CHAPTER I

INTRODUCTION

1.1 Background

One of the most important properties of creams and lotions are that they must have textures that are appealing to consumers; that is, it must not be too "thin", dispensed easily out of its packaging, and easily spread on to skin or hair. Cationic surfactants and fatty alcohol emulsions are commonly used in lotions and creams. Such emulsions can form different structures (i.e. lamellar phase). Of interest is how to manipulate rheological properties of such emulsions either throuh processing and/or addition of polymer such as hydroxyethyl cellulose. Understanding how to manipulate the rheological properties of these emulsions will allow us to more effectively process products so as to have better appeal to consumers.

If two immiscible liquids are mixed together in a container and then shaken, a close examination will reveal that one of the two phases has become a collection of droplets that are dispersed in the other phase; an emulsion has been formed *(Hunter, 1993)*. Emulsion has long been of a great practical interest because of their widespread occurrences in everyday life. Some important and familiar emulsions include those occurring in foods (milk, mayonnaise, etc.), cosmetics (creams, lotions and conditioners), pharmaceuticals (soluble vitamin and hormone products), and agricultural products (insecticide and herbicide emulsion formulations).

Emulsions are a special kind of colloidal dispersion: one in which a liquid is dispersed in a continuous phase *(Hunter, 1993)*. The dispersed phase

is sometimes referred to as the internal (disperse) phase, and the continuous phase as the external phase. Emulsion systems usually contain emulsifying agents (surfactants, surface active agents) to stabilize the dispersion of the two insoluble liquids. The surfactants are used to stabilize the emulsion systems. Two types of emulsion can be readily distinguished in principle, depending upon which kind of liquid forms the continuous phase *(Bennett, 1968)*.

1) Oil-in-water emulsion (O/W) for oil droplets dispersed in water such as lotions, conditioners, mayonnaise, milk and etc.

2) Water-in-oil emulsions (W/O) for water droplets dispersed in oil such as moisturizing creams, hormone products, paints, and etc.

a)   b)

where [ ] = water, and [■] = oil

Figure 1.1 The two simplest kinds of emulsion: a) Oil-in-water;

b) Water-in-oil.

1.2   Physical Characteristics of Emulsions

1.2.1   Appearance

A considerable range of appearances is possible, depending upon the droplet sizes and the difference in refractive indices between the phases. An emulsion can be transparent if the refractive index of each phase is the

same, or alternatively, if the dispersed phase is made up of droplets that are sufficiently small compared with the wavelength of the illuminating light.

1.2.2 Droplet or Particle Sizes

Emulsion droplets usually have diameters greater than 0.2 micron and may be larger than 50 micron. The particle size of the dispersed phase is dependent on the method of manufacture, the type and the concentration of emulsifier used. The droplet or particle size of an emulsion is one of its most important characteristics because it can affect the appearance, the rheological properties and the stability of the emulsion. As the particle size in the dispersed phase of an emulsion decreases, its appearance changes from white to transparent. Correspondingly, smaller particle sizes usually favor greater stability. Particle size can be determined by using light scattering techniques.

The relationship between appearance of emulsions and the particle size can be shown in Table 1.1. Their relationship is helpful to gain a qualitative estimate of emulsion particle size at a glance.

Table 1.1 The relationship between appearance and the particle size of emulsion

Particle size	Appearance
Macroglobules	Two phases may be distinguished
Larger than 1 micron	Milky white emulsion
1 to appox. 0.1 micron	Blue-white emulsion
0.1 to 0.005 micron	Gray semitransparent(translucent)
0.005 micron and smaller	Transparent

1.2.3 Rheological Properties

The rheological properties of an emulsion are very important. Too high viscosity of an emulsion is troublesome, it causes a resistance to flow, an undesirable property for which an emulsion is formulated. So the knowledge of the rheological properties of an emulsion is important in the production and use of the emulsion. The choice of mixer-type, size, optimum speed, and power requirements will affect the rheological properties of the emulsion. The ultimate use of emulsion dictates the rheological properties necessary for an acceptable product.

A fluid, that is, a liquid or a gas, is a substance that undergoes continuous deformation under the action of an applied shear force or stress. In other words, when a fluid is subjected to shear, it deforms continuously *(Barnes, 1989).* On the other hand, a solid deforms with a finite strain under the action of an applied shear force and retains its original shape upon the cessation of the applied shear force. The manner by which a fluid obeys a given shear-stress-shear-rate relationship determines its class within the rheological classification of a fluid.

1) Newtonian fluids

A fluid is said to be Newtonian if it obeys Newton's law of viscosity, given by

$$\tau = \eta \dot{\gamma} \qquad\qquad 1)$$

where τ is the shear stress (Pa or dyn/cm^2), $\dot{\gamma}$ is the shear strain rate exerted on the fluids (s-1), and η is constant and is referred to as the fluid dynamic or shear viscosity (Pa.s or cP). A Newtonian fluid is one in which the flow is independent of the amount of strain rate such as water at 20 C has viscosity equal to 1 cP.

2) Non-Newtonian fluids

Non-Newtonian fluids follow by the Ostwald-de Waele equation, commonly called the power law, given as

$$\tau = K\gamma \cdot [\gamma]^{n-1} \qquad\qquad 2)$$

or
$$\eta = K\gamma^{n-1} \qquad\qquad 3)$$

where **n** is called the power-law index, and **K** is a constant. When n = 1, a Newtonian fluid is obtained. For pseudoplastic fluid, n is less than unity whereas dilatant fluid, n is more than unity.

Many fluids encountered in emulsions exhibit complex or non-Newtonian behavior. A non-Newtonian fluids is one in which the viscosity is a function of the amount of shear and the time of applying it. The behavior characteristic of non-Newtonian fluids places them in five major classes as follows:

Plastic: The shearing stress of a plastic or Bingham plastic fluid must exceed some minimum value before it flows which shown in figure 1.2. In practice, few materials exhibit this behavior such as synthetic resins, ketchup and etc.

Pseudoplastic: Pseudoplastic behavior is frequently encountered. The consistency, or apparent viscosity, of this behavior decreases instantly with increasing strain rate which shown in figure 1.2.

Dilatant: The opposite of pseudoplastic substance is a dilatant material. Suspensions of starch in water and silicone bouncing exhibit dilatant flow characteristics. The apparent viscosity increases instantaneously with increasing rate of shear. This behavior can be shown in figure 1.2

Thixotropic: The apparent viscosity in a thixotropic substance decreases with time to some minimum value at a constant strain rate such as mayonnaise, paint, hand cream and etc. The behavior can be shown in figure 1.3.

Rheopectic: The apparent viscosity of a rheopectic fluid increases with time to some maximum value at a constant strain rate which shown in figure 1.3.
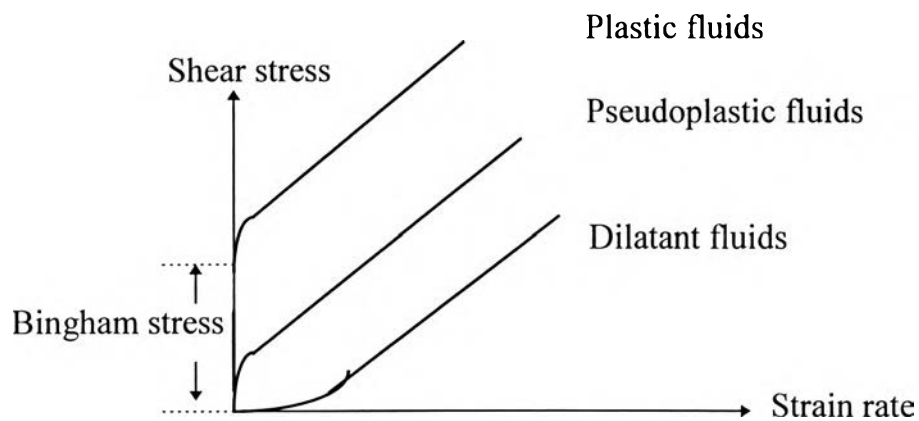

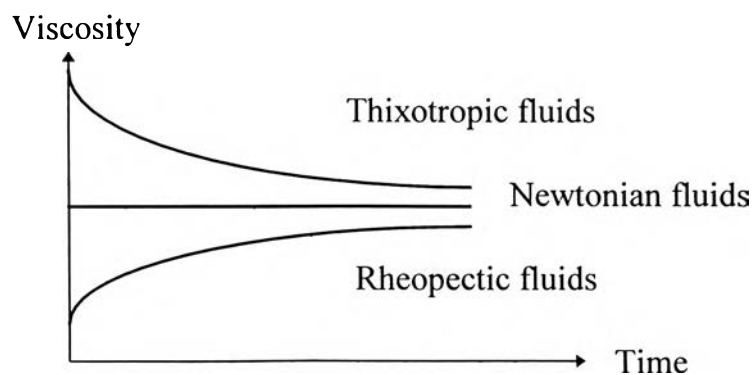Figure 1.2 Flow behavior of non-Newtonian fluids.

Figure 1.3 Viscosity profiles of time dependent fluids compared with Newtonian fluids.

1.2.4 Stability

Stability is one of the key problems of the formulator or manufacturer of emulsions. An emulsified product loses a great deal of its appeal to the user if it separates into two layers, changing in consistency, or discolor before or while it is used. Any emulsion is inherently unstable and will eventually break down to form two layers. The two immiscible layers is "thermodynamically" stable but not "stable" in the formulator's eyes. Emulsion is unstable because the system has a large interfacial surface area and an interfacial surface energy which is proportional to this area.

Colloidal dispersion can come together in very different ways. In the definition of emulsion stability, stability is considered against two different processes *(Hunter, 1993)*: flocculation and coalescence. **In flocculation** two or more droplets clump together, touching only at certain points, and with virtually no change in total surface area. Flocculation is sometimes referred to as coagulation. It can lead to creaming. Creaming is the separation of dispersed droplets from the continuous phase and results from a density difference between the two liquid phases. **In coalescence** two or more droplets fuse together to form a single larger unit with a reduced total surface area. It ultimately leads to two separate liquid layers which is called breaking.

A change in the system which reduces the total surface energy will bring the system into more "stable" state. The total surface energy is reduced if the emulsion drops coalesce, because surface energy is reduced when two drops join to make one drop. One way in which surface active agents promote the stability of emulsion is by reducing the total surface energy of the system.
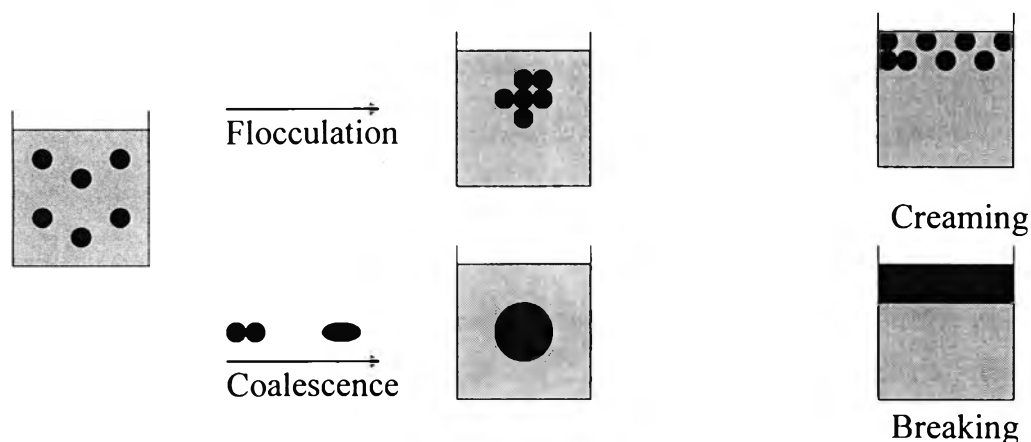
Figure 1.4 Schematic presentation of emulsion instability.

1.3   Emulsifying Agents or Surface Active Agents

Surface active agents or surfactants are characterized by the presence of two portions in the same molecule, one polar and the other non-polar *(Porter, 1994)*.The polar part is the hydrophilic part which may carry a positive or negative charge, giving rise to cationic or anionic surfactants respectively. The non-polar part of the molecule is normally a hydrocarbon chain which is the hydrophobic part.

Surfactants are classified according to the nature of the polar (hydrophilic) part of the molecule when dissociated in water. They can be divided into 4 types *(Porter, 1994)*.

1) Anionic Surfactant :   A surfactant molecule whose polar group is negatively charged; for example, sodium stearate, sodium dodecyl sulfate, sodium dodecyl bezene sulfonate.
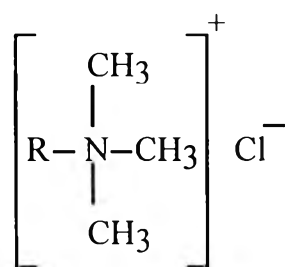
2) Cationic Surfactant :   A surfactant molecule whose polar group is positively charged; for example, cetyltrimethylammonium chloride, laurylamine hydrochloride.

3) Nonionic Surfactant : A surfactant molecule whose polar group is not electrically charged; for example, polyoxyethylene alcohol alkylphenol ethoxylate.
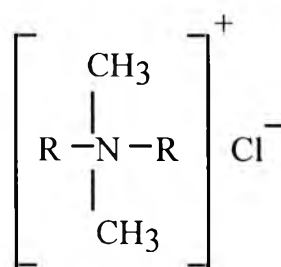
4) Zwitterionic or Amphoteric Surfactant : A surfactant molecule whose polar group contains both negatively and positively charged groups. The charge depends on solution pH. It is positively charged at low pH but is electrically neutral, having both positive and negative charges at intermediate pH. For high pH, it is negatively charged. For example, they are lauramidopropylbetaine, cocoamido-2-hydroxypropyl sulfobetaine.

1.4 Cationic surfactants and the lamellar phase

Cationic surfactants are widely used in aqueous and nonaqueous systems as emulsifier. The type of cationic surfactants which are commonly used in cosmetic creams and lotions are the quaternary ammonium compounds: monoalkyl, dialkyl, trialkyl quats.

$$\left[\begin{array}{c} CH_3 \\ | \\ R-N-CH_3 \\ | \\ CH_3 \end{array} \right]^{+} Cl^{-} \qquad \left[\begin{array}{c} CH_3 \\ | \\ R-N-R \\ | \\ CH_3 \end{array} \right]^{+} Cl^{-}$$

Monoalkyl quats   Dialkyl quats

Monoalkyl quats are normally used in hair preparations such as hair conditioners(Fox, 1990). CTAC or cetyltrimethyl ammonium chloride is know to be strongly adsorbed on the hair surface resulting in a diminished comb-to-hair friction under wet and dry conditions. This leads to a lessening of

electrical charging off the hair surface and, in consequence, a reduction in flyaway. This benefit is co-existent with an improvement in ease of dry combing. The other function of CTAC is to emulsify the fatty alcohol, which gives the lamellar phase-high viscosity finished product. This leaves the product from being too thin.

CTAC can form lamellar phase in the presence of fatty alcohol *(Fox, 1990)*, with high viscosity and pseudoplastic rheological properties. This phase is the most important of all liquid crystalline phase for emulsion stability. It is formed when there is a surplus of emulsifier in the system. Change in the viscosity induces changes in the properties of product that is very important in processing and stability of emulsion. Control of the presence of the lamellar phase occurring in the systems can influence the rheology of product.
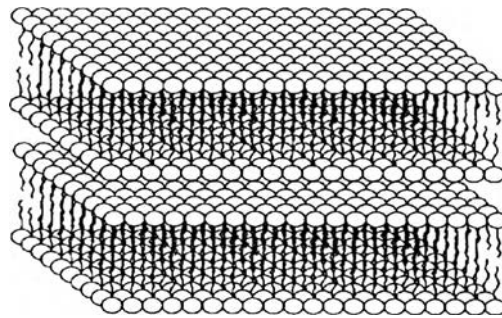

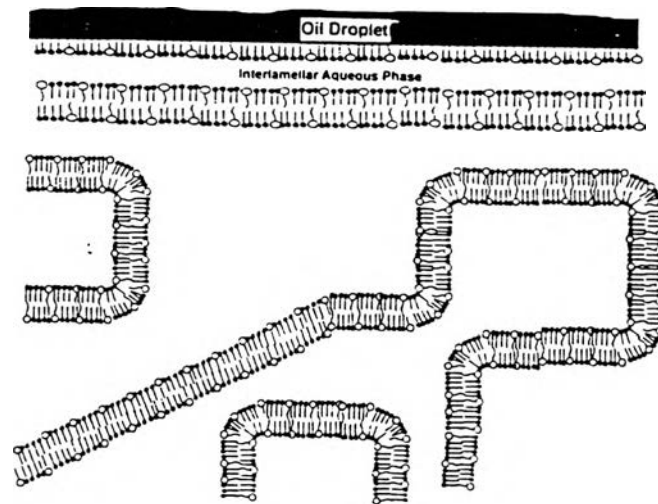Figure 1.5 The structure of lamellar liquid crystalline phase.

Figure 1.6 Schematic of lamellar gel structuring of an aqueous emulsion.

Knowing the structure of emulsion can help understand the rheology of emulsion systems. The relationship between structure and rheology is shown in figure 1.7, which displays the water-in-oil and oil-in-water emulsion having a low viscosity. Viscosity will increase when the lamellar phase occurs, so the lamellar phase gives high viscosity for emulsion products. The lamellar phase is birefringence so it can be identified by a polarizing or optical microscope which has high resolution and a good depth of field such as a laser scanning microscope *(Lochhead, 1994)*.
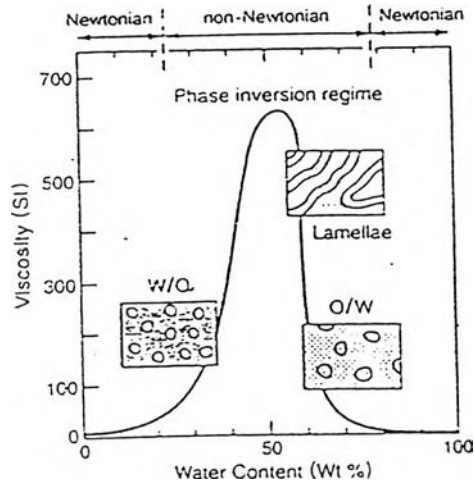
Figure 1.7 Relationship between rheology and structure.

1.5 Water-soluble polymer and the lamellar phase

Water-soluble polymers represent an important class of raw materials for the cosmetic industry. They are used as rheology modifiers. So rheology properties can change in the presence of a polymer. On the other hand, each application depends on the unique polymer solution properties such as the ability to stabilize colloidal dispersions, the ability to adsorb at interfaces, the ability to thicken emulsion system, the ability to act as a unique emulsion and to build three-dimensional molecular network structures which offer preferred rheology.

1.6   Applications

Emulsion is very important and used in many application such as in cosmetic formulations, consumer products, drug releases, foods industries, paints industries, agricultural products, and enhance oil recovery. On the other hand, emulsions are difficult to manufacture. A small deviation in temperature or mixing speed or small amounts impurities can prevent the formation of a stable emulsion. Emulsions are sensitive in varying degrees to heat, and age. Aging of emulsion causes the properties of emulsion to change with time in storage. Aging may refer to changes in composition due to oxidation, precipitation of components, bacterial action, or evaporation of components that have low boiling points or any of aggregation, coalescence, creaming, or chemical changes. Aged emulsion frequently have larger droplets sizes. The production of good, stable emulsions, therefore, is the combination of science and art.

1.7   Literature Survey

Lin and Eads (1997) studied polymer/surfactant interactions involving the nonionic polymers polyethylene glycol (PEG) and polypropylene glycol (PPG) and the surfactant potassium oleate in aqueous solution. They found that in the absence of the polymer, the surfactant solution was viscoelastic. Threadlike micelle was investigated by Cryo-transmission electron microscope. Addition of PEG or PPG induces a viscoelastic-to-Newtonian liquid transition. PEG is more effective than the more hydrophobic polymer, PPG, in inducing this transition. Cryo-TEM images showed a threadlike-to-spherical micelle transition in these polymer/surfactant system.

Jamieson et al. (1995) studied a cationic surfactant in aqueous solution by rheological and imaging techniques. They found that the system becomes gel-like above a threshold surfactant concentration, as evidenced by the appearance of an apparent yield stress and a viscosity which was highly non-Newtonian. Hysteresis was observed in the shear stress vs. shear strain rate measurements: the formation of shear-induced microstructures at high shear rates may cause shear thickening. Electron micrographs indicated three distinct structures in the sample; lamellar, large onion-like globules, and small nodules. These structures were discussed in the context of the rheological data. The density of the globular structures in sheared samples was observed to be larger than in unsheared samples.

Lin (1995) found that branched worm-like micelles occurred in aqueous solutions of alkylamine oxide and alkyl ethoxylate sulfate mixtures by cryo-transmission electron miroscopy (cryo-TEM). These branched micelles formed interconnected micellar networks at high solution pH or salt concentrations. The networks are similar to the bilayer structures in the bicontinuous phase. The rheological properties of these branched worm-like micelles and their networks were also studied. The branched micelle solutions exhibited weak viscoelasticity and an apparent yield stress value. However, no real yield stress value was observed. When a dense micellar network formed, the solution exhibited well-defined Maxwell behavior.

In studying water-in-oil and oil-in-water emulsions of mineral oil and water, *Sherman (1991)* found that the viscosity of emulsions can also increase on aging when the dispersed particles of an emulsion aggregate, part of the continuous phase is immobilized by being trapped between the aggregated particles. This has the same effect as decreasing the continuous phase concentration, and as a consequence the viscosity increases.

Mukherjee and Sharma (1990) , working with kerosene-in-water emulsions stabilized by sodium oleate and gelatin, they found that the particle size of the dispersed phase when homogenized, with a resultant increase in viscosity.

Axon (1990) reported that the viscosity of oil-in-water emulsions containing 70% disperse phase increased with increasing concentration of emulsifying agent. In emulsions prepared with equal oil and a number of univalent soaps as emulsifiers, an increase in soap concentration produced in most cases an increase in viscosity, the magnitude varying with the type of soap and the nature of internal phase.

Munzel and Amann (1989) have postulated the formation of gels in oil-in-water systems by the incorporation of water-in-oil emulsions into the micelles formed by oil-in-water emulsifiers, theorizing that in this way the micelles are "stiffened" and form rigid structural units that crosslink to form the three-dimensional gel network resulting in the "semisolid" gel-like state assumed by the aqueous phase. On microscopic examination of a liquid emulsion of cetostearyl alcohol in mineral oil and cetomacrogol 1000 or cetrimide in water. *Talman and Rowan (1986)* found "filaments" which they assumed to be cetostearyl alcohol complexed with the surfactant in the aqueous phase.

Sherman (1989) has shown that inversion depends on the emulsifier concentration, and in general a higher emulsifier concentration will permit the incorporation of a large internal phase before inversion takes place. *Davies and Beacher (1988)* also have shown that the type of emulsifier affects the quantity of internal phase that can exist before inversion occurs. For example, with emulsifiers having a low HLB number, like the sorbitan monoesters, phase inversion will occur at lower internal-oil-phase volumes and the concentration of the emulsifier is increased.

Talman et al. (1987) examined the rheology of emulsions containing lauryl, oleyl, and cetostearyl alcohol as oil-soluble components and found that the viscosity can be controlled by adding cetostearyl alcohol. This increases the yield value and plastic viscosity of the emulsion studied.

Schambil et al. (1986) reported the mixture of cetyl and steary alcohol increases the viscosity and stability of emulsion instead of using cetyl alcohol or stearyl alcohol alone. He examined that only the crystals of cetostearyl alcohol are able to contribute to emulsion stability and the microscopical observation showed that third phase consists of a lamellar liquid crystal. He also found that increasing the emulsifier concentration induces in some cases a change from thixotropic to newtonian and rheopectic behavior. The viscosity effects and the long term stability of cosmetic emulsions do not depend on the properties of fatty alcohol alone but the mixed phases formed by the emulsifier and the alcohol.

Eccleston (1982) studied on liquid paraffin in water emulsions stabilized by PEG 1000 monostearate and alcohols (myristyl:C14, cetyl:C16, stearyl:C18, and cetostearyl). Ternary systems prepared by dispersing each fatty alcohol and surfactant in water were examined during 30 days, using a Ferranti-Shirley cone and plate viscometer. Microscopical diffusion experiments investigated interaction between PEG 1000 monostearate solution and each alcohol at high and low temperature. He found that the rheological properties of each ternary system were similar. Formulations prepared form pure C14, C16, C18 or cetostearyl alcohols were semisolid immediately after preparation. Flow curves were in the form of anticlockwise hysteresis loops with spur points. On aging for 24 hr., structure built-up over a time scale similar to that observed in diffusion experiments, so that apparent viscosity increased. However, on further aging the pure C14, C16, alcohol system were

not as stable as those prepared with cetostearyl alcohol. In contrast, the pure C18 systems were mobile liquids and the emulsion cracked within days.

1.8 Objectives

One of the most important properties of creams and lotions are that they must have textures that are appealing to consumers; that is, it must not be too "thin", dispensed easily out of its packaging, and easily spread on to skin or hair. Cationic surfactants and fatty alcohol emulsions are commonly used in lotions and creams. Such emulsions can form different structures (i.e. lamellar phase). Of interest is how to manipulate rheological properties of such emulsions either throuh processing and/or addition of polymer such as hydroxyethyl cellulose. Understanding how to manipulate the rheological properties of these emulsions will allow us to more effectively process products so as to have better appeal to consumers.

<u>Objectives</u>

1. To investigate rheological and optical properties of cationic surfactant (CTAC) and fatty alcohol (FA) emulsion system.

2. To investigate rheological and optical properties of cationic surfactant (CTAC) and fatty alcohol (FA) mixtures in the presence of hydroxyethyl cellulose (HEC) and modified hydroxyethyl cellulose (modified HEC).

<u>System studied are</u> :

1. CTAC/FA = 0.7/y   (y = 2.0-8.0%)

2. CTAC/FA/HEC = 0.7/y/z   (y = 2.0- 8.0% ; z = 0-1.5 %)

3. CTAC/FA/Modified HEC = 0.7/y/z   (y = 2.0- 8.0% ;

z = 0- 1.5 %)

4. CTAC/FA = 1.05/y (y = 2.0-8.0%)

5. BTAC/FA = 0.7/y   (y = 2.0-8.0%)

6. BTAC/FA = 1.05/y (y = 2.0-8.0%)