dyn/cm. That value was reduced to 7.2 dyn/cm 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 dyn/cm 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. 13.

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 (Table 2). Results are shown in Fig. 14.

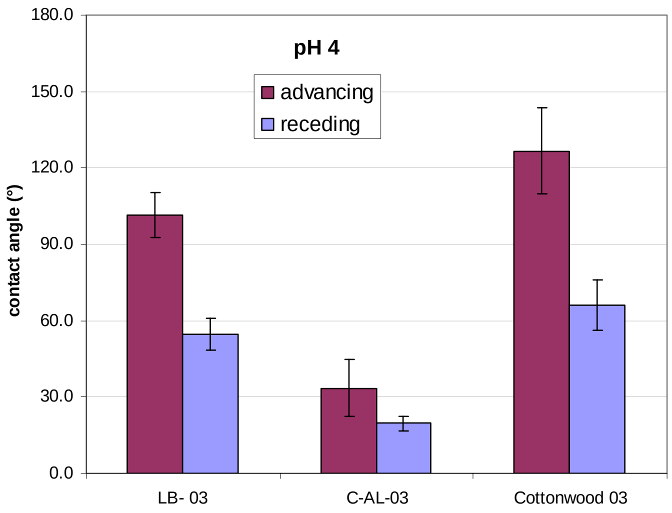


Figure 14. Decane/buffer contact angles for mica exposed to {pH 4, 0.01 M} buffer for 24 hrs, then to one of three crude oils for 21 days at ambient temperature. Crude oil was removed by rinsing with toluene.

Interfacial tensions for these three crude oils are shown in Fig. 15. Two experiments with Cottonwood-03, equilibrated with synthetic sea water in one case and with a synthetic reservoir brine in the other, show very high rates of IFT decrease, suggesting that this oil may be contaminated with some surface active material, as received. The other measurements were made with {pH 6, 0.1M} buffers.

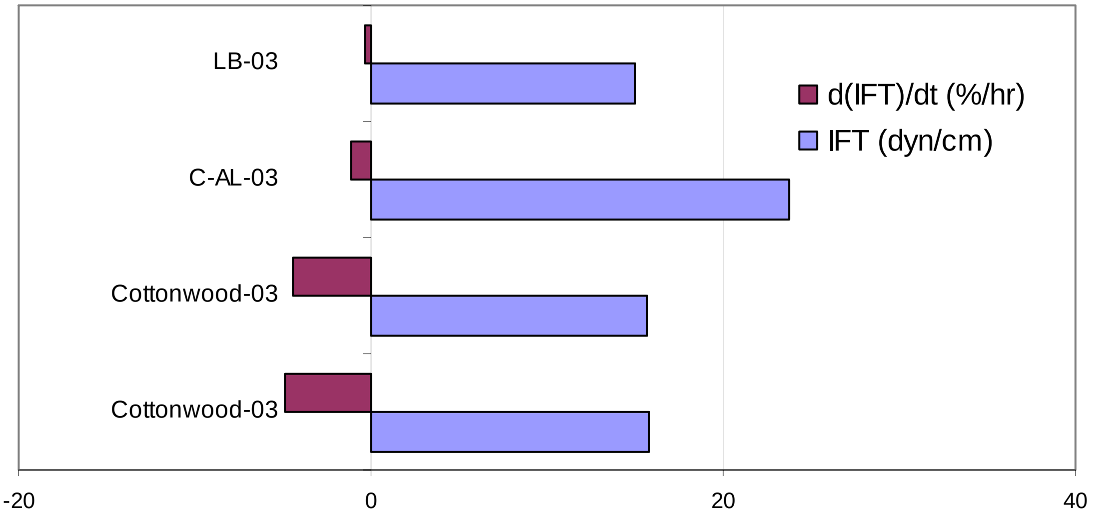


Figure 15. Interfacial tension measured by the pendent drop method and changes in IFT with time for the three crude oils used in this study. Cottonwood-03 may have some surfactant contamination.

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. 16. 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.

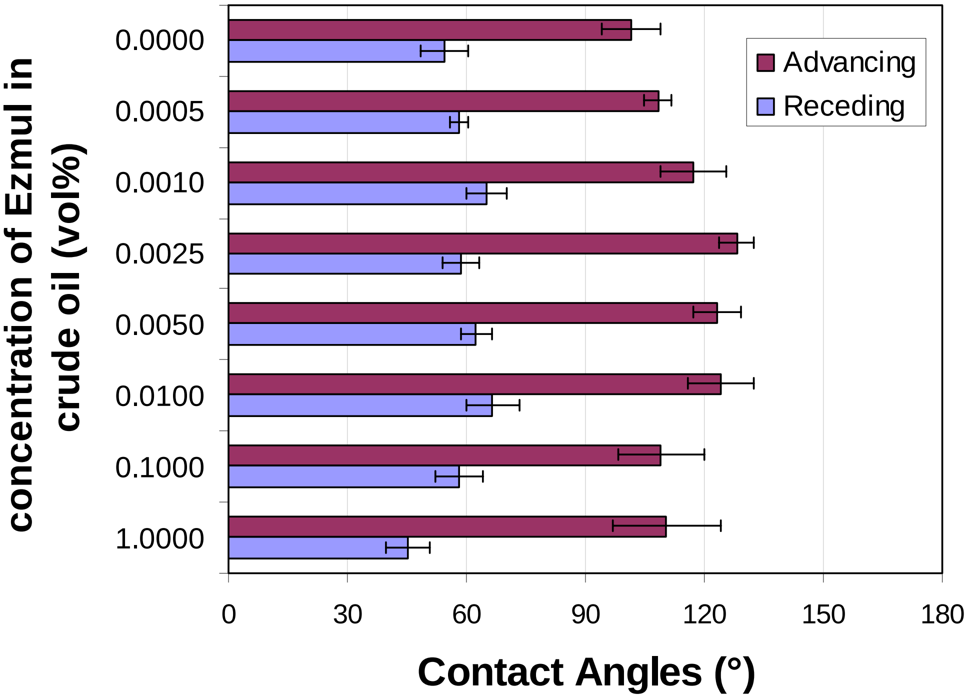
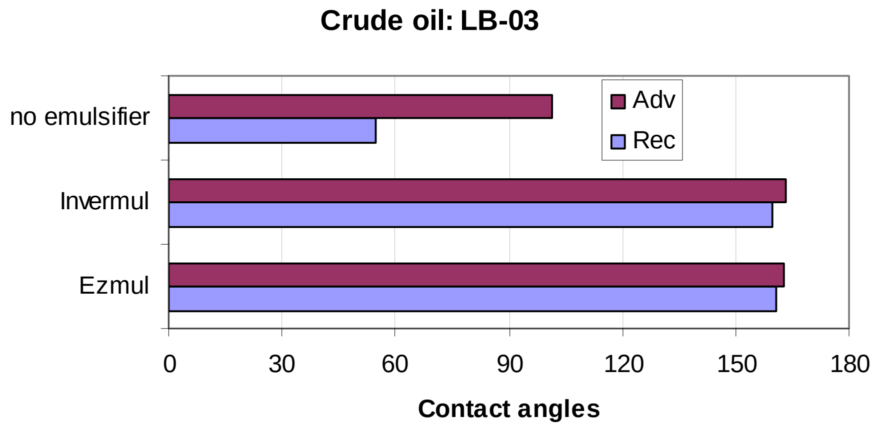


Figure 16. Contact angles for mica surfaces aged in LB-03 crude oil to which varying amounts of Ez Mul were added. Mica was aged for 24 hrs in {pH 4, 0.01 M} buffer, 21 days in oil plus Ez Mul, rinsed with toluene, and submerged in decane. Contact angles were measured with decane and {pH 6, 0.1M} buffer.

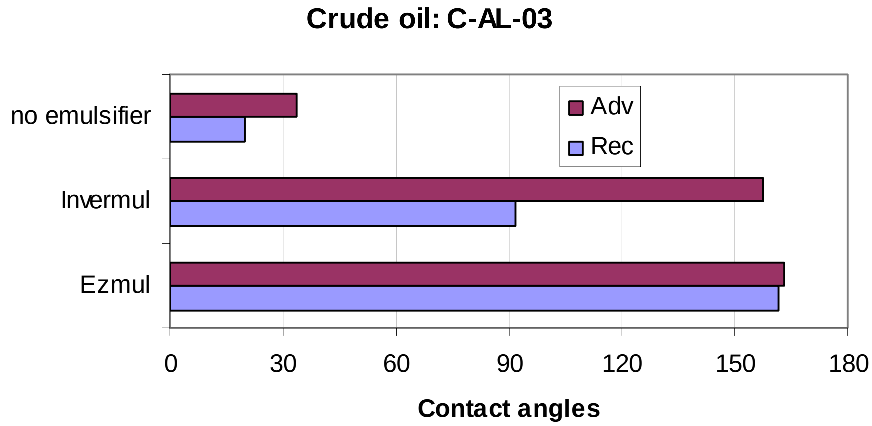
Changes in wetting toward more oil-wet conditions were more dramatic if surfaces were exposed to the emulsifier after they had been treated with crude oil (Fig. 17). All of the mica samples were equilibrated first with {pH 4, 0.01M} buffer for 24 hrs, then with one of the three crude oils for 21 days. Bulk crude oil was removed by rinsing with toluene, then each surface was submerged in one of three decane solutions (Table 6). Contact angles were measured with the aqueous phases shown in Table 6.

Table 6. Test fluids for the contact angle measurements shown in Fig. 17

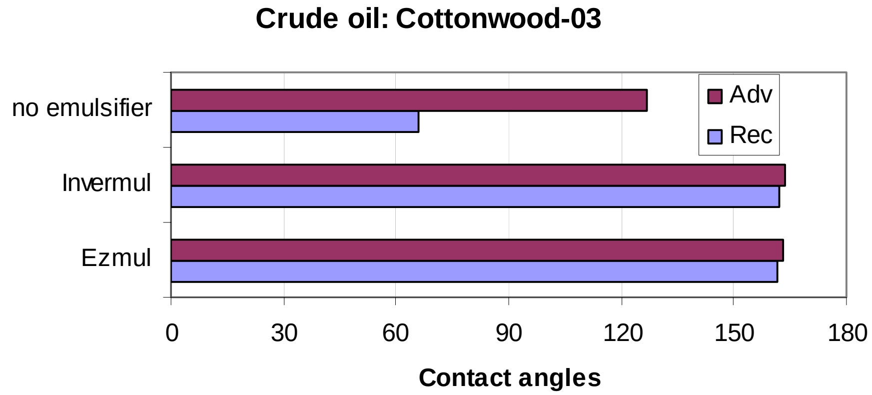
	oleic phase	**aqueous phase**
no emulsifier	decane	{pH 4, 0.01M}
Invermul	0.03vol% solution in decane	{pH 4, 0.01M} equilibrated with the Invermul solution for 12 days
Ez Mul	0.03vol% solution in decane	{pH 4, 0.01M} equilibrated with the Ez Mul solution for 12 days



(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 17. 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%).

3.2 Surfactants of known structure

3.2.1 Contact angle tests

The first requirement in selecting surfactants of known structure for further study was that they be soluble in decane. Some of those initially selected (Table 4) had limited decane solubility and were not considered further. Decane solutions were prepared by equilibration of an excess of surfactant (about 5% by weight) with decane.

The decane solutions thus produced were used in several ways. Mica was immersed in the solution and contact angles were measured with a drop of distilled water. Results for CAM-2 were similar to those for TAM-2 (Table 7). A second group of experiments involved exposure of mica to decane surfactant solutions (for at least 30 and not more than 60 min) followed by a step in which the surfaces were rinsed with toluene. Finally the mica surfaces were submerged in fresh decane. Measurement of the residual effect of surfactant were made with a drop of distilled water. Both CAM-2 and TAM-2 made mica fairly oil-wet. The water-advancing contact angles were reduced somewhat when the surfaces were rinsed with toluene although in neither case was toluene effective in restoring strongly water-wet conditions (Table 7).

Table 7. Water-advancing angles on mica surfaces submerged in decane solutions of surfactants.

Surfactant	θ_A (deg)	toluene rinse
CAM-2	144	no
TAM-2	145	no
CAM-2	67	yes
TAM-2	126	yes

In the remaining experiments, decane surfactant solutions were equilibrated with distilled water, pH 4, or pH 8 aqueous buffers. Equilibrated decane and aqueous phases were removed from the top and bottom of a separatory funnel, respectively. Equilibration times varied widely with the stability of the emulsions formed by different combinations of surfactant and buffer. Contact angles were measured with a number of combinations of these preequilibrated phases and fresh solutions including cases where both decane and aqueous drop were preequilibrated (designated “PE” or “PE of both” in Fig. 18 and 19) and preequilibrated decane solution contacted with a drop of fresh aqueous phase (designated “PE decane” in Fig. 18 and 19).

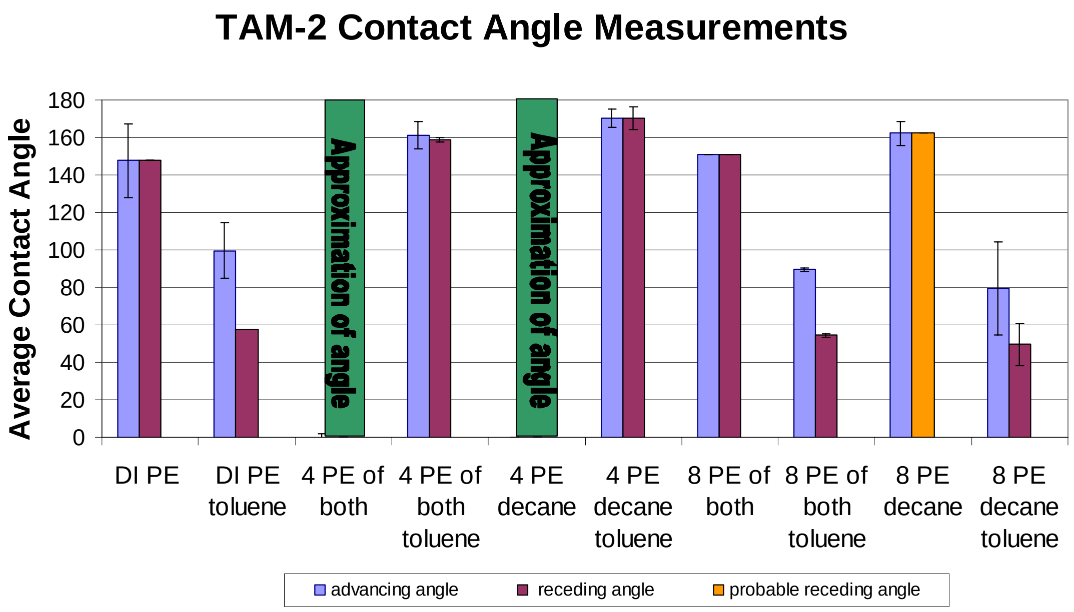


Figure 18. **Water-advancing and receding contact angles measured on mica after exposure to decane solutions of TAM-2. Pre-equilibration of both decane and aqueous drop is designated "PE" or "PE of both." Pre-equilibrated decane solution contacted with a drop of fresh aqueous phase is designated "PE decane." Samples with the designation "toluene" were removed from the surfactant solution, rinsed with toluene and contact angles were measured in decane.**

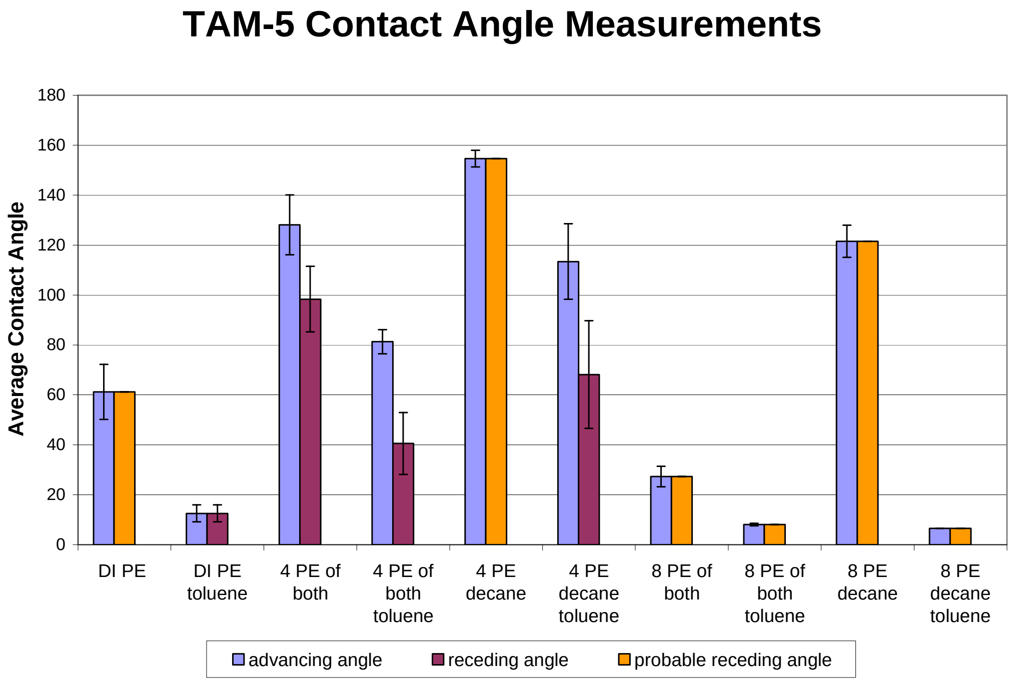


Figure 19. **Water-advancing and receding contact angles measured on mica after exposure to decane solutions of TAM-5. Pre-equilibration of both decane and aqueous drop is designated "PE" or "PE of both." Pre-equilibrated decane solution contacted with a drop of fresh aqueous phase is designated "PE decane." Samples with the designation "toluene" were removed from the surfactant solution, rinsed with toluene and contact angles were measured in decane.**

Results for CAM-2 (not shown) were similar to TAM-2 (Fig. 18). Differences in the length of the hydrocarbon "tails" evidently had less influence on the adsorption and retention of these materials than did differences in the polar head groups. In all cases, higher contact angles were measured on surfaces that had been exposed to TAM-2, with only 2 ethoxy groups, than on those exposed to TAM-5, which has 5 ethoxy groups. These observations suggest that it is the nitrogen (probably in its positively charged form) that is responsible for adsorption and that additional ethoxy groups may sterically hinder effective adsorption. In general, the toluene rinse decreases contact angles, but washing with toluene is not effective in returning the mica to its original, strongly water-wet condition. Additional analysis of these contact angle data will be made when more results, including some duplicate experiments, are available.

3.2.2 Surface tensions

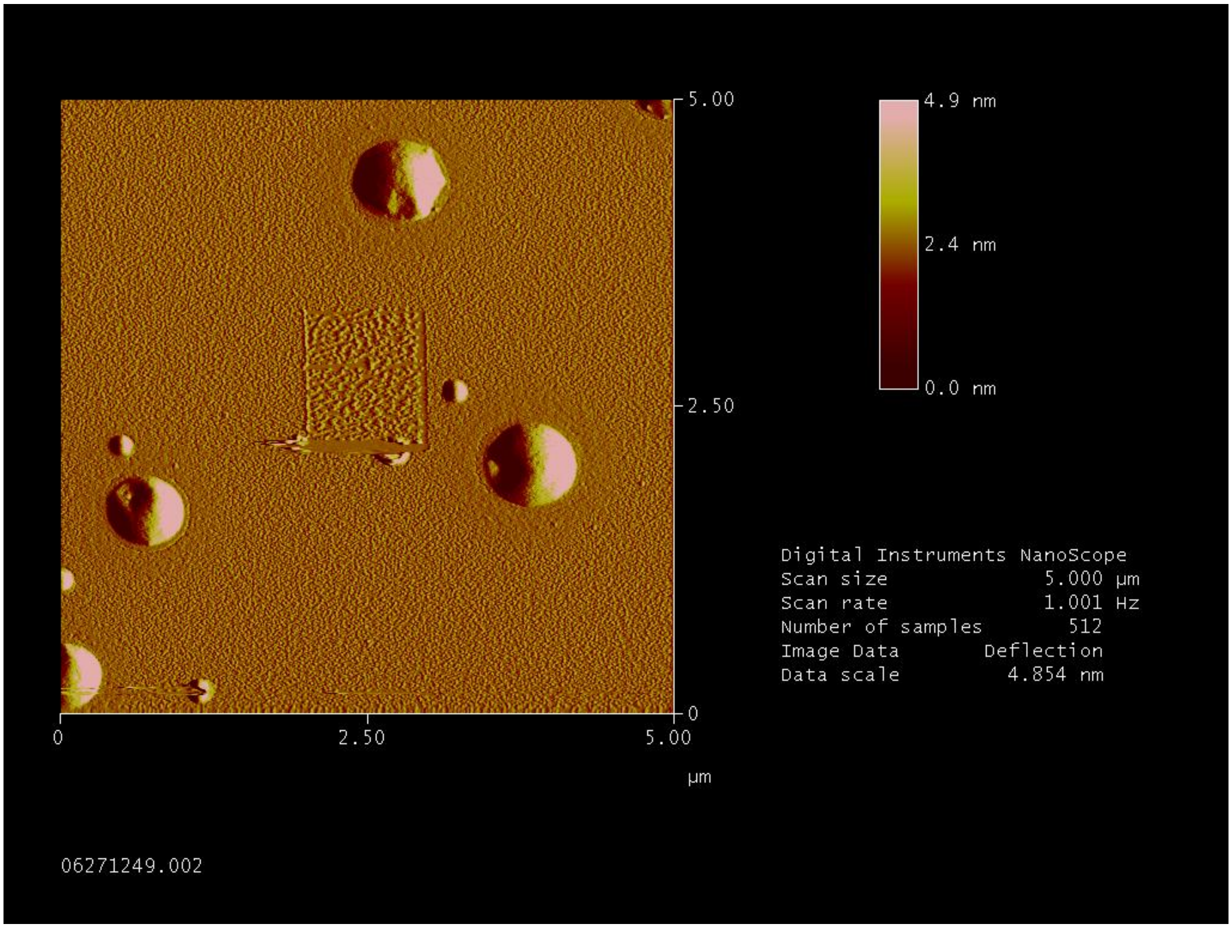
The surfactants shown in Fig. 1 should be positively charged at low pH and neutral at high pH. The pK_a values (pH at which concentrations of the charged and neutral forms are equal) are not know, but can be estimated from those of other compounds. For example, the pK_a for 2-ethoxyethylamine is 6.26; that for diethanolamine is 8.88. Since the brine pH values used in these tests were 4 and 8, it is likely that the surfactants were positively charged at pH 4. At pH 8 both charged and neutral species may be present. Table 8 shows surface tensions of aqueous solutions after equilibration with decane solutions of the three polyethoxylated amine surfactants measured with the duNouy ring. Without surfactant, all aqueous buffers and distilled water had surface tensions above 72 dynes/cm. The reduction in surface tension reflects the amount of surfactant extracted into the aqueous phase and its accumulation at the air/water interface.

Table 8. Surface tension of aqueous solutions of fixed pH after equilibration with surfactant-saturated decane solutions.

Surfactant	pH	Tension (dyn/cm)
CAM-2	4	31.9
TAM-2	4	34.0
TAM-5	4	40.8
CAM-2	8	34.2
TAM-5	8	34.2

3.2.3 AFM

Mica surfaces treated with the decane surfactant solutions and with surfaces rinsed with toluene after exposure to surfactant solutions have been imaged both in contact mode and in tapping mode. In both cases, the surfaces were allowed to dry in air before being glued to the metal sample puck. Experiments followed the guidelines provided in PRRC 01-15. Initial experiments in contact mode showed large areas of essentially clean mica for the surfaces exposed to the decane surfactant solutions, then allowed to dry without further treatment. Similarly treated surfaces that had been rinsed with toluene appeared to be coated with a layer of surfactant, as shown in Fig. 20 for mica that was exposed to a decane solution of CAM-2. The central area was deliberately scraped by increasing the imaging force in a prior scan of that 1μm by 1μm area. Although the adsorbed surfactant could not be removed, it did appear to aggregate under the increased pressure. Surfactant appears to be adsorbed evenly over the rest of the surface. The nearly micron-sized droplets may be remnants of the toluene used to rinse the surface.



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Digital Instruments NanoScope
Scan size              5.000 µm
Scan rate              1.001 Hz
Number of samples       512
Image Data        Deflection
Data scale          4.854 nm
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Figure 20. CAM-2 (preequilibrated with pH 8 buffer) rinsed with toluene, θ_A = 125°.

These observations—i.e. surfactant remaining on the toluene-rinsed mica surfaces, but not on the unrinsed surfaces—seem to be the reverse of what the contact angle observations would lead us to expect, since water-advancing angles were lower on the toluene-rinsed surfaces than on the unrinsed ones. It is likely, however, that the decane, which evaporates more slowly than toluene, was not sufficiently dry and that all the adsorbed surfactant was removed in the first imaging scan whereas the toluene-rinsed surfaces were dryer and hence more amenable to contact mode imaging.

A similarly treated sample exposed to TAM-2 is shown in Fig. 21. In this case the image was made in what is known as tapping mode. The image on the left shows the height or topographic information; on the right is a phase image that would show chemical boundaries, if these existed. In this case, coverage appears to be quite uniform although the results of a previous tapping scan on the central $1 \mu m^2$ area are evident in the phase image. Tapping mode is often used to minimize disturbance of soft surface samples, but some disturbance is apparently occuring even so.

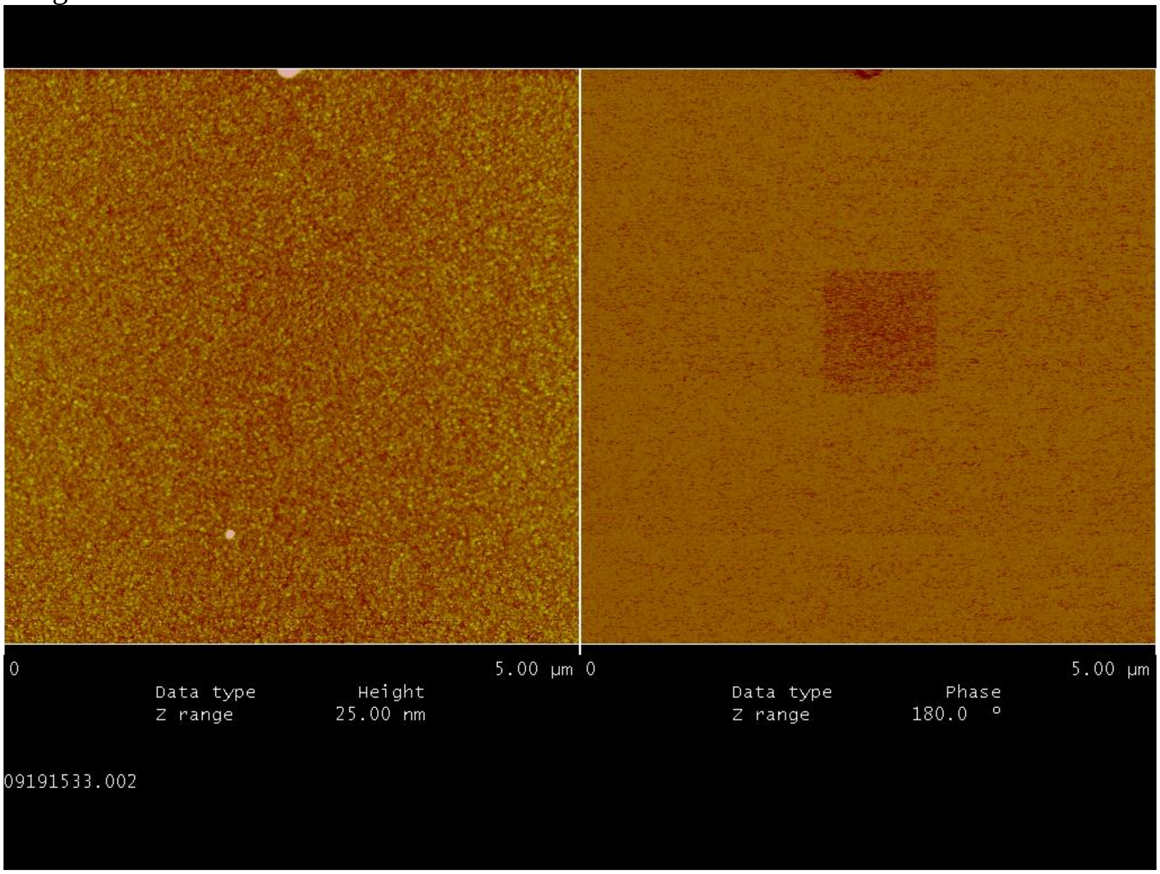

Figure 21. TAM-2 (preequilibrated with pH 8 buffer) rinsed with toluene, θ_A = 151°.

At this stage, the AFM is providing some interesting a thought provoking images, but it is not yet clear how to interpret and use the information provided. A more detailed review of the many images obtained is in progress.

3.3 Base oils and asphaltene stability

The materials used to replace diesel or other crude oil-based products in synthetic oil-based muds are chosen to meet environmental regulations, among other specifications. The toxicity of aromatic compounds has caused regulators to focus on their exclusion from the base oils from which drilling fluids are formulated. This might result in incompatibility between the base oil and some crudes causing destabilization of asphaltenes. Synthetic base oil products have been tested for compatibility with two crude oils; the results are summarized in Table 9 and are compared with n-paraffins in Figures 22 (tests with Minnelusa-99 at 60°C) and 23 (tests with C-F-03 at 20°C). All but two of the synthetic base oils precipitated asphaltenes. The two that did not appear to destabilize asphaltenes were the original Petrofree, an ester-based fluid, and Petrofree LV, also an ester-based fluid with lower viscosity than the original Petrofree.

Table 9. Onset of asphaltene flocculation in mixtures with base oils.

Product designation	Crude oil	T°C	P_{RI}	$f_{v,oil}$
Accolade	C-F-03	20	1.4588	0.28
Biobase 240 (C-14)	C-F-03	20	1.475	0.6
Biobase 560 (LP)	C-F-03	20	1.4737	0.65
EDC 99DW	C-F-03	20	1.4722	0.51
GOM 4 comp blend - IO	C-F-03	20	1.4754	0.59
LVT mineral oil	Minnelusa-99	60	1.4637	0.49
Petrofree	C-F-03	20	no onset	
Petrofree LV	C-F-03	20	no onset	
Petrofree SF	Minnelusa-99	60	1.4589	0.7
SF Base	C-F-03	20	1.4768	0.68
XP-07	C-F-03	20	1.4785	0.71

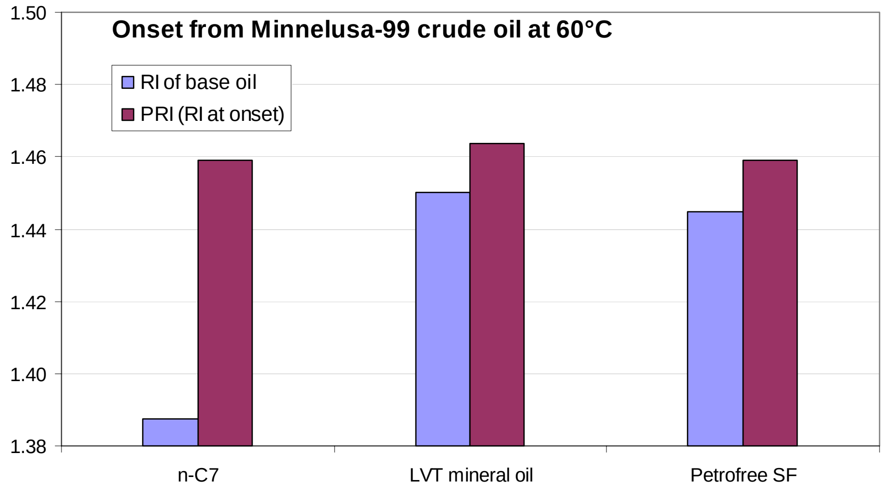

Figure 22. RIs at the onset of asphaltene flocculation (P_{RI}) from Minnelusa-99 crude oil induced by LVT mineral oil and Petrofree SF are comparable to the onset condition with n-C_7. Also shown is the RI of each precipitant.

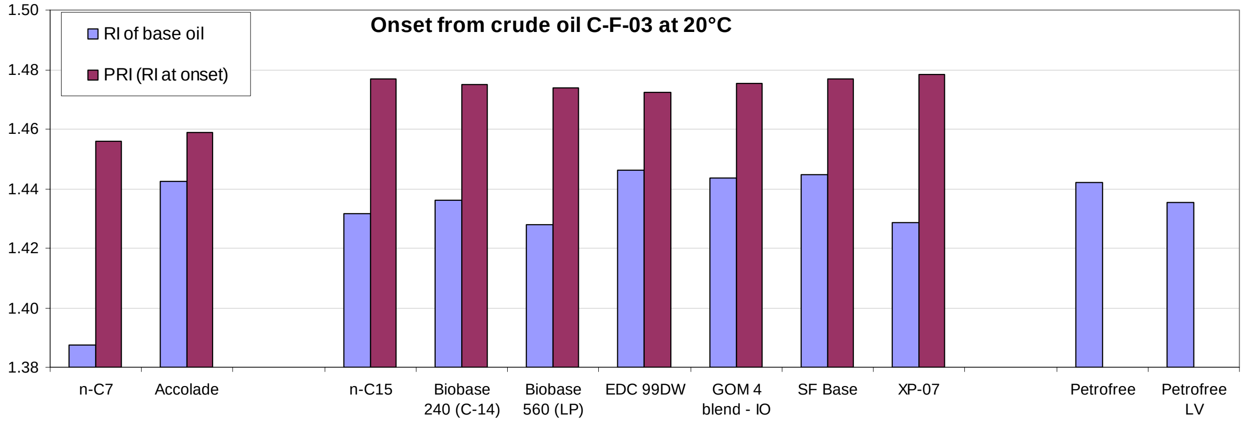

Figure 23. P_{RI} for the onset from C-F-03 crude oil induced by Accolade is comparable to the onset condition with n-C_7. P_{RI} for flocculation from C-F-03 crude oil induced by six other SBM base oils are comparable to the onset conditions with n-C_{15}. No flocculation was observed with Petrofree or Petrofree LV. Also shown is the RI of each precipitant or solvent.

Most of the base oils began to precipitate asphaltenes at solubility conditions that are similar to n-pentadecane. Accolade, LVT mineral oil and Petrofree SF produced asphaltene instability at a lower value of RI of the onset mixture (P_{RI}), more similar to n-heptane. Note that in all three cases, much more of the base oil than n-heptane would be required to initiate precipitation because the refractive indices (RI) of these products are much higher than the RI of n-heptane and the RI of a mixture is approximately equal to the sum of the RIs of the components multiplied by their volume fractions. So the amounts of these base oils that destabilize asphaltenes are greater than the amount of n-heptane required, but the instability occurs at similar solubility conditions, as indicated by the P_{RI}.

Destabilizing the asphaltenes when drilling fluid mixes with crude oil could provide a mechanism for wetting alteration that does not depend on contact with the surface-active materials in the drilling fluid. Surface precipitation of asphaltenes can cause changes in wetting by crude oil components beyond what would otherwise occur (Buckley *et al.*, 1998; Al-Maamari and Buckley, 2003)

All but two of the synthetic base oils precipitated asphaltenes. The two that did not appear to destabilize asphaltenes were the original Petrofree, an ester-based fluid, and Petrofree LV, also an ester-based fluid with lower viscosity than the original Petrofree. With respect to drilling under Arctic conditions, the latter product may be one that should be considered in cases where asphaltene stability is likely to be an issue.

4. Summary

Surface studies of surfactants, both commercial products used in SBM formulations and polyethoxyamines of known structure, are making good progress. In addition, SBM base oils—without surfactants—have been tested to determine their influence on asphaltene stability. Some of the main observations from these studies are listed below.

Commercial SBM and OBM surfactants:

- IFT and CMC values vary as a function of pH and define two main surfactant groups. In all likelihood, the same surfactants are used in multiple products, given different names by different distributors and for different applications (e.g., OBM and SBM). Exact formulations may vary, but the trends of CMC and IFT are similar within the two groups.
- All of the products tested make mica surfaces less water-wet; under some conditions surfaces became oil-wet.
- Non-equilibrium effects can play a large role in the observed wetting conditions. Equilibration times of 4 to 12 days appeared to be sufficient to eliminate these transient effects. Contact angles were lower (weakly water-wet) after equilibration of the surfactant solution and aqueous buffer.
- Addition of one surfactant product (Ez Mul) to a crude oil increased contact angles only slightly.
- Contact angles measured in Ez Mul or Invermul solutions in decane on mica surfaces that had previously been treated with crude oil were substantially higher than similar measurements in the absence of surfactant.
- Contamination with Invermul reduced interfacial tensions and caused slow changes in IFT that continue of several hours.

Polyethoxyamines:

- Exposure of mica surfaces to decane solutions of three polyethoxyamines produced oil-wet surfaces. Contact angles depend on the details of surfactant exposure and on pre-equilibration history.
- Atomic forces microscopy can be used to image mica surfaces after exposure to surfactant solution. Interpretation of these images is in progress.
- Toluene removes some, but not all of the adsorbed surfactant. A search for more efficient cleaning methods is underway.

SBM base oils:

- All of the SBM base oils tested caused asphaltene flocculation except the ester-based products.
- Flocculation occurs at conditions that are similar—in terms of P_{RI} (and thus in terms of solubility)—to n-heptane or n-pentadecane.

The results of these surface tests are being used to guide testing in porous media. The results of ongoing porous media testing of both surfactants and base oils will be the subject of the our next report.

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