

**Deanship of Graduate Students
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**Phase Behavior of Mixed Nonionic Surfactants Using
Sucrose Ester, Field of Application: Water-Diesel
Fuel.**

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Sucrose Ester, Field of Application: Water-Diesel Fuel.

Prepared by:

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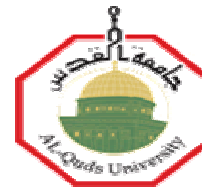
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Thesis approval

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Dedication:

I would like to dedicate this work to ***my parents***, who gave me confidence from the beginning and gave me the ability to continue studying and work efficiently, my family, my friend ***Dr. Ibrahim Afaneh*** who believing in me all the time.

Finally, don't go where the path takes you, go where there is no path and leave your footprints behind.

Salam wadaa'h

Declaration:

I certify that this thesis submitted for the degree of Master is my own research, expect 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:

Salam A'Mar Wadaa'h Muhammad Salem

Date / /2012.

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Abstract:

This study aims to investigate microemulsion formulas serves water-Diesel fuel; using minimum amount of nonionic strongly hydrophilic sugar ester surfactant. The sugar ester in this study is the commercial sucrose monolaurate (1695); was studied with glycerol monooleate (M300K) nonionic hydrophobic surfactant. The oil phases are n-heptane (model oil) and diesel. Co-surfactants also were used including hydrophilic alcohol ethoxylates (C₁₈E₁₀₀), propionic acid, butanol and 1-pentanol.

In this research, we firstly studied the effect of different percentage of surfactants on the phase behavior of the systems water/mixed surfactant / n-heptane at different temperature 25, 37 and 45°C. We also explored the effect of adding co-surfactant on the phase behavior of the systems water/sucrose monolaurate (1695) / Diesel at 25°C. Lastly the Phase behavior of sucrose monolaurate (1695) studied as a function of temperature and surfactant concentration; that presented in the form of the well known 'fish' diagram. Anisotropy was detected using visual inspection, cross polarizers and polarizing microscope. The hydrodynamic diameter of microemulsion micelle also was determined using dynamic light scattering.

Water-Diesel fuel microemulsion was formulated using minimum amount of strongly hydrophilic sugar ester surfactant (1695) values as low as 10 wt% at 25°C. and the average hydrodynamic diameter of microemulsion micelle equals 10.86 nm at 25°C.

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Abbreviations, Symbols and Terminology:

HLB: Hydrophile–Lipophile balance.

CMC: Critical micelle concentration.

L1: Spherical normal micelles.

L2: Reversed micelle.

H1: Normal hexagonal phase.

H2: Reversed hexagonal phase.

L α : Lamellar phase.

I1: Normal micellar cubic liquid crystalline phase.

I2: Reversed micellar cubic liquid crystalline phase.

V1: Normal bicontinuous cubic phase.

V2: Reversed bicontinuous cubic phase.

SE: Sucrose ester.

L1695: Sucrose monolaurate.

M300K: Monoolein.

1 Φ : One-phase area.

NO x : Nitrogen oxides emissions.

W m + O: Water continuous micellar solution with excess oil.

M Φ : Multi phase.

nm: Nanometer.

σ : Electrical conductivity.

μ S: Microsiemens.

mm: Millimeter.

O/W: Oil in water.

W/O: Water in oil.

$\underline{2}$: O/W type coexists with excess oil.

$\bar{2}$: W/O type coexists with excess water.

\bar{V} : Surfactant concentration.

ppm : Part per million.

Wt%: Weight percent.

K: Kelvin.

δ : Co-surfactant concentration.

d_H : Hydrodynamic diameter.

DLS: Dynamic light scattering.

Chapter One:

Introduction

1. Introduction:

1.1. Surfactant:

Surface active agent or simply "**Surfactant**", is a general term used to describe molecules that interact with an interface. These consist of two parts, one of which is highly soluble in one of the phases while the other is not [Goodwin, 2004]¹. Their structures consist of a hydrophobic tail which is usually a hydrocarbon, and polar hydrophilic head group which may be ionic, non-ionic and zwitterionic. Fig.1.1.

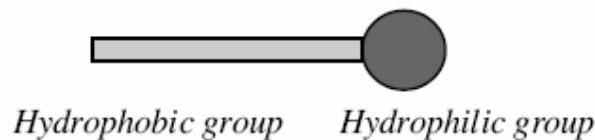


Figure.1.1. Schematic illustration of surfactant molecule

Adsorption of a surfactant at the water/oil interface produces a surface with a significant very low interfacial energies, the formation of this type of low interfacial energy surface is the basis of the stability of most oil and water emulsions and all microemulsions. Fig.1.2. [Richard, *et al.* 2004]²

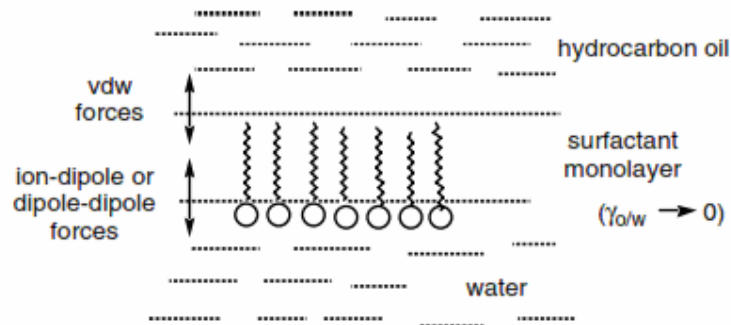


Figure.1.2. Illustration of the effect of an adsorbed surfactant layer on the interfacial energy between oil and water [Richard, *et al.* 2004]².

The most useful chemical classification of surfactant is based on the nature of the hydrophilic part (head), with subgroups based on the nature of the hydrophobic part (tail). The four basic classes of surfactants are [Myers, 2006]³: Anionic in which the hydrophilic part is a negatively charged group such as carboxyl (RCOO^-M^+), Cationic the hydrophilic part is a positive charge as for example, the quaternary ammonium halides ($\text{R}_4\text{N}^+\text{X}^-$), nonionic the hydrophilic has no charge, but derives its water solubility from highly polar groups such as R-Polyol groups including sugars and amphoteric (zwitterionic). The molecule contains, or can potentially contain both a negative charge and a positive charge, such as the sulfobetaines ($\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^-$).

With a wide variety of surfactant structures available, it is not surprising that the selection of a suitable surfactant for a given application can become a significant problem. Thus an empirical numbering system has been developed to enable the correct type of surfactant to be chosen. The system is called the 'hydrophile-lipophile balance' (HLB).

1.2. Self-Assembled Surfactant Structures:

In aqueous solution dilute concentrations of surfactant act much as normal electrolytes, but at higher concentrations very different behaviour results. This behaviour is explained in terms of the formation of organized aggregates of large numbers of molecules called micelles Fig.1.3. In which the lipophilic parts of the surfactants associate in the interior of the aggregate leaving hydrophilic parts to face the aqueous medium. Meanwhile, That happens at a specific, higher, surfactant concentration, known as the critical micelle concentration (CMC). Besides, the physico-chemical properties of surfactants vary markedly above and below the CMC value [Schramm, *et al.*2003]⁴.

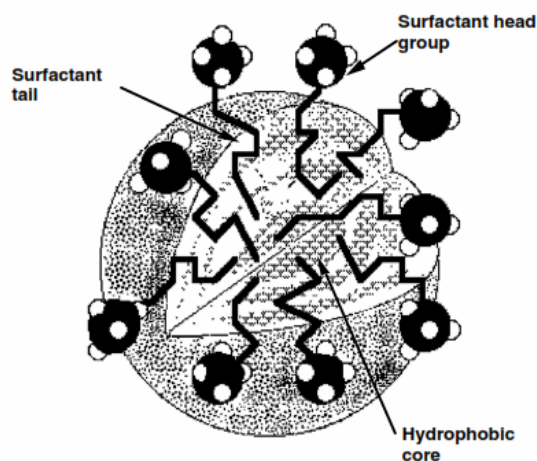


Figure.1.3.Schematic diagram of a surfactant micelle [Schramm, *et al.*2003]⁴.

In addition, acting surfactants at oil/water interface formed a large number of self-assembled structure depending on the type of surfactants [Borne, 2002]⁵. Spherical normal micelles (L₁) are formed at high water content (oil/water), while reversed micelle (L₂) are formed at low water content (water/oil), between these two extremes different isotropic and anisotropic liquid crystalline phases with decreased water content or increased temperature or electrolyte concentration may be formed. The following sequence of anisotropic liquid crystalline phase may take place for the surfactant systems Fig.1.4:

Normal hexagonal phase (H_1) → lamellar phase ($L\alpha$) → reversed hexagonal phase (H_2). Isotropic discrete reversed micellar cubic liquid crystalline phase (I_2) and normal (I_1) can appear between the micellar and the hexagonal phases of both the reversed and normal types. The normal bicontinuous cubic phase (V_1) and reversed (V_2) occur on each side of lamellar phase.

The variation and complexity of these structures has led to much research on potential industrial applications. However, microemulsion is the most important structures in which single low viscous isotropic phase formed in L_1 and L_2 regions of the phase diagram.

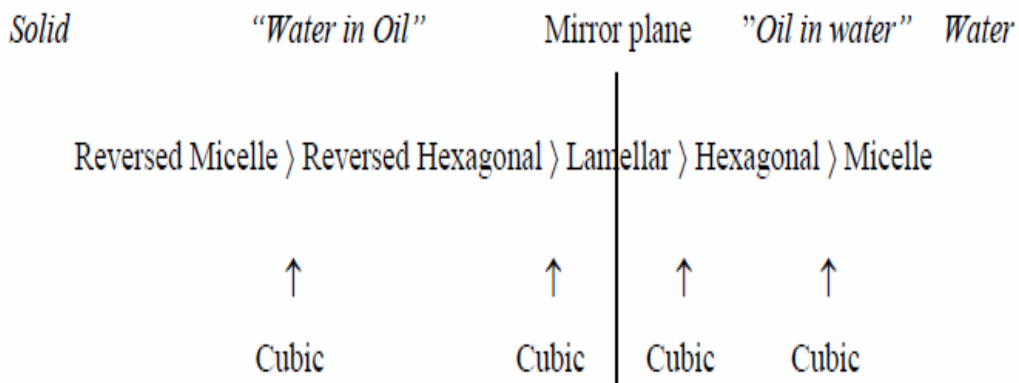


Figure.1.4. The fontell scheme, showing the idealized sequence of association structures of surfactants [Borne, 2002]⁵.

The critical packing parameter can be used as a guide to the aggregate Architecture for a given surfactant. Represented by eq (1). Where a the cross sectional area of head group for surfactant, lc extended chain length and v a hydrocarbon volume.

$$R = \frac{v}{alc} \dots \dots \dots \text{eq (1)}.$$

Typical values and their corresponding aggregate structures are [Richard, *et al.*2004]²:

$\mathbf{v}/\mathbf{alc} < 1/3$Spherical micelles.

$1/3 < \mathbf{v}/\mathbf{alc} < 1/2$Poly-dispersed cylindrical micelles.

$1/2 < \mathbf{v}/\mathbf{alc} < 1$ Vesicles, oblate micelles or bilayers.

$\mathbf{v}/\mathbf{alc} > 1$Inverted structures.

1.3. Sugar-Based Surfactants:

Sugar-based surfactants are characterized by having the hydrophilic sugar head group and the hydrophobic alkyl chain. This structural feature provides unique physicochemical properties to these surfactants. Among the characteristic properties of Sugar-based surfactants, a frequently remarked fact is that they can be produced from renewable resources and exhibit excellent ecological behavior. Certainly, there is currently a clear tendency to replace conventional surfactants with more environmentally benign compounds. Although interest in Sugar-based surfactant was traditionally, they have recently become the object of increasing attention for many researchers.

The behavior of Sugar-based surfactants is also critically influenced by the nature of the substituent groups bound to the individual monosaccharides. These substituents can be of natural origin or seminatural quality. Whether they are natural or seminatural, the classification of Sugar-based surfactants falls into one of five categories, based primarily on the polysaccharide charge. These include: anionic, cationic, nonionic, amphoteric, and hydrophobically modified Sugar-based surfactants [Gruber, 1999]⁶. It is clear from an industrial perspective that only a few carbohydrates fulfill the criteria of price, quality, and availability. Today, the most important sugar-based surfactants are alkyl polyglycosides, sorbitan esters, and sucrose esters.

1.4. Sucrose Ester Surfactants:

Sucrose ester (SE), nonionic surfactants, contain sucrose as the hydrophilic group and a fatty acid as the hydrophobic [Fanun, *et al.* 2006a] ⁷, They are tasteless, odorless, nontoxic and non irritant to eyes and skin, biodegradable and approved as food, pharmaceutical and cosmetics emulsifiers in most countries of the world. An advantageous property of sucrose ester surfactants is their weak temperature dependence of the head group hydration, also temperature insensitive microemulsions were formulated using this surfactant [Fanun, *et al.* 2006b] ⁸.

The manufacture of sucrose esters is quite challenging because the sucrose molecule is very temperature sensitive. And due to its high functionality with eight hydroxyl groups, selectivity in the esterification reaction is difficult to achieve Fig.1.5. General chemical pathways are either direct esterification with fatty acids or trans-esterification of sucrose with fatty acid methyl ester. The major producers for sucrose esters are Dai-Ichi Kogyo Seiyaku and Mitsubishi in Japan[Ruiz, 2009] ⁹. The fats may react with one or more primary hydroxyl groups of sucrose to form mono-, di- or poly-esters. And these surfactants offer a full range of hydrophilic–lipophilic balances (HLB) values from 1 to 16[Fanun, *et al.* 2006b] ⁸.

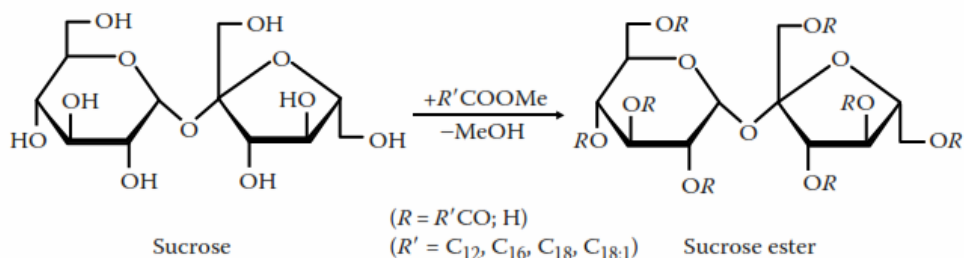


Figure.1.5. Synthesis of sucrose esters by base catalyzed trans-esterification with Fatty acid methyl esters (R'COOMe) are usually carried out in solvents (e.g., dimethyl formamide), microemulsions or solvent free[Ruiz, 2009] ⁹.

Sucrose monolaurate (L1695) Fig.1.6. is the result of the reaction between sucrose and lauric acid used as a powerful emulsifier [Fanun, *et al.* 2006b]⁸. It is a strongly hydrophilic nonionic surfactant; its solubility in many classes of oils is very low requiring the use of a co-surfactant to augment its solubility in oils and create water/sucrose laurate/oil microemulsion [Fanun, *et al.* 2006a]⁷.

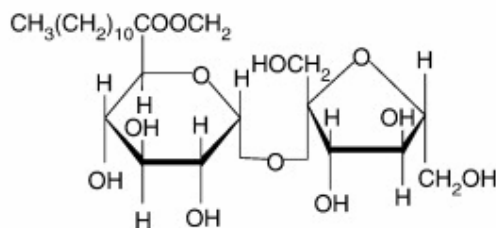


Fig.1.6.Chemical structure of sucrose monolaurate [Fanun, *et al.* 2006b]⁸.

Table.1.1.shows the properties and composition of Sucrose monolaurate (L1695) used in this research project.

Table. 1.1. Properties and composition of sucrose monolaurate (L1695) [Fanun, *et al.* 2006b]⁸.

HLB	CMC($\times 10^{-3}$) (mol/dm ³)	Purity of combined fatty acids (%)	Ester composition (%)		Melting point (°C)	
			Monoester	Di, tri and polyester	Start point	Peak point
16	0.5	Lauric 95				
			80	20	35	47

Using polarizing microscope and Low angle X-ray, Thelma and his team investigated phase behavior of L1695/water system over the temperature range 0-100°C in all concentration[Herrington, *et al.*1988]¹⁰.They predicted three an isotropic region (H₁, L_α, and L_β), while one isotropic region L₁.

Fanun and Salah Al-Diyn group demonstrated the effect of temperature in the presences of different types of oils in the phase behavior of the system water/sucrose laurate (L1695)/ethoxylated mono-di-glyceride (EMDG)/oil [Fanun, *et al.* 2006a] ⁷. Where the mixing ratio of ethoxylated monodi-glyceride/sucrose laurate (EMDG\L1695) was varied, they found a synergistic effect of the mixed surfactant that a mixture of surfactants enhances the surfactants partitioning at the interface, increases the stability of the amphiphilic film, and enhances the mutual solubilization of water and oil. This also will decrease the phase inversion temperature and increases the efficiency of the mixed surfactants.

The pseudo ternary phase diagram of the water/sucrose laurate/ethoxylated-mono-di-glyceride/peppermint oil system studied at 25°C Fig1.7. [Fanun, 2010c] ¹¹. The phase behavior indicates the presence of an isotropic and low-viscosity area that is a microemulsion region (1Φ); the remainder of the phase diagram represents a multiphase region composed of the water continuous micellar solution with excess oil designated by ($W_m + O$).

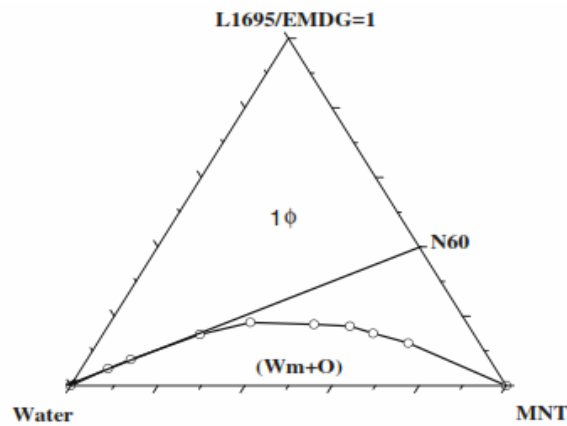


Fig1.7.Pseudoternary phase diagram of the water/sucrose laurate/ethoxylated mono-di-glyceride/peppermint oil system [Fanun, 2010c] ¹¹.

The phase behavior as function of temperature and oil content in the water/sucrose laurate/ethoxylated mono-di-glycerides/caprylic-capric triglyceride system was investigated [Fanun, 2007d]¹². The types of microstructures formed along the one phase microemulsion channel were examined using self-diffusion NMR. The very large variations in the relative diffusion coefficients of water and oil on varying their weight fractions indicates microstructural transitions from O/W structure at low oil to water ratio to W/O at high ratio passing through a bicontinuous structure.

1.5. Monoolein (M300K) Surfactant:

Monoolein (M300K) is a synthetic surface-active chemical widely used as a nonionic surfactant. It is prepared by esterifying glycerin with food-grade oleic acid in the presence of a suitable catalyst to form a monoglyceride ester; glycerol monooleate is clear amber or pale yellow liquid, and also glycerin is completely soluble in water, while oleic acid is insoluble in water. Hence the hydrophilic-lipophilic balance (HLB) of glycerol monooleate is 3.8 [OMRI, 2001]¹³ Fig.1.8.

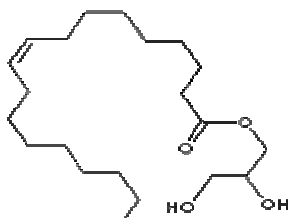


Fig.1.8. Chemical structure of glycerol monooleate.

Hong Qiu *et al* .reported the phase diagram of monoolein/water system over the temperature range from -15 to 55°C and 0-50% (w/w) water composition ranges [Qiu, *et al.*2000]¹⁴. The pure phases found in this system determined By X-ray diffraction include: the LC phase, the L α phase, two inverted bicontinuous cubic Phases belonging to space groups Ia3d and Pn3m and the fluid isotropic (FI) phase.

In another study the binary phase diagram of the monoolein/water system at 25 °C was demonstrated [Borne, *et al.*2000]¹⁵. The samples were examined by visual inspection and between cross polarizer sheets in order to verify sample homogeneity and identify anisotropic and isotropic phases. From these examinations, they acquired a number of anisotropic and isotropic phases involve bicontinuous cubic phase; lamellar phase, reversed micellar phase and hydrated lipid crystals.

1.6. Microemulsion:

Though historically microemulsion has been studied for along time, their importance was not acknowledged until the work of schulman in 1943 with his definition of microemulsion [Satya, *et al.* 2006] ¹⁶. Microemulsions are macroscopically isotropic mixtures of at least a hydrophilic, a hydrophobic and an amphiphilic component. Their thermodynamic stability and their nanostructure are two important characteristics that distinguish them from ordinary emulsions which are thermodynamically unstable [Cosima, 2009] ¹⁷.

The interfacial tension of microemulsion has to be ‘ultra-low’, with typical values being in the range from 10^{-4} up to 10^{-2} mNm⁻¹, while the particle size range from 5–50 nm [Goodwin, 2004] ¹. There are four kinds of microemulsion: Oil-in-water microemulsion with upper excess oil (Winsor I), bicontinuous microemulsion (Winsor III), water-in-oil microemulsion with the low excess water (Winsor II) and the single phase with water, oil and surfactant (Winsor IV) [Winsor, 1954] ¹⁸. Though microemulsion macroscopically homogeneous are heterogeneous on the sub-microscope scale and the stability of the microemulsion can be influenced by adding of salt, other additives, temperature or pressure.

Microemulsion, based on nonionic surfactants, has been extensively investigated. In almost all nonionic microemulsion the nonionic surfactants used are single surfactants. However, mixed nonionic surfactants are also used [Fanun, 2008e] ¹⁹. Phase behavior of nonionic amphiphiles is characterized by the change in the distribution of the amphiphile between the water-rich and oil-rich phase with the change in temperature [Fanun, *et al.* 2006a] ⁷. Upon increasing temperature the phase behavior sequence will depend on the total amphiphile concentration. At low amphiphile concentration the sequence will be: Winsor I- Winsor III- Winsor II, while at high amphiphile concentration the sequence will be: Winsor I- Winsor IV- Winsor II.

Microemulsions are usually characterized by ternary phase diagram, which three edges are the components of a microemulsion; namely oil, water and surfactant. Any co-surfactant used are usually grouped together With the surfactant at a fixed ratio and treated as a pseudo-component [Kai, 2010] ²⁰. Fig.1.9.

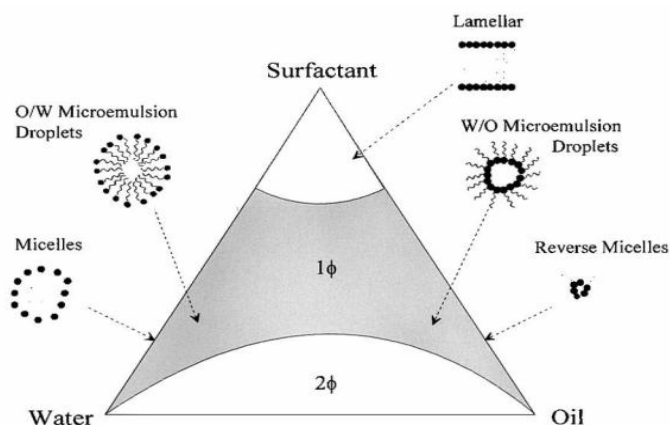


Fig .1.9. Ternary phase diagram of microemulsion [Kai, 2010]²⁰.

One of the central questions of microemulsion formulation has been, and still is, the quest for high efficiency, which means finding microemulsions in which a minimum amount of surfactant is necessary for solubilising oil in water or vice versa [Ruiz, 2009]⁹. A rapid method for quantifying the efficiency of a system is to determine the X –point by recording a T (γ)-section at an oil/ (water +oil) volume fraction $\Phi = 0.5$. Fig .1.10. [Cosima, 2009]¹⁷.

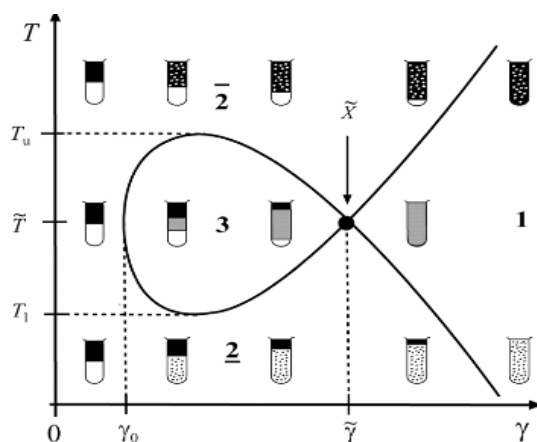


Fig .1.10. T (γ) -section at a constant oil/ (water + oil) volume fraction of $\Phi = 0.5$, for nonionic surfactant [Cosima, 2009]¹⁷.

Characterization of microemulsions is very important especially for industrial processes. This includes both macroscopic measurements and microenvironment methods. Macroscopic measurements involving viscosity, conductivity, as well as dielectric measurements, cross polarizers for birefringence and polarizing microscope. On the other hand, microenvironment studies can involve pulsed field NMR, scattering methods such as light scattering, neutron scattering and X-ray scattering.

Cross polarizers and polarizing microscope can be used to distinguish between microemulsion and different types of surfactant association structure that appear during the construction of phase diagram. 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, *et al.*2001]²¹. While Dynamic light scattering can also be applied to obtain the hydrodynamic radius of the micelle, by measuring the intensity fluctuation of scattered light by the micelles when these undergo Brownian diffusion [Gruber, 1999]⁶.

Kayali *et al.* Used visual inspection as well as cross polarizers to detect anisotropy for water, L 123 – 4S (a alkyl polypropylene oxide sulfate C₁₂ (PO)₄SO₄), decane system at 25°C [Kayali, *et al.* 2012a]²². His work shows that three one phase regions, the anisotropic lamellar liquid crystalline phase L_α, the isotropic L₁ micellar liquid and L₃ sponge phase.

Anisotropy for systems containing sodium bis (2- ethylhexyl sulfosuccinate) (AOT), with the cationic hydrotrope tetraethyl ammonium chloride (TEAC), in the presence of water and heptane was detected using cross polarizers and polarized microscopy [Kanan, *et al.* 2012]²³.

The value of the hydrodynamic radius for the water + propylene glycol/sucrose Laurate/ethoxylated mono-Di-Glyceride/ peppermint Oil +ethanol system was determined with value as low as 11nm; using Dynamic light scattering; at aqueous phase volume fraction and temperature equal 90% and 25°C respectively[Fanun, 2010i]²⁴.

1.7 Alcohol Conventional Effects:

Three effects of an alcohol additive in the formulation of microemulsion have been mentioned so far [Cosima, 2009]¹⁷. First, it contributes to the general formulation as a co-surfactant, slightly hydrophilic contribution for methanol and ethanol; lipophilic contribution for n-butanol and longer linear alcohols. And second, as a co-solvent. The alcohol co-adsorbs with the surfactant at the interface and thus changes the overall interaction of the amphiphilic film with the adjacent solvents. The longer the alcohol, the lower its tendency to act as co-surfactant, because it is rather solubilised in the oil phase. Consequently, the co-surfactant effect may be said to fade away. As the alcohol mostly partitions into the water or oil phase it behaves either as a co-solvent. When such alcohol co-solvents are present in small proportion, they might not mix uniformly in the bulk of the oil or water phase and they could exhibit a third effect so-called lipophilic linker Fig.1.11.

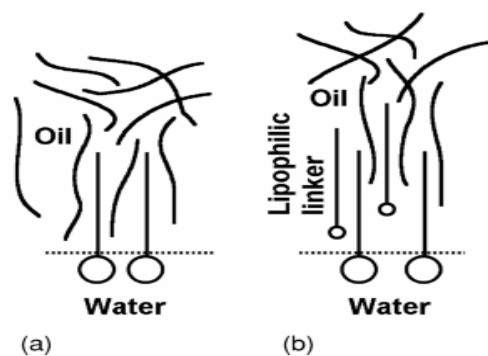


Figure.1.11. Solubilisation improvement of a conventional surfactant (a) by a lipophilic linker (b) [Cosima, 2009]¹⁷.

The high surfactant concentration required to formulate a microemulsion, usually 20% or more, remains a major concern for the user. In addition, much of the work on microemulsions has employed alcohols as co-surfactants and as co-solvent in order to decrease surfactant film rigidity, thus promoting microemulsion formation and delay the occurrence of liquid crystalline phases. Alcohol can also reduce the time needed for equilibration to be reached in multi phase systems. [Kayali, *et al.* 2012b]²⁵. However, for application like water-diesel fuel, alcohol may be desirable to be use at low percent, because their volatility, flammability.

Microemulsion stabilized by sugar surfactants usually contains a co-surfactant. Without a co-surfactant only o/w-microemulsions are formed, which is mainly due to the fact that the high hydrophilicity of sugar surfactants cannot be changed significantly by temperature variation [Ruiz, 2009]⁹. It was found that sucrose esters are not able to form w/o microemulsion without co-surfactants. However, sucrose esters, in the presence of alcohols and cetearyl octanoate as the oil phase, were able to solubilize large amounts of water up to 45 wt. % [Garti, *et al.*2000]²⁶.

Fanun reported the effect of ethanol in formulation of mixed nonionic surfactants microemulsion. The systems were water/sucrose laurate/ethoxylated mono-di-glyceride/oleic phase [Fanun, 2008e]¹⁹. The oleic phase was R (+)-limonene, isopropylmyristate, and caprylic-capric triglyceride; these oils were mixed with ethanol at different mixing ratios (w/w). The total area of the monophasic microemulsion increases with the increase in the ethanol/oil mixing ratio (w/w).

Pseudoternary phase diagram of the water + propylene glycol/ L1695/ Benzaldehyde + ethanol system was determined at 37°C [Fanun, 2008f]²⁷. Where the weight ratios of Water/propylene glycol and that of benzaldehyde/ethanol equal 2 and 1, respectively. The isotropic and low viscosity area is presented in the phase diagram as a microemulsion one phase area (1 Φ). The remainder of the phase diagram represents the turbid region, represented as multiphase (M Φ) conventional emulsions based on visual identification. Fig.1.12.

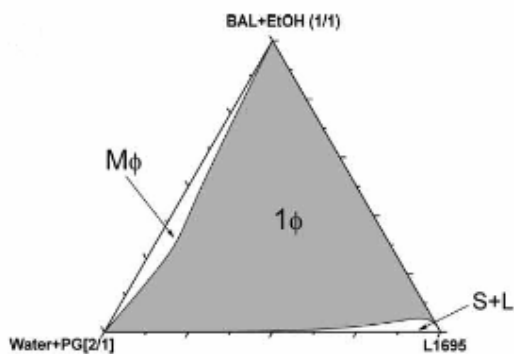


Figure.1.12. Pseudoternary phase diagram of the water + propylene glycol/ L1695/benzaldehyde + ethanol at 37°C [Fanun, 2008f]²⁷.

In 2009 Fanun investigated the pseudo ternary phase diagram of the water + propylene glycol/ sucrose laurate/peppermint oil + ethanol systems at 25°C[Fanun, 2009g] ²⁸. The mixing ratios (w/w) of water/propylene glycol and that of ethanol/oil equal 1 and 2, respectively. The phase behavior indicates the presence of an isotropic and low-viscosity area that is a microemulsion one-phase region, the remainder of the phase diagram represents a two-phase region composed of water continuous micellar solution with excess oil designated by .Fig.1.13.

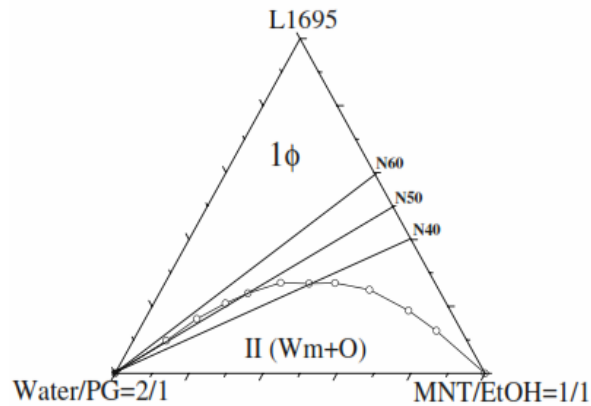


Figure.1.13. the pseudo ternary phase diagram of the water + propylene glycol/ sucrose laurate/peppermint oil + ethanol systems at 25°C[Fanun, 2009g] ²⁸.

1.8 Application of Microemulsion:

Microemulsions have found numerous applications in different fields due to their unique properties that are low interfacial tension, high thermodynamic stability, high interfacial area, and the ability to dissolve immiscible liquids.

Within the last 30 years, microemulsions have also become increasingly significant in industry. Besides their application in enhanced oil recovery, they are used as lubricants, cutting oils and corrosion inhibitors, coatings and textile finishing, in detergency, cosmetics, agrochemicals, food, pharmaceuticals, environmental remediation and detoxification, analytical applications as liquid membranes and in biotechnology [Moulik, *et al.*2006]²⁹.

In details, the water molecules solubilized in the interior of the water pool have properties different from those of bulk water. This makes reverse microemulsion applicable to many fields such as water –diesel fuels [Ding, *et al.*2007]³⁰.

1.9 Alternative Fuel (Water-Diesel Fuel):

During the past several decades, there has been a considerable increase in research and development in areas of environmentally acceptable alternative fuels; Synthetic fuels were of prime interest in the 1970s, due to a sudden shortage of petroleum supply kindled by an oil embargo in 1973, as well as public concern about Dwindling petroleum reserves, Although synthetic fuels seemed to be a most promising solution to the conservation of petroleum resources or at least, frugal use of the resources and the development of additional sources for conventional liquid fuels [Lee, *et al.*2007] ³¹.The Concerns of global warming via greenhouse gases have further intensified the issue of environmental acceptance of fuel consumption. Hence, efforts have been made to reduce emissions of air pollutants associated with combustion processes whose sources include electric power generation and vehicular transportation.

The problem is incomplete combustion, the long-chain hydrocarbons used as diesel fuel do not burn as easily as the lighter ones found in petrol. Some of the carbon therefore ends up as soot, rather than carbon dioxide, and oxygen that should be combining with carbon combines with nitrogen from the air instead. One possibility for the simultaneous improvement of combustion efficiency and reduction of emission of noxious substances is the use of special fuels; especially fuels which consist of a mixture of aqueous and non-aqueous phases, such fuels allow an efficient combustion process in spite of comparatively low combustion temperatures.

The investigations of different groups have shown that the increase of the oxygen content in blend fuels with additives such as ester, ether, acetals, alcohols etc. cause the reduction of soot emissions, hence The addition of water leads to a reduction of nitrogen oxide and soot emissions Simultaneously[Bemert, *et al.*2009] ³².

One way to add water to air–fuel mixtures is to use water-in diesel Fuels. These fuels are generated by mixing vigorously the two main components and stabilizing them by adding relatively small amounts of emulsifiers, i.e. surfactants and polymers. The two main components are blend into a system consisting of fine, or ultra fine, water drops dispersed in diesel forming either an emulsion or a microemulsion [Ochoterena, *et al.* 2010]³⁵. The amount of water dispersed in diesel with in the range of 5–15% for an emulsion or a microemulsion water-diesel fuel [Lif, *et al.* 2010a]³³.

However, for practical use and environmental concerns, the surfactants used should burn readily without forming smoke and should not contain sulfur or nitrogen. Thus, they should contain only carbon, hydrogen and oxygen and they should preferably not have aromatic rings in their structure. Nonionic surfactants based on aliphatic hydrocarbon tails, such as alcohol ethoxylates, fatty acid ethoxylates and *sugar esters* of fatty acids, are typical candidates [Lif, *et al.* 2006b]³⁴.

The advantageous effects of water on the combustion of diesel- fuel have been repeatedly studied over the past thirty years. Unfortunately, emulsions do not exhibit long-term stability as they separate into an aqueous and an oily phase after a certain time. However, the thermodynamic instability of emulsions has remained an unsolved problem. Thus the best way to produce a homogeneous mixture of two immiscible liquids as water and fuel is a microemulsion [Bemert, *et al.* 2009]³².

1.10 Water-In-Diesel Microemulsion:

Microemulsion-based fuel formulations date back to 1976 when Gillberg and Friberg published a paper on the use of water in-diesel microemulsions as fuel [Lif, *et al.*2006b]³⁴. The main advantage with the microemulsion concept is the thermodynamic stability which means that there should be no risk of phase separation on storage as long as the temperature is under control [Lif, *et al.*2010a]³³. Only the chemical stability of the single components could be a limiting factor [Bemert, *et al.*2009]³⁴. Fortunately incorporating water into the fuel as microemulsion provides opportunity to use water-in-diesel fuels in diesel engine vehicles with no major modifications of the engines [Ochoterena, *et al.*2010]³⁵.

In diesel fuels (a typical diesel hydrocarbon Equivalent to dodecane), many problems are overcome due to the high combustion temperatures (160–325°C) [Bidyut, *et al.*2001]³⁶. Hence, water incorporated in fuel as Microemulsion vaporizes during combustion and acts as a heat sink. In the case of combustion of fuel in an internal combustion engine; water is also expected to assist in fuel atomization due to microexplosions phenomenon, which occurs during the evaporation of the water inside droplets of fuel gives a membrane of oil Fig.1.14. This lowers the peak combustion temperatures, which results in a drastic reduction in nitrogen oxides (NO_x) emissions, reduces the particulate soot formation and improves the combustion efficiency [Ding, *et al.*2007]³⁰.

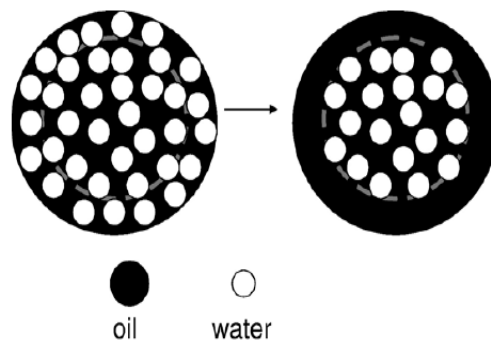
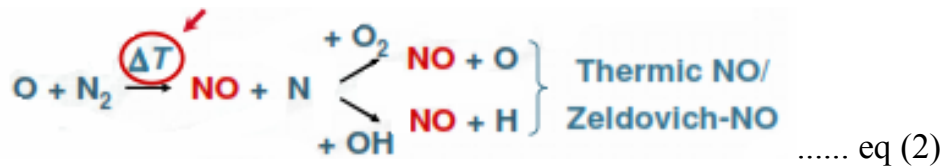
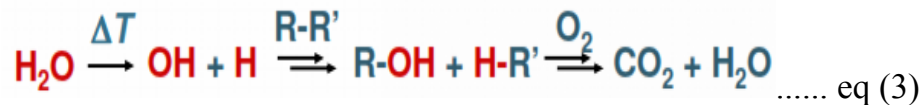


Figure.1.14. Formation of the oil membrane in the atomization process after fuel injection in the cylinder. Evaporation of water microdroplets in the periphery gives a membrane of oil [Lif, *et al.*2006b]³⁴.

Excess heat vaporizes water, this lowers combustion temperature, and less thermal energy for this initial step available so a decrease of 30% of nitrogen oxides produced according to Zeldovich eq (2) [Aljabarin, 2010]³⁷:



On the other hand, the formation of hydroxyl radicals by water dissociation, enhancing the oxidation of soot [Ochoterena, *et al.*2010]³⁵. Hence, high combustion temperature splits water into radicals; this accelerates the degradation of fuel molecules to form short chain alcohol; and hydrocarbons eq (3) [Pascal, *et al.*2009]³⁸:



Another advantages of microemulsion as fuel, are its capacity in increasing the octane number of gasoline and the analog octane number on diesel. The presence of water-diesel fuel improves air-fuel contact and increase the flash point of the fuel and it is normal that diesel microemulsion contain water soluble cetane number improvers which mean higher performance efficiency [Bidyut, *et al.*2001]³⁶. An important criterion for a microemulsion to be used as fuel is that the one-phase region extends over a wide temperature range [Bemert, *et al.* 2009]³². Despite the Wide range of advantages, a microemulsion formulation requires considerably more surfactant than an emulsion. However, the commercial water in-diesel fuels are all emulsions [Lif, *et al.*2010a]³³.

There are many reports about microemulsion fuel systems containing anionic, cationic and nonionic surfactant [Andheria, *et al.* 1995]³⁹. Diesel is composed of a broad range of paraffinic and aromatic hydrocarbons making it difficult for a single surfactant to do the job especially at low concentrations. Combining more than one surfactant can facilitate the formulation of microemulsion that is stable over a wide range of temperatures [Kayali, *et al.* 2012c]⁴⁰.

Recently, Anna Lif and coworkers have developed suitable formulations of microemulsion diesel fuel by using FT-diesel as model oil [Lif, *et al.* 2010a]³³. The novel C₈P₂E₄ amphiphile was combined with a range of other surfactants in order to search for systems that would be useful to prepare water in FT-diesel microemulsion. Particularly interesting results were obtained when C₈P₂E₄ was used together with an etheramine surfactant based on a C₈₋₁₀ hydrocarbon tail. When the etheramine surfactant and C₈P₂E₄ were combined in a 70:30 weight ratio a microemulsion with an Existence Region of 22°C could be obtained with as little as 14% total surfactant together with 10% water and 76% FTdiesel.

In 2010, Raul Ochoterena and coworkers reported a formulation of water-in-diesel microemulsion used as fuels of engine vehicles with no major modifications of the engines [Ochoterena, *etal.* 2010]³⁵. The microemulsion fuel was prepared by dissolving the additives in the diesel, adding the water and then mixing with a propeller agitator. Where the composition of microemulsion are 10% additives consist of a mixed penta (ethylene glycol) monoundecyl ether and sorbitan monooleate, water 10% and diesel 80%. However, the results from the emission tests show large reductions in soot emissions were observed, but the NO_x emissions were barely affected when the microemulsion fuels were combusted compared to those detected when regular diesel fuel was used.

Zhaoyun *et al.* investigated Synergistic effect for the mixtures of polyglycerol esters of fatty acids (PGEFs) with sodium oleate solubilizing water in gasoline meanwhile they study The effect of series of alcohols on water amounts solubilized in the microemulsion [Ding, *et al.* 2007]³⁰. As a result of these experiments, TGDIS/sodium oleate/1-butanol the best synergistic effect in solubilizing water in water-in-gasoline microemulsion system. The best weight ratio of TGDIS/sodium oleate was about 6:4. At this condition, the maximum solubilization capacity of water in the TGDIS/ Sodium oleate/1-butanol/gasoline/water microemulsion system was 2.402 g at 16°C, when the amount of the mixed surfactants and gasoline were 0.740 and 6.000 g respectively.

Newly Kayali *et al.* investigated bicontinuous and water in diesel microemulsion were formulated at $\delta = 0.10$, using single nonionic alkyl poly glycol ethers combined with hydrophilic alcohol ethoxylates [Kayali, *et al.* 2012c]⁴⁰; This work shows that the addition of hydrophilic alcohol ethoxylates as a co-surfactant was necessary to initiate the formation of both continuous and w/diesel microemulsions in the formula of water, diesel and the nonionic surfactant CiEj. Varying the mass fraction of co-surfactant in the surfactant/co-surfactant mixture, δ , between 0.05 to 0.16 gave approximately similar surfactant efficiency.

1.11. Objectives:

Obtaining microemulsion formulas serves water-Diesel fuel using conventional surfactants is a very sophisticated process. In general, this formula must improve the combustion efficiency, reduce the nitrogen oxides (NO_x) emission, and also lower soot and particulate contents in the exhaust; As well as the surfactants used should burn readily without forming smoke and should not contain sulfur or nitrogen. Thus, the selection of suitable surfactants for water-Diesel fuel can become a significant problem.

The main objective of this study is the preparation of suitable, stable and applicable microemulsion formula serves water-Diesel fuel; using nonionic strongly hydrophilic sugar ester surfactant (L1695); To obtain this formula there are specific objectives needed to be achieved:

- To estimate phase diagram of the best components concentration for microemulsion preparation.
- To Study the Phase behavior as a function of temperature and surfactant concentration, that presenting in the form of the well known 'fish' diagram which is a vertical section taken from the ternary phase diagram at constant water/oil ratio.
- To determine the surfactant ratios which have highly solubilization capacity as well as highly surfactant efficiency.
- To formulate microemulsion formula serves water-Diesel fuel.
- To Use the following instruments to identify, approve and justify the output results: dynamic light scattering, crossed polarizers and polarizing microscope.

Chapter Two:

Methods and Experiments

2. Methods and Experiments:

2.1 Materials:

Sucrose monolaurate (sucrose dodecanoate) (L1695) Mol. Wt 561.1 was obtained from Mitsubishi-Kasei Food Corp., (Mie, Japan). Mol. Mazol 300 K (glycerol monooleate) Mol. Wt 355.96 was purchased from BASF Corporation (Gurnee, Illinois, USA). Polyoxyethylene (100) stearyl ether, C₁₈E₁₀₀, Brij S 100 (M Wt ~4670) was obtained from Sigma-Aldrich, Sweden.

N-heptane 99% was obtained from Fink leman LTD Chemical. 1-pentanol 99% was from MP Biomedicals, Inc, Propionic acid (POA) 98% and N-butanol 99% were purchased from Sigma Chemicals Co (ST.Louis, USA), Diesel was obtained from a local gas station in Bethlehem, Palestine. Aqueous solutions were prepared using deionized water supplied by a Milli-Q water purification system (Milli pore system, AL-quds University) $\sigma < 3 \mu\text{S}$. All components were used as supplied without further purification.

2.2 Instruments and Equipments:

Balance, Vortex, cross polarizers, Test tubes, a thermostated water baths, polarizing microscope, Zetasizer Nano S (ZEN 1600) by Malvern Instruments Ltd. (Worcestershire, United Kingdom).

2.3 Procedures:

2.3.1 Constructing of Phase Diagram:

The phase behavior of the systems consisting of water (with or without co-surfactant), oil (or model oil), surfactant (or mixed surfactants) may be described on a phase tetrahedron whose apexes respectively represent the pure components. 1g of a mixture consisting of oil (or model oil), surfactant (or mixed surfactants) at different weight ratios were prepared in culture tubes sealed with Viton lined screw caps and stirred at high temperature (45°C) by vortex until clear solution was obtained. Titrating these samples with MQ water which was added drop wise until its solubilization limit was reached. Vigorous stirring followed all of the aqueous phase additions on a vortex mixer. The time for equilibration between each addition was typically, from a few minutes up to 24 h.

Phase diagram was investigated at three temperatures 25, 37 and 45°C. Detecting number of phase by bare eye. The anisotropy by cross polarizers and polarizing microscope. The single isotropic sample which will be dark under cross polarizers 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 cross polarizers and polarizing microscope. Detect the boundary of single phase; finally draw the phase diagram using Origin Pro 8.1 software.

2.3.2 Constructing of Fish Phase Diagram:

The samples were prepared by weighing appropriate amounts of surfactant, co-surfactant and MQ water in 10 mm glass test tubes with screw caps, shake with a vortex for 1-2 minutes. The appearance of the solution was checked visually for transparency and between cross polarizers for birefringence. After that, diesel was added at water/oil wt. ratio of 1:1 for bicontinuous microemulsion and at 1:9 wt. ratios for w/o droplet microemulsion. The determinations of the phase diagrams were carried out in a thermostated water bath with temperature control up to 0.1°C. Samples at a given compositions were checked as a function of temperature by visual inspection in transmitted light and between cross polarizers to detect the presence of anisotropic phases.

Following the notations used previously for 'fish' diagram [Cosima, 2009]¹⁷, at low temperature o/w type coexists with excess oil (denoted by $\underline{2}$). At high temperature, w/o type coexists with excess water $\bar{2}$. At intermediate temperature the three phase microemulsion appears (denoted by 3). At higher surfactant concentrations, at the fish tail, the one phase region appears (denoted by 1). The surfactant concentration at which this first occurs is denoted by $\tilde{\gamma}$. Phase separation between the regions $\underline{2}$ and $\bar{2}$ is usually very slow in such systems and may take weeks. In the present work these regions were not studied in details, instead the investigations were directed towards the fish tail region where the three- phase and the one phase regions meet.

2.3.3 Dynamic Light Scattering:

Zetasizer Nano S (ZEN 1600) by Malvern Instruments Ltd. (Worcestershire, United Kingdom) was used for the measurements of the size of dispersed particles. The equipment comprises a 4mW, 633nm He-Ne laser. Size measurement range between 0.6 nm to 6 μm , size measurement angle equals 173° , concentration range for size measurement was between 0.1ppm (0.00001vol%) – 40 wt% and temperature measurement range between 275 K to 363 K. 1.5 ml microemulsion sample was introduced in a disposable polystyrene cuvettes and measured at temperatures range between 273 and 323 K by steps of 5 K. The particle hydrodynamic diameters calculated from the translational diffusion coefficient (D) using the Stokes-Einstein relationship eq (4) [Gruber, 1999]⁶:

$$d_H = k_B T / 6 \pi \eta D \quad \dots\dots \text{eq (4)}$$

Where d_H is the hydrodynamic diameter, k_B is Boltzmann's constant, T is the absolute temperature and η is the solvent viscosity. The results are averages of 3 experiments.

Chapter Three:

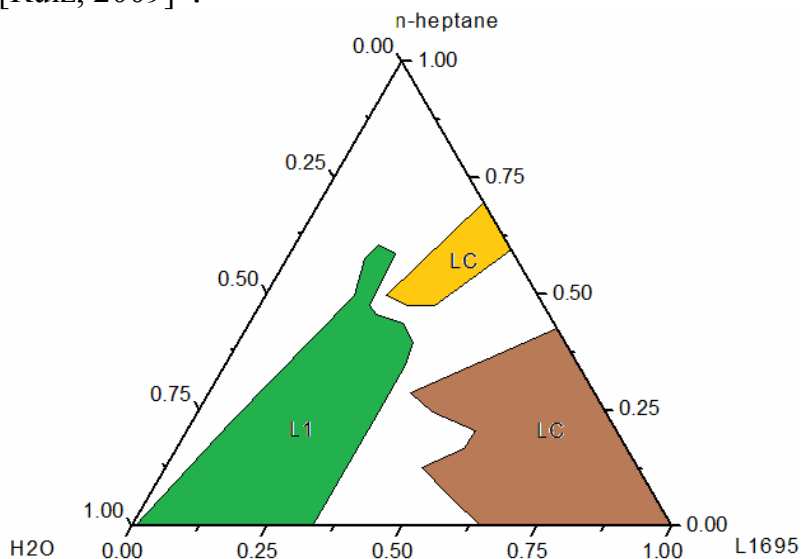
Results and Discussions

3. Results and Discussions:

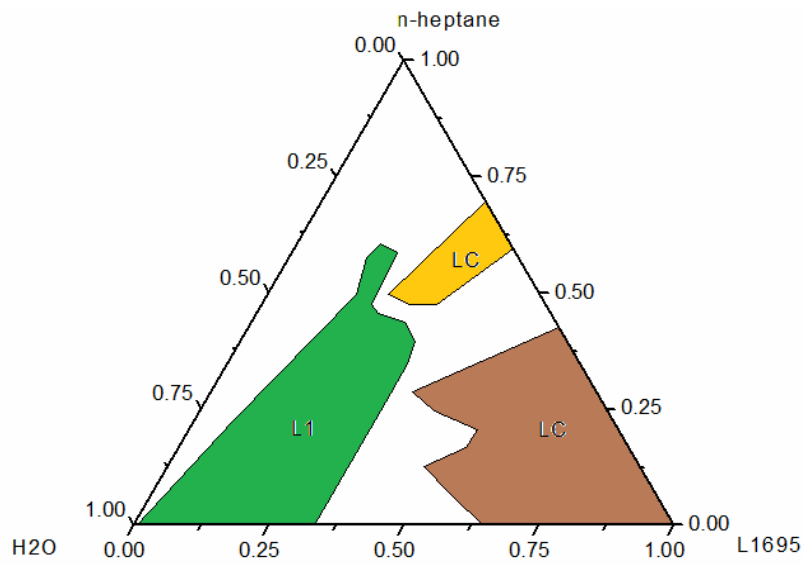
3.1 Phase Diagram of Water/Sucrose Monolaurate (L1695)/N-heptane System.

The presence of temperature insensitivity for a lauryl sucrose ester/hexadecane system was investigated [Kyoung, *et al.*1995]⁴¹. We reported the ternary phase diagram of water/sucrose monolaurate (L1695)/n-heptane system at 25, 37 and 45°C; using n-heptane as model oil Fig 3.1. Sucrose monolaurate produces temperature insensitive phase behavior at three different temperatures as expected.

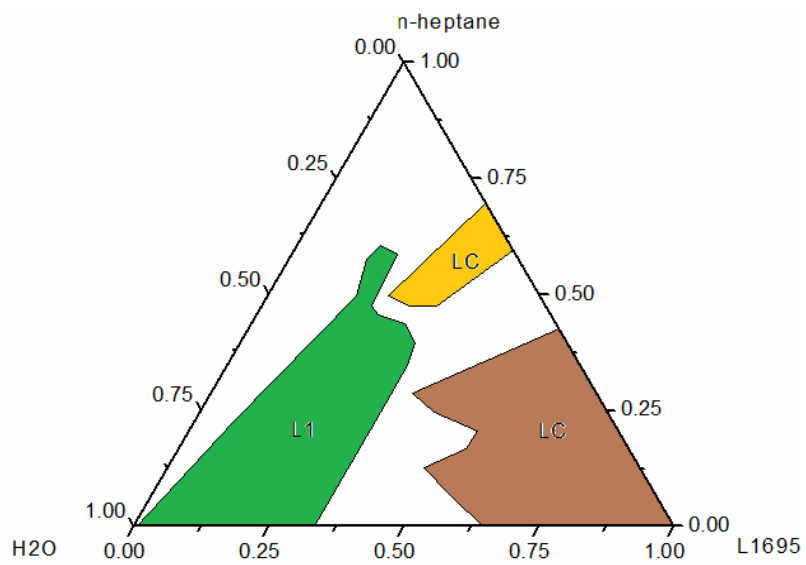
Binary phase behavior of L1695/water predict three an isotropic region H_1 , L_{α} , and L_{β} . Meanwhile, one isotropic region L_1 [Herrington, *et al.* 1988]¹⁰. In our work the resulting phase indicated the presence L_1 , semisolid anisotropic LC and highly viscous anisotropic LC. Thus, the remainder of the phase diagram represents the turbid region based on visual identification. No co-surfactant was used in order to simplify the system; without co-surfactant only o/w microemulsions (L_1) are formed, which is mainly due to the fact that the high hydrophilicity of sugar surfactants cannot be changed significantly by temperature variation[Ruiz, 2009]⁹.



(a)



(b)



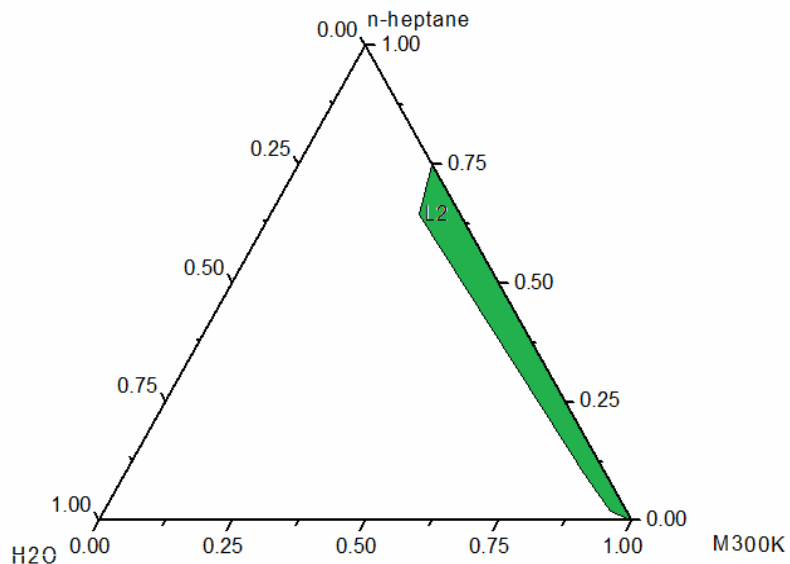
(c)

Figure 3.1. Ternary Phase diagram of water/sucrose monolaurate (L1695)/n-heptane system; (a) 25°C, (b) at 37°C and (c) at 45°C.

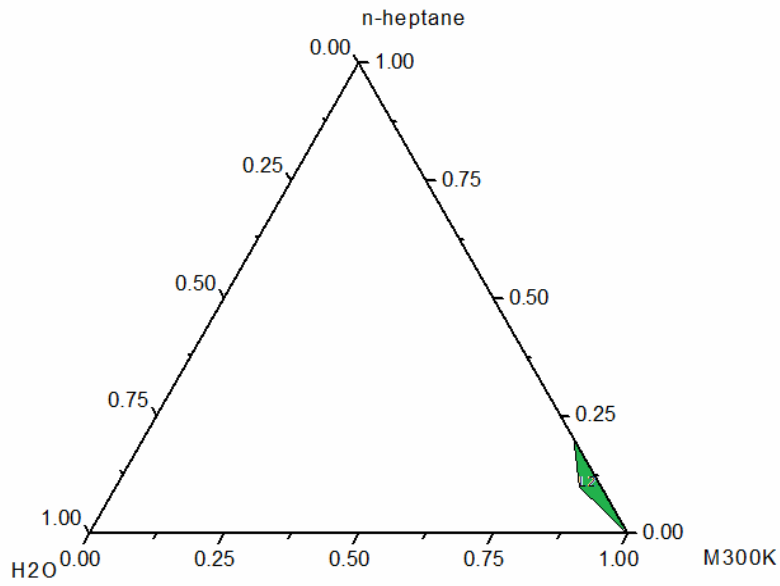
3.2 Phase Diagram of Water/ Glycerol Monooleate (M300 K)/N-heptane System.

Binary phase diagram of the glycerol monooleate/water system demonstrated that; a narrow area of reversed micelle (L₂) was formed [Borne, *et al.*2000]¹⁵. Ternary phase diagram was studied upon addition of water to M300K/n-heptane system at 25, 37 and 45°C Fig 3.2. The result was single clear isotropic region (L₂). The L₂ region decreases with increasing temperature, which refers to the fact that at low temperatures the non-ionic surfactant is mainly soluble in water, while it is mainly soluble in oil at high temperatures. Thus, an increase in temperature turns a non-ionic surfactant from hydrophilic into hydrophobic [Cosima, 2009]

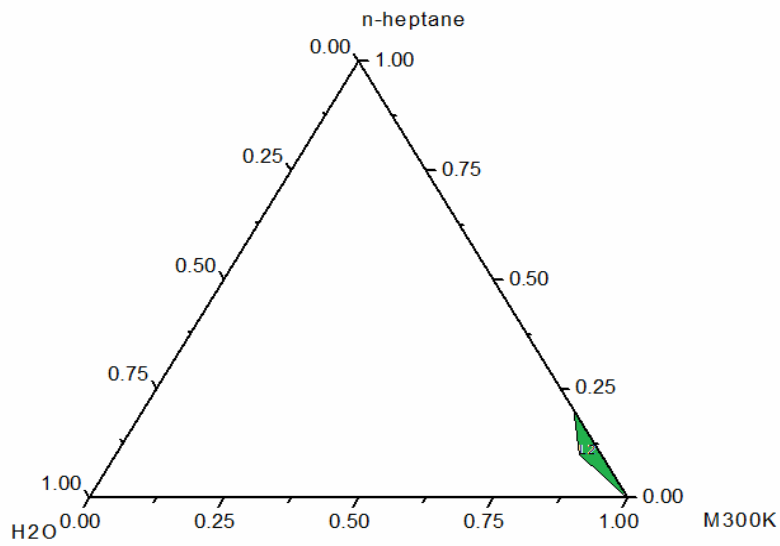
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(a)



(b)



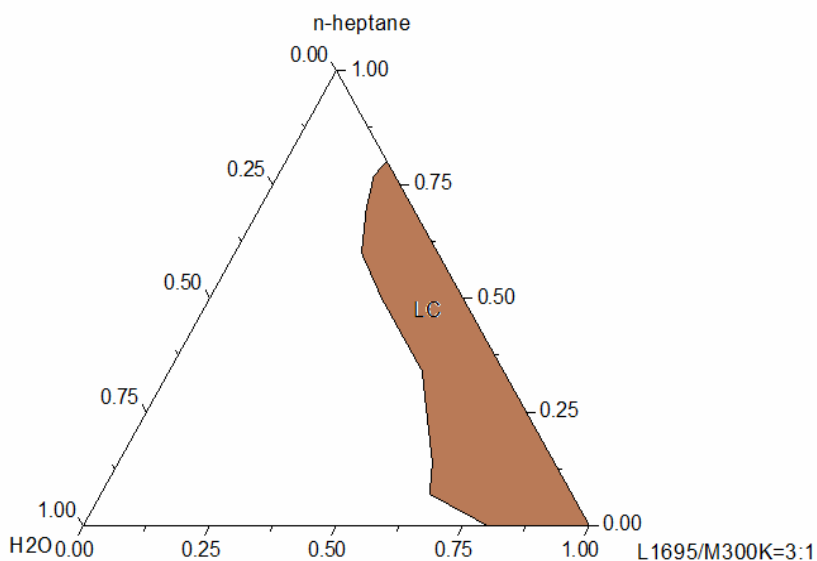
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Figure 3.2. Ternary Phase diagram of water/ glycerol monooleate (M300K)/n-heptane system; (a) 25°C, (b) at 37°C and (c) at 45°C.

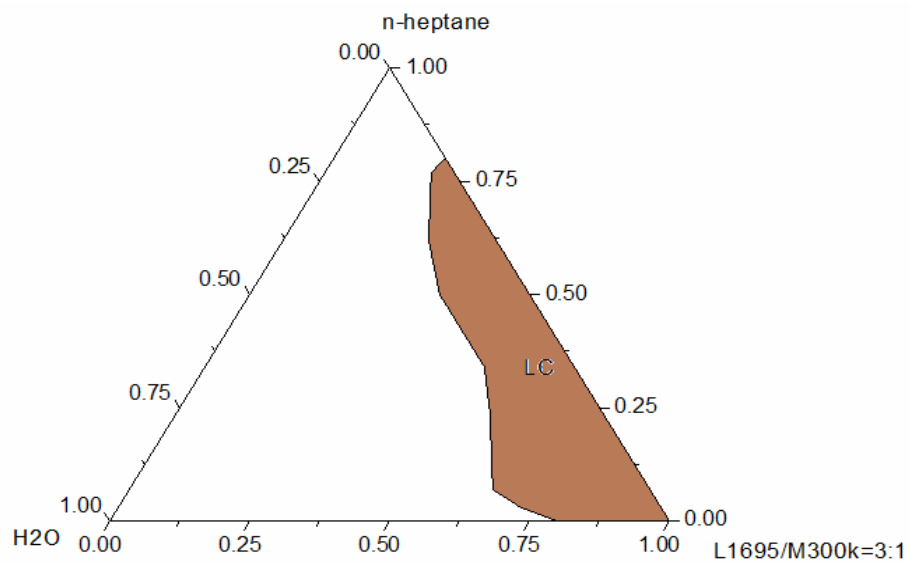
3.3. Phase Diagram of Water/ Mixed Nonionic Surfactant/N-heptane Systems.

Temperature is not the appropriate parameter to tune the mean curvature of the amphiphilic film of nonionic surfactant and with it the phase behaviour of the system. Instead, the mixing of two surfactants of different hydrophilicity is the appropriate method to drive the quaternary system through the phase inversion [Cosima, 2009]¹⁷. On the other hand, mixtures are often made on purpose to attain some intermediate property or some synergetic effect. The Phase behavior of water/ sucrose monolaurate/M300K /peppermint oil system was investigated as function of temperature and the weight ratio of M300K in the mixed surfactant; This phase behavior indicated that mixing M300K with L1695 improves the water solubilization but doesn't affect the temperature insensitivity of L1695[shakarnah, 2012]⁴².

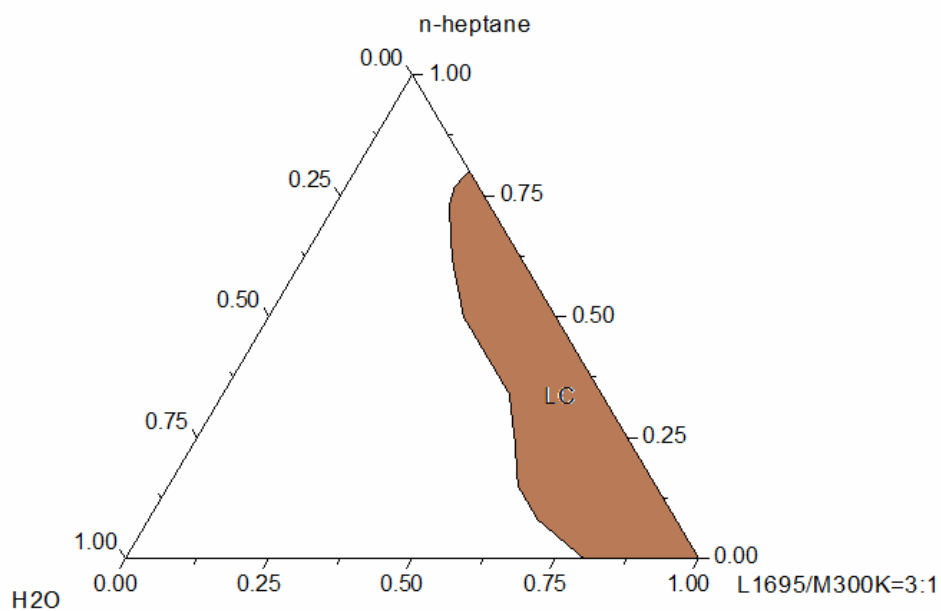
The Phase diagram of water/sucrose monolaurate (L1695) + glycerol monooleate (M300 K) /n-heptane at 25, 37 and 45°C is presented in Fig 3.3. The weight ratio of L1695/M300K equals 3:1. The phase diagram indicated the presence of semisolid isotropic LC region. Thus the remainder of the phase diagram represents the turbid region based on visual identification. In addition; there is slightly difference between phase diagrams at three different temperatures. This indicated that mixing M300K with L1695 at 3:1 weight ratio doesn't affect the temperature insensitivity of L1695.



(a)



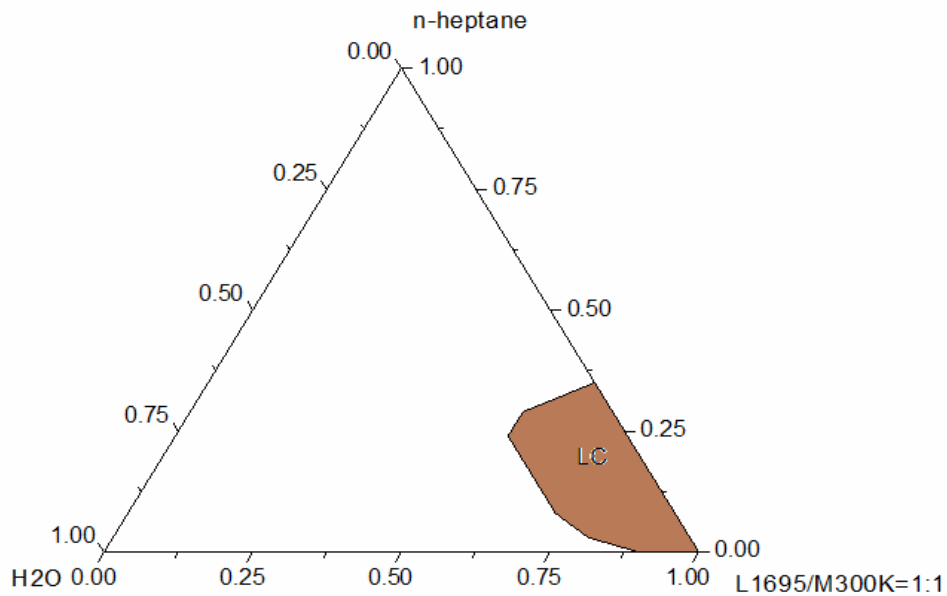
(b)



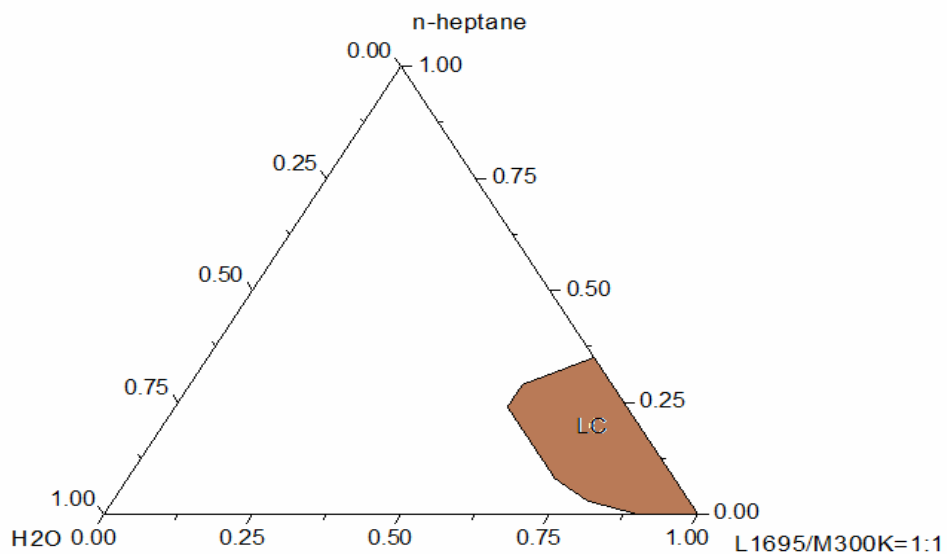
(c)

Figure 3.3. Ternary Phase diagram of water/ sucrose monolaurate (L1695)/glycerol monooleate (M300K)/n-heptane system; (a) 25°C, (b) at 37°C and (c) at 45°C. The weight ratio of L1695/M300K equals 3:1.

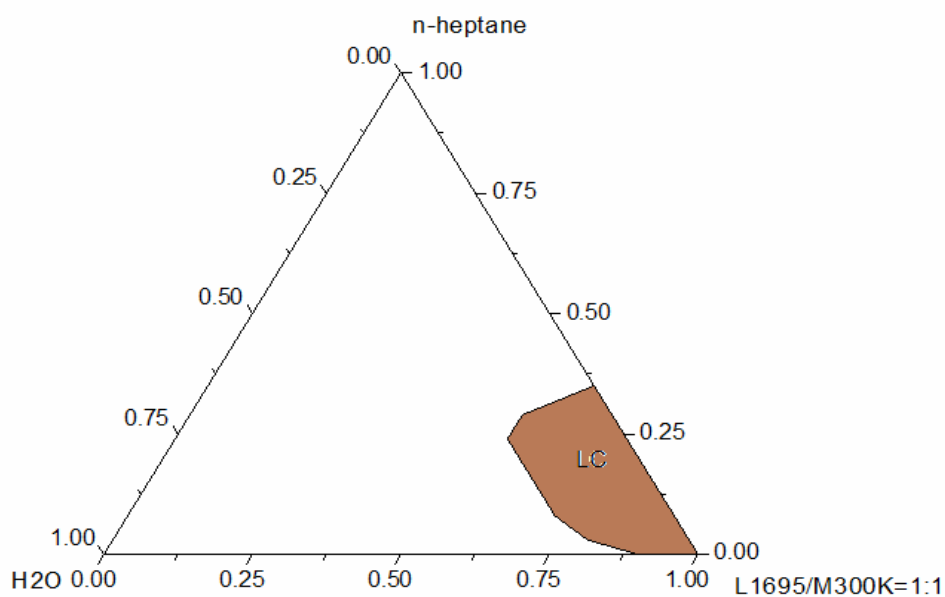
Fig 3.4. Presents the Phase diagram of water/sucrose monolaurate (L1695) + glycerol monooleate (M300K) /n-heptane at 25, 37 and 45°C. The weight ratio of L1695/M300K equals 1:1. The phase diagram indicated the presence of semisolid isotropic LC region. Thus, the remainder of the phase diagram represents the turbid region based on visual identification. However, the semisolid isotropic LC region shrinks more compared to Fig 3.3. and there is no difference between phase diagrams at three different temperatures. This indicated that mixing M300K with L1695 at 1:1 weight ratio doesn't affect the temperature insensitivity of L1695.



(a)



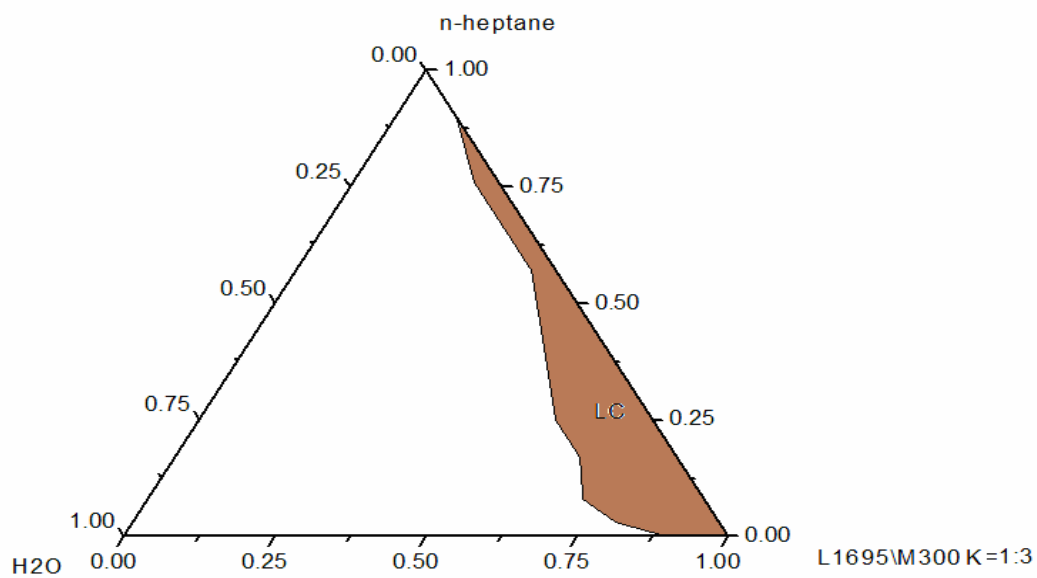
(b)



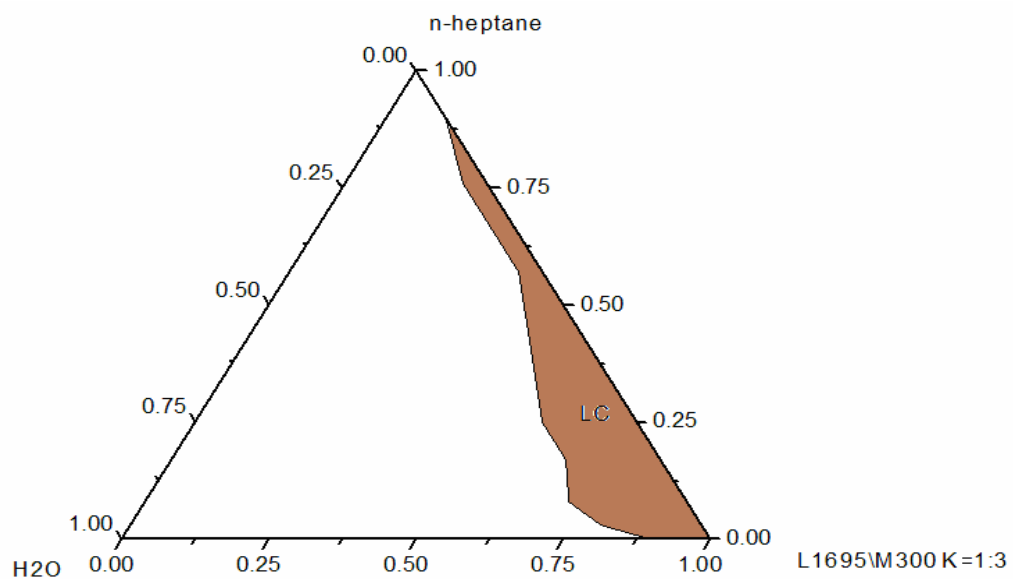
(c)

Figure 3.4. Ternary Phase diagram of water/ sucrose monolaurate (L1695)/glycerol monooleate (Mazol 300 K)/n-heptane system; (a) 25°C, (b) at 37°C and (c) at 45°C. The weight ratio of L1695/M300K equals 1:1.

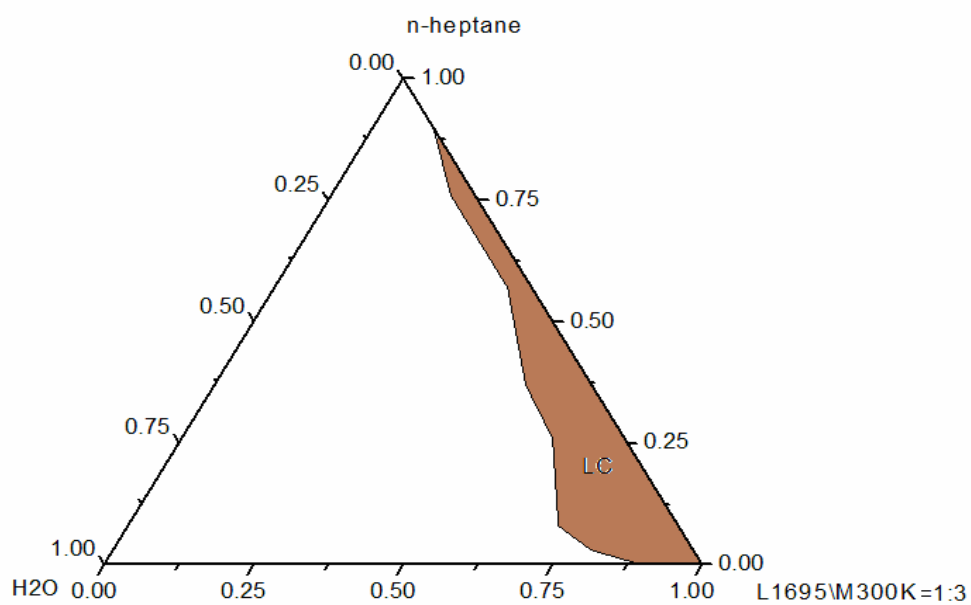
Fig 3.5. presents the Phase diagram of the water/sucrose monolaurate (L1695) + glycerol monooleate (M300K) /n-heptane at 25, 37 and 45°C. The weight ratio of L1695/M300K equals 1:3. The phase diagram indicated the presence of viscous anisotropic LC region. Thus the remainder of the phase diagram represents the turbid region based on visual identification. In addition there is slightly difference between phase diagram at three different temperatures. This indicated that mixing M300K with L1695 at 1:3 weight ratio doesn't affect the temperature insensitivity of L1695.



(a)



(b)



(c)

Figure 3.5. Ternary Phase diagram of water/sucrose monooleate (L1695)/glycerol monooleate (M300K)/n-heptane system; (a) 25°C, (b) at 37°C and (c) at 45°C. The weight ratio of L1695/M300k equals 1:3.

3.4. Phase Diagram of Water/Sucrose Monolaurate (L1695)/ Diesel System.

The observed ternary phase diagram at 25°C is shown Fig.3.6. The compositions in L₁ and isotropic LC region will shift to transparent solution and semisolid paste respectively upon mixing. No co-surfactant was used in order to simplify the system, without co-surfactant only o/w microemulsions (L₁) are formed. Hence, this result compared with Fig 3.1. Was exactly identical.

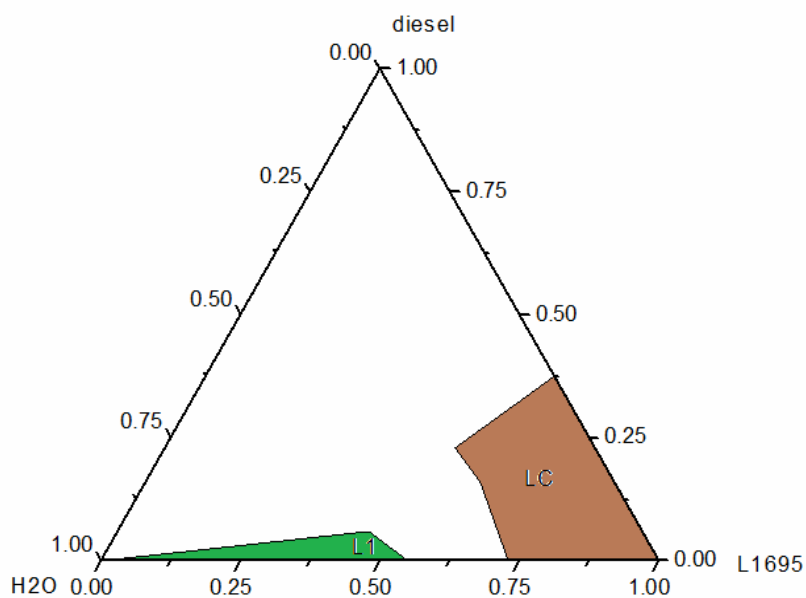
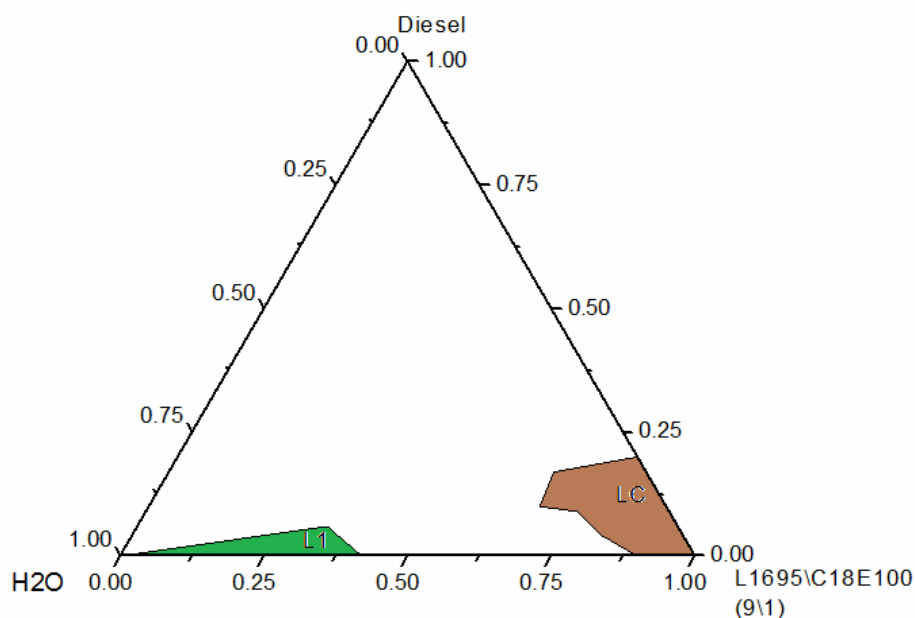


Figure 3.6. Ternary Phase diagram of water/sucrose monolaurate (L1695)/diesel system at 25°C.

3.5. Phase Diagram of Water/Sucrose Monolaurate (L1695): C₁₈E₁₀₀ (9:1)/ Diesel System.

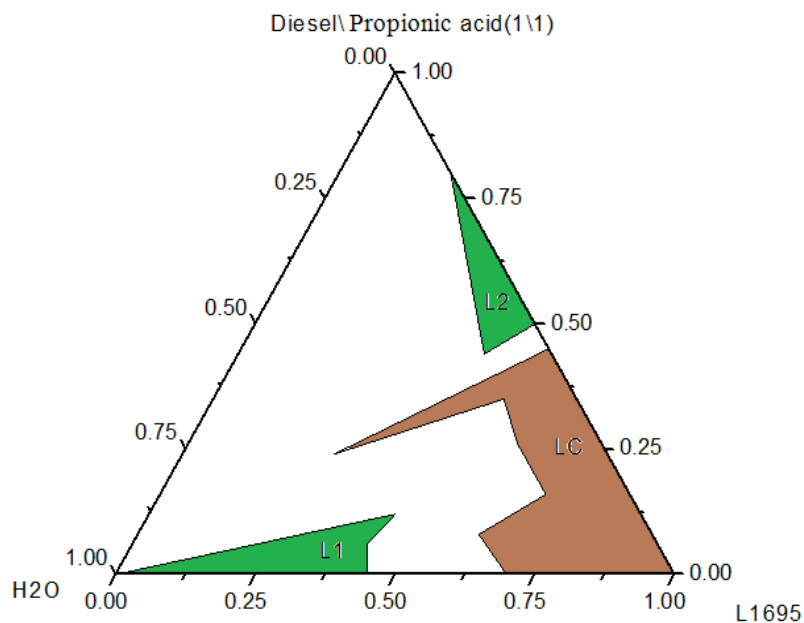
Water in diesel microemulsion was formulated using single nonionic alkyl poly glycol ethers combined with hydrophilic alcohol ethoxylates (C₁₈E₁₀₀) at $\delta = 0.10$ as a co-surfactant [Kayali, *et al.*2012c]⁴⁰. Small quantities of hydrophilic alcohol ethoxylates were added to surfactant caused a drastic shift of the one-phase region to lower surfactant concentration [Christian, *et al.*2008]⁴³. We reported Ternary phase diagram of water/sucrose monolaurate (L1695): C₁₈E₁₀₀ (9:1)/ Diesel system at 45°C Fig 3.7, this Phase diagram was studied at 45°C In order to increase the hydrophobicity of surfactant, which attaches to the fact that an increase in temperature turns a non-ionic surfactant from hydrophilic into hydrophobic [Cosima, 2009]¹⁷, thus obtains w/o microemulsion (L₂) at lower surfactant concentration. The phase diagram indicated the presence of L₁ and semisolid anisotropic LC regions. However, the L₁ and semisolid anisotropic LC regions shrinks more compared to Figure 3.6. No w/o microemulsions (L₂) obtained. This indicates the temperature insensitivity of L1695.



3.7. Phase diagram of water/ sucrose monolaurate (L1695): C₁₈E₁₀₀ (9:1)/diesel system 45°C.

3.6. Phase Diagram of Water/Sucrose Monolaurate (L1695) / (Diesel/Propionic Acid (1:1)) System.

Phase diagram of system containing sucrose monolaurate as surfactant and Propionic acid as co-surfactant was constructed with different types of oils. They demonstrated that using propionic acid as co-surfactant increase the total monophonic area [shakarnah, 2012]⁴². Figure 3.8. Present the Phase diagram of water/sucrose monolaurate (L1695)/ (diesel/ Propionic acid (1:1)) at 25°C. The phase diagram indicated the presence L1, L2 and semisolid anisotropic LC regions. However, w/o microemulsion (L2) was obtained at fairly high surfactant concentration equals~ 20%.



3.8. Phase diagram of water/ sucrose monolaurate (L1695)/ (diesel/Propionic acid (1:1)) system 25°C.

3.7. Phase Diagram of Water/Sucrose Monolaurate (L1695)/ (Diesel/Medium Chain Alcohol) Systems.

The composition of the amphiphilic film is the tuning parameter of the mean curvature in quaternary temperature-insensitive systems [Cosima, 2009] ¹⁷. Fig 3.9. Schematically shows the change of the curvature with increasing fraction of alcohol in the amphiphilic film of water/sucrose monolaurate (L1695)/(diesel/medium chain alcohol) system. Knowing that the head group area of alcohols is smaller than that of sucrose monolaurate (L1695), one observes that an increasing fraction of alcohol in the mixed interfacial film causes a decrease of the mean curvature from $H > 0$ for o/w-microemulsion to $H < 0$ for w/o-microemulsion.

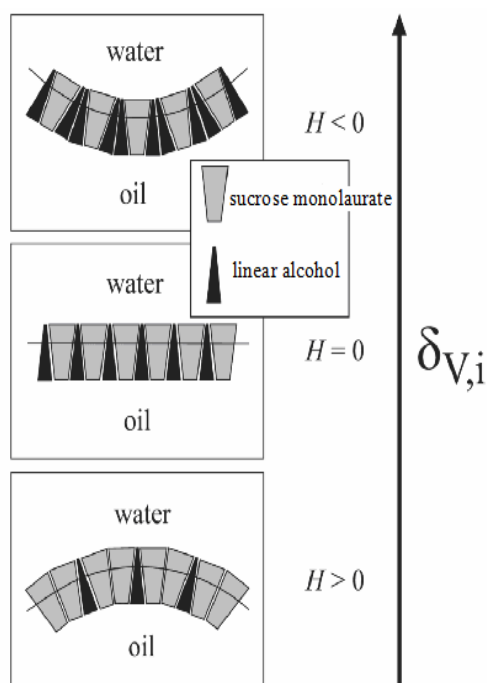


Figure 3.9. Mean curvature H of sucrose monolaurate (L1695) film at the water/oil interface as a function the composition of the internal interface $\delta v, i$.

3.7.1 Phase Diagram of Water/Sucrose monolaurate (L1695)/ (Diesel/Butanol (1:1)) System.

Huge microemulsion region was shown in the ternary phase diagram of water/sucrose monolaurate (L1695)/ (dodecane/butanol (1:1)) system [Garti,*etal.*2000]²⁶. Fig 3.10. Presents the phase diagram of the water/sucrose monolaurate (L1695)/ (diesel/ butanol (1:1)) at 25°C. The phase diagram indicated the presence of low viscous isotropic and semisolid anisotropic LC regions. The remainder of the phase diagram represents the turbid region based on visual identification. In addition, the shape of low viscous isotropic region leads to that water-in-oil to bicontinuous to oil-in-water droplets transitions occur upon addition of aqueous phase.

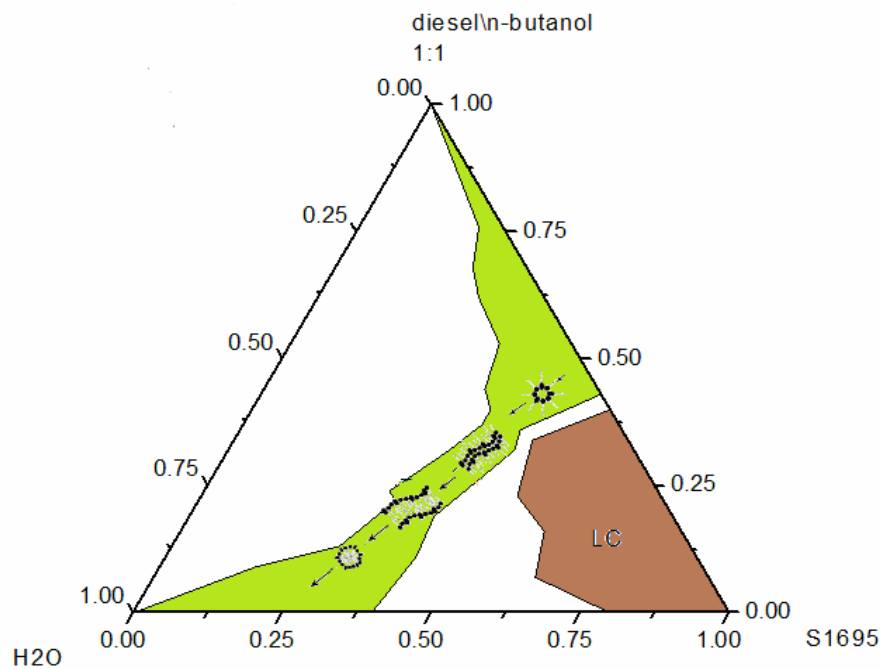


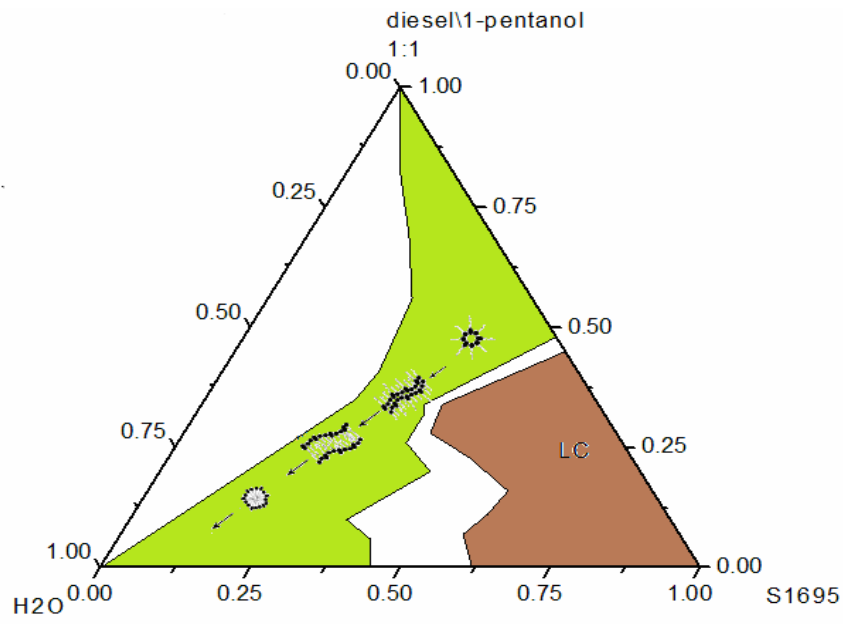
Figure 3.10.Phase diagram of the water/sucrose monolaurate (L1695)/(diesel/ butanol (1:1)) at 25°C.

3.7.2 Phase Diagram of Water/Sucrose Monolaurate (L1695)/ (Diesel/1-Pentanol) Systems. At Different Weight Ratio of Diesel/1-Pentanol that are: (a) 1:1 (b) 3:1 (c) 9:1.

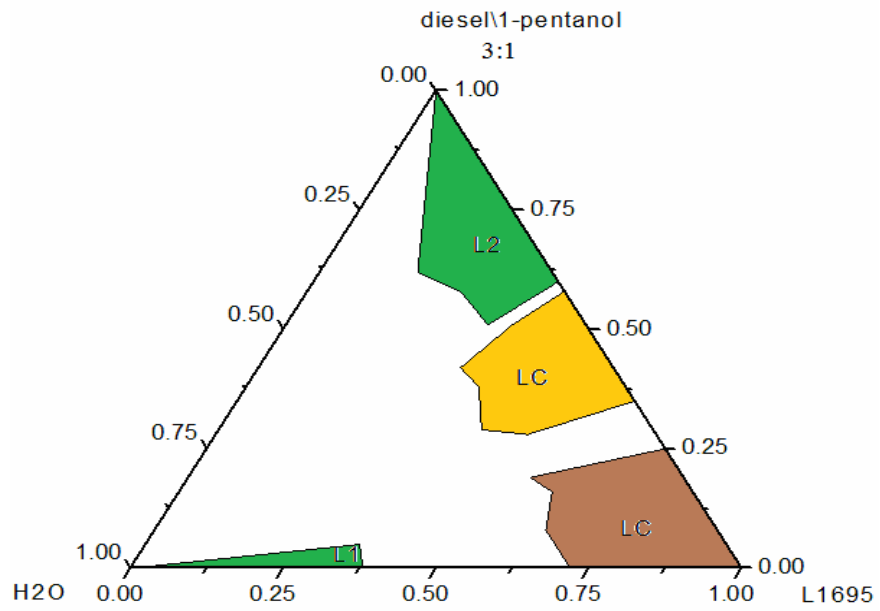
The effect of different mixing ratios of ethanol in formulation water/sucrose laurate/ethoxylated mono-di-glyceride/oleic phase system was investigated, the total area of the monophasic microemulsion increases with the increase the ethanol/oil mixing ratio [Fanun, 2008e]¹⁹.

Fig 3.11. (a) Presents the Phase diagram of the water/sucrose monolaurate (L1695)/ (diesel/1-pentanol (1:1)) at 25°C. The phase diagram indicated the presence of low viscous isotropic and semisolid anisotropic LC regions. The remainder of the phase diagram represents the turbid region based on visual identification. In addition the shape of low viscous isotropic region leads to that water-in-oil to bicontinuous to oil-in-water droplets transitions occur upon addition of water. However, the low viscous isotropic region and semisolid anisotropic LC regions expands more compared to Figure 3.10.

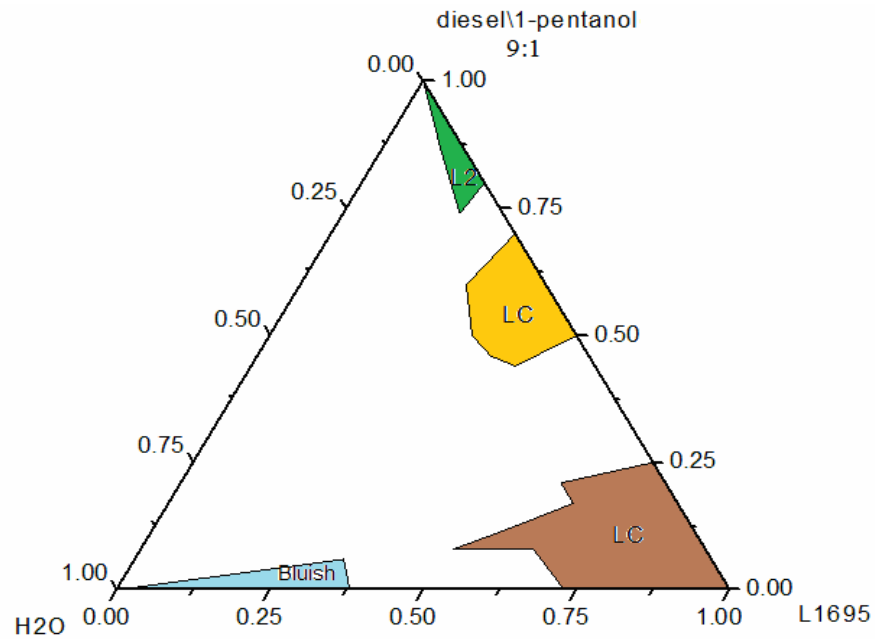
Fig 3.11. (b) Presents the Phase diagram of the water/sucrose monolaurate (L1695)/ (diesel/1-pentanol (3:1)) at 25°C. The phase diagram indicated the presence of L₁, L₂, semisolid anisotropic and highly viscous anisotropic LC regions. The remainder of the phase diagram represents the turbid region based on visual identification. While Fig 3.11. (c) Presents the Phase diagram of the water/sucrose monolaurate (L1695)/ (diesel/1-pentanol (9:1)) at 25°C. The phase diagram indicated the presence of L₂, Bluish low viscous isotropic, semisolid anisotropic and highly viscous anisotropic LC regions. The remainder of the phase diagram represents the turbid region based on visual identification. Each of L₂ and highly viscous anisotropic LC regions shrink more compared to Figure 3.11. (b) Thus a semisolid anisotropic LC region expands more. The appearance of Bluish nanostructure diesel microemulsion is shown in Fig. 3.12.



(a)



(b)



(c)

Figure 3.11.Phase diagram of water/ sucrose monolaurate (L1695)/ (diesel/1-pentanol) system. At different weight ratio of diesel/1-pentanol that are (a) 1:1 (b) 3:1 (c) 9:1.



Fig. 3.12.Photo for sample representing Bluish nanostructure diesel microemulsion.

3.8. The Effect of 1-Pentanol on the Solubilization Capacity of W/O Microemulsion in Water/Sucrose Monolaurate (L1695)/ (Diesel/ 1-Pentanol) System.

Because 1-pentanol as co-surfactant had best effect in enhancing solubilizing of water Fig 3.11, it was chosen for further investigation. the effect of different weight ratio of diesel/1-pentanol on the solubilization capacity of w/o micremulsion system at 10% of surfactant was examined in water/ sucrose monolaurate (L1695)/ (diesel/ 1-pentanol) system Fig. 3.13. The maximum amount of water solubilized was 12% at 25% of 1-pentanol; before this point the solubilization capacity appears to increase rapidly with the increase of 1-pentanol weight ration. While, after this point any increase of 1-pentanol weight ration shows sharp degrees in the solubilization capacity.

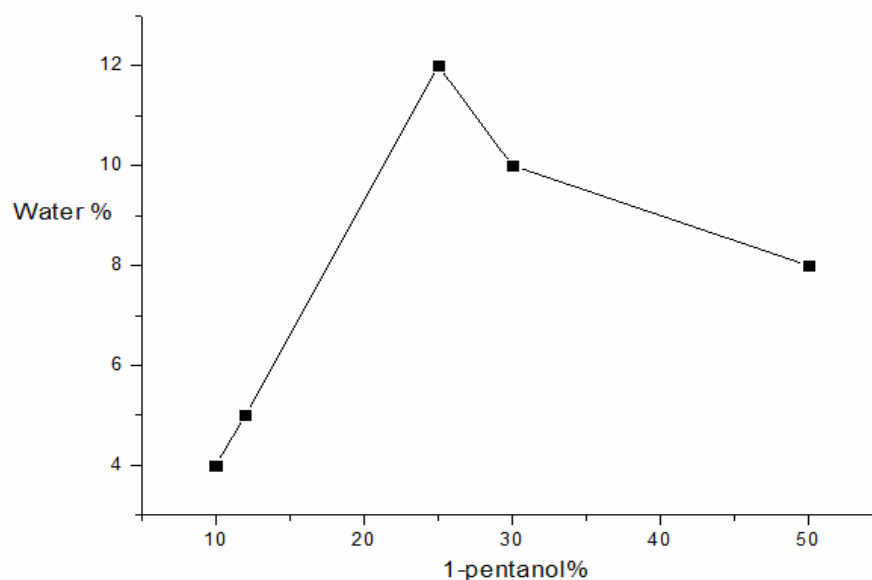


Figure 3.13. Represents the Effect of 1-pentanol on the solubilization capacity of w/o microemulsion in water/ sucrose monolaurate (L1695)/ (diesel/ 1-pentanol) system.

3.9. W/O Droplet Microemulsions.

The efficiency of sucrose monolaurate in solubilizing equal amounts of water and limonene oil as a function of temperature was reported, isotropic low viscous region was shown at 25 wt% of L1695 with narrow temperature window between 70°C to 72°C [Fanun, *et al.*2006a]⁷. In our work Phase behavior studied as a function of temperature and sucrose monolaurate concentration will be presented in the form of the well known ‘fish’ diagram; which is a vertical section taken from the ternary phase diagram at constant water/oil ratio.

Phase diagram of water in oil microemulsion was formulated with sucrose monolaurate (L1695) at water to diesel wt. ratio of 1:1 using n-butanol at $\delta = 0.50$ as a co-surfactant. Only two phase emulsions were produced in the absence of the co-surfactant. Fig.3.14 shows the minimum amount of surfactant needed to reach the one phase microemulsion to be 40 wt. % at 25°C with the temperature window widening between 10°C to 100°C at 40 wt. % surfactant.

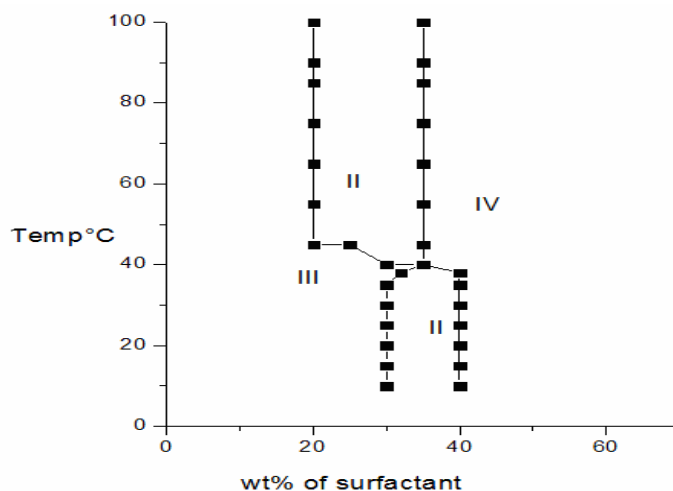


Figure 3.14. Phase diagram of water-diesel- L1695 at water to diesel wt. ratio of 1:1 with n-butanol at $\delta = 0.50$

Newly, a formula was tried by changing the co-surfactant to 1-pentanol at water to diesel wt. ratio of 9:1 Fig.3.15. Shows the phase diagram using 1-pentanol at $\delta = 0.25$. The minimum amount of surfactant is shifted to 10wt. %; however the temperature window is narrower ranging between 10 °C to 35 °C at 10 wt. % surfactant.

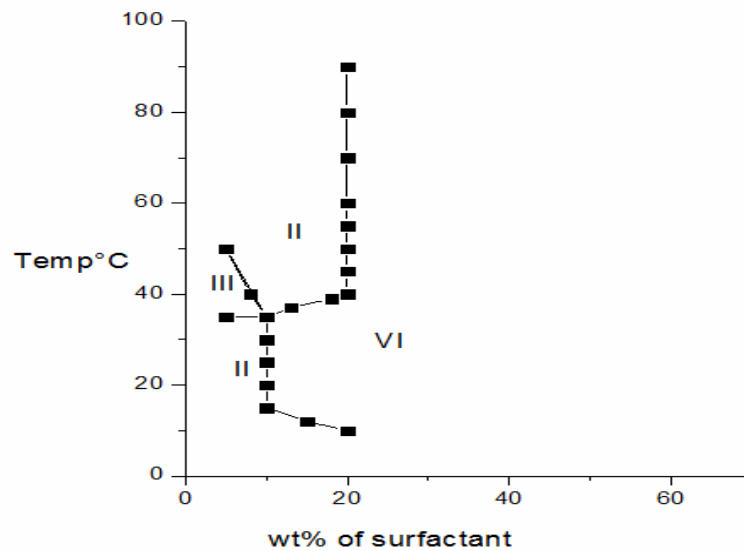


Figure 3.15.Phase diagram of water-diesel- L1695 at water to diesel wt. ratio of 9:1 with 1-pentanol at $\delta = 0.25$

The appearance of the water in diesel microemulsion at 10 wt. % sucrose monolaurate (L1695) with 1-pentanol at $\delta = 0.12$ is shown in Fig3.16. (a), was so similar to the 100 % diesel, Fig3.16. (b) That it was so difficult to distinguish between them by visual inspection. The formulation of w/diesel without the addition of co-surfactant resulted in a two phase system as shown in Fig3.16. (c).

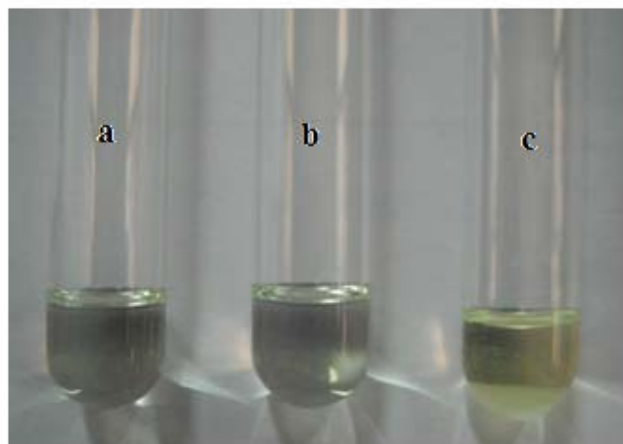


Figure 3.16.Photos for samples representing water in diesel microemulsion (a), 100% diesel (b), and a two phase mixture in the absence of the co-surfactant (c).

3.10. Dynamic Light Scattering (DLS):

Dynamic light scattering can be applied to obtain the hydrodynamic radius of the micelle, by measuring the intensity fluctuation of scattered light by the micelles when these undergo Brownian diffusion [Gruber, 1999]⁶. In this part, we used the *DLS* technique to investigate the microemulsion system, as a function of temperature at aqueous phase volume fraction equals 0.90 Fig.3.6. The values of the average hydrodynamic diameter (d_H) as function of temperature in the aqueous phase rich region are presented in. Fig.3.17. increases with temperature increase indicating that the tails of the surfactants molecules residing on different droplets or fusion of droplets which lowers the curvature energy makes the micelles grow in size as the temperature increases the microemulsion droplets deform by thermal fluctuations. The droplets may undergo attractive interactions that lead to aggregation between the droplets. Similar results of the behavior of the hydrodynamic diameter as Functions of temperature were reported in previous study [Fanun, 2010i]²⁴.

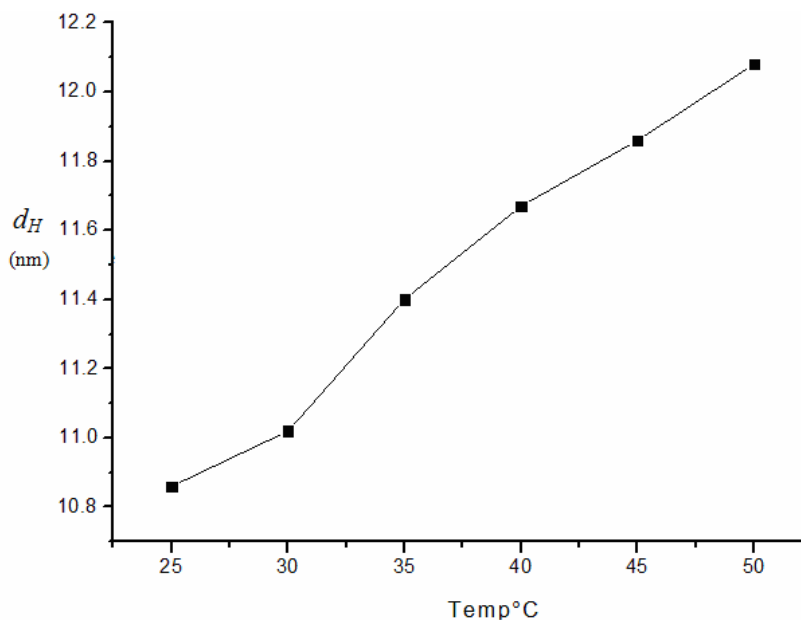


Fig.3.17. the values of the verge hydrodynamic diameter (d_H) as function of temperature in the aqueous phase rich region equals 0.90.

Fig 3.18 shows the intensity size distribution obtained from three repeated measurements of the microemulsion at 25°C. The results show very repeatable intensity size distributions with z-average diameters of 10.86 nm. The z-average diameter is the mean hydrodynamic diameter and is calculated according to the International Standard on dynamic light scattering ISO13321.

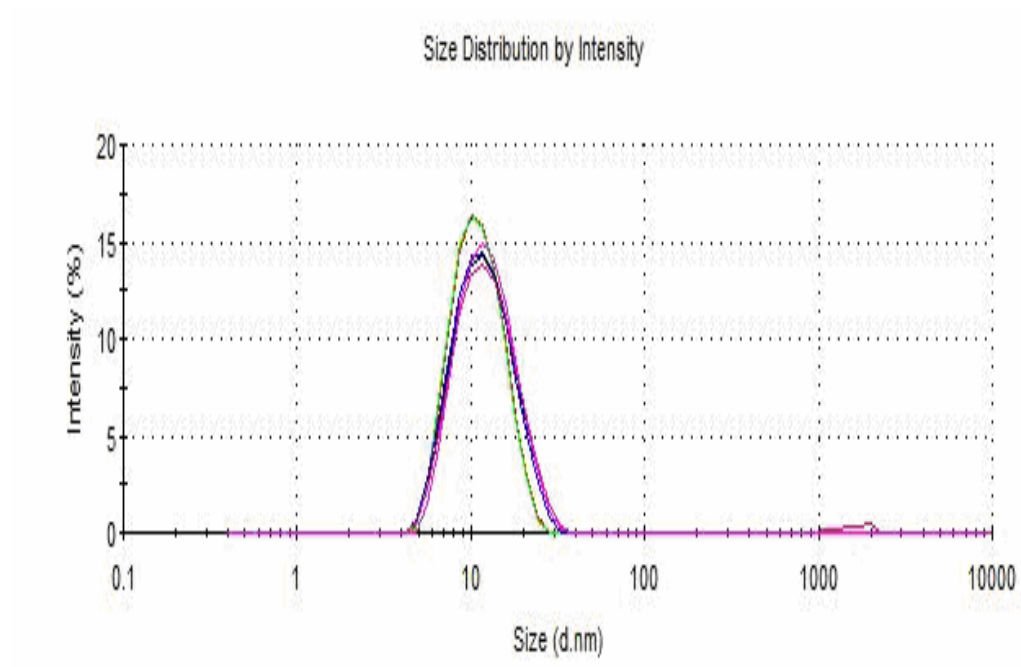


Figure 3.18 shows the intensity size distribution obtained from microemulsion sample at 25°C.

3.11.1 Conclusion

This work shows that the addition of medium chain alcohol as a co-surfactant at different mass fraction in the diesel/ alcohol mixture is necessary to initiate the formation water in diesel microemulsions in the formula of water, diesel and sugar ester nonionic surfactant due to temperature insensitivity of sugar ester; In addition, medium chain alcohol is used as "tuning parameter "to change H_o and to increase the flexibility of the surfactant film. An increasing fraction of alcohol in the mixed interfacial film causes a decrease of the mean curvature from $H_o > 0$ for o/w-microemulsion to $H_o < 0$ for w/o-microemulsion .

Water in diesel microemulsions were formulated using 10 wt% of single sugar ester surfactant (L1695); combined with $\delta = 0.12$ of co-surfactant (1-pentanol) at 25°C. At last the reasonable amount of surfactant required to form water in diesel microemulsion provide realistic options in the search for alternative fuel that would reduce the level of both nitrogen oxides and soot in the emission.

3.11.2 Future work

Combustion experiments can be performed on such formulation. In order to investigate suitable, stable and applicable microemulsion formula serves water-Diesel fuel.

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الملخص العربي:

تهدف هذه الدراسة الى البحث عن صيغ لمستحلب ذو جزيئات بالغة الصغر (ميكرو املشن) تعمل في وقود الماء-الديزل باستخدام أقل كمية ممكنة من منشط السطوح (surfactant) سكر الإستر الغير أيوني شديد المحبة للماء سكر الإستر المستخدم هو (sucrose monolaurate (1695))، والذي درس مع منشط السطوح المسمى ((glycerol monooleate (M300K)) الغير أيوني الكاره للماء. الزيوت المستخدمة هي الهيبنتان (model oil) والديزل. وكذلك استخدمت مساعدات السطوح المنشطة (Co-surfactants), وتشمل: إيثوكسيالات الكحول المحبة للماء (C18E100), حمض البروبيونيك, البيوتانول و 1-بينتانول.

خلال هذه البحث تم دراسة تأثير النسب المختلفة لمنشطات السطوح على سلوك الطور (phase behavior) للأنظمة الماء\مزيج السطوح الغير أيونية\الهيبنتان على درجات حراره مختلفة 45,37,25 °س. وكذلك تم اكتشاف تأثير إضافة مساعدات منشطات السطوح على سلوك الطور للأنظمة الماء\((sucrose monolaurate (1695))\الديزل على درجة حرارة 25 °س. واخيرا تم دراسة سلوك منشط السطح((sucrose monolaurate (1695)) بدلالة كل من درجة الحرارة وتركيز منشط السطح، والتي مثلت على شكل سلوك الطور المسمى ('fish' diagram). تم تعيين المناطق المتباينة الخواص (Anisotropy) لهذه الأنظمة عن طريق ميكروسكوب الاستقطاب (polarizing microscope). وتم قياس القطر الهيدروديناميكي للمستحلب بواسطة جهاز يسمى (Dynamic light scattering).

تم صياغة مستحلب وقود الماء-الديزل باستخدام كمية قليلة من منشط السطوح سكر الإستر الغير أيوني شديد المحبة للماء ((sucrose monolaurate (1695)) والتي تصل الى 10% على درجة حرارة 25 °س. حيث يبلغ القطر الهيدروديناميكي للمستحلب 10,86 نانوميتر على درجه حرارة 25 °س.

5. Arabic abstract:

العنوان:

"سلوك الطور لمزيج السطوح الغير أيونية باستخدام سكر الإستر. مجال التطبيق وقود الماء-الديزل".

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إشراف : البروفيسور إبراهيم كيالي.

مشرف ثاني :الدكتور خالد كنعان.

