

CHAPTER I

INTRODUCTION

1.1 Background

Emulsions are disperse systems in which oil and water are held together in finely distributed form by surface-active substances. Besides oil, water and emulsifiers, as consistency agent, they function by building up a lamellar-structure in the matrix phase (Eccleston 1990). This research work continues from previous research that they study the rheological properties of cationic surfactant and fatty alcohol mixtures with aging time. They investigate the effect of cationic surfactant concentration, and different types of cationic surfactant were compared. The emulsion structure will affect to the rheological properties and they change with aging time until reaching equilibrium condition. The effect of added polymer (HEC) and modified polymer also were studied (Nakarapanich 1998).

In this research, we reported new results on the rheological properties of different emulsion systems with longer aging time. The effect of annealing on the rheological properties with aging time was also reported.

1.2 General Aspect

1.2.1 Cationic Surfactants and the Lamellar Phase

The word SURFACTANT is a short term for surface-active agent. Surfactants have a characteristic molecular structure consisting of a structural group that has very little attraction for the solvent, known as a lyophobic group (solvent-hating), together with a group that has strong attraction for the solvent called the lyophilic group (solvent-loving). This known as an

amphipathic structure. Surfactants can be classified into four classes: anionic surfactants; cationic surfactants; nonionic surfactants; and zwitterionic surfactants.

1.2.2 Water-Soluble Polymer

Polymers exhibiting water solubility are not limited to polyelectrolytes but a diverse class of important structures, ionic and nonionic, of both synthetic and biological origins. Some water-soluble polymers contain monomers that have amphiphilic character themselves. In this case, solvation of the polymer may involve the hydrophobic interaction, in which the local structure of water in the neighborhood of the hydrophobic portion of the segment is thought to play a role. Addition of other solution components, such as salt, cosolvents, or surfactants, or changing the molecular weight of the polymer, can affect the solubility strongly.

1.2.3 The Polymer and Surfactant Interactions

The main driving force for polymer-surfactant interaction is believed to be the reduction of the interfacial area between the hydrophobic polymer segments and the solvent water by association of these segments with the exposed hydrophobic parts of aggregation surfactants. Here the hydrophobicity of the polymer chain plays a major role, although steric requirements at the micellar surface and the perturbation of the hydration sheath by the surfactant head groups and counterions may influence the free energy transfer of the polymer from the aqueous to the micellar phase. Since the hydrophobic polymer strands are believed to replace water molecules structured around the micellar head groups, stabilization of the micelle upon binding to a polymer strand results from a reduction of interfacial tension between the hydrophobic core and water. Furthermore, specific interactions

such as hydrogen binding between the polymer and the head groups may also play a role.

1.2.4 Rheological Properties of Emulsions

The cosmetic technologist is often concerned with two aspects of flow property, namely, the behavior in the container and the behavior when applied to the skin or hair. For example, when a cream is applied to the skin, the emulsion breakdown or perhaps inversion occurs resulting in a change in flow behavior which is sensed by the skin as a pleasant or unpleasant sensation. It may be difficult, but usually possible, to define and measure the necessary flow properties of the product in the container, it is impossible to define objectively those flow properties required to ensure consumer acceptance.

However, it is important to recognize the various basic types of flow behavior, and also to be aware of the factors which determine the flow properties of emulsion.

1.2.4.1 Types of Flow Behavior

The coefficient of viscosity of the fluid is defined as the force per unit area required to maintain unit difference in velocity between two parallel layers. With ideal liquids, the viscosity is independent of the shear rate produced by the stress applied. This is called Newtonian flow and exhibited by simple liquids. However, most emulsions do not behave as simple liquids. Figure 1 shows the various basic types of flow behavior.

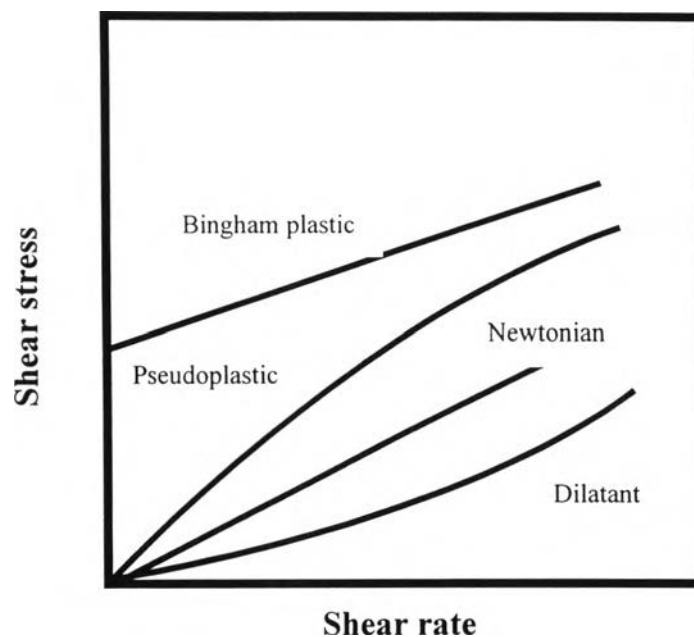


Figure 1.1 Various types of flow behavior.

With Newtonian liquids the plot of shearing stress against rate of shear is a straight line passing through the origin, the viscosity is given by the slope of the line. A Bingham plastic material resists deformation until the limiting stress is reached. As a nonnewtonian material, a pseudo-plastic material does not show a yield value, but its viscosity decreases with increasing of shear rate to a limiting value at which the viscosity usually becomes independent of the shear rate. Most cosmetic emulsions exhibit pseudo-plasticity in some form or other. In the case of dilatant systems, the viscosity increases with shear rate. Dilatant cosmetic emulsions are quite rare. Generally for non-Newtonian systems, viscosity is dependent on the shear rate.

1.2.4.2 Factors Influencing the Flow Behavior of Emulsions

There are some important factors or characteristics of emulsion systems which can affect flow behavior. Sherman (1955) has listed six factors which he considers as contribution to the viscosity of emulsion systems.

- 1) The viscosity of the continuous phase
- 2) The viscosity of the disperse phase
- 3) The volume concentration of the disperse phase
- 4) The particle size distribution
- 5) The nature of the emulsifying agent

These factors vary in their contribution. In certain products one factor such as the viscosity of the continuous phase may alone determine the viscosity of the product. However, in most products several factors are involved. These factors are not only determined by the formulation used, but also by the method of preparation.

1) Viscosity of the continuous phase

This is the prime determination factor that the viscosity of an emulsion is proportional to the continuous phase viscosity η_0 . Other factors such as particle size distribution and phase volume fraction can be important when η_0 is low, but this contributes less when η_0 is very high.

2) Viscosity of the disperse phase

Theoretically this is of no importance if the disperse phase droplets behave as rigid spheres, but if the disperse phase is considered as consisting of deformable liquid droplets, then internal phase viscosity can contribute substantially in determination of emulsion viscosity. However, most cosmetic emulsion, it has no practical significance in this respect.

3) Concentration of disperse phase

The viscosity increases with increasing disperse phase concentration, and then increasing to a maximum value after which inversion usually occurs.

4) Particle size distribution

Homogenization of a coarse emulsion produces a change in droplet size distribution. The reduction in median diameter results in an increased interfacial area, and the mutual interaction of droplets offers an increased resistance to shear stresses, i.e. the viscosity increases. The particle size distribution of solid components included in certain cosmetic emulsions is also of importance in defining viscosity. For example, homogenization of a heavily pigmented O/W foundation cream will not only alter the particle size distribution of the dispersed oil phase, but also modify the pigment dispersion. Both will affect viscosity. Also in a W/O cream containing waxes, homogenization may reduce the aggregation of crystallites, thereby modifying the viscosity of the continuous phase. Thus, in practice, the net effect of homogenization of cosmetic emulsions can be the sum of several separate effects which either support or oppose each other.

5) Nature of the emulsifier

Both types of emulsifying agent and the level at which it is used to affect the flow properties of emulsion systems as well as other properties. For example, water in mineral oil emulsion containing 60 percent weight of water, stabilized with calcium soap will normally be a thick cream. A similar system stabilized with sorbitan sesquioleate will be much softer. This difference is due not only to differences in particle size distribution, but also to the nature of the interfacial film. Calcium soap gives a rigid interfacial film, whereas the sorbitan sesquioleate interfacial film is more flexible. As in the case above, changes in the nature of the interfacial film contribute to overall effects on viscosity as well as stability.

1.2.4.3 Optical properties

The opaque appearance of normal emulsions arises from the differing refractive indices of the two phases. If the two phases have identical refractive, but different optical dispersive powers, highly colored transparent emulsion are obtained. These are not encountered in cosmetic practice. Transparent systems are obtained irrespective of refractive index considerations, when the droplet size reduced below approximately 0.05μ diameter.

With normal emulsions, the appearance changes with changes in droplet size, as indicated below in Table 1.

Table 1 Effect of droplet size on physical appearance of emulsion.

Particle size diameter	Appearance
$>0.05 \mu$	Transparent
$0.05 - 0.1 \mu$	Grey, translucent
$0.1 - 1.0 \mu$	Bluish-white
$1.0 - 50 \mu$	Milky white, the opacity decreasing with increasing particle size

The opacity of emulsions is also, within limits, dependent on the concentration of the disperse phase. Generally speaking, with any given two phases, the opacity of the emulsion increases as the disperse phase concentration increases to a maximum limiting value as defined by the particle size distribution, after which the opacity becomes independent of disperse phase concentration. The critical concentration at which opacity becomes independent of disperse phase concentration increases with increasing droplet size. For fine emulsions, having droplet size around 1μ , opacity is independent of disperse phase concentration from about 5 percent disperse phase upwards.

1.3 Literature Survey

Schambil (1986) reported that cosmetic oil-in-water emulsions often contained cetostearyl alcohol (1/1 mixture of cetyl and stearyl alcohol) to increase the viscosity and the stability. It is known that using cetyl alcohol or stearyl alcohol alone instead of their mixtures, a very disadvantageous behavior can be observed. The difference in stability at a constant temperature supposed to be connected with the polymorphism of the alcohol was postulated. Further on, it was assumed that only the crystals of cetostearyl alcohol were able to contribute to the emulsion stability by accumulation at the interface. Rheological measurements with several long chain alcohols showed that the highest yield values and the highest apparent viscosity of oil-in-water emulsions were obtained with cetostearyl alcohol.

Goddard and co-workers (1991) studied the system of cat-HEC in combination with anionic surfactants. It was concluded from this study that the anionic surfactants binded to the cationic charges of the polymer and the tails of the surfactant acted again as crosslinks between different polymer coils. If enough surfactant was added to compensate the charges completely, the system phase separated with excess anionic surfactant. A single-phase solution was obtained.

Goddard and Leung (1992) showed that systems with even stronger elastic properties could be obtained with HEC when the polymer was substituted with cationic groups which also carried a hydrophobic alkyl group. With an increasing concentration of anionic surfactant such systems became viscoelastic, then phase separated and finally became single phase again and behave as very strong stiff hydrogels. Rheological measurement showed that the storage modulus (G') were much higher than the loss modulus (G'') over a frequency range of several decades and that the absolute values of the moduli were more than ten times larger than for those systems which were only hydrophobically or cationically modified.

Hoffmann (1994) investigated and compared rheological properties of different kinds of viscoelastic surfactant solutions. The first system (type 1) consisted of entangled flexible rodlike micelles in an isotropic micellar phase (L1- phase), while the second (type 2) consisted of tightly packed uni- and multilamellar vesicles (dilute L-phase). The rodlike micelles can be formed with a nonionic, a zwitterionic and an ionic surfactant or with a combination of two surfactants. The systems of type 2 had a yield stress value and the samples did not flow, if the applied shear stress was below the yield stress value. At small stress values the systems of type 2 behaved like true permanent networks, while the systems of type 1 behave like temporary networks. It is evident that the microstructures in both cases must be very different. The network with the elastic properties in the systems of type 2 consisted of tightly packed uni- and multilamellar vesicles. In normal temporary networks in viscoelastic surfactant solutions the modulus I determined by entropy elastic forces, while in the type 2 the modulus was given by energy elastic forces. In case 1 the modulus was independent of the ionic strength, while in case 2 the modulus broke down with increasing ionic strength. The different viscoelastic behaviors became evident with increasing deformation of the sample. While the strain of the entropy elastic solution was about 100% until the modulus started to decrease at a strain value of about 10%. At higher strains, the systems started to flow. Thus, the yield stress was about 10% of the shear modulus.

Kevin (1994) reported that long-chain surfactants are playing an increasingly important role in the formulation of personal-care products. These ingredients, based on a C_{22} rather than a C_{12} - C_{18} fatty moiety, were less water-soluble than the more traditional uric- to stearic-based analogs. Their more hydrophobic nature provided some superior hair conditioning and surfactant-type thickening properties. These properties were dependent on limited water solubility. Properties of two surfactants were based on a long-chain (C_{22}) fatty

moiety. Behenyl methyl ammonium methosulfate, a mild quaternary material, offered both conditioning and emulsifying properties.

Kastner (1995) compared the solution behavior and the macroscopic properties of samples of hydroxyethyl cellulose (HEC) which were modified by perfluoroalkyl chains (F-HMHEC), by cationic groups (cat-HEC), and by hydrophobically modified cationic side chains (cat-HMHEC). They found that the viscosity increased with hydrophobic and ionic modifications of the HEC, and the entanglement concentration C^* , decreased by hydrophobic substitution. On addition of ionic surfactants the viscosity of the modified HEC solutions increased even more. Yield stress values sometimes were found for the F-HMHEC samples with anionic and cationic surfactants and the cat-HEC and cat-HMHEC samples with oppositely charged (anionic) surfactants. The results of the observed polymer-surfactant interactions were interpreted in terms of association between the oppositely charged and/or the hydrophobic parts of both compounds.

Goldszal (1995) reported that the thermal behavior of two non-ionic cellulose: ethyl(hydroxyethyl)cellulose (EHEC) and methylcellulose (MC) in dilute aqueous solutions. These polymers exhibited a lower critical solution temperature; i.e. demixing occurred by raising the temperature. The interaction with a cationic surfactant was investigated: various amounts of cetyltrimethyl ammonium bromide (CTAB) were added to the dilute polymer solutions corresponding to surfactant concentrations below and above the CMC. By increasing the temperature they showed that these two polymers behave in a very different way: a micellization followed by a chain collapse was observed for EHEC. The surfactant interacted strongly with EHEC, which reduced the aggregation and swelled the coils, while only a fraction of the MC sample was sensitive to CTAB.

Martino (1995) reported that the lamella phases formed with SHBS, DDAB and $C_{12}E_5$ at relatively high surfactant concentration and at 25 °C broke up as water was gradually replaced with propylene glycol. In addition, the SHBS lamellar phase became unstable at progressively lower temperatures as propylene glycol content increased. The break-up of the lamellar phase accompanied a reduction in the lamellar repeat distance for the ionic surfactants, but the repeat distance was constant for the nonionic surfactant. With $C_{12}E_5$, the stability of the lamellar phase resulted from their balance between van der Waals attractions and steric repulsions. It was seen that a reduction in the van der Waals attraction forces perhaps was accompanied by a reduction in the elastic constant of the surfactant membrane, leading to the break-up of the lamellar phase. In the ionic surfactant mixtures, both intra- and inter-aggregate interactions were responsible for lamellar stability. They established that the addition of propylene glycol decreased the electrostatic repulsive forces between lamellar and disturbed the hydration shell around the ionic aggregate head groups by breaking the water hydrogen bonding network.

Hoffmann (1996) studied the macroscopic properties of aqueous solutions of hydroxyethyl cellulose (HEC) and of modified HEC samples, which carried cationic groups (cat-HEC) or a cationic and hydrophobic group and their interactions with ionic surfactants (SDS and STS). He reported that HEC did not interact with ionic surfactants. The cat-HEC samples showed strong interaction with oppositely charged surfactant molecules. The viscosity and the elasticity increased with increasing surfactant concentration.

Nakarapanich (1998) investigated the rheological and optical properties of CTAC/FA, CTAC/FA/HEC, CTAC/FA/modified HEC and BTAC/FA in terms of aging time and concentration. It was found that aging allows a growth of lamellar structures toward equilibrium size within seven days. Fatty alcohol induces lamellar or vesicle structure, instead of rod-like micelles formed by the cationic in the absence of fatty alcohol content. Both

entanglement storage modulus and zero shear viscosity increase with fatty alcohol until reaching a saturation state. The effect of adding HEC is to disrupt lamellar formation due to interaction between the polymer and cationic surfactant, inducing polymer chain expansion and surfactant will not be available to stabilize the lamellar structure, which led to smaller lamellar sizes. On the other hand, the effect of adding modified HEC is to induce the formation of interconnected lamellar structure. In the BTAC/FA system, beautiful and symmetric sunflower-like structures were noted. Whereas in the CTAC/FA systems, the aggregates of lamellar and vesicle structures were observed.

1.4 Objectives

The objective of this work was to study the influence of emulsion type and structure on the rheological properties with aging time. The several types of emulsion were compared with different types of cationic surfactant, and the emulsion with added polymer (HEC). The effect of annealing also was conducted by heating up the emulsions to various temperatures: 40, 53 (melting point of FA) and 80 °C respectively and cooling down to room temperature. Then the rheological properties were studied in terms of aging time by using Rheometer at room temperature. The Laser Scanning Microscope was used to study the morphology, which is related to the rheological properties.