CHARACTERIZATION OF PHASE AND EMULSION BEHAVIOR, SURFACTANT RETENTION, AND OIL RECOVERY FOR NOVEL ALCOHOL ETHOXYCARBOXYLATE SURFACTANTS

Final Technical Report

For the Period October 01, 1997 to August 31, 2001

Lebone T. Moeti (PI) and Ramanathan Sampath (CoPI)

September 28, 2001

Grant No. DE-FG26-97FT97278

For

AAD Document Control
U.S. Department of Energy
National Energy Technology Laboratory
P.O. Box 10940, MS 921-143
Pittsburgh, PA 15236-0940

By

Department of Engineering
Clark Atlanta University
Atlanta, GA 30314
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturers, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
CHARACTERIZATION OF PHASE AND EMULSION BEHAVIOR, SURFACTANT RETENTION, AND OIL RECOVERY FOR NOVEL ALCOHOL ETHOXYCARBOXYLATE SURFACTANTS

ABSTRACT

This final technical report describes work performed under DOE Grant No. DE-FG26-97FT97278 during the period October 01, 1997 to August 31, 2001 which covers the total performance period of the project. During this period, detailed information on optimal salinity, temperature, emulsion morphologies, effectiveness for surfactant retention and oil recovery was obtained for an Alcohol Ethoxycarboxylate (AEC) surfactant to evaluate its performance in flooding processes. Tests were conducted on several AEC surfactants and NEODOX (23-4) was identified as the most suitable hybrid 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 to identify the optimal salinity and temperature, and the temperature and salinity intervals in which all three phases coexisted. NEODOX 23-4 formed three phases between 4 and 52.5°C. It formed an aqueous rich microemulsion phase at high temperatures and an oleic rich microemulsion phase at low temperatures - a characteristic of the ionic part of the surfactant. The morphology measurement system was set-up successfully at CAU. The best oil/water/surfactant system defined by the above phase work was then studied for emulsion morphologies. Electrical conductivities were measured for middle and bottom phases of the NEODOX 23-4/dodecane/10mM water system and by mixing measured volumes of the middle phase into a fixed volume of the bottom phase and vice versa at room temperature. Electrical conductivity of the mixture decreased as the fraction of volume of the middle phase was increased and vice versa. Also inversion phenomena was observed. These experiments were then repeated for bottom/middle (B/M) and middle/bottom (M/B) conjugate pair phases at 10, 15, 25, 30, 35, 40, and 45°C. Electrical conductivity measurements were then compared with the predictions of the conductivity model developed in this project. The M/B and B/M morphologies and their inversion hysteresis lines conformed to the previously postulated dispersion morphology diagram; that is, within experimental uncertainties, the two emulsion inversion lines in phase volume-temperature space met at a critical point that coincided with the upper critical end point for the phases. Coreflooding measurements were performed by our industrial partner in this project, Surtek, Golden, CO which showed poor hydrocarbon recovery (38.1%) for NEODOX 23-4. It was also found that NEODOX 23-4 surfactant adsorbed too much to the rock (97.1% surfactant loss to the core), a characteristic of the non-ionic part of the surfactant.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>EXECUTIVE SUMMARY</td>
<td>1</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>2</td>
</tr>
<tr>
<td>EXPERIMENTAL METHODS</td>
<td>4</td>
</tr>
<tr>
<td>RESULTS AND DISCUSSIONS</td>
<td>11</td>
</tr>
<tr>
<td>OUTCOMES OF THE PROJECT</td>
<td>25</td>
</tr>
<tr>
<td>CONCLUSIONS AND SIGNIFICANCE</td>
<td>26</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>26</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>26</td>
</tr>
</tbody>
</table>
EXECUTIVE SUMMARY

In this semi-annual report, the work performed under DOE Grant No. DE-FG26-97FT97278 during the period October 01, 1997 to August 31, 2001 which covers the total performance period of this project 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 surfactants 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 research were to characterize the phase and emulsion behavior, and surfactant retention and oil recovery capabilities of novel alcohol ethoxycarboxylate surfactants.

During the performance period, tests were conducted on several AEC surfactants and NEODOX (23-4) was identified as the most suitable hybrid 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 to identify the optimal salinity and temperature, and the temperature and salinity intervals in which all three phases coexisted. The best oil/water/surfactant system defined by the above phase work was then studied for emulsion morphologies. Electrical conductivities were measured for middle and bottom phases of the NEODOX 23-4/dodecane/10mM water system and by mixing measured volumes of the middle phase into a fixed volume of the bottom phase and vice versa. Also inversion phenomena was observed. Electrical conductivity measurements were then compared with the predictions of the conductivity model developed in this project. Coreflooding measurements were performed by our industrial partner in this project, Surtek, Golden, CO which showed poor surfactant and hydrocarbon recovery for NEODOX 23-4.
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 focusing 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_c and T_u—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 \( \text{C}_{13}\text{H}_{27} \text{(OC}_{2}\text{H}_{4})_{2}\text{OH/n-tetradecane/aqueous 10 mM Nace} \) at temperatures from 298 K down to 285 K, near the lower critical end-point temperature \( (T_c = 283.6 \text{ K}) \). 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 sought to characterize novel alcohol ethoxycarboxylate (AEC) surfactants that are commercially available. In this study, detailed information on optimal salinity, temperature, adsorption coefficient, oil recovery, and emulsion morphologies for these surfactants were obtained and their performance in terms of cost-effectiveness, adsorptivity, and oil recovery efficiency in flooding processes were evaluated. The specific objectives were:

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 were carried out to meet the project objectives. Objectives 1 and emulsion morphology work in Objective 2 were accomplished by CAU. Coreflooding experiments were completed by Surtek, our industrial partner in this project. The successful accomplishment of the objectives provides a detailed and unique database to assess the potentials of ethoxycarboxylate surfactants for oil recovery. It was found that the emulsion morphologies for conjugate pair phases and their inversion hysteresis lines conformed to the previously postulated dispersion morphology diagram. It was also found that NEODOX 23-4 surfactant showed lower surfactant and hydrocarbon recovery in coreflooding processes.

EXPERIMENTAL METHODS

This study was unique in that detailed information on optimal salinity, temperature, emulsion morphologies, effectiveness for surfactant retention and oil recovery was obtained for an Alcohol Ethoxycarboxylate (AEC) surfactant to evaluate its performance in flooding processes. Measurements for optimal salinity, temperature, emulsion morphologies were accomplished by CAU. Coreflooding experiments were completed by Surtek, our industrial partner in this project.

CAU Measurements

AEC is a hybrid surfactant that exhibits both ionic and non-ionic characteristics. Typical NEODOX AECs are: NEODOX 1-4, NEODOX 23-4, NEODOX 23-6, NEODOX 25-6, NEODOX 25-11, NEODOX 45-6, NEODOX 91-5, and NEODOX 91-7. These surfactants differ in critical
micelle concentration, foaming and wetting time. Tests were conducted at several temperatures (25, 30, 35, and 40°C) on these surfactants to identify a surfactant that yields almost equal volumes of top, middle, and bottom phases when mixed with oil (dodecane) and water. 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 dodecane and water.

Following the selection of this surfactant, salinity scans were performed at CAU to examine the ionic effect of the surfactant and to identify the optimal salinity and temperature in which all three phases coexisted. About 10 samples of equal volume of dodecane 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°C.

Following the salinity experiments, measurements were made with the optimal salinity for various surfactant concentrations to examine the non-ionic effect of the surfactant and to identify the optimal temperature in which all three phases coexisted. The small salt concentration was used to improve the sensitivity and accuracy of the conductivity measurements by increasing the conductivity differences between the conjugate phases of the emulsions.

Following the optimal salinity and temperature scans, the morphology measurement system was set up as shown in Figures 1 and 2. Only a brief description of the measurement system and the experimental procedures involved is provided below. More details can be obtained elsewhere [6,17]. A typical experiment involved gravimetric preparation of a mixture of the surfactant, dodecane, and water (brine solution); equilibration of the mixture in a large, thermostated buret until phase separation was complete (at least 48 hours); and careful separation of the layers. A Princeton Applied Research Model 124A lock-in amplifier and a radiometer conductivity cell with platinized electrodes were used to measure the conductances. Emulsion volume fractions were changed by additions from a buret of one of the conjugate phases to the sample, which was contained in a jacketed, thermostated beaker. The sample was mixed thoroughly by continuous magnetic stirring and circulation through a pump. The conductivity of the emulsions was measured 5 minutes after each phase addition. The measurement frequency was 2 kHz, at which electrode polarization effects were negligible for conductivities smaller than 100 mS.cm⁻¹. The temperature was controlled within 0.1°C by a Lauda M2 thermostat bath.

**Surtek Measurements**

The best dodecane/surfactant/water chemical system selected by CAU was tested using coreflooding techniques to measure the effectiveness for surfactant retention and oil recovery in flooding processes.

Linear corefloods were performed to determine the adsorption of chemical onto the rock surface and the amount of hydrocarbon recovery. Surfactant was injected into brine and dodecane saturated core (Figure 3). The porous media was Berea sandstone. Surfactant solutions were injected at different injection rates to define fluid rheology as the ability of the solution to flow
through porous media. Oil recovery was determined by a mass balance and by modified Dean-Stark extraction of the core after the displacement studies. Effluent sample surfactant concentration was analyzed for surfactant concentration with the adsorption determined by mass balance.

Radial corefloods were conducted to estimate the additional amount of oil production due to the injection of surfactant solution into core in the radial direction (Figure 4). To estimate the potential oil recovery, two volumes of each surfactant solution was injected for a total of four radial corefloods. A polymer (polyacrylamide) was added to the surfactant solution for mobility control. Surfactant was injected into brine and dodecane saturated core. Effluent sample surfactant concentration was analyzed to determine adsorption and to facilitate analysis of the oil recovery potential.
Figure 1. Preparation of the Top, Middle, and Bottom Phases
Figure 2. Conductivity Measurement System
Figure 3. Linear Coreflood Measurement System
Figure 4. Radial Coreflood Measurement System
RESULTS AND DISCUSSIONS

CAU Results

Figure 5 presents the results of the tests conducted at 20EC on several AEC surfactants to identify the best surfactant(s) for emulsion experiments that yield the best proportion in volume for top, middle, and bottom phases when mixed with oil and water. It can be seen that NEODOX 23-4 gives the best quantity of all the three phases when mixed with dodecane and water.

Figure 6 presents the results of the salinity scans conducted at 20EC to identify the optimal salinity in which all three phases coexist for this surfactant. It can be seen that 10mM NaCl concentration in water gives the best quantity of all the three phases when mixed with dodecane and water.

Figure 7 presents the results of the temperature scans conducted with 10mM NaCl solution to identify the optimal temperature in which all three phases coexist for this surfactant. As can be seen, the temperature scans resulted in a temperature-surfactant concentration plot that yields a typical alpha shape curve that demonstrates the existence of 1, 2, or 3 phases in the system between the temperature range of 4 and 52.5EC. It forms aqueous rich microemulsion phase at high temperatures and oleic rich microemulsion phase at low temperatures - a characteristic of the ionic part of the surfactant.

Figures (8-15) present the results of the electrical conductivity measurements conducted at 10,15,20,25,30,35,40, and 45EC on the bottom and middle conjugate pair phases of the NEODOX 23-4/dodecane/10mM water chemical system. As can be seen, electrical conductivity of the mixture decreases as the fraction of volume of the middle phase was increased and vice versa. Also inversion phenomena was observed except for the last case. Because the conductivities of the two phases (Figure 15) are much closer at this temperature, the change of emulsion conductivity at inversion is much smaller than that observed at other temperatures tested here. These experiments were then repeated for top/bottom and top/middle conjugate pair phases. The conductivity of the top phase was found negligible, much below the measurement threshold of the experimental system. No significant changes were observed in the measured conductivity to changes in incremental volume of the top phase in the conjugate pair experiments.

Modeling efforts that were established in previous studies [6,17-19] to predict electrical conductivities and inversion phenomena were reviewed. A theoretical model to predict the conductivity measurements using Maxwell equations [20] was developed in this study. Electrical conductivity measurements were then compared with the predictions of the conductivity model. As can be seen in Figures (8-15), a good agreement was obtained between the predicted emulsion conductivities and the measured values. This provides considerable confidence that the morphology assignments are correct.
Figure 5. Surfactant vs. Phase volume at 20°C
Figure 6. Salinity Scans at 20°C

- **Bottom**
- **Middle**
- **Top**

**NaCl concentration in H₂O(mM)**

**B, M, T Layer (ml)**

**Figure 6. Salinity Scans at 20°C**
Figure 7. Alpha Diagram
Figure 8. Conductivities at 10°C of Emulsions of the Bottom and Middle Phases of Neodox 23-4/Dodecane/aqueous 10 mM NaCl
Figure 9. Conductivities at 15°C of Emulsions of the Bottom and Middle Phases of Neodox 23-4/Dodecane/aqueous 10 mM NaCl
Figure 10. Conductivities at 20°C of Emulsions of the Bottom and Middle Phases of Neodox 23-4/Dodecane/aqueous 10 mM NaCl
Figure 11. Conductivities at 25°C of Emulsions of the Bottom and Middle Phases of Neodox 23-4/Dodecane/aqueous 10 mM NaCl
Figure 12. Conductivities at 30°C of Emulsions of the Bottom and Middle Phases of Neodox 23-4/Dodecane/aqueous 10 mM NaCl
Figure 13. Conductivities at 35°C of Emulsions of the Bottom and Middle Phases of Neodox 23-4/Dodecane/aqueous 10 mM NaCl
Figure 14. Conductivities at 40°C of Emulsions of the Bottom and Middle Phases of Neodox 23-4/Dodecane/aqueous 10 mM NaCl
Figure 15. Conductivities at 45°C of Emulsions of the Bottom and Middle Phases of Neodox 23-4/Dodecane/aqueous 10 mM NaCl
Figure 16. Hysteresis lines between M/B and B/M inversions of the system Neodox 23-4/Dodecane/aqueous 10 mM NaCl
# Table1: Temperatures and Volume Fractions of Inversions

<table>
<thead>
<tr>
<th>Temperature EC</th>
<th>$Q_{B/M:\overline{M}/B}$</th>
<th>$Q_{M/B:\overline{B}/M}$</th>
<th>$aQ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.81</td>
<td>0.77</td>
<td>0.04</td>
</tr>
<tr>
<td>15</td>
<td>0.785</td>
<td>0.75</td>
<td>0.035</td>
</tr>
<tr>
<td>20</td>
<td>0.755</td>
<td>0.725</td>
<td>0.03</td>
</tr>
<tr>
<td>25</td>
<td>0.72</td>
<td>0.69</td>
<td>0.03</td>
</tr>
<tr>
<td>30</td>
<td>0.678</td>
<td>0.65</td>
<td>0.028</td>
</tr>
<tr>
<td>35</td>
<td>0.645</td>
<td>0.62</td>
<td>0.025</td>
</tr>
<tr>
<td>40</td>
<td>0.61</td>
<td>0.59</td>
<td>0.02</td>
</tr>
<tr>
<td>45</td>
<td>0.565</td>
<td>0.56</td>
<td>0.005</td>
</tr>
<tr>
<td>52.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.000</td>
</tr>
</tbody>
</table>
The temperatures and phase volume fractions (Q) at which inversions were found are summarized in Table 1. These data are plotted in Figure 16, along with the phase upper critical end point (Q_{uc} = 0.5, T_{uc} = 52.5^\circ C). In drawing Figure 16, it was assumed that the emulsion inversion upper critical end point occurred at Q_{iuc} = Q_{uc}, T_{iuc} = T_{uc}. As illustrated by Figure 16, this is plausible, and perhaps a rigorously correct, assumption. With this assumption, the inversion hysteresis lines of Figure 16 closely resemble to the previously postulated dispersion morphology diagram [18-19]; i.e., the M/B and B/M inversion hysteresis lines in phase volume-temperature space meet at a critical point that coincided with the upper critical end point for the phases.

**Surtek Results**

Surtek, our industrial partner in this project, conducted a detailed analysis of the data obtained in their coreflooding measurements. Their findings are as follows: NEODOX 23-4 showed poor oil recovery (38.1%) and very high surfactant loss to the core (97.1%) in Radial Core Flooding experiments. Oil Recovery in Linear Corefloods injecting large pore volumes of NEODOX 23-4 resulted in high oil recovery, however, high retention of the surfactant (44.5%) was again observed.

**OUTCOMES OF THE PROJECT**

Ms. Junli Chen, a graduate student from the Department of Chemistry, CAU, was identified and supported as a Graduate Research Assistant in this project for over two years, and the student recently graduated.

Several experiments and theoretical analyses were conducted in this project and the experimental results were compared with predictions. These activities resulted in several conference presentations and are listed below.


CONCLUSIONS AND SIGNIFICANCE

Detailed information on optimal salinity, temperature, emulsion morphologies, effectiveness for surfactant retention and oil recovery was obtained for an Alcohol Ethoxycarboxylate (AEC) surfactant to evaluate its performance in flooding processes. Tests were conducted on several AEC surfactants and NEODOX (23-4) was identified as the most suitable hybrid surfactant that yielded the best proportion in volume for top, middle, and bottom phases when mixed with oil and water. Temperature and salinity scans were then performed to identify the optimal salinity and temperature, and the temperature and salinity intervals in which all three phases coexisted. NEODOX 23-4 formed three phases between 4 and 52.5°C. It formed aqueous rich microemulsion phase at high temperatures and Oleic Rich microemulsion phase at low temperatures. The best oil/water/surfactant system defined by the above phase work was then studied for emulsion morphologies. Electrical conductivities were measured for middle and bottom phases of the NEODOX 23-4/dodecane/10mM water system and by mixing measured volumes of the middle phase into a fixed volume of the bottom phase and vice versa at 10, 15, 20, 25, 30, 35, 40, and 45°C. Electrical conductivity of the mixture decreased as the fraction of volume of the middle phase was increased and vice versa. Also inversion phenomena was observed. Electrical conductivity measurements were then compared with the predictions of the conductivity model developed in this project. The M/B and B/M morphologies and their inversion hysteresis lines conformed to the previously postulated dispersion morphology diagram; that is, within experimental uncertainties, the two emulsion inversion lines in phase volume-temperature space met at a critical point that coincided with the upper critical end point for the phases. Coreflooding measurements were performed by our industrial partner in this project, Surtek, Golden, CO which showed poor surfactant and hydrocarbon recovery for NEODOX 23-4.

ACKNOWLEDGMENTS

This work was supported under FETC/DOE grant No. DE-FG26-97FT97278. Technical discussions provided by Mr. Purna Halder, National Petroleum Technology Office, Tulsa, Oklahoma, and Dr. Duane Smith, National Energy Technology Laboratory, Morgantown, WV are acknowledged. Financial support provided to Junli Chen in the form of a research assistantship is gratefully acknowledged.

REFERENCES


17. Johnson, G. K., A Study of Three-Phase Emulsion Behavior, Ph.D. Dissertation, 1993, West Virginia University, Morgantown, WV.

