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# QUANTIFICATION OF NON-IDEAL MIXING IN SODIUM DI (2-ETHYLHEXYL) SULFOSUCCINATE – ANIONIC SURFACTANT MIXTURES

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# QUANTIFICATION OF NON-IDEAL MIXING IN SODIUM DI (2-ETHYLHEXYL) SULFOSUCCINATE – ANIONIC SURFACTANT MIXTURES

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BY

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# Dedication

To my parents, my brother who believed in me, instilled in me the virtues of perseverance and commitment and relentlessly encouraged me to strive for excellence.

To my lovely friends and host family for their friendship, kindness and affection throughout this journey.

And to my late friend Samir Anand.

Thank you for your love, support, encouragement and sacrifices.

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# Table of Contents

Acknowledgements .......... iv

List of Tables .......... vii

List of Figures .......... viii

Abstract .......... xiv

Chapter 1: Introduction .......... 1

- 1.1 Problem Statement .......... 5

Chapter 2: Literature Review .......... 6

- 2.1 HLD equation origin .......... 6
- 2.2 Linear Mixing Rules and K, Cc value determination of mixtures .......... 7
- 2.3 Evaluation of Non-idealities in surfactant mixtures .......... 11

Chapter 3: Experimental Procedure .......... 15

- 3.1 Materials Used .......... 15
- 3.2 Microemulsion Phase Study (Salinity Scan) .......... 17
- 3.3 Evaluation of Non-Idealities in Anionic Mixtures .......... 18

Chapter 4: Results and Discussion .......... 20

- 4.1 Microemulsion Phase Study (Salinity Scan) .......... 20
  - 4.1.1 K and Cc values of reference surfactants .......... 20
  - 4.1.2 AOT/AMA (10:90) .......... 21
  - 4.1.3 AOT/AMA (30:70) .......... 23
  - 4.1.4 AOT/AMA (50:50) .......... 26
  - 4.1.5 AOT/AMA (70:30) .......... 29
  - 4.1.6 AOT/ALFOTERRA-8-41S (10:90) .......... 30

4.1.7 AOT/ALFOTERRA-8-41S (30:70) .......... 33
4.1.8 AOT/ALFOTERRA-8-41S (50:50) .......... 35
4.1.9 AOT/ALFOTERRA-8-41S (70:30) .......... 38
4.1.10 AOT/ISALCHEM 123-2 (10:90) .......... 40
4.1.11 AOT/ISALCHEM 123-2 (30:70) .......... 43
4.1.12 AOT/ISALCHEM 123-2 (50:50) .......... 45
4.1.13 AOT/ISALCHEM 123-2 (70:30) .......... 48
4.2 K and Cc vs. mole fraction of AOT .......... 50
4.3 Quantification of Non-Ideality .......... 62
Chapter 5: Conclusion .......... 66
References .......... 68
Appendix A: Supplementary Tables .......... 70

# List of Tables

Table 1: Molecular Structures ........................................................................ 15

Table 2: Additional Surfactant Information ................................................... 17

Table 3: K and Cc values of reference surfactants ......................................... 20

Table 4: K and Cc values obtained from AOT/AMA mixture ....................................... 51

Table 5: K and Cc values obtained from AOT/ALFOTERRA 8-41S mixture .............. 52

Table 6: K and Cc values obtained from AOT/ISALCHEM 123-2 mixture ................. 53

Table 7: Standard deviations of $K_{AOT}$ ........................................................... 54

Table 8: Standard deviations of $Cc_{AOT}$ ......................................................... 57

Table 9: Margules Parameters ........................................................................ 70

Table 10: Gibbs Free Energy of AOT/AMA in Hexane ................................................ 70

Table 11: Gibbs Free Energy of AOT/AMA in Octane ................................................. 71

Table 12: Gibbs Free Energy of AOT/ALFOTERRA 8-41S in Hexane........................ 71

Table 13: Gibbs Free Energy of AOT/ALFOTERRA 8-41S in Octane ........................ 71

Table 14: Gibbs Free Energy of AOT/ALFOTERRA 8-41S in Decane........................ 72

Table 15: Gibbs Free Energy of AOT/ISALCHEM 123-2 in Hexane........................... 72

Table 16: Gibbs Free Energy of AOT/ISALCHEM 123-2 in Octane............................ 73

Table 17: Gibbs Free Energy of AOT/ISALCHEM 123-2 in Decane ........................... 73

# List of Figures

Figure 1: Structure of Surfactant ........................................................................ 1

Figure 2: Structure of Extended Surfactant ..................................................... 4

Figure 3: Comparison of the optimum salinity ($S*$) obtained from the prediction using HLD and the experimental values in (a) AMA/AOT/octane system, and (b) the AMA/AOT/decane system. Total surfactant concentration of 0.07 M was kept constant at 25 ◦C [4]. ........................................................................................................ 9

Figure 4: Optimal salinity shift for SDHS(or AMA)-AOT and SDHS-SO mixtures as a function of AOT and SO with 0.1M total surfactant concentration in Decane at 25°C [9]. ............................................................................................................ 9

Figure 5: Excess Gibbs free energy as a function of mole fraction of non-ionic surfactant. Solid lines represent Margules 2 parametric equation [11]. ......................... 13

Figure 6: Salinity scan for AOT/AMA at $X_{AOT}$ = 0.1 in Hexane at 25°C...................... 21

Figure 7: Salinity scan for AOT/AMA at $X_{AOT}$ = 0.1 in Heptane at 25°C..................... 21

Figure 8: Salinity scan for AOT/AMA at $X_{AOT}$ = 0.1 in Octane at 25°C....................... 22

Figure 9: $\ln S^*_{mix}$ as a function of EACN for AOT/AMA mixture at $X_{AOT}$ = 0.1 .......... 22

Figure 10: Salinity scan for AOT/AMA at $X_{AOT}$ = 0.3 in Pentane at 25°C. ................. 23

Figure 11: Salinity scan for AOT/AMA at $X_{AOT}$ = 0.3 in Hexane at 25°C.................... 24

Figure 12: Salinity scan for AOT/AMA at $X_{AOT}$ = 0.3 in Heptane at 25°C.................. 24

Figure 13: Salinity scan for AOT/AMA at $X_{AOT}$ = 0.3 in Octane at 25°C..................... 25

Figure 14: $\ln S^*_{mix}$ as a function of EACN for AOT/AMA mixture at $X_{AOT}$ = 0.3 ........ 25

Figure 15: Salinity scan for AOT/AMA at $X_{AOT}$ = 0.5 in Hexane at 25°C.................... 26

Figure 16: Salinity scan for AOT/AMA at $X_{AOT}$ = 0.5 in Octane at 25°C..................... 27

Figure 17: Salinity scan for AOT/AMA at $X_{AOT}$ = 0.5 in Decane at 25°C. .................. 27

Figure 18: $lnS^*_{mix}$ as a function of EACN for AOT/AMA mixture at $X_{AOT}$ = 0.5 ........ 28

Figure 19: Salinity scan for AOT/AMA at $X_{AOT}$ = 0.7 in Hexane at 25°C. .................. 29

Figure 20: $lnS^*_{mix}$ as a function of EACN for AOT/AMA mixture at $X_{AOT}$ = 0.7 ........ 29

Figure 21: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT}$ = 0.1 in Hexane at 25°C. ........................................................................................................ 30

Figure 22: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT}$ = 0.1 in Octane at 25°C. ........................................................................................................ 31

Figure 23: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT}$ = 0.1 in Decane at 25°C. ........................................................................................................ 31

Figure 24: $lnS^*_{mix}$ as a function of EACN for AOT/ALFOTERRA mixture at $X_{AOT}$ = 0.1 ........................................................................................................ 32

Figure 25: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT}$ = 0.3 in Hexane at 25°C. ........................................................................................................ 33

Figure 26: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT}$ = 0.3 in Octane at 25°C. ........................................................................................................ 33

Figure 27: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT}$ = 0.3 in Decane at 25°C. ........................................................................................................ 34

Figure 28: $lnS^*_{mix}$ as a function of EACN for AOT/ALFOTERRA mixture at $X_{AOT}$ = 0.3 ........................................................................................................ 34

Figure 29: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT}$ = 0.5 in Hexane at 25°C. ........................................................................................................ 35

Figure 30: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT}$ = 0.5 in Octane at 25°C. ........ 36

Figure 31: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT}$ = 0.5 in Decane at 25°C. ........ 36

Figure 32: $\ln S^*_{mix}$ as a function of EACN for AOT/ALFOTERRA mixture at $X_{AOT}$ = 0.5 ........ 37

Figure 33: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT}$ = 0.7 in Hexane at 25°C. ........ 38

Figure 34: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT}$ = 0.7 in Octane at 25°C. ........ 38

Figure 35: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT}$ = 0.7 in Decane at 25°C. ........ 39

Figure 36: $\ln S^*_{mix}$ as a function of EACN for AOT/ALFOTERRA mixture at $X_{AOT}$ = 0.7 ........ 39

Figure 37: Salinity scan for AOT/ISALCHEM 123-2 at $X_{AOT}$ = 0.1 in Hexane at 25°C. ........ 40

Figure 38: Salinity scan for AOT/ISALCHEM 123-2 at $X_{AOT}$ = 0.1 in Octane at 25°C. ........ 41

Figure 39: Salinity scan for AOT/ISALCHEM 123-2 at $X_{AOT}$ = 0.1 in Decane at 25°C. ........ 41

Figure 40: $\ln S^*_{mix}$ as a function of EACN for AOT/ISALCHEM 123-2 mixture at $X_{AOT}$ = 0.1 ........ 42

Figure 41: Salinity scan for AOT/ISALCHEM 123-2 at $X_{AOT}$ = 0.3 in Hexane at 25°C. ............ 43

Figure 42: Salinity scan for AOT/ISALCHEM 123-2 at $X_{AOT}$ = 0.3 in Octane at 25°C. ............ 43

Figure 43: Salinity scan for AOT/ISALCHEM 123-2 at $X_{AOT}$ = 0.3 in Decane at 25°C. ............ 44

Figure 44: $\ln S^*_{mix}$ as a function of EACN for AOT/ISALCHEM 123-2 mixture at $X_{AOT}$ = 0.3 ............ 44

Figure 45: Salinity scan for AOT/ISALCHEM 123-2 at $X_{AOT}$ = 0.5 in Hexane at 25°C. ............ 45

Figure 46: Salinity scan for AOT/ISALCHEM 123-2 at $X_{AOT}$ = 0.5 in Octane at 25°C. ............ 46

Figure 47: Salinity scan for AOT/ISALCHEM 123-2 at $X_{AOT}$ = 0.5 in Decane at 25°C. ............ 46

Figure 48: $\ln S^*_{mix}$ as a function of EACN for AOT/ISALCHEM 123-2 mixture at $X_{AOT}$ = 0.5 ............ 47

Figure 49: Salinity scan for AOT/ISALCHEM 123-2 at $X_{AOT}$ = 0.7 in Hexane at 25°C. ............ 48

Figure 50: Salinity scan for AOT/ISALCHEM 123-2 at $X_{AOT}$ = 0.7 in Octane at 25°C. ............ 48

Figure 51: Salinity scan for AOT/ISALCHEM 123-2 at $X_{AOT}$ = 0.7 in Decane at 25°C. ............ 49

Figure 52: $\ln S^*_{mix}$ as a function of EACN for AOT/ISALCHEM 123-2 mixture at $X_{AOT}$ = 0.7 ......... 49

Figure 53: $K_{AOT}$ as a function of $X_{AOT}$ ($K_{AOT}$ @ X = 1 are extrapolated)......... 55

Figure 54: $Cc_{AOT}$ as a function of $X_{AOT}$ ($Cc_{AOT}$ @ X = 1 are extrapolated)......... 56

Figure 55: $S^*_{mix}$ as a function of $X_{AOT}$ in pentane, hexane, heptane, octane and decane in AOT/AMA mixture. $S^*_{mix}$ actual is represented as hollow and $S^*_{mix}$ experimental are represented as solid data points. ......... 58

Figure 56: $S^*_{mix}$ as a function of $X_{AOT}$ in hexane, octane and decane in AOT/ALFOTERRA 8-41S mixture. $S^*_{mix}$ actual is represented as hollow and $S^*_{mix}$ experimental are represented as solid data points. ......... 58

Figure 57: $S^*_{mix}$ as a function of $X_{AOT}$ in hexane, octane and decane in AOT/ISALCHEM 123-2 mixture. $S^*_{mix}$ actual is represented as hollow and $S^*_{mix}$ experimental are represented as solid data points. ......... 59

Figure 58: $\ln S^*_{mix}$ as a function of $X_{AOT}$ for AOT/AMA, AOT/ALFOTERRA 8-41S and AOT/ISALCHEM 123-2 mixtures in Hexane......... 60

Figure 59: $\ln S^*_{mix}$ as a function of $X_{AOT}$ for AOT/AMA, AOT/ALFOTERRA 8-41S and AOT/ISALCHEM 123-2 mixtures in Octane......... 60

Figure 60: $\ln S^*_{mix}$ as a function of $X_{AOT}$ for AOT/AMA, AOT/ALFOTERRA 8-41S and AOT/ISALCHEM 123-2 mixtures in Decane. ......... 61

Figure 61: Normalized Gibbs free energy as a function of $X_{AOT}$ for AOT/AMA, AOT/ALFOTERRA 8-41S and AOT/ISALCHEM 123-2 mixtures in Hexane. The solid lines represent the Margules rules fit......... 62

Figure 62: Normalized Gibbs free energy as a function of $X_{AOT}$ for AOT/AMA, AOT/ALFOTERRA 8-41S and AOT/ISALCHEM 123-2 mixtures in Octane. The solid lines represent the Margules rules fit. .......... 63

Figure 63: Normalized Gibbs free energy as a function of $X_{AOT}$ for AOT/AMA, AOT/ALFOTERRA 8-41S and AOT/ISALCHEM 123-2 mixtures in Decane. The solid lines represent the Margules rules fit. .......... 63

# Abstract

HLD equation was first introduced by Salager [1], however for predicting the HLD parameters from known parameters of a surfactant in a binary anionic-anionic mixture, Acosta [8] suggested linear mixing rules which can be applied to the HLD equation. The linear mixing rules have been shown to work for various anionic-anionic surfactants. However, while performing a phase behavior with Sodium di(2-ethylhexyl) sulfosuccinate or commercially known as AEROSOL-OT or AOT, a deviation from ideal mixing has been observed. In order to quantify this non-ideality, a microemulsion phase study (salinity scan) was performed on AOT. AOT cannot form a middle phase microemulsion by itself, hence AOT was mixed with a reference surfactant to obtain Winsor III microemulsions. The reference surfactants used to perform the salinity scan were a twin-tailed surfactant and two linear chained alkyl sulfates. The twin-tailed reference surfactant used was Sodium dihexyl sulfosuccinate or commercially also known as AMA and the linear chained alkyl sulfates were ALFOTERRA 8-41S and ISALCHEM 123-2. The salinity scan was performed at 25°C at different mole fractions of AOT i.e. 0.1, 0.3, 0.5 and 0.7 in different oils namely pentane, hexane, heptane, octane and decane. After performing the salinity scan and determining the $K_{AOT}$ and $Cc_{AOT}$ using the linear mixing rules, it was observed that the linear mixing rules fail to satisfy the HLD equation in the case of an AOT mixture. Deviations from ideal-mixing were quantified in terms of Gibbs free energy and negative normalized Gibbs free energy values were obtained for all the three systems indicating the existence of strong driving forces in AOT-anionic mixtures to make microemulsions at room temperature. The largest deviations were observed in the AOT/AMA mixture probably because of low packing. It was also

observed that a mixture of high Cc and low Cc valued surfactants irrespective of their structural differences showed to have much lower deviations from non-ideal mixing as compared to two similarly structured surfactants like AOT/AMA.

# Chapter 1: Introduction

Salager [3] states that the name Surfactant denotes surface active agent. A surfactant molecule sits at the interface of the oil and the aqueous phase and hence lowering the interfacial surface tension between both the phases. Surfactants have two parts as a part of their structure, one polar and the other non-polar hence they are also called amphipathic molecules. The surfactant sits at the oil and aqueous phase interface with its polar head which is hydrophilic in the water and the non-polar tail being hydrophobic in the oil phase. Surfactants are like bridging agents which reduce the IFT between both the phases and the interfacial energy hence enabling a molecule to sit at the interface. It hence decreases the forces required to increase the interfacial are by 1 unit.

Surfactants can be categorized into 1) Ionic Surfactants (Anionic, Cationic), 2) Non-Ionic Surfactants, 3) Zwitterionic Surfactants. An Ionic surfactant is of two types anionic and cationic, which means the headgroup either has a negative or positive net charge on it. A Non-Ionic surfactant has a headgroup no net charge on it. A zwitterionic surfactant has a headgroup with both positive charges on it.

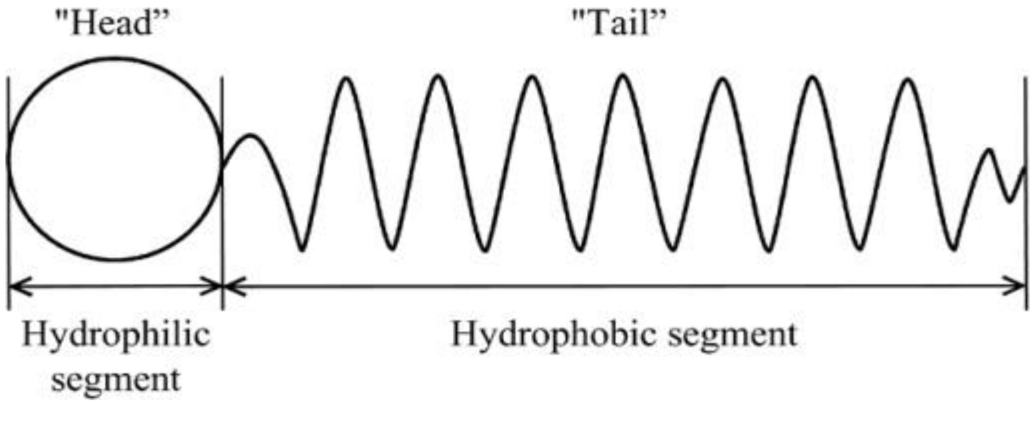


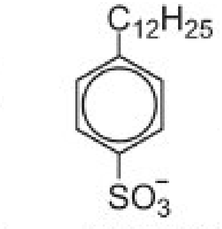
**Figure 1: Structure of Surfactant**

There are 3 types of surfactants, namely:

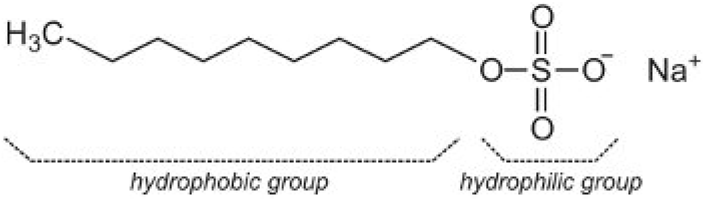
1) Anionic Surfactants:

These surfactants are negatively charged surfactants. The headgroups of these surfactants have a negative charge. These types of surfactants are mostly used in the laundry/detergent/cosmetic industries since these surfactants show high cleaning properties [2]. There are four types of common anionic surfactants:

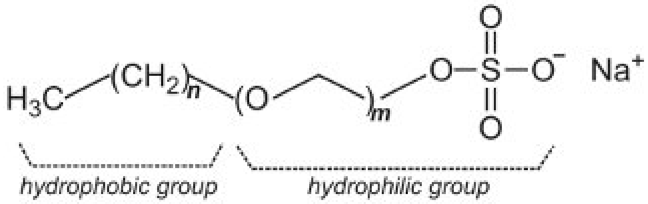
a) Alkylbenzene sulfonates



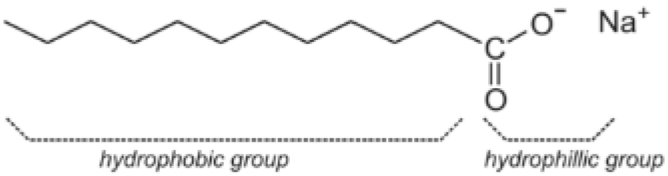
b) Alkyl sulfates



c) Alkyl ether sulfates



d) Soap



2) Cationic Surfactants:

Cationic surfactants have a positive headgroup. Cationic surfactants are used as hair conditioners, soaps etc. The function of a hair conditioner is to add back oil to the hair, hence the cationic surfactants are used for the same purpose as these are positively charged while the hair is negatively charged and hence would bind with cationic surfactant letting it stay on its surface [2].

3) Amphoteric Surfactants

Salager [3] defines amphoteric surfactants as surfactants which have two functional groups i.e. both anionic and cationic. Amphoteric surfactants are pH dependent, mostly behaving like an anionic at alkaline pH and cationic at acidic pH. The amino acid amphoteric surfactants are largely used in pharmaceutical companies as they are highly biocompatible in nature. Whereas the betaines are very mild in nature hence used in baby products such as baby shampoos etc.

Another class of surfactants are the “Extended surfactants”. Extended surfactants have intermediate polarity groups, such PO (Propylene Oxides) and EO (Ethylene Oxide) which are sited between hydrocarbon tail and hydrophilic head group. Because of their unique structures, it is extended out further to both the oil phase and water phase, hence giving a smoother transition amidst the hydrophobic and hydrophilic regions in the interface, hence giving a condition of solubilizing hydrophilic and hydrophobic phases. The Gibbs adsorption equation leads to an expectation that the interfacial region thickening, between these two phases would result to a reduction of IFT and increase in adsorption. Even though their molecular weights are large, they are soluble in water and can be formulated without any precipitation even in high salt concentration [5].

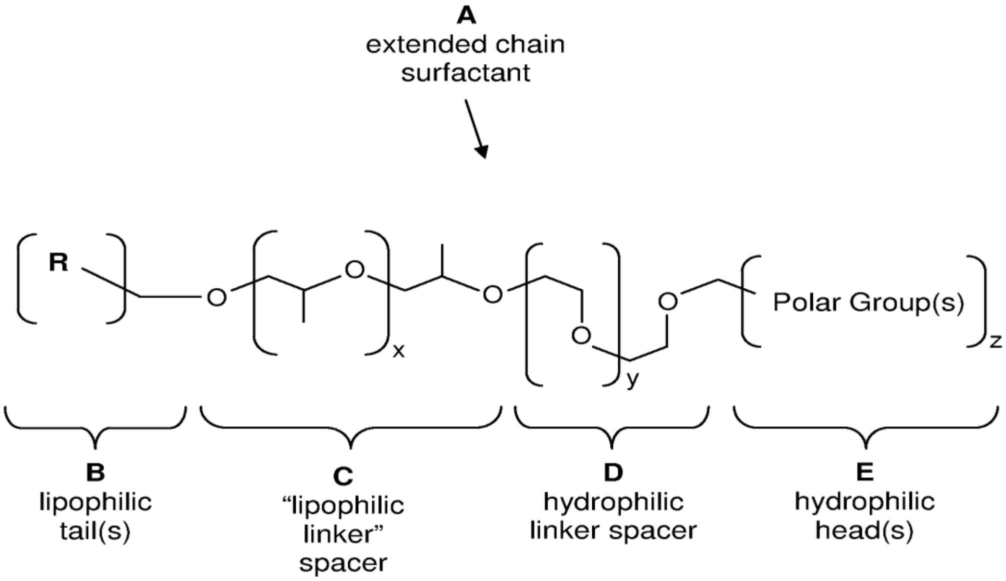


**Figure 2: Structure of Extended Surfactant**

"Reference surfactants" are such surfactants which can form middle phase (Winsor III) microemulsion by themselves. The most commonly used reference surfactants used in our lab are AMA, ALFOTERRA 8-41S, ALFOTERRA 10-41S and through this project we have tried to introduce another reference surfactant named ISALCHEM 123-2. All the mentioned surfactants are anionic in nature.

## 1.1 Problem Statement

Sodium di(2-ethylhexyl) sulfosuccinate or commonly known as AEROSOL-OT (AOT) has been shown to have deviations from the linear mixing rules commonly used in the HLD equation. Fatoumata [6] and Dr. Su showed that the $K_{AOT}$ and $Cc_{AOT}$ values of AOT were not constant with increasing molar ratios of AOT in an AOT/AF 8-41S mixture. However, the AOT used in [6] was 75% active and had some unknown solvent in it, hence in this work, phase behavior of 100% pure AOT (wax) was studied, when mixed with Sodium di-hexyl sulfosuccinate or known as AMA which is a twin-tailed surfactant and with two linearly chained alkyl sulfates namely ALFOTERRA 8-41S and ISALCHEM 123-2.

So, here in this work we tried to determine the $K_{AOT}$ and $Cc_{AOT}$ values for different mole fractions of AOT in AOT/AMA, AOT/ALFOTERRA-8-41S and AOT/ISALCHEM 123-2 mixtures at 25ºC and hence try to investigate and verify the accuracy of the linear mixing rule in the HLD theory. And also later, we quantified the non-ideality in terms normalized Gibbs free energy i.e. $G_{EX}/RT$.

# Chapter 2: Literature Review

## 2.1 HLD equation origin

The HLD concept was first introduced by J. L. Salager et. al. [1], it is a thermodynamically derived correlation to describe a microemulsion system at optimal formulation conditions. HLD negative, positive and zero values represent Type I, II and III microemulsions, respectively. A Type 1 microemulsion consists of oil swollen micelles in aqueous solution, in equilibrium with the excess oil phase; a Type 2 microemulsion consists of water swollen reverse micelles in a non-aqueous phase, in equilibrium with an excess water phase; a Type 3 microemulsions consists of a separate surfactant phase containing significant volumes of oil and water, in equilibrium with separate oil and water phases. The HLD equation is:

$HLD = \ln(S) - K(EACN) - f(A) + C_c - \alpha_t(T - T_{ref})$ for ionic surfactants

**(Equation 1)**

$HLD = \mathrm{b}S - K(EACN) - f(A) + C_c - \alpha_t(T - T_{ref})$ for non-ionic surfactants

**(Equation 2)**

where:

EACN = Equivalent Alkane Carbon Number; for an alkane, this value is simply the number of carbon atoms (e.g., hexane=6) while for aromatics and other cyclic compounds the value varies (e.g. cyclohexane = 3, benzene = 0).

T = temperature in degrees C.

$T_{ref}$ = reference temperature, always 25°C.

$\alpha_t$ = empirical temperature constant; typically taken to be ~0.01 for ionics, -0.06 for ethoxylates and 0 for polysaccharide surfactants.

S = salinity in g/100 ml.

Cc = characteristic curvature of surfactant. A more positive Cc represents a surfactant that prefers to be soluble in oil, while a more negative Cc represents a surfactant that prefers to be soluble in water. The term characteristic curvature is intended to convey the molecules intrinsic tendency to introduce curvature at an oil/water interface, and is closely related to the Israelachvili [14] dimensionless packing factor of the surfactant.

K, b = an empirical constant

### 2.2 Linear Mixing Rules and K, Cc value determination of mixtures

Straight long tailed surfactants generally form liquid crystals, gels or viscous microemulsions when mixed in the oil phases sometimes also at optimal conditions. These kind of microemulsions can take weeks to equilibrate and also sometimes even after equilibration, it becomes difficult to observe a clear middle phase and hence making it difficult to determine the HLD microemulsions [7].

Hence, in order to solve this issue, Acosta [8] proposed the linear mixing rule assumption. He used AMA i.e. Sodium di-hexyl sulfosuccinate as his reference surfactant since AMA can form clear middle phases by itself, hence could be used as a co-surfactant hence making it easier to determine the HLD parameters of the interested surfactant.

The linear mixing rules can be written in the following way:

$$lnS*_{mix} = K_{mix}(EACN) - Cc_{mix} \quad \textbf{(Equation 3)}$$

Where,

$$lnS*_{mix} = \sum x_i \, lnS*_i \quad \textbf{(Equation 4)}$$

$$K_{mix} = \sum x_i K_i \quad \textbf{(Equation 5)}$$

$$Cc_{mix} = \sum x_i * Cc_i \quad \textbf{(Equation 6)}$$

Here,

'i' = surfactant in the mixture,

'$x_i$' = mole fraction of surfactant in the mixture

As shown by Manish [7], $\ln S^*_{mix}$ obtained from the microemulsion phase study (Salinity scan) were plotted against the EACN of different oils used. The slope hence obtained was the $K_{mix}$ and the intercept obtained was $Cc_{mix}$. Using the linear mixing rules, K and Cc of the surfactant of interest were back calculated using eq. (5) & (6).

Witthayapanyanon [4] and Mavaddat [9] in the past have worked with AOT-AMA mixtures both of which are di-alkyled twin tailed anionic surfactants. They had showed the $\ln S_{mix}$ AOT/AMA vs. mole fraction correlation in limonene(EACN=5.7) and decane (EACN=10) at 25˚C respectively, both of whose data match with our current results.

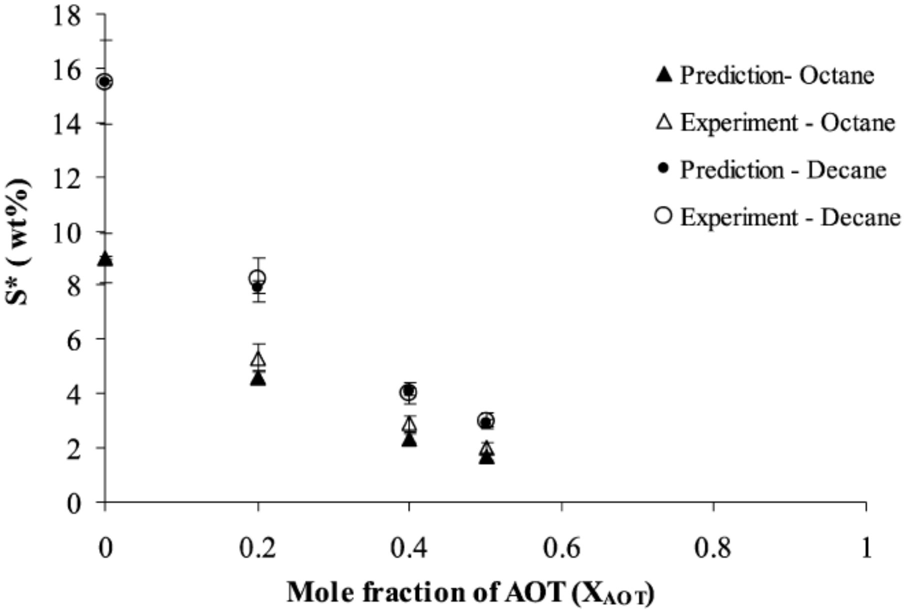


**Figure 3: Comparison of the optimum salinity (*S∗*) obtained from the prediction using HLD and the experimental values in (a) AMA/AOT/octane system, and (b) the AMA/AOT/decane system. Total surfactant concentration of 0.07 M was kept constant at 25 ◦C [4].**

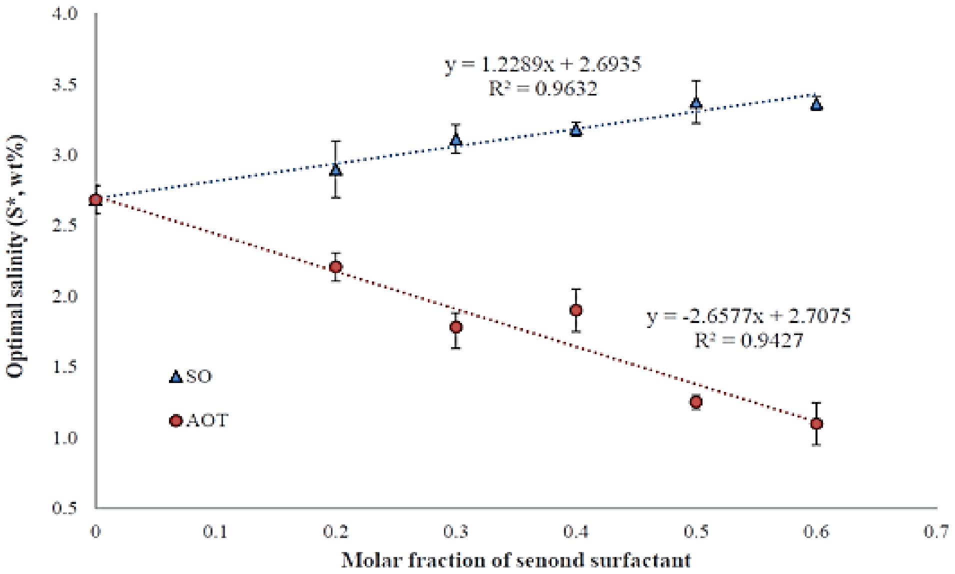


**Figure 4: Optimal salinity shift for SDHS(or AMA)-AOT and SDHS-SO mixtures as a function of AOT and SO with 0.1M total surfactant concentration in Decane at 25°C [9].**

However, a same $K_{AMA}$ and $K_{AOT}$ value was used by Witthayapanyanon [4], Mavaddat [9] , Acosta [8] and Steven Abbott [10] which was 0.17. Also, the $Cc_{AMA}$ and $Cc_{AOT}$ values used in the literature so far are $Cc_{AMA}$ = 0.93(AMA) [4] and $Cc_{AOT}$ = 2.42 [4], 1.67 [9], 2.55 [10]. Whereas, our $K_{AMA}$ = 0.072 and $Cc_{AMA}$ = -1.51 whereas $K_{AOT}$ and $Cc_{AOT}$ have been shown to be varying with $X_{AOT.}$ However, the negative slope of $S^{*}_{mix}$ observed in Fig. (3) and Fig. (4) can be seen to match with our results in this work.

One of the main reason behind this discrepancy is the theoretical approach used to determine the $K_{AOT}$ and $Cc_{AOT}$. As shown in [4] and [9], the $\ln S*_{mix}$ of the AOT/AMA mixture were plotted against $X_{AOT}$ to determine the $K_{AOT}$ and $Cc_{AOT}$. Hence, as per the following equation:

$lnS*_{mix} = lnS*_1 + \{(K_2 - K_1)(EACN) + (Cc_1 - Cc_2)\}x_2$ **(Equation 7)**

Where,

Slope = $(K_2 - K_1)(EACN) + (Cc_1 - Cc_2)$ **(Equation 8)**

Intercept = $lnS*_1 = (K_1)(EACN) - Cc_1$ **(Equation 9)**

and EACN = 5.7 for Limonene in [4], 10 for Decane in [9]

Here, the $K_1$ or $K_{AMA}$ and $K_2$ or $K_{AOT}$ were both taken as 0.17.

Whereas, the method used to determine $K_{AOT}$ and $Cc_{AOT}$ in our study is as per the procedure showed by Manish [7]. Where, $\ln S*_{mix}$ vs EACN was plotted. Hence, as per the below equation,

$lnS*_{mix} = K_{mix}(EACN) - Cc_{mix}$

Where,

Slope = $K_{mix} = x_1 * K_1 + x_2 * K_2$ **(Equation 10)**

Intercept = $Cc_{mix} = x_1 * Cc_1 + x_2 * Cc_2$ **(Equation 11)**

Here, $K_1 = K_{AMA} = 0.072$

$K_2 = K_{AOT}$ = To be determined

$Cc_1 = Cc_{AMA} = -1.51$

$Cc_2 = Cc_{AOT}$ = To be determined

And EACN = 5, 6, 7, 8, 10

We decided to follow this method, as it is always better to use a more accurate specific K value for any surfactant species instead of assuming a common value.

## 2.3 Evaluation of Non-idealities in surfactant mixtures

HLD parameters can be determined for anionic-anionic mixture by using a simple linear mixing rule [10, 18, 22]:

$$HLD_{mix} = X_1 HLD_1 + X_2 HLD_2 \qquad \textbf{(Equation 12)}$$

Where,

$X_1$ = mole fraction of surfactant 1

$X_2$ = mole fraction of surfactant 2

Because of the inherent structural differences between a non-ionic and anionic surfactant molecule, a synergistic, non-ideal mixing behavior may have a dramatic effect on the overall calculated HLD and require a factor to correct for this non-ideality. Acosta et. al [11] used the following equation for an anionic-nonionic system, however in our case, the modified overall HLD equation would be as follows, where "a" and "n" refer to anionic and nonionic, respectively, and $G_{EX}/RT$ represents the excess free energy normalized by RT and $X_a$ and $X_n$ are the mole fractions of the surfactants in the mixture.

$$HLD_{mix} = X_a HLD_a + X_n HLD_n + G_{EX}/RT \qquad \textbf{(Equation 13)}$$

At the optimum salinity for the overall mixture, S*$_{mix}$, HLD$_{mix}$ = 0 and the equation above can be rearranged as the following equation.

$$\frac{G_{EX}}{RT} = -X_a HLD_a - X_n HLD_n$$ **(Equation 14)**

For an ideal mixture, when S*$_{mix}$ is used to calculated HLD$_a$ and HLD$_n$, G$_{EX}$/RT = 0. However, for a non-ideal mixture, G$_{EX}$/RT will be a nonzero value representing the excess free energy of bringing a mole of surfactant from the oil phase to the aqueous phase, normalized by RT. A positive value for G$_{EX}$/RT indicates the real mixture is more hydrophobic than the ideal mixture, and a negative value indicates the real mixture is more hydrophilic than the ideal mixture [11].

However, for our study, since we have observed a non-ideal mixing in AOT-anionic reference surfactant mixtures, hence for our study, we decided to use eq. (13) for our AOT mixtures, thus changing the equation to,

$$HLD_{mix} = X_{Ref\ Surfactant} HLD_{Ref\ Surfactant} + X_{AOT} HLD_{AOT} + G_{EX}/RT$$

**(Equation 15)**

At the optimum salinity for the overall mixture, S*$_{mix}$, HLD$_{mix}$ = 0 and the eq. (14) can be rearranged as the following equation.

$$\frac{G_{EX}}{RT} = -X_{Ref\ Surfactant} HLD_{Ref\ Surfactant} - X_{AOT} HLD_{AOT}$$ **(Equation 16)**

As discussed in [12], Margules polynomial equation is one of the simplest methods in classical thermodynamics which can be used to quantify the correlation between Gibbs free energy and surfactant mole fraction. The 2 parametric Margules equation can show a non-symmetric deviation that includes both positive and negative deviations. It is represented as eq. (17). As shown by Acosta et. al [11], the deviations from non-ideal behavior can be fitted using a 2-parameters Margules equation. Acosta et. al [11], tried to quantify the normalized Gibbs free energy $G_{EX}/RT$ for a binary anionic-non-ionic mixture. The equation used was as follows:

$$G_{EX}/RT = A_1 X_i X_{ni}^2 + A_2 X_{ni} X_i^2 \quad \textbf{(Equation 17)}$$

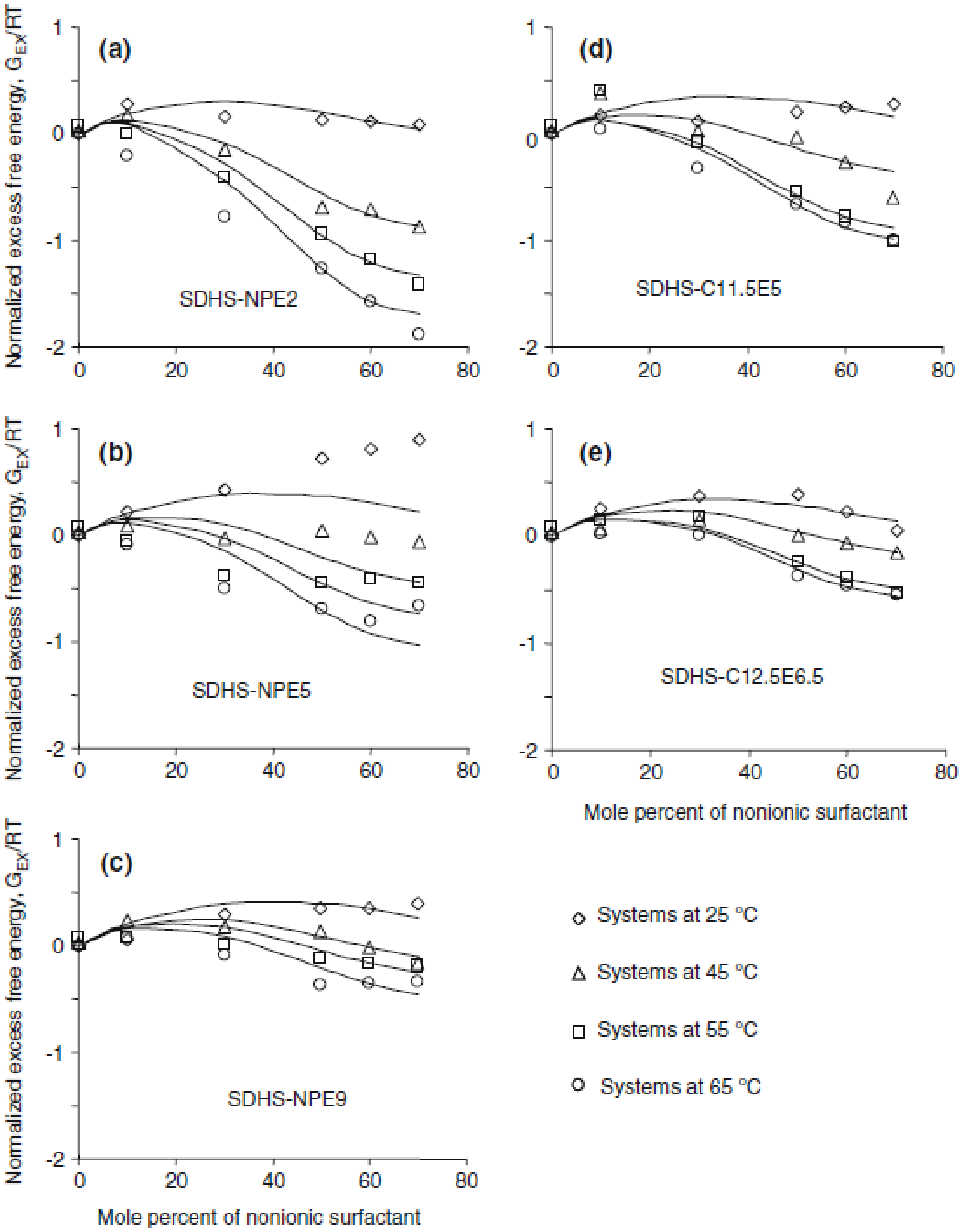


**Figure 5: Excess Gibbs free energy as a function of mole fraction of non-ionic surfactant. Solid lines represent Margules 2 parametric equation [11].**

Fig. (5) are some of his results, where he tried to fit the experimentally calculated $G_{EX}$/RT using the Margules 2 parameter expression. As, discussed in case of the SDHS-nonionic mixture used, at the 25°C, a positive deviation i.e. positive values of $G_{EX}$/RT were observed, hence suggesting that this system was thermodynamically not favorable at room temperature. In our study, we tried to use this methodology for an AOT- reference anionic surfactant mixture.

# Chapter 3: Experimental Procedure

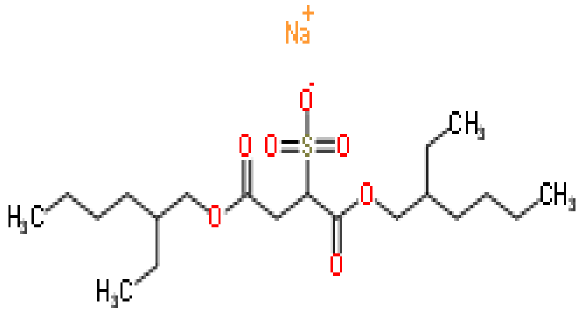
## 3.1 Materials Used

The surfactants used for this study are AOT (Sodium di(2-ethylhexyl) sulfosuccinate), AMA (Sodium dihexyl sulfosuccinate), ALFOTERRA 8-41S and ISALCHEM 123-2.

All of these are commercially available surfactants. The anionic reference surfactant which can be used is ALFOTERRA 8-41S (ALFOTERRA K2-41S), an extended surfactant having propoxylated (PO) / ethoxylated (EO) spacer arms; the EO helps bulk up the head and increase water solubility and hardness tolerance; the PO spacer allows an increase in lipophilicity without inducing precipitation or other phase separation. To the best of our knowledge, ISALCHEM 123-2 on the other hand, is the only surfactant without a PO group which forms middle phase by itself.

Their structures are as shown below:

**Table 1: Molecular Structures**

| NAME | STRUCTURE |
|---|---|
| AOT |  |

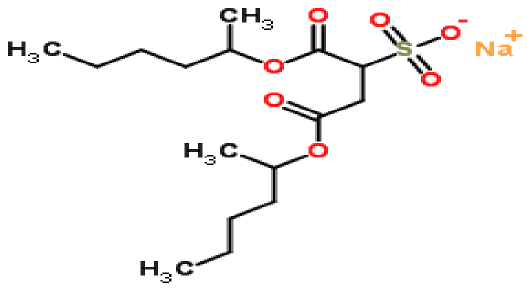
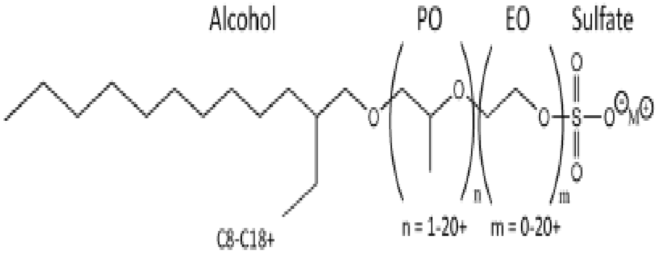
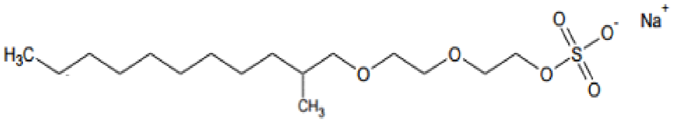
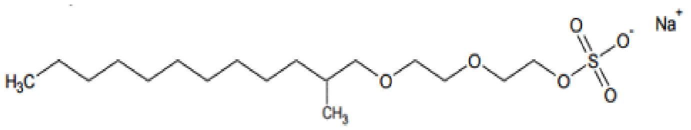
| | |
|---|---|
| AMA | <br> |
| ALFOTERRA 8-41S | <br> <br>**General structure of ALFOTERRA® Surfactant** |
| ISALCHEM 123-2 | C12 branched (ethoxy)<br><br> <br>C13 branched (ethoxy)<br><br> <br>Isalchem 123-2 Paste (95% Branched; branch may be C1 to C4 but always on the 2nd carbon)<br>$C_{12}$ $C_{13}$ alcohol. With 2 EO groups. |

**Table 2: Additional Surfactant Information**

| Name | Supplier | M.W(g/mole) | Activity(%) |
|---|---|---|---|
| AOT (wax) | FISCHER CHEMICALS | 444.54 | 100 |
| AMA | SIGMA ALDRICH | 388.45 | 80 |
| ALFOTERRA 8-41S | SASOL | 508.56 | 32.2 |
| ISALCHEM 123-2 | SASOL | 397.1 | 70.18 |

### 3.2 Microemulsion Phase Study (Salinity Scan)

Salinity scans were conducted on the given surfactants to determine the optimal salinity for evaluating the hydrophilic-lipophilic deviation (HLD) parameters, K and Cc. 5 mL of oil phase was added into each vial that contained 5 mL of aqueous phase composed of test surfactant, reference surfactant, sodium chloride, and deionized water. The vials were shaken by hand and then allowed to equilibrate for at least 24 hours at room temperature, 25 ± 2 °C. For each salinity scan, the vial with equal amount of oil and water solubilized in the middle phase was determined as the optimal formulation; for systems with slow equilibration rates the vial with the fastest coalescence rate was taken as the system at optimum. The salinity at the optimal formulation was defined as the optimal salinity, S*. During the salinity scan, the total surfactant concentration for AOT/AMA mixture at $X_{AOT}$ = 0.1, 0.3, 0.5 and 0.7 were fixed at 0.1M, 0.15M, 0.12M and 0.15M respectively. The total surfactant concentrations for all mole fractions of AOT in the

AOT/ALFOTERRA 8-41S mixture were fixed at 0.03M. Lastly, the total surfactant concentrations for all mole fractions of AOT in the AOT/ISALCHEM 123-2 mixture were fixed at 0.04M. The CMC of AOT has been measured as 2.65 µM in water at room temperature [13], hence in our entire work, we have kept our AOT concentrations above the CMC.

### 3.3 Evaluation of Non-Idealities in Anionic Mixtures

Because of the inherent structural differences between an AOT molecule and an anionic reference surfactant molecule, a synergistic, non-ideal mixing behavior may have a dramatic effect on the overall calculated HLD and require a factor to correct for this non-ideality. The modified overall HLD can be shown as in eq. (15), where $G_{EX}/RT$ represents the excess free energy normalized by RT and $X_{AOT}$ and $X_{Ref\ Surfactant}$ are the mole fractions of the surfactants in the mixture. At the optimum salinity for the overall mixture, $S_{mix}*$, $HLD_{mix} = 0$ and the eq. (15) can be rewritten as eq. (16).

For an ideal mixture, when $S_{mix}*$ is used to calculated $HLD_{Ref\ Surfactant}$ and $HLD_{AOT}$, $G_{EX}/RT = 0$. However, for a non-ideal mixture, $G_{EX}/RT$ will be a nonzero value.

One example of our calculations is ($X_{AOT}$ values given in Appendix-Table (10)),

$$\frac{G_{EX}}{RT} = -X_{AMA}HLD_{AMA} - X_{AOT}HLD_{AOT}$$

$$\Rightarrow \frac{G_{EX}}{RT} = -(0.9)(-0.0104) - (0.1)(6.0527)$$

$$\Rightarrow \frac{G_{EX}}{RT} = -0.595$$

The term $(G_{EX}/RT)_{AOT\text{-}AMA}$ in the above example was calculated after a salinity scan with hexane at room temperature. The optimum salinity occurs at 6.1 g/100 mL and $(G_{EX}/RT)_{AOT\text{-}AMA} = -0.66512$.

For determining the Margules parameters $A_1$ and $A_2$, the experimental $G_{EX}/RT$ values were plotted against $X_{AOT}.X_{Ref\ Surfactant}^2$ and $X_{AOT}^2.X_{Ref\ Surfactant}$, keeping intercept as 0. Hence giving us two line equations,

$$\frac{G_{EX}}{RT} = m_1.X_{AOT}.X_{Ref\ Surfactant}^2 \qquad \textbf{(Equation 18)}$$

$$\frac{G_{EX}}{RT} = m_2.X_{Ref\ Surfactant}.X_{AOT}^2 \qquad \textbf{(Equation 19)}$$

Adding eq.(18) and eq.(19), we get,

$$2\frac{G_{EX}}{RT} = m_1.X_{AOT}.X_{Ref\ Surfactant}^2 + m_2.X_{Ref\ Surfactant}.X_{AOT}^2$$

$$\Rightarrow \frac{G_{EX}}{RT} = \frac{m_1}{2}.X_{AOT}.X_{Ref\ Surfactant}^2 + \frac{m_2}{2}.X_{Ref\ Surfactant}.X_{AOT}^2$$

$$\Rightarrow \frac{G_{EX}}{RT} = M_1.X_{AOT}.X_{Ref\ Surfactant}^2 + M_2.X_{Ref\ Surfactant}.X_{AOT}^2 \qquad \textbf{(Equation 20)}$$

Where,

$m_1$ = Slope obtained from plotting $G_{EX}/RT$ values $X_{AOT}.X_{Ref\ Surfactant}^2$

$m_2$ = Slope obtained from plotting GEX/RT values $X_{AOT}^2.X_{Ref\ Surfactant}$

$M_1 = m_1/2 = A_1$

$M_2 = m_2/2 = A_2$

$G_{EX}/RT_{Margules}$ was then calculated using eq. (17) and were fitted to $G_{EX}/RT$. The results will be further discussed in the results/discussion section.

# Chapter 4: Results and Discussion

## 4.1 Microemulsion Phase Study (Salinity Scan)

### 4.1.1 K and Cc values of reference surfactants

**Table 3: K and Cc values of reference surfactants**

| Reference Surfactant | K | Cc |
|---|---|---|
| **AMA** | 0.072 | -1.51 |
| **AF 8-41S** | 0.057 | -2.4 |
| **ISALCHEM 123-2** | 0.06 | -2.31 |

As it can be seen, that the experimentally determined K and Cc values of AMA in our case are very different from the values reported by Acosta [8] i.e. 0.17 and -0.98 respectively. Also, it can be observed that the Cc values of ALFOTERRA 8-41S < ISALCHEM 123-2 < AMA hence denoting that ALFOTERRA 8-41S > ISALCHEM 123-2 > AMA in terms of hydrophilicity. However, the K values are in the same range. These K and Cc values of the reference surfactants given in Table (3), upon mixing them with AOT at different mole fractions, will be used to determine $K_{AOT}$ and $Cc_{AOT}$.

### 4.1.2 AOT/AMA (10:90)

| | | | | | |
|---|---|---|---|---|---|
| 5.8 | 6 | S* = 6.1* | 6.3 | 6.5 | 6.7 |

**Figure 6: Salinity scan for AOT/AMA at $X_{AOT}$ = 0.1 in Hexane at 25°C**

| | | |
|---|---|---|
| 6.7 | S* = 7* | 7.2 |

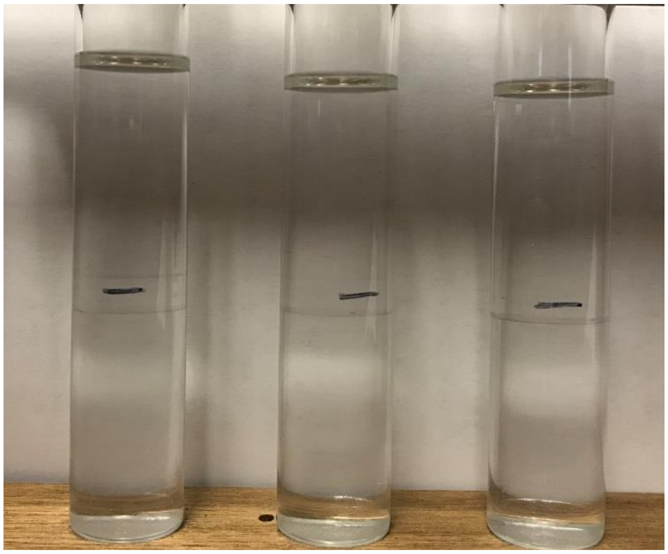


**Figure 7: Salinity scan for AOT/AMA at $X_{AOT}$ = 0.1 in Heptane at 25°C**

|  |  |  |  |  |
|---|---|---|---|---|
| 7.1 | 7.2 | 7.5 | 7.7 | S* = 7.8* |

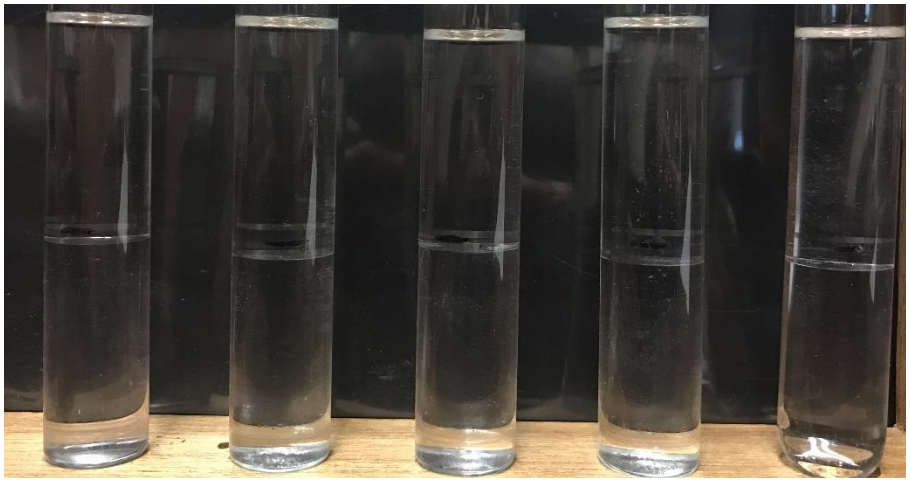


**Figure 8: Salinity scan for AOT/AMA at $X_{AOT}$ = 0.1 in Octane at 25°C.**

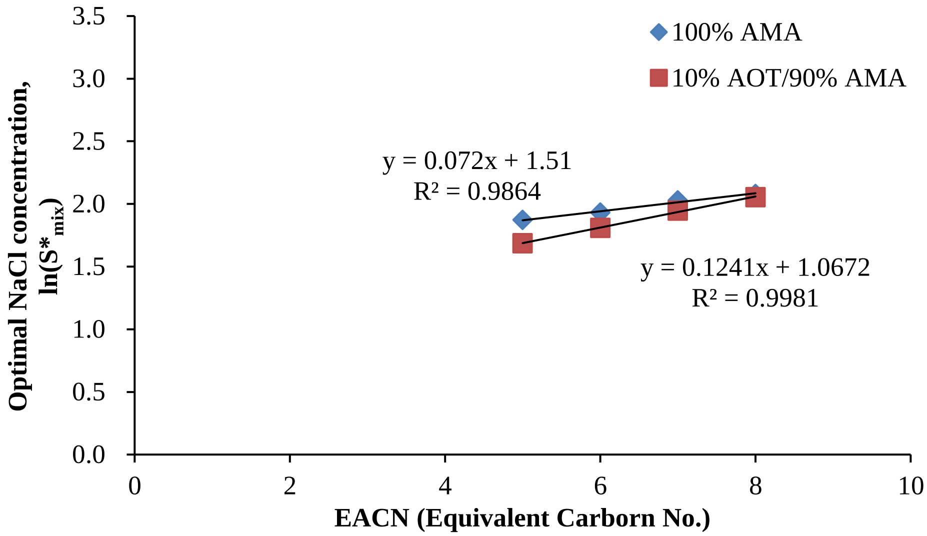


**Figure 9: $\ln S^*_{mix}$ as a function of EACN for AOT/AMA mixture at $X_{AOT}$ = 0.1**

The plot of $\ln S^*_{mix}$ vs. EACN gives us the slope and intercept of eq. (3), which are as follows:

$$\text{Slope} = K_{mix} = x_1 * K_1 + x_2 * K_2 \qquad \textbf{(Equation 21)}$$

Intercept = $Cc_{mix} = x_1 * Cc_1 + x_2 * Cc_2$ **(Equation 22)**

Where,

$K_1 = 0.072$ & $Cc_1 = -1.51$

Thus, upon substitution in eq. (21) & (22) we get,

$K_2 = K_{AOT} = 0.59$

$Cc_2 = Cc_{AOT} = 2.92$

4.1.3 AOT/AMA (30:70)

| | |
|---|---|
| 2.2 | S* = **2.3*** |

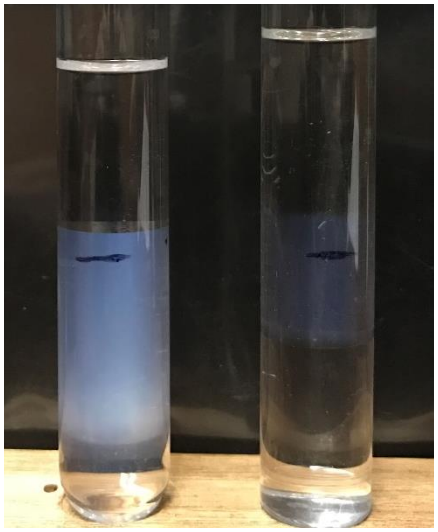


**Figure 10: Salinity scan for AOT/AMA at $X_{AOT}$ = 0.3 in Pentane at 25°C.**

|  |  |  |  |
|---|---|---|---|
| 2 | 2.2 | 2.4 | S* = **2.8*** |

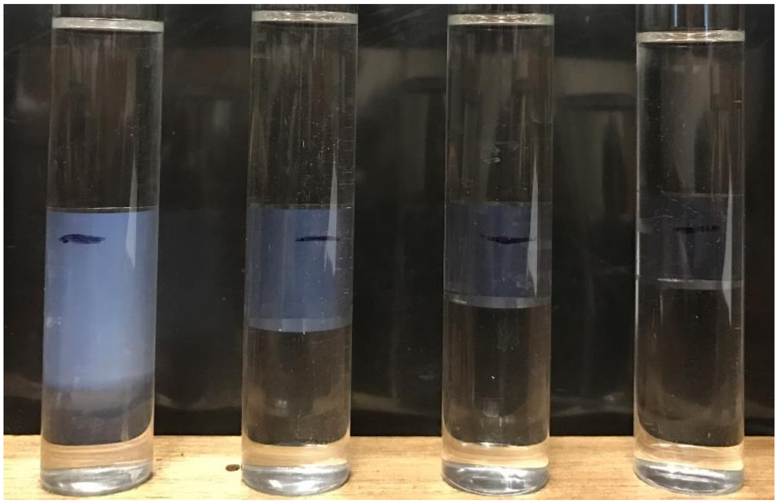


**Figure 11: Salinity scan for AOT/AMA at $X_{AOT}$ = 0.3 in Hexane at 25°C.**

|  |  |  |  |
|---|---|---|---|
| S* = **3.2** | 3.4 | 3.6 | 3.8 |

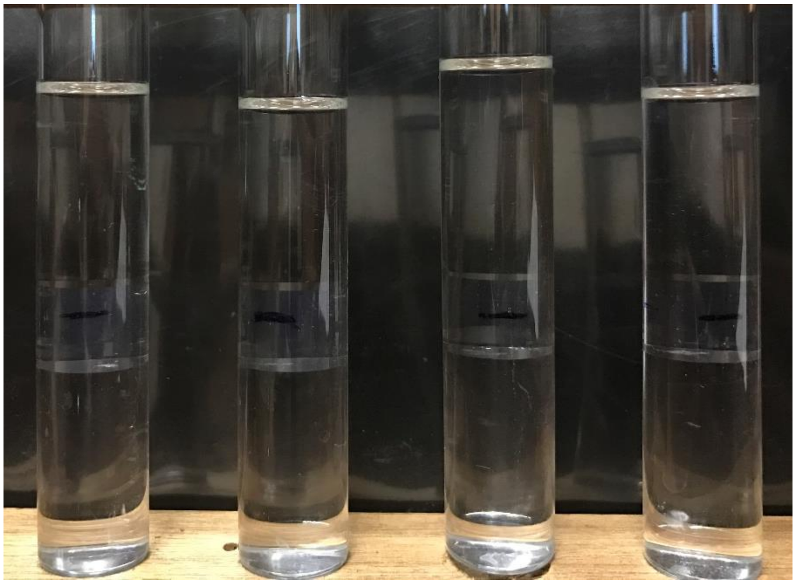


**Figure 12: Salinity scan for AOT/AMA at $X_{AOT}$ = 0.3 in Heptane at 25°C.**

S* = **4.5**

**Figure 13: Salinity scan for AOT/AMA at $X_{AOT}$ = 0.3 in Octane at 25°C.**

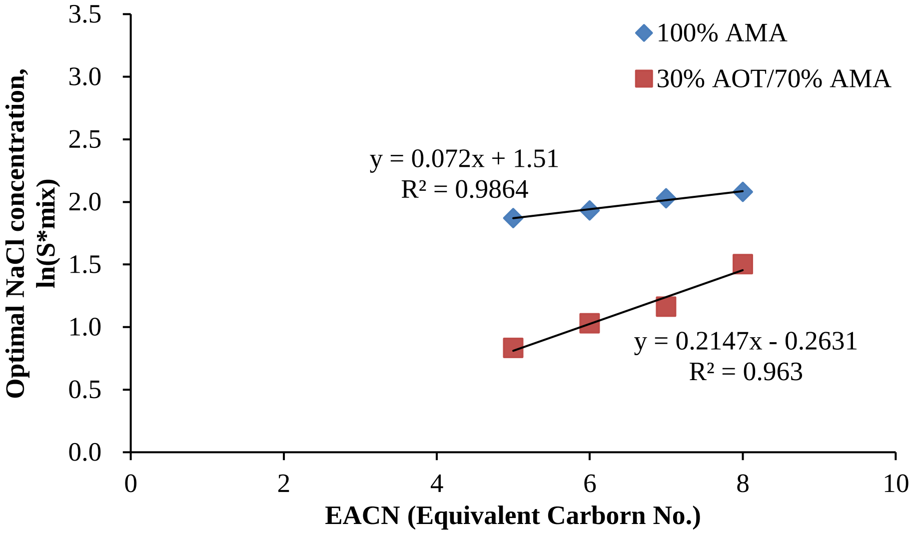


**Figure 14: $\ln S^*_{mix}$ as a function of EACN for AOT/AMA mixture at $X_{AOT}$ = 0.3**

The plot of $\ln S^*_{mix}$ vs. EACN gives us the slope and intercept of eq. (3), which are as follows:

Slope $= K_{mix} = 0.2147$

Intercept $= Cc_{mix} = 0.2631$

Where,

$K_1 = 0.072$ & $Cc_1 = -1.51$

Thus, upon substitution in eq. (21) & (22) we get,

$K_2 = K_{AOT} = 0.55$

$Cc_2 = Cc_{AOT} = 4.40$

### 4.1.4 AOT/AMA (50:50)

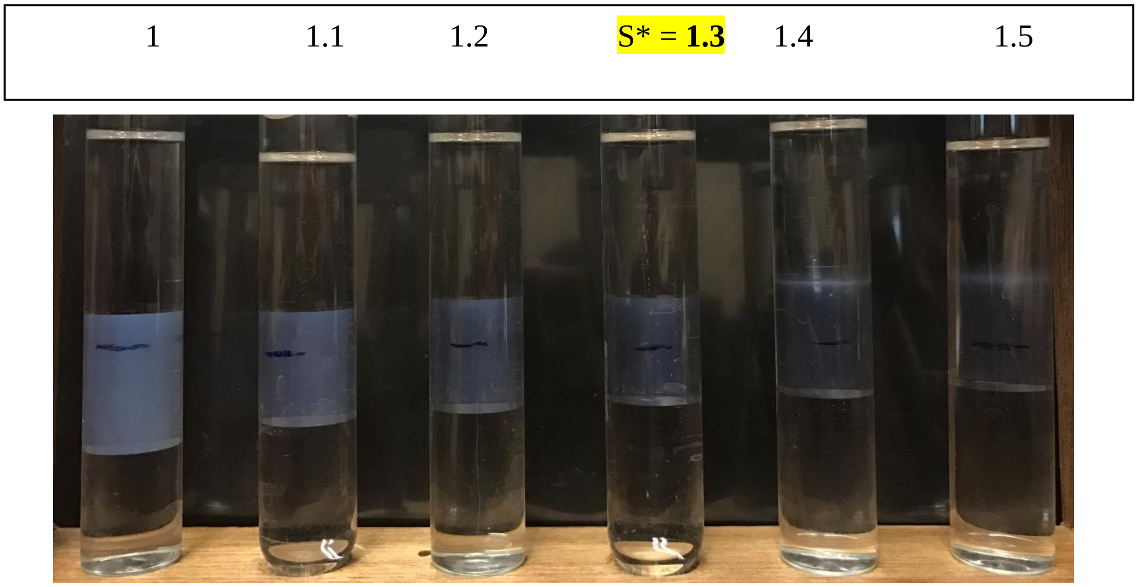


**Figure 15: Salinity scan for AOT/AMA at $X_{AOT} = 0.5$ in Hexane at 25°C.**

1.5 1.6 1.7 1.8 S* = **1.9** 2

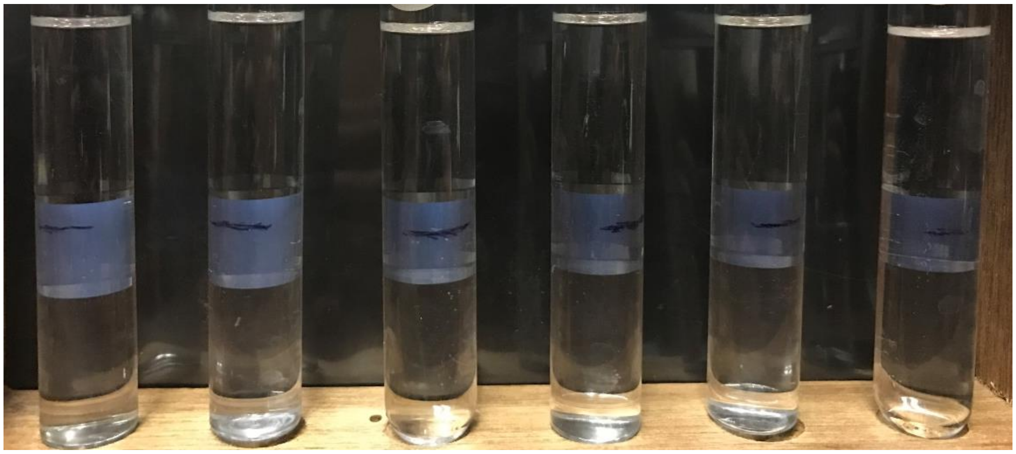


**Figure 16: Salinity scan for AOT/AMA at $X_{AOT}$ = 0.5 in Octane at 25°C.**

2.5 2.6 2.7 2.8 S* = **2.9** 3

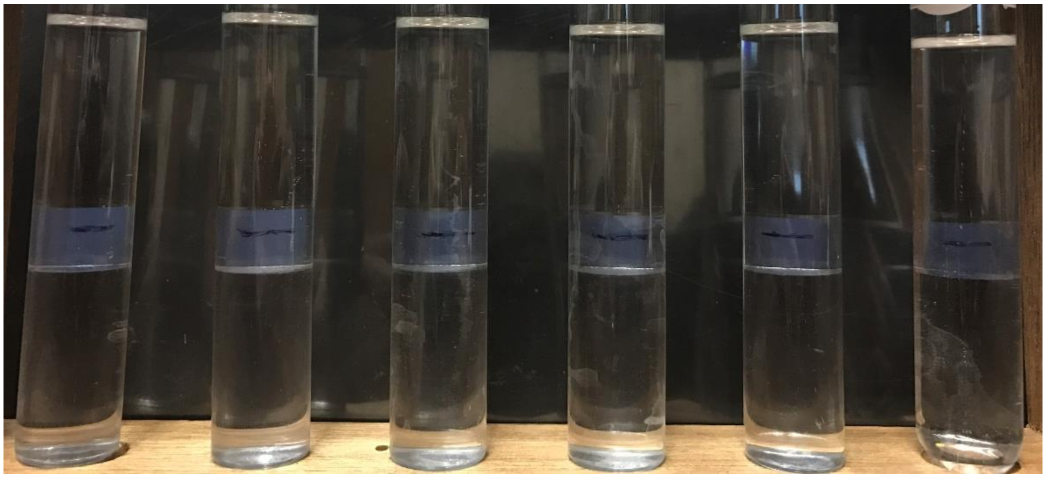


**Figure 17: Salinity scan for AOT/AMA at $X_{AOT}$ = 0.5 in Decane at 25°C.**

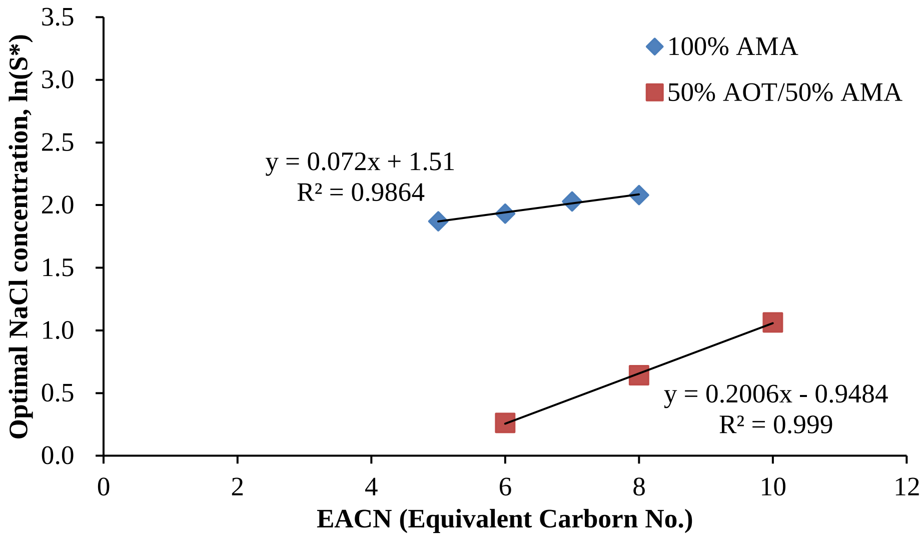


**Figure 18: $\ln S^*_{mix}$ as a function of EACN for AOT/AMA mixture at $X_{AOT}$ = 0.5**

The plot of $\ln S^*_{mix}$ vs. EACN gives us the slope and intercept of eq. (3), which are as follows:

Slope $= K_{mix} = 0.2006$

Intercept $= Cc_{mix} = 0.9484$

Where,

$K_1 = 0.072$ & $Cc_1 = -1.51$

Thus, upon substitution in eq. (21) & (22) we get,

$K_2 = K_{AOT} = 0.33$

$Cc_2 = Cc_{AOT} = 3.41$

### 4.1.5 AOT/AMA (70:30)

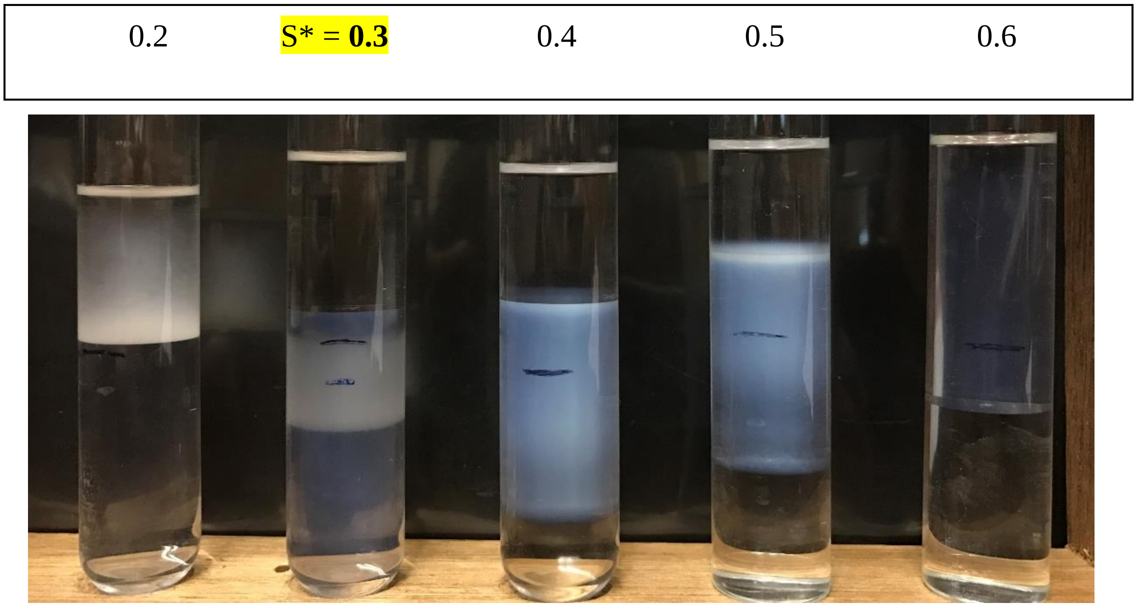


**Figure 19: Salinity scan for AOT/AMA at $X_{AOT}$ = 0.7 in Hexane at 25°C.**

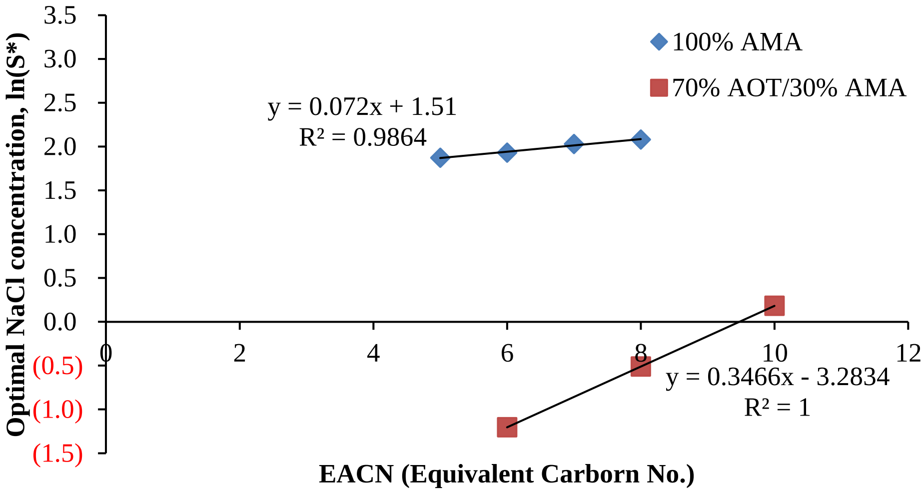


**Figure 20: $\ln S^*_{mix}$ as a function of EACN for AOT/AMA mixture at $X_{AOT}$ = 0.7**

The plot of $\ln S^*_{mix}$ vs. EACN gives us the slope and intercept of eq. (3), which are as follows:

Slope $= K_{mix} = 0.3466$

Intercept = $Cc_{mix} = 3.2834$

Where,

$K_1 = 0.072$ & $Cc_1 = -1.51$

Thus, upon substitution in eq. (21) & (22) we get,

$K_2 = K_{AOT} = 0.46$

$Cc_2 = Cc_{AOT} = 5.34$

### 4.1.6 AOT/ALFOTERRA-8-41S (10:90)

| | | | | | |
|---|---|---|---|---|---|
| 13 | 13.1 | 13.2 | S* = **13.3** | 13.4 | 13.5 |

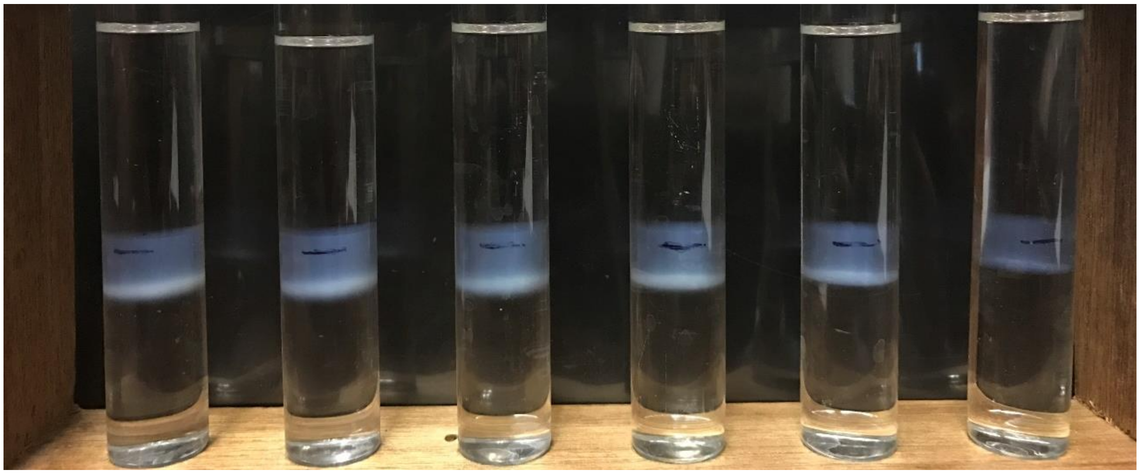


**Figure 21: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT}$ = 0.1 in Hexane at 25°C.**

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| 15 | 15.1 | S* = **15.2** | 15.3 | 15.4 | 15.5 |

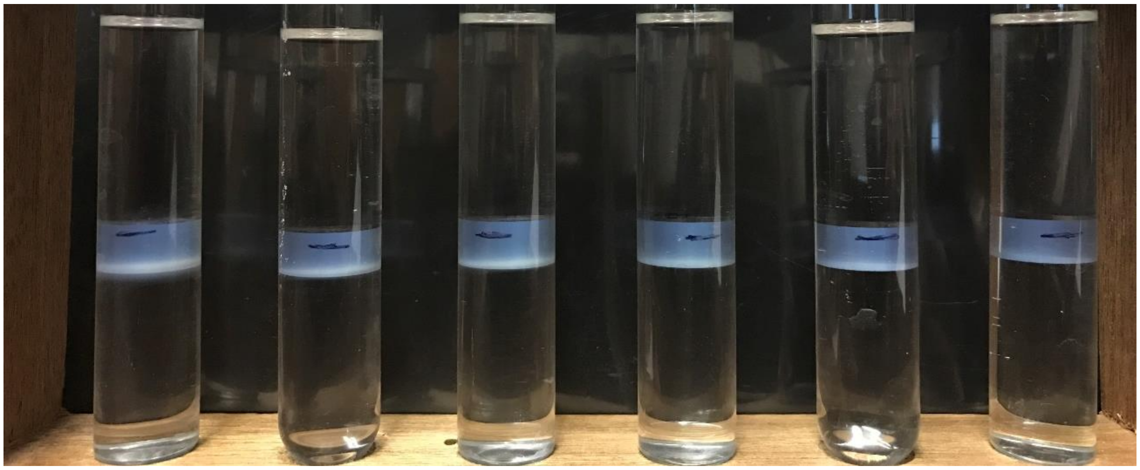


**Figure 22: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT}$ = 0.1 in Octane at 25°C.**

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| 16.8 | 16.9 | 17 | S* = **17.1** | 17.2 | 17.3 |

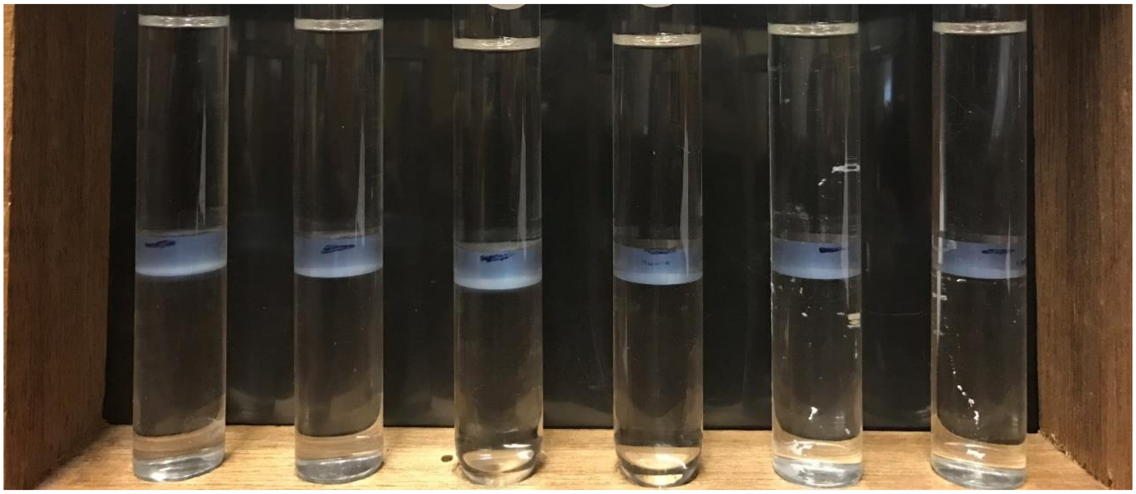


**Figure 23: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT}$ = 0.1 in Decane at 25°C.**

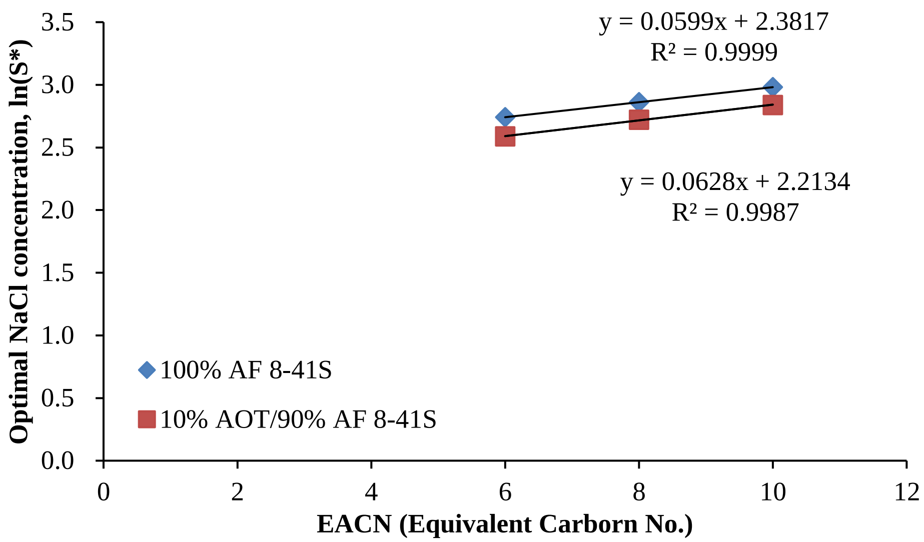


**Figure 24: $\ln S^*_{mix}$ as a function of EACN for AOT/ALFOTERRA mixture at $X_{AOT}$ = 0.1**

The plot of $\ln S^*_{mix}$ vs. EACN gives us the slope and intercept of eq. (3), which are as follows:

Slope $= K_{mix} = 0.0628$

Intercept = $Cc_{mix} = 2.2134$

Where,

$K_1 = 0.057$ & $Cc_1 = -2.40$

Thus, upon substitution in eq. (21) & (22) we get,

$K_2 = K_{AOT} = 0.12$

$Cc_2 = Cc_{AOT} = -0.53$

### 4.1.7 AOT/ALFOTERRA-8-41S (30:70)

| | | | | | |
|---|---|---|---|---|---|
| 8 | S* = **8.2** | 8.3 | 8.4 | 8.5 | 8.6 |

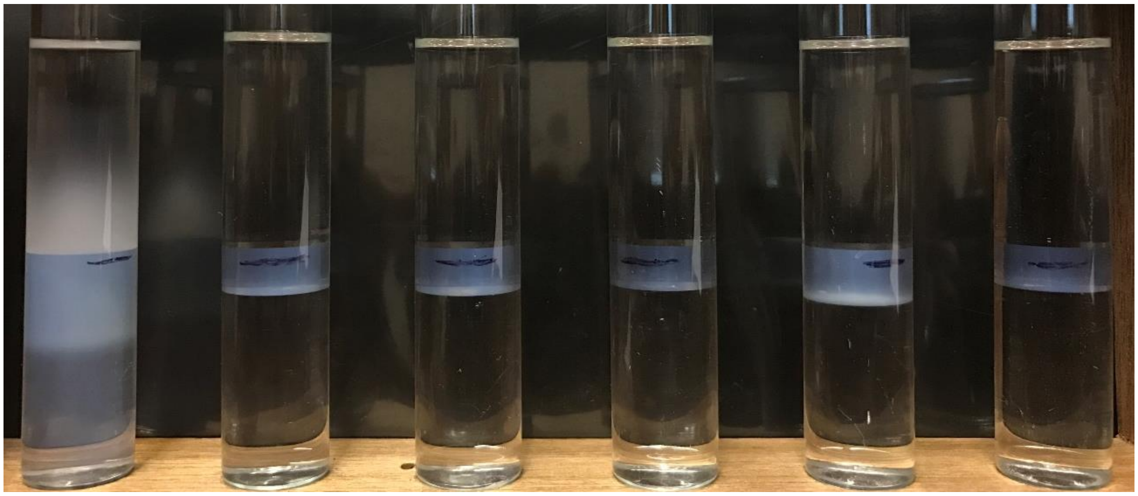


**Figure 25: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT}$ = 0.3 in Hexane at 25°C.**

| | | |
|---|---|---|
| 10.5 | S* = **10.6** | 10.7 |

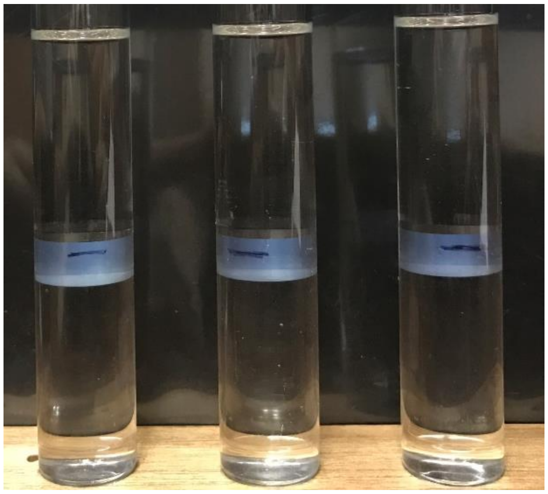


**Figure 26: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT}$ = 0.3 in Octane at 25°C.**

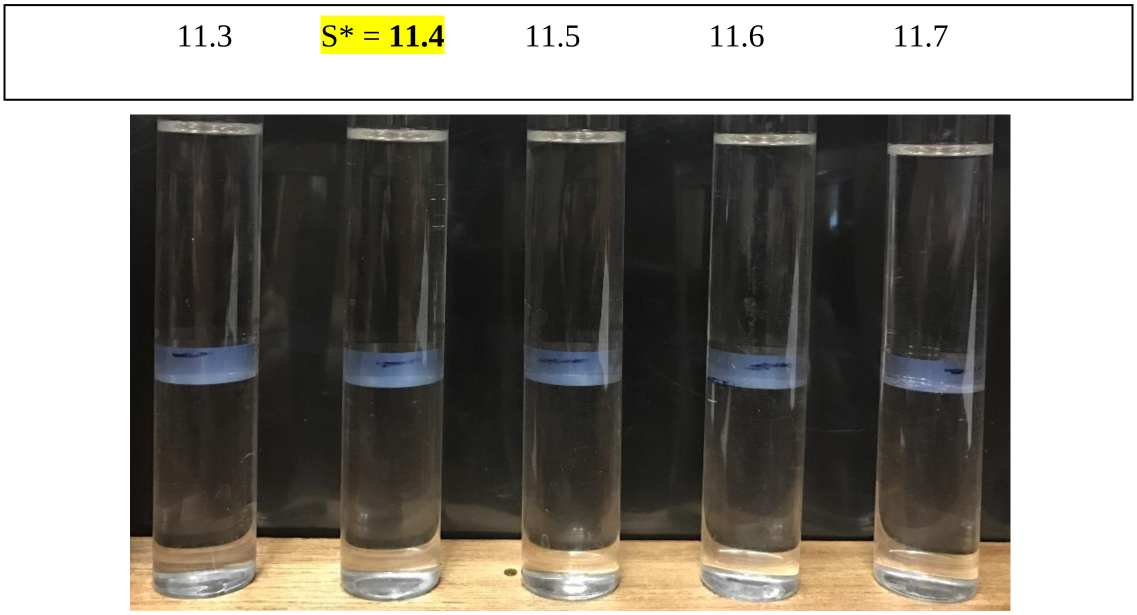


**Figure 27: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT}$ = 0.3 in Decane at 25°C.**

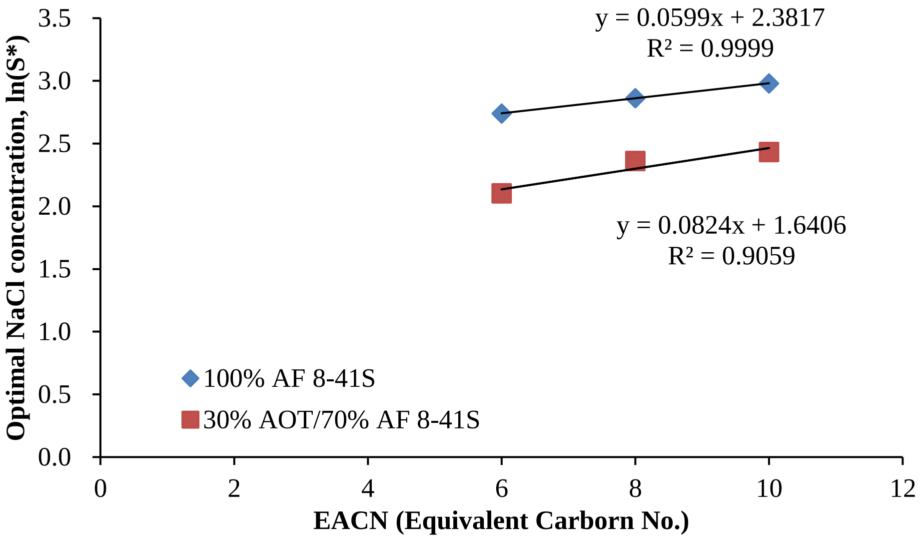


**Figure 28: lnS*$_{mix}$ as a function of EACN for AOT/ALFOTERRA mixture at $X_{AOT}$ = 0.3**

The plot of $\ln S^*_{mix}$ vs. EACN gives us the slope and intercept of eq. (3), which are as follows:

Slope $= K_{mix} = 0.0824$

Intercept $= Cc_{mix} = 1.6406$

Where,

$K_1 = 0.057$ & $Cc_1 = -2.40$

Thus, upon substitution in eq. eq. (21) & (22) we get,

$K_2 = K_{AOT} = 0.14$

$Cc_2 = Cc_{AOT} = 0.13$

### 4.1.8 AOT/ALFOTERRA-8-41S (50:50)

| | | | | | |
|---|---|---|---|---|---|
| 4 | 4.1 | 4.2 | 4.3 | S* = **4.4** | 4.5 |

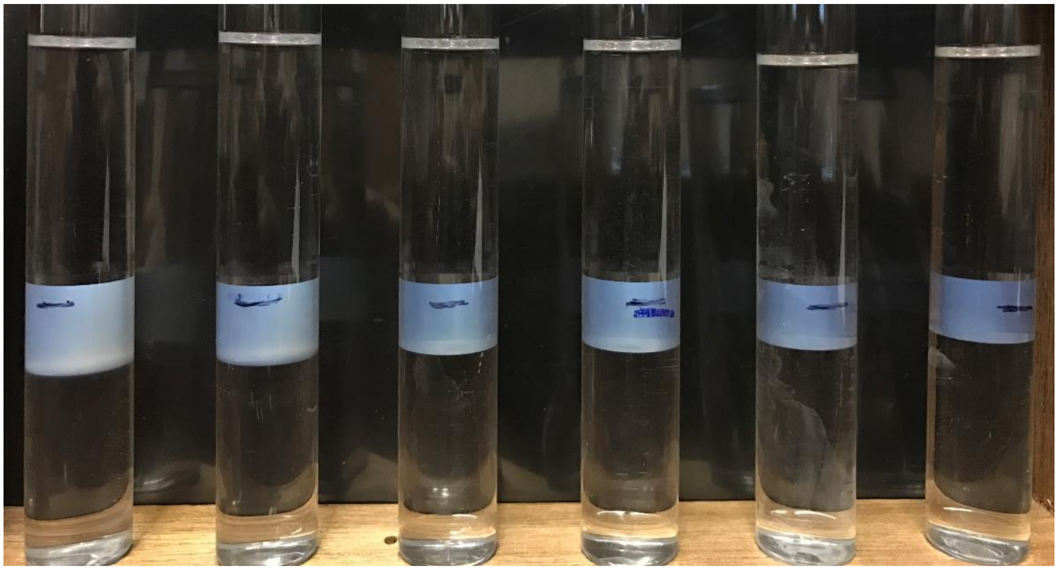


**Figure 29: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT} = 0.5$ in Hexane at 25°C.**

| | | | | |
|---|---|---|---|---|
| 5.3 | 5.4 | 5.5 | S* = **5.6** | 5.7 |

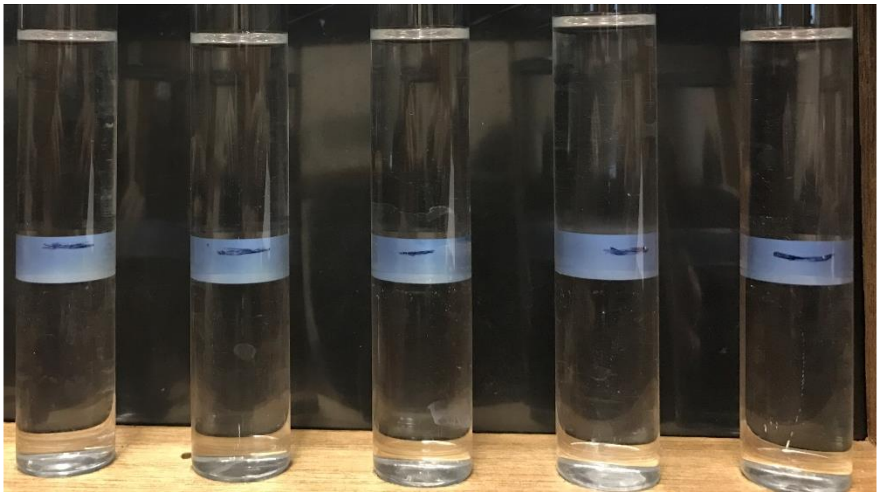


**Figure 30: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT}$ = 0.5 in Octane at 25°C.**

| | | | | | |
|---|---|---|---|---|---|
| 6.5 | 6.6 | 6.7 | S* = **6.8** | 6.9 | 7 |

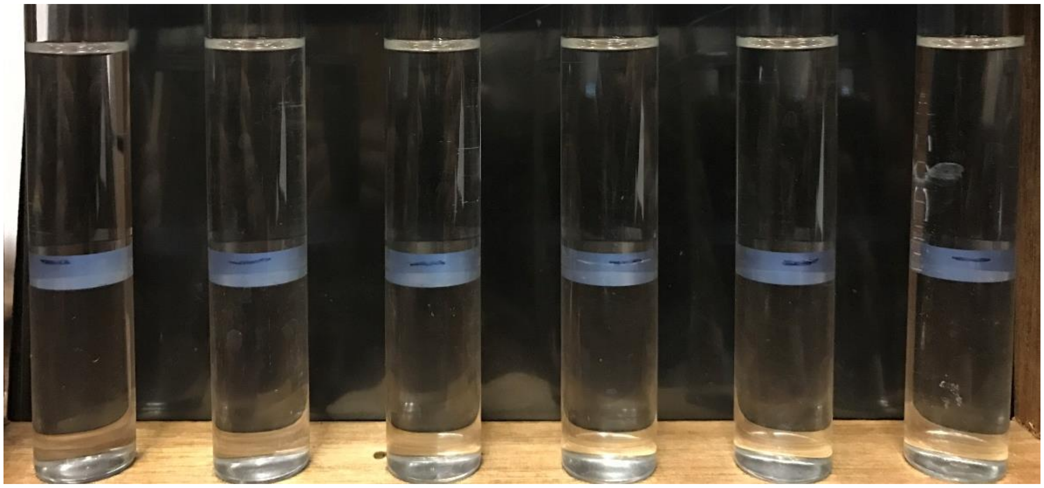


**Figure 31: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT}$ = 0.5 in Decane at 25°C.**

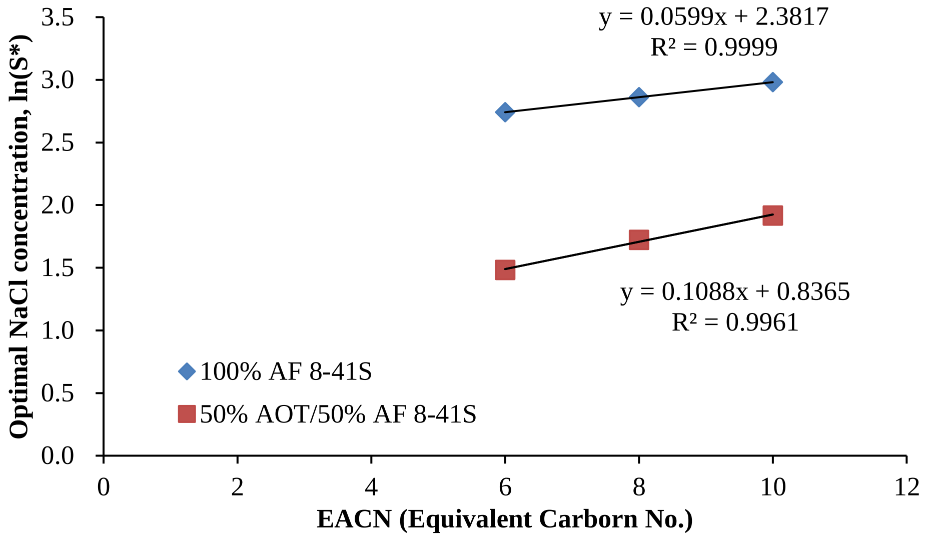


**Figure 32: $\ln S^*_{mix}$ as a function of EACN for AOT/ALFOTERRA mixture at $X_{AOT}$ = 0.5**

The plot of $\ln S^*_{mix}$ vs. EACN gives us the slope and intercept of eq. (3), which are as follows:

Slope $= K_{mix} = 0.1088$

Intercept $= Cc_{mix} = 0.8365$

Where,

$K_1 = 0.057$ & $Cc_1 = -2.40$

Thus, upon substitution in eq. eq. (21) & (22) we get,

$K_2 = K_{AOT} = 0.16$

$Cc_2 = Cc_{AOT} = 0.73$

### 4.1.9 AOT/ALFOTERRA-8-41S (70:30)

| | | | | | |
|---|---|---|---|---|---|
| 1 | 1.1 | 1.2 | 1.3 | S* = **1.4** | 1.5 |

**Figure 33: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT}$ = 0.7 in Hexane at 25°C.**

| | | | | |
|---|---|---|---|---|
| 1.7 | 1.8 | S* = **1.9** | 2 | 2.1 |

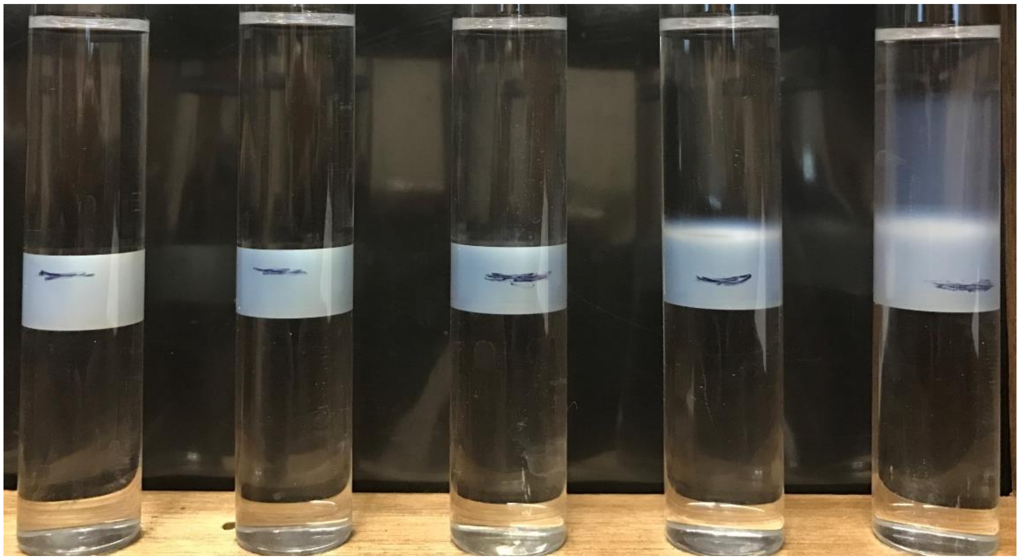


**Figure 34: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT}$ = 0.7 in Octane at 25°C.**

| | | | | |
|---|---|---|---|---|
| 3.8 | S* = **3.9** | 4 | 4.1 | 4.2 |

**Figure 35: Salinity scan for AOT/ALFOTERRA 8-41S at $X_{AOT}$ = 0.7 in Decane at 25°C.**

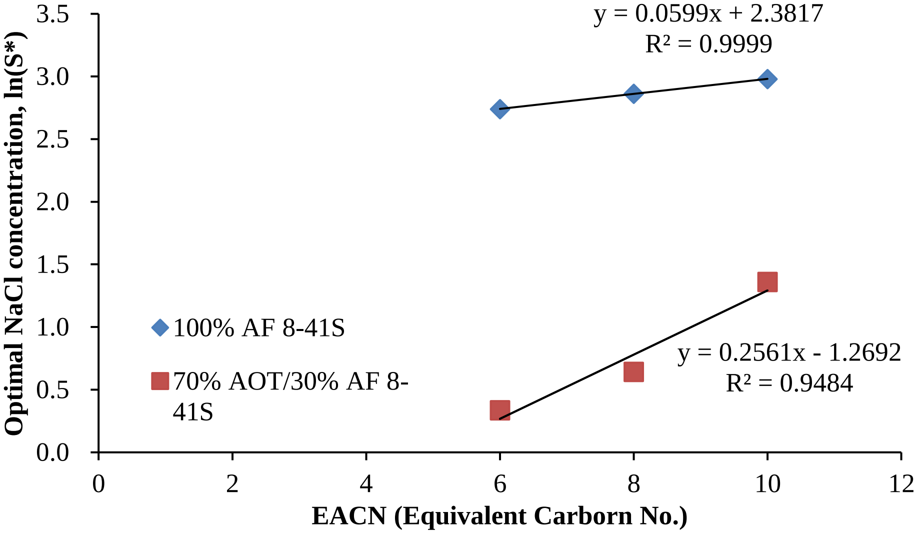


**Figure 36: $\ln S^*_{mix}$ as a function of EACN for AOT/ALFOTERRA mixture at $X_{AOT}$ = 0.7**

The plot of lnS*$_{mix}$ vs. EACN gives us the slope and intercept of eq. (3), which are as follows:

Slope $= K_{mix} = 0.2561$

Intercept $= Cc_{mix} = 1.2692$

Where,

$K_1 = 0.057$ & $Cc_1 = -2.40$

Thus, upon substitution in eq. eq. (21) & (22) we get,

$K_2 = K_{AOT} = 0.34$

$Cc_2 = Cc_{AOT} = 2.84$

### 4.1.10 AOT/ISALCHEM 123-2 (10:90)

| | | | | | |
|---|---|---|---|---|---|
| 11.9 | **S* = 12.0** | 12.1 | 12.2 | 12.3 | 12.4 |

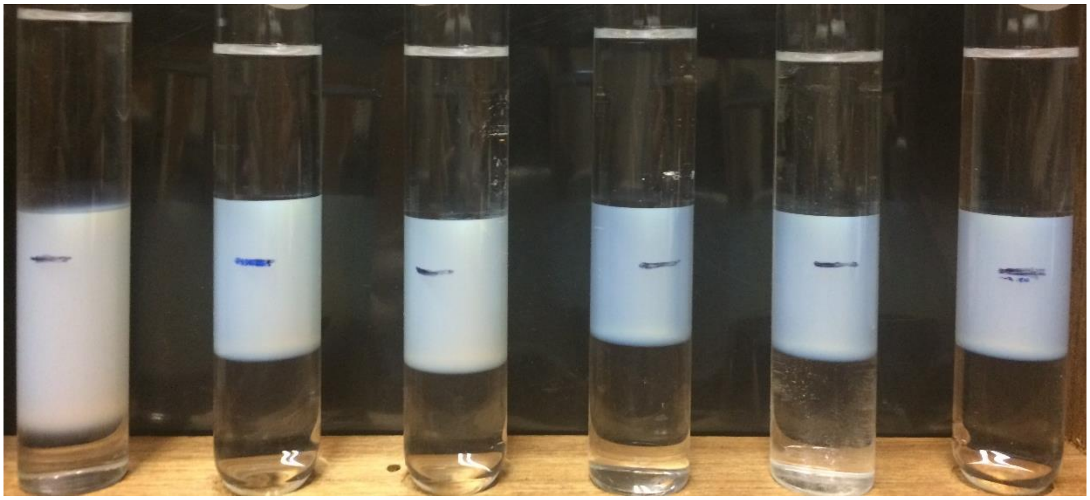


**Figure 37: Salinity scan for AOT/ISALCHEM 123-2 at X$_{AOT}$ = 0.1 in Hexane at 25°C.**

| | | | | |
|---|---|---|---|---|
| 13.6 | 13.7 | 13.8 | S* = **13.9** | 14 |

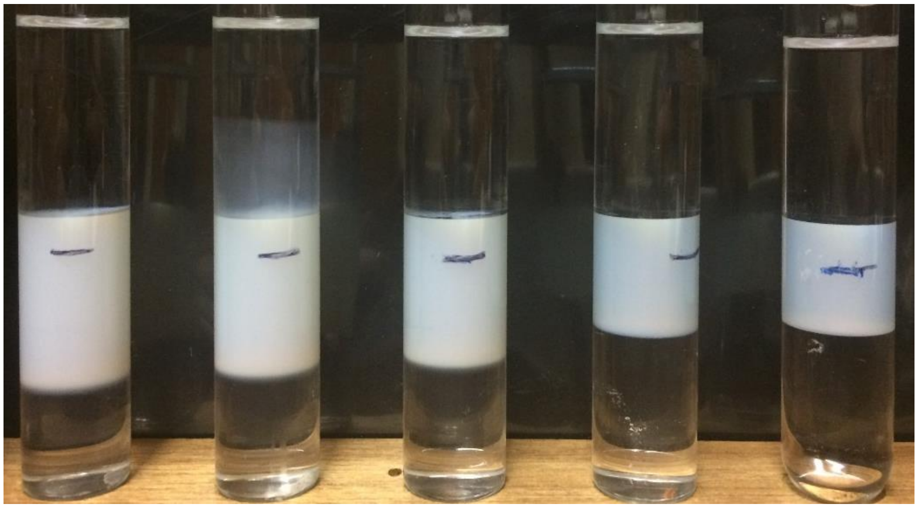


**Figure 38: Salinity scan for AOT/ISALCHEM 123-2 at $X_{AOT}$ = 0.1 in Octane at 25°C.**

| | | | | |
|---|---|---|---|---|
| S* = **15** | 15.2 | 15.4 | 15.6 | 15.8 |

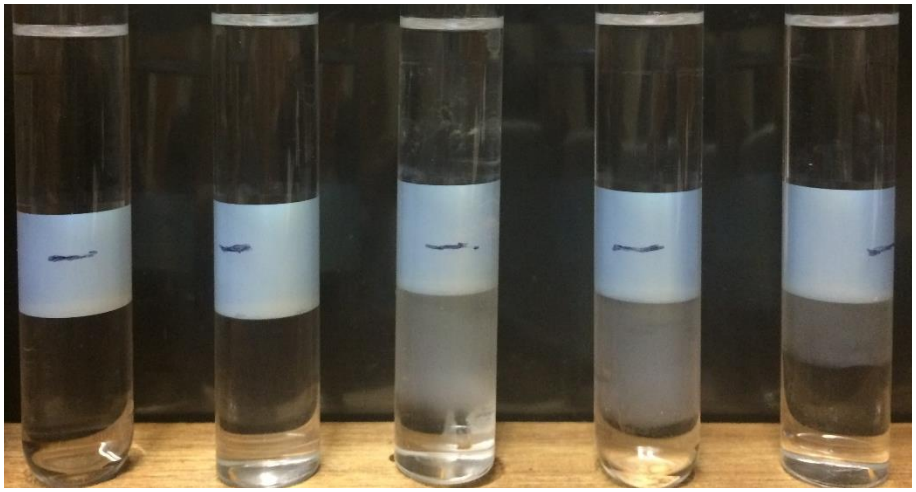


**Figure 39: Salinity scan for AOT/ISALCHEM 123-2 at $X_{AOT}$ = 0.1 in Decane at 25°C.**

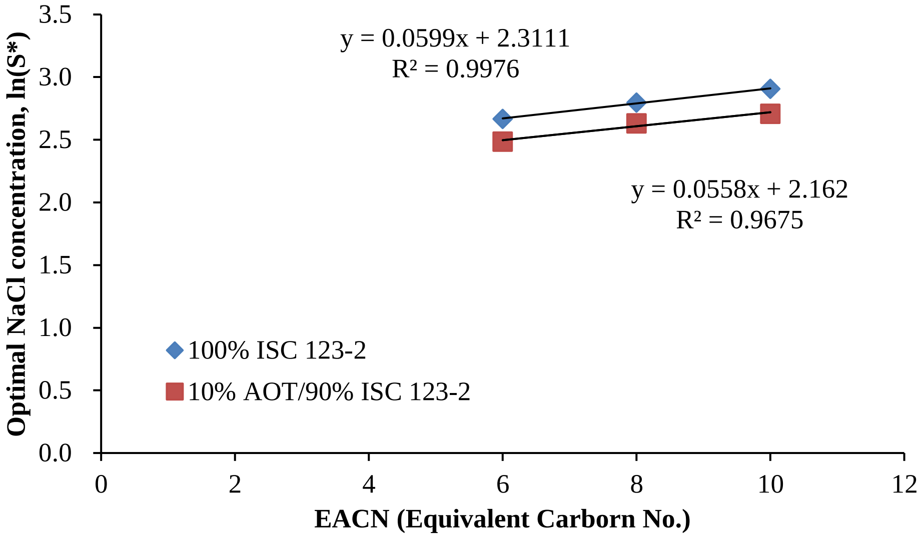


**Figure 40: lnS*$_{mix}$ as a function of EACN for AOT/ISALCHEM 123-2 mixture at X$_{AOT}$ = 0.1**

The plot of lnS*$_{mix}$ vs. EACN gives us the slope and intercept of eq. (3), which are as follows:

Slope $= K_{mix} = 0.0558$

Intercept = $Cc_{mix} \ = 2.162$

Where,

$K_1 = \ 0.06$ & $Cc_1 = \ -2.31$

Thus, upon substitution in eq. eq. (21) & (22) we get,

$K_2 \ = \ K_{AOT} \ = \ 0.02$

$Cc_2 \ = \ Cc_{AOT} \ = \ -0.83$

### 4.1.11 AOT/ISALCHEM 123-2 (30:70)

| S* = **7.1** |
|---|

**Figure 41: Salinity scan for AOT/ISALCHEM 123-2 at $X_{AOT}$ = 0.3 in Hexane at 25°C.**

| 8.5 | 8.6 | S* = **8.7** | 8.8 | 8.9 | 9 |
|---|---|---|---|---|---|

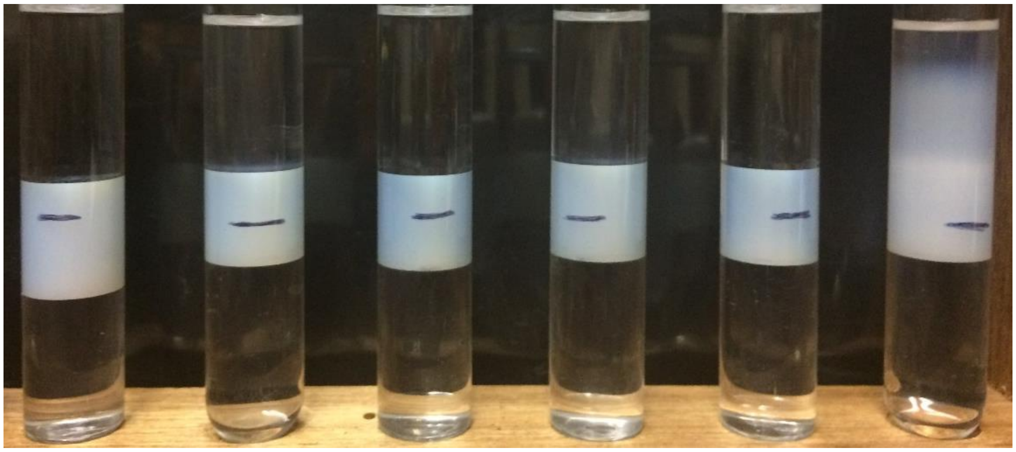


**Figure 42: Salinity scan for AOT/ISALCHEM 123-2 at $X_{AOT}$ = 0.3 in Octane at 25°C.**

| | |
|---|---|
| S* = **10.5** | 10.6 |

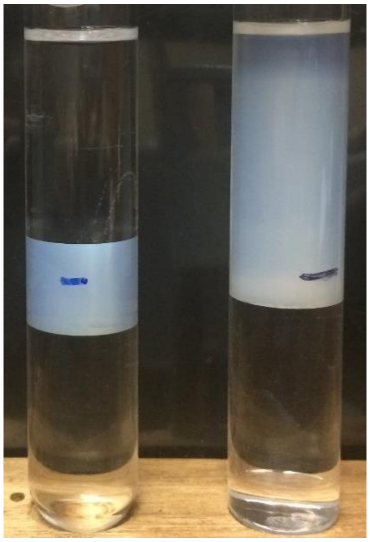


**Figure 43: Salinity scan for AOT/ISALCHEM 123-2 at $X_{AOT}$ = 0.3 in Decane at 25°C.**

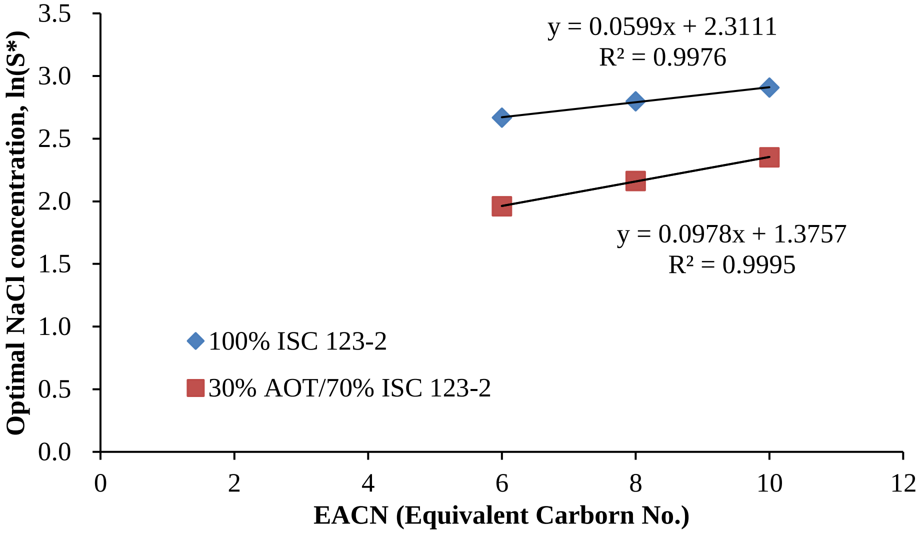


**Figure 44: $\ln S^*_{mix}$ as a function of EACN for AOT/ISALCHEM 123-2 mixture at $X_{AOT}$ = 0.3**

The plot of $\ln S^*_{mix}$ vs. EACN gives us the slope and intercept of eq. (3), which are as follows:

Slope $= K_{mix} = 0.0978$

Intercept = $Cc_{mix} = 1.3757$

Where,

$K_1 = 0.06$ & $Cc_1 = -2.31$

Thus, upon substitution in eq. eq. (21) & (22) we get,

$K_2 = K_{AOT} = 0.19$

$Cc_2 = Cc_{AOT} = 0.80$

### 4.1.12 AOT/ISALCHEM 123-2 (50:50)

| | | | |
|---|---|---|---|
| 2.6 | 2.7 | 2.8 | S* = **2.9** |

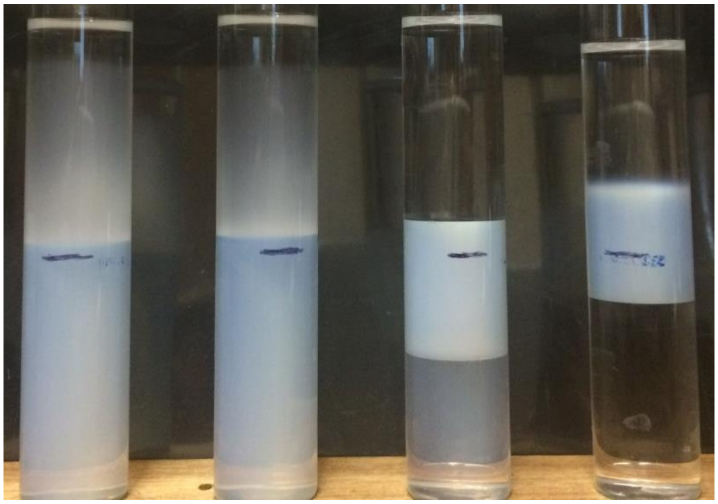


**Figure 45: Salinity scan for AOT/ISALCHEM 123-2 at $X_{AOT}$ = 0.5 in Hexane at 25°C.**

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| 3.5 | 3.6 | 3.7 | S* = **3.8** | 3.9 | 4 |

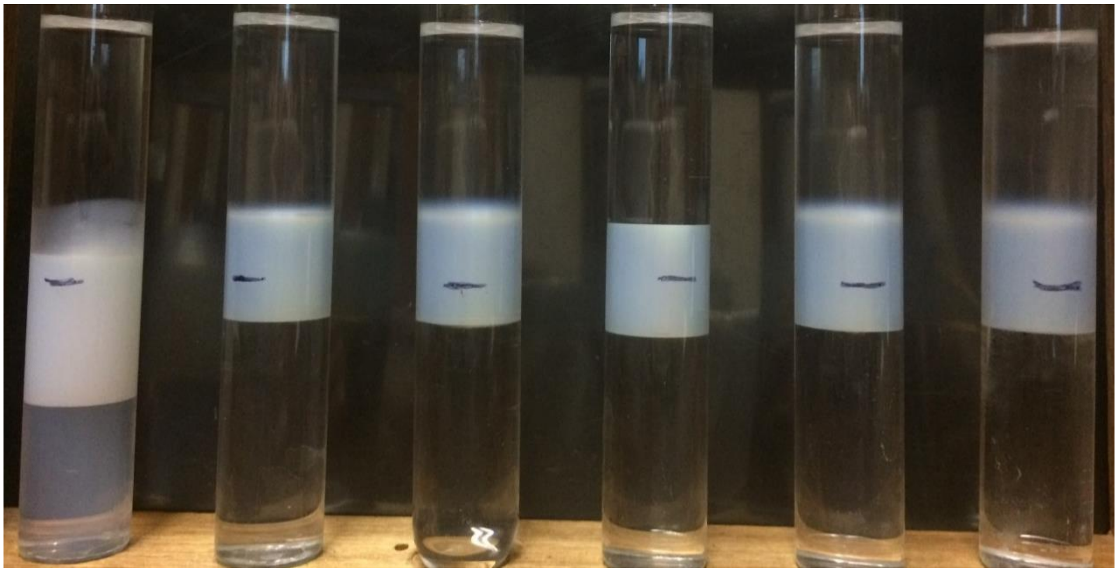


**Figure 46: Salinity scan for AOT/ISALCHEM 123-2 at $X_{AOT}$ = 0.5 in Octane at 25°C.**

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| 4.5 | 4.6 | S* = **4.7** | 4.8 | 4.9 | 5 |

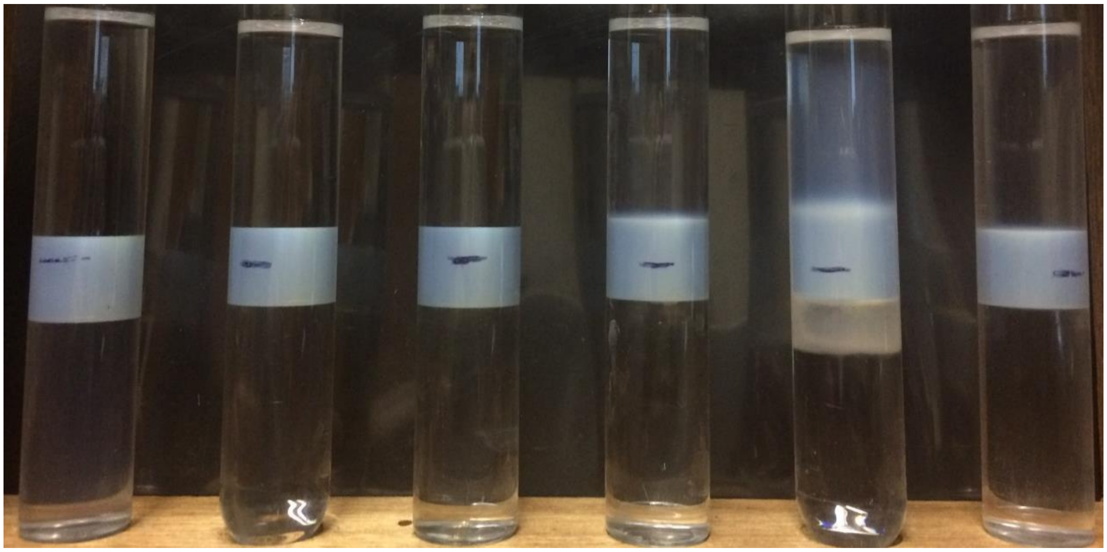


**Figure 47: Salinity scan for AOT/ISALCHEM 123-2 at $X_{AOT}$ = 0.5 in Decane at 25°C.**

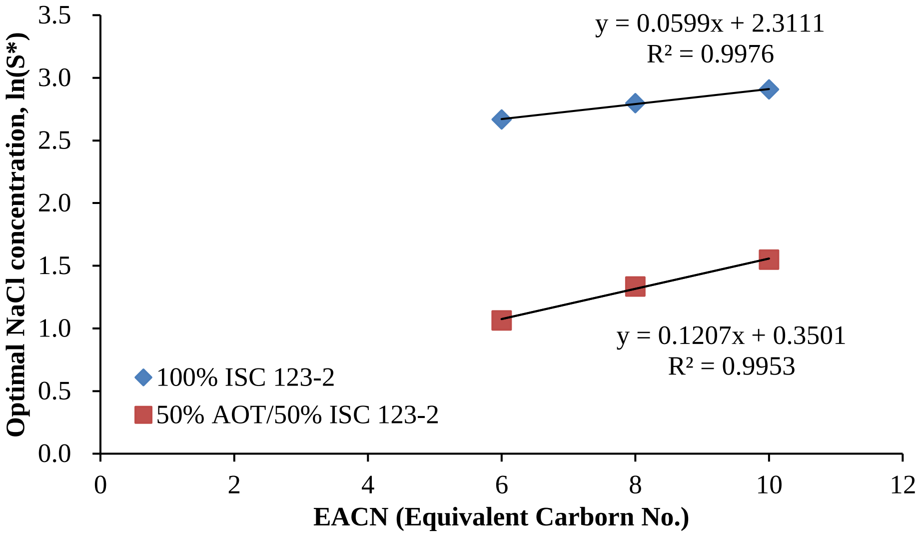


**Figure 48: $\ln S^*_{mix}$ as a function of EACN for AOT/ISALCHEM 123-2 mixture at $X_{AOT} = 0.5$**

The plot of $\ln S^*_{mix}$ vs. EACN gives us the slope and intercept of eq. (3), which are as follows:

Slope $= K_{mix} = 0.1207$

Intercept = $Cc_{mix} = -0.3501$

Where,

$K_1 = 0.06$ & $Cc_1 = -2.31$

Thus, upon substitution in eq. eq. (21) & (22) we get,

$K_2 = K_{AOT} = 0.18$

$Cc_2 = Cc_{AOT} = 1.61$

4.1.13 AOT/ISALCHEM 123-2 (70:30)

S* = **1.5** 1.6

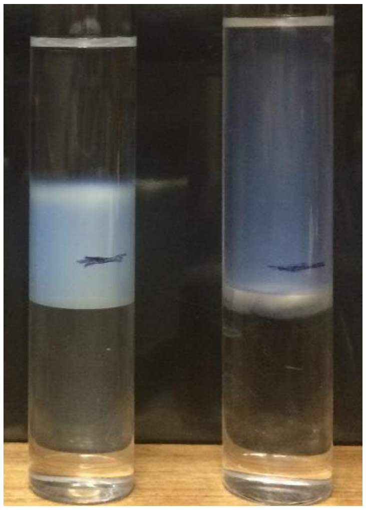


**Figure 49: Salinity scan for AOT/ISALCHEM 123-2 at $X_{AOT}$ = 0.7 in Hexane at 25°C.**

1.5 1.7 1.8 S* = **1.9** 2

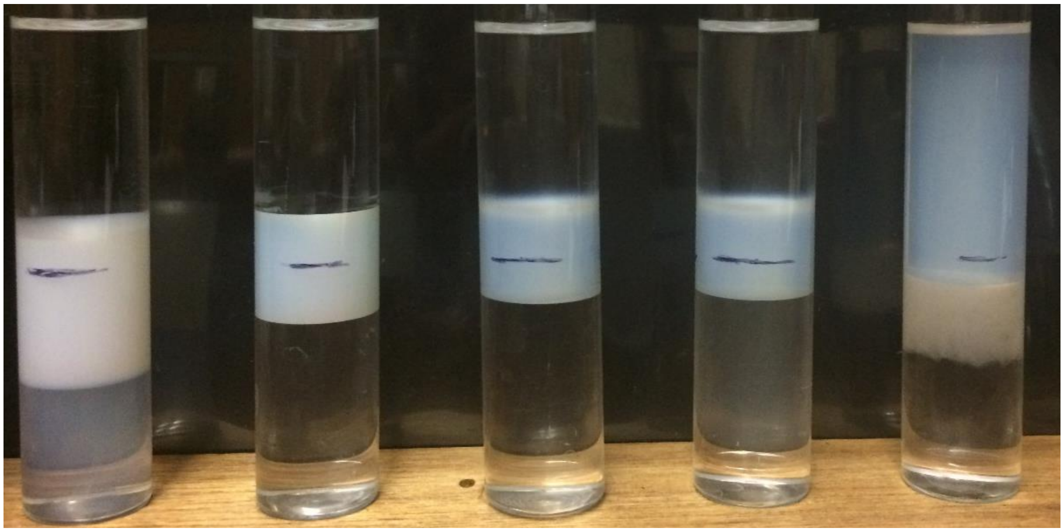


**Figure 50: Salinity scan for AOT/ISALCHEM 123-2 at $X_{AOT}$ = 0.7 in Octane at 25°C.**

| | | | | |
|---|---|---|---|---|
| 2.8 | 2.9 | S* = 3 | 3.1 | 3.2 |

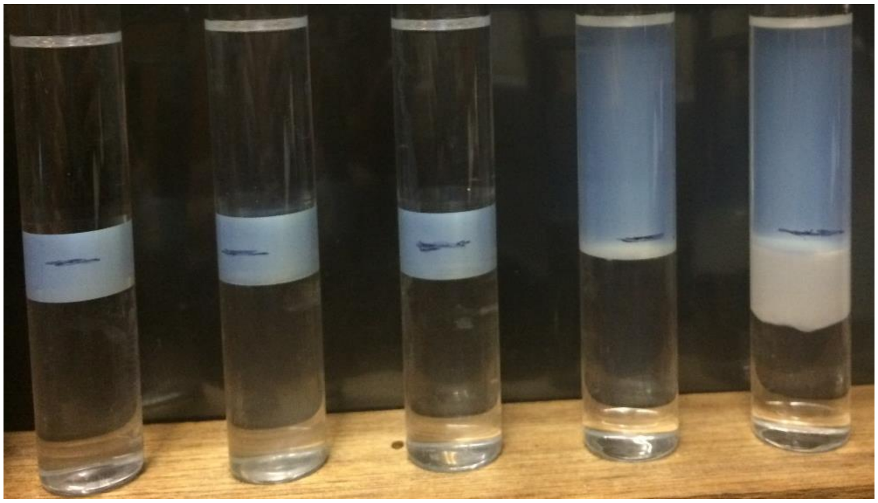


**Figure 51: Salinity scan for AOT/ISALCHEM 123-2 at $X_{AOT}$ = 0.7 in Decane at 25°C.**

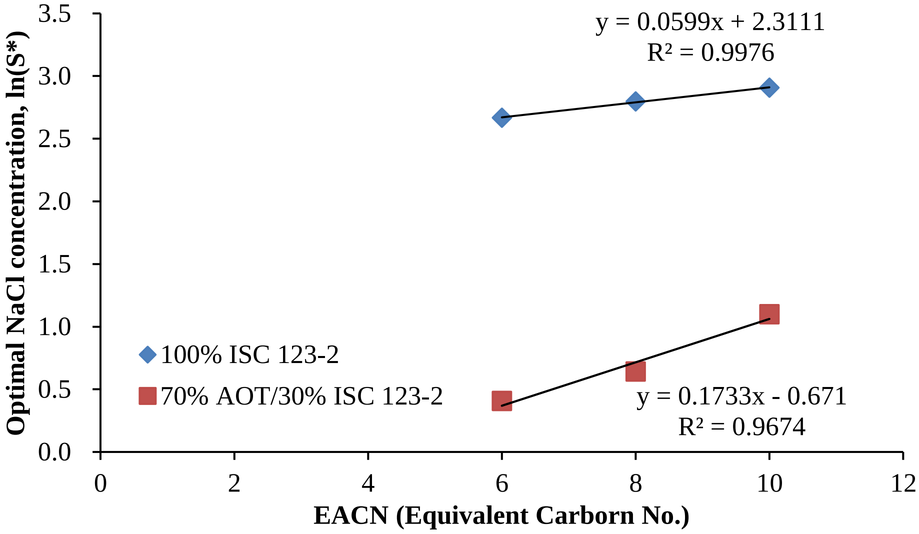


**Figure 52: $\ln S^*_{mix}$ as a function of EACN for AOT/ISALCHEM 123-2 mixture at $X_{AOT}$ = 0.7**

The plot of $\ln S^*_{mix}$ vs. EACN gives us the slope and intercept of eq. (3), which are as follows:

Slope $= K_{mix} = 0.1733$

Intercept = $Cc_{mix} = 0.671$

Where,

$K_1 = 0.06$ & $Cc_1 = -2.31$

Thus, upon substitution in eq. eq. (21) & (22) we get,

$K_2 = K_{AOT} = 0.22$

$Cc_2 = Cc_{AOT} = 1.95$

### 4.2 K and Cc vs. mole fraction of AOT

As, mentioned before, AOT is incapable of forming middle phases by itself. Hence, in order to characterize it in terms of the HLD parameters, we formulated an AOT-reference surfactant mixture with AMA, ALFOTERRA 8-41S and ISALCHEM 123-2, and performed a salinity scan with pentane, hexane, heptane, octane and decane at 25°C, at varied mole fractions of AOT.

- AOT/AMA

For, mole fractions 0.1 and 0.3 of AOT, decane was not used as it was observed by one of our postdoc Dr.Su, that at higher salt concentrations decane with AOT/AMA mixtures forms coacervates at the optimal salinity i.e. at the Winsor III formulation. Hence, it was suggested by him not to use decane for higher salt concentrations for AMA/AOT mixture. Whereas, for mole fractions 0.5 and 0.7 decane could be use since the formulation now requires less salt at higher concentration of AOT. Then the $\ln S_{mix}$ vs. $X_{AOT}$ were plotted and a linear regression was applied. The slope $K_{mix}$ and intercept $Cc_{mix}$ were obtained from the graph. As discussed earlier, linear mixing rules were applied and $K_{AOT}$ and $Cc_{AOT}$ were obtained from $K_{mix}$ and $Cc_{mix}$. Below, is the summary of the $K_{mix}$, $Cc_{mix}$, $K_{AOT}$ and $Cc_{AOT}$ of the AOT/AMA mixture.

**Table 4: K and Cc values obtained from AOT/AMA mixture**

| $X_{AOT}$ | $K_{mix}$ | $Cc_{mix}$ | $K_{AOT}$ | $Cc_{AOT}$ |
|---|---|---|---|---|
| **0** | 0 | 0 | 0.072 | -1.51 |
| **0.1** | 0.12 | -1.07 | 0.59 | 2.92 |
| **0.3** | 0.21 | 0.26 | 0.55 | 4.40 |
| **0.5** | 0.20 | 0.95 | 0.33 | 3.41 |
| **0.7** | 0.35 | 3.28 | 0.46 | 5.34 |
| **1** | 0.42 | 4.98 | 0.30 | 5.90 |

As, can be seen in Table (4), the $K_{AOT}$ values are significantly decreasing with increase in mole fraction of AOT showing that the linear mixing rules do not apply in this case as is generally expected in case of an anionic-anionic surfactant mixture. Also, as it can be observed, the $Cc_{AOT}$ keeps increasing as the AOT concentration increases, which makes sense as AOT is highly hydrophobic and a higher value of Cc denotes higher hydrophobicity at higher AOT mole fraction.

- AOT/ALFOTERRA 8-41S

A salt scan was performed for AOT/ALFOTERRA 8-41S AT 25°C, with three different oils like hexane, octane and decane for different mole fractions of AOT 0.1, 0.3, 0.5 and 0.7. Then the $\ln S_{mix}$ vs. $X_{AOT}$ were plotted and a linear regression was applied. The slope

$K_{mix}$ and intercept $Cc_{mix}$ were obtained from the graph. As discussed earlier, linear mixing rules were applied and $K_{AOT}$ and $Cc_{AOT}$ were obtained from $K_{mix}$ and $Cc_{mix}$. Below, is the summary of the $K_{mix}$, $Cc_{mix}$, $K_{AOT}$ and $Cc_{AOT}$ of the AOT/ALFOTERRA 8-41S mixture.

**Table 5: K and Cc values obtained from AOT/ALFOTERRA 8-41S mixture**

| $X_{AOT}$ | $K_{mix}$ | $Cc_{mix}$ | $K_{AOT}$ | $Cc_{AOT}$ |
|---|---|---|---|---|
| **0** | 0 | 0 | 0.057 | -2.4 |
| **0.1** | 0.0628 | -2.2134 | 0.12 | -0.53 |
| **0.3** | 0.0824 | -1.6406 | 0.14 | 0.13 |
| **0.5** | 0.1088 | -0.8365 | 0.16 | 0.73 |
| **0.7** | 0.2561 | 1.2692 | 0.34 | 2.84 |
| **1** | 0.3095 | 2.5203 | 0.394 | 4.0055 |

As, can be seen in Table (5), the $K_{AOT}$ values increase with increase in mole fraction of AOT showing that the linear mixing rules do not apply in this case as is generally expected in case an anionic-anionic surfactant mixture. However, it is interesting to observe that the $K_{AOT}$ values are less than that of AOT/AMA. Also, as it can be observed, the $Cc_{AOT}$ keeps increasing as the AOT concentration increases, also $Cc_{AOT}$ of this system are less than the $Cc_{AOT}$ values obtained from the AOT/AMA system. The possible, reason behind these lower values maybe because the tail length of AMA is small and hence is not able to contribute to the overall curvature as much as the long tailed ALFOTERRA 8-41S does.

- AOT/ISALCHEM 123-2

A salt scan was performed for AOT/ISALCHEM 123-2 at 25°C, with three different oils like hexane, octane and decane for different mole fractions of AOT 0.1, 0.3, 0.5 and 0.7. Then the $\ln S_{mix}$ vs. $X_{AOT}$ were plotted and a linear regression was applied. Upon applying the linear mixing rules, $K_{AOT}$ and $Cc_{AOT}$ were obtained from $K_{mix}$ and $Cc_{mix}$. Below, is the summary of the $K_{mix}$, $Cc_{mix}$, $K_{AOT}$ and $Cc_{AOT}$ of the AOT/ISALCHEM 123-2 mixture.

**Table 6: K and Cc values obtained from AOT/ISALCHEM 123-2 mixture**

| $X_{AOT}$ | $K_{mix}$ | $Cc_{mix}$ | $K_{AOT}$ | $Cc_{AOT}$ |
|---|---|---|---|---|
| **0** | 0 | 0 | 0.06 | -2.31 |
| **0.1** | 0.0558 | -2.162 | 0.02 | -0.83 |
| **0.3** | 0.0978 | -1.3757 | 0.19 | 0.8 |
| **0.5** | 0.1207 | -0.3501 | 0.18 | 1.61 |
| **0.7** | 0.1733 | 0.671 | 0.22 | 1.95 |
| **1** | 0.2245 | 2.0532 | 0.3295 | 3.6275 |

As, can be seen in Table (6), the varied $K_{AOT}$ values again show that the linear mixing rules fail yet again in this system too. $K_{AOT}$ values are less than that of AOT/AMA. Also, as it can be observed, the $Cc_{AOT}$ are less than that of AOT/AMA.

- Discussion on $K_{AOT}$ and $Cc_{AOT}$

As can be seen from the above Table, that the experimentally derived K values of AOT using AMA, ALFOTERRA 8-41S and ISALCHEM 123-2 as a reference surfactant vary drastically with varied molar fraction of AOT, which should not be the case as per the HLD theory according to which K should remain constant and independent of the change in mole fraction of a surfactant. This clearly negates the commonly used linear mixing rules when using an anionic-anionic mixture. The $K_{AOT}$ determined from all the AOT-anionic reference surfactant mixtures were plotted against each other just to compare them more vividly. These data points were plotted with the standard deviations of the individual $K_{AOT}$ values calculated using the LINEST function on Excel.

**Table 7: Standard deviations of $K_{AOT}$**

| | **Std. Deviation of $K_{AOT}$** |
|---|---|
| **AOT/AMA** | 0.084202 |
| **AOT/ALFOTERRA 8-41S** | 0.050596 |
| **AOT/ISALCHEM 123-2** | 0.047854 |

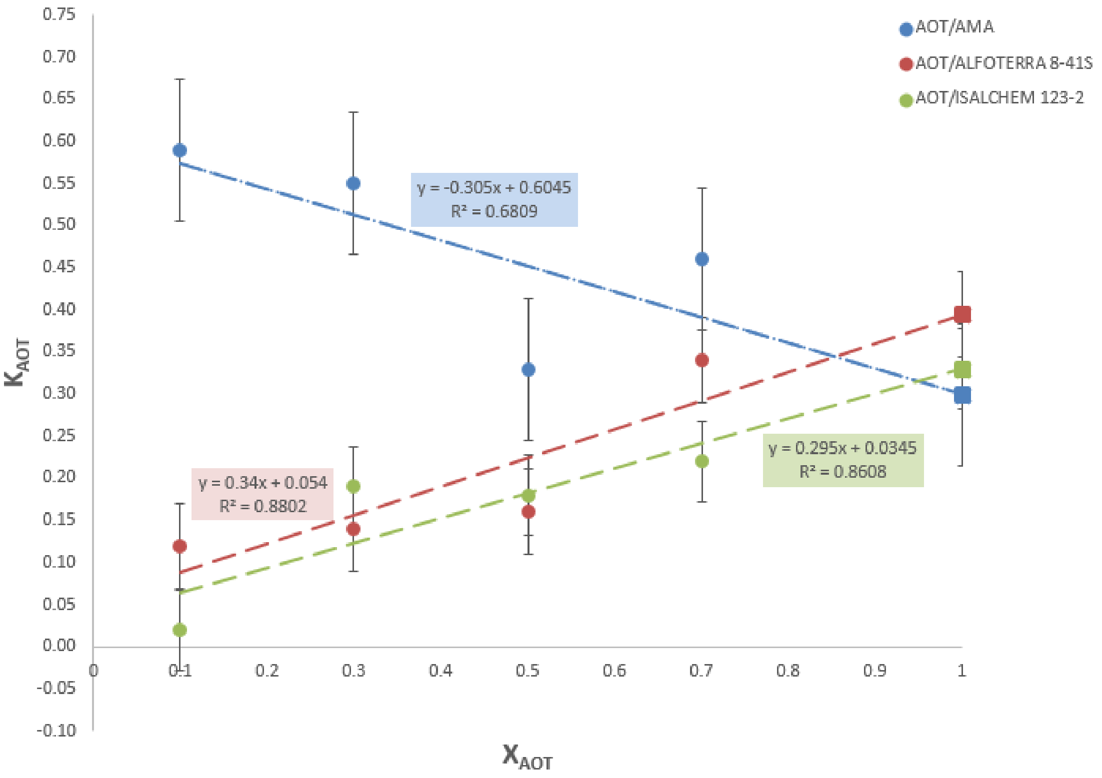


**Figure 53: $K_{AOT}$ as a function of $X_{AOT}$ ($K_{AOT}$ @ X = 1 are extrapolated)**

Since, AOT cannot form middle phase microemulsions by itself, hence upon applying the linear regression to the $K_{AOT}$ values, the $K_{AOT}$ values at 100% concentration were extrapolated using the regression equation $K_{AOT} = -0.305X_{AOT} + 0.6045$ from AOT/AMA mixture, $K_{AOT} = 0.34X_{AOT} + 0.054$ from AOT/ALFOTERRA 8-41S and $K_{AOT} = 0.295X_{AOT} + 0.0345$ from AOT/ISALCHEM 123-2 mixture where $X_{AOT}$ was equalized to 1, hence giving us the $K_{AOT}$ = 0.3, 0.39, 0.33 values of the AOT pure species respectively. The reason why the AOT/ALFOTERRA 8-41S and AOT/ISALCHEM 123-2 show similar trend is because of their similar structures also; it can be observed that the ALFOTERRA 8-41S has almost the same no. of carbon atoms in the tail as the

ISALCHEM 123-2 because of 4 PO groups attached to it which contributes to better miscibility of the surfactant in the oil.

Similarly, $Cc_{AOT}$ values have been plotted against $X_{AOT}$ as shown below.

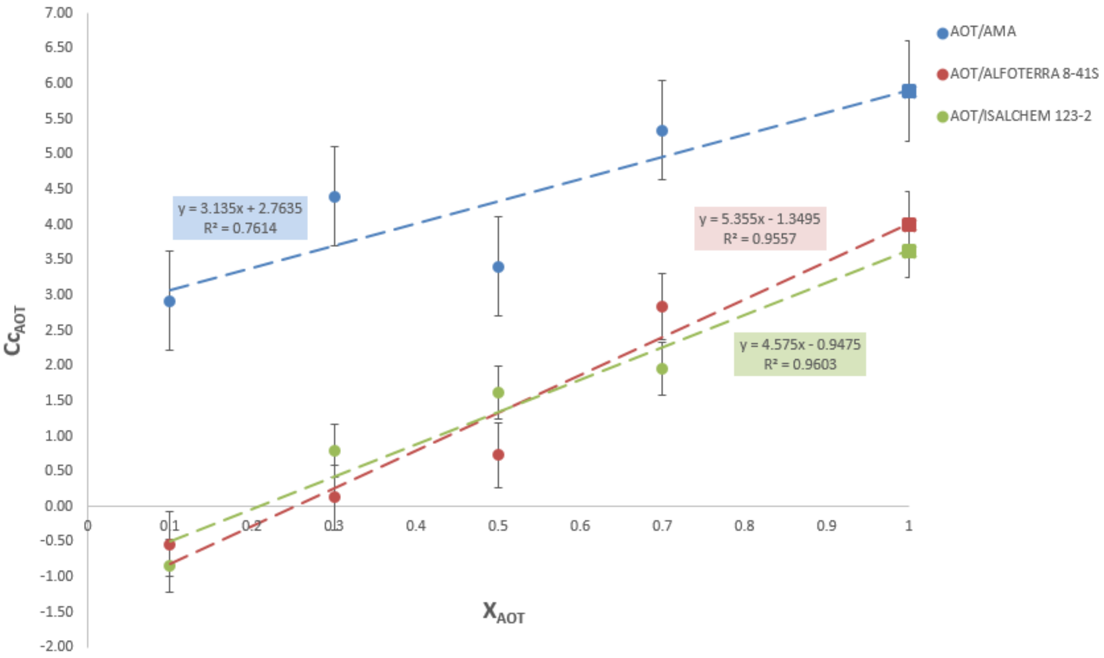


**Figure 54: $Cc_{AOT}$ as a function of $X_{AOT}$ ($Cc_{AOT}$ @ X = 1 are extrapolated)**

Upon applying the linear regression to the Cc values, the $Cc_{AOT}$ at 100% concentration was extrapolated using the regression equation $Cc_{AOT} = 3.135X_{AOT} + 2.7635$ in the AOT/AMA mixture, $Cc_{AOT} = 5.355X_{AOT} - 1.3495$ in the AOT/ALFOTERRA 8-41S mixture and $Cc_{AOT} = 4.575X_{AOT} - 0.9475$ in the AOT/ISALCHEM 123-2 mixture where $X_{AOT}$ was equalized to 1, hence giving us the $Cc_{AOT}$ = 5.9, 4.01, 3.63 of the AOT pure species respectively. Now these values are our hypothetical $Cc_{AOT}$ of pure AOT values (had it had the capacity to form middle phases by itself).

Also, the $Cc_{AOT}$ values were plotted with their respective standard deviation values using the LINEST function on Excel as shown below in the Table (8).

**Table 8: Standard deviations of $Cc_{AOT}$**

| | **Std. Deviation of CcAOT** |
|---|---|
| **AOT/AMA** | 0.707868 |
| **AOT/ALFOTERRA 8-41S** | 0.46507 |
| **AOT/ISALCHEM 123-2** | 0.375122 |

- Accuracy of HLD

Since, now we have our extrapolated or hypothetical $K_{AOT}$ and $Cc_{AOT}$ (pure species) values, we plugged $K_{AOT\ @\ X=1}$ and $Cc_{AOT\ @\ X=1}$ values in their respective HLD equations to back calculate $S^*_{mix}$, so as to verify these expected optimal salinities with the actual optimal salinities that we have got which are $S^*_{mix}$ actual. Below is the graph, where the solid data points are the $S^*_{mix}$ expected values in the respective oils and the hollow data points are the actual optimal salinities i.e. $S^*_{mix}$ actual.

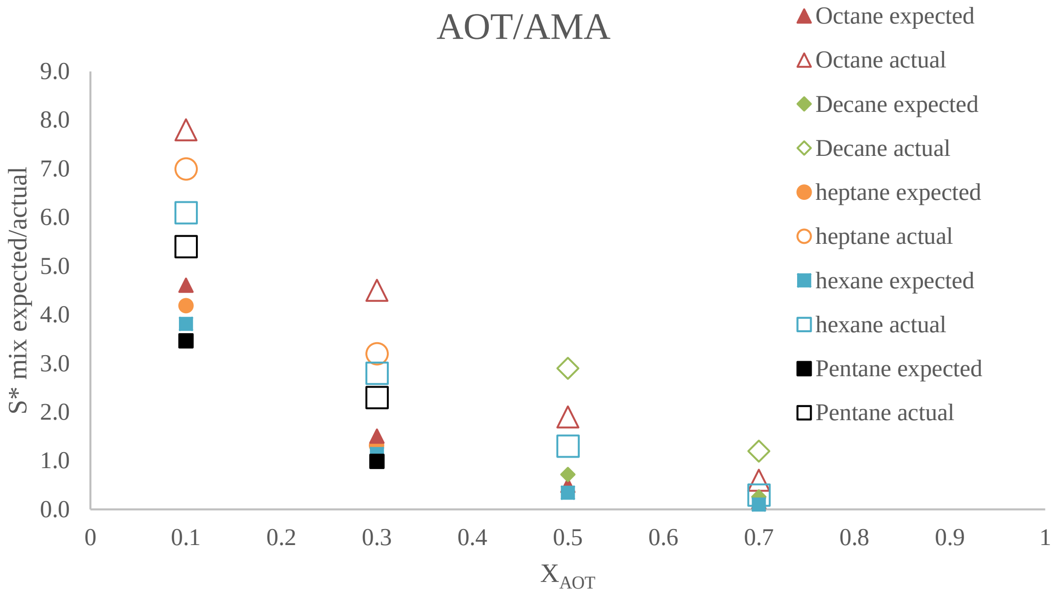


**Figure 55: $S^{*}_{mix}$ as a function of $X_{AOT}$ in pentane, hexane, heptane, octane and decane in AOT/AMA mixture. $S^{*}_{mix}$ actual is represented as hollow and $S^{*}_{mix}$ experimental are represented as solid data points.**

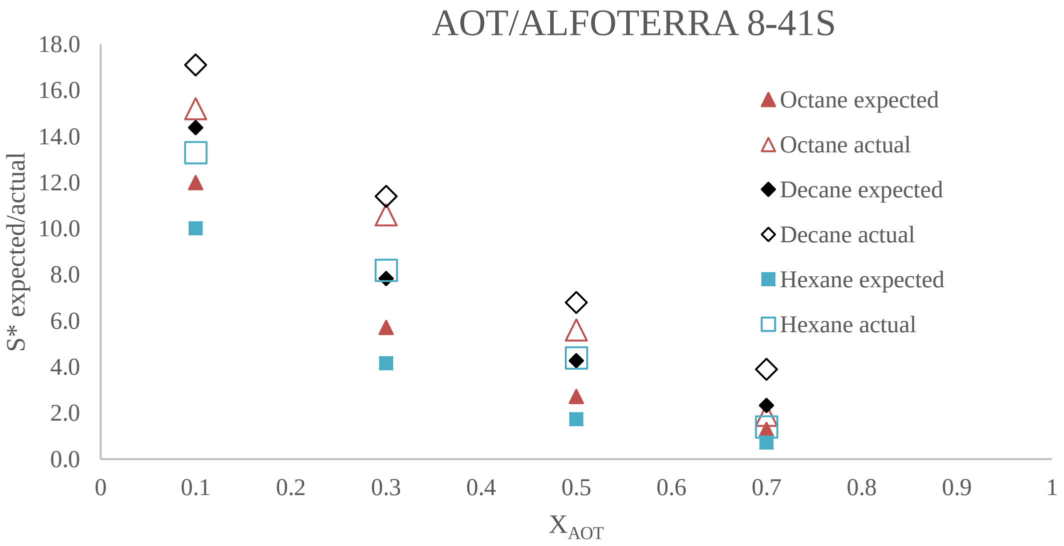


**Figure 56: $S^{*}_{mix}$ as a function of $X_{AOT}$ in hexane, octane and decane in AOT/ALFOTERRA 8-41S mixture. $S^{*}_{mix}$ actual is represented as hollow and $S^{*}_{mix}$ experimental are represented as solid data points.**

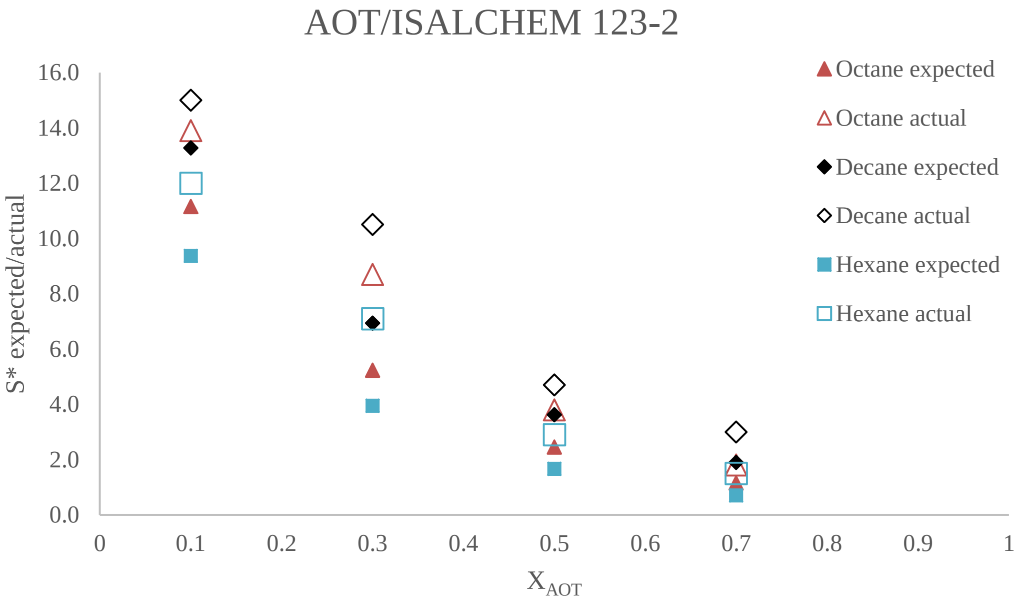


**Figure 57: $S^*_{mix}$ as a function of $X_{AOT}$ in hexane, octane and decane in AOT/ISALCHEM 123-2 mixture. $S^*_{mix}$ actual is represented as hollow and $S^*_{mix}$ experimental are represented as solid data points.**

Clearly, the $S^*_{mix}$ actual values are way off from that of expected or calculated. This clearly suggests a need for a correction factor to the HLD equation in case of these AOT mixtures, for better accuracy in predicting the optimal salinity using HLD equation. These values are in good agreement with the data shown in [4] and [9]. Further $\ln S^*_{mix}$ was plotted against $X_{AOT}$ for different AOT mixtures in different oils as shown below.

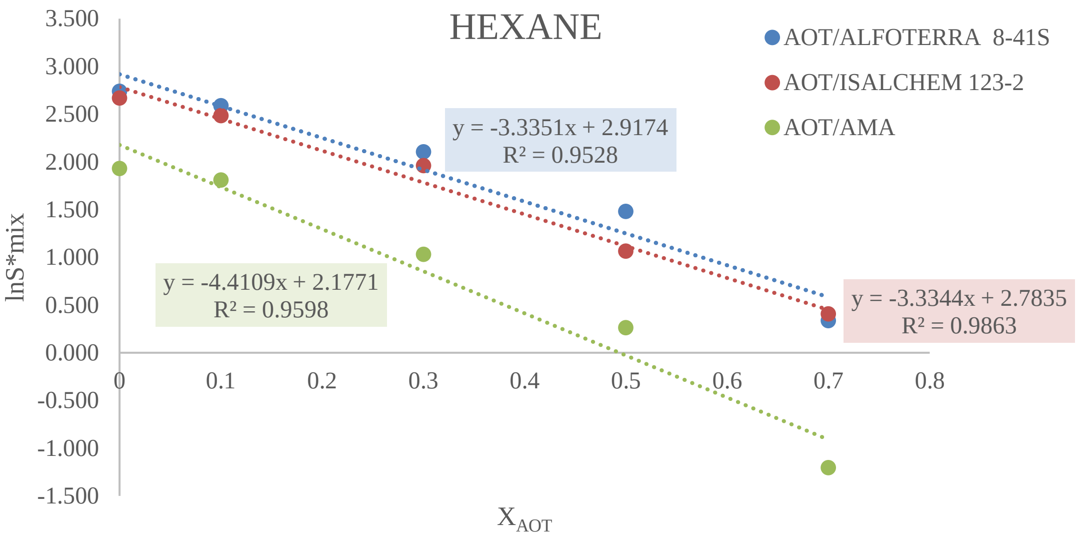


**Figure 58: $\ln S^*_{mix}$ as a function of $X_{AOT}$ for AOT/AMA, AOT/ALFOTERRA 8-41S and AOT/ISALCHEM 123-2 mixtures in Hexane.**

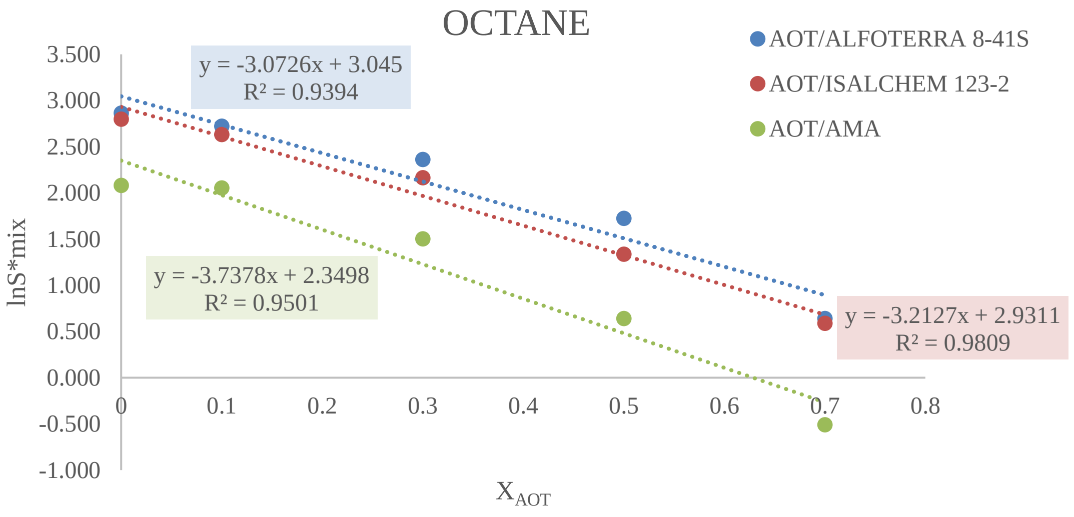


**Figure 59: $\ln S^*_{mix}$ as a function of $X_{AOT}$ for AOT/AMA, AOT/ALFOTERRA 8-41S and AOT/ISALCHEM 123-2 mixtures in Octane.**

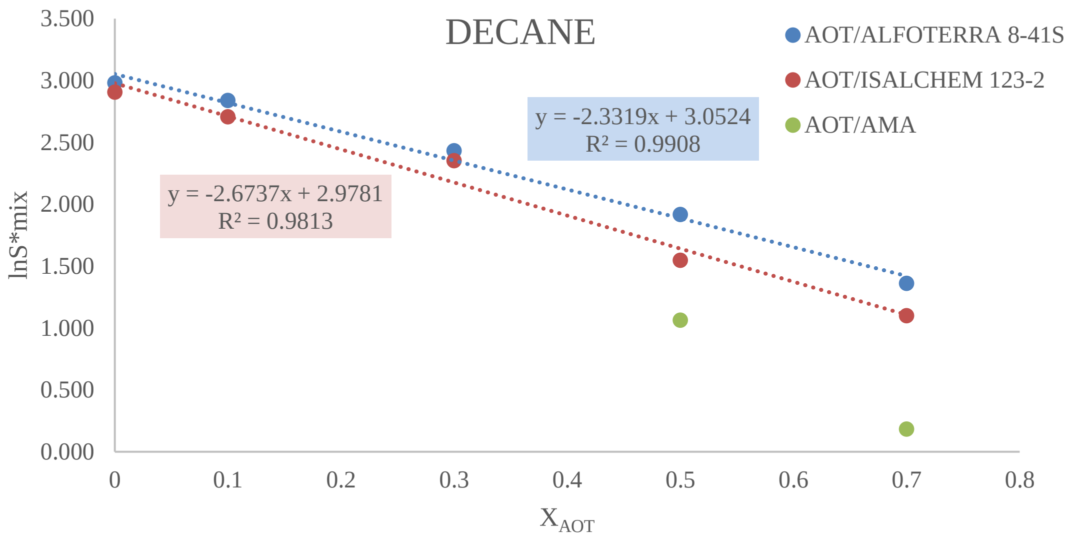


**Figure 60: $\ln S^*_{mix}$ as a function of $X_{AOT}$ for AOT/AMA, AOT/ALFOTERRA 8-41S and AOT/ISALCHEM 123-2 mixtures in Decane.**

When substituting eq. (5) and (6) in eq. (3). We get,

$$\ln S*_{mix} = \left(X_{AOT}K_{AOT} + X_{Ref\ Surfactant}K_{Ref\ Surfactant}\right)(EACN) - (X_{AOT}Cc_{AOT} + X_{Ref\ Surfactant}Cc_{Ref\ Surfactant})$$

$$\Rightarrow \quad = \left(K_{AOT}.EACN - Cc_{AOT} - K_{Ref\ Surfactant}.EACN + Cc_{Ref\ Surfactant}\right)X_{AOT} + (K_{Ref\ Surfactant}.EACN - Cc_{Ref\ Surfactant}) \qquad \textbf{(Equation 23)}$$

Hence, it can be inferred from the above equation that $\ln S*_{mix}$ is linearly dependent on $X_{AOT}$ in case of linear mixing. However, in Fig. (58),(59) and(60) one can notice that $\ln S^*_{mix}$ is not really linearly depending on $X_{AOT}$, hence showing a non-linear mixing behavior. However, to quantify this non-ideality, we felt the need of calculating the Gibbs free energy and fit it with the Margules 2 parametric polynomial equation.

### 4.3 Quantification of Non-Ideality

The Gibbs free energy were calculated using eq. (15), and were fitted using Margules 2 parametric Margules equation eq. (17). Appendix A (Tables 10-17) are the tabulated values of $G_{EX}/RT_{Experimental}$ and $G_{EX}/RT_{Margules}$ for different mixtures in different oils. The experimentally calculated $G_{EX}/RT$ were equated to the Margules equation eq. (17), and then individual $A_1$ and $A_2$ which are nothing but the Margules parameter were calculated. The Margules parameters are tabulated in Appendix A (Table. 9). Below are the plots of Gibbs free energy calculated experimentally and Gibbs free energy calculated from the Margules equation.

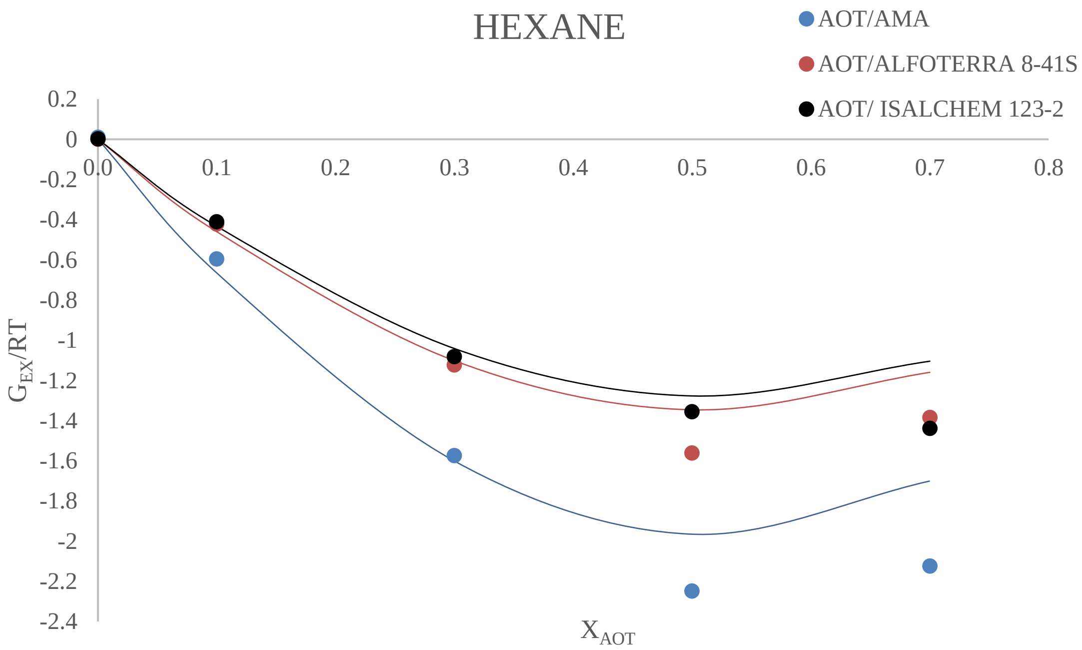


**Figure 61: Normalized Gibbs free energy as a function of $X_{AOT}$ for AOT/AMA, AOT/ALFOTERRA 8-41S and AOT/ISALCHEM 123-2 mixtures in Hexane. The solid lines represent the Margules rules fit.**

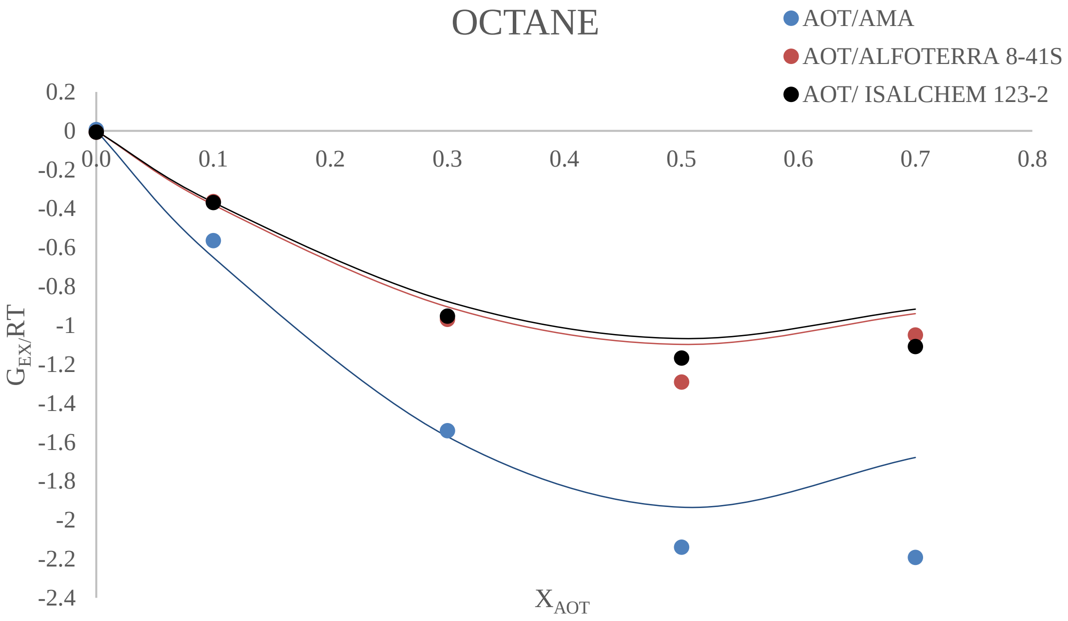


**Figure 62: Normalized Gibbs free energy as a function of $X_{AOT}$ for AOT/AMA, AOT/ALFOTERRA 8-41S and AOT/ISALCHEM 123-2 mixtures in Octane. The solid lines represent the Margules rules fit.**

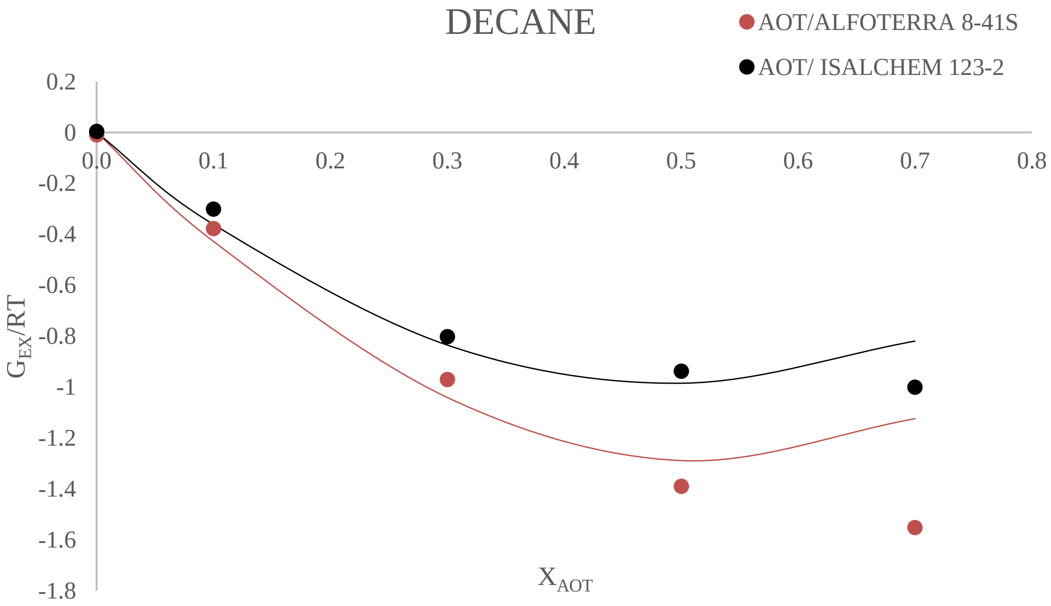


**Figure 63: Normalized Gibbs free energy as a function of $X_{AOT}$ for AOT/AMA, AOT/ALFOTERRA 8-41S and AOT/ISALCHEM 123-2 mixtures in Decane. The solid lines represent the Margules rules fit.**

In the above plots, the solid smoothened lines are the Margules polynomial fit whereas the scattered plot is the experimentally calculated Gibbs free energy.

There are a lot of interesting observations which can be made about figures (61), (62) and (63). The Gibbs free energy of these three AOT systems are negative which indicates that the mixture of AOT showed non-ideal mixing behavior with the mixture exhibiting a more hydrophilic character than the pure components since the AOT mixtures needed more salt. The negative values also show that the driving force of making microemulsions increases, with increasing mole fraction of AOT. It was observed that AOT/ISALCHEM 123-2 showed the least deviations. ISALCHEM 123-2 is the only surfactant without a PO group, to the best of our knowledge to have formed a middle phase by itself. Hence, in this work, it can be observed that the one additional EO group helps pack the ISALCHEM 123-2 monomer better with the AOT monomer than in the AOT/ALFOTERRA 8-41S mixture, so as to give it a slightly less deviation than the AOT/ALFOTERRA 8-41S system. The Gibbs free energy of the AOT/AMA microemulsion is more negative than AOT/ALFOTERRA 8-41S and AOT/ISALCHEM 123-2. One of the possible reasons behind such a large deviation in AMA/AOT can be because of inefficient packing of AOT and AMA monomers in the micelles. Also, it has been found in the past that the AOT monomers form vesicles in aqueous phase. The linear chained alkyl sulfates seem to be packing better with AOT monomers than the AMA monomers, hence showing that it is effective to mix a high Cc surfactant with a low Cc surfactant for desired optimal formulations. In hexane and octane, the Gibbs free energy seem to be increasing and converging when approaching the pure component state, whereas in decane the Gibbs free energy of the AOT/ALFOTERRA 8-41S and AOT/ISALCHEM 123-2 mixtures seem to be asymptotically increasing with increasing mole fractions of AOT indicating a possibility of an unknown synergy between the surfactant molecules and the oil. It’s also interesting to see that the trend is quite similar to that observed by Acosta et. al. [11] for the SDHS-nonionic mixture at 65°C.

# Chapter 5: Conclusion

- Linear mixing rules fail to satisfy the HLD equation in case of AOT mixtures.
- $K_{AOT}$ values when plotted against EACN, showed a negative slope in case AOT/AMA whereas, $K_{AOT}$ values showed a positive slope in case AOT/ALFOTERRA 8-41S and AOT/ISALCHEM 123-2. However, interestingly all the three slopes converged to approximately similar value when approaching the pure species composition i.e. at 100% AOT, which sounds legit as K value of a pure species should be a constant.
- $Cc_{AOT}$ showed a positive slope in all the three studied systems. However, the $Cc_{AOT}$ in case AOT/AMA were found to be higher than the other two systems, probably because AMA has a comparatively shorter tail length than ALFOTERRA 8-41S and ISALCHEM 123-2 and hence, won't have contributed to the curvature as well, as the other two surfactants because of their longer tail lengths.
- The deviations in AOT/AMA were higher than that in AOT/ALFOTERRA 8-41S and AOT/ISALCHEM 123-2, possibly because of the inefficient packing of AMA molecules with the AOT molecules.
- The high negative values of Gibbs free energy of the AOT mixtures also denote that the driving forces of these microemulsions are high when we mix these surfactants together.
- The asymptotic increase in the Gibbs free energy of AOT/ALFOTERRA 8-41S and AOT/ISALCHEM 123-2 mixtures in decane, indicate the possibility of an unknown synergy between the decane and the surfactant monomers, because of

the higher alkane no. of the oil and hence suggesting a need for further investigation on the possible unknown interactions that may be existing in these systems.

- It’s also interesting to note that a twin tailed structured surfactant mixes better with a linear chained surfactant than a mixture of two linear chained surfactants, hence showing that irrespective of their different structures, a high Cc surfactant can be mixed with a low Cc surfactant to achieve the desired optimum formulation.

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# Appendix A: Supplementary Tables

## Table 9: Margules Parameters

| | 6 | | 8 | | 10 | |
|---|---|---|---|---|---|---|
| | $A_1$ | $A_2$ | $A_1$ | $A_2$ | $A_1$ | $A_2$ |
| AOT/AMA | -8.454 | -7.272 | -8.38 | -7.095 | -- | -- |
| AOT/ALFOTERRA 8-41S | -5.731 | -5.041 | -4.6 | -4.179 | -5.653 | -4.66 |
| AOT/ISALCHEM 123-2 | -5.483 | -4.735 | -4.504 | -4.034 | -3.848 | -3.379 |

## Table 10: Gibbs Free Energy of AOT/AMA in Hexane

| $X_{AOT}$ | $G_{EX}/RT_{Experimental}$ | $G_{EX}/RT_{Margules}$ |
|---|---|---|
| 0 | 0.010478588 | 0 |
| 0.1 | -0.595848148 | -0.665118 |
| 0.3 | -1.574900813 | -1.601586 |
| 0.5 | -2.248192838 | -1.96575 |
| 0.7 | -2.12522546 | -1.700874 |

## Table 11: Gibbs Free Energy of AOT/AMA in Octane

| $X_{AOT}$ | $G_{EX}/RT_{Experimental}$ | $G_{EX}/RT_{Margules}$ |
|---|---|---|
| 0 | 0.006558458 | 0 |
| 0.1 | -0.564059761 | -0.650115 |
| 0.3 | -1.540282298 | -1.570905 |
| 0.5 | -2.140397714 | -1.934375 |
| 0.7 | -2.192304526 | -1.678845 |

## Table 12: Gibbs Free Energy of AOT/ALFOTERRA 8-41S in Hexane

| $X_{AOT}$ | $G_{EX}/RT_{Experimental}$ | $G_{EX}/RT_{Margules}$ |
|---|---|---|
| 0 | 0.001159976 | 0 |
| 0.1 | -0.421882425 | -0.4598955 |
| 0.3 | -1.122878263 | -1.1020485 |
| 0.5 | -1.560972282 | -1.3464375 |
| 0.7 | -1.384232573 | -1.1599665 |

## Table 13: Gibbs Free Energy of AOT/ALFOTERRA 8-41S in Octane

| $X_{AOT}$ | $G_{EX}/RT_{Experimental}$ | $G_{EX}/RT_{Margules}$ |
|---|---|---|
| 0 | -0.006200881 | 0 |
| 0.1 | -0.363060336 | -0.3799467 |
| 0.3 | -0.968646817 | -0.9042159 |

| | | |
|---|---|---|
| 0.5 | -1.291233739 | -1.0974875 |
| 0.7 | -1.048607985 | -0.9395631 |

### Table 14: Gibbs Free Energy of AOT/ALFOTERRA 8-41S in Decane

| **$X_{AOT}$** | **$G_{EX}/RT_{Experimental}$** | **$G_{EX}/RT_{Margules}$** |
|---|---|---|
| 0 | -0.010618636 | 0 |
| 0.1 | -0.378814619 | -0.42837795 |
| 0.3 | -0.971739245 | -1.04125665 |
| 0.5 | -1.390520624 | -1.28924375 |
| 0.7 | -1.553319178 | -1.12467285 |

### Table 15: Gibbs Free Energy of AOT/ISALCHEM 123-2 in Hexane

| **$X_{AOT}$** | **$G_{EX}/RT_{Experimental}$** | **$G_{EX}/RT_{Margules}$** |
|---|---|---|
| 0 | 0.002771793 | 0 |
| 0.1 | -0.411046051 | -0.432927 |
| 0.3 | -1.08123818 | -1.041579 |
| 0.5 | -1.356219472 | -1.277375 |
| 0.7 | -1.438344038 | -1.104411 |

## Table 16: Gibbs Free Energy of AOT/ISALCHEM 123-2 in Octane

| $X_{AOT}$ | $G_{EX}/RT_{Experimental}$ | $G_{EX}/RT_{Margules}$ |
|---|---|---|
| 0 | -0.007281335 | 0 |
| 0.1 | -0.368892085 | -0.3673341 |
| 0.3 | -0.951543842 | -0.8768697 |
| 0.5 | -1.166891201 | -1.0674125 |
| 0.7 | -1.107685066 | -0.9163833 |

## Table 17: Gibbs Free Energy of AOT/ISALCHEM 123-2 in Decane

| $X_{AOT}$ | $G_{EX}/RT_{Experimental}$ | $G_{EX}/RT_{Margules}$ |
|---|---|---|
| 0 | 0.00309894 | 0 |
| 0.1 | -0.301265974 | -0.3614238 |
| 0.3 | -0.802993319 | -0.8354976 |
| 0.5 | -0.938481784 | -0.985325 |
| 0.7 | -1.00084892 | -0.8198484 |