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Phase Behavior of Extended Surfactant with Cationic Hydrotrope

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M.Sc Thesis

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Phase behavior of extended surfactant with cationic hydrotrope

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Dedication

I would like to dedicate this work to my father Husam and my mother Rehab, and my husband, Dr. Sami Al-bahar and my beloved children Asma` and Qays, and my brothers Yousef and Younis , and my sisters Ola and Fathiya, in recognition of their efforts for encourage me to complete this master thesis…thank you all…

Hala H Y Sheqwar

Declaration

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

Signed:____________________.

Hala Husam Eldden Yousef (sheqwara) Bahar

Date: / /2010

Acknowledgment

First of all I thank God, the merciful and the passionate, who gave me the strength and patience in order to fight the first degree of science.

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I do not forget of course graciousness of my family, my father and my mother for life-long support and praying to demand luck and success for me, their firm and kind-heart personality has affected me deeply.

My devoted husband Dr. Sami Albahar who gave me love affection and support without complain. And gave me the appropriate conditions to study, in order to complete my thesis. This work would not have happened without his contribution, **Thank you Sami.**

Big love to my beloved children Asma` and Qais who were the background of my full happiness.

Abstract

Phase behavior for systems containing Sodium bis (2- ethylhexyl sulfosuccinate) (AOT), with the cationic hydrotrope, Tetraethyl ammonium chloride (TEAC) in the presence of water and heptane were studied. Formulations of microemulsion for such systems and for systems containing the so called "extended surfactant" were carried out at different salt concentrations. Anisotropy was detected using cross polarizers and polarized microscopy. Ultralow interfacial tension for microemulsion were measured, first theoretically using Chun-Huh equation, and then experimentally using spinning drop experiments.

The presence of short chain hydrotropes (TEAC) was found to destabilize the liquid crystalline region, present in AOT/water/heptane phase diagram. Ultralow interfacial tension were found for the microemulsion formulated with surfactant concentration as low as 0.5% for both AOT and "extended surfactant" systems.

The effect of temperature on the phase behavior of microemulsion formed with AOT system was studied and found to behave in opposite manner compared to the nonionic surfactant.

For both systems formation of alcohol free microemulsion were configured, at low surfactants mixture concentration, and low salt concentration, which are applicable in most applied and chemical processing such as EOR and SEAR where presence of alcohol complicates the mentioned fields.

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Abbreviations

HLB	Hydrophilic Lipophilic Balance
CMC	Critical micelle concentration.
PIT	Phase inversion temperature.
L1	Normal micelle.
L2	Inverse micelle.
LC	Liquid crystal.
O\W	Oil in water microemulsion.
W\O	Water in oil microemulsion.
IFT	Interfacial tension.
Catanionic	Cationic-anionic surfactant mixture.
WOR	Water: oil ratio.
AOT	Sodium bis (2-ethylhexyl) sulfosuccinate (Aerosol)
TEAC	Tetra ethyl ammonium chloride.
EOR	Enhanced oil recovery.
SEAR	Surfactant enhanced aquifer remediation.

Chapter One
Introduction

Chapter one

1. Introduction

1.1 Surfactants

Surfactants are a blend of "**surf**ace **act**ing **a**ge**nt**" [Rosen, 2004][1]. They are usually organic compounds that are amphiphilic, because they contain both non polar hydrophobic groups (their "tails") which is in general a hydrocarbon chain of the alkyl or alkylbenzene type, sometimes with halogen atoms and even a few nonionized oxygen atoms , and polar hydrophilic groups (their "heads") contain O, S, P, or N Fig. (1.1), included in functional groups such as alcohol, thiol, ether, ester, acid, sulfate, sulfonate, phosphate, amine, amide etc. Therefore, they are soluble in both organic solvents and water. They have tendency to migrate at interface because of there dual polar –apolar affinity, so that the polar group lies in water and the apolar group is placed out of it, and eventually in oil. Fig. (1.2)

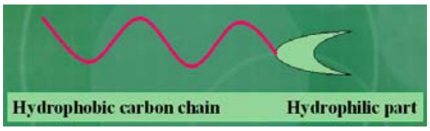


Figure 1.1: Schematic illustration of surfactant molecule.

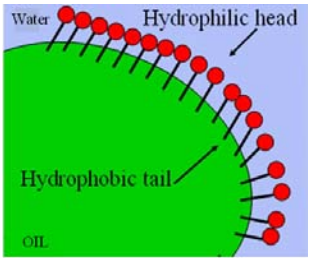


Figure 1.2: Surfactant molecules tend to adsorb to the surface of oil droplets. The hydrophilic heads stick out into the water phase, while the hydrophobic tails stick into the oil phase.

1.2 Classifications of surfactants

Surfactants are commonly classified into four categories, according to the presence of charged groups in its head [Clint, 1992][2]: anionic (negatively charged), cationic (positively charged), nonionic (uncharged) and amphoteric (presents both positive and negative charges at a neutral pH).
1- **Anionic** surfactants which have negative charge when ionized in solution such as a sulfate, sulfonate, or carboxylate (soap) group attached to them.
2- **Cationic** surfactants that have positive charge in their head group, for example the quaternary ammonium groups which are widely used,
3- **Nonionic** surfactants that do not provide ions in aqueous solution and are mainly derived from the reaction of alcohols, alkylphenols and amines with ethylene oxide and/or propylene oxide.
4- **Amphoteric** (zwitterionic) surfactants are compounds that contain both acidic and basic groups in their structures, they exhibit anionic or cationic features, depending on the pH of the solution, the main are acyl ethylenediamines and alkyl amino acids.

Recently there is an introduction of a new class of surfactant, called **polymeric surfactants** or **surface active polymers** [Piirma, 1992][3], which result from the association of one or several macromolecular structures, have hydrophilic and lipophilic characters, they are now very commonly used formulating products such as cosmetics, paints, foodstuffs, and petroleum production.

Also surfactants can be classified according to chemical structure into [Gurgel 2004][4] Fig.(1.3):

- Single chain double chain, triple chain surfactants.
- Gemini surfactants. These surfactants possess two head-groups, each one having one tail, and linked by a short hydrophobic chain.
- Bolaform surfactants. When the molecule presents two head-groups linked together by one or two long hydrocarbon chains.
- Asymmetric surfactants. When the molecule has one or more chiral centers in their polar head-groups.

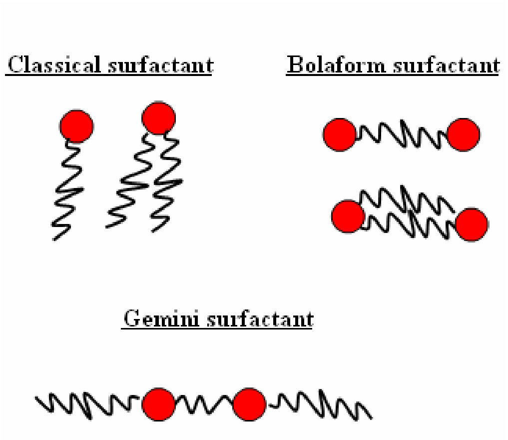


Figure1.3: Classification of surfactant according to chemical structure**.**

1.3 Uses of surfactants

Surfactants find applications in almost every chemical industry; they must have certain hydrophilic-lipophilic balance (HLB), chiefly between 1-40 which can be calculated by Griffin equation. eq. (1.1)

HLB=7+$\sum$ hydrophilic group number + $\sum$ lipophilic group number ………(eq.1.1)

Such uses as in detergents, paints, dyestuffs, paper coatings, inks, plastics and fibers, personal care and cosmetics, agrochemicals, pharmaceuticals, food processing, etc. In addition, they play a vital role in the oil industry, e.g. in enhanced and tertiary oil recovery, oil slick dispersion for environmental protection, among others.

Their role in detergency is well known Fig. (1.4) that the hydrophobic ends attach themselves to the soil particles present in or on the fabrics being washed, while the hydrophilic ends are attracted to the water. So the surfactants molecules surround the soil particles, break them up and force them away from the surface of the fabric, then suspend the soil particles in the wash water [Arthur, 2008][5].

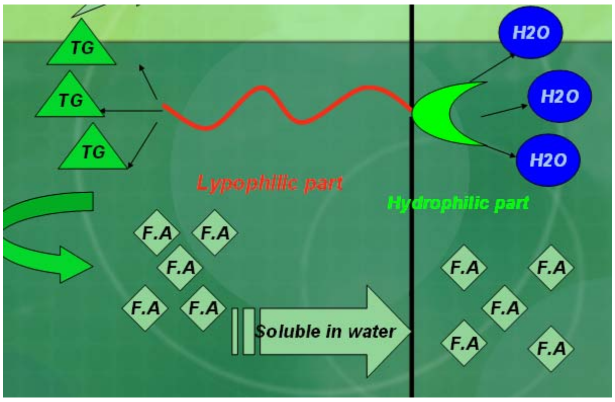


Figure1.4: Detergency action

1.4 Surfactant association structure

Surfactants can assemble in the solution into aggregates above its critical micelle concentration or CMC, and above critical temperature concentration or kraft temperature [Lindblom, *et al*., 1979][6] Fig. (1.5). Examples of such aggregates are vesicles and micelles (self assembled structures), which behaves as isotropic solution. While below the CMC most of the surfactant molecules are unassociated.

Micelles are one of the main types of structures formed by the self-association of amphiphiles Fig. (1.6). They consist of core of hydrophobic chains, shielded from the contact with water by hydrophilic head groups, which may be ionic or non-ionic. Micelles can either be spherical or elongated into rod-like shape. In the opposite way inverse micelle which have hydrophilic core and hydrophobic chain toward outside oil phase. This difference in shape depends on numerous features of the surfactants and their surrounding environment.

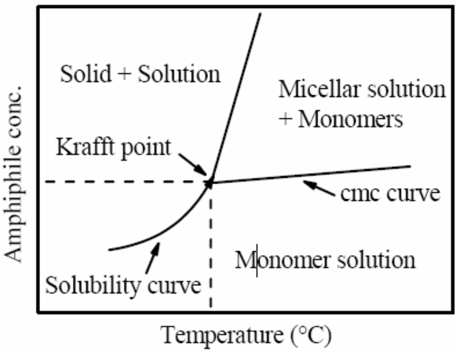


Figure 1.5: Phase diagram for an ionic surfactant solution.

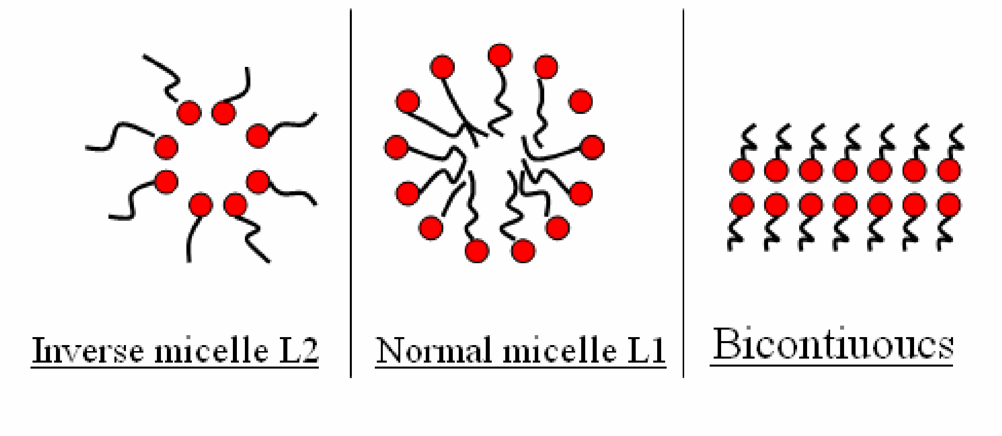


Figure 1.6: Illustration of micelle and inverse micelle and bicontiuous

. For many amphiphiles at higher concentration, the aggregation number increases and the micelles tend to form a rod-like conformation which leads to hexagonal or lamellar aggregates, and even vesicles Fig. (1.7).
Each surfactant molecules has a characteristic CMC at a given temperature and electrolyte concentration. The most common technique for measuring the CMC is by determining the surface tension, which shows break at the CMC, after which it remains constant with further increases in concentration.

A useful concept for characterizing micelle geometry is the packing parameter (***R***), which was shown by Israelachvilli *et al.* [Israelachvilli et.al, 1976][7] they considered that surfactants molecules can be regarded as a two –piece structure, polar head and hydrophobic tail. Represented by eq.1.2 that for surfactant cross sectional area of head group ***a*°,** a hydrocarbon volume ***v*** and extended chain length ***lc*** the value of ($R<1/3$) spherical micelle will be formed, and ($1/3<R <1/2$) cylindrical micelle formed, and ($1/2<R\leq1$) lamellar structure or bilayer is formed, and ($R>1$) inverse micelle is formed. Fig. (1.8)

$R= v\backslash a^{\circ}\, lc$ ………………… *eq*. (1.2)

So the aggregation of particular surfactants is greatly depending on the molecular structure and the concentration of surfactants.

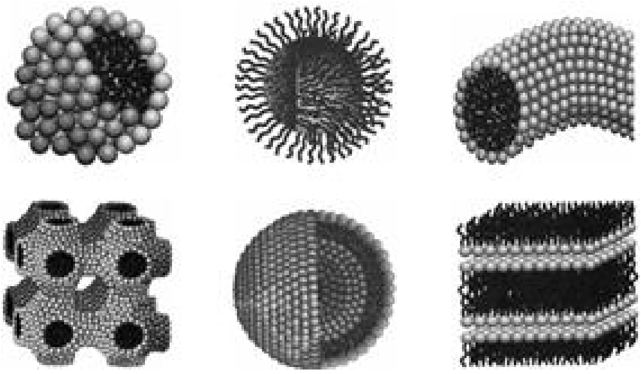


Figure 1.7: Surfactant association structure

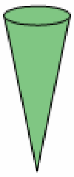
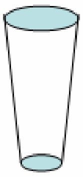
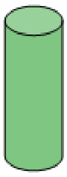
R Packing parameter	R<1\3	1\3<R <1\2	1\2<R≤1	R>1
structure				
Micelle structure	Spherical	Cylindrical	Lamellar	Inverse

Figure 1.8: Schematic of surfactant structures and shapes derived from various packing parameter.

1.5 Extended surfactants and AOT

1.5.1. Extended surfactants:

Are special types of surfactants, which are characterized by the presence of one or more intermediate-polarity groups, such as a number of ethoxylate groups (EO) and/or propoxylate groups (PO) between the hydrophilic head and the hydrophobic tail Fig.(1.9); it has large molecular weight with high water solubility, which is able to dissolve very hydrophobic oils. It is used for the formulation of microemulsions with high solubilization capacity and ultralow interfacial tension (IFT) and lower optimum salinity which are desirable in most formulations [Witthayapanyanon, *et al*., 2006][8], because they have low critical micelle concentrations (CMC) compared with other conventional surfactants.

The use of extended surfactants will replace the uses of hydrophilic and lipophilic linkers, which are used to increase the surfactant-water and surfactant-oil interactions by extending the hydrophilic head group and hydrophobic tail respectively.

Graciaa *et al*. [Graciaa, *et al*., 1993a][9], [Graciaa, *et al*., 1993b][10] was the first to study the use of a lipophilic linker to extend the length of the surfactant tail into the oil phase without affecting water solubility of the surfactant; by using a long-chain alcohol.

The combination of hydrophilic and lipophilic linkers act as an additional surfactant, so the system will need reduced amount of the main surfactant, which is necessary for oil solubilization in middle phase microemulsion and producing ultra low interfacial tension [Acosta, *et al.,* 2002][11],[Acosta, *et al*., 2004][12] . Most of these linkers are long or short chain alcohols which are undesirable in most formulation, so the use of extended surfactant is the best choice.
[Scorzza, *et al*., 2002][13], [Huang, *et al*., 2004][14].

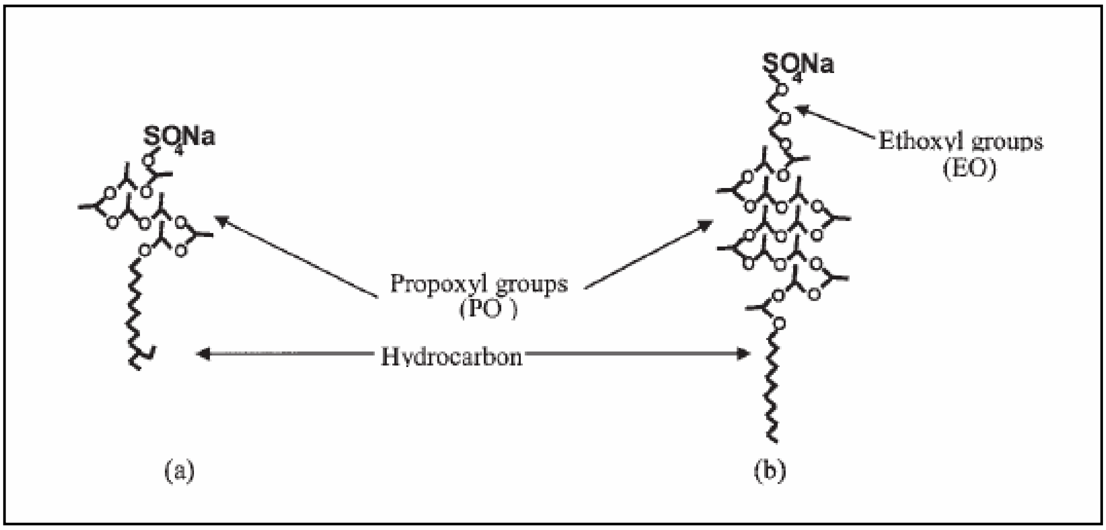


Figure 1.9: Structure of extended surfactants: (a) alkyl-PO sulfate C14-15-(PO)8-SO4Na, (b) alkyl-PO-EO sulfate C12-(PO)14- (EO)2-SO4Na. [Witthayapanyanon, *et al.,* 2006]7.

ALFOTERRA® [Sasol North America, 2009][15] is the trade name of Sodium alkyl polypropylene oxide sulfate Fig. (1.10) extended Surfactant, yellow clear liquid, which exhibit improved solubilization of oily materials in an aqueous medium by extending the interface. The monobranched alkyl hydrophobe allows for greater interaction with the oil phase while maintaining good solubility. These two factors give the surfactant unique emulsification properties and ultra-low interfacial surface tensions. ALFOTERRA® can be used in a wide variety of industrial and personal care applications including: Enhance Oil Recovery, Soil Remediation, proven extremely effective in the solubilization of oily contaminants from aquifers and subsurface soil, oil/seed extraction, good emulsifier for triglycerides and other hydrophobic oils, dry cleaning, may be used for dry cleaning solvent replacement due to the excellent mobilization of hydrophobic stains, industrial cleaning. Personal care formulations, additive in cleaning formulations. It may also be utilized in mining, textile processing, lubricants, leather processing, metal working, and a variety of other applications.

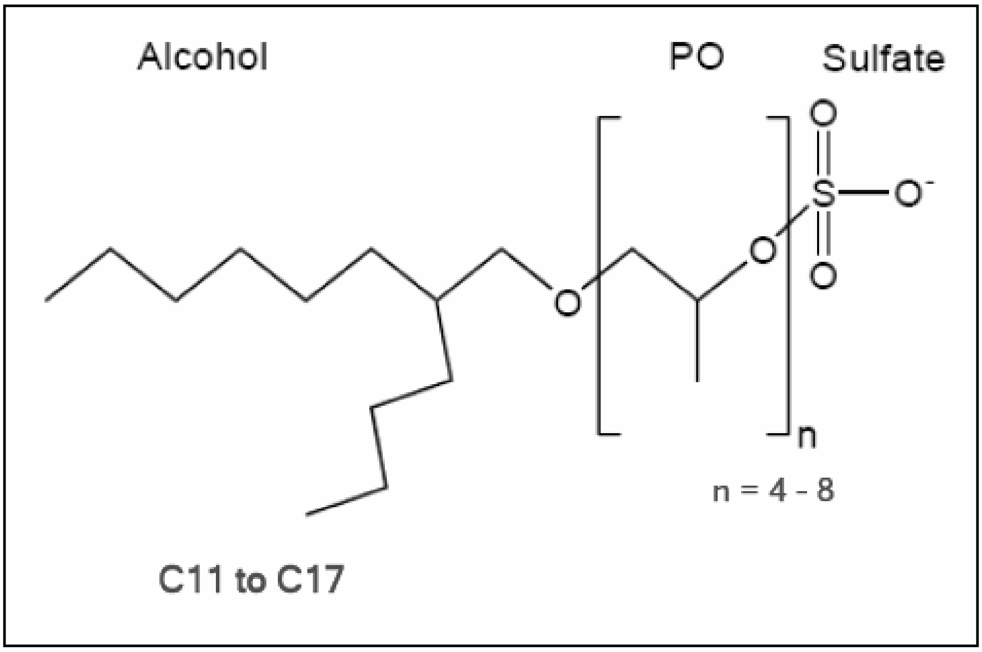


Figure 1.10: Alfotera; Sodium alkyl polypropylene oxide sulfate. [Sasol North America, 2009]14

1.5.2. Aerosol (AOT):

AOT Fig.(1.11) which is named as sodium bis (2-ethylhexyl) sulfosuccinate. White, wax-like, plastic solid, having a characteristic odour suggestive of octanol [Cytec Industries, 2005][16]. Used as emulsifying agent, wetting agent ,emulsion and suspension polymerization, in paint formulations, in dry cleaning and spotting, in dispersion of colors and dyes in plastics, and in lubricants, coolants, and rust inhibitors . It is sparingly soluble in water; freely soluble in ethanol and glycerol.

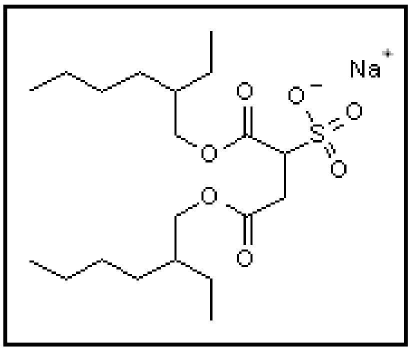


Figure 1.11: Aerosol (AOT): sodium bis (2-ethylhexyl) sulfosuccinate [Cytec Industries, 2005] 15

Ternary Phase behavior of AOT with different hydrocarbon\water systems has been studied widely, because of its unique properties of having balanced hydrophilic and lipophilic portion. It is well known that it has large area of inverse micelle of a spherical form, which has many applications, and it form lamellar liquid crystal which some times limit its uses [Luan, *et al.*, 2003][17] Fig.(1.12).

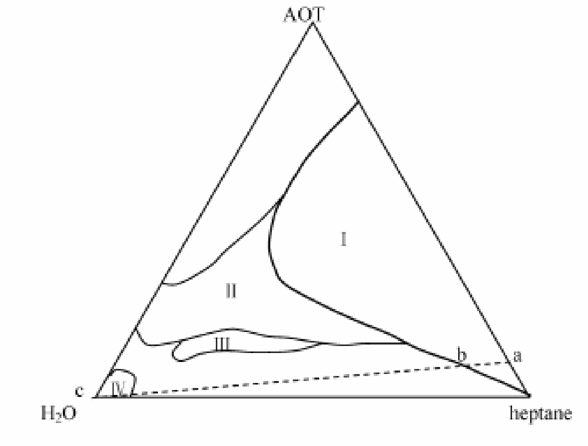


Figure 1.12 .ternary phase diagram H2O/AOT/ n-heptane [Luan, et al.,2003]16. The regions of I, II, III, and IV represent the reversed micelle, the liquid crystal, the bicontinuous phase, and the O/W microemulsion, respectively

Also binary phase behavior of AOT /water system shows that it has large area of lamellar liquid crystal Fig. (1.13) [Petrov, *et al.*, 2002][18], [Franses, and Hart, 1983][19]. So Many researches have been done to study the phase behavior of AOT /water/hydrocarbon, with different additive to enhance the application of AOT or to modify new uses of this anionic surfactant.

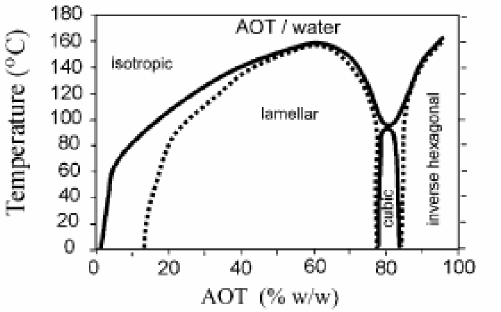


Figure 1.13: Binary phase diagram of Aerosol OT/water system the main ordered phase is the lamellar, with a pocket of bicontinuous cubic and inverse hexagonal phases at high concentrations, and it form isotropic solution at high temperature. [Petrov, *et al.*, 2002]17

Most microemulsion containing ionic surfactants required alcohol or some other cosurfactant and/or salt for their formation and stability. An exception is AOT which can form microemulsion that exhibits ultralow interfacial tension without any cosurfactants addition.

Arthur R. Malheiro, *et al.* studied the behavior of The Aerosol OT + *n*-Butanol + *n*-Heptane + Water System [Malheiro, *et al.*, 2007][20], this pseudo-ternary system was applied to the synthesis of carbon-supported Pt70Fe30 nanoparticles.

Sabatini D.A. *et al.*, studied the salinity of 3% AOT, 2% alkyl diphenyl oxide disulfonate (ADPODS), and 2% Span 80 System with 1:1 ratio hexadecane to water [Tongcumpou, *et al.*, 2003] [21] they found that the optimal salinity was at 5% NaCl.

Hanan M. El-Laithy constructed a pseudoternary microemulsion system using aerosol OT/medium-chain triglycerides with oleic acid/glycerol monooleate and water [Laithy, 2003][22], and applied it as drug delivery.

Mercedes Velázquez M. *et al.*, studied the behavior of AOT and ethylene glycol [Velázquez, *et al.*, 2007][23] by Dynamic light scattering and Cryo-TEM measurements. In this work they show that small unilamellar vesicles predominate in pure Aerosol OT solutions and in dilute polymer solutions mixed with AOT.

Khan A. *et al.* studied the phase equilibria of anionic sodium dodecyl sulfate (SDS) and cationic didodecyldimethylammonium bromide (DDAB), [Marquse, *et al.*, 1993][24] they investigate that addition of cationic DDAB to solutions of spherical SDS micelles may induce a micellar growth to rodlike aggregates. Puig' J.E. *et.al*, studied the effect of NaCl concentration on the surface tension of aqueous AOT with various concentration at 25ºC.[Puig, *et al.*, 1985] [25] Fig.(1.14)

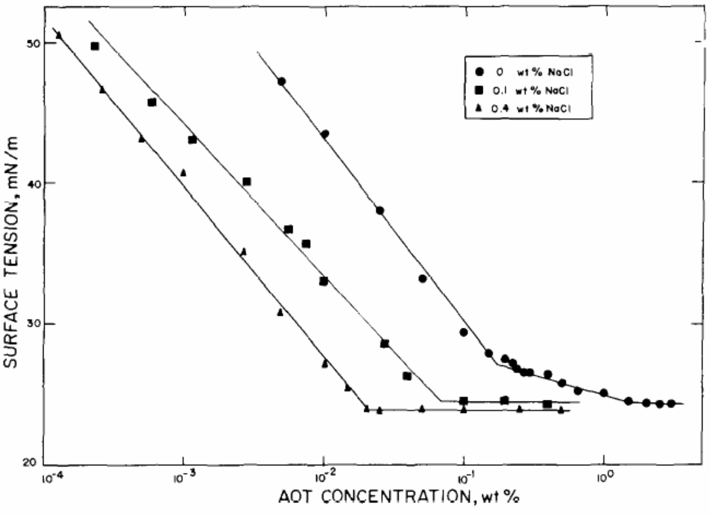


Figure 1.14: Surface tension as a function of the logarithm of the surfactant concentration of preparations of AOT in water and in aqueous NaCl at 25°C. .[Puig, *et al.,* 1985]24.

Shinoda K. *et al.* [Kunieda and Shinoda, 1980][26] studied solution behavior of AOT in brine-isooctane in connection with microemulsions and ultralow interfacial tensions; they found that microemulsion occurs at 0.5%AOT and 0.5% NaCl at 40°C.Fig. (1.15)

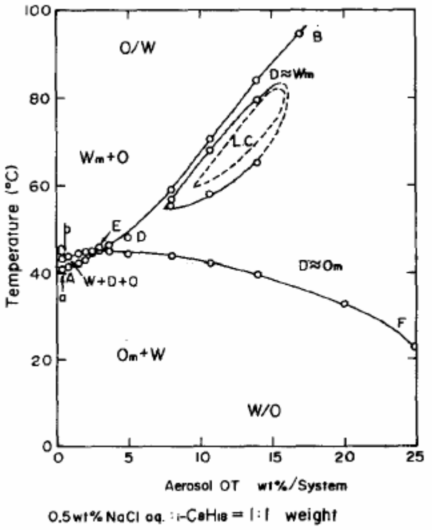


Figure 1.15.The effect of the concentrations of Aerosol OT on the equiweight mixture of isooctane and 0.5 wt% NaC1 aqueous solutions as a function of temperature. [Kunieda and Shinoda, 1980]25.

Kunieda *et al.* have reported that the HLB of AOT depends on the ratio of AOT and water [Kunieda and Sato*,* 1979][27] when the amount of water is low, AOT is lipophilic; it becomes hydrophilic as the amount of water increases.

1.6 Tetra ethyl ammonium chloride

Quaternary ammonium compounds are any of a group of ammonium salts in which organic radicals have been substituted for all four hydrogen of the original ammonium cataion [Chemicalland21, 2008][28]. They have a central nitrogen atom which is joined to four organic radicals and one acid radical. They are prepared by treatment of an amine with an alkylating agent. They show a variety of physical, chemical, and biological properties and most compounds are soluble in water and strong electrolytes. They have tendency of locating at the interface of two phases (liquid–liquid), to introduce continuity between the two different phase, These compounds are used as; Surface-active agents**,** solvents **,**intermediates**,** active Ingredient for conditioners**,** antistatic agent**,** detergent sanitizers**,** softener for textiles and paper products**,** antimicrobials**,** disinfection agents**,** pigment dispersers. Hydrotropes are used in powdered detergents to reduce hygroscopy, in pastes to reduce viscosity, and in dishwashing and fine fabric hand washing liquids to avoid precipitation at low temperature.

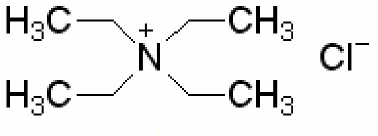


Figure 1.16: Tetraethylammonium chloride (TEAC) [Chemicalland21, 2008] 27.

TEAC may be considered as Cationic surfactant which is extremely useful for some specific uses, but they are not good detergents nor foaming agents, and they cannot be mixed in formulations which contain anionic surfactants except when a catanionic complex synergetic action is sought

In most cases they are used as **cationic hydrotropes** which are substances that help other to become compatible with water. For instance, it is well known that short alcohols and urea are able to cosolubilize organic compounds such as perfumes. They enter the micelles as cosolubilizing agents [Hassan, *et al.,* 2002][29]. As the molecular weight (or length) of the hydrophobic portion of the hydrotrope is increased, the hydrotrope begins to behave more like a second surfactant and can alter the self-assembly in solution, leading to the formation of vesicles.

1.7 Microemulsions

The concept of microemulsion was first introduced by Hoar and Schulman in 1943 [Hoar and Schulman 1943][30], which was defined later as a thermodynamically stable isotropic, transparent, with low viscosity, fine dispersions of two immiscible phases (water and oil) stabilized by surfactant compounds which hold the mixture in single phase, this phase has ultra low interfacial tension and large interfacial area and high solubilization capacity. Microemulsion consist of various structure from swollen micelle as bicontinuous to inverse micelle, with size of (10-200nm) in diameter. Because the droplet size of microemulsion is smaller than the wave length of visible light so the mixture is transparent and can't be observed by optical microscope [Yamamoto and Tanaka, 2001][31], so microemulsion is macroscopically homogenous, but microscopically heterogonous .The stability of the microemulsion can be influenced by addition of salt, other additives, temperature or pressure.

The surfactant molecule give the mixture of microemulsion both hydrophile and lipophile properties, Shinoda recorded the concept of HLB temperature or phase inversion temperature (PIT), at which hydrophile-lipophile properties are balanced and at this point the solution has maximum solubilization capacity of oil and water and ultralow interfacial tension, this point could be achieved by temperature changes in non-ionic surfactants, and by salinity scan in ionic surfactants system.

When hydrophilic surfactant is used, oil in water (O/W) microemulsion is formed, while when lipophilic surfactant is used water in oil (W/O) microemulsion is formed, and finally when a surfactant has balance hydrophil-lipophile property in a water\oil system, a surfactant phase or middle phase which has bicontinous structure is formed.

The easiest way to graphically represent microemulsion system, at well defined temperature and pressure is constructing phase diagram [Wennerstrom, 2007][32], with varying composition an equilateral triangle is the usual format of the diagram. The vertices of the triangle is correspond to pure components, and each of it s sides represents possible compositions of binary mixtures, including micelles and reverse micelles. Any point inside triangle represents a ternary mixture in specific proportions for each component. In the following figure a ternary phase diagram for an ideal three-component system, in which some possible aggregates are shown, single phase O/W microemulsion are formed in the L1 region of the diagram and W/O microemulsion appear in L2 region. Liquid crystals may be present in Lc region, with high surfactant concentration. Fig. (1.17)

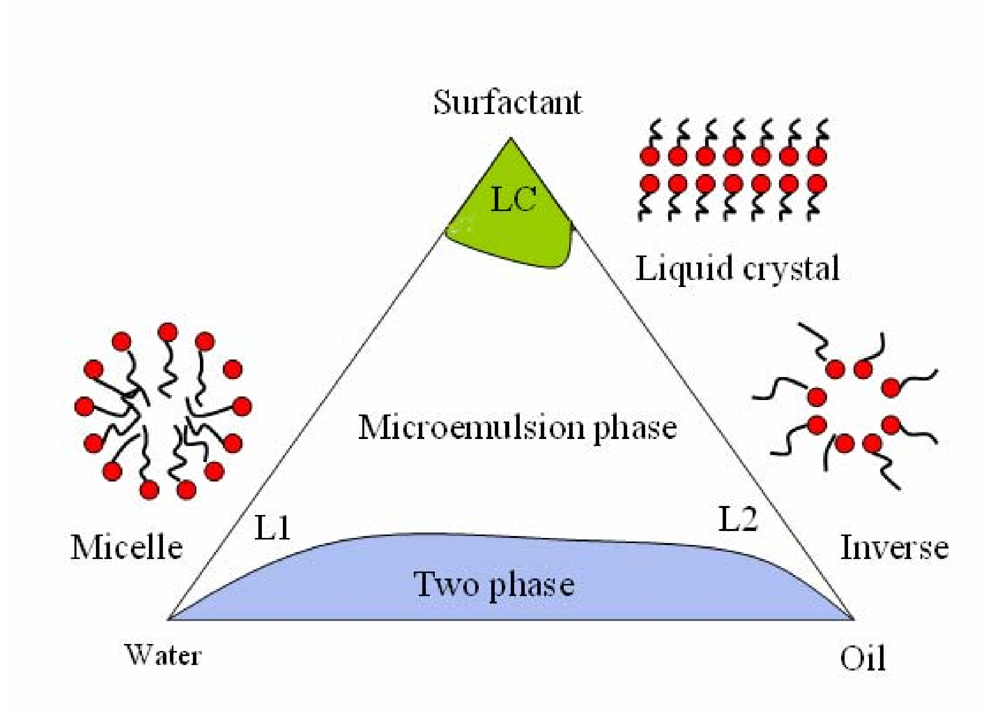


Figure 1.17: Schematic representation of ternary phase diagram

A lot of research was dedicated to the phase behavior of surfactant \oil\water systems in term of brine salinity, oil alkane carbon number, surfactant characteristic parameters, and as well as temperature.

1.8. Winsor classification of microemulsion

Microemulsion can be classified into four main categories [Winsor, 1954][33], fig (1.18, 1.19)

Winsor I: with two phases, the lower (o/w) microemulsion phase in equilibrium with the upper excess oil.

Winsor II: with two phases, the upper microemulsion phase (w/o) in equilibrium with excess water;

Winsor III: with three phases, middle microemulsion phase (surfactant phase) in equilibrium with upper excess oil and lower excess water; ultralow interfacial tension and a bicontinuous structure.

Winsor IV: in single phase, with oil, water and surfactant homogeneously mixed, with high surfactant concentration.

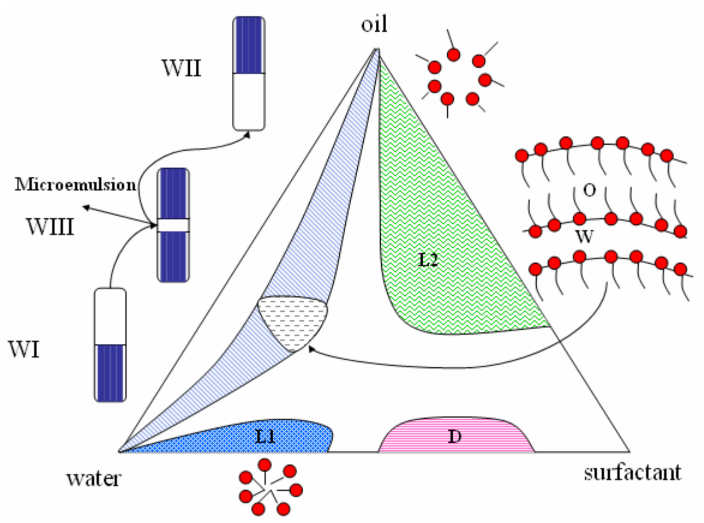


Figure.1.18. type I and type II and type III microemulsion according to Winsor.

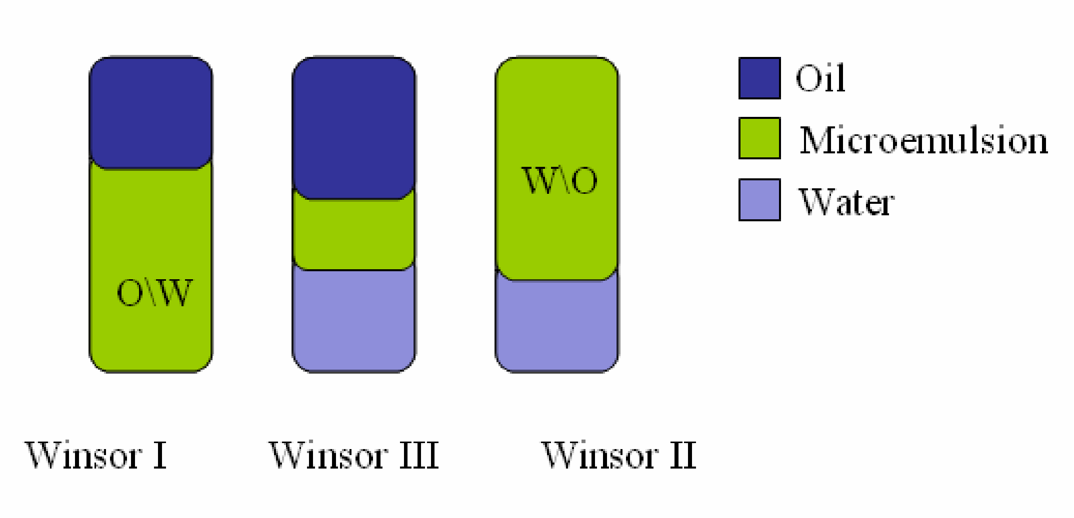


Figure 1.19.Illustration of Winsor

Electrolyte concentration is commonly used as the scan variable for a microemulsion system when ionic surfactants, whereas temperature is often used for nonionic surfactant systems. In both cases, as increasing (salinity or temperature), the water solubility of the surfactant decreases and oil solubility increases. They use HLB number to characterize water solubility; change in such parameter (salinity or temperature), will reverse the direction of the natural curvature of the surfactant film from oil-in-water to water-in-oil and hence produce an inversion in phase continuity of the microemulsion. Fig. (1.20)

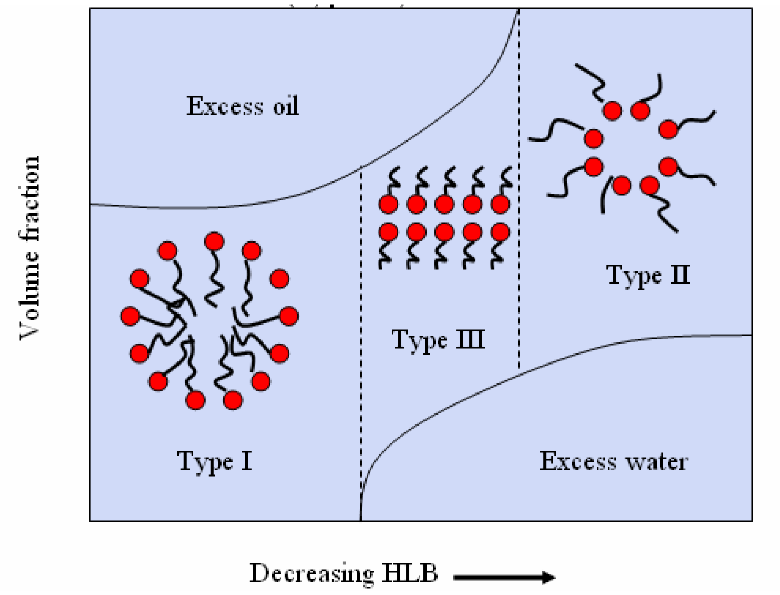


Figure 1.20: Phase behavior showing the transition from oil in water (type I) to bicontinuous structure (type III) and water in oil structure (type II)

The surfactant phase or middle phase has ultra low interfacial tension which can be predicted by Chun-Huh equation,(eq.1.3)

$$IFT = \frac{c}{(V_x \backslash V_s)^2} \quad \ldots\ldots 1.3$$

Where IFT related to interfacial tension, c is constant characteristic for surfactant equal 0.3 mN\m, Vx volume of solubilized oil or water in middle phase, Vs volume of surfactant uses. The results obtained from Chun-Huh equation usually compatible with results obtained from other methods such du Nouy ring , pendant drop , laser light scattering , dynamic drop , and spinning drop method [Trejo and Fadrique, 2007][34], which is one of the most accurate and direct methods to measure low interfacial tension. In typical spinning drop tensiometers, a glass tube is mostly filled with the aqueous phase (the denser phase) and a small drop of the oil phase (the lighter) is placed inside this tube Fig.(1.21). The drop is located at the middle of the tube at a high speed and the shape of the drop is measured after elongation stops, from which the interfacial tension can be calculated. This method works for typical water–surfactant–oil systems in which surface tensions below 10^{-2} mN/m.

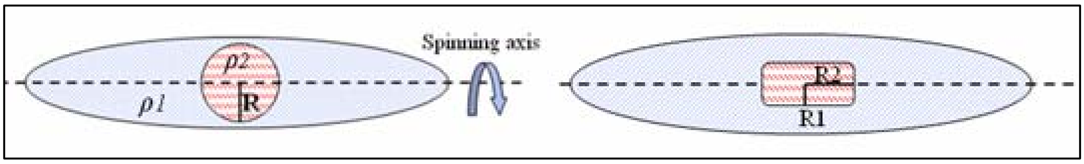


Figure 1.21: Principle of spinning drop tensiometer.

The surface or interfacial tensions are calculated using Eq.(1.4) suggested by Vonnegut under the following considerations [Vonnegut 1942][35].The elongation of the bubble stops when the centrifugal forces are balanced by the surface tension forces, assuming that the length of the bubble is large compared with the radius (***L***_***R***) so it can be treated like a circular cylinder, and a negligible effect of gravity at increased speeds of rotation, then it is possible to write an expression for the total energy of the bubble and solve it for the equilibrium shape with the minimum energy.

$$\sigma = \frac{\Delta\rho\omega^2 R^3}{4} \quad \dots \quad 1.4$$

Where σ is the interfacial tension, $\Delta\rho$ the density difference between phases, ω the angular velocity and R is the cylinder radius.

1.9. Applications of microemulsions

There are many applications found in the recent years using microemulsion such as in enhanced oil recovery EOR, as a fuels ,as coatings and textile finishing, as lubricants, cutting oils and corrosion inhibitors, in detergency, in cosmetics, in agrochemicals, in food ,in pharmaceuticals in environmental remediation SEAR and, detoxification, in analytical applications, in biotechnology..[Bidyut, *et al.*, 2001][36]. So a lot of research carried out in all areas to take advantage of the unique characteristics of microemulsion.

The most worthable application which has a large economic potential is in EOR, in which a considerable amounts of oil are trapped in porous rocks of oil reservoir, and then a surfactant solution is injected, the IFT must be lower than 10^{-2}mN\m in order to remove this residual oil from pores.

In surfactant-enhanced aquifer remediation SEAR, surfactant solutions are injected underground to remove organic phase contaminants stranded in soils [Shiau, *et al.,* 1994][37]. Such of the organic contaminants, e.g. trichloroethylene (TCE) or perchloroethylene (PCE).

1.10 Catanionic surfactant mixtures.

It is common practice to prepare formulations for various applications by mixing surfactants. It allows synergetic effects, such as increased oil solubilization, foaming, emulsification, washing abilities, and desired structural organizations in mixed systems. Previous studies on mixed surfactants have shown that the interfacial activity is exceeded that of single surfactant systems [Rosen, 1992][38].

Oppositely charged surfactants should never be mixed because of the potential for precipitation of the insoluble surfactant [Scamehorn and Harwell 2005][39], precipitation is generally found only near equimolar compositions [Jonsson, *et al.,* 1991][40] , and when use symmetrical anionic/cationic system (cationic and anionic surfactants with the same carbon chain) [Yatcilla*, et al.,* 1996][41], and this precipitation can sometimes be block mixture application.

K.L. Stellner *et al.* studied mixtures of anionic and cationic surfactants [Stellner, *et al.*, 1988][42], over a wide range of concentrations in order to develop a model that could provide complete phase boundaries for precipitation of that system

In fact synergism of anionic/nonionic and cationic/nonionic, anionic/amphoteric and anionic/cationic mixtures has also been observed for various systems. Also Mixtures of anionic and cationic surfactants in water display interesting phase behavior and a range of microstructures, including small micelles, rod-like micelles, lamellar phases and vesicles**.**

Synergism increases with the degree of charge difference [Mehretab and Loprest, 1988][43], upon mixing anionic and cationic surfactants, and increasing tail length differences .that mean with anionic-cationic mixture with the same tail length the interaction between head groups and tail chains are very high which lead to formation of liquid crystal precipitation

Lucassen-Reynders *et al.* studied the surface tensions of several mixtures of SDS (sodium dodecyl sulfate) and DTAB (dodecyl trimethylammonium bromide) [Lucassen, *et al.,* 1981][44]. Fig (1.22) shows the relationship between surface tension, concentration and mixing ratios (SDS/DTAB), it need concentration of 4.5 mol/m3 of SDS alone to reach a surface tension of 50 mN/m, where as to reach the same surface tension it need only 9 X10-^{3}mol/m3 of the equimolar mixture

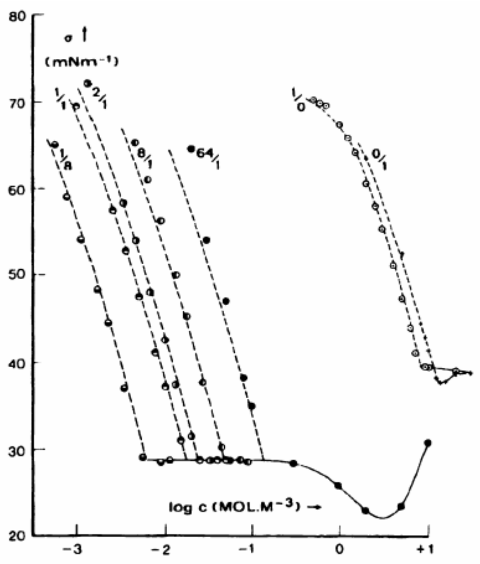


Figure 1.22 Surface tension for mixtures of SDS/DTAB. Mixing ratios 1:8, 1:1, 2:1, 8:1, 64:1, 1:0, 0:1, respectively. [Lucassen,*et al*.. 1981] 43

Surfactant mixture present as monomer at low concentration, when it reach CMC micelle start to formed, above CMC precipitation may occur. fig. (1.23)

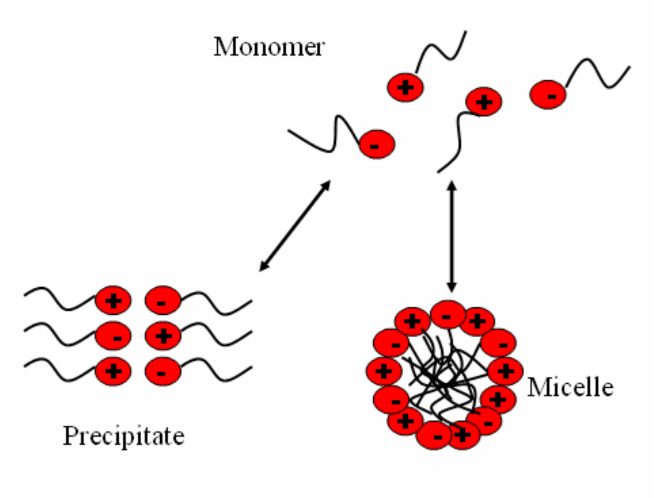


Figure 1.23: Basic equilibrium in a cationic/anionic system.

Short chain cationic hydrotropes were used in combination with novel surfactants, prepared by Shell to formulate microemulsion with model oil and crude oil from Texas wells. [Kayali, *et al*., 2010a].[45]

Two types of molecular interactions lead to the formation of precipitate phases (liquid crystals, and gels) one is electrostatic attraction between the anionic and cationic surfactant head group, and Van der Waals hydrophobic interactions between the surfactant tail groups.

Electrostatic interactions is increased by increasing charge difference between head groups, that mean the most interaction is between anionic and cationic head groups, and decreased by increasing distance between head groups. While the Van der Waals interaction is increased by increasing the number of carbons in each tail, and decreased by increasing distance between tail chains. [Doan, *et al.,* 2003][46].

1.11 Objectives

Single surfactants do lower the interfacial tension of the oil\water systems, but addition of a second surfactant or hydrotrpes of a completely different nature lowers the interfacial tension further which enhanced the main system applications.

Formation of alcohol-free microemulsions mixtures of anionic and cationic surfactants has important applications in pharmaceutical preparations and photochemical studies where the presence of alcohol is undesirable. This system exhibit several unique properties that they have lower critical micelle concentrations (CMC) than do single pure surfactants; they are usually more surface active than either pure surfactant; and they can produce microstructures that do not form by pure components (such as vesicles and rod-like micelles), and diminished the formation of liquid crystal .These properties can be used in many ways. For example the (CMC) may be useful in detergency applications, and the vesicles could be used for controlled drug release, Also in EOR and SEAR liquid crystal must not be formed during application.

Many studies were done to avoid precipitation of mixed anionic-cationic systems, but they add alcohol to avoid liquid crystal formation. So the main purpose of this research is to develop alcohol- free anionic-cationic systems in order to form middle- phase microemulsions without the formation of liquid crystal or gel.

Also as we mentioned CMC of the mixed surfactant system is lower than either pure one, that mean it need lower amount of each surfactant in order to formulate microemulsion, which is of great significance in economic terms.

Chapter Two
Methods and Experiments

Chapter Two

2.Method and Experimental

2.1 Materials

Sodium bis (2-ethylhexyl) sulfosuccinate (Aerosol AOT) 99% $CH_3(CH_2)_3CH(C_2H_5)CH_2O_2CCH_2CH(SO_3Na)CO_2CH_2CH(C_2H_5)(CH_2)_{33}$ mol. Wt 444.56 Obtained from Sigma. Tetraethyl ammonium chloride (TEAC) 98%, $(C_2H_5)_4$NH3Cl mol. Wt.165.71 , obtained from sigma also.
Sodium alkyl polypropylene oxide sulfate, C12-13H25-27 (PO)4 SO4 Na,
(L 123-4S) consisting of a branched hydrocarbon chain. Its purity is 32.5% with 0.1 wt. % Na2SO4, 2.5 % free oil and 64.9 wt %water. the surfactant was denoted by Sasol North America inc (Westlake, Louisiana).polypropylene oxide quaternary ammonium chloride (Variquat CC-9 NS) its purity is >90% donated by Evonik-Deguss, Germany .Heptane 99% obtained from sigma , and distilled water obtained from chemistry lab of al-quds University.

2.2 Instruments and equipments

Balance, Vortex, cross polarizer, Centrifuge. Shaker, Test tubes, spinning drop tensiometer from department of physical chemistry, cologne university-Germany. (Spining Drop Tensiometer SITE100, revolution speed 15000 rpm, measuring range 10^{-6} mN/m. capillary diameter 3.5 mm, Temperature range 0 to 100°C). [Engelskirchen, *et al.,* 2007][47].

2.3 Procedure

2.3.1. Constructing ternary phase diagrams:

Samples were prepared by weighing appropriate amounts of each component into 5 ml glass tubes with screw caps at room temperature 25ºC, the samples were mixed by vortex and stand until equilibrate; any bubbles formed must be removed by centrifuge. Detecting number of phases by naked eye. By polarizer detect the anisotropy. The single isotropic sample which will be dark under cross polarizer will be regarded to either cubic or micelle which can be distinguished by viscosity. The anisotropic lamellar liquid crystal and hexagonal liquid crystal are determined by the polarizer. Detect the boundary of single phase, finally draw the phase diagram.

2.3.2. Fish phase diagram (1:1) molar ratio of surfactant mixture WOR=1 by salinity scan and interfacial tension measurement:

Sample were prepared by weighing appropriate amount of each components into 10 ml glass tubes (1:1) molar ratio of surfactant mixture and water\ Heptane (1:1) weight ratio, and different concentrations of NaCl at room temperature 25ºC were added, the samples were mixed by vortex for 1-2 minutes until the surfactant was completely dissolved, and then mixed on shaker over night (24h), then put on a stand until equilibrate; Then by visual observation detect the number of phases, also we noted the transition of phases from under optimum to optimum to over optimum which correspond to winsor I to winsor III to winsor II respectively . Also we observed number of phases at 15ºC, 25 ºC and at 40ºC, after leave the samples 24 hours in water bath.

For calculating the IFT using Chun-Huh equation the solubilization parameter (Vx/Vs) can be obtained by measuring the amount of solublized oil or water ,by knowing the amount of oil or water after equilibrium and subtract it from the original oil or water added, then we compensate in the Chun-Huh equation .

For measuring IFT by spinning drop tensiometer between brine and heptane with different NaCl concentration at 25ºC, a drop of the less dense liquid (heptane) is suspended in a glass tube containing brine solution. On rotating the whole mass, the drop of heptane moves to the centre. With increasing speed of revolution, the drop elongates, the maximum speed with high elongation were recorded .this speed will equal to angular velocity, and the radius of elongated drop is R value in the Vonnegut equation, from which we can calculate the surface tension. In the same way surface tension between brine and middle phase will be measured at different NaCl at 25ºC also.

Chapter Three
Results and Discussion

Chapter Three

3. Result and discussions

3.1 Ternary Phase diagram of AOT/ TEAC/ water

Binary phase diagram of AOT\water show that; it has large area of lamellar liquid crystal [Petrov, P.G., 2002]17, we study Ternary phase diagram upon addition of cationic hydrotrope to AOT\water system at 25ºC. the result was single clear isotropic phase Fig.(3.1), obtained until addition of 0.05 g AOT to a well stirred mixture of 0.75 g water and 0.25 g TEAC , at this point upon addition of another 0.05 AOT surfactant the mixture turned rapidly to a single turbid phase. Further addition of AOT the mixture appeared to be very thick, which attach to the fact that AOT surfactant is very hydrophobic and it's solubility in water doesn't exceed 1.3%.. While addition of TEAC cationic hydrotropes increase the solubility of AOT and increase the ability for forming L1 phase.

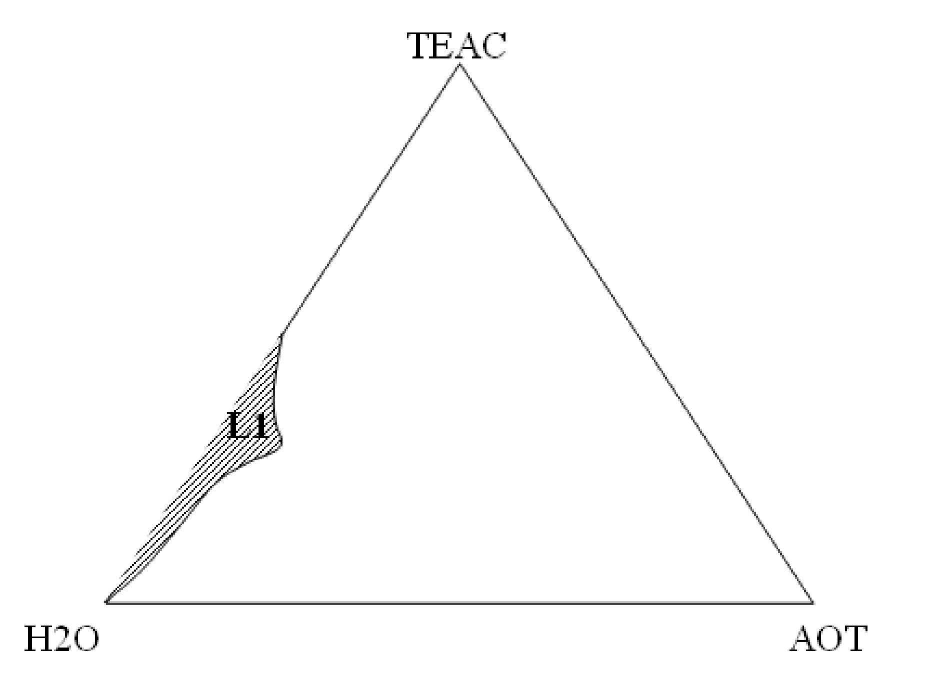


Figure 3.1: The isothermal phase diagram of three component system AOT/TEAC/water at 25ºC.L1 represents the normal micelle area.

3.2 Ternary phase diagram AOT/Water /Heptane system

A ternary phase diagram of AOT/water/heptane system has been constructed previously [Luan, Y., 2003]16. In our lab the resulting phase diagram resemble the previous one except no L1 isotropic region will appeare in our model Fig.(3.2). So it can provide a clear picture of a system of certain composition, the regions of L2, LC, represent the reversed micelle and the liquid crystal respectively. At the point of 25% surfactant and 25% water and 50% heptane, additional surfactant will change the liquid crystal to inverse micelle structure. Large area of liquid crystal has been detected as expected.

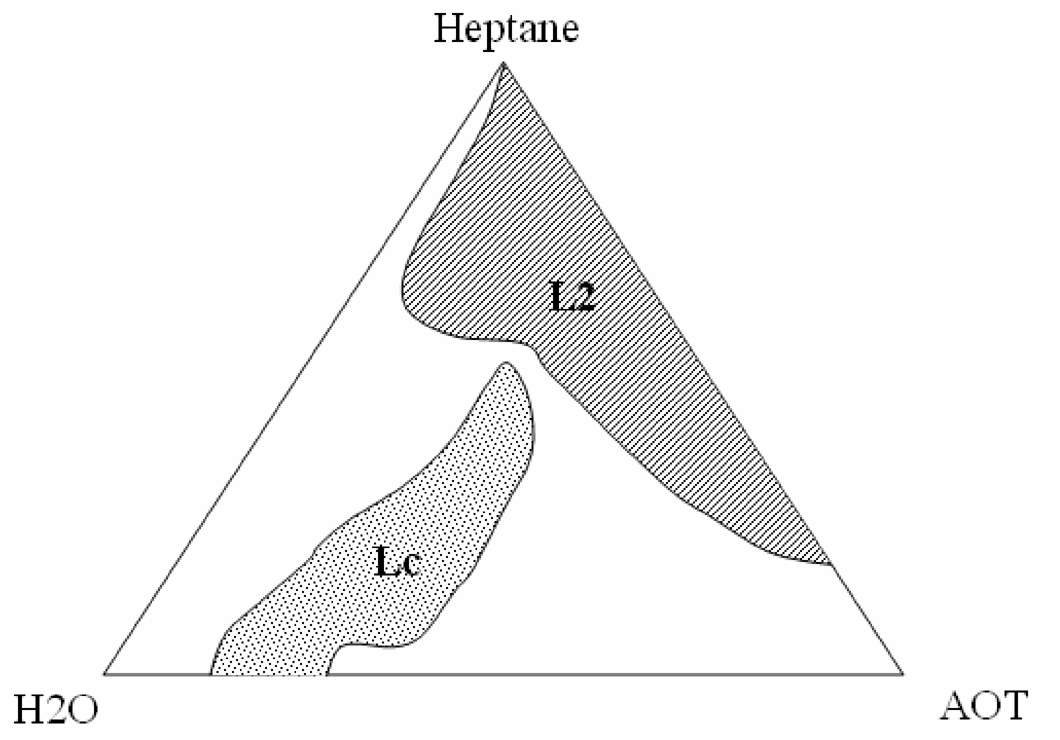


Figure 3.2: Ternary phase diagram of a system H2O/Water/Heptane at 25C, L2, Lc, represent the reversed micelle and the liquid crystal respectively.

3-3 Ternary Phase diagram of AOT/TEAC (1:1) molar ratio \water /Heptane

The observed ternary phase diagram at 25ºC is shown in Fig. (3.3), the composition in L1 and L2 region will immediately shift to transparent solution upon mixing. The samples compositions are presented in weight percent concentrations. The triangle sides correspond to the different binary axes; thus, the bottom side corresponds to the water/AOT: TEAC (1:1) molar ratio system and the right correspond to heptane/AOT: TEAC (1:1) molar ratio system, and left ones correspond to heptane /water system.

Interesting phases were determined comparing it to Fig (3.2). The addition of hydrophobic TEAC substance will change properties of AOT in equimolar ratio. TEAC increase flexibility of AOT surfactant film by increasing solubilization and penetration of oil. So decreasing the rigidity of surfactant film of AOT, which will reduce formation of LC. In our system the liquid crystal region will diminished completely and be replaced by small area of normal micelle L1 region.

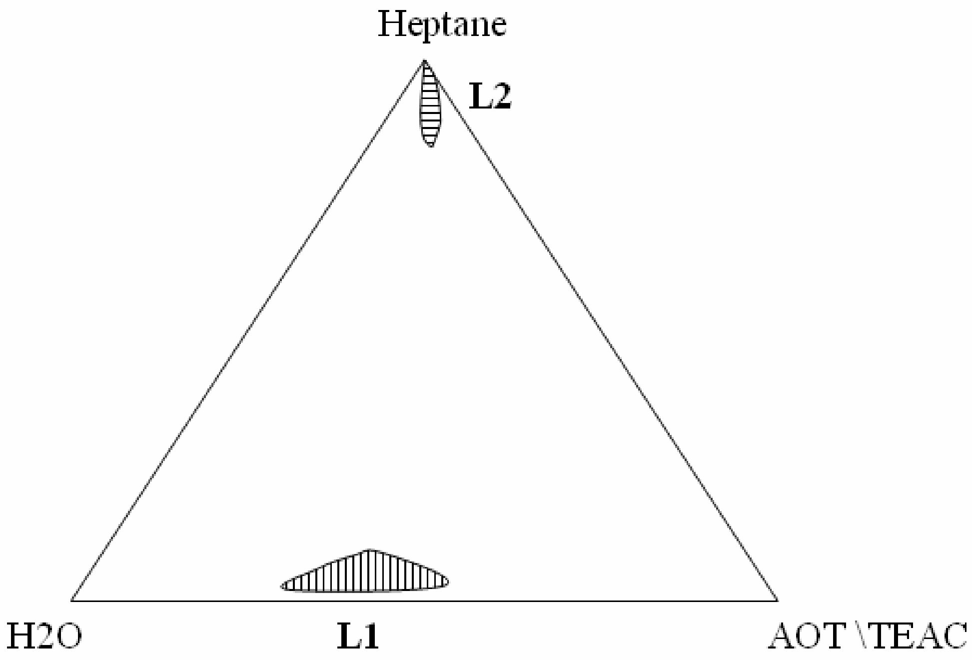


Figure 3.3: ternary phase diagram of H2O/heptane/AOT: TEAC (1:1) molar ratio, L1 and L2 represent micelle and inverse micelle respectively.

AOT molecule has double branched and long tail chain, and TEAC is a small hydrophobic molecule with small hydrocarbon side. According to hydrotrope properties it will be located at water oil interface with the main surfactant (AOT) Fig. (3.4), this will decrease the electrostatic attraction of the head groups of AOT, consequently the vander waal attraction of tail chains of AOT will be decreased also because the tail will be apart from each other, and thus synergistic effect will be obtained ,which will enable additional solubilization of oil, and enhance formation of middle phase microemulsion Fig. (3.5).

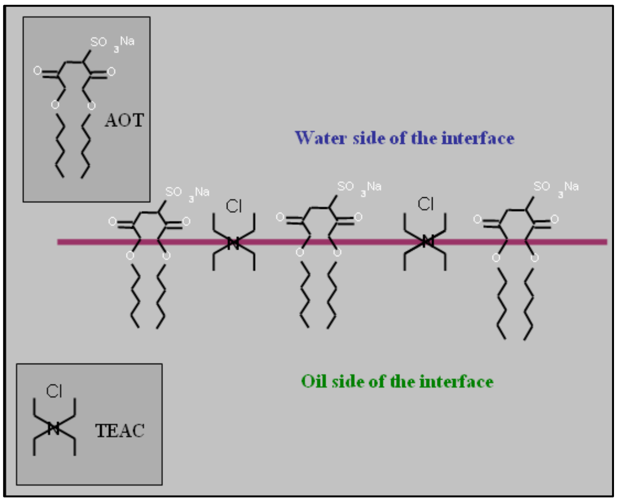


Figure 3.4: TEAC located at the water/oil interface as well as AOT.

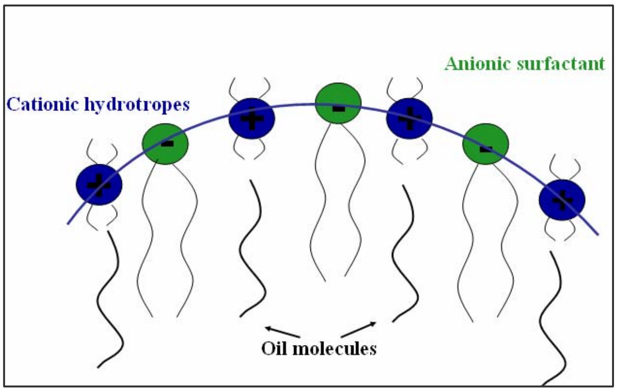


Figure 3.5: Anionic/ Cationic model which enable solubilization of additional oil, and formation of middle phase microemulsion.

3-4 Fish phase diagram of AOT/TEAC (1:1) molar ratio WOR=1 by salinity scan and interfacial tension measurement

The effect of salt concentration and temperature on phase behavior of AOT with cationic hydrotrope TEAC equal molar ratio, and WOR=1 using heptane as a model oil was noted in order to understand the whole solution behavior of surfactant mixture. It was compared with previous work by kayali I *et al.*, [Kayali, et al., 2010 b][48], which were exactly identical. In previous work of Shinoda and Kunieda [Shinoda and Kunieda,1987][49],they studied the effect of salt concentration on the phase behavior of brine\AOT\ decane system by constructing fish phase diagram, they found that middle phase microemulsion occurs at 2 wt% AOT with brine 0.7% NaCl at 42ºC .

Our systems of salinity scan containing 0.5% AOT: TEAC (1:1) molar ratio show matches with conventional winsor I, III, II Fig. **(**3.6, 3.7, 3.8**)**, at 15, 25, 45 ºC, the optimal salinities were 0.22, 0.27, 0.29 wt % NaCl respectively. The equilibrium attained after 24 hr in water bath. While without TEAC no winsor premises occurs at the same salt concentration. [Kayali, et al., 2010 b]47.

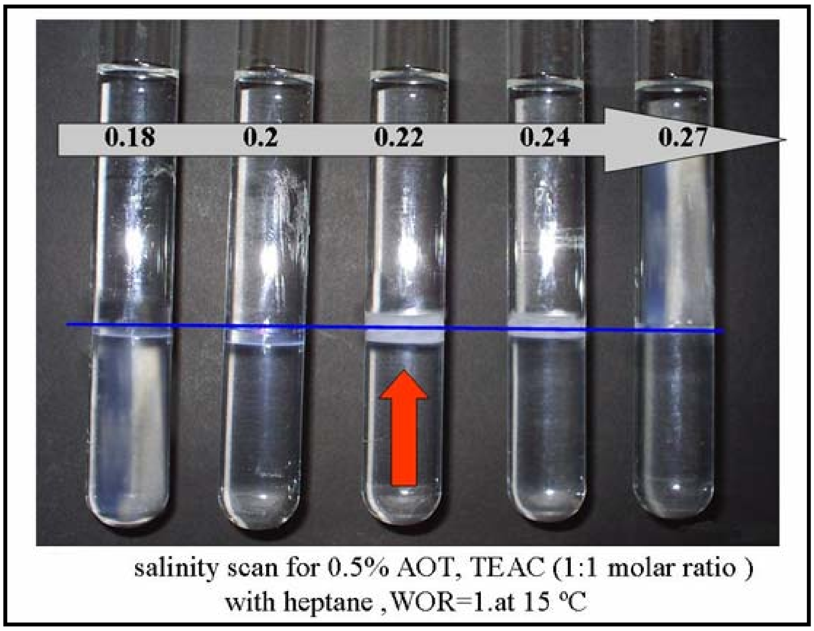


Figure 3.6: salinity scan for 0.5% AOT/TEAC (1:1) molar ratio with heptane WOR=1 at 15ºC, the arrow indicates the optimal salinity at 0.22 wt % NaCl. The horizontal line represents the amount of original oil and water

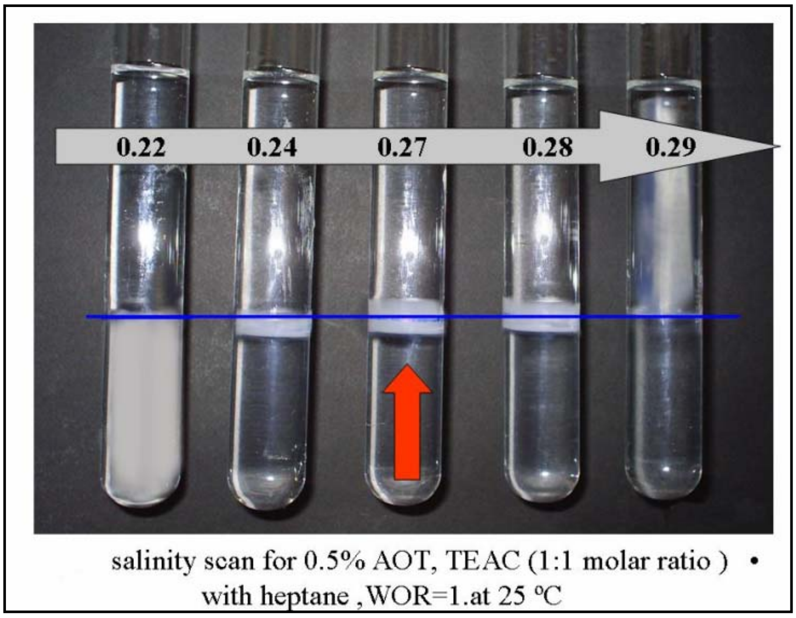


Figure 3.7: salinity scan for 0.5% AOT/TEAC (1:1) molar ratio with heptane WOR=1 at 25ºC, the arrow indicates the optimal salinity at 0.27 wt % NaCl. The horizontal line represents the amount of original oil and water.

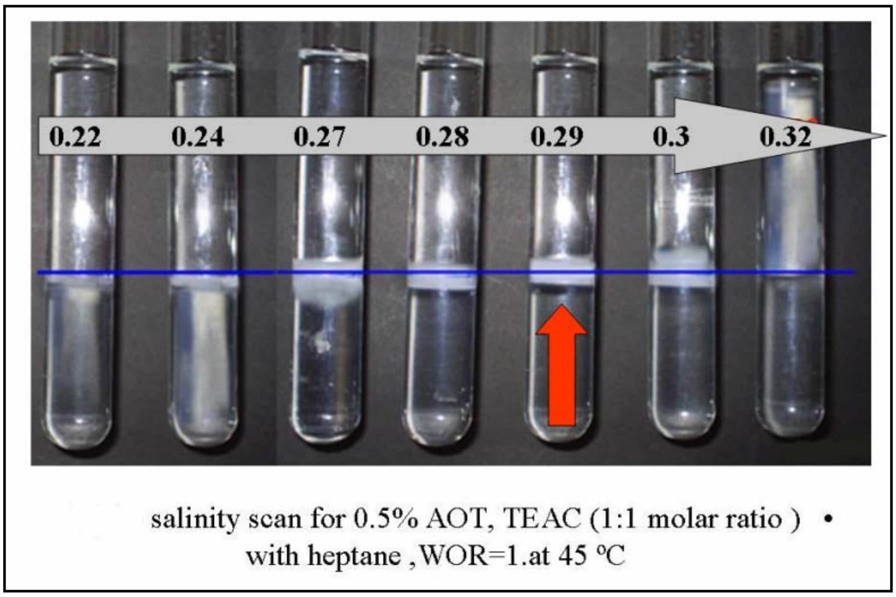


Figure 3.8: salinity scan for 0.5% AOT/TEAC (1:1) molar ratio with heptane WOR=1 at 40ºC, the arrow indicates the optimal salinity at 0.29 wt % NaCl. The horizontal line represents the amount of original oil and water.

Also the effects of surfactant mixture concentration in different brine aqueous solutions were studied by constructing fish phase diagram Fig. (3.9) the middle phase microemulsion (Winsor III) is formed with wide range of surfactant mixture starting concentration from 0.4% surfactant mixture until reaching 9% surfactant mixture. While in Shinoda study the maximum concentration of surfactant was 6.5% AOT solution alone [Shinoda and Kunieda, 1987]48, so addition of TEAC to AOT solution will change behavior of solution completely.

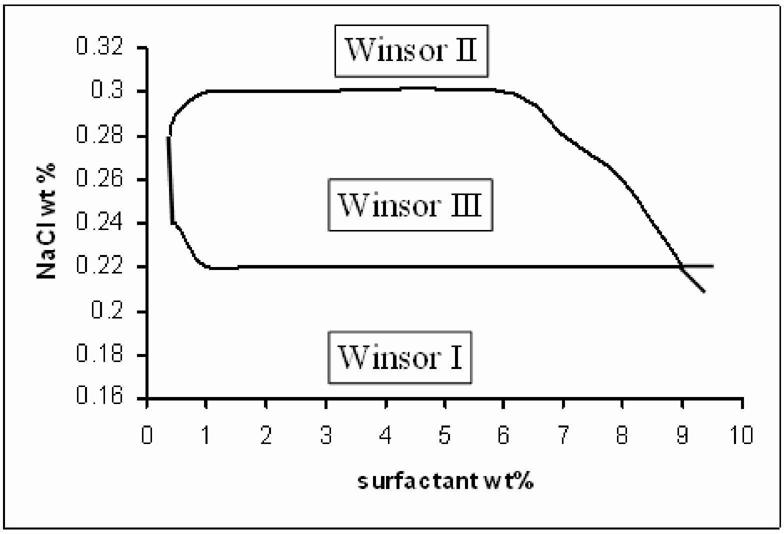


Figure 3.9: phase diagram of AOT/TEAC (1:1) molar ratio (surfactant %), with brine/heptane (1:1) weight ratio, as a function of salt concentration (NaCl %) at 25ºC.

AOT is an ionic surfactant; it is highly affected by salt concentration, at low salt concentration below 0.22% NaCl the AOT brine solution mixture is soluble in water, and it form micelles which coexist with excess oil, we assume this phase Winsor I Fig.(3.9), so AOT is more hydrophilic at this point, and upon addition of TEAC cationic hydrotope (1:1) molar ratio to AOT solution the hydrophilic lipophilic value (HLB) will increase, and thus the mixture need lower salt concentration in order to form middle phase microemulsion.

On the contrary at high salt concentration, above 0.3% NaCl non-aqueous reversed miceller solution coexist with an excess water phase (Winsor II), because of increasing lipophilic properties of AOT, so at this point the (HLB) is decreased, and the addition of equimolar ratio of TEAC, the lipophilcity is also reduced largely, but still behaves as Winsor II .

In between the above two phases (0.22-0.3% NaCl), an intermediate phase consisting of three phase region of water, surfactant and oil (winsor III) is present at hydrophilic lipophilic balanced point (HLB). Bellow this phase the natural curvature of the surfactant film (Ho<0) (winsor I), and above it (Ho >0) (winsor II) .This phase is claimed to termed surfactant phase or middle phase because it contain the total amount of surfactant in the mixture, with minimum amount of solubilized oil and solubilised water. The weight % of surfactant in the middle phase will range from 5.2-6 wt % according to salt concentration table (3.1)

The unique balanced hydrophile-lipophile properties of AOT, will produce solution behavior similar to non-ionic surfactant at constant brine concentration, that behave in reverse way. AOT is dissolved in the oil phase at low temperature and forms reversed micellar solution (w/o), with excess water. Contrariwise AOT is dissolved in the water phase at high temperature forming (o/w) microemulsion in equilibrium with excess oil.

Figure 3.10 shows phase behavior of AOT/TEAC (1:1 molar ratio) with constant salt concentration (WOR=1), at different temperatures. At 15ºC the system was hydrophobic, the surfactant mixture dissolved in oil phase in equilibrium with excess water. The hydrophilicity increased by increasing temperature, until reaching 45ºC the surfactant mixture became more hydrophilic forming (o/w) microemulsion in equilibrium with excess oil.

Previous study of Shinoda showed that AOT/brine/oil system had hydrophobic properties below 45 ºC, while had hydrophilic properties above 45ºC. In our model by addition of TEAC (1:1) molar ratio, the system became more hydrophilic by increasing temperature, which is above 25ºC the surfactant became more hydrophilic, and below it the surfactant became more hydrophobic.

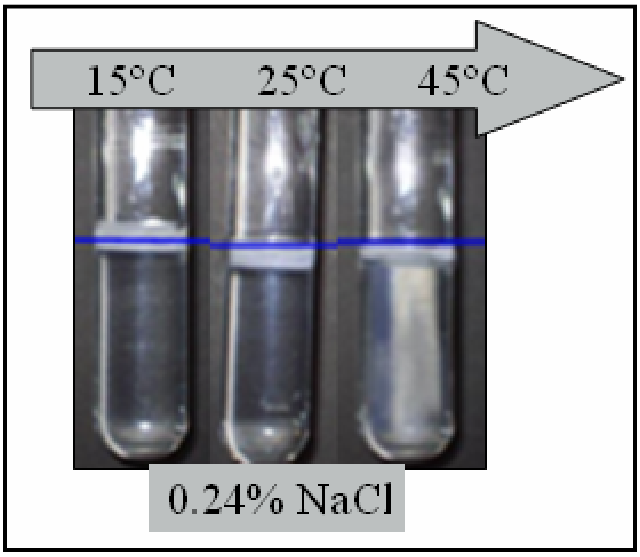


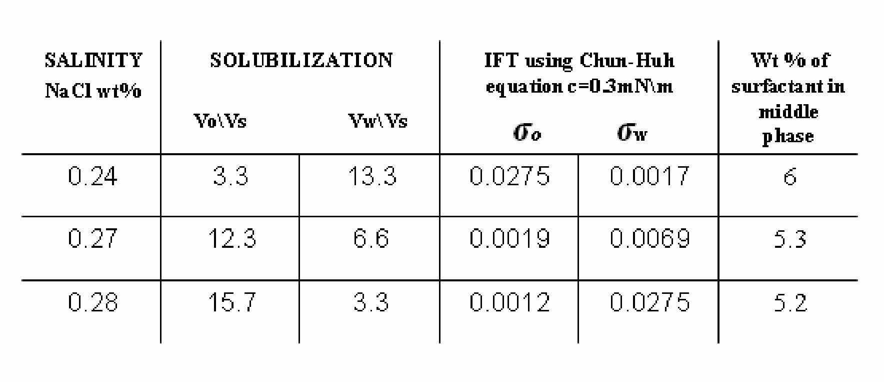
Figure 3.10 phase behavior of AOT/TEAC (1:1) molar ratio, WOR=1, at constant salt concentration (0.24% NaCl), at 15ºC, 25 ºC, 45 ºC.

The solubilization ratio and interfacial tension at the middle phase can be predicted using Chun-Huh equation at middle phase, tab. (3.1) as the following:

$$\sigma_{mo} = c \setminus (V_o \setminus V_s)^2 , \quad \sigma_{mw} = c \setminus (V_w \setminus V_s)^2$$

Where *σ mo* is the IFT between the oil phase and surfactant phase, and *(V o/ Vs)* is the ratio of solubilized oil to the volume of total surfactant, *σ mw* the IFT between the water phase and surfactant phase, *(Vw/Vs)* is the ratio of solubilized water to the volume of total surfactant, *c* is constant equal o.3 mN/m, which found to be consistent with this type of system [Liu, *et al.,* 2008][50].

Table 3.1: Solubilization ratio and IFT for a system AOT/TEAC (1:1) molar ratio WOR=1 at 25ºC using Chun-Huh equation, and wt% of surfactant in the middle phase assuming all surfactant in the middle phase



SALINITY NaCl wt%	SOLUBILIZATION		IFT using Chun-Huh equation c=0.3mN\m		Wt % of surfactant in middle phase
	Vo\Vs	Vw\Vs	σ_o	σ_w	
0.24	3.3	13.3	0.0275	0.0017	6
0.27	12.3	6.6	0.0019	0.0069	5.3
0.28	15.7	3.3	0.0012	0.0275	5.2

The above results are illustrated in Fig. (3.11) it shows that IFT between heptane and middle phase (σ *mo*) falls down with increasing salinity, from 0.0275 to 0.0012 mN\m. While IFT between water and middle phase *(σ mw)* rise up by increasing salinity from 0.0017 to 0.0275 mN\m. the figure shows that the IFT at 0.265 is equal at water and oil side which mean this point is the middle phase.

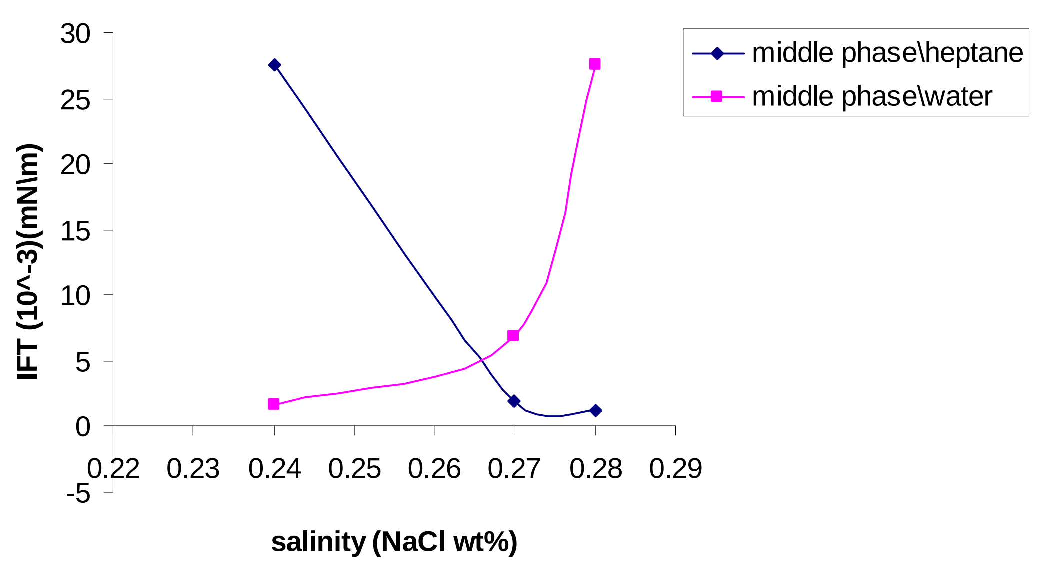


Figure 3.11: IFT verse NaCl wt % concentration as predicted by Chun-Huh equation, for a system 0.5% AOT: TEAC (1:1) molar ratio, WOR=1

These IFT results were confirmed using spinning drop tensiometer Table (3.2), the results are consistent to Chun-Huh result calculations, that both methods produce ultralow interfacial tension, which mean this system is applicable in many industrial field that need ultralow IFT for their formulations.

For measuring the IFT by spinning drop tensiometer, 5ml of brine was injected into glass tube of spinning drop with one drop of middle phase at 0.24, 0.27, 0.28% NaCl. And allow rotating horizontally until maximum elongation of middle phase drop, at this point the angular velocity measured was compensated in Vonnegut equation, and then we obtained IFT. The same procedure was done between middle phase and heptane. The results are illustrated in Table (3.2)

Table 3.2: IFT using spinning drop tensiometer, between brine and heptane, and between brine and middle phase for a system 0.5% AOT: TEAC (1:1) molar ratio, WOR=1

Salinity NaCl%	IFT (brine\ heptane) (mN\m)	IFT (brine\middle phase) (mN\m)
0.24	0.014	0.0009
0.28	0.0049	0.0002
0.30	0.012	0.006

Spinning drop results are illustrated in Fig. (3.12), the IFT between brine and middle phase fall down until reached optimum salinity (0.28% NaCl) which equal 0.0002 mN\m, after this point the IFT rise up again. Also the IFT between brine and heptane has ultralow value equal 0.0048 mN\m.

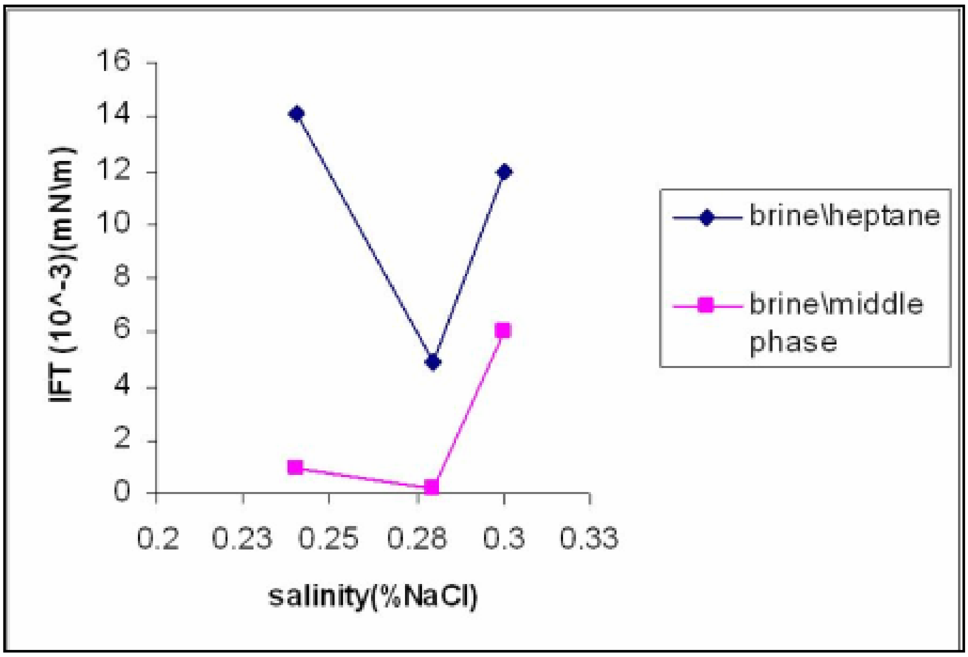


Figure 3.12: IFT between brine/Heptane, and brine\middle phase, for a system containing 0.5% AOT: TEAC (1:2) molar ratio, WOR=1**.**

3-5 Phase behavior of L123-4S/Variquat-cc9 (1:1) molar ratio WOR=1 by salinity scan and interfacial tension measurement

Phase behavior of extended surfactant by salinity scan can produce ultralow IFT close to 0.001 mN\m at optimum salinity, while for conventional surfactant AOT the IFT remains above 1 mN/m [Witthayapanyanon, *et al.,* 2006]7, this means the side chain of polyethylene –polypropylene oxide of extended surfactants give special properties of ultralow IFT and high solubilization capacity, and low CMC, such information will replaced in detergency and EOR where concentrated amount of surfactant is needed.

While studying Phase behavior of extended surfactant L123-4S with cationic hydrotropes Variquat-cc9 (1:1) molar ratio at low concentration reached 0.5% with water: heptane (1:1) weight ratio, the system produced ultralow IFT close to 0.00075 mN\m at optimum salinity, which are compatible with I.kayali *et al.* study [Kayali , *et al*. 2010c] [51]. The system meets winsor premises transition from winsor I to winsor III to winsor II fig. (3.13), it shows that it has optimal salinity at 3.25% NaCl concentration.

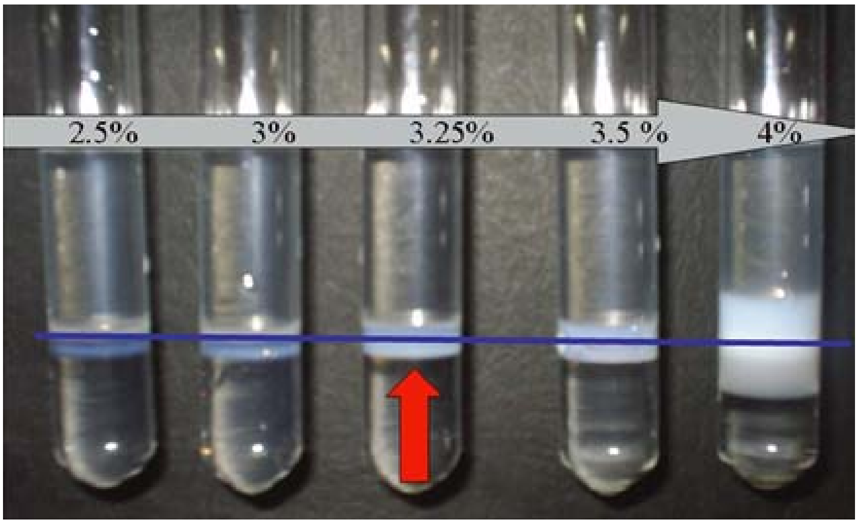


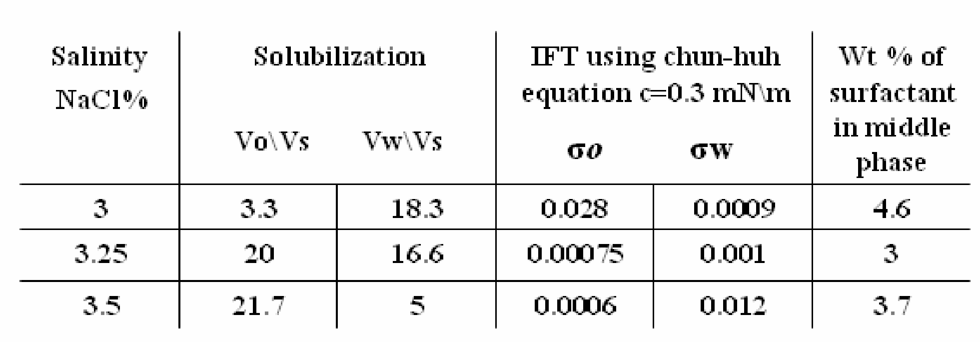
Figure 3.13: salinity scan for 0.5% L123-4S/variquate-cc9 (1:1) molar ratio with heptane WOR=1 at 25ºC, the arrow indicates the optimal salinity at 3.25 wt % NaCl. The horizontal line represents the amount of original oil and water.

On the other hand, by comparing this system with previous AOT/TEAC system, the conventional AOT /TEAC system behaves as extended surfactant and will produce ultralow IFT close to 0.0002 mN/m at optimum salinity, but with lower salt concentration than extended surfactant does.

Solubilization parameter and the IFT by chun-huh equation were determined in Table (3.3), it is clear that the solubilization ratio is rise up from 3.3 (ml of heptane \ml of surfactant) at 3% NaCl to 21.7 at 3.5% NaCl, which will reduce the IFT to its lower value 0.0006 mN\m between heptane and middle phase. Contrariwise between water and middle phase the solubilization ratio fall down from higher value 18.3 at 3% NaCl to lower one 5 at 3.5% NaCl Fig.(3.14).

These observations were correlated to phase behavior of most anionic surfactants, which at low salt concentration; below 2.5% NaCl the mixture were highly hydrophilic and the surfactant dissolved in water, forming micelles coexist with excess oil, we assume this phase winsor I. on the contrary at higher salt concentration; above 4% the mixture became more hydrophobic and the surfactant dissolved in heptane forming inverse micelle with excess water, we assume this phase winsor II. In between these two phases (2.5-4% NaCl) precisely at 3.25% NaCl ,the surfactant mixture has balanced hydrophilic-lipophilic properties (HLB) level, this phase is called winsor III or surfactant phase where the total amount of surfactant is present, and it range from 3-4.6%. Table (3.3)

Table 3.3: Solubilization ratio and IFT for a system L123-4S/variquate-cc9 (1:1) molar ratio WOR=1 at 25ºC using Chun-Huh equation, and wt% of surfactant in the middle phase assuming all surfactant in the middle phase



Salinity NaCl%	Solubilization		IFT using chun-huh equation c=0.3 mN\m		Wt % of surfactant in middle phase
	Vo\Vs	Vw\Vs	σo	σw	
3	3.3	18.3	0.028	0.0009	4.6
3.25	20	16.6	0.00075	0.001	3
3.5	21.7	5	0.0006	0.012	3.7

Predicted IFT by Chun- huh equation were illustrated in Fig.(3.14), it had the lowest value at optimum 3.25% NaCl which produced approximately 0.001 mN/m.

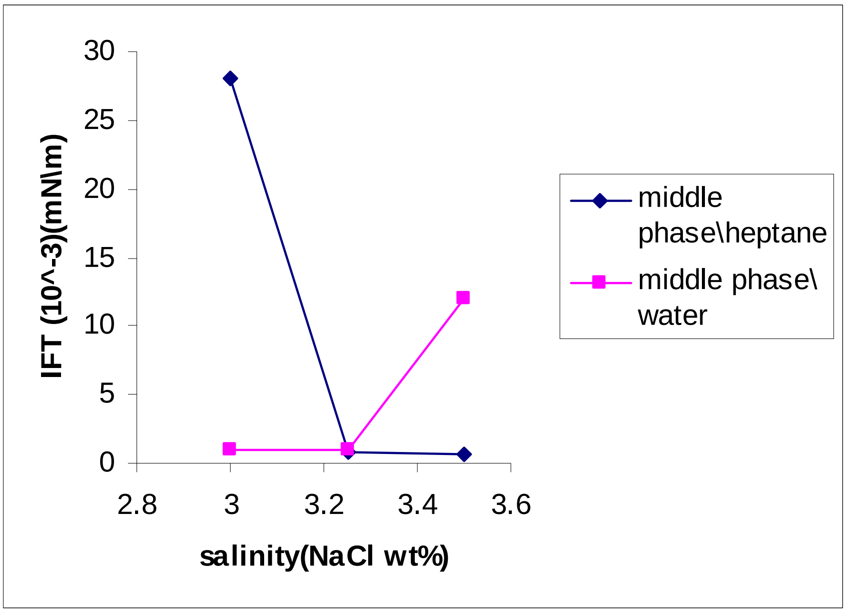
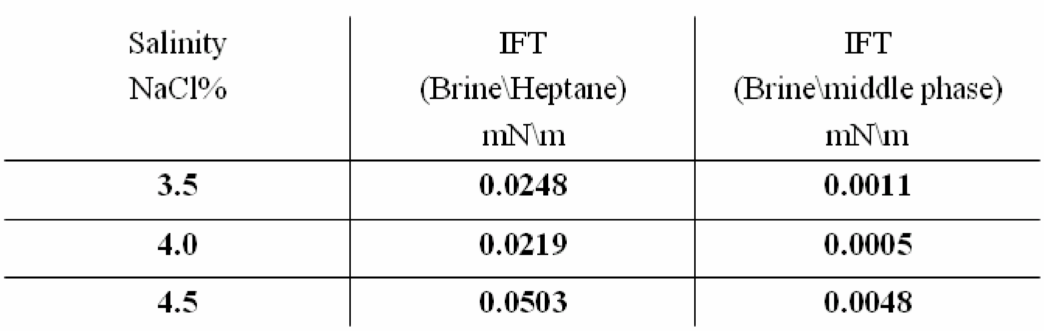


Figure 3.14: IFT versus NaCl wt % concentration as predicted by Chun-Huh equation, for a system 0.5% L123-4S/variquate-cc9 (1:1) molar ratio, WOR=1

For measuring the IFT by spinning drop tensiometer, 5ml of brine was injected into glass tube of spinning drop with one drop of middle phase at 3.5, 4.0, 4.5% NaCl. And allow rotating horizontally until maximum elongation of middle phase drop occurred, at this point the angular velocity measured was compensated in Vonnegut equation, and then we obtained IFT. The same procedure was done between middle phase and heptane. The results are illustrated in Table (3.4).

Table 3.4: IFT using spinning drop tensiometer, between brine and heptane, and between brine and middle phase for a system 0.5% L123-4S/variquate-cc9 (1:1) molar ratio, WOR=1 by spinning drop tensiometer



Salinity NaCl%	IFT (Brine\Heptane) mN\m	IFT (Brine\middle phase) mN\m
3.5	**0.0248**	**0.0011**
4.0	**0.0219**	**0.0005**
4.5	**0.0503**	**0.0048**

Fig. (3.15) illustrates IFT between brine and middle phase reached optimum salinity (4% NaCl) which equal 0.0005 mN\m, after this point the IFT rise up again. Also the IFT between brine and heptane has ultralow value equal 0.0048 mN\m.

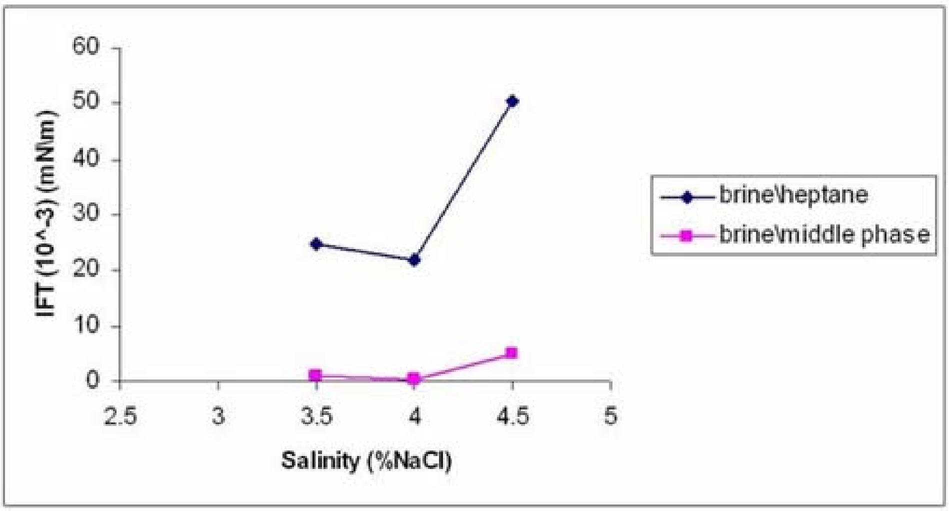


Figure 3.15: IFT between brine/Heptane, and brine\middle phase, for a system containing 0.5% L123-4S/variquate-cc9 (1:1) molar ratio, WOR=1**.**

3-6 Conclusion and future work

3-6-1 Conclusion

Cationic hydrotropes can be added to anionic surfactant for formulating alcohol free middle phase microemulsion with ultralow IFT, and high solubilization capacity, At minimum surfactant concentration.

TEAC short chain cationic hydrotrope can be added to anionic AOT in (1:1) molar ratio at 0.5% surfactant concentration, and low salt concentration(0.2-0.3% NaCl), to produce ultralow IFT equal to 0.001 mN/m and even less. Such system can also produce middle phase microemulsion at different temperature which will be more hydrophilic by increasing temperature in constant brine solution.

In the same way addition of variquat-cc9 short chain cationic hydrotrope to 0.5% extended surfactant L123-4S in equimolar ratio with WOR=1 and different salt concentration will produce middle phase microemulsion with ultralow IFT.

Finally we can conclude that addition of short chain cationic hydrotropes will change properties of AOT completely, which considered as conventional surfactant, while addition of TEAC to AOT solution will raise its level to extended surfactant by producing ultralow IFT and high solubilization capacity.

3-6-2 Future work

Both systems can be applied in EOR and SEAR efficiently at low surfactants concentration, without formation of liquid crystal and without addition of alcohol which will complicate the mentioned fields.

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الملخص العربي

العنوان:

سلوك السطوح الممتدة(extended surfactant) مع المركبات المحبة للماء
(hydrotrope)موجبة الشحنة

اعداد:
هالة حسام الدين يوسف (شقوارة) بحر.

اشراف:
د.ابراهيم الكيالي

الملخص:

هذه الدراسة تناولت سلوك الانظمة المحتوية على مواد منشطة للسطوح (surfactant) سالبة الشحنة، مع مركبات محبة للماء (hydrotrope) موجبة الشحنة، بوجود الماء والزيت (heptane). النظام الاول يحتوي على عوامل منشطة سالبة الشحنة تسمى (AOT) مع مركبات محبة للماء (hydrotrope) موجبة الشحنة(TEAC)، مع الماء والزيت(heptane) فتكون من خلالها مستحلب ذات جزيئات بالغة الصغر(ميكرو املشن) (microemulsion) . والشيء نفسه حصل لعوامل منشطة تسمى العوامل المشطة للسطوح الممتدة (extended surfactant) على تراكيز ملح مختلفة.

تم تعيين المناطق المتباينة الخواص (anisotropy) لهذه الانظمة عن طريق ميكروسكوب الاستقطاب (polarize microscopy) وتم قياس التوتر السطحي منخفض القيمة لهذه المستحلبات (microemulsion) نظريا بواسطة معادلة (chun-huh) ، وتم التحقق من النتائج عمليا بواسطة تجربة (spinning drop) . وجود المركبات المحبة للماء (hydrotrope) (TEAC) قصيرة الذيل ، ادت الى اختفاء منطقة (liquid crystal) الموجودة في الرسم الثلاثي االاطوار (ternary phase diagram) للنظام (AOT/water/heptane) .

التوتر السطحي منخفض القيمة لهذه المستحلبات تكون بتراكيز ضئيلة من العوامل المنشطة (surfactant) تصل الى (0.5%) للنظامين (AOT) و (extended surfactant) . تم دراسة تاثير الحرارة على المستحلبات (microemulsion) بوجود (AOT) ، وجد ان (AOT) يتصرف بشكل معاكس للعوامل المنشطة الغير متأينة(nonionic).

اهمية الدراسة تكمن في تطبيقها في مجالات تحتاج عادة الى تراكيز عالية من العوامل المنشطة للسطوح لتكوين المستحلبات (microemulsion) و بوجود الكحول. هذه الانظمة احتوت على تراكيز ضئيلة من المواد المنشطة للسطوح(surfactant) بدون الحاجة لاستعمال الكحول غير المرغوب فيه .ومن هذه المجالات؛ تنقية المياه الجوفية من الشوائب العضوية، واستخراج البترول من حقول النفط .

J. Chem. Soc., Faraday Trans. 2, 1976, 72, 1525 - 1568,
Theory of self-assembly of hydrocarbon amphiphiles into micelles and bilayers
Jacob N. Israelachvili, D. John Mitchell and Barry W. Ninham