CALIFORNIA INSTITUTE OF TECHNOLOGY

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Cost Effective Surfactant Formulations for Improved Oil Recovery in Carbonate Reservoirs

DOE Project: DE-FC26-04NT15521

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Co-PI: Yongchun Tang
Senior Staff: Patrick Shuler and Mario Blanco
Postdoctoral Scholars: Yongfu Wu

California Institute of Technology

FINAL REPORT

October 2004 – March 2007

- Covering the period October 2004 – March 2007
- Compiled by Patrick Shuler
- Sections written by Patrick Shuler
- Issued May 2007

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1 EXECUTIVE SUMMARY

This report summarizes work during the 30 month time period of this project. This was planned originally for 3-years duration, but due to its financial limitations, DOE halted funding after 2 years. The California Institute of Technology continued working on this project for an additional 6 months based on a no-cost extension granted by DOE.

The objective of this project is to improve the performance of aqueous phase formulations that are designed to increase oil recovery from fractured, oil-wet carbonate reservoir rock. This process works by increasing the rate and extent of aqueous phase imbibition into the matrix blocks in the reservoir and thereby displacing crude oil normally not recovered in a conventional waterflood operation.

The project had three major components: 1) developing methods for the rapid screening of surfactant formulations towards identifying candidates suitable for more detailed evaluation, 2) more fundamental studies to relate the chemical structure of acid components of an oil and surfactants in aqueous solution as relates to their tendency to wet a carbonate surface by oil or water, and 3) a more applied study where aqueous solutions of different commercial surfactants are examined for their ability to recover a West Texas crude oil from a limestone core via an imbibition process.

The first item, regarding rapid screening methods for suitable surfactants has been summarized as a Topical Report. One promising surfactant screening protocol is based on the ability of a surfactant solution to remove aged crude oil that coats a clear calcite crystal (Iceland Spar). Good surfactant candidate solutions remove the most oil the quickest from the surface of these chips, plus change the apparent contact angle of the remaining oil droplets on the surface that thereby indicate increased water-wetting. The other fast surfactant screening method is based on the flotation behavior of powdered calcite in water. In this test protocol, first the calcite power is pre-treated to make the surface oil-wet. The next step is to add the pre-treated powder to a test tube and add a candidate aqueous surfactant formulation; the greater the percentage of the calcite that now sinks to the bottom rather than floats, the more effective the surfactant is in changing the solids to become now preferentially water-wet. Results from the screening test generally are consistent with surfactant oil recovery performance reported in the literature.

The second effort is a more fundamental study. It considers the effect of chemical structures of different naphthenic acids (NA) dissolved in decane as model oils that render calcite surfaces oil-wet to a different degree. NAs are common to crude oil and are at least partially responsible for the frequent observation that carbonate reservoirs are oil-wet. Because pure NA compounds are used, trends in wetting behavior can be related to NA molecular structure as measured by solid adsorption, contact angle and our novel, simple flotation test with calcite. Experiments with different surfactants and NA-treated calcite powder provide information about mechanisms responsible for sought after reversal to a water-wet state. Key findings include: 1) more hydrophobic NA's are more prone to induce oil-wetting, and 2) recovery of the model oil from limestone core was better with cationic surfactants, but one nonionic surfactant, Igepal CO-530, also had favorable results. This portion of the project included theoretical calculations to investigate key basic properties of several NAs such as their acidic strength and their relative water/oil solubility, and relate this to their chemical structure.

The third category of this project focused on the recovery of a light crude oil from West Texas (McElroy Field) from a carbonate rock (limestone outcrop). For this effort, the first item was to establish a suite of surfactants that would be compatible with the McElroy Field brine. Those were examined further for their ability to recover oil by imbibition. Results demonstrate several types of promising candidates, and that within a given series of nonionic surfactants the oil recovery appears to be related to the HLB of each surfactant. For the McElroy brine and crude oil system, higher HLB (more water soluble) surfactants perform better than in earlier imbibition tests performed with the model oil and a fresh water or low salinity brine. We speculate that this difference mostly is because a more water soluble surfactant is required to be compatible with higher salinity of the McElroy brine (over 3 wt% salt).

TABLE OF CONTENTS

Attachments:

1. Topical Report –- “Screening Methods for Selection of Surfactant Formulations for IOR from Fractured Carbonate Reservoirs”

2. Paper SPE 99612 -- Study of Wetting Behavior and Surfactant EOR in Carbonates with Model Compounds

2 INTRODUCTION

The goal of this project is to develop cost-effective chemical formulations that will recover incremental oil beyond a waterflood operation from carbonate reservoirs. The specific target for this improved technology are large, domestic carbonate reservoirs that are at a mature point in their waterflood operations, most especially those that are fractured reservoirs and with the matrix blocks in an oil-wet state. For such reservoirs, the waterflood is usually very inefficient, in part, because the injection water can not imbibe into the porous, matrix blocks due to their oil-wet condition.

Adding the right surfactants to the injection water will change the wettability of the carbonate reservoir surfaces to a water-wet condition and decrease the interfacial tension (IFT) so as to increase the penetration of the injected aqueous phase into the rock matrix holding trapped oil. The oil forced out of the oil-rich matrix blocks due to the imbibition of the aqueous (chemical) solution then moves into the fracture/high permeability network. These flow networks act as a "highway" to convey the newly mobilized oil to a production well. If properly designed, this process will increase significantly the recovery of this oil otherwise not recovered by waterflood.

About 80% of carbonate reservoirs are classified as neutral to oil-wet (Standnes and Austand, 2002), and an oil-wetting condition is even more likely to be the case in cooler, more shallow reservoirs (Austad and Standnes, 2002). This means chemical formulations that can alter successfully carbonate minerals from oil- to water-wet conditions should be effective IOR agents for a large number of oil reservoirs. For example, there are many large, shallow (cooler, less than 60 ^{o}C), carbonate reservoirs in the Permian Basin which have all of the characteristics mentioned above that makes them potential candidate locations for this chemical IOR process: 1) mature waterfloods with poor recovery, 2) fractured formations or have significant thief zones, and 3) high oil saturation remaining in the porous matrix due to its oil-wet condition.

Three different topic areas are included in this final report: 1) development of rapid screening methods to identify suitable candidates for further testing, 2) a more fundamental study of the nature of oil-wetting on carbonates by model naphthenic acids (NA), and then the alteration to a more wetting nature by surfactants, and 3) a more practical application where different commercial surfactants are tested for their ability to recover a light West Texas crude oil from an outcrop limestone core.

2.1 Rapid Screening Methods to Identify Better Surfactants for Oil Recovery

This body of work is given in detail in a Topical Report that was provided to DOE during Year 1 of this project. This is provided as Attachment 1 to this final report.

An Abstract for the findings of this Topical Report is given below:

This topical report presents details of the laboratory work performed to complete Task 1 of this project; developing rapid screening methods to assess surfactant performance for IOR (Improved

Oil Recovery) from fractured carbonate reservoirs. The desired outcome is to identify surfactant formulations that increase the rate and amount of aqueous phase imbibition into oil-rich, oil-wet carbonate reservoir rock. Changing the wettability from oil-wet to water-wet is one key to enhancing this water-phase imbibition process that in turn recovers additional oil from the matrix portion of a carbonate reservoir.

The common laboratory test to evaluate candidate surfactant formulations is to measure directly the aqueous imbibition rate and oil recovery from small outcrop or reservoir cores, but this procedure typically requires several weeks. Two methods are presented here for the rapid screening of candidate surfactant formulations for their potential IOR performance in carbonate reservoirs. One promising surfactant screening protocol is based on the ability of a surfactant solution to remove aged crude oil that coats a clear calcite crystal (Iceland Spar). Good surfactant candidate solutions remove the most oil the quickest from the chips, plus change the apparent contact angle of the remaining oil droplets on the surface that thereby indicate increased water-wetting. The other fast surfactant screening method is based on the flotation behavior of powdered calcite in water. In this test protocol, first the calcite power is pre-treated to make the surface oil-wet. The next step is to add the pre-treated powder to a test tube and add a candidate aqueous surfactant formulation; the greater the percentage of the calcite that now sinks to the bottom rather than floats, the more effective the surfactant is in changing the solids to become now preferentially water-wet. Results from the screening test generally are consistent with surfactant performance reported in the literature.

2.2 Study of Weting Behavior and Surfactant EOR in Carbonates with Model Compounds

The experimental body of this work is given in detail in a SPE paper (SPE 99612) that was presented at the SPE/DOE Symposium of Improved Oil Recovery at Tulsa, Oklahoma April 22-24, 2006. This paper has been submitted to SPE for peer review, and has been accepted for publication pending a review of the revisions recently provided by the authors. This is provided as Attachment 2 to this final report.

From the Abstract for the paper SPE 99612:

This study focuses on the mechanisms responsible for enhanced oil recovery (EOR) from fractured carbonate reservoirs by surfactant solutions, and methods to screen for effective chemical formulations quickly. One key to this EOR process is the surfactant solution reversing the wetting of the carbonate surfaces from oil-wet to water-wet conditions. This effect allows the aqueous phase to imbibe into the matrix spontaneously and expel oil bypassed by a waterflood.

This study used different naphthenic acids (NA) dissolved in decane as a model oil to render calcite surfaces oil-wet. Because pure compounds are used, trends in wetting behavior can be related to NA molecular structure as measured by solid adsorption, contact angle and a novel, simple flotation test with calcite. Experiments with different surfactants and NA-treated calcite powder provide information about mechanisms responsible for sought after reversal to a water-

wet state. Results indicate this flotation and a calcite chip cleaning test are rapid screening tools to identify better EOR surfactants for carbonates.

Also complementary theoretical calculations were performed to rationalize the different properties and behavior of the various model NA species studies. A description of this theoretical effort was not included in the SPE paper, and is summarized here in Section 3, based on information provided in previous interim reports to DOE.

2.3 Oil Recovery Test of a Light West Texas Crude Oil

This third portion o the project study focused on the recovery of a light crude oil obtained from West Texas (McElroy Field) from a carbonate rock (limestone outcrop). For this effort, the first item was to establish a suite of surfactants that would be compatible with the McElroy Field brine. Those were examined further for their ability to recover oil by imbibition. Results demonstrate there are several types of promising candidate surfactants, and that within a given series of nonionic surfactants the oil recovery appears to be related to the HLB of each surfactant. For the McElroy brine and crude oil system, higher HLB (more water soluble) surfactants perform better than in earlier imbibition tests performed with the model oil and a fresh water or low salinity brine. We speculate that this difference mostly is because a more water soluble surfactant is required to be compatible with higher salinity of the McElroy brine (over 3 wt% salt).

The results for this portion of the project were presented in previous interim reports to DOE, and the results of this effort are summarized here in Sections 4 and 5 of the Final Report.

3. THEORETICAL CHEMISTRY CALCULATIONS / MODEL NAPHTHENIC ACIDS

3.1 Introductory Remarks

One goal of the project was pointed towards gaining a better fundamental understanding about the wetting behavior of carbonate minerals, and how that changes with exposure to oil and aqueous surfactant solutions. That is, how is it that certain components in the oil (e.g. naphthenic acids (NAs) and asphaltenes) promote the mineral surface to be oil-wet? What are the atomistic-level processes that can alter that oil-wet condition to the desired outcome of becoming strongly water-wet via exposure to an aqueous surfactant solution? From a better understanding of these processes and in particular, coupling these wetting behavior phenomena to chemical structures, we will improve our ability to forecast the performance of different candidate surfactant ideas.

For this more fundamental portion of the project we select model compounds and components so that we can focus on the fundamental chemistry without having too many complicating chemical parameters. This simplified chemistry approach will make it practical to perform theoretical calculations about the characteristics of model NA species. These specific naphthenic (carboxylic) acids act as model compounds such as those that may be in a crude oil and

contribute to the oil-wetting commonly observed by crude oils. Initially we consider pure calcite (calcium carbonate) as the mineral surface.

Among the suite of carboxylic acids compounds considered are shown below:

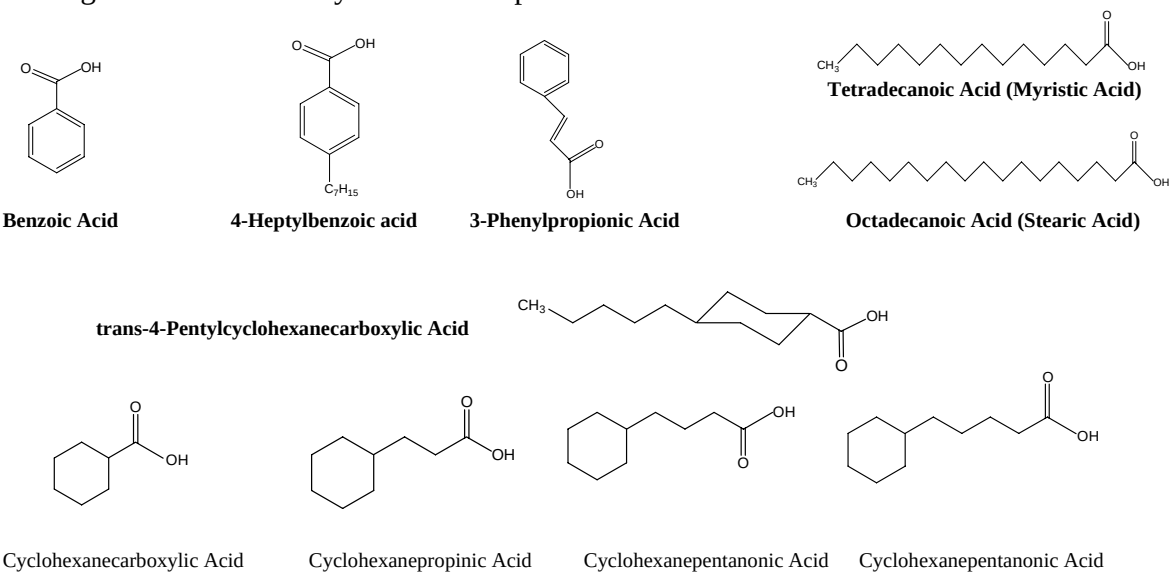

Figure 1. Structures of model naphthenic acids (NA)

The literature suggests that NAs can create an oil-wet condition via their carboxylate group binding to the carbonate mineral surface. Then the hydrophobic (e.g. alkyl chain) protruding from the surface creates effectively an oil-like coating (Standes and Austad, 2000).

3.2 Computer Calculations for Naphthenic Acid (NA) Properties

Basic characteristics of each NA include their dissociation from an acid form to a carboxylate anion in water, and their affinity for water versus a non-polar phase. The wetting behavior of various NA compounds in turn may well be directly related to, or can be correlated to these basic chemical characteristics. A first objective of the modeling effort then is to predict the acidity and solubility of any NA, just based on its chemical structure. The notion is that predicting these basic chemical characteristics may aid in predicting their oil-wetting propensity on carbonates.

The former characteristic, acidity, may be quantified by the pKa (acid dissociation constant).

$$HA \leftrightarrows H^+ + A^- \qquad pKa = -\log \{ [H^+][A^-] / [HA] \}$$

where HA represents the undissociated NA, [A-] the carboxylate anion, and [H+] is the hydronium ion released from the acid. The lower the pKa, the stronger the acid. This property may be determined via an acid-base titration.

The latter characteristic, partitioning coefficient may be quantified by the so-called LogP, which is defined as

$$\log P = \log \{ [HA]_{\text{n-octanol}} / [HA]_{\text{water}} \}$$

The physical meaning of logP is the log of the ratio of the equilibrium concentration of a species in n-octanol to its concentration in an equal volume of fresh water at 25 ºC. The larger the value of logP, the greater is its concentration in the n-octanol versus water. The practical implication for our purposes is that the larger the logP, the greater the solubility of the NA in the hydrocarbon versus the aqueous phase.

These important properties of various NA may be estimated based on molecular dynamic calculation methods (Ma, et. al., 2003) developed recently for a different DOE supported project at California Institute of technology that concerns developing new refinery processes to reduce NA concentration in crude oils.

Acidities (pKa) and partitioning (logP) of various naphthenic acids (NAs) have been studied utilizing the first-principle density functional theory (DFT), in combination with the Poisson-Bolzmann continuum-solvation model to take the solvent effect into account. The *ab-inito* calculated gas-phase deprotonation energy provides a probe for the structural dependence of acidity, and theoretically predicted pKa values are in good agreement with experimental data for NA having measured values. Comparing the calculated solvation energy in water and n-octanol provides the logP value. Calculated results for pKa and log P are given below.

Table 1. Results of calculated pKa and logP of 10 selected carboxylic acids

Number	Chemical Name	dG	in water	in 1-Octanol	Edeprot	pka	logP	M.W
		(kcal/mol)	(kcal/mol)	(kcal/mol)	(kcal/mol)			(a.u.)
1	Benzoic Acid	-264023.56	-6.808	-9.387	343.69	**3.91**	**1.87**	122.100
1-anion		-263679.87	-80.51					
2	4-Heptylbenzoic Acid	-436618.30	-5.584	-9.129	342.96	**3.89**	**2.57**	220.310
2-anion		-436275.34	-78.58					
3	3-Phenylpropionic Acid	-312577.12	-8.246	-10.922	350.93	**4.40**	**1.94**	148.160
3-anion		-312226.19	-88.51					
4	Cyclohexanecarboxylic Acid	-266266.12	-5.499	-8.106	350.74	**4.39**	**1.89**	128.170
4-anion		-265915.38	-85.59					
5	Cyclohexanepropionic Acid	-315577.38	-5.144	-7.820	350.45	**4.38**	**1.94**	156.230
5-anion		-315226.93	-84.95					
6	Cyclohexanebutyric Acid	-340234.02	-4.861	-7.785	350.40	**4.36**	**2.12**	170.250
6-anion		-339883.62	-84.65					
7	Cyclohexanepentanonic Acid	-364889.57	-4.601	-7.828	350.20	**4.35**	**2.34**	184.280
7-anion		-364539.37	-84.20					
8	trans-4-Pentylcyclohexanecarboxylic Acid	-389545.45	-4.724	-7.690	349.41	**4.33**	**2.15**	198.310
8-anion		-389196.04	-83.57					
9	Tetradecanoic Acid (Myristic Acid)	-439605.67	-3.729	-6.902	350.77	**4.39**	**2.30**	228.400
9-anion		-439254.90	-83.84					
10	Octadecanoic Acid (Stearic Acid)	-538227.48	-2.780	-6.780	349.30	**4.39**	**2.90**	284.480
10-anion		-537878.17	-81.43					

The results are that the pKa values are similar among different NAs, ranging from 3.8 - 4.5. The acidity of these NA components exhibit little structural dependence. The steric hindrance is the predominant effect for saturates, yielding a difference of the calculated E_{deprot} of ~ 2.0 kcal/mol in the dilute gas-phase. Species with aromatic rings increase acidity (decrease pKa) due to the electron-withdrawing effect (4 ~ 6 kcal/mol decreasing of the calculated gas-phase E_{deprot}). The solvent effect, on the other hand, reduces these differences, rendering a ~1.0 difference of calculated pKa value for saturates and aromatics, corresponding to a Gibbs' free energy difference of 1.5 kcal/mol in aqueous solutions.

As expected, the molecular simulations predict that the partitioning of NA species between n-octanol and water (logP) increases with increasing hydrophobicity of the NA. For example, in the homologous series of cyclohexanoic acids, the logP increases from 1.89, 1.94, 2.12, and 2.34 as the length of the added alkyl chain goes from 0, 3, 4, and 5 carbons, respectively. In fact, we find the correlation between calculated logP and just the molecular weight is good (r^2 almost 0.9 -- see figure below), especially considering these selected carboxylic acids include aliphatics, saturated ring, and aromatic ring type compounds. Similarly in the literature, Havre (2003), reports a trend of partitioning between water and oil that is strongly related to the number of carbons, with a mild secondary effect of one-ring structures being slightly more hydrophilic than multiple rings.

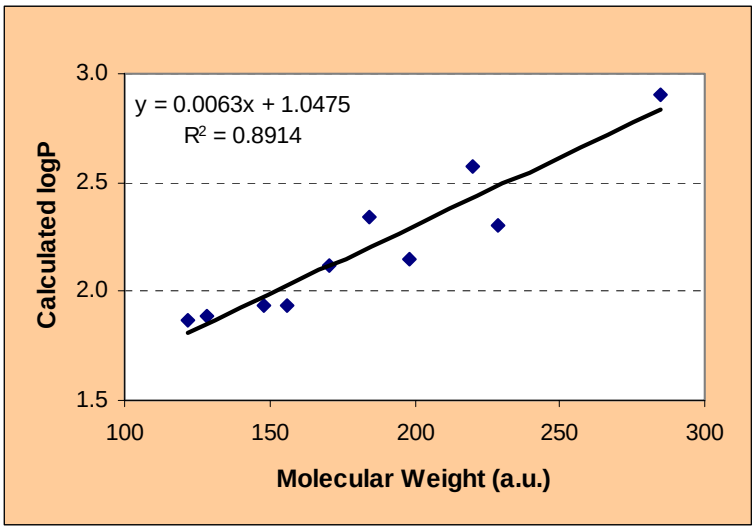

Figure 2. Correlation between calculated logP and the molecular weight of the 10 carboxylic acids considered.

Recommended for future study is to develop a molecular description of the calcite surface so that it may be included in any further molecular dynamic calculations that will examine the interaction energies between NA and calcite (to probe mechanisms associated with induced oil-wetting). Yet other future calculations could focus on subsequent energy interactions with this altered surface and candidate surfactants (to probe chemical mechanisms associated with the attempt to reverse the wetting and become a water-wet surface).

4. EXPERIMENTAL METHODS FOR CRUDE OIL STUDY

4.1 Brine Compatibility

A number of different commercial surfactants were screened for their compatibility with two different synthetic brines. One of these is representative of the McElroy Field and the other mimics the formation brine found in the Vacuum Field. Both of these fields are operated by Chevron and are located in the Permian Basin in West Texas.

The recipe for the McElroy brine is as follows:

Table 2. Recipe for Synthetic McElroy Reservoir Brine

	MW	mg/l		Ions	mg/l
NaCl	58.5	20000		Total Na	8819
Na2SO4	142	2950		Ca	1197
CaCl2.2H2O	147	4400		Mg	400
MgCl2.6H20	203.3	3350		SO4	1994
				Total Cl	15432
pH adjusted to	7			TDS	27483

The recipe for the Vacuum Field reservoir water has a much higher salt content.

Table 3. Recipe for Synthetic Vacuum Field Brine

	MW	mg/l		Ions	mg/l
NaCl	58.5	106350		Total Na	42785
Na2SO4	142	3000		Ca	2993
CaCl2.2H2O	147	11000		Mg	598
MgCl2.6H20	203.3	5000		SO4	2028
				Total Cl	71596
				TDS	120000
		Check the pH.		Adjust to	pH near 7

As shown above, this brine is 12 wt% Total Dissolved Solids (TDS), whereas the McElroy brine is a bit less than 3 wt%.

The test procedure for brine compatibility was to add the candidate surfactants at a concentration of 0.5 wt% (active basis) to the subject brine. After vigorous hand mixing the test tubes are set aside and allowed to sit. One series of test tubes were at room temperature, another placed in an oven held at 50 C, and a third set of test tubes stored at 75 C.

The clarity of each test tube was monitored, and notes were taken of the appearance of each solution after sitting static for one week at its respective temperature

4.2 Calcite Chip Cleaning Test for McElroy Crude Oil

This test method was developed and described in detail in the Topical Report that is included here as Attachment 1.

Just briefly, the procedure is to soak Iceland Spar calcite chips with McElroy crude oil and aging for 2 days at 80 ºC. This allows the crude oil to form an adherent film on the chips. Next, the chips are removed from the crude oil and the excess oil is allowed to drain off. Each treated chip is placed into a different surfactant test solution (0.1 wt% active basis) in synthetic McElroy brine. The apparent percentage of the chip area cleaned is noted at a series of different time intervals (see table below). Those surfactant solutions showing the most complete, quickest cleaning are the top candidates for the upcoming more involved oil recovery tests from cores.

4.3 Oil Recovery Tests for McElroy Crude Oil

In this test series, we evaluate the ability of several surfactants to recover the McElroy Field crude oil from limestone cores. These 1" x 2" cores were cut from a slab of Texas Crème limestone and provided by PTS (Petroleum Testing Service). The air permeability of these cores is fairly low, ranging from 5 – 20 md. The limestone cores were first dried at 120°C for 2 hours to remove adsorbed moisture. After cooling to room temperature, the cores were placed in a vacuum system for 4 hours and the crude oil was introduced and allowed to penetrate the cores over night to create a fully oil saturated condition. Then the saturated cores were placed into Amott cells containing the different surfactant solutions at a concentration of 0.2 wt% in synthetic McElroy brine. The details about this brine are given below.

As the aqueous phase imbibes into the core, oil is expelled and captured in the volumetric burette attached to the top of the cell. The Amott cells were maintained at room temperature and the oil recovery was monitored versus time.

5. RESULTS AND DISCUSSION FOR CRUDE OIL STUDY

5.1 Brine Compatibility

Table 4. Surfactant compatibility tests with McElroy Field

Test for Surfactant ---- Brine Compatibility McElroy Field -- Chevron -- Located in Texas Brine (TDS = 27483)						
Surfactants	**Manufacturer**	**HLB**	**wt.%**	**Clarity**		
Cationics(0.5 wt.%)				25 癈	50 癈	75 癈
C_8-trimethyl Amo Bromide	Alfa Aesar		99.0	**clear**	**clear**	**clear**
C_{10}-trimethyl Amo Bromide	Alfa Aesar		98.0	**clear**	**clear**	**clear**
C_{12}-trimethyl Amo Bromide	Aldrich		98.0	**clear**	**clear**	**clear**
C_{10}-triphenyl Phos Bromide	Avocado		98.0	s. cloudy	s. cloudy	**clear**
C_{12}-triphenyl Phos Bromide	Avocado		98.0	s. cloudy	s. cloudy	**clear**
ARQUAD 12-50	Akzo Nobel	17.1	62.5	**clear**	**clear**	**clear**
ARQUAD 18-50	Akzo Nobel	15.7	54.2	**clear**	**clear**	**clear**
ARQUAD C-50	Akzo Nobel	16.5	61.4	**clear**	**clear**	**clear**
ARQUAD S-50	Akzo Nobel	15.6	63.0	**clear**	**clear**	**clear**
ARQUAD T-50	Akzo Nobel	14.2	55.7	**clear**	**clear**	**clear**
ETHOMEEN C/12	Akzo Nobel	6.4	100.0	cloudy	cloudy	cloudy
ETHOMEEN C/15	Akzo Nobel	14.0	100.0	**clear**	s. cloudy	cloudy
Anionics(0.5 wt.%)						
Sodium Dodecyl Sulfate	Sigma(R)		99.0	inslouble	**clear**	**clear**
Sodium 1-decanesulfonate	Alfa Aesar(R)		99.0	inslouble	cloudy	**clear**
AEROSOL® OT-B	*CYANAMID*		99.6	inslouble	s. cloudy	s. cloudy
AEROSOL® GPG	*CYANAMID*		70.0	s. cloudy	s. cloudy	s. cloudy
AEROSOL® TR-70	*CYANAMID*		74.8	s. cloudy	cloudy	s. cloudy
AEROSOL® OT-S	*CYANAMID*		76.8	s. cloudy	cloudy	s. cloudy
AEROSOL® MA-80	*CYANAMID*		86.8	**clear**	**clear**	**clear**
AEROSOL® OT 75%	*CYANAMID*		73.9	s. cloudy	s. cloudy	s. cloudy
Nonionics(0.5 wt.%)						
Igepal® CO-520	Rhone-Poulenc	10.0	100.0	cloudy	s. cloudy	cloudy
Igepal® CO-530	Rhone-Poulenc	10.8	100.0	cloudy	s. cloudy	cloudy
Igepal® CO-630	Rhone-Poulenc	13.0	100.0	**clear**	s. cloudy	s. cloudy
Igepal® CO-710	Rhone-Poulenc	13.6	100.0	**clear**	**clear**	s. cloudy
Neodol® 1-3	Norman, FOX Co.	8.7	94.2	s. cloudy	s. cloudy	s. cloudy
Neodol® 1-5	Norman, FOX Co.	11.2	96.8	s. cloudy	s. cloudy	s. cloudy
Neodol® 1-7	Norman, FOX Co.	12.8	98.3	**clear**	s. cloudy	s. cloudy
Neodol® 1-9	Norman, FOX Co.	13.9	98.9	**clear**	**clear**	**clear**
Neodol® 23-6.5	Norman, FOX Co.	12.1	99.9	**clear**	s. cloudy	s. cloudy
Neodol® 25-3	Shell Chemicals	7.8	98.8	s. cloudy	cloudy	s. cloudy
Neodol® 25-7	Norman, FOX Co.	12.3	99.6	**clear**	**clear**	s. cloudy
Neodol® 25-9	Norman, FOX Co.	13.1	99.4	**clear**	**clear**	s. cloudy
Tergitol® 15-S-3	Union Carbide	8.3	98.7	s. cloudy	s. cloudy	**clear**
Tergitol® 15-S-5	Union Carbide	10.6	99.8	v. s. cloudy	s. cloudy	s. cloudy
Tergitol® 15-S-7	Union Carbide	12.4	98.8	**clear**	s. cloudy	s. cloudy
Tergitol® 15-S-9	Union Carbide	13.3	102.0	**clear**	v.s. cloudy	v. s. cloudy
Tergitol® 15-S-12	Union Carbide	14.7	100.2	**clear**	**clear**	**clear**
Tergitol® 15-S-20	Union Carbide	16.4	100.0	**clear**	**clear**	**clear**
Tergitol® 15-S-40	Union Carbide	18.0	99.9	**clear**	**clear**	**clear**
Triton™ X-35	Rohm & Hass	7.8	100.3	cloudy	s. cloudy	v. s. cloudy
Triton™ X-45	Union Carbide	9.8	100.2	cloudy	cloudy	v. s. cloudy
Triton™ X-100	Rohm & Hass	13.4	99.8	**clear**	s. cloudy	cloudy
Triton™ X-114	Aldrich(R)	12.3	100.5	s. cloudy	s. cloudy	cloudy
Triton™ X-165	Rohm & Hass	15.5	58.4	**clear**	**clear**	**clear**
Triton™ X-405	Aldrich(R)	17.6	70.1	**clear**	**clear**	**clear**
Triton™ X-705	Sigma(R)	18.4	70.4	**clear**	**clear**	**clear**
Tween® 21	ICI Chemicals	13.3	98.0	s. cloudy	cloudy	cloudy
Tween® 61	Sigma(R)	9.6	97.9	inslouble	cloudy	cloudy
Tween® 80	ICI Chemicals	15.0	98.6	**clear**	**clear**	**clear**
Tween® 81	ICI Chemicals	10.0	95.8	cloudy	cloudy	cloudy

Table 5. Surfactant compatibility tests with high salinity brine, 120,000 mg/l

Test for Surfactant ---- Brine Compatibility High Salt Brine (TDS = 120,000 mg/L)						
Surfactants	**Manufacturer**	**HLB**	**wt.%**	**Clarity**		
Cationics(0.5 wt.%)				25 癈	50 癈	75 癈
C_8-trimethyl Amo Bromide	Alfa Aesar		99.0	**clear**	**clear**	**clear**
C_{10}-trimethyl Amo Bromide	Alfa Aesar		98.0	**clear**	**clear**	**clear**
C_{12}-trimethyl Amo Bromide	Aldrich		98.0	**clear**	**clear**	**clear**
C_{10}-triphenyl Phos Bromide	Avocado		98.0	s. cloudy	cloudy	s. cloudy
C_{12}-triphenyl Phos Bromide	Avocado		98.0	s. cloudy	cloudy	s. cloudy
ARQUAD 12-50	Akzo Nobel	17.1	62.5	**clear**	**clear**	**clear**
ARQUAD 18-50	Akzo Nobel	15.7	54.2	s. cloudy	**clear**	**clear**
ARQUAD C-50	Akzo Nobel	16.5	61.4	**clear**	**clear**	**clear**
ARQUAD S-50	Akzo Nobel	15.6	63.0	**clear**	**clear**	**clear**
ARQUAD T-50	Akzo Nobel	14.2	55.7	**clear**	**clear**	**clear**
ETHOMEEN C/12	Akzo Nobel	6.4	100.0	cloudy	cloudy	cloudy
ETHOMEEN C/15	Akzo Nobel	14.0	100.0	**clear**	cloudy	cloudy
Anionics(0.5 wt.%)						
Sodium Dodecyl Sulfate	Sigma(R)		99.0	insloluble	s. cloudy	**clear**
Sodium 1-decanesulfonate	Alfa Aesar(R)		99.0	insloluble	cloudy	**clear**
AEROSOL® OT-B	*CYANAMID*		99.6	insloluble	**clear**	s. cloudy
AEROSOL® GPG	*CYANAMID*		70.0	s. cloudy	s. cloudy	s. cloudy
AEROSOL® TR-70	*CYANAMID*		74.8	s. cloudy	s. cloudy	s. cloudy
AEROSOL® OT-S	*CYANAMID*		76.8	s. cloudy	s. cloudy	s. cloudy
AEROSOL® MA-80	*CYANAMID*		86.8	s. cloudy	s. cloudy	s. cloudy
AEROSOL® OT 75%	*CYANAMID*		73.9	s. cloudy	s. cloudy	s. cloudy
Nonionics(0.5 wt.%)						
Igepal® CO-520	Rhone-Poulenc	10.0	100.0	cloudy	cloudy	s. cloudy
Igepal® CO-530	Rhone-Poulenc	10.8	100.0	cloudy	s. cloudy	s. cloudy
Igepal® CO-630	Rhone-Poulenc	13.0	100.0	**clear**	s. cloudy	cloudy
Igepal® CO-710	Rhone-Poulenc	13.6	100.0	**clear**	s. cloudy	cloudy
Neodol® 1-3	Norman, FOX Co.	8.7	94.2	s. cloudy	s. cloudy	v. s. cloudy
Neodol® 1-5	Norman, FOX Co.	11.2	96.8	s. cloudy	s. cloudy	s. cloudy
Neodol® 1-7	Norman, FOX Co.	12.8	98.3	**clear**	s. cloudy	s. cloudy
Neodol® 1-9	Norman, FOX Co.	13.9	98.9	**clear**	s. cloudy	s. cloudy
Neodol® 23-6.5	Norman, FOX Co.	12.1	99.9	s. cloudy	s. cloudy	s. cloudy
Neodol® 25-3	Shell Chemicals	7.8	98.8	s. cloudy	s. cloudy	v. s. cloudy
Neodol® 25-7	Norman, FOX Co.	12.3	99.6	**clear**	s. cloudy	s. cloudy
Neodol® 25-9	Norman, FOX Co.	13.1	99.4	**clear**	s. cloudy	s. cloudy
Tergitol® 15-S-3	Union Carbide	8.3	98.7	s. cloudy	s. cloudy	v. s. cloudy
Tergitol® 15-S-5	Union Carbide	10.6	99.8	s. cloudy	s. cloudy	v. s. cloudy
Tergitol® 15-S-7	Union Carbide	12.4	98.8	s. cloudy	cloudy	v. s. cloudy
Tergitol® 15-S-9	Union Carbide	13.3	102.0	**clear**	s. cloudy	v. s. cloudy
Tergitol® 15-S-12	Union Carbide	14.7	100.2	**clear**	s. cloudy	s. cloudy
Tergitol® 15-S-20	Union Carbide	16.4	100.0	**clear**	**clear**	s. cloudy
Tergitol® 15-S-40	Union Carbide	18.0	99.9	**clear**	**clear**	**clear**
Triton™ X-35	Rohm & Hass	7.8	100.3	cloudy	v.s. cloudy	**clear**
Triton™ X-45	Union Carbide	9.8	100.2	cloudy	s. cloudy	s. cloudy
Triton™ X-100	Rohm & Hass	13.4	99.8	**clear**	cloudy	cloudy
Triton™ X-114	Aldrich(R)	12.3	100.5	cloudy	s. cloudy	s. cloudy
Triton™ X-165	Rohm & Hass	15.5	58.4	**clear**	**clear**	cloudy
Triton™ X-405	Aldrich(R)	17.6	70.1	**clear**	**clear**	**clear**
Triton™ X-705	Sigma(R)	18.4	70.4	**clear**	**clear**	**clear**
Tween® 21	ICI Chemicals	13.3	98.0	s. cloudy	cloudy	cloudy
Tween® 61	Sigma(R)	9.6	97.9	insloluble	s. cloudy	s. cloudy
Tween® 80	ICI Chemicals	15.0	98.6	**clear**	**clear**	cloudy
Tween® 81	ICI Chemicals	10.0	95.8	cloudy	cloudy	cloudy

As expected, there are many more of the candidate surfactants compatible with the lower salinity case of the synthetic McElroy brine than the synthetic brine representative for the Vacuum Field. Also, as expected, as the water solubility of the surfactant increases (as indicated by an increase in its reported HLB value), this surfactant becomes more compatible. One important feature for the nonionic surfactants is that as the temperature increases, this generally decreases their solubility. The temperature at which these surfactants begin to create a cloudy appearance is termed the "cloud point".

The remainder of the project study with crude oil focused on the McElroy oil case, and so these are the brine compatibility results of direct relevance to this project.

5.2 Calcite Chip Cleaning Test for McElroy Crude Oil

Table 6. Surfactant screening test via cleaning of calcite chips coated with McElroy oil

Test for Surfactant ---- Calcite Chips Cleaning McElroy Field -- Chevron -- Located in Texas Brine (TDS = 27483)								
Surfactants	**2 hours**	**6 hours**	**24 hours**	**2 days**	**5 days**	**10 days**	**14 days**	**25 days**
Cationics								
1. C_8-trimethyl Amo Bromide	2%	10%	15%	15%	15%	15%	15%	15%
2. C_{10}-trimethyl Amo Bromide	2%	6%	10%	10%	12%	12%	15%	15%
3. C_{12}-trimethyl Amo Bromide	1%	5%	5%	6%	8%	8%	10%	12%
4. C_{10}-triphenyl Phos Bromide	3%	6%	6%	8%	10%	10%	25%	40%
5. C_{12}-triphenyl Phos Bromide	3%	5%	6%	10%	10%	10%	15%	15%
6. ARQUAD 12-50 17.1	1%	6%	8%	12%	15%	15%	20%	30%
7. ARQUAD 18-50 15.7	1%	6%	7%	15%	20%	20%	30%	30%
8. ARQUAD C-50 16.5	0%	5%	6%	6%	8%	8%	12%	12%
9. ARQUAD S-50 15.6	1%	4%	5%	8%	10%	10%	15%	15%
10. ARQUAD T-50 14.2	1%	3%	7%	10%	25%	75%	80%	90%
11. ETHOMEEN C/12 6.4	30%	50%	70%	80%	80%	80%	80%	80%
12. ETHOMEEN C/15 13.9	50%	80%	85%	85%	85%	85%	85%	90%
Anionics								
13. Sodium Dodecyl Sulfate	0%	0%	0%	0%	0%	0%	0%	0%
14. Sodium 1-decanesulfonate	1%	3%	6%	15%	15%	15%	15%	15%
Nonionics								
15. ALCODET 218 13.6	4%	5%	10%	10%	15%	15%	30%	35%
16. ALCODET SK 12.7	5%	8%	15%	15%	20%	20%	30%	35%
17. Antarox LF-222 n/a	2%	10%	15%	50%	60%	60%	75%	75%
18. Igepal® CA-620 12.0	2%	6%	7%	20%	20%	20%	30%	35%
19. Igepal® CA-630 13.0	5%	6%	8%	15%	15%	35%	40%	40%
20. Igepal® CO-520 10.0	4%	10%	25%	50%	60%	70%	80%	80%
21. Igepal® CO-530 10.8	5%	10%	25%	50%	70%	80%	85%	90%
22. Igepal® CO-630 13.0	3%	15%	20%	40%	45%	50%	60%	70%
23. Igepal® CO-710 13.6	5%	20%	30%	40%	55%	60%	70%	70%
24. Neodol® 1-3 8.7	40%	80%	90%	90%	92%	93%	95%	96%
25. Neodol® 1-5 11.2	6%	10%	15%	20%	20%	20%	30%	40%
26. Neodol® 1-7 12.8	6%	15%	25%	55%	65%	65%	70%	70%
27. Neodol® 1-9 13.9	5%	15%	30%	70%	75%	75%	80%	80%
28. Neodol® 23-6.5 12.1	1%	5%	8%	12%	12%	12%	15%	15%
29. Neodol® 25-3 7.8	5%	60%	70%	85%	85%	87%	90%	90%
30. Neodol® 25-7 12.3	4%	50%	60%	75%	80%	80%	86%	88%
31. Neodol® 25-9 13.1	4%	20%	25%	55%	60%	65%	75%	80%
32. Tergitol® 15-S-3 8.3	4%	6%	40%	75%	75%	75%	75%	75%
33. Tergitol® 15-S-5 10.6	10%	20%	60%	60%	70%	85%	88%	90%
34. Tergitol® 15-S-7 12.4	3%	5%	50%	70%	70%	70%	70%	70%
35. Tergitol® 15-S-9 13.3	1%	2%	30%	50%	60%	60%	65%	65%
36. Tergitol® 15-S-12 14.7	1%	2%	20%	40%	40%	40%	40%	40%
37. Tergitol® 15-S-20 16.4	3%	5%	10%	30%	45%	45%	45%	65%
38. Tergitol® NP-4 8.9	2%	7%	10%	10%	20%	40%	45%	50%
39. Tergitol® NP-6 10.9	3%	70%	80%	90%	95%	96%	97%	98%
40. Tergitol® NP-9.5 13.1	4%	40%	50%	50%	65%	65%	70%	70%
41. Tergitol® NP-10 13.2	4%	10%	40%	60%	60%	70%	70%	75%
42. Triton™ BG-10 n/a	0%	0%	0%	20%	30%	30%	30%	50%
43. Triton™CG-110 n/a	0%	0%	0%	10%	30%	30%	30%	50%
44. Triton™ X-35 7.8	2%	20%	30%	40%	60%	65%	65%	70%
45. Triton™ X-45 9.8	30%	70%	75%	85%	85%	85%	90%	90%
46. Triton™ X-100 13.4	2%	15%	20%	60%	65%	65%	75%	75%
47. Triton™ X-114 12.3	2%	15%	30%	60%	70%	75%	80%	80%
48. Triton™ X-165 15.5	3%	4%	10%	20%	25%	30%	50%	55%

The results above identify a number of these surfactants with promising performance. The better products include among the cationic surfactants 3 different products from Akzo Nobel:

	% Cleaning	
Product	6 hours	10 days
ARQUAD T-50	3	75
ETHOMEEN C/12	50	80
ETHOMEEN C15	80	85

It is somewhat surprising that not more of the cationic surfactants would exhibit good performance in this chip-cleaning screening test. Previous experience for other systems showed that usually the cationic surfactants are more effective, but more costly than nonionic surfactant products.

Among the nonionic surfactants, several exhibited good performance, with the best products including:

		% Cleaning	
Product	HLB	6 hours	10 days
Neodol 1-3	8.7	80	93
Neodol 25-3	7.8	60	87
Neodol 25-7	12.3	50	80
Tergitol NP-6	10.9	70	96
Triton X-45	9.8	70	85

In this case, the optimum HLB is approximately 10 for the nonionic surfactants tested. These product seem to be “on the edge” with respect to their solubility in the McElroy synthetic brine. Having a marginal solubility in the brine could be preferred as it would tend to drive the surfactant to have increased interaction with the oil and reservoir rock surfaces.

5.3 Oil Recovery Tests for McElroy Crude Oil

In this test series, we evaluate the ability of several surfactants to recover McElroy crude oil via imbibition from outcrop Texas Crème limestone cores. The photograph below illustrates oil recovery that occurs after about two weeks of soaking time with these surfactant samples.

(a) (b)

Figure 3. Photographs of 8 different Amott cell experiments taken a) at the start of the imbibition experiment and b) after about 3 weeks of elapsed time.

This shows visually that there can be a substantial difference in performance among the surfactants that were included in this evaluation.

The Figures 4 - 9 show the percent oil recovery versus time for some of the surfactant solutions tested in this project. The results are plotted both versus time on arithmetic and as a logarithmic scale. Figures 8 and 9 provide a comparison of repeat oil recovery imbibition experiments with the two primary alcohol nonionic surfactants Neodol 1-7 and 1-9.

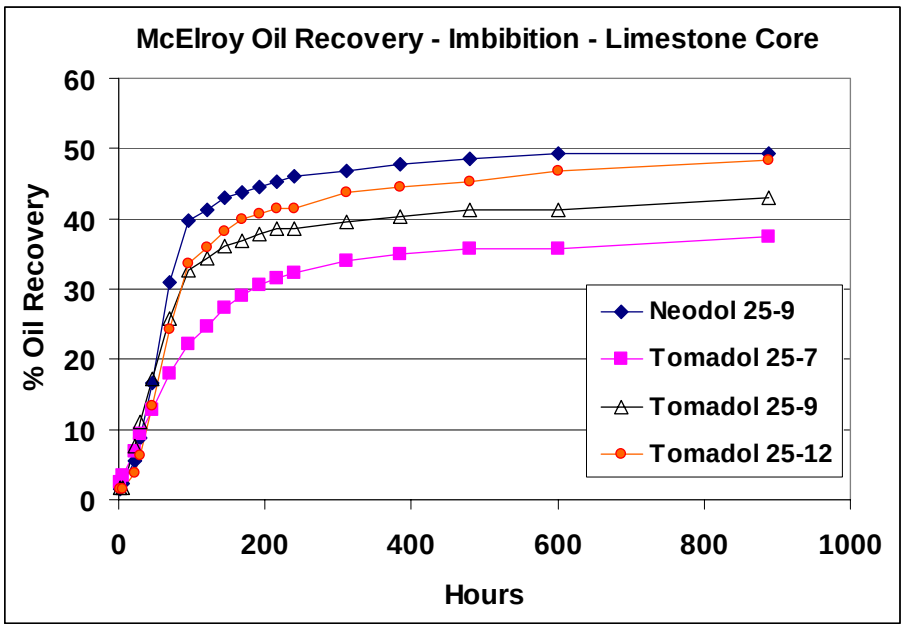

Figure 4. Oil recovery via imbibition from a limestone core saturated with McElroy crude oil. Results for 4 different nonionic surfactants.

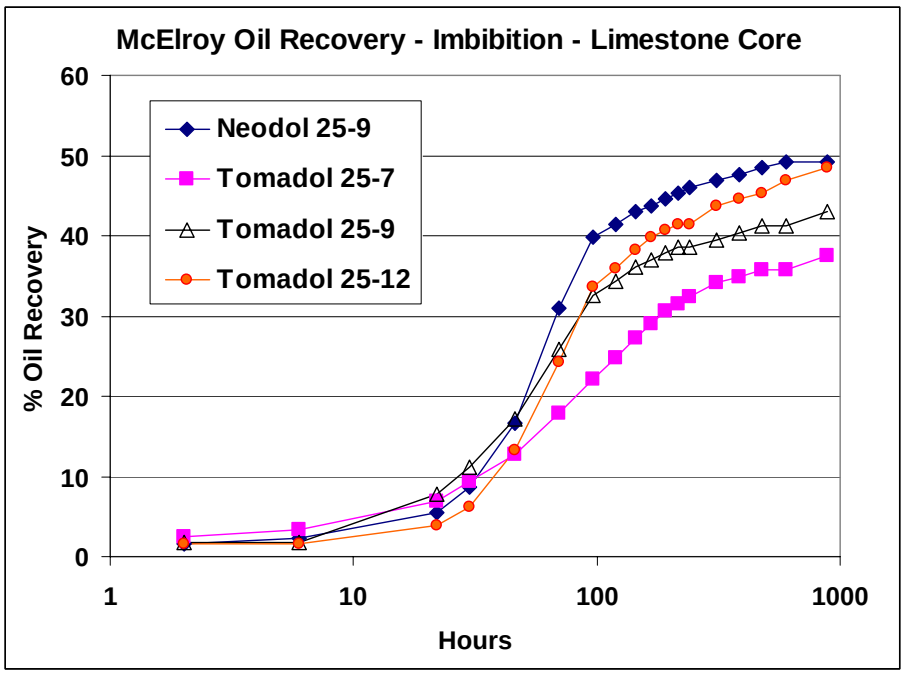

Figure 5. Oil recovery via imbibition from a limestone core saturated with McElroy crude oil. Results for 4 different nonionic surfactants. Log scale used for the time scale.

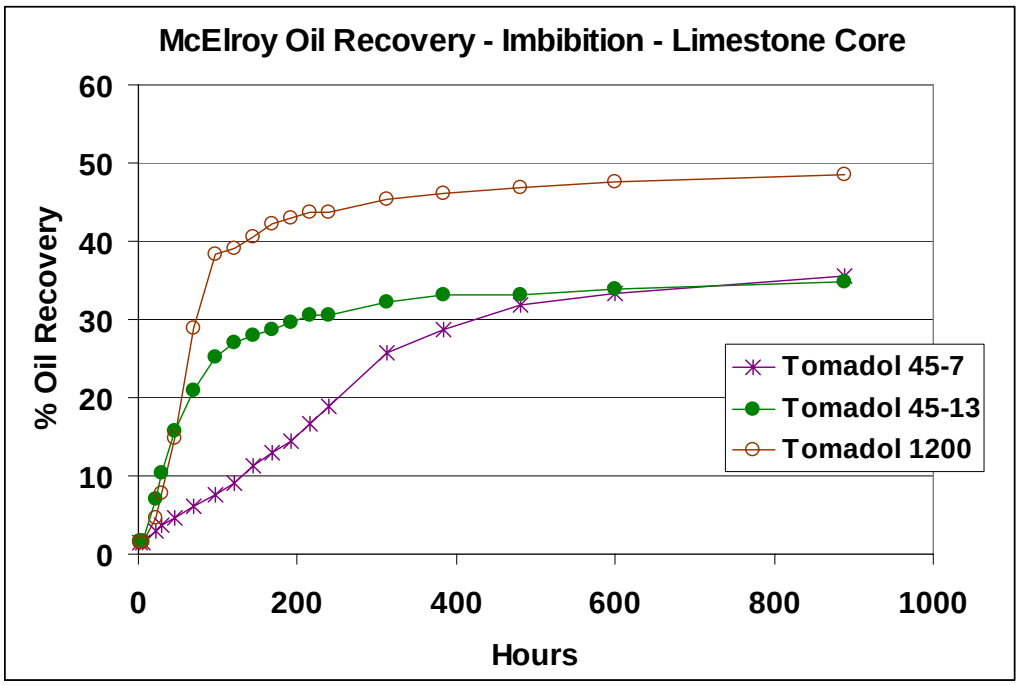

Figure 6. Oil recovery via imbibition from a limestone core saturated with McElroy crude oil. Results for 3 different nonionic surfactants.

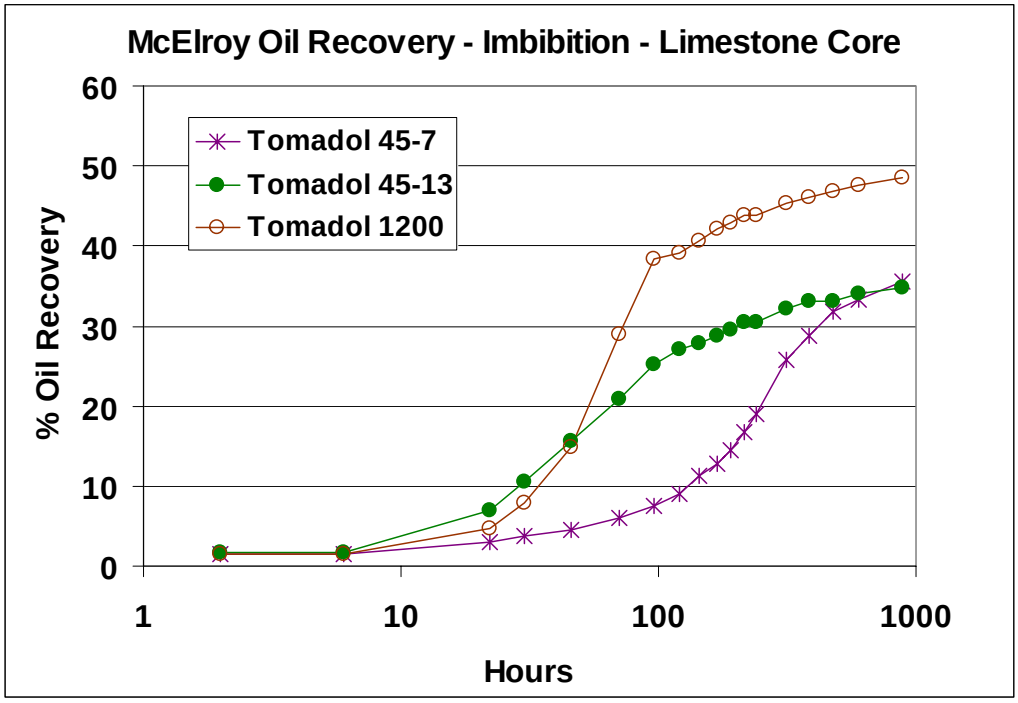

Figure 7. Oil recovery via imbibition from a limestone core saturated with McElroy crude oil. Results for 3 different nonionic surfactants. Log scale used for the time scale.

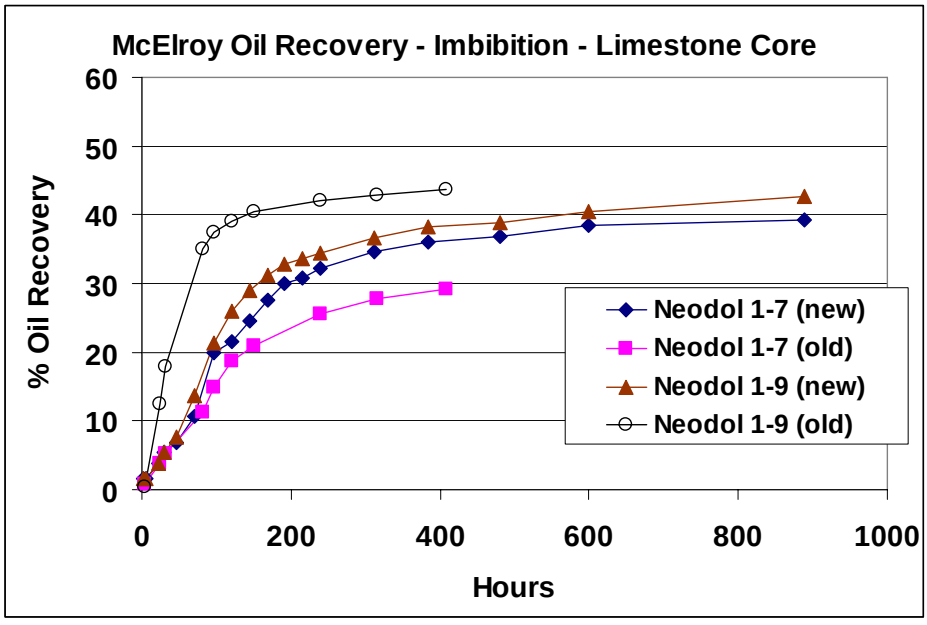

Figure 8. Oil recovery via imbibition from a limestone core saturated with McElroy crude oil. Comparison of results of oil recovery for Neodol 1-7 and Neodol 1-9 from the previous and current set of experiments.

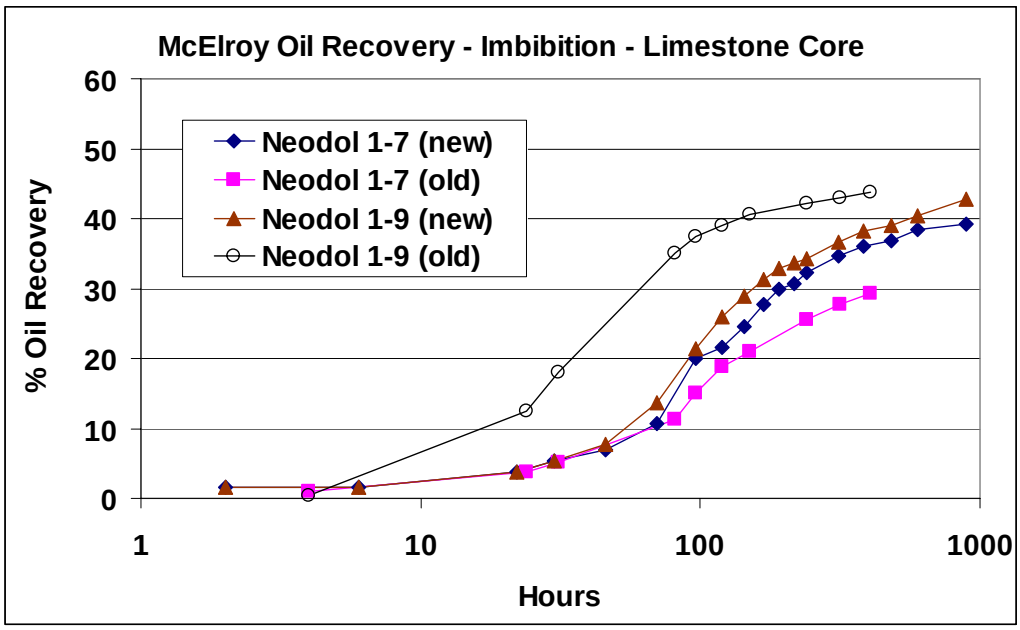

Figure 9. Oil recovery via imbibition from a limestone core saturated with McElroy `crude oil. Comparison of results of oil recovery for Neodol 1-7 and Neodol 1-9 from the previous set and current set of experiments. Log scale used for the time elapsed.

The oil recoveries do not show a large range of response. This is in part due to the deliberate selection biased towards surfactants thought to be potentially good oil products. That is, the only surfactants evaluated for oil recovery were those where their other behavior would suggest a high probability of good performance to displace oil by imbibition.

Similar to the general behavior we reported previously for the model oil system (NA in n-decane), we find one useful way to characterize the surfactants is by their HLB. The table below compares the oil recovery and HLB for different classes of ethoxylated nonionic surfactants.

Table 7. Comparison of Oil Recovery and Surfactant HLB for Different Classes of Nonionic Surfactants

Primary Alcohols	% Oil Recovery	HLB
Neodol 1-5	25.4	11.2
Neodol 1-7 (a)	32.7	12.8
Neodol 1-9 (b)	40.9	13.9
Neodol 23-6.5	27.0	12.1
Tomadol 25-7 *	34.9	12.3
Neodol 25-9 *	47.7	13.1
Tomadol 25-9 *	40.4	13.0
Tomadol 25-12 *	44.5	14.4
Tomadol 45-7 *	28.8	11.6
Tomadol 45-13 *	33.1	14.4
Secondary Alcohols		
Tergitol 15-S-7	25.1	12.4
Tergitol 15-S-9	18.6	13.3
Tergitol 15-S-12	33.6	14.7
Tergitol 15-S-20	34.3	16.4
Nonyl phenols ehtoxylated		
Igepal CO-630	31.0	13.0
Tergitol NP-9.5	26.5	13.1
Tergitol NP-10	32.6	13.2
Tomadol 1200 *	46.1	13.6

* surfactants tested in the most recent period
(a) average of previous and new run -- 29.2% and 36.1%
(b) average of previous and new run -- 43.7% and 38.2%

Figure 10 below shows the oil recovery tends to increase with an increase in the HLB of these selected nonionic surfactants, at least over the range of HLB we tested here. Earlier oil recovery tests in this project using a model oil / fresh water system showed a similar behavior of having an "optimum" HLB of the nonionic surfactant for best oil recovery. However, the HLB for best performance with the model oil and fresh water system was found generally to be lower, more in the range of 10 - 12. This is consistent with the idea that a higher HLB surfactant would be a better match for a system where the aqueous phase is a higher salinity and by itself reduces the surfactant solubility of the treatment solution.

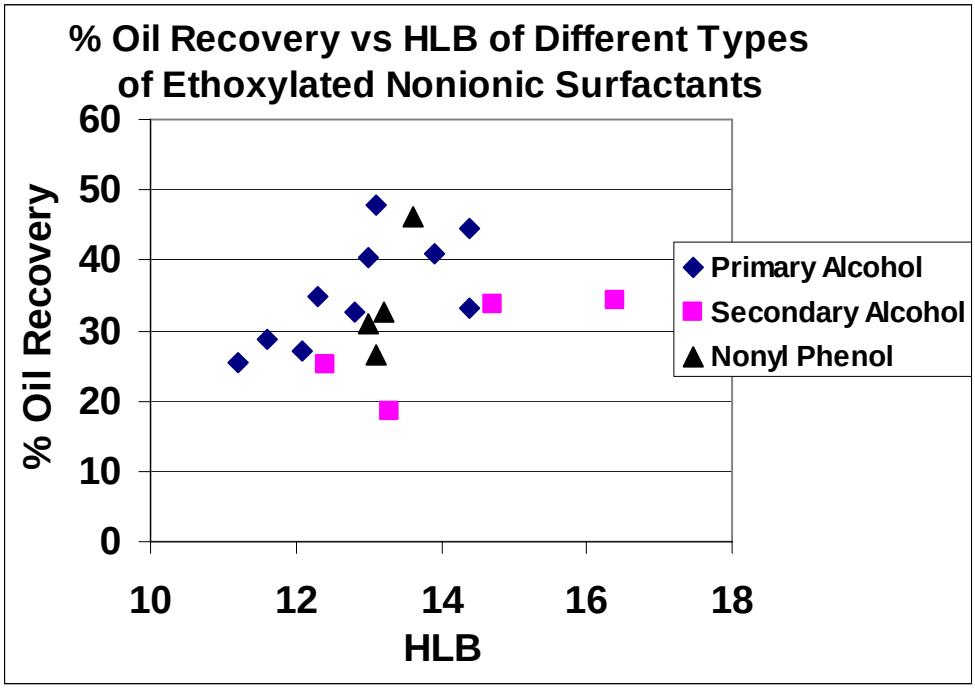

Figure 10. Recovery of McElroy crude oil by imbibition for 408 hours from limestone core versus the HLB for different types of nonionic surfactants (0.2 wt% in a synthetic McElroy brine). Experiments conducted at room temperature.

The results shown in Figure 10 indicate that the type (general structure) of the nonionic surfactant makes a difference in its performance. In particular, the primary alcohol type (linear alkyl chain) performs better than a secondary one (branched alkyl chain). The nonyl phenol type appears to have roughly the same performance as the primary alcohol-based ethoxylated surfactants.

6.0 CONCLUSIONS

The conclusions for this project are subdivided into its three major components:

Conclusions regarding the test methods created to evaluate surfactant properties and their potential as oil recovery agents for fractured carbonates:

1. One screening test was developed for surfactant recovery performance based on the relative ability of different chemical formulations to remove oil that is coating a clear calcite chip. These tests can be designed to be relatively simple and quick to perform (only a few days exposure time) and provide a measure of relative performance of removing oil coating a carbonate mineral surface, and thereby an indication of the surfactant's ability to recover incremental oil via enhancing aqueous phase imbibition into carbonate porous media.

2. A second surfactant screening test was developed based on the ability of an aqueous chemical solution to make an oil-wet calcite powder water-wet. This method also is a

relatively quick and easy procedure to screen surfactant for their potential performance as EOR agent for carbonate reservoirs. The general procedure is to render a powdered carbonate material oil-wet, and then add it to a surfactant solution. After agitating and aging this suspension, the success in converting the powder to a water-wet condition is indicated by the fraction of the powder that is made to sink. This is compared to the blank case with no surfactant in which almost all of the powder (still oil-wet) will float.

Conclusions regarding the study with model oil compounds (naphthenic acids in n-decane) for their wetting behavior on carbonate surfaces and recovery of the model oil from limestone cores:

1. Adsorption of naphthenic acids on calcite surface in n-decane media is in the order: cyclohexanepropionic acid > cyclohexanebutyric acid > cyclohexanepentanoic acid. Because these three naphthenic acids are analogues in term of molecular structure, this indicates that adsorption of the NAs decreases with increase of alkyl chain length from 2 $-CH_2-$ to 4 $-CH_2-$ groups.

2. In term of volume percentage of calcite powder floating on water, the oil-wettability of calcite powder treated with different naphthenic acids is in the order: trans-4-pentylcyclohexane carboxylic acid ~ cyclohexanepentanoic acid > cyclohexanebutyric acid > cyclohexanepropionic acid > cyclohexanecarboxylic acid. It is almost in reverse order of adsorption on calcite surface. This indicates that their ability to alter calcite surface to become oil-wet depends on their molecular structures.

3. Contact angle and novel flotation test results are consistent in ranking oil-wet conditions. At equilibrium, contact angle of water on the calcite surface treated with naphthenic acids is in the order: trans-4-pentylcyclohexanecarboxylic ~ cyclohexanepentanoic > cyclohexanebutyric > cyclohexanepropionic > cyclohexanecarboxylic > fresh calcite surface. The untreated calcite surface has the smallest contact angle for water, which is 21°. This is exactly in the same order as the flotation results.

4. Among the 12 selected surfactants studies, cationic surfactants are generally more efficient in recovering model oil from a limestone core than the others, but one nonionic surfactant, Igepal CO-530 has also been found to be very efficient for oil recovery. For the two quaternary phosphonium cationic surfactants, C_{10}TPPB and C_{12}TPPB, these phosphonium surfactants with bulky head groups recovered the model oil in limestone cores most efficiently.

5. The results of wettability alteration using different surfactant aqueous solutions in a simple flotation test are consistent with oil recovery by spontaneous imbibition of the selected surfactant aqueous solutions. For example, cationic Arquad T-50 and nonionic Igepal CO-530 are efficient in altering wettability of treated calcite powder from oil-wet to water-wet condition, and they also are efficient in oil recovery.

Concluding remarks regarding the oil recovery tests:

1. Oil recovery tests with McElroy oil in outcrop limestone cores show a similar trend as with

our previous results using a model oil phase (n-decane and a naphthenic acid mixture). The performance of each series of nonionic surfactants can be related to some fair degree to the HLB of the (nonionic) surfactant. The better performing surfactants can recover almost half of either the model oil or the McElroy crude oil from a 1"by 2" limestone core in an Amott imbibition cell within a couple of weeks.

2. The oil recovery performance may depend upon the general type of surfactant structure. The data indicate ethoxylated surfactants based on primary alcohol or nonyl phenol are more efficient that those based on secondary alcohols for recovery of the McElroy crude oil.

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Attachments

Attachment 1

Topical Report –- "Screening Methods for Selection of Surfactant Formulations for IOR from Fractured Carbonate Reservoirs"

Paper SPE 99612 -- Study of Wetting Behavior and Surfactant EOR in Carbonates with Model Compounds

Attachment 1

Topical Report –- "Screening Methods for Selection of Surfactant Formulations for IOR from Fractured Carbonate Reservoirs"

ABSTRACT

This topical report presents details of the laboratory work performed to complete Task 1 of this project; developing rapid screening methods to assess surfactant performance for IOR (Improved Oil Recovery) from fractured carbonate reservoirs. The desired outcome is to identify surfactant formulations that increase the rate and amount of aqueous phase imbibition into oil-rich, oil-wet carbonate reservoir rock. Changing the wettability from oil-wet to water-wet is one key to enhancing this water-phase imbibition process that in turn recovers additional oil from the matrix portion of a carbonate reservoir.

The common laboratory test to evaluate candidate surfactant formulations is to measure directly the aqueous imbibition rate and oil recovery from small outcrop or reservoir cores, but this procedure typically requires several weeks. Two methods are presented here for the rapid screening of candidate surfactant formulations for their potential IOR performance in carbonate reservoirs. One promising surfactant screening protocol is based on the ability of a surfactant solution to remove aged crude oil that coats a clear calcite crystal (Iceland Spar). Good surfactant candidate solutions remove the most oil the quickest from the chips, plus change the apparent contact angle of the remaining oil droplets on the surface that thereby indicate increased water-wetting. The other fast surfactant screening method is based on the flotation behavior of powdered calcite in water. In this test protocol, first the calcite power is pre-treated to make the surface oil-wet. The next step is to add the pre-treated powder to a test tube and add a candidate aqueous surfactant formulation; the greater the percentage of the calcite that now sinks to the bottom rather than floats, the more effective the surfactant is in changing the solids to become now preferentially water-wet. Results from the screening test generally are consistent with surfactant performance reported in the literature.

Screening Methods for Selection of Surfactant Formulations for IOR from Fractured Carbonate Reservoirs

DOE Project: DE-FC26-04NT15521

Topical Report June 2005

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Co-PI: Yongchun Tang
Senior Staff: Patrick Shuler and Mario Blanco
Postdoctoral Scholars: Yongfu Wu and Seung Soon Jang
California Institute of Technology

1.0 EXECUTIVE SUMMARY

This topical report presents details of the laboratory work performed to complete Task 1 of this project; namely developing rapid screening methods to assess surfactant performance for IOR (Improved Oil Recovery) from fractured carbonate reservoirs. The desired action is to have the chemical (surfactant) additive increase the rate and amount of aqueous phase imbibition into oil-rich, oil-wet carbonate reservoir rock, and thereby displace some of the oil normally still trapped in place after a conventional waterflood. A key to improve the rate of water imbibition is to have the surfactant change the mineral surfaces from an oil-wet to a water-wet condition. The normal laboratory test to mimic the field process measures the aqueous imbibition rate and oil recovery from small outcrop or reservoir cores, but this is a very time consuming procedure.

Two methods are presented here for the rapid screening of candidate surfactant formulations for their potential IOR performance. One promising surfactant screening protocol is based on the ability of a surfactant solution to remove aged crude oil that coats a clear calcite crystal (Iceland Spar). Good surfactant candidate solutions exhibit the greatest and fastest removal of oil from the calcite chip, plus change the apparent contact angle of the remaining oil droplets on the surface so as to indicate a more water-wet condition. Screening tests were performed both with a heavy crude oil from the San Joaquin Valley and a light oil from McElroy Field, a major carbonate field in the Permian Basin. This technique was used successfully to screen almost 250 different surfactants. The observations from this surfactant screening test are largely consistent with the oil recovery performance results reported in the literature.

The other fast surfactant screening method is based on the flotation behavior of powdered calcite in water. In this test protocol, first the calcite power is pre-treated to make the surface oil-wet. The next step is to add the pre-treated powder to a test tube and add a candidate aqueous formulation and shake the suspension. The calcite powder that is still oil-wet stays at the top of the water column. The greater the percentage of the calcite that now sinks to the bottom rather than floats, the more effective the surfactant is in changing the solids to become now preferentially water-wet. Those surfactant solutions that are efficient in altering the wettability to a water-wet condition are then better candidates for further testing as agents to promote rapid imbibition of an aqueous phase into oil-saturated carbonate porous media.

2.0 INTRODUCTION

The goal of this ongoing project is to develop cost-effective chemical formulations that will recover incremental oil beyond a waterflood operation from carbonate reservoirs. About 80% of carbonate reservoirs are classified as neutral to oil-wet (Standnes and Austand, 2002), and an oil-wetting condition is even more likely to be the case in cooler, more shallow reservoirs (Austad and Standnes, 2000). The particular target for this improved technology is large, domestic carbonate reservoirs that are at a mature point in their waterflood operations, most especially those that are fractured reservoirs and with the matrix blocks in an oil-wet state. For such reservoirs, the waterflood is usually very inefficient, in part, because the injection water can not imbibe into the porous, matrix blocks due to their oil-wet condition.

Adding the right surfactants to the injection water will change the wettability of the carbonate reservoir surfaces to a water-wet condition and decrease the interfacial tension (IFT) so as to increase the penetration of the injected aqueous phase into the rock matrix holding trapped oil. The oil forced out of the oil-rich matrix blocks due to the imbibition of the aqueous (chemical) solution then is forced into the fracture/high permeability network. These flow networks act as a "highway" to convey the newly mobilized oil to a production well. If properly designed, this process will increase significantly the recovery of this oil otherwise not recovered by a conventional waterflood.

The conventional procedure to evaluate candidate surfactant solutions is to immerse an outcrop or reservoir core sample high in oil saturation into a container (Amott cell) containing a surfactant solution held at reservoir temperature (Austad and Standes, 2002, Chen, 2000, Hirasaki, and Zhang, 2004, Seethpalli, 2004). The amount of oil produced moves into a graduated burette attached to the top of the container. The oil recovered is monitored versus time; of course the greater the volume and the faster the oil produced, the better the surfactant performance. This test has the advantage of being a fair physical analog to the actual field conditions, but a major disadvantage is that the time required to perform this test (requires several days or even weeks).

The objective of Task 1 of this project is to develop rapid screening methods to evaluate quickly and conveniently candidate surfactant formulations for their potential performance as IOR agent for fractured carbonate reservoirs. This report summarizes the procedures and results of two such rapid screening test methods.

3.0 FAST METHODS FOR CHEMICAL FORMULATION SCREENING

3.1 Calcite Chip Screening Method to Evaluate Surfactant Performance for Changing Carbonate Mineral to Become Water-Wet

3.1.1 Procedure for Calcite Chip Screening Method

The developed test procedure and the rationale for these procedures are:

1. Select clear calcite crystals (Iceland Spar), roughly ½" on each edge. These calcium carbonate crystals come from Ward's Natural Science (Catalog 46-1437), and are attractive for this screening test program because they are inexpensive and are clear with flat smooth sides. This means it is easy to see where the oil is removed from the surface, and to observe and estimate the contact angle of the oil drops that remain on the surface.

2. Soak the crystals in warm (80 ºC) crude oil. This will render the surface oil-wet and provide a target for removal by candidate chemical formulations. The heavy crude selected comes from Midway-Sunset Field (identified as Fee oil) located in the San Joaquin Valley (SJV), and was supplied by Chevron. This heavy oil is typical of that located in shallow sandstone formations and that are produced by steam flood projects in SJV. It has a relatively high viscosity and significant asphaltene and naphthenic acid content (has a high acid number of approximately 4). In this test the oil covers the calcite crystal completely and forms a layer of "sticky" oil that wets the surface well and adheres to the crystal. The concept is that this heavy, high acid number oil provides a more difficult screening test than with a chip coated with lighter oil. For the heavy oil the chips were aged for one day. Fewer, similar tests were performed with the McElroy crude oil; some of these calcite chips were aged with McElroy crude oil for only one day and some for one week.

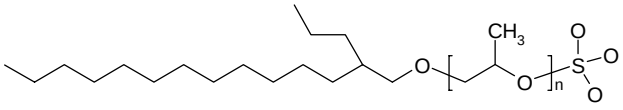
3. Pick out a single crystal with a pair of tweezers and let the excess hot oil drain off. Place the crystal into a small bottle containing 20 grams of surfactant solution. Our default conditions are 0.1 wt% (active) of surfactant in a synthetic brine (2 wt% NaCl, with 20 ppm of calcium). Some tests involving McElroy oil used a synthetic McElroy brine as the make-up water for surfactant solutions (see table below).

Table 1. Recipe for McElroy Field synthetic field brine:

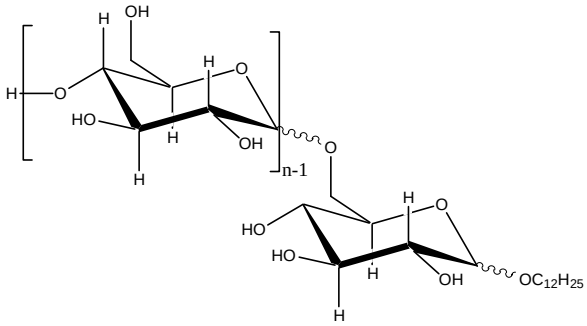
Salt	mg/l		Ion	mg/l
NaCl	20000		Na	8838
Na2SO4	2950		Ca	1197
CaCl2.2H2O	4400		Mg	400
MgCl2.6H20	3350		SO4	1000
NaHCO3	70		Cl	18835
TDS	30770		HCo3	51

4. Monitor at room temperature the appearance of the crystal versus elapsed time (e.g. 8 hours, 1 day, 3 days, 1 week, 1 month and 2 months). In particular, note the percent of the crystal surface that is cleared of oil and visible, and also estimate the contact angle of the remaining oil drops on the crystal surfaces. Note by our convention 0º refers to the oil drop spreading on the surface (completely oil-wet) and 180º refers to the oil not wetting the calcite crystal. Also observe if the bulk aqueous solution remains clear or discolored, thereby indicating some of the oil is solubilized into the surfactant solution, and if there is floating crude oil visible on top of the aqueous phase (indicates removal of some crude as free oil from the calcite chip).

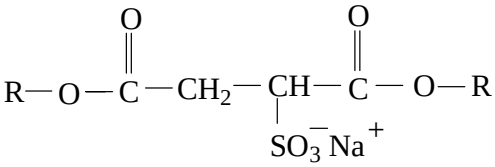
The figure below provides chemical structure information for many of the products tested with the screening tests.



Branched alkyl propoxylated sulfates (Alfoterra)

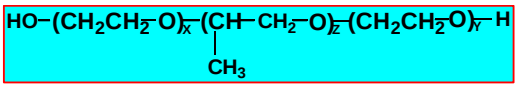


alkyl polyglycoside (APG)



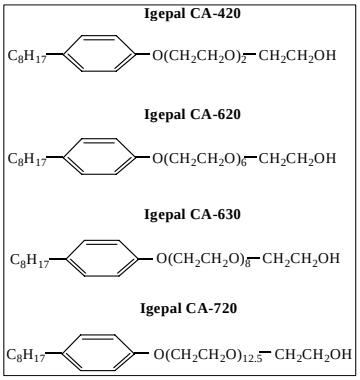
Sulfosuccinate Surfactant (Aerosol Series)

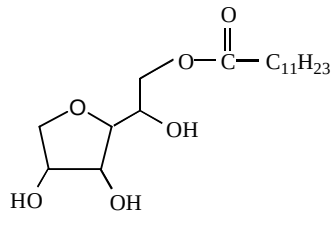
Aerosol MA-80 R = branched C6 Aerosol OT-B R = branched C8
Aerosol TR-70 R=linear C13



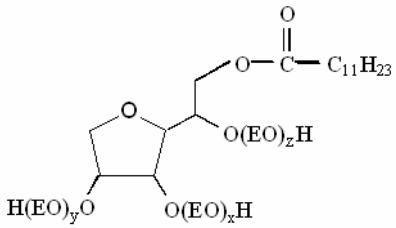
Pluronic block co-polymers of EO – PO – EO

Examples of Igepal series of surfactants (octyl- and nonyl-phenol ethoxylates)





Example of SPAN surfactant (SPAN 20)



Example Structure of Tween Surfactants

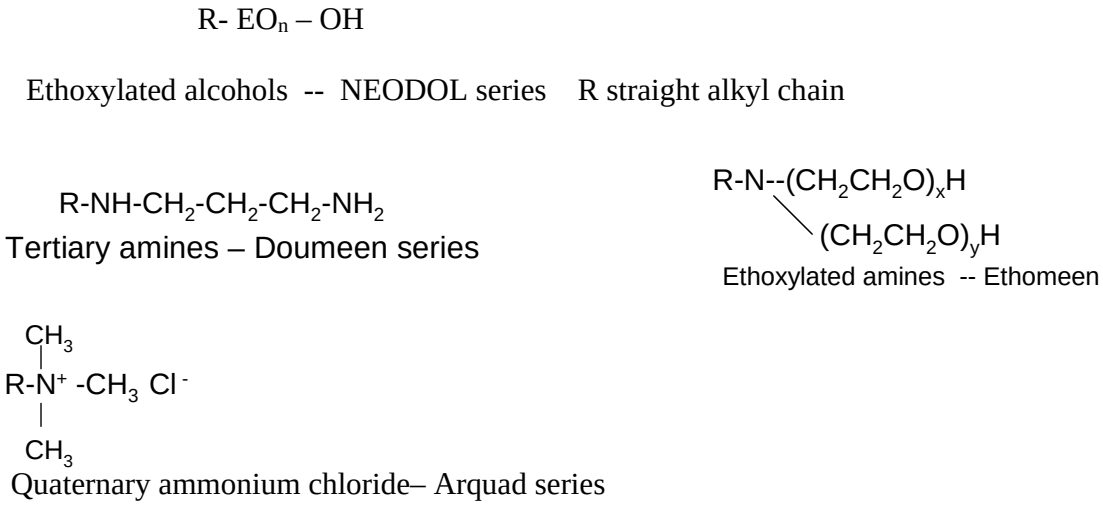


Figure 1. Chemical Structure of Selected Surfactants

3.1.2. ***Results/Discussion - Calcite Chip Screening Method – Heavy Oil***

The photographs below illustrate the test procedure and observations used to evaluate the surfactant solution performance.

Figure 2. (Left) -- calcite crystal initially coated with a heavy oil and immersed in a surfactant solution
(Right) - calcite crystal after several weeks exposure to an efficient surfactant. Almost all of the surface of the crystal is visible.

Figure 3. Photograph of calcite crystal after being submerged in an efficient surfactant solution for one month. Note the blob of oil leaving the surface and oil on top.

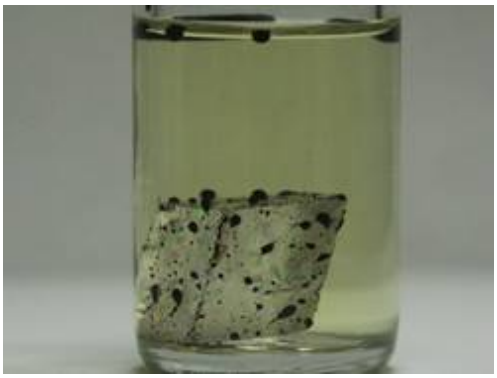


Figure 4. Photograph showing a calcite crystal with only a few drops of heavy crude oil still on the surface. The contact angle of the oil drops are estimated by eye.

The graph immediately below shows an example of the data collected for each of the surfactant solutions versus time. As expected, the percent of the area cleaned and the increase in contact angle of the oil droplets remaining on the surface both increase with length of exposure.

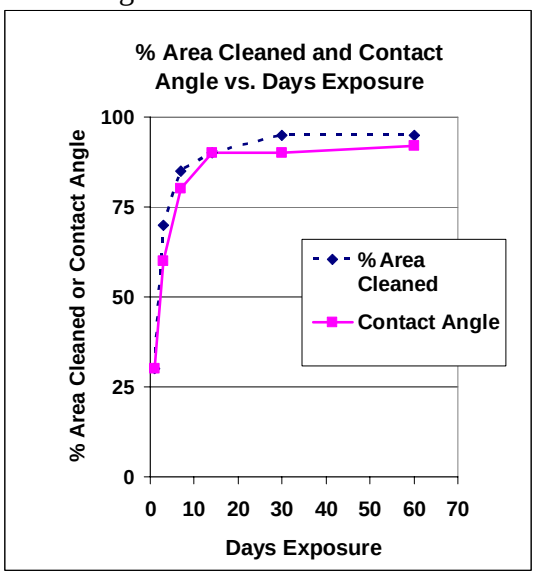


Figure 5. Example of raw data collected -- response for a Neodol 25-3 (nonionic ethoxylated alcohol) surfactant solution.

Appendix A has a complete list of the surfactant-cleaning results for calcite chip results with the heavy oil pre-treatment.

Data tends observations:
1. There is a rough correlation between the percent of the area cleared of heavy oil and the estimated contact angle of the oil remaining on the crystal. See the figure below. It would be expected that surfactant solutions that clean the crystal surface also are acting to increase the

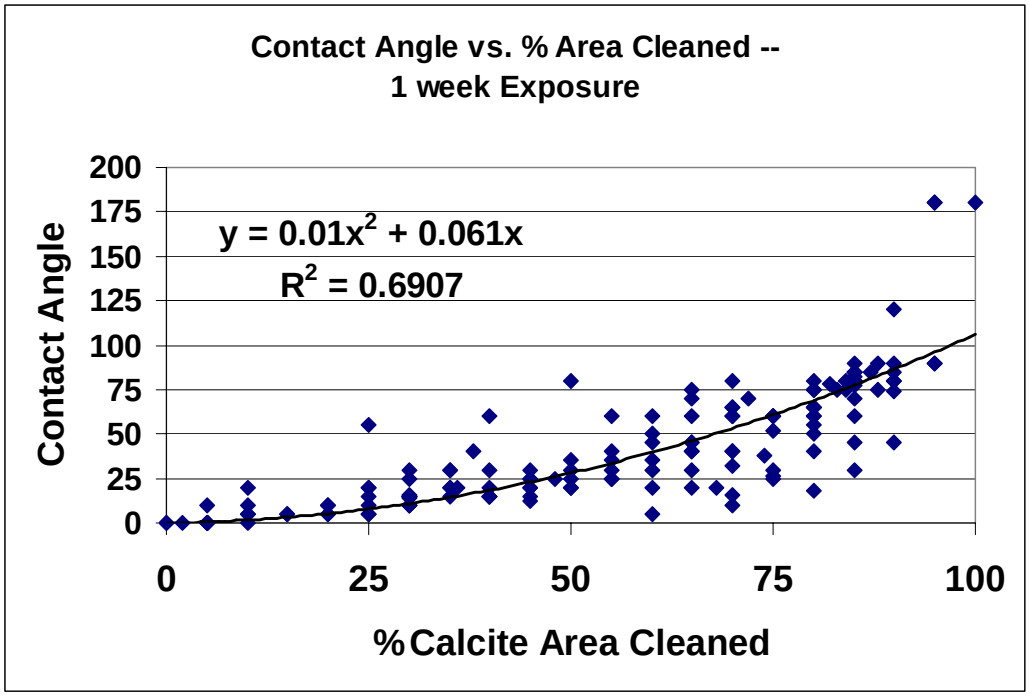


Figure 6. Correlation between contact angle of oil remaining and the percent of the calcite crystal area cleaned.

oil contact angle (decrease the oil-wetting). Those chemical systems that both clean the surface and change the contact angle the fastest are judged to be have the best performance. Some (nonionic) surfactant solutions had the effect of cleaning the surface quickly, but created only a modest increase in oil contact angle. A lesser change in the contact angle is thought to be less desirable as this means that larger large blobs of oil can still be attached strongly to the calcite surface, and so this solution would not be expected to be as efficient in displacing oil.

2. The early time results are a good predictor of the relative performance at longer exposure times. That is, the best performing surfactants early on are also among the best much later.

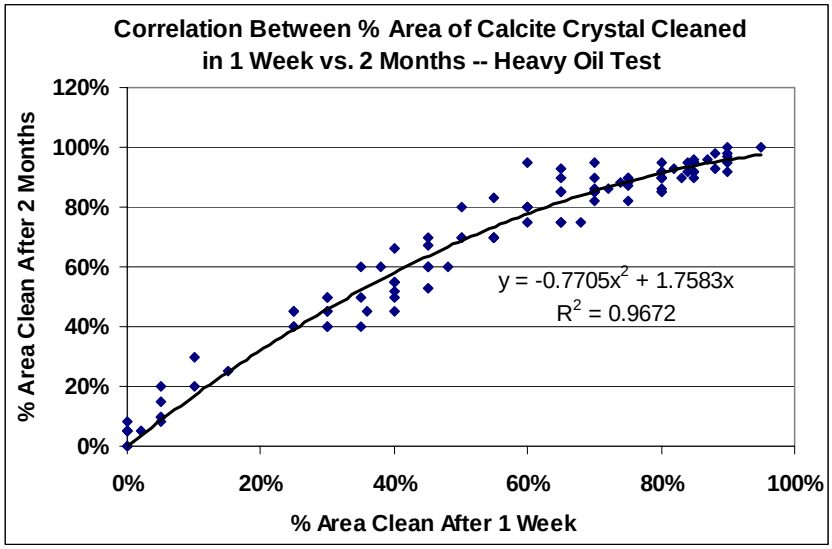


Figure 7. Strong correlation between the percent of cleaning at 1 week and 2 months The r^2 is 0.967 if using a quadratic fit, and still over 0.9 if restricted to a simple linear fit.

The practical implication of this observation is that one could do this screening test procedure for just one week and arrive at almost the same conclusions regarding the relative performance among the surfactant solutions tested.

2. The trends of surfactant type/structure and their performance found with this screening test are consistent generally with that reported in the literature.

Several authors describe imbibition oil recovery tests where a carbonate core containing crude oil is immersed in a candidate surfactant solution (e.g. Chen, 2000, Seethepalli, 2004, and Standnes, and Austad, 2000). Their results generally match our observations, such as:

- Cationic surfactants can be efficient, but create a strong emulsion effect as evidenced by the aqueous solution becoming dark.
- Nonionic and anionic surfactants generally maintain clear aqueous solutions and the recovered oil floats to the top as a separate phase.
- With the better surfactant systems, the oil is seen to "stream" off the crystal.

More specifically, we find in common with these other studies:

- The "blank" case (no surfactant) shows virtually no oil recovery.
- Cationic surfactants such as the CTAB series (trimethyl, alkyl ammonium salts) with a long alkyl chain length have very good performance.
- The hyamine type of cationic surfactants have poor performance
- A small number of the branched alkyl propoxylated sulfate anionic surfactants (Sasol manufactures) show good performance.
- SDS (sodium dodecyl sulfate) anionic surfactant has poor performance.
- Several nonionic surfactants (such as from the Neodol series of ethoxylated alcohols) which have been used in successful field experiments) have good performance in our

screening test. We found for our test system that better performance is favored with nonionic surfactants having a HLB ranging 10 – 12.

These common observations provide support for the validity of the simple screening test that we developed here; good and not so good IOR surfactants identified with our simple and fast screening test appear to be consistent with literature data about the same relative performance in the more complicated, but more realistic imbibition oil displacement tests.

3. Other observations about results with heavy oil/calcite chip tests.

Many of the samples used in these screening tests had nonionic surfactants. One general observation was that in these tests samples with a nonionic surfactant having a HLB in the range of 10 – 15 have a better probability of good performance (larger percent of calcite chip surface being cleaned). See the figure below.

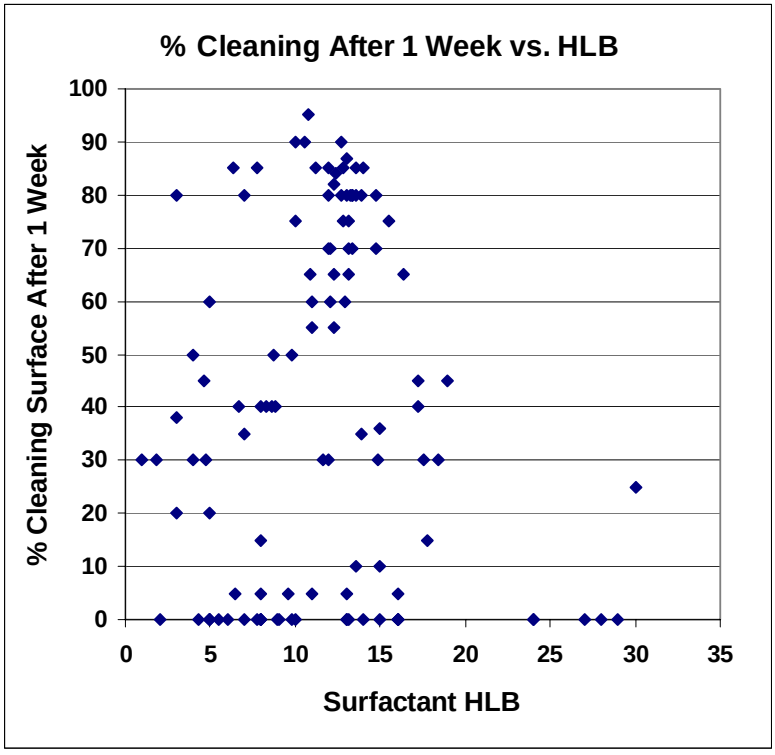


Figure 8. Cleaning efficiency of calcite chip coated with heavy oil versus the HLB of nonionic surfactants tested. Best performance seen with HLB 10 – 15.

These results encompass different types of nonionic surfactants such as alkyl ethoxylated octyl and nonyl-phenols, linear ethoxylated alcohols, secondary alcohol ethoxylated alcohols, alkyl polyglycosides, sorbitan, polyethoxylated thioethers, and block copolymers of polyethylene and ethylene oxides. Results are given below for selected groups of surfactants. Each group of surfactants is sorted from best to worst by the percent cleaning of the calcite chip after 1 week: Most of the tables below include observed chip area cleaned and the estimated contact angle also after 1month of exposure time.

Table 2. Results for calcite chip cleaning and oil contact angle for Neodol series of surfactants

Ref. No	Surfactant (Trade Name)	Chemical Description	Manufacturer	HLB	No. Carbons	No. EO	Area% of crystal cleaned 1 wk.	Area% of crystal cleaned 1 mth	Contact Angle (Degrees) 1 wk.	Contact Angle (Degrees) 1 mth
199	Neodol 1-5	C11 linear primary alcohol ethoxylate	Norman, Fox & Co	11.2	11	5	85%		60	
200	Neodol 1-7	C11 linear primary alcohol ethoxylate	Norman, Fox & Co	12.8	11	7	85%		70	
133	Neodol 25-3	C12-15 linear primary alcohol ethoxylate	Shell Chemicals	7.8	13.5	3	85%	95%	80	90
201	Neodol 1-9	C11 linear primary alcohol ethoxylate	Norman, Fox & Co	13.9	11	9	80%		65	
134	Neodol 1-7	C11 linear primary alcohol ethoxylate	Norman, Fox & Co	12.8	11	7	75%	81%	60	70
132	Neodol 23-6.5	C12-13 linear primary alcohol ethoxylate	Norman, Fox & Co	12.1	12.5	6.5	70%	92%	80	90
136	Neodol 25-7	C12-15 linear primary alcohol ethoxylate	Norman, Fox & Co	12.3	13.5	7	65%	87%	40	70
204	Neodol 25-9	C12-15 linear primary alcohol ethoxylate	Norman, Fox & Co	13.1	13.5	9	65%		70	
202	Neodol 23-6.5	C12-13 linear primary alcohol ethoxylate	Norman, Fox & Co	12.1	12.5	6.5	60%		45	
203	Neodol 25-7	C12-15 linear primary alcohol ethoxylate	Norman, Fox & Co	12.3	13.5	7	55%		25	
198	Neodol 1-3	C11 linear primary alcohol ethoxylate	Norman, Fox & Co	8.7	11	3	50%		80	

No. Carbons – length alkyl chain EO – number ethoxy groups Contact angle - oil on chip

One of these nonionic surfactants has been used in a field test of this process (Chen, 2000).

Table 3. Results for calcite chip cleaning and oil contact angle for Tergitol series of surfactants

Ref. No	Surfactant (Trade Name)	Chemical Description	Manufacturer	HLB	No. Carbons	No. EO	Area% of crystal cleaned 1 wk.	Area% of crystal cleaned 1 mth	Contact Angle (Degrees) 1 wk.	Contact Angle (Degrees) 1 mth
107	Tergitol® 15-S-5	C12-C14 seconary alcohol ethoxylate	Union Carbide	10.6	12-14.	5	90%	98%	90	150
108	Tergitol® 15-S-7	C12-C14 seconary alcohol ethoxylate	Union Carbide	12.4	12-14.	7	84%	93%	80	90
110	Tergitol® 15-S-12	C12-C14 seconary alcohol ethoxylate	Union Carbide	14.7	12-14.	12	80%	88%	65	70
109	Tergitol® 15-S-9	C12-C14 seconary alcohol ethoxylate	Union Carbide	13.3	12-14.	9	80%	84%	75	83
111	Tergitol® 15-S-20	C12-C14 seconary alcohol ethoxylate	Union Carbide	14.7	12-14.	20	70%	84%	40	50
112	Tergitol® 15-S-40	C12-C14 seconary alcohol ethoxylate	Union Carbide	16.4	12-14.	40	65%	82%	30	35
106	Tergitol® 15-S-3	C12-C14 seconary alcohol ethoxylate	Union Carbide	8.3	12-14.	3	40%	50%	20	30

The results with these secondary ethoxylated alcohols reinforce the notion that there is an optimum HLB. Note that it is the samples with either the low (EO = 3) or high end of ethoxylate groups (EO = 20, 40) and HLB that perform much worse than the other surfactants.

Table 4. Results for calcite chip cleaning and oil contact angle for ethoxylated octylphenol surfactants

No.	Name	Chemical	Num EO	HLB	Area% of crystal cleaned 1 wk.	Area% of crystal cleaned 1 mth	Contact Angle (Degrees) 1 wk.	Contact Angle (Degrees) 1 mth
127	Triton X-114	Ethoxylated octylphenol, octoxynol-8	8	12.3	82%	91%	78	89
51	Igepal? CA-630	Octoxynol-9	9	13.0	80%	90%	65	90
50	Igepal? CA-620	Octoxynol-7	7	12.0	80%	90%	60	80
126	Triton X-100	Ethoxylated octylphenol, octoxynol-9	9	13.4	80%	90%	75	90
128	Triton X-165	Ethoxylated octylphenol, octoxynol-16	16	15.5	75%	90%	60	80
123	Triton? X-15	Ethoxylated octylphenol, octoxynol-1	1	4.9	60%	75%	20	30
125	Triton X-45	Ethoxylated octylphenol, octoxynol-5	5	9.8	50%	66%	35	50
129	Triton X-405	Ethoxylated octylphenol, octoxynol-40	40	17.6	30%	43%	15	16
130	Triton X-705	Ethoxylated octylphenol, octoxynol-70	70	18.4	30%	38%	15	20
49	Igepal? CA-420	Octoxynol-3	3	8.0	5%	15%	0	15
124	Triton? X-35	Ethoxylated octylphenol, octoxynol-3	3	7.8	0	0	0	0

Table 5. Results for calcite chip cleaning and oil contact angle for ethoxylated nonylphenol surfactants

No.	Name	Chemical	Num EO	HLB	Area% of crystal cleaned		Contact Angle (Degrees)	
					1 wk.	1 mth	1 wk.	1 mth
12	Igepal? CO-530	Nonoxynol-6	6	10.8	95%	95%	90	150
13	Igepal? CO-630	Nonoxynol-9	9	13.0	87%	94%	85	100
14	Igepal? CO-710	Nonoxynol-11	11	13.6	85%	86%	80	90
116	Tergitol? NP-10	Ethoxylated nonylphenol, nonoxynol-10	10	13.2	80%	88%	60	80
11	Igepal? CO-520	Nonoxynol-5	5	10.0	75%	85%	60	80
115	Tergitol? NP-9.5	Ethoxylated nonylphenol, nonoxynol-9.5	9.5	13.1	70%	82%	65	80
114	Tergitol? NP-6	Ethoxylated nonylphenol, nonoxynol-6	6	10.9	65%	75%	20	25
143	Tergitol? NP-9	Ethoxylated nonylphenol, nonoxynol-9	9	12.9	60%	90%	60	90
9	Igepal? CO-210	Nonoxynol-2 (1.5 EO)	1.5	4.6	45%	55%	20	27
16	Igepal? CO-880	Nonoxynol-30	30	17.2	45%	55%	25	43
10	Igepal? CO-430	Nonoxynol-4	4	8.8	40%	50%	15	46
17	Igepal? CO-887	Nonoxynol-30	30	17.2	40%	45%	15	27
15	Igepal? CO-730	Nonoxynol-15	15	15.0	36%	42%	20	40
117	Tergitol? NP-13	Ethoxylated nonylphenol, nonoxynol-13	13	13.9	35%	40%	20	25
18	Igepal? CO-897	Nonoxynol-40	40	17.8	15%	24%	5	20
113	Tergitol? NP-4	Ethoxylated nonylphenol, nonoxynol-4	4	8.9	0	5%	0	0

The results with these ethoxylated octyl- and nonyl-phenols also show this same trend; a HLB range of approximately 10 – 13 produces the best cleaning and a larger oil drop contact angle, whereas HLB values outside of this range are not as effective either in cleaning the chip or increasing the contact angle of the oil drops remaining on the chip.

The Alcodet series of thioether surfactants also showed promising results. Perhaps the sulfur linkages are beneficial to performance by interacting with some of the sulfur containing components in the crude oil. Also the range of HLB (11 - 13) for these particular Alcodet surfactants should be favorable, given the results of other nonionic surfactants tested under these conditions.

Table 6. Results for calcite chip cleaning and oil contact angle for Alcodet series of surfactants

Ref. No	Surfactant (Trade Name)	Chemical Description	Manufacturer	HLB	Area% of crystal cleaned		Contact Angle (Degrees)	
					1 wk.	1 mth	1 wk.	1 mth
2	ALCODET SK	PEG 8 isolauryl,thioether	Rhodia, Inc.	12.7	90%	90%	75	80
6	ALCODET MC-2000	POE thioether	Rhone-Poulenc	12.0	85%	92%	85	95
3	ALCODET 218	PEG 10 isolauryl, thioether	Rhone-Poulenc	13.6	80%	83%	75	80
5	ALCODET HSC-1000	POE thioether	Rhone-Poulenc	12.0	70%	85%	60	90
4	ALCODET 260	PEG 6 isolauryl, thioether	Rhone-Poulenc	11.0	60%	75%	50	65

Sorbitan type of surfactants (SPAN and Tween series) generally was not very good performers, with the exception of Tween 21 and 81.

Table 7. Results for calcite chip cleaning and oil contact angle for the Sorbitan and the Tween series of surfactants

Ref. No	Surfactant (Trade Name)	Chemical Description	Manufacturer	HLB	Area% of crystal cleaned		Contact Angle (Degrees)	
					1 wk.	1 mth	1 wk.	1 mth
92	SPAN® 20	Sorbitan monolaurate	ICI Chemicals	8.6	40%	60%	60	75
93	SPAN® 40	Sorbitan monopalmitate	SIGMA	6.7	40%	50%	30	45
94	SPAN® 60	Sorbitan monostearate	ICI Chemicals	4.7	30%	45%	15	18
97	SPAN® 85	Sorbitan trioleate	ICI Chemicals	1.8	30%	47%	15	20
95	SPAN® 80	Sorbitan monooleate	ATLAS Chemicals	4.3	0	0	0	0
96	SPAN® 83	Not Available	Aldrich	n/a	0	5%	0	5
101	Tween® 81	POE (5) Sorbitan monooleate	ICI Chemicals	10.0	90%	94%	80	92
98	Tween® 21	POE (4) Sorbitan monolaurate	ICI Chemicals	13.3	70%	85%	60	70
102	Tween® 85	POE (20) Sorbitan trioleate	Aldrich	11.0	55%	68%	40	45
99	Tween® 60	POE (20) Sorbitan monostearate	Unknown	14.9	30%	38%	10	15
100	Tween® 61	POE (4) Sorbitan monostearate	ATLAS Chemicals	9.6	5%	9%	0	5

The Pluoronic series of block polyethylene and ethylene co-polymers were not effective in these tests. The relatively high molecular weight of these products may play a role in decreasing their performance. Another feature of these surfactants is that it does not follow the rule of thumb of best performance when the HLB ranges from 8 – 15. The few Pluronic products with a positive result have HLB values as low as 1 and as high as 30.

Table 8. Results for calcite chip cleaning and oil contact angle for Pluoronic series of surfactants

Ref. No	Surfactant (Trade Name)	Chemical Description	Manufacturer	HLB	Area% of crystal cleaned		Oil Contact Angle	
					1 wk.	1 mth	1 wk.	1 mth
173	Pluronic L 122	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	4.0	30%	85%	30	30
167	Pluronic L 43	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	12.0	30%	75%	10	20
170	Pluronic L 101	Block copolymers of propylene, ethylene oxides	BASF	1.0	30%	70%	16	18
163	Pluronic F 38	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	30.0	25%	50%	5	10
172	Pluronic L 121	Block copolymers of propylene, ethylene oxides	BASF	5.0	20%	40%	10	18
166	Pluronic L 42	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	8.0	15%	40%	5	10
168	Pluronic L 44	Block copolymers of propylene, ethylene oxides	BASF	16.0	5%	20%	0	10
169	Pluronic L 63	Block copolymers of propylene, ethylene oxides	BASF	11.0	5%	15%	0	10
189	Pluronic L-72	Block copolymers of propylene, ethylene oxides	BASF	6.5	5%	15%	10	10
190	Pluronic L-81	Block copolymers of propylene, ethylene oxides	BASF	2	0	10%	5	5
191	Pluronic L-92	Block copolymers of propylene, ethylene oxides	BASF	5.5	0	5%	5	5
175	Pluronic 17R2	Block copolymers of propylene, ethylene oxides	BASF	n/a	0	0	0	0
164	Pluronic F 77	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	24.0	0	0	0	0
179	Pluronic F-108	Block copolymers of propylene, ethylene oxides	BASF	27.0	0	0	0	0
176	Pluronic F-68	Block copolymers of propylene, ethylene oxides	BASF	29.0	0	0	0	0
177	Pluronic F-87	Block copolymers of propylene, ethylene oxides	BASF	24.0	0	0	0	0
178	Pluronic F-88	Block copolymers of propylene, ethylene oxides	BASF	28.0	0	0	0	0
171	Pluronic L 103	Block copolymers of propylene, ethylene oxides	BASF	n/a	0	0	0	0
184	Pluronic L-31	Block copolymers of propylene, ethylene oxides	BASF	5	0	0	0	0
185	Pluronic L-44	Block copolymers of propylene, ethylene oxides	BASF	16	0	0	0	0
186	Pluronic L-61	Block copolymers of propylene, ethylene oxides	BASF	16	0	0	0	0
187	Pluronic L-62	Block copolymers of propylene, ethylene oxides	BASF	7	0	0	0	0
188	Pluronic L-64	Block copolymers of propylene, ethylene oxides	BASF	15	0	0	0	0
165	Pluronic P 104	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	13.0	0	0	0	0
182	Pluronic P-103	Block copolymers of propylene, ethylene oxides	BASF	9	0	0	0	0
183	Pluronic P-123	Block copolymers of propylene, ethylene oxides	BASF	8	0	0	0	0

Three series of anionc surfactants evaluated included the NEODOX (alkyl ethoxy carboxylate) series made by Shell, Alfoterra (alkyl propxylated sulfate) made by Sasol, and the Aerosol surfactant series (sodium sulfosuccinates) from Cyanamid. The first two had no outstanding candidates, and the third series did have a couple of surfactants with encouraging results. See the Tables below.

Table 9. Results for calcite chip cleaning and oil contact angle for the NEODOX surfactant series

Surfactant			Area% of crystal cleaned		Oil Contact Angle	
Ref. No	(Trade Name)	Manufacturer	1 wk.	1 mth	1 wk.	1 mth
210	NEODOX 23-6	Westhollow Tech.	95%	96%	90	90
212	NEODOX 25-11	Westhollow Tech.	65%	65%	40	40
211	NEODOX 25-6	Westhollow Tech.	90%	90%	45	45
213	NEODOX 91-5	Westhollow Tech.	85%	85%	30	40
214	NEODOX 91-7	Westhollow Tech.	75%	75%	25	40

Table 10. Results for calcite chip cleaning and oil contact angle for the Alfoterra branched alkyl propoxy sulfate surfactant series

Surfactant			Area% of crystal cleaned		Oil Contact Angle	
Ref. No	(Trade Name)	Manufacturer	1 wk.	1 mth	1 wk.	1 mth
55	Alfoterra? 13	Sasol, Inc.	0	0	0	0
56	Alfoterra? 15	Sasol, Inc.	0	0	0	0
57	Alfoterra? 18	Sasol, Inc.	0	0	0	0
58	Alfoterra? 23	Sasol, Inc.	0	0	0	0
59	Alfoterra? 25	Sasol, Inc.	0	0	0	0
60	Alfoterra? 28	Sasol, Inc.	0	0	0	0
61	Alfoterra? 33	Sasol, Inc.	25%	35%	20	20
62	Alfoterra? 35	Sasol, Inc.	25%	35%	20	25
63	Alfoterra? 38	Sasol, Inc.	0	0	0	0
64	Alfoterra? 43	Sasol, Inc.	0	0	0	0
65	Alfoterra? 45	Sasol, Inc.	0	0	0	0
66	Alfoterra? 48	Sasol, Inc.	0	0	0	0
67	Alfoterra? 53	Sasol, Inc.	35%	45%	20	27
68	Alfoterra? 55	Sasol, Inc.	5%	10%	0	5
69	Alfoterra? 58	Sasol, Inc.	0	0	0	0
70	Alfoterra? 63	Sasol, Inc.	45%	50%	25	27
71	Alfoterra? 65	Sasol, Inc.	2%	5%	0	5
72	Alfoterra? 68	Sasol, Inc.	0	0	0	0

Table 11. Results for calcite chip cleaning and oil contact angle for Aerosol series of surfactants

Ref. No	Surfactant (Trade Name)	Chemical Description	Manufacturer	Area% of crystal cleaned		Contact Angle (Degrees)	
				1 wk.	1 mth	1 wk.	1 mth
81	AEROSOL® OT 75%	Dioctyl ester of sodium sulfosuccinic acid	Cyanamid	80%	84%	50	54
79	AEROSOL® OT-S	Dioctyl sodium sulfosuccinate	Cyanamid	70%	88%	65	80
76	AEROSOL® OT-B	Dioctyl ester of sodium sulfosuccinic acid	Cyanamid	65%	92%	75	90
78	AEROSOL® TR-70	Bis(tridecyl) ester of sodium sulfosuccinic acid	Cyanamid	45%	60%	20	30
80	AEROSOL® MA-80	Dihexyl sodium sulfosuccinate	Cyanamid	25%	35%	15	22

It might be with more formulation effort that the other anionic surfactant series, such as the Alfoterra surfactants then would be effective. Note that the literature reports this series of anionic surfactants have good oil recovery performance characteristics for carbonate formations when formulated at high pH. In that way they can create a very low interfacial tension and not suffer from excessive solid adsorption (Hirasaki, 2004 and Seethepalli , 2004).

The best ”chip cleaning” and largest contact angle effect occurred with tests using several of the cationic surfactants, especially the alkyl-trimethyl ammonium chlorides. . See below.

Table 12. Results for calcite chip cleaning and oil contact angle for cationic surfactants

Ref. No	Surfactant (Trade Name)	Chemical Description	Manufacturer	Area% of crystal cleaned		Contact Angle (Degrees)
				1 wk.	1 mth	1 wk.
225	**ARQUAD T-50**	Tallowalkyl - trimethyl ammonium chloride	Akzo Nobel	100%		180
222	**ARQUAD 18-50**	Octadeycl - trimethyl ammonium chloride	Akzo Nobel	95%		180
223	**ARQUAD C-50**	Cocoalkyl - trimethyl ammonium chloride	Akzo Nobel	95%		180
224	**ARQUAD S-50**	Soyalkyl - trimethyl ammonium chloride	Akzo Nobel	90%		120
74	**C10-triphenyl bromide**	Decyl triphenylphosphonium bromide	AVOCADO	85%	90%	80
73	**C12-triphenyl bromide**	Dodecyl triphenylphosphonium bromide	AVOCADO	85%	95%	77
75	**Trimethyl amm bromide**	Trimethyl(tetradecyl) ammonium bromide	SIGMA	88%	98%	90

This is consistent with some literature reports that have discussed some quaternary amines having good performance characteristics in recovering crude oil from carbonate (chalk) cores via imbibition (Austad, 2002, Standnes, 2000, and Standes, 2002).

For comparison, consider the performance of two other amine surfactants. The Doumeen series of surfactants is a diamine and the Ethomeen series is a tertiary amine (see Figure 1).

Table 13. Results for calcite chip cleaning and oil contact angle for amine surfactants

Ref. No	Surfactant (Trade Name)		Manufacturer	HLB	Area% cleaned 1 wk.		Oil Contact Angle 1 wk.
226	DUOMEEN O	N-oleyl-1,3-propane diamine	Akzo Nobel	15.2	75%		30
227	DUOMEEN T	Tallow-1,3-diamino propane	Akzo Nobel	15.6	50%		20
215	ETHOMEEN C/12	Tertiary amines ethylene oxide, cocoalkyl	Akzo Nobel	12.2	85%		45
216	ETHOMEEN C/15	Tertiary amines ethylene oxide, cocoalkyl	Akzo Nobel	13.5	85%		85
218	ETHOMEEN S/12	Tertiary amines ethylene oxide, soyalkyl	Akzo Nobel	10.0	50%		25
219	ETHOMEEN S/15	Tertiary amines ethylene oxide, soyalkyl	Akzo Nobel	11.1	45%		15
220	ETHOMEEN S/25	Tertiary amines ethylene oxide, soyalkyl	Akzo Nobel	14.7	0		0
217	ETHOMEEN C/25	Tertiary amines ethylene oxide, cocoalkyl	Akzo Nobel	16.8	0		0

The performance of these surfactants ranges from nil to very good (Ethomeen C/12 and C/15). The better chemical performance occurs for members with nominal HLB of 12.2 and 13.5, inside the optimum HLB range reported above in this document.

3.1.3 Results/Discussion - Calcite Chip Screening – McElroy Oil

Other experiments used the calcite chip (Iceland Spar) coated and aged with McElroy crude oil testing some of the same surfactants as before. There is a 2-by-2 matrix of 4 different run conditions:

Chip Aging Time at 80 ºC	1 Day	7 Days
Water Chemistry	2 wt% NaCl	Synthetic McElroy Brine

The complete listing of results for the cleaning experiments with these chips is given in Appendix B.

Results for the faster test protocol (where calcite chips pre-aged for only 24 hours with McElroy oil) are shown in the table below. For this situation the calcite chips are cleaned relatively quickly. The calcite chips aged for 7 days with McElroy oil however, showed hardly any response (see Appendix B), even after a week or more with exposure to a surfactant solution

Table 14. Performance in cleaning calcite chips coated with aged McElroy oil. Results sorted by best to worst for both samples with 2 wt% NaCl brine and synthetic McElroy brine. Calcite chips pre-treated with McElroy oil for 24 hours at 80 ºC . Percent of chip cleaned after 1 day in surfactant solutions at RT in 2 wt% NaCl and synthetic McElroy brine shown below.

McElroy Oil Age 24 hours at 80 C on Calcite Chips

Brine 2.0 wt%			**Synthetic McElroy Brine**		
Surfactant Name	HLB	24 hours	Surfactant Name	HLB	24 hours
Igepal? CO-530	10.8	95%	Triton X-114	12.3	93%
Tergitol? 15-S-7	12.4	95%	Neodol? 1-7	12.8	90%
Neodol? 1-7	12.8	92%	Tergitol? 15-S-7	12.4	90%
Tergitol? 15-S-9	13.3	92%	Tergitol? 15-S-9	13.3	85%
Neodol? 25-7	12.3	90%	SIL WET? L-77	n/a	85%
Tergitol? 15-S-5	10.6	90%	ALCODET SK	12.7	85%
Neodol? 25-9	13.1	85%	Igepal? CO-630	13	80%
Tergitol? 15-S-12	14.7	85%	Neodol? 1-9	13.9	80%
Triton X-114	12.3	85%	Neodol? 25-9	13.1	80%
ALCODET SK	12.7	85%	Tergitol? 15-S-5	10.6	80%
ALCODET 218	13.6	85%	Triton X-100	13.4	80%
Igepal? CO-630	13	80%	Neodol? 25-7	12.3	75%
Igepal? CO-710	13.6	80%	NEODOX? 25-6	n/a	75%
Neodol? 1-9	13.9	80%	ARQUAD T-50	n/a	75%
NEODOX? 25-11	n/a	80%	Igepal? CO-530	10.8	70%
SIL WET? L-77	n/a	80%	Tergitol? 15-S-12	14.7	70%
Triton X-165	15.5	75%	ALCODET 218	13.6	70%
NEODOX? 25-6	n/a	70%	Triton X-405	17.6	65%
Tergitol? 15-S-20	14.7	70%	NEODOX? 25-11	n/a	60%
Triton X-100	13.4	70%	Triton X-165	15.5	60%
Triton X-405	17.6	70%	Tergitol? 15-S-20	14.7	55%
ARQUAD T-50	n/a	65%	Igepal? CO-710	13.6	50%
SIMULSOL SL 4	n/a	20%	TritonTM BG-10	n/a	10%
TritonTM BG-10	n/a	10%	Agrimul? PG 2067	13.6	5%
Agrimul? PG 2067	13.6	10%	SIMULSOL SL 4	n/a	5%
SIMULSOL SL 55	n/a	10%	C_{10}-triphenyl-bromide	n/a	0%
C_{10}-triphenyl-bromide	n/a	0%	SIMULSOL AS 48	n/a	0%
SIMULSOL AS 48	n/a	0%	SIMULSOL SL 55	n/a	0%
AVERAGE		**68%**			**60%**

Similar to the results shown earlier for the heavy oil-coated calcite chips, nonionic surfactants with a HLB in the range of 10 – 15 are relatively effective. The average HLB is 12.7 for the nonionic surfactants that remove 80% or more of the McElroy oil from these chips after a 1 day, whether the surfactant is dissolved in 2 wt% brine or a synthetic McElroy brine. On average, the chip cleaning is more efficient if the brine is 2 wt% NaCl (average of 68% cleaning) rather than

synthetic McElroy brine (average of 60% cleaning). Somewhat contrary to the heavy oil results, the cationic surfactants are inferior rather than superior to the nonionic surfactants. For example, the Arquad T-50 has decent efficiency when tested versus the chips coated with McElroy oil, but it is not as good as the best Tergitol and Neodol surfactants. Recall that the Arquad T-50 was one of the particularly good products for cleaning the chips coated with the heavy oil.

3.2 Screening Method Based on Calcite Powder Flotation

3.2.1 Introductory Remarks

Task 2 of this project is pointed towards gaining a better fundamental understanding about the wetting behavior of carbonate minerals, and how that changes with exposure to oil and aqueous surfactant solutions. That is, how is it that certain components in the oil (e.g. naphthenic acids (NAs) and asphaltenes) promote the mineral surface to be oil-wet? What are the chemical processes that can alter that oil-wet condition to the desired outcome of becoming strongly water-wet via exposure to an aqueous surfactant solution? Standes and Austad (2000, 2002) for example, have addressed the surfactant wetting mechanisms with a carbonate surface covered by a naphthenic acid.

One outcome from conducting the experimental portion of this Task 2 has been the development of another rapid, efficient method to screen surfactant formulations for IOR performance in carbonates (i.e. screen surfactants for their ability to alter the surface from an oil-wet to a water–wet condition). The general concept is to pre-treat a powdered calcite material with a NA compound to render it oil-wet. This powder then will float on top when agitated in water because it is oil-wet. If, however, the aqueous phase contains an efficient water-wetting surfactant, then some of the calcite powder now will sink to the bottom. More details about all of the work associated with this Task 2 are given in the first semi-annual and the third quarter report for Year 1. The literature (Skvarla and Kmet, 1991, and Ozkan and Yekeler, 2003) describes the flotation action that can occur with a carbonate mineral that has been contacted with a naphthenic acid (such as sodium oleate).

3.2.2 Experimental Procedure – Calcite Flotation Test

The first step in this procedure is to select the hydrocarbon and the treatment details that will make the calcite powder initially oil-wet. To test this concept, we first selected a series of specific naphthenic (carboxylic) acids as model compounds, and that may be present in a crude oil and contribute to oil-wetting behavior in actual reservoirs. Powdered calcite (calcium carbonate) was selected as the mineral surface and formulations with single surfactant products as agents to induce water-wetting behavior. Per details below, based on the results of the first test, cyclohexanepentanonic acid was selected as the oil-wetting agent for part two of the test.

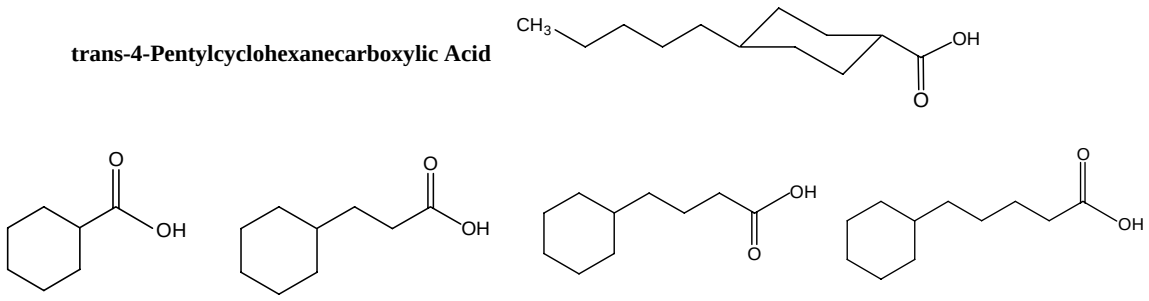
The second step in the procedure is to then use the cyclohexanepentanonic acid oil-wet treated calcite powder as the starting material. This powder almost all floats when dispersed in water. However, when this powder is exposed to effective aqueous surfactant solutions, all or a

significant fraction of the powder sinks, thereby indicating conversion of the solid to a water-wet state.

These flotation tests (as was the calcite chip cleaning tests) all were performed at room temperature. These same procedures could be adapted easily to elevated temperatures.

Experimental Procedure to Select Oil-Wetting Agent NA

A selected suite of naphthenic acid (NA) compounds included in the study are shown below:



Cyclohexanecarboxylic Acid Cyclohexanepropinic Acid Cyclohexanebutyric Acid Cyclohexanepentanonic Acid

Figure 9. Structures of model naphthenic acids (NA)

The literature suggests that NAs can create an oil-wet condition via their carboxylate group binding to the carbonate mineral surface. Then the hydrophobic (e.g. alkyl chain) group protruding from the surface creates effectively an oil-like coating (Standes and Austad, 2000).

The first portion of this test development program is to measure the wetting behavior induced by the different chemical structures of the selected NA compounds. The general procedure to do this via flotation behavior is:

1. Prepare naphthenic acid solution in decane. Solutions were made from 0.005 - 0.067 M, which is equivalent to acid numbers of 0.45 - 5.1 for the selected naphthenic acids.

2. Mix 10.0 ml naphthenic acid-decane solution with 0.5 g calcite powder (first pre-heated at 120 °C for 2 hours) in a test tube. The average size of the powder is 5 microns, with a surface area of 1.6 sq. m/gram. Then shake the test tube at room temperature for 12 hours in order to establish adsorption to its equilibrium.

3. Put the test tube containing calcite powder with adsorbed naphthenic acid in an oven at 85 °C to remove extra solvent until a constant weight is obtained. Cool it to room temperature for the flotation test.

4. Add 10 g distilled water to a test tube with calcite powder and shake it vigorously for 2 minutes. Then leave the test tube stand vertically for several hours. The volume of calcite powder in bottom (water-wet portion) and top (oil-wet portion) are measured.

Per the procedure above (Steps 3 and 4), several tests were performed to compare the tendency of the calcite powder treated with different NA compounds to float. See the photos below.

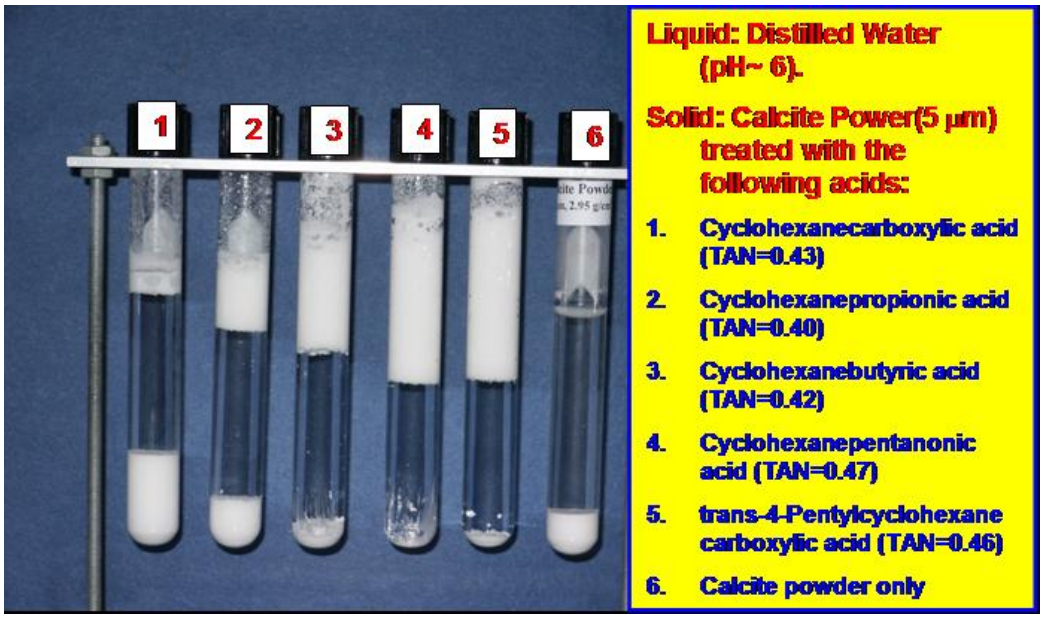


Figure10. Flotation of calcite powder treated by different NAs at TAN of about 0.45

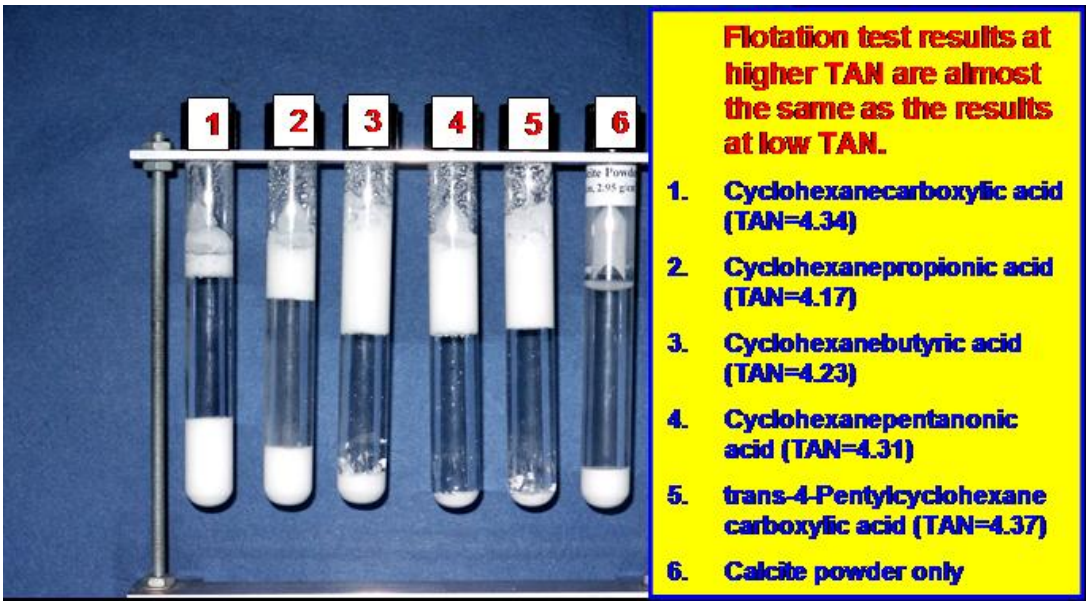


Figure 11. Flotation of calcite powder treated by different NAs at TAN of about 4.5

The volume percent of the powdered calcite observed to be floating at the top (called "oil-wet percentage") for all of the acid numbers examined are shown in the plots below, both in terms of the NA molar concentration and expressed as total acid number, TAN.

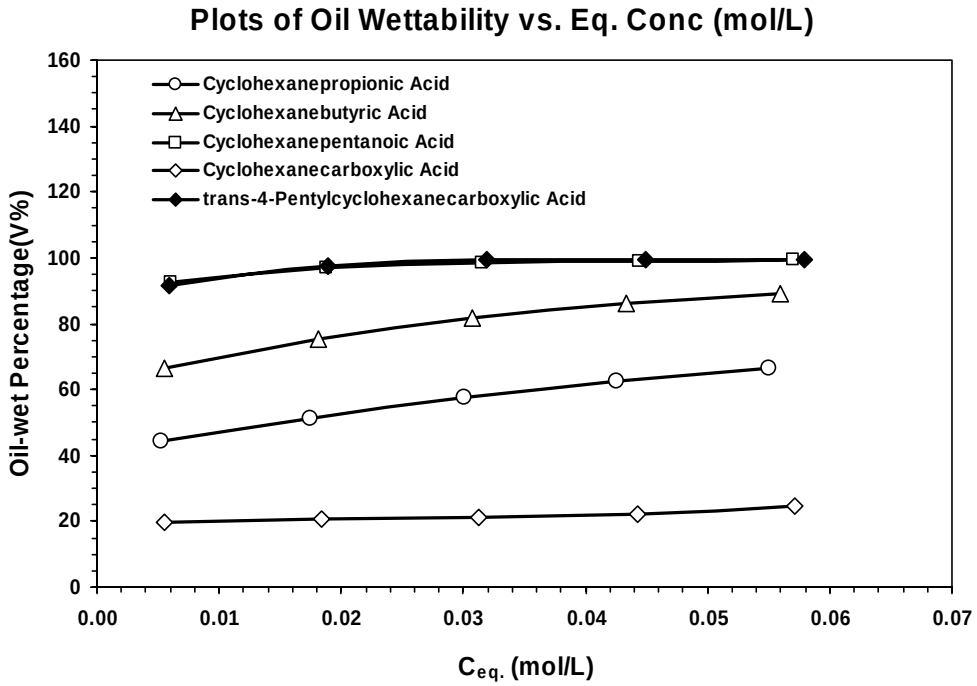


Figure 12. Flotation of calcite powder treated by different NAs versus molar concentration.

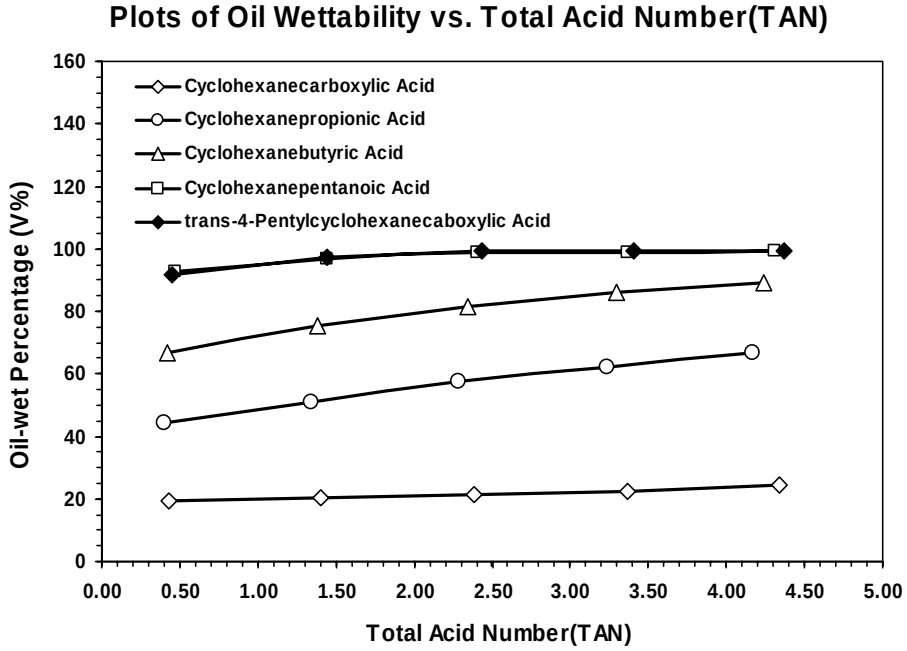


Figure 13. Flotation of calcite powder treated by different NAs versus their TAN.

The greater the hydrophobic character of the NA, the greater the percentage of the treated calcite powder that floats in distilled water. Based on these above results, we selected powdered calcite pre-treated with cyclohexanepentanonic acid as the "standard" initially oil-wet material for the second part of the overall test procedure which tests the performance of surfactants. Thus, the "blank" result when testing surfactants and additives to the aqueous phase is nearly 100% of the powder remains at the top.

Experimental Procedure to Screen Surfactant Performance

In the surfactant screening test, one prepares a quantity of treated calcite powder, and then observes how that powder behaves when dispersed into different surfactant candidate solutions.

1. Clean new calcite crystals. Wash the crystals with heptane and toluene separately, and then dry the samples in an oven at 85 °C for an hour.

2. Prepare a 0.066 M cyclohexanepentanonic acid solutions in decane (equivalent to total acid number, TAN, of about 5).

3. Immerse the clean calcite crystal in the naphthenic acid solution in decane for 24 hours at room temperature. Take the crystals out of the solutions carefully. Dry the treated crystals in an oven at 85 °C for an hour to remove all extra solvent.

4. Add 1 gram of this pre-treated calcite powder (now oil-wet) to a test tube.

5. Add 10 grams of surfactant solution and shake vigorously.

6. Allow to settle over night. Note the volume fraction of calcite powder that has sunk or is floating. If there is foam at the top (often there is), then proceed to Step 7. The foam should be broken because it may induce a false reading. Any foam could hold some of the water-wet calcite powder to remain floating at the top and not allow it to sink.

7. For the case when there is some foam at the top, gently tilt and rotate the test tube to gradually break the bubbles. Carefully replace the test tube and allow it sit for 2 hours or more. Take a final reading of the percent of solids floating or now at the bottom. Those aqueous chemical solutions that cause more of the solids to sink are judged to be Superior candidates that merit further testing.

3.2.3 Results and Discussion – Calcite Flotation Test

The results of the flotation test response are shown in the table below.

Table 15. Results of surfactant flotation test. Calcite powder pre-treated with cyclohexanepentanoic acid is exposed to different aqueous surfactant solutions. The percent of the powder that then sinks to the bottom of the test tube indicate the success in converting the solid to a water-wet condition.

Wettability Alteration Test (Flotation) for Selected Surfactants				
		Percent of Calcite Powder that Sinks		
		Surfactant Concentration		
No.	Surfactants	100 ppm	50 ppm	20 ppm
1	Alcodet(R) SK	0	0	
2	Alcodet(R) MC-2000	95%	55%	
3	Alkamide(R) WRS-166	0	0	
4	Igepal(R) CO-530	100%	95%	2%
5	Arquard(R) C-50	100%	50%	
6	Arquard(R) T-50	100%	100%	60%
7	Neodol(R) 1-5	95%	45%	
8	Neodol(R) 1-7	95%	40%	
9	Neodol(R) 25-7	100%	80%	
10	Neodol(R) 25-9	100%	80%	
11	Neodox(R) 23-6	0%	0%	
12	Sil wet(R) L-77	100%	80%	
13	Sil wet(R) L-7614	100%	30%	
14	Tergitol(R) 15-S-3	100%	70%	
15	Tergitol(R) 15-S-5	100%	65%	
16	Tergitol(R) 15-S-7	100%	45%	
17	Tergitol(R) 15-S-20	75%	50%	
18	Tergitol(R) 15-S-40	50%	40%	
19	Triton(R) BG-10	0%	0%	
20	C_{12}TAB	60%	45%	
21	Sodium Dodecyl Sulfate	0%	0%	

The results are shown for surfactant concentrations of 100 ppm and less. At 100 ppm surfactant concentration we see a spread of results, but several surfactants still show 100% effectiveness. There is more spread of results at the 50 and 25 ppm level. These results then are internally consistent, with respect to a decrease of performance as the surfactant dosage rate decreases. Note that at higher dosages this procedure does not discriminate performance and hence is not a useful test; for example, we found at 1000 ppm active surfactant concentration that all of these products tested were 100% effective.

Some of the trends with respect to changes of performance with the surfactant chemical structure are expected. For example, within the Tergitol series we see that the performance is poorer for the two products (Tergitol 15-S-20 and Tergitol 15-S-40) with a large number of EO (ethoxy) groups (20 and 40, respectively) and relatively high HLB (14.7 and 16.4, respectively). Per earlier findings with the calcite chip cleaning test, these appear to be too water soluble. One inconsistency, however, is that the Tergitol 15-S-3 with only 3 EO groups and a low HLB of 8.3

performs the best among this series of surfactants. The calcite chip results would suggest this surfactant is not water soluble enough for good performance.

The Arquad T-50 (a cationic quaternary amine) was the best performing surfactant in this flotation test. Having a quaternary amine as a good surfactant is consistent with the calcite chip heavy oil test results (and other literature). For the calcite chip results with heavy oil the Arquad C-50 was almost as good as the Arquad T-50, but not so for the flotation test. Note that the difference is in the alkyl chain, with the C-50 based on coconut oil (circa C12) and the T-50 based on a tallow oil (circa C15). One other common result is that the pure cationic compound, C_{12}TAB (dodecly trimethyl ammonium bromide), has moderate performance for both the flotation and calcite cleaning screening tests.

4.0 CONCLUSIONS

1. One screening test was developed for surfactant recovery performance based on the relative ability of different chemical formulations to remove oil that is coating a clear calcite chip. These tests can be designed to be relatively simple and quick to perform (only a few days exposure time) and provide a measure of relative performance of removing oil coating a carbonate mineral surface, and thereby an indication of the surfactant's ability to recover incremental oil via enhancing aqueous phase imbibition into carbonate porous media.

2. A second surfactant screening test was developed based on the ability of an aqueous chemical solution to make an oil-wet calcite powder water-wet. This method also is a relatively quick and easy procedure to screen surfactant for their potential performance as EOR agent for carbonate reservoirs. The general procedure is to render a powdered carbonate material oil-wet, and then add it to a surfactant solution. After agitating and aging this suspension, the success in converting the powder to a water-wet condition is indicated by the fraction of the powder that is made to sink. This is compared to the blank case with no surfactant in which almost all of the powder (still oil-wet) will float.

5.0 REFERENCES

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APPENDIX A.

LIST OF CALCITE CHIP – HEAVY OIL CLEANING RESULTS WITH SURFACTANTS

WETTABILITY ALTERATION

No.	Surfactant (Trade Name)	Chemical Description	Manufacturer	HLB	Area% of oil-wet to water-wet						Crude oil contact angle on calcite surface (deg. 0 = spreading, 180 = non-wet to oil)					
					24 hrs	3days	1 wk.	2 wks	1 mth	2 mth	24 hrs	3days	1 wk.	2 wks	1 mth	2 mth
240	ABIL B 88183	Polysiloxane polyether copolymer	Goldschmidt	n/a	0	0	0	0			0	0	0	0		
241	ABIL B 88184	Polysiloxane polyether copolymer	Goldschmidt	n/a	0	0	0	0			0	0	0	0		
239	ABIL B 8851	Polysiloxane polyether copolymer	Goldschmidt	n/a	0	0	0	0			0	0	0	0		
242	ABIL EM 90	Cetyl dimethicone copolyol	Goldschmidt	5.0	0	0	0	0			0	0	0	0		
77	AEROSOL® GPG	Dioctyl ester of sodium sulfosuccinic acid	Cyanamid	anionic	25%	45%	55%	70%	80%	83%	30	40	60	70	75	
80	AEROSOL® MA-80	Dihexyl sodium sulfosuccinate	Cyanamid	anionic	10%	20%	25%	30%	35%	40%	5	10	15	20	22	
81	AEROSOL® OT 75%	Dioctyl ester of sodium sulfosuccinic acid	Cyanamid	anionic	20%	70%	80%	82%	84%	86%	18	48	50	52	54	
76	AEROSOL® OT-B	Dioctyl ester of sodium sulfosuccinic acid	Cyanamid	anionic	25%	50%	65%	85%	92%	93%	20	50	75	88	90	
79	AEROSOL® OT-S	Dioctyl sodium sulfosuccinate	Cyanamid	anionic	30%	60%	70%	85%	88%	90%	30	50	65	70	80	
78	AEROSOL® TR-70	Bis(tridecyl) ester of sodium sulfosuccinic acid	Cyanamid	anionic	25%	35%	45%	50%	60%	70%	15	20	20	25	30	
245	Agniqul® PG 9116	Alkyl polyglycosides	Cognis	13.1	0	0	0	0			0	0	0	0		
243	Agrimul® PG 2062	Alkyl polyglycosides	Cognis	11.6	0	0	30%	30%			0	0	10	cloudy		
244	Agrimul® PG 2067	Alkyl polyglycosides	Cognis	13.6	0	0	10%	20%			0	0	20	20		
3	ALCODET 218	PEG 10 isolauryl, thioether	Rhone-Poulenc	13.6	75%	80%	80%	80%	83%	85%	60	75	75	78	78	
4	ALCODET 260	PEG 6 isolauryl, thioether	Rhone-Poulenc	11.0	50%	55%	60%	70%	75%	80%	35	40	50	60	65	
5	ALCODET HSC-1000	POE thioether	Rhone-Poulenc	12.0	40%	50%	70%	80%	85%	85%	28	35	60	80	90	
6	ALCODET MC-2000	POE thioether	Rhone-Poulenc	12.0	75%	80%	85%	90%	92%	92%	70	80	85	92	95	
2	ALCODET SK	PEG 8 isolauryl,thioether	Rhodia, Inc.	12.7	76%	85%	90%	90%	90%	92%	62	68	74	78	80	
55	Alfoterra? 13	Branched alcohol propoxylate sulfate(3 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0	0	0	0	0	0	
56	Alfoterra? 15	Branched alcohol propoxylate sulfate(5 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0	0	0	0	0	0	
57	Alfoterra? 18	Branched alcohol propoxylate sulfate(8 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0	0	0	0	0	0	
58	Alfoterra? 23	Branched alcohol propoxylate sulfate(3 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0	0	0	0	0	0	
59	Alfoterra? 25	Branched alcohol propoxylate sulfate(5 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0	0	0	0	0	0	
60	Alfoterra? 28	Branched alcohol propoxylate sulfate(8 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0	0	0	0	0	0	
61	Alfoterra? 33	Branched alcohol propoxylate sulfate(3 PO)	Sasol, Inc.	anionic	15%	20%	25%	30%	35%	45%	10	15	20	20	20	
62	Alfoterra? 35	Branched alcohol propoxylate sulfate(5 PO)	Sasol, Inc.	anionic	10%	20%	25%	30%	35%	45%	10	15	20	25	25	
63	Alfoterra? 38	Branched alcohol propoxylate sulfate(8 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0	0	0	0	0	0	
64	Alfoterra? 43	Branched alcohol propoxylate sulfate(3 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0	0	0	0	0	0	
65	Alfoterra? 45	Branched alcohol propoxylate sulfate(5 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0	0	0	0	0	0	
66	Alfoterra? 48	Branched alcohol propoxylate sulfate(8 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0	0	0	0	0	0	
67	Alfoterra? 53	Branched alcohol propoxylate sulfate(3 PO)	Sasol, Inc.	anionic	15%	35%	35%	40%	45%	50%	10	15	20	25	27	
68	Alfoterra? 55	Branched alcohol propoxylate sulfate(5 PO)	Sasol, Inc.	anionic	0%	0%	5%	10%	10%	15%	0	0	0	5	5	
69	Alfoterra? 58	Branched alcohol propoxylate sulfate(8 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0	0	0	0	0	0	
70	Alfoterra? 63	Branched alcohol propoxylate sulfate(3 PO)	Sasol, Inc.	anionic	10%	35%	45%	50%	50%	53%	15	20	25	27	27	
71	Alfoterra? 65	Branched alcohol propoxylate sulfate(5 PO)	Sasol, Inc.	anionic	0	0	2%	2%	5%	5%	0	0	0	0	5	
72	Alfoterra? 68	Branched alcohol propoxylate sulfate(8 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0	0	0	0	0	0	
1	ALKAMIDE WRS-166	Oleamide DEA(Anionic/Nonionic)	Rhone-Poulenc	n/a	80%	85%	90%	95%	95%	98%	70	75	80	83	87	
23	Antarox 17-R-2	Alkoxylated glycols,Meroxipol 172	Rhodia, Inc.	8.0	10%	30%	40%	45%	47%	50%	5	10	15	20	25	
22	Antarox 31-R-1	Alkoxylated glycols,Meroxipol 131	Rhodia, Inc.	4.0	10%	35%	50%	60%	68%	70%	5	20	30	35	40	
25	Antarox L-61	Alkoxylated glycols,poloxymer 181	Rhone-Poulenc	3.0	10%	28%	38%	55%	58%	60%	10	15	40	48	50	
26	Antarox L-62	Alkoxylated glycols,poloxymer 182	Rhone-Poulenc	7.0	10%	25%	35%	45%	55%	60%	8	20	30	40	48	

WETTABILITY ALTERATION

No.	Surfactant (Trade Name)	Chemical Description	Manufacturer	HLB	Area% of oil-wet to water-wet						Crude oil contact angle on calcite surface (deg. 0 = spreading, 180 = non-wet to oil)					
					24 hrs	3days	1 wk.	2 wks	1 mth	2 mth	24 hrs	3days	1 wk.	2 wks	1 mth	2 mth
27	Antarox L-64	Alkoxylated glycols, Polyoxymer 184	Rhone-Poulenc	15.0	0%	5%	10%	15%	20%	20%	0	0	10	15	20	
29	Antarox LA-EP-15	Modified oxyethylated straight chain alcohol	Rhodia, Inc.	7.0	15%	75%	80%	85%	90%	92%	10	45	55	65	75	
30	Antarox LA-EP-16	Modified oxyethylated straight chain alcohol	Rhodia, Inc.	13.1	15%	70%	75%	80%	85%	88%	10	40	52	63	75	
24	Antarox LF-222	Ethoxylated alkylphenols	Rhodia, Inc.	n/a	45%	80%	85%	90%	93%	95%	20	75	80	85	90	
28	Antarox P-104	Alkoxylated glycols, Polyoxymer 334	Rhone-Poulenc	13.0	0	0	0	0	0	0	0	0	0	0	0	
221	ARQUAD 12-50	N-alkyl trimethyl ammonium chloride	Akzo Nobel	cationic	Very Cloudy	Very Cloudy	Very Cloudy				N/A	N/A	180	180		
222	ARQUAD 18-50	N-alkyl trimethyl ammonium chloride	Akzo Nobel	cationic	N/A	90%	95%	95%			N/A	120	180	180		
223	ARQUAD C-50	N-alkyl trimethyl ammonium chloride	Akzo Nobel	cationic	cloudy	90%	95%	95%			N/A	95	180	180		
224	ARQUAD S-50	N-alkyl trimethyl ammonium chloride	Akzo Nobel	cationic	cloudy	80%	90%	90%			N/A	90	120	120		
225	ARQUAD T-50	N-alkyl trimethyl ammonium chloride	Akzo Nobel	cationic	cloudy	90%	100%	100%			N/A	100	180	180		
228	Bio Soft N-411	Isopropylamine salt of linear alkylbenzenesulfonicacid	STEPAN	anionic	0	0	0	0			0	0	0	0		
233	BLO	(Not available)	ISP Corp.	n/a	25%	30%	45%	60%			5	10	12	30		
74	C10-triphenyl bromide	Decyl triphenylphosphonium bromide	AVOCADO	cationic	33%	80%	85%	85%	90%	95%	30	75	80	85	90	
73	C12-triphenyl bromide	Dodecyl triphenylphosphonium bromide	AVOCADO	cationic	30%	77%	85%	92%	95%	96%	25	45	77	88	90	
155	Calamide C	Coconut diethanolamide	PILOT	Nonionic	0	0	0	0	0		0	0	0	0	0	
156	Calamide CW-100	Modified coconut dialkanolamide	PILOT	Nonionic	0	0	0	0	0		0	0	0	0	0	
157	Calamide CWT	Modified coco amide soap superamide	PILOT	Nonionic	0	10%	15%	30%	40%		cloudy	cloudy	cloudy	cloudy	cloudy	
158	Calamide F	Vegetable oil diethanolamide	PILOT	Nonionic	15%	35%	65%	85%	92%		15	30	60	70	80	
159	Calamide O	Coco/oleic diethanolamide	PILOT	Nonionic	0	0	0	0	0		0	0	0	0	0	
160	Calfax 10L-45	Sodium n-decyl diphenyl oxide disulfonate	PILOT	anionic	0	10%	20%	30%	40%		0	0	5	10	20	
161	Calfax 16L-35	Sodium n-hexa-decyldiphenyl disulfonate	PILOT	anionic	0	5%	10%	20%	30%		0	0	5	10	15	
162	Calfax DB-45	Sodium dodecyl diphenyl oxide disulfonate	PILOT	anionic	0	0	0	0	0		0	0	0	0	0	
148	Calfoam EA-603	Ammonium alcohol ether sulfate	PILOT	anionic	0	0	0	0	0		0	0	0	0	0	
149	Calfoam ES-603	Sodium alcohol ether sulfate	PILOT	anionic	0	0	0	0	0		0	0	0	0	0	
147	Calimulse EM-22	Sodium branched alkylbenzenesulfonate	PILOT	anionic	0	0	0	0	0		0	0	0	0	0	
146	Calimulse PRS	Isopropylamine sulfonate	PILOT	anionic	0	0	0	0	0		0	0	0	0	0	
145	Caloxylate N-9	Nonylphenol ethoxylate, 9 moles	PILOT	anionic	10%	20%	35%	55%	75%		0	15	30	45	55	
150	Calsoft AOS-40	SodiumC14-C16 olefin sulfonate	PILOT	anionic	0	0	0	0	0		0	0	0	0	0	
151	Calsoft L-40 Slurry	Sodium dodecyl-Benzene sulfonate	PILOT	anionic	0	0	0				0	0	0			
152	Calsoft LAS-99	Dodecylbenzene sulfonic acid, linear	PILOT	anionic	10%	20%	30%	40%	50%		5	15	25	35	40	
153	Calsoft T-60	Triethanolamine alkylaryl sulfonate	PILOT	anionic	0	0	0	0	0		0	0	0	0	0	
154	Calsoft TSA-99	Linear tridecyl benzene sulfonic acid	PILOT	anionic	15%	45%	55%	70%	85%		5	20	30	35	45	
193	DERMOL 2022	(Not available)	ALZO International	n/a	0	15%	25%	45%			0	5	5	15		
195	DERMOL DGDIS	Polyglycerol-2 diisostearate	ALZO International	n/a	0	0	0	0			0	0	0	10		
196	DERMOL DGMIS	Diglycerol-2 monoisostearate	ALZO International	n/a	0	0	0	0			0	0	0	0		
192	DERMOL DO	(Not available)	ALZO International	n/a	20%	50%	60%	70%			5	5	5	20		
194	DERMOL NGDI	Neopentyl diisostearate	ALZO International	n/a	0	0	0	20%			0	0	0	20		
208	DOWFAX 2A0	Dodecyl diphenyl oxide disulfonic acid	DOW Chemicals	anionic	0	10%	35%	35%			0	10	15	20		
207	DOWFAX 2A1	Sodium dodecyl diphenyloxide disulfonate	DOW Chemicals	anionic	0	0	0	0			0	0	0	0		
206	DOWFAX 8390	Sodium n-hexadecyldiphenyloxide disulfonate	DOW Chemicals	anionic	0	0	0	0			0	0	0	0		

WETTABILITY ALTERATION

No.	Surfactant (Trade Name)	Chemical Description	Manufacturer	HLB	Area% of oil-wet to water-wet						Crude oil contact angle on calcite surface (deg. 0 = spreading, 180 = non-wet to oil)					
					24 hrs	3days	1 wk.	2 wks	1 mth	2 mth	24 hrs	3days	1 wk.	2 wks	1 mth	2 mth
209	DOWFAX C6L	Sodium hexyl diphenyloxide disulfonate	DOW Chemicals	anionic	0	0	0	0			0	0	0	0		
226	DUOMEEN O	N-oleyl-1,3-propane diamine	Akzo Nobel	15.2	65%	75%	75%	75%			25	30	30	30		
227	DUOMEEN T	Tallow-1,3-diamino propane	Akzo Nobel	15.6	30%	50%	50%	70%			15	20	20	20		
137	Dynol® 604	(Not available)	Air Products	n/a	0	0	0	0	0	0	0	0	0	0	0	
246	Elmsorb® 2500	(Not available)	Cognis	n/a	0	0	0	0			0	0	0	0		
247	Elmsorb® 2503	(Not available)	Cognis	n/a	10%	15%	20%	30%			5	5	5	20		
248	Elmsorb® 2515	(Not available)	Cognis	n/a	0	0	25%	45%			0	0	55	0		
138	ENVIROGE MAD01	(Not available)	Air Products	n/a	0	0	0	0	0	0	0	0	0	0	0	
215	ETHOMEEN C/12	Tertiary amines ethylene oxide, cocoalkyl	Akzo Nobel	12.2	50%	80%	85%	85%			30	40	45	45		
216	ETHOMEEN C/15	Tertiary amines ethylene oxide, cocoalkyl	Akzo Nobel	13.5	25%	80%	85%	85%			30	75	85	85		
217	ETHOMEEN C/25	Tertiary amines ethylene oxide, cocoalkyl	Akzo Nobel	16.8	0	0	0	0			0	0	0	0		
218	ETHOMEEN S/12	Tertiary amines ethylene oxide, soyalkyl	Akzo Nobel	10.0	35%	40%	50%	50%			15	20	25	20		
219	ETHOMEEN S/15	Tertiary amines ethylene oxide, soyalkyl	Akzo Nobel	11.1	0	10%	45%	90%			0	5	15	30		
220	ETHOMEEN S/25	Tertiary amines ethylene oxide, soyalkyl	Akzo Nobel	14.7	0	0	0	5%			0	0	0	15		
19	Ethoxylated Oleic Acid	Ethoxylated Oleic Acid	Rhone-Poulenc	n/a	45%	55%	65%	75%	80%	85%	20	28	45	70	75	
232	Fluid Q4-3667	(Not available)	Dow Corning	n/a	0	0	0	0			0	0	0	0		
236	GANEX V-216	PVP/hexadecane copolymer	ISP Corp.	10.0	0	0	0	0			0	0	0	0		
238	GANEX V-220	PVP/eicosene copolymer	ISP Corp.	8.0	0	0	0	0			0	0	0	0		
237	GANEX WP-660	(Not available)	ISP Corp.	n/a	0	0	0	0			0	0	0	0		
250	Hyamine® 1622	Di(isobutylphenoxythyl)dimethylbenzylammonium chloride	EM Science	cationic	0	5%	10%	20%			0	0	5	30		
49	Igepal? CA-420	Octoxynol-3	Rhone-Poulenc	8.0	0%	0%	5%	10%	15%	20%	0	0	0	5	15	
50	Igepal? CA-620	Octoxynol-7	Rhone-Poulenc	12.0	25%	55%	80%	85%	90%	90%	30	55	60	70	80	
51	Igepal? CA-630	Octoxynol-9	Rhone-Poulenc	13.0	27%	60%	80%	85%	90%	95%	30	55	65	75	90	
52	Igepal? CA-720	Octoxynol-12	Rhone-Poulenc	14.6	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	
9	Igepal? CO-210	Nonoxynol-2 (1.5 EO)	Rhone-Poulenc	4.6	25%	35%	45%	50%	55%	60%	10	14	20	24	27	
10	Igepal? CO-430	Nonoxynol-4	Rhone-Poulenc	8.8	20%	30%	40%	45%	50%	55%	5	10	15	30	46	
11	Igepal? CO-520	Nonoxynol-5	Rhone-Poulenc	10.0	60%	70%	75%	80%	85%	90%	45	50	60	70	80	
12	Igepal? CO-530	Nonoxynol-6	Rhone-Poulenc	10.8	80%	88%	95%	95%	95%	100%	75	85	90	120	150	
13	Igepal? CO-630	Nonoxynol-9	Rhone-Poulenc	13.0	80%	83%	87%	92%	94%	96%	70	78	85	90	100	
14	Igepal? CO-710	Nonoxynol-11	Rhone-Poulenc	13.6	76%	82%	85%	86%	86%	90%	60	75	80	88	90	
15	Igepal? CO-730	Nonoxynol-15	Rhone-Poulenc	15.0	22%	30%	36%	40%	42%	45%	10	15	20	30	40	
16	Igepal? CO-880	Nonoxynol-30	Rhone-Poulenc	17.2	30%	40%	45%	50%	55%	60%	12	18	25	36	43	
17	Igepal? CO-887	Nonoxynol-30	Rhone-Poulenc	17.2	20%	33%	40%	45%	45%	45%	6	11	15	24	27	
18	Igepal? CO-897	Nonoxynol-40	Rhone-Poulenc	17.8	0%	10%	15%	20%	24%	25%	0	0	5	15	20	
38	Lubrhophos LL-550	Free acid of complex org. phosphate alcohol	Rhone-Poulenc	anionic	23%	55%	60%	70%	75%	80%	20	30	30	35	40	
36	Lubrhophos LP-700	Complex org phospha ester of ethoxylated phenol, acid free	Rhone-Poulenc	n/a	10%	50%	55%	60%	65%	70%	5	20	25	30	35	
35	Lubrhophos LB-400	Org phosphate ester of ethoxylated oleyl alcohol, acid free	Rhone-Poulenc	n/a	20%	60%	72%	80%	84%	86%	20	60	70	80	85	
37	Lubrhophos LK-500	Org phosphate ester of ethoxylated hexanol, acid free	Rhone-Poulenc	n/a	10%	45%	48%	50%	56%	60%	5	20	25	25	28	
249	Mednique 2062	(Not available)	Cognis	n/a	0	0	5%	5%			0	0	0	5		
20	Miranol DM Conc 45%	Sodium stearoamphoacetate(Amephoteric)	Rhone-Poulenc	amepho	20%	70%	83%	85%	87%	90%	8	60	75	80	80	

WETTABILITY ALTERATION

No.	Surfactant (Trade Name)	Chemical Description	Manufacturer	HLB	Area% of oil-wet to water-wet: 24 hrs	3days	1 wk.	2 wks	1 mth	2 mth	Crude oil contact angle on calcite surface (deg. 0 = spreading, 180 = non-wet to oil): 24 hrs	3days	1 wk.	2 wks	1 mth	2 mth
21	Miranol FBS	Disodium cocoamphopropionate(Amephoteric)	Rhone-Poulenc	amepho	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	
8	MIRANOL JS CONC.	Sodium cocoamphohydroxypropysulfonate	Rhodia, Inc.	anionic	0	0	0	0	0	0	0	0	0	0	0	
7	MIRANOL, CS CONC.	Sodium cocoamphohydroxypropysulfonate	Rhodia, Inc.	anionic	0	0	0	0	0	0	0	0	0	0	0	
54	Miratain BET-D 33	Not Available(Amphoteric)	Rhone-Poulenc	amphoteric	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	
31	Mirataine BB	Laury/myristylamido propyl betain	Rhone-Poulenc	amphoteric	0	0	0	0	0	0	0	0	0	0	0	
34	Mirataine BET-O 30	Oleamido propyl betain	Rhone-Poulenc	amphoteric	0	0	0	0	0	0	0	0	0	0	0	
33	Mirataine BET-W	Cocoamido propyl betain	Rhone-Poulenc	amphoteric	0	0	0	0	0	0	0	0	0	0	0	
32	Mirataine COB	Coco/oleamido propyl betain	Rhone-Poulenc	amphoteric	0	0	0	0	0	0	0	0	0	0	0	
198	Neodol 1-3	C11 linear primary alcohol ethoxylate	Norman, Fox & Co	8.7	0	40%	50%	55%			0	60	80	85		
199	Neodol 1-5	C11 linear primary alcohol ethoxylate	Norman, Fox & Co	11.2	15%	75%	85%	85%			15	50	60	60		
200	Neodol 1-7	C11 linear primary alcohol ethoxylate	Norman, Fox & Co	12.8	10%	70%	85%	85%			15	50	70	70		
134	Neodol 1-7	C11 linear primary alcohol ethoxylate	Norman, Fox & Co	12.8	10%	60%	75%	80%	81%	82%	10	45	60	65	70	
201	Neodol 1-9	C11 linear primary alcohol ethoxylate	Norman, Fox & Co	13.9	0	10%	80%	40%			0	5	65	80		
132	Neodol 23-6.5	C12-13 linear primary alcohol ethoxylate	Norman, Fox & Co	12.1	10%	25%	70%	85%	92%	95%	10	3	80	85	90	
202	Neodol 23-6.5	C12-13 linear primary alcohol ethoxylate	Norman, Fox & Co	12.1	5%	15%	60%	60%			0	20	45	85		
133	Neodol 25-3	C12-15 linear primary alcohol ethoxylate	Shell Chemicals	7.8	30%	70%	85%	90%	95%	95%	30	60	80	90	90	
135	Neodol 25-3S	(Not available)	Shell Chemicals	n/a	0	5%	10%	20%	25%	30%	0	0	0	5	10	
136	Neodol 25-7	C12-15 linear primary alcohol ethoxylate	Norman, Fox & Co	12.3	25%	55%	65%	85%	87%	90%	24	35	40	60	70	
203	Neodol 25-7	C12-15 linear primary alcohol ethoxylate	Norman, Fox & Co	12.3	10%	45%	55%	70%			15	20	25	60		
204	Neodol 25-9	C12-15 linear primary alcohol ethoxylate	Norman, Fox & Co	13.1	0	30%	65%	55%			0	30	70	70		
210	NEODOX 23-6	(Not available)	Westhollow Tech.	n/a	85%	90%	95%	96%			75	87	90	90		
212	NEODOX 25-11	(Not available)	Westhollow Tech.	n/a	35%	65%	65%	65%			30	40	40	40		
211	NEODOX 25-6	(Not available)	Westhollow Tech.	n/a	80%	85%	90%	90%			40	40	45	45		
213	NEODOX 91-5	(Not available)	Westhollow Tech.	n/a	75%	85%	85%	85%			25	30	30	40		
214	NEODOX 91-7	(Not available)	Westhollow Tech.	n/a	70%	75%	75%	75%			20	25	25	40		
205	Norfox F-221	Complex fatty amido ester	Norman, Fox & Co	5.0	0	0	0	0			0	0	0	0		
197	Octyl Stearate	Octyl Stearate	CRODA	n/a	10%	45%	70%	83%			5	10	10	20		
175	Pluronic 17R2	Block copolymers of propylene, ethylene oxides	BASF	n/a	0	0	0	0	0		0	0	0	0	0	
163	Pluronic F 38	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	30.0	10%	15%	25%	30%	50%		0	5	5	5	10	
164	Pluronic F 77	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	24.0	0	0	0	0	0		0	0	0	0	0	
179	Pluronic F-108	Block copolymers of propylene, ethylene oxides	BASF	27.0	0	0	0	0	0		0	0	0	0	0	
176	Pluronic F-68	Block copolymers of propylene, ethylene oxides	BASF	29.0	0	0	0	0	0		0	0	0	0	0	
177	Pluronic F-87	Block copolymers of propylene, ethylene oxides	BASF	24.0	0	0	0	0	0		0	0	0	0	0	
178	Pluronic F-88	Block copolymers of propylene, ethylene oxides	BASF	28.0	0	0	0	0	0		0	0	0	0	0	
170	Pluronic L 101	Block copolymers of propylene, ethylene oxides	BASF	1.0	5%	20%	30%	45%	70%		0	15	16	17	18	
171	Pluronic L 103	Block copolymers of propylene, ethylene oxides	BASF	n/a	0	0	0	0	0		0	0	0	0	0	
172	Pluronic L 121	Block copolymers of propylene, ethylene oxides	BASF	5.0	0	15%	20%	25%	40%		0	10	10	15	18	
173	Pluronic L 122	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	4.0	10%	20%	30%	65%	85%		5	10	30	30	30	
166	Pluronic L 42	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	8.0	0	5%	15%	25%	40%		0	0	5	5	10	
167	Pluronic L 43	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	12.0	5%	10%	30%	50%	75%		0	5	10	15	20	
168	Pluronic L 44	Block copolymers of propylene, ethylene oxides	BASF	16.0	0	0	5%	10%	20%		0	0	0	5	10	
169	Pluronic L 63	Block copolymers of propylene, ethylene oxides	BASF	11.0	0	0	5%	8%	15%		0	0	0	5	10	
184	Pluronic L-31	Block copolymers of propylene, ethylene oxides	BASF	5	0	0	0	0	0		0	0	0	0	0	
185	Pluronic L-44	Block copolymers of propylene, ethylene oxides	BASF	16	0	0	0	0	0		0	0	0	0	0	
186	Pluronic L-61	Block copolymers of propylene, ethylene oxides	BASF	16	0	0	0	0	0		0	0	0	0	0	
187	Pluronic L-62	Block copolymers of propylene, ethylene oxides	BASF	7	0	0	0	0	0		0	0	0	0	0	
188	Pluronic L-64	Block copolymers of propylene, ethylene oxides	BASF	15	0	0	0	0	0		0	0	0	0	0	
189	Pluronic L-72	Block copolymers of propylene, ethylene oxides	BASF	6.5	0	0	5%	10%	15%		10	10	10	10	10	
190	Pluronic L-81	Block copolymers of propylene, ethylene oxides	BASF	2	0	0	0	5%	10%		5	5	5	5	5	
191	Pluronic L-92	Block copolymers of propylene, ethylene oxides	BASF	5.5	0	0	0	0	5%		5	5	5	5	5	

WETTABILITY ALTERATION

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					24 hrs	3days	1 wk.	2 wks	1 mth	2 mth	24 hrs	3days	1 wk.	2 wks	1 mth	2 mth
165	Pluronic P 104	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	13.0	0	0	0	0	0		0	0	0	0	0	
182	Pluronic P-103	Block copolymers of propylene, ethylene oxides	BASF	9	0	0	0	0	0		0	0	0	0	0	
183	Pluronic P-123	Block copolymers of propylene, ethylene oxides	BASF	8	0	0	0	0	0		0	0	0	0	0	
180	Pluronic P-84	Block copolymers of propylene, ethylene oxides	BASF	14.0	0	0	0	0	0		0	0	0	0	0	
181	Pluronic P-85	Block copolymers of propylene, ethylene oxides	BASF	16	0	0	0	0	0		0	0	0	0	0	
39	Rhodacal 330	Isopropylamine branched alkylbenzene aryl sulfonate	Rhodia, Inc.	anionic	0%	20%	30%	32%	36%	45%	0	10	15	15	20	
40	Rhodacal IPAM	Isopropylamine salt of linear alkylbenzene sulfonic acid	Rhodia, Inc.	anionic	0%	0%	0%	2%	5%	5%	0	0	0	0	0	
47	Rhodameen OA-910	PEG-30 oleamine(Cationic)	Rhone-Poulenc	16.4	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	
48	Rhodameen PN-430	PEG-5 hydrogenated tallow amine(Cationic)	Rhone-Poulenc	cationic	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	
41	Rhodamoxb LO	Lauryl dimethylamine oxide (nonionic/cationic)	Rhodia, Inc.	non/cat	10%	20%	25%	35%	40%	40%	5	10	10	15	20	
42	Rhodapex CD-128	Ammonium capryleth sulfate (Anionic)	Rhone-Poulenc	anionic	15%	40%	60%	70%	75%	80%	10	25	35	50	60	
43	Rhodapex CO-436	Ammonium nonoxynol-4 sulfate(Anionic)	Rhone-Poulenc	anionic	0	0	0	0	0	0	0	0	0	0	0	
45	Rhodaquat DAET-90	Not Available(Cationic)	Rhone-Poulenc	cationic	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	
46	Rhodaquat M242C/29	Cetrimonium chloride(Cationic)	Rhone-Poulenc	cationic	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	
44	Rhodaquat T	Ditallow imidazolinium(Cationic)	Rhone-Poulenc	cationic	10%	35%	45%	55%	65%	67%	10	20	30	35	40	
53	RHODOPOL 23	Xanthan gum	Rhone-Poulenc	n/a	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	
103	SDS	Sodium dodecyl sulfonate	Aldrich	anionic	0	0	0	0	0	0	0	0	0	0	0	
85	SIL WET® L-7001	Silicone glycol copolymer	Union Carbide	5~8	25%	50%	65%	72%	74%	75%	15	35	45	50	55	
83	SIL WET® L-720	Silicone glycol copolymer	Union Carbide	5~8	23%	50%	70%	76%	80%	82%	12	15	16	17	18	
84	SIL WET® L-722	Silicone glycol copolymer	Union Carbide	5~8	25%	55%	68%	73%	75%	75%	15	20	20	20	20	
86	SIL WET® L-7500	Silicone glycol copolymer	Union Carbide	5~8	25%	50%	55%	60%	65%	70%	20	3	35	40	45	
87	SIL WET® L-7600	Silicone glycol copolymer	Union Carbide	5~8	30%	66%	74%	82%	85%	88%	25	35	38	39	39	
88	SIL WET® L-7602	Silicone glycol copolymer	Union Carbide	5~8	30%	65%	70%	80%	85%	85%	18	32	40	45	52	
89	SIL WET® L-7605	Silicone glycol copolymer	Union Carbide	5~8	30%	55%	75%	80%	84%	87%	20	24	26	28	30	
90	SIL WET® L-7607	Silicone glycol copolymer	Union Carbide	5~8	35%	60%	70%	81%	83%	85%	20	30	32	34	35	
91	SIL WET® L-7614	Silicone glycol copolymer	Union Carbide	5~8	0	0	5%	5%	5%	10%	0	0	0	5	6	
82	SIL WET® L-77	Silicone glycol copolymer	Union Carbide	5~8	30%	75%	80%	85%	90%	92%	10	16	18	20	20	
92	SPAN® 20	Sorbitan monolaurate	ICI Chemicals	8.6	20%	35%	40%	52%	60%	66%	20	40	60	70	75	
93	SPAN® 40	Sorbitan monopalmitate	SIGMA	6.7	10%	25%	40%	45%	50%	52%	5	25	30	35	45	
94	SPAN® 60	Sorbitan monostearate	ICI Chemicals	4.7	10%	20%	30%	40%	45%	50%	5	15	15	17	18	
95	SPAN® 80	Sorbitan monooleate	ATLAS Chemicals	4.3	0	0	0	0	0	0	0	0	0	0	0	
96	SPAN® 83	Not Available	Aldrich	n/a	0	0	0	5%	5%	5%	0	0	0	0	5	
97	SPAN® 85	Sorbitan trioleate	ICI Chemicals	1.8	10%	25%	30%	40%	47%	50%	10	15	15	20	20	
229	Surfactant 190	(Not available)	Dow Corning	n/a	0	0	0	10%			0	0	0	10		
230	Surfactant 193	(Not available)	Dow Corning	n/a	0	0	0	40%			0	0	0	10		
231	Surfactant 5103	(Not available)	Dow Corning	n/a	0	0	0	0			0	0	0	0		
234	Surfadone LP-100	Caprylyl pyrrolidone	ISP Corp.	6.0	0	0	0	0			0	0	0	0		
235	Surfadone LP-300	Lauryl pyrrolidone	ISP Corp.	3.0	20%	65%	80%	83%			10	30	40	40		
141	Surfynol? 2502	(Not available)	Air Products	n/a	0	0	0	5%	5%	8%	0	0	0	0	5	
139	Surfynol® 440	PEG-3.5 tetramethyl decynediol	Air Products	8	0	0	0	0	0	0	0	0	0	0	0	
140	Surfynol® 465	PEG-10 tetra- methyl decynediol	Air Products	13	0	0	5%	5%	8%	8%	0	0	0	5	5	
142	Surfynol? SE-F	Surfactant blend	Air Products	4 ~ 5	0	0	0	0	0	0	0	0	0	0	0	

WETTABILITY ALTERATION

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					24 hrs	3days	1 wk.	2 wks	1 mth	2 mth	24 hrs	3days	1 wk.	2 wks	1 mth	2 mth
110	Tergitol® 15-S-12	C12-C14 seconary alcohol ethoxylate	Union Carbide	14.7	60%	75%	80%	86%	88%	90%	50	65	65	70	70	
111	Tergitol® 15-S-20	C12-C14 seconary alcohol ethoxylate	Union Carbide	14.7	40%	60%	70%	82%	84%	85%	35	35	40	45	50	
106	Tergitol® 15-S-3	C12-C14 seconary alcohol ethoxylate	Union Carbide	8.3	25%	30%	40%	45%	50%	55%	12	15	20	25	30	
112	Tergitol® 15-S-40	C12-C14 seconary alcohol ethoxylate	Union Carbide	16.4	40%	55%	65%	80%	82%	85%	20	25	30	35	35	
107	Tergitol® 15-S-5	C12-C14 seconary alcohol ethoxylate	Union Carbide	10.6	75%	80%	90%	95%	98%	100%	80	80	90	120	150	
108	Tergitol® 15-S-7	C12-C14 seconary alcohol ethoxylate	Union Carbide	12.4	65%	80%	84%	90%	93%	95%	60	70	80	88	90	
109	Tergitol® 15-S-9	C12-C14 seconary alcohol ethoxylate	Union Carbide	13.3	58%	75%	80%	82%	84%	85%	50	70	75	80	83	
104	Tergitol® MIN FOAM 1X	Propoxylated & ethoxylated fatty acids, alcohols	Union Carbide	n/a	75%	80%	85%	90%	95%	95%	70	90	90	91	92	
105	Tergitol® MIN FOAM 2X	Propoxylated & ethoxylated fatty acids, alcohols	Union Carbide	n/a	70%	80%	85%	90%	95%	95%	70	85	85	90	90	
116	Tergitol? NP-10	Ethoxylated nonylphenol, nonoxynol-10	Union Carbide	13.2	50%	70%	80%	86%	88%	90%	40	55	60	70	80	
117	Tergitol? NP-13	Ethoxylated nonylphenol, nonoxynol-13	Union Carbide	13.9	10%	25%	35%	40%	40%	40%	5	15	20	25	25	
113	Tergitol? NP-4	Ethoxylated nonylphenol, nonoxynol-4	Union Carbide	8.9	0	0	0	5%	5%	5%	0	0	0	0	0	
114	Tergitol? NP-6	Ethoxylated nonylphenol, nonoxynol-6	Union Carbide	10.9	35%	50%	65%	70%	75%	75%	15	15	20	23	25	
143	Tergitol? NP-9	Ethoxylated nonylphenol, nonoxynol-9	Union Carbide	12.9	20%	50%	60%	85%	90%	95%	15	45	60	85	90	
115	Tergitol? NP-9.5	Ethoxylated nonylphenol, nonoxynol-9.5	Union Carbide	13.1	45%	60%	70%	82%	82%	85%	40	50	65	70	80	
174	Tetronic 701	Block copolymers of propylene, ethylene oxides	BASF	3.0	5%	10%	20%	30%	40%		0		10	15	20	
75	Trimethyl amm bromide	Trimethyl(tetradecyl) ammonium bromide	SIGMA	cationic	35%	82%	88%	95%	98%	98%	40	70	90	120	150	
144	Triton H-66	Phosphate ester, potassium salt	Union Carbide	anionic	20%	40%	50%	75%	80%	80%	10	15	20	30	30	
126	Triton X-100	Ethoxylated octylphenol, octoxynol-9	Rohm & Hass	13.4	40%	55%	80%	88%	90%	92%	25	50	75	85	90	
127	Triton X-114	Ethoxylated octylphenol, octoxynol-8	Aldrich	12.3	40%	60%	82%	90%	91%	93%	30	50	78	85	89	
128	Triton X-165	Ethoxylated octylphenol, octoxynol-16	Rohm & Hass	15.5	40%	55%	75%	85%	90%	90%	25	30	60	70	80	
129	Triton X-405	Ethoxylated octylphenol, octoxynol-40	Aldrich	17.6	15%	24%	30%	38%	43%	45%	10	12	14	15	16	
125	Triton X-45	Ethoxylated octylphenol, octoxynol-5	Union Carbide	9.8	20%	35%	50%	60%	66%	70%	20	30	35	45	50	
130	Triton X-705	Ethoxylated octylphenol, octoxynol-70	SIGMA	18.4	15%	20%	30%	35%	38%	40%	10	10	15	15	20	
131	Triton XL-80N	Propoxylated & ethoxylated fatty acids, alcohols	Union Carbide	n/a	40%	80%	84%	88%	90%	92%	35	65	75	80	85	
118	Triton? BG-10	Alkylpolyglucoside	Dow Chemicals	n/a	58%	80%	90%	95%	96%	97%	50	75	85	90	90	
120	Triton? CF-87	Alkylaryl ether, modified	D.C. Atkins Son	12.7	45%	65%	80%	85%	88%	90%	50	67	80	85	90	
119	Triton? CG-110	Alkylpolyglucoside	Dow Chemicals	n/a	55%	75%	88%	90%	92%	93%	50	70	75	80	80	
121	Triton? N-101	(Not available)	Union Carbide	n/a	45%	65%	85%	90%	91%	92%	45	70	82	87	88	
122	Triton? QS-44	Phosphate surfactant in free acid form	Union Carbide	n/a	0	0	0	0	0	0	0	0	0	0	0	
123	Triton? X-15	Ethoxylated octylphenol, octoxynol-1	Union Carbide	4.9	35%	50%	60%	70%	75%	75%	15	20	20	30	30	
124	Triton? X-35	Ethoxylated octylphenol, octoxynol-3	Rohm & Hass	7.8	0	0	0	0	0	0	0	0	0	0	0	
98	Tween® 21	POE (4) Sorbitan monolaurate	ICI Chemicals	13.3	40%	60%	70%	80%	85%	86%	45	60	60	65	70	
99	Tween® 60	POE (20) Sorbitan monostearate	Unknown	14.9	10%	25%	30%	35%	38%	40%	5	10	10	15	15	
100	Tween® 61	POE (4) Sorbitan monostearate	ATLAS Chemicals	9.6	0	0	5%	8%	9%	10%	0	0	0	0	5	
101	Tween® 81	POE (5) Sorbitan monooleate	ICI Chemicals	10.0	70%	80%	90%	92%	94%	95%	70	75	80	90	92	
102	Tween® 85	POE (20) Sorbitan trioleate	Aldrich	11.0	30%	50%	55%	60%	68%	70%	25	35	40	40	45	

Note: TBM= to be determined

APPENDIX B.

LIST OF CALCITE CHIP – McELROY CRUDE OIL CLEANING RESULTS WITH SURFACTANTS

Wettability Alteration Test for McElroy Crude Oil in 2%wt. NaCl Solution

Calcite Crystals aged in McElroy Crude Oil at 85 癈 for **24 hours** March 8, 2005

Surfactant Name	HLB	Area% from Oil-wet to Water-wet						Solution appearance
		1 hour	2 hours	8 hours	24 hours	3 days	1 week	
Igepal? CO-530	10.8	75%	85%	92%	95%	96%	96%	slightly yellow
Igepal? CO-630	13	65%	65%	80%	80%	82%	85%	clear
Igepal? CO-710	13.6	70%	75%	80%	80%	85%	86%	clear
Neodol? 1-7	12.8	85%	90%	90%	92%	93%	95%	clear
Neodol? 1-9	13.9	72%	75%	80%	80%	83%	85%	clear
Neodol? 25-7	12.3	85%	90%	90%	90%	90%	90%	clear
Neodol? 25-9	13.1	80%	80%	85%	85%	92%	92%	clear
NEODOX? 25-6	n/a	50%	50%	65%	70%	80%	82%	clear
NEODOX? 25-11	n/a	70%	75%	78%	80%	80%	80%	clear
Tergitol? 15-S-5	10.6	72%	72%	90%	90%	90%	90%	slightly yellow
Tergitol? 15-S-7	12.4	85%	90%	92%	95%	92%	92%	clear
Tergitol? 15-S-9	13.3	85%	87%	90%	92%	93%	93%	clear
Tergitol? 15-S-12	14.7	77%	80%	85%	85%	85%	85%	clear
Tergitol? 15-S-20	14.7	65%	65%	70%	70%	70%	70%	clear
Triton X-100	13.4	50%	55%	65%	70%	70%	72%	clear
Triton X-114	12.3	65%	70%	80%	85%	85%	85%	slightly yellow
Triton X-165	15.5	60%	65%	70%	75%	80%	80%	clear
Triton X-405	17.6	50%	50%	60%	70%	75%	75%	clear
SIL WET? L-77	n/a	80%	80%	80%	80%	83%	83%	clear
TritonTM BG-10	n/a	5%	5%	10%	10%	20%	30%	clear
Agrimul? PG 2067	13.6	0%	0%	5%	10%	20%	30%	clear
ALCODET SK	12.7	80%	85%	85%	85%	86%	85%	slightly yellow
ALCODET 218	13.6	75%	80%	86%	85%	85%	85%	clear
ARQUAD T-50	n/a	15%	20%	45%	65%	70%	70%	slightly yellow
C_{10}-triphenyl-bromide	n/a	0%	0%	0%	0%	0%	0%	clear
SIMULSOL AS 48	n/a	0%	0%	0%	0%	0%	0%	clear
SIMULSOL SL 4	n/a	15%	15%	15%	20%	30%	40%	clear
SIMULSOL SL 55	n/a	0%	0%	0%	10%	25%	25%	cloudy

Wettability Alteration Test for McElroy Crude Oil in McElroy **Synthetic Brine**								
Calcite Crystals aged in McElroy Crude Oil at 85 癈 for **24 hours** March 8, 2005								
		Area% from Oil-wet to Water-wet						Solution
Surfactant Name	HLB	1 hour	2 hours	8 hours	24 hours	3 days	1 week	appearance
Igepal? CO-530	10.8	55%	55%	65%	70%	70%	70%	slightly yellow
Igepal? CO-630	13	65%	65%	75%	80%	80%	80%	clear
Igepal? CO-710	13.6	20%	30%	40%	50%	80%	80%	clear
Neodol? 1-7	12.8	80%	85%	87%	90%	90%	92%	clear
Neodol? 1-9	13.9	70%	70%	75%	80%	85%	85%	clear
Neodol? 25-7	12.3	55%	65%	70%	75%	82%	87%	clear
Neodol? 25-9	13.1	60%	65%	76%	80%	82%	82%	clear
NEODOX? 25-6	n/a	50%	50%	70%	75%	78%	78%	clear
NEODOX? 25-11	n/a	30%	40%	50%	60%	60%	60%	clear
Tergitol? 15-S-5	10.6	75%	75%	80%	80%	85%	86%	slightly cloudy
Tergitol? 15-S-7	12.4	80%	85%	90%	90%	92%	92%	clear
Tergitol? 15-S-9	13.3	75%	78%	80%	85%	90%	90%	clear
Tergitol? 15-S-12	14.7	50%	50%	60%	70%	75%	75%	clear
Tergitol? 15-S-20	14.7	45%	45%	50%	55%	70%	75%	clear
Triton X-100	13.4	50%	75%	80%	80%	85%	85%	clear
Triton X-114	12.3	**90%**	**92%**	**92%**	**93%**	**95%**	**95%**	**slightly yellow**
Triton X-165	15.5	50%	50%	60%	60%	65%	70%	clear
Triton X-405	17.6	50%	55%	55%	65%	70%	73%	clear
SIL WET? L-77	n/a	70%	80%	80%	85%	88%	88%	clear
TritonTM BG-10	n/a	0%	0%	0%	10%	20%	30%	clear
Agrimul? PG 2067	13.6	0%	0%	0%	5%	15%	30%	clear
ALCODET SK	12.7	50%	75%	85%	85%	90%	92%	slightly yellow
ALCODET 218	13.6	40%	40%	60%	70%	70%	70%	clear
ARQUAD T-50	n/a	15%	15%	60%	75%	75%	75%	slightly yellow
C_{10}-triphenyl-bromide	n/a	0%	0%	0%	0%	10%	15%	clear
SIMULSOL AS 48	n/a	0%	0%	0%	0%	10%	15%	clear
SIMULSOL SL 4	n/a	0%	0%	0%	5%	15%	30%	clear
SIMULSOL SL 55	n/a	0%	0%	0%	0%	5%	20%	cloudy

Wettability Alteration Test for McElroy Crude Oil in **2.0wt.% NaCl** Solution							
Calcite Crystals aged in McElroy Crude Oil at 85 癈 for **7 days**							
		Solution	Area% from Oil-wet to Water-wet				
Surfactant Name	HLB	appearance	24 hours	3 days	1 week	2 weeks	1 month
Igepal? CO-530	10.8	cloudy	0%	2%	7%	15%	40%
Igepal? CO-630	13	clear	0%	0%	2%	5%	10%
Igepal? CO-710	13.6	clear	0%	0%	0%	3%	8%
Neodol? 1-7	12.8	clear	0%	0%	0%	3%	10%
Neodol? 1-9	13.9	clear	0%	0%	2%	5%	15%
Neodol? 25-7	12.3	clear	0%	0%	5%	10%	20%
Neodol? 25-9	13.1	clear	0%	0%	0%	5%	10%
NEODOX? 25-6	n/a	clear	0%	0%	5%	15%	35%
NEODOX? 25-11	n/a	clear	0%	0%	0%	0%	0%
Tergitol? 15-S-5	10.6	slightly clou	0%	2%	10%	20%	50%
Tergitol? 15-S-7	12.4	clear	0%	2%	6%	15%	30%
Tergitol? 15-S-9	13.3	clear	0%	0%	0%	3%	10%
Tergitol? 15-S-12	14.7	clear	0%	0%	0%	0%	2%
Tergitol? 15-S-20	14.7	clear	0%	0%	0%	0%	2%
Triton X-100	13.4	clear	0%	0%	2%	4%	10%
Triton X-114	12.3	cloudy	0%	0%	0%	0%	3%
Triton X-165	15.5	clear	0%	0%	0%	0%	0%
Triton X-405	17.6	clear	0%	0%	0%	3%	6%
SIL WET? L-77	n/a	slightly clou	0%	0%	0%	0%	2%
TritonTM BG-10	n/a	clear	0%	0%	0%	0%	0%
Agrimul? PG 2067	13.6	clear	0%	0%	0%	0%	0%
ALCODET SK	12.7	clear	0%	0%	0%	0%	3%
ALCODET 218	13.6	clear	0%	0%	0%	0%	0%
ARQUAD T-50	n/a	clear	0%	0%	0%	0%	0%
C_{10}-triphenyl-bromide	n/a	clear	0%	0%	0%	0%	0%
SIMULSOL AS 48	n/a	clear	0%	0%	0%	0%	0%
SIMULSOL SL 4	n/a	clear	0%	0%	2%	5%	0%
SIMULSOL SL 55	n/a	cloudy	N/A	N/A	N/A	N/A	N/A

Wettability Alteration Test for McElroy Crude Oil in McElroy Synthetic Brine							
Calcite Crystals aged in McElroy Crude Oil at 85 癈 for 7 days							
		Solution	Area% from Oil-wet to Water-wet				
Surfactant Name	HLB	appearance	24 hours	3 days	1 week	2 weeks	1 month
Igepal? CO-530	10.8	cloudy	0%	0%	0%	0%	0%
Igepal? CO-630	13	clear	0%	0%	0%	0%	5%
Igepal? CO-710	13.6	clear	0%	0%	0%	0%	3%
Neodol? 1-7	12.8	clear	0%	0%	0%	3%	10%
Neodol? 1-9	13.9	clear	0%	0%	0%	0%	3%
Neodol? 25-7	12.3	clear	0%	3%	10%	20%	45%
Neodol? 25-9	13.1	clear	0%	5%	15%	30%	70%
NEODOX? 25-6	n/a	clear	0%	0%	0%	0%	0%
NEODOX? 25-11	n/a	clear	0%	0%	0%	0%	0%
Tergitol? 15-S-5	10.6	slightly clou	0%	0%	0%	0%	0%
Tergitol? 15-S-7	12.4	clear	0%	0%	0%	2%	10%
Tergitol? 15-S-9	13.3	clear	0%	0%	0%	3%	10%
Tergitol? 15-S-12	14.7	clear	0%	0%	5%	10%	20%
Tergitol? 15-S-20	14.7	clear	0%	0%	0%	5%	15%
Triton X-100	13.4	clear	0%	0%	2%	6%	12%
Triton X-114	12.3	cloudy	0%	0%	0%	0%	0%
Triton X-165	15.5	clear	0%	2%	10%	20%	40%
Triton X-405	17.6	clear	0%	3%	7%	12%	25%
SIL WET? L-77	n/a	slightly clou	0%	0%	0%	0%	2%
TritonTM BG-10	n/a	clear	0%	0%	0%	0%	0%
Agrimul? PG 2067	13.6	clear	0%	0%	0%	0%	0%
ALCODET SK	12.7	clear	0%	0%	0%	0%	2%
ALCODET 218	13.6	clear	0%	0%	0%	0%	6%
ARQUAD T-50	n/a	clear	0%	0%	0%	0%	0%
C_{10}-triphenyl-bromide	n/a	clear	0%	0%	0%	0%	0%
SIMULSOL AS 48	n/a	clear	0%	0%	0%	0%	0%
SIMULSOL SL 4	n/a	clear	0%	0%	2%	5%	15%
SIMULSOL SL 55	n/a	cloudy	N/A	N/A	N/A	N/A	N/A

ATTACHMENT 2

Paper SPE 99612 -- Study of Wetting Behavior and Surfactant EOR in Carbonates with Model Compounds

SPE 99612

A Study of Wetting Behavior and Surfactant EOR in Carbonates with Model Compounds

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This paper was prepared for presentation at the 2006 SPE/DOE Symposium on Improved Oil Recovery held in Tulsa, Oklahoma, U.S.A., 22–26 April 2006.

Abstract

This study focuses on the mechanisms responsible for enhanced oil recovery (EOR) from fractured carbonate reservoirs by surfactant solutions, and methods to screen for effective chemical formulations quickly. One key to this EOR process is the surfactant solution reversing the wetting of the carbonate surfaces from oil-wet to water-wet conditions. This effect allows the aqueous phase to imbibe into the matrix spontaneously and expel oil bypassed by a waterflood.

This study used different naphthenic acids (NA) dissolved in decane as a model oil to render calcite surfaces oil-wet. Because pure compounds are used, trends in wetting behavior can be related to NA molecular structure as measured by solid adsorption, contact angle and a novel, simple flotation test with calcite. Experiments with different surfactants and NA-treated calcite powder provide information about mechanisms responsible for sought after reversal to a water-wet state. Results indicate this flotation and a calcite chip cleaning test are rapid screening tools to identify better EOR surfactants for carbonates.

The study considers the application of surfactants for enhanced oil recovery (EOR) from carbonate reservoirs. This technology provides a new opportunity for EOR, especially for fractured carbonate where waterflood response typically is poor and the matrix is a high oil-saturation target for this process.

Introduction

Typically only about a third of the original oil in place (OOIP) is recovered by primary and secondary recovery processes, leaving two-thirds trapped in reservoirs as residual oil. About half of world's discovered oil reserves are in carbonate reservoirs and many of these reservoirs are naturally fractured.[1] According to a recent review of 100 fractured reservoirs,[2] carbonate fractured reservoirs with high matrix porosity and low matrix permeability especially could use enhanced oil recovery (EOR) processes. The oil recovery from these reservoirs is typically very low via conventional technology, due in part to fractured carbonate reservoirs (about 80%) being originally oil-wet, or at least, mixed wettability. Injected water will not penetrate easily into the oil-wet porous matrix and so can not displace the oil in place.

Wettability of carbonate reservoirs has been widely recognized an important parameter in oil recovery by flooding technology.[3-6] Because altering the wettability of rock surface to preferentially water-wet conditions is critical to oil recovery, alteration of reservoir wettability by surfactants has been intensively studied and many research papers have been published[7]. Vijapurapu and Rao at Louisiana University studied the capability of certain ethoxy alcohol surfactants to alter wettability of the Yates reservoir rock from strongly oil-wet to water-wet.

They reported that the advancing contact angle of water can be reduced from 158° to 39° by addition of the surfactant at a concentration of 3500 ppm.[8] Seethepali and co-workers at University of Houston reported that several anionic surfactants (SS-6656, Alfoterra 35, 38, 63 65 and 68) in the presence of Na_2CO_3 can change a calcite surface wetted by a West Texas crude oil to intermediate/water-wet conditions as well as or even better than an efficient cationic surfactant.[9] Zhang and co-workers at Rice University investigated also the effect of electrolyte concentration, surfactant concentration and water/oil ratio on wettability alteration. They reported that wettability of calcite surface can be altered to about intermediate oil-wet to preferentially water-wet condition with alkaline/anionic surfactant systems. Adsorption of anionic surfactants on a dolomite surface can be significantly reduced in the presence of sodium carbonate.[10]

Xie and co-workers at University of Wyoming reported that after imbibition of reservoir brine had ceased, immersion of a core in surfactant solution can produce an additional recovery of 5 to 10% OOIP, and they ascribed this additional oil recovery to increased water wetness of the core.[11] Enrique and co-workers examined wettability conditions of solid/brine/n-dodecane systems at various surfactant concentrations and different ionic strength. They concluded that the wettability in solid/oil/brine systems could be changed by diffusion, through the aqueous phase, of surfactant species that were originally present in the oil phase while the gradual adsorption of these molecules on the solid walls modifies the surface energy. [12]

Standnes studied spontaneous imbibition (SI) into preferential oil-wet carbonate porous medium when it is exposed to a water-phase containing cationic surfactants of the type CnTAB (alkyl trimethyl ammonium bromide) and developed a simple analytical model to obtain quantitative information about SI rates of aqueous surfactant solution.[13] Standnes and Austad studied non-toxic and low cost amines as wettability alteration surfactants in carbonates. They reported that C_{10}-amine was compatible with high salinity brine at pH<7 in the temperature range of 20 – 70 °C, but C_{12}-amine was unstable at similar conditions. 1.0 wt.% C_{10}-amine dissolved in brine at pH=6.5 imbibed spontaneously into oil-wet reservoir dolomite cores at 20 and 40 °C, and the oil recovery varied between 50 – 75% of OOIP depending on the core properties. The mechanism for the wettability alteration using C_{10}-amine is proposed to be desorption of strongly adsorbed carboxylate groups from the carbonate surface by the formation of ion-pairs with the surfactant monomer.[14]

Bryant and co-workers studied wettability alteration induced by adsorption and removal of amine surfactants of known molecular structure on mica surfaces that were exposed to decane solutions of the surfactants. They reported that only weak surfactant adsorption occurred from non-aqueous solutions. Differences among the molecular structures were greater for increased levels of ethoxylation; differences due to hydrocarbon chain length were negligible. They also reported that stronger adsorption, higher contact angles and more stable surfactant layers could be demonstrated when mica was exposed to aqueous surfactant solutions, depending on the pH of the aqueous phase. Low pH conditions that promote protonation of the surfactant amine groups produced the greatest wettability alteration. Above a pH of 8 or 9, no adsorbed surfactant molecule remained on mica surface.[15] Ashayer and co-workers studied the influence of partitioning and adsorption of surfactant molecules (alkyl ether carboxylic acid with four ethylene oxide groups in its chain) on the wetting phenomena. Their experiments showed two different mechanisms responsible for wettability alteration. The first one is due to the adsorption of surfactant at the oil-water interface. The second one is due to the adsorption of surfactant molecules on the solid surface, but this is much slower than the former one. The wettability

alteration from water-wet to oil-wet increases as the salinity increases. This may help explain less oil production at higher salinity.[16]

It is generally accepted that adsorption of polar compounds onto rock surface has a significant effect on the wettability of reservoirs.[17-24] In other words, the wettability of hydrocarbon reservoirs depends on the specific interactions in the oil/rock/brine systems. Naphthenic acids are the products of extensive oxidation of crude oil and play an important role in wettability control of reservoirs. Carboxylic groups in naphthenic acids from the crude oil are the most strongly adsorbed material onto the rock surface, and they may act as "anchor" molecules for other surface-active components present in the crude oil. However, there is only limited knowledge of the influence of organic acids on the three-phase system of oil/brine/rock.

In this paper we will present and discuss (1) adsorption of naphthenic acids (NAs) on calcite powder from n-decane (model oil) at room temperature and the relationship between molecular structure of naphthenic acids and their adsorption from non-aqueous media. (2) wettability of the calcite powder treated with various naphthenic acids and the influence of molecular structure of naphthenic acids on the wettability of calcite surface. (3) contact angle of water on the surface of a calcite crystal treated with various naphthenic acids and the surface energy of the calcite surfaces. These data combined with molecular simulation provide a prediction of the influence of molecular structure of naphthenic acids on calcite surface energy. In addition, reversion of the wettability from oil-wet back to water-wet by use of surfactant aqueous solution is also presented and discussed. Furthermore, data are presented for some selected surfactants on recovery of model oil from limestone core via a spontaneous imbibition test.

Experimental

Materials: Calcite crystals (Iceland Spar) used in our study for measurement of contact angle are purchased from WARD's Natural Science (Rochester, NY). Calcite powder for measurements of adsorption of naphthenic acids from non-aqueous phase and flotation test is purchased from Alfa Aesar Company (Ward Hill, MA) and are activated at 120 °C for 2 hours before used for experiments. The powder has a density of 2.93 g/cm^3 and ~5 μm particle size, and the specific surface area was determined to be 1.67 m^2/g.

Naphthenic acids studied in this research are purchased from Aldrich, Inc. (St. Louis, MO) and used without any purification. The naphthenic acids we investigated are: (1) cyclohexanecarboxylic. (2) cyclohexanepropionic acid. (3) cyclohexanebutyric acid. (4) cyclohexanepentanoic acid. (5) trans-4- pentylcyclohexanecarboxylic acid. Their molecular structures and related parameters are list in Table 1.

Surfactants investigated are mainly divided between a series of cationic and nonionic chemicals.

Measurement of adsorption of naphthenic acids (NAs) on calcite surface from non-aqueous phase: (1) Prepare naphthenic acid solution in n-decane. Solutions were made from 0.005 - 0.067 M, which is equivalent to acid numbers of 0.45 - 5.1 for the selected naphthenic acids. (2) Mix 10.0 ml naphthenic-decane solution with 0.5 g calcite powder in a test tube. Then shake the test tube at room temperature for 12 hours in order to establish adsorption equilibrium. (3) Separate the solution and calcite powder after adsorption via a centrifuge. Remove the supernatant solution for analysis of the equilibrium concentration of NAs via GC-MS (Hewlett-Packard HP-G 1800A GCD system). Naphthalene ($C_{10}H_8$) was used as internal standard.

Flotation test for wettability of calcite powder with adsorption of naphthenic acids: After the measurement of adsorption, the separated calcite powder in test tubes was dried at 85

°C to remove all n-decane. 10 ml of distilled water was added to the tube and the tube was shaken vigorously for 2 minutes. After allowing the test tubes to stand vertically, the volume of calcite powder in the bottom (water-wet portion) and top (oil-wet portion) were measured. After allowing the test tube to sit for 2 hours, a final reading was taken for the volume percentage of solids at the top and the bottom.

Measurement of contact angle of calcite surface: (1) Clean new calcite crystals. Wash the crystals with heptane and toluene separately, and then dry the samples in an oven at 85 °C for an hour. (2) Prepare various naphthenic acid solutions in decane at 6.62×10^{-2} M, which is equivalent to a total acid number (TAN) of 5 for all selected naphthenic acids. (3) Immerse the clean calcite crystal in each naphthenic acid solution in decane for 24 hours at room temperature. Take the crystals out of the solutions carefully and dry them in an oven at 85 °C for an hour to remove all extra solvent. (4) Measure advancing contact angle of water on the treated calcite crystal surface at room temperature by use of an Advanced Goniometer (Model 500, Rame-Hart, Inc.). The crystal sample was placed in a chamber saturated with distilled water. The contact angle was recorded every one minute until the change of contact angle is less than 0.2° within a 10 minute interval. (5) Break a large calcite crystal to small pieces in order to get a fresh surface. Measure advancing contact angle of water on the new surface using the same method as described in step 4.

Model oil for surfactant performance testing: Based on the results of the experiments described above, a model oil composition was selected that changes the calcite surface to an oil-wet condition. The model oil used for the remainder of the study that investigated surfactant effects was selected: cyclohexanepentanoic acid at 1.48 wt% in –decane. This is equivalent to a TAN of 4.5.

Flotation test of wettability alteration by selected surfactant aqueous solutions: Aqueous surfactant solutions were added to test tubes at different concentrations (100, 50 and 25 ppm) containing powdered calcite treated with the model oil. After shaking the test tube vigorously for 2 minutes, it was left sit for 2 hours or more. The volume of calcite powder in bottom and top was measured. If there is foam at the top, the bubbles were broken before taking a reading. The more the powder sunk, the better the surfactant's performance in reversing wettability.

Interfacial tension (IFT) measurement: In order to study equilibrium phase behavior at the oil and aqueous solution interface, the model oil and surfactant aqueous solution were mixed in a test tube in 1:1 volume ratio. The test tubes were shaken at room temperature and left standing for at least two weeks to achieve phase equilibrium. The IFT between the top oil layer and bottom water layer was measured by a spinning drop interfacial tensiometer, Model 510 from Temco, Inc. An oleic phase drop (2 μl) was placed into a glass tube containing the aqueous phase, and spun at high speed. Rotation continued until reaching an equilibrium condition (typically in less than 2 hours), as indicated by no drop shape change for 30 minutes at the test temperature of
30 ^{o}C.

Spontaneous imbibition test of model oil recovery: The last series of experiments compares the ability of each of these different surfactants to recover the model oil phase from a limestone cores. These 1" x 2" cores were cut from a slab of limestone obtained by New Mexico Travertine. The air permeability of these cores is fairly low, ranging from 5 – 20 md. The limestone cores were first dried at 120°C for 2 hours to remove adsorbed moisture. After cooling to room temperature, the cores were placed in a vacuum system for 4 hours and the model oil

was introduced and allowed to saturate the cores over night. Then the saturated cores were placed into Amott cells (see Figure 1) containing the various surfactant solutions at a concentration of 0.4 wt% in distilled water. As the aqueous phase imbibes into the core, oil is expelled and captured in the volumetric burette. The cells were maintained at room temperature and the oil recovery was monitored versus time.

Results and Discussion

Adsorption of naphthenic acids on calcite surface from n-decane media: Adsorption isotherms of selected NAs on calcite surface from n-decane are shown in Figure 2. In general, adsorption of the NAs on calcite surface from n-decane media is in the order: cyclohexanepropionic acid > cyclohexanebutyric acid > cyclohexanepentanoic acid > cyclohexanecarboxylic acid > trans-4-pentylcyclohexane carboxylic acid. Because cyclohexanepropionic acid, cyclohexanebutyric acid, cyclohexanepentanoic acid and cyclohexanecarboxylic acid are analogues, it indicates that adsorption of the NAs decreases with increase of alkyl chain length with exception of cyclohexanecarboxylic acid. This may be explained by the interaction between alkyl chain of NA and n-decane molecules. The longer the alkyl chain, the stronger the interaction between acid and solvent molecules; this reduces the adsorption of NA on the calcite surface. As to the exception of cyclohexanecarboxylic acid, the steric exclusion of cyclohexane ring directly connected to the carboxyl group in its molecules has a significant influence on the adsorption on calcite surface, which dramatically reduces adsorption of cyclohexanecarboxylic acid. The same reason may also be an explanation of the small adsorption of trans-4-pentylcyclohexane carboxylic acid. In other words, the adsorption may be related to interaction in term of solubility of the NA in the solvent phase (n-decane), with the added feature that the NA species will form dimer compounds in the non-aqueous media. The adsorption layer is formed by orientation of carboxyl groups toward calcite surface because the surface carries positive charges.[23]

For engineering purposes, the adsorption isotherms are also plotted as adsorption amount (mg of NA per g calcite powder) versus total acid number (TAN) and are shown in Figure 3. TANs were calculated by amount (in mg) of KOH required to neutralize NA in 1 mL of the oil. From these plots, it can seen that the adsorption amount in mg/g is still in the order of cyclohexanepropionic acid > cyclohexanebutyric acid > cyclohexanepentanoic acid > cyclohexanecarboxylic acid ~ trans-4-pentyl cyclohexane carboxylic acid. Due to its greater molecular weight, the mass of adsorption of trans-4-pentylcyclohexanecarboxylic acid is very close to cyclohexanecarboxylic acid. In addition, adsorption of these two NAs has very little change with an increase of their TANs. For the other three NAs, their adsorption amount increases gradually with increase of the TANs.

Flotation test of calcite powder treated with different naphthenic acids: We developed a simple flotation test to demonstrate the relative change in wetting for a calcite surface caused by exposure to different NA chemical structures. This test method uses the concept that with a powdered calcite sample rendered oil-wet, that this material will float when contacted with water. The general procedure for this flotation test method has been described in the previous part.

Photos of the flotation test of calcite powder treated with different NAs are shown in Figures 4(a) and 4(b). Tubes 1 to 5 contain powdered calcite samples treated with the 5 selected NAs separately. Volume of oil-wet (floating) powder for the 5 investigated NAs is in the order: trans-4-pentylcyclohexane carboxylic acid ~ cyclohexanepentanoic acid > cyclohexane butyric acid >

cyclohexanepropionic acid > cyclohexane carboxylic acid. It is almost in reverse order of adsorption on calcite surface. This indicates that their ability to alter calcite surface to become oil-wet is not related directly to their adsorption on calcite surface, but depends on their molecular structures. For example, although its adsorption is smallest among the five investigated acids, trans-4-pentylcyclohexane carboxylic acid can alter calcite powder to be almost completely oil-wet. On the other hand for the blank sample, powdered calcite sample with no NA treatment completely sink in the water (tube 6). This indicates that calcite surface is originally water-wet.

The volume percentages of the oil-wet portion at different equilibrium NA molar concentration and different TAN are shown in Figures 5 and 6, respectively. From the figures, it can be seen that the wettability alteration of calcite surface by selected NAs increases gradually with an increase of equilibrium concentration (or TAN) for cyclohexanepropionic and cyclohexanebutyric acids. But the wettability changes very slightly for trans-4-pentylcyclohexanecarboxylic, cyclohexanepentanoic and cyclohexanecarboxylic acids.

Wettability of calcite crystal (Iceland Spar) surfaces treated with different NAs: The contact angle of water on the solid surface is a common measure of surface wettability. This was done on the calcite crystal surface treated with different NAs and the results are shown in Figure 7. Note that: (1) after 50 minutes when an equilibrium reached, the contact angle of water on the calcite surface treated with the selected NAs is in the order: trans-4-pentylcyclohexanecarboxylic > cyclohexanepentanoic > cyclohexanebutyric > cyclohexanepropionic > cyclohexanecarboxylic > fresh calcite surface (without treatment of NA). This is exactly in the same order as the flotation results. The untreated calcite surface has the smallest contact angle for water, which is 21°. (2) the contact angle decreases with time for the various NAs. This may be due to trace amounts of the adsorbed NA layer on the calcite being transferred from the treated surface to the water phase due to solubility effect. As this occurs, there is less NA on the surface and so the contact angle gradually decreases until reaching an equilibrium condition where no more phase transfer occurs. One piece of supporting evidence is that the contact angle changes very little for the blank samples.

Furthermore, these results indicate, as expected, that the degree of induced oil-wetting increases as the NA is more hydrophobic. For example, cyclohexanepentanoic acid (alkyl chain with 5 carbons) increases water contact angle more than the cyclohexanepropionic acid (alkyl chain only 3 carbons) or cyclohexanecarboxylic acid (no alkyl chain). It is recognized that such increase of water contact angle is due to decrease of surface energy of calcite surface. This calcite surface energy can be evaluated by Neumann's Equation-of-State:[25]

$$\cos\theta = -1 + 2\sqrt{\gamma_{SV}/\gamma_{LV}}\, e^{-\beta(\gamma_{LV}-\gamma_{SV})^2}$$

where, γ_{LV} is surface tension of water, 72 dyne/cm at 25 °C, and γ_{SV} is the interfacial tension at the interface of solid and vapor. In our case, it can be used for evaluation of the surface energy of calcite surface; β is a constant of 0.0001247 m^4/mJ^2. Although this constant was originally obtained with polymer surfaces, it can has been used for γ_{SV} calculation of natural surfaces such as apatite crystals.[26] The calculated surface energy data of calcite surface treated with various NAs are listed in Table 3. From these data, one can find that fresh calcite surface

has the highest surface energy. It indicates again that calcite surface is originally water wet. For the surfaces treated with NAs, the surface energy decreases with an increase of $–CH_2–$ group numbers in NA molecules. For example, calcite surface treated with cyclohexanecarboxylic acid has almost the same energy as fresh surface because there is no $–CH_2–$ group in the molecule. On the other hand, the surface treated with trans-4-pentylcyclohexanecarboxylic acid has the lowest energy (has one $–CH_3$ and four $–CH_2–$ groups).

We also seek to relate the observed data to theoretical calculations about the NA compounds and their interaction with calcite. Calculations of Log P were performed in our research. Log P is the log of the ratio of the partitioning of a compound between n-octanol and fresh water at 25 °C. This means that compounds with a larger Log P have a greater affinity for an organic phase than for water. Thus a larger Log P indicates the compound is more hydrophobic. POLARIS with Qeq charges was employed as the model for simulation. The geometries were obtained from Dreiding minimizations of structures as built. Plot of the calculated Log P vs. the measured contact angle is shown in Figure 8. There is a good linear relationship between contact angle and Log P. For this series of NAs, more $–CH_2–$ groups in the molecule make NA more hydrophobic and increases the Log P. Consequently, the NA makes calcite surface lower energy and more oil-wet.

Wettability alteration using surfactant aqueous solutions at different concentrations: In order to investigate the ability of surfactants to reverse the treated calcite surface to water-wet conditions, 8 surfactants were selected. Calcite powder was treated with model oil (n-decane containing 1.48 wt.% cyclohexanepentanoic acid, TAN=4.50). The wettability alteration results are listed in Table 4. Of the surfactants tested by this procedure, the commercial cationic surfactant, Arquad T-50 has the best performance, with just a 25 ppm concentration altering more than half of the oil-wet powder to become water-wet. Of the nonionic surfactants, the Igepal CO-530 has the best performance, showing at 50 ppm, about 95% oil-wet powder can be altered to water-wet. The one anionic surfactant, sodium dodecyl sulfate (SDS), has essentially no effect on changing the wetting of the treated calcite powder.

One factor that could be important to the wetting reversal and imbibition performance of a surfactant is its ability to remove the oil-wetting component (NA compound) from the carbonate surface. Presumably if these components are stripped away from the surface, then the carbonate would become the desired water-wet condition. This is exactly the mechanism proposed for the action of cationic surfactants.[27, 28] These authors speculate that the cationic surfactants form ion-pairs with the dissociated NA anions in the aqueous phase, and that this action provides a means to transport the adsorbed NA from the surface. These same authors hypothesize that the mechanism for wetting reversal for nonionic and anionic surfactants is not the removal of the surface-absorbed NA species, but instead these surfactants co-adsorb on the carbonate surface. This so-called bilayer adsorption where the surfactants have strong hydrophobic-hydrophobic interaction with the adsorbed NA species, leaves the polar head group of the surfactants sticking out into the bulk solution. The hydrophilic groups of these adsorbed surfactants then provide a water-wet layer near the surface.

Measurements were performed via GC-MS to examine the fate of the adsorbed NA on the calcite surface. The starting point is the test tube samples from the flotation test described above. Because all of the NA starts on the calcite powder, any NA detected in the aqueous surfactant solution must represent NA lifted off the calcite surface. The GC-MS method is calibrated by running samples of known concentration of cyclohexanepentanoic acid solution dissolved in n-decane. Unknown samples are taken from the aqueous surfactant solutions in the previous

calcite powder flotation test. Results are shown in Table 5. All of the samples show detectable amounts of NA are transported into aqueous phase. As expected, the cationic surfactants desorbed more of the NA from the calcite surfaces, as strong ion-pairing should have enhanced that process. The anionic SDS surfactant appears to have removed a significant amount of the NA, but still had little success in changing the wetting as indicated by the flotation test. This is because strong adsorption of SDS itself on calcite surface makes the powder remain oil-wet condition. This was demonstrated in a simple test: mix 1 g of new calcite powder with 10 g of 100 ppm surfactant aqueous solution in a test tube and shake it vigorously. For the SDS all of the calcite powder floats on the aqueous phase. However, for other cationic and nonionic surfactants, the powder sinks in the aqueous phase.

Spontaneous imbibition test of porous limestone cores:

As a follow-up to the flotation test, 12 surfactants were selected for spontaneous imbibition test to evaluate their ability to recover oil from porous limestone core. Experimental procedures were described in the previous part. All surfactant solutions were prepared with distilled water at 0.4 wt.% concentration and the test was conducted at room temperature, 24°C. The selected surfactants are seven ionic surfactants, including one anionic and six cationic surfactants, and five anionic surfactants. Most of them are commercial products. Molecular structure, critical micelle concentration, HLB values, IFT results as well as cumulative oil recovery are listed in Table 6.

In general, the results show (1) Oil recovery by use of cationic surfactants is between 40 and 60%, except for n-decyl trimethylammonium bromide (C_{10}TAB), which can recover only 12% of the oil. (2) Oil recovery by use of nonionic surfactants is between 10 and 20%, except for nonylphenoxypoly ethanol (Igepal CO-530), which has around 50% oil recovery. (3) Oil recovery by the sodium dodecyl sulfate (SDS) is low, only 6.8% of the oil. (4) There is some rough correlation between the observed oil recovery and the IFT. Surfactants with high oil recovery (>40%) show generally a low IFT (~0.5 dyne/cm). However, for the cationic surfactants, n-decyl triphenylphosphonium bromide (C_{10}TPPB) and n-dodecyl triphenylphosphonium bromide (C_{12}TPPB), their oil recovery is higher than 50%, but the IFT is also high, at 3.56 and 2.02 mN/m, respectively. The low IFT cases may include gravity effects in their oil recovery, whereas case with high IFT likely have oil recovery controlled by a uniform imbibition process. (5) There is no obvious relationship between oil recovery and critical micelle concentration (CMC). Molar concentrations of these surfactants at 0.4 wt.% were calculated and are listed in the table. They all are higher then CMC of the surfactants except for C_{10}TAB and C_{12}TAB. For the C_{10}TAB, however, it may show less oil recovery in part because it is far below its CMC; if the mechanism relies on this cationic surfactant forming aqueous complxes between its monomers and the adsorbed NA, then not maximizing its monomer concentration could hurt its performance. For nonionic surfactants, their molar concentrations are greater than their CMC by two or three orders of magnitude.

The cumulative oil recovery curves for ionic and nonionic surfactants are shown in Figure 9 and 10, respectively. Among the 5 cationic surfactants, during the early time (less than 5 days), the recovery rates are almost the same. This may indicate that early oil recovery is governed by gravity forces and imbibition of water near the surface and subsurface around the limestone core. Once the pores are filled by surfactant aqueous solution, the surfactant molecules will move to next pores. As the process continues, the recovery rate will depend significantly on diffusion rate of surfactant molecules. A faster diffusion results in a higher recovery rate. A stronger diffusion results in a further penetration of surfactant molecules in the porous core, and

consequently, a greater cumulative recovery. It is expected that such diffusion rate and penetration extent is proportional to the concentration gradient in porous structure. For a given surfactant and a porous core, higher surfactant concentration should improve oil recovery performance for these 5 cationic surfactants. In addition, higher temperature will also increase the diffusion rate and extent of surfactant penetration. Therefore, oil recovery is expected to be further enhanced by both an increase of surfactant concentration and temperature.[27]

The 4 cationic surfactants, C_{10}TAB, C_{12}TAB, ARQUAD C-50 and ARQUAD T-50, are quaternary ammonium salts with different alkyl chains. The shorter chain C_{10}TAB has relatively poor recovery as compared to these other 3 products. The other two cationic surfactants, C_{10}TPPB and C_{12}TPPB, show the best performance in this test series. These are quaternary phosphonium salts with a C10 and C12 straight alkyl chain, respectively. Because of their very bulky hydrophilic head, their molecules can not pack tightly at oil/water interface. Therefore, both of them do not produce a low IFT at the interface. The mechanism responsible for oil recovery by this kind of phosphonium surfactants is currently unknown. But this, perhaps, indicate a new direction of candidate selection for EOR in fractured carbonate reservoirs.

The SDS is included as a benchmark anionic surfactant for our test program. This solution recovers only 7% of the oil. Its poor performance may due in part to strong adsorption of SDS on the limestone surface due to a strong electrostatic attraction. Therefore, SDS molecules are prevented from diffusing into the core pores and forcing oil recovery.

For the five nonionic surfactants used in our spontaneous imbibition test, they are ethoxylated primary or secondary alcohols with a linear or a branched alkyl chain as shown in Table 6. Among them, Tergitol® 15-S-3, Tergitol® 15-S-7, Tergitol® 15-S-40 and Neodol® 25-7 recover limited amounts of oil from the limestone core. The Igepal® CO-530 (Rhodia, Inc.) has by far the best performance of these nonionic surfactants, recovering as much as 50% from limestone core. This is comparable to the oil recovery by the cationic surfactants, C_{12}TAB, ARQUAD C-50 and ARQUAD T-50. Note that this observation is consistent with the result of the wettability alteration flotation test discussed in the previous section of this paper. Another feature of the Igepal® CO-530 is that it has about the lowest IFT in our test series of surfactants.

Conclusions

1 Adsorption of naphthenic acids on calcite surface in n-decane media is in the order: cyclohexanepropionic acid > cyclohexanebutyric acid > cyclohexanepentanoic acid. Because these three naphthenic acids are analogues in term of molecular structure, this indicates that adsorption of the NAs decreases with increase of alkyl chain length from 2 $-CH_2-$ to 4 $-CH_2-$ groups. As to cyclohexanecarboxylic and trans-4-pentylcyclohexane carboxylic acids, their adsorption is almost the same at different experimental concentration. Again, adsorption of trans-4-pentylcyclohexanecarboxylic acid is greater than that of cyclohexanecarboxylic acid because the former has a straight alkyl chain with 5 carbons in the molecules.

2 In term of volume percentage of calcite powder floating on water, the oil-wettability of calcite powder treated with different naphthenic acids is in the order: trans-4-pentylcyclohexane carboxylic acid ~ cyclohexanepentanoic acid > cyclohexanebutyric acid > cyclohexanepropionic acid > cyclohexanecarboxylic acid. It is almost in reverse order of adsorption on calcite surface. This indicates that their ability to alter calcite surface to become oil-wet is not related directly to their adsorption on calcite surface, but depends on their molecular structures. As to calcite powder without treatment of naphthenic acid, it is originally water wet.

3. Contact angle and novel flotation test results are consistent in ranking oil-wet condition. At equilibrium, contact angle of water on the calcite surface treated with naphthenic acids is in the order: trans-4-pentylcyclohexanecarboxylic ~ cyclohexanepentanoic > cyclohexanebutyric > cyclohexanepropionic > cyclohexanecarboxylic > fresh calcite surface. The untreated calcite surface has the smallest contact angle for water, which is 21°. This is exactly in the same order as the flotation results.
4. Among the 12 selected surfactants, cationic surfactants are generally more efficient in recovering model oil from limestone core than the others, but one nonionic surfactant, Igepal CO-530 has also been found to be efficient for oil recovery. For the two quaternary phosphonium cationic surfactants, C_{10}TPPB and C_{12}TPPB, these phosphonium surfactants with bulky head groups recovered the model oil in limestone cores most efficiently.
5. The results of wettability alteration using different surfactant aqueous solutions in a simple flotation test are consistent with oil recovery by spontaneous imbibition of the selected surfactant aqueous solutions. For example, cationic Arquad T-50 and nonionic Igepal CO-530 are efficient in altering wettability of treated calcite powder from oil-wet to water-wet condition, and they also are efficient in oil recovery.

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Table 1. Molecular Structures of Naphthenic Acids Investigated

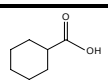
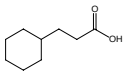
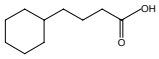
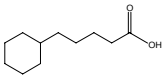
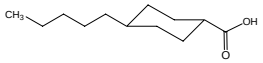
Naphthenic Acids	Molecular Structure	F.W.	m.p. (°C)	b.p. (°C)
Cyclohexanecarboxylic Acid		128.17	31	232
Cyclohexanepropionic Acid		156.23	15	276
Cyclohexanebutyric Acid		170.25	31	>110
Cyclohexanepentanoic Acid		184.28	16	126
trans-Pentylcyclohexanecarboxylic Acid		198.31	52	>110

Figure 1(a), 1(b). Amott Cells used in imbibition oil recovery tests

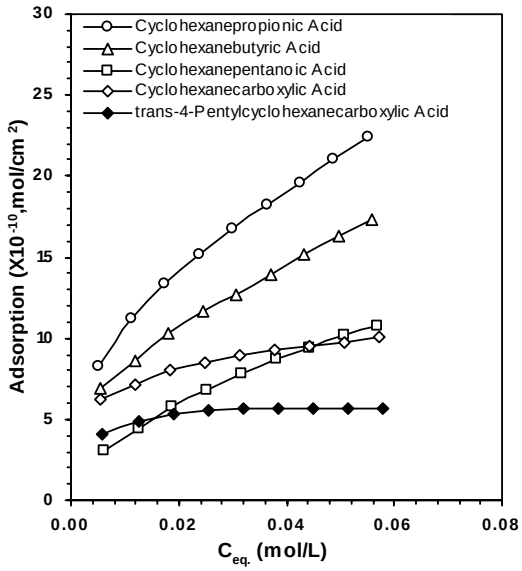


Figure 2. Aadsorption isotherms of naphthenic acids on calcite in n-Decane solution (23 °C, 16 hours)

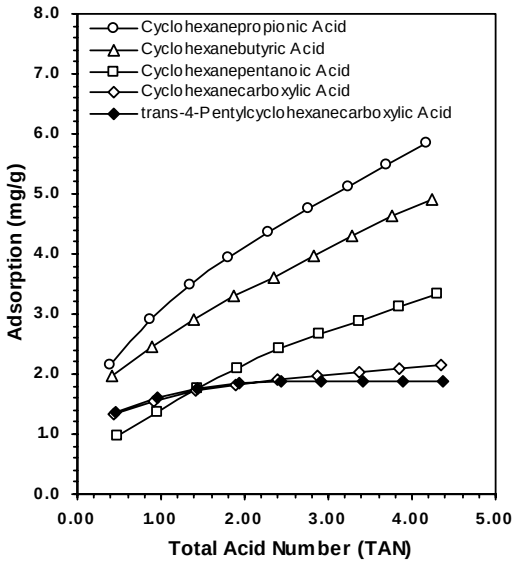


Figure 3. Adsorption isotherms of naphthenic acids in n-Decane on calcite (mass adsorption vs. TAN) (23 °C, 16 hours)

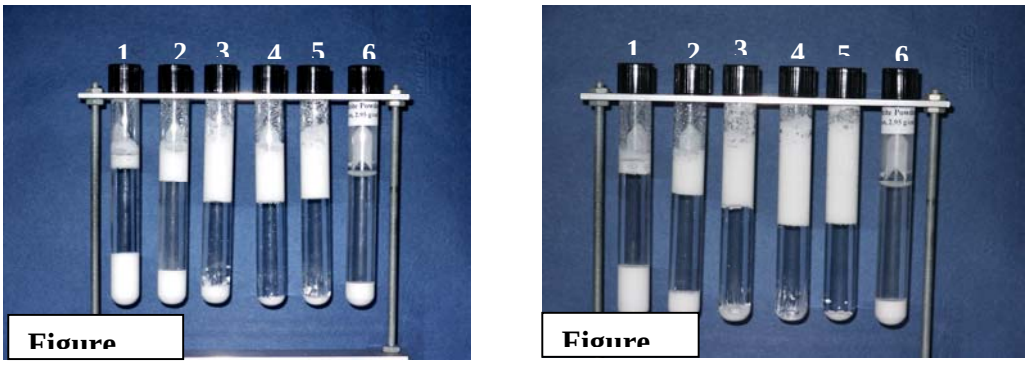


Figure 4. Flotation test of calcite powder treated with NA at different concentrations [Figure 4(a): TAN 0.4 ~ 0.5; Figure 4(b): 4 ~ 4.5]. Liquid phase: distilled water (pH~ 6). Solid treated with NA: (1) cyclohexanecarboxylic acid; (2) cyclohexanepropionic acid; (3) cyclohexanebutyric acid; (4) cyclohexanepentanonic acid; (5) trans-4-Pentylcyclohexane carboxylic acid; (6) without treatment.

Figure 5. Oil-wet (v/v) vs. eq. concentration (M)

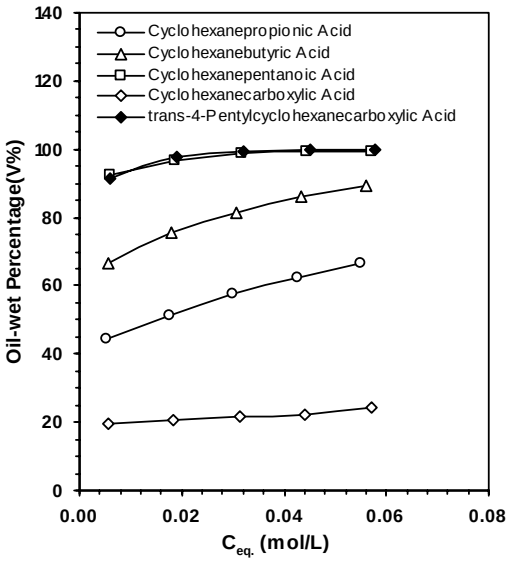


Figure 6. Oil-wet (v/v) vs. total acid number (TAN)

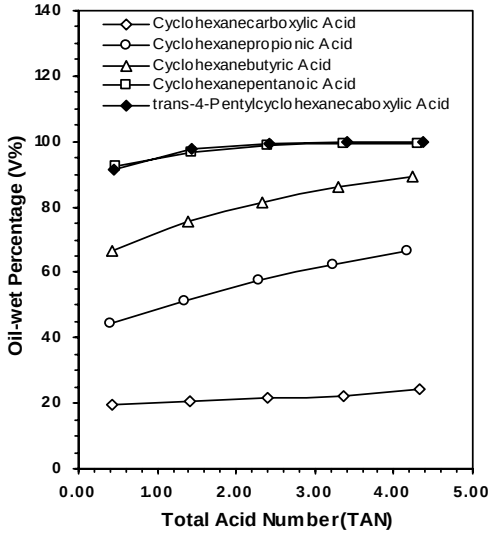


Figure 7. Water Contact Angles on Calcite Surface

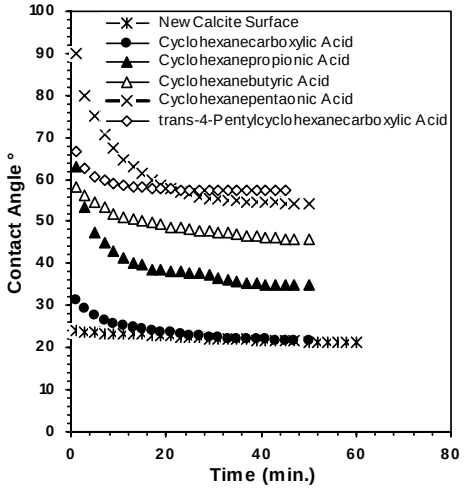


Table 2. Adsorption, Oil-wettability and Contact Angle

Calcite with Naphthenic Acids	Γ_{max} (mol/cm^2)	Oil-wet	Water-wet	θ
Cyclohexane carboxylic acid	1.01×10^{-9}	19%	81%	22
Cyclohexane propionic acid	2.25×10^{-9}	67%	23%	35
Cyclohexane butyric acid	1.73×10^{-9}	89%	11%	46
Cyclohexane pentanoic acid	1.08×10^{-9}	99%	1%	55
trans-4-pentylcyclohexane carboxylic acid	0.57×10^{-9}	99%	1%	57

Table 3. Interfacial Tension (γ_{ow}) of Calcite Surfaces Measured by Water Contact Angle at T=25 °C

Surfaces Treated with Naphthenic Acids	θ	γ_{ow} (mg/cm^2)
New chalk surface without NA	21°	47.6
Cyclohexanecarboxylic acid (Log P=0.8858)	22°	47.1
Cyclohexanepropionic acid (Log P=1.4398)	39°	41.3
Cyclohexanebutyric acid (Log P=1.9216)	46°	35.4
Cyclohexanepentanoic acid (Log P=2.4962)	53°	30.1
trans-4-pentylcyclohexane carboxylic acid (Log P=5.9581)	57°	49.0

Figure 8. Plot Log P vs Water Contact Angles on Calcite Surface for Various NAs

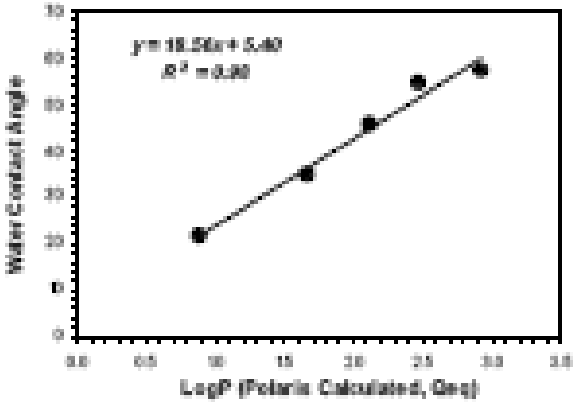


Table 4. Wettability Alteration to Water-wet by Use of Surfactant Solution (T=25 °C)

Surfactant	Type	Percentage of Positive Imbibition (water-wet)		
		100 ppm	50 ppm	25 ppm
Arquad T-50	Cationic	100%	100%	60%
CuTAB	Cationic	60%	45%	N/D*
Igepal CO-530	Nonionic	100%	95%	5%
Neodol 25-7	Nonionic	100%	60%	N/D
Tergitol 15-S-3	Nonionic	100%	70%	N/D
Tergitol 15-S-7	Nonionic	100%	45%	N/D
Tergitol 15-S-40	Nonionic	50%	40%	N/D
S.D.S.	Anionic	0%	0%	N/D

* N/D: not determined.

Table 5. Concentration of Cyclohexanepentanoic Acid in Aqueous Solution Desorbed by Surfactant

Surfactant	Type	Cyclohexanepentanoic acid	
		Conc. (ppm)	Mass (µg)
Arquad T-50	Cationic	260	2.6
CuTAB	Cationic	330	3.3
Igepal CO-530	Nonionic	160	1.6
Neodol 25-7	Nonionic	270	2.7
Tergitol 15-S-3	Nonionic	N/D	N/A*
Tergitol 15-S-7	Nonionic	N/D	N/A
Tergitol 15-S-40	Nonionic	N/D	N/A
S.D.S.	Anionic	240	2.4

* N/A: not available.

Figure 9. Oil Recovery Measured by Spontaneous Imbibition Test (Ionic Surfactant, 0.4 wt.%, 25 °C)

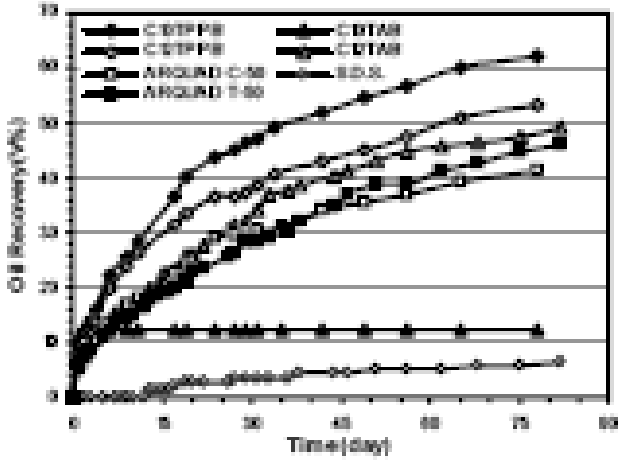


Figure 10. Oil Recovery Measured by Spontaneous Imbibition Test (Nonionic Surfactant, 0.4 wt.%, 25 °C)

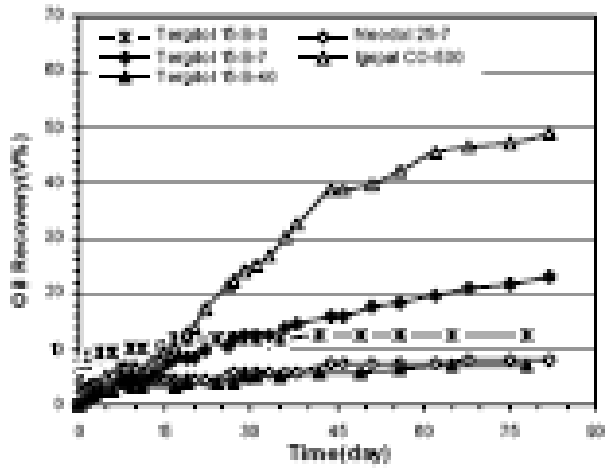
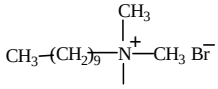
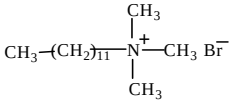
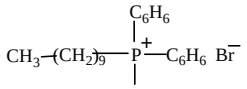
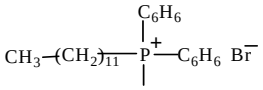
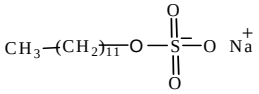
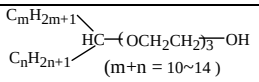
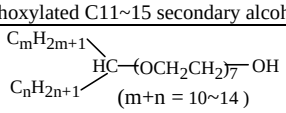
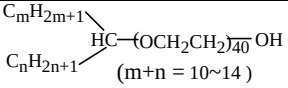
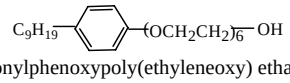
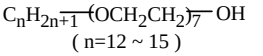


Table 6. Molecular Structure, Critical Micelle Concentration and Related Parameters of Selected Surfactants, and Oil Recovery Results for Model Oil by Use of the Surfactants at 0.4 wt.% and Room Temperature

Surfactants & Molecular Structures	Symbol or Trade Name	C.M.C. (at 25°C)	Conc. at 0.4 wt.%	Oil Recovery and IFT
 n-Decyl Trimethylammonium Bromide	**C_{10}TAB** (Cationic) M.W. =280.3	6.8×10^{-2} M	1.43×10^{-2} M	**12.1%(v/v)** IFT=2.67 mN/m
 n-Dodecyl Trimethylammonium Bromide	**C_{12}TAB** (Cationic) M.W.=308.35	1.6×10^{-2} M	1.30×10^{-2} M	**48.5%(v/v)** IFT=0.59 mN/m
 n-Decyl Triphenylphosphonium Bromide	**C_{10}TPPB** (Cationic) M.W.=483.45	1st: 7.3×10^{-3} M 2nd: 1.5×10^{-2} M	8.27×10^{-3} M	**62.0%(v/v)** IFT=3.56 mN/m
 n-Dodecyl Triphenylphosphonium Bromide	**C_{12}TPPB** (Cationic) M.W.=511.50	1st: 1.8×10^{-3} M 2nd: 2.7×10^{-3} M	7.82×10^{-3} M	**52.5%(v/v)** IFT=2.02 mN/m
ARQUAD® C-50 Coconut oil alkyl (C_{12}-C_{14}) trimethylammonium chloride	M.W.=278.0 (Cationic) HLB=16.5	4.5×10^{-3} ~2.0×10^{-2} M	1.44×10^{-2} M	**41.0%(v/v)** IFT=0.53 mN/m
ARQUAD® T-50 Trimethyl tallowalkyl(C_{16}-C_{18}) ammonium chloride	M.W.=340.0 (Cationic) HLB=14.2	<1.3×10^{-3} M	1.18×10^{-2} M	**46.0%(v/v)** IFT=0.69 mN/m
 Sodium Dodecyl Sulfate	**S.D.S.** (Anionic) M.W.=288.4	8.2×10^{-3} M	1.39×10^{-2} M	**6.8%(v/v)** IFT=4.77 mN/m
 Ethoxylated C11~15 secondary alcohol	**Tergitol 15-S-3** (Nonionic) HLB=8.3 M.W.=336.0	>5.6×10^{-5} M	1.19×10^{-2} M	**12.8%(v/v)** IFT=4.44 mN/m
 Ethoxylated C11~15 secondary alcohol	**Tergitol 15-S-7** (Nonionic) HLB=12.4 M.W.=515.0	>8.4×10^{-5} M	7.77×10^{-3} M	**22.5%(v/v)** IFT=1.39 mN/m
 Ethoxylated C11~15 secondary alcohol	**Tergitol 15-S-40** (Nonionic) HLB=18.0 M.W.=2004	>1.4×10^{-4} M	2.00×10^{-3} M	**5.7%(v/v)** IFT=11.5 mN/m
 Nonylphenoxypoly(ethyleneoxy) ethanol	**Igepal CO-530** (Nonionic) HLB=10.8 M.W.=484.0	7.5×10^{-5} M	8.26×10^{-3} M	**49.5%(v/v)** IFT=0.33 mN/m
 (n=12 ~ 15) C_{12} – C_{15} linear primary alcohol ethoxylate	**Neodol 25-7** (Nonionic) HLB=12.5 M.W.=515.0	<8.2×10^{-5} M	7.77×10^{-3} M	**8.2%(v/v)** IFT=2.02 mN/m