CALIFORNIA
INSTITUTE OF
TECHNOLOGY

DOE CONTRACT DE-FC26-04NT15521
DR. WILLIAM GODDARD III, PRINCIPAL
INVESTIGATOR, CALTECH

# Cost Effective Surfactant Formulations for Improved Oil Recovery in Carbonate Reservoirs

- Covering the period October 2005 – March 2006 – First Semi-Annual Report for Year 2
- Compiled by Patrick Shuler
- Sections written by Patrick Shuler and Yongfu Wu
- Issued April 2006

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**Cost Effective Surfactant Formulations for Improved Oil Recovery in Carbonate Reservoirs**
**DOE Project: DE-FC26-04NT15521**

**Progress Report April 2006**

PI: William A. Goddard III
Co-PI: Yongchun Tang
Senior Staff: Patrick Shuler and Mario Blanco
Postdoctoral Scholars: Yongfu Wu, Baojun Bai, Seung Soon Jang

**California Institute of Technology**

**First Semi-Annual Report / Year 2 October 2005 – March 2006**

## 1.0 EXECUTIVE SUMMARY

This report updates work during the 13 – 18 month time period of this 3-year project. The objective of this project is to improve the performance of chemical 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.

During this time period, experiments continued to investigate the fundamental mechanisms of how model oil components (naphthenic acids, NA) that induce oil-wetting on carbonates and how surfactant solutions then have the desirable function of reversing the surface to become water-wet (Task 2). These experiments included completion of a comparison of oil recovery capability versus other metrics for EOR candidate surfactants. For example, we observed the simple surfactant performance screening method we developed based on calcite powder flotation gave reasonable prediction of oil recovery ability for a series of surfactant systems. In a parallel theoretical investigation in Task 2, calculations showed that the binding energy is very similar for a series of different naphthenic acids (NAs) that render carbonates oil-wet to a different degree. It suggests binding of a NA to calcite is controlled by the carboxylate group interaction common to all NA molecules, and it supports our experimental finding that the oil-wetting induced by a NA is related to (increases with) its degree of hydrophobic character. The results from this Task 2 will be presented at the SPE/DOE IOR meeting in Tulsa next April. This SPE 99612 paper is attached to this progress report.

Other experiments attempted to improve on our chip cleaning surfactant screening method. The original test soaks a single calcite crystal coated with a crude oil in a test surfactant solution; better surfactants spontaneously clean the chip surface faster. In the improved test being developed, multiple oil-coated calcite ships are added to an Amott imbibition test cell with a candidate surfactant solution. The performance of the surfactant is judged not only by the visual evidence of how well it cleans the chips, but this method also provides a volumetric measurement of oil recovery versus time. Our first attempt at applying this technique was only partially successful because we selected heavy oil as a test fluid. Its high viscosity impeded its

movement into the volumetric burette, so the oil recovery data are uncertain. This new method should be useful for light oil samples where the oil can easily move into the collection burette.

Other experiments investigated candidate surfactants and their compatibility with different test brines (Task 4). Some 50 surfactants with demonstrated laboratory success as potential EOR agents for carbonates were mixed into two different brines. One brine is a synthetic brine (Total Dissolved Solids, TDS = 27, 500 mg/l) that mimics the dissolved salt composition of the produced and injection water at Chevron's McEroy Field in the Permian Basin. This was selected as we now have both the oil and rock samples from this field from which to build a case study, plus it is a useful benchmark as its salinity is similar to sea water. The second test brine has a much higher salinity (TDS = 120,000 mg/l, roughly 4 times sea water) and hardness in order to challenge these candidate surfactants with regards to compatibility of field brines. The salt concentration of target carbonate reservoirs in domestic reservoirs can be very high, and one goal is to develop surfactant formulations suitable for these more challenging conditions. The other feature of this test is to find surfactants compatible with these brines at room temperature (such as when prepare solutions at a surface facility) and at elevated conditions (when surfactant solutions are inside a reservoir). The compatibility tests identified several surfactants compatible with one or both of these saline brines, and over a temperature range from 25 to 70 °C.

Yet other laboratory testing is in progress with the Chevron McElroy Field case as an example potential field application target. Building on the brine compatibility testing mentioned above, those surfactants passing that test are being evaluated as oil recovery agents for this field. Specifically, the screening methods previously developed (calcite chip cleaning and calcite powder flotation) in this project are being used to reduce the number of candidates for the next step of evaluation. This will be a series of oil recovery performance tests from model carbonate core material, and then finally in field cores.

One major accomplishment for this reporting period was organizing and hosting a workshop about chemical EOR at the California Institute of Technology. This venue attracted participants from several oil companies, including Chevron, Shell, ExxonMobil, Occidental, and Breitburn Energy. Feedback from the attendees was very positive.

## 2.0 BACKGROUND

The goal of this proposed 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 will be 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 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 50 ºC), 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.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Highlights of Efforts and Results by Task for this Reporting Period

**Task 1** – Months 1-9
*Develop and demonstrate an experimental method for screening of wettability alteration by candidate chemical formulations, and verify results with contact angles measurements.*

-- Task 1 was completed on schedule with a Topical Report issued in July, 2005 regarding two methods for fast screening of surfactants. **More details are provided below** about follow up work for a third screening method that is a variation of the other screening tests.

**Task 2** -- Months 4 - 27
*Use molecular simulation software to estimate the relative ability of different classes of surfactant to alter carbonate surfaces to become water-wet.*

-- Experiments with model naphthenic acid compounds (NA) as oil-wetting agents on calcite were completed, as well as a study of the ability of selected surfactants to reverse treated surfaces to a more water-wet condition and recover oil from limestone cores. A **copy of SPE paper 99612 detailing this work is attached to this progress report. This paper will be presented at the SPE IOR meeting in Tulsa in April, 2006.**

-- New theoretical calculations indicate the binding energy of various NA molecules to a calcite surface is almost independent of NA molecular structure. **More details are given below.**

**Task 3** – Months 7 - 20
*Make test tube samples to observe phase behavior and IFT for the most promising candidate chemical formulations.*

-- Phase behavior and IFT measurements were included as part of the test program in the experimental program in Task 2. The attached paper SPE 99612 documents this work.

**Task 4 -** Months 13 - 23
*Evaluate the best surfactants found from Tasks 1 – 3 and perform test tube measurements of compatibility of these chemicals over a range of brine compositions.*

-- First experiments performed to screen a number of promising oil recovery agents for their compatibility with higher salinity brines. **More details are provided below** about these early experimental results. We target a potential application for this technology at Chevron's McElroy Field that is located in the Permian Basin.

**Task 5** – Months 14 - 33
*Conduct oil displacement tests, with brine only, and with surfactant solutions.*

--- Additional data were collected for the oil recovery tests versus elapsed time that were reported in the previous progress report to DOE. The new data do not change the relative performance results for the surfactants reported previously.

**Task 6** – Months 32 - 36
*Conduct additional oil displacement tests to optimize chemical efficiency in carbonate mineral porous media.*
--- Nothing to report for this time period.

### 3.2 More Details of Results -- Task 1, Screening Methods to Predict Relative Oil Recovery Performance by Candidate Surfactants

Previous work was documented in a Topical Report completed in July, 2005 for two different methods to screen surfactants as potentially good agents for oil recovery from carbonate porous media. One of these is based on the ability of aqueous chemical formulations to clean calcite chips previously soaked and aged in a crude oil. The second method is based on the ability of such test solutions to sink (make water-wet) calcite powder pre-treated to be oil-wet.

This period we attempted to improve on the first test method. The concept is to use several chips coated with oil that are placed in an Amott imbibition cell filled with an aqueous surfactant solution. The initial amount of oil on the chips is determined by weight (total oil around 4 grams). As in the first method, the speed at which the surfactant solution makes a calcite surface appears clean in one measure of performance. But now another metric is to measure the volume of oil recovered as seen in the burette above the cell, just as in an oil recovery test using a core. This provides a more quantitative measure of surfactant performance. In the first attempt to use this technique, we soaked and aged the calcite chips in a heavy oil (from Midway Sunset Field near Bakersfield, the same oil sample as used before in this project). The figure below is a photograph of the Amott cells filled with these treated calcite chips after some exposure time.

**Figure 1.** Amott cells filled with calcite chips coated with heavy crude oil and surrounded by surfactant solution. Oil removed is collected in burettes. The tests are performed at room temperature.

One problem with this test series is that the heavy oil has very high viscosity at room temperature, and so has difficulty in moving from the chips into the collection burette. As can be seen in the above photograph, the oil appears as streaks in the burette rather than as a clean oil-water interface. We would suggest using a light oil (lower viscosity) as a better test medium.

The oil recovery results for these tests are given below. Again the values have some uncertainty due to the problems in collecting a clean oil phase in the burette.

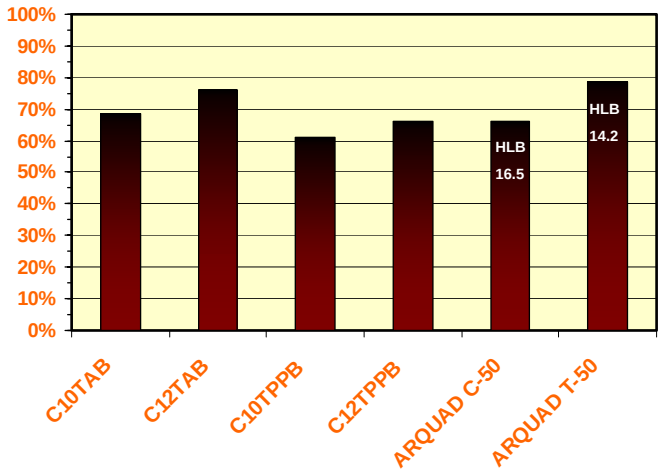
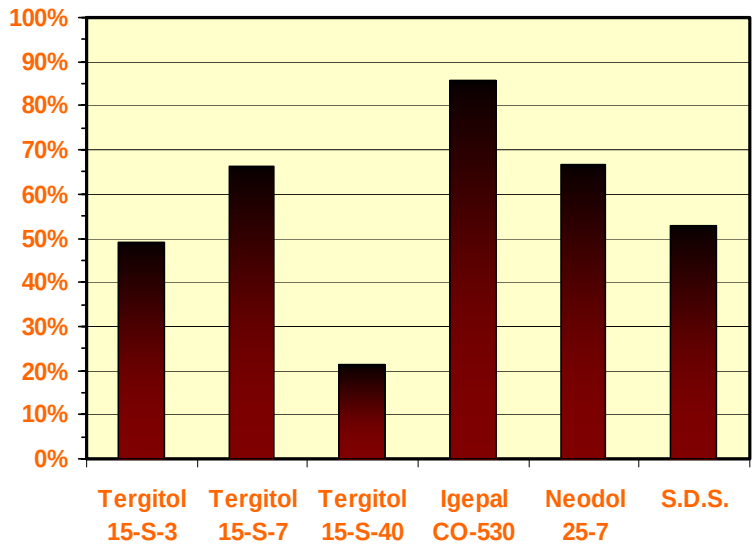



**Figure 2.** Oil recovery with a series of cationic surfactant solutions from calcite chips coated with a heavy oil after 14 days




| | | | | | |
|---|---|---|---|---|---|
| **HLB** | **8 .3** | **12.4** | **16.0** | **10.8** | **12.3** |

**Figure 3.** Oil recovery with a series of nonionic and SDS (anionic) surfactant solutions from calcite chips coated with a heavy oil after 14 days

In spite of the uncertainties in oil recovered, the results are reasonable. In general the cationic surfactants have better performance. Also within the nonionic surfactants we see the Igepal CO-530 with the best oil recovery, consistent with the model oil study reported in the previous progress report. There is also the trend that matches previous heavy oil calcite chip testing that among the Tergitol series of products that the 15-S-7 has the better performance. This continues the theme that there is a preferred range of surfactant HLB.

## 3.3 More Details of Results -- Task 2, Mechanistic Study of Wetting Phenomena

### 3.3.1 *SPE 99612 – Paper to be presented at SPE/DOE IOR Meeting*

We completed a final draft of a paper to be presented at the SPE/DOE IOR meeting for next April in Tulsa. This paper reports mainly the results of the several experimental studies aimed at Task 2 of this project; namely systematic measurements with simplified chemistry (model compounds) so as to be able to focus on the mechanisms surrounding oil and water wetting and oil recovery for carbonate materials.

The text of this paper is attached to this progress report as Attachment 1. The abstract is given below:

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

Yongfu Wu, SPE; Patrick J. Shuler, SPE; Mario Blanco; Yongchun Tang; William A. Goddard, III, California Institute of Technology

**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.

### 3.3.2 *Further Theoretical Study – Binding Energy of Naphthenic Acids (NAs) To a Calcium Carbonate Surface*

During this quarter, there was an additional theoretical investigation to model the binding of various naphthenic acids (NAs) to a calcite surface. The reason this is of interest is that the details of how a NA is docked onto a calcium carbonate surface should influence its ability to alter that surface to an oil-wet condition. Our experiments and those reported in the literature clearly show that a calcite surface is naturally water-wet, but then becomes oil-wet with exposure to NAs. Once having a better understanding of how such a surface becomes oil-wet in the first place is required information to then go on to the next step; modeling how it is that surfactants can interact with a NA coated surface and make it then more water-wet.

We employed Density Functional Theory (DFT) with the Becke 3 LYP (B3LYP) functional to estimate binding energetics of the various NAs acids under consideration. We use a high level basis set: LACVP** with polarization functions. To correct for basis set superposition errors we used a counterpoise correction (labeled BSSE). The model used for calcite is a fixed atom model (Figure 4). The coordinates are taken from the crystallographic x-ray data for calcite.

Procedure:

The geometries of the NAs were fully optimized first within a force field (molecular mechanics) keeping the calcite atoms (Figure 4) fixed. Charges were formally assigned to the Ca+2 atoms and Qeq charges were used for all other atoms. After the Molecular Mechanics minimizations the clusters were further minimized within the DFT B3LYP level, keeping the calcite atoms fixed to better simulate the conditions under a calcite surface. The geometry and positions of the atoms in the NA were fully optimized. The acid was modeled as dissociated with the proton transferred to the calcite completely in all cases.

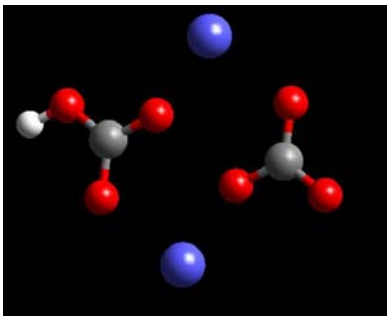


**Figure 4.** Calcite Model. Two calcium +2 ions and two carbonate moieties, one protonated, represent the calcite surface. Coordinates from the x-ray crystallographic structure for calcite.

**Results:**

The binding energy results are shown in Table 1. All binding energies of the naphthenic acid are within 2 Kcal/mol of one another. (CHBA=cyclohexanebutyric acid, CHPA=cyclohexanepropionic acid, CHPNA=cyclohexylpentanoic acid, CHCA=cyclohexane carboxylic acid, TPCHA=trans-pentylcyclohexane carboxylic acid). CHPNA shows the best binding and CHCA the lowest, but the differences are not significant. Binding geometries are illustrated in Figure 5.

These results indicate that differences in water contact angle and wetting of the calcite are not largely due to differences in binding energetics but rather more to differences in partitioning between the aqueous solvent and the calcite surface. This explains and is consistent with the results presented previously on the LogP correlation with contact angles previously reported (equivalent to saying more hydrophobic NAs promote stronger oil-wetting action).

**Table 1:** Calcite binding energies for various Naphthenic acids.

| | DFT(b3lyp) Hartrees | Binding Kcal/mol |
|---|---|---|
| chba_2Ca | -1143.302145 | -160.55893 |
| chba BSSE | -541.8270162 | |
| Ca BSSE | -601.2192618 | |
| | | |
| chca_2Ca | -1025.358402 | -159.87708 |
| chca BSSE | -423.8847168 | |
| Ca BSSE | -601.2189051 | |
| | | |
| chpa_2Ca | -1103.988841 | -161.37257 |
| chpa BSSE | -502.5130661 | |
| Ca BSSE | -601.2186114 | |
| | | |
| chpna_2Ca | -1182.619002 | -161.7521 |
| chpna BSSE | -581.1426466 | |
| Ca BSSE | -601.2185868 | |
| | | |
| tpcha_2Ca | -1221.934351 | -160.2225 |
| tpcha BSSE | -620.4599286 | |
| Ca BSSE | -601.219092 | |

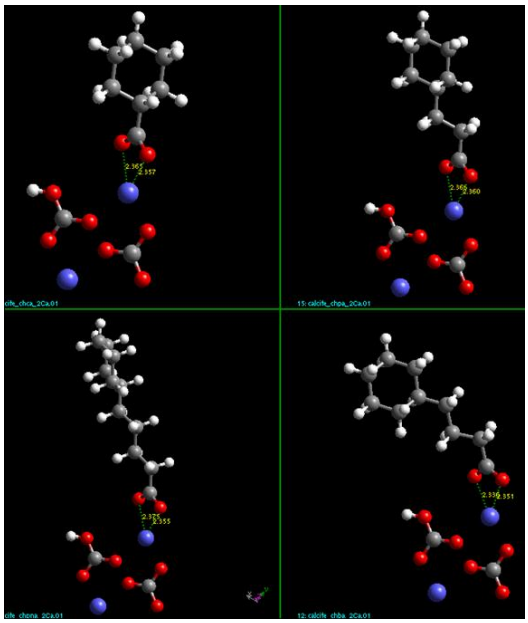


**Figure 5.** Representative naphthenic acid binding geometries to calcite, minimized with Quantum Mechanics DFT B3LYP using a high level basis set.

### 3.4 More Details of Results -- Task 4, Surfactant-Brine Compatibility

One important consideration in the selection of an EOR surfactant for application in carbonate reservoirs is the compatibility with the injection and reservoir brine. Ideally, the surfactant will dissolve completely and form a clear solution with the injection water. It is not acceptable that the surfactant will itself precipitate or cause other components in the injection water to create any suspended solids. Besides a loss of valuable material, such solids may deposit and cause blockage in surface facilities or cause plugging in injection wells. The injected surfactant solution may be near the ambient temperature, or it may somewhat elevated if it is re-injected produced water still carrying sensible heat. The chemical should be compatible over the entire range of temperature that the injection water will experience. Hence our evaluation consider compatibility from 25 – 70 °C, which should encompass typical temperatures from its surface mixing to in-situ conditions in most all target carbonate reservoirs.

The reservoir brine will be similar in composition to the injection water if the main source of the injection water is produced water. This is often the case with domestic onshore reservoirs under mature waterfloods. For the case where the reservoir brine has a significantly different dissolved salt composition, the surfactant should be compatible with this in-situ brine, and in mixtures with the surfactant/injection water stream. Specifically, undue precipitation of the surfactant in-situ due to an incompatibility with the reservoir brine is undesirable because this represents a loss of active material and would be expected to reduce the effectiveness of the surfactant treatment.

Two synthetic brines were selected to test as test matrices. One is based on the brine composition typical of the McElroy Field in the Permian Basin. Its composition is given below:

| | 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 |

This is a saline brine, approaching a TDS not unlike sea water. Some domestic carbonate reservoirs have a fresher brine, but many are even higher salinity.

The second test brine was created with much higher salinity, a TDS of 120,000 mg/l. The motivation for selecting this second brine composition is that it provides a much harder challenge in selection of suitable surfactants, plus it mimics a not uncommon case of target reservoirs with associated oil field brines very high salinity.

| | 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 |
| adjust to pH 7 | | | | | |

The test procedure was to dissolve 50 different surfactants of interest at a concentration of 0.5 wt% in an active basis into the two compatibility test brines and mixed at room temperature. After a few days the optical clarity was noted. These same samples then were exposed to higher temperatures of 50 and 70 °C for a few days, and again the optical clarity was observed.

Results for surfactants tested are presented in Tables 2 and 3 for the McElroy brine and the high salinity brine. Ideally, candidate surfactants will show clear solutions over the span of temperatures and up to the very high salinity considered. The practical requirement will depend upon the specific reservoir. For example, for the McElroy Field, the surfactant should be compatible with that brine, and over the range from 25 °C to that reservoir temperature, 40 °C. Some significant trends:

- The cationic surfactants tested have the better compatibility
- Surfactant compatibility is more problematic at the very salinity
- Nonionic surfactants are less compatible at high temperature (exceed their cloud point)
- Nonionic surfactants are more compatible as increase their HLB; a minimum HLB of about 14 is required to be compatible with the McElroy brine at all temperatures. The minimum HLB is more in the neighborhood of 17 for compatibility with the 120,000 mg/l brine at even 70 °C.

Recall from previous reports that in our previous testing of oil-cleaning and oil recovery that for the nonionic surfactants the best performance was with HLB values more in the range of 10 – 12. This may reflect that these tests were confined to room temperature and in brines no more than 2 weight percent sodium chloride where the surfactant compatibility is less difficult.

Table 2. Surfactant compatibility tests with McElroy Field

| Test for Surfactant ---- Brine Compatibility<br>McElroy Field -- Chevron -- Located in Texas Brine (TDS = 27483) | | | | | | |
|---|---|---|---|---|---|---|
| **Surfactants** | **Manufacturer** | **HLB** | **wt.%** | **Clarity** | | |
| **Cationics(0.5 wt.%)** | | | | 25 °C | 50 °C | 75 °C |
| $C_8$-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 3. Surfactant compatibility tests with high salinity brine, 120,000 mg/l

| Test for Surfactant ---- Brine Compatibility<br>High Salt Brine (TDS = 120,000 mg/L) | | | | | | |
|---|---|---|---|---|---|---|
| **Surfactants** | **Manufacturer** | **HLB** | **wt.%** | **Clarity** | | |
| **Cationics(0.5 wt.%)** | | | | 25 °C | 50 °C | 75 °C |
| $C_8$-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 | insloubl e | s. cloudy | **clear** |
| Sodium 1-decanesulfonate | Alfa Aesar(R) | | 99.0 | insloubl e | cloudy | **clear** |
| AEROSOL® OT-B | *CYANAMID* | | 99.6 | insloubl e | **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 | insloubl e | 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 |

### 3.5 Update on Experimental Study for Surfactant Oil Recovery Mechanisms

Data collection has been completed for the oil recovery portion of the experimental program. In these tests, the so-called model oil (a naphthenic acid dissolved in n-decane) saturates limestone cores. These cores are placed in Amott cells containing different surfactant solutions. The oil recovery is then monitored versus time, with the better surfactant solutions providing more, quicker oil recovery. The details about this evaluation program and results are given in the SPE paper 99612 (see Attachment 1 in this report). Longer time data did not show any significant additional oil recovery beyond that reported in the SPE paper.

In addition, repeat oil recovery experiments were performed for selected surfactants. These repeat experiments showed generally very good agreement with the first set of results. The differences are somewhat greater recovery for the C12TAB surfactant and lower recovery for the C10TPPB with the repeat experiments.

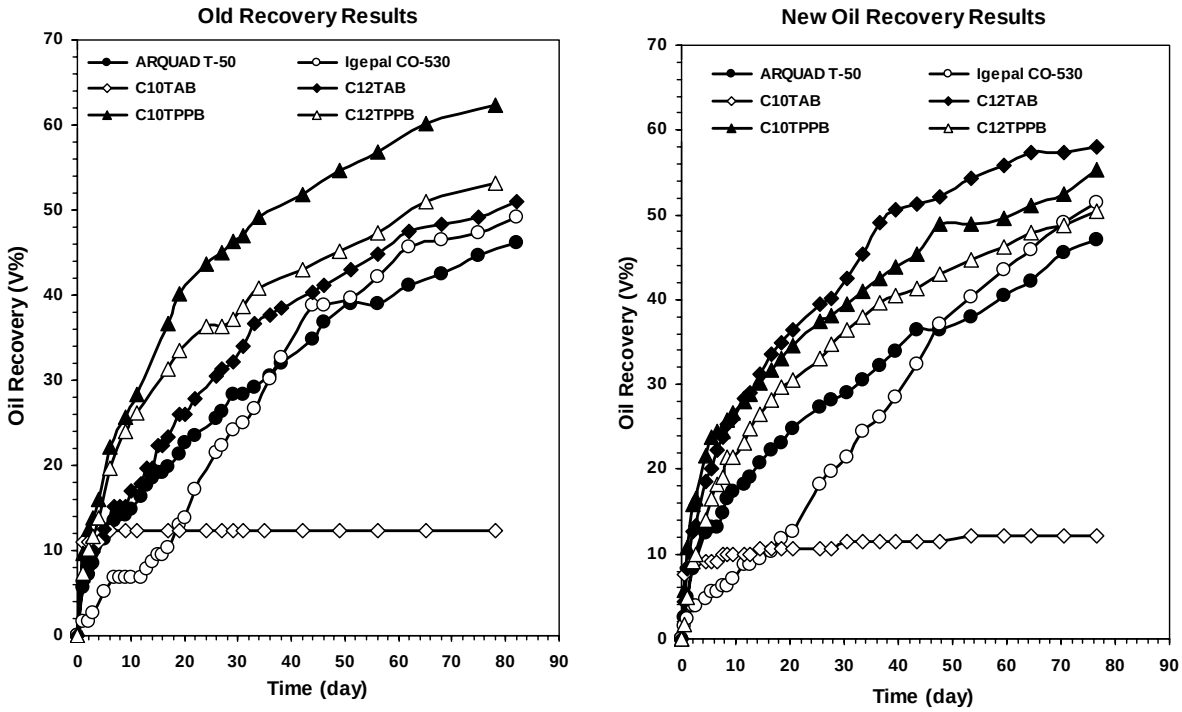



**Figure 6.** Comparison of the recovery of the model oil from limestone cores via surfactant solution imbibition

Thus these results still show the same oil recovery relative performance among the surfactants tested. Based on these and some previous results, we have filed a provisional patent for some types of surfactants as preferred oil recovery agents for fractured carbonate reservoirs.
The oil recovery results after 76 days (data taken from graphs above) are summarized below:

| Product | % Oil Recovery by Imbibition First Test | Repeat Test |
|---|---|---|
| C10TAB | 12.4 | 12.2 |
| C12TAB | 49.2 | 58.0 |
| C10TPPB | 62.3 | 55.4 |
| C12TPPB | 53.1 | 50.4 |
| Arquad T-50 | 44.7 | 47.1 |
| Igepal CO-530 | 47.4 | 51.4 |

### 3.6 Experimental Study to Optimize Surfactant Type for Field Case

Work is in progress to optimize the surfactant selection for Chevron's McElroy Field that is located in the Permian Basin. Per above in Table 2, we have already identified a number of surfactants for their compatibility with a synthetic McElroy brine. Starting with this list of compatible surfactants (either clear or slightly cloudy), further work has progressed with our rapid screening methods for oil recovery performance.

These next tests include the so-called calcite chip-cleaning method. 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. The photograph below shows some of the calcite chips exposed to surfactant after 24 hours exposure.

**Figure 7.** Photograph of some calcite chips coated with McElroy oil after 24 hours exposure to different nonionic surfactant solutions.

**Table 4.** Surfactant screening test via cleaning of calcite chips coated with McElroy oil

| Test for Surfactant ---- Calcite Chips Cleaning<br>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.

### 3.7 Conclusions for Work Performed this Reporting Period

1. A variation of a calcite chip screening method for surfactant performance was developed. This new approach uses several such chips in an imbibition cell so that the oil recovery is added as a performance metric to the visual observation of the clearness of the calcite surfaces. We recommend trying this method next with a light oil so that the recovered oil may be collected and measured accurately.

2. The theoretical calculations indicate the binding energy of naphthenic acids (NAs) to a carbonate surface is almost the same for the several molecules considered. Because our experiments demonstrate significant differences among the NAs in their ability to generate

an oil-wet condition on carbonate surfaces, it shows NA binding energy is not a primary factor related to carbonate wetting.

3. Of the 50 different surfactants tested for brine compatibility in a 3 and 12 wt% brine, the cationic types performed better. For the nonionic surfactants, the compatibility decreased with the higher salinity and temperature. The compatibility can be related roughly to the HLB of the nonionic surfactant.

4. The oil recovery performance testing for the surfactant mechanism study (a model oil from a limestone outcrop core) was reproducible and suggested certain cationic and nonionic surfactants have promising results.

5. The oil recovery performance testing for the surfactant mechanism study (a model oil from a limestone outcrop core) was reproducible and suggested certain cationic and nonionic structures are preferred.

6. Early screening studies of a number of surfactant products suitable for a potential application at McElroy Field show promising results. Further screening and more detailed study is in progress to identify commercial surfactants that could be applied in the field.

### 3.8 <u>References for Results and Discussion Presentation</u>

Austad, T. and Standnes, D.C.: "Spontaneous Inhibition of Water into Oil-Wet Carbonates", presented at 7th International Symposium on Reservoir Wettability, Freycinet, Tasmania, Australia, March 12-15, 2002.

Standnes, D.C. and Austad, T.: "Wettability alteration in chalk. 2. Mechanism for wettability alteration from oil-wet to water-wet using surfactants", *J. Pet.Sci. Eng.*, 28,123-143, 2000.

Standnes, D.C. and Austad, T.: "Non-toxic and Low-cost Amines as Wettability Alteration Chemicals in Carbonates", presented at 7th International Symposium on Reservoir Wettability, Freycinet, Tasmania, Australia, March 12-15, 2002.

Wu, Yongfu, Patrick J. Shuler, Mario Blanco; Yongchun Tang; William A. Goddard, III: "A Study of Wetting Behavior and Surfactant EOR in Carbonates with Model Compounds". Paper SPE 96612, presented at the SPE IOR Meeting, Tulsa, OK, April 24 – 26, 2006.

## 4.0 COST AND SCHEDULE AND MILESTONE STATUS

So far, we are on target to meet the milestones for this project. These are:

1. Develop a convenient rapid screening test for chemical performance (Month 9 - Done)
2. Complete study to use molecular simulation methods to estimate wetting ability of different surfactants. (Month 27)

3. Complete phase behavior/IFT study of most promising surfactant formulations (Month 20).
4. Complete brine compatibility tests of the best surfactants (Month 23).
5. Complete the initial oil displacement tests to demonstrate incremental recovery beyond waterflood with carbonate porous media (Month 33).
6. Complete additional oil recovery tests with carbonate porous media to optimize chemical efficiency and incremental oil recovery (Month 36).

The budget information and status for the project are shown below:

DOE- Surfactant EOR in Carbonates
Budget Period: 10/1/04 – 3/31/06
Approved Budget: $648,466
DOE share: $518,773
Non-Fed share: $129,693
Funding Received from DOE: $518,773
Actual Costs Incurred for period 10/1/04 - 3/31/06: $528,992
Cost Sharing for period: $132,248
Total Costs for period: $661,240

## 5.0 SUMMARY OF SIGNIFICANT ACCOMPLISHMENTS THIS TIME PERIOD

1. Development of yet another (a third) method for rapid screening of surfactants as Candidates for EOR in carbonate reservoirs. The initial attempt at using this approach was only partially successful due to the high viscosity of the crude oil used in the test. This screening method may be more useful for lighter, lower viscosity oils.

2. Compatibility tests identified several specific surfactant types and structures suitable for even very high salinity oil field brines, and over the range of temperatures expected in many carbonate reservoirs.

3. We completed a SPE paper that will be presented at the IOR meeting next April that reports our findings about chemical mechanisms associated with wetting on carbonate surfaces.

4. We hosted a chemical EOR workshop and had participation from several oil companies. Feedback from this effort was positive.

## 6.0 FUTURE WORK / POTENTIAL PROBLEMS

The focus for the next quarter will be or on 1) completing the SPE paper and submit for the upcoming SPE/DOE IOR meeting, 2) further effort on the theoretical study of the chemical mechanisms surrounding oil and surfactant solution wetting on carbonate minerals, and 3) more emphasis on the remaining experimental tasks concerning chemical compatibilities, IFT, and oil recovery. There are no serious problems anticipated for completion of the scheduled tasks.

## 7.0 TECHNOLOGY TRANSFER ACTIVITIES

We did receive several cores from Chevron from their McElroy Field located in the Permian Basin. We already had done some preliminary tests with that crude oil and have several EOR candidate surfactants in mind. After doing some additional scoping work, we will do some demonstration tests of oil recovery using these reservoir cores.

A significant effort was undertaken to organize and present a one-day chemical EOR workshop for industrial participants. This event was hosted by the California Institute of Technology and held on February 16 on campus at the Beckman Institute. The agenda for this event is given in Attachment 2. We had several oil companies participating both as attendees and also in some cases as presenters. If DOE is interested, we can provide further details, such as the meeting proceedings, or even repeat the workshop for another audience.

## 8.0 ACKNOWLEDGMENTS

As always, we would like to thank the DOE for their financial support and guidance throughout this project, and the useful technical discussions and samples being provided by the two industrial collaborators for this project, Chevron and Akzo Nobel.

**ATTACHMENT 1**

# PAPER SPE 99612

SPE 99612

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

Yongfu Wu, SPE; Patrick J. Shuler, SPE; Mario Blanco; Yongchun Tang; William A. Goddard, III
California Institute of Technology

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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.
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## 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 $6.62 \times 10^{-2}$ 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-pentylcyclohexane carboxylic > cyclohexanepentanoic > cyclohexanebutyric > cyclohexanepropionic > cyclohexanecarboxylic > fresh calcite surface (without treatment of NA). This is exactly in the same order as the flotation results listed in Table 2. 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, $\gamma_{LV}$ is surface tension of water, 72 dyne/cm at 25 °C, and $\gamma_{SV}$ 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; $\beta$ 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 $\gamma_{SV}$ 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.

Quantam mechanic (QM) calculations also were performed to estimate the binding energy between these NAs and the calcite surface. Binding energy calculations for all of these NAs are within 2 kcal/mol of one another (less than 2% variation), and hence not considered to be significantly different. These results indicate that differences in water contact angle and wetting of the calcite surface are not due to differences in binding energetics but rather to differences in partitioning between the aqueous solvent and the calcite surface. These findings are consistent with the LogP correlation with contact angles discussed above.

**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 1000 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 mN/m). 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 , because of the steric exclusion of cyclohexane ring connected directly to –COOH in cyclohexanecarboxylic acid and stronger interaction between solvent molecules and alkyl chian in trans-4-pentylcyclohexane carboxylic acids, their adsorption is relatively lower than the others.

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-pentylcyclohexane carboxylic ~ 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.

## Acknowledgements

This work was conducted at the California Institute of Technology and financially supported by the Department of Energy of Energy grant DE-FC26-04BC15521. The authors thank Chevron and Akzo Nobel for their collaboration on this project.

## References

1. Roehl, P. O. and Choquette, P. W.: *"Carbonate Petroleum Reservoirs"*, Springer-Verlag, New York City(1985).
2. Allan, J. and Sun, S. Q.: *"Controls on Recovery Factor in Fractured Reservoirs: Lessons Learned from 100 Fractured Fields*", paper SPE 84590 presented at SPE ATCE, Denver, CO, 5-8 October, 2003.
3. Tong, Z. X.; Morrow, N. R. and Xie, X.: *"Spontaneous Imbibition For Mixed-Wettability States In Sandstones Induced By Adsorption From Crude Oil"*, presented at the 7th International Symposium on Reservoir Wettability, Tasmania, Australia, 12-14 March, 2002.

4. Morrow, N.R. and Mason, G.: "*Recovery of Oil by Spontaneous Imbibition*", Current Opinion in Colloid and Interface Science, 6, 2001, 321-337.

5. Zhou, X., Morrow, N. R. and Ma, S.: "*Interrelationship of Wettability, Initial Water Saturation, Aging Time and Oil Recovery by Spontaneous Imbibition and Waterflooding"* SPE Journal, 5(2), June 2000, 199-207.

6. Hirasaki, G. and Zhang, D. L.: "*Surface Chemistry of Oil Recovery from Fractural, Oil-Wet, Carbonate Formations"*, SPE Journal, 9(2), June 2004, 151-162.

7. Spinler, E. A. and Baldwin, B. A.: "*Surfactant Induced Wettability Alteration in Porous Media*", in "Surfactant Fundamentals and Application in the Petroleum Industry", Ed. by Schramm, L. L., Cambridge University Press, 2000, 159-202.

8. Vijapurapu, C. and Rao, D. N.: "*Compositional Effects of Fluids on Spreading, Adhesion and Wettability in Porous Media"*, Colloids & Surface A: Physicochem. Eng. Aspects, 2004(241), 335-342.

9. Seethepalli, A.; Adibhatla, B. and Mohanty, K. K.: "*Wettability Alteration During Surfactant Flooding of Carbonate Reservoirs*", paper SPE 89423 presented at SPE/DOE 14th Symposium on Improved Oil Recovery, Tulsa, OK, 17-21 April, 2004.

10. Zhang, D. L.; Liu, S.; Puerto, M. Miller, C. A. and Hirasaki, G. J.: "*Wettability Alteration and Spontaneous Imbibition in Oil-Wet Carbonate Formations*", presented at the 8th International Symposium on Reservoir Wettability, Houston, Texas,16-18 May, 2004.

11. Xie, X.; Weiss, W. W.; Tong, Z and Morrow, N. R.: "*Improved Oil Recovery from Carbonate Reservoirs by Chemical Stimulation*", paper SPE 89424 presented at SPE/DOE 14th Symposium on Improved Oil Recovery, Tulsa, OK, 17-21 April, 2004.

12. Enrique, S-S.; Armando, D-O.; Hermilo, P-A.; Issac, K-S. and Fernando, R-G.: "*Wettability of Solid/Brine/n-Dodecane System: Experimental Study of the Effects of Ionic Strength and Surfactant Concentration*", Colloids & Surfaces A: Physicochem Eng. Aspects, 2004(241), 343-349.

13. Standnes, D. C.: "*Analysis of Oil Recovery Rates for Spontaneous Imbibition of Aqueous Surfactant Solutions into Preferential Oil-Wet Carbonates by Estimation of Capillary Diffusivity Coefficients*", Colloids & Surfaces A: Physicochem Eng. Aspects, 2004(251), 93-101.

14. Standnes, D. C. and Austad, T.: "*Non-toxic and Low Cost Amines as Wettability Alteration Chemicals in Carbonates*", presented at the 7th International Symposium on Reservoir Wettability, Tasmania, Australia, 12-14 March, 2002.

15. Bryant, E. M.; Bowman, R. S. and Buckley, J. S.: "*Wetting Alteration of Mica Surfaces with Polyethoxylated Amine Surfactants*", presented at the 8th International Symposium on Reservoir Wettability, Houston, Texas, 16-18 May, 2004.

16. Ashayer, R.; Grattoni, C. A. and Luckham, P. F.: "*Wettability Changes During Surfactant Flooding*", presented at the 6th International Symposium on Evaluation of Reservoir Wettability and Its Effect on Oil Recovery, Socorro, New Mexico, 27-28 September, 2000.

17. Morrow, N. R.: "*Wettability and Its Effect on Oil Recovery*", JPT, 42(12), December 1990, 1476-1484.

18. Anderson, W. G.: "*Wettability Literature Survey-Part I: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability*", JPT, 38(11), October 1986, 1125-1144.

19. Madsen, L.; G.-M., L.; Gron, C.; Lind, I. and Engell, J.: "*Adsorption of Polar Aromatic Hydrocarbons on Synthetic Calcite*", Org. Geochem., 24(12), 1996, 1151-1155.

20. Madsen, L. and Lind, I.: "*Adsorption of Carboxylic Acids on Reservoir Minerals from Organic and Aqueous Phase*", SPE Reservoir Evaluation & Engineering, Feb. 1998, 47-51.

21. Thomas, M. M.; Clouse, J. A. and Longo, J. M.: "*Adsorption of Organic Compounds on Carbonate Minerals 1. Model Compounds and Their Influence on Mineral Wettability*", Chemical Geology, 1993, 109, 201-213.

22. Zou, L.; Han, B.; Yan, H.; Kasperski, K. L. Xu, Y. and Hepler, L. G.: "*Enthalpy of Adsorption and Isotherms for Adsorption of Naphthenic Acid onto Clays*", J. Colloid & Interface Science, 1997, 190, 472-475.

23. Legens, C.; Toulhoat, H.; Cuiec, L.; Villieras, F. and Palermo, T.: "*Wettability Change Related to the Adsorption of Organic Acids on Calcite: Experimental and Ab Initio Computational Studies*", paper SPE 49319 presented at ATCE, New Orleans, Louisiana, 27-30 September, 1998.

24. Zhang, P. and Austad, T.: "*The Relative Effects of Acid Number and Temperature on Chalk Wettability*", paper SPE 92999 presented at SPE International Symposium on Oilfield Chemistry, Houston, Texas, 2-4 February, 2005.

25. Li, D. and Neumann, A. W.: "*Equation of state for interfacial tensions of solid-liquid systems*", Advances in Colloid and Interface Science, 1992(39), 299-345.

26. Suzuki, T.; Hirose, G. and Oishi, S.: "*Contact Angle of Water Droplet on Apatite Single Crystals*", Materials Research Bulletin, 2004(39), 103-108.

27. Standnes, D. C. and Austad, T.: "*Wettability Alteration in Chalk: 2. Mechanism for Wettability Alteration from Oil-wet to Water-wet Using Surfactants*", J. of Petroleum Science & Engineering, 2000(28), 123-143.

28. Standnes, D. C. and Austad, T.: "*Wettability Alteration in Carbonates: Interaction between Cationic Surfactants and Carboxylates as a Key Factor in Wettability Alteration from Oil-wet to Water-wet*", Colloids & Surfaces A: Physicochemical & Engineering Aspects, 2003(216),243-259.

**Table 1. Molecular Structures of Naphthenic Acids Investigated**

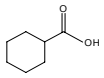
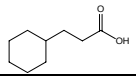
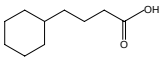
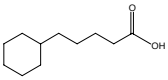
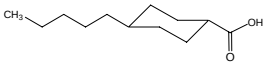
| Naphthenic Acids | Molecular Structure | F.W. | m.p. (°C) | b.p. (°C) |
|---|---|---|---|---|
| Cyclohexanecarboxylic Acid |  | 128.17 | 31 | 232 |
| Cyclohexanepropionic Acid |  | 156.23 | 15 | 276 |
| Cyclohexanebutyric Acid |  | 170.25 | 31 | >110 |
| Cyclohexanepentanoic Acid |  | 184.28 | 16 | 126 |
| trans-4-pentylcyclohexanecarboxylic Acid |  | 198.31 | 52 | >110 |

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

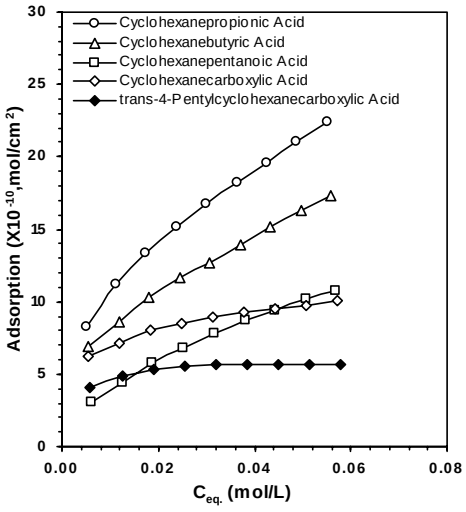



Figure 2. Adsorption isotherms of naphthenic acids on calcite in n-Decane solution (23 °C, 16 hours)

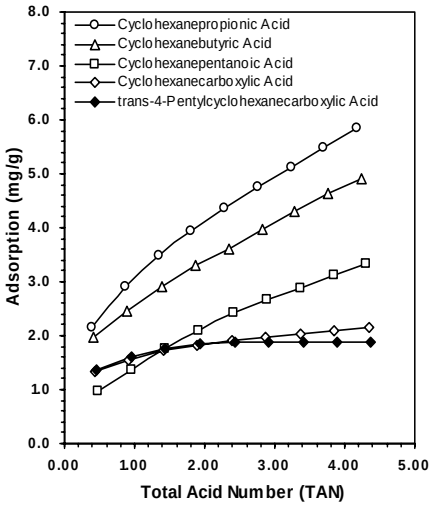
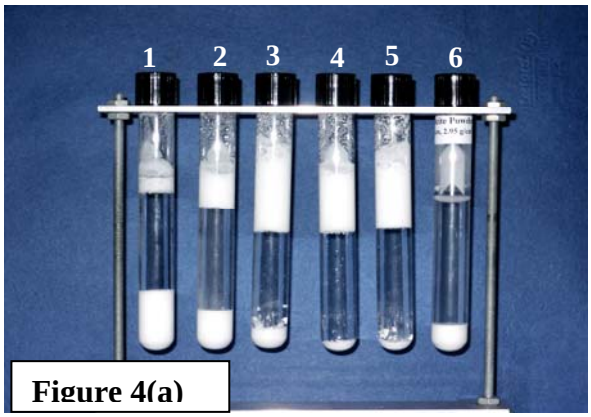



Figure 3. Adsorption isotherms of naphthenic acids in n-Decane on calcite (mass adsorption vs. TAN) (23 °C, 16 hours)



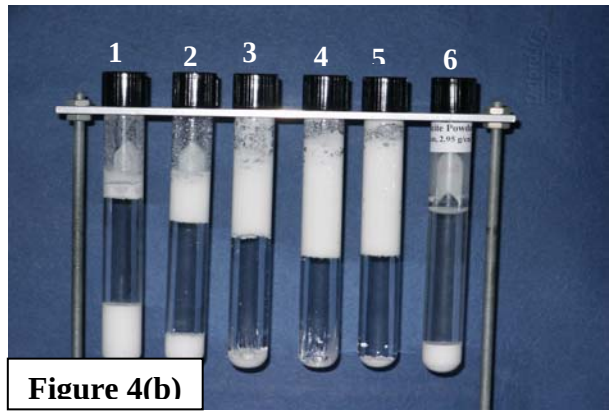




Figure 4. Flotation test of calcite powder treated with NA at different concentrations [Figure 4(a): TAN 0.4 ~ 0.5; Figure 4(b): 4 ~ 4.5]. Liquid phase: distilled water (pH~ 6). Solid treated with NA: (1) cyclohexanecarboxylic acid; (2) cyclohexanepropionic acid; (3) cyclohexanebutyric acid; (4) cyclohexanepentanonic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

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

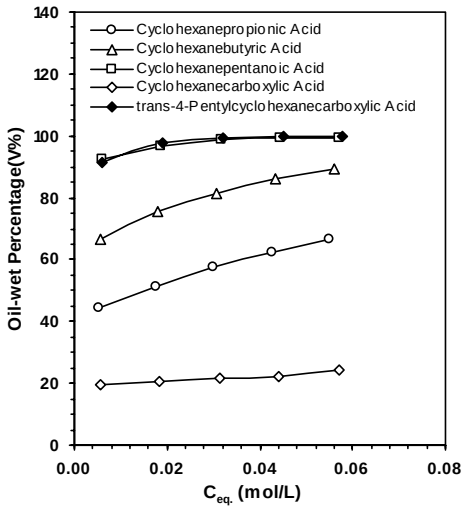



Figure 6. Oil-wet (v/v) vs. total acid number (TAN)

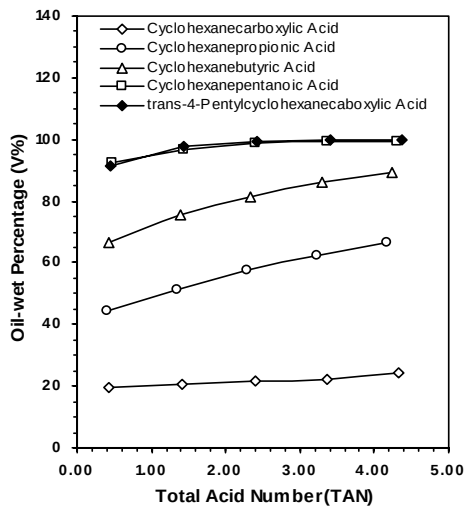



Figure 7. Water Contact Angles on Calcite Surface

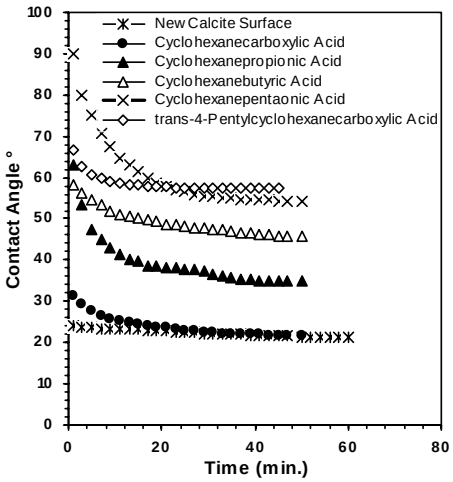



Table 2. Adsorption, Oil-wettability and Contact Angle

| Calcite with Naphthenic Acids | $\Gamma_{max}$ (mol/cm$^2$) | Oil-wet | Water-wet | $\theta$ |
|---|---|---|---|---|
| Cyclohexane carboxylic acid | $1.01\times10^{-9}$ | 19% | 81% | 22 |
| Cyclohexane propionic acid | $2.25\times10^{-9}$ | 67% | 33% | 35 |
| Cyclohexane butyric acid | $1.73\times10^{-9}$ | 89% | 11% | 46 |
| Cyclohexane pentanoic acid | $1.08\times10^{-9}$ | 99% | 1% | 55 |
| trans-4-pentylcyclohexane carboxylic acid | $0.57\times10^{-9}$ | 99% | 1% | 57 |

Table 3. Interfacial Tension ($\gamma_{SV}$) of Calcite Surfaces Measured by Water Contact Angle at T=25 °C

| Surfaces Treated with Naphthenic Acids | $\theta$ | $\gamma_{SV}$ (erg/cm$^2$) |
|---|---|---|
| New clcite surface without NA | 21° | 67.6 |
| Cyclohexanecarboxylic acid (Log P=0.8859) | 22° | 67.2 |
| Cyclohexanepropionic acid (Log P=1.6690) | 35° | 61.3 |
| Cyclohexanebutyric acid (Log P=2.1216) | 46° | 55.4 |
| Cyclohexanepentanoic acid (Log P=2.4961) | 55° | 50.1 |
| trans-4-pentylcyclohexane carboxylic acid (Log P=2.9291) | 57° | 49.0 |

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

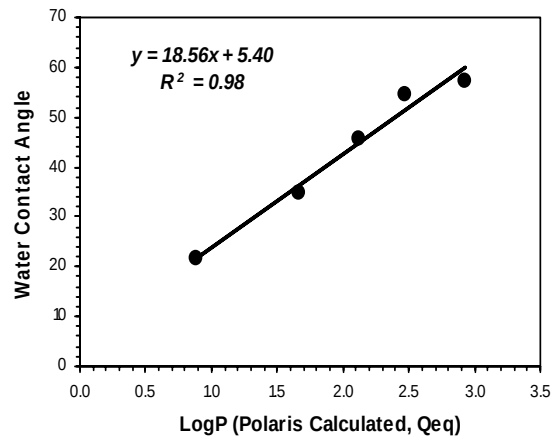



Table 4. Wettability Alteration to Water-wet by Use of Surfactant Solution (T=25 °C)

| Surfactant | Type | Percentage of Powder that Sinks(water-wet) | | |
|---|---|---|---|---|
| | | 100 ppm | 50 ppm | 25 ppm |
| Arquad T-50 | Cationic | 100% | 100% | 60% |
| $C_{12}$TAB | Cationic | 60% | 45% | N/D* |
| Igepal CO-530 | Nonionic | 100% | 95% | 2% |
| Neodol 25-7 | Nonionic | 100% | 80% | 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 (mg) |
| Arquad T-50 | Cationic | 260 | 2.6 |
| $C_{12}$TAB | 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 Surfactants, 0.4 wt.%, 25 °C)

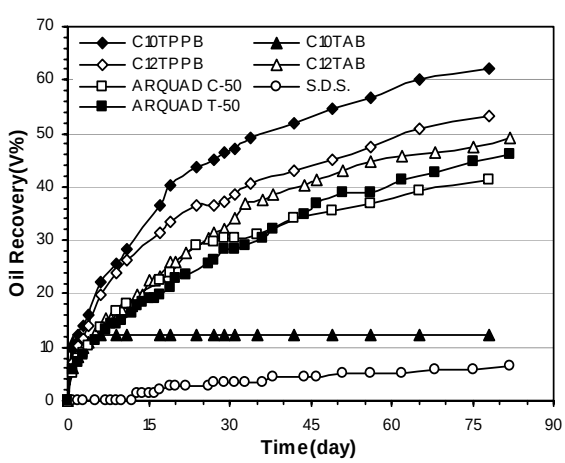



Figure 10. Oil Recovery Measured by Spontaneous Imbibition Test (Nonionic Surfactants, 0.4 wt.%, 25 °C)

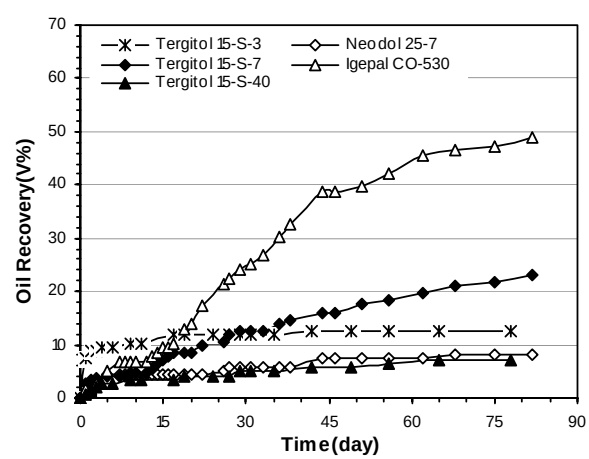
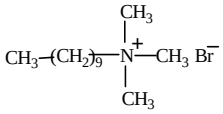
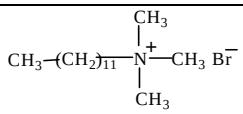
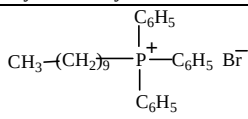
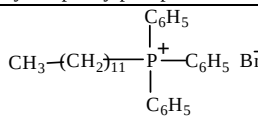
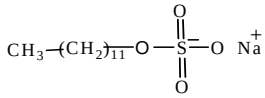
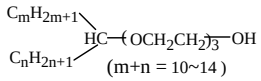
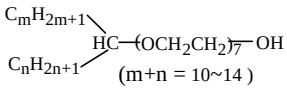
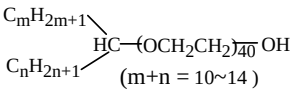
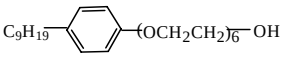
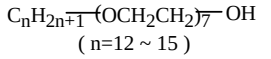


Table 6. Molecular Structure, Critical Micelle Concentration and Related Parameters of Selected Surfactants, and Oil Recovery Results for Model Oil by Use of the Surfactants at 0.4 wt.% and Room Temperature

| **Surfactants & Molecular Structures** | **Symbol or Trade Name** | **C.M.C. (at 25°C)** | **Conc. at 0.4 wt.%** | **Oil Recovery and IFT** |
|---|---|---|---|---|
|  <br>n-Decyl Trimethylammonium Bromide | **$C_{10}$TAB**<br>(Cationic)<br>M.W. =280.3 | $6.8\times10^{-2}$ M | $1.43\times10^{-2}$ M | **12.1%(v/v)**<br>IFT=2.67 mN/m |
|  <br>n-Dodecyl Trimethylammonium Bromide | **$C_{12}$TAB**<br>(Cationic)<br>M.W.=308.35 | $1.6\times10^{-2}$ M | $1.30\times10^{-2}$ M | **48.5%(v/v)**<br>IFT=0.59 mN/m |
|  <br>n-Decyl Triphenylphosphonium Bromide | **$C_{10}$TPPB**<br>(Cationic)<br>M.W.=483.45 | 1st: $7.3\times10^{-3}$ M<br>2nd: $1.5\times10^{-2}$ M | $8.27\times10^{-3}$ M | **62.0%(v/v)**<br>IFT=3.56 mN/m |
|  <br>n-Dodecyl Triphenylphosphonium Bromide | **$C_{12}$TPPB**<br>(Cationic)<br>M.W.=511.50 | 1st: $1.8\times10^{-3}$ M<br>2nd: $2.7\times10^{-3}$ M | $7.82\times10^{-3}$ M | **52.5%(v/v)**<br>IFT=2.02 mN/m |
| **ARQUAD® C-50**<br>Coconut oil alkyl ($C_{12}$-$C_{14}$) trimethylammonium chloride | M.W.=278.0<br>(Cationic)<br>HLB=16.5 | $4.5\times10^{-3}$<br>~$2.0\times10^{-2}$ M | $1.44\times10^{-2}$ M | **41.0%(v/v)**<br>IFT=0.53 mN/m |
| **ARQUAD® T-50**<br>Trimethyl tallowalkyl($C_{16}$-$C_{18}$) ammonium chloride | M.W.=340.0<br>(Cationic)<br>HLB=14.2 | <$1.3\times10^{-3}$ M | $1.18\times10^{-2}$ M | **46.0%(v/v)**<br>IFT=0.69 mN/m |
|  <br>Sodium Dodecyl Sulfate | **S.D.S.**<br>(Anionic)<br>M.W.=288.4 | $8.2\times10^{-3}$ M | $1.39\times10^{-2}$ M | **6.8%(v/v)**<br>IFT=4.77 mN/m |
|  <br>Ethoxylated C11~15 secondary alcohol | **Tergitol 15-S-3**<br>(Nonionic)<br>HLB=8.3<br>M.W.=336.0 | >$5.6\times10^{-5}$ M | $1.19\times10^{-2}$ M | **12.8%(v/v)**<br>IFT=4.44 mN/m |
|  <br>Ethoxylated C11~15 secondary alcohol | **Tergitol 15-S-7**<br>(Nonionic)<br>HLB=12.4<br>M.W.=515.0 | >$8.4\times10^{-5}$ M | $7.77\times10^{-3}$ M | **22.5%(v/v)**<br>IFT=1.39 mN/m |
|  <br>Ethoxylated C11~15 secondary alcohol | **Tergitol 15-S-40**<br>(Nonionic)<br>HLB=18.0<br>M.W.=2004 | >$1.4\times10^{-4}$ M | $2.00\times10^{-3}$ M | **5.7%(v/v)**<br>IFT=11.5 mN/m |
|  <br>Nonylphenoxypoly(ethyleneoxy) ethanol | **Igepal CO-530**<br>(Nonionic)<br>HLB=10.8<br>M.W.=484.0 | $7.5\times10^{-5}$ M | $8.26\times10^{-3}$ M | **49.5%(v/v)**<br>IFT=0.33 mN/m |
|  <br>( n=12 ~ 15 )<br>$C_{12}$ – $C_{15}$ linear primary alcohol ethoxylate | **Neodol 25-7**<br>(Nonionic)<br>HLB=12.5<br>M.W.=515.0 | <$8.2\times10^{-5}$ M | $7.77\times10^{-3}$ M | **8.2%(v/v)**<br>IFT=2.02 mN/m |

# ATTACHMENT 2

# AGENDA FOR CHEMCIAL EOR WORKSHOP

**TECHNICAL AGENDA CHEMICAL EOR WORKSHOP**

**CALIFORNIA INSTITUTE OF TECHNOLOGY**

**FEBRUARY 16, 2006 Beckman Institute Auditorium**

**Topics and Speakers**

| | | |
|---|---|---|
| 9:00 – 9:10 | Opening remarks | Yongchun Tang/Caltech |
| 9:10 – 9:35 | Overview of EOR Trends | Pat Shuler/Caltech |
| 9:35– 10:15 | Overview Chemical EOR | Rien Faber/Shell Netherlands |
| 10:15 – 10:35 | Break | |
| 10:35 – 11:10 | Chemical Flooding – China Focus | Qimeng Wang/Daqing, China presenter, Pat Shuler/Caltech |
| 11:10 – 11:45 | Surfactant Polymer Project Minas Field | Gabriel Prukop/Chevron USA |
| 11:45 – 1:00 | Lunch and Posters | |
| 1:00 – 1:20 | Molecular Design of EOR Chemicals | Bill Goddard/Caltech |
| 1:20 – 1:50 | Surfactant EOR in Carbonate Reservoirs | Yongfu Wu/Caltech |
| 1:50 – 2:20 | Conformance Control – Pre-formed Particle Gel (PPG) Technology | Baojun Bai/Caltech |
| 2:20 – 2:50 | Conformance Control - Bright Water Technology | Rick Ng/Chevron USA |
| 2:50 – 3:10 | Conformance Control – Foam Gels | Francois Friedmann/Caltech |
| 3:10 – 3:30 | Break | |
| 3:30 – 4:00 | Tracer Technology for EOR Projects | Raymond Lovie/Tracerco UK |
| 4:00 - 4:30 | Microbial EOR | Xiang-Dong Fang/Caltech |
| 4:30 – 5:00 | Workshop Wrap Up | Pat Shuler/Caltech |