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Bridging the Gap between Chemical Flooding and Independent Oil Producers

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Abstract

Ten Kansas oil leases were selected for the study of the application of chemical flooding. The ten leases represent both sandstones and carbonate reservoirs and are distributed across the state. Interviews with technical employees of 47 independent oil production companies which represent 45% of the 2008 Kansas oil production, were the key component of the selection process. A successful waterflood was the best general indicator of favorable characteristics of a reservoir/lease for application of chemical flooding. Rationale for focusing on waterfloods and additional criteria for selection of leases are presented. Efforts are ongoing to identify and collect geological and engineering data for each lease so that it can be utilized during the design process. Laboratory tests to formulate efficient chemical systems were conducted. Acid numbers were measured for the crude oils and phase behavior studies were conducted with thirteen surfactants and two crude oils. Values of the total acid numbers for nine of the crude oils are low and indicate the use of alkali in the chemical formulations for the purpose of producing soap is not warranted. Phase behavior studies were conducted to identify surfactants that show high performance with crude oils from the Trembley and Wahrman leases. The influence of several parameters for formulating a chemical system was established. Measurements of viscosity and interfacial tension verified visual observations and evaluations that are made during phase behavior studies. Several chemical systems were identified for the Trembley crude oil that met the primary criteria of an efficient system for residual oil recovery. Less satisfactory results were obtained with the Wahrman crude oil where the phase-behavior criteria were met except for the chemical system at optimal salinity was not a one-phase solution before mixing with the crude oil.

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Executive Summary

The principle objective of Task 2 was the selection of ten oil leases in Kansas that are considered to be good candidates for application of chemical flooding. Formulation of efficient chemical systems and designs for field applications will be conducted for a few of these leases. Two approaches were used to identify and evaluate potential leases/reservoirs. The first was a broad approach where a database of pertinent information on Kansas oilfields was assembled from available public information. Geological and engineering analysis of the database would then provide a resource base for chemical flooding and target specific reservoirs for study. Sufficient information was lacking in public data for this analysis. The second approach was to consult with technical employees of companies producing the largest amounts of oil in Kansas to determine specific leases that would be candidates for chemical flooding. This approach was completed by contacting and interviewing personnel from 47 independent oil production companies that produced more than 45 % of the oil in Kansas in 2008.

It became evident that successful waterfloods are the best indicator of favorable characteristics of a reservoir/lease for application of chemical flooding, both as a general criterion for specific rock formations and for specific leases. Rationale for focusing on waterfloods and additional criteria for selection of leases are presented.

Ten oil leases were selected for study which represent both sandstones and carbonate reservoirs. Three different sandstone beds and four different carbonate units are represented in central and western Kansas. Two reservoirs in eastern Kansas are in two different sandstone layers in the Cherokee Group.

General procedures were developed and specific arrangements were made with personnel of the production companies to collect oil samples that contained no or the minimal amounts of treatment chemicals in order to reduce or eliminate effects the treatment chemicals might have on the laboratory testing. Crude oil samples were collected from 9 of the leases. Efforts are ongoing to identify and collect technical data for each lease so that it can be utilized for the development of reservoir models and simulation studies scheduled in Task 4. Reservoir data are being collected from the operators and from public sources by our geologists. A series of spreadsheets summarizing available geologic and engineering have been developed.

Laboratory tests to formulate efficient chemical systems were conducted as part of Task 3. Acid numbers were measure for the crude oils and phase behavior studies were conducted with thirteen surfactants and two crude oils. Values of the total acid numbers for nine of the crude oils are low and indicate the use of alkali in the chemical formulations for the purpose of producing soap is not warranted.

Phase behavior studies were conducted to identify surfactants that show high performance with crude oils from the Trembley and Wahrman leases. The influence of parameters in a chemical system such as component concentrations and molecular structure on optimal salinity, solubilization parameters and equilibrium times was established. These trends will be used to expedite future phase behavior studies. Measurements of viscosity and interfacial tension verified visual observations and evaluations that are made during phase behavior studies. The use of alkali in the formulations improved the phase behavior results. Alkali shortened equilibration

times, increased solubilization ratios and enhanced fluidity of the microemulsion phases. Several chemical systems were identified for the Trembley crude oil that met the primary criteria of an efficient system for residual oil recovery. These formulations will be tested for compatibility with polymer and then tested for residual oil recovery in flow experiments. Less satisfactory results were obtained with the Wahrman crude oil where the phase-behavior criteria were met except for the chemical system at optimal salinity was not a one-phase solution before mixing with the crude oil.

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. Ten Kansas oil leases were selected for the study of the application of chemical flooding. The selection process was the focus of Task 2. Laboratory tests to formulate efficient chemical systems were conducted as part of Task 3.

Progress, Results and Discussion

Task 2. Identify and Select Candidate Reservoirs

The principle objective of Task 2 was the selection of approximately ten oil leases in Kansas for which laboratory studies will be conducted on the crude oils from those leases in the effort to design efficient chemical formulations for flooding applications. Two approaches were used to identify and evaluate potential leases/reservoirs. The first was a broad approach where a database of pertinent information on Kansas oilfields was assembled from available public information. Geological and engineering analysis of the database would then provide a resource base for chemical flooding and target specific reservoirs for study. The second approach was to consult with technical employees of companies producing the largest amounts of oil in Kansas to determine specific leases that would be candidates for chemical flooding. Personal contacts with personnel from the oil producers proved the best approach. Sufficient information was lacking in public data for analysis. The selection processes are described.

It became evident through our work that successful waterfloods are the best indicator of favorable characteristics of a reservoir/lease for application of chemical flooding, both as a general criterion for specific rock formations and for specific leases. Rationale for focusing on waterfloods and additional criteria for selection of leases are presented.

A. Geological Prospects for Chemical Flooding in Kansas

Geological characteristics and oil production mechanisms were used to classify and select producing horizons that are favorable to chemical flooding. Engineers and geologists from several of the largest independent oil producers confirmed the production mechanisms and classifications.

Oil is produced in Kansas from rocks ranging from Proterozoic to Permian in age (Figure 1). The stratigraphic intervals shown in Figure 1 may include many different units, some of which

are fundamentally different reservoir types. Table 1 indicates many subdivisions of the stratigraphic systems, stages, and groups that are productive and highlights the intervals that are known to waterflood well.

Each productive horizon has one or more characteristic types of traps and drive mechanisms. For example, both limestone and dolomite of the Arbuckle Group, the most prolific unit, and chert or chert breccia of the Mississippian Osagean Stage, produce from high points on an overlying unconformity surface. Some such high points are faulted blocks, while others are residual highs on karsted unconformity surfaces. Strong water drive provides energy for production in most Arbuckle Group fields, whereas Mississippian reservoirs have weaker water drives. Both the Arbuckle and Osagean are generally not good candidates for flooding processes.

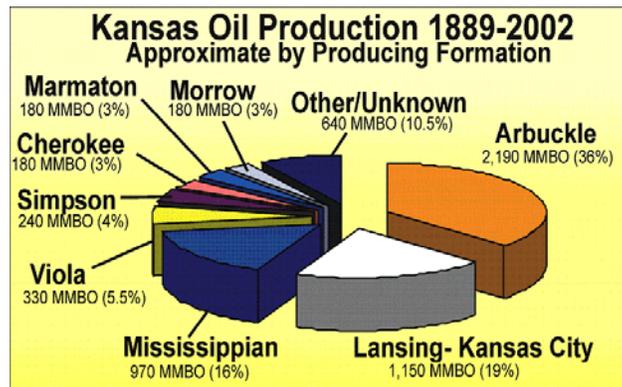


Figure 1 - Oil production in Kansas by stratigraphic unit. (Kansas Geological Survey).

To the extent that the most likely targets for successful chemical floods are oilfields that waterflood well, a few characteristic combinations of lithology, trap and drive are most promising among those in Kansas. Among the sandstone producing units in Kansas, good waterfloods are common in Chesteran (Mississippian) and in Morrowan and Cherokee and other Pennsylvanian sandstones. However, productive Permian sandstone may also be a candidate; the 650 ft. sandstone in the El Dorado Field has been flooded (Van Horn, 1983). Cherokee reservoirs are concentrated in southeastern Kansas, east of the Nemaha uplift. Most of the oil production comes from elongate sandstone bodies that probably fill valleys. Other pre-Marmaton, post-Atokan Pennsylvanian reservoirs on the margins of the Central Kansas Uplift are either assigned to the Cherokee Group or the informal Pennsylvanian basal conglomerate. Recently, development has occurred in channel-like sandstones of Cherokee age rocks in Ness County, first pointed out by Walters et al. (1979). The Pennsylvanian basal conglomerate is a discontinuous sheet of residual breccia, sandstone, and clay that thickens and thins over underlying irregularities in karsted Mississippian rocks. Beach and shallow marine sandstones of the Simpson Group (Ordovician) waterflood well, at least in the Tobias Field, but other lower Paleozoic units, limestone or dolomite for the most part (Viola, Hunton) do not.

Many grainstone reservoirs in the Lansing and Kansas City groups (Missourian, referred to as LKC), the Fort Scott Limestone and other Marmaton Group reservoirs (Desmoinesian), and the Topeka Limestone (Virgilian) have also waterflooded well. Oolitic grainstone is a common reservoir type in Lansing and Kansas City group reservoirs. Some such reservoirs are bending-

fold anticlinal traps over faulted basement highs, perhaps with preferential development of oolites on the highs. Others are isolated oolite or other grainstone bodies.

Table 1 - Stratigraphic chart of oil producing formations in Kansas. Commonly waterflooded formations in central and western Kansas are highlighted.

Era	System	Stage	Group	Producing Rock Units
Mesozic	Cretaceous		Colorado	Niabrara
Paleozoic	Permian	Guadalupian		
		Leonardian	Nippewalla	
			Sumner	Red Cave
		Wolfcampian	Chase	Herington, Krider, Winfield, Towanda, Fort Riley
			Council Grove	Neva, Cottonwood
		Virgilian	Admire	Indian Cave
			Wabaunsee	Langdon, Tarkio, Willard, White Cloud, Howard, Severy
			Shawnee	Topeka, Elgin, Hoover, Toronto
			Douglas	Ireland, Stalnaker
		Missourian	<i>Lansing</i>	
	<i>Kansas City</i>		Layton, Perry Gas	
	Pleasanton		Cleveland, Knobtown, Hepler	
	<i>Marmaton</i>		New Albany, Wayside, Bandera, Weiser, Pawnee, Peru, Fort Scott, Oswego	
	<i>Cherokee</i>		Mulky Coal, <i>Prue</i> , Bevier Coal, <i>Squirrel</i> , <i>Cattleman</i> , <i>Bartlesville</i> , Weir-Pittsburg, <i>McLouth</i> , Riverton Coal, <i>Burgess</i>	
	Atokan			
	Morrowan	<i>Morrow</i>		
				<i>Basal Pennsylvanian Conglomerate</i> , Gorham
	Mississippian	Chesteran	<i>Chester</i>	
		Meramecian		Saint Genevieve, Saint Louis, Spergen, Warsaw
		Osagian		
		Kinderhookian		
Devonian			Misener	
Silurian		Hunton		
Ordovician			Maquoketa	
			Viola	
		<i>Simpson</i>		
Cambrian		Arbuckle		
			Reagan	
			Granite Wash	

B. Databases of Kansas Oilfields and Reservoirs

Databases of Kansas oil fields and oil reservoirs were assembled with the purpose to select reservoirs and individual oil leases using the producing horizons that were identified above to be favorable for chemical flooding. Databases were assembled in Excel spreadsheets from a database derived from public data and maintained by the Kansas Geological Survey (KGS). KGS's database can be queried by the public at <http://www.kgs.ku.edu>. KGS obtains field names, counties in which the field is located and producing zones from public records that the Kansas Corporation Commission requires when wells are initially drilled. Production data are obtained from public records from the Kansas Department of Revenue where production is given by lease. The information is cross referenced by location and is accessible online in an Excel spreadsheet named *Kansas Oilfields.xls* at <http://www.torp.ku.edu>. There are 6,536 oilfields listed, one per row. Production data and producing zones (reservoirs) are listed for each field along with additional information listed in Table 2. A second spreadsheet named *Kansas Reservoir.xls* is also available that lists 9,765 producing zones (or reservoirs). Production figures in this database are for all the reservoirs in the field and are listed only once in one of the producing zones (reservoirs) for that field.

Several issues made the development of a representative database of Kansas oil reservoirs from public data impractical for our purpose. The number of producing zones (reservoirs) for each oilfield ranged from one to ten. Producing zones were identified when the well was initially completed and subsequent completions in other zones are not usually known. Oilfields with the largest oil production commonly had many oil producing zones (reservoirs). Oil production from an oilfield could not be reliably allocated to individual reservoirs with the public data. This was the primary issue that prevented the establishment of a resource base for chemical flooding. It was concluded that types of information derived from the public records was not sufficient to identify reservoirs and leases for chemical flooding applications.

Table 2 – Information listed in the database of Kansas oilfields.

Field name
Producing zones (up to 9 zones)
Discovery date
Total cumulative oil production (bbls)
Total cumulative gas production (mcf)
Area (acres)
Total number of wells
2008 oil production (bbls)
Number of oil wells in 2008
2008 gas production (mcf)
Number of gas wells in 2008
Location by county (up to 19)

C. Identification of Chemical Flooding Prospect through Interviews with Oil Producers

The Top 30 oil producers in Kansas were contacted to discuss chemical flooding applications for their leases. The Top 30 producers were determined using 2008 data obtained from the Kansas Geological Survey. Only one company of the Top 30 did not respond to our repeated attempts to

contact. Production by the Top 30 was generally in central and western Kansas and production in eastern Kansas was not represented. Eastern Kansas oil production is characterized by shallow depths and oils with lower API gravities than in central and western Kansas which brings different opportunities for chemical flooding applications. We identified the Top 10 oil producers in eastern Kansas and contacted them as well as other producers that responded to our calls for participation. A listing of the oil companies that were contacted is given in Table 3. The 47 companies that were contacted represented more than 45 % of the oil produced in Kansas. It is noted that more than 5,500 companies produced oil in Kansas in 2008.

Initial contacts were conducted by telephone followed by email to (1) describe and explain the chemical flooding process, (2) determine and confirm general chemical flooding prospects in Kansas from the company's waterflooding applications (3) inform company personnel about possible positive benefits from participating in this design project, and (4) identify their best performing waterfloods as prospects for our design work. Follow up meetings with many of the companies, both in-person and by phone, were conducted to assess their data on their prospective leases as well as determine their interest and their ability to support a chemical flood application. Criteria for the selection of leases are given in the following section.

Cooperation and support of independent oil producers is a key component of this project. The process to contact and interview oil producers was time intensive but worth the effort in terms of identifying prospects for chemical flooding as well as educating independent oil producers and generating interest in this project and chemical flooding applications. The personnel contacted represent a significant portion of the oil produced in Kansas.

D. Criteria for Selection of Leases

The performance of a chemical flood is a function of the microscopic efficiency of the chemical system to mobilize and displace contacted oil and the macroscopic efficiency of the chemical slug to contact the reservoir volume. Formulation of the chemical system for microscopic efficiency is addressed in Task 3 of this program. Mobility control for better sweep of the reservoir by including polymer during the formulation of the chemical system is also addressed in Task 3. Assuming that efficient chemical systems can be formulated, reservoirs with efficient sweep are the best candidates for chemical flooding so that the integrity of the chemical slug as it flows through the reservoir can be maintained.

It became evident during our initial interviews with oil producers that a successful waterflooding application was the best indicator of favorable characteristics for chemical flooding, both as a general criterion for specific rock formations and for a particular lease. Waterfloods were targeted because an oil operator has previously made the assessment that the reservoir would respond favorably to a flooding process and reservoir information is more common in waterflooded leases/units. A well-performing waterflood that has good sweep efficiency implies favorable fluid flow characteristics that are required for high performance of the slug-type process of chemical flooding.

Technical personnel from the oil companies were asked to survey their company's waterflooded properties and present what they determined were their best-performing leases/units. In these interviews, which were typically in person, we assessed the performance of the waterfloods and

Table 3 –Oil Producers contacted/interviewed for discussions of chemical flooding opportunities.

Kansas Rank	Name	2008 KS oil production (bbls)	City	State	% of KS production
1	Murfin Drilling Company	1,067,615	Wichita	KS	3.62
2	Vess Oil Corporation	1,020,954	Wichita	KS	3.47
3	Berexco	1,002,979	Wichita	KS	3.41
4	EOG Resources	814,645	Oklahoma City	OK	2.77
5	American Warrior	702,850	Garden City	KS	2.39
6	Anadarko Petroleum Corporation	586,161	Houston	TX	1.99
7	OXY USA	580,231	Houston	TX	1.97
8	Hartman Oil Company	383,870	Garden City	KS	1.30
9	McCoy Petroleum Corporation	378,387	Wichita	KS	1.28
10	Ritchie Exploration	373,282	Wichita	KS	1.27
11	John O. Farmer	362,605	Russell	KS	1.23
12	Mull Drilling Company	334,238	Wichita	KS	1.13
13	Lario Oil & Gas Company	323,614	Wichita	KS	1.10
14	Merit Energy Company	318,999	Dallas	TX	1.08
15	Woolsey Operating Company	317,614	Wichita	KS	1.08
16	Presco Western	301,961	Boulder	CO	1.03
17	T-N-T Engineering	298,368	Wichita Falls	TX	1.01
18	Mai Oil Operations	294,190	Dallas	TX	1.00
19	Herman L. Loeb	286,317	Lawrenceville	IL	0.97
20	Cimarex Energy Company	261,136	Tulsa	OK	0.89
21	Carmen Schmitt	257,725	Great Bend	KS	0.88
22	Abercrombie Energy	252,239	Wichita	KS	0.86
23	Elysium Energy	251,869	Denver	CO	0.86
24	PetroSantander (USA)	239,486	Houston	TX	0.81
25	Falcon Exploration	237,963	Wichita	KS	0.81
26	L.D. Drilling	227,863	Great Bend	KS	0.77
27	Palomino Petroleum	222,512	Newton	KS	0.76
28	Larson Operating Company	214,895	Olmitz	KS	0.73
29	Oil Producers Inc. of Kansas	211,341	Wichita	KS	0.72
30	Pintail Petroleum, Ltd.	204,604	Wichita	KS	0.69
31	Trans Pacific Oil Corporation	199,759	Wichita	KS	0.68

**Continued on next page.

Table 3 –Oil Producers contacted/interviewed for discussions of chemical flooding opportunities. (continued).

Kansas Rank	Eastern Kansas Rank	Name	2008 KS oil production (bbls)	City	State	% of KS production
66	1	Haas Petroleum	100,107	Kansas City	MO	0.34
70	2	Laymon Oil II	93,284	Neosho Falls	KS	0.32
75	3	D. E. Exploration	81,956	Wellsville	KS	0.28
89	4	Colt Energy	68,389	Fairway	KS	0.23
48	5	Stelbar Oil Corporation	147,584	Wichita	KS	0.50
165	6	Trimble & Maclaskey Oil	31,801	Gridley	KS	0.11
108	7	M.A.E. Resources	49,848	Parker	KS	0.17
110	8	Viva International	49,084	Lenexa	KS	0.17
135	9	Enerjex Kansas	39,205	Overland Park	KS	0.13
101	10	Piqua Petro	55,328	Piqua	KS	0.19
142	11	R J Enterprises	37,236	Garnett	KS	0.13
172	12	Town Oil Company	30,306	Paola	KS	0.10
183	13	Thomas Well Service	28,385	Mclouth	KS	0.10
193	14	KLM Exploration Co.	25,631	Mclouth	KS	0.09
204	15	Ensminger Oil	24,421	Moran	KS	0.08
208	16	Verde Oil Company	23,638	Savonburg	KS	0.08
Total % KS oil production represented						45.55

the state of the wells and surface equipment and determined the types of data they had available. In addition, we judged their interest and the capability of the oil company to engage in a relatively expensive chemical flooding project. This process allowed for the survey of a significant number of leases/units in Kansas and to narrow the selection to leases/units that have favorable characteristics for chemical flooding.

All of the selected leases/units met the following criteria:

- The waterflood showed a substantial, sustained oil recovery response.
- The condition of the wells and surface equipment were satisfactory. There were no or limited number of plugged wells.
- The timing for a chemical flood in the year 2012 or so was appropriate.
- The oil company expressed considerable interest and was judged capable of participating in a chemical flooding application.

An objective of this project is to provide public information about the design of chemical floods to independent oil operators and this influenced the lease selections. A range of reservoir types with both sandstones and carbonate rocks was preferred. Three different sandstone beds and four different carbonate units are represented in central and western Kansas. The reservoirs in eastern Kansas are two different sandstone layers in the Cherokee Group.

Assessment of a demonstration project for chemical flood is improved if the flood is contained within the specified pattern area. An effective way to satisfy this criterion is to use leases where containment is identified. Several small reservoirs were identified where the fluid containment was strongly indicated. These reservoirs appear to be representative of the larger resource of the same producing formation and are prime candidates for a demonstration project. Leases in larger reservoirs were also selected if there was reservoir information, usually based on injection and production data, that a chemical flood could be contained in the lease.

Two additional sandstone reservoirs were selected in eastern Kansas. Many of the reservoirs in eastern Kansas were heavily fractured at discovery to accelerate primary production rates. Also, many of the reservoirs are waterflooded but the waterflood performance is often poor in part due to the fracturing practices at discovery. The eastern Kansas leases were selected for economic considerations due to the shallow depths and much lower development and operating costs as compared to the rest of the state.

E. Leases Selected for Laboratory Studies

Ten leases were selected for investigating the application of chemical flooding in Kansas. General information about the ten leases and the oil company operating the lease are given in Table 4. Locations of the oilfields containing the leases are shown in Figure 2. The leases are presently under waterflood and represent most of the oil-producing horizons in Kansas that we have identified as targets for chemical flooding applications (see Table 1).

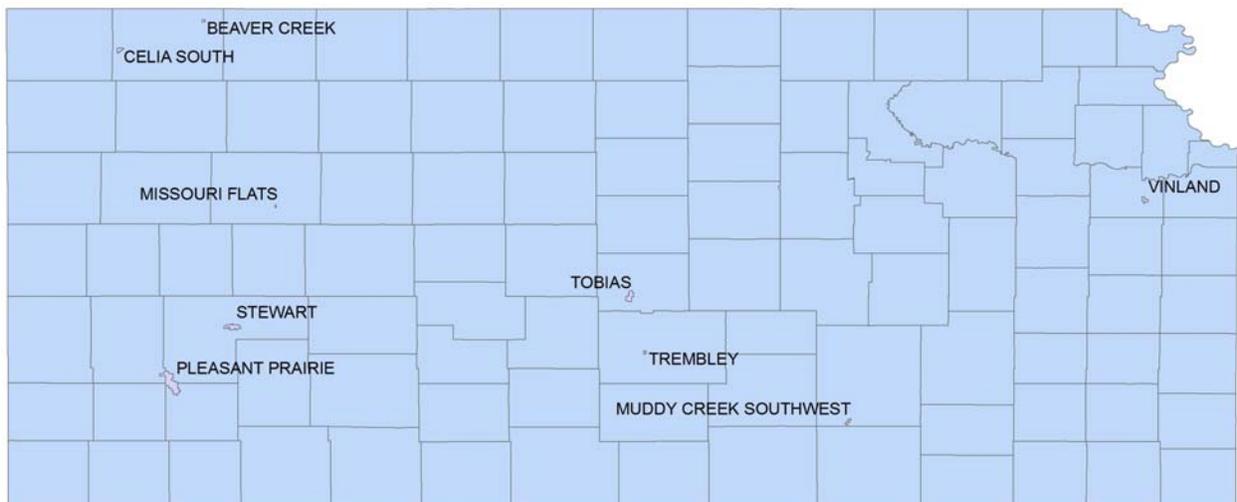


Figure 2 - Location of oilfields containing the selected leases.

Table 4 - Leases selected for laboratory studies.

Lease/Unit	Trembley	Wahrman	Missouri Flats	Tobias	Celia South	Chester Waterflood	Pleasant Prairie – Chester Unit	Stewart	Woodhead	Muddy Creek SW
Operator	Berexco	Vess	Merit	Berexco	Murfin	Cimerex	Oxy	PetroSantander	Colt	Stelbar
County	Reno	Rawlins	Gove	Rice	Rawlins	Haskell	Haskell	Finney	Douglas	Butler
Field name	Trembley	Beaver Creek	Missouri Flats	Tobias	Celia South	Pleasant Prairie	Pleasant Prairie	Stewart	Vinland	Muddy Creek SW
Res. temp (°F)	110 - 115	110 - 118	118	105	138		120	108 - 120		105
Oil gravity (API)	37.3 - 35.8	33	38	35	27.5		35.7	27	27.9	38
Producing wells	4	2	7	5	19		6		14	5
Injection wells	3	1	4	5	8		4		8	2
TA wells	0	0	1	2	4		0		18 + 23	0
Net area (acre)		30	1260		1440			1550	160	160
Avg thickness (ft)	5		47	12	5		29.3	18.5	5	20
Zone	LKC “J” - Hertha	LKC “J”	Lansing & Marmaton	Simpson Sand	Cherokee Lime	Chester Sand	Chester Sand	Morrow	Cherokee Squirrel	Cherokee Bartlesville
Rock type	Limestone	Limestone	Limestone	Sandstone	Limestone	Sandstone	Sandstone	Sandstone	Sandstone	Sandstone
Comments	6' to 10' local porous zone in Hertha (LKC “J”) Limestone.	Thin (4') porous zone at top of LKC “J” zone or Hertha Limestone. Geologist's log implies grainstone or packstone.	Few logs have been scanned. Available materials suggest production from several different LKC layers.	Multiple producing horizons. Only interested in Simpson waterflood. No new wells since 1985.	Thin zone: few feet. Cherokee limestone wells IP at 100 bopd. Also produces from LKC B zone. No new wells since 1983.	Long, narrow field, apparently a fluvial sandstone filling an incised valley. 70' thick, but only partially saturated. Cimerex Chester waterflood is continuous with Oxy’s Pleasant Prairie Chester Unit.		The reservoir fills a valley eroded into underlying limestones. Rock appears to have fluvial characteristics. May actually be Atokan rather than Morrowan.	Shallow field, 600 to 700'. Logs are mostly gamma-unscaled neutron; few quantitative logs. Very dense well spacing.	Bartlesville sandstone is at about 2850', consists of a number of stringers, generally fining upward. May be incised-valley fill sandstone like other Bartlesville reservoirs.

F. Sample and Data Collection

Oil samples were collected from 9 of the leases. One sample remains to be collected. Laboratory studies to formulate efficient chemical systems for the oils are underway in Task 3.1.

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 specific arrangements were made with office and field personnel of the production companies to collect crude oil samples that contained no or the 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.

Oil collection procedures varied according to each situation. Generally, the oil collection procedures were to suspend chemical treatment of the well for one or two applications and then collect the sample at the wellhead just before the subsequent treatment. Water was separated from the oil using barrel-testing equipment at the wellhead if equipped or using 5-gallon buckets and siphoning the oil into collection jugs.

Efforts are underway to identify and collect technical data for each lease so that it can be utilized during the design process. The laboratory study to formulate chemical systems requires several critical data for each lease, which include the reservoir temperature, salinity and hardness of the injected water and mineralogy of the reservoir rock. These data are usually not readily known by the operators and efforts by the operators and our staff are ongoing to determine these data both timely and accurately by reviewing reports and obtaining analyses of injected brines.

Reservoir data are required for the future development of reservoir models for simulation studies scheduled in Task 4. Reservoir data are being collected from public sources by our geologist and from the operators. Communications with the operators are ongoing to determine of the types of data that are available and to collect these data. Petra® analysis and display software for oilfields is being employed by our staff to match the operators' software of five of the leases.

G. Geological Investigations of Reservoirs

The objectives of the geological study are 1) to identify specific producing horizons, their continuity and their suitability for chemical flood, 2) to use studies of cores to improve the understanding of the particular reservoirs, and 3) to gather the petrophysical data necessary for future modeling studies. Basic geological mapping of reservoirs, using log information in Petra¹, a subsurface geological information system, will provide information on continuity. Sedimentological studies of cores will provide information on vertical continuity of reservoirs, depositional environments, and obvious diagenetic features that may be relevant. Core permeability-core porosity relationships will form the basis for log porosity-permeability estimators, which will allow mapping of porosity and permeability, to accompany log-based petrophysical studies of initial fluid saturation in the reservoirs. Mineralogical studies of cores will also help predict interaction with any injected chemicals. Where cores are unavailable for

¹ Petra is a commercial software package sold by IHS. Mention or use of this product should not be construed as an endorsement by The University of Kansas.

the particular reservoir in question, cores from nearby fields that produce from the same reservoirs may be helpful.

We are querying the database of the Kansas Geological Survey (KGS) to gather all publicly available data on the chosen leases. We are emphasizing scanned well logs and cores. If paper copies of logs are available, but not yet scanned, we are attempting to get scanned copies of them from operators or arranging to have them scanned at the KGS. Few digital logs are available for the leases in question, because of their age and because of standard oil-field practice in Kansas. Scanned logs can be digitized in Petra for use in petrophysical calculations. We are also collecting any results or indications of drill-stem tests, pressure measurements, and re-completions of wells in different zones. Some discrepancies exist between operator and KGS records of the number and locations of wells in the leases, particularly in eastern Kansas. We are attempting to identify those discrepancies and then can pursue them with the operators. Cores are either in the custody of the operators or are part of the collection of the KGS here in Lawrence. If core petrophysical data are not available from the KGS, they may be available from the operators, themselves. The Walters Digital Library of the Kansas Geological Society in Wichita has data that are not in public records. We have not yet examined Walters Library records, but they generally provide access to those data at a reduced rate, compared to the normal rate for non-members, for research and educational purposes.

Geologic studies began in earnest in August, 2009, although some work had begun in June, 2009. To date, we have developed a series of spreadsheets summarizing available geologic data for the project. We have also created Petra projects for the various reservoirs that are under study, and have begun to load logs and make maps and cross-sections with the available information.

Task 3: Design Efficient Chemical Formulations for selected Oil/Brine/Reservoir.

Task 3.1: Conduct laboratory tests using crude oils and field brines.

Laboratory tests to formulate efficient chemical systems through phase behavior studies using crude oils from the selected leases are the main focus of this task. Acid numbers were measured for the crude oils and phase behavior studies were conducted with crude oils from the Trembley and Wahrman leases.

A. Acid Numbers of the Crude Oils

Alkali is a potential component of chemical formulations depending on conditions. Alkali can reduce surfactant retention in carbonate-containing rocks and can react with acidic crude oils to produce surface-active soaps which can reduce surfactant loading of the system.

The acid number of a crude oil can be used to assess the responsiveness of the oil to soap production. A non-aqueous phase titration method [Fan and Buckley] is used to determine the total acid number of a crude oil and an aqueous phase titration [Liu et al.] is used to determine the effective acid number. The effective acid number measures the amount of soap extracted into an aqueous phase after the oil is reacted with strong base and the value is less than the total acid number.

Total acid numbers were measured for the nine crude oils that have been collected and the results are given in Table 5. Values of the acid numbers are low and indicate the use of alkali in the chemical formulations for the purpose of producing soap is not warranted. Effective acid numbers were not measured since the total acid numbers were so low.

Table 5 – Acid numbers of crude oils of the leases.

Lease/Unit name	Acid number (mg KOH/g of oil)
Trembley	0.08
Wahrman	0.11
Missouri Flats	0.09
Tobias	0.07
Celia South	0.07
Chester Waterflood	0.03
Pleasant Prairie Chester Unit	0.03
Stewart	0.21
Muddy Creek SW	0.02
Woodhead	not measured yet

B. Formulation of Chemical Systems for Crude Oils

Surfactants evaluated. Surfactant samples for this study were obtained from Stepan Company and Sasol North America. The surfactants were anionic and have been shown to have beneficial attributes for high oil recoveries in core floods in a variety of rock type with very little surfactant loss due to adsorption.(Hirasaki, Pope et al. 2006; Levitt, Jackson et al. 2006; Flaaten, Nguyen et al. 2008). A list of the surfactants selected for screening is provided in Table 6. The first column

lists the trade name of the surfactants and the alcohol hydrophobe used to prepare them, the second column lists their common chemical name, and the third column lists an abbreviated chemical representation of the molecule. The subscript on C gives the range of the number of carbons in hydrophobe. Some of the surfactants contained various degrees of propoxylation of the hydrophobe. Propoxylation is employed to decrease the hydrophilic nature of the molecule. The number of moles of propoxylene oxide (PO) added to hydrophobe are included in the chemical representation as (PO)_n, where *n* is the number of moles. All the anionic surfactants contained either sulfate or sulfonate hydrophilic groups. More information about molecular formula and structure of some of the surfactants can be found in study by Levitt (Levitt et al., 2006).

Table 6 - List of surfactants that were evaluated in the laboratory screening experiments with Trembley and Wahrman crude oils.

Trade Name (Supplier), Alcohol hydrophobe	Common Chemical Name	Abbreviated* Chemical Representation
Alfoterra® 123-8S (Sasol), Isalchem 123™	Alcohol Propoxy Sulfate	C ₁₂₋₁₃ -(PO) ₈ -SO ₄ ⁻
Alfoterra® 145-4S (Sasol), Isalchem 145™	Alcohol Propoxy Sulfate	C ₁₄₋₁₅ -(PO) ₄ -SO ₄ ⁻
Alfoterra® 145-8S (Sasol), Isalchem 145™	Alcohol Propoxy Sulfate	C ₁₄₋₁₅ -(PO) ₈ -SO ₄ ⁻
Alfoterra® 167-4S (Sasol), Isalchem 167™	Alcohol Propoxy Sulfate	C ₁₆₋₁₇ -(PO) ₄ -SO ₄ ⁻
Alfoterra® 167-7S (Sasol), Isalchem 167™	Alcohol Propoxy Sulfate	C ₁₆₋₁₇ -(PO) ₇ -SO ₄ ⁻
Petrostep S-1 (Stepan)	Alcohol Propoxy Sulfate	
Petrostep S-3 (Stepan)	Internal Olefin Sulfonate	
Petrostep S-2 (Stepan)	Internal Olefin Sulfonate	
Petrostep C-1 (Stepan)	Alpha Olefin Sulfonate	
Petrostep C-5 (Stepan)	Alpha Olefin Sulfonate	
Petrostep S-8B (Stepan)	Alcohol Propoxy Sulfate	
Petrostep S-8C (Stepan)	Alcohol Propoxy Sulfate	
Petrostep S-13C (Stepan)	Alcohol Propoxy Sulfate	

* see text for abbreviations.

Criteria for phase behavior studies. 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 a field application. High solubilization or uptake of a phase in a middle-phase microemulsion indicates a low interfacial tension between the microemulsion and the respective phase (Healy, Reed et al. 1976). Therefore, high solubilizations of both phases must be exhibited in lab screening by the surfactant formulation. The microemulsion phase that is so essential for effective mobilization and displacement of residual oil must form readily and coalesce quickly in lab screening and must also exhibit fluidity and homogeneity i.e. absence of viscous phases, gels and macroemulsions.

Laboratory screening entails the combination of carefully chosen surfactant formulations with the oil being evaluated and observing viscosity of the microemulsion phases and quantifying the solubilization of the pure phases in the microemulsion phase. Both properties are critical to achieve an effective chemical flood. A good measure of degree of solubilization of water and oil phase is by way of solubilization parameters. Solubilization parameters, also referred to as solubilization ratios, of water, P_w , and oil, P_o , are defined as the ratio of the volume of respective phase solubilized by the microemulsion phase to the volume of surfactant present in the microemulsion phase.

$$P_w = V_w / V_s = \frac{\text{volume of water in microemulsion phase}}{\text{volume of surfactant in microemulsion phase}}$$

$$P_o = V_o / V_s = \frac{\text{volume of oil in microemulsion phase}}{\text{volume of surfactant in microemulsion phase}}$$

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 can be controlled by varying the concentration of electrolyte. Increasing electrolyte concentrations in the aqueous phase containing surfactant reduces the solubility of surfactants in the aqueous phase which can lead to three distinct types of microemulsions formed as salinity increases from low to high. Winsor classified the three phases as Type I, Type III and Type II (Green and Willhite 1998). Type I is an oil-in-water microemulsion that forms at low electrolyte concentration, Type II is a water-in-oil microemulsion that forms at high electrolyte concentrations and Type III is a bicontinuous microemulsion that forms at intermediate electrolyte concentrations. For anionic surfactants, a transition Type I → Type III → Type II is observed as electrolyte concentration is increased (Nelson and Pope 1978). For this transition it is necessary that surfactant concentration relative to oil and water phase is low enough such that the composition of formulation lies in the three phase region of a pseudoternary diagram (Green and Willhite 1998). Equal solubilization parameters for oil and water are attained in the Type III regime. The electrolyte concentration at which the solubilization parameters are equal is called the optimum salinity (S^*) and the value of solubilization parameter at the optimum salinity is termed optimum solubilization parameters or optimum solubilization ratios (σ^*).

Flaaten et al (2008) summarize the laboratory screening criteria that needs to be satisfied as the following:

1. An optimum solubilization parameter of at least 10 mL/mL must be aimed for as it correlates to an ultra low IFT of about 0.003 dynes/cm
2. Microemulsion, type III, phase must coalesce and equilibrate quickly, preferably in less than 7 days
3. Microemulsion phase must have free flowing interfaces with oil and water and appear non-viscous and macroemulsion free, and
4. The aqueous surfactant slug must be a one-phase clear homogeneous mixture.

To obtain an optimum surfactant slug it is necessary to study and understand the effects of variables such as total surfactant concentration, surfactant ratios, co-solvent concentration, alkali concentration, types of electrolyte etc. on phase behavior observed with screening experiments. After successful screening results, the identified surfactant formulation must be tested in core floods to determine the oil recovery performance.

Experimental methods. An approach similar to that discussed by Levitt et al. (Levitt, Jackson et al. 2006) is used for phase behavior experiments. Ten mL borosilicate Fisher brand pipets, flame sealed at the bottom end are used to contain the formulations comprising an aqueous phase and an oleic phase in 1:1 ratio by volume. Several pipets are required to screen each formulation for a range of salinities, thus termed salinity scan. A series of aqueous phase containing fixed surfactants, co-solvents and alkali concentrations but varying electrolyte concentration are added to the pipets first and the initial aqueous phase levels are marked. After mixing the aqueous solution on a vortex mixer, aqueous phase appearance/behavior is recorded and then an equal volume of oil is added.

The pipet is brought to reservoir temperature before they are mixed by tilting completely several times and 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 with time. At the time solubilization stops changing for both phases the microemulsion phase is considered to have equilibrated.

After equilibration is established, properties of the microemulsion phase are evaluated by both qualitative and quantitative examination. Initially, pipets are scanned for presence of any *macroemulsions*, gels or other viscous phases. Also, a quick evaluation of the viscosity of the type III microemulsion phase is performed by tilting and twisting a pipet and noting the fluidity and dispersion behavior of aqueous and microemulsion phase interface nearest to optimum salinity as shown in Figure 3. Optimum solubilization parameters, optimum salinity and equilibration time are determined and used as signs of of microemulsion phase properties, for instance, solubilization parameters are related to IFT and equilibration time to viscosity of the microemulsion. For selected formulations, actual measurement of viscosities and IFT measurements are performed to corroborate the qualitative assessment.

Optimum salinity and solubilization parameters are determined by plotting solubilization parameters as a function of salinity (Green and Willhite, 1998). Figure 4 is an example of a solubilization parameter plot. A picture of the phase behavior pipets for this plot is shown in



Figure 3 - Visual examination of type III microemulsion fluidity by tilting and twisting the pipet.

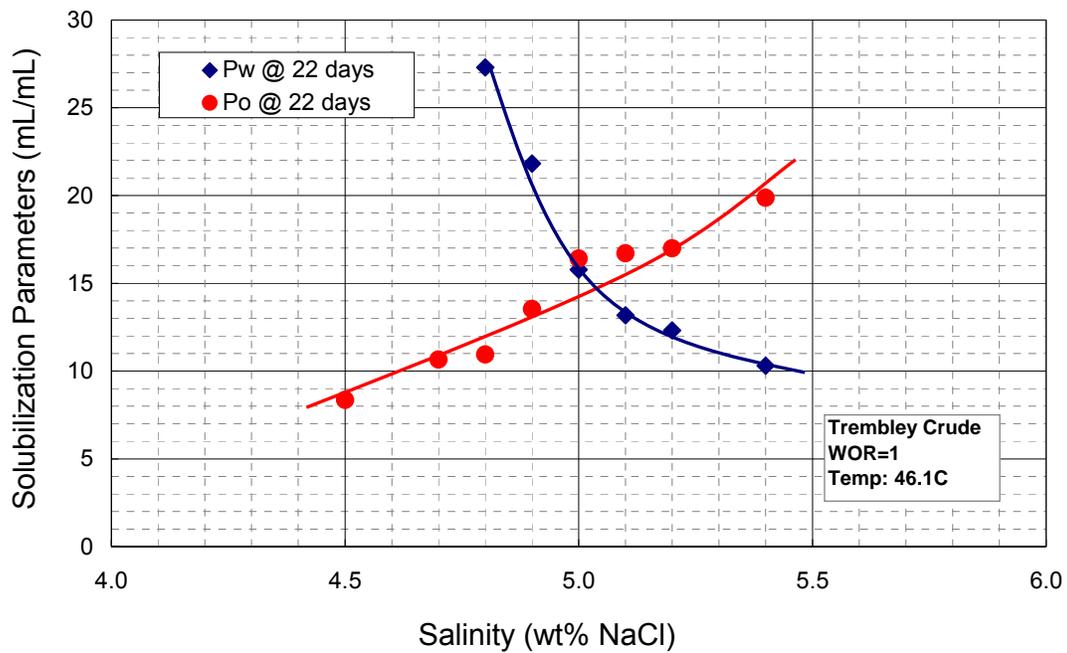


Figure 4 - Solubilization Parameters plot for formulation (A3) containing 0.625 wt% Alfoterra® 123-8s, 0.375 wt% Petrostep® S-2, 0.75 wt% IBA and 0.05 wt% NaOH with Trembley crude oil @ 46.1 °Celsius after equilibrating for 22 days.

Figure 5. The aqueous formulation contained 0.625 wt% Alfoterra® 123-8s surfactant, 0.375 wt% Petrostep® S-2 co-surfactant, 0.75 wt% IBA and 0.05 wt% NaOH in aqueous phase and was screened with Trembley crude oil at 46.1 Celsius using a WOR of 1. Optimum salinity and optimum solubilization parameter are read at the point where the two curves intersect in Figure 4. Equilibration time, another parameter sought in the lab screening, is obtained from plotting the solubilizations of water and oil against time for the salinity value nearest to optimum salinity as shown in Figure 6. It is generally observed that solubilization values stabilize quicker near optimum salinity.

C. Screening Results for Trembley Crude Oil

Surfactant screening was conducted with crude oil from the Trembley Lease in the Trembley Field in Reno County, Kansas. The lease produces from the Lansing Kansas City formation which is a limestone formation. The 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 slightly acidic with an acid number of 0.08 mg KOH /g oil.

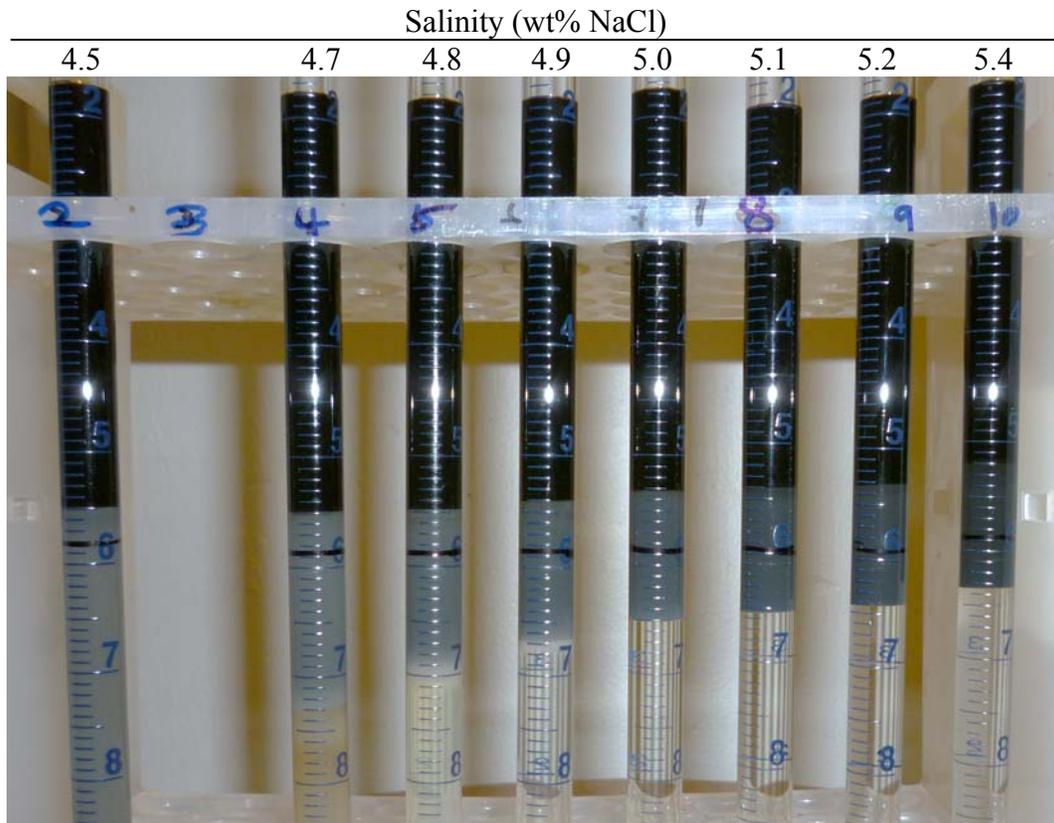


Figure 5 - Photo of a salinity scan for a formulation(A3) containing 0.625 wt% Alfoterra® 123-8s, 0.375 wt% Petrostep® S-2, 0.75 wt% IBA and 0.05 wt% NaOH with Trembley crude oil @ 46.1 °Celsius after equilibrating for 22 days.

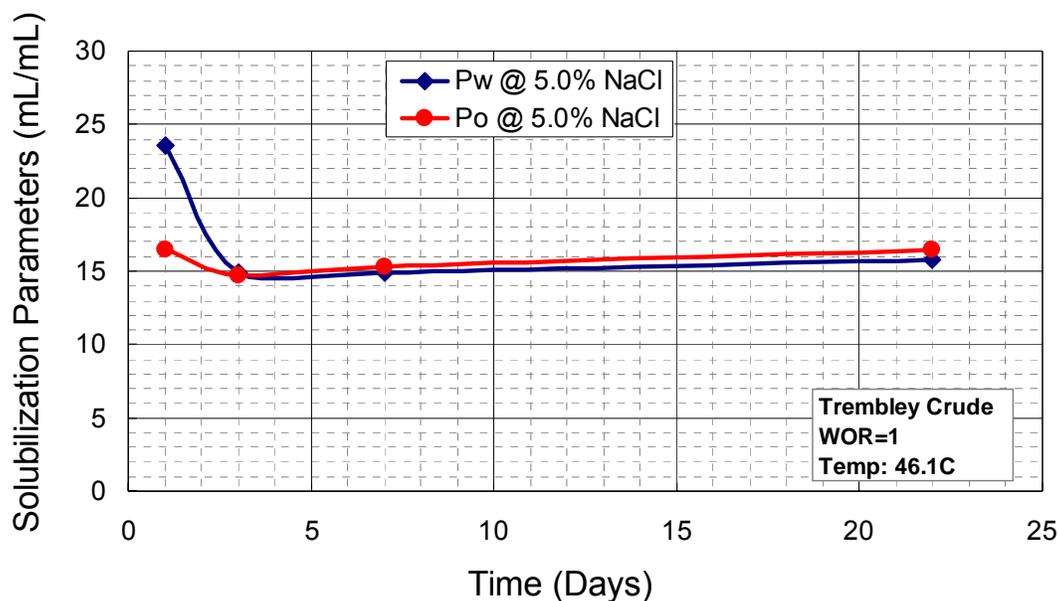


Figure 6 - Determination of equilibration time for a formulation(A3) containing 0.625 wt% Alfoterra® 123-8s, 0.375 wt% Petrostep® S-2, 0.75 wt% IBA and 0.05 wt% NaOH with Trembley crude oil @ 46.1 °Celsius.

Alcohol propoxy sulfates and olefin sulfonates were used in the surfactant screening experiments with Trembley crude oil. Each formulation contained a primary surfactant to form microemulsion by solubilizing the oil and aqueous phases and a co-surfactant to enhance equilibration times, reduce viscosity of microemulsion phase and allow optimization of surfactant slug to the field brine application. A co-solvent such as sec-butyl alcohol (SBA) or iso-butyl alcohol (IBA) was also added to the formulations to reduce unwanted liquid crystalline phases and macroemulsions. Alkali was added to achieve higher solubilization and reduction of equilibration times.

Primary surfactants tested with Trembley crude oil were Petrostep® S-1, Alfoterra® 123-8s, Petrostep® 8-B, Petrostep® 8-C and Petrostep® 13-C belonging to the class of branched propoxy alcohol sulfates. Co-surfactants tested include an internal olefin sulfonate, Petrostep S-2, and two alpha olefin sulfonates, Petrostep® C-1 and C-5. SBA and IBA were used as co-solvent and sodium hydroxide (NaOH) and sodium carbonate (Na₂CO₃) were tested as alkali. More than ninety salinity scans were conducted with the various surfactants and the Trembley crude oil. Examples of combinations of surfactant, co-surfactant, co-solvent and alkali with the Trembley oil at a water-to-oil ratio (WOR) of 1 are presented in Table 7. Formulations that are being considered for testing in core flooding for this oil are labeled A1 to A4 in the table.

Petrostep S-1 (A1 and A2), Alfoterra® 123-8s (A3) and Petrostep S-13C (A4) were the most successful primary surfactant when combined with Petrostep S-2 as co-surfactant. At a total surfactant concentration of 1 wt% and at surfactant-to-co-surfactant ratios of 5:3, 5:3 and 3:1, the optimum solubilization ratios were the highest and their equilibration time were short as well. Optimum salinities of Series A1 to A4 are between 3 and 5 wt% NaCl using similar surfactant-to-co-surfactant ratios except for formulation A4. Addition of alkali to these systems was

necessary to attain quick equilibration. Optimum amount of alkali was found to be between 0.02 wt% - 0.05 wt% NaOH and 0.2 wt% - 1 wt% Na₂CO₃.

Alcohol concentrations in the formulations in Table 7 were at the level that was deemed necessary to alleviate viscous phases and macroemulsions. Formulation A3 required the minimum amount of alcohol and gave comparable results to A1, A2 and A4. Minimum use of alcohol is desired to minimize the cost of the surfactant slug and therefore emphasis will be on using the formulation with lowest requirement of alcohol that still satisfies the necessary phase behavior criteria for success.

Table 7 - Quantitative results of the laboratory screening experiments/salinity scans performed on Trembley oil with various surfactant combinations at 46.1 °Celsius

	Formulation	Solubilization ratio (mL/mL)	Time to equilibrate (days)	Optimal salinity (wt% NaCl)
	1.25% Petrostep® S1, 0.75% Petrostep® S2, 2% SBA	Did not equilibrate and viscous		
	0.62% Petrostep® S1, 0.38% Petrostep® S2, 2% SBA	7.5	>50	4.66
A1	0.62% Petrostep® S1, 0.38% Petrostep® S2, 2% SBA, 0.05 wt% NaOH	15	3	4.6
A2	0.62% Petrostep® S1, 0.38% Petrostep® S2, 2% SBA, 1 wt% Na ₂ CO ₃	14	6	4.22
	0.62% Alfoterra® 123-8s, 0.38% Petrostep®S2, 2% SBA	11	14	4.47
A3	0.62% Alfoterra® 123-8s, 0.38% Petrostep® S2, 0.75% IBA, 0.05 wt% NaOH	15	3	5
	0.62% Alfoterra® 123-8s, 0.38% Petrostep® C1, 0.75% IBA, 0.25 wt% NaOH	Did not equilibrate and viscous		
	0.62% Alfoterra® 123-8s, 0.38% Petrostep® C5, 0.75% IBA, 0.25 wt% NaOH	13	3	9.72
	0.62% Petrostep® S8-B, 0.38% Petrostep® S2, 0.75% IBA, 0.25 wt% NaOH	13	3	5.25
	0.62% Petrostep® S8-C, 0.38% Petrostep® S2, 0.75% IBA, 0.25 wt% NaOH	12	3	4.8
A4	0.67% Petrostep® S13-C, 0.33% Petrostep® S2, 1.5% IBA, 0.2 wt% NaOH	14.9	3	3.15

Stability of the injected chemical system. A one-phase surfactant slug is generally considered a requirement so as to maintain the composition while injection into the reservoir. The aqueous surfactant formulations prior to adding oil are examined for visual homogeneity and clarity at salinities up to and higher than the optimal salinity (S*) at room temperature (surface facilities) and at reservoir temperature. Haziness of the aqueous phase is observed when the *salinity limit* is

reached and with time the hazy aqueous phase separates into a surfactant rich layer and excess brine. Chemical formulations for the Trembley oil would probably be injected at optimal salinity so the salinity limit of the injected system needs to be higher than optimal salinity.

Salinity limits determined for the chemical systems under consideration are shown in Table 8. The salinity scans for the aqueous stability tests were prepared at 0.25 wt % and 0.5 wt% NaCl increments and the highest salinity at which the aqueous phase was a clear, one-phase solution is given in the table. Salinity limits for aqueous stability were above optimum salinity at both room temperature and at reservoir temperature for three of the formulations. Solubilities of the surfactants were reduced at the elevated temperature.

Table 8 - Aqueous stability limit of surfactant formulations A1, A2 A3 and A4 under consideration for Trembley crude oil at room temperature and their optimum salinity at reservoir temperature, 46.1 °C, are compared.

	Formulation	Optimal salinity (wt% NaCl)	Salinity limit for aqueous stability (wt % NaCl)	
			@ room temperature	@ 46.1 °C
A1	0.62% Petrostep® S1, 0.38% S2, 2% SBA, 0.05 wt% NaOH	4.6	6	5
A2	0.62% Petrostep® S1, 0.38% S2, 2% SBA, 1 wt% Na ₂ CO ₃	4.18	5.5	4.75
A3	0.62% Alfoterra® 123-8s, 0.38% S2, 0.75% IBA, 0.05 wt% NaOH	5	5	4.5
A4*	0.67% Petrostep® S13-C, 0.33% S2, 1.5% IBA, 0.05 wt% NaOH	3.4*	4.0	3.5

Effect of co-surfactant on phase behavior. Screening experiments performed in the lab used two surfactants simultaneously, a primary surfactant and a co-surfactant. Having a surfactant and co-surfactant blend has been shown to provide various benefits (Hirasaki, Miller et al. 2008). A good co-surfactant reduces tendency of a macroemulsion or viscous phase being formed instead of microemulsion and could also replace or reduce the need for co-solvent (alcohol) that is added to reduce viscosity of the microemulsion phase. Co-surfactants also allow for the adjustment of optimum salinity to target field conditions. The co-surfactants that we have used are more hydrophilic than the primary surfactant and therefore increasing their proportion shifts the optimal salinity to higher values.

Table 9 presents selected screening results that illustrate the effect of varying the surfactant-to-co-surfactant ratio. In salinity scans 16, 17 and 18 of Group #25, the surfactant-to-co-surfactant ratio was varied. Run #25-16 had a viscous middle phase and did not equilibrate to form a fluid type III microemulsion, however, higher proportion of co-surfactant in Runs #25-17 and #25-18, gave fluid type III microemulsions. Note that alcohol concentration is the same in all series.

These results indicate that co-surfactant helped reduce viscosity of the microemulsion phase and promoted coalescence to a stable microemulsion that would otherwise require additional alcohol co-solvents. This improvement may be attributed to the disorder that is created by different molecular structures such as carbon chain length and branching of the surfactant and co-surfactant at the water and oil interface disallowing them to pack closely to form viscous phases (Hirasaki, Miller et al. 2008).

Optimum salinity increased as the surfactant ratio (primary surfactant: co-surfactant) decreased as shown by the salinity scans of both Groups #25 and #33 in Table 9. The other significant impact of using co-surfactant was on alcohol requirement. Both #33-5 and #33-6 had 1 wt% total surfactant and had similar solubilization ratios and equilibration times but #33-5 required half the amount of alcohol as #33-6 due to the higher proportion of co-surfactant. This is a significant reduction in alcohol when considering economics of field applications.

Use of lower surfactant ratios may have the drawback of reducing optimum solubilization as reflected in Runs #25-17 and #25-18. This effect is compensated for as the requirement for alcohol is less as demonstrated by Runs #33-5 and #33-6.

Table 9 - The effect of varying surfactant-to co-surfactant ratios on solubilization ratios, optimum salinity and equilibration time; Trembley crude oil at 46.1°C.

Series	Surfactant		Co-Surfactant	Co-Solvent*	Ratio	Alkali	Sol. ratio (mL/mL)	Equil. time (days)	Optimal salinity (wt% NaCl)
	Petrostep S1 (wt%)	Petrostep S-13C (wt%)	Petrostep S2 (wt%)	(wt%)	surf.-to-co-sur.f.	NaOH (wt%)			
#25-16	0.75		0.25	2 (SBA)	3:1	0.25	Did not equilibrate/viscous		
#25-17	0.625		0.375	2 (SBA)	5:3	0.25	15	5	4.18
#25-18	0.5		0.5	2 (SBA)	1:1	0.25	11.6	10	5.72
#33-6		0.75	0.25	1.5 (IBA)	3:1	0.2	14.9	3	3.15
#33-5		0.625	0.375	0.75 (IBA)	5:3	0.2	14.2	5	4.55

* Isobutyl alcohol (IBA) or sec-butanol (SBA)

Effect of co-solvent on phase behavior. Co-solvents such as short chain alcohols are added to the surfactant formulation to avoid formation of liquid crystalline phases and reduce viscosity of the microemulsion phase both with and without oil (Eicke 1987). The short alcohol molecules participate along with the surfactant/co-surfactant at the interface between oil and water in microemulsions. Shorter co-solvent molecules separate longer surfactant molecules and prevent them from packing together to form ordered structures with increased viscosities. Co-solvents also add flexibility at the oil-water interface to allow for the formation of spherical microemulsion micelles (Prince 1977). Drawback of adding alcohol to formulation as co-solvent is that it reduces solubilizations and therefore raises the interfacial tension between the microemulsion and the respective phase (Salter 1977). The amount of co-solvent can and should be minimized by using branched surfactants and co-surfactants in order to minimize cost and harmful affects of chromatographic separation of alcohol in the reservoir (Hirasaki, Miller et al. 2008).

In screening experiments with Trembley crude oil, formulations containing 0.63 wt% Petrostep S-13C surfactant, 0.37 wt% Petrostep S-2 as co-surfactant and isobutyl alcohol (IBA) as the co-solvent was studied for co-solvent effects. The reduction in optimum solubilization ratio was significant when co-solvent concentration was increased from 0.25 wt% aqueous to 0.75 wt% as shown in Table 10. A concentration of 0.75 wt% IBA was considered necessary to obtain non-viscous microemulsion phase that still has ultra low IFT as the optimum solubilization was still above 10 mL/mL. Viscosity of the microemulsion was inspected by tilting the pipets as well as by actual measurement on a sample retrieved from the pipet with the composition nearest to optimum salinity. The measurement showed viscosities were not significantly different at low and high alcohol concentration near optimum salinity.

Table 10 - Effect of varying co-solvent (IBA) concentration on the phase behavior of formulation containing surfactant Stepan 13-C, co-surfactant S2, alkali and Trembley crude oil at 46.1 °C.

Series	Surf.	Co-surf.	Co-solvent	Ratio	Alkali	Sol. ratio (mL/mL)	Equil. time (days)	Optimal salinity (wt% NaCl)	Viscosity near optimum (cp)
	Petrostep S-13C (wt%)	Petrostep S2 (wt%)	Isobutyl alcohol (wt%)	surf.-to-co-surf.	NaOH (wt%)				
#30-6	0.625	0.375	0.25	5:3	0.2	20.2	3	4.9	8.0
#30-5	0.625	0.375	0.5	5:3	0.2	17.9	3	4.83	8.9
#33-5	0.625	0.375	0.75	5:3	0.2	14.2	5	4.55	8.9

Effect of alkali on phase behavior. An alkali such as sodium hydroxide (NaOH) or sodium carbonate (Na₂CO₃) is added to the formulation to increase the pH of the injected surfactant slug which gives the benefit of reduced adsorption of anionic surfactant on rock matrix and also generates natural surfactant by reacting to naphthenic acid for acidic crude oils (Hirasaki, Miller et al. 2008). Another significant benefit that may further enhance chemical flooding is the shorter equilibration time and higher solubilization ratios exhibited by microemulsion phases in the presence of alkali even with oils with low acid numbers (Jackson 2006).

Many formulations containing Petrostep S-1 and Petrostep S-2 with SBA as the co-solvent were studied initially without alkali added. This surfactant combination met acceptable phase behavior criteria except for equilibration times that were several weeks or more. Addition of alkali considerably shortened the equilibration times to acceptable durations. Several series of salinity scans at different values of alkali are given in Table 11. Run #16-36 without alkali took on the order of 50 days to equilibrate. Equilibration times were reduced to a week or less for the series containing various amounts of alkali, while optimum solubilization ratios were increased. An addition of up to 0.05 wt% NaOH or 0.2 wt% Na₂CO₃ to these formulations almost doubled the optimum solubilization ratio. A comparison of effect of alkali is depicted in Figure 7. Microemulsion phases were observed to be more fluid with alkali. Higher alkali concentrations may not improve these results further as comparisons in Table 11 suggest. Changes in the optimum salinity values are mostly due to the addition of alkali salts that are not reflected in the salinity values.

Table 11 - Effect of varying alkali concentration for two types of alkali on the phase behavior of formulation containing surfactant Petrostep S-1, co-surfactant Petrostep S-2, and Trembley crude oil at 46.1 °C where WOR=1.

Series	Surfactant		Co-Solvent	Ratio	Alkali			Sol. ratio (mL/mL)	Equil. time (days)	Optimal salinity (wt% NaCl)
	Petrostep S-1 (wt%)	Petrostep S2 (wt%)	Sec-butyl alcohol (wt%)	surf.-to-co-surf.	Type	(wt%)	pH			
#16-36	0.625	0.375	2	5:3	None	0.00	9.3	7.5	>50	4.65
#27-10	0.625	0.375	2	5:3	NaOH	0.02	11.6	15.0	7	5.00*
#27-4	0.625	0.375	2	5:3	NaOH	0.05	11.7	15.0	3	4.60
#27-5	0.625	0.375	2	5:3	NaOH	0.2	12.3	14.6	3	4.35
#27-6	0.625	0.375	2	5:3	NaOH	1	12.7	14.8	3	3.10
#27-7	0.625	0.375	2	5:3	Na ₂ CO ₃	0.05	10.4	slow to equilibrate >6		5.00
#27-8	0.625	0.375	2	5:3	Na ₂ CO ₃	0.2	10.6	16.0	6	4.80
#27-9	0.625	0.375	2	5:3	Na ₂ CO ₃	1	11.0	14.0	6	4.20

* Value higher than expected.

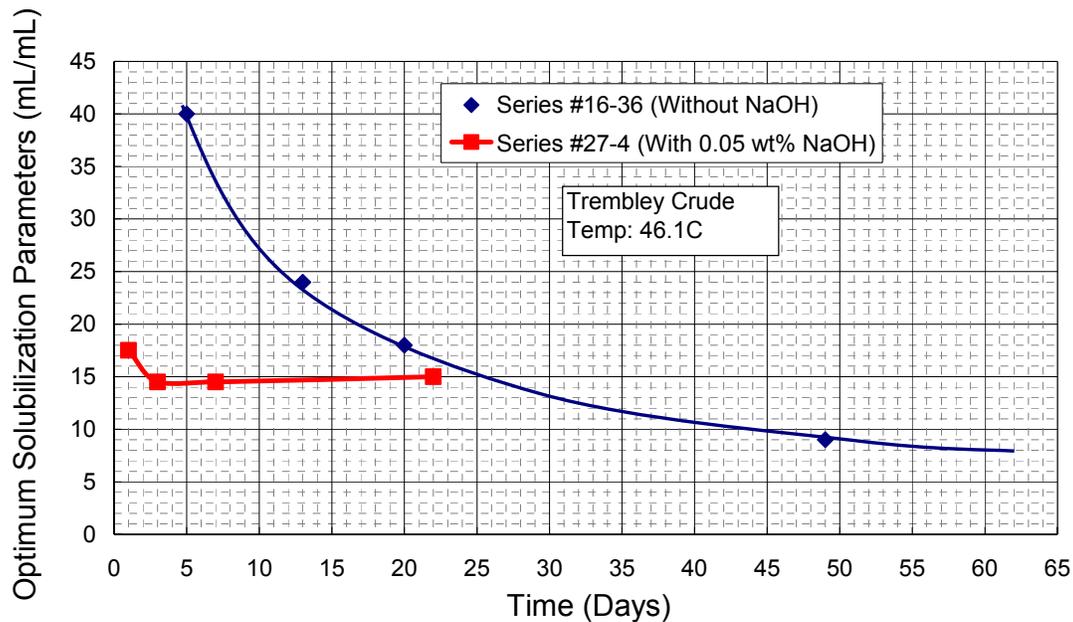


Figure 7 - Comparison of time required (equilibration time) for optimum solubilization ratio to attain a stable value with and without alkali for the same formulation.

Interfacial tension (IFT) measurements. IFT measurement between the aqueous and microemulsion phases was performed for a formulation containing 0.62% Petrostep S1, 0.38% Petrostep S2, 2% SBA, 0.5 wt% NaOH and Trembley crude oil with WOR=1 at 4 % salinity. The solubilization of water and oil were 13.5 mL/mL and 21 mL/mL, respectively, for this sample. The IFT value measured using spinning drop tensiometer was 0.0006 dynes/cm, which is ultra low and satisfies the assumption that a solubilization ratio of above 10 mL/mL correlates to ultra low IFT. Figure 8 is a picture of the spinning microemulsion drop contained in the aqueous phase.

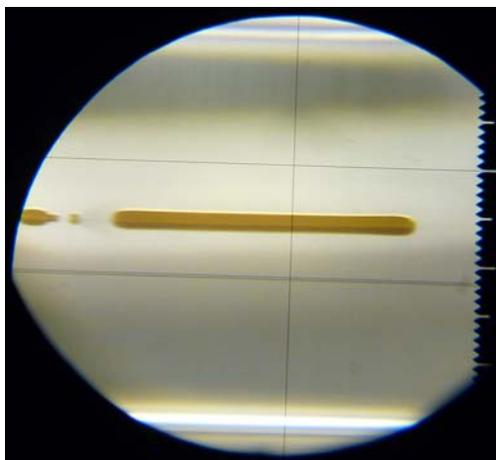


Figure 8 - A picture of spinning drop in action during IFT measurement between aqueous and microemulsion phase from the same pipet. The formulation contained 0.62% Petrostep S1, 0.38% Petrostep S2, 2% SBA, 0.5 wt% NaOH and Trembley crude oil with WOR=1 at 4 % salinity and 46.1 °C.

Viscosity measurements. Viscosities of the microemulsion phases were measured to identify the range of viscosities that may be encountered during chemical flooding. A Brookfield DV –I+ cone-and-plate viscometer was used for viscosity measurement at the reservoir temperature. Samples were quickly transferred from the pipets to the viscometer and run at several shear rates, however, only the first measurement obtained at 75 sec^{-1} were compared as they were the least affected due to evaporation of alcohol. Samples were retrieved from the same pipets that were used for salinity scans.

Viscosity of middle phase microemulsions for salinity scans A2 and A3 are shown in Figure 9 as a function of salinity. Viscosities of the microemulsions were highest at the phase transition boundaries and minimum values were found close to the optimum salinity. Viscosity values of the microemulsions ranged from 7 to 11 cp which is two to three times the value of the Trembley crude oil of 4.1 cp. Viscosity values of the microemulsions are considered suitable for chemical flooding applications.

The viscosities showed non-Newtonian behavior particularly at the lower salinities close to the type I-to-type III transition and less non-Newtonian behavior near optimum salinity. This behavior is similar to that observed by Bennet et al. for microemulsions. (Bennett et al. 1981).

Summary Several surfactants and co-surfactants were tested in systematic laboratory screening with the Trembley crude oil. Effects of surfactant-to-co-surfactant ratio, co-solvent concentration and alkali on microemulsion phase properties were studied in order to formulate efficient systems chemical flooding. Criteria for good performance of a surfactant formulation in laboratory screening were defined as low viscosity microemulsion phase, optimum solubilization ratio of above 10mL/mL, and equilibration time of less than seven days. Best performing surfactants were Alfoterra 123-8s, Petrostep S1 and Petrostep S-13C when combined with co-surfactant Petrostep S2. Both sec-butyl alcohol and isobutyl alcohol were used as co-solvents to

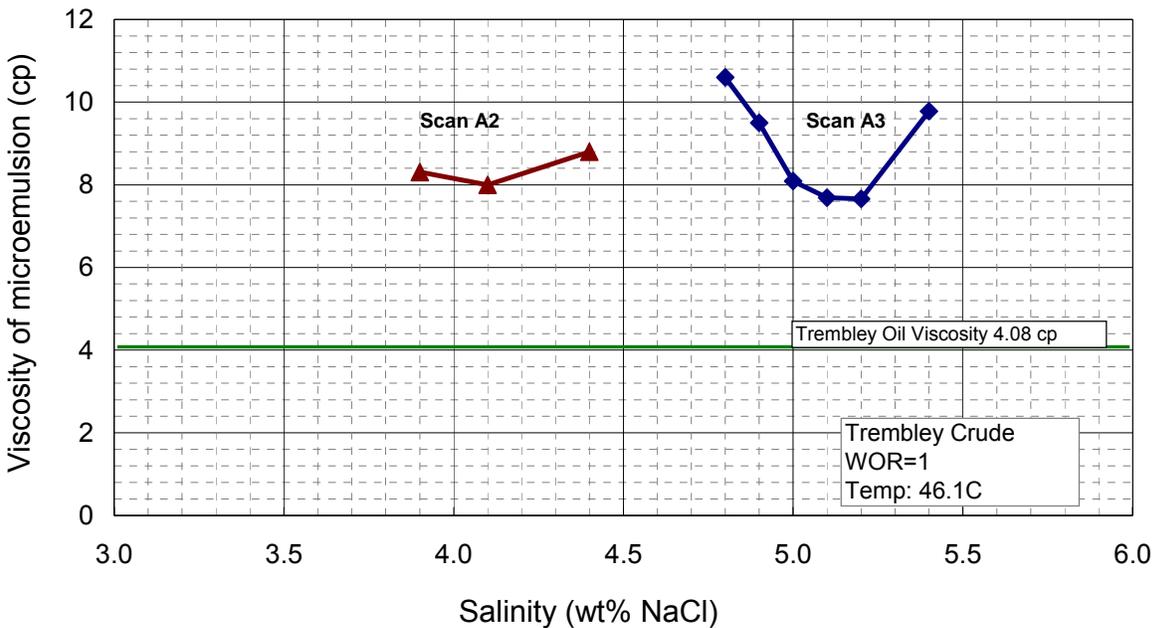


Figure 9 - Microemulsion viscosity for formulation A2 and A3 and corresponding microemulsion volume fraction is shown. Viscosities were measured at a shear rate of 75 s^{-1} .

avoid macroemulsions and gels, while addition of alkali was necessary to achieve quick equilibration of the microemulsion phase. Addition of alkali had the added benefits of increased optimum solubilization ratio and enhanced fluidity of the microemulsion phase.

Viscosities of microemulsion phases from two selected salinity scans were in the range 7 to 11 cp and considered acceptable for flooding applications. Interfacial tension between the microemulsion phase and the lower aqueous phase of a sample with water solubilization parameter of 13.5 mL/mL was about 0.0006 dynes/cm, which is ultra low as expected.

Future work will include testing identified surfactant formulations in synthetic field brine containing divalent cations and adding polymer to formulation for mobility control. Formulations will then be tested in Berea core floods for performance of residual oil recovery.

D. Screening Results for Wahrman Crude Oil

Wahrman crude oil from Beaver Creek Field is produced from Lansing-Kansas City formation, which is limestone formation. The reservoir temperature is 43.3°C . Wahrman oil is light with an API gravity of 35.2 at 25°C . Viscosity of the Wahrman oil is 13.9 cP at 25°C ; 8.5 cp at the reservoir temperature 43.3°C .

Six primary surfactants and four co-surfactants were used in salinity scans for the Wahrman oil to select the optimal surfactants. Information about the ten surfactants is given in Table 6.

Petrostep S1 and Alfoterra® 123-8S were selected to conduct further tests as primary surfactants with co-surfactant Petrostep S2. This was based on phase behavior screening of many of the combinations in Table 6. Using the primary surfactants Alfoterra 145-4S, Alfoterra 145-8S, Alfoterra 167-4S, and Alfoterra 167-7S with Petrostep S2 as the co-surfactant, the microemulsion phases that formed were visually more viscous and these primary surfactants were not selected for further study. The optimum solubility parameter was low and microemulsion phases were visually viscous when Petrostep S3 was used as a co-surfactant with Petrostep S1 as the main surfactant. Petrostep S3 has a longer carbon chain than S2 and is more suitable for heavier crude oils

No microemulsion phases formed when Petrostep C1, Petrostep C5 serve as co-surfactant with Alfoterra® 123-8S as the primary surfactant. These scans were conducted at a surfactant ratio of 3 and salinity range between 1.5 and 9.5% NaCl. Micro-emulsion phases may form at higher salinities but the aqueous phase before mixing with crude oil at reservoir temperature was not stable.

Effect of surfactant structure on optimal salinity. The Alfoterra series of surfactants has various lengths of carbon chain and varying number of propoxylene oxide (PO) groups which allows for the determination of the effect of structure on phase behavior parameters. Salinity scans were conducted with the Alfoterra series combined with Stepan S2 co-surfactant and 2.5% SBA co-solvent at surfactant ratios of 5:3 and 9:3. The effect of the number of carbons in the molecules on optimal salinity is shown in Figure 10 for the primary surfactants that contain 7 or 8 PO groups (Alfoterra 123-8S, Alfoterra 145-8S, Alfoterra 167-7S). Optimal salinity decreases with increasing average molecule size indicating increased hydrophobicity.

Effect of total surfactant concentration on phase behavior. Tests with different total surfactant concentrations with different ratios of primary surfactant to co-surfactant (termed surfactant ratios) were conducted by using Petrostep S1 and Petrostep S2. The total surfactant concentration ranged from 0.5% to 2% and the surfactant ratios ranged from 1 to 3. Optimal solubilization parameters for these run are presented in Figure 11. Optimal solubilization parameters increase as total surfactant concentration increased. The small increase in the solubilization parameter between 1 and 2% surfactant concentration was not considered beneficial even though the optimal solubilization parameters for 1% total surfactant concentration was sometimes just below 10 mL/mL. Also, formulations with 2% total surfactant required more alcohol co-solvent and the middle phase microemulsions were more viscous than at lower surfactant concentrations.

Effect of surfactant ratio on optimal salinity. Salinity scans were conducted at selected surfactant ratios with Petrostep S1 and Alfoterra 123-8S as the primary surfactant and Petrostep S2 as co-surfactant. Alkali was added to the scans at surfactant ratios greater than 4. Optimal salinities for these scans are shown in Figure 12 as a function of the surfactant ratio. Optimal salinity decreased as primary surfactant/co-surfactant ratio increased. Surfactant ratios can be used to adjust the optimal salinity to appropriate levels for field application if the other criteria such as solubilization parameters and aqueous phase stability are also satisfied.

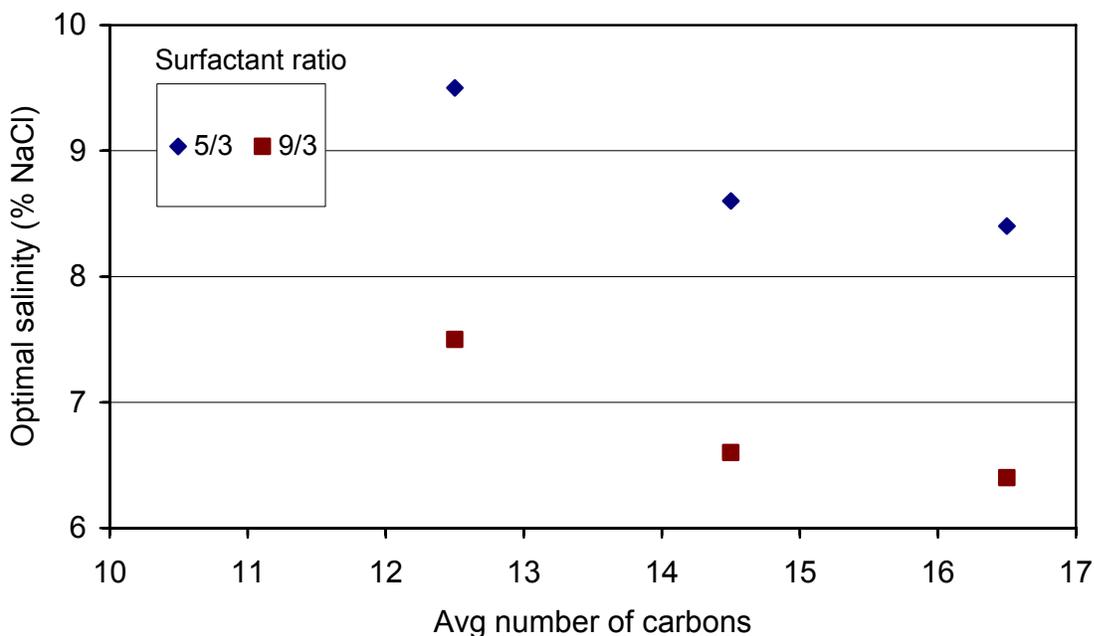


Figure 10 – The effect of carbon chain length on optimal salinity for two surfactant ratios. 1% total surfactant concentration, primary surfactants were from the Alfoterra series, Petrostep S2 co-surfactant and 2.5% SBA.

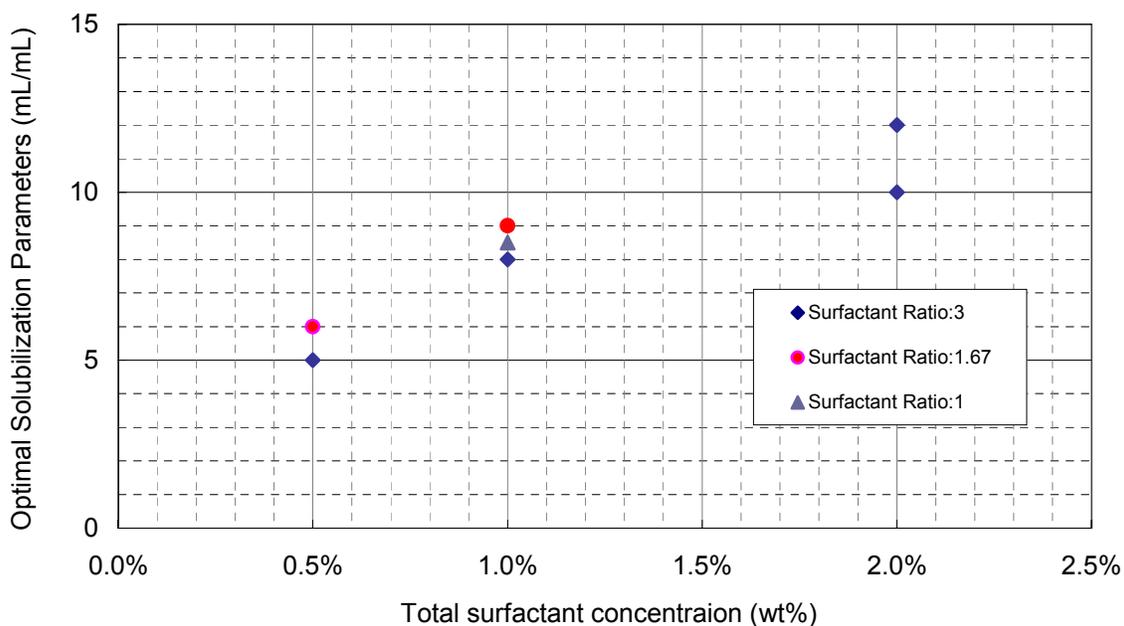


Figure 11 - Optimal solubilization parameters for different total surfactant concentration with different surfactant ratios of Petrostep S1 and Petrostep S2; SBA concentrations were 2 times the surfactant concentration.

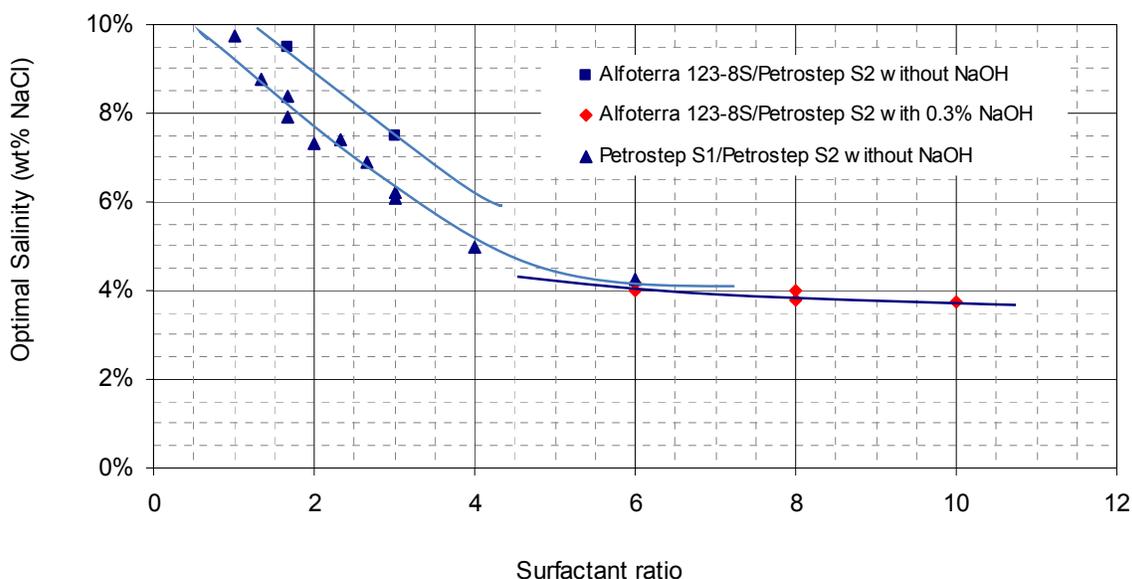


Figure 12 - Optimal salinity changes with surfactant ratio in surfactant system with 1% total surfactant concentration and 2.5% SBA.

Effect of co-solvent (alcohol) on phase behavior. Sec-butyl alcohol (SBA) was used as the co-solvent in all tests with the Wahrman oil. It was found that 0.5% SBA was not sufficient for 1% surfactant concentrations as the middle-phase microemulsions were viscous and contained liquid crystals, therefore, higher concentrations of SBA were studied. The effect of SBA concentration on the optimal solubilization parameters is shown in Figure 13 for a Petrostep S1-Petrostep S2 formulation. Solubilization parameters decrease with co-solvent (SBA) concentration. The effect of SBA concentration on optimal salinity for three surfactant formulations is shown in Figure 14. Higher SBA concentrations reduce optimal salinities. Minimum co-solvent (alcohol) concentrations are desired for economic reasons but the co-solvent is often required to reduce micro-emulsion phase viscosity and to dissolve the surfactants to obtain clear aqueous phases before mixing with oil.

Effect of alkali on phase behavior. The effect of alkali on equilibration times is shown in Figure 15 for a system containing Alfoterra 123-8S, Petrostep S2 and SBA: Without sodium hydroxide, the middle-phase microemulsion formed at 2 days; the tube close to optimal salinity formed middle phase first followed by the tubes above optimal salinity and then the tubes below optimal salinity. With sodium hydroxide, the middle-phase microemulsion formed the following day and equilibrated after 2 days. The middle phases with NaOH also look more fluid with clear lower interfaces with the aqueous phase. With sodium hydroxide or not, upper interfaces

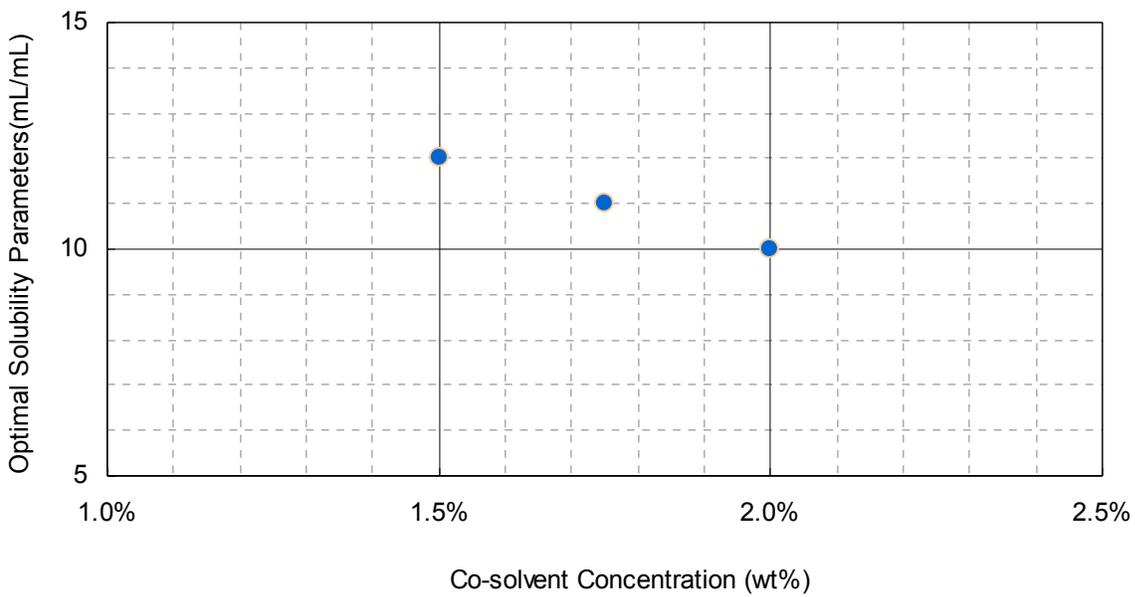


Figure 13 - Optimal solubility parameters change as co-solvent (SBA) concentration with 0.625% Petrostep S1, 0.375% Petrostep S2.

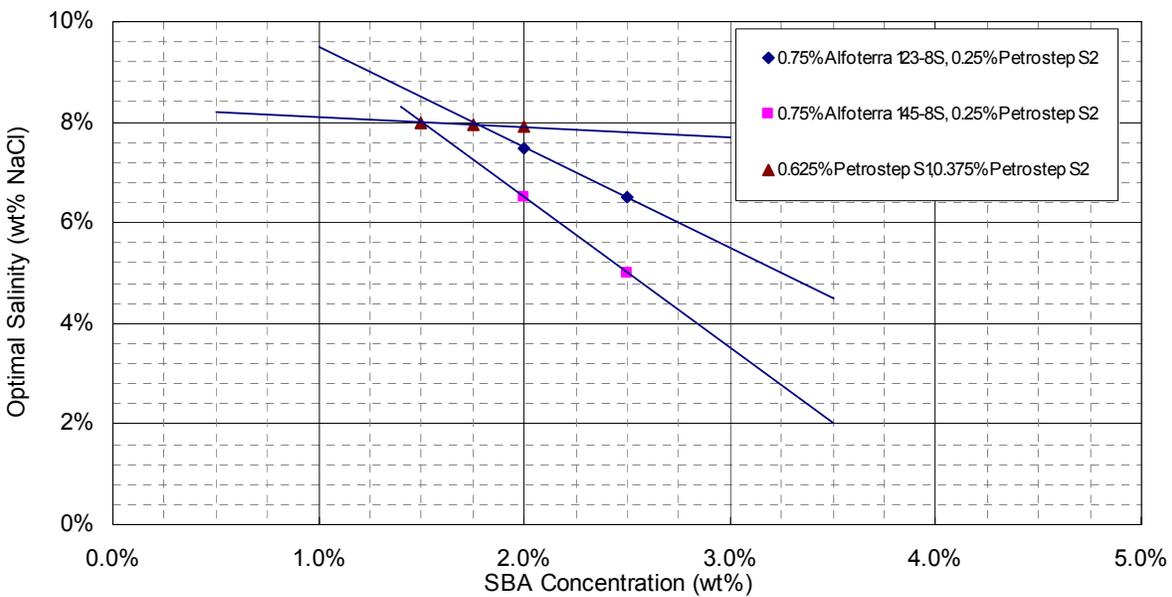


Figure 14 - Optimal salinity changes as co-solvent (SBA) concentration with different surfactant systems.

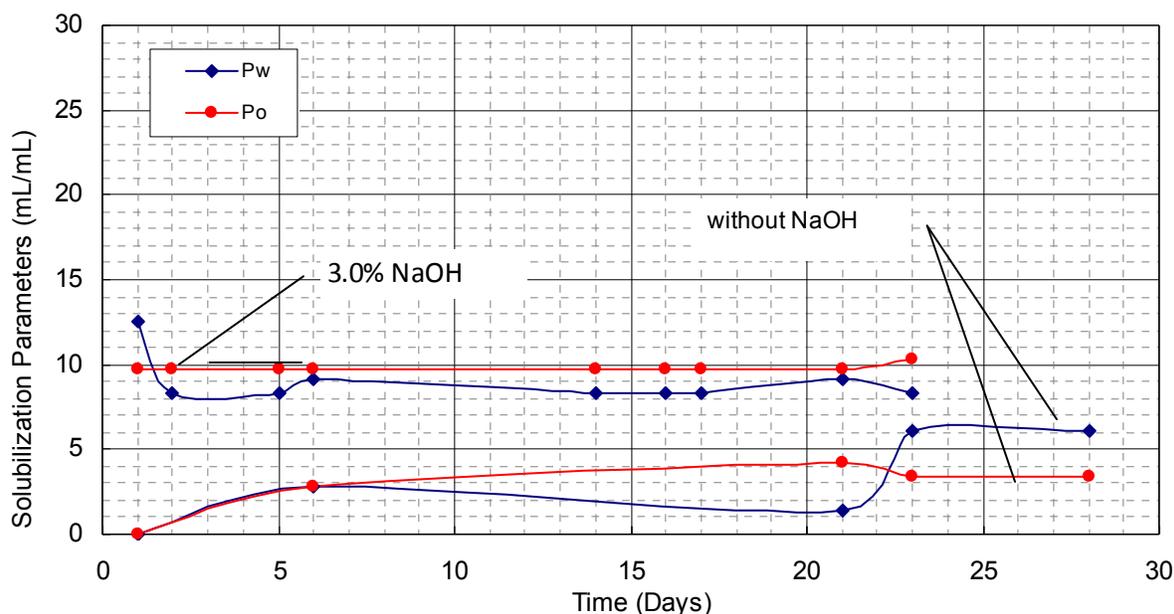


Figure 15 - Equilibration time for surfactant system: 0.857% Alfoterra 123-8S, 0.143% Pestrostep S2, 2% SBA with and without NaOH.

between the microemulsion and the oil phase always equilibrate faster than lower interface between the microemulsion and water phase. When sodium carbonate was added to surfactant formulation of Pestrostep S1 and Pestrostep S2, it does not show advantage of improving optimal solubility parameters or the broadening of the phase Type III region.

Stability of the injected chemical system. The chemical system should remain a one-phase solution during mixing and injection into the reservoir. This criterion is tested by observing the chemical system prior to mixing with crude oil. The criterion is attained if the chemical system remains a clear one-phase solution at room temperature and at reservoir temperature. The appearance of the chemical system is noted prior to mixing with oil during salinity scans. Generally, the surfactant systems are stable, one-phase solutions at low salinity values. As the salinity is increased, the systems become hazy and, with time, often will separate into two liquid phases. The salinity limit for aqueous stability is the highest salinity for which a clear, one-phase solution is observed. For most applications, the salinity limit should be above the optimal salinity to eliminate phase separations during the injection process.

Two surfactant systems were investigated extensively for the Wahram crud oil: (1) [Pestrostep S1, Pestrostep S2, SBA] and (2) [Alfoterra 123-8S, Pestrostep S2, SBA, NaOH]. These systems at a range of concentrations have fluid middle-phase microemulsion and relatively high solubilization ratios. However, the aqueous phases of these systems before mixing with Wahram crude oil at optimal salinity are not clear at room temperature and will separate into two liquid phases at reservoir temperature (43.3°C). Several attempts aimed to obtain one-phase solutions (prior to

mixing with oil) at the optimal salinity were conducted. The surfactant ratio was increased to reduce the optimal salinity, the SBA (co-solvent) concentration was increased to increase the solubility of the surfactants and the effects of the addition of alkali, both NaOH and Na₂CO₃, on the aqueous stability were checked. The effect of the surfactant ratio on both the optimal salinity and the salinity limit for aqueous stability are shown in Figure 16. The surfactant ratio was increased to reduce the optimal salinity to values below the salinity limit for aqueous stability. The salinity limit also decreased with surfactant ratio as shown in Figure 16. This and the other attempts to find a chemical system that meets all of the phase behavior criteria were not successful.

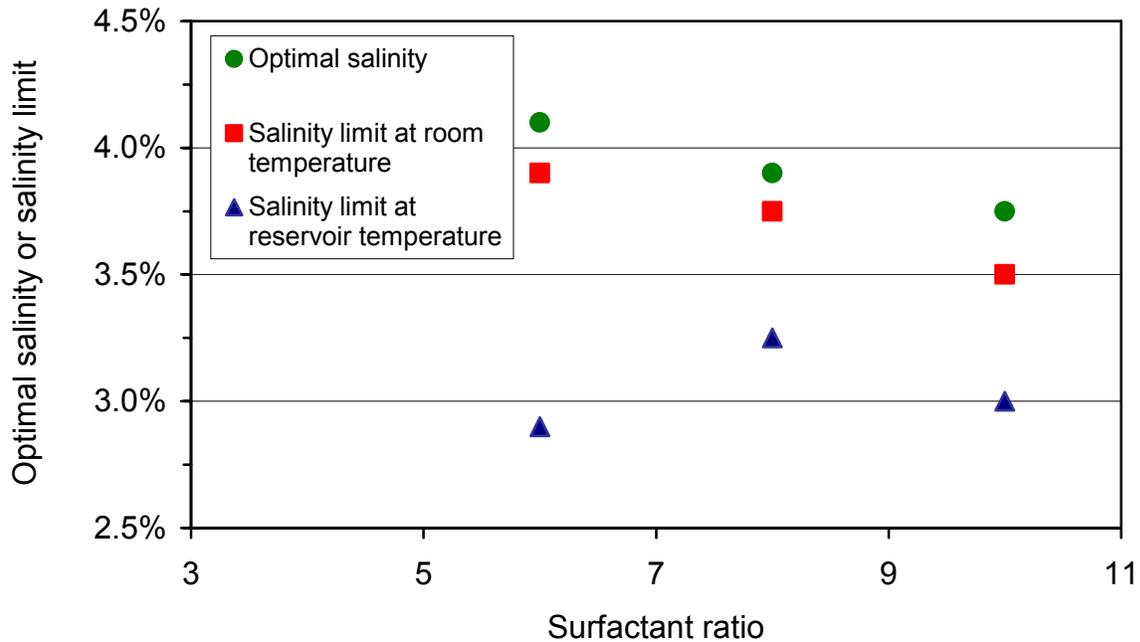


Figure 16 – The effect of surfactant ratio on optimal salinity and the salinity limit for aqueous stability.

Interfacial tension (IFT) measurements. Ultra low interfacial between different phases (lower phase and middle phase, middle phase and upper phase) is crucial for high oil recovery in surfactant flooding. In order to verify that ultra low interfacial tension is obtained, IFT values were measured by the spinning drop method. Vonnegut (1942) gave equation to calculate IFT measured by spinning drop tension-meter, which is:

$$\gamma = \frac{\pi(\rho_1 - \rho_2)d^3\omega^2}{4}$$

γ = interfacial tension

ρ_1 = density of outer phase

ρ_2 = density of inside phase

d = droplet diameter

ω = rotation angular speed

The spinning drop method requires the outer phase (more dense phase) be clear in order to see and measure the dimensions of the spinning drop. Microemulsions of crude oil systems are opaque and therefore only the IFT between the microemulsion phase and a clear lower aqueous phase can be measured. Large samples (40ml) were prepared for certain surfactant system so as to obtain large enough samples of the microemulsion phase to measure IFT. The IFT values are given in Table 12 for two systems. Both IFT values are smaller than 10^{-3} dyne/cm, which is a general criterion for efficient recovery of residual oil.

Table 12 - IFT measurement for two surfactant systems.

Main Surfactant(wt%) Petrostep S1	Co-surfactant(wt%) Petrostep S2	Co-solvent(wt%) SBA	Salinity (NaCl wt%) (optimal)	IFT(dyne/cm)
0.727%	0.273%	2%	6.75%	2.55×10^{-4}
0.625%	0.375%	2%	8.00%	3.38×10^{-4}

Viscosity measurements. Gels or viscous phases are detrimental to the efficient propagation of the chemical slug through the reservoir. Presence of viscous and/or gel phases are determined by visual inspection during salinity scans by tipping the tubes and observing the fluidity of the interfaces and sometimes inverting the tubes to determine the presence of gels.

Viscosities of middle phase microemulsions were measured to verify the visual inspections. Large samples were prepared to obtain larger volumes of the microemulsion phase for measurement. Viscosities at three salinities that bracket the optimal salinity of a formulation containing Petrostep S1 and Petrostep S2 are shown in Figure 17. Viscosity of microemulsion phases were about 20 cp, two to three times the viscosity of the Wahrman crude oil at reservoir temperature (8.16 cp).

Summary. Phase behavior studies with the Wahrman crude oil narrowed the focus to two surfactant systems: (1) 0.625% Petrostep S1, 0.375% Petrostep S2, 2% SBA and (2) 0.89% Alfoterra 123-8S, 0.11% Petrostep S2, 2.5% SBA, 0.3% NaOH. Both these systems produced good fluid microemulsion phases with optimal solubilization ratios around 10 which showed satisfactory results of viscosity and IFT measurements. However, these chemical systems at optimal salinities were not one-phase solutions before mixing with the crude oil. Further testing will be required to identify chemical formulations that meet all of the criteria of an efficient system for the Wahrman crude oil.

The influence of several of the parameters for formulating a chemical system on the phase behavior results such as optimal salinity and solubilization parameters was established. These trends will expedite future work with the Wahrman crude oil and the other crude oils from the leases under study.

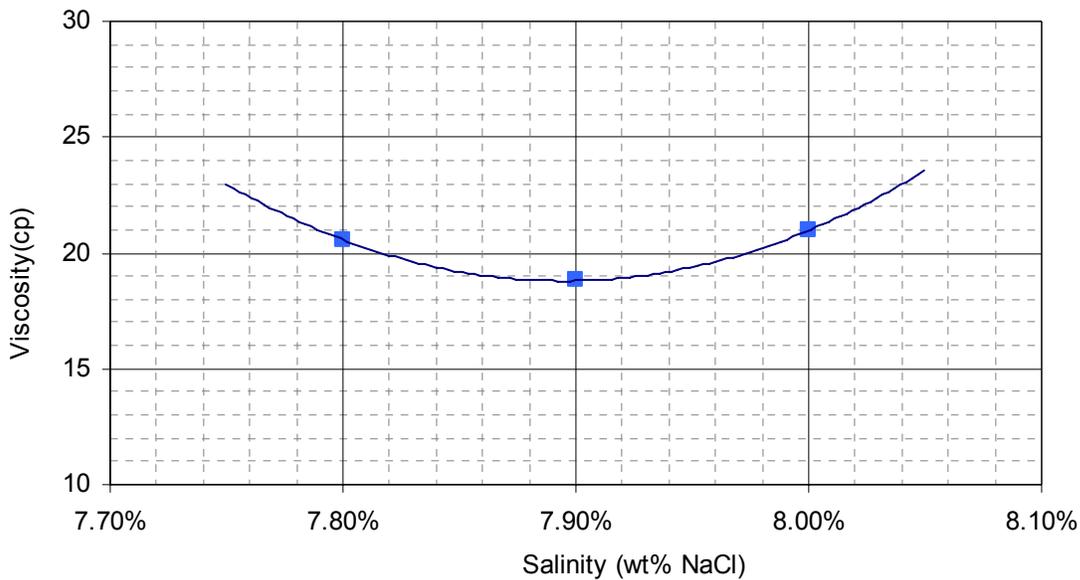


Figure 17 - Viscosity of micro-emulsion phase at different salinity for surfactant system: 0.625% Petrostep S1, 0.375% Petrostep S2, 2% SBA after equilibrating 8 days. Measured at a shear rate of 30 sec^{-1} .

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