

CHAPTER II

LITERATURE SURVEY

Schambil (1986) found that for cosmetic oil-in-water emulsions containing cetostearyl alcohol (1/1 mixture of cetyl and stearyl alcohol), viscosity and stability were improved. Rheological measurements showed that the emulsions possessed structural viscosity. Increasing the emulsifier concentration induced, in some cases, a change from thixotropic to newtonian and rheopectic behaviors. At medium emulsifier concentrations, fluid and stable emulsions were obtained. These results showed that the viscosity effect and the long-term stability of cosmetic emulsions did not depend on the properties of the fatty alcohol alone but the mixed phase formed by the emulsifier and the alcohol.

The factors that affected the flow characteristics (rheology) of emulsions were observed by Tadros (1994). These factors were the volume fraction of the dispersed phase, the viscosity of the dispersed droplets, the droplet size distribution, the viscosity and the chemical composition of the medium, the interfacial rheology of the emulsifier film, the concentration and nature of the emulsifier. The viscoelastic properties of concentrated sterically stabilized oil-in-water (o/w) and water-in-oil (w/o) emulsions were described by plots of the complex modulus (G^*), the storage modulus (G') and the loss modulus (G'') versus frequency. Results showed a transition from predominantly viscous to predominantly elastic response at a critical volume fraction (ϕ) value. The viscoelastic properties of weakly flocculated emulsions were obtained by the addition of a free polymer to a sterically stabilized emulsion. Above a critical volume fraction of the free polymer, there was a rapid increase in the storage modulus, which determined the onset of depletion flocculation.

Kelvin (1994) studied the important role of long chain surfactants in the formulation of personal care product. A long chain (C22) fatty used was behenyltrimethyl ammonium methosulfate as a cationic surfactant. The C22 quat is nonirritating and can be used in a variety of skin care applications whereas C18 quat is highly irritating. The use of C22 instead of C18 fatty moiety substantially raised the melting point of the resulting quaternary derivative. Comparing with erucamidopropyl hydroxysultain and betaine hydroxysultaine, he found, that because of a hydroxysultaine contained both strong positive and negative charges, its molecules may have binded to hair and complexed with the quaternary conditioning agents. Presumably, the cationic portion of the hydroxysultaine molecule binded to the negatively charged sites present on the hair, leaving the ionic group free to be attracted to some other positively charges or cationic moiety.

The influence of the ionic charge on the phase behavior of C12E4/hexanol/water system at low surfactant concentration was investigated by Mercedes (1995). Replacing a nonionic surfactant with a cationic surfactant and adding NaBr salt changed the ionic strength of the system. The bicontinuous bilayers (L3) phase disappeared in the presence of the cationic surfactant and it appeared again when the charges were screened with NaBr salt. On the contrary, the micelle structure (L1) phase was only present in the presence of cationic surfactant. The resulting lamellar phase showed very different macroscopic properties with the hexanol concentration and with the cationic surfactant the lamellar phase was a plastic system with yield stress value.

Goldzal *et al.* (1996) reported that the thermal behavior of two non-ionic celluloses: 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 cetyltrimethylammonium bromide (CTAB) were added to the dilute polymer solutions corresponding to surfactant concentrations below and above the CMC. At elevated temperatures, they showed that these two polymers behaved in very different ways: a micellization followed by a chain collapse was observed for EHEC. The surfactant interacted strongly with EHEC, which reduced the aggregation and swelled the coil, while only a fraction of the MC sample was sensitive to CTAB.

Kastner *et al.* (1996) studied the macroscopic properties of aqueous solutions of several modified hydroxyethyl cellulose (HEC) samples and their interactions with anionic and cationic surfactants by using solubility, electric birefringence, rheology, and surface tension measurements. The modified HEC samples carried cationic groups (cat-HEC A), cationic and hydrophobic groups at the same substituent (cat-HMHEC, C). For the cat-HEC, polymers sample A behaved like a typical polyelectrolyte, while polymer samples B and C combined the solution properties of both charged and hydrophobic polymers. The hydrophobic and cationic parts of samples B and C interacted synergistically with the anionic surfactant molecules, resulting in stronger viscoelastic properties than for only cationic HEC. Differences were also found for these hydrophobic and cationic derivatives depending on whether the charges and the hydrophobic parts were separately attached at the polymer backbone (Sample B) or belonged to one substituent (Sample C).

Rajinder (1997) investigated the rheological behavior of fine (small droplets) and coarse (large droplets) emulsions, and their mixtures on both oil-in-water and water-in-oil emulsions. The viscosity and storage modulus increased substantially upon reducing of the droplet size. The shear-thinning effect in both emulsions also increased upon the reduction of the droplet size. The low-shear viscosity of the mixed fine and coarse emulsions exhibited a minimum at a certain proportion of fine emulsion in the mixture. The minimum value of viscosity was much larger in the case of oil-in-water

emulsion. The storage and loss moduli of mixed oil-in-water emulsions showed a minimum at a certain proportion of fine emulsion only at high frequencies but in the case of water-in-oil emulsions, these moduli did not show minimum value.

Eccleston (1997) reported that the structured and semisolid emulsions intended for application to the skin and mucus membranes were generally complex mixtures of excipients whose stability and bioavailability varied greatly. Surfactants and fatty amphiphiles combined to form mixed emulsifiers. The emulsifying waxes have the ability to promote emulsification at the time of manufacture such as the stabilization of oil droplets, control stability during a shelf-like and control the rheological properties of the system by their interaction with water and other excipients in the external phase.

The rheological behavior of a lamellar liquid crystalline surfactant-water system was studied by Nemeth *et al.* (1998). The repeat distance of lamellar as a function of surfactant concentration and temperature was measured by small-angle X-ray scattering. The rheological characteristics were measured at different temperatures with systems containing surfactant at different concentrations. The frequency-dependent storage and loss moduli were found to be characteristic of the lamellar phase in the linear viscoelastic region. The results were analyzed on the basis of the Jones-McLeish's slip-plane theory. Trends of the fitted constants were discussed based of the general knowledge on the interactions in dispersions stabilized by non-ionic surfactants, and the structure of lamellar liquid crystalline samples. Time-dependent compliance was also measured. The instantaneous elasticity measured in the creep test was compared with that predicted from oscillatory tests. Burger's model was used to describe the time-dependent compliance.

Bulavin *et al.* (1998) studied the micellar solutions of 1-bromo-4-tridecylpyridine in water and salt-water solutions by the small angle neutron scattering. Results showed that micellar electrical charge decreased with

increasing solution ionic strength but did not change with increasing temperature. However, these results also showed a suddenly decrease in the fractional micellar change with increase in surfactant concentration and a decrease in the electrostatic parameters of micelles (Coulomb potential and charge through counterion absorption) with increasing ionic strength of the solution.

Huseyin and Birgul (1998) observed pH changes as a function of concentration for sodium dodecyl sulfate (SDS) and cetylmethylammonium bromide (CTAB) by addition of 1 N HCl and 1 N KOH. The pH values increased up to the critical micelle concentration (CMC) for the SDS/HCl system and decreased for the CTAB/KOH system. In the SDS/HCl and CTAB/KOH systems, the micellar phase had a fixed composition and was homogenous and monodisperse above the CMC. However, in the SDS/KOH and CTAB/HCl systems, pH values increased continuously and gradually below and above the CMC. The properties of the micellar phase changed as a function of concentration, giving rise to inhomogeneity and polydispersity.

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. Aging allowed a growth of lamellar structures toward equilibrium size within seven days. Fatty alcohol induced lamellar or vesicle structures, instead of rod-like micelles formed by the cationic in the absence of fatty alcohol content. Both entanglement storage modulus and zero shear viscosity increased with fatty alcohol unit reaching saturation state. The effect of adding HEC was to disrupt lamellar formation due to interaction between the polymer chain and cationic surfactant, inducing polymer chain expansion and surfactant was not available to stabilize the lamellar structure, leading to smaller lamellar sizes. On the other hand, the effect of adding modified HEC was to induce the formation of interconnected lamellar structure. In the BTAC/FA system, beautiful and symmetric

sunflower-like structures were observed. In the CTAC/FA system, the aggregates of lamellar and vesicle structures were observed. In addition, the effect of annealing temperature of CTAC/FA, BTAC/FA and CTAC/FA/HEC were observed by Barameesangpet (1999). The emulsions were annealed at 40, 53 and 80°C. The entanglement storage modulus and zero shear viscosity differed slightly from initially, then returned to their initial values as a function of annealing time. This were correlated with the change from lamellar network structures to droplets of FA surrounded with lamellar aggregates. On aging, the lamellar network morphology recovered.

The phase transition process of molecular assembly comprising cetyltrimethylammonium choride (CTAC), cetyl alcohol (C₁₆OH) and water was analyzed by Yamagata and Senna (1999a and 1999b) on the basis of dynamic viscoelasticity, mainly by using the Cole-Cole plots. The assembly prepared at 75°C showed onionlike multilamellar vesicles immediately after preparation and transformed into a rosary network of vesicles and fused into lamellar after aging. The dynamic modulus (G') of the assembly monotonically increased with frequency while the loss modulus (G'') showed two peaks. The Cole-Cole plots expressed by two arcs, indicating the coexistence of two different relaxation mechanisms. The viscoelastic behavior on the longer time scale corresponded to the network of multilamellar vesicles and that on the shorter time scale corresponded to the lamellar. They also studied the effect of temperature on the development of the internal structure of the cetyltrimethylammonium choride/cetyl alcohol/water system. CTAC was added to a saturated solution containing an excess of aggregated spherical white solid globules of cetyl alcohol to give a semitranslucent gel (STG) spontaneously without stirring. Its internal structure was compared by morphology and thermal properties with ternary mixture system (TMS) of the same composition but prepared by mixing and stirring at 75°C. While dispersed particles in the TMS were multilamellar vesicles, the STG consisted

of anisotropic lamellar. The melting point was lower for the lamellar structure than for the vesicles structure because of the higher water content between lamellar so the interlamellar water content played a critical role in the structure difference between the two assemblies.

Regev and Guillemet (1999) studied bilayers structural evolution of a single-tail nonionic surfactant cocodiethanolamide-water system by using cryo-transmission electron microscopy (cryo-TEM), small-angle X-ray scattering, light scattering, and rheological measurements. The result was discussed in terms of surfactant geometry and membrane flexibility. It was found that, with increasing surfactant concentration, unilamellar vesicles turned into multilamellar vesicles while a lamellar phase was clearly observed in the TEM micrographs at higher surfactant concentration.