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New Correlation for Predicting the Best Surfactant and Co-solvent Structures to Evaluate for Chemical EOR

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New Correlation for Predicting the Best Surfactant and Co-solvent Structures to Evaluate for Chemical EOR

by

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Dedication

To my family and my friends.
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Abstract

New Correlation for Predicting the Best Surfactant and Co-solvent Structures to Evaluate for Chemical EOR

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The focus of this study was the development of an improved correlation that more accurately quantifies the relationships between optimum salinity, optimum solubilization ratios, chemical formulation variables such as surfactant and co-solvent structures, and the EACN. Entrained in this study are improved correlations for co-solvent partition coefficients and correlations for the optimum salinity and solubilization ratio with EACN. Several trends in the oil-water partition coefficient were observed with the alcohol type (IBA and phenol), the number of ethylene oxide groups in the co-solvent, the EACN of the oil, temperature, and salinity. New EACN measurements were made using optimized formulations containing various combinations of primary surfactants, co-surfactants, co-solvents and alkali. The new EACN measurements ranged from 11.3 to 21.1. These new data significantly expand the total number of reliable EACN values available to understand and correlate chemical EOR formulation results. An improved correlation that more accurately quantifies the relationship between surfactant structure, co-solvents, oil, temperature, and optimum salinity was developed using a new and much larger high quality formulation dataset now available from studies done in recent years in the Center for Petroleum and Geosystems Engineering at the University of Texas at Austin. The correlation is useful for understanding the now very large number of microemulsion phase
behavior experiments as well as the uncertainties associated with these data, and for suggesting new chemical structures to develop and test.
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Chapter 1: Introduction

The focus of this study was the development of an improved correlation that more accurately quantifies the relationships between optimum salinity, optimum solubilization ratios, chemical formulation variables such as surfactant and co-solvent structures, and the EACN. Entrained in this study are improved correlations for co-solvent partition coefficients and correlations for the optimum salinity and solubilization ratio with EACN. A more accurate and predictive correlation was needed for the purpose of screening chemicals to test for specific applications of chemical enhanced oil recovery processes. A predictive correlation is also useful for understanding the now very large number of microemulsion phase behavior experiments as well as the uncertainties associated with these data, and for suggesting new chemical structures to develop and test.

In Chapter 3, new measurements of the partition coefficients of the newer alcohol ethoxylates currently being used for chemical enhanced oil recovery were presented and analyzed. These data are needed to model and design surfactant-polymer (SP), alkaline-surfactant-polymer (ASP) and alkaline-co-solvent-polymer (ACP) processes. Several trends in the oil-water partition coefficient ($K_{ow}$) were observed with the alcohol type (IBA and phenol), the number of ethylene oxide groups in the co-solvent, the EACN of the oil, temperature, and salinity. This was a useful first step in the development of a correlation to help minimize the number of measurements needed for co-solvent selection. The ideal value for the $K_{ow}$ is 1 based on previous studies taking into account considerations such as minimizing the chromatographic separation of the co-solvent and surfactant when a chemical slug is injected into an oil reservoir. The $K_{ow}$ values measured in this study ranged from 0.01 to 6.06 depending on the variables listed above. The co-solvent partition coefficient between the surfactant pseudo component (micellar interface) and water ($K_{pw}$) was found to be approximately 10, an order of magnitude greater than the $K_{ow}$. This meant that the concentrations of co-solvents in the excess water and oil phases were approximately equal, and that the concentrations in the surfactant pseudo component was approximately 10 times that in both excess water and oil phases. These results show that the co-solvent clearly prefers the interface created by the presence of surfactants.
In Chapter 4, new measurements of the equivalent alkane carbon number (EACN) of several different crude oils as well as dilutions of these crude oils is presented and discussed. An improved procedure based on the results of the different EACN measurements was proposed and implemented. The new measurements were made using optimized formulations containing various combinations of primary surfactants, co-surfactants, co-solvents and alkali. The new EACN measurements ranged from 11.3 to 21.1. These new data significantly expand the total number of reliable EACN values available to understand and correlate chemical EOR formulation results such as the correlations presented in Chapter 5.

In 2012, Solairaj developed a correlation that quantified the relationship between certain surfactant and oil properties, temperature, and optimum salinity. The correlation was developed from multivariable regression of phase behavior data from optimized surfactant formulations using inactive oils. The correlation did not account for the effect of co-solvent and hydrophobe branching on the optimum salinity. The correlation captured the known trends of certain surfactant attributes such as the number of ethylene oxide groups, the number of propylene oxide groups, and the carbon number of the hydrophobe.

In Chapter 5, an improved correlation that more accurately quantifies the relationship between surfactant structure, co-solvents, oil, temperature, and optimum salinity was developed using a new and much larger high quality formulation dataset now available from studies done in recent years in the Center for Petroleum and Geosystems Engineering at the University of Texas at Austin. First, the old correlation was tested using the new expanded dataset. Next several attempts to improve the old correlation were made. Further attempts to improve the correlation by incorporating the optimum salinity and EACN correlation from Chapter 4 were made. Lastly, a new 2014 correlation was developed that more accurately represent hydrophobe structures and directly addresses head groups. The preliminary trends seem to agree with experimental observations. As such, the 2014 correlation is a better predictive tool than the 2012 correlation. The
correlation also models the solubilization ratio, which is a more important design factor for a formulation than the optimum salinity. The predicted optimum solubilization ratio trends seem to agree with those observed experimentally.

In Chapter 6, an overall summary of this research and the overall conclusions of this research are presented as well as suggestions for future work.
Chapter 2: Background and Literature Review

2.1 Surfactant Theory

Surfactants or surface active agents are amphiphilic compounds that exhibit both lipophilic and hydrophilic characteristics. Surfactants have a hydrophobic tail and a hydrophilic head group. Surfactants are able to reduce the interfacial tension (IFT) between oil and water. A good surfactant must interact with oil and water equally and strongly. The balance between oil and water interactions are characterized by the hydrophilic-lipophilic balance (HLB) and with the Winsor R ratio.

Hydrophilic-lipophilic balance (HLB) is a concept introduced by Griffin in 1949, which assigns surfactants an empirical value ranging from 0 (extreme lipophilicity) to 20 (extreme hydrophilicity) based on the lipophilic and hydrophilic nature of segments of the surfactant molecule. This theory is widely used to illustrate the relative hydrophilicity and lipophilicity of surfactants.

In 1954, Winsor introduced the R ratio, defined as the ratio of the interaction energy (A) between the surfactant (c) and oil (o) and the interaction energy between the surfactant and water (w).

\[ R = \frac{A_{co}}{A_{cw}} \]

Winsor showed that there were only 3 types of ternary diagrams when a surfactant is mixed with oil and water to form a thermodynamically stable microemulsion. He labeled these three types of microemulsions as Type I, Type II, and Type III. The different phase transitions are encountered when scanning from \( R < 1 \) to \( R > 1 \).

In Winsor type I (also called Type II(-)), \( R \) is less than 1, and an oil-in-water (water external) microemulsion exists with an excess oil phase. The oil solubilization ratio \( \sigma_o \) is \( V_o/V_s \), where \( V_o \) is the volume of solubilized oil and \( V_s \) is the volume of surfactant in the microemulsion. The \( \sigma_o \) increases with increasing \( R \).

In Winsor type II (also called Type II(+)\)), \( R \) is greater than 1, and a water-in-oil (oil external) microemulsion exists with an excess water phase. The water solubilization
ratio $\sigma_w$ is $V_w/V_s$ where $V_w$ is the volume of solubilized water. The $\sigma_w$ increases with decreasing $R$.

In Winsor Type III, $R$ is approximately 1. The microemulsion is bicontinuous in both oil and water and exists with excess oil and excess water. The oil solubilization ratio $\sigma_o$ approach a vertical asymptote at the type III and type II boundary, and the water solubilization ratio $\sigma_w$ approach a vertical asymptote at the type I and type III boundary. At $R = 1$, the oil and water interactions are balanced and $\sigma_o$ and $\sigma_w$ are equal. This salinity in a salinity scan is called the optimum salinity ($S^*$), and the oil and water solubilization ratios are equal to the optimum solubilization ratio ($\sigma^*$).

Huh (1979) developed a theory for predicting the interfacial tension from the solubilization ratios. The equation is

$$\gamma = C/\sigma^2$$

Where $C$ is typically about 0.3 dynes/cm. Thus, the IFT at both the water-microemulsion interface and the oil-microemulsion interface is equally low at the optimum salinity. The Huh equation is not valid if the microemulsion is not at equilibrium. Typically, $\sigma^*$ must exceed 10 cc/cc or the IFT must be less than 0.003 dynes/cm to be effective in oil recovery experiments used to study enhanced oil recovery using surfactants. The ones that exhibit such high solubilization ratios are referred to as ultra-low IFT systems.

The oil and water solubilization ratios must be measured when the fluids are at equilibrium for the values to be valid and useful. To do so, the solubilization ratios are monitored over time. The rate of coalescence of the microemulsion is qualitatively assessed. When the solubilization ratios are constant with time, they are widely assumed to be at equilibrium. However, other tests can be done to verify equilibrium and it is good practice to do so. For example, if the fluids are at equilibrium at a specific constant temperature, then first increasing and then decreasing the temperature to its original value will not change the phase behavior or fluid properties including the solubilization ratios. Before the fluids have fully equilibrated, it is very common to observe macroemulsions, which are not equilibrium fluids, but which may persist for long periods of time if highly viscous. The entire middle phase may initially be a macroemulsion, or there may be a
middle phase microemulsion that is surrounded on the top or bottom by a small macroemulsion. When the macroemulsions are viscous and persistent, they are highly undesirable for enhanced oil recovery applications. This tends to be more common when the temperature is low. Co-solvents and co-surfactants are effective in breaking the macroemulsions, especially if they are branched or twin tailed.

Microemulsion phase transitions are brought about by changing the electrolyte composition or concentration (salinity, hardness), temperature, pressure, surfactant composition (e.g. the ratio of two surfactants is changed), co-solvent concentration, and oil composition. The salinity changes are most often used in what are called salinity scans or microemulsion phase behavior experiments. In the salinity scans, all other variables—surfactants, co-solvents, oil, and temperature—are fixed and only the salinity is varied. The salinity can be changed by adding salts such as NaCl or CaCl2, by adding alkali such as Na2CO3, or by blending different complex oilfield brines, or by any combination of these options. The salinity scans are conducted in sealed glass pipettes with salinity increment of 5000 ppm or less.

2.2 Surfactant Structures

There is a wide variety of surfactants, which are classified by their ionic type: anionic, nonionic, cationic, and amphoteric (zwitterionic). Anionic surfactants are by far the most commonly used surfactants in chemical EOR. Combined with alkali, anionic surfactants show low adsorption on negatively charged rocks (Hirasaki et al., 2011). There are three main anionic head groups: sulfonate, sulfate, and carboxylate.

Sulfonate Surfactants

Sulfonate surfactants commonly used for EOR have two types of structures: alkyl aryl sulfonates such as alkylbenzene sulfonate (ABS) or alkyl xylene sulfonates (AXS) and olefin sulfonates such as internal olefin sulfonates (IOS) and alpha olefin sulfonate (AOS).

The general structure of ABS surfactants is a benzene sulfonate bonded in the para position to an alkyl chain. The number of carbons of the alkyl chains is a distribution typically supplied by the manufacturer. The alkyl chain, which is a twin-tail, can be linear
or slightly branched. The position of the benzene sulfonate on the alkyl chain is random. The alkyl chain of ABS surfactants used for EOR typically have an average of 11 to 30 carbons. The benzene is in general electron withdrawing and affects the properties of the surfactant.

In IOS surfactants, the sulfonate head group is attached in close proximity to either a randomly positioned internal double bond or a hydroxyl group on the carbon chain. The former is an alkene sulfonate and the latter is a hydroxyalkane sulfonate in approximately 2:3 ratio. Because of the random position of the sulfonate functionality, IOS molecules are a distribution of positional isomers. In addition the number of carbons of the chain is a distribution typically supplied by the manufacturer. The chains typically have an average of 15 to 28 carbons. Due to dispersion of the sulfonate group on the alkane chain, these surfactants behave as twin-tailed or branched molecules.

AOS surfactants, in contrast, have a sulfonate group at the terminal carbon with the double bond or the hydroxyl group in close proximity inside the chain. In an analogous manner to IOS, the two main components, i.e. the alkene sulfonate and the hydroxyalkane sulfonate are produced approximately in a 2:3 ratio. The chains can be varied from 12 to 18 carbons. As with other linear surfactants, this linear structure is unfavorable for EOR applications due to its lower aqueous stability, tendency for gel formation, among other things.

**Sulfate and Carboxylate Surfactants**

Modern sulfate and carboxylate surfactants used for EOR are alcohol alkoxy sulfate/carboxylate surfactants. Typically, block of propylene oxide (PO) groups, followed by ethylene oxide (EO) groups, separate the alcohol or the hydrophobe from the head group. The PO and EO groups extend the lipophilic and hydrophilic portions of the surfactant and create a more gradual lipophilic to hydrophilic transition. The groups, PO to some extent and EO more so, enhance the aqueous stability of the surfactant in the presence of calcium which can complex with the anionic group. There are variations of alcohol alkoxy sulfates with blocks of only PO or EO groups, and there are also variations of
alcohol alkoxy sulfates/carboxylates which contain a block of butylene oxide (BO). In addition to the number of PO and EO groups, the alcohol or hydrophobe can be tailored to suit the application.

There are several different hydrophobe structures for alcohol alkoxy sulfate/carboxylate but only four were studied in the present work: near-midpoint branched, slightly branched, bent, and aromatic hydrophobes.

The (near) midpoint branched hydrophobes are the Guerbet alcohols and epoxide alcohols. These are considered to be large and approximate midpoint branched hydrophobes. The Guerbet alcohols are synthesized in the Guerbet reaction in which two primary aliphatic alcohols are dimerized forming a β-branched dimer alcohol. The epoxide alcohols are formed by the condensation of an alcohol with a 1,2 linear alkyl epoxide molecule. Guerbet alkoxy sulfate and carboxylate surfactants have high performance and low costs and work exceptionally well with high EACN oils, which require large hydrophobes and branched structures (Adkins et al., 2010 and Adkins et al., 2012). The hydrophobes range from 16 to 32 carbons.

The slightly branched hydrophobes include C13 tridecyl alcohol (TDA), C16-17 (Neodol 67), and C12-13 (Neodol 23) hydrophobes. The synthesis of these hydrophobes vary by manufacturer, but the hydrophobes are all slightly branched, possessing varying degrees of methyl branches. The hydrophobe is typically combine with propoxy sulfates.

A bent hydrophobe, specifically the oleyl alcohol, is a C18 alcohol with a cis double bond at the 9-10 carbon position, which creates a bend in the molecule that imparts a branching effect. Consequently, they exhibit surfactant behavior reminiscent of a large hydrophobe surfactant.

Aromatic hydrophobes, specifically tristyrylphenol, has been demonstrated to be highly effective with waxy and high acid number crude oils to exhibit ultra-low IFT and low microemulsion viscosities with surrogate and live oils (Liyanage et al., 2012). They show special affinity towards oils containing high levels of resins and asphaltenes.
2.3 Co-solvent Properties

Co-solvents used in micellar solutions and microemulsions are nonionic molecules, typically short chain alcohols (carbon chain length 6 or less) and their ethoxylate analogs. The simple alcohols range from methanol to hexanol. The alcohol ethoxylates are various butanol isomer (normal-BA, IBA, SBA) ethoxylates and phenol ethoxylates. The number of ethylene oxide groups range from 1 to 20. Recently, a mono propoxy (1-PO) version of these alcohol ethoxylates has been introduced into phase behavior studies.

Co-solvents serve many purposes in chemical EOR formulations. Co-solvent help prevent or break macroemulsions which reduces the time required for microemulsions to coalesce or equilibrate (Bourrel & Schechter 1988). This is especially beneficial for EOR when the macroemulsions, gels, or liquid crystals have a high viscosity. Co-solvents also reduce the microemulsion viscosity and prevent or minimize non-Newtonian rheology (Walker et al 2012) (Fortenberry et al., 2013). Co-solvents also alter phase behavior, often increasing the solubility of the surfactant in brine (Sahni 2010). A fundamental requirement for EOR applications is that the aqueous surfactant solution is clear and stable at or above the optimum salinity. This requirement is called the aqueous stability requirement. Co-solvents are often needed for aqueous stability, especially when as usual polymer is also in the aqueous solution. However, co-solvents increase the IFT and decreases solubilization ratios (Levitt et al. 2009). For alkaline polymer flooding, co-solvents widen the type III window and reduce the bulk emulsion viscosity and the interfacial viscosity (Fortenberry et al, 2013).

The partitioning of co-solvents is important in the design and optimization of chemical EOR formulations and floods. In a microemulsion, the co-solvent that is not in the microemulsion is not actively contributing to the microemulsion properties. An effective co-solvent would preferentially partition into the microemulsion phase. The definition of the oil-water partition coefficient (\(K_{ow}\)) and the microemulsion-water partition coefficient (\(K_{mw}\)) are as follows:
\[ K_{ow} = \frac{C_{Ao}}{C_{Aw}} \]
\[ K_{mw} = \frac{C_{Am}}{C_{Aw}} \]

Where,

- \( K_{ij} \) is the partition coefficient of alcohol between phase \( i \) and phase \( j \).
- \( C_{Ak} \) is the co-solvent concentration in phase \( k \), ppm.
- The water, oil, and microemulsion phases are \( o \), \( w \), and \( m \) respectively.

Satoh (1984) and Prouvost et al. (1984) assumed the microemulsion phase consisted of three pseudo components: oil, water, and surfactant (membrane pseudophase). The oil and water pseudo components were assumed to have the same co-solvent concentrations as the excess oil and excess water phases of a type III microemulsion. The surfactant pseudo component was assumed to be composed of only surfactant and co-solvent, acting like the volume of the micellar interface. It was assumed that the co-solvent in the surfactant pseudo component was directly influencing the microemulsion properties. The co-solvent partition coefficient between the surfactant pseudo component and the excess water is required to calculate the co-solvent concentration of the surfactant pseudo component. The equation is

\[ K_{pw} = \frac{C_{Ap}}{C_{Aw}} \]

Where,

- \( C_{ap} \) is the concentration of co-solvent in the surfactant pseudo component \( p \).

Satoh (1984) modeled and simulated that the \( K_{pw} \) was higher than the \( K_{ow} \), which meant that the alcohol was strongly interacting with the surfactants. His models also showed for isobutyl alcohol (IBA) and for isoamyl alcohol (IAA) that the \( K_{pw} \) was approximately 10 times the \( K_{ow} \) for surfactant concentrations 1% or less, and they also showed that the \( K_{ow} \) and \( K_{pw} \) for IAA were an order of magnitude higher greater than those for IBA. Finally, he showed that a 1:1 ratio of IBA and IAA, yielding approximate \( K_{ow} \) of 1 and \( K_{pw} \) of 10, were more favorable than pure IBA or pure IAA.
2.4 Oil EACN

TAN

The crude oils are categorized as inactive or active. An active crude oil is defined as having total acids number (TAN) greater than 0.15 mg KOH per g oil. An inactive crude oil is defined as having TAN less than 0.15 mg KOH per g oil. These units represent the milligrams of potassium hydroxide required to titrate the acids in 1 gram of the oil. The soaps are formed by the titration or saponification of esters and carboxylic acids in crude oils. The soaps that are generated are typically large hydrophobe carboxylate soaps which are typically very hydrophobic, as seen by low optimum salinities in activity diagrams. Activity diagrams show the salinity scans of a formulation with many different concentrations of oil. As the oil concentration increases, the ratio of soap to surfactant increases. Typically, the optimum salinity of the activity diagram shifts to lower salinities with increasing oil concentration.

In ASP for active oils, alkali, typically sodium carbonate or sodium metaborate, is used to generate soaps, which work with the surfactants to produce ultra-low IFT. With inactive oils, the use of alkali does not generate a significant amount of soaps to influence the formulation, but alkali is used for other purposes like reducing surfactant adsorption.

EACN

Crude oils are also categorized by their dilutions and composition. Live crude oils are the crude oil as it exists in the reservoir at reservoir temperature and pressure. The live oils have dissolved solution gas, which are a range of light components. Dead crude oils are the live oils equilibrated at standard conditions, and, thus, are missing light components. The dead crude oils have a higher molecular weight and different microemulsion phase behavior properties than the live oils. Surrogate oils are the dead crude oils diluted with specific diluents to achieve similar microemulsion phase behavior properties as with the live oils.

In 1976, Cayias et al. introduced the equivalent alkane carbon number (EACN) concept. He observed a strong correlation between the effects of surfactants on the IFT
behavior and the mole fraction weighted EACN for several alkane and non-alkane mixtures of pure hydrocarbons. The empirical equation Cayias et al developed for calculating the EACN of hydrocarbons is:

\[
\text{EACN} = \text{Number of Carbons} - 2 \times \text{Number of Rings} - \frac{4}{3} \times \text{Number of Double Bonds}
\]

The EACN of an oil is the carbon number of the alkane with the same optimum salinity based on phase behavior experiments using the same surfactant.

In 1977, Salager reported an empirical equation relating the optimum salinity with the EACN of the oil and the parameters characterizing the alcohol and surfactant.

\[
\ln S^* = K (EACN) + f(A) - \sigma + \cdots
\]

The slope \(K\) of \(\ln(S^*)\) versus EACN was reported as 0.16±0.01 for alkylaryl sulfonates. He made other attempts to quantify the slope between other surfactants and found that they were slightly different. \(f(A)\) was a function of the alcohol \(A\) type and concentration, and \(\sigma\) was a characteristic surfactant parameter. The Salager equation effectively captured the change of optimum salinity with alcohol and surfactant types over a range of EACNs. In his equation, the alcohol function was independent of the surfactant parameter.

Puerto et al (1983) developed a three-parameter method for characterizing oils. They made mixtures of equivalent oils that matched the optimum salinity, solubilization ratio, oil molar volume, and the oil viscosity. The three parameter model is useful for making surrogate oils to match live oils, but it requires far more data and still has uncertainties associated with it, so it has not been used very much by other labs. Also, until very recently very few reliable microemulsion phase behavior experiments using live crude oils were available to validate it or any other approach for making surrogate oils.

Jang, et al (2014) has recently published a much larger set of phase behavior data using a variety of live oils at high pressure. These data confirm that the EACN equation does not apply to solution gas components such as methane. However, the EACN equation is still useful for the heavier hydrocarbon components used to make surrogate
oils. For this reason and for simplicity EACN has been used in this research study for the purposes of correlating microemulsion phase behavior data using crude oils without solution gas components (dead and surrogate oils). It has been found to still be a very valuable measurement for this purpose.
Chapter 3: Co-solvent Partitioning Study

3.1 Purpose

The purpose of this chapter was to find a better way to select co-solvents to optimize the phase behavior of microemulsions based on their partition coefficients. Alcohols were the only commonly used co-solvents until recent years, so partition coefficients were not available for the newer co-solvents. Thus the first step was to make new measurements and develop a correlation with alcohol type (IBA and phenol), the number of ethylene oxide groups in the co-solvent, the EACN of the oil, temperature, and salinity. Such a correlation should be useful to minimize the number of measurements needed for co-solvent selection.

The analytical method for the study was high performance liquid chromatography (HPLC) with UV-Vis and evaporative light scattering detectors. HPLC analysis enabled the quantification of analyte concentrations by means of calibration curves. Calibration curves correlate the detector signal to the analyte concentration and are constructed from multiple known concentrations of analyte. The HPLC method yielded high resolution and relatively well separated chromatograms. The high quality of the chromatograms allowed for relatively easy and reliable deconvolution of the chromatograms, which enabled a more thorough analysis. Deconvolution is further explained in Section 3.6.

Sections 3.7-3.10 are devoted to the study of partitioning of co-solvents between oil and water. The last section discusses the results of co-solvent partitioning in type III microemulsion systems.

3.2 Materials

Table 3.1 shows the co-solvents used in this study. The co-solvents are phenol ethoxylates (Ph-xEO), isobutyl alcohol ethoxylates (IBA-xEO), and phenol monopropoxy ethoxylates (Ph-1PO-xEO).
Table 3.1 List of Co-solvents

<table>
<thead>
<tr>
<th>Co-solvent</th>
<th>Manufacturer</th>
<th>Lot#</th>
<th>Received Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobutanol + 1EO</td>
<td>Huntsman</td>
<td>8741-66-38</td>
<td></td>
</tr>
<tr>
<td><strong>Isobutyl Alcohol + 3EO</strong></td>
<td>Harcros</td>
<td></td>
<td>12/10/2013</td>
</tr>
<tr>
<td>Unneutralized</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Isobutyl Alcohol + 5EO</strong></td>
<td>Harcros</td>
<td></td>
<td>12/10/2013</td>
</tr>
<tr>
<td>Unneutralized</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Isobutanol + 7EO</strong></td>
<td>Harcros</td>
<td></td>
<td>June 19 2013</td>
</tr>
<tr>
<td>Unneutralized</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isobutanol = 19.38%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EO = 80.62%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol + 10EO NRE</td>
<td>Harcros</td>
<td>624201310</td>
<td>6/24/2013</td>
</tr>
<tr>
<td>Narrow range Ethoxylate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activity 50%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Using 3/1/2013 Sample</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol-20EO</td>
<td>Harcros</td>
<td>709201320</td>
<td>7/19/2013</td>
</tr>
<tr>
<td>Narrow Range Ethoxylate (NRE)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activity = 20%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diluted using 5012013 batch</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol + 4EO</td>
<td>Harcros</td>
<td>08092012</td>
<td></td>
</tr>
<tr>
<td>P-2 = 65.27%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EO = 24.73%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100% Active</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol + 2EO</td>
<td>Harcros</td>
<td></td>
<td>October 24, 2013</td>
</tr>
<tr>
<td>Phenol = 51.65</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EO = 48.35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100% active</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activity = 100%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol + 1PO + 5EO</td>
<td>Harcros</td>
<td></td>
<td>August 15, 2014</td>
</tr>
<tr>
<td>Phenol+1PO = 40.85%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EO = 59.51%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW = 372</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol + 1PO + 2EO</td>
<td>Harcros</td>
<td></td>
<td>August 15, 2014</td>
</tr>
<tr>
<td>Phenol+1PO = 63.32</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EO = 36.68%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW = 240</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The co-solvent partition coefficients were measured with ABK, CN, and KPK crude oils and their surrogate oils. The crude oils were filtered through 0.45 µm. The surrogate oil diluents were toluene, octane, and hexadecane.

3.3 Procedure

**Calibration Samples**

Calibration curves for each co-solvent were made from 8 calibration samples ranging from concentrations of 250 ppm to 2000 ppm co-solvent in 46000 ppm NaCl. The samples were kept refrigerated to prevent the evaporation of analytes.

**Oil/Water Partitioning Samples**

The oil/water partitioning samples were made in triplicates. The samples were made by mixing 2 ml of oil and 2 ml of 5000 ppm co-solvent in an aqueous solution. The samples were mixed and aged for 3-4 days. The aqueous phase of each sample was extracted via glass Pasteur pipettes and diluted by a factor of 4 (by mass) with 46,000 ppm NaCl brine. The samples were filtered through 0.45 µm filters into HPLC vials.

**Oil/Water/Microemulsion Partitioning Samples**

The type III microemulsion samples were made by mixing 4 ml of dead or surrogate oil with 4 ml of surfactant (including co-solvent) aqueous solution. The salinity and electrolyte corresponded to that of the optimum salinity, which had been determined earlier by phase behavior experiments (salinity scans). The samples were mixed and aged at constant temperature until the solubilization ratios remained constant within the uncertainty of the observations, which indicated the phase behavior was at or close to equilibrium. The samples were aged for approximately 40 days. Plots of the solubilization ratios versus time are shown Section 3.11.

The aqueous and microemulsion phases were extracted separately via thin stainless steel syringes. The phases were extracted from the lowest point in the vial. First, the bulk
of the aqueous phase was extracted. Then, the remaining aqueous phase and a bit of the microemulsion-aqueous interface was extracted, leaving behind uncontaminated microemulsion. Finally, the microemulsion phase was extracted, but leaving behind the oil-microemulsion interface. The aqueous phase was diluted by a factor of 4 (by mass) with the deionized water. The microemulsion was diluted by a factor of approximately 7 (by mass) with 10% IPA and deionized water solution, which was used to help solubilize the oil. The diluted microemulsion phase was centrifuged at 2000 rpm for 10 minutes to separate any excess oil that remained, which could not be injected in the HPLC. The diluted aqueous phase samples and the diluted and separated microemulsion phase samples were filtered through 0.45 µm filters into HPLC vials.

3.4 High Performance Liquid Chromatography Analysis

Dionex Ultimate 3000 UHPLC was used to analyze the co-solvent samples using Acclaim Mixed-Mode HILIC-1 column (4.6 X 150 mm, 5µm) attached to the guard column. A solvent gradient of 0.1M ammonium acetate (pH 5.5) and acetonitrile shown in Figure 3.1 was used. The temperature and flow rate were held constant at 30°C and 1 mL/min. The evaporative light scattering detector (Agilent 1260 infinity ELSD) and the UV-Vis diode array detector (DAD) were used to detect the analyte. With this stationary phase and solvent gradient, the more lipophilic components elute first.

The phenol ethoxylates are aromatic and therefore absorb ultraviolet and visible light. The phenol ethoxylate samples were analyzed with the DAD at a wavelength of 260 nm, which had the highest absorptivity. The absorbance follows the Beer-Lambert law, and so the DAD signal is directly proportional to the molar concentration of components.

The ELSD atomize/nebulize the analyte and measures the scattering of light. The ELSD can be used to detect all nonvolatile components. The butyl ethoxylates are not UV-Vis absorbing and were analyzed by the ELSD. The ELSD signal is proportional to the square of the mass concentration of the components.
HPLC analysis revealed that the co-solvents are composed of a distribution of alcohol ethoxylates and that co-solvents with a greater average number of ethylene oxide groups had a broader distribution of components. Figure 3.2 is a comparison of HPLC chromatograms of 750 ppm Phenol-2EO, 4EO, and 6EO.

The peaks were assumed to differ by 1 ethylene oxide group. The peak with a retention time of 3.6 minutes was experimentally determined to be phenol. As mentioned before, the more lipophilic components, those with fewer number of ethylene oxide groups, eluted first.
HPLC analysis further revealed that the distribution of the components in the aqueous phase significantly changed when equilibrated with oil because the components had different partition coefficients. Figure 3.3 compares the chromatograms of phenol-4EO calibration samples to the chromatogram of a sample equilibrated with oil.

The peak heights and areas of the calibration samples scaled linearly with the total co-solvent concentration, which meant that the distribution of components were identical. However, the peak heights and areas of the oil/water sample were relatively higher and larger for the components with longer retention times. This shift or skewing of the distribution towards components with higher average number of ethylene oxide groups simply indicates that the more hydrophilic components, those with more ethylene oxide groups, had lower partition coefficients.

The cumulative or total area was used to calculate the concentration in the extracted and diluted aqueous phase. The concentrations in the oil and aqueous phase were determined by mass balance. The cumulative partition coefficient was the quotient of these concentrations. Despite how the sample distributions were different from the calibration
distributions, the areas were assumed to be scalable. More explicitly, this meant that the areas of all peaks were equivalently weighted, which was not true because the corresponding molecules differ in the number of ethylene oxide groups. The cumulative partition coefficient was assumed to be a representative average partition coefficient for the distribution.

This was a reasonable assumption for narrow distributions, as the range of molecules and partition coefficients were small. However, with broader distributions, the cumulative partition coefficients were more heavily biased, as the range of molecules and partition coefficients were much more significant.

3.5 Cumulative Partitioning Data

The effects of alcohol type (phenol and IBA), the number of ethylene oxide groups, temperature, and salinity on the partition coefficients were systematically studied with ABK, KPK, and CN crude oils. The effects of EACN were studied with ABK and KPK crude oils and with toluene, octane, and hexadecane. Most of the sample conditions were at a temperature of 55°C, a salinity and electrolyte of 46000 ppm NaCl, and co-solvent concentration of 5000 ppm. These conditions were typical of most formulations and reservoir conditions, and it was set as the base conditions.

The co-solvent partition coefficients ($K_{ow}$) of phenol ethoxylates and isobutanol ethoxylates between brine at salinities of 46000 and 60000 ppm NaCl and ABK oil (EACN = 10) at 55°C and 85°C are given in Tables 3.2 and 3.3, respectively.
Table 3.2 Phenol-xEO with ABK oil

<table>
<thead>
<tr>
<th>Oil</th>
<th>Co-solvent</th>
<th>Salinity</th>
<th>Temperature</th>
<th>K_{ow}</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABK</td>
<td>Phenol-2EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.71</td>
</tr>
<tr>
<td>ABK</td>
<td>Phenol-4EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.50</td>
</tr>
<tr>
<td>ABK</td>
<td>Phenol-6EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.05</td>
</tr>
<tr>
<td>ABK</td>
<td>Phenol-10EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.02</td>
</tr>
<tr>
<td>ABK</td>
<td>Phenol-20EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.03</td>
</tr>
<tr>
<td>ABK</td>
<td>Phenol-4EO</td>
<td>60000 ppm</td>
<td>55</td>
<td>0.50</td>
</tr>
<tr>
<td>ABK</td>
<td>Phenol-4EO</td>
<td>60000 ppm</td>
<td>85</td>
<td>0.98</td>
</tr>
<tr>
<td>ABK</td>
<td>Phenol-2EO</td>
<td>46000 ppm</td>
<td>85</td>
<td>1.45</td>
</tr>
<tr>
<td>ABK</td>
<td>Phenol-4EO</td>
<td>46000 ppm</td>
<td>85</td>
<td>0.81</td>
</tr>
<tr>
<td>ABK</td>
<td>Phenol-6EO</td>
<td>46000 ppm</td>
<td>85</td>
<td>0.18</td>
</tr>
<tr>
<td>ABK</td>
<td>Phenol-4EO</td>
<td>46000 ppm</td>
<td>25</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Table 3.3 IBA-xEO with ABK

<table>
<thead>
<tr>
<th>Oil</th>
<th>Co-solvent</th>
<th>Salinity</th>
<th>Temperature</th>
<th>K_{ow}</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABK</td>
<td>IBA-1EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.12</td>
</tr>
<tr>
<td>ABK</td>
<td>IBA-3EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.06</td>
</tr>
<tr>
<td>ABK</td>
<td>IBA-5EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.01</td>
</tr>
<tr>
<td>ABK</td>
<td>IBA-7EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.03</td>
</tr>
</tbody>
</table>

The effect of co-solvent concentration on the partition coefficient can be seen from the results given in Table 3.4. The cumulative partition coefficients of 5000 ppm, 1250 ppm and 500 ppm of phenol-4EO with ABK crude oil at the base conditions were determined to not be significantly different within experimental error i.e. the cumulative partition coefficients were found to be independent of concentration. Furthermore, in Section 3.7, the partition coefficients of individual components making up the co-solvent were measured and were determined to not significantly differ with the overall co-solvent
composition. This indicates that the interference effect from other components is negligible, and that the components can be treated independently.

Table 3.4 Phenol-4EO with ABK Concentration Scan

<table>
<thead>
<tr>
<th>Oil</th>
<th>Co-solvent</th>
<th>Salinity</th>
<th>Temperature</th>
<th>K_{ow}</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABK</td>
<td>5000 ppm Ph-4EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.50</td>
</tr>
<tr>
<td>ABK</td>
<td>1250 ppm Ph-4EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.54</td>
</tr>
<tr>
<td>ABK</td>
<td>500 ppm Ph-4EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.47</td>
</tr>
</tbody>
</table>

The results in Table 3.5 show the effects of salinity on the partition coefficient of phenol-4EO with ABK crude oil at 55°C. These results will be discussed in more detail in Section 3.9.

Table 3.5 Phenol-4EO with ABK Salinity Scan

<table>
<thead>
<tr>
<th>Oil</th>
<th>Co-solvent</th>
<th>Salinity</th>
<th>Temperature</th>
<th>K_{ow}</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABK</td>
<td>Phenol-4EO</td>
<td>0 ppm</td>
<td>55</td>
<td>0.34</td>
</tr>
<tr>
<td>ABK</td>
<td>Phenol-4EO</td>
<td>1000 ppm</td>
<td>55</td>
<td>0.36</td>
</tr>
<tr>
<td>ABK</td>
<td>Phenol-4EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.50</td>
</tr>
<tr>
<td>ABK</td>
<td>Phenol-4EO</td>
<td>60000 ppm</td>
<td>55</td>
<td>0.50</td>
</tr>
<tr>
<td>ABK</td>
<td>Phenol-4EO</td>
<td>150000 ppm</td>
<td>55</td>
<td>1.76</td>
</tr>
</tbody>
</table>

The partition coefficients of phenol ethoxylates with KPK, ABK, and CN dead and surrogate oils are given in Tables 3.6, 3.7 and 3.8. The partition coefficient of phenol ethoxylates with the surrogate oil diluents toluene, hexadecane and octane are given in Table 3.9. The sample conditions were predominantly the base case conditions, except for the CN samples, which used 30,000 ppm NaBO2. These experiments were designed to study the relationship between partition coefficients and the oil phase properties. The results are discussed in Section 3.10.
Table 3.6 Phenol-xEO with KPK Dead and Surrogate Oils

<table>
<thead>
<tr>
<th>Oil</th>
<th>EACN</th>
<th>Co-solvent</th>
<th>Salinity</th>
<th>Temperature</th>
<th>K&lt;sub&gt;ow&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>KPK+12%Tol</td>
<td>9.12</td>
<td>Phenol-2EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>1.38</td>
</tr>
<tr>
<td>KPK+12%Tol</td>
<td>9.12</td>
<td>Phenol-2EO</td>
<td>46000 ppm</td>
<td>68</td>
<td>1.83</td>
</tr>
<tr>
<td>KPK+12%Tol</td>
<td>9.12</td>
<td>Phenol-4EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.98</td>
</tr>
<tr>
<td>KPK+12%Tol</td>
<td>9.12</td>
<td>Phenol-6EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.12</td>
</tr>
<tr>
<td>KPK</td>
<td>12.35</td>
<td>Phenol-2EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>1.15</td>
</tr>
<tr>
<td>KPK</td>
<td>12.35</td>
<td>Phenol-4EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.61</td>
</tr>
<tr>
<td>KPK+20%C16</td>
<td>13.14</td>
<td>Phenol-4EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.44</td>
</tr>
<tr>
<td>KPK+20%C8</td>
<td>10.74</td>
<td>Phenol-4EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Table 3.7 Phenol-xEO with ABK + 20% Toluene and ABK + 20% Hexadecane

<table>
<thead>
<tr>
<th>Oil</th>
<th>EACN</th>
<th>Co-solvent</th>
<th>Salinity</th>
<th>Temperature</th>
<th>K&lt;sub&gt;ow&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABK+20%Tol</td>
<td>6.54</td>
<td>Phenol-4EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>1.09</td>
</tr>
<tr>
<td>ABK+20%Tol</td>
<td>6.54</td>
<td>Phenol-6EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.07</td>
</tr>
<tr>
<td>ABK+20%C16</td>
<td>11.22</td>
<td>Phenol-2EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.82</td>
</tr>
<tr>
<td>ABK+20%C16</td>
<td>11.22</td>
<td>Phenol-4EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.51</td>
</tr>
<tr>
<td>ABK+20%C16</td>
<td>11.22</td>
<td>Phenol-6EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.08</td>
</tr>
<tr>
<td>ABK+20%C8</td>
<td>9.11</td>
<td>Phenol-4EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Table 3.8 Phenol-xEO with CN

<table>
<thead>
<tr>
<th>Oil</th>
<th>EACN</th>
<th>Co- solvent</th>
<th>Salinity</th>
<th>Electrolyte</th>
<th>Temperature</th>
<th>K&lt;sub&gt;ow&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td>13.45</td>
<td>Phenol-2EO</td>
<td>30000 ppm</td>
<td>NaBO2</td>
<td>55</td>
<td>0.76</td>
</tr>
<tr>
<td>CN</td>
<td>13.45</td>
<td>Phenol-2EO</td>
<td>30000 ppm</td>
<td>NaBO2</td>
<td>85</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Table 3.9 Phenol-xEO with Pure Hydrocarbons

<table>
<thead>
<tr>
<th>Oil</th>
<th>EACN</th>
<th>Co-solvent</th>
<th>Salinity</th>
<th>Temperature</th>
<th>K&lt;sub&gt;ow&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>1</td>
<td>Phenol-4EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>6.06</td>
</tr>
<tr>
<td>Toluene</td>
<td>1</td>
<td>Phenol-6EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>2.61</td>
</tr>
<tr>
<td>C8</td>
<td>8</td>
<td>Phenol-4EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.24</td>
</tr>
<tr>
<td>C16</td>
<td>16</td>
<td>Phenol-4EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.18</td>
</tr>
</tbody>
</table>

The experiments in Table 3.10 measured the cumulative partition coefficient of phenol monopropoxy ethoxylates (Ph-1PO-xEO) with ABK crude oil and KPK surrogate oil at the base conditions. The insertion of a propylene oxide group to the phenol ethoxylates seemed to double the partition coefficients. Figure 3.4 illustrates the difference of the partition coefficient of phenol monopropoxy ethoxylates and phenol ethoxylates.

Table 3.10 Phenol-wPO-xEO with ABK and KPK

<table>
<thead>
<tr>
<th>Oil</th>
<th>Co-solvent</th>
<th>Salinity</th>
<th>Temperature</th>
<th>K&lt;sub&gt;ow&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABK</td>
<td>Ph-1PO-2EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>1.24</td>
</tr>
<tr>
<td>KPK+12%Tol</td>
<td>Ph-1PO-2EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>3.02</td>
</tr>
<tr>
<td>ABK</td>
<td>Ph-1PO-5EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.30</td>
</tr>
<tr>
<td>KPK+12%Tol</td>
<td>Ph-1PO-5EO</td>
<td>46000 ppm</td>
<td>55</td>
<td>0.70</td>
</tr>
</tbody>
</table>
Figure 3.4 Partition Coefficient of Phenol Monopropoxy Ethoxylates and Phenol Ethoxylates

3.6 Deconvoluted Partitioning Data

The chromatograms had moderate resolution or separation. The peaks were slightly overlapping, which muddled the signals corresponding to different peaks. The chromatograms were mathematically separated into individual peaks corresponding to the different components. This was accomplished by fitting multiple normal (Gaussian) distributions to all local maximums of the chromatogram. The retention time (the average), the bandwidth (the standard deviation), and the scaling factor (the area) for each peak were determined using Excel solver by minimizing the square of the residual between the calculated (the sum of all peaks) and the chromatogram. The components present in the small fractions had correspondingly small peak areas and large relative errors, so the values associated with these components were often excluded. Figure 3.5 shows an example of the solved peaks and a comparison with the chromatogram.
The chemical compositions of the co-solvents were not measured, because it would have required the pure components via standard addition or an internal standard. However, the chemical compositions were not required to calculate the partition coefficients of individual components.

The calibration sample chromatograms were deconvoluted. Since the distributions of the calibration samples were identical, the concentrations of individual components were proportional to the total concentration. Then, calibration curves (unique to co-solvent composition) of the deconvoluted signal versus the relative concentration were constructed for each component. The calibration curves of phenol-4EO component for the phenol-2EO, Phenol-4EO, and phenol-6EO co-solvents were different, because the co-solvent compositions were different.

Using the component calibration curves, the deconvoluted signal was converted to a relative concentration in the aqueous phase, $C_{aw}^*$. $C_{aw}^*$ and the extrapolated initial concentration in the aqueous phase $C_{awt}$ were used in the following equation, derived from mass balance, to determine the partition coefficient of the component.
The deconvolution of the chromatograms and the determination of the individual component partition coefficients eliminates the bias present in the cumulative partition coefficients and more clearly presents the data.

There were many sources of error in these experiments. There was human error in the determination of the baselines for the chromatograms. This was often made worse by significant baseline drift. The most severe source of error was the reduction of the effective length of the column or the number of theoretical plates with time due to overuse. This effectively reduced the retention times and increased the standard deviations of the peaks, resulting in more overlapping peaks, which were more difficult to deconvolute. Therefore, the error was likely increasing with time, but periodically measured calibration samples showed no overall signal loss. The increased error in deconvolution resulted in fewer of the lower signal peaks being used. Because of the limited time available the standard errors for the partition coefficient values were not quantified.

### 3.7 Effects of Ethylene oxide groups

The data presented in the following sections are the averages of triplicate measurements. Again, the values of low-concentration components were often excluded. Also, components with small partition coefficients were also excluded, because of the large error associated with such a small the co-solvent concentration in the oil. As a result, the Ph-10EO and Ph-20EO chromatograms were not analyzed by the deconvolution.

Figure 3.6 and Figure 3.7 show the partition coefficients of phenol ethoxylates with ABK crude oil (EACN = 10) at 55°C and 85°C in 46,000 ppm NaCl brine. The data for each component was from a combination of phenol-2EO, phenol-4EO, and phenol-6EO co-solvents. The cumulative partition coefficients were plotted to illustrate the bias of using the cumulative areas.
Figure 3.6 Partition Coefficient of Phenol-xEO with ABK oil at 55°C and 46000 ppm NaCl Brine

Figure 3.7 Partition Coefficient of Phenol-xEO with ABK oil at 85°C and 46000 ppm NaCl Brine

Figure 3.8 shows the partition coefficients of phenol ethoxylates with toluene (EACN = 1) at 55°C and 46000 ppm NaCl. The data for each component was from a combination phenol-4EO and phenol-6EO co-solvents.
Figure 3.8 Partition Coefficient of Phenol-xEO with Toluene at 55°C and 46000 ppm NaCl Brine

Figure 3.9 shows the partition coefficients of phenol ethoxylates with KPK + 12% toluene (EACN = 9.12) at 55°C and 46000 ppm NaCl brine. The data for each component was from a combination of phenol-2EO, phenol-4EO, and phenol-6EO co-solvents.
Figure 3.9 Partition Coefficient of Phenol-xEO with KPK+12% Toluene at 55°C and 46000 ppm NaCl Brine

Figure 3.10 shows the partition coefficients of phenol ethoxylates with KPK dead crude oil (EACN = 9.12) at 55°C and 46000 ppm NaCl brine. The data for each component was from a combination of phenol-2EO and phenol-4EO co-solvents.

Figure 3.10 Partition Coefficient of Phenol-xEO with KPK at 55°C and 46000 ppm NaCl Brine
Figure 3.11 shows the partition coefficients of phenol ethoxylates with ABK + 20% toluene (EACN = 6.54) at 55°C and 46000 ppm NaCl. The data for each component was from a combination of phenol-4EO and phenol-6EO co-solvents.

![Figure 3.11 Partition Coefficient of Phenol-xEO with ABK+20% Toluene at 55°C and 46000 ppm NaCl Brine](image)

Figure 3.11 Partition Coefficient of Phenol-xEO with ABK+20% Toluene at 55°C and 46000 ppm NaCl Brine

Figure 3.12 shows the partition coefficients of phenol ethoxylates with ABK + 20% hexadecane (EACN = 11.22) at 55°C and 46000 ppm NaCl. The data for each component was from a combination of phenol-2EO, phenol-4EO, and phenol-6EO co-solvents.
Figure 3.12 Partition Coefficient of Phenol-xEO with ABK+20% Hexadecane at 55°C and 46000 ppm NaCl Brine

These data show that the partition coefficients of identical components from different compositions were not significantly different. This indicates that the interference effect from other components is negligible, and that the components can be treated independently.

The partition coefficient (K_{ow}) decreases as the number of ethylene oxide groups (NEO) increases. The trend is approximately linear when plotted as the logarithm of K_{ow} vs NEO. The cumulative partition coefficients of phenol-2EO and phenol-4EO co-solvents were consistent with the component trends, but the cumulative partition coefficients of phenol-6EO co-solvent were consistently underestimated. This was likely due to the bias of using the cumulative areas, as the phenol-6EO distribution was broader and would be more biased.
3.8 Effects of Temperature

Figure 3.13 compares the partition coefficient of phenol ethoxylates at different temperatures with ABK crude oil (EACN = 10) at 46,000 ppm NaCl brine. The data at 25°C was derived from only phenol-4EO co-solvents and seem to deviate from the trends.

![Figure 3.13 Partition Coefficient of Phenol-xEO with ABK at Multiple Temperatures and 46000 ppm NaCl Brine](image)

Figure 3.14 shows the partition coefficient of phenol ethoxylates at 55 and 85°C with ABK crude oil (EACN = 10) at a different salinity of 60,000 ppm NaCl brine. The datasets were derived from phenol-4EO co-solvents.
Figure 3.14 Partition Coefficient of Phenol-4EO with ABK at 55 and 85°C and 60,000 ppm NaCl Brine

Figure 3.15 shows the partition coefficient of phenol ethoxylates at 55 and 85°C for CN crude oil (EACN = 13.45) at 30,000 ppm NaBO2 brine. The datasets were derived from phenol-2EO co-solvents.

Figure 3.15 Partition Coefficient of Phenol-2EO with CN at 55 and 85°C and 30,000 ppm NaBO2 Brine
Figure 3.16 shows the partition coefficient of phenol ethoxylates at 55 and 68°C for KPK + 12% Toluene (EACN = 9.12) with 46,000 ppm NaCl brine. The datasets were derived from phenol-2EO co-solvents.

Figure 3.16 Partition Coefficient of Phenol-2EO with KPK+12% Toluene at 55 and 68°C and 46000 ppm NaCl Brine

It seems clear that increasing temperature increases the partition coefficient of phenol ethoxylates. It also seems that from Figures 3.14-3.16, that the increase of partition coefficient is larger for components with larger NEO.

3.9 Effects of Salinity

Figure 3.17 shows the partition coefficient of phenol ethoxylates at multiple salinities with ABK crude oil (EACN = 10) at 55°C. The data was derived from phenol-4EO co-solvents. Figure 3.18 shows the cumulative partition coefficients versus salinity.
3.10 Effects of Oil EACN

The effects of temperature, the number of ethylene oxide groups, and salinity on the co-solvent partition coefficients as shown above was determined first. The oil phase was studied next. The ABK and KPK dead oils were diluted with toluene, octane, and hexadecane to make oils with a wide range of EACNs to determine if partition coefficients
scaled with EACN. Octane and hexadecane were chosen because they bracket the ABK and KPK dead oil EACNs.

The oils were diluted with pure hydrocarbons to adjust the EACN. Pure hydrocarbons were studied first. Figure 3.19 shows the partition coefficients of phenol ethoxylates with toluene, octane, and hexadecane at 55°C and in 46000 ppm NaCl.

![Figure 3.19 Partition Coefficients of Phenol-xEO with Pure Toluene, Octane, and Hexadecane](image)

Figure 3.20 shows the partition coefficients of phenol ethoxylates with KPK dead oil (EACN = 12.35), KPK + 12% toluene (EACN = 9.12), KPK + 20% octane (EACN = 10.74), and KPK + 20% hexadecane (EACN = 13.19) at 55°C and 46,000 ppm NaCl brine. The KPK dead oil data fall between the toluene and octane dilution.
Figure 3.20 Partition Coefficients of Phenol-xEO with Multiple EACN KPK Oils at 55°C and 46000 ppm NaCl Brine

Figure 3.21, Figure 3.22, and Figure 3.23 show the change of partition coefficients with mole and volume fraction of toluene, octane, and hexadecane with KPK crude oil at the base conditions. The plotted partition coefficients were the values predicted by the exponential trends shown in Figure 3.20.

Figure 3.21 Partition Coefficient of Phenol-xEO with Mixtures of KPK and Toluene at 55°C and 46000 ppm NaCl Brine
Figure 3.22 Partition Coefficient of Phenol-xEO with Mixtures of KPK and Octane at 55°C and 46000 ppm NaCl Brine

Figure 3.23 Partition Coefficient of Phenol-xEO with Mixtures of KPK and Hexadecane at 55°C and 46000 ppm NaCl Brine

Figure 3.24 depicts the partition coefficients of phenol ethoxylates with ABK dead oil (EACN = 10), ABK + 20% toluene (EACN = 6.54), ABK + 20% octane (EACN = 9.33), and ABK + 20% hexadecane (EACN = 11.22) at 55°C and 46000 ppm NaCl. This is a combination of Figure 3.6, Figure 3.11, Figure 3.8, and Figure 3.12.
Figure 3.24 Partition Coefficients of Phenol-xEO with Multiple EACN ABK Oils at 55°C and 46000 ppm NaCl Brine

Figure 3.25 and Figure 3.26 show the change of partition coefficient with mole and volume fraction of toluene and hexadecane with ABK crude oil at the same conditions.

Figure 3.25 Partition Coefficient of Phenol-xEO with Mixtures of ABK and Toluene at 55°C and 46000 ppm NaCl Brine
Figure 3.26 Partition Coefficient of Phenol-xEO with Mixtures of ABK and Octane at 55°C and 46000 ppm NaCl Brine

Figure 3.27 Partition Coefficient Versus Mole/Volume Fraction Hexadecane with ABK at 55°C and 46000 ppm NaCl

Figure 3.19 shows that the partition coefficients of phenol ethoxylates with toluene are significantly greater than octane and hexadecane. More experiments are required to determine the correlation between co-solvent partition coefficients and oil EACN.

The partition coefficients scaled well with both the volume fraction and the mole fraction of diluent. However, since EACN scales with the mole fraction of diluent, the mole fraction relationship is favored. More experiments with different fractions of diluent are required to confirm this relationship.
3.11 Partitioning of Co-solvents in Microemulsions

In Dwarakanath et al. (2008), the co-solvent concentrations in the excess water and microemulsion phases in a phase behavior salinity scan up to the optimum salinity were measured using gas chromatography with flame ionization detector. They measured the oil-water partition coefficient of their co-solvent to be 0.31. They show a marked increase of co-solvent concentration in the microemulsion phase from type I to type III, and a markedly lower co-solvent concentration in the excess water phase in type III. In addition, using a simple mass balance of their data shows that the partition coefficient of co-solvent between the type I microemulsion and excess oil was approximately 0.75. This study shows that co-solvents and surfactants have a significantly effect on each other.

In this section, the microemulsion-water partition coefficients of phenol-2EO and phenol-4EO co-solvents were determined for two optimized surfactant formulations with the CN and ABK crude oils studied previously. The formulations and optimum salinity conditions for the three oils are show in Table 3.11.

<table>
<thead>
<tr>
<th>Crude Oil</th>
<th>Formulation</th>
<th>Expected Optimum Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABK (EACN = 10)</td>
<td>0.66% C28(O)-25PO-25EO-COO 0.3% C15-18 IOS 0.4% C19-23 IOS 0.6% Phenol-4EO</td>
<td>60000 ppm NaCl (\sigma_o = 9) and (\sigma_w = 6) 85 C</td>
</tr>
<tr>
<td>CN (EACN = 13.45)</td>
<td>0.4% C18-45PO-30EO-COO 0.6% C19-28 IOS 0.5% Phenol-2EO</td>
<td>30000 ppm NaBO2 (\sigma_o = 12) and (\sigma_w = 12) 85 C</td>
</tr>
</tbody>
</table>

Figure 3.28 shows the phase behavior results for ABK crude oil. The formulation had 0.6% phenol-4EO co-solvent. The oil/water partition coefficient for phenol-4EO at these conditions was determined to be 0.98. Figure 3.29 shows the solubilization ratios of one of the microemulsion samples with time. The solubilization ratios indicate this sample
was below the optimum salinity since the value for oil is less than the value for water. The aqueous and microemulsion phases were extracted after 38 days of aging.

![Figure 3.28 ABK Phase Behavior with Phenol-4EO](image)

![Figure 3.29 Solubilization Ratios of ABK Microemulsion Sample Versus Time](image)

Figure 3.28 ABK Phase Behavior with Phenol-4EO

Figure 3.29 Solubilization Ratios of ABK Microemulsion Sample Versus Time

Figure 3.30 shows the phase behavior results for CN crude oil. The formulation had 0.5% phenol-2EO co-solvent. The oil/water partition coefficient for phenol-2EO at these
conditions was determined to be 1.00. The CN type III microemulsion samples showed solubilization ratios consistent with the optimum salinity. Figure 3.31 shows the solubilization ratios of one of the microemulsion samples with time. The aqueous and microemulsion phases were extracted after 38 days of aging.

![Figure 3.30 CN Phase Behavior with Phenol-2EO](image1)

![Figure 3.31 Solubilization Ratios of CN Microemulsion Sample Versus Time](image2)
The co-solvent concentrations in the excess water and microemulsion phases were determined from HPLC analysis. With deconvolution, the concentrations of the individual co-solvent components in these phases were determined. Through mass balance, the cumulative and individual concentrations of co-solvents in the excess oil phase were calculated. The calculation starts with a mass balance equation and two volume balance equations:

\[ C_w C_{a1wi} = C_w^* C_{a1w}^* + C_{ME}^* C_{a1ME}^* + C_o^* C_{a1o}^* \]
\[ C_w + C_o = 1 \]
\[ C_w^* + C_{ME}^* + C_o^* = 1 \]

Where,

\( C_w \) and \( C_o \) are the initial volume fractions of the water and oil phases
\( C_w^* \), \( C_{ME}^* \), and \( C_o^* \) are the volume fractions of the water, microemulsion, and oil phases at equilibrium (designated by *)
\( C_{a1wi} \) is the concentration of co-solvent 1 in the initial water phase
\( C_{a1w}^* \), \( C_{a1ME}^* \), and \( C_{a1o}^* \) are the concentrations of co-solvent 1 in the water, microemulsion, and oil phases at equilibrium (designated by *)

The concentration of co-solvent 1 in the oil phase at equilibrium, \( C_{a1o}^* \), and the partition coefficient of co-solvent between oil and water, \( K_{ow} \), and between microemulsion and water, \( K_{mw} \), are

\[ C_{a1o}^* = \frac{C_w C_{a1wi} - C_w^* C_{a1w}^* - C_{ME}^* C_{a1ME}^*}{C_o^*} \]
\[ K_{ow} = \frac{C_{a1o}^*}{C_{a1w}^*} \]
\[ K_{mw} = \frac{C_{a1ME}^*}{C_{a1w}^*} \]

The concentration of co-solvent in the microemulsion \( C_{aME} \) includes the co-solvent in the solubilized water and oil. The concentration of co-solvent participating at the
interface, described earlier as the surfactant pseudo component, is more useful and interesting.

The following simplifying assumptions were made to calculate the co-solvent concentration in the surfactant pseudo component.

a) The co-solvent concentrations in the excess water and excess oil phases were the same as those in the solubilized water and oil in the microemulsion.

b) The pure surfactants have the density of water. Therefore the surfactant mass fraction equals the surfactant volume fraction.

c) The surfactant pseudo component contains only surfactant and partitioned co-solvent

d) The surfactant pseudo component maintains the volume of the pure surfactant. Therefore, the co-solvent does not swell the phase volume.

e) The volume fraction of the surfactant pseudo component is negligible compared to the volume fraction of water.

The calculation started with a similar mass balance:

\[
C_w C_{a1wi} = C_w C_{a1w}^* + C_p C_{a1p}^* + C_o C_{a1o}^* \\
C_w + C_o = 1
\]

Where,

- \(C_w, C_o, \text{ and } C_p\) are the initial volume fractions of water, oil, and surfactant pseudo component
- \(C_{a1wi}\) is the concentration of co-solvent 1 in the initial water phase
- \(C_{a1w}^*, C_{a1p}^*, \text{ and } C_{a1o}^*\) are the concentrations of co-solvent 1 in the water, surfactant pseudo, and oil phases at equilibrium (designated by *)

The volume fraction of surfactant pseudophase is

\[
C_p = C_w \sum_{i=1}^{n} C_{si}
\]

Where,
Csi is the weight fraction of surfactant i initially in the aqueous phase
n is the number of surfactant components

The concentration of co-solvent 1 in the surfactant pseudo component is

\[ C_{a1p}^* = \frac{C_w C_{a1w} - C_w C_{a1w}^* - C_o C_{a1o}^*}{C_p} \]

The co-solvent partition coefficient between the surfactant pseudo component and water is

\[ K_{pw} = \frac{C_{a1p}^*}{C_{a1w}^*} \]

Table 3.12 shows the partitioning of phenol-4EO co-solvent in ABK type III microemulsion. The results for phenol-1EO to phenol-5EO components are shown in Figure 3.32. Since the compositions of the co-solvents were not quantified, the concentrations of the phenol ethoxylate components are expressed as normalized concentrations, which are the sample component concentrations normalized by the initial component concentrations. For ABK, there was initially 0.6% phenol-4EO co-solvent and 1.36% surfactant. The excess water, microemulsion, and excess oil volume fractions were 0.46, 0.07, and 047, respectively. Only the data for phenol-1EO to phenol-5EO components are shown because the signals were large and reliable. The relative proportion of each component can be seen by the initial concentration signal relative to the cumulative initial concentration signal.

Figure 3.33 shows the oil-water partition coefficients for phenol-4EO components with ABK oil at 85C and 60,000 ppm NaCl brine in the absence of surfactants (shown previously in previously in Figure 3.15) and in the presence of surfactants. The oil-water partition coefficients with and without surfactants seemed to agree within uncertainty of the measurements. The data for the individual components also seemed to agree with the cumulative data.
Table 3.12 Partitioning of Phenol-4EO Co-solvent in ABK Type III Microemulsion

<table>
<thead>
<tr>
<th></th>
<th>Ph-1EO</th>
<th>Ph-2EO</th>
<th>Ph-3EO</th>
<th>Ph-4EO</th>
<th>Ph-5EO</th>
<th>Cumulative</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Concentration Signal</td>
<td>268.14</td>
<td>444.36</td>
<td>368.88</td>
<td>219.70</td>
<td>98.95</td>
<td>1564.42</td>
</tr>
<tr>
<td>Normalized Initial Concentration</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>Normalized Concentration in Excess Water</td>
<td>0.417</td>
<td>0.473</td>
<td>0.530</td>
<td>0.594</td>
<td>0.704</td>
<td>0.503</td>
</tr>
<tr>
<td>Normalized Concentration in ME</td>
<td>0.796</td>
<td>0.948</td>
<td>0.991</td>
<td>0.971</td>
<td>0.910</td>
<td>0.897</td>
</tr>
<tr>
<td>Normalized Concentration in Excess Oil</td>
<td>0.541</td>
<td>0.465</td>
<td>0.404</td>
<td>0.344</td>
<td>0.245</td>
<td>0.442</td>
</tr>
<tr>
<td>Normalized Concentration in Interface</td>
<td>3.096</td>
<td>4.544</td>
<td>4.893</td>
<td>4.585</td>
<td>3.779</td>
<td>3.556</td>
</tr>
<tr>
<td>Kow</td>
<td>1.30</td>
<td>0.98</td>
<td>0.76</td>
<td>0.58</td>
<td>0.35</td>
<td>0.88</td>
</tr>
<tr>
<td>Kmw</td>
<td>1.91</td>
<td>2.00</td>
<td>1.87</td>
<td>1.63</td>
<td>1.29</td>
<td>1.78</td>
</tr>
<tr>
<td>Kpw</td>
<td>7.42</td>
<td>9.60</td>
<td>9.25</td>
<td>7.72</td>
<td>5.38</td>
<td>7.07</td>
</tr>
</tbody>
</table>

Figure 3.32 Results of ABK Type III Microemulsion
Figure 3.33 Oil-Water Partition Coefficients of Phenol-4EO with ABK with and without Surfactants

Table 3.13 shows the results of the CN type III microemulsion. The results for phenol to phenol-4EO components are shown in Figure 3.32. This experiment initially had 0.5% or 5000 ppm phenol-2EO and 1% total surfactant. The excess water, microemulsion, and excess oil volume fractions were 0.46, 0.11, and 0.43, respectively. The component data seemed to agree with the cumulative data.

Figure 3.35 shows the oil-water partition coefficients for phenol-2EO components with CN oil at 85°C and 63,000 ppm NaBO2 brine in the absence of surfactants (shown previously in previously in Figure 3.16) and in the presence of surfactants. The oil-water partition coefficients with and without surfactants seemed to agree within uncertainty of the measurements. The data for the individual components also seemed to agree with the cumulative data.
Table 3.13 Partitioning of Phenol-2EO Co-solvent in CN Type III Microemulsion

<table>
<thead>
<tr>
<th></th>
<th>Phenol</th>
<th>Ph-1EO</th>
<th>Ph-2EO</th>
<th>Ph-3EO</th>
<th>Ph-4EO</th>
<th>Cumulative</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Concentration Signal (AU)</td>
<td>260.18</td>
<td>722.05</td>
<td>452.84</td>
<td>170.20</td>
<td>55.50</td>
<td>1699.65</td>
</tr>
<tr>
<td>Normalized Initial Concentration</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>Normalized Concentration in Excess Water</td>
<td>0.404</td>
<td>0.475</td>
<td>0.540</td>
<td>0.584</td>
<td>0.597</td>
<td>0.397</td>
</tr>
<tr>
<td>Normalized Concentration in ME</td>
<td>0.693</td>
<td>0.837</td>
<td>0.897</td>
<td>0.883</td>
<td>0.797</td>
<td>0.650</td>
</tr>
<tr>
<td>Normalized Concentration in Excess Oil</td>
<td>0.554</td>
<td>0.443</td>
<td>0.359</td>
<td>0.316</td>
<td>0.325</td>
<td>0.380</td>
</tr>
<tr>
<td>Normalized Concentration in Interface</td>
<td>4.275</td>
<td>8.167</td>
<td>10.103</td>
<td>9.974</td>
<td>7.794</td>
<td>5.217</td>
</tr>
<tr>
<td>Kow</td>
<td>1.38</td>
<td>0.94</td>
<td>0.67</td>
<td>0.54</td>
<td>0.55</td>
<td>0.96</td>
</tr>
<tr>
<td>Kmw</td>
<td>1.71</td>
<td>1.76</td>
<td>1.66</td>
<td>1.51</td>
<td>1.33</td>
<td>1.64</td>
</tr>
<tr>
<td>Kpw</td>
<td>10.43</td>
<td>17.15</td>
<td>18.70</td>
<td>17.05</td>
<td>13.04</td>
<td>13.06</td>
</tr>
</tbody>
</table>

Figure 3.34 Results of CN Type III Microemulsion
Figure 3.35 Oil-Water Partition Coefficients of Phenol-2EO with CN with and without Surfactants

For both ABK and CN, the oil-water partition coefficients were approximately 1 and the pseudo component-water partition coefficients were approximately 10. This meant that the concentrations of co-solvents in the excess water and oil phases were approximately equal, and that the concentrations in the pseudo component was approximately 10 times that in both excess water and oil phases. Also, for both microemulsions, the co-solvent components in the center of the distribution were the most abundant in the pseudo component, as the lower EO number components were more drawn to the excess oil phase and the higher EO number components were more drawn to the excess water phase. The results show that co-solvent clearly prefers the interface created by the presence of surfactants.

One of the largest source of uncertainty are with the phase volumes. In the oil-water samples, the phase volumes were equal and showed no measureable change with age, and the uncertainty of the co-solvent concentration in the oil phase was largely only dependent of the co-solvent concentration in the aqueous phase. However, in the microemulsion samples, there was an additional phase, and the volumes and the precision of the volumes changed significantly, and the co-solvent concentration in the oil phase was dependent on
3 phase volumes and the concentrations in the water and microemulsion phases. Thus, the uncertainty in results for the microemulsion samples were significantly higher than that for the oil and water samples.

In addition to this, the uncertainty in the results for individual components was affected by the uncertainty in the deconvolution, and the uncertainty in the cumulative co-solvent results was affected by the distribution bias discussed previously.

In the future, the partition coefficients of co-solvents with other oils should be measured to better understand how the partition coefficient relates with oil. The next step would be to develop a correlation on the component level with the number of ethylene oxide groups, the temperature, the salinity, and the oil. Using the HPLC, the composition of the different co-solvents can be quantified using an internal standard or by standard addition with the pure components (if obtainable). With both the composition data and the correlation, the cumulative partition coefficient of the co-solvents could be estimated with any oil at any temperature and salinity. This would greatly improve co-solvent selection and optimization.

The phenol-monopropoxy ethoxylate co-solvents showed promise of having higher partition coefficients than the equivalent phenol ethoxylate co-solvent. The effects of the propylene oxide group on microemulsion properties should be studied. Other co-solvents can be studied with these methods. Samples of n-butanol ethoxylates, including triethylene glycol monobutyl ether (TEGBE) and ethylene glycol monobutyl ether (EGBE), with ABK oil were made. However, due to complications the HPLC, the elutions of the analyte peaks approached that of the carrier fluid and the signal was overwhelmed by noise. No meaningful data were measured for n-butanol ethoxylates. However, modifications to the HPLC injection volumes, the solvent gradient program, and the ELSD could fix these problems for n-butanol ethoxylates. Fortunately, the chromatograms for IBA ethoxylates with similar number of ethylene oxide groups were of higher resolution. However, the partition coefficients were much lower than that of phenol ethoxylates with equivalent number of ethylene oxide groups, so the uncertainty was much higher for them.
The partitioning of co-solvents should be studied with other oils, with other formulations and with type I and type II microemulsions. It would be interesting to see the effects of poorly optimized formulations and imbalanced oil-water partitioning co-solvents on the partitioning to the surfactant pseudo component and the microemulsion. Finally, it would be incredibly useful to relate the co-solvent partitioning to the surfactant pseudo component and the microemulsion with the microemulsion viscosity.

The effects of temperature and salinity on the partition coefficients of co-solvent components with different numbers of ethylene oxide groups may reveal fundamental properties, which can be related to the ethylene oxide groups in surfactants.

The uncertainty of this data should be quantified, and this procedure could be optimized to reduce uncertainty. For example, the procedure currently yields values with very large uncertainty for high-EO and low partition coefficient co-solvents. By increasing the oil to water ratio, a larger difference between the initial and final aqueous co-solvent concentrations could be measured, which would reduce the uncertainty.

The HPLC solvent gradient program should also be optimized to improve the resolution, which would greatly reduce the dependence of the individual component data on the mathematical deconvolution.
Chapter 4: Equivalent Alkane Carbon Number Study

4.1 Purpose

The equivalent alkane carbon number (EACN) of an oil is the carbon number of
the alkane with the same optimum salinity based on phase behavior experiments using
the same surfactant. The empirical rule developed by Cayias et al. (1976) for the EACN of
pure non-alkanes is:

\[
\text{EACN} = \text{Number of Carbons} - 2 \times \text{Number of Rings} - \frac{4}{3} \times \text{Number of Double Bonds}
\]

The purpose of measuring the EACN of crude oils is to create surrogate oils that
match the live oil EACN. Using these surrogate oils allows for more efficient screening of
surfactant formulations since it is not practical to test a large number of surfactants using
live oil at high pressure.

Table 4.1 shows the typical diluents used in surrogate oils and their respective
EACNs. Alkanes with carbon numbers of 6 and greater have shown a strong correlation
between the logarithm of optimum salinity and EACN. Toluene, cyclohexane, and decalin
are commonly used diluents in surrogate oils. They are used to mimic the light components
in the live oils to match the live oil EACN and often to match the live oil viscosities. The
dead crude oils studied range from EACN of 10 to EACN of 21.1.

<table>
<thead>
<tr>
<th>Diluent</th>
<th>EACN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>1</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>4</td>
</tr>
<tr>
<td>Decalin</td>
<td>6</td>
</tr>
<tr>
<td>Hexane</td>
<td>6</td>
</tr>
<tr>
<td>Octane</td>
<td>8</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>16</td>
</tr>
</tbody>
</table>
The EACN of a mixture of n components is the mole weighted average of the EACN of each component.

\[ \text{EACN} = \sum_{i}^{n} x_i \text{EACN}_i \]

With the same surfactant formulation, crude oils and pure hydrocarbons tend to exhibit different microemulsion phase behavior properties. However, moderate dilutions of the crude oils with pure hydrocarbons tend to exhibit microemulsion properties comparable to those with the crude oil. Pure hydrocarbons are added to the dead crude oil to adjust its EACN to the value desired for the surrogate oil. The EACN of the surrogate oil is given by the following equation in terms of the mole fractions of each oil.

\[ \text{EACN}_{DO+d} = x_d \text{EACN}_d + x_{DO} \text{EACN}_{DO} \]

The optimum salinity is plotted versus the EACN for each oil. The EACN of the diluted oils are functions of the dead oil EACN, which is the unknown variable. The dead oil EACN is the value that yields the best fit (maximum R-squared) between the logarithm of optimum salinity and EACN.

### 4.2 Procedure

**Determination of Oil Molecular Weight**

The viscosity of the crude oils were measured at 25°C to estimate the oil molecular weight using an empirical correlation developed by Closmann et al., which relates the crude oil viscosity at 25°C and the crude oil molecular weight. The correlation works effectively over a broad range of oil viscosities. In the paper, the oil molecular weights were determined by gas chromatography. The empirical equation for the molecular weight (MW) from the oil viscosity at 25°C (μ) is as follows:
\[ MW = 140.5 + 53.7\ln(\mu) - 1.915\ln(\mu)^2 \]

The crude oil viscosities were measured with the TA ARES Rheometer at different shear rates to find out if the oil was Newtonian. For crude oils with melting points higher than 25°C, the viscosity at 25°C was extrapolated from viscosity measurements at multiple temperatures above the melting point using an exponential fit.

**Oil Dilutions**

A minimum of three alkane diluents were used. Two of the alkane diluents were chosen with EACN’s that would bracket the dead oil EACN. This enabled estimation of dead oil EACN by interpolation rather than by extrapolation, which has more uncertainty. In addition, the molar concentrations of the non-alkane diluents were chosen such that their probable EACNs were within the bracketed region for the same reason. The mole fraction of the bracketing alkanes were enlarged to bracket a bigger EACN range.

Excessively large perturbations to the EACN from which the formulation was optimized adversely affect the nature of the phase behavior, for example, by increasing the IFT at the optimum, by significantly affecting the microemulsion viscosity, or by developing non-classical phase behavior. Conversely, overly small perturbations would yield small measurable differences and greater relative error. Dilution concentrations between 10 to 40 mole percent seemed to be optimal.

**Formulation Screening and Phase Behavior Preparation**

The formulations for EACN determination were screened for ultra-low IFT, fast separation, and classical phase behavior. The aqueous stability limit was unimportant for this purpose. Formulations that had been tested in coreflood experiments and shown to reduce the Sorc below 5% typically met all the required screening criteria.

The formulations with inactive oils used a fixed water oil ratio. The oil phase was composed of the dead crude oil diluted to the desired mole fraction. However, the formulations predicated upon the saponification of naphthenic acids were treated
differently, because the substitution of the crude oil with diluent would affect the soap to surfactant ratio. Therefore, the ratio of dead crude oil to aqueous surfactant phase was held constant, and the diluents were added separately, using the densities and molecular weights, to obtain the desired mole fractions.

Using the known optimum salinity of the formulation from past experiments, the approximate dead oil EACN from the correlation in section 4.4, and the relationship between optimum salinity with EACN in section 4.2, the optimum salinities of the oil EACN scans were roughly estimated to optimize the precision of the measurements.

**Mixing and Emulsion Testing**

The interfaces of the phases were recorded over time to determine the rate of change. When the volumes and optimal salinity had stabilized, the fluids were assumed to be approximately at equilibrium. In addition to plotting the oil and water solubilization ratios, the emulsion test was used to identify the sample with the lowest IFT or the sample closest to the optimum salinity. The optimum solubilization ratios were taken as the intercept of the oil and water solubilization ratios.

**4.3 EACN Determination Results**

The EACN of several crude oils were determined. The formulations, oil properties, and results are shown in Table 4.2. The temperatures shown are the temperature at which the experiments were aged, which were typically but not necessarily the reservoir temperature. All formulations used either sodium carbonate or sodium metaborate as the alkali. The table indicates whether or not the oil was active, and because there was alkali, all active oil formulations also generated soap. The TAN in mg KOH per g oil is given in Table 4.2 if reported or measured. The reported oil API gravity is also given in Table 4.2. The oil molecular weight in grams per mole was calculated from either GC data or the Closmann viscosity correlation when not available from a PVT report.

Experiments 1 through 10 were measured by an earlier and different procedure, where the soap to surfactant ratios were not always held constant. The data from these
Experiments were still useful. Experiments 11-19 used the procedure described in the previous section. Thus, active oil formulations in these experiments maintained constant soap to surfactant ratios. In addition to the optimum salinity, the optimum solubilization ratios were measured and showed a strong correlation with EACN. The fluidity or the viscosity of the microemulsion phase was qualitatively observed to decrease with increasing EACN, but the microemulsion viscosities were not quantified.

Table 4.2 EACN Determination Experiments

<table>
<thead>
<tr>
<th>Crude</th>
<th>Formulation</th>
<th>Temperature (°C)</th>
<th>Active</th>
<th>TAN</th>
<th>API gravity</th>
<th>Oil MW</th>
<th>DO EACN</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 BGM</td>
<td>0.25% C12-13-13PO-SO4 0.25% C20-24 IOS 0.5% IBA</td>
<td>55</td>
<td>Y</td>
<td>25</td>
<td>448</td>
<td>19.4</td>
<td></td>
</tr>
<tr>
<td>2 CHSU</td>
<td>Large Hydrophobe Carboxylic Acid, Internal Olefin Sulfonate</td>
<td>110</td>
<td>N</td>
<td>30</td>
<td>263</td>
<td>10.9</td>
<td></td>
</tr>
<tr>
<td>3 KPK</td>
<td>0.5% C28-35PO-10EO-COO 0.5% C19-23 IOS</td>
<td>68</td>
<td>N</td>
<td>23.5</td>
<td>269</td>
<td>12.4</td>
<td></td>
</tr>
<tr>
<td>4 SAMA</td>
<td>Large Hydrophobe Carboxylic Acid, Internal Olefin Sulfonate</td>
<td>78</td>
<td>N</td>
<td>222</td>
<td>11.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 PCN</td>
<td>1% C16-7PO-14EO-SO4</td>
<td>38</td>
<td>Y</td>
<td>5.14</td>
<td>16.8</td>
<td>410</td>
<td>19.3</td>
</tr>
<tr>
<td>6 HSE</td>
<td>0.15% C28-25PO-55EO COO-0.15% IOS 19-23 1% IBA-5EO</td>
<td>100</td>
<td>Y</td>
<td>3.5</td>
<td>-</td>
<td>500</td>
<td>17.0</td>
</tr>
<tr>
<td>7 BAR</td>
<td>0.125% C28-35PO-20EO-SO4 0.125% C28-35PO-50EO-SO4 0.125% C15-18 IOS 0.125% C19-23 IOS 0.5% TEGBE</td>
<td>100</td>
<td>Y</td>
<td>2.08</td>
<td>32.6</td>
<td>310</td>
<td>11.0</td>
</tr>
<tr>
<td>8 CHSN</td>
<td>0.5% C12-13-13PO-SO4 0.4% C19-23 IOS 1% IBA</td>
<td>55</td>
<td>N</td>
<td>-</td>
<td>37</td>
<td>230</td>
<td>10.3</td>
</tr>
<tr>
<td>9 LIBT</td>
<td>0.5% C28-45PO-30EO-COO 0.15% C15-18 IOS 0.35% C19-23 IOS</td>
<td>100</td>
<td>N</td>
<td>-</td>
<td>308</td>
<td>14.5</td>
<td></td>
</tr>
<tr>
<td>10 LEW</td>
<td>0.5% C13-13PO-SO4 0.15% C15-18 IOS 0.35% C19-23 IOS 1% SBA</td>
<td>90</td>
<td>N</td>
<td>37</td>
<td>243</td>
<td>14.8</td>
<td></td>
</tr>
<tr>
<td>11 LCI</td>
<td>30% 0.5% C12-13 13PO-Sulfate 0.5% C19-23IOS 0.5% Phenol-6EO</td>
<td>55</td>
<td>Y</td>
<td>1.18</td>
<td>25.3</td>
<td>339</td>
<td>15.0</td>
</tr>
<tr>
<td>12 LCI</td>
<td>25% 0.5% C12-13 13PO-Sulfate 0.5% C19-23IOS 0.5% Phenol-6EO</td>
<td>55</td>
<td>Y</td>
<td>1.18</td>
<td>25.3</td>
<td>339</td>
<td>15.0</td>
</tr>
</tbody>
</table>
Table 4.2, cont.

<p>| | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>RBD</td>
<td>0.55% C13-13PO-SO4 0.2% C20-24 IOS 0.75% Phenol-2EO</td>
<td>25</td>
<td>N</td>
<td></td>
<td>263</td>
<td>11.3</td>
</tr>
<tr>
<td>14</td>
<td>LDN</td>
<td>0.5% C13-13PO-SO4 0.5% C20-24 IOS 2% IBA</td>
<td>38</td>
<td>N</td>
<td>0.168</td>
<td>33.8</td>
<td>267</td>
</tr>
<tr>
<td>15</td>
<td>OB</td>
<td>0.5% TDA-13PO-SO4 0.5% C20-24 IOS 1% TEGBE</td>
<td>38</td>
<td>Y</td>
<td></td>
<td>412</td>
<td>21.1</td>
</tr>
<tr>
<td>16</td>
<td>CN</td>
<td>0.4% C18-45PO-30EO-COO-0.5% C19-23 IOS 0.5% Phenol-2EO</td>
<td>100</td>
<td>N</td>
<td>0.15</td>
<td>29</td>
<td>318</td>
</tr>
<tr>
<td>17</td>
<td>LBU</td>
<td>0.25% TDA-13PO-SO4 0.5% C15-18 IOS 1% TEGBE</td>
<td>55</td>
<td>Y</td>
<td>2.05</td>
<td>15</td>
<td>435</td>
</tr>
<tr>
<td>18</td>
<td>MN</td>
<td>0.4% C28-35PO-10EO-COO-0.6% C19-28 IOS 1% TEGBE</td>
<td>85</td>
<td>N</td>
<td></td>
<td>323</td>
<td>20.0</td>
</tr>
<tr>
<td>19</td>
<td>HSE</td>
<td>1% IBA-5EO</td>
<td>85</td>
<td>Y</td>
<td>3.5</td>
<td></td>
<td>566</td>
</tr>
</tbody>
</table>

In the literature, optimum solubilization ratios are typically shown as linear or inverse relationships with EACN. However, linear trends predict negative solubilization ratios at high enough EACN, and inverse trends approach infinite solubilization ratios as the EACN approaches 0. Exponential trends have more realistic limits, predicting a finite solubilization at 0 EACN and approaching zero solubilization ratio with increasing EACN.

In terms of modeling, exponential trends are nearly linear for most EACN ranges studied here and capture the horizontal asymptote of the inverse trends. Therefore, exponential trends do not significantly contradict the literature trends. For these reasons, the natural logarithm of the solubilization ratio as well as the optimum salinity was modeled as a linear function of EACN using the following equations:

\[
\ln S^* = mEACN + B
\]

\[
\ln \sigma^* = nEACN + C
\]

Where,

m and n are the slopes of optimum salinity and solubilization ratio with EACN.
B and C are the intercepts of the optimum salinity and solubilization ratio with EACN

These exponential lines were plotted through the center of mass (x, log y) of each EACN data set. The slope of the lines was determined by minimizing the square error between the experimental values and the correlation values. The standard deviation was calculated from the residuals (Y experimental – Y Predicted). Table 4.3 shows the determined slopes and standard deviations.

Table 4.3 Parameters m and n Determined from Least Squares Regression of Data

<table>
<thead>
<tr>
<th></th>
<th>Slope</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimum Salinity</td>
<td>0.084</td>
<td>3000 ppm</td>
</tr>
<tr>
<td>Optimum Solubilization Ratio</td>
<td>-0.14</td>
<td>2.7 cc/cc</td>
</tr>
</tbody>
</table>

The slope and standard deviation were determined using all the EACN experimental data shown in Table 4.2. These experiments include 17 different oils, 19 unique formulations, and 86 data points.

The optimum solubilization ratio correlation was determined using EACN experiments 9 through 18 shown in Table 4.2. These experiments used 9 different oils, 10 unique formulations, and 44 data points. The sample size for the optimum solubilization ratio correlation was much smaller in part because the data for older experiments was either unavailable or unreliable and in part because the solubilization ratios were typically more scattered and had more outliers.

LEW crude oil is an inactive and light oil. The EACN was determined using an older procedure. The different oils were made using 12.8 wt% toluene, hexane, decane, and pentadecane. The toluene dilution phase behavior scan did not exhibit ultra-low interfacial tension from emulsion test and therefore was not used in the EACN determination. The formulation was originally designed with the dead oil, and the toluene
dilution could have been too large of a perturbation to the EACN. The optimum salinity and solubilization ratios are shown in Figure 4.1.

The oil dilutions are shown in blue. The exponential trend line used to determine the dead Oil EACN though minimization of $R^2$ is shown by the dashed blue line. The dead oil EACN data point is shown in grey and indicates whether the dead oil EACN was determined by interpolation or extrapolation. The exponential correlations with the Table 4.3 slopes going through the center of mass of the data are shown with dashed orange lines. Together, these lines indicate how well the correlations match the experimental results. It seems that the optimum salinity and solubilization ratio correlations capture the trends in the data rather well.

![Figure 4.1 LEW EACN Determination](image)

LIBT crude oil crude oil is also an inactive light oil. The EACN was determined with the same method and diluents except 15 wt% diluents were used. The toluene dilution phase behavior scan also did not exhibit ultra-low interfacial tension based on the emulsion test and therefore was not used in the EACN determination. The formulation also was originally designed with the dead oil, and the toluene dilution could have been too large of a perturbation to the EACN to produce ultra-low IFT. The results are shown in Figure 4.2.
In both the LEW and LIBT experiments, the EACN of the toluene dilution was over perturbed and the EACN of the pentadecane dilution was barely greater than the dead oil EACN. The toluene dilutions needed to be reduced. Both experiments would have benefited from a larger positive EACN perturbation.

These observations paved the way for the procedure now used for EACN determination. The EACN of the toluene dilution is typically kept within the bracketing alkane dilutions, and a fairly large mole fraction (0.35) of hexadecane is typically used. Octadecane and other higher carbon number alkanes are typically not used because they are solid at room temperature and are difficult to handle.

The subsequent EACN determination experiments were conducted with the procedure detailed in this chapter. The molecular weights were determined by the Closmann correlation. The solubilization ratios were monitored over

RBD crude oil is an inactive light oil. The different oils were made from 0.175 mole fraction (7 wt%) of toluene, 0.35 of hexane, 0.3 of octane, and 0.35 of hexadecane. All dilutions exhibited viscous macroemulsions or gels in the type II region. The toluene and hexane dilutions did not exhibit ultra-low IFT and were likely over perturbed. The solubilization ratio of the octane dilution was considered an outlier and was not used in the correlation. Figure 4.3 show the results for the dead oil and the octane and hexadecane
dilutions of the dead oil. This non-ideal behavior could explain the deviation of the results from the trends.

![Graph showing optimum solubility and EACN relationship for different dilutions of dead oil.](image1)

Figure 4.3 RBD EACN Determination

LDN is an inactive light oil. The different oils were made from 0.175 mole fraction (7 wt%) of toluene, 0.35 of hexane, 0.3 of octane, and 0.35 of hexadecane. All dilutions exhibited ultra-low IFT and classical phase behavior, and all the data was used for the correlations shown in Figure 4.4. The correlations seemed to capture the trends in the data rather well.

![Graph showing optimum solubility and EACN relationship for different dilutions of dead oil.](image2)

Figure 4.4 LDN EACN Determination

OB is a moderately active medium gravity oil. The EACN was determined using the procedure detailed in this chapter for active oils. The dead oil volume was held constant.
at 30%, and the diluents were added at the appropriate volumes to achieve the desired mole fractions. The oil dilutions were 0.24 mole fraction of toluene, 0.35 of decalin, 0.41 of hexane, 0.35 of octane, and 0.40 of hexadecane. The salinity scans showed some non-ideality, where the solubilization ratios in the type I region were not smooth. The formulation was barely passable. The toluene dilution exhibited non-ideal behavior and was not used. The dead oil EACN was not successfully bracketed by alkanes. The solubilization ratio of the hexane dilution was considered an outlier. The results are shown in Figure 4.5.

![Figure 4.5 OB EACN Determination](image)

CN crude oil is an inactive light oil. The different oils were made from 0.15 mole fraction (5 wt%) of toluene, 0.35 of hexane, 0.3 of octane, and 0.35 of hexadecane. All dilutions exhibited ultra-low IFT and classical phase behavior, and all the data was used for the correlations, shown in Figure 4.6. The correlations seemed to capture the trends in the data rather well.
LBU is an active medium gravity crude oil. The EACN was determined using the procedure detailed in this chapter for active oils. The dead oil volume was held constant at 30%, and the diluents were added at the appropriate volumes to achieve the desired mole fractions. The oil dilutions were 0.15 mole fraction of toluene, 0.31 of decalin, 0.37 of hexane, 0.31 of octane, and 0.37 of hexadecane. All dilutions exhibited ultra-low IFT and classical phase behavior, but the toluene dilution significantly deviated from the trend. The apparent EACN of toluene or the EACN value for toluene that allows the optimum salinity to correlate with the other data was calculated to be 2.5. The results without toluene are shown in Figure 4.7.

The optimum solubilization ratio data deviate from the correlation. The solubilization ratios were calculated by dividing the oil volume by the surfactant volume and were therefore artificially inflated because the soap volume were not considered. The true solubilization ratios are thus lower than the computed values. However, the soap to surfactant ratio was kept constant, so the trends would still reflect the surfactant and soap normalized solubilization ratios.
MN is an inactive crude oil that is a solid at room temperature. The oil dilutions were 0.175 mole fraction of toluene, 0.35 of hexane, 0.30 of octane, and 0.35 of hexadecane. All dilutions exhibited ultra-low IFT and classical phase behavior. The dead oil EACN was not successfully bracketed by alkanes. The results are shown in Figure 4.8. The correlations seemed to capture the trends in the data.

HSE is an active heavy crude oil. The formulation used was an alkali/co-solvent/polymer (ACP) formulation. The alkali reacts with the oil to generate soap. The EACN of this oil was previously determined in experiment 6 in Table 4.2 using an alkali/surfactant/polymer formulation at 100°C. In the previous experiment, the EACN was determined to be 17, so different diluents were chosen to bracket the dead oil EACN. The
EACN was determined using the procedure detailed in this chapter for active oils. The dead oil volumes were held constant at 30%, and the diluents were added at the appropriate volumes to achieve the desired mole fractions. The oil dilutions were 0.3 mole fraction of decalin, 0.36 of octane, 0.31 of hexadecane, and 0.36 of octadecane. The scanning electrolyte increment was 1000 ppm, which offered very high resolution. All dilutions exhibited ultra-low IFT. The results are shown in Figure 4.9.

Since surfactants were not use in this experiment, the solubilization ratios were calculated using an estimate of the soap volume in the middle phase. The soap volume generated per volume of oil was calculated to be 0.03 ml soap/ml oil using the total acid number (TAN) following the methods described in Mohammadi 2008. The TAN is the milligrams of potassium hydroxide (KOH) required to titrate 1 gram of oil. The moles of KOH were assumed to be equivalent to the moles of soap. The molecular weight was assumed to be 500 g/mol, which is consistent with a C30 carboxylate. The soap density was assumed to be 1 g/cc, which is consistent with the densities assumed for surfactants.

These solubilization ratios are similar for all values of EACN and did not agree with the correlation between solubilization ratios and EACN of surfactant formulations shown here and in the literature. Soaps may not exhibit the same trends as surfactants. For this reason, these solubilization ratio data were not used in the regression analysis to determine the slope of solubilization ratio versus EACN.

Figure 4.9 HSE EACN Determination
Parallel correlation lines with the slopes m and n given in Table 4.3 were able to capture the trends in optimum salinity and solubilization ratio with EACN. This was especially true for the experiments with phase behavior of the best quality. The correlations deviated more with active oil experiments, but the confounding factor could be the higher oil viscosities, slower separation, and differences in the rate of saponification. The data of different oils with different formulations were captured by these parallel correlation lines with only different y-intercepts. This demonstrates that the slopes of the correlation lines are independent of the formulation, oil, and temperature and that the intercepts are functions of the formulation and temperature.

The correlations predict the dependence of optimum salinity and solubilization ratio on EACN outside the measured range, but should be used with caution because an over perturbation of EACN (values far from the original optimized formulation) results in non-classical phase behavior and poor correlations.

The LEW, LIBT, RBD, and OB experiments had one or more oil dilutions that exhibited non-classical phase behavior or high IFT. Table 4.4 shows the diluents, the diluent mole fractions, and EACNs of these dilutions and the nearest EACN dilutions that exhibited classical phase behavior or low IFT. For comparison, the most negatively perturbed oil dilutions for the other crude oils are shown. The high IFT oil dilutions were more negatively perturbed than the nearest low IFT oil dilution, except for OB. In OB, decalin and hexane dilutions, although being more negatively perturbed seemed more ideal.

The LEW, LIBT, and RBD formulations were optimized with the dead crude oils. The OB formulation was optimized with 20wt% decalin diluted crude oil (EACN = 14.66). The RBD oil dilutions all exhibited viscous macroemulsions or gels in the type II region, indicating that the formulation was not well optimized. However, the dead oil and the octane and hexadecane dilutions all exhibited ultra-low IFT. The OB oil dilutions showed slightly non-classical phase behavior and was considered barely passable. The RBD and OB formulations were not well optimized.

Based on LEW and LIBT, negative EACN perturbations greater than -3.5 can cause the onset of non-classical phase behavior. However, the toluene dilution with MN had a
negative perturbation of -4.90 and still exhibited classical phase behavior. The MN formulation was very well optimized and exhibited fast separation, ultra-low IFT, and fluid microemulsions. The maximum allowable negative EACN perturbation likely depends on the quality of the formulation.

Table 4.4 EACN Perturbation

<table>
<thead>
<tr>
<th>Oil</th>
<th>DO</th>
<th>EACN</th>
<th>Diluent</th>
<th>Mole Fraction</th>
<th>High IFT Oil Dilutions</th>
<th>EACN</th>
<th>ΔEACN</th>
<th>Nearest Low IFT Oil Dilutions</th>
<th>Mole Fraction</th>
<th>EACN</th>
<th>ΔEACN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lewis Creek</td>
<td>14.8</td>
<td>10.95</td>
<td>Toluene</td>
<td>0.279</td>
<td></td>
<td>Hexane</td>
<td>0.293</td>
<td>12.22</td>
<td>-2.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiBT</td>
<td>14.5</td>
<td>9.49</td>
<td>Toluene</td>
<td>0.293</td>
<td>5.01</td>
<td>Hexane</td>
<td>0.387</td>
<td>11.21</td>
<td>-3.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RBD</td>
<td>11.3</td>
<td>9.59</td>
<td>Toluene</td>
<td>0.350</td>
<td>-1.71</td>
<td>Octane</td>
<td>0.300</td>
<td>10.31</td>
<td>-0.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RBD</td>
<td>11.3</td>
<td>9.44</td>
<td>Hexane</td>
<td>0.175</td>
<td>-1.86</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OB</td>
<td>21.1</td>
<td>16.18</td>
<td>Toluene</td>
<td>0.245</td>
<td>-4.92</td>
<td>Decalin</td>
<td>0.346</td>
<td>15.88</td>
<td>-5.22</td>
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<td></td>
</tr>
<tr>
<td>OB</td>
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<td></td>
<td></td>
<td>Hexane</td>
<td>0.406</td>
<td>14.97</td>
<td>-6.13</td>
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</tr>
<tr>
<td>LDN</td>
<td>12.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Hexane</td>
<td>0.350</td>
<td>10.16</td>
<td>-2.24</td>
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<td></td>
</tr>
<tr>
<td>CN</td>
<td>13.45</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Hexane</td>
<td>0.350</td>
<td>10.84</td>
<td>-2.61</td>
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<td></td>
</tr>
<tr>
<td>LBU</td>
<td>13</td>
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<td></td>
<td></td>
<td></td>
<td>Hexane</td>
<td>0.370</td>
<td>10.41</td>
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<td>MN</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Hexane</td>
<td>0.350</td>
<td>15.10</td>
<td>-4.90</td>
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<td></td>
</tr>
<tr>
<td>HSE</td>
<td>17.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Decalin</td>
<td>0.305</td>
<td>13.99</td>
<td>-3.51</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The determinations of several other crude oils were attempted, but they exhibited non-classical phase behavior and high IFT. These experiments typically occurred when the original oil and original surfactant batches were not available.

4.4 Oil Molecular Weight and EACN Trend Analysis

In addition to correlations with the optimum salinity and solubilization ratio, a correlation between the oil molecular weight and EACN was developed. Figure 4.10 shows the dead oil EACN versus the oil molecular weights from Table 4.2. The oil molecular weights were calculated from acquired GC data, or calculated from the Closmann viscosity equation when they were not available from PVT reports. As a comparison, Figure 4.10 shows the EACN and molecular weight relationship for alkanes (C_nH_{2n+2}), unsaturated hydrocarbons (C_nH_{n+2}), and partially unsaturated hydrocarbons consisting of 10 fully saturated carbons (C_{10+n}H_{22+n}). It is clear that crude oils have a lower EACN to molecular
weight ratio than pure alkanes and a higher EACN to molecular weight ratio than unsaturated hydrocarbons. The linear correlation through the data shown as a dashed blue line shares the same EACN to molecular weight ratio as the partially unsaturated hydrocarbons.

The crude oils seem to exhibit a combination of both alkane and unsaturated hydrocarbon behaviors. These results seem to agree with the conclusions that the phase behavior of pure hydrocarbons differ from that of crude oils.

Figure 4.10 Correlation of Oil EACN and Oil Molecular Weight

This correlation between the dead oil EACN and the oil molecular weight however weak is useful for predicting the EACN and screening formulations of new oils. This can also be a valuable tool for understanding the effects of diluents in surrogate oils and live oils. The combination of the optimum salinity and molecular weight correlations with
EACN would enable the prediction of the optimum salinity shift with different oil dilutions and the design of more efficient salinity scans for EACN determination.

In summary, the optimum salinity and solubilization ratio data correlated with EACN, and especially so with the highest quality data from exceptionally well optimized formulations. The data was regressed to obtain the slopes m and n in Table 4.2. This is equivalent to saying the lines on a semi-log plot are parallel and independent of the formulation, oil and temperature. The y-intercepts are a function of the formulation and temperature.

However, the correlations for optimum salinity and solubilization ratios do not capture all aspects of microemulsion phase behavior, and EACN only empirically captures some of the oil interactions. Future works should be aimed at studying the influences of oil compositions by utilizing GC and SARA analysis data and quantifying the trends between microemulsion viscosity and EACN.

The optimum salinity and solubilization ratios are subjective and have a large uncertainty, which is often made worse by non-classical phase behavior. At best, the accuracy of the optimum salinity, determined by emulsion test, is limited to the salinity increment of the scan. The optimum solubilization ratios were taken as the intercept of the oil and water solubilization ratios, which are subjectively drawn. Non-classical phase behavior often further complicates the interpretation of the change of solubilization ratio with salinity. The most significant source of error occurs because the phase behaviors are not fully equilibrated. This is a large systematic error that can result in an uncertainty of ±50%. These experiments were specifically monitored over an extended period of time, and the reported optimum salinity and solubilization ratios were taken when the phase volumes had settled.
Chapter 5: Optimum Salinity Correlation

5.1 Purpose

Solairaj (2012) developed a correlation that quantified the relationship between certain surfactant and oil properties, temperature, and optimum salinity. The correlation was developed from multivariable regression of phase behavior data from optimized surfactant formulations using inactive oils. The correlation did not account for the effect of co-solvent and hydrophobe branching on the optimum salinity. The correlation captured the known trends of certain surfactant attributes such as the number of ethylene oxide groups, the number of propylene oxide groups, and the carbon number of the hydrophobe. Solairaj did not attempt to correlate the solubilization ratio data from these same phase behavior experiments. Furthermore, much more phase behavior data are available now than at the time he developed the correlation with optimum salinity.

The purpose of this study was to find an improved correlation that more accurately quantifies the relationship between surfactant structure, co-solvents, oil, temperature, and optimum salinity. A correlation was developed using a new and much larger high quality dataset. First, the old correlation was tested using the new expanded dataset. Next several attempts to improve the old correlation were made. These modified correlations are discussed and the results presented below. Lastly, a new correlation was developed and the results using it with the new dataset are presented and discussed.

5.2 The 2012 Correlation Equation

Solairaj et al. (2012) used the following equation to correlate the phase behavior data:

\[ N_c = a_1 N_{PO} + a_2 N_{EO} + a_3 (T - Tr) + a_4 \log(S^*) + a_5 EACN + C \quad (1) \]

Where,

- \( a_1, a_2, a_3, \ldots a_m \) are regression coefficients
- \( C \) is the intercept
Nc is the mole weighted average number of carbons in the hydrophobe of the surfactant mixture (\(Nc = \sum_{i=1}^{n} x_i Nc_i\), where \(x_i\) and \(Nc_i\) is the mole fraction and carbon number in the hydrophobe of surfactant \(i\))

NPO is the mole weighted average number of propylene oxide groups of the surfactants mixture (\(NPO = \sum_{i=1}^{n} x_i NPO_i\), where \(x_i\) and \(NPO_i\) is the mole fraction and number of propylene oxide groups of surfactant \(i\))

NEO is the mole weighted average number of ethylene oxide groups of the surfactants mixture (\(NEO = \sum_{i=1}^{n} x_i NEO_i\), where \(x_i\) and \(NEO_i\) is the mole fraction and number of ethylene oxide groups of surfactant \(i\))

\(T-Tr\) is the difference in aged temperature in Celsius and a reference temperature of 21°C

\(\log(S^*)\) is the logarithm (in base 10) of the optimum salinity in ppm

EACN is the equivalent alkane carbon number of the oil

The coefficients of the 2012 correlation were determined from multivariable regression of the phase behavior data for 34 optimized formulations using inactive oils with known or estimated values of EACN. Many other data were not used because the oils were active or the oil EACN had not been measured yet at the time. At the time this study was completed, the number of optimized formulations with complete and useable data (Dataset 47) was 124 (out of a total of more than 1200 formulations in the complete dataset). Thus, the useable dataset is almost four times larger than it was in 2012.

Table 5.1 shows the 2012 correlation coefficients, standard errors, and normalized standard errors evaluated with the 2012 dataset and with dataset 47. Table 5.1 also shows the values from the same multivariable regression of dataset 47. Figure 3.1 shows a comparison of the calculated versus experimental NC of the 2012 dataset and Dataset 47 with the 2012 correlation coefficients. The coefficient of determination (\(R^2\)) decreased from 0.878 with the 2012 dataset to 0.210 with Dataset 47. In addition, the normalized standard errors have increased for all parameters.
In the tables, the standard error (SE) is the standard deviation of the coefficient (Coeff). The normalized standard error (NSE) is the absolute value of the quotient of the standard error and the coefficient. Normalized standard errors greater than 1 indicate that one standard error away would result in a positive to negative or negative to positive sign change of the coefficient. This means that the variable is very weakly correlated and is likely statistically insignificant. Typically, normalized standard errors greater than 1 will be shown in red. The statistical significance of coefficients were evaluated based on the normalized standard errors and qualitatively based on the predicted trends. The table also shows the sample size (N) of the dataset used for the regressions and the R-squared value corresponding to the calculated versus experimental NC, which are plotted in the figures.

Figure 5.2 compares the calculated versus experimental NC of dataset 47 with the 2012 coefficients and the dataset 47 coefficients. The R² increased from 0.210 with the 2012 coefficients to 0.584 with the dataset 47 coefficients. Comparing the 2012 dataset coefficients and the dataset 47 coefficients, the relative magnitudes of the coefficients of NPO and NEO remained approximately 2:1, and the coefficients for temperature remained 0.03. However, the coefficient for the Log(S*) changed from -10.75 to 0.52, which would yield a negative correlation with EACN, which does not follow experimental observations. This could be explained by confounding factors such as co-solvents and head groups, which were not accounted for in this correlation.

Table 5.1 Coefficients of 2012 Correlation with Original Dataset and Dataset 47

<table>
<thead>
<tr>
<th>Coeff</th>
<th>SE</th>
<th>NSE</th>
<th>Coeff</th>
<th>SE</th>
<th>NSE</th>
<th>Coeff</th>
<th>SE</th>
<th>NSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept, C</td>
<td>65.60</td>
<td>7.54</td>
<td>0.11</td>
<td>65.60</td>
<td>11.02</td>
<td>0.17</td>
<td>20.22</td>
<td>6.55</td>
</tr>
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<td>NPO, a1</td>
<td>-1.30</td>
<td>0.12</td>
<td>0.09</td>
<td>-1.30</td>
<td>0.30</td>
<td>0.23</td>
<td>-1.45</td>
<td>0.18</td>
</tr>
<tr>
<td>NEO, a2</td>
<td>-0.59</td>
<td>0.12</td>
<td>0.21</td>
<td>-0.59</td>
<td>0.43</td>
<td>0.73</td>
<td>-0.76</td>
<td>0.26</td>
</tr>
<tr>
<td>T-Tref, a3</td>
<td>0.03</td>
<td>0.01</td>
<td>0.34</td>
<td>0.03</td>
<td>0.02</td>
<td>0.57</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>Log S*, a4</td>
<td>-10.75</td>
<td>1.59</td>
<td>0.15</td>
<td>-10.75</td>
<td>2.31</td>
<td>0.22</td>
<td><strong>0.52</strong></td>
<td>1.38</td>
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<td>EACN, a5</td>
<td>0.48</td>
<td>0.10</td>
<td>0.21</td>
<td>0.48</td>
<td>0.11</td>
<td>0.24</td>
<td>0.14</td>
<td>0.07</td>
</tr>
<tr>
<td>N</td>
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<td>124</td>
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<tr>
<td>R-squared</td>
<td>0.878</td>
<td>0.210</td>
<td>0.584</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
Figure 5.1 Original Dataset and Dataset 47 with 2012 Correlation Equation and 2012 Coefficients
Figure 5.2 The 2012 Dataset and Dataset 47 with the 2012 Correlation Equation and Regressed Coefficients

5.3 The 2012 Correlation Equation with Additional Parameters

The first confounding factor studied was the surfactant head group. The sulfate and carboxylate anions have different hydrophilicity due to differences in partial charge and different dissociation constants with pH. Dataset 47 was divided into two subsets based on the head group of the primary surfactant, a primary sulfate surfactant subset and a primary carboxylate surfactant subset. The primary surfactants were always the largest carbon number surfactant molecule in the formulations.

The same multivariable regression was applied to the sulfate and carboxylate subsets. The results are shown in Table 3.1. Figure 5.3 shows the calculated versus experimental NC for the two subsets. Individually, the correlations for the sulfate and carboxylate subsets have significantly higher $R^2$ than the correlation for the combined
dataset 47. In addition, the sulfate and carboxylate subset correlations more closely agree with experimental observations, notably with slope of the logarithm of optimum salinity versus EACN.

Table 5.2 Regression Coefficients of Sulfate and Carboxylate Subsets

<table>
<thead>
<tr>
<th></th>
<th>Sulfates</th>
<th></th>
<th>Carboxylates</th>
<th></th>
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<tr>
<td></td>
<td>Coefficient</td>
<td>SE</td>
<td>NSE</td>
<td>Coefficient</td>
</tr>
<tr>
<td>Intercept, C</td>
<td>31.54</td>
<td>7.60</td>
<td>0.24</td>
<td>35.03</td>
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<tr>
<td>NPO, a1</td>
<td>-0.80</td>
<td>0.14</td>
<td>0.18</td>
<td>-3.18</td>
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<td>NEO, a2</td>
<td>0.79</td>
<td>0.37</td>
<td>0.46</td>
<td>-1.30</td>
</tr>
<tr>
<td>T-Tref, a3</td>
<td>0.00</td>
<td>0.02</td>
<td>3.99</td>
<td>0.02</td>
</tr>
<tr>
<td>Log S*, a4</td>
<td>-3.01</td>
<td>1.60</td>
<td>0.53</td>
<td>-1.54</td>
</tr>
<tr>
<td>EACN, a5</td>
<td>0.32</td>
<td>0.10</td>
<td>0.30</td>
<td>0.31</td>
</tr>
<tr>
<td>N</td>
<td>55</td>
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<td></td>
<td>69</td>
</tr>
<tr>
<td>R-squared</td>
<td>0.718</td>
<td></td>
<td></td>
<td>0.814</td>
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</table>

Figure 5.3 2012 Correlation With Sulfate and Carboxylate Subsets
The carboxylate and sulfate correlations showed significantly less scatter (higher R²) than the combined correlation. In addition, the Log(S*) versus EACN slopes for the sulfate and carboxylate correlations were 0.1 and 0.2, respectively. In terms of natural log of the optimum salinity, the slopes were 0.24 and 0.46, respectively. Despite being greater than the slope determined in Chapter 4, the slopes show a positive correlation between Log(S*) and EACN, whereas the combined correlation showed an unphysical negative correlation.

Having separate equations for the different primary surfactant head groups limits the applicability. For example, neither equation could reasonably represent a formulation with sulfate surfactants and soaps (carboxylates). In addition, the equation still does not directly address the head groups, specifically the sulfonate head groups, and would be difficult to extend to more complicated surfactant molecules with multiple head groups, such as Gemini surfactants.

Separation of the dataset by primary surfactant head group did significantly improve the correlation, but that may have been the result of the reduction of the sample size. The improvement does not prove that the head group was the confounding factor. In fact, it was more likely that certain head groups were used preferentially with certain hydrophobes and certain reservoir conditions, such as sulfates with C13 hydrophobes and carboxylates with higher reservoir temperatures. This would significantly bias the sulfate and carboxylate subsets and subsequently the correlations, which was evident in the disparity of the coefficients of the two equations. Ideally, the difference of head groups would have manifested itself as differences in the intercept, but differences were mainly in the coefficients for NPO, NEO, LogS*, and EACN which imply deeper confounding factors.

**Correlation Equation 2**

Equation 2 incorporates the effects of the total molar concentration of co-solvent, independent of co-solvent properties. The two main properties of co-solvents are the number of carbons in the alcohol and the number of ethylene oxide group
shown in Chapter 3 to significantly affect the partitioning and concentration in the pseudo surfactant phase.

Surfactants at the optimum salinity are predominantly in the middle phase microemulsion. For pure or nearly pure surfactants, the optimum salinity and the optimum solubilization ratio are insensitive to the total surfactant concentration, because the total surfactant concentration does not affect the hydrophilic-lipophilic balance, and the solubilization ratio is normalized to the surfactant concentration. Unlike the nearly pure surfactants used in this study, co-solvents partition between all three phases, and the phase volumes and initial concentrations affect the equilibrium concentrations. The participating fraction of the co-solvents would be proportional to the total molar concentration of co-solvent, Ca.

\[ N_c = a_1 N_{PO} + a_2 N_{EO} + a_3 (T - Tr) + a_4 \text{LOG}(S^*) + a_5 \text{EACN} + a_6 C_a + C \]  \hspace{1cm} (2)

Where

- \( C_a \) is the total molar concentration of co-solvent (moles of co-solvent per milliliter of sample) \( C_a = (1 - Co) \sum_j \frac{C_{aj}}{MW_j} \) where \( C_{aj} \) and \( MW_j \) are the initial aqueous mass fraction and the molecular weight of co-solvent \( j \) and \( Co \) is the volume fraction of oil

Table 5.3 shows the regression coefficients of Dataset 47 and the sulfate and carboxylate subsets. The addition of \( C_a \) improved the \( R^2 \) for all three cases, but the \( \text{Log}(S^*) \) coefficient for dataset 47 still resulted in a nonphysical negative correlation between \( \text{Log}(S^*) \) and EACN. Figure 3.1 and 3.2 show the calculated versus experimental NC for Dataset 47 and the sulfate/carboxylate subsets.
Table 5.3 Equation 2 Regression Coefficients

<table>
<thead>
<tr>
<th></th>
<th>Sulfates + Carboxylates</th>
<th>Sulfates</th>
<th>Carboxylates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coef</td>
<td>SE</td>
<td>NSE</td>
</tr>
<tr>
<td>C</td>
<td>14.44</td>
<td>7.01</td>
<td>0.49</td>
</tr>
<tr>
<td>NPO, a1</td>
<td>-1.11</td>
<td>0.24</td>
<td>0.21</td>
</tr>
<tr>
<td>NEO, a2</td>
<td>-0.55</td>
<td>0.27</td>
<td>0.50</td>
</tr>
<tr>
<td>T-Tref, a3</td>
<td>0.05</td>
<td>0.01</td>
<td>0.27</td>
</tr>
<tr>
<td>Log S*, a4</td>
<td>1.21</td>
<td>1.39</td>
<td>1.16</td>
</tr>
<tr>
<td>EACN, a5</td>
<td>0.13</td>
<td>0.07</td>
<td>0.49</td>
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<tr>
<td>Ca, a6</td>
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<td>4415</td>
<td>0.47</td>
</tr>
<tr>
<td>N</td>
<td>124</td>
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<td></td>
</tr>
<tr>
<td>R²</td>
<td>0.600</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.4 Equation 2 Dataset 47
Figure 5.5 Equation 2 Sulfate and Carboxylate Subsets

**Correlation Equation 3**

Equation 2 captured the effect of co-solvent concentrations. Equation 3 starts to incorporate specific properties of the co-solvents in an attempt to better improve the correlation without significantly increasing the number of regression parameters. The effect of the co-solvent properties on the correlation must scale directly with the co-solvent concentration. As the co-solvent concentration approaches zero, the effect and the parameter must approach zero. The influence of surfactants is independent of concentration and, therefore, would not have the same limits.

The number of carbons and the number of ethylene oxide groups are the two co-solvent properties that were studied. All co-solvents are composed of a primary alcohol with some number of carbons, but not all co-solvents have ethylene oxide groups. Therefore, the number of carbons in the co-solvent was the first property to be incorporated. The incorporated parameter is the mole averaged number of carbons of the
co-solvent, $N_{Ca}$, coupled (multiplied) with the total molar concentration, $Ca$, as shown in Equation 3.

$$N_c = a_1 NPO + a_2 NEO + a_3 T + a_4 \log(S^*) + a_5 EACN + a_6 C_{Ca} N_{Ca} + C \quad (3)$$

Where

$C_{Ca}N_{Ca}$ is the product of the total molar concentration $Ca$ and the mole average number of carbons (excluding the carbons in the EO groups) of the co-solvents

($N_{Ca} = \sum_{j=1}^{n} y_j N_{Caj}$, where $y_j$ and $N_{Caj}$ are the mole fraction and the number of ethylene oxide groups of co-solvent $j$)

Table 5.4 shows the regression coefficients of Dataset 47 and the sulfate and carboxylate subsets with Equation 3. The incorporation of $N_{Ca}$ did not significantly affect the $R^2$, the coefficients, or the normalized standard errors.

<table>
<thead>
<tr>
<th></th>
<th>Sulfates + Carboxylates</th>
<th>Sulfates</th>
<th>Carboxylates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coef</td>
<td>SE</td>
<td>NSE</td>
</tr>
<tr>
<td>C</td>
<td>13.60</td>
<td>6.97</td>
<td>0.51</td>
</tr>
<tr>
<td>NPO, $a_1$</td>
<td>-1.08</td>
<td>0.23</td>
<td>0.21</td>
</tr>
<tr>
<td>NEO, $a_2$</td>
<td>-0.51</td>
<td>0.27</td>
<td>0.53</td>
</tr>
<tr>
<td>T-Tref, $a_3$</td>
<td>0.05</td>
<td>0.01</td>
<td>0.26</td>
</tr>
<tr>
<td>Log $S^*$, $a_4$</td>
<td>1.30</td>
<td>1.39</td>
<td>1.07</td>
</tr>
<tr>
<td>EACN, $a_5$</td>
<td>0.14</td>
<td>0.07</td>
<td>0.48</td>
</tr>
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<td>$C_{Ca}N_{Ca}$, $a_6$</td>
<td>2721</td>
<td>1112</td>
<td>0.41</td>
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<tr>
<td>$N$</td>
<td>124</td>
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<td></td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.605</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Correlation Equation 4**

Equation 4 adds a parameter for the number of ethylene oxide groups of the co-solvent, NEOa, coupled with the total molar concentration, $Ca$. 82
\[
N_c = a_1N_{PO} + a_2N_{EO} + a_3T + a_4\log(S^*) + a_5EACN + a_6C_{a}N_{Ca} + \\
a_7C_{a}N_{EOa} + C
\]  
(4)

Where,

\( C_{a}N_{EOa} \) is the product of the total molar concentration \( C_{a} \) and the mole weighted average number of ethylene oxide groups of the co-solvents \( (N_{EOa} = \sum_{j=1}^{n} y_{j}N_{EOaj}, \) where \( y_{j} \) and \( N_{EOaj} \) is the mole fraction and number of ethylene oxide groups of co-solvent \( j \) \)

Table 5.5 shows the regression coefficients for Dataset 47 and the sulfate and carboxylate subsets using Equation 4. The addition of the \( C_{a}N_{EOa} \) term gave essentially the same value for \( R^2 \) and increased the normalized standard errors of several coefficients, but did not significantly affect the trends of individual variables.

Table 5.5 Equations 4 Regression Coefficients

<table>
<thead>
<tr>
<th></th>
<th>Sulfates + Carboxylates</th>
<th>Sulfates</th>
<th>Carboxylates</th>
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<tbody>
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<td>NSE</td>
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<tr>
<td>C</td>
<td>11.58</td>
<td>6.89</td>
<td>0.59</td>
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<tr>
<td>NPO, a1</td>
<td>-1.04</td>
<td>0.23</td>
<td>0.22</td>
</tr>
<tr>
<td>NEO, a2</td>
<td>-0.43</td>
<td>0.27</td>
<td>0.63</td>
</tr>
<tr>
<td>T-Tref, a3</td>
<td>0.05</td>
<td>0.01</td>
<td>0.25</td>
</tr>
<tr>
<td>Log(S*), a4</td>
<td>0.18</td>
<td>0.07</td>
<td>0.37</td>
</tr>
<tr>
<td>EACN, a5</td>
<td>1.43</td>
<td>1.36</td>
<td>0.95</td>
</tr>
<tr>
<td>C_{a}N_{Ca}, a6</td>
<td>3644</td>
<td>1160</td>
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</tr>
<tr>
<td>C_{a}N_{EOa}, a7</td>
<td>14544</td>
<td>6180</td>
<td>0.42</td>
</tr>
<tr>
<td>N</td>
<td>124</td>
<td></td>
<td>69</td>
</tr>
<tr>
<td>R^2</td>
<td>0.623</td>
<td></td>
<td>0.748</td>
</tr>
</tbody>
</table>

The slopes of \( \ln(S^*) \) versus EACN for all of the above equations are shown in Table 5.6. For comparison, the slope of \( \ln(S^*) \) versus EACN determined in Chapter 4 was 0.084. The slope of the 2012 correlation is in agreement with a slope of 0.084. The slopes
of the combined Dataset 47 correlations remained negative. The slopes for the sulfate and carboxylate correlations were all overestimated, but those for the sulfate correlations were much lower and in more agreement with 0.084 than those for the carboxylate correlations.

Table 5.6 Slopes of Ln(S*) Versus EACN

<table>
<thead>
<tr>
<th>Equation</th>
<th>2012 Dataset</th>
<th>Dataset 47</th>
<th>SO4 Subset</th>
<th>COO Subset</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.103</td>
<td>-0.620</td>
<td>0.245</td>
<td>0.464</td>
</tr>
<tr>
<td>2</td>
<td>-0.247</td>
<td>0.200</td>
<td>1.035</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>-0.248</td>
<td>0.208</td>
<td>1.181</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>-18.293</td>
<td>0.159</td>
<td>1.430</td>
<td></td>
</tr>
</tbody>
</table>

The coefficients for temperature, EACN, and Log(S*) typically had large normalized standard errors, which implies that some of the variables did not have a significant effect on the accuracy of the correlation. Another possibility is that the equations or underlying assumptions are fundamentally incorrect or the formulation properties were imperfectly weighted or parameterized.

Several other forms of co-solvent concentration were parameterized, such as the total mass concentration,

\[ Camt = (1 - Co) \sum_j^n C_{aj}, \]

the mole fraction of co-solvent (moles of co-solvent divided by the moles of co-solvent and surfactant):

\[ Caf = (1 - Co) \frac{\sum_j^m C_{aj}}{\sum_j^m \frac{C_{aj}}{MW_j} + \sum_i^n \frac{C_{si}}{MW_i}}, \]

and the mass fraction of co-solvent (mass of co-solvent divided by the mass of co-solvent and surfactant):

\[ Camf = (1 - Co) \frac{\sum_j^m C_{aj}}{\sum_j^m \frac{C_{aj}}{MW_j} + \sum_i^n \frac{C_{si}}{MW_i}}. \]

These different parameters yielded results very similar to those presented above.
The addition of the total molar concentration of co-solvent parameter $C_a$ significantly increased $R^2$ and improved the trends. Using the product of the carbon number of the co-solvent and the total molar concentration $C_aN_{Ca}$ instead of $C_a$ had relatively little effect on the $R^2$, the trends, and standard errors. The addition of the $C_aN_{EOa}$ parameter resulted in slight improvements to the $R^2$ but at the cost of substantially increased normalized standard errors. The normalized standard error for $C_aN_{EOa}$ in both the sulfate and carboxylate subset equations were greater than 1, implying the parameter was not statistically significant.

Based on simplicity, the value of $R^2$ for each regression, the trends predicted for individual variables, and the standard errors of the coefficients, Equation 2 is considered a better choice for correlating the data than either Equation 3 or 4.

5.4 The 2012 Correlation Equation with Optimum Salinity and EACN Relationship

Many papers have shown an approximate linear trend between the logarithm of optimum salinity and EACN. Furthermore, the slope of this trend is nearly the same for the various formulations examined in Chapter 4. Therefore, it seemed reasonable to incorporate this linear equation using a constant slope based on all of the data into Equations 1 through 4. This combination reduces the number of coefficients by one and ensures the regression of the data does not yield a non-physical slope. For example, the algebraic combination with Equation 1 with Equation 5 is shown below.

$$\ln S^* = mEACN + B$$ (5)

$$Nc = a1NPO + a2NEO + a3T + a4 \log S^* + a5 EACN + C$$
$$Nc = a1NPO + a2NEO + a3T + a4 (m EACN + b) + a5EACN + C$$
$$Nc = a1NPO + a2NEO + a3T + (m*a4+a5) EACN + C+b$$
$$Nc = a1NPO + a2NEO + a3T + a6 EACN + K$$
Correlation Equation 5a

Equation 5a is the combination of Equations 5 and 1. Optimum salinity is not explicitly in the equation but can easily be calculated.

\[
NC = a_1N_{PO} + a_2N_{EO} + a_3T + a_4EACN + C \tag{5a}
\]

Table 5.7 shows the regression coefficients of Dataset 47 and the sulfate and carboxylate subsets with Equation 5a. The \( R^2 \) for the combined Dataset 47 for equation 5a was much higher than that of Equation 1. The \( R^2 \) for the subsets were largely unchanged.

<table>
<thead>
<tr>
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<th>Sulfates + Carboxylates</th>
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<tbody>
<tr>
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<td>Coef</td>
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</tr>
<tr>
<td>C</td>
<td>22.64</td>
<td>1.17</td>
<td>0.05</td>
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<tr>
<td>NPO, a1</td>
<td>-1.46</td>
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<tr>
<td>NEO, a2</td>
<td>-0.70</td>
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<td>0.29</td>
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<tr>
<td>T-Tref, a3</td>
<td>0.03</td>
<td>0.01</td>
<td>0.33</td>
</tr>
<tr>
<td>EACN, a4</td>
<td>0.13</td>
<td>0.07</td>
<td>0.50</td>
</tr>
<tr>
<td>N</td>
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<td></td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.764</td>
<td></td>
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</tr>
</tbody>
</table>

Correlation Equation 5b

Equation 5b is a combination of Equations 5 and 2. Compared to Equation 5a, Equation 5b incorporates co-solvent concentration.

\[
NC = a_1N_{PO} + a_2N_{EO} + a_3T + a_4EACN + a_5C_5 + C \tag{5b}
\]

Table 5.8 shows the regression coefficients of Dataset 47 and the sulfate and carboxylate subsets with Equation 5b. The equation predicts trends that follow experimental observations, and the normalized standard errors are all less than 1. Compared to Equation 2, Equation 5b has approximately the same \( R^2 \) for the sulfate and
carboxylate subsets with one less coefficient and better represents experimental observations. Figure 5.6 and Figure 5.7 show the calculated versus experimental NC for Dataset 47 and the sulfate/carboxylate subsets.

Table 5.8 Equation 5b Regression Coefficients

<table>
<thead>
<tr>
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<th>Sulfates</th>
<th>Carboxylates</th>
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<tr>
<td></td>
<td>Coef</td>
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<td>NSE</td>
</tr>
<tr>
<td>C</td>
<td>20.34</td>
<td>1.64</td>
<td>0.08</td>
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<td>NPO, a1</td>
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<td>0.23</td>
<td>0.19</td>
</tr>
<tr>
<td>NEO, a2</td>
<td>-0.43</td>
<td>0.24</td>
<td>0.55</td>
</tr>
<tr>
<td>T-Tref, a3</td>
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<td>0.01</td>
<td>0.27</td>
</tr>
<tr>
<td>EACN, a4</td>
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<td>0.07</td>
<td>0.52</td>
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<td>Ca, a5</td>
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<tr>
<td>N</td>
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</tr>
<tr>
<td>R²</td>
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Figure 5.6 Equation 5b with Dataset 47
Figure 5.7 Equation 5b with Sulfate and Carboxylate Subsets

The Equation 5b was studied in more detail. Table 5.9 shows the ranges of the parameters for dataset 47 and the subsets. It is clear that the sulfate subset has fewer formulations with ethylene oxide groups than the carboxylate subset. The experimental temperatures of the sulfate subset were much lower than that of the carboxylate subset. The average concentration of co-solvent was higher for the sulfate subset than the carboxylate subset.
Table 5.9 Equation 5b Analysis

<table>
<thead>
<tr>
<th></th>
<th>Dataset 47</th>
<th>Sulfate</th>
<th>Carboxylate</th>
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<tr>
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<td>Med</td>
<td>Mean</td>
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<tr>
<td>NC</td>
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<td>18.77</td>
</tr>
<tr>
<td>NPO</td>
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<td>3.64</td>
<td>3.98</td>
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<tr>
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<tr>
<td>T-Tr</td>
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<tr>
<td>Ca*10^5</td>
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<td>2.18</td>
<td>4.82</td>
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</table>

Figure 5.8 shows the calculated versus experimental NC of the three sets. The data still show more scatter than the smaller dataset used in 2012. Figure 5.9 shows the effect of each parameter on the calculated NC. The range of parameters shown was the minimum to the maximum of their corresponding sets. The other parameters were fixed at the average.

All of the equations predicted strong negative relationships between NC and NPO, implying both parameters have similar influences on the development of a good formulation. The predicted effects of NEO on NC were much weaker than that of NPO, which is consistent with typical experimental observations when developing a new formulation. For the sulfate equation, the predicted NEO trend was likely based off of insufficient data.

The equations also predicted a positive relationship between NC and the temperature, the EACN and the co-solvent concentration. These trends are consistent with those observed by Solairaj (2012). Higher temperatures increase the water-anionic head group attraction and, thus, require a larger hydrophobe to maintain hydrophilic-lipophilic balance. Higher oil EACN requires larger hydrophobes to interact with the oil. Larger hydrophobes are also required to offset the negative effects of co-solvents.
Figure 5.8 Equation 5b Correlation
Correlation Equation 5C

Equation 5c is a combination of Equations 5 and 3, which attempts to incorporate the mole averaged number of carbons of the co-solvents.

\[
NC = a_1\text{NPO} + a_2\text{NEO} + a_3T + a_4\text{EACN} + a_5\text{CaN}_{\text{Ca}} + C \quad (5c)
\]
Table 5.10 shows regression coefficients of Dataset 47 and the sulfate and carboxylate subsets with Equation 5c. Equation 5c and Equation 5b have similar $R^2$, coefficients, and normalized standard errors.

Table 5.10 Equation 5c

<table>
<thead>
<tr>
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<th>Sulfates + Carboxylates</th>
<th>Sulfates</th>
<th>Carboxylates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coef</td>
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<tr>
<td>C</td>
<td>19.96</td>
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<td>-1.14</td>
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<td>NEO, a2</td>
<td>-0.39</td>
<td>0.24</td>
<td>0.62</td>
</tr>
<tr>
<td>T_Tref, a3</td>
<td>0.04</td>
<td>0.01</td>
<td>0.26</td>
</tr>
<tr>
<td>EACN, a4</td>
<td>0.13</td>
<td>0.07</td>
<td>0.50</td>
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<tr>
<td>CaNaCa, a5</td>
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</tr>
<tr>
<td>$R^2$</td>
<td>0.602</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Correlation Equation 5D**

Equation 5d is a combination of Equations 5 and 4, which adds a parameter for the mole averaged number of ethylene oxide groups of the co-solvents.

\[
NC = a_1NPO + a_2NEO + a_3T + a_4EACN + a_6CaNaCa + a_7CaNEOa + C \quad (5d)
\]

Table 5.11 shows the regression coefficients of Dataset 47 and the sulfate and carboxylate subsets with Equation 5d. The $CaNEOa$ parameter for the sulfate and carboxylate subsets had very high normalized standard errors, implying that the coefficient was not significant and could be taken out. Equation 5b and 5c had approximately the same $R^2$ but 1 fewer parameter. The improvements to equation 5d for dataset 47 were not enough to justify the addition of the extra parameter.
Table 5.11 Equation 5d

<table>
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<tr>
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<td>Coef</td>
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<td>NSE</td>
</tr>
<tr>
<td>C</td>
<td>18.60</td>
<td>1.72</td>
<td>0.09</td>
</tr>
<tr>
<td>NPO, a1</td>
<td>-1.11</td>
<td>0.22</td>
<td>0.20</td>
</tr>
<tr>
<td>NEO, a2</td>
<td>-0.30</td>
<td>0.24</td>
<td>0.80</td>
</tr>
<tr>
<td>T-Tref, a3</td>
<td>0.04</td>
<td>0.01</td>
<td>0.26</td>
</tr>
<tr>
<td>EACN, a4</td>
<td>0.17</td>
<td>0.07</td>
<td>0.39</td>
</tr>
<tr>
<td>CₐNₐCa, a5</td>
<td>3362</td>
<td>1129</td>
<td>0.34</td>
</tr>
<tr>
<td>CₐNₐEOₐ, a6</td>
<td>14278</td>
<td>6178</td>
<td>0.43</td>
</tr>
<tr>
<td>N</td>
<td>124</td>
<td>56</td>
<td>69</td>
</tr>
<tr>
<td>R²</td>
<td>0.619</td>
<td>0.734</td>
<td>0.881</td>
</tr>
</tbody>
</table>

Summary

The combination of the Log(S*) and EACN parameters significantly increased the R², reduced the standard errors, and improved the predicted trends. Equation 5b seemed to be the most significant based on R², standard errors, trends, and simplicity. It is more significant than equation 2 because there was a larger sample size for the number of parameters. The NₐCa and NₐEOₐ co-solvent parameters did not significantly improve the correlation. The co-solvent type and the number of ethylene oxide groups influence phase behavior properties through the co-solvent partition coefficient. It is also well known that co-solvent affects both the microemulsion viscosity and solubilization ratios and these are both extremely important, but not captured in any of the above equations. For these and other reasons, a new correlation was developed.

5.5 The 2014 Correlation Equations

In the 2012 correlation equation and its modifications shown above, the surfactant hydrophobes were parameterized by the number of carbon atoms, but not the structure of the hydrophobe such as branching, which is known to be very important. The carbon atoms of slightly branched, midpoint branched, aromatic, unsaturated, and linear hydrophobes were all weighted equally. The equation also did not directly account for the surfactant
head groups. More importantly, the optimum solubilization ratio (IFT) was not correlated even though it is more important than optimum salinity since the most essential attribute of an effective formulation is ultra-low IFT.

The general correlation equations, Equations 6 and 7, developed in Chapter 4 correlated the optimum salinity and the solubilization ratio at the optimum with the EACN of the oil.

\[
\ln S^* = 0.084EACN + B \quad \text{or} \quad S^* = Be^{0.084EACN} \tag{6}
\]

\[
\ln \sigma^* = -0.14EACN + C \quad \text{or} \quad \sigma^* = Ce^{-0.14EACN} \tag{7}
\]

Where B and C are the intercepts and functions of the surfactants and the co-solvents. The main difference between the two versions of the equations is how the constants B and C scale with \(S^*\) and \(\sigma^*\). In the versions on the left, B and C scale directly with logarithms of \(S^*\) and \(\sigma^*\), and in the versions on the right, B and C scale with \(S^*\) and \(\sigma^*\).

In this section, new correlation equations were developed to quantify the B and C intercepts in the above Equations 6 and 7. This is equivalent to correlating both the optimum salinity and solubilization ratio with the formulation variables. In addition, these two equations incorporate the effects of hydrophobe structure and the effect of the surfactant head groups. The motive behind this approach is to have a correlation that can be used to predict the best surfactants and co-solvents to test experimentally when developing a new formulation with an oil with a particular EACN.

**Structure of the Equations**

The intercepts B and C are the mole weighted averages of the pure component intercepts \(B_{\text{eff}}\) and \(C_{\text{eff}}\).

\[
B = \sum_{i=1}^{N} B_{\text{eff}i}x_i
\]
\[ C = \sum_{i=1}^{N} C_{eff i} x_i \]

Where,

- \( B_{eff} \) and \( C_{eff} \) is the effective intercept of pure component \( i \)
- \( x_i \) is the mole fraction of component \( i \) participating in the surfactant pseudo component
- \( N \) is the total number of surfactant and co-solvent components

The mole fraction, \( x \), was calculated with respect to the components participating in the surfactant pseudo component. All of the surfactant was assumed to participate, but only a fraction of the co-solvent was assumed to participate due to partitioning into the excess oil and excess water phases.

**Determination of the fraction of participating co-solvent**

In a type III microemulsion, the co-solvent partitions between the excess water, excess oil, and the microemulsion. The microemulsion is composed of solubilized water and oil and a surfactant pseudo component. The solubilized water and oil were assumed to have co-solvent concentrations equal to that of the excess water and excess oil phases. As shown in Section 3.11, the co-solvent preferentially partitions into the surfactant pseudo component or the interface created by the surfactants. Only the co-solvent in the surfactant pseudo component was assumed to be participating or influencing the phase behavior. The participating fraction of co-solvent is a function of the water oil ratio, the oil-water partition coefficient \( (K_{ow}) \), and the surfactant pseudo component-water partition coefficient \( (K_{pw}) \).

Since the correlation of partition coefficients with EACN was inconclusive, the partition coefficients were assumed to be those measured in Section 3.11.

a) \( K_{ow} = 1 \)

b) \( K_{pw} = 10 \)

The simplifying assumptions made in Section 3.11 were used to calculate the moles of participating co-solvent
a) The co-solvent concentrations in the excess water and excess oil phases were the same as those in the solubilized water and oil in the microemulsion.

b) The pure surfactants have the density of water. Therefore the aqueous surfactant mass fraction equals the aqueous surfactant volume fraction.

c) The surfactant pseudo component contains only surfactant and partitioned co-solvent.

d) The surfactant pseudo component maintains the volume of the pure surfactant. Therefore, the co-solvent does not swell the phase volume.

e) The volume fraction of the surfactant pseudo component is negligible compared to the volume fraction of water.

The calculation of the moles of co-solvent started with a mass balance and three general equations:

\[ C_w C_{a1wi} = C_w C_{a1w}^* + C_p C_{a1p}^* + C_o C_{a1o}^* \]

\[ C_w + C_o = 1 \]

\[ K_{ow} = \frac{C_{a1o}}{C_{a1w}^*} \]

\[ K_{pw} = \frac{C_{a1p}}{C_{a1w}^*} \]

Where,

\( C_w, C_o, \text{ and } C_p \) are the volume fractions of water, oil, and surfactant pseudo component

\( C_{a1wi} \) is the concentration of alcohol 1 in the initial water phase

\( C_{a1w}^*, C_{a1p}^*, \text{ and } C_{a1o}^* \) are the concentrations of alcohol 1 in the water, surfactant pseudo, and oil phases at equilibrium (designated by *)

The volume fraction of surfactant pseudophase is

\[ C_p = C_w \sum_{i}^{n} C_{si} \]

Where,
$C_{si}$ is the weight fraction of surfactant $i$ initially in the aqueous phase

$n$ is the number of surfactant components

The concentration of co-solvent 1 in the surfactant pseudo component is

$$C_{a1p}^* = \frac{K_{pw}C_{a1wi}}{1 + K_{pw} \sum_i C_{si} + K_{ow} \frac{C_o}{C_w}}$$

And the moles of co-solvent 1 in the surfactant pseudo component is the product of the concentration ($C_{a1p}^*$) and the volume fraction of the surfactant pseudo component ($C_w \sum_i^n C_{si}$):

$$moles_{a1p} = \frac{K_{pw}C_{a1wi}C_w \sum_i^n C_{si}}{1 + K_{pw} \sum_i C_{si} + K_{ow} \frac{C_o}{C_w}}$$

In the future, with a more complete co-solvent correlation, better estimates of $K_{ow}$ and $K_{pw}$ can be used to calculate the participating amount of co-solvents.

**Surfactant and Co-solvent Parameterization**

The surfactant and co-solvent components were divided into the following categories for the purposes of weighting the hydrophobe carbon numbers:

1. Internal olefin sulfonates (IOS)
2. Alkyl benzene sulfonates (ABS)
3. Midpoint branched hydrophobe anionic surfactants (large hydrophobe alkoxy sulfates/carboxylates)
4. Slightly branched hydrophobe anionic surfactants (short hydrophobe alkoxy sulfates/carboxylates)
5. Bent hydrophobe anionic surfactants (oleyl alcohol alkoxy sulfates/carboxylates)
6. Aromatic large hydrophobe anionic surfactants (tristyrylphenol alkoxy sulfates/carboxylates)
7. Co-solvents
The hydrophobe carbon numbers of each category component were weighted differently. However, the propylene oxide groups and ethylene oxide groups of category 3-6 components were weighted equally. The ethylene oxide groups of category 7 components were assigned a different weighting factor than that for category 3-6 components. The anionic head groups – IOS, ABS, sulfate, and carboxylate – were assigned unique constants. The head group constants for category 7 components were assumed to be 0.

Beff and Ceff share the same equations for each category but have different valued weighting factors. The following equations are expressed only in terms of Beff. The equations are the same for Ceff.

IOS and ABS are distributions of different sized hydrophobe surfactants and different isomers. ABS differs from IOS, having a benzene separating the sulfonate and the hydrophobe. In molecular dynamics simulations by Jang et al. (2004), and Huibers (1999), the benzene ring reduced the partial charge of the sulfonate group from -0.658 to -0.733. In addition, the benzene ring also partially contributes to the lipophilicity.

The equation for category 1 - internal olefin sulfonate surfactants is

\[ \text{Beff} = A_{\text{NC_IOS}} \cdot \text{NC}_{\text{IOS}} + A_{\text{IOS}} \]

Where

- \( \text{NC}_{\text{IOS}} \) is the average number of carbons in the IOS surfactant
- \( A_{\text{NC_IOS}} \) is the weighting factor for the IOS hydrophobe
- \( A_{\text{IOS}} \) is the constant for the IOS head group

The equation for category 2 – alkyl benzene sulfonate surfactants is
\( \text{Beff} = A_{\text{NC,ABS}} \text{NC}_{\text{ABS}} + A_{\text{ABS}} \)

Where

- \( \text{NC}_{\text{ABS}} \) is the average number of carbons excluding those in the benzene ring
- \( A_{\text{NC,ABS}} \) is the weighting factor for the ABS hydrophobe
- \( A_{\text{ABS}} \) is the constant for the ABS head group

Category 3-6 components are anionic sulfate or carboxylate surfactants. They typically have a block of propylene oxide groups followed by a block of ethylene oxide groups separating the hydrophobe and the anionic head group. Some of these surfactants have blocks of only propylene oxide groups or blocks of only ethylene oxide groups.

Category 3 – midpoint branched hydrophobes include most large hydrophobe surfactants, such as Guerbet alcohols, which range from 16 to 32 carbons, and epoxide alcohols, which were typically 28 carbons. The Guerbet and epoxide alcohol hydrophobes are both approximately midpoint branched and were given the same weighting factor, \( A_{\text{NC,L}} \) for large hydrophobe. The equations for the category 3 sulfate and carboxylate versions are

\[
\begin{align*}
\text{Beff} &= A_{\text{NC,L}} \text{NC}_{\text{L}} + A_{\text{PO}} \text{PO} + A_{\text{EO}} \text{EO} + A_{\text{SO4}} \\
\text{Beff} &= A_{\text{NC,L}} \text{NC}_{\text{L}} + A_{\text{PO}} \text{PO} + A_{\text{EO}} \text{EO} + A_{\text{COO}}
\end{align*}
\]

Where

- \( \text{NC}_{\text{L}} \) is the average number of carbons in the hydrophobe
- \( \text{PO} \) is the number of propylene oxide groups
- \( \text{EO} \) is the number of ethylene oxide groups
- \( A_{\text{NC,L}} \) is the weighting factor for the large hydrophobes
- \( A_{\text{PO}} \) is the weighting factor for the propylene oxide groups
- \( A_{\text{EO}} \) is the weighting factor for the ethylene oxide groups
\( A_{SO4} \) is the constant for the sulfate head group
\( A_{COO} \) is the constant for the carboxylate head group

Category 4 – slightly branched hydrophobes include most short hydrophobes, such as tridecyl alcohol (TDA), C16-17 (Neodol 67), C12-13 (N23), and other roughly linear hydrophobes with a few methyl branches. These hydrophobes were given the weighting factor, \( A_{NC_S} \), for short hydrophobe. The equations for the category 4 sulfate and carboxylate versions are

\[
\begin{align*}
\text{Beff} &= A_{NC_S} \text{NC}_s + A_{PO} \text{ PO } + A_{EO} \text{ EO } + A_{SO4} \\
\text{Beff} &= A_{NC_S} \text{NC}_s + A_{PO} \text{ PO } + A_{EO} \text{ EO } + A_{COO}
\end{align*}
\]

Where
\( \text{NC}_s \) is the average number of carbons in the hydrophobe
\( A_{NC_S} \) is the weighting factor for the short hydrophobes

Category 5 – bent hydrophobes are limited to C18 oleyl alcohol. A cis double bond between the 9\(^{th}\) and 10\(^{th}\) carbon creates a bend in the molecule. The equation for category 5 sulfate and carboxylate versions are

\[
\begin{align*}
\text{Beff} &= A_{NC_B} \text{NC}_B + A_{PO} \text{ PO } + A_{EO} \text{ EO } + A_{SO4} \\
\text{Beff} &= A_{NC_B} \text{NC}_B + A_{PO} \text{ PO } + A_{EO} \text{ EO } + A_{COO}
\end{align*}
\]

Where
\( \text{NC}_B \) is the average number of carbons in the hydrophobe
\( A_{NC_B} \) is the weighting factor for the bent hydrophobes

Category 6 – aromatic large hydrophobes are limited to C30 tristyrylphenol (TSP) alcohol. The equation for category 6 sulfate and carboxylate versions are
\[ \text{Beff} = A_{NC,T} \ NC_T + A_{PO} \ PO + A_{EO} \ EO + A_{SO4} \]
\[ \text{Beff} = A_{NC,T} \ NC_T + A_{PO} \ PO + A_{EO} \ EO + A_{COO} \]

Where

- \( NC_T \) is the average number of carbons in the hydrophobe
- \( A_{NC,T} \) is the weighting factor for the TSP hydrophobes

Category 7 – co-solvents are typically various isomers of simple alcohols, various butanol isomer ethoxylates, and phenol ethoxylates. The number of carbons of the most frequently used co-solvents ranges from 4 to 6. The number of ethylene oxide groups range from 0 to as much as 20. The ethylene oxide groups were weighted differently than those in anionic surfactants. The hydroxide head group was assumed to have a constant of 0. The equation for co-solvents is

\[ \text{Beff} = A_{NC,a} \ NCa + A_{NEO,a} \ EOa \]

Where

- \( NCa \) is the average number of carbons in the primary alcohol of the co-solvent
- \( EOa \) is the number of ethylene oxide groups in the co-solvent
- \( A_{NC,a} \) is the weighting factor for the carbons of the primary alcohol of the co-solvent
- \( A_{NEO,a} \) is the weighting factor for the number of ethylene oxide groups of the co-solvent

Nonionic surfactants typically have larger hydrophobes and larger blocks of propylene oxide and ethylene oxide groups than co-solvents. The hydrophobe, PO, and EO could be parameterized as some combination of those in categories 3-7. Due to the ambiguity, nonionic surfactants were not used in the development of the correlation.

Additional modifications and categories would allow for more complex surfactant molecules like Gemini surfactants. The structures of Gemini surfactants are variations of two linear hydrophobe propoxy anionic surfactant molecules cross-linked with ethylene
oxide groups. The head group constants would be doubled to account for the two anionic head groups. A new weighting factor for the hydrophobe would be required, which would likely be some combination of those for category 3 and category 4 hydrophobes, because the cross-linkages give the hydrophobes some degree of independence and some degree of midpoint branching. In addition, a new weighting factor for the number of ethylene oxide groups would be required, because the ethylene oxide groups are more centralized and have a different function. The weighting factor for number propylene oxide groups would be unchanged. The incorporation of any complex surfactant molecule would require a large sample size of data for the number of additional parameters.

The weighting factors were determined from multivariable regression using Dataset 54. The aromatic (tristyrylphenol) hydrophobe surfactants were not used in the development of the correlation, because these surfactants were typically used with waxy and active oils. Active oils were not used in the initial developments of the correlation, because the soaps had not been characterized. An important distinction from the procedure of the previous equations is that a regression constant or an intercept, \( C \), of 0 was imposed. The slopes versus EACN were constrained to 0.084 and -0.14 for the optimum salinity and optimum solubilization ratio.

Another important difference is that there is no parameter for temperature. Temperature of course has a big influence on phase behavior properties, but it was intentionally left out of the initial correlation for simplicity. In future studies, temperature can be introduced by making the head group constants first order functions of temperature.

The total number of regression parameters or weighting factors was 13.

Table 5.12 shows the weighting factors (\( A_j \)) and the corresponding properties (\( Z_j \)). The equations being solved by multivariable regression analysis are shown below.

Where,

- \( P \) is the total number of \( j \) parameters
- \( N \) is the total number of \( i \) components in the formulation
- \( M \) is the total number of formulations or experiments
Table 5.12 Equation Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Weighting Factor $A_j$</th>
<th>Property $Z_j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$A_{NC,IOS}$</td>
<td>NC$_{IOS}$</td>
</tr>
<tr>
<td>2</td>
<td>$A_{IOS}$</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>$A_{NC,ABS}$</td>
<td>NC$_{ABS}$</td>
</tr>
<tr>
<td>4</td>
<td>$A_{ABS}$</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>$A_{NC,L}$</td>
<td>NC$_{L}$</td>
</tr>
<tr>
<td>6</td>
<td>$A_{NC,S}$</td>
<td>NC$_{S}$</td>
</tr>
<tr>
<td>7</td>
<td>$A_{NC,B}$</td>
<td>NC$_{B}$</td>
</tr>
<tr>
<td>8</td>
<td>$A_{NPO}$</td>
<td>PO</td>
</tr>
<tr>
<td>9</td>
<td>$A_{NEO}$</td>
<td>EO</td>
</tr>
<tr>
<td>10</td>
<td>$A_{SO4}$</td>
<td>1</td>
</tr>
<tr>
<td>11</td>
<td>$A_{COO}$</td>
<td>1</td>
</tr>
<tr>
<td>12</td>
<td>$A_{NC,a}$</td>
<td>NC$a$</td>
</tr>
<tr>
<td>13</td>
<td>$A_{NEO,a}$</td>
<td>EO$a$</td>
</tr>
</tbody>
</table>

\[
X = \begin{bmatrix}
\sum_{i=1}^{N} Z_{1i} * x_{1i} \\
\vdots \\
\sum_{i=1}^{N} Z_{1M} * x_{1M} \\
\vdots \\
\sum_{i=1}^{N} Z_{Pi} * x_{Pi} \\
\vdots \\
\sum_{i=1}^{N} Z_{PM} * x_{PM}
\end{bmatrix}
\]

\[
A = \begin{bmatrix}
A_{1} \\
\vdots \\
A_{P}
\end{bmatrix}
\]

\[
B = XA
\]

\[
C = XA
\]

\[
Y_{S^*} = \ln \begin{bmatrix}
S_{1}^{*} \\
\vdots \\
S_{M}^{*}
\end{bmatrix} - 0.084 \begin{bmatrix}
EACN_{1} \\
\vdots \\
EACN_{M}
\end{bmatrix}
\]

or

\[
Y_{S^*} = \begin{bmatrix}
S_{1}^{*} \div e^{0.084 \cdot EACN_{1}} \\
\vdots \\
S_{M}^{*} \div e^{0.084 \cdot EACN_{M}}
\end{bmatrix}
\]

\[
Y_{\sigma^*} = \ln \begin{bmatrix}
\sigma_{1}^{*} \\
\vdots \\
\sigma_{M}^{*}
\end{bmatrix} + 0.14 \begin{bmatrix}
EACN_{1} \\
\vdots \\
EACN_{M}
\end{bmatrix}
\]

or

\[
Y_{\sigma^*} = \begin{bmatrix}
\sigma_{1}^{*} \div e^{-0.14 \cdot EACN_{1}} \\
\vdots \\
\sigma_{M}^{*} \div e^{-0.14 \cdot EACN_{M}}
\end{bmatrix}
\]

The weighting factor vector (A) is determined by finding the minimum of the square difference between B and $Y_{S^*}$ for the optimum salinity correlation (Equation 6).
Similarly, the weighting factor vector is determined by finding the minimum of the square difference between $C$ and $Y_{o^+}$ for the optimum solubilization ratio correlation (Equation 7).

The Dataset

The dataset, referred to as Dataset 54, was populated with equilibrated phase behavior data. Phase behavior experiments were assumed to be equilibrated if the optimum salinity and optimum solubilization ratio were no longer changing with time or if the phase behavior experiments were aged the duration that similar oil, temperature and co-solvent phase behavior experiments took to equilibrate. Typically, the age of the phase behavior experiment had to exceed 30 days, but it varied depending on the co-solvent concentration and temperature. Future studies should consider the equilibration of the phase behavior even more carefully than was possible in the limited time available for this study and insist on rigorous documentation of how long each formulation takes to equilibrate.

Incomplete or inconsistent data were filtered out. Each experiment, surfactant, co-solvent, and brine were assigned unique keys. The exact brine compositions at both the optimum salinity and the aqueous stability limit were calculated. Formulations with nonionic surfactants and those using temporary aqueous solubilizers like MA-80 were excluded from the dataset.

Table 5.13 shows the distribution of the oil and formulation types of Dataset 54, the distribution of formulations with and without co-solvents, and the frequency of different surfactant hydrophobes. The formulations in Dataset 54 did not generate soaps.
Table 5.13 Dataset 54

<table>
<thead>
<tr>
<th>Surfactant Combinations of Dataset 54</th>
<th>105</th>
<th>14</th>
<th>17</th>
<th>136</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASP no soap</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SP inactive oil</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SP active oil</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>105</td>
<td>14</td>
<td>17</td>
<td>136</td>
</tr>
<tr>
<td>With Co-solvent</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Without Co-solvent</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Large Hydrophobe</td>
<td>76</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Small Hydrophobe</td>
<td>65</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bent Hydrophobe</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IOS hydrophobe</td>
<td>126</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ABS Hydrophobe</td>
<td>43</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.14 shows the combinations of the different surfactant head groups and hydrophobes for dataset 54. L, B, and S represent large, bent, and short hydrophobes, respectively. The formulations on the main diagonal contained one or more surfactants with similar hydrophobes and the same head group. Dataset 54 did not contain formulations with short hydrophobe alkoxy carboxylate surfactants. The 17 formulations with a short hydrophobe sulfate and a large hydrophobe carboxylate also all contained an ABS. Thus, most of the formulations are a combination 2 different types of surfactants.

Table 5.14 Surfactant Combinations of Dataset 54

<table>
<thead>
<tr>
<th>SO4 L</th>
<th>SO4 B</th>
<th>SO4 S</th>
<th>COO L</th>
<th>COO B</th>
<th>IOS</th>
<th>ABS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO4 L</td>
<td>1 (+IOS)</td>
<td></td>
<td></td>
<td>15</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>SO4 B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>SO4 S</td>
<td>2</td>
<td></td>
<td>17(+ABS)</td>
<td>38</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>COO L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>32</td>
<td>6</td>
</tr>
<tr>
<td>COO B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>IOS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>ABS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
</tr>
</tbody>
</table>
Table 5.15 The Range of Properties in Dataset 54

<table>
<thead>
<tr>
<th></th>
<th>Min</th>
<th>Median</th>
<th>Mean</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC_L</td>
<td>24</td>
<td>28</td>
<td>27.95</td>
<td>32</td>
</tr>
<tr>
<td>NC_S</td>
<td>12.5</td>
<td>13</td>
<td>13.08</td>
<td>16.5</td>
</tr>
<tr>
<td>PO</td>
<td>7</td>
<td>25</td>
<td>25.72</td>
<td>45</td>
</tr>
<tr>
<td>EO</td>
<td>0</td>
<td>10</td>
<td>11.56</td>
<td>60</td>
</tr>
<tr>
<td>Ca (wt%)</td>
<td>0</td>
<td>0.75</td>
<td>0.87</td>
<td>2</td>
</tr>
<tr>
<td>NCa</td>
<td>4</td>
<td>4</td>
<td>4.65</td>
<td>6</td>
</tr>
<tr>
<td>NEOa</td>
<td>0</td>
<td>2</td>
<td>2.25</td>
<td>6</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>24</td>
<td>73</td>
<td>66.76</td>
<td>110</td>
</tr>
<tr>
<td>EACN</td>
<td>3.9</td>
<td>12.4</td>
<td>12.9</td>
<td>20.0</td>
</tr>
<tr>
<td>S* (ppm TDA)</td>
<td>6100</td>
<td>30000</td>
<td>33250</td>
<td>101800</td>
</tr>
<tr>
<td>σ* (cc/cc)</td>
<td>5</td>
<td>16</td>
<td>17</td>
<td>37</td>
</tr>
</tbody>
</table>

5.6 Discussion of Results

The multivariable regression analysis for the weighting factors were conducted using MATLAB. Both versions of the optimum solubilization ratio equations had similar normalized standard errors and similar $R^2$ for the predicted and calculated intercept $C$ and $B$. Although with similar $R^2$, the optimum salinity equations, showed varying degrees of scatter especially with $S^* > 50,000$ ppm TDS. The $S^*$ equation that showed the least scatter for the entire range and the similarly scaled $σ^*$ equation that were used are:

$$S^* = B e^{0.084EACN}$$

$$σ^* = C e^{-0.14EACN}$$

The main difference between the two versions of the equations is how the constant $B$ and $C$ scale with $S^*$ and $σ^*$. In this form, $B$ and $C$ scale directly with $S^*$ and $σ^*$, and in the other 2 versions $B$ and $C$ scale with the logarithms of $S^*$ and $σ^*$.

Table 5.16 shows the regressed weighting factors (coefficients) and standard errors for the $S^*$ and $σ^*$ intercept equations, $B$ and $C$. The $R^2$ for the calculated versus experimental $B$ and $C$ equations and for the calculated versus experimental $S^*$ and $σ^*$ are shown below.
Table 5.16 Weighting Factors for the Equations for $S^*$ and $\sigma^*$ Intercept Equations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Optimum Salinity</th>
<th>Optimum Solubilization Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{NC_L}$</td>
<td>-3094</td>
<td>634</td>
</tr>
<tr>
<td>$A_{NC_S}$</td>
<td>-4914</td>
<td>1260</td>
</tr>
<tr>
<td>$A_{NC_B}$</td>
<td>-3335</td>
<td>1387</td>
</tr>
<tr>
<td>$A_{NPO}$</td>
<td>-1129</td>
<td>479</td>
</tr>
<tr>
<td>$A_{NEO}$</td>
<td>4138</td>
<td>652</td>
</tr>
<tr>
<td>$A_{SO4}$</td>
<td>88872</td>
<td>21066</td>
</tr>
<tr>
<td>$A_{COO}$</td>
<td>139833</td>
<td>26412</td>
</tr>
<tr>
<td>$A_{NC_IOS}$</td>
<td>-4193</td>
<td>327</td>
</tr>
<tr>
<td>$A_{IOS}$</td>
<td>96032</td>
<td>7159</td>
</tr>
<tr>
<td>$A_{NC_ABS}$</td>
<td>263</td>
<td>567</td>
</tr>
<tr>
<td>$A_{ABS}$</td>
<td>-3062</td>
<td>8634</td>
</tr>
<tr>
<td>$A_{NC_a}$</td>
<td>3050</td>
<td>523</td>
</tr>
<tr>
<td>$A_{NEO_a}$</td>
<td>8753</td>
<td>2087</td>
</tr>
<tr>
<td>$R^2 - B, C$</td>
<td>0.802</td>
<td>0.524</td>
</tr>
<tr>
<td>$R^2 - S^<em>, \sigma^</em>$</td>
<td>0.683</td>
<td>0.005</td>
</tr>
</tbody>
</table>

The weighting factors or coefficients for the optimum salinity correlation have interesting patterns. With the exception of the weighting factors related to ABS surfactants, the weighting factors for surfactant head groups and ethylene oxide groups are positive and the weighting factors for surfactant hydrophobes and propylene oxide groups are negative. It seems that the positive weighting factors correspond to hydrophilic parameters which increase the surfactant-water interactions, and the negative weighting factors correspond to the lipophilic parameters which increase the surfactant-oil interactions. Based on the weighting factors, the carbons and the ethylene oxide groups of co-solvents seem to both increase the hydrophilic interactions. The normalized standard errors for the weighting factors were small with the exception of those related to ABS surfactants. Although ABS surfactants comprised a significant portion of the formulation data, their normalized standard errors imply that their statistical significance is small.

Figure 5.10 and Figure 5.11 shows the calculated versus experimental intercept $B$ and optimum salinity $S^*$. In both figures, the linear best fit lines (dashed blue) were constrained to $y$-intercepts of 0, which was imposed by regression. In Figure 5.11, lines of $\pm 10,000$ ppm of the best fit line are shown by dashed orange and dashed grey lines, which
encompass approximately 80% of the data. 10,000 ppm is double the typical salinity increment of the phase behavior experiments. The optimum salinity is determined by the emulsion test and can typically be narrowed to 1 salinity increment or ± 5,000 ppm. Considering the uncertainty of the optimum salinity measurement and the uncertainty of the parameters, the calculated optimum salinity is in remarkably good agreement with the experimental optimum salinity.

Figure 5.10 Calculated Versus Experimental S* Correlation Intercept B
More important than the optimum salinity is the optimum solubilization ratio $\sigma^*$. The weighting factors for the optimum solubilization ratio show an opposite trend. With the exception of the weighting factors related to ABS surfactants, the weighting factors for surfactant head groups are negative and the weighting factors for surfactant hydrophobes are positive. These results seem to agree with how increasing the lipophilic interactions tends to increase the optimum solubilization ratios. The normalized standard errors for the weighting factors of the number of ethylene oxide groups of surfactants ($A_{\text{NPO}}$), the number of carbon atoms of ABS surfactants ($A_{\text{NC,ABS}}$), and the number of carbon atoms of co-solvents ($A_{\text{NC,a}}$) were greater than 1, which implies that these parameters have a low statistical significance. The normalized standard errors for the weighting factors of the number of carbon atoms of the bent hydrophobe ($A_{\text{NC,B}}$), the ABS surfactant head group ($A_{\text{ABS}}$), and the number of ethylene oxide groups of the co-solvent ($A_{\text{NEO,a}}$) were moderately large, which implies that these parameters have a moderate uncertainty.

Figure 5.12 and Figure 5.13 show the calculated versus experimental values of intercept C and the optimum solubilization ratio $\sigma^*$. In both figures, the linear best fit lines (dashed blue) were constrained to y-intercepts of 0, which was imposed by regression. The

![Figure 5.11 Calculated Versus Experimental Optimum Salinity](image-url)
calculated and experimental intercepts \( C \) are in remarkably good agreement with the exception of 2 points at approximately \((480, 230)\). The calculated and experimental \( \sigma^* \) are incredibly scattered. However, lines of \( \pm 50\% \) of the best fitting line, shown by dashed orange and dashed grey lines, encompass approximately 85\% of the data. The uncertainty in optimum solubilization ratio measurements is significantly greater than that in the optimum salinity measurements. The optimum solubilization ratios are systematically overestimated if the phase separation is not careful monitored with time to verify that the fluids are at equilibrium. Considering the large uncertainty of the optimum solubilization ratio measurements, the uncertainty of the parameters, and the large uncertainty of the \( \sigma^* \) versus EACN correlation, the correlation seems to do a fair job of capturing trends.

![Figure 5.12 Calculated Versus Experimental \( \sigma^* \) Correlation Intercept \( C \)](image-url)
Figure 5.13 Calculated Versus Experimental Optimum Solubilization Ratio

The following figures show the predictions using equations for $S^*$ and $\sigma^*$, assuming actual surfactants and co-solvents. Blocks of X’s indicate the variables that are changing. The base case formulation was

0.5% TDA-35PO-20EO-SO4
0.5% C19-23 IOS
0.5% IBA-2EO
EACN = 16
30% Oil

Figure 5.14 shows the change of $S^*$ and $\sigma^*$ with the short and large hydrophobes. Increasing the number of carbons decreases $S^*$ and increases $\sigma^*$, but at different rates. Short hydrophobes are nearly linear, and the addition of a carbon atom results in the increase of hydrophobe length by 1 carbon. However, for large hydrophobes, which are near midpoint branching, the addition of 1 carbon results in an increase of hydrophobe length by an average of half a carbon. The slopes seem to scale with the average hydrophobe carbon
length. The lines of the large hydrophobe surfactants were nearly half as steep as those of the small hydrophobe surfactants.

The results suggest that sulfate surfactants yield higher solubilization ratios, which is logical because the sulfate-water interaction is typically stronger than the carboxylate-water interaction, as seen by the more negative partial charge of sulfate (-1.131) than carboxylate (-0.923) through molecular dynamic simulations in Huibers, 1999. This is also supported by the difference of the dissociation constants of the sulfate and carboxylate head groups.

The results also show that with nearly double the number of carbons as the short hydrophobe surfactants, large hydrophobes surfactants would achieve the same solubilization ratio or IFT. Despite how the optimum salinities and solubilization ratios can be roughly matched, the other microemulsion phase behaviors like the microemulsion viscosity could be very different. Branched hydrophobes typically help reduce microemulsion viscosities.

Figure 5.14 Optimum Salinity and Solubilization Ratio Versus Hydrophobe Carbon Number

Figure 5.15 show the effects of changing the number of propylene oxide (PO) groups for different hydrophobes and head group surfactants. The results indicate that increasing the number of PO groups significantly increases \( \sigma^* \) and decreases \( S^* \), but the effect decreases as the size of the hydrophobe increases. Also the number of PO groups has
a greater effect on $\sigma^*$ with carboxylate surfactants than with sulfate surfactants. This also shows that the head groups have a large influence on the $S^*$ and $\sigma^*$.

Interestingly this linear correlation captures the experimentally observed diminishing returns of increasing the number of PO groups on the $S^*$ and $\sigma^*$. This is caused numerically by increasing the surfactant molecular weight, which reduces the molar concentration of the fixed weight percentage of the primary surfactant.

![Figure 5.15 Optimum Salinity and Solubilization Ratio Versus Number of PO Groups](image)

Figure 5.16 shows the effects of changing the number of ethylene oxide (EO) groups for the same surfactants shown above. The results indicate that increasing the number of EO groups significantly increases $S^*$ with a very small and mixed effect on $\sigma^*$. Despite the small influences on $S^*$ and $\sigma^*$, the number of EO groups is a very important design parameter, especially for the aqueous stability.
Figure 5.16 Optimum Salinity and Solubilization Ratio Versus Number of EO Groups

Figure 5.17 shows the effects of varying the primary surfactant to co-surfactant fractions of several common co-surfactants, C15-18 IOS, C19-23 IOS, C19-28 IOS, and C19-23 ABS, while maintaining 1% total surfactant concentrations. This is an extrapolation of our data, as almost all formulations used contained two or more surfactants at relatively similar concentrations. The primary surfactants are shown to have higher $S^*$ and higher $\sigma^*$ than the co-surfactants.

Figure 5.17 Optimum Salinity and Solubilization Ratio versus Co-surfactant Concentration

Figure 5.18 shows the effect of varying the co-solvent concentration. It seems that increasing the co-solvent concentration increases the optimum salinity and decreases the
σ*. Probably because of the imposed $K_{ow}$ and $K_{pw}$, the different co-solvents all seem to have relatively the similar effects on σ*.

Figure 5.18 Optimum Salinity and Solubilization Ratio versus Co-solvent Concentration

**Summary**

The 2014 correlations seem to be a significant improvement to the 2012 correlation. The 2014 correlation more accurately represent hydrophobe structures and directly addresses head groups. The preliminary trends seem to agree with experimental observations. As such, the 2014 correlation is a better predictive tool than the 2012 correlation. The correlation also models the solubilization ratio, which is a more important design factor for a formulation than the optimum salinity. The predicted optimum solubilization ratio trends seem to agree with those observed experimentally.

More data is required as the sample size for the number of parameters is nearly 10:1. With more data, the confidence in the weighting factors will increase. The correlation also needs to be evaluated with fresh data to see if the correlation still holds and is still predictive.

The handling of co-solvents needs to be improved. The assumptions for the partition coefficients were the best guesses based on the two experiments in Chapter 3. With a better co-solvent partitioning correlation, the predictions of the effects of co-solvents would significantly improve. This would also likely reduce the standard errors of the co-solvent coefficients.
On top of better quantifying the participating concentration of co-solvents in the surfactant pseudo component, the actual influences of the alcohol and number of EO groups of the co-solvent may be quantified on the optimum salinity and solubilization ratio. For example, an IBA ethoxylate and phenol ethoxylate can be designed to have similar partition coefficients and similar surfactant pseudo phase concentrations, but the effects of the alcohols could have different effects, which may become apparent.

Although temperature has a large influence on the phase behavior properties, it was intentionally left out of the correlation equations for simplicity. However, temperature can easily be introduced in several ways. The effects on co-solvent partition coefficients seem to be significant, and will be incorporated in better estimates of the partition coefficients. The effects on the head group-water interaction is significant. The temperature increases the head group-water interaction, which often requires larger hydrophobes to maintain hydrophilic-lipophilic balance.

Temperature can be incorporated into the head group weighting factor as first order functions of temperature. For example:

\[
\begin{align*}
A_{IOS} &= A_{IOS} + A_{IOS,T}(T - T_r) \\
A_{ABS} &= A_{ABS} + A_{ABS,T}(T - T_r) \\
A_{SO4} &= A_{SO4} + A_{SO4,T}(T - T_r) \\
A_{COO} &= A_{COO} + A_{COO,T}(T - T_r)
\end{align*}
\]

For simplicity, initial development, and the conservation of parameters, the weighting factors for the temperature effect on the head groups can be assumed to be equal to \(A_{HG,T}\):

\[
A_{HG,T} = A_{HG,IOS} = A_{HG,ABS} = A_{HG,SO4} = A_{HG,COO}
\]

In exactly the same way, the weighting factor could be determined by multivariable regression. And the effects of temperature can be quantified on the intercepts B and C and \(S^*\) and \(\sigma^*\). With this, all of the parameters in the 2012 correlation and more would be captured. This would also likely reduce the scatter of the data and be more predictive. If proven to be significant, the weighting factors for the different head groups could be individual regressed.
The correlation can also be extended to active oils and used to quantify certain soap properties like the effective hydrophobe size and structure. The quantification of the molar concentration of soaps in oils has already been established in Mohammadi 2008. Formulation data for active oil formulations could be used to find the effective B and effective C of the soap. With the soaps quantified for individual oils, the correlation could potentially be extended to ACP formulations. It would be interesting to see how the soap properties vary between oils. These results combined with the GC oil compositions and the SARA analysis could be used to explore correlations between certain chemicals and the microemulsion properties.

The correlation could also be extended to live oils. The effects of solution gas and pressure on the optimum salinity and solubilization ratios would be extremely useful and could potentially bridge the gap between surrogate oil and live oil phase behaviors.

This parameterization concept could potentially be extended to aqueous stability limits and to microemulsion viscosities. In an aqueous stability limit correlation synergistic effects are incredibly important and also incredibly difficult to capture. There is an abundance of data, since aqueous stability limit is independent of the oil and is relatively easy to acquire and analyze. The aqueous composition, especially the divalent ions, would be crucial for the correlation.

The microemulsion viscosities have been qualitatively observed to correlate with EACN. This trend may be more easily captured with the current equation, but microemulsion data is extremely scarce. However there have been recently efforts to measure more microemulsion viscosity data, because the direct influence on surfactant retention.
6.1 Co-solvent Partitioning Summary and Conclusions

Chapter 6: Summary and Conclusions

In Chapter 3, new measurements of the partition coefficients of the newer alcohol ethoxylates currently being used for chemical enhanced oil recovery were presented and analyzed. These data are needed to model and design surfactant-polymer (SP), alkaline-surfactant-polymer (ASP) and alkaline-co-solvent-polymer (ACP) processes. Several trends in the oil-water partition coefficient were observed with the alcohol type (IBA and phenol), the number of ethylene oxide groups in the co-solvent, the EACN of the oil, temperature, and salinity. This was a useful first step in the development of a correlation to help minimize the number of measurements needed for co-solvent selection. The ideal value for the oil-water partition coefficient is 1 based on previous studies taking into account considerations such as minimizing the chromatographic separation of the co-solvent and surfactant when a chemical slug is injected into an oil reservoir. The values measured in this study ranged from 0.01 to 6.06 depending on the variables listed above.

Through deconvolution, more data was extracted from the chromatograms, specifically for the individual alcohol ethoxylate components making up the co-solvent. These data show that the partition coefficients of identical components from different compositions were not significantly different and that the interference effect from other components was negligible.

The cumulative chromatogram data and the data derived from deconvolution show that the oil-water partition coefficient ($K_{ow}$) decreases as the number of ethylene oxide groups (NEO) increases. The trend is approximately linear when plotted as the logarithm of $K_{ow}$ vs NEO. In addition, increasing the temperature increases the co-solvent partition coefficients, more so for those co-solvents with a higher NEO. The partition coefficients were also shown to increase quadratically with salinity.

The partition coefficients of phenol ethoxylates were measured with three different crude oils and several different surrogate oils made from dilutions with toluene, octane,
and hexadecane. The partition coefficients of the phenol ethoxylates with toluene were significantly greater than those with octane and hexadecane. The EACNs of the crude oils were bracketed by octane and hexadecane. However, the partition coefficients of phenol ethoxylates with the crude oils were greater than with either octane or hexadecane. The partition coefficients with the surrogate oils correlated well with both the volume fraction and the mole fraction of the pure components. Thus, the logarithm of the partition coefficients of phenol ethoxylates did not correlate with EACN in the same way as was measured in Dwarakanath et al. (1998). Data with different dilutions of the same diluent are required to determine whether the mole or volume fraction is better. More experiments are required to determine the correlation between co-solvent partition coefficients and oil EACN.

The co-solvent concentrations in the excess water and microemulsion phases of type III microemulsions with two different oils were measured. Both were optimized microemulsion formulations. The oil-water partition coefficient (K_{ow}) and surfactant pseudo component-water partition coefficient (K_{pw}) were calculated from mass balance. The K_{ow} for both oils in the presence of surfactants were approximately 1, which remarkably agreed with the K_{ow} in the absence of surfactants. The K_{pw} for both microemulsions were approximately 10, an order of magnitude greater than the K_{ow}. This meant that the concentrations of co-solvents in the excess water and oil phases were approximately equal, and that the concentrations in the pseudo component was approximately 10 times that in both excess water and oil phases. Also, for both microemulsions, the co-solvent components in the center of the distribution were the most abundant in the pseudo component, as the lower EO number components were more drawn to the excess oil phase and the higher EO number components were more drawn to the excess water phase. The results show that the co-solvent clearly prefers the interface created by the presence of surfactants.

There were many sources of error in these experiments. There was human error in the determination of the baselines for the chromatograms. This error was often made worse by significant baseline drift. The most severe source of error was the reduction of the
effective length or the number of theoretical plates of the column with time due to overuse. This effectively reduced the retention times and increased the standard deviations of the peaks, resulting in more overlapping peaks, which were more difficult to deconvolute. Therefore, the error was likely increasing with time, but periodically measured calibration samples showed no overall signal loss. The increased error in deconvolution resulted in fewer of the lower signal peaks being used. Because of the limited time available, the standard errors for the partition coefficient values were not quantified.

One of the largest sources of uncertainty in the measurement of the partition coefficients for the microemulsion samples is the uncertainty of the phase volumes. In the oil-water samples, the phase volumes were equal and showed no measurable change with age, and the uncertainty of the co-solvent concentration in the oil phase was largely only dependent of the co-solvent concentration in the aqueous phase. However, in the microemulsion samples, there was an additional phase, and the volumes and the precision of the volumes changed significantly, and the co-solvent concentration in the oil phase was dependent on three phase volumes and the concentrations in the water and microemulsion phases. Thus, the uncertainty in the results for the microemulsion samples was significantly higher than that for the oil and water samples. In addition to this, the uncertainty in the results for individual components with different NEO was affected by the uncertainty in the deconvolution, and the uncertainty in the cumulative co-solvent results was affected by the distribution bias discussed previously.

In the future, the partition coefficients of co-solvents with other oils should be measured to better understand how the partition coefficient depends on the oil. The next step would be to develop a correlation on the component level with the number of ethylene oxide groups, the temperature, the salinity, and the oil. Using the HPLC, the composition of the different co-solvents can be quantified using an internal standard or by standard addition with the pure components (if obtainable). With both the composition data and the correlation, the cumulative partition coefficient of the co-solvents could be estimated with any oil at any temperature and salinity. This would greatly improve co-solvent selection and optimization.
The phenol-monoproproxy ethoxylate co-solvents showed promise of having higher partition coefficients than the equivalent phenol ethoxylate co-solvent. The effects of the propylene oxide group on microemulsion properties should be studied. Other co-solvents can be studied with these methods. Samples of n-butanol ethoxylates, including triethylene glycol monobutyl ether (TEGBE) and ethylene glycol monobutyl ether (EGBE), with ABK oil were made. However, due to complications the HPLC, the elutions of the analyte peaks approached that of the carrier fluid and the signal was overwhelmed by noise. No meaningful data were measured for n-butanol ethoxylates. However, modifications to the HPLC injection volumes, the solvent gradient program, and the ELSD could fix these problems for n-butanol ethoxylates. Fortunately, the chromatograms for IBA ethoxylates with similar number of ethylene oxide groups were of higher resolution. However, the partition coefficients were much lower than that of phenol ethoxylates with equivalent number of ethylene oxide groups, so the uncertainty was much higher for them.

The partitioning of co-solvents should be studied with other oils, with other formulations and with type I and type II microemulsions. Observing what the effects of poorly optimized formulations and imbalanced partitioning between oil and water have on the partitioning to the surfactant pseudo component and the microemulsion would also be worthwhile. Finally, it would be incredibly useful to relate the co-solvent partitioning to the surfactant pseudo component and the microemulsion with the microemulsion viscosity. In addition, the effects of temperature and salinity on the partition coefficients of co-solvent components with different numbers of ethylene oxide groups may reveal fundamental properties, which can be related to the ethylene oxide groups in surfactants.

The uncertainty of this data should be quantified, and this procedure could be optimized to reduce uncertainty. For example, the procedure currently yields values with very large uncertainty for high-EO and low partition coefficient co-solvents. By increasing the oil to water ratio, a larger difference between the initial and final aqueous co-solvent concentrations could be measured, which would reduce the uncertainty.
The HPLC solvent gradient program should also be optimized to improve the resolution, which would greatly reduce the dependence of the individual component data on the mathematical deconvolution.

6.2 Oil EACN Summary and Conclusions

In Chapter 4, new measurements of the equivalent alkane carbon number (EACN) of several different crude oils as well as dilutions of these crude oils were presented and discussed. An improved procedure based on the results of the different EACN measurements was proposed and implemented. The new measurements were made using optimized formulations containing various combinations of primary surfactants, co-surfactants, co-solvents and alkali. The new EACN measurements ranged from 11.3 to 21.1. These new data significantly expand the total number of reliable EACN values available to understand and correlate chemical EOR formulation results such as the correlations presented in Chapter 5.

Strong correlations of both the optimum salinity \( S^* \) and the optimum solubilization ratio \( \sigma^* \) with the EACN of the oil were observed in these experiments. Using the experimental data, the natural logarithm of the solubilization ratio and the natural logarithm of the optimum salinity were modeled as linear functions of EACN. The correlation equations are

\[
\ln S^* = 0.084EACN + B \quad \text{or} \quad S^* = Be^{0.084EACN}
\]

\[
\ln \sigma^* = -0.14EACN + C \quad \text{or} \quad \sigma^* = Ce^{-0.14EACN}
\]

The correlation lines on a semi-log plot are parallel. The slopes are independent of the formulation, oil and temperature and the y-intercepts B and C are a function of the formulation and temperature. The slopes of these correlation equations were determined through minimization of the square error between the experimental values and the correlation values. The standard deviation of the residuals (Y experimental – Y Predicted) was 3000 ppm for the optimum salinity correlation, which was based on the results of 17
different oils, 19 unique formulations, and 86 data points. The standard deviation of the residuals was 2.7 cc/cc for the optimum solubilization ratio correlation, which was based on the results of 9 different oils, 10 unique formulations, and 44 data points. These correlation equations were integral in the development of the optimum salinity and solubilization ratio correlations of Chapter 5.

Finally, the dead oil EACN and the oil molecular weight data were analyzed. A weak correlation between the dead oil EACN and the oil molecular weight was found. The correlation showed that the EACN to molecular weight ratio of crude oils behaves as a combination of pure alkanes and unsaturated hydrocarbons. This correlation is valuable for predicting the EACN of an oil before a formulation has been developed for it, and as a guide for which formulations to initially test for a new oil. Once a formulation has been developed, then the EACN can be measured, but at least one suitable formulation must be developed for the oil before a reliable EACN of the oil can be measured.

The correlations for optimum salinity and solubilization ratios do not capture all aspects of microemulsion phase behavior, and EACN only empirically captures some of the oil interactions. Future research should be aimed at studying the influences of oil composition by utilizing GC and SARA analysis data and quantifying the trends between microemulsion viscosity and EACN.

The optimum salinity and solubilization ratios have a large uncertainty, which is often made worse by non-classical phase behavior. At best, the accuracy of the optimum salinity, determined by the emulsion test, is limited to the salinity increment of the salinity scan. The optimum solubilization ratios were determined by plotting the oil and water solubilization ratios, drawing curves through the data for each ratio, and assuming the optimum value is where the curves cross. This procedure is uncertain for several reasons and often does not agree with the lowest IFT as estimated from the emulsion test. Non-classical phase behavior often further complicates the interpretation of the change of solubilization ratio with salinity. The most significant source of error occurs because the fluids are not fully equilibrated. This is a large systematic error that can result in an uncertainty of up to ±50%. The new experiments were specifically monitored over an
extended period of time, and the reported optimum salinity and solubilization ratios were taken when the phase volumes appeared to be constant.

Phase behavior measurements were also made using only alkali and co-solvent (no surfactant) for an active oil that yields soap when reacted with the alkali. These data are needed for the new alkaline-co-solvent-polymer (ACP) process. The results did not conform to the typical behavior of the surfactant formulations so they were not used in the correlations, but they are nevertheless valuable data that merit additional study to understand the phase behavior as well as for other purposes.

More work needs to be done in developing a co-solvent structure(s) that will not negatively impact, or in the very least minimally affect the solubilization ratio when added to the surfactant formulation. If the new structures could also be more efficient relative to the ones used currently, the overall cost of the formulation can be lowered, thus making the CEOR process economically more attractive. Incorporating more than one propylene oxide group in the co-solvent may be one way of achieving this goal.

6.3 Summary and Conclusions of the 2012 Correlation and Modifications

Solairaj (2012) developed a correlation that quantified the relationship between certain surfactant and oil properties, temperature, and optimum salinity. The correlation was developed from multivariable regression of phase behavior data from optimized surfactant formulations using inactive oils. The correlation did not account for the effect of co-solvent and hydrophobe branching on the optimum salinity. The correlation captured the known trends of certain surfactant attributes such as the number of ethylene oxide groups, the number of propylene oxide groups, and the carbon number of the hydrophobe. Solairaj did not attempt to correlate the solubilization ratio data from these same phase behavior experiments. Furthermore, much more phase behavior data are available now than at the time he developed the correlation with optimum salinity. The purpose of this study was to find an improved correlation that more accurately quantifies the relationship between surfactant structure, co-solvents, oil, temperature, and optimum salinity. A correlation was developed using a new and much larger high quality formulation dataset
now available from studies done in recent years in the Center for Petroleum and Geosystems Engineering at the University of Texas at Austin.

First, the old correlation was tested using the new expanded dataset. The $R^2$ for the expanded dataset was significantly greater than the original much smaller dataset. The coefficients of the old equation were updated by regressing with the new dataset. The $R^2$ improved, but several trends predicted by the correlation with variables such as EACN appeared to be non-physical. Several confounding factors were studied, such as the head group of the primary surfactant. The dataset was divided into subsets based on the head group of the primary surfactant, a sulfate subset and a carboxylate subset. Similarly evaluated, the individual sulfate and carboxylate correlations predicted a higher $R^2$ and all of the trends appeared to be physically correct. Because of these positive results, both the entire dataset and the individual sulfate and carboxylate subsets were subsequently run for all modifications.

A series of modifications were made to the equation. The first (Equation 2) was the addition of the total molar concentration of co-solvent $C_a$ (moles of co-solvent per volume of sample). Next, (Equation 3) the mole average number of carbons of the co-solvent ($N_{Ca}$) was incorporated with $C_a$ parameter, becoming $C_aN_{Ca}$. Finally, (Equation 4) a new parameter for the mole average number of ethylene oxide groups of the co-solvent ($N_{EOa}$) similarly combined with $C_a$ parameter, becoming $C_aN_{EOa}$, was added.

The addition of the total molar concentration of co-solvent parameter $C_a$ significantly increased $R^2$ and improved the trends. The substitution of $C_aN_{Ca}$ for $C_a$ had relatively little effect on $R^2$, the trends, and standard errors. The addition of the $C_aN_{EOa}$ parameter resulted in slight improvements to $R^2$ but at the cost of substantially increased normalized standard errors. The normalized standard error for $C_aN_{EOa}$ in both the sulfate and carboxylate subset equations were greater than 1, implying the parameter was not statistically significant. Based on simplicity, the value of $R^2$ for each regression, the trends predicted for individual variables, and the standard errors of the coefficients, Equation 2 is considered a better choice for correlating the data than either Equation 3 or 4.
In the equations, the combined dataset correlations predicted non-physical optimum salinity versus EACN trends, and the sulfate and carboxylate correlations consistently overestimated the slope of optimum salinity versus EACN. Using the correlation developed in Chapter 4, the logarithm of optimum salinity and the EACN parameters were algebraically combined in the original correlation and the modifications Equations 2-4, becoming Equations 5a-5d. This effectively constrains the Log(S*) and EACN and reduces the number of regression parameters by one.

The combination of the Log(S*) and EACN parameters significantly increased the \( R^2 \), reduced the standard errors, and improved the predicted trends. Equation 5b seemed to be the most significant based on \( R^2 \), standard errors, trends, and simplicity. It is more significant than equation 2 because there was a larger sample size for the number of parameters. The \( N_{Ca} \) and \( N_{EOa} \) co-solvent parameters did not significantly improve the correlation. The alcohol type and the number of ethylene oxide groups influence phase behavior properties through the co-solvent partition coefficient. It is also well known that co-solvent affects both the microemulsion viscosity and solubilization ratios and these are both extremely important, but not captured in any of the equations. For these and other reasons, a new correlation was developed.

### 6.4 Summary and Conclusions of the 2014 Correlation Equation

In the 2012 correlation equation and its modifications, the surfactant hydrophobes were parameterized by the number of carbon atoms, but not the structure of the hydrophobe such as branching, which is known to be very important. The equation also did not directly account for the surfactant head groups. More importantly, the optimum solubilization ratio (IFT) was not correlated even though it is more important than optimum salinity since the most essential attribute of an effective formulation is ultra-low IFT.

The new 2014 correlation developed in this research study is built off of the optimum salinity and solubilization ratio correlations with EACN.

\[
\ln S^* = 0.084EACN + B \quad \text{or} \quad S^* = Be^{0.084EACN}
\]
\[ \ln \sigma^* = -0.14EACN + C \quad \text{or} \quad \sigma^* = Ce^{-0.14EACN} \]

The formulation variables were all incorporated in the y-intercepts B and C. B and C are the mole average weighted effective B and effective C of the pure components participating in the surfactant pseudo component, which includes all of the surfactants, but only a portion of the co-solvents. As shown in chapter 3, the co-solvent partitions between the excess water, excess oil, and the microemulsion phases. In the microemulsion phase, only the co-solvent in the surfactant pseudo component was assumed to be participating. The oil-water partition coefficient (K\text{ow}) was assumed to be 1 and the surfactant pseudo component-water partition coefficient (K\text{pw}) was assumed to be 10, taken from the results in Chapter 3.

The carbon atoms of small (slightly branched), large (midpoint branched), bent (oleyl alcohol), aromatic (tristeryl phenol), IOS and ABS hydrophobes were all assigned different weighting factors. The different anionic head groups were also assigned unique weighting factors. The effective B and effective C were the combinations of the products of the weighting factors and the corresponding parameters.

The weighting factors were determined from multivariable regression of a slightly larger dataset with a sample size of 136. The 2014 correlation for optimum salinity is a significant improvement to the 2012 correlation. The 2014 correlation more accurately represents hydrophobe structures and directly addresses head groups. The trends appear to agree with qualitative experimental observations. As such, the 2014 correlation is a better predictive tool than the 2012 correlation. Most significantly, a new correlation for the solubilization ratio was developed, which is a more important design factor for a formulation than the optimum salinity. The predicted trends also appear to agree with qualitative experimental observations.

More data are required as the sample size for the number of parameters is nearly 10:1. With more data, weighting factors could be more accurately and confidently
quantified. The correlations also need to be evaluated with new independently measured
data to evaluate their predictive accuracy.

The handling of co-solvents needs to be improved. The assumptions for the
partition coefficients were the best guesses based on the experiments presented in
Chapter 3. With a better co-solvent partitioning correlation, the predictions of the effects
of co-solvents would significantly improve. This would also likely reduce the standard
errors of the co-solvent coefficients.

On top of better quantifying the participating concentration of co-solvents in the
surfactant pseudo component, the actual influence of the alcohol and number of EO
groups of the co-solvent may be quantified on the optimum salinity and solubilization
ratio. For example, certain IBA ethoxylates and phenol ethoxylates could be selected to
have similar partition coefficients and similar concentrations in the surfactant pseudo
component, but the effects of the actual co-solvent on the microemulsion phase behavior
has yet to be explicitly addressed.

Although temperature has a large influence on the phase behavior properties, it was
intentionally left out of the correlation equations for simplicity. However, temperature can
be introduced in several ways. Temperature can be incorporated into finding better
estimates of the co-solvent partition coefficients.

Temperature also has significant effects on the head group-water interaction. The
head group-water interaction increases as temperature increases, which often requires
larger hydrophobes to maintain hydrophilic-lipophilic balance. Temperature can be
incorporated into the head group weighting factor as first order functions of temperature.
For example:

\[
A_{\text{IOS}} = A_{\text{IOS}} + A_{\text{IOS},T}(T - T_r)
\]
\[
A_{\text{ABS}} = A_{\text{ABS}} + A_{\text{ABS},T}(T - T_r)
\]
\[
A_{\text{SO4}} = A_{\text{SO4}} + A_{\text{SO4},T}(T - T_r)
\]
\[
A_{\text{COO}} = A_{\text{COO}} + A_{\text{COO},T}(T - T_r)
\]
For simplicity, initial development, and the conservation of parameters, the weighting factors for the temperature effect on the head groups can be assumed to all be equal to $A_{HG,T}$:

$$A_{HG,T} = A_{HG,IOS} = A_{HG,ABS} = A_{HG,SO4} = A_{HG,COO}$$

The weighting factor could be determined by multivariable regression. And the effects of temperature can be quantified on the intercepts $B$ and $C$ and $S^*$ and $\sigma^*$. With temperature the correlation would capture all of the parameters in the 2012 correlation plus hydrophobe branching, co-solvents, and head groups. The addition of temperature would likely reduce the scatter of the data and be more predictive. If proven to be significant, the weighting factors for the different head groups could be regressed individually. A correlation with this level of functionality would be incredibly useful for the expedient optimization of formulations.

The correlation can also be extended to active oils and used to quantify certain soap properties like the effective hydrophobe size and structure. The quantification of the molar concentration of soaps in oils has already been established in Mohammadi 2008. Formulation data for active oil formulations could be used to find the effective $B$ and effective $C$ of the soap. With the soaps quantified for individual oils, the correlation could potentially be extended to ACP formulations. It would be interesting to see how the soap properties vary between oils. These results combined with the GC oil compositions and the SARA analysis could be used to explore correlations between certain chemicals and the microemulsion properties.

The correlation could also be extended to live oils. The effects of solution gas and pressure on the optimum salinity and solubilization ratios would be extremely useful and could potentially bridge the gap between surrogate oil and live oil phase behaviors.

This parameterization concept could potentially be extended to aqueous stability limits and to microemulsion viscosities. In an aqueous stability limit correlation synergistic effects are incredibly important and also incredibly difficult to capture. There is an abundance of data, since aqueous stability limit is independent of the oil and is
relatively easy to acquire and analyze. The aqueous composition, especially the divalent ions, would be crucial for the correlation.

The microemulsion viscosities have been qualitatively observed to correlate with EACN. This trend may be more easily captured with the current equation, but microemulsion viscosity data is relatively scarce. However recently there have been efforts to measure more microemulsion viscosity data, because of its direct influence on surfactant retention.
Works Cited


