

CHAPTER II THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Theoretical Background

2.1.1 Castor Oil

Castor oil is extracted from the seeds of the *Ricinus communis* plant. Typically 50 % of the seed weight is oil and 70 % of the oil is composed of *triricinoleate* (Figure 2.1). Castor oil is a viscous, pale yellow non-volatile. It has a good shelf life and does not turn rancid unless subjected to excessive heat. The largest exporter of castor oil is India and other major producers are China and Brazil including Thailand as shown in Table 2.1. Castor oil has many properties that make it perfect for use in cosmetics. Castor oil has unique properties that is when dry it forms a solid film that can have water-binding abilities, grabbing moisture from the air and holding it close to the skin. It is rarely associated with skin irritation or allergic reactions, but can have a slightly sticky feel on skin. Moreover castor oil is an inexpensive, eco-friendly, biodegradable oil, that has many uses in our modern world.

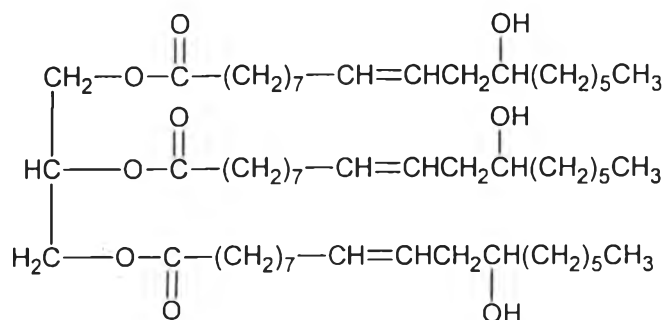


Figure 2.1 Structure of triricinoleate.

Table 2.1 Production volume of castor oil by major producer (Razdi, W. 2012)

Major Producers	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000
	'000t	'000t	'000t	'000t	'000t	'000t	'000t	'000t	'000t	'000t	'000t
India	192	239	232	242	271	333	344	278	304	294	324
China	77	86	93	97	97	82	73	83	80	91	105
Brazil	77	73	54	28	28	22	21	43	21	19	52
Thailand	18	18	19	18	16	14	10	9	9	7	5
E.U.	20	16	14	12	14	11	9	10	7	8	8
Others	54	52	49	41	20	21	22	19	20	23	23
Total	438	484	461	438	446	483	479	442	441	442	517

2.1.2 Sunflower Oil

Sunflower oil is a non-volatile oil compressed from sunflower (*Helianthus annuus*) seeds. It is commonly used in cosmetic formulations as an emollient. This oil is a monounsaturated (MUFA)/polyunsaturated (PUFA) mixture of mostly oleic acid (omega-9)-linoleic acid (omega-6) group of oils (Figure 2.2). The refined oil is pale yellow. The oil contains appreciable quantities of vitamin E, sterols, squalene, and other aliphatic hydrocarbons, terpene and methyl ketones (chiefly methyl nonyl ketone). In cosmetics, it has smoothing properties and is considered noncomedogenic. Only the high oleic variety possesses shelf life sufficient for commercial cosmetic formulation.

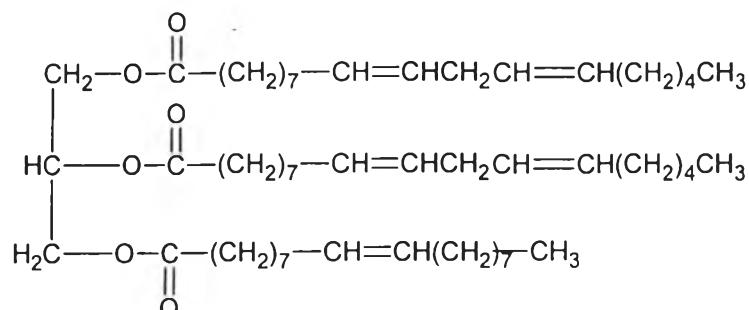


Figure 2.2 The structure of the fatty acids linoleic acid (with is doubly unsaturated) and oleic acid.

2.1.3 Cleansing Skin with Oil

Cleansing skin with water and some additive which improve cleansing effect is not enough efficiency to get rid of the grease, dust that does not dissolve in water and water-proof make-up products. Accordingly oil is need to get rid of dirt.

• *2.1.3.1 Advantage of cleansing skin with oil are:*

1) Cleansing oil helps to balance your skin's natural sebum production while every kind of impurity is done away with. The oil that has hardened with dust particles deep within your skin pores comes out easily when you massage your skin with oil. This prevents blemishes and pimples while giving you a glowing and beautiful skin.

2) Cleansing oil has greasing effect that can decrease the loss of water from skin and keeps your skin hydrated with vitamin E and antioxidants thus making skin soft and condition.

2.1.3.2 Disadvantage of clearing skin with oil are:

- 1) Price of natural oil for make oil remover is high
- 2) Oil leave a greasy feeling after use

2.1.4 Self-emulsifying Oil

2.1.4.1 Self-emulsifying Cleansing Oil

The main component of self-emulsifying cleansing oil is compose of oil and surfactant. When mix it with water it turns to be water in oil emulsion or oil in water emulsion. The system of emulsion depends on type and volume of oil and surfactant. The difference of type and component of emulsion affects the cleansing power and satisfaction.

2.1.4.2 Emulsion

An emulsion is a thermodynamically unstable mixture of two immiscible fluids with one fluid being dispersed in the other. In such systems, the distribution of the particles must be stable in the reasonable period. Surfactants play an important role in making a stable of immiscible fluids system.

2.1.4.3 Emulsion System

Typically there are two common systems of emulsion; first, an oil-in-water emulsion, wherein the oil is the dispersed phase and water is the medium phase. Second, they can form a water-in-oil emulsion, wherein water is the dispersed phase and oil is the continuous phase.

2.1.4.4 Emulsion Process

1) Surface free energy is a process that one liquid is dispersed as droplets in another liquid. This process cannot happen by itself, it have to use the force like shaking to increase the surface free energy for disturbed boundaries between the two surfaces. This fluid boundaries break into another and separate into spherical particles but this process is rather unstable.

2) Coalescence of emulsions is a process that two or more emulsion droplets become joined together forming larger droplets and separate into two phases (Figure 2.3). When the droplets approach each other very closely, the liquid film between them undergoes some fluctuation, and when the film thickness approaches a critical value, film collapse occurs resulting in its rupture. This process can occur very fast by itself without protection of energy barrier.

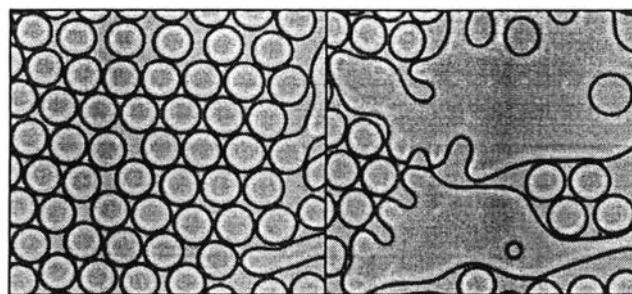


Figure 2.3 Propagation of drop coalescence in a two-dimensional emulsion.

2.1.5 Surfactant

A surfactant is a compound that lowers the surface tension which is the force of cohesion exhibited by the molecules of a liquid, increasing the contact between the liquid and another substance. There are a wide variety of these compounds that work with oil, water, and an assortment of other liquids. Surfactants are contain both hydrophobic groups or water insoluble component (their tails) and hydrophilic groups or water soluble component (their heads) (Figure 2.4).

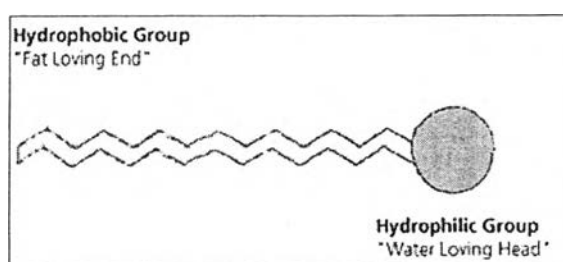


Figure 2.4 Structure of surfactant.

2.1.5.1 *Surfactant Process*

- 1) Mechanical barrier are stabilized by films that form around droplets at interface to prevent droplet joined together forming larger droplets and reduce in the rate of emulsion breakdown.
- 2) Thermodynamic action decreased surface energy by reduce interfacial tension of oil and water.

2.1.5.2 Surfactant Classification

Type of surfactant depending on their charge characteristics, surface-active molecules may be anionic, cationic, non-ionic or zwitterionic (ampholytic) (Figure 2.5). The most commonly of anionic surfactants have carboxylate, sulfate, sulfonate and phosphate polar groups in combination with counterions. In cationic surfactants, the charge is carried on a nitrogen. In non-ionic surfactants are those with one or more poly(oxyethylene) chains as their hydrophilic part. Zwitterionic and amphoteric surfactants possess polar head groups which on ionisation may impart both positive and negative charges. The positive charge is almost always carried by an ammonium group and the negative charge is often a carboxylate.

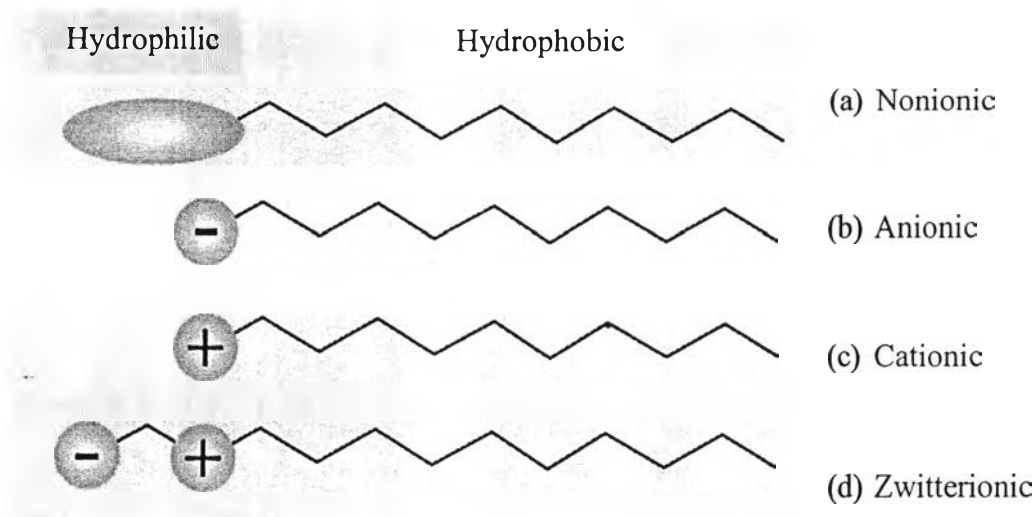


Figure 2.5 Surfactant classification according to the composition of their head: (a). nonionic (no charged), (b). anionic (negative charge) (c). cationic (positive-charged), (d). zwitterionic (two oppositely charged groups).

Nonionic surfactants that used in this study are

1) Sorbitan Monooleate (SPAN[®] 80)

Sorbitan monooleate is a nonionic surfactant and emulsifier often used in foods and cosmetics. This synthetic compound is a viscous liquid. Sorbitan monooleate is derived from polyethoxylated sorbitan (hydrophilic groups) and oleic acid (the lipophilic groups) (Figure 2.6). The critical micelle concentration of polysorbate 80 in pure water is reported as 0.012 mM. In foods, sorbitan monooleate is used as an emulsifier. In Health and Beauty, it widely used in personal care products. Water in oil (W/O) emulsifier, particularly recommended for unsaturated lipid components such as oleyl alcohol or vegetable oils. Dispersing agents for insoluble liquids in other lipophilic liquids. Sorbitan monooleate is used as wetting agents and dispersants for pigments in color cosmetics and zinc oxide/titanium dioxide in sun care products.

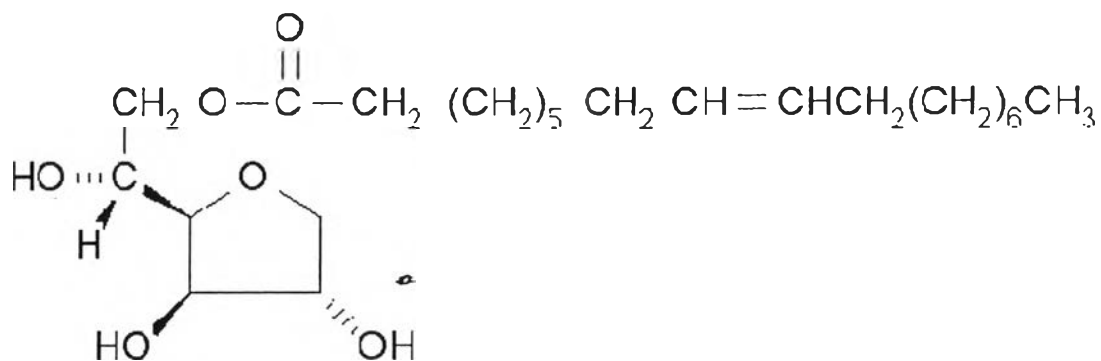


Figure 2.6 Structure of sorbitan monooleate (SPAN[®] 80).

2) Polyoxyethylene Lauryl Ether (Dehydol[®])

Polyoxyethylene Lauryl ether is a synthetic polymer composed of lauryl alcohol and PEG (polyethylene glycol) (Figure 2.7). Due to the presence of PEG, it refers the different of HLB value that use to measure of the degree of surfactant which is hydrophilic or lipophilic. Therefore the high lipophilic is arranged as follows: Dehydol[®] LS 2 TH > Dehydol[®] LS 5 TH > Dehydol[®] LS 7 TH

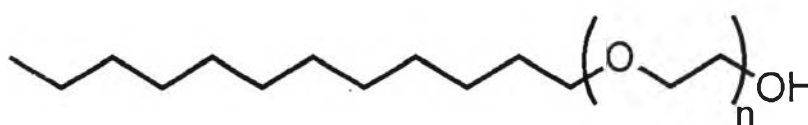


Figure 2.7 Structure of polyoxyethylene lauryl ether (Dehydol[®]).

Table 2.2 Specific properties of polyoxyethylene lauryl ether

Product Name	Chemical Description / INCI Name	Properties		
		Density (g/cm ³) @70 °C	HLB	Cloud Point (°C)
Dehydol LS 1 TH	Fatty alcohol C12-14 approx. 1 mole EO / Laureth-1	0.837	3.6	-
Dehydol LS 2 TH	Fatty alcohol C12-14 approx. 2 mole EO / Laureth-2	0.869	6.1	-
Dehydol LS 3 TH	Fatty alcohol C12-14 approx. 3 mole EO / Laureth-3	0.89	7.9	51-53
Dehydol LS 5 TH	Fatty alcohol C12-14 approx. 5 mole EO / Laureth-5	0.924	10.3	68.73
Dehydol LS 7 TH	Fatty alcohol C12-14 approx. 7 mole EO / Laureth-7	0.949	12.1	52-58

2.1.5.3 Surfactant Aggregation

The surfactant molecules that dispersed in a liquid colloid are aggregate to form micelle. A typical micelle in aqueous solution forms an aggregate with the hydrophilic "head" regions in contact with surrounding solvent, sequestering the hydrophobic single-tail regions in the micelle center. In Figure 2.8 shows typical changes in surfactant self-assembly and morphologies formed with decreasing water content in the system.

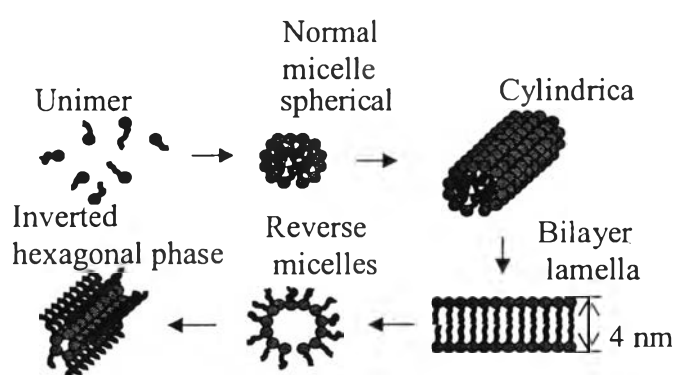


Figure 2.8 Aggregation of surfactant.

2.1.5.4 Hydrophilic-Lipophilic Balance (HLB)

For measure the degree to which it is hydrophilic or lipophilic, the hydrophilic-lipophilic balance is used to calculating values for the different regions of the molecule. The HLB value can be used to predict the surfactant properties of a molecule follow by Table 2.3.

Table 2.3 The properties of surfactant depend on HLB value

HLB Value	Surfactant Properties
< 10	Lipid soluble (water insoluble)
> 10	Water soluble (lipid insoluble)
4 to 8	Anti-foaming agent
7 to 11	W/O (water in oil) emulsifier
11 to 14	Wetting agent
12 to 15	Detergent
12 to 16	O/W (oil in water) emulsifier
16 to 20	Solubiliser or Hydrotrope

2.2 Literature Review

2.2.1 The Study of Pseudo-ternary Phase Diagram Behavior

2.2.1.1 *Effect of Surfactants Types and Concentrations*

Vegetable oil-based microemulsions using carboxylate-based extended surfactants and their potential as an alternative renewable biofuel was studied by Attaphong *et al.* (2012). This study showed that in reverse micellar microemulsion system, which including of canola oil, the linear alkyl propoxylated ethoxylated carboxylate surfactants and the branched alkyl propoxylated ethoxylated carboxylate surfactants, the linear surfactants are used less amount of surfactant than branched extended surfactants to solubilize all components and produce a single phase microemulsion. Moreover, decreasing the number of EO groups in surfactant leads to a reduction in of the amount of surfactant needed to obtain single phase microemulsions.

Syed *et al.* (2014) investigated identification of phases of various oil, surfactant/co-surfactant and water system by ternary phase diagram. From their results, a large area of transparent/clear solution was formed in the oil rich regions and found to be attached to the borders of the diagrams where water and oil ratio was low and the surfactant ratio was high.

In 2014, Ahmad *et al.* studied about stability of thermodynamic. Thermodynamic stability occurs when a system is in its lowest energy state, or in chemical equilibrium with its environment. The process is thermodynamically driven by the requirement of surfactant to maintain an aqueous phase concentration equivalent to its critical micelle concentration but it can lead to show phase separation upon infinite dilution.

Mayer *et al.* (2013) investigated the influence of surfactant concentration on lipid digestion. Vitamin E acetate was relatively stable to digestion by lipase and the non-ionic surfactant was slowly digested, which can be attributed to hydrolysis of the ester bonds linking the hydrophilic head group to the hydrophobic tail group. Studied about concentration of surfactant on vitamin E bioaccessibility, from results suggest that the high levels of surfactant present in the nanoemulsions led to the formation of colloidal structures in the mixed micelle phase that were able to encapsulate vitamin E acetate thereby leading to a high bioavailability.

2.2.1.2 Effect of Co-surfactant Types

Zhu *et al.* (2014) studied the formation of Rhamnolipid-based water-containing castor oil/diesel microemulsion. They formed the microemulsion by used n-butanol, n-pentanol, n-hexanol as a co-surfactant and the results was n-heptanol and n-octanol can form single phase microemulsion successfully. From their results, they stated that different carbon chain lengths of linear alcohols affected the superficial area of palisades region because the increment of chain length might decrease the standard Gibbs free energy of transferring from oil phase to an interfacial region (The smaller value of Gibbs free energy, the grater spontaneous formation of microemulsion).

Attaphong *et al.* (2012) investigated about influence of structure of co-surfactant and they found that the number of carbon chain length of co-surfactant has more influence on the phase behavior than the branching of co-surfactant.

The effect of alcohol chain length of co-surfactant was investigated by Yaghmur *et al.* (2002). The increment of alcohol chain length from

ethanol to butanol was increase the solubilization of system while pentanol and hexanol got the opposite results. They stated that this process seem to be limited since the long chain length of alcohol affects the large attractive interaction among droplet by limiting the actual radius to smaller values than the critical radius.

Ahmad *et al.* (2014) investigated the solubilization capacity and they found that the solubilization was dependent on co-surfactant structure (content, configuration of the polar head group and the hydrocarbon moiety) and type of oils. Their results shows solubilization capacity value that propylene glycol monocaprylate was found to have maximum solubilization capacity value while glycerol monooleate had least solubilization capacity value. This was perhaps due to shorter carbon chain length of propylene glycol monocaprylate, leading to its higher solubilization resulting in its high water absorption capacity.

In 2013, Saberi *et al.* studied the effect of co-surfactant such as propylene glycol and ethanol on formation, stability, and properties to form vitamin E acetate-loaded nanoemulsions by spontaneous emulsification. For propylene glycol, the smallest droplets with narrow unimodal distributions were formed at an 30 % co-solvent concentration while ethanol in aqueous phase and organic phase the smallest droplets with broadening of the unimodal distributions were formed at 20 % and 5 % co-solvent concentration respectively. The least percentage of co-solvent in organic phase because it was no longer completely soluble in the oil phase.

Nanoemulsion Components Screening and Selection: a Technical Note was studied by Azeem *et al.* (2009). When the chain length was increased from ethanol to isopropyl alcohol, it increased the area of the existence of the nanoemulsion. However, with n-butanol, a considerable decrease in the area was observed. Also, increasing the number of hydroxyl groups as we move from isopropyl alcohol to propylene glycol reduced the nanoemulsion area.

The stability of emulsions in the presence of additives was studied by Gasic *et al.* (2002). The influence of different additives on the effective HLB values of non-ionic emulsifiers was studied. In the system with xylene as the oil

phase. Ethanol, glycerol and ethylene glycol (5, 10, 15 and 20 %) were used as additives. From their result, it can be concluded that ethanol and ethylene glycol tend to increase the effective HLB, with the influence of the former being stronger. The influence of both additives became stronger as their concentration increased. The influence of glycerol was just the opposite.

Yang *et al.* (2013) investigated the phase behavior with the increment of glycerol concentration. They found that increasing of glycerol concentration made the viscosity increase and affect the microemulsion system by decrease the interfacial tension, retards droplet encounters and produce smaller droplets due to during the mixing and homogenization stages adding glycerol to the continuous phase caused foaming of the emulsions containing which was attributed to the ability of the high viscosity aqueous phase to trap air bubbles formed.

Syed *et al.* (2014) investigated the concentration of co-surfactant on phase behavior. The addition of co-surfactant like propylene glycol and the decreasing of HLB value of the surfactant system increased the microemulsion zone compared to the surfactant system.

2.2.1.3 Effect of Surfactant/Co-surfactants Ratios (S:Co Ratios)

The phase behavior of castor oil-based ionic liquid microemulsion was study by Wang *et al.* (2014). Their results showed that the mass ratio between surfactant and co-surfactant ratio affected the single-phase areas. The decreasing amount of co-surfactant (n-butanol) was increase the single phase region because hydroxyl of ricinoleic acid, the main fatty acid esters in castor oil, was soluble with surfactant (TX-100) so low interfacial tension was produced without co-surfactant.

Nanoemulsion Components Screening and Selection: a Technical Note was studied by Azeem *et al.* (2009). They were found that the presence of the co-surfactant/surfactant and its type can thus affect the phase behavior of the nanoemulsion by attributed to differences in the packing of surfactant and co-surfactant at the interface.

In 2012, Nguyen *et al.* investigated about phase separation. Two of the surfactants used in this study were 1-octanol and oleyl amine. The experimental results show that at a total surfactant/co-surfactant concentration lower than 0.4 % v/v, phase separation occurs. Additionally, ethanol caused the phase separation because it is very hydrophilic, it tends to separate out and the surfactant concentration used is not high enough to be able to solubilize ethanol into the hydrophobic oil phase.

In 2012, Moghimipour *et al.* investigated about preparation and evaluation of tretinoin microemulsion based on pseudo ternary phase diagram. This study demonstrated that physicochemical properties were dependent upon the contents of surfactant and co-surfactant ratios, water and, oil percentage in formulations. Phase diagrams indicated more width microemulsion region with a rise in surfactant and co-surfactant ratios.

2.2.1.4 Effect of Castor Oil/Sunflower Oil Ratios (C:S Ratios)

The studied of Attaphong *et al.* (2012) about effect of vegetable oils on phase behavior suggested that vegetable oils containing triglycerides are highly hydrophobic because long and bulky alkyl chains of triglyceride structure thus micellar solubilization of triglycerides has been less efficient than other organic phases. Accordingly, when increasing ratio of vegetable oil, increasing in surfactant to form a single phase microemulsion were required.

Zhu *et al.* (2014) studied the co-surfactant (short chain alcohol) and surfactant ratio (C/S ratio) on microemulsion phase formed. They varied C/S ratio from 0.0-1.0 and found the results that C/S ratio below than 0.4 got the two phase emulsion whereas more than 0.6 was decrease the single phase region. Because, when the boundary of the micelles was saturated by alcohol, the excessive amounts of alcohol would be dissolved in the aqueous phase. The excessive molecule of alcohol might separate the surfactant molecules too far. The phase layer would become unstable and the decrease the water solubilization.

Ahmad *et al.* (2014) investigated the effect of surfactant and co-surfactant mass ratio on phase behavior. From their result proved that surfactant

and co-surfactant mass ratio found to be a key factor in influencing the phase properties. When co-surfactant concentration was doubled to value 1:2, the total nanoemulsifying area decreased slightly when compared to value 1:1 but spontaneity of self-emulsification was improved. However when surfactant concentration was doubled as compared to co-surfactant with value 2:1, large increase in nanoemulsifying area was observed than value 1:1. When surfactant concentration was further increased to Km value 3:1 and 4:1, the nanoemulsifying area in the phase diagrams gradually decreased. These effect was attributed to the differences in the packing of surfactant and co-surfactant at the water and oil interface.

The formation of vegetable oil-based ionic liquid microemulsion (ILMs) was determined by Wang *et al.* (2014). They form ILMs with ionic liquid and vegetable oil such as castor oil, jatropha oil and soybean oil. Their results showed that the size of the microemulsion region followed the sequence: castor oil-based ILMs > jatropha oil-based ILMs > soybean oil-based ILMs.

Syed *et al.* (2014) investigated the structure of oil that use to form microemulsion and they found that the oil which contains long-chain triglycerides of oleic acid such as mineral and olive oil was not successful to obtain microemulsions while the molecular weight of mineral and olive oil is most probably too high to assist in the formation of microemulsion.

Azeem *et al.* (2009) were found that, it was also observed that decreasing the oil level led to an increase in the area of nanoemulsion formation. This fact suggested that the oil constitutes the inner phase of the nanoemulsion droplets.

Syed *et al.* (2014) investigated identification of phases of various oil by ternary phase diagram. They attempted to obtain microemulsions using mineral and olive oil and it was not successful because they were contains long-chain triglycerides of oleic acid. Thus, the molecular weight of mineral and olive oil is most probably too high to assist in the formation of microemulsion.

Influence of Oil Polarity on Droplet Growth in Oil-in-Water Emulsions Stabilized by a weakly adsorbing biopolymer or a nonionic surfactant was

observed by Chanamai *et al.* in 2001. They studied about the influence of oil type (n-hexadecane, 1-decanol, n-decane), and emulsifier type (Tween 20, gum arabic) on droplet growth in oil-in-water emulsions. They found that droplet growth in emulsions containing oil molecules of relatively high polarity and high water solubility (decanol) depended on emulsifier type.

Aubrun *et al.* (2004) investigated about nanoemulsions a new vehicle for skincare products. The oil phase of cosmetic products is usually made of a mixture of oils in order to optimize their skin application properties. Low molecular weight oils were light and dry whereas high molecular weight oils were heavy and greasy. However oil which have low molecular had perfect touch more than high molecular weight oils but it was increased in the ripening rate. Furthermore, low molecular weight oils lead to unstable nanoemulsions unlike high molecular weight oils.

2.2.2 Study of Microemulsion Characterization

The ratio of vegetable oil and diesel oil on diameter of reverse micelle and viscosity was investigated by Zhu *et al.* (2014). The increment of castor oil in system was increase the diameter of the reverse micelle due to the hydrophobic and hydrophilic substance of castor oil were dissolve in the reverse micelle system under the action of surfactant and co- surfactant. In addition, the higher concentration of castor oil was increased the viscosity as well. It could be infer that the excessive amounts of castor oil were dissolved in the aqueous phase, the separation of surfactant molecule might occur.

Syed *et al.* (2014) found the hydrophilic-lipophilic balance (HLB) of the selected surfactant reflects the stability of the system and can be obtained when the HLBs of the surfactant and oil are similar. The stability of emulsions is improved if a combination of surfactants is used because solubilization reaches the maximum and the smallest particles are formed when the HLB of a surfactant is optimal in a given oil-water system. Likewise, a type of oil, whether it is triglyceride form or long chain hydrocarbon, can change the physical properties of the systems.

Mayer *et al.* (2013) investigated turbidity of vitamin E-loaded nanoemulsions. The optical properties of the nanoemulsions containing 20 % ethanol appeared to be less transparent than the ones containing 30 % PG 7 times because emulsion formation and emulsion stability are governed by different physical mechanisms.

In 2014, Ahmad *et al.* studied about effect of Km value on mean droplet size. The increment of mean globule size is due to high sufficient concentration of surfactant to carry out self-emulsification but it has delayed emulsification rate.

Azeem *et al.* (2009) studied the droplet size of nanoemulsion from pseudo ternary phase diagrams of Capryol 90 (oil), water, Tween 20 (surfactant), and Carbitol (co-surfactant). All formulations were in the nano range. The droplet size increased with increase in the concentration of the oil in the formulations. The low polydispersibility values observed indicated uniformity of droplet size.

Mayer *et al.* (2013) examined the influence of surfactant-to-oil ratio on the behavior of vitamin E acetate delivery systems under simulated gastrointestinal (GIT) conditions. From the results, the nanoemulsions containing 5 % and 10 % surfactant were optically opaque suggesting that they contained relatively large droplets and may have been some particle aggregation, whereas the one containing 20 % surfactant was translucent, indicating that it contained smaller droplets.

The ζ -potential measurements indicated that oil droplets coated by non-ionic surfactants (Tween 80) have a slight negative charge at acidic pH, which was attributed to adsorption of OH⁻ ions or the presence of anionic impurities (such as free fatty acids, bile salts and phospholipids) at the particle surfaces.

Rao *et al.* (2011) studied in size of droplets of flavor oil microemulsion, nanoemulsion and emulsion. As the emulsifier concentration was increased, the population of smaller droplets increased while the population of larger ones diminished until it eventually disappeared. This trend might be expected

because there would be more surfactant present to cover the oil-water interface, thus enabling small droplets to be formed.

Anisa *et al.* (2010) investigated about affect of viscosity and droplet diameter on water-in-oil (w/o) emulsions. From their experiment, The increment of water affect the viscosity increased linearly due to hydrogen bonds were increase, leading to decrease in the molecular distances of the emulsion system as well as an increase of resistance to flow. Moreover, the decreased in viscosity would be brought about the broadening of the droplet size distribution.