

Characterization of Phase and Emulsion Behavior, Surfactant Retention, and Oil Recovery for
Novel Alcohol Ethoxycarboxylate Surfactants

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ABSTRACT

This semi-annual technical progress report describes work performed at Clark Atlanta University under DOE Grant No. DE-FG26-97FT97278 during the period April 01, 1998 to October 01, 1998 which covers the second six months of the project. Presently work is in progress at the EOR Laboratory, Clark Atlanta University (CAU), to characterize phase and emulsion behavior for a novel, hybrid (ionic/non-ionic), alcohol ethoxycarboxylate surfactant (NEODOX 23-4 from Shell Chemical Company). During this reporting period, salinity scans were completed for 0, 5, 10, 20, 50, 100, 250, 500, 1000, 2000, 3000, 4000, 5000, and 6000 mM salt concentrations at 20, 25, and 30 °C to identify optimal salinity intervals in which all three phases coexist for this surfactant. Temperature scans were also performed at 20 mM salt concentration for various surfactant concentrations ranging from 0 to 60 weight percent at temperatures ranging from 5 to 50 °C to identify optimal surfactant concentration and temperature intervals in which all three phases coexist. This resulted in an "alpha" curve with an interval of temperature in which all three phases coexisted. Presently, temperature scans are being repeated at 100, 250, 500, 1000, and 5000 mM salt concentrations to see whether increase in salt concentration has any effect on the temperature interval. This will provide us better understanding and experimental control of the many variables involved in this research in the future. Following completion of the temperature scans, phase studies will be conducted at CAU, and coreflooding experiments at the facility of our industrial partner, Surtek, Golden, CO.

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EXECUTIVE SUMMARY

In this semi-annual report, the work performed under DOE Grant No. DE-FG26-97FT97278 during the period April 01, 1998 to October 01, 1998 which covers the second six months of the project is described and the major accomplishments are highlighted summarizing the most important research results.

Many surfactants will simultaneously form three coexisting liquid phases when mixed with oil and water within a well defined salinity and temperature interval. At the mean temperature of this interval one finds--for thermodynamic reasons--a maximum of the mutual solubility between water and oil. The middle phase, which contains the greatest concentration of surfactant, is called a microemulsion. Typically the microemulsion reduces the interfacial tension between oil and water by about three or four orders of magnitude. These ultralow tensions allow the oil-rich (top) phase to be pushed through porous media by the aqueous (bottom) phase, and the three liquid phases flow as macroemulsions. The microemulsion phase can also form two-phase, or three-phase, macroemulsion structures or morphologies when mixed with either one, or both, of the other two phases, depending on the temperature, relative volumes of the phases, and other factors. Formation of a wrong morphology or inversion from the desired morphology to the wrong morphology is also possible. Investigation of these morphologies, when they occur, and their flow through porous media are of considerable interest in Enhanced Oil Recovery (EOR).

Selection of effective surfactants and a better understanding of the formation of their emulsions with crude oils are of paramount importance for progress towards EOR. Alcohol ethoxycarboxylates (AEC) are novel and are hybrids exhibiting both ionic (carboxylate) and non-ionic (ethoxy) characteristics depending on the conditions of the applications. These surfactants have not yet been tested for their suitability in enhanced oil recovery. The objectives of this proposal are to characterize the phase and emulsion behavior, and surfactant retention and oil recovery capabilities of novel alcohol ethoxycarboxylate surfactants. The successful accomplishment of the objectives will provide a detailed and unique database for alcohol ethoxycarboxylate surfactants for oil recovery. If the surfactant is found effective, the database would be of immense value for developing cost-effective surfactant flooding processes.

Presently work is in progress at the EOR Laboratory, Clark Atlanta University (CAU), to characterize phase and emulsion behavior for NEODOX (23-4) alcohol ethoxycarboxylate surfactant. Temperature scans at various salt concentrations are being performed to identify the optimal temperature interval in which all three phases coexist, and to investigate the effect of increase in salt concentration on the temperature interval. Following completion of the temperature scans, phase studies will be conducted at CAU, and coreflooding experiments will be conducted at the facility of our industrial partner, Surtek, Golden, CO.

INTRODUCTION

The Department of Energy has been sponsoring fundamental and applied research in the enhanced oil recovery area. Recently, the DOE 's National Petroleum Technology Office, Tulsa, Oklahoma, has been interested in research focussing on the use of novel surfactants for effective oil recovery. If better surfactants can be found, the potential for surfactant flooding is great.

After an oil well loses its self flow (primary recovery by natural forces), and secondary flow (secondary recovery by pressurization using water flood and gas), approximately 2/3 of the original oil remains in the reservoir. This accounts for an estimated 327 billion barrels in the United States. Much of the remaining oil can be collected by enhanced oil recovery techniques such as surfactant flooding. Effective emulsifying surfactants and a better understanding of the formation of their emulsions with the crude are of paramount importance to economically recover the abundant residual oil in reservoirs.

Mixtures of water, oils, amphiphiles, and salt may separate into three coexisting liquid phases within a well defined temperature interval, the mean temperature of which may depend sensitively but systematically on the nature of the oil and the amphiphile and on the salt concentration. At the mean temperature of this interval one finds--for thermodynamic reasons--a maximum of the mutual solubility between water and oil and a minimum of the interfacial tension between the aqueous and the oil-rich phase. Both of these properties are of considerable interest for both research and industrial application.

Emulsions and other fluid-fluid dispersions have long been used in many different commercial products and processes, such as liquid-liquid extractions, foods, medicines, paints, cosmetics, and the production and transport of petroleum. One of the most novel applications is the use of dispersions of supercritical CO₂ to improve oil recoveries from miscible flood enhanced oil recovery [1]. Each of these applications depends on the formation of a dispersion of the desired morphology, for example, an "oil-in-water" or a "water-in-oil" emulsion. Formation of the "wrong" morphology or inversion from the desired morphology to the "wrong" morphology causes the product or process to fail.

Many, if not most, of the two-phase emulsions commonly encountered at various temperatures in systems of nonionic surfactant, oil, and water form in systems that also can form [2] triconjugate oil-rich top phase (T), water-rich bottom phase (B), and middle-phase microemulsion (M). For such systems, two-phase emulsions may form in any of the various two-phase regions [3-4] that surround a stack of tie triangles in the triangular-prismatic phase diagram. For temperatures between lower and upper critical points T_{lc} and T_{uc} --the range over which phases T, M, and B coexist--there are three two-phase regions and thus six nonmultiple, two phase emulsion morphologies [5]. For such systems the plotting of phase boundaries and of boundaries between different emulsion morphologies in accordance with the phase rule introduces a rigorous way of showing how the occurrence of each of the six two-phase morphologies depends on temperature and composition. For the limiting tie lines (i.e., the sides of the tie triangle), where the three-phase and two-phase regions

meet, the six two-phase morphologies are formed by the triconjugate phases taken pairwise: T/M, M/T; B/T, T/B; and M/B, B/M [6].

One of the widely observed phenomena of emulsion inversion is inversion hysteresis [7]. For example, the phase volume fractions at which the inversions A/B to B/A and B/A to A/B occur are somewhat different. If the pair of phase volume fraction points at which the pair of conjugate inversions occur are measured at different temperatures, the resulting measurements form a pair of inversion hysteresis lines in phase volume fraction-temperature space. The fractional phase volume at which inversion occurs is believed to depend on many different factors, such as the temperature, structure and concentration of the emulsifying amphiphile, salinity, and "oil" composition. The factors that control dispersion morphology and inversion are now well understood [6]. Qualitatively, dispersion inversion has long seemed to be a catastrophic event. The properties of an A/B (A-in-B) dispersion are very different from the properties of a B/A (B-in-A) dispersion, and the inversion from one morphology to the other is often abrupt and irreversible. Inversion is marked by a sudden change in the physical properties (e.g., electrical conductivity) of the dispersion, indicating an abrupt change in the structure of the dispersion [6]. Smith et al. [6,8-10] demonstrated for several oil/water/surfactant systems that elementary catastrophe theory provides a unifying framework to explain these phenomena in systems of variable oil/water ratio and amphiphile concentration at constant temperature and pressure. Smith et al. [2] hypothesized that wherever a phase critical point occurs, there will be a "critical point" for dispersion inversion, also; that is, pairs of dispersion inversion hysteresis lines meet at a point, and this point coincides with the critical point for the two phases of the dispersion.

Recently, experiments were performed [6] for the surfactant/oil/water system $C_6H_{13}(OC_2H_4)_2OH/n$ -tetradecane/aqueous 10 mm NaCl at temperatures from 298 K down to 285 K, near the lower critical end-point temperature ($T_{lc} = 283.6$ K). Morphologies and phase volume fractions at which inversion occurred were determined for (macro)emulsions formed by the middle-phase microemulsion (M) and water-rich bottom phase (B) by means of electrical conductivity measurements. The M/B and B/M morphologies and their inversion hysteresis lines were found to conform to the dispersion morphology diagram previously postulated by Smith et al. [2]; that is, within experimental uncertainties, the two emulsion inversion lines in phase volume-temperature space met at a "critical point" that coincided with the lower critical end point for the phases.

The phase behavior, interfacial tension, and solution physical parameters only define a single interface in the oil recovery process, the water-oil interface. In an oil and water filled reservoir system, two other interfaces exist, the oil-rock and water-rock interface. The effect of these two interfaces on the oil recovery process are just as important, if not more important, than the water-oil interface [11-14]. Linear and radial corefloods are used to test the effect of the two rock interfaces on the oil recovery potential of the surfactant systems. Linear corefloods provide adsorption coefficients of chemicals onto the rock surface and define fluid rheology as the ability of the solution to flow through porous media. Radial corefloods to estimate oil recovery potential are preferable to linear corefloods for a number of reasons [11-16]. The pore volume of a radial core is greater than that of a linear core, making measurement of the injected and produced fluids volumes more accurate.

The flow patterns in a radial core allow expansion of the interface between the injected surfactant and the fluid in the core to occur in a similar manner as in a vertical well in the field. When fractional pore volumes of chemical are injected, chemical banks thin in a manner analogous to a vertical well in the field allowing dispersion, dilution, and other potentially deleterious effects to occur.

The Shell Chemical Company produces NEODOL ethoxylates that are non-ionic surfactants. These surfactants are relatively inexpensive. A number of them have been tried in oil recovery. NEODOX Alcohol Ethoxycarboxylates (AEC) have recently been produced by the Shell Chemical Company by an oxidative reaction of alcohol ethoxylate with air or oxygen and have not yet been tested for their suitability in oil recovery. These surfactants are >90% purity. These novel surfactants are hybrid exhibiting both ionic (carboxylate) and non-ionic (ethoxy) characteristics depending on the conditions of the applications. They exhibit good alkaline stability, electrolyte tolerance, good emulsification, and temperature stability that make them highly suitable for enhanced oil recovery. The ionic part of these hybrid surfactants would make them adsorb less on rocks. Emulsions formed by these surfactants can easily be broken by adjusting the pH in order to recycle the oil, water, and the surfactant. These surfactants are novel and Shell does not have technical data such as salinity scans, temperature-surfactant concentration plots, and adsorption coefficient for these surfactants.

This project seeks to characterize novel alcohol ethoxycarboxylate (AEC) surfactants that are commercially available. Detailed information on optimal salinity, temperature, adsorption coefficient, oil recovery, and emulsion morphologies for these surfactants is needed to evaluate their performance in terms of cost-effectiveness, adsorptivity, and oil recovery efficiency in flooding processes. The specific objectives are:

- 1) Perform salinity and temperature scans to obtain optimal salinity and temperature at which all three phases coexist.
- 2) Perform emulsion morphology and coreflooding experiments for the oil/water/surfactant system that gives the best results in objective 1.

Experiments and analyses are being carried out to meet the project objectives. Objectives 1 and phase work will be accomplished by CAU. Coreflooding experiments will be accomplished by Surtek, our industrial partner in this project. The successful accomplishment of the objectives will provide a detailed and unique database for ethoxycarboxylate surfactants for oil recovery. If the surfactant is found effective, the database would be of immense value for developing cost-effective surfactant flooding processes.

PROGRESS TO DATE

The hybrid surfactant research program discussed above began at Clark Atlanta University in October 1997. Laboratory space to set up the proposed surfactant characterization measurement system in the Research Science Center was made available. A Ph.D. student in Chemistry was identified and is supported as a Graduate Research Assistant in this project. Her contribution towards this project will form her Ph.D. thesis. The test matrix to perform salinity and temperature scans was

established. Supply requests to obtain refined hydrocarbon, surfactant, and crude were processed, and supplies obtained. Temperature bath control unit to perform temperature scans was obtained on loan from Federal Energy Technology Center, Morgantown, WV. The setting up of the temperature control unit and associated chiller with water circulation line was completed. Tests were conducted on several hybrid surfactants, and NEODOX (23-4) was identified as one of two best surfactants for future experimental work that yielded almost equal volumes of top, middle, and bottom phases when mixed with oil and water. Current literature in the subject area, and modeling efforts that were established in previous studies to predict electrical conductivities and inversion phenomena were reviewed. These activities resulted in a student poster paper and a conference paper that were presented at the Sixth Annual Historically Black Colleges and Other Minority Institutions Symposium, April 28-29, 1998, Ocean City, MD. Recently, salinity scans were completed, and temperature scans are in progress.

WORK PERFORMED DURING THIS REPORTING PERIOD

More tests at several temperatures (25, 30, 35, and 40 EC) to select the optimum NEODOX surfactant were continued from the previous reporting period. NEODOX (23-4) was identified as the most suitable surfactant that yielded the best proportion in volume for top, middle, and bottom phases when mixed with oil and water. Following the selection of this surfactant, temperature and salinity scans were performed at CAU to identify the optimal salinity and temperature, and the temperature and salinity intervals in which all three phases coexisted. About 10 samples of equal volume of crude and water with initially 2% concentration of surfactant were tested for optimal salinity by varying the salinity with NaCl from 1 to 10%, or greater. The temperature of the water bath in these experiments was set at 20, 25, 30, and 35 EC. Following the salinity experiments, measurements were made with 20mM salinity for various surfactant concentrations. The small salt concentration may be used to improve the sensitivity and accuracy of the conductivity measurements by increasing the conductivity differences between the conjugate phases of the emulsions. The resulting temperature vs. surfactant concentration plot yielded a typical alpha shape curve that demonstrated the existence of 1, 2, or 3 phases in the system. More temperature scans to high salt concentrations are being performed to investigate the effect of increase in salt concentration on the temperature interval. The best oil/water/surfactant system defined by the above phase work will then be studied for core flooding, and emulsion morphologies. Core flooding measurements will be conducted by our industrial partner, Surtek, CO, to characterize surfactant retention and oil recovery. Measurements for emulsion morphologies will be performed by CAU. Briefly, electrical conductivities will be measured for top/bottom, top/middle, and middle/bottom phases that form the sides of the tie triangle diagram by mixing measured volumes of the pre-equilibrated phases.

OUTCOMES TO DATE

1. Chen, J., Sampath, R., Moeti, L., and Smith, D., Investigation of Phase and Emulsion Behavior for Novel Alcohol Ethoxycarboxylate Surfactants, Technology Transfer Session, Historically Black Colleges/Universities and Other Minority Institutions Annual Symposium, April 28-29, 1998, Ocean City, MD.

2. Sampath, R., Moeti, L., Smith, D., and Pitts, M., Characterization of Surfactants for Enhanced Oil Recovery, Technology Transfer Session, Historically Black Colleges/Universities and Other Minority Institutions Annual Symposium, April 28-29, 1998, Ocean City, MD.

PLANS FOR THE NEXT REPORTING PERIOD

Phase work is scheduled to be performed at CAU, and coreflooding experiments at the facility of our industrial partner, Surtek, Golden, CO in the next reporting period.

SUMMARY AND CONCLUSIONS

The project is progressing well. During this reporting period, salinity scans were completed for a range of salt concentrations at several temperatures to identify optimal salinity intervals in which all three phases coexisted. Temperature scans were also performed to identify optimal surfactant concentration and temperature intervals in which all three phases coexist. Presently, more temperature scans from low to high salt concentrations are being performed to see whether increase in salt concentration has any effect on the temperature interval.

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