

## CHAPTER IV

### FURTHER DISCUSSION

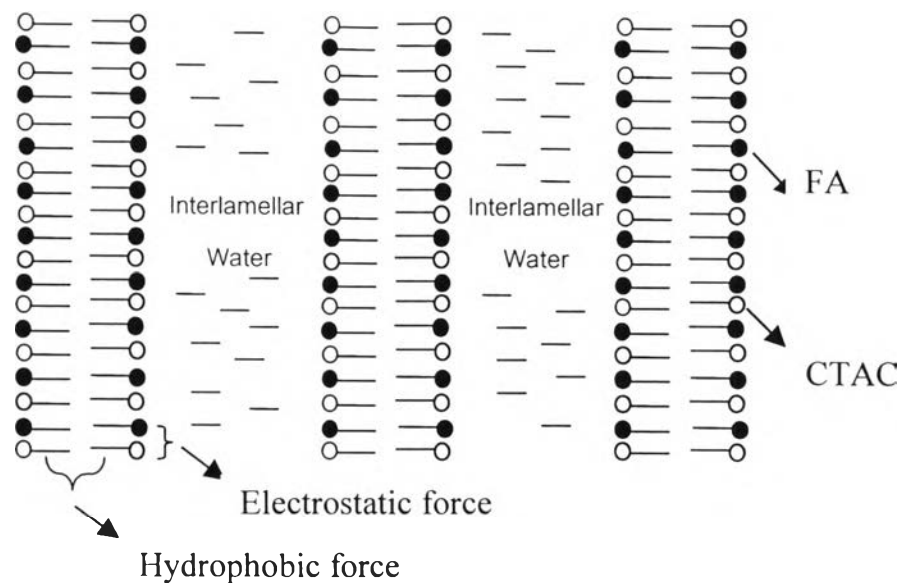
In this chapter, we will discuss possible mechanisms for the lamellar crystalline formation and the effect of annealing.

#### **4.1 Possible Mechanisms of Component Interaction**

##### **4.1.1 Surfactant and Crystalline Phase**

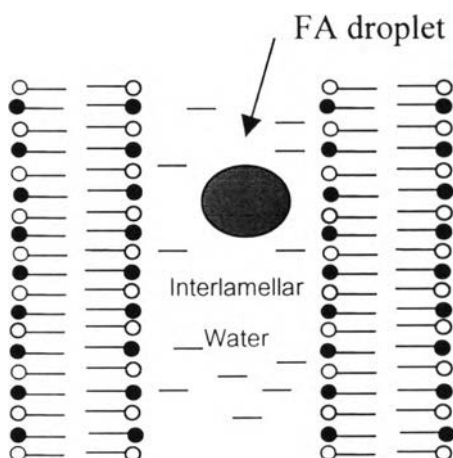
Rheological measurements have proved to be particularly valuable in the microstructure analysis of complex O/W emulsion. Such measurements together with optical measurements have allowed us to better assess the emulsion microstructures. In general, the interaction force between the ionic surfactant and emulsifier such as FA mainly consists of the electrostatic force between charges and the hydrophobic force of hydrophobic portion (Gillian 1997).

For the CTAC/FA system with low FA concentration, in the competition for space at the oil-water interface, two kinds of surface-active species will tend to interact in the bulk phase and at the interphase, leading to formation of a lamellar structure between CTAC and FA through the electrostatic force and the hydrophobic force and their hydrophilic head groups are exposed to the water as shown in Figure 4.1.

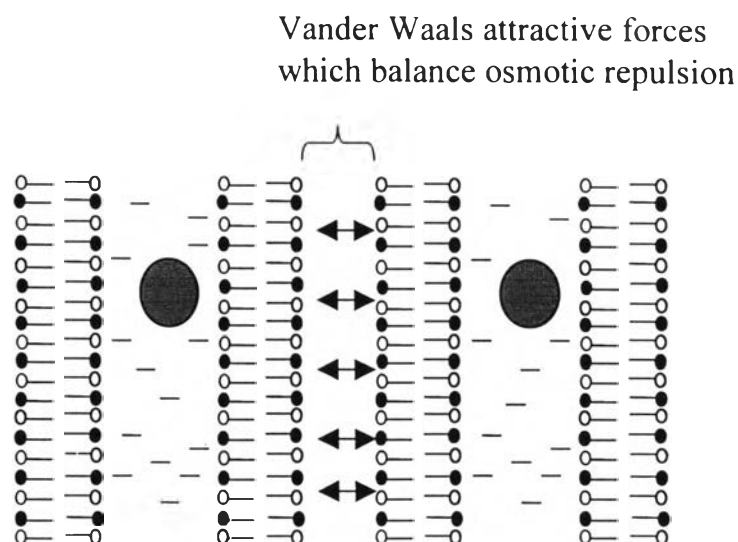


**Figure 4.1** Schematic diagram of lamellar structure formed from low fatty alcohol concentration with cationic surfactant (CTAC).

For the system with high FA concentration, CTAC interacts with FA to form lamellar structure until CTAC is all used up. There are the droplets of FA left in the system, which are surrounded, with lamellar structures by a specific interaction. Later on, each of lamellar structure comes close together and links each other to form a network type structure at equilibrium condition as shown in Figure 4.2.

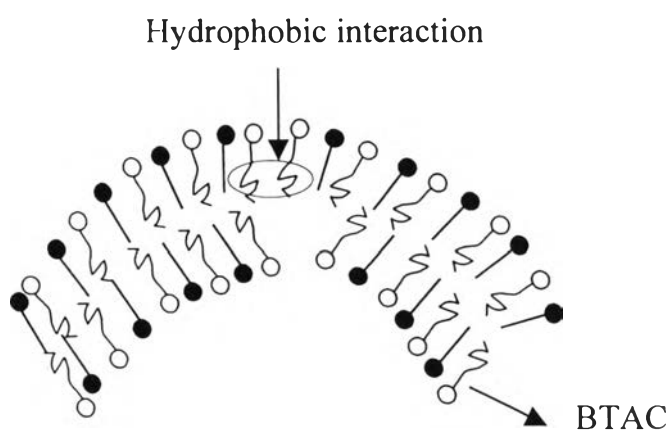


**Figure 4.2a** Schematic diagram of lamellar structure formed from a high fatty alcohol concentration with cationic surfactant (CTAC).



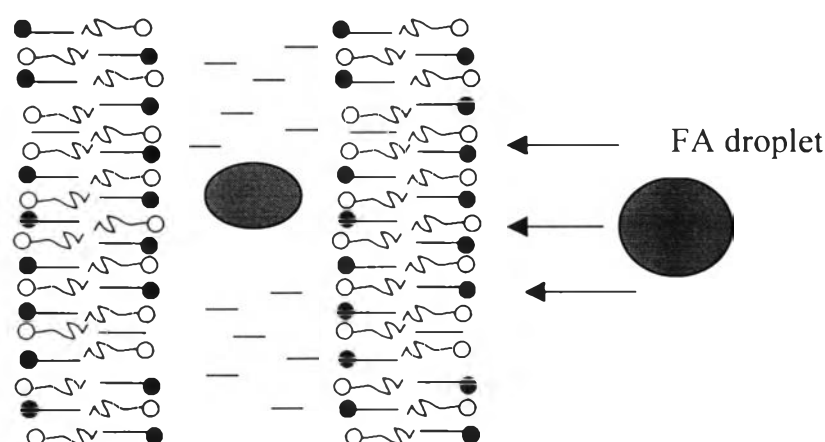
**Figure 4.2b** Schematic diagram of interconnected lamellar structure formed from a high fatty alcohol concentration with cationic surfactant (CTAC).

For the BTAC/FA system at low fatty alcohol concentration, the structure of this system slightly differs from CTAC/FA system. BTAC has a longer carbon chain than CTAC and can interact with a lesser degree with FA. The structure looks like continuous lamellar aggregate or vesicle. It is partly due to the interaction between carbon chains of BTAC by hydrophobic force as shown in Figure 4.3.



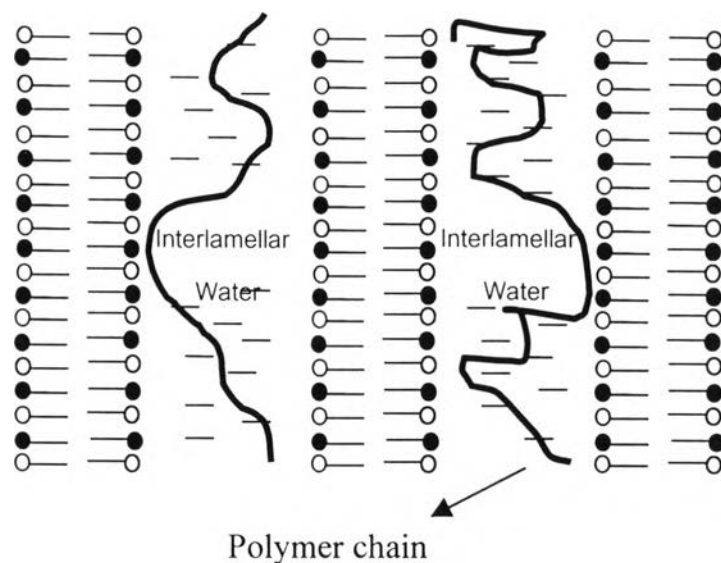
**Figure 4.3** Schematic diagram of lamellar structure formed from low fatty alcohol concentration with cationic surfactant (BTAC).

For BTAC/FA system at high FA concentration, the structure looks like a droplet of FA surrounded by lamellar aggregates. The excess fatty alcohol exists in the middle of structure with same kind of driving force. Therefore, the droplet size of fatty alcohol increases until it reaches equilibrium as shown in Figure 4.4.



**Figure 4.4** Schematic diagram of lamellar structure formed from high fatty alcohol concentration with cationic surfactant (BTAC).

In the case of emulsion system of CTAC/FA with HEC polymer, there are lamellar structures in the system and HEC polymer can not interact with CTAC and FA. These polymer chains are in the aqueous phase locating between the lamellar structures. Therefore, the interruption of lamellar formation or lamellar aggregation to form network will be disrupted by polymer chain as shown in Figure 4.5.

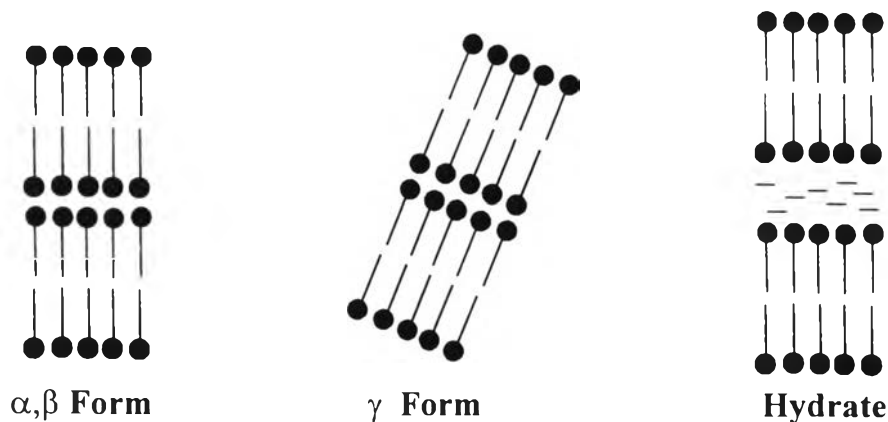


**Figure 4.5** Schematic diagram of lamellar structure formed from fatty alcohol concentration with cationic surfactant (CTAC) with polymer additive (HEC).

## 4.2 Possible Mechanisms for the Effect of Annealing Study

### 4.2.1 Fatty Alcohol Mixed Emulsifiers

The pure long-chain alcohols exist in at least three polymorphic forms (Eccleston 1986). The high temperature  $\alpha$  form separates first from the melt and is stable over a narrow temperature range. At lower temperatures the  $\beta$  form, in which the hydrocarbon chains are non-rotating, and the tilted  $\gamma$  form can coexist, although the  $\beta$  form is usually in excess. Transition temperatures are lower with homologous admixtures such as cetostearyl alcohol, and in the presence of water where they exhibit limited swelling to form crystalline hydrates (Figure 4.6). Thus, the pure cetyl or stearyl alcohol in water may be in the  $\beta$  and  $\gamma$  crystalline forms at room temperature (25 °C) whilst the  $\alpha$  modification is the stable form with mixed homologue alcohols such as cetostearyl alcohol.

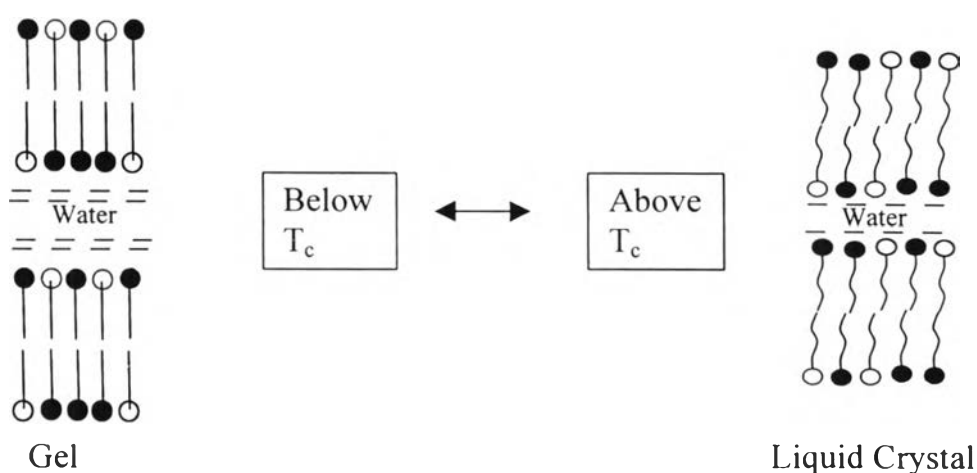


**Figure 4.6** Schematic illustration of the polymorphic structures formed by fatty alcohol amphiphiles. In excess water the  $\alpha$ -crystals swell to form the  $\alpha$ -crystalline hydrate.

On heating, the gel phase transforms at a specific temperature, the transition temperature, to a lamellar liquid crystalline phase. This phase, in which the hydrocarbon chains are molten and in a dynamic disordered state, does not swell as extensively as the low-temperature gel phase. Generally, the gel to liquid crystalline transition temperature is well above 40-50 °C (Eccleston 1986).

In practice, emulsions are prepared by mixing the molten component at high temperature and then cooling it down to room temperature. At the high temperature, emulsion droplets are stabilized by the mixed interfacial film at the oil droplet-water interface. During the cooling process the excess FA forms micelles or liquid crystalline phases that further stabilize the emulsion. When the temperature falls below the transition temperature the liquid crystals convert to the gel phase with the simultaneous absorption of additional water. The system sometimes changes from a milky dispersion to a semisolid emulsion at the transition temperature.

Therefore, after the heating and cooling cycle, the viscoelastic gel networks may be compared by at least three phases (i) crystalline hydrates of fatty amphiphile in equilibrium with (ii) swollen lamellar crystalline gel phase of surfactant and fatty alcohol and (iii) free bulk water (Eccleston 1986).



**Figure 4.7** Schematic illustration of lamellar swollen  $\alpha$ -crystalline gel phase and the lamellar liquid crystalline phase that form spontaneously when a fatty alcohol is dispersed in water in the presence of small quantities of ionic surfactant.  $T_c$  = gel-liquid crystalline transition temperature.  $\bigcirc$ — Surfactant,  $\bullet$ — Fatty alcohol.

In this experiment, the emulsions were heated to various temperature of 40, 53 (melting point of FA), and 80 °C and cooled down to room temperature. From micrographs, we see that the melting of the fatty alcohol causes changes in the morphology. Fatty alcohol is a mixture of cetyl and stearyl. It must therefore have a broad melting range, and perhaps only one of these species is melted at 53 °C. Clearly, if a poorly soluble material was mixed below its melting point, it will not have much opportunity to interact with the CTAC and hence to influence the morphology. However, above the melting point more effective mixing will occur, and therefore it is expected that the morphology will change on heating above 53 °C.