

# CHARACTERIZATION OF SURFACTANTS FOR ENHANCED OIL RECOVERY

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## ABSTRACT

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).

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. Temperature and salinity scans are planned at CAU to identify the optimal salinity and temperature, and the temperature and salinity intervals in which all three phases coexist for this surfactant. Core flooding measurements will be conducted by our industrial partner, Surtek, CO, to characterize surfactant retention and oil recovery. In this paper, details of our previous work and results of the current activities in the subject matter are presented.

## INTRODUCTION

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 CO<sub>2</sub> 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. [6,8,10-11] 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.

## RELATED RESEARCH

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.

Details of the emulsion measurement system, its components, and basic methods employed for calibration and data analysis can be obtained elsewhere [6,12]. Briefly, oil, water, and surfactant were mixed in ratios that resulted in three conjugate phases coexisting at the temperature of interest. Electrical conductivities were measured for middle/bottom and bottom/middle phases by mixing measured volumes of the pre-equilibrated phases. Emulsion morphologies were identified by comparison of the measured emulsion conductivities with conductivities predicted by equations that contain no adjustable parameters [6,12-14]. Inversions were detected as abrupt, discontinuous jumps of the measured emulsion conductivities between the two theoretical curves (Figure 1). Experiments were repeated for several temperatures close to the lower critical end-point temperature,  $T_{lc}$ . Measured phase conductivities for bottom and middle phases, and temperature data were used to fit a critical scaling theory equation [6] to obtain  $T_{lc}$  (Figure 2). The emulsion inversion phase volume fraction and temperature data were then plotted and the critical point for emulsion inversion was found to coincide with the phase critical point,  $T_{lc}$  (Figure 3), thus proving the earlier hypothesis proposed by Smith et al. [2]. These findings are important for progress towards effective surfactant flooding and the information was disseminated to the researchers in the field in a paper [6] published in the *Journal of Physical Chemistry*.

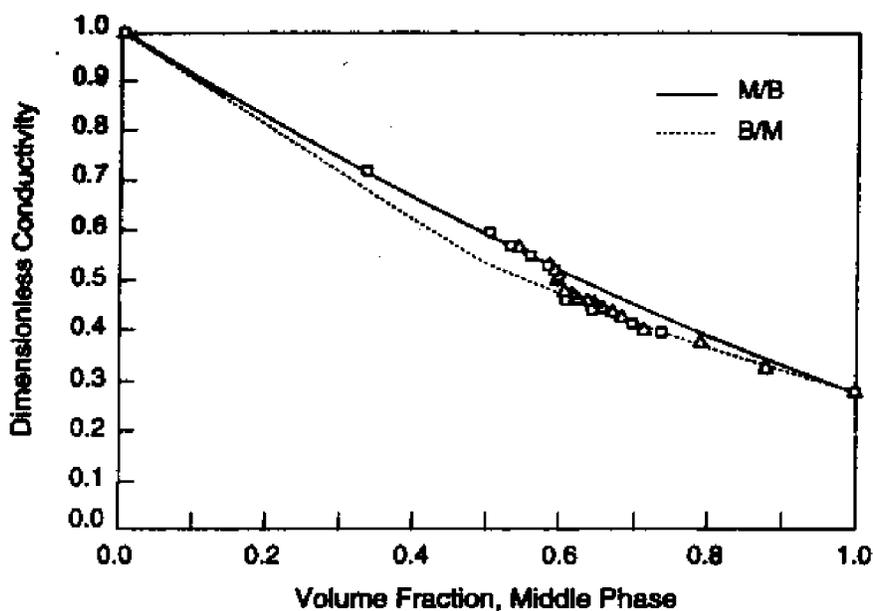
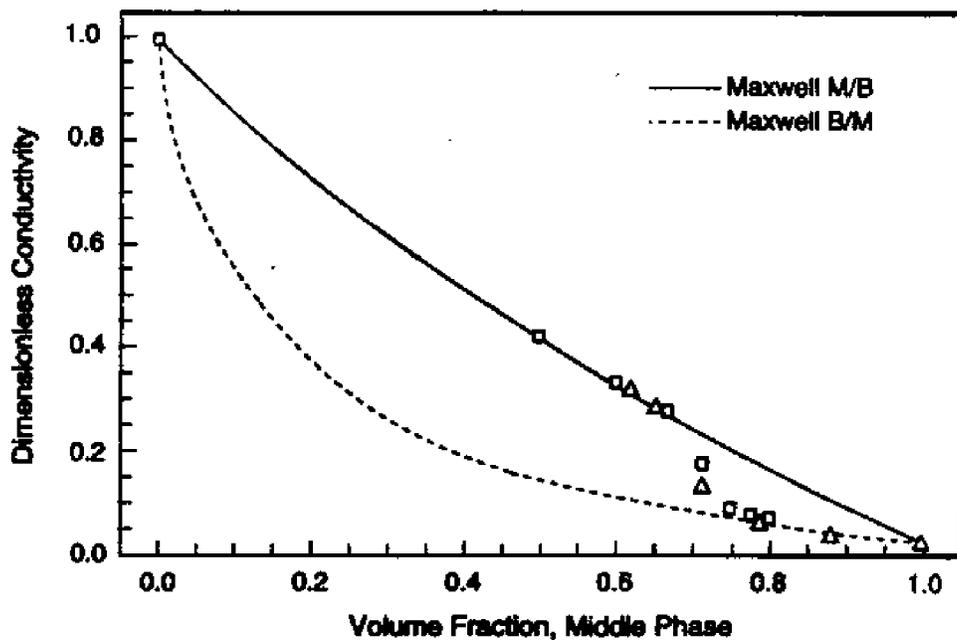


Figure 1. (a) Conductivities at 298.2 K of emulsions of the bottom and middle phases of  $C_6H_{13}(OC_2H_4)_2OH/n$ -tetradecane/aqueous 10 mm NaCl: squares, emulsions titrated with M; triangles, emulsions titrated with B; lines, predictions of the Maxwell equation (reference 6) for M/B and B/M morphologies, respectively. (b) Same as part a, except  $T = 285.2$  K.

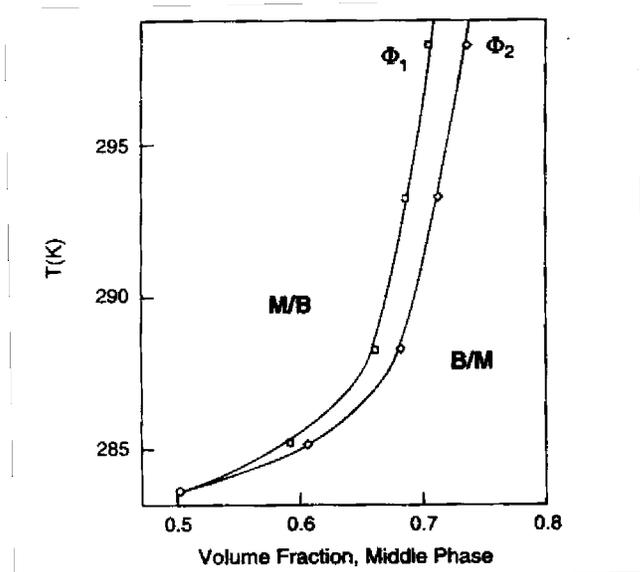


Figure 2. Hysteresis lines for M/B  $\leftrightarrow$  B/M inversions of the system  $C_6H_{13}(OC_2H_4)_2OH/n$ -tetradecane/aqueous 10 mm NaCl: points, measured; lines, model (reference 6).

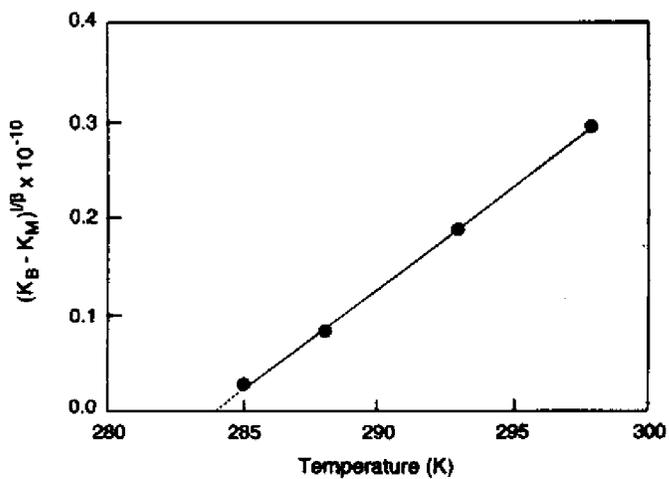


Figure 3. Fit of Critical Scaling Theory equation (reference 6) to the phase conductivities to get the value of the lower phase critical end-point temperature,  $T_{lc} = 283.6$  K

## PRESENT WORK

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 [15-18]. 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 [15-20]. 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.

Selection of effective surfactants and a better understanding of the formation of their emulsions with crude oils are important for progress towards Enhanced Oil Recovery (EOR). NEODOX Alcohol Ethoxycarboxylates (AEC) have recently been produced by the Shell Chemical Company by an oxidative reaction of alcohol ethoxylate with air or oxygen. These novel surfactants are hybrids exhibiting both ionic (carboxylate) and non-ionic (ethoxy) characteristics depending on the conditions of the applications. The non-ionic part of these surfactants 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 should 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 have not yet been tested for their suitability in enhanced oil recovery. Detailed information on optimal salinity, temperature, and emulsion morphologies is needed to evaluate their performance in flooding processes.

Presently work is in progress at the EOR Laboratory, Clark Atlanta University (CAU), to characterize phase and emulsion behavior for a NEODOX hybrid surfactant available from Shell Chemical Company. Temperature and salinity scans are planned at CAU to identify the optimal salinity and temperature, and the temperature and salinity intervals in which all three phases coexist for this surfactant. About 10 samples of equal volume of crude and water with initially 2% concentration of surfactant are 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 is set at 35 °C. Following the salinity experiments, measurements will be made with zero salinity or 10 mm NaCl in water 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 will yield a typical alpha shape curve that will demonstrate the existence of 1, 2, or 3 phases in the system. 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.

In addition to Enhanced Oil Recovery, the surfactant research program on-going at Clark Atlanta University has potential application in environmental chemical engineering in the future. Many surfactants will simultaneously form three liquid phases when mixed with a non-polar (i.e., organic) liquid and water at an appropriate temperature, and salinity. The organic liquid may be a chlorinated hydrocarbon (i.e., dense non-aqueous phase liquid, or DNAPL), or a light non-aqueous phase liquid (LNAPL). Knowledge gained in our research program would pave the way for the investigation of the effective removal of DNAPL or LNAPL pollutants for environmental remediation in the future.

## **ACCOMPLISHMENTS**

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. A temperature bath with a 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, associated chiller, and phase separation glassware with water circulation lines is in progress. Current literature in the subject area, and modeling efforts that were established in previous studies to predict electrical conductivities and inversion phenomena were reviewed.

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