Oil & Natural Gas Technology

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Quarterly Report

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Bridging the Gap between Chemical Flooding and Independent Oil Producers

Submitted by:
University of Kansas Center for Research, Inc.
2385 Irving Hill Rd
Lawrence, KS 66045-7563

Prepared for:
United States Department of Energy
National Energy Technology Laboratory

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Office of Fossil Energy

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EXECUTIVE SUMMARY

The task to identify, evaluate and select oil leases in Kansas that will be the subjects of study during the remainder of this project was accomplished. The selection process was accomplished through contacts and interviews with technical personnel from oil production companies. Ten leases were selected for laboratory studies to design chemical systems for flooding applications. Crude oil samples were collected from nine of the leases. Phase behavior studies and related physical measurements using crude oils from three of the selected leases were initiated. Preliminary results from these laboratory studies using crude oil from the Trembley lease are described.

INTRODUCTION

This research project aims to demonstrate the potential of "next generation" chemical flooding processes and will provide the design work that is necessary for Independent Oil Producers to make an informed assessment for implementation of a pilot or demonstration project. Laboratory testing is a major focus of the design process and this testing will be conducted to design proper chemical formulations for specific oils/reservoirs. Field response to chemical flooding will be determined through reservoir simulations. Economics of pilot/demonstration and field applications will be evaluated. Laboratory, simulation and economic results will be dispersed through technical papers and presentations to independent oil operators. Designs of chemical floods provide the basis for demonstration projects and a starting point for independent oil operators to implement the new chemical flooding technology. We anticipate government-sponsored field projects to demonstrate the benefits of new chemical flooding technologies to Independent Oil Producers.

The Project Management Plan was updated (Task 1) during the first quarter of the project. Task 2 was completed and Task 3 was initiated during the third quarter of the project (April – June 2009). Progress and results of these two tasks are reported below.

PROGRESS, RESULTS AND DISCUSSION

Task 2. Identify and Select Candidate Reservoirs

Ten oil leases in Kansas were selected to be the subjects of study during the remainder of this project. General information about the leases and the Independent Oil Producer operating each lease are given in Table 1. The leases are under various stages of waterflood and represent most of the oil-producing horizons in Kansas that we have identified as targets for chemical flooding applications. Each of the leases was judged by the operators as their best, or one of their top performing and efficient waterfloods. An efficient waterflood is an excellent indicator of favorable flow characteristics, a key requirement for an efficient chemical flood. We have determined that the personnel of the companies operating the selected leases are interested in chemical flooding technology and appear to have the financial backing and technical personnel to implement the technology.

Most of the leases had chemical treatment programs that often included corrosion inhibitors in the production well and emulsion breakers for the flow lines and separation facilities. General procedures were developed and arrangements were made with office and field personnel of the production companies to collect crude oil samples that contained no or minimal amounts of treatment chemicals. This was done in order to reduce or eliminate any effect the treatment chemicals might have on the laboratory testing in Task 3. Oil samples from nine of the leases have been collected. Efforts are underway to identify and collect available technical data for each lease so that it can be utilized during the design process.

Table 1 - Selected leases for laboratory studies.

Lease/Unit	Formation	Field	County	Oil Operator
Trembley	Lansing-Kansas City	Trembley	Reno	Berexco
Celia South WF	Cherokee Lime	Celia South	Rawlins	Murfin
Tobias	Simpson sand	Tobias	Rice	Berexco
Missouri Flats	Lansing	Missouri Flats NE	Gove	Merit
Wahrman	Lansing-Kansas City	Beaver Creek	Rawlins	Vess
Stewart	Morrow sand	Stewart	Finney	PetroSantander
Muddy Creek SW	Bartlesville	Muddy Creek	Butler	Stelbar
Woodhead	Squirrel	Vinland	Douglas	Colt Energy
Pleasant Prairie Chester Unit	Chester	Pleasant Prairie	Haskell	Oxy
Chester Waterflood	Chester	Pleasant Prairie	Haskell	Cimarex

Task 3: Design Efficient Chemical Formulations for selected Oil/Brine/Reservoir.
Task 3.1: Conduct laboratory tests using crude oils and field brines.

Phase behavior studies and related physical measurements using crude oils from three of the selected leases were initiated. Preliminary results from the laboratory studies using crude oil from the Trembley lease are described.

Introduction. Crude oil from the Trembley Lease in the Trembley Field in Reno County, Kansas was selected for surfactant screening. This crude oil is light, having an API gravity of 37.6 and a low viscosity of 4.06 cp at reservoir temperature of 46.1 Celsius. The oil is not reactive with alkali as the acid number determined for this oil was a mere 0.08 mg KOH /g oil.

Several criteria need to be met for a success when screening surfactants (co-surfactants and co-solvents) for effectiveness in chemical flooding. The performance of a chemical formulation depends directly on the ability of the formulation to solubilize sufficient volumes of both oil and aqueous phases especially at the electrolyte concentration to be encountered in field application. High solubilization or uptake of a phase in the microemulsion phase indicates a low interfacial tension between the microemulsion and the respective phase. The microemulsion phases must also form readily and coalesce quickly after contacting the aqueous solution containing surfactants with the oil. The formed phases must also exhibit fluidity and homogeneity i.e. absence of viscous phases, gels and macroemulsions.

Laboratory screening entails combining surfactant formulations with the oil being evaluated and observing the physical attributes of the phases involved such as viscosity, interfacial tension between phases and quantifying the solubilization of the pure phases in the microemulsion phase. The degree of solubilization of the water and oil phases brought about by the presence of surfactant is expressed in terms of solubilization parameters. Solubilization parameters of water and oil, P_w and P_o, are defined as the ratio of the volume of the respective phase solubilized by the microemulsion phase to the volume of surfactant present in the microemulsion phase. It is assumed for this calculation that all of the surfactants are contained in the microemulsion phase.

An optimum solubilization is achieved when the uptake of oil and water phases is equal in the microemulsion phase. When working with anionic surfactants, uptake of the two phases is controlled by the concentration of electrolyte. Increasing electrolyte concentrations in aqueous phase containing surfactant reduces the solubility of surfactants in the aqueous phase which leads to three distinct types of microemulsions forming as salinity increases from low to high. Winsor classified the three phases as Type I, Type III and Type II. Type I is an oil-in-water microemulsion formed at low electrolyte concentration, Type II is a water-in-oil microemulsion formed at high electrolyte concentrations and Type III is a bicontinous microemulsion with both oil and aqueous phase solubilized and is formed at intermediate electrolyte concentrations. The transition Type I→ Type III → Type II is seen as electrolyte concentration is increased. Equal solubilization parameters for oil and water are obtained in the Type III regime. The electrolyte concentration at which the solubilization parameters are equal is called optimum salinity and the value of solubilization parameter at the optimum salinity is termed optimum solubilization parameters or ratios. An optimum solubilization parameter of at least 10 cc/cc is aimed for which is sufficient to give ultra low interfacial tensions [Flaaten et al.]. In addition, the surfactant formulations are studied for the effects of parameters such as total surfactant concentration, surfactant ratios, co-solvent concentration, alkali concentration, types of electrolyte etc. on phase behavior of the systems in order to improve formulations.

Experimental Methods. An approach similar to discussed by Flaaten et al. is used for phase behavior experiments. 10 mL borosilicate Fisherbrand pipettes are used to contain the formulations, comprising of an aqueous phase and an oleic phase in 1:1 ratio by mass. The aqueous phase contains surfactants, co-solvents and electrolyte. Sample preparation began by preparing four grams of the aqueous phase. After mixing the aqueous solution on a vortex mixer, aqueous phase behavior is recorded and then an equal mass of oil is added. The formulations are mixed well on the first day and after that left to equilibrate in an oven at reservoir temperature. In subsequent days, interface levels are recorded from time to time to determine the solubilization of the oil and water phases. Each series has a unique concentration of surfactants and co-solvent (SBA) while concentration of electrolyte, namely NaCl, is increased gradually within a series until all the three microemulsion phases are observed i.e. Winsor Type I, Type II and Type III. The main tasks of this laboratory approach to screening is to determine the optimum salinity, solubilization parameters, equilibration times and viscosities of the phases.

Surfactants Petrostep S1 and Petrostep S2 obtained from the Stepan Company were selected for initial testing with Trembley crude. Petrostep S1 is a branched alcohol propoxy sulfate and Petrostep S2 is an internal olefin sulfonate. These surfactants were selected as the starting surfactants for screening with Trembley crude because earlier studies have found them to have favorable properties and performance for EOR application at temperatures and oil properties similar to those of the Trembley crude oil. Screening experiments performed in the lab used the two surfactants simultaneously as that gives certain advantages, foremost being the control of optimum salinity and second being the reduced use of co-solvents such as sec-butanol (SBA) that are essential for reducing viscous phases and equilibration time. SBA was the co-solvent used in all of the studies.

A photo of the pipettes for a salinity scan using Petrostep surfactants and the Trembley oil is shown in Figure 1. The phase volumes in the pipettes are measured and the solubilization parameters were calculated and plotted in Figure 2 as a function of salinity. Optimum salinity and the optimum solubilization parameter are determined at the point where the two curves intersect.

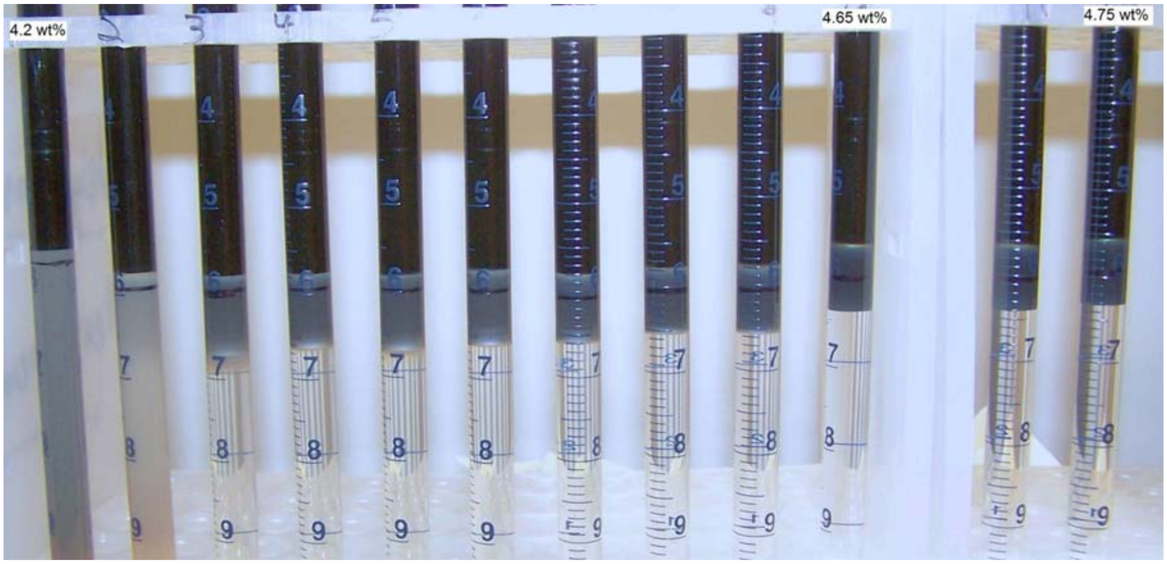

Figure 1. Photo of a salinity scan for a formulation containing 0.625 wt% Petrostep S1, 0.375 wt% Petrostep S2 and 2 wt% SBA with Trembley crude oil @ 46.1 Celsius after equilibrating for 49 days. Salinity from 4.2 to 4.75 wt% NaCl (left to right) at increments of 0.05 wt% NaCl.

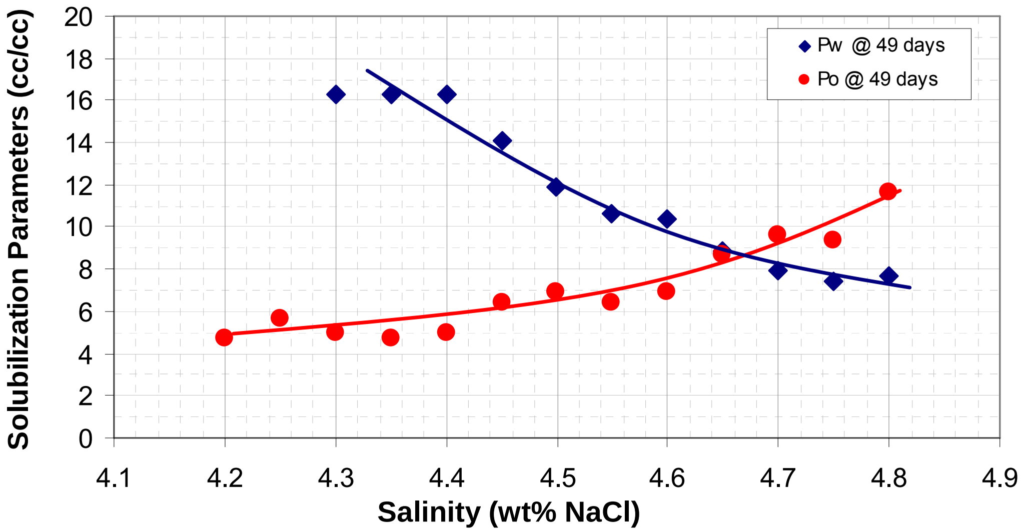

Figure 2. Solubilization parameters for salinity scan for a formulation containing 0.625 wt% Petrostep S1, 0.375 wt% Petrostep S2 and 2 wt% SBA with Trembley crude oil @ 46.1 Celsius after equilibrating for 49 days.

Effect of Total Surfactant Concentration and Surfactant Ratios. A total surfactant concentration of 2 wt % in the aqueous phase was used in initial screening experiments. Slow coalescence and viscous phases were observed in the pipettes at this concentration of total surfactant. Gels were observed in some of the tubes. It was suspected that the concentration of co-solvent (SBA) was not sufficient to reduce the viscous and gel phases for the 2 % total surfactant series. In subsequent experiments the total surfactant concentrations were reduced to 1.0 wt% and 0.5 wt% and the relative amount of co-solvent (SBA) was increased in the attempt to reduce equilibration times and promote more fluidity at the interfaces.

Lower total surfactant concentrations showed quicker equilibration and more fluidity at interfaces and, in general, the SBA requirement was also reduced at lower concentrations. Optimum solubilization ratios were improved slightly by reducing total surfactant concentration. This was likely a result of lower co-solvent (SBA) requirement.

After allowing sufficient time to equilibrate, more than 100 days for series containing 2% total surfactant and approximately 50 to 80 days for series containing 1.0 wt% to 0.5 wt% surfactant, it was observed that as the surfactant concentration was decreased there was a shift towards lower optimum salinities at a was observed for a particular ratio of Petrostep 1 to Petrostep 2. This is illustrated in Figure 3. A significant shift in optimum salinity was observed when the surfactant concentration was reduced from 1.0 wt% to 0.5 wt%.

The main impact of varying the ratios of surfactants was on the optimum salinity of the formulations. As Petrostep S1 is more hydrophobic increasing its concentration drives the optimum salinity to lower values while opposite for Petrostep S2 is observed. This effect is also shown in Figure 3.

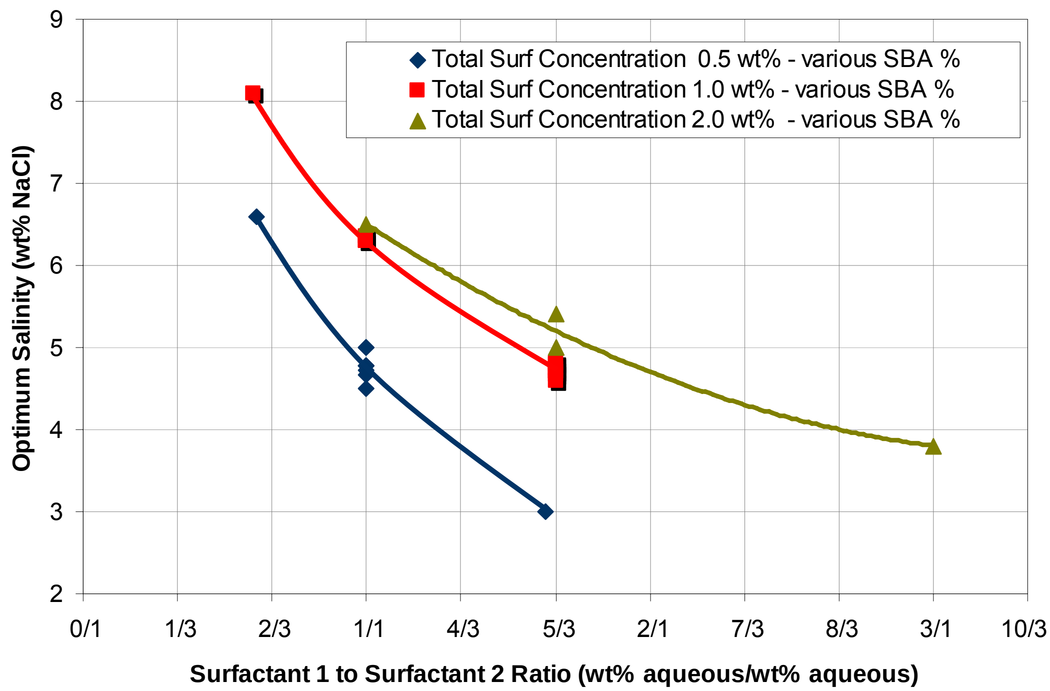

Figure 3. Effect of varying Petrostep S1 to Petrostep S2 ratio on optimum salinity with various SBA concentrations. Oil is Trembley crude oil @ 46.1 Celsius.

Additional co-solvent (SBA) was required to speed up equilibration and avoid viscous phases at higher ratios of Petrostep S1 to Petrostep S2,. For instance, at a Petrostep S1 to Petrostep S2 ratio of 3:1, gels and viscous phases formed and long equilibration times were observed for all surfactant concentrations, even at relatively high SBA concentrations. Another major disadvantage of higher ratios of Petrostep S1 was low solubilization values that were observed for all surfactant concentrations. Moving towards higher ratios of Petrostep S2 gave better solubilization, relatively quicker equilibration and was less likely to form viscous and gel phases.

Effect of Co-Solvent Concentration. Sec-butanol (SBA) was used as co-solvent in all the experiments and was essential to mitigate viscous phases and gels which in turn promoted faster coalescence times. However, use of co-solvent also often reduced the solubilization of oil and water in the microemulsions. For Trembley oil, high SBA concentrations were required, relative to total surfactant concentration, to decrease equilibration times and to alleviate gels and macro emulsions. Coalescence times were not reduced as much as desired even though SBA concentration was increased to three times the value of the total surfactant concentration.

Figures 4 and 5 illustrate the effect of SBA on optimum solubilization parameter for salinity scans containing 1.0 wt% and 0.5 wt% total surfactant, respectively. Some of the series had to equilibrate more than 60 days before they reached a stable solubilization of each phase. For a ratio of 1:1 of Petrostep S1 and Petrostep S2, a significant reduction in the optimum solubilization parameters was observed on increasing SBA concentration. A less dramatic change was observed for the 5:3 ratio of Petrostep S1 to Petrostep S2. The effect of the amount of alcohol on optimum salinity was insignificant for the series studied.

Equilibration Times. Equilibration times were ascertained by plotting optimum solubilization parameters versus time from mixing. One such graph is shown in Figure 6 for a salinity scan that required more than 50 days to reach equilibrium. The optimum solubilization parameter was significantly lower after 50 days than at early times. A general rule of thumb is that solubilization parameters have to be on the order of 10 or higher in order for interfacial tensions to be low enough for efficient recovery of oil. Slow equilibration times are an issue that is being addressed by testing other surfactants and co-solvents.

Measurements of interfacial tension and viscosity. Qualitative assessment of the viscosity of phases in salinity scans tubes are made visually. Gels and very viscous phase are detrimental to the performance of the system and these are easily observed in the tubes. Similarly, interfacial tensions between the phases can be assessed by correlation with the solubilization parameters and by visual inspection of the interfaces. These qualitative assessments need to be verified by actual measurements.

Samples for viscosity and interfacial tension measurements were prepared in 20-mL scintillation vials to provide sufficient sample volumes. These samples equilibrated faster than the same system in pipettes, possibly due to larger cross section available for coalescence.

The spinning drop tensiometer in our laboratory was constructed in-house several years ago and has not recently been used. The tensiometer was tested for its ability to control temperature and the performance was tested with the n-butanol-water system. The spinning drop tensiometer performs accurate measurements and has temperature control to within 0.2Celcius at 46 Celsius. This is approximately the highest temperature we expect to investigate during this project.

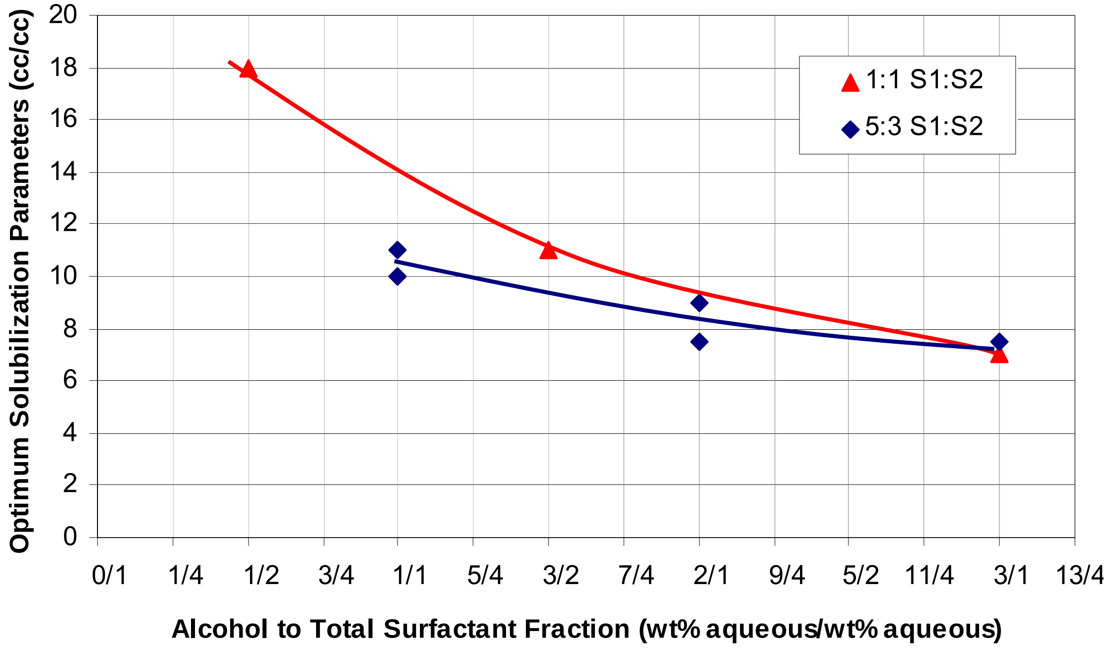

Figure 4. Effect of co-Solvent (SBA) concentration on optimum solubilization parameter at 1% total surfactant concentration and two ratios of Petrostep S1 to Petrostep S2.

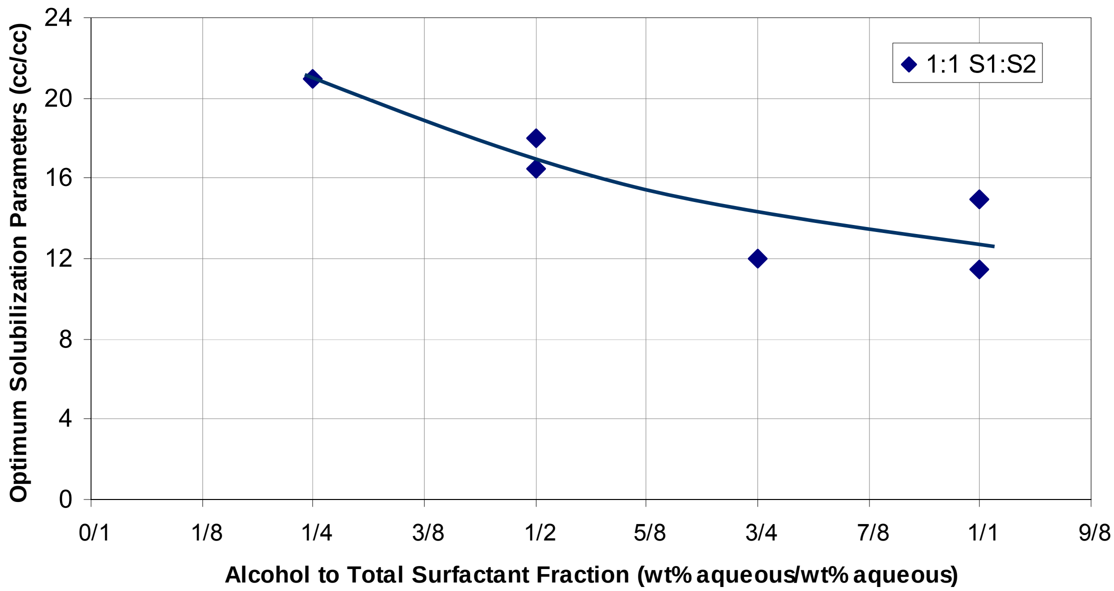

Figure 5. Effect of co-solvent (SBA) concentration on optimum solubilization parameter at 0.5% total surfactant concentration and different alcohol:surfactant ratios.

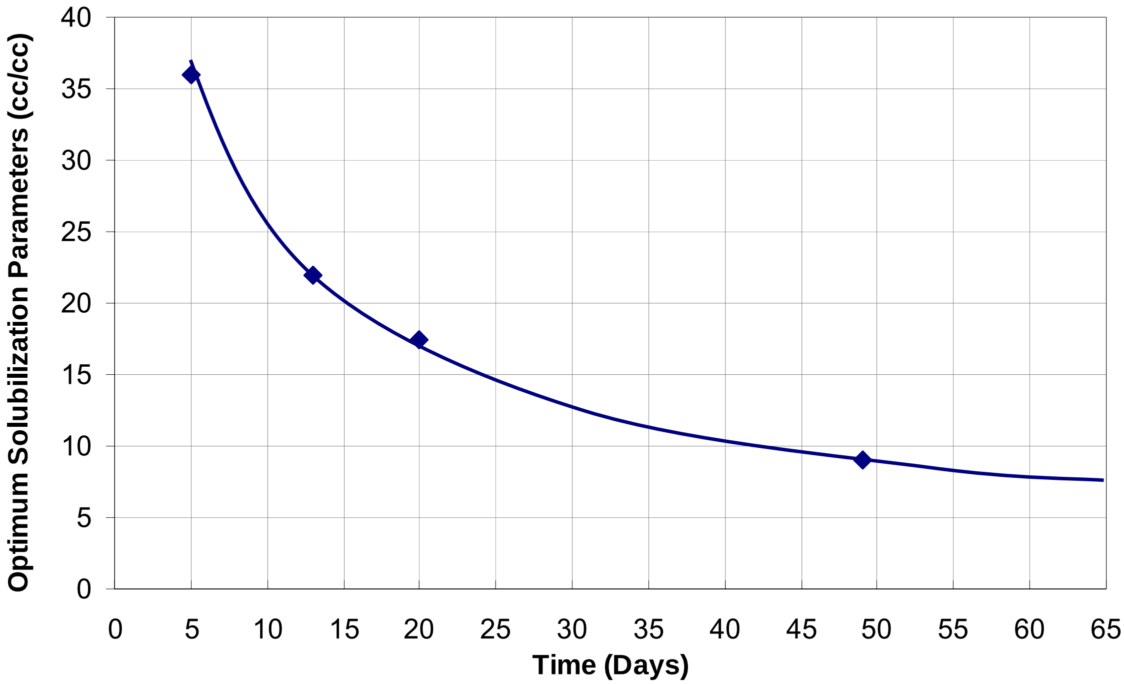

Figure 6. Optimum solubilization parameters plotted against time to estimate equilibration time for salinity scans containing 0.625 wt% Petrostep S1, 0.375 wt% Petrostep S2 and 2.0 wt% SBA at 46.1 Celsius with Trembley crude oil.

Interfacial tension measurement between lower and middle phase of a system containing 0.5 wt% of Petrostep S1, 0.5 wt% of Petrostep S2 and 0.5 wt% of SBA and at a salinity of 6.2 % NaCl were conducted after allowing the sample to equilibrate. This system was very close to optimum salinity. The measured IFT value was 0.002 dynes/cm which is low as expected and indicates a system with high-performance potential.

Interfacial tension can only be measured between the lower and middle phases for crude oil systems. Interfacial tension between the middle and upper phases can not be measure due to the opacity of middle phase in crude oil systems which does not allow the viewing and measurement of the diameter of the upper phase drop in the tensiometer.

Viscosities of Type III/middle phase microemulsions in the range close to the optimum salinity were measured for selected a series. Figures 7 shows the viscosities of four samples which contain a total of 0.5 wt% surfactant in 1:1 ratio of Petrostep S1 and Petrostep S2 and 0.125 wt% SBA. The optimal salinity was about 4.83 % NaCl as shown in Figure 8 where the solubilization parameters for a salinity scan of the same system are shown. Viscosities values of the middle phase microemulsions for this system were approximately twice the value of the crude oil (4.1 cp) at reservoir temperature.

Another series which contained a similar formulation except that SBA was in double concentration. Viscosities from this series are shown in Figure 9. The increased SBA concentration resulted in lower viscosity values.

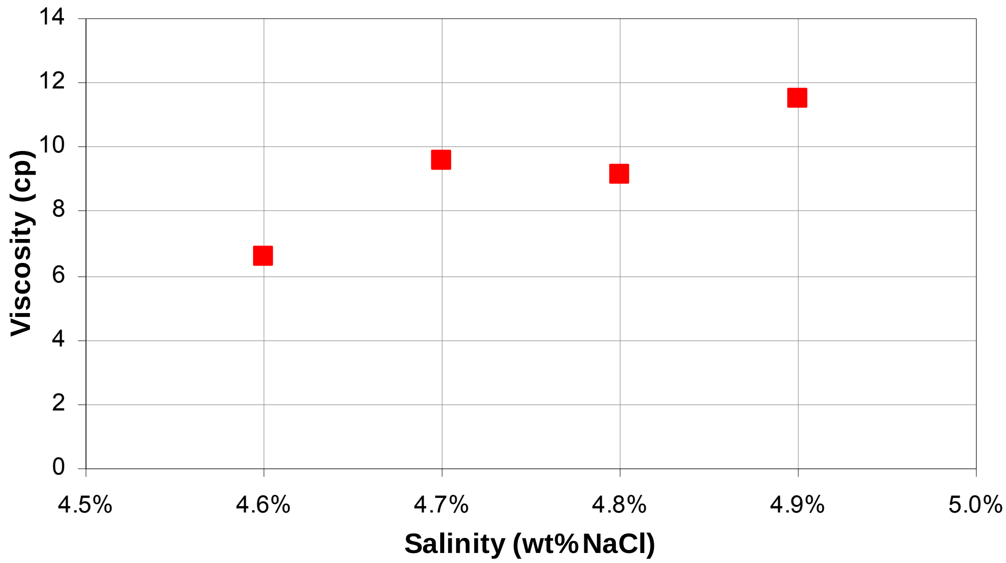

Figure 7. Viscosities of microemulsion phase close to optimum salinity for samples containing 0.25 wt% Petrostep S1, 0.25 wt% Petrostep S2 and 0.125 wt% SBA at 46.1 Celsius- Trembley Oil. Measurements conducted at a shear rate of 75 s^{-1}.

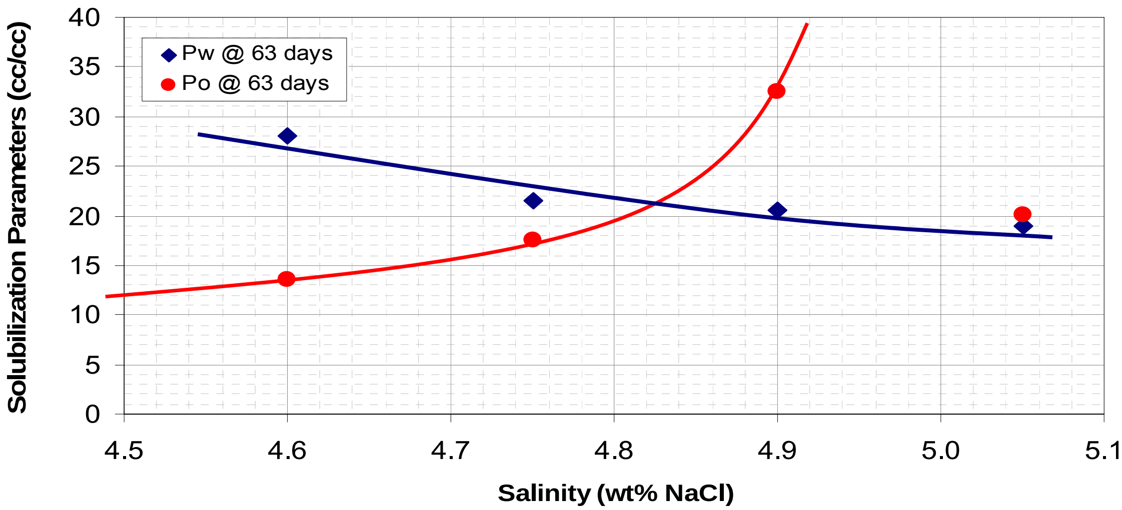

Figure 8. Salinity scan for samples containing 0.25 wt% Petrostep S1, 0.25 wt% Petrostep S2 and 0.125 wt% SBA at 46.1 Celsius - Trembley Oil.

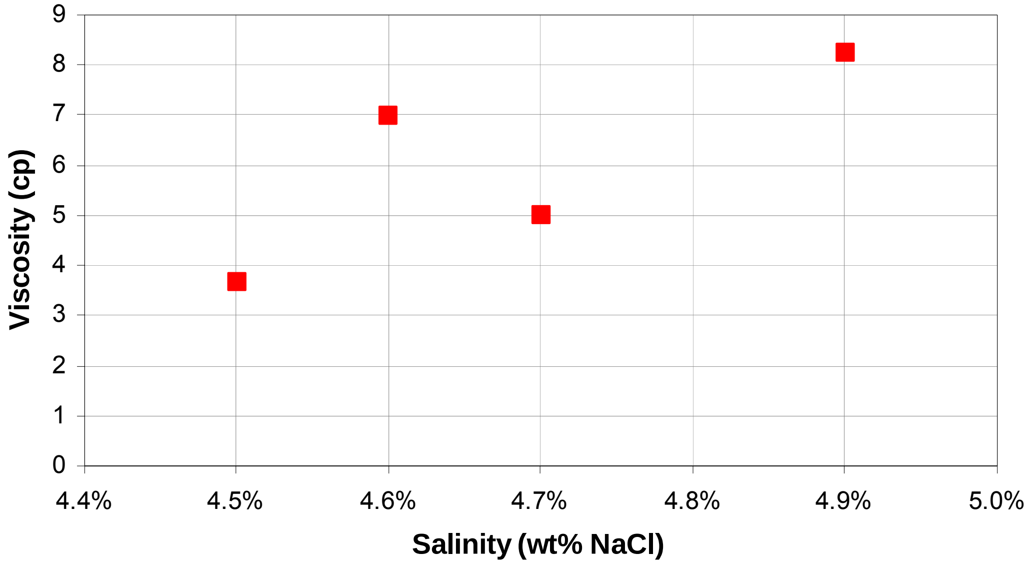

Figure 9. Viscosities of type III microemulsion close to optimum salinity for samples containing 0.25 wt% Petrostep S1, 0.25 wt% Petrostep S2 and 0.25 wt% SBA at 46.1 Celsius with Trembley Oil. Measurements conducted at a shear rate of 75 s^{-1}.

Future work. Two surfactants, Petrostep S1 and Petrostep S2, and one co-solvent SBA have been tested in formulations with Trembley crude oil. Stable microemulsion were achieved which showed good properties except for possibly equilibration/coalescence times that were longer than values suggested in the literature. More surfactants are now available in our inventory and their performance with the Trembley crude and crude oil from the other selected leases will be evaluated.

REFERENCES

Flaaten, Adam K., Quoc P. Nguyen, Gary A. Pope, and Jieyuan Zhang: "A Systematic Approach to Low-Cost, High-Performance Chemical Flooding." SPE/DOE Symposium on Improved Oil Recovery, 20-23 April 2008, Tulsa, Oklahoma, USA.

MILESTONE STATUS

Task	Project milestone Description	Planned		Actual		Comments, explanation of deviations from plan
		Start Date	End date	Start Date	End date	
1	Project Management Plan updated	10/1/08	11/30/08	10/08	12/08	The Project Management Plan was updated and approved.
2	Development of database of KS reservoirs – Critical 1	10/1/08	3/31/09	11/08	3/09	Databases were prepared and are available online. The databases not effective in the process to select leases for Task 3.
2	Reservoirs/leases selected for study – Critical 2	10/1/08	6/30/09	1/09	6/09	Ten leases were selected for study in Task 3.
3.1	Acid numbers of oils determined	3/31/09	9/30/09	5/09		Equipment was secured and procedures were tested on crude oil samples from three of the selected leases.
3.1	Phase behavior studies completed – Critical 3	3/31/09	9/30/10	1/09		Phase behavior studies were initiated for crude oils from three selected leases
3.1	Efficient chemical formulations designed for a minimum of two crude oils based on phase behavior studies.- Critical 4	3/31/09	9/30/10			
3.1	Flow tests completed in lab rocks	6/30/09	9/30/10			
3.2	Flow tests completed in reservoir rocks	6/30/10	3/31/11			
3.2	Efficient chemical formulations designed for a minimum of two applications based on flow experiments.- Critical 5	6/30/10	3/31/11			
4	Simulations completed – Critical 6	12/31/10 3/	6/30/11			
4	Economics completed	3/31/11	9/30/11			

SCHEDULING AND WORKLOAD ISSUES

The level of effort to contact and interview personnel from interested oil companies was underestimated. However, this process was concluded on time.

Laboratory studies were started earlier than scheduled by three graduate students due to a timing issue between the start date of the project and the availability of graduate students at the start of the school year(August 18). One of the graduate students left school to take care of his parents due to the death of his brother. We do not expect the student will return to school and continue his research project. His work will be continued by other personnel.

National Energy Technology Laboratory

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880

One West Third Street, Suite 1400
Tulsa, OK 74103-3519

1450 Queen Avenue SW
Albany, OR 97321-2198

2175 University Ave. South
Suite 201
Fairbanks, AK 99709

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