CHAPTER I

INTRODUCTION

1.1 Background

Nowadays, surfactant-based liquid crystals have a broad range of applications, especially in cosmetics and food industries. One of the most important systems are those in which bilayers of surfactants are formed. Possible structures are the lamellar mesophase, the bicontinuous cubic phase, the liposome phase and the onion phase (Nemeth *et al.*, 1998). Rheological properties of such systems are very important since they must have textures that are appealing to consumers; that is, it must not be too thin, can dispense easily out of its packaging, and easily spreads on to skin or hair. Moreover, it helps to save energy required to package the product.

1.2 Cosmetics Emulsion

1.2.1 Definition of Emulsion (IUPAC, 1972):

An emulsion is a dispersion of droplets of one liquid in another one with which it is incompletely miscible. Emulsions of droplets of an organic liquid (an oil) in an aqueous solution are indicated by the symbol O/W and emulsions of aqueous droplets in an organic liquid as W/O. In emulsions the droplets often exceed the usual limits for colloids in size (Israelachvili, 1994).

For cosmetic emulsions, they cover a whole range of systems from simple two-phase liquid systems to complicated poly-phase systems. However, all of them are characterized by possessing two major phases, one aqueous and the other lipid in nature (Clark, 1963).

1.2.2 Emulsifying Agents or Surfactants

A surfactant is a substance that, when present at low concentration in a system, has the properties of adsorbing onto the surfaces or interfaces of the system and of altering to a marked degree the surfaces or interfacial free energies of those surfaces or interfaces (Rosen, 1988).

Surfactant has a characteristic molecular structure consisting of two structure portions: lyophobic group or hydrophobic group and lyophilic group or hydrophilic group. The chemical structures of the hydrophobic and hydrophilic portions of the surfactant molecule vary with the nature of the solvent and the conditions of use (Clint, 1992).

The hydrophobic part of surfactant is usually a long chain hydrocarbon residue; the hydrophilic part is an ionic or highly polar group. Depending on the nature of the hydrophilic group, surfactants are classified as

1. Anionic surfactant: The surfactant has a negative charge on the hydrophilic group

2. Cationic surfactant: The surfactant has a positive charge on the hydrophilic group

3. Zwitterionic or Amphoteric surfactant: Both positive and negative charges may be present on the hydrophilic group

4. Nonionic surfactant: No ionic charge on the hydrophilic group

The adsorption of a surfactant on a surface depends upon the concentration. At very low concentrations, the surfactant molecule lies flat on the surface. As the concentration increases, the number of surfactant molecules on the surface increases and begins to orient. If the concentration continues to increase, the surfactant molecules in the solution will form an ordered structure known as a micelle. This particular concentration is known as the critical micelle concentration or CMC. At above CMC, there is no apparent change in adsorption at hydrophobic surfaces, but at hydropholic

surfaces more than one layers of surfactant molecules can form micelle (Porter, 1994).

1.2.3 The Shape of Micelles in Solution

There are many factors that can affect the structure and the shape of a micelle such as the temperature, the type of surfactant and its concentration, other ions in solution and other water-soluble organic compounds, e.g. alcohol.

However, the shape of micelles can be described by the geometrical packing of the hydrophilic and hydrophobic groups. The area occupied by the hydrophobic group and the hydrophilic group was defined by the hydrophilic group area (a_o), the maximum length of the alkyl chain (l_c) and the alkyl chain volume (V_c). These relations can be expressed in table 1.1 (Ananthapadmanabhan, 1992).

Table 1.1 The Structure of Micelles at Various Geometrical Packing

Value of V_c/a_ol_c	Structure of Micelles
< 1/3	spherical micelles
1/3 – 1/2	cylindrical micells
1/2 - 1	bilayers/Vesicles
> 1	inverted micelles

Depending upon the surfactant concentration, the basic surfactant aggregate structures or the shape of micelle can be diverted into 2 types. First, spherical and cylindrical micelles are formed at low surfactant concentrations. Second, hexagonal, cubic, lamellar and gel phases are formed at higher surfactant concentrations. Structures of these latter types, with cubic, hexagonal and lamellar phases are known as mesophase or lyotropic (solvent-

induced) liquid crystals. The name liquid crystal is highly descriptive of the physical state of these phases. The degree of ordering of molecules is intermediate between simple viscous liquid and crystalline elastic solid. Hexagonal and lamellar phases are very common and are birefringent so that their existence are readily demonstrated by the polarizing microscope. Cubic phases are isotropic and they can occur in several different parts of the phase diagram (Clint, 1992).
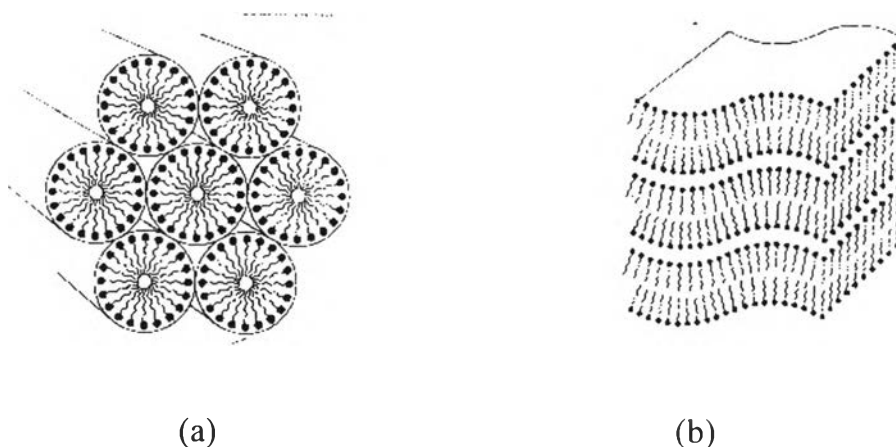

(a)   (b)

Figure 1.1 Schematic drawing of the structure of (a) hexagonal phase and (b) lamellar phase.

1.2.4. Emulsion Stability

Stability of emulsions is very important for the formulator or cosmetic chemists whether the stability during storage or the stability in use is concerned. An emulsion of two liquids without a stabilizer will be easy to break into two liquid layers. Emulsion is unstable because the system has a change in interfacial surface area and an interfacial surface energy, which is proportional to this area.

There are four types of emulsion instability: creaming, flocculation, coalescence and inversion.

" Creaming" is a common occurrence with fluid emulsions. It is the separation of dispersed droplets from the continuous phase under the

action of gravity. For example, in W/O systems, the disperse phase gravitates to the bottom of the container, giving a water-rich system. This is known as downward creaming.

"Flocculation" is the first stage leading to irreversible breakdown of the emulsion. In this system, a number of droplets will have aggregated together whilst still preserving their identity as discrete particles. The formation of aggregates in this manner will automatically accelerate the rate of creaming, as the effective radius of the particles will have increased.

"Coalescence" can follow upon flocculation, when each aggregate combines to form a single droplet. The process of flocculation, followed by coalescence, may repeat until complete phase separation has taken place.

"Inversion" or phase inversion is a particular form of instability in which the emulsion types changes, for example, from O/W to W/O or vice versa and this system will decrease the viscosity of emulsions (Clark, 1963).

1.2.5 Liquid Crystal Stabilization

Friberg *et al.* (1969) demonstrated that a sudden increase in emulsion stability arose in the concentration range where a liquid-crystalline phase could be separated from the emulsion. The viscosity of these liquid-crystalline compositions is usually high. The lamellar phase has pseudoplastic rheology and it is the most important of all liquid-crystalline phase for the emulsion stability. The presence of a liquid-crystalline phase causes a reduction in the available London-Van-der-Waals energy for coalescence, in combination with the high viscosity of the liquid-crystal layer, the time for coalescence is increased dramatically (Robert, 1994).

1.2.6. Vesicles and Liposomes

In cosmetic emulsions such as hair condition and fabric softener, cationic surfactants in the form of quaternary ammonium compounds have been shown to form vesicles and liposomes structures (Clint, 1992). Vesicles can be imaged as lamellar micelles bent around and joined up in a sphere, leaving an aqueous solution inside the sphere and one outside. Liposomes are concentric spheres of vesicles. The simple pictures of these structures are given in Figure 1.2. The geometric of the surfactant needed to form such structures is one whose size of the hydrophobic group is nearly the same size as the size of the hydrophilic group (Porter, 1994). The reason that the lamellar or bilayers form spheres is that the edge of bilayer sheet with the hydrophobic groups inside will have their hydrophobic groups exposed to the water. The only way that the hydrophobic groups can avoid the water is by forming into a sphere (Kahler et al., 1992).
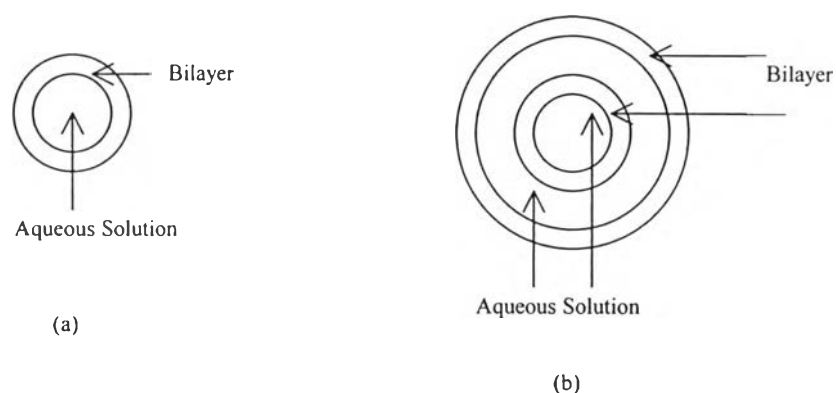

Figure 1.2 Schematic drawing of the structure of (a) vesicles structure and (b) liposomes phase.

1.3 Major Raw Materials in Hair-Care Product

1.3.1 Cationic Surfactants

Unlike anionic or amphoteric surfactants, cationic surfactants cannot be used generally for cleaning applications. Due to their conditioning

properties, cationic surfactants show a high substantively to natural surfaces such as skin and hair. They can act as emollients for the skin or as conditioning agents on the hair. Cationic surfactants, in the form of quaternary ammonium salts or "quats" are widely used in hair condition. Quats can be thought of as ammonium salts with the hydrocarbon molecules replaced by alkyl groups. At least one group is a hydrophobic molecule with a long hydrocarbon chain (12-22 carbons) (Williams and Schmitt, 1996).

A quats abililty to condition comes from the hydrophobic nature of the long chain of hydrocarbon group and the cationic charge of the polar head group (hydrophilic group). In aqueous cosmetic formulations, quats dissociate into their ionic components. The cation is attached to the hydrocarbon chain, which is attracted to anionic charges present in hair's protein structures. This electrostatic interaction, coupled with the fatty nature of a molecule's hydrocarbon portion, inhibits rinse-off (Randy and Perry, 1995).

The fatty portion of the quats deposites on the hair surface. The benefits of quats are evident when hair cuticle is smoothed resulting in softer feel with easier combing ability, reduces static electrical build up and also reduces fly-away and improves manageability. The disadvantages of quats are the incompatibility between quats and anionic surfactants, a relatively high potential for skin and eye irritation (Randy and Perry, 1995). Quats are usually obtained by the reaction between methyl chloride, dimethyl sulfate and tertiary amines. The most important cationic surfactants in conditioners are cetyltrimetyl ammonium chloride or CTAC. This surfactant shows a light to moderate conditioning ability combined with an excellent water solubility. The substantivity and conditioning properties are improved as the carbon chain length increases.

1.3.2 Fatty Alcohol

Fatty alcohol, mainly cetyl alcohol ($C_{16}OH$) and stearyl alcohol ($C_{18}OH$) can be used as consistency regulators and co-emulsifiers in cosmetics emulsions, for example, cream, lotions and hair conditioners. The so-called natural fatty alcohol is obtained by hydration of fatty acid methyl esters. Mixtures of cetyl and stearyl alcohols combined with surfactants are known as self-emulsifying. Fatty alcohol interacts with a cationic surfactant, the mixture is mainly used in hair rinse formulations. They give a texture and a body to the formulation and acts as consistency regulator. This behavior comes from high viscosity and lamellar liquid crystalline phase of the finished product (Williams and Schmitt, 1996).

1.3.3 Water Soluble Polymer

Water- soluble polymers have been widely used as thickeners in food and cosmetic industries. They are used as rheology-modifies in gels; conditioning shampoos and liquid makeup; and as conditioners for hair and skin. Each of these applications depends on the unique polymer solution properties such as the ability to adsorb at interfaces, and the ability to stabilize colloidal dispersions. The interaction between a surfactant and a polymer gives a self-association in aqueous solution and generates the association structures of high molecular weight and displays the substantial increase in viscosity of cosmetic emulsion (Robert, 1992).

1.4 Rheology of Cosmetics Emulsion

Cosmetics chemist is concerned with two aspects of rheological properties, namely, the behavior in the container and the behavior when applied to the skin or hair. To understand the various types it is necessary to determine rheological properties of emulsion.

The viscosity η of a fluid is defined as the force per unit area required to maintain unit difference in velocity between two parallel layers. If a shearing stress τ results in a velocity difference of du (cm per sec) between two layers dx (cm) apart, then

$$\tau = \eta(du/dx) \quad \text{or} \quad \tau = \eta\dot\gamma \quad\quad\quad (1.1)$$

For ideal liquids, the shearing stress is proportional to the shear rate $\dot\gamma$ or velocity gradient, in other words, the viscosity is constant and it is independent of the shear rate. This behavior is known as Newtonian. In contrast, most emulsions do not behave as simple liquids but they show various types of flow behavior, and they are called non-Newtonian fluids (Clark, 1963). Figure 1.3 illustrates the various types of fluid characteristics.
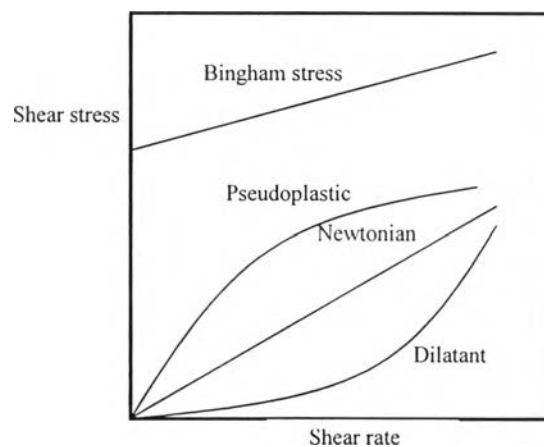

Figure 1.3 Various types of fluid characteristics.

For Newtonian liquids, the plot of shearing stress versus rate of shear is a straight line passing through the origin and the slope of the line is the viscosity. A bingham plastic material resists deformation until limiting stress is applied, whereupon it behaves as a Newtonian material. This plastic will not flow until a critical yield stress is exceeded. A critical yield stress required to produce flow is called "Bingham stress". However, a pseudo-plastic

material does not show a yield value, but its viscosity decreases with increasing rate of shear. For dilatant plastics, the viscosity increases with the rate of shear. Most cosmetic emulsions exhibit pseudo-plasticity in some form or other while dilatant cosmetic emulsions are quite rare, but highly dispersed phase W/O systems such as cosmetic lotions can produce this character.

For some materials, viscosity decreases with time at a constant stress then it is referred to as being thixotropic. "Thixotropic" flow is a common feature of many cosmetic emulsions. Alternatively, the viscosity of a "rheopectic" system increases with the time of applied stress but this behavior is quite rare in cosmetic emulsions.

1.5 Factors Influencing the Rheological Behavior of Emulsions

Sherman (1955) has listed six factors, which can influence rheological behavior of emulsions.

(1) The viscosity of the continuous phase

This is the most important rheological property of emulsions. The viscosity of an emulsion is proportional to the continuous phase viscosity. The proportionality factor is never less than unity. Other factors such as particle size distribution and phase volume fraction can be important when continuous phase viscosity is low, but contribute less when continuous phase viscosity is very high.

(2) The viscosity of the disperse phase

This factor plays an important role when the disperse phase is considered as consisting of deformable liquid droplets but not important if the disperse droplets behave as rigid spheres.

(3) The concentration of the disperse phase

The emulsion viscosity will increase with increasing disperse

phase concentration, slowly at first, and then increasing steeply to a maximum value after the phase inversion occurs.

(4) The particle size distribution

Homogenization of a coarse emulsion produces a change in droplet size distribution. The interaction of droplets offers an increased resistance to shear stresses i.e. the viscosity increases. The viscosity of the emulsion can be clearly defined if the system contains uniform size droplets. Thus for practical proposes, homogenization method can give the emulsion system to a standard viscosity specification.

(5) Nature of emulsifier

The type of emulsifying agent and the level at which it is used affect the rheological properties of emulsions system. The change of emulsifier will change the nature of the interfacial film and results in the change of viscosity of emulsions.

(6) Electroviscous effect

The presence of electrically charged disperse phase droplet results in an apparent change in their volume. The electroviscous effects would be greater for emulsions having a fine particle size compared with coarse emulsions.

1.6 Applications

Today's cosmetic emulsions are still of interest to chemist whether its composition or the flow properties during storage or in use. To control, adjust and predict the flow properties during manufacturing, such as mixing, pumping, filling or packing of emulsions require a good knowledge of the flow properties. The physical behavior of emulsions products needs also to be understood, such as pouring or extrusion from packs, draining, and leveling in use (Howard, 1994).

1.7 Objectives

To investigate rheological and optical properties of CTAC/FA, BTAC/FA, CTAC/FA/HEC and BTAC/FA/HEC emulsions. In particular, we investigate in terms of entanglement storage modulus (G_N^o), Bingham stress (τ_B) and zero shear viscosity (η_o) of these emulsions and to correlate these properties with various structures formed.

1.8 Scope of Work

We investigated the following effects:
(a) The effect of fatty alcohol concentrations
(b) The effect of temperature
(c) The effect of annealing temperature
(d) The effect of pH