Characteristic Curvature Evaluation of Anionic Surfactants for Enhanced Oil Recovery Applications

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Abstract

Application of microemulsions in hydrocarbon production has re-gained its appeal with recent market interest in chemical enhanced oil recovery (cEOR). A core principal of this microemulsion application is to significantly decrease the interfacial tension between resident crude oil and connate water, resulting in the drastic improvement of hydrocarbon flow within a reservoir. A method to determine the characteristic curvature (Cc) value for anionic surfactants using hydrophilic-lipophilic difference (HLD) concepts and known Cc values as designing tools in formulating surfactant candidates for cEOR in mature oilfields is investigated. Cc values for a set of alkyl alkoxy sulfate (AAS) and alkyl alkoxy carboxylate (AAC) surfactants were determined by thorough analysis of various microemulsion systems containing equal volumes of toluene and aqueous solution. Variable parameters included a ratio of a reference surfactant (in this case, sodium dihexyl sulfosuccinate or SDHS) to a tested AAS or AAC surfactant and system salinity. At each studied surfactant ratio, an optimal salinity at which the surfactant system exhibits an equivalent solubilization potential for the aqueous and organic phase was visually observed. Based on a deviation of the optimal salinity of surfactant mixtures from the reference surfactant, the Cc values of tested surfactant were calculated and identified as hydrophobic. A preparation methodology, Winsor-type microemulsion classification, results for Cc evaluation, and potential HLD application in cEOR will be discussed.

Keywords: EOR, Surfactants, Characteristic Curvature

1. Introduction

Microemulsions are isotropic, thermodynamically stable, heterogeneous multicomponent fluid systems that offer a potential avenue for improved flow of oil and gas of mature production sites. Improved production using microemulsions can be made possible via the formulation of surface-active agents, surfactants, whose purpose is widespread in industrial applications. Primarily, surfactants are utilized with the goal of improving solubilization of two immiscible phases such as resident crude and connate water [1]. In addition to synergistic mixing properties, their power to reduce the interfacial tension that exists between these phases is of interest to oil production scientists and engineers. Increased revenue from wells that have exhausted the benefits from natural drive and artificial lift techniques is the driving force behind refining surfactant formulations used in chemical enhanced oil recovery. Combination of oil and water phases permits the evaluation of properties signature to biologic or synthetic surfactants, which include characteristic curvature (Cc). Characteristic Curvature is a reflection of a surfactant's hydrophilic or lipophilic nature [2]. Characteristic curvature is a measure of the tendency for the surfactant to form intermediate aggregates, normal micelles, or reverse micelles [3]. Cc provides guidance to the most efficient means of minimizing the Gibbs free energy for a system by optimizing solvation requirements [4]. The information from surfactant characterization is then used by chemists, petrochemical, and reservoir engineers in design of the most

efficient formulation to improve recoverable hydrocarbons from a formation. The purpose of this study is to establish a library of Cc values to be used in a calculation algorithm to screen for the most effective surfactants given certain reservoir parameters. The value from this research not only improves existing knowledge as it pertains to formulation synthesis, but it also drastically reduces the turn-around-time associated with analytics for commercial applications.

Variation of parameters that foster an environment in which characteristic curvature can be assessed are concentration and brine salinity. Altering the concentration and salinity gradient facilitate the analysis of ionic surfactant systems. With regard to nonionic surfactant systems, methodologies may implore the manipulation of the thermal gradient in addition to the concentration. Variations to the aforementioned parameters will directly affect the surfactant's solubility potential in both aqueous and organic phases. Presence of a three-phase system provides insight into the optimal performance for a certain surfactant formulation. Previous studies have been made into characterization models for microemulsions that include hydrophilic-lipophilic balance (HLB), phase-inversion temperature (PIT), the cohesive ratio, and the interaction energy ratio, which was introduced in research conducted by Hoar and Schulman in 1943 [5].

1.1 Winsor-Type Microemulsion Systems

Based on the phase behavior evaluation of surfactant-oil-water (SOW) systems, microemulsions can be classified into one of four types. Winsor microemulsions are formed from the careful preparation of a SOW system once it has reached an equilibrated state. Microemulsions are thereby classified into Winsor-Type I, II, III, or IV depending on the degree of solubilization of the immiscible phases and the prevalence of the third phase. The differences in Winsor-Type microemulsions result from the surfactant's affinity to a particular phase; this behavior allows for the characterization of micelle types present in solution.

Winsor-Type I present a system in which the surfactant has formed oil-in-water (O/W) microemulsions and solubilized readily with the aqueous component. O/W microemulsions are conceptualized as swollen regular micelles containing oil droplets surrounded by water [6]. Winsor-Type II models a system in which the surfactant has forged water-in-oil (W/O) microemulsion and solubilized with the organic component. W/O microemulsions can be visualized as swollen reverse micelles containing water droplets surrounded by oil. Winsor-Type III microemulsions describes a state in which the surfactant molecule has solubilized both oil and water into a third phase that resides between the excess oil and excess water phases. Winsor-Type III microemulsions describe a behavior in which the third phase is said to be bi-continuous. SOW systems existing in a Winsor-Type III state are oftentimes diagrammed using tie-triangles in which relative volumes of each phase are directly proportional to their proximity of the overall composition to each corner of the tie-triangle. Tie-Triangles are included in Figure-1 for reference [6].
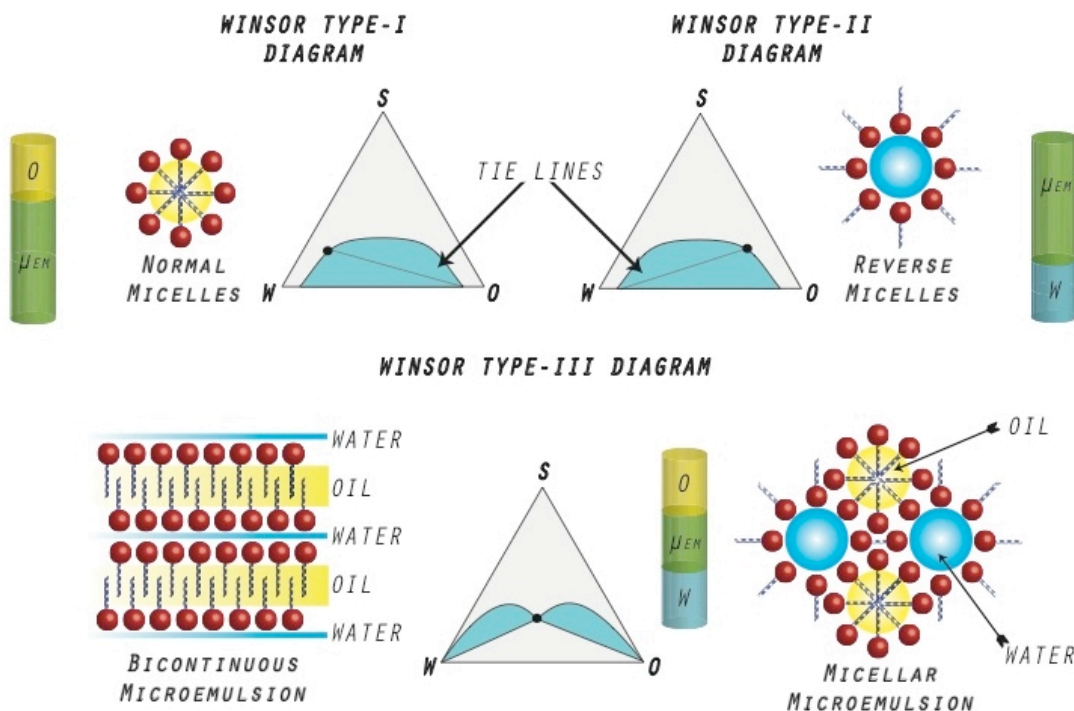
Figure 1. Ternary Diagrams of Winsor-Type Microemulsion Systems
Figure 1. Winsor type-I, type-II, and type-III ternary diagrams for systems of surfactant, oil, and water. Associated micelle configuration of the microemulsion phase and physical manifestation in test tubes also depicted.

Changes to the concentration of any component of the microemulsion system will shift the phase-equilibrium point (black region) about the phase envelope (blue region). Optimal salinity will occur in type-III systems with the phase-equilibrium point located at the centermost point of the ternary plot.

Winsor-Type IV microemulsions are a special case of Winsor-Type III in which the concentration of surfactant in solution is elevated once the optimal salinity has been determined and the bi-continuous molecular arrangement predominates in solution with the apparent presence of a single phase.

1.2 HLD concept and optimal salinity

The general HLD equation of state is useful for performance assessment of anionic surfactants. The general HLD equation is useful in predicting phase behavior of microemulsion systems and is shown in equation (1).

$$HLD = \ln(S) - K(EACN) - f(a) + \sigma - a_T(\Delta T) \tag{1}$$

In the formula, the HLD is determined by the electrolyte concentration, S, present in the aqueous phase. K is defined as an empirical constant characterized by the head group of the surfactant molecule, and EACN is the equivalent alkane carbon number; in the case of toluene, the *EACN* will be 1. In the use of alcohol to achieve surfactant solubility, *f(a)* represents an adjustment to the HLD based on the alcohol type and concentration. The characteristic curvature parameter is defined by σ. An adjustment to the temperature must be made in the event that the tested temperatures is not 25°C. The temperature correction is achieved through the product of the empirical temperature constant, a_T, and the difference in tested to reference temperature (ΔT). For simplification purposes, this study was performed at the reference temperature of 25°C using toluene in the absence of alcohols. Adjusting (1) the HLD will be calculated by using equation (2).

$$HLD = \ln(S) - K(1) + \sigma \tag{2}$$

   In this study, the HLD relationship will be tested for a single (reference) surfactant system as well as for a mixed surfactant system. It is important to note that since the tests evaluate optimal salinity, the HLD is zero as the ratio between organic and aqueous phases in the microemulsion is equivalent. Further simplification of the HLD equation is made for single surfactant systems via equation (3).

$$\ln(S^*) = K(EACN) - \sigma \tag{3}$$

For mixed surfactant systems, (3) must be tailored to account for the ratio of primary surfactant to co-surfactant and are represented in equation (4) by X_1 and X_2 respectively. K_1 and K_2 are the empirical partition coefficients describing the allocation of surfactant to the aqueous and oleic phases; σ_1 and σ_2 are the characteristic curvature parameters for each surfactant respectively.

$$\ln(S_{mix}{}^*) = \left(X_1 K_1 + X_2 K_2\right) - \left(X_1\sigma_1 + X_2\sigma_2\right) \tag{4}$$

By subtracting (3) from (4) the slope of the characteristic curvature between test and reference surfactant is obtained. This slope can be plotted against the molar concentration of the test anionic surfactant in order to determine the difference in characteristic curvatures. Knowing the characteristic curvature for SDHS then allows the quantification of the characteristic curvature of AAS-1 via equation (5).

$$\ln\left(S^* \Big/ S_{mix}{}^*\right) = X_2\left(\sigma_1 - \sigma_2\right) \tag{5}$$

   From reference, Acosta [7] reports the value for Cc of SDHS to be -0.92. Negative values for Cc are characteristic of hydrophilic surfactants that tend to form oil-in-water microemulsions (normal micelles), whereas positive values of Cc are signature to hydrophobic surfactants having an affinity to form water-in-oil Microemulsions (reverse micelles).
   Calculated values for constants used in the HLD calculation are depicted in Table-1 from HLD-NAC (net-average curvature) model used by Kiran [8]. Optimal salinity for anionic surfactants refers to the electrolyte concentration of a specified SOW system where the solubility of both aqueous and organic phases is equivalent and the HLD is 0. The benefit to measuring the optimal salinity of a surfactant is that its application can be optimized as per the reservoir conditions. Because surfactants solubility can be affected by factors such as reservoir salinity, temperature, and hydrocarbon composition it is imperative that application of surfactant type be optimized. Parameters will vary depending on whether the surfactant being used in application is cationic, anionic, nonionic, or amphoteric; this is one of the primary reasons for understanding phase behavior for any SOW system.

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Table 1. Parameters Calculated from HLD-NAC model for SDHS, Toluene, Water Microemulsions

Parameter	Value	Units
S	20	g/100 mL
K	0.17	-
$EACN$	1	-
$f(a)$	0	-
a_T	0.01	$°C^{-1}$
ΔT	0	$°C$
$Ccl = \sigma_1$	-0.92	-

1.3 Oilfield application

Regarded for application versatility in cEOR, microemulsions are also present in additional components of oilfield production and maintenance.

In production environments, microemulsion have been utilized as a fluid-management tool by providing improved relative permeability to oil and gas when integrated into the composition of a drilling fluid additive. Such drilling fluid additives can target fluid loss, shale inhibition, coagulants, and flocculating agents. Facilitating the energy required to carry forward squeezing cementing operations, microemulsions (ME) improve the displacement efficiency of injected fluid from prop-packs and strata by lowering the effective pressure required to maintain the carrying capacity at optimal conditions [9].

Transport conduit maintenance in pipelining operations also benefit from the use of specially tailored formulations. Controlling asphaltene deposition in pipelines spanning large distances is mitigated by flux of a concentrated surfactant rich ME system for solubilization is common in the field of flow assurance. In de-scaling and fracturing operations, emulsified ME scale inhibitors and matrix acidizing agents release the active agents into the formation once the injected fluids reach reservoir temperature. Novel application techniques are ongoing in the field of gas hydrate production with recent advances being made via injection of an H_2O-CO_2 ME formulation into the methane hydrate that destabilizes the crystal lattice structure and forms CO_2 hydrates [10].

2. Methodology

2.1 materials

The following anionic surfactants were obtained from Sigma Aldrich (Milwaukee, WI) at the given concentrations shown without further purification: sodium dihexyl sulfosuccinate SDHS (80 wt. % solution in water). Alkyl alkoxy sulfates AAS-1 and AAS-2 were obtained from BASF Corporation (Florham Park, NJ), Alkyl alkoxy carboxylate AAC-1 was also obtained from BASF. Sodium Chloride obtained from BDH Chemicals (Houston, TX). Toluene (99.9% reagent grade) obtained from Fisher Scientific. Table-2 shows the molecular structure, density, equivalent alkane carbon number, and molar weight for the organic phase used in this experiment. This information is necessary in accurately calculating the characteristic curvature value for anionic surfactants.

Table 2. Selected Properties and Molecular Structures for Organic Phase Studied

Organic Phase	Chemical Structure	Density, 25°C (g/mL)	EACN	Molecular Mass (g/mol)
Toluene C_7H_8 (99.9% pure)		0.865	1	92.14

2.2 experimental methods

Phase behavior tests were carried out in 20mL borosilicate flat-bottomed test tubes with Teflon-lined screw caps. Test tube contents included equal volumes of aqueous solution and toluene (5 mL each) facilitated by the use of single-channel Novus Finn pipette, precision pipettes. Salt scans were performed by variations in the sodium chloride concentration at constant temperate and pressure within a specific reference to test surfactant ratio.

Ratios varied from 100-percent SDHS to 60-percent SDHS, with AAS-1, AAS-2, or AAC-1 making up the difference in content. Preparation of the aqueous phase included the use of deionized water, 20 wt.% sodium chloride, 0.2 M SDHS, and 0.2 M AAS-1 all diluted in deionized water; all parameters were adjusted to evaluate intervals of interest. Upon proper solubilization of all aqueous components, 0.5 mL of toluene was introduced into the flat-bottomed test tubes and the initial area of interface was marked. Addition of the remaining 4.5 mL of toluene enabled the gentle mixing of all contents, which were then left to equilibrate over a time period ranging from 3-10 days. After the systems reached equilibrium, relative phase heights were observed and quantified to determine the optimal condition. The optimal salinity is signature to the highest value for the middle phase having equal volumes of organic and aqueous in its composition. In the event that an optimal salinity was unclear, presence of Winsor Type-I, II, or III indicated a possible avenue for fine adjustment salt scans. The following SDHS to AAS-1 ratios were evaluated in addition to a single system containing SDHS alone to verify the optimal salinity for the reference surfactant: (95% SDHS to 5% AAS-1), (90% SDHS to 10% AAS-1), (85% SDHS to 15% AAS-1), (80% SDHS to 20% AAS-1), (70% SDHS to 30% AAS-1), (60% SDHS to 40% AAS-1). All ratios were tested at electrolyte concentration ranging from 1.0% to 5.0% in 1.0% increments. Intermediate salinities were used in producing fine scans to better evaluate optimum salinity.

Evaluation of AAS-2 was conducted at a surfactant concentration of 0.05 M due to the high molecular weight of the anionic surfactant. SDHS was also prepared at 0.05 M to establish comparative baseline from system to system. The ratios of SDHS to AAS-2 tested include the following: (98% SDHS to 2% AAS-2), (96.5% SDHS to 3.5% AAS-2), (95% SDHS to 5% AAS-2), (93.5% SDHS to 6.5% AAS-2), (92% SDHS to 8% AAS-2), (90% SDHS to 10% AAS-2), (85% SDHS to 15% AAS-2), (80% SDHS to 20% AAS-2), (70% SDHS to 30% AAS-2), (60% SDHS to 40% AAS-2).

Analysis of AAC-1 was conducted at a surfactant concentration of 0.2 M and due to the intermediate molecular weight, the anionic surfactant required significant mixing for proper solubilization. SDHS was also prepared at 0.2 M for this series of microemulsions. The ratios of SDHS to AAC-1 tested include: (97.5% SDHS to 2.5% AAC-1), (90% SDHS to 10% AAC-1), (87.5% SDHS to 12.5% AAC-1), (85% SDHS to 15% AAC-1), (80% SDHS to 20% AAC-1), (70% SDHS to 30% AAC-1), (60% SDHS to 40% AAC-1).

3. Results and Discussion

Figure-2 presents the optimum salinity of the various SDHS-Test Surfactant system formulations as a function of the molar fraction of Test Surfactant (X_2) present in the various mixtures. As depicted by (5) the slope of the curve established by various optimal salinities supports the linear mixing rule hypothesis. Equation (5a) and (5b) are used to solve for the characteristic curvature of AAS-1, AAS-2, and AAC-1.

$$-2.3646 = X_2(-0.92 - \sigma_2) \tag{5a}$$

$$\sigma_2 = 2.3646 - 0.92 = 1.4446 \tag{5b}$$

The slopes expressed in Figure-2 are equivalent to the difference between Cc_1 and Cc_2. From reference, Cc_1 is -0.92, and therefore Cc_2 is +1.4446 when X_2 has a value of 1.
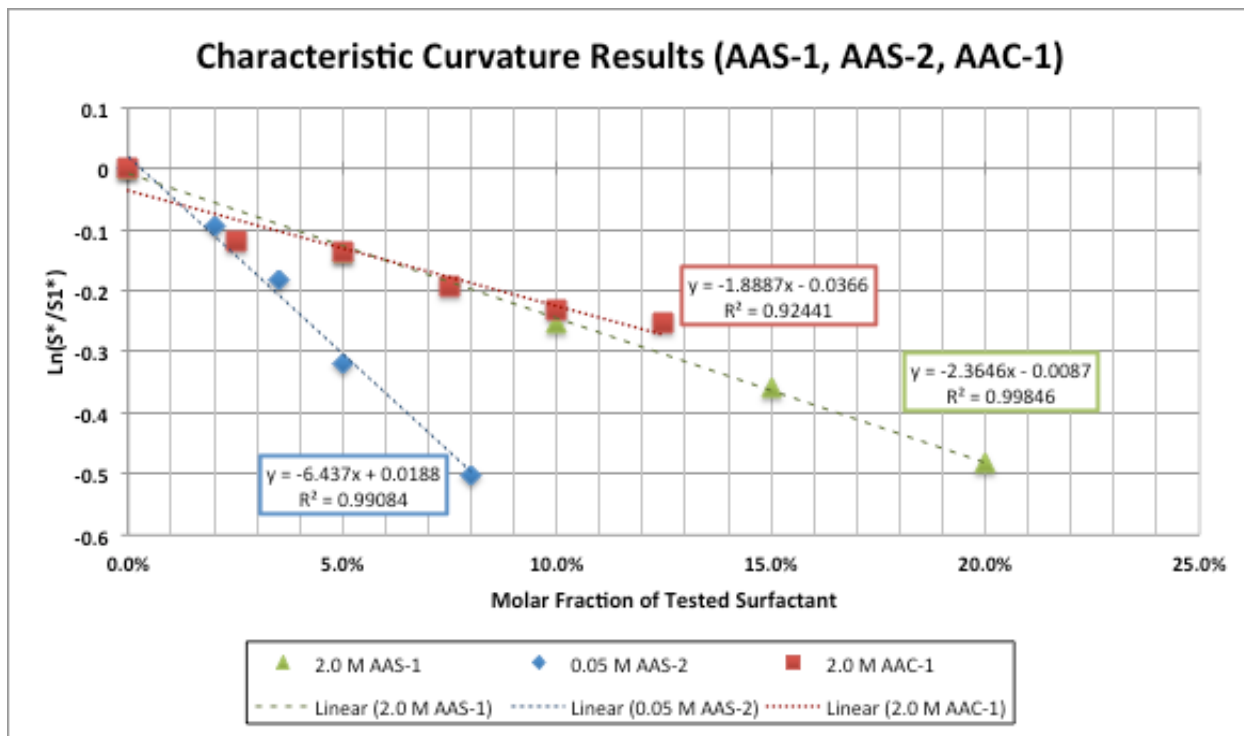
Figure 2. Plot of Optimal Salinity for SOW Systems containing AAS-1, AAS-2, AAC-1 with SDHS and Toluene
Figure 2. Optimal Salinity plots facilitate the calculation of the characteristic curvature parameter specific to an anionic surfactant. By employing linear mixing rules with various reference-test surfactant ratios and the slope of the line generated by various optimal points, calculation of characteristic curvature is achieved.

In systems containing toluene-AAS-1-SDHS, gel production took place at ratios of 70% SDHS and 30% AAS-1, as well as those containing 60% SDHS and 40% AAS-1. Presence of gels in a system scan indicates reduced solubilization capacity of the microemulsion at low concentrations of AAS-1. These results are consistent with research [9]. Results for SDHS and AAS-1 microemulsion electrolyte scans are displayed in Figure-3.

Using (5), the Cc value for AAS-2 was determined to be +5.517. The same process was used to determine the Cc value for AAC-1, which was found to be +0.9687. The optimal salinity electrolyte scans for both AAS-2 and AAC-1 are shown in Figure-4 and Figure-5 respectively.
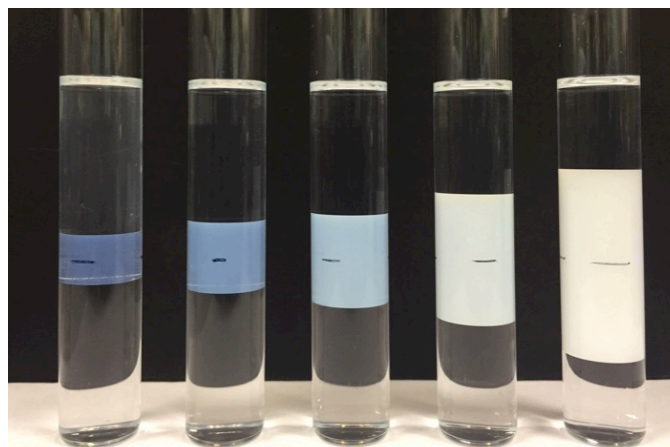

Figure 3. Electrolyte Scan for Optimal Salinity Ratios of 0.2 M SDHS and 0.2 M AAS-1 Microemulsions.
Figure 3. Optimal Salinity results for AAS-1 anionic surfactant. Ratios of SDHS and AAS-1, from left to right, include: 100:0, 95:5, 90:10, 85:15, and 80:20.
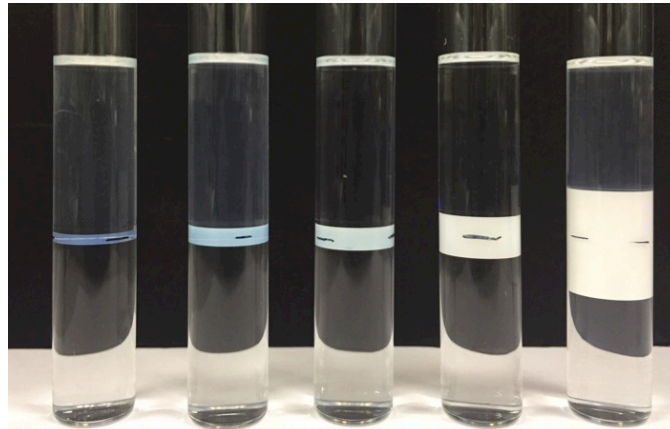
Figure 4. Electrolyte Scan for Optimal Salinity Ratios of 0.05 M SDHS and 0.05 M AAS-2 Microemulsions.
Figure 4. Optimal Salinity results for AAS-2 anionic surfactant. Ratios of SDHS and AAS-2, from left to right, include: 100:0, 98:2, 96.5:3.5, 95:5, and 92:8.
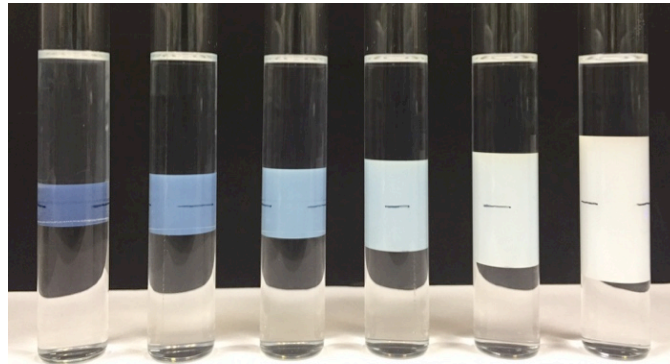

Figure 5. Electrolyte Scan for Optimal Salinity Ratios of 0.2 M SDHS and 0.2 M AAC-1 Microemulsions.
Figure 5. Optimal Salinity results for AAC-1 anionic surfactant. Ratios of SDHS and AAC-1, from left to right, include: 100:0, 95:5, 97.5:2.5, 95:5, 92.5:7.5, 90:10, and 87.5:12.5.

4. Conclusion

Through evaluation of phase behavior for a binary system of anionic surfactants, the characteristic curvature values for AAS-1, AAS-2, and AAC-1 surfactants were obtained. AAS-1 has a Cc value of +1.4446, AAS-2 had a Cc value of +5.517, and AAC-1 had a Cc value of +0.9687. In the conditions used throughout this research, all test surfactants possess properties signature to hydrophobic surfactants that have an affinity for the oleic phase and are susceptible to the formation of reverse micelles. Numerically, a larger Cc value does not necessarily indicate increased complexity in molecular structure. Relationships between families of surface chemistry, their respective Cc values, and the oleic phases in which they are most appropriate are the subject matter of continued field research.

AAS-1, AAS-2 and AAC-1 are all viable candidates for cEOR application with the capability of reducing interfacial tension between resident crude and connate water in mature oilfields. It can be expected to observe a drop in the interfacial tension between reservoir fluids from about 20-25 mN/m, to as low as 0.001 mN/m using combinations of surfactants in the field [12]. In addition to improving displacement efficiency of subsequent driving polyacrylamide chemistry in a surfactant-polymer (SP) or alkali-surfactant-polymer (ASP) flood, lowered IFT also is indicative of an altered state of wettability for the formation and subsequently lowered interfacial viscosity. Modifications to wettability and interfacial tension, along with application to reservoir stimulation are within the capacity of the chemistry presented in this paper.

5. Acknowledgments

6. References

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