

**Deanship of Graduate Studies  
Al-Quds University**



**(Phase Behavior of a Newly Developed Extended  
Surfactant: Potential Applications in Enhanced Oil  
Recovery and Aquifer Remediation)**

**Hani Mahmoud Ibrahim Roumiyh**

**M.Sc. Thesis**

**Jerusalem– Palestine**

**1434 / 2013**

**Deanship of Graduate Studies  
Al-Quds University**



**(Phase Behavior of a Newly Developed Extended  
Surfactant: Potential Applications in Enhanced Oil  
Recovery and Aquifer Remediation)**

**Hani Mahmoud Ibrahim Roumiyh**

**M.Sc. Thesis**

**Jerusalem– Palestine**

**1434 / 2013**

**(Phase Behavior of a Newly Developed Extended  
Surfactant: Potential Applications in Enhanced Oil  
Recovery and Aquifer Remediation)**

Prepared by:  
**(Hani Mahmoud Ibrahim Roumiyh)**

B.Sc.: Chemistry (Al-Quds University) (Palestine)

Supervisor: Prof. Ibrahim Kayali

A thesis Submitted in Partial fulfillment of requirement for  
the degree of Master of Applied and Industrial Technology,  
Al-Quds University

1434/2013



**Thesis Approval**

**(Phase Behavior of a Newly Developed Extended Surfactant: Potential Applications in Enhanced Oil Recovery and Aquifer Remediation)**

Prepared By: Hani Mahmoud Ibrahim Roumiyh  
Registration No.: 20913716

Supervisor: Prof. Ibrahim Kayali

Master thesis submitted and accepted, Date: / 01 / 2013

The names and signatures of examining committee members are as follows:

1- Head of Committee: Prof. Ibrahim Kayali	Signature .....
2- Internal Examiner: Dr. Wadie Sultan	Signature .....
3- External Examiner: Dr. Hatem Maraqah	Signature .....

Jerusalem-Palestine

1434/2013

## **Dedication:**

I would like to dedicate this work to my father, my mother and my wife in recognition of their efforts for encourage me to complete this master thesis.

Thank you all ...

Hani Mahmoud Ibrahim Roumiyh

**Declaration:**

I Certify that this thesis submitted for the degree of Master, is my own research, except where otherwise acknowledged, and that this study (or any part of the same) has not been submitted for a higher degree to any other university or institution.

Signed:

(Hani Mahmoud Ibrahim Roumiyh)

Date: 15 / 01 / 2013

## **Acknowledgments:**

I thank God, who gave me the strength and patience for achieving these thesis requirements.

I would like to thank and appreciate all members of the Department of Chemistry at Al-Quds University especially my supervisor Prof. Ibrahim Kayali for the effort and encouragement.

## **Abstract**

Phase behavior of a newly developed extended surfactant of alkyl polypropylene oxide polyethylene oxide sulfate (X-AES) with a small quantity of cationic hydrotrope was studied for their applications in enhanced oil recovery (EOR) and aquifer remediation process. Formulation of microemulsion with high level of extraction efficiency of crude oil is the main interest objective in this research.

Ternary phase diagram, salinity scan, interfacial tension and adsorption on clay are used to preferably compare between formulations, also using visual inspection as well as cross polarizers to detect anisotropy.

The results show that X-AES with Variquat cc-9 as cationic hydrotrope are preferred candidates for EOR applications as it can give ultra low interfacial tension at optimum salinity. The minimum surfactant concentration needed to initiate middle phase formation was low, as much as 0.05 wt.%, and the adsorption of this surfactants mixture on Kaolin clay can be neglected at this low concentration. Interfacial tension (IFT) calculation using Huh equation showed a minimum value of 0.0004 mN/m between diesel and brine.

X-AES-Variquate cc-9 mixture have been identify as promising EOR surfactant using this screening method.



## Table of Contents

Chapter No.	Title	Page No.
-	Declaration	i
-	Acknowledgement	ii
-	Abstract	iii
-	Table of content	iv
-	List of tables	v
-	List of figures	vi
-	List of appendix	viii
-	List of abbreviations	ix
1.	Introduction: 1.1 Enhanced oil recovery 1.2 Surfactants enhanced aquifer remediation (SEAR) 1.3 Microemulsion 1.4 Extended surfactants 1.4.1 Properties of extended surfactants 1.4.2 Extended surfactants synthesis 1.4.3 Role of extended surfactants in microemulsion application 1.5 Aims of the study	1 2 6 8 11 12 13 14 14
2.	Literature review	15
3.	Materials and method: 3.1 Materials 3.2 Instruments and equipments 3.3 Procedure 3.3.1 Constructing ternary phase diagram 3.3.2 Fish phase diagram 3.4 Methodology	22 23 23 23 23 24 24
4.	Results and discussion: 4.1 Ternary phase diagram of X-AES/TEAC/Water at 25 °C 4.2 Ternary phase diagram of X-AES/Variquat cc-9/Water at 25°C 4.3 Ternary phase diagram of X-AES/Diesel/Water at 25 °C 4.4 Ternary phase diagram of X-AES:Variquat cc-9/Diesel/Water at 25 °C 4.5 Ternary phase diagram of X-AES:Variquat cc-9/Diesel/Water at 50 °C 4.6 Acid value for diesel 4.7 Fish diagram 4.8 Surfactants adsorption onto Kaolin Clay	26 28 30 30 31 32 32 33 40
5.	Summary and conclusion 5.1 Conclusion 5.2 Future work	43 44 45
-	References	46
-	Appendix - Definition	49
-	Arabic abstract	51

## List of Tables

<b>Table No.</b>	<b>Table Name</b>	<b>Page No.</b>
1.1	Classification and microbial origin of biosurfactants	7
2.1	Properties of the Extended Surfactants	20
4.1	Solubilization ratio and interfacial tension IFT for a system containing 1.0% of X-AES (71%)/Variquat cc-9 (4:1) wt. % WOR=1 with fixed amount of Sodium borate 0.5% at 25°C.	39
4.2	Surfactants adsorption on Kaolin clay	40

## List of Figures

Figure No.	Figure name	Page No.
1.1	Oil production, 1 <sup>o</sup> , 2 <sup>o</sup> and 3 <sup>o</sup> oil recovery process.	3
1.2	Some enhanced oil recovery methods.	5
1.3	Experimental setup for sand column washing.	8
1.4	Three types of phase behavior for surfactant (S), oil (O) and water (W) system according to Winsor.	9
1.5	Phase behavior along a salinity scan test tube aspect and phase diagrams.	9
1.6	General structure for extended surfactant.	11
1.7	CMC of extended surfactant as a function of propylene oxide number (PON).	12
1.8	Cloud point of extended surfactants as a function of PON.	13
2.1	Partial ternary phase diagram of water, L <sub>123</sub> -4S:TBAB (1:1 molar ratio) and decane at 25°C.	17
2.2	An increase in solubilization by stretching the surfactant interior to increase the penetration into the oil and water phases. (A) First generation: anionic–nonionic extended surfactant; (B) second generation: sugar-based extended surfactant. EO, ethylene oxide.	18
2.3	Effect of added NaCl on phase behavior of 1 wt.% solutions of X-AES / sodium dodecyl benzene sulfonate.	19
4.1	Ternary phase diagram of X-AES/TEAC/Water at 25 °C.	28
4.2	Schematic phase diagram of the extended surfactant X-AES/Water system.	29
4.3	Ternary phase diagram of AOT/TEAC/Water at 25 °C.	29
4.4	Ternary phase diagram of X-AES/Variquat cc-9 and Water at 25 °C.	30
4.5	Ternary phase diagram of X-AES/Diesel/Water.	31
4.6	Ternary phase diagram of X-AES:Variquat cc-9/Diesel/Water at 25 °C.	31
4.7	Ternary phase diagram of X-AES:Variquat cc-9/Diesel/Water at 50 °C.	32
4.8	Example of a naphthenic acid.	33
4.9	Effect of added NaCl on phase behavior of X-AES:Variquat cc-9 [8:2] and 0.5% sodium borate solution.	34
4.10	Microemulsion fish phase diagram of X-AES:Variquat cc-9 [8:2] and 0.5% sodium borate using diesel WOR=1.	34
4.11	Salinity scan for 0.50% X-AES, Variquat cc-9 (8:2 wt./wt.), with diesel, WOR = 1.	36
4.12	Salinity scan after equilibration of equal volumes of diesel and aqueous solutions containing 1.0 wt.% X-AES, Variquat cc-9 (8:2 wt./wt.), and wt.% NaCl as indicated.	37
4.13	Salinity scan for 1.0% X-AES, Variquat cc-9 (5:5 wt./wt.), with diesel, WOR = 1.	38
4.14	IFT versus NaCl wt.%, for a system of 1.0%	39

	AES:Variquat cc-9 (4:1) wt.% ratio, WOR= 1 with fixed quantity of Sodium borate 0.5%.	
4.15	S-shaped adsorption isotherm for an ionic surfactant on an oppositely charged substrate.	41
4.16	Adsorption of X-AES : Variquat cc-9 (8:2 wt./wt.) onto kaolin clay.	41

## List of Appendices

<b>Appendices No.</b>	<b>Appendices name</b>	<b>Page No.</b>
1.	Definition	49

## List of Abbreviations

No.	Abbreviations	Read as
1.	CMC	Critical micelle concentration
2.	$N_c$	Capillary number
3.	PO	Propylene oxide
4.	EO	Ethylene oxide
5.	IFT	Inter facial tension
6.	EOR	Enhanced oil recovery
7.	LPG	Liquefied petroleum gas
8.	SEAR	Surfactants enhanced aquifer remediation
9.	EACN	Equivalent alkane carbon number
10.	NAPL	Non-aqueous phase liquids
11.	DNAPL	Dense non-aqueous phase liquids
12.	SAD	Surfactant affinity difference
13.	WOR	Water:Oil ratio
14.	TEAC	Tetra ethyl ammonium chloride
15.	$C_{\mu}C$	Critical microemulsion concentration
16.	$\xi$	Characteristic length
17.	$E_r$	Interfacial rigidity
18.	$\sigma$	Surfactant characteristic
19.	AOT	Sodium bis (2-ethylhexyl) sulfosuccinate
20.	X-AES	Anionic extended surfactants
21.	USP-34	United state pharmacopeia
22.	RI	Refractive index
23.	wt.	Weight
24.	TDS	Total dissolved solid

# **Chapter One**

## **Introduction**

## 1.1 Enhanced Oil Recovery

Oil recovery processes as an industrial view from a reservoir can be divided into three main stages:

- 1- Primary oil recovery process:  
This is the first stage in oil recovery process, in this stage the oil is recovered due to the natural gases pressure in the reservoir without any additional external pressure.
- 2- Secondary oil recovery process (Water flooding):  
Usually this second stage started when the first stage ended or stopped as a result of decrease the natural pressure in the reservoir, when the pressure in the reservoir reach a point where the expelling process of the oil is not achievable water is injected to re-pressurize the remain oil.
- 3- Tertiary oil recovery process (Enhanced oil recovery (EOR)):  
The amount of oil still present in the reservoir after the primary and secondary stages is estimated to be about 65%, because of this high lost percent of oil and because of the decline of oil discovery during the last decades, there is a great need to recover at least apportion of the remained quantity of the oil, and this is the main idea of the third stage of oil recovery. Tertiary oil recovery methods mean to increase the mobility of the oil in order to enhance extraction of the oil from processed reservoirs.

The illustration and written descriptions of the various methods of oil production have been simplified in Fig. (1.1) below:

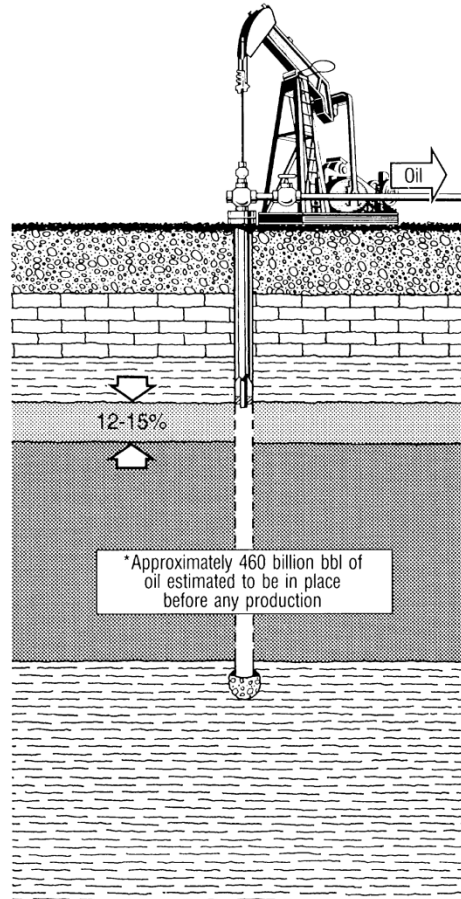


# OIL PRODUCTION

Improved technology through research is enhancing oil recovery.

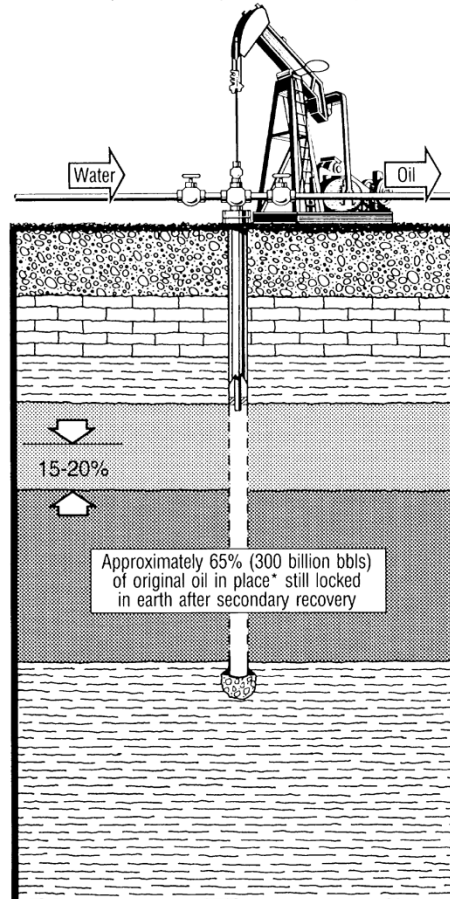
## PRIMARY RECOVERY

Produces 12-15% of the original oil-in-place\*



## SECONDARY RECOVERY

Another 15-20% of the original oil-in-place\* may be produced by waterflooding



## ENHANCED OIL RECOVERY (EOR)

An additional 4-11% of the original oil-in-place\* may be produced using current and advanced technology

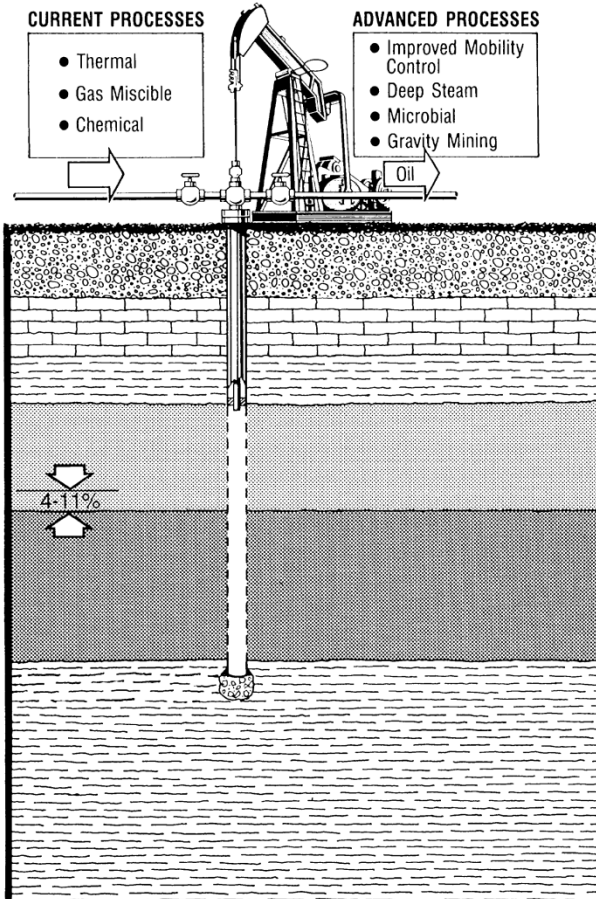


Fig. 1.1: Oil production, 1<sup>o</sup>, 2<sup>o</sup> and 3<sup>o</sup> oil recovery processes (Enhanced oil recovery information, 1986).

Enhanced oil recovery or tertiary oil recovery stage can be divided according to the field of application, the properties of the crude oil and the properties of the reservoir divided into two major groups (Pillai, et al., 1999):

- 1- Thermal processes
- 2- Chemical flooding processes

Thermal recovery processes in which energy have to be introduced are the most advance in the field experimentation, these method consist of adding heat to a reservoir in order to reduce the viscosity of the crude oil and eventually vaporize it (Salager, 1977). Thermal methods include as a main advances techniques: in-situ composition and steam injection, specifically steam injection still dominate as the preferred EOR methods for heavy oil reservoir (Alvarado and Manrique, 2010).

Chemical flooding processes may contains caustic flooding, surfactant flooding and polymer flooding, these processes may consist of various chemicals specially surfactants and polymers, usually as dilute solution, polymer and surfactants can be used as diluted solution to increase the amount of oil recovered in some formation.

Chemicals preparations in chemical flooding processes may form a mixture which typically contains surfactants, co-surfactant, polymer, and electrolyte and / or alkaline those are often mixed into the fresh water or formation brine is used in EOR (Flaaten, 2007).

The co-surfactants in formulation for enhanced oil recovery acts to prevent gel formation and reduce equilibrium time. Alkali agents can be used to enable in-situ soap generation from crude components.

The neutral electrolytes are adjusted to achieve optimum salinity and thus minimum interfacial tension. Injection of alkaline or caustic solution into reservoir will result in the production of soap of organic acid in crude oil which may lower interfacial tension (IFT) enough to increase oil recovery from reservoir (Pillai, et al., 1999).

Fig. (1.2) below is a simplified chart illustrate some types of enhanced oil recovery methods generally sorted in petroleum industry, generally combination of two major method in recovery process is helpful and useful to overcome the interfacial effect and alter the viscosity which ease the mobility of trapped oil in pores of rocks (Gurgel, et al., 2008).

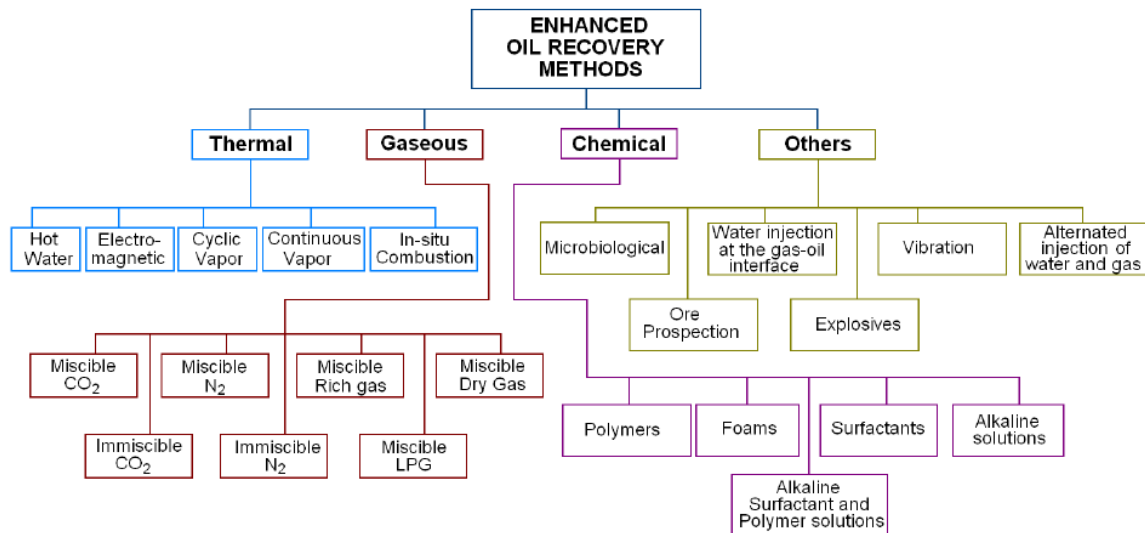


Fig. 1.2: Some enhanced oil recovery methods (LPG = Liquefied petroleum gas).

Oil remains trapped in geological reservoir because of high interfacial tension (IFT) between crude oil and brine, by decreasing the value of IFT to a very low values getting what is known as ultralow interfacial tension ( $\sim 10^{-3}$  mN m<sup>-1</sup>), a large amount of crude oil from reservoir can be recovered, so lowering the tension between the water and the oil is the driving force that enables the researchers for getting applicable method to increase the recovered quantity of trapped oil (Moulik and Rakshit, 2006).

Many considerations must be taken when selecting a suitable method for enhanced oil recovery (Gurgel, et al., 2008). Especially in surfactant flooding techniques, some of these considerations are the adsorption phenomena which occurs within the reservoir porous medium which affects the interfacial tension and interfacial rheology, this phenomena reduces the efficiency of the process because of surfactant loss by adsorption, other important issue have to be consider the concentration of the surfactant to be used and its efficiency The efficiency of surfactant affected by surfactant type, CMC values, the solubility of surfactant, temperature and Kraft point of the surfactant. The choice of the more appropriate surfactants to be used in EOR application must have fulfillment study to all these aspects (Gurgel, et al., 2008).

Oil recovery processes are function of displacement, which are dependent on three major forces: capillary forces, gravitational or buoyancy forces, and viscous forces (Martel and Gelinias, 1996).

Capillary forces cause oil trapping and they resist its mobilization. Three functions are affecting this capillary forces, first oil/aqueous phase interfacial tension, second water-solid contact angle in the presence of oil (wettability) and third the radius of the pore containing the interface (Martel and Gelinias, 1996). The ratio of viscous forces, which favor oil mobilization to capillary forces, which favor oil trapping, is quantified by the capillary number ( $N_c$ ).

Gravitational forces are hydrostatic in nature; viscous forces are created by the flow of the displacing fluid in porous media. Capillary forces can be reduced by lowering interfacial tension or by changing wettability (Martel and Gelinias, 1996).

Microemulsion is also a potential candidate because it has benefits as a special formulation that can be effective in this field of oil recovery.

Application of microemulsion in EOR is usually limited by the cost of surfactants used in the preparation of microemulsion, their adsorption and loss onto the rock.

Chemical flooding processes are the most complex methods to be applied as an oil recovery techniques because there are many sensitive and important parameters have to be controlled (Salager, 1977). Since every crude oil is unique therefore a unique chemical EOR formulation and technique have to be designed for specific crude oil, equivalent alkane carbon number (EACN) are used to characterize and identify crude oil, evaluating this parameter, which is analogous to the alkane carbon number (ACN) indicated the hydrophobicity of the oil phase, to affect optional salinity and solubilization ratio. Also many considerations must be taken when selecting a suitable method for EOR such as heterogeneous geological nature of the oil reservoir (Gurgel, et al., 2008).

## **1.2 Surfactants Enhanced Aquifer Remediation (SEAR)**

The presence of non aqueous phase liquids is one of the principle problems associated with ground water remediation efforts since these non aqueous liquids have low aqueous solubility. Aqueous solution with or without additives are employed to solubilize contaminants in soil and aquifer. The efficiency of extracting the contaminants depends on important factors such as the hydraulic conductivity of the treated soil, high permeability (greater than  $1 \times 10^{-3}$  cm/s) the solubility of excited pollutants and if these pollutants are originally solubilized in water or not, the chemistry of binding these pollutants and the hydrogeology of the site to be treated, soil pH and soil type and the particle size, high clay and matter contents all of these factors are key factors in removal efficiency processes. Removing mechanisms of many organic contaminants is controlled by the solubility of these contaminants in water, additives are used to enhance efficiencies by reduce the time of treating a site and a large variety of contaminants can be treated comparing of using water alone. The liquid contaminants remains as a separate phases called non-aqueous phase liquids (NAPL's), non-aqueous phase liquids which sink below water are denser and called denser non-aqueous phase liquids (DNAPL), and those are lighter called lighter non-aqueous phase liquids (LNAPL), some of these contaminants are chlorinated solvents, such as trichloroethylene, polycyclic aromatic hydrocarbons, and other contaminants become more complicated such as mixtures of metals.

The additives used to enhance the contaminants removing process must be effective, low cost, low toxicity and biodegradable, these additives include surfactants, polymers organic and inorganic acid, sodium hydroxide and complexing agents such as EDTA (Mulligan, et al., 2001).

Numerous studies and research have indicated that surfactants enhance recoveries of non-aqueous phase liquids (NAPL's) especially DNAPL by reducing the interfacial tension between DNAPL and ground water, the forcing idea to be applied here is reducing or damaging the capillary forces which restrict the mobility of DNAPL, when these forces are reduced or removed the contaminants are mobilized and collected in separate extraction wells (Mulligan, et al., 2001).

Several technologies exist to treat water after pumped from the ground to remove hydrocarbons and metals (Mulligan, et al., 2001).

Some of the major of these technologies are ion exchange, sodium hydroxide or sodium sulfide precipitation, ultra filtration, activated carbon adsorption, reverse osmosis (Mulligan, et al., 2001).

Overall, desirable surfactant characteristics used for SEAR include low toxicity, biodegradability, low adsorption to soil, solubility at ground-water temperatures, effective at concentration lower than 3%, low CMC and low surface tensions (Mulligan, et al., 2001).

Some interest and useful surfactants used in SEAR are called Biosurfactants which are biologically produced from yeast or bacteria from different substrate like sugar, oils and alkanes, composition and yields depend on the fermentor design, pH, temperature, composition of the nutrients, most of these biosurfactants are neutral and anionic and few are cationic, their CMCs generally ranging from 1 – 200 mg/L and have ranging molecular weights of 500 – 1500, these biosurfactants were effective in oil recovery and transformation of crude oil by effective reduction in the interfacial tension values between crude oil and water (Mulligan, et al., 2001).

Table (1.1) below give an example of these surfactants.

Table 1.1 Classification and microbial origin of biosurfactants (Mulligan, et al., 2001).

Surfactant class	Microorganism
Trehalose lipids	Arthrobacter paraffineus
Rhammolipids	Pseudomonas aeruginosa
Sophorose lipids	Candida apicole
Glucose-, fructose-, saccharose lipids	R. erythropolis
Cellobiose lipids	Ustilago maydis
Polyol lipids	Rhodotorula glutinous
Diglycosyl diglycerides	Lactobacillus fermentii
Lipopolysaccharides	Acinetobacter calcoaceticus
Lipopeptides	Bacillus pumilis
Ornithine, lysine peptides	Streptomyces sioyaensis
Phospholipids	T. thiooxidans
Sulfonylipids	Capnocytophage
Fatty acids	Penicillum spiculisporum

Surfactant solution compatibility with aquifer material, ground-water temperature, and salinity must be verified before using surfactants as SEAR, during the application of the surfactant solution in fields the surfactant solution may mobilize the fine minerals particles that can restrict the ground water flow, polyvalent cations may adsorbed on sediment particles causing surfactant precipitation leading to deficiency of the washing solution (Martel and Gelinias, 1996).

Interfacial tension can be reduced between DNAPL and ground water by using surfactants, also the surfactant ease and enhance the solubility of the contaminants which may aid in extraction them from an aquifer (Fountain, et al., 1996).

As an application of technology a sand column techniques is a necessary pre-work before lab scale or pilot scale application this column technique simulate the effect of contaminated porous aquifer.

Fig. (1.3) below show an experimental setup for sand column washing (Martel and Gelinas, 1996).

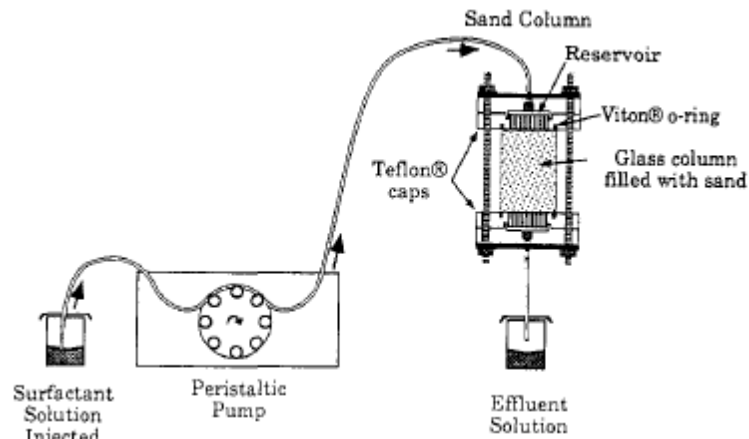


Fig. 1.3: Experimental setup for sand column washing.

### 1.3 Microemulsion

Microemulsions are isotropic, thermodynamically stable dispersions of two immiscible liquids containing appropriate amounts of surfactants (Sharma and Shah, 1985). It was first introduced in 1959 by Jack H. Shulman at Columbia University (Lee, 2010).

Since microemulsions are thermodynamically stable it does not need a high energy or shear condition for their formation (Lee, 2010).

Microemulsions appear clear unlike emulsion, and have a droplet size around 10 nm (Lee, 2010). With a dispersed phase which consists of small droplets with diameter in the range of 100-1000 Å (Sharma and Shah, 1985). These unique properties of microemulsion make it the most interest field of scientific research (Lee, 2010). The most interest properties of microemulsion such as low interfacial tension, high thermodynamic stability and the ability to dissolve immiscible liquid give microemulsion potential application as a drug delivery vehicles and many application in food industry and in the petrochemical industry (Lee, 2010).

Microemulsions are typically classified into three main categories, or Winsor-type systems. Winsor's type I microemulsion consist of oil swollen micelles in water with excess water, where as a type II system consists of water swollen inverse micelles in oil with excess oil. Type III microemulsion system, middle phase microemulsion or Winsor III appears with an excess of both water and oil (Salager, et al., 2005).

Fig. (1.4) Illustrate the three types of phase behavior for surfactant (S) – oil (O) – water (W) system according to Winsor. Shading indicates the surfactant rich phase, and R is Winsor ratio, that indicates the ratio of interaction between surfactants at interface and oil, and the interaction between surfactants and water.  $R = A_{co}/A_{cw}$ , where  $A_{co}$  indicates the interaction between the surfactant adsorbed at the interface and the oil phase per unit area of interface, and where  $A_{cw}$  does likewise for the water phase (Salager, et al., 2005).

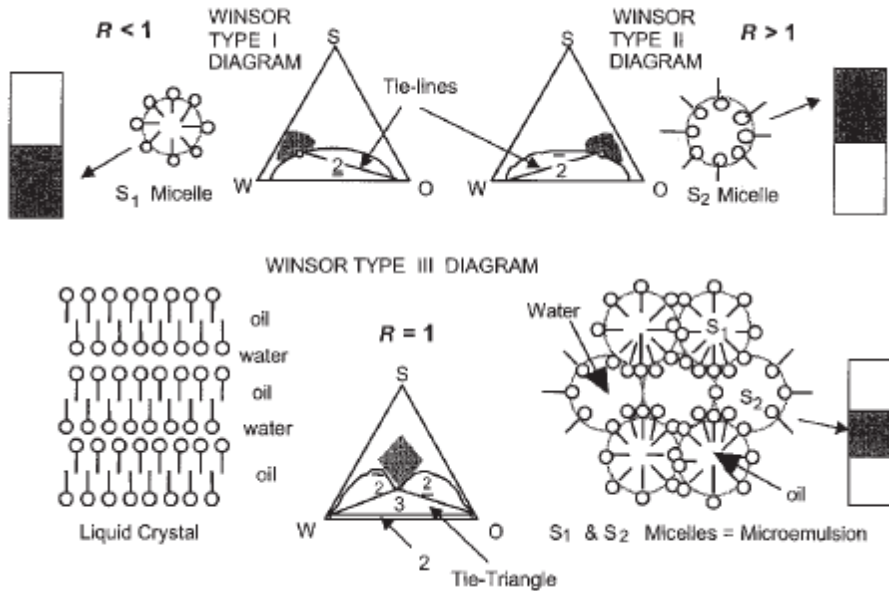


Fig. 1.4: Three types of phase behavior for surfactant (S), oil (O) and water (W) system according to Winsor.

When  $R=1$  a maximum solubilization and a very low interfacial tension occurs (Salager, et al., 2005).

Fig. (1.5) Illustrate phase behavior along a salinity scan test tube aspect and phase diagrams (Salager, et al., 2005).

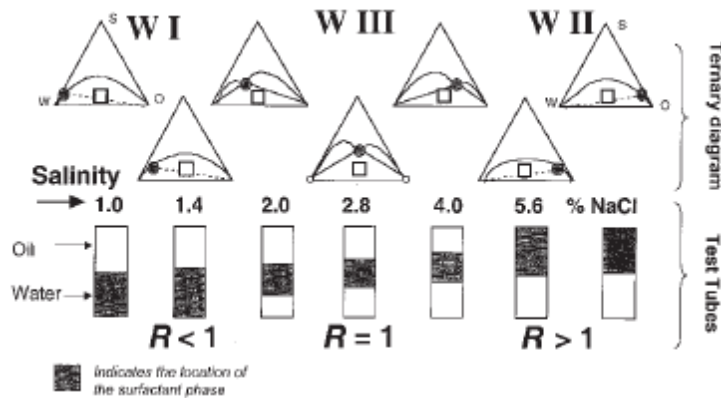


Fig. 1.5: Phase behavior along a salinity scan test tube aspect and phase diagrams.

Interest in the application of microemulsion in enhanced oil recovery continues to grow (Salager, et al., 2005).

The zero net-curvature condition for the surfactant layer between the oil and water, is the most favorable when highly solubilization are concerned (Salager, et al., 2005).

Three types of microemulsion can be formed oil in water, water in oil and middle-phase microemulsion. Middle-phase microemulsion occurs when the Winsor's ratio  $R=1$ , and when the  $SAD = 0$  (Kanicky, et al., 2001), where  $SAD$  is the Surfactant affinity difference.

Surfactant affinity difference (SAD):

Ultra-low interfacial tension and maximum oil mobilization can be predicted using numerical empirical correlation. This correlation (Surfactant affinity difference) is a measure of the difference between the standard chemical potentials or the Gibbs free energy of surfactant in the oil and water phase.

$$SAD = \mu_w - \mu_o = \Delta G_{(Water \rightarrow Oil)} = -RTL \ln K_p$$

Where  $\mu_w$  and  $\mu_o$  are the chemical potential of the surfactant in the water and oil phase, respectively,  $K_p$  is the partition coefficient of surfactant between water and oil at the corresponding temperature.

SAD actually represents the free energy of transfer of a surfactant molecule from the water to the oil.

At a  $SAD = 0$ , the surfactant affinity for the water phase exactly equals its affinity for the oil phase, thus resulting in the optimum formulation (Ultra-Low interfacial tension). The sign of the SAD indicates the dominant affinity of the surfactant, whereas the value denotes the magnitude of deviation from an optimum formulation. A  $SAD < 0$  means that surfactant – oil interactions dominate, while a  $SAD > 0$  indicates that surfactant – water interactions prevail.

Many factors which change the hydrophobic balance of the surfactants may enable us to move from one type to another.

These factors are illustrated below:

- 1) Chain length of surfactants  
Longer chain length would take us from Winsor I to Winsor II.
- 2) Polarity of aqueous phase (Water)  
The addition of short chain alcohol can cause increase in polarity of water and then transfer from Winsor I to Winsor II.
- 3) Temperature and electrolyte concentration  
The increasing in temperature for a non-ionic surfactants or increasing in electrolyte concentration for ionic surfactants would take us from Winsor I to Winsor II also (Goodwin, 2004).

Many numerical equations can be used to calculate the values of interfacial tension (IFT), scientist Huh (1979) develop an equation that used to estimate IFT using optimal solubility, this equation is given as:

$$\gamma = 0.3 / (\sigma^*)^2$$

where  $\gamma$  is IFT and  $\sigma^*$  is oil or water solubilization ratio at optimal salinity (Flaaten, 2007).

Another research indicates that interfacial tension can be calculated using Vannegut equation (1942):

$$\gamma = \pi (\rho_1 - \rho_2) R_d^3 \omega^2 / 4$$

$\gamma$  = Interfacial tension

$\rho_1$  = Density of continuous phase



$\rho_2$  = Density of droplet phase  
 $R_d$  = Droplet diameter  
 $\omega$  = Rotational speed (Flaaten, 2007).

All the above results of scientific research were obtained to ease the dealing of IFT values in equation forms, since these values are of great importance in microemulsion techniques.

### 1.4 Extended Surfactants

Extended chain surfactant is a new generation of surfactants which have an intermediate polarity linking chain (Polypropylene oxide (PO), Polyethylene oxide (EO)) inserted between lipophilic tail and hydrophilic head.

The general formula of extended surfactants is:  $R-(PO)_x-(EO)_y-O-SO_3-A$

Where R is a linear or branched, saturated or unsaturated aliphatic or aromatic hydrocarbon having from 8-20 carbon atoms.

A: is a cationic species such as alkaline earth metal.

X: is the number of propylene oxide group (Degree of propoxylation) ranging from 5-15,

and Y: is the average degree of ethoxylation ranging from 1-5 (Smith and Hand, 2006).

General structure for extended surfactant is shown below in Fig. (1.6) (Quintero, et al., 2009).

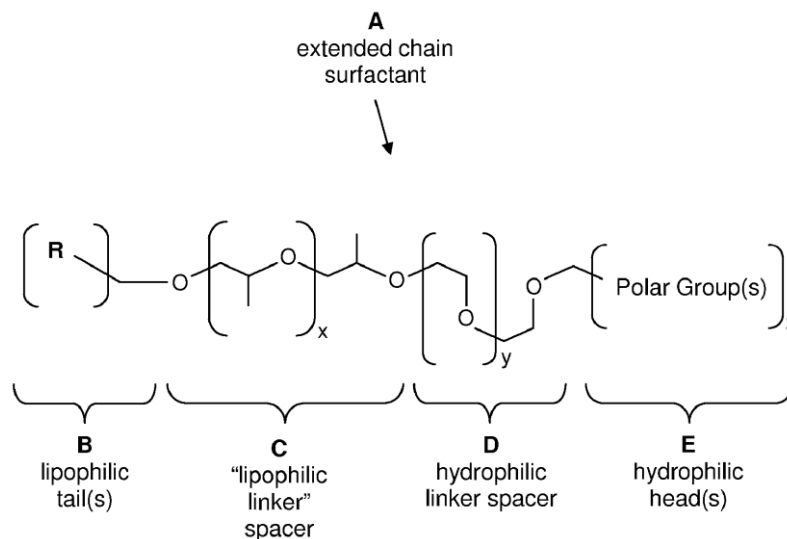


Fig. 1.6: General structure for extended surfactant.

The first generation of extended surfactants was found to produce a high solubilization with long hydrocarbon and polar oil, which is presented in the form:

Alkyl-polypropylene oxide-polyethylene oxide sulfate sodium salt (Salager, et al., 2005).

The second generation of extended surfactants which are recently been synthesized are more bio-friendly polar groups, such as glucose, galactose, xylitol or carboxylate (Salager, et al., 2005).

Using extended surfactant alter using hydrophilic and lipophilic linkers, which are used to increase surfactant-water and surfactant-oil interaction.

#### 1.4.1 Properties of extended surfactants

Extended surfactants exhibit a critical micelle concentration (CMC) and a cloud point that changes with the number of propylene oxide groups per molecule (Perez, et al., 1995).

As the number of propylene oxide group increase, the CMC decreases.

In Fig. (1.7) we see the variation in CMC as a function of number of propylene oxide group per molecules (Perez, et al., 1995).

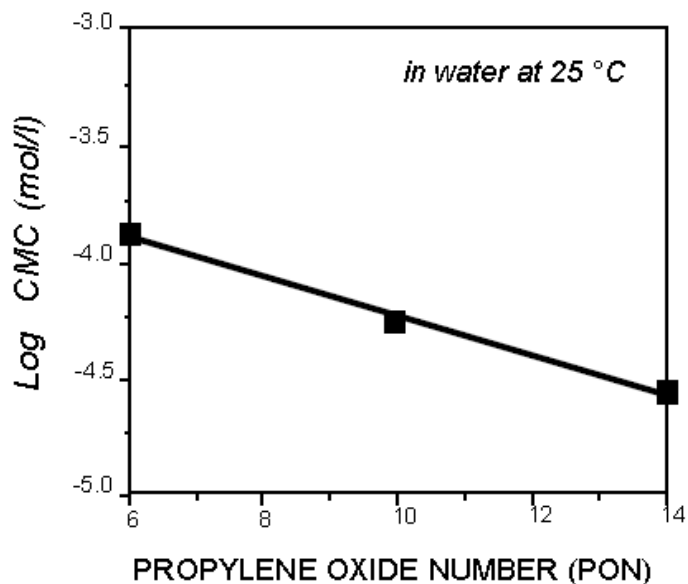


Fig. 1.7: CMC of extended surfactant as a function of propylene oxide number (PON).

The cloud point temperature decreases when the number of propylene oxide groups increases.

Fig. (1.8) indicate the relation between cloud point temperature and number of propylene oxide group, where 712 SN, 713 SN and 714 SN contain 6, 10 and 14 group of PO, respectively (Perez, et al., 1995).

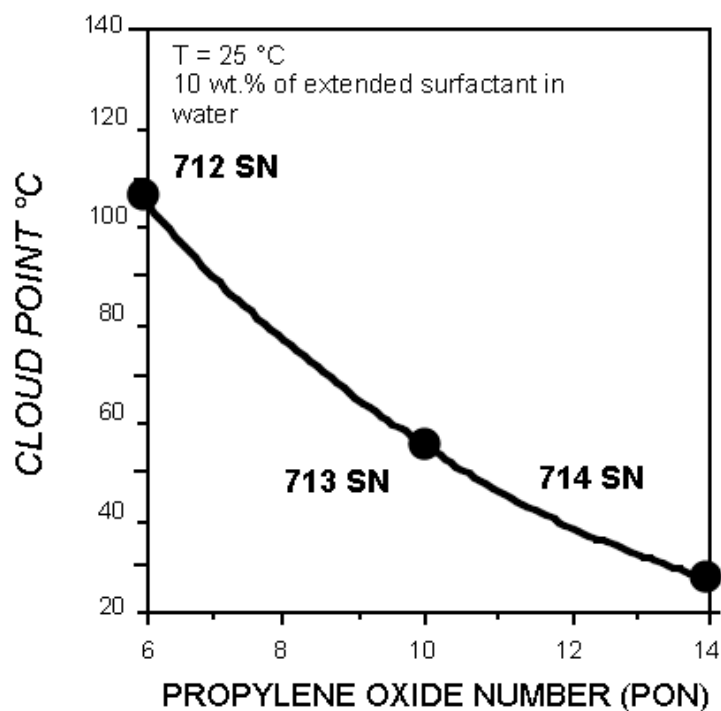


Fig. 1.8: Cloud point of extended surfactants as a function of PON.

The cloud point decrease is approximately 10 °C per propylene oxide group (Minana-Perez, et al., 1995).

Intermediate-polarity group (PO / PO-EO) in extended surfactants structure offer a smoother interfacial transition from a polar aqueous to non polar oil region, that's why it capable to form middle-phase microemulsions with high solubilization, ultralow IFT and lower optimum salinity for a wide range of oil (triglyceride, vegetable oil and long chain alkane) (Witthayapanyanon, et al., 2009).

With the additional of PO groups in surfactant, extended surfactants are likely to evidence higher characteristic length ( $\xi$ ) (Thicker surfactant membrane) and more rigid surfactant membrane ( $E_r$ ) (Witthayapanyanon, et al., 2009).

Increasing the number of EO group in surfactant molecule increase the optimum salinity and the tolerance for divalent cations, preventing precipitation problem. Whereas PO group increase the size and area of the surfactant and thus tend to promote lower IFT over a wide range system (Flaaten, 2007).

#### 1.4.2 Extended surfactants synthesis

Extended chain surfactants can be prepared by reaction of appropriate alcohol with propylene oxide at 120 °C and ethylene oxide at 160 °C in the presence of a base catalyst (Sodium hydroxide, potassium hydroxide, sodium methoxide) to produce an alkoxyated alcohol (Smith and Hand, 2006).

Alkoxyated alcohol can be reacting with chlorosulfonic acid (CSA) or  $\text{SO}_3$  and neutralized by NaOH to produce the extended chain surfactants (Smith and Hand, 2006).

### 1.4.3 Role of extended surfactants in microemulsion application

Extended surfactants ease forming microemulsion in a wide range of efficient applications, such as EOR, SEAR, laundry detergent, liquid-liquid extraction, alternative fuel and plant oil extraction.

### 1.5 Aims of the Study

1. Prepare alcohol-free microemulsion using newly developed extended surfactant sodium alkyl polypropylene oxide polyethylene oxide sulfate [ $C_{12} (PO)_{14} (EO)_2 SO_4Na$ ] (X-AES) and short chain cationic hydrotrope with a low amount of surfactants and reach ultra low IFT.
2. Study the phase behavior of X-AES and cationic hydrotrope (Variquat cc-9 and TEAC) with water.
3. To investigate phase behavior of X-AES, diesel and water ternary system.
4. Investigate the effect of addition hydrotrope cationic surfactants on phase behavior of system containing sodium alkyl polypropylene oxide polyethylene oxide sulfate and diesel.
5. Construct a ternary phase diagram of a mixture of extended surfactant and cationic hydrotrope, diesel and water at 25 °C.
6. Reach the optimum salinity TDS < 12000 ppm.
7. Construct a phase diagram of anionic extended surfactant, cationic hydrotrope, diesel and water at 50 °C.
8. Prepare middle phase microemulsion using mixture of sodium alkyl polypropylene oxide polyethylene oxide sulfate and cationic hydrotrope with diesel by salinity scan method and determine the properties of this system.
9. Reach middle phase microemulsion at a minimum equilibrium time and low salt concentration.
10. Determine the main properties of the formulated microemulsion.
11. Investigate the adsorption of surfactants system onto Kaolin Clay.
12. Prepare and give the optimum microemulsion formulations and to investigate them in EOR and SEAR project.

# **Chapter Two**

## **Literature Review**

This chapter provided literature review on the theory and methods used in this research. The main topics cover in this chapter are preparation of microemulsion using extended surfactants and characterize its properties for EOR and SEAR application, the second is review of literature that study cationic hydrotrope and its benefits in microemulsion formulation as flooding fluids for EOR.

Microemulsions are a thermodynamic stable dispersion of oil and water stabilized by surfactants with a combination of additives or co-surfactant. Middle phase microemulsion with its unique properties, in particular their ability to significantly reduce interfacial tension (IFT) and enhance the solubilization of hydrophilic and lipophilic ingredients make it a key component of successful technologies in various applications such as an enhanced oil recovery (EOR) and surfactant enhanced aquifer remediation (SEAR).

Ultra low interfacial tension system using sodium alkyl polypropylene oxide sulfate and sodium alkyl polypropylene oxide polyethylene oxide sulfate has been formulated with a wide range of oil, which exhibit low critical micelle concentration (CMC), low critical microemulsion concentration ( $C_{\mu}C$ ) compared with conventional surfactants, and it was also found that introduce PO and EO in the extended surfactants yielded ultralow IFT and lower optimum salinity. In this research they observe that there is a slight increase in the IFT above  $C_{\mu}C$  for extended surfactants used, and indicate that the physical explanation for this phenomenon is still unknown (Witthayapanyanon, et al., 2006).

Extended surfactants which consisting of both EO and PO groups in surfactants structure have a dual ionic and nonionic characteristic (Witthayapanyanon, et al., 2006).

Evaluating of both equilibrium and kinetic aspects of extended surfactant based microemulsion was studied by Witthayapanyanon, et al., 2009 and they found that extended surfactant resulted in a relatively rigid interfacial membrane compared with conventional surfactants.

The interfacial morphology of the extended surfactant membrane, both the characteristic length ( $\xi$ ) and interfacial rigidity ( $E_r$ ) parameters will increase with the increase in length of the polypropylene oxide spacer (Witthayapanyanon, et al., 2009).

Witthayapanyanon introduce an accurate model to determine the hydrophilic-lipophilic nature of extended surfactants. Hydrophilic-Lipophilic Deviation (HLD) approach can be used to determine the surfactant characteristic ( $\sigma$ ) and the  $\sigma/k$  parameter of extended surfactants (Witthayapanyanon, et al., 2008).

Recently it was found that the addition of a small amount (modest quantity) of cationic hydrotrope surfactants to anionic extended surfactants will increase solubilization of oil and brine in microemulsion and lower IFT at optimal salinity (Kayali, et al., 2010).

Adding cationic surfactants to anionic surfactant has a disadvantage, that some of the ion pairs formed may partition into the oil phase instead of remaining at the internal interfaces in microemulsion (Kayali, et al., 2010).

Many studies indicate the synergistic effect of cationic hydrotrope (Polypropylene oxide ammonium chloride) and anionic extended surfactants (Sodium alkyl polypropylene oxide sulfate) to prepare microemulsion with a minimum amount of 0.20 wt. % surfactant and ultra low IFT (Kayali, et al., 2011).

Using optical microscopy (Klaus, et al., 2009/2010) investigated phase behavior of extended surfactants in water at all concentrations from dilute and semi dilute up to concentrate phases, and at different temperatures from 0 – 90 °C they examined formation of liquid crystal by two methods, the first way by increasing surfactant concentration and the other is by increasing temperature.

In their pioneer work on extended surfactants they found that X-AES formed many types of mesophases like H1,  $L_\alpha$ , V2, H2 when mixed with water without other component by increasing temperature or concentration (Klaus, et al., 2010).

A comprehensive description of different phase formed using X-AES and its properties (Shape, size and area per molecule) were studied by (Klaus, et al., 2010).

A ternary phase diagram was determined at ambient condition for alkyl polypropylene oxide sulfate combined with tetrabutyl ammonium bromide with water and decane as shown in Fig. (2.1) below (Kayali, et al., 2011). According to this study lamellar liquid crystalline phase will disappear when using cationic hydrotrope surfactant with extended surfactants.

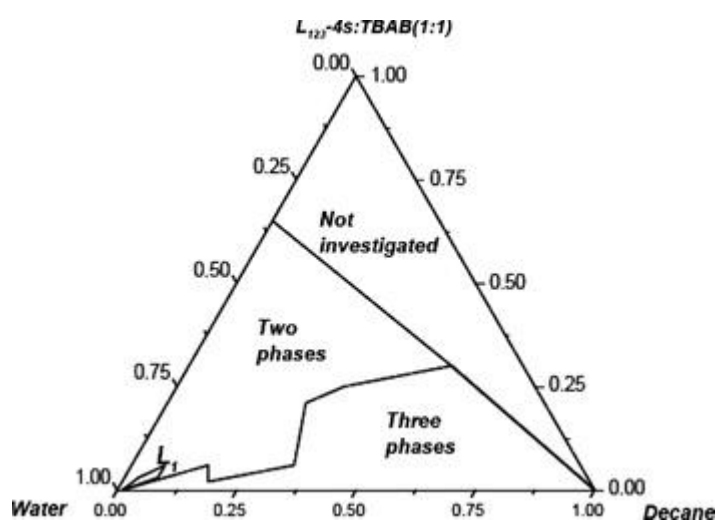


Fig. 2.1: Partial ternary phase diagram of water,  $L_{123}$ -4S:TBAB (1:1 molar ratio) and decane at 25°C. (Kayali, et al., 2011).

The presence of a smooth, blurred and expanded transition across the interfacial region from polar to non-polar phases can be improved solubilization in microemulsion (Salager, et al., 2005).

Extended surfactants with a poly-propylene oxide chain inserted between the conventional alkyl and ether sulfate groups, exhibit a critical micelle concentration and a cloud point that changes with the number of propylene oxide group per molecule. These surfactants show three phase behavior at optimum formulation with hexadecane, ethyl oleate and with triglyceride oil, such as soya oil (Minana-Perez, et al., 1995).

X- AES surfactant exhibits a cloud-point temperature that decreases with increasing surfactant concentration before adding electrolytes (Klaus, et al., 2011).

Extended surfactants are found to enhance the interaction on the oil side of the interface, formation of that because microemulsion is now possible with triglyceride oils or very long chain hydrocarbons (Minana-Perez, et al., 1996).

Fig. (2.2) below illustrate the two generation of extended surfactants, with second generation which exhibit a higher biocompatibility than did the first generation.

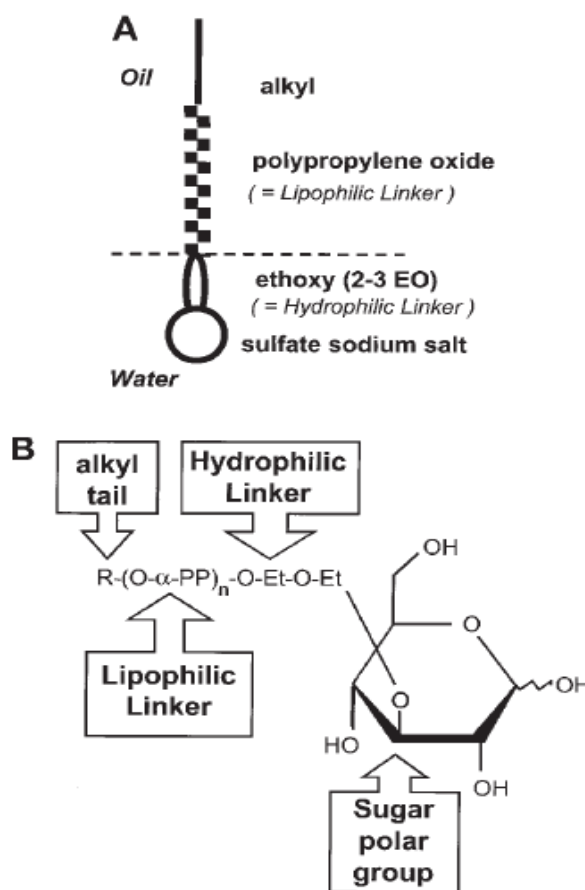


Fig. 2.2: An increase in solubilization by stretching the surfactant interior to increase the penetration into the oil and water phases. (A) First generation: anionic–nonionic extended surfactant; (B) second generation: sugar-based extended surfactant. EO, ethylene oxide. (Salager, et al., 2005).



Kayali, et al., 2011 studied water-diesel microemulsion using anionic extended surfactants and cationic hydrotrope, for their application in EOR. Since the presence of precipitation or liquid crystal in injected solution lead to non uniform distribution and many complicate the transport process, they test the equilibrium phase behavior of aqueous solution containing 1.0 wt% of X-AES and Sodium dodecyl benzene sulfonate as a function of NaCl as in Fig. (2.3) below and they found that both surfactants individually exhibit precipitate above 2.0 wt% of NaCl, whereas no precipitation or cloudiness occurs when using a mixture of X-AES - Sodium dodecyl benzene sulfonate at wt. ratio of 1:1 as NaCl content increase up to 5 wt% (Kayali, et al., 2011).

For SEAR and EOR processes, ultralow interfacial tension values near 0.01 mN/m are necessary for any successful displacement of oil (Kayali, et al., 2011).

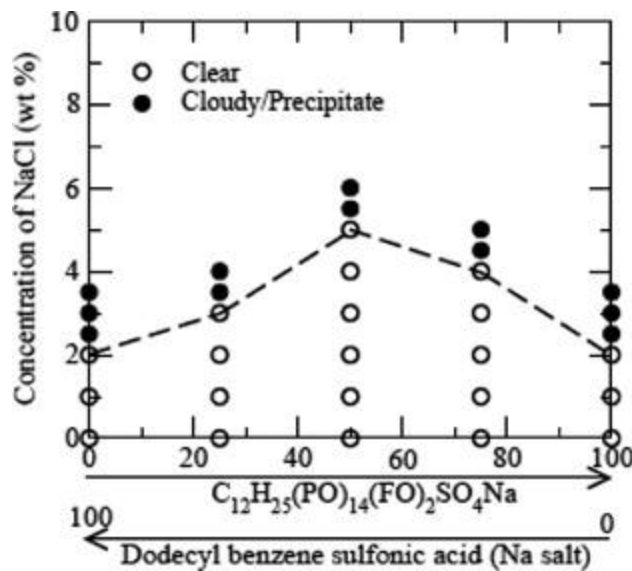


Fig. 2.3: Effect of added NaCl on phase behavior of 1 wt% solutions of X-AES / sodium dodecyl benzene sulfonate.

When using sodium octane sulfonate with X-AES in a ratio of 0.27:0.73 (SOS:X-AES) the region of one phase enlargement to about 20 wt. % of NaCl (Kayali, et al., 2011). The main idea is by using sulfonate with X-AES it increase salt resistance.

Choosing the type of hydrotrope used can adjust the optimal salinities according to crude oil required (Kayali, et al., 2011).

Table (2.1) summarize numbers of extended surfactants and its some properties and characteristics obtained from many articles deal with these topics.

Table 2.1 Properties of the Extended Surfactants. These data obtained from [(Witthayapanyanon, et al., 2009), (Witthayapanyanon, et al., 2008), (Witthayapanyanon, et al., 2006), (Do, et al., 2008), (Arpornpong, et al., 2010) and (Phan, et al., 2011)]

Extended surfactants	Alkyl No.	% Branch	No. of PO groups	No. of EO groups	% Active	MW	Ai (A <sup>2</sup> )	HLB	$\sigma$	No salt		0.2 M NaCl	
										CMC	Area per molecule	CMC	Area per molecule
C <sub>12,13</sub> H <sub>25,27</sub> (PO) <sub>3</sub> SO <sub>4</sub> Na	12-13	0	3	0	-	-	-	39.55	-1.77	-	-	-	-
C <sub>12,13</sub> H <sub>25,27</sub> (PO) <sub>8</sub> SO <sub>4</sub> Na	12-13	0	8	0	29.1	712.8	-	38.80 31.6	-0.78	130	153	14	68
C <sub>14,15</sub> H <sub>29,31</sub> (PO) <sub>8</sub> SO <sub>4</sub> Na	14-15	0	8	0	29.6	715.5	-	30.6	-	33	133	5	116
C <sub>12,13</sub> H <sub>25,27</sub> (PO) <sub>4</sub> SO <sub>4</sub> Na	12-13	100	4	0	30.0	527	-	-	-	-	-	-	-
C <sub>12,13</sub> H <sub>25,27</sub> (PO) <sub>8</sub> SO <sub>4</sub> Na	12-13	100	8	0	30.7	766	-	-	-	-	-	-	-
C <sub>14,15</sub> H <sub>29,31</sub> (PO) <sub>4</sub> SO <sub>4</sub> Na	14-15	100	4	0	30.0	553	-	-	-	-	-	-	-
C <sub>14,15</sub> H <sub>29,31</sub> (PO) <sub>8</sub> SO <sub>4</sub> Na	14-15	100	8	0	29.5	783	-	-	-	-	-	-	-
C <sub>12,13</sub> H <sub>25,27</sub> (PO) <sub>4</sub> SO <sub>4</sub> Na	12-13	0	4	0	27.3	519	-	-	-	-	-	-	-
C <sub>12,13</sub> H <sub>25,27</sub> (PO) <sub>4</sub> SO <sub>4</sub> Na, 50 B	12-13	50	4	0	30.0 28.1	527	144.9	-	-	-	-	-	-
C <sub>12,13</sub> H <sub>25,27</sub> (PO) <sub>8</sub> SO <sub>4</sub> Na, 50 B	12-13	50	8	0	30.7	766	61.73	-	-	-	-	-	-
C <sub>12,13</sub> H <sub>25,27</sub> (PO) <sub>8</sub> SO <sub>4</sub> Na, 100 B	12-13	100	8	0	30.6	667	96.14	-	-	-	-	-	-
C <sub>12</sub> H <sub>25</sub> (PO) <sub>14</sub> (EO) <sub>2</sub> SO <sub>4</sub> Na	12	0	14	2	24.1	1104	31.8	39.51 38.6	0.74	80	200	8	147
C <sub>12</sub> H <sub>25</sub> (PO) <sub>10</sub> (EO) <sub>2</sub> SO <sub>4</sub> Na	12	0	10	2	24.1	-	-	39.2	-	-	-	-	-
C <sub>12</sub> H <sub>25</sub> (PO) <sub>12</sub> (EO) <sub>2</sub> SO <sub>4</sub> Na	12	0	12	2	24.2	-	-	38.7	-	-	-	-	-
C <sub>10</sub> (PO) <sub>18</sub> (EO) <sub>2</sub> SO <sub>4</sub> Na	10	0	18	2	22.5	-	-	38.91	1.99	-	-	-	-
C <sub>10</sub> (PO) <sub>14</sub> (EO) <sub>2</sub> SO <sub>4</sub> Na	10	0	14	2	22.4	-	-	39.5	-	-	-	-	-
C <sub>10</sub> (PO) <sub>10</sub> (EO) <sub>2</sub> SO <sub>4</sub> Na	10	0	10	2	17.4	-	-	40.1	-	-	-	-	-
C <sub>16</sub> H <sub>33</sub> (PO) <sub>2.9</sub> SO <sub>4</sub> Na	16	0	2.9	0	22.2	-	-	37.7	-	-	-	-	-
C <sub>16</sub> H <sub>33</sub> (PO) <sub>4.5</sub> SO <sub>4</sub> Na	16	0	4.5	0	23.2	-	-	37.4	-	-	-	-	-
C <sub>16</sub> H <sub>33</sub> (PO) <sub>5.5</sub> SO <sub>4</sub> Na	16	0	5.5	0	24.7	-	-	37.3	-	-	-	-	-
C <sub>16</sub> H <sub>33</sub> (PO) <sub>8.2</sub> SO <sub>4</sub> Na	16	0	8.2	0	24.1	-	-	36.9	-	-	-	-	-
C <sub>16</sub> H <sub>33</sub> (PO) <sub>10.7</sub> SO <sub>4</sub> Na	16	0	10.7	0	24.2	-	-	36.5	-	-	-	-	-
C <sub>16,17</sub> (PO) <sub>4</sub> (EO) <sub>5</sub> COONa	16-17	0	4	5	-	-	184	19.3	-	0.020	-	-	-
C <sub>16,17</sub> (PO) <sub>4</sub> SO <sub>4</sub> Na	16-17	0	4	0	-	-	55	37.3	-	0.070	-	-	-

Kayali, et al., 2010 study phase behavior of system that contains sodium bis (2-ethylhexyl) sulfosuccinate (AOT) as a primary surfactant and tetraethyl ammonium chloride as cationic hydrotrope co-surfactant as a function of alkane carbon number and salt concentration at ambient condition, they found that 10mM of AOT need to formulate microemulsion with high alkane carbon number such as heptanes, octane and nonane.

Velasquez, et al., 2009 study the effect of temperature and other variables on the optimum formulation of anionic extended surfactant/ alkane/ brine systems, they found that extended surfactants with alkyl polypropylene oxide sulfate type obey the linear correlation  $\ln S = k \cdot ACN$  for optimum formulation, an increase in temperature found to produce a decrease in surfactant hydrophilicity.

Wu, et al., 2010 investigate Alkyl alcohol propoxylated sulfate surfactants as candidates for enhanced oil recovery application, the result show that these anionic surfactants can create low interfacial tension at dilute concentrations even at high salinity, without requiring an alkaline agent or co-surfactant.

# **Chapter Three**

## **Materials and Method**

### 3.1 Materials

Chemicals components used in this research for microemulsion preparation are chosen based on their molecular design and evaluated based upon both the aqueous phase behavior and microemulsion phase behavior with diesel as a module.

Sodium alkyl polypropylene oxide polyethylene oxide sulfate used as extended surfactants for this research,  $C_{12}(PO)_{14}(EO)_2SO_4Na$ , pale yellow to colorless solution consists of 23.6% active, the surfactant was donated by Huntsman Petrochemical Corp. (Houston, TX, USA) and was used as received from the manufacturer without any analysis.

Tetraethyl ammonium chloride (TEAC) was obtained from SIGMA, assay > 98.0%, melting point > 300°C and used as received.

Polypropylene oxide quaternary ammonium chloride (Variquat cc-9 NS) purity >90% was donated by Evonik-Deguss, Germany.

Diesel was obtained from Al-Huda station in Al-Beirh.

Distilled water obtained from Quality Control lab of Jerusalem Pharmaceuticals was used as the aqueous phase to prepare all stock solutions, Sodium chloride was from Merck, Germany.

Sodium hydroxide, assay  $\geq 99\%$ , sodium carbonate, assay  $\geq 99.9\%$  and di-sodium tetraborate decahydrate ( $Na_2B_4O_7 \cdot 10H_2O$ ), Molecular weight 381.37, assay 99.5-103.0 all of these materials are from Merck KGaA Germany, and used as received.

Kaolin clay was obtained from Wbbminerals, United Kingdom, and used as received. The compositions of this clay (Assay) are as follow:

$SiO_2 = 48.00\%$

$TiO_2 = 0.04\%$

$Al_2O_3 = 36.46\%$

$Fe_2O_3 = 0.85\%$

$CaO = 0.06\%$

$MgO = 0.39\%$

$K_2O = 2.40\%$

$Na_2O = 0.10\%$

### 3.2 Instruments and equipments

Analytical balance (Acculab Vicon Vic-303), Vortex mixer (mrc Laboratory Equipment VM-1000), Cross polarizer, Polarizer microscope (Olympus), Shaker, Water bath, Oven, pH meter 691 (Metrohm SWISS made), KF Titrino 701 (Metrohm SWISS made), Centrifuge, conductivity meter LF 538 (WTW), mrc K7135 Refractometer, Brookfield viscometer, 10 mm glass test tubes with screw caps.

### 3.3 Procedure

#### 3.3.1 Constructing ternary phase diagram

Sample of anionic extended surfactants was placed in oven at 30-40 °C for many days with fan ventilation (Vacuum condition) to reach a desired concentration of surfactants.

Sample were prepared by weighing appropriate amounts of each component into 10 mm glass test tubes with screw caps at ambient condition 25°C and at 50°C, the samples were mixed by vortex then stand until equilibrate. Detecting number of phases by naked eye. Polarized microscope was used to detect anisotropy. Finally draw the phase diagram using OriginPro 7.5 program develop by OriginLab Corporation.

### **3.3.2 Fish phase diagram**

WOR=1 by salinity scan using surfactant mixture.

Samples were prepared by weighing appropriate amount of each component into 10 mm glass test tubes molar ratio of surfactant mixture and water / diesel (1:1)

To calculate IFT Chun-Huh equation will be used, the solubilization parameter  $V_x/V_s$  can be obtained by measuring the amount of solubilized oil or water, by knowing the amount of oil or water after equilibrium and abstract it from the original oil or water added.

### **3.4 Methodology**

To determine the appropriate ratio of anionic and cationic surfactants which will be used to prepare middle phase microemulsion with brine and diesel we prepare ternary phase diagram of water, cationic surfactant and anionic extended surfactant. We examine transparency of system visually.

Ternary phase diagram for water, acceptant mixture of anionic extended surfactant with cationic and diesel also will be prepared. These phase behavior will be studied at ambient condition and at 50 °C.

All samples will be weighted in 10 mm glass test tube with screw caps, shake with a vortex for 1-2 minutes then diesel will be added and mix gently on a mixer for 12 hours, then the tubes will put in an upright position to allow to settle.

Polarized light will be used to detect birefringence phases if it appears.  
Salinity scan method will be used to prepare middle phase microemulsion.

Mixture of X-AES and Variquat cc-9 Preparation:

Two compensation was used in this research, one by mixing X-AES:Variquat cc-9 in ratio 4:1 wt./wt., and the other combination is 1:1 wt./wt..

Since we expected a small quantity of hydrotrope, most of experiments done on 4:1 w/w ratio.

Acid value determination:

Reference: USP-34 Pharmacopeia.

Procedure: Dissolve about 10.0 g of diesel, accurately weighed, in 50 mL of a mixture of equal volumes of alcohol and ether, which has been neutralized to phenolphthalein with 0.1 N sodium hydroxide contained in a flask.

Calculate the acid value by the formula:

$$\text{Acid value} = 56.11 V * N/W$$

In which 56.11 is the molecular weight of potassium hydroxide; V is the volume, in mL; N is the normality of the sodium hydroxide solution; and W is the weight, in g, of the diesel taken.

#### Surfactants adsorption onto Kaolin Clay

A quantity of Kaolin clay was dried in an oven at 120°C for two hours, then one gram of clay is used for 20g of surfactants solution. This sample was shaken for 24 hours on shaker at ambient condition. Then the test tube was centrifuged to separate the solution and clay. Surfactant adsorbed mass was determined.

# **Chapter Four**

## **Results and Discussion**



Selection and screening of surfactants for EOR application undergo three stage procedures, first by testing a list of surfactants based upon surfactant structure, activity, knowledge and physicochemical condition of reservoir. That's because extended surfactant is choosing for this research, since it can increase solubilization, as well as a broader region of ultra-low IFT can be a chive with low amount of surfactant.

The second step is done using phase behavior experiments, with calculation of IFT, measure viscosity and equilibration time are used to evaluate candidates. In this stage alkali and other additives may be added to optimize performance.

The final phase involves oil recovery experiments (Core flood) in reservoir cores; this stage is lifted for future work.

Chemicals for EOR application are commonly characterized in phase behavior experiments by evaluating the microemulsion created with oil, water and surfactants.

The most important step in chemical formulation for an EOR application is to work well in phase behavior before being tested in a core flood experiment. To obtain an optimal formulation a strategic design methodology is required.

Surfactants cause the solubilization of water and oil with each other, and form the primary component in phase behavior studies, so choosing the proper surfactants mixture ratio is very important, since the most desirable phase behavior is microemulsion with low viscosity and the absence of high viscosity gel or other viscous phases, this viscous phases retard transport in porous media and also promote high retention, so we tested many hydrotrope surfactants (TEAC and Variquat cc-9) to compare and chose the best mixture and the best ratio of these surfactants; the primary or the main surfactant which is the extended surfactant and secondary which is the co-surfactant (Cationic hydrotrope).

#### Concentrated X-AES:

A suitable amount of Sodium alkyl polypropylene oxide polyethylene oxide sulfate  $C_{12}(PO)_{14}(EO)_2SO_4Na$  was dried in an oven at temperature range of 30-40 °C with vacuum condition for many days to evaporate water from the sample, this is the way how a concentrated X-AES is obtained to be use in this research, weight variation between the weight of the sample before and after evaporation is used to calculate the concentration of the extended surfactant, which is a 71% X-AES, further tests are done on the dried samples using available instruments as: KF titrino titer, which is used to determine the actual quantity of water in the finished sample, the result show that sample contains 26.66% water.

Refractive index used generally to identify oily sample or solvent, and used here for further characterization for the concentrated sample of X-AES, the result show that RI equal to 1.431.

Injection composition of microemulsion can be represented on equilibrium ternary diagrams with coordinates water, surfactant and oil. That portion of such a diagram having economic significance, divides into a single phase region and a multiphase region. Within the single phase region, micellar structure is studied in relation to effects of salinity and co-surfactant on viscosity, optical birefringence and conductivity. Within the multiphase region, effects on phase behavior, interfacial tension and solubilization parameter are determined as functions of salinity.

#### 4.1 Ternary phase diagram of X-AES/TEAC/Water at 25 °C

A Ternary phase diagram obtained by addition of water to alkyl polypropylene oxide poly ethylene oxide sodium sulfate, which is the extended surfactant (X-AES 71%), and Tetraethyl ammonium chloride TEAC at 25 °C, the result is a single clear isotropic region as in Fig. (4.1) below, and lamellar liquid crystal phase at moderate concentration of X-AES on binary system with water.

L1 micelle isotropic region will appear at low surfactants concentration, when the X-AES concentration increases at binary system (Water and X-AES) a viscous one phase region appears, when the sample tested by polarized microscope a shiny crystal as Maltese cross patterns is shown.

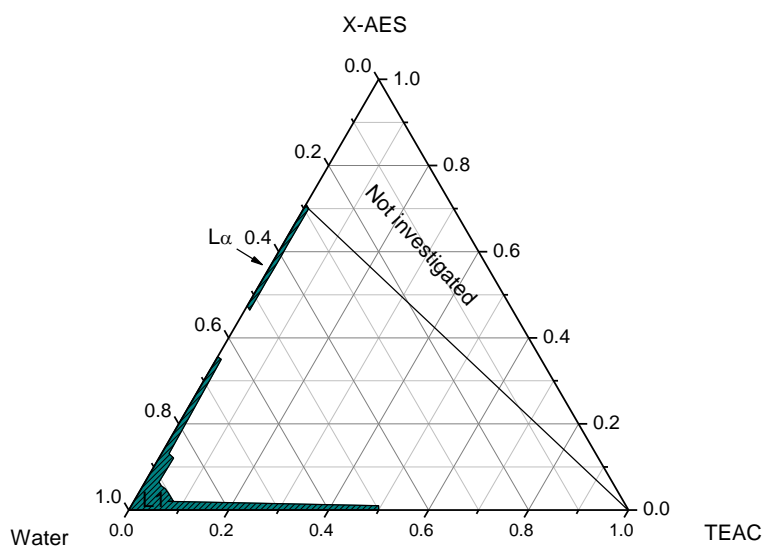


Fig. 4.1: Ternary phase diagram of X-AES/TEAC/Water at 25 °C.

On binary system of X-AES (71%) and water, a region of viscous single phase is appears labeled as  $L\alpha$  and when a small quantity of TEAC is added to X-AES and titrated with water milky suspension (Two phase) appears. This because of solid nature of TEAC. In order to have a high concentrated sample, we evaporate the water from the original surfactant the maximum concentration we could reach was 71% that why the uninvestigated region appears in the obtained phase diagram.

The Fig. (4.2) below adopted from a research paper (Klaus, et al., 2009) dealing with the same problem, the research results complies with what is obtained in our work in extended surfactant treatment, even the result of the research paper were tested using optical microscope.

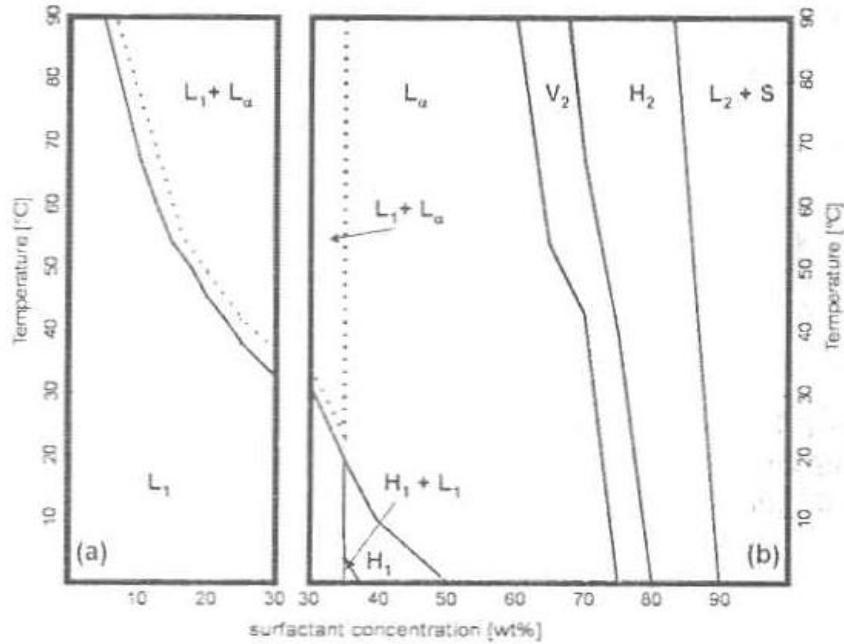


Fig. 4.2: Schematic phase diagram of the extended surfactant X-AES/Water system.

At 25 °C, L1 appear from zero up to 34% of extended surfactant, where as Lα appear at higher concentration upper than 35% to 70%.

In Fig. (4.3) below, ternary phase diagram for AOT / TEAC and water adapted from (Kanan, et al. studied phase behavior of extended surfactant with cationic hydrotrope, our result complies with their result related to TEAC and water.

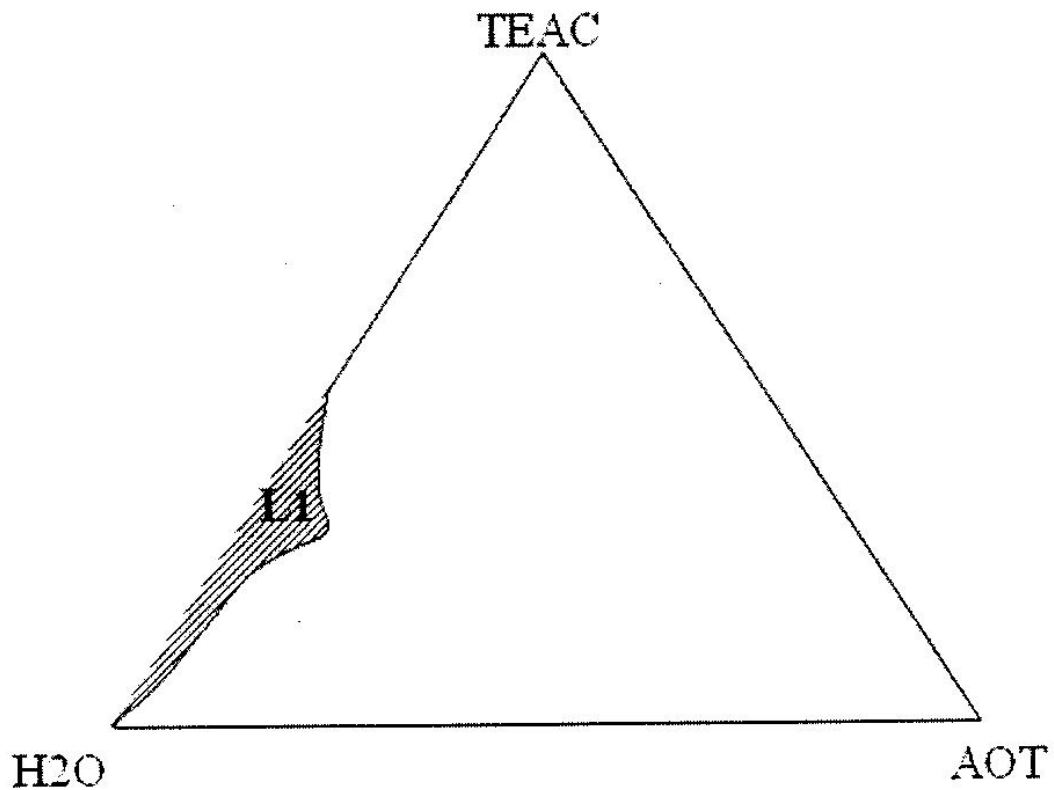


Fig. 4.3: Ternary phase diagram of AOT/TEAC/Water at 25 °C.

## 4.2 Ternary phase diagram of X-AES/Variquat cc-9/Water at 25 °C

The extended surfactant X-AES used in this research has a long hydrocarbon chain compared with hydrotrope used either TEAC or Variquat cc-9, this give hydrotrope its properties to be located at water oil interface, and this will decrease the electrostatic attraction of the head group of the main surfactant and thus synergistic effect will be obtained which will enable additional solubilization of oil.

Fig. (4.4) below illustrate ternary phase diagram of X-AES / Variquat cc-9 with water, many one phase region appears, initially by clear isotropic phase (micelle solution L1, conductivity = 10.1 mS/cm) in high concentration of water, secondary by huge region of inverse micelle L2 (Conductivity = 5.2 mS/cm), despite of no oil present and a high percent of water up to 50% presence in this region inverse micelle is observed, third by a small one phase region presence in high concentration of X-AES, which is an isotropic low viscous liquid, this lead to fact that addition of hydrotrope prevent the formation of liquid crystal.

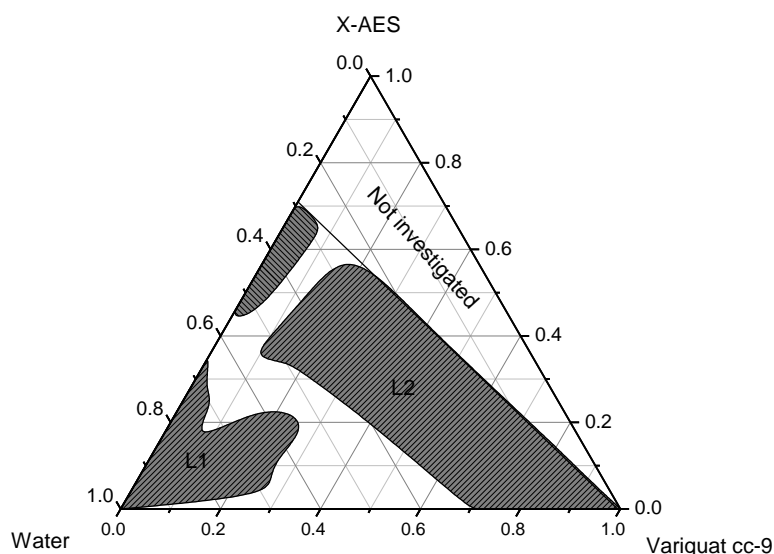


Fig. 4.4: Ternary phase diagram of X-AES/Variquat cc-9 and Water at 25 °C.

Huge one phase regions appear in the above ternary phase diagram consisting of different types of lyotropic phases, comparing with TEAC phase diagram shown previously, this behavior of spreading large one phase regions due to the more hydrophilic nature of Variquat cc-9 than TEAC.

The minimum quantity of Variquat cc-9 (Ratio to X-AES) used and give large area of isotropic one phase is 2:8 wt./wt. (Variquat cc-9:X-AES), so this ratio used for further investigation and considered as the best ratio of hydrotrope.

## 4.3 Ternary phase diagram of X-AES/Diesel/Water at 25 °C

Ternary phase diagram upon addition of water to a combination of sodium alkylpolypropylene oxide polyethylene oxide sulfate and diesel as oil model was done. The results are illustrated below in Fig. (4.5), which show three regions of one phase, one of them is gel and the others is water like, after this gel tested between crossed polarizer it show that region is anisotropic and has Maltese cross patterns under polarized microscope.

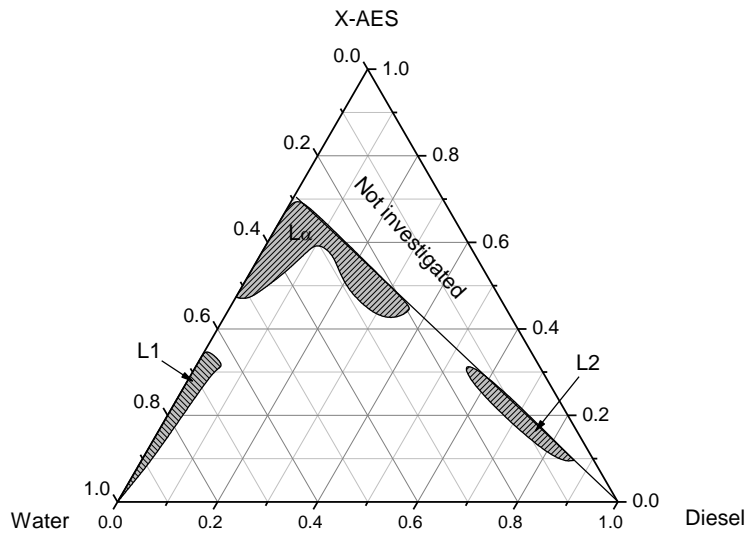


Fig. 4.5: Ternary phase diagram of X-AES/Diesel/Water.

On the other hand from the figure above, 10% of X-AES is sufficient to solubilize 10% of water in diesel.

#### 4.4 Ternary phase diagram of X-AES:Variquat cc-9/Diesel/Water at 25 °C

The observed ternary phase diagram at 25 °C is shown in Fig. (4.6), which was prepared using combination of X-AES (71%) with Variquat cc-9 [8:2 wt./wt.] as surfactant.

The ratio of anionic extended surfactant (X-AES (71%)) to cationic hydrotrope (Variquat cc-9) concentration was systematically varied in phase behavior experiments, so we chose that ratio depends on high single phase sample with the lowest quantity of variquat cc-9 as mentioned before.

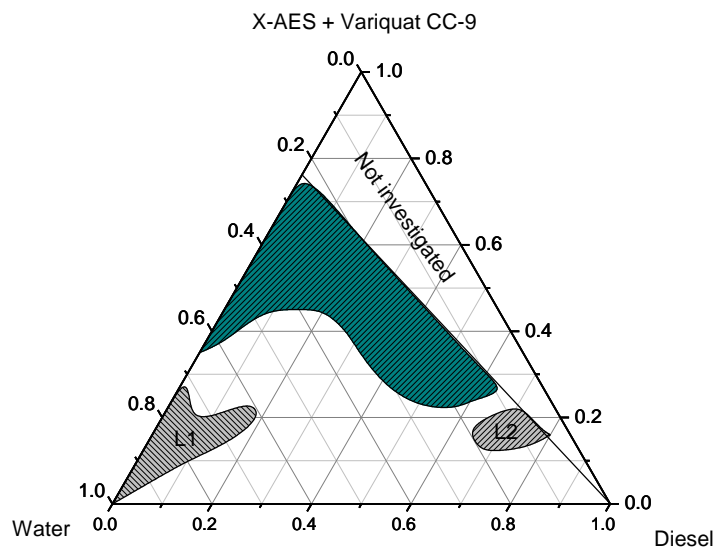


Fig. 4.6: Ternary phase diagram of X-AES:Variquat cc-9/Diesel/Water at 25 °C.

Isotropic regions appear in figure above labeled by L1, L2 and large area of isotropic viscous liquid region. The combination of X-AES with variquat cc-9 can prevent liquid crystal formation and enhance solubility of diesel with water, since 60% of diesel can mix with 20% of water using 20% of surfactants to give clear thermodynamic stable microemulsion.

#### 4.5 Ternary phase diagram of X-AES:Variquat cc-9/Diesel/Water at 50 °C

Effect of the temperature on the phase behavior of X-AES and Variquat cc-9:

The hydrophilic head of the X-AES is sulfate group, which is hydrolyzed above 60 °C, so we study the phase diagram at 50 °C, this make this type of surfactants limited to low reservoir temperature applications.

An increase in temperature is known to increase the hydrophilicity of ionic surfactants, in spite that there is an opposite effect on ionic extended surfactants by increasing temperature, from this point the effect of temperature on phase diagram of X-AES:Variquat cc-9/Diesel/Water were studied, the result shown below in Fig. (4.7), with same ratio as above from X-AES and Variquat cc-9.

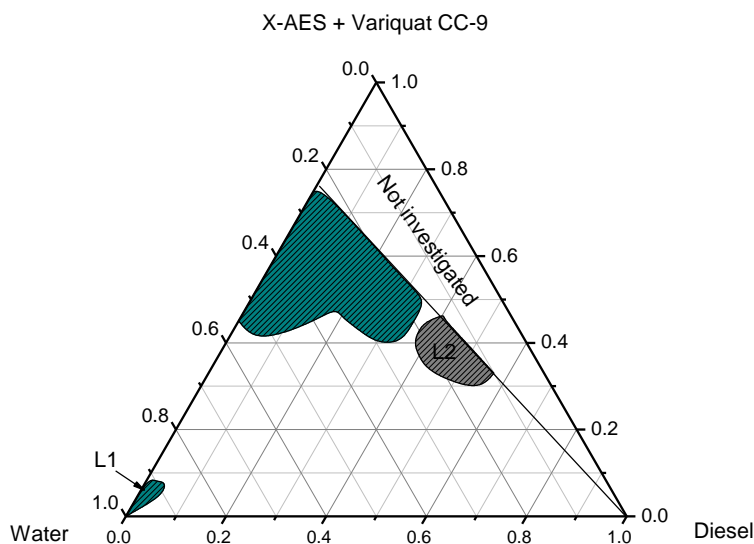


Fig. 4.7: Ternary phase diagram of X-AES:Variquat cc-9/Diesel/Water at 50 °C.

One phase region was shrinking and become smaller by increasing temperature. More surfactants concentration needs to formulate one phase region. As at 25 °C L1 and L2 appears and faint shiny under polarized microscope region appears.

#### 4.6 Acid value for diesel

The addition of alkali to a formulation solution for EOR serves to increase both electrolyte strength and pH. The optimal salinity then will achieve with little amount of NaCl. In addition that using NaOH or sodium carbonate as example of alkali agent help to saponify naphthenic acid present in diesel, so work as alternative surfactants.

Naphthenic acid is unspecific mixture of several cyclopentyl and cyclohexyl carboxylic acids with molecular weight of 120 up to 700 g/ mole. An example of Naphthenic acid is described in Fig. (4.8) below:

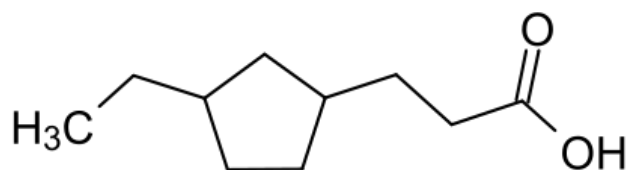


Fig. 4.8: Example of a naphthenic acid.

The composition of naphthenic acid varies with the crude oil composition and the condition during refining and oxidation. Naphthenic acids are present in crude oil and leads to corrosion problems within the oil refineries, so for this reason and to enhance surfactant efficiency we try to convert it to soap.

The acid number of the crude oil (mg of KOH required for neutralizing 1g of oil) is often used as an indicator of the naphthenic / carboxylic acid concentration that could potentially be saponified.

To determine the acidity of diesel as reflection of naphthenic acid and other acids represent in the oil; acid value can be used.

Test method and calculation of acid value for diesel are doing according to USP-34 Pharmacopeia, the result show that acid value for diesel is 0.3 mL of 0.1N NaOH require to neutralize 10g of diesel.

We use sodium borate as alkali agent for further investigation, to optimize formula for core flooding and to draw fish diagram using optimum surfactants combination as in phase diagram early.

Using sodium carbonate as alkali agent have many disadvantages, one of them is precipitation of calcium carbonate when anhydrite is present in the rock. However it may be possible to use sodium metaborate to avoid this problem.

Oil recovery mechanisms in alkali flooding are complicated and there are at least eight postulated recovery mechanisms, these include emulsification with entrainment, emulsification with entrapment, emulsification with coalescence, wettability reversal, wettability gradients, oil-phase swelling, disruption of rigid films and low interfacial tensions.

#### 4.7 Fish diagram

The effect of salt concentration on phase behavior of X-AES with cationic hydrotrope Variquat cc-9 with different ratio, and WOR=1 using diesel as a model oil was noted in order to understand the whole solution behavior of surfactant mixture.

Fig. (4.9) shows the equilibrium phase behavior at ambient condition of oil free aqueous solutions containing many surfactants concentration, varies from 0.01% to 25.0% of surfactants mixture (X-AES:Variquat cc-9 [8:2 wt./wt.]) with a fixed quantity of 0.5% of Sodium borate. In the absence of electrolytes, X-AES exhibits a cloud-point temperature that decreases with increasing surfactant concentration, but here at ambient conditions and with addition electrolyte we see that when surfactants concentration increases precipitation appears at lower electrolyte concentration.

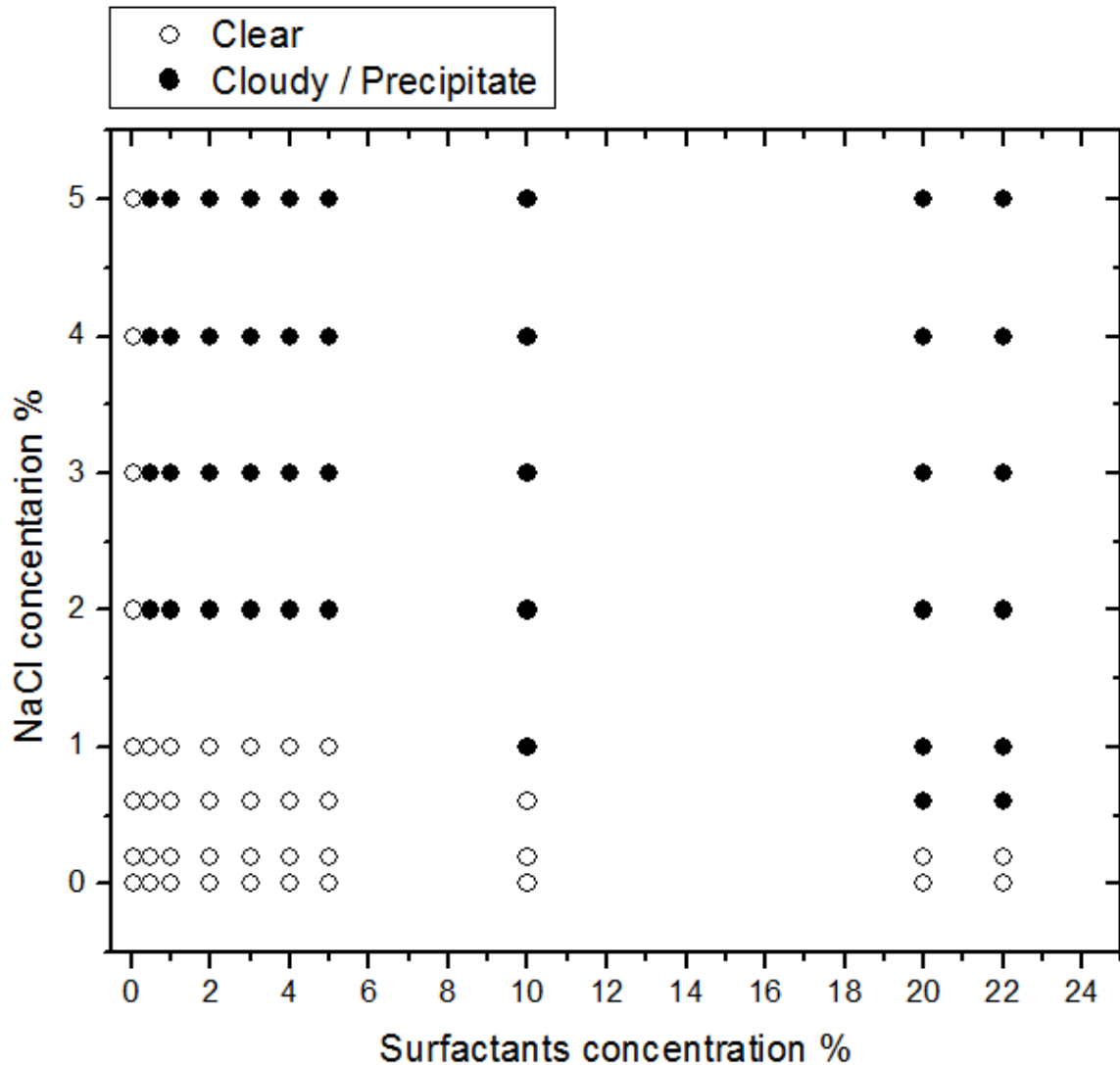


Fig. 4.9: Effect of added NaCl on phase behavior of X-AES:Variquat cc-9 [8:2] and 0.5% sodium borate solution.

Salinity scans (Based on the whole volume) of the above solution equilibrated with equal weight of diesel were prepared at room temperature, the Fig. (4.10) below shows the results.



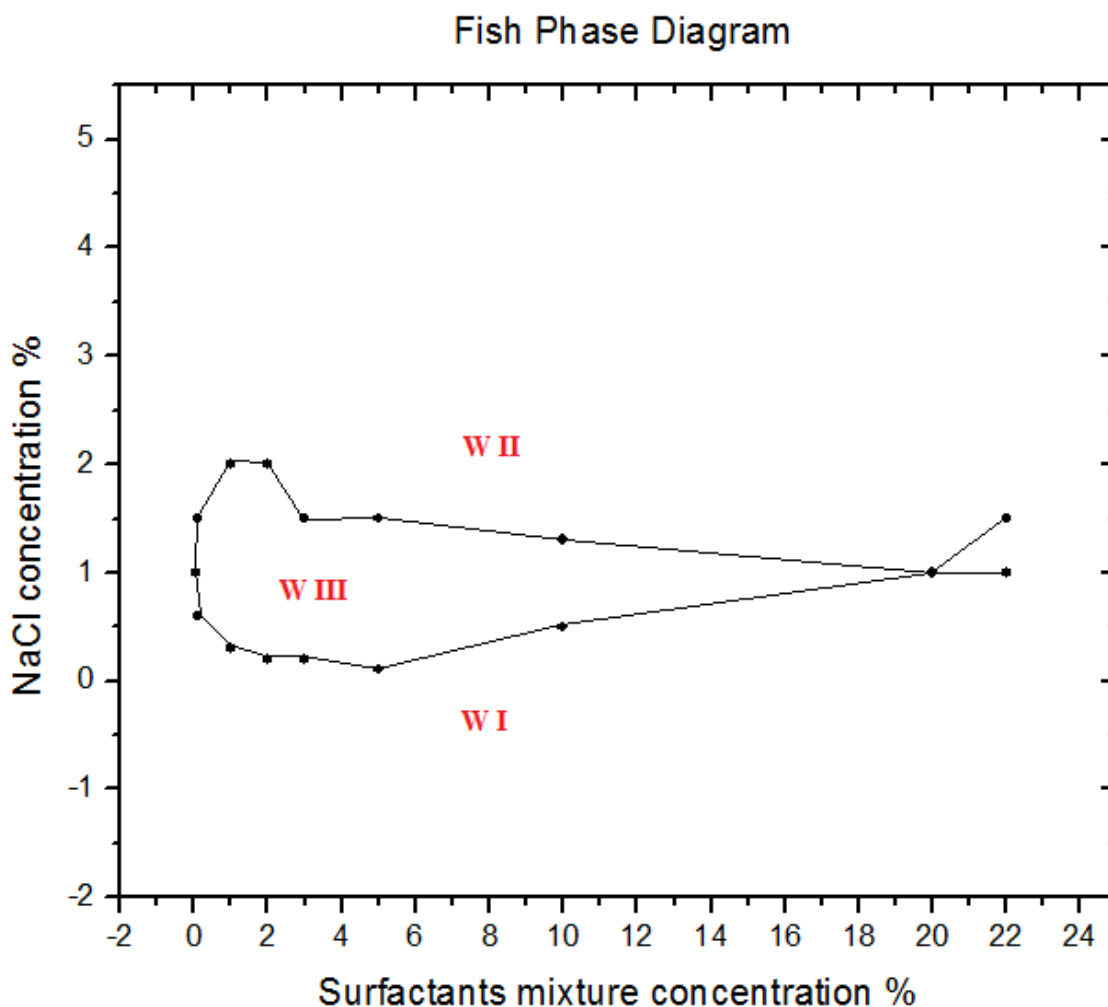


Fig. 4.10: Microemulsion fish phase diagram of X-AES:Variquat cc-9 [8:2] and 0.5% sodium borate using diesel WOR=1.

The minimum surfactants concentration needed to start forming middle phase was 0.05 wt.%, and the minimum surfactants concentration needed to form one phase (Winsor IV) was 20.0 wt.% of surfactants mixture. The equilibrium time was reached within 15 days.

Phase behavior at ambient temperature of salinity scan containing 0.50 wt.% of X-AES 71%, Variquat cc-9 (8:2 wt./wt.) with equal weight ratios of water and diesel was observed. Fig. (4.11) shows a typical Winsor I, III and II microemulsion sequence using sodium chloride from 1.0% at the left hand up to 8.0% at right hand, the optimum salinity was shown at 3.0% of NaCl and equilibrium was reached within 15 days.

To understand phase behavior of X-AES with addition of hydrotrope (Variquat cc-9) and sodium borate, blank solution was prepared to investigate the effects of Variquat cc-9 and sodium borate on phase behavior.

In the absence of variquat cc-9 salinity scan of 1.0 % of X-AES was investigated with WOR=1 with diesel as module, the salinity scan of (0.0 – 4.5 wt.%) were tested, the middle phase appears with optimum salinity at 2.0% of NaCl, and no effect for the addition of Variquat cc-9 on optimum salinity, whereas addition of sodium borate cause a slightly shift in optimum salinity.

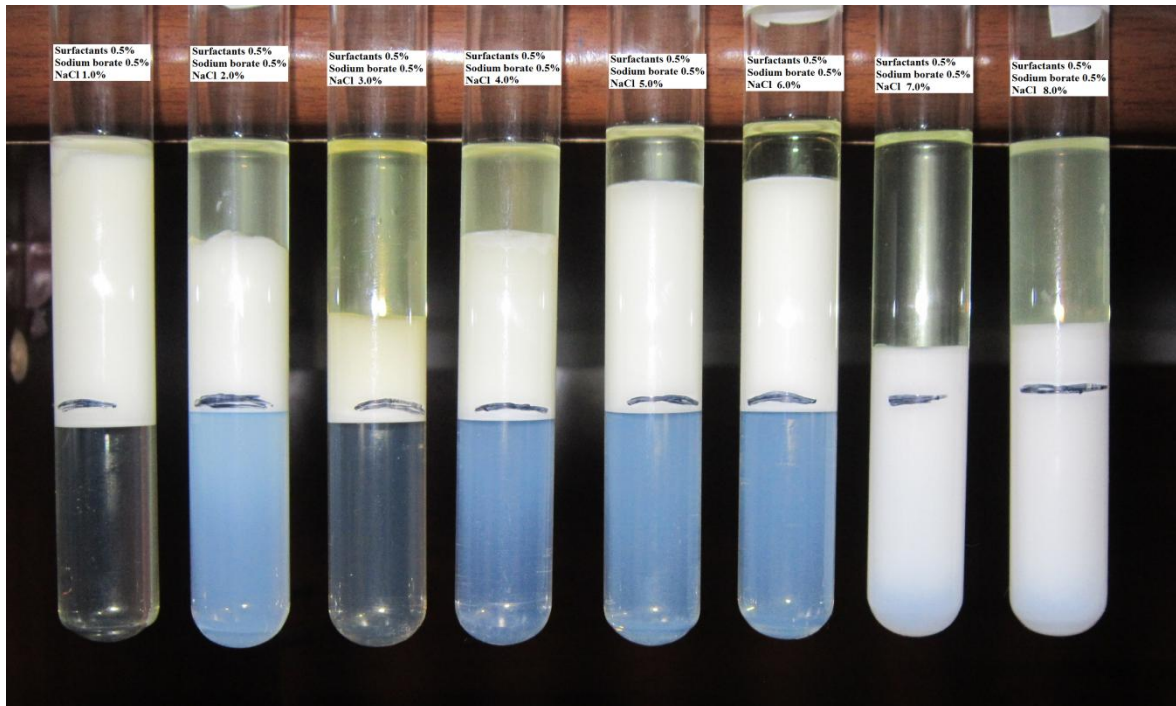


Fig. 4.11: Salinity scan for 0.50% X-AES, Variquat cc-9 (8:2 wt./wt.), with diesel, WOR = 1.

### Effect of sodium hydroxide and sodium carbonate

The phase behavior experiments reported tested the addition of sodium hydroxide and sodium carbonate in combination with surfactants. The focus of this research was on sodium borate which is the primary alkali chemical used for these experiments. Diesel contains naphthenic acids that may saponify upon the addition of sodium borate and generate in-situ soap. The addition of sodium carbonate is desirable because it has been shown to reduce anionic surfactant adsorption on reservoir rocks (Jackson, 2006). One of disadvantage of use sodium carbonate is the precipitation of sodium carbonate after the dissolution of high concentration of calcium in brine water around reservoir.

Fig. (4.12) show the salinity scan for 1.0% of surfactants mixture (X-AES 71% + Variquat cc-9 [8:2] wt./wt.) with 0.5% as a constant individual quantity of sodium borate, sodium hydroxide and sodium carbonate, it has been shown that no Winsor III was formulated with this quantity of alkaline agent, this because of high quantity of sodium ion in formulation. This problem can be go over by decreasing the alkaline agent used, considering acid value for oil used. On the other hand optimum salinity of the system can be changed according to salinity of reservoir by varying the alkalinity agent or its concentration.

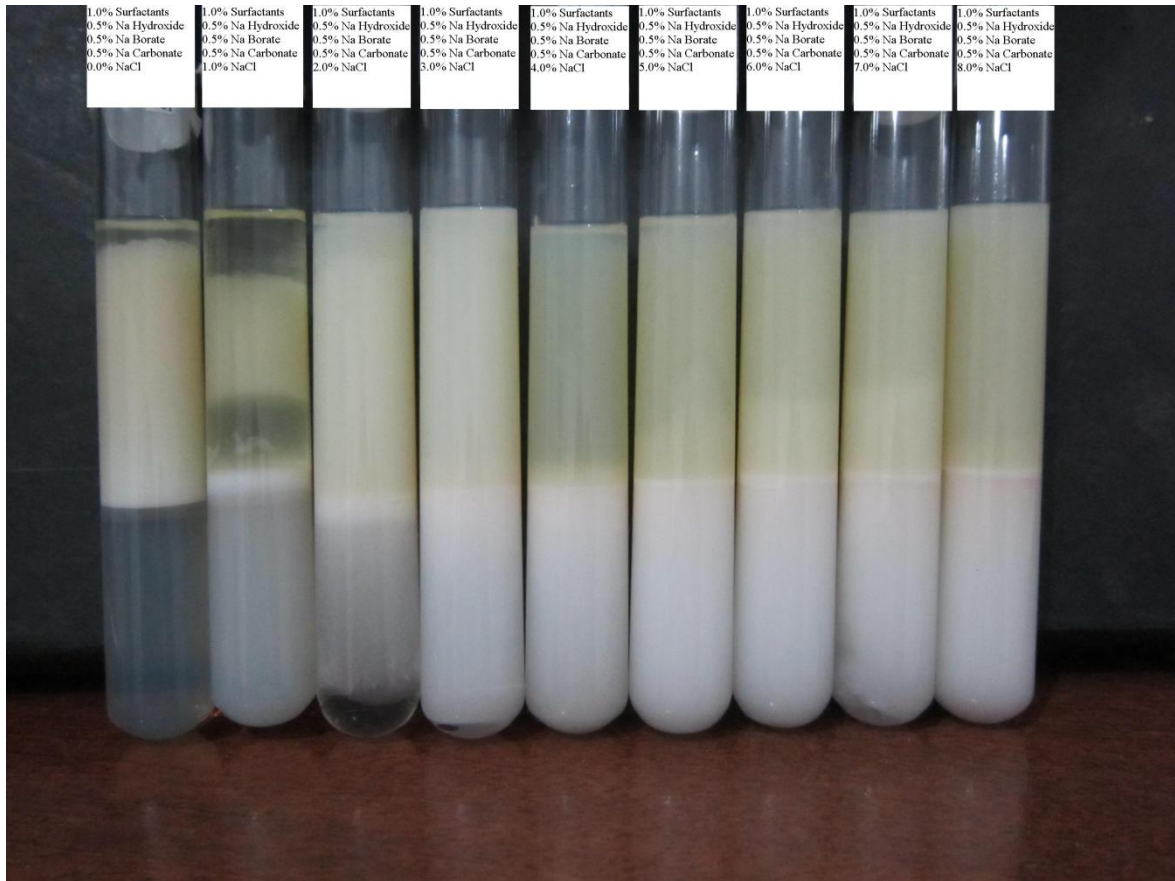


Fig. 4.12: Salinity scan after equilibration of equal volumes of diesel and aqueous solutions containing 1.0 wt.% X-AES, Variquat cc-9 (8:2 wt./wt.), and wt.% NaCl as indicated.

These results indicate that alkali addition contributes electrolytes to act as a NaCl equivalent.

One of the challenge in EOR fluid is to find surfactant blends that reach optimum salinity at a total dissolved solid (TDS) < 12000 ppm, so the effects of surfactants mixture ratio were studied, using (1:1) wt. /wt. of X-AES 71% and Variquat cc-9, the results shown in Fig. (4.13) below.

Salinity scan of 1.0% of surfactants (X-AES 71% + Variquat cc-9 [1:1]) is shown below, there is no clear Winsor III microemulsion formed with this surfactants combination ratio.

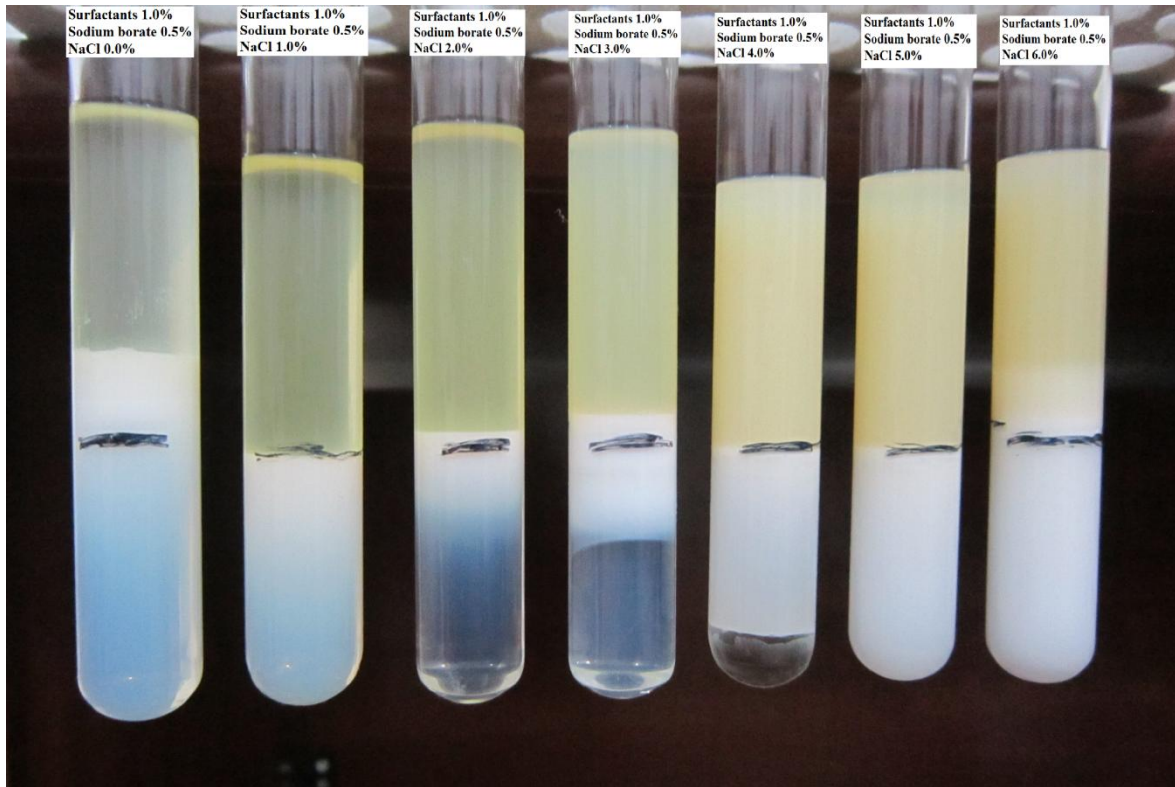


Fig. 4.13: Salinity scan for 1.0% X-AES, Variquat cc-9 (5:5 wt./wt.), with diesel, WOR = 1.

In general for actual field reservoir, the optimal salinity must match salinity field brine.

### Calculation of IFT ( $\gamma$ ) and Solubilization Parameter

Interfacial tension ( $\gamma$ ) and solubilization ratio can be calculated using Huh equation that describes relationship between solubilization ratio and IFT as follow:

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

Solubilization ratios were introduced to describe the microemulsion phase behavior– Phase behavior testing seeks to establish the salinity where the Winsor type III middle phase microemulsion is largest (i.e. maximum volume oil and water solubilized per volume surfactant).

Winsor III microemulsion needs in general a solubilization ratio equal to or greater than 10 at optimal salinity, and an equilibration time of less than 7 days to be suitable for EOR process.

Table 4.1 below show the result of IFT measurement for a system of X-AES (71%)/Variquat cc-9 (4:1) wt.% WOR=1 with fixed amount of Sodium borate 0.5% at 25°C using Huh equation [ $\gamma_o = C/(V_o/V_s)^2$ ,  $\gamma_w = C/(V_w/V_s)^2$ ], with assuming  $C = 0.3$  mN/m and all surfactants in the middle phase.

Where  $\gamma_o$  is the IFT between the oil phase and surfactant phase, and  $(V_o/V_s)$  is the ratio of solubilized oil to the volume of total surfactant and  $\gamma_w$  is the IFT between the water phase

and surfactant phase, ( $V_w/V_s$ ) is the ratio of solubilized water to the volume of total surfactant.

The oil solubilization ratio is applied for Winsor type I and type III behavior, where as water solubilization ratio is applied for Winsor type III and type II behavior.

According to Huh equation a solubilization ration of 10 or greater corresponds to an IFT of 0.003 dynes/ cm or lower. This typically the target IFT necessary to recover residual oil.

Table 4.1: Solubilization ratio and interfacial tension IFT for a system containing 1.0% of X-AES (71%)/Variquat cc-9 (4:1) wt. % WOR=1 with fixed amount of Sodium borate 0.5% at 25°C.

Salinity NaCl %	Solubilization		IFT using Chun-Huh equation $C=0.3$ mN/m	
	$V_o/V_s$	$V_w/V_s$	$\gamma_o$	$\gamma_w$
2.0	21.0	29.0	$6.8 \times 10^{-4}$	$3.6 \times 10^{-4}$
3.0	26.5	25.3	$4.3 \times 10^{-4}$	$4.7 \times 10^{-4}$
4.0	31.4	22.5	$3.0 \times 10^{-4}$	$5.9 \times 10^{-4}$
5.0	32.4	18.1	$2.9 \times 10^{-4}$	$9.2 \times 10^{-4}$

Fig. (4.14) below show the relation between IFT and NaCl concentration, it shows that IFT between diesel and middle phase  $\gamma_o$  decrease from  $6.8 \times 10^{-4}$  to  $2.9 \times 10^{-4}$  by increasing salinity, while IFT between water and middle phase  $\gamma_w$  increase with increasing salinity, from  $3.6 \times 10^{-4}$  to  $9.2 \times 10^{-4}$ .

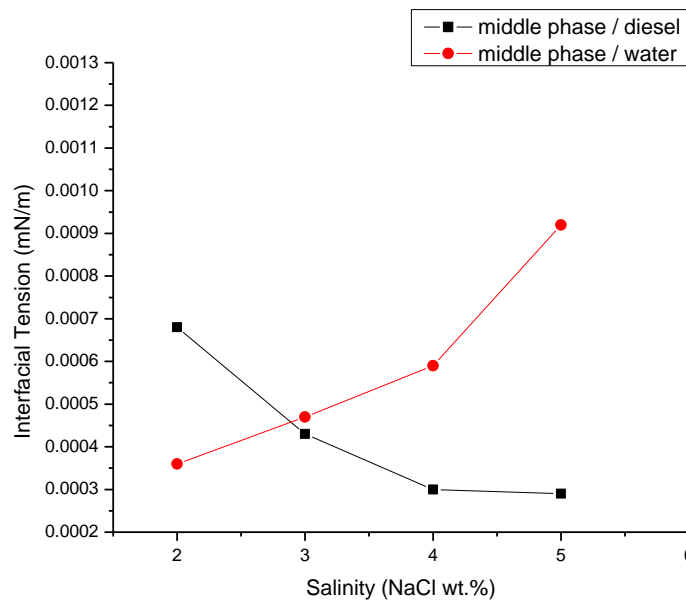


Fig. 4.14: IFT versus NaCl wt.%, for a system of 1.0% AES:Variquat cc-9 (4:1) wt.% ratio, WOR= 1 with fixed quantity of Sodium borate 0.5%.

Table 4.1 and Fig. (4.14) show ultralow interfacial tension, which mean this system is applicable in many industrial field that need ultralow IFT for their formulation.

#### 4.8 Surfactants adsorption onto Kaolin Clay

Adsorption is an important physical process leading to surfactant loss during a surfactant EOR flooding, so surfactants adsorption onto positively charged kaolin clay is evaluated in terms of estimation of material loss in the rock during fluid flow.

Adsorption of X-AES with Variquat cc-9 (8:2 wt/wt) surfactants onto kaolin clay was measured at 25 °C and the results are shown below in Table 4.2.

The long hydrophobic chain in X-AES that contains polypropylene oxide group make surfactant more hydrophobic chain, this weakens the interaction between the polar head of surfactant molecules and the specific sites on the kaolin clay surface (Wu, et al., 2010), that's because adsorption of surfactants on solid surfaces can modify their hydrophobicity and surface charge (Zhang and Somasundaran, 2006).

Table 4.2: Surfactants adsorption on Kaolin clay

	Surfactants concentration %			
	0.5	1.0	5.0	10.0
Adsorption of surfactants on kaolin Clay [mg/g]	0.0	5.0	30.0	26.0

We see from the above results in table 4.2 that when the surfactants concentration increase, the quantity of surfactants adsorbed on kaolin clay as a module increases. Whereas at 0.5% surfactants the adsorption was zero, this give this formula another advantage, since there is no loss at low concentration of surfactants.

Fig. (4.15) below show the ideal curve for adsorption isotherm, which is identical to our result in Fig. (4.16) which illustrate the S-shape of surfactants adsorption.



## Adsorption isotherm

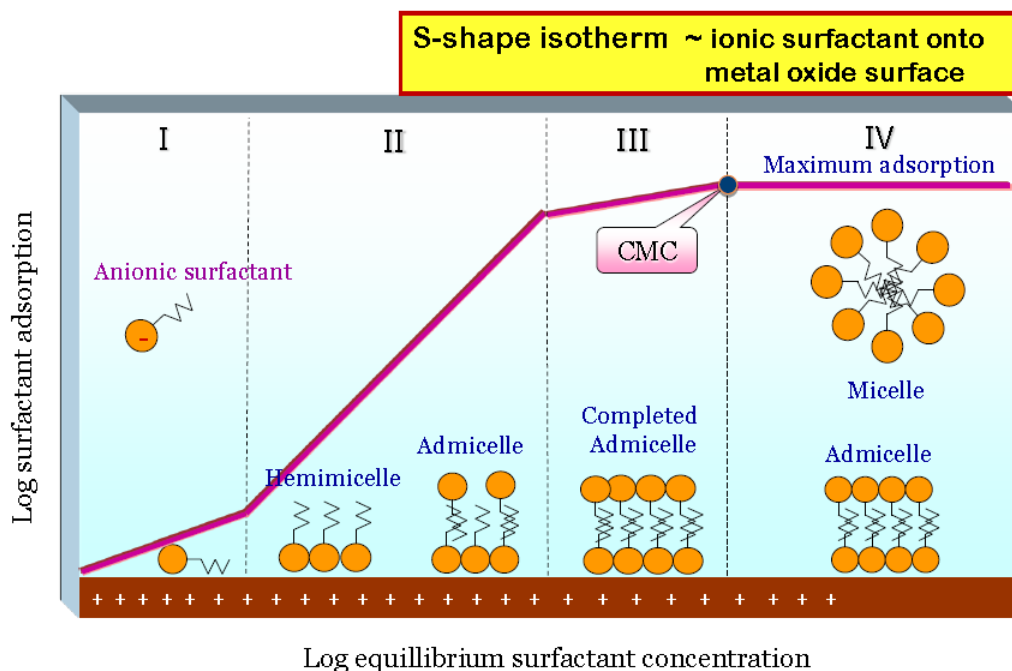


Fig. 4.15: S-shaped adsorption isotherm for an ionic surfactant on an oppositely charged substrate.

The adsorption of surfactants (X-AES + Variquat cc-9 8:2 wt./wt.) onto kaolin clay is shown in Fig. (4.16) below:

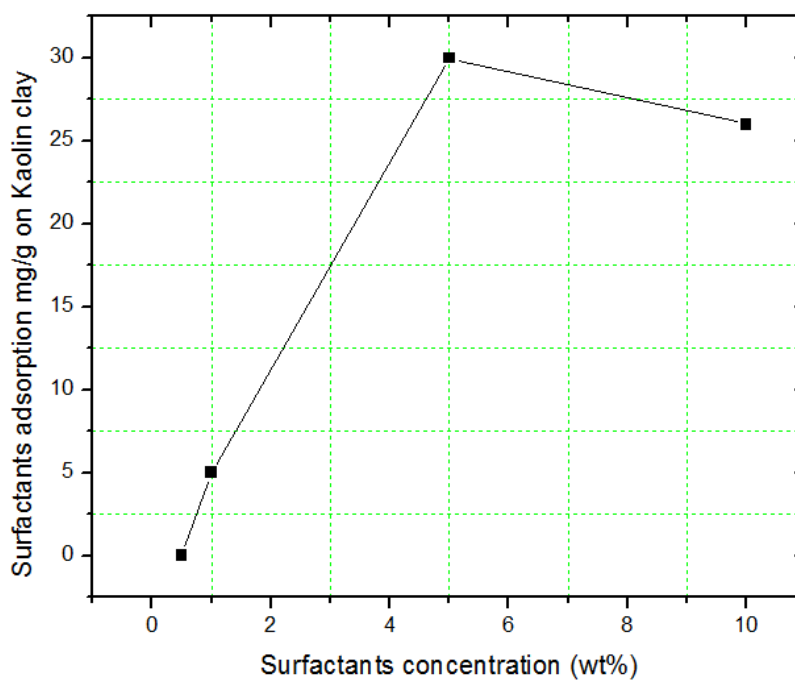


Fig. 4.16: Adsorption of X-AES : Variquat cc-9 (8:2 wt./wt.) onto kaolin clay.

From Fig. (4.16), it can be seen that the adsorption isotherms of surfactants demonstrate the classical S-shaped isotherm. In spite of strong affinity of sulfate head group for

adsorption on positively charged surface, the adsorbed quantity of surfactants can be neglected.

The magnitude of surfactants adsorption increases by increasing the surfactants concentration up to 30mg/g at 5% then decreases to 26mg/g at 10%, this trend due to the two mechanisms of surfactant adsorption, one at low bulk surfactant concentration, which is due to the interaction between the polar head of the amphiphile molecule and some specific site of the surface. The second mechanism at higher bulk surfactant concentrations, aggregates are formed at the interface as a result of lateral interactions between hydrophobic chains. On the other hand, adsorption of surfactant on mineral surfaces also depends on many factors, several physiochemical processes can be expected to occur, such as ion-exchange, electrostatic adsorption and dissolution of the clay constitute. At high concentration of surfactants when micelles formed it can dissolve some of the complex precipitate on the surface. As a result, the adsorption decreases at high concentrations.



# **Chapter Five**

## **Summary and Conclusion**

The research helped to understand many of the objectives that motivated this work in the field of chemical EOR.

Systematic experiments were done to observe the phase behavior of extended surfactant with diesel for EOR applications. Phase behavior observations used to screen surfactants for favorable attributes such as low microemulsion viscosity, short equilibration time, ultralow IFT and absence of viscous gel or macroemulsions.

A systematic study with phase behavior experiments helped understand how different chemical components and environmental conditions affect microemulsion properties and phase behavior performance.

Co-surfactants as cationic hydrotrope, alkali can be added to improve performance. Additional information such as optimum salinity, surfactants adsorption and solubilization ratios used to optimize formula.

## 5.1 Conclusion

Alkyl polyethylene oxide polypropylene oxide sodium sulfate extended surfactant is promising surfactant to use in EOR and SEAR applications. Presence of polyethylene oxide and polypropylene oxide within the surfactant structure give it unique properties with high solubilization capacity.

Extended anionic surfactant (X-AES) combined with a short chain cationic hydrotrope (Variquat cc-9) 4:1 wt./wt. produced middle phase microemulsion at low surfactants concentrations 0.05 wt.% without alcohol and with high solubilization capacity and ultra low IFT values, 0.0004 mN/m or less, measured between brine and diesel. Minimize the depletion of the injected surfactant, can be achieved using these combination of surfactants (Alkyl polyethylene oxide polypropylene oxide sodium sulfate and Variquat cc-9).

We are able to form both Winsor type III and IV microemulsions at ambient conditions without the addition of alcohols and at relatively low electrolyte concentrations.

Generally, adsorption of these surfactants on Kaolin Clay increases with an increase in surfactants concentrations.

In the absence of electrolytes, X-AES exhibits a cloud-point temperature that decreases with increasing surfactant concentration, but here at ambient conditions and with addition of electrolyte we see that when surfactants concentrations increase precipitation appears at lower electrolyte concentration.

Several alkali types were tested in phase behavior to determine how they can affect phase behavior parameters. Sodium borate found to has advantages over NaOH and Na<sub>2</sub>CO<sub>3</sub> since it is efficient to saponify Naphthenic acid present in diesel and has low pH range comparing to other alkali agents which prevent surfactants damage at high pH range. Another benefit for using sodium borate preventing Calcium ions precipitation.

## **5.2 Future work**

The optimum formulation as mentioned above can be applied in EOR and SEAR efficiently at low surfactants concentrations, it seems promising to contribute to future commercial projects or flooding experiments.

## References

1	Alvarado, V. Manrique, E. (2010): “Enhanced oil recovery: An update review”. <i>Energies</i> , <b>3</b> . pp. 1529-1575.
2	Arpornpong, N. Charoensaeng, A. Sabatini, D. Khaodhiar, S. (2010): “Ethoxy carboxylate extended surfactant: Micellar, adsorption and adsolubilization properties”. <i>Journal of Surfactants and Detergents</i> , <b>13</b> . pp. 305-311.
3	Do, L. Withayyapayanon, A. Harwell, J. Sabatini, D. (2008): “Environmentally friendly vegetable oil microemulsions using extended surfactants and linkers”. <i>Journal of Surfactants and Detergents</i> , <b>12</b> . pp. 91-99.
4	<b>Enhanced oil recovery information</b> (April, 1986): National Institute for Petroleum and Energy Research. Oklahoma
5	Flaaten, A. (2007): <b>Experimental study of microemulsion characterization and optimization in enhanced oil recovery: A design approach for reservoirs with high salinity and hardness</b> . University of Texas, Austin.
6	Fountain, J. Starr, R. Middleton, T. Beikirch, M. Taylor, C. Hodge, D. (1996): “A controlled field test of surfactant-enhanced aquifer remediation”. <i>Ground Water</i> , <b>34-5</b> . pp. 910-916.
7	Goodwin, J. W. (2004): <b>Colloids and interfaces with surfactants and polymers – An introduction</b> , First edition. John Wiley and Sons, Ltd., England.
8	Gurgel, A. Moura, M. Dantas, T. Barros Neto, E. Dantas Neto, A. (2008): “A review on chemical flooding methods applied in enhanced oil recovery”. <i>Brazilian Journal of Petroleum and Gas</i> , <b>2</b> . pp. 83-95.
9	Jackson, A. (2006): <b>Experimental study of the benefits of sodium carbonate on surfactants for enhanced oil recovery</b> . University of Texas, Austin.
10	Kanan, K. Yousef, H. Kayali, I. (2012): “Nanostructured microemulsion phase behavior using AOT or extended surfactant combined with cationic hydrotrope”. <i>Journal of Surface Engineered Materials and Advanced Technology</i> , <b>2</b> . pp. 53-60.
11	Kanicky, J. Lopez-Montilla, J. Pandey, S. Shah, D. (2001): Surface chemistry in the petroleum industry. In: K. Holmberg (Editor). <b>Handbook of Applied Surface and Colloid Chemistry</b> (pp. 251-267). John Wiley and Sons, Ltd., England.
12	Kayali, I. Liu, S. Miller, C. (2010): “Microemulsions containing mixtures of propoxylated sulfates with slightly branched hydrocarbon chains and cationic surfactants with short hydrophobes or PO chains”. <i>Colloids and Surfaces A: Physicochemical and Engineering Aspects</i> , <b>354</b> . pp. 246-251.
13	Kayali, I. Qamhieh, K. Habjoqa, F. AlBawab, A. Olsson, U. Bemert, L. Strey, R. (2012): “Phase behavior of microemulsions formulated with sodium alkyl polypropylene oxide sulfate and a cationic hydrotrope”. <i>Journal of Dispersion Science and Technology</i> , <b>33</b> . pp. 369-373.
14	Kayali, I. Qamhieh, K. Olsson, U. (2010): “Microemulsion phase behavior of aerosol-ot combined with cationic hydrotrope in the dilute region”. <i>Journal of Dispersion Science and Technology</i> , <b>31</b> . pp. 183-187.

15	Kayali, I. Qamhieh, K. Olsson, U. (2011): "Formulating middle phase microemulsions using extended anionic surfactant combined with cationic hydrotrope". <i>Journal of Dispersion Science and Technology</i> , <b>32</b> . pp. 41-46.
16	Kayali, I. Qamhieh, K. Olsson, U. Bemert, L. Strey, R. (2012): "Water-diesel microemulsions stabilized by an anionic extended surfactant and a cationic hydrotrope". <i>Journal of Dispersion Science and Technology</i> , <b>33</b> . pp. 516-520.
17	Klaus, A. Tiddy, G. Rachel, R. Trinh, A. Maurer, E. Touraud, D. Kunz, W. (2011): "Hydrotrope-Induced inversion of salt effects on the cloud point of an extended surfactant". <i>American Chemical Society</i> , <b>27</b> . pp. 4403-4411.
18	Klaus, A. Tiddy, G. Touraud, D. Schramm, A. Stuhler, G. Drechsler, M. Kunz, W. (2009): "Phase behavior of an extended surfactant in water and a detailed characterization of the dilute and semidilute phases". <i>American Chemical Society</i> , <b>26-8</b> . pp. 5435-5443.
19	Klaus, A. Tiddy, G. Touraud, D. Schramm, A. Stuhler, G. Kunz, W. (2010): "Phase behavior of an extended surfactant in water and a detailed characterization of the concentrated phases". <i>American Chemical Society</i> , <b>26-22</b> . pp. 16871-16883.
20	Lee, K. (November, 2010): <b>Applications and use of microemulsions</b> . Department of Chemical Engineering and Chemical Technology, Imperial College London.
21	Martel, R. Gelin, P. (February, 1996): "Surfactant solutions developed for NAPL recovery in contaminated aquifers". <i>Ground Water</i> , <b>34</b> . pp. 143-154.
22	Minana-Perez, M. Graciaa, A. Lachaise, J. Salager, J. (1995): "Solubilization of polar oils with extended surfactants". <i>Colloids and Surfaces A: Physicochemical and Engineering Aspects</i> , <b>100</b> . pp. 217-224.
23	Minana-Pereze, M. Graciaa, A. Lachaise, J. Salager, J. (1996): System containing mixtures of extended surfactants and conventional nonionics – Phase behavior and solubilization in microemulsion. In: Roger de Lluria (Editor), <i>World Surfactants Congress</i> , June 3-7 1996. A.E.P.S.A.T., Spain. pp. 226-234.
24	Moulik, S. Rakshit, A. (2006): "Physicochemistry and applications of microemulsions". <i>Journal Science Technology</i> , <b>22</b> . pp. 159-186.
25	Mulligan, C. Yong, R. Gibbs, B. (2001): "Surfactant-enhanced remediation of contaminated soil: a review". <i>Engineering Geology</i> , <b>60</b> . pp. 371-380.
26	Phan, T. Attaphong, C. Sabatini, D. (2011): "Effect of extended surfactant structure on interfacial tension and microemulsion formation with triglycerides". <i>Journal of American Oil Chemical Society</i> , <b>88</b> . pp. 1223-1228.
27	Pillai, V. Kanicky, J. Shah, D. (1999): Applications of microemulsions in enhanced oil recovery. In: P. Kumar, K. Mittal (Editor). <b>Handbook of microemulsion science and technology</b> (pp. 743-754). Marcel Dekker, Inc. New York.
28	Quintero, L. Clark, D. Salager, J. Forgiarini, A. (23 July, 2009): "Mesophase fluids with extended chain surfactants for downhole treatments". United States Patent, Pub. No.: US 2009/0183877 A1.
29	Salager, J. (1977): <b>Physico-chemical properties of surfactant-water-oil mixtures: Phase behavior, microemulsion formation and interfacial tension</b> . University of Texas, Austin.
30	Salager, J. Anton, R. Sabatini, D. Harwell, J. Acosta, E. Tolosa, L. (January,

	2005): “Enhancing solubilization in microemulsions – State of the art and current trends”. <i>Surfactants and Detergents</i> , <b>8-1</b> . pp. 3-21.
31	Shan, D. Sharma, M. (1985): <b>Introduction to Macro- and microemulsions</b> . Departments of Chemical Engineering and Anesthesiology, University of Florida, Gainesville, FL 32611.
32	Smith, G. Hand, K. (21 September 2006): “Enhanced solubilization using extended chain surfactants”. United States Patent, Pub. No.: US 2006/0211593 A1.
33	Velasquez, J. Scorzza, C. Vejar, F. Forgiarini, A. Anton, R. Salager, J. (2010): “Effect of temperature and other variables on the optimum formulation of anionic extended surfactant-alkane-brine systems”. <i>Journal of Surfactants and Detergents</i> , <b>13</b> . pp. 69-73.
34	Witthayapanyanon, A. Acosta, E. Harwell, J. Sabatini, D. (2006): “Formulation of ultralow interfacial tension systems using extended surfactants”. <i>Journal of Surfactants and Detergents</i> , <b>9</b> . pp. 331-339.
35	Witthayapanyanon, A. Harwell, J. Sabatini, D. (2008): “Hydrophilic-Lipophilic deviation (HLD) method for characterizing conventional and extended surfactants”. <i>Journal of Colloid and Interface Science</i> , <b>325</b> . pp. 259-266.
36	Witthayapanyanon, A. Phan, T. Heitmann, T. Harwell, J. Sabatini, D. (2010): “Interfacial properties of extended-surfactant-based microemulsions and related macroemulsions”. <i>Journal of Surfactant and Detergent</i> , <b>13</b> . pp. 127-134.
37	Wu, Y. Lglauer, S. Shuler, P. Tang, Y. Goddard, W. (2010): “Branched alkyl alcohol propoxylated sulfate surfactants for improved oil recovery”. <i>Tenside Surfactants and Detergents</i> , <b>47</b> . pp. 152-161.
38	Zhang, R. Somasundaran, P. (2006): “Advances in adsorption of surfactants and their mixtures at solid/solution interfaces”. <i>Advances in Colloid and Interface Science</i> , <b>123-126</b> . pp. 213-229.

## **Appendices**

### **Definition**

These are some definition used in this research thesis:

The glossary from National Institute for Petroleum and Energy Research was used as a basis for these definitions.

**Acid number:** A measure of reactivity of crude oil with caustic solution, in terms of milligrams of potassium hydroxide that are neutralized by one gram of crude oil.

**Adsorption:** The physical/chemical phenomenon whereby a molecule or aggregate of molecules attaches itself to the rock surface.

**Aquifer:** A subsurface rock interval that will produce water; many oil reservoirs are under laid by an aquifer.

**Capillary forces:** Interfacial forces between immiscible fluid phases, resulting in pressure differences between the two phases.

**Caustic consumption:** The amount of caustic lost from reacting chemically with the minerals in the rock, the oil, and the brine.

**Corefloods:** Laboratory flow test through small samples (cores) of porous rock.

**Displacement efficiency:** Ratio of the amount of oil moved from the zone swept by the recovery process to the amount of oil present in the swept zone prior to start of the process.

**Lithology:** The geological characteristics of the reservoir rock.

**Modified alkaline flooding:** The addition of a cosurfactant and/or polymer to the alkaline flooding process.

**Non-Newtonian:** A fluid that exhibits a change of viscosity with flow rate.

**Preflush:** A conditioning slug injected into a reservoir as the first step of an EOR process.

**Pressure gradient:** Rate of change of pressure with distance.

**Reservoir:** A rock formation below the earth's surface containing petroleum or natural gas.

**Reservoir simulation:** Analysis and prediction of reservoir performance with a computer model.

**Retention:** The loss of chemical components due to adsorption onto the rock's surface, precipitation, or to trapping within the reservoir.

**Screening guide:** A list of reservoir rock and fluid properties critical to an EOR process.

**Slug:** A quantity of fluid injected into a reservoir during enhanced oil recovery.

Stripper well: A well that produces (strips from the reservoir) less than 10 barrels of oil per day.



## Arabic abstract

سلوك المواد الفعالة على السطوح من النوع الممتد حديثة التطوير: أهم التطبيقات في تحسين عمليات استخراج النفط وتنقية المياه الجوفية.

لقد تم دراسة سلوك المواد الفعالة على السطوح حديثة التطوير (X-AES) مع استخدام كمية صغيرة من المواد موجبة الشحنة قصيرة الذيل وامكانية تطبيقها في تحسين عملية استخراج النفط وتنقية المياه الجوفية. الهدف الأساسي في هذه الدراسة هو تحضير مستحلب يمتاز بقدرة عالية على استخلاص النفط الخام. استخدام نظام الشكل الثلاثي، البحث الملحي، التوتر السطحي بين الطبقات والإدمصاص استخدمت للمفاضلة بين التراكيب. كما أنه تم استخدام النظر والضوء المستقطب لتمييز وتعيين المناطق المتباينة الخواص. بينت النتيجة أن استخدام خليط من المواد الفعالة على السطوح بنوعيتها الممتد وقصيرة الذيل مفضل في حالة استخراج النفط الخام حيث يمكن أن يؤدي إلى توتر سطحي منخفض بين السطوح عند درجة الملوحة المثالية. أقل كمية من المواد الفعالة على السطوح يمكنها تكوين نظام متوسط هي 0.05% كما ويمكن الغاء كمية المواد الفعالة على السطوح الممتصة على السطح عند هذا الحد من التركيز. إن قراءة التوتر السطحي المقاس نظريا كانت 0.0004 م-نيوتن لكل م بين الديزل والمحلول الملحي. هذه المواد الفعالة على السطوح يمكن اعتبارها على أنها مواد واعدة بناء على طرق التقييم المستخدمة.