

Colloid Stability: The Role of Surface Forces  
By Th. F. Tadros  
Published by Wiley-VCH  
ISBN 3527314644, 9783527314645

energy of the system can be minimized by changing to a packing geometry of cylindrical units. The formation of the lamellar phase is the result of relieving the "strain" of increasing the volume fraction even further. This argument explains the sequence  $L_1 \rightarrow$  hexagonal  $\rightarrow$  lamellar for the  $C_{12}E_6$ -water system.

## 6.4

### Formulation of Liquid Crystalline Phases

The formulation of liquid crystalline phases is based on the application of the above concepts. However, one must take into account the penetration of the oil between the hydrocarbon tails (which affects the volume and hence  $a$  of the chain) and also hydration of the head group, which affects  $a_0$ .

The most useful liquid crystalline phases are those of the lamellar structure, which can bend around the droplets, producing an energy barrier against coalescence and Ostwald ripening. As mentioned above, these lamellar liquid crystals can also extend in the bulk phase, forming a "gel" network that prevents creaming or sedimentation. These liquid crystalline phases also provide the optimum consistency for sensorial application. Due to the high water content of the liquid crystalline structure (water incorporated between several bilayers), it can also provide increased skin hydration.

The key to producing lamellar liquid crystals is to use mixtures of surfactants with different  $P$  values (different HLB numbers) whose composition can be adjusted to produce the right units.

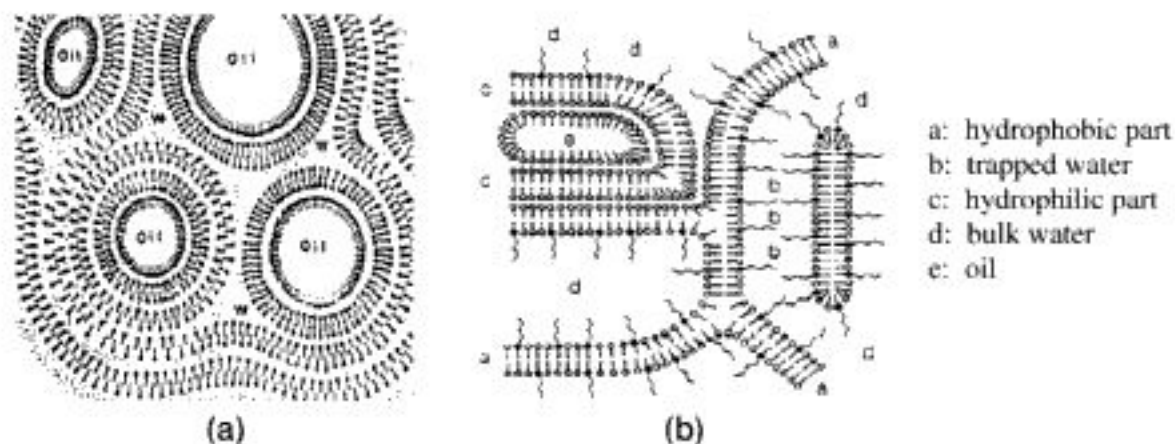
Using the above concepts, we have developed two different types of liquid crystals in oil-in-water (O/W) emulsions: oleosomes and hydrosomes. These structures were obtained by using several surfactant mixtures whose concentration ratio and total concentration were carefully adjusted to produce the desired effect. These systems are described below.

#### 6.4.1

##### Oleosomes

These are multilayers of lamellar liquid crystals surrounding the oil droplets that become randomly distributed as they progress into the continuous phase. The rest of the liquid crystals produce the "gel" phase that is viscoelastic. The oleosomes are produced using a mixture of Brij 72 (Steareth-2), Brij 721 (Steareth-21), a fatty alcohol and a minimum of a specific emollient. The nature of the emollient is crucial; it should be a medium to polar oil such as Arlamol E (PPG-15 stearyl ether) or Estol 3609 (triethylhexanoin). Very polar oils such as Prisorine 2034 (propylene glycol isostearate) and Prisorine 2040 (glyceryl isostearate) disturb the oleosome structure. Nonpolar oils such as paraffinic oils inhibit the formation of oleosomes.

The oleosomes are anisotropic and they can be identified using polarizing microscopy. Figure 6.2 shows a schematic diagram of the oleosomes.



**Figure 6.2** Schematic representation of (a) oleosomes and (b) hydrosomes.

#### 6.4.2

#### Hydrosomes

In this case a “gel” network is produced in the aqueous phase by the lamellar liquid crystals. The surfactant mixture is dispersed in water at high temperature (80 °C) and this creates the lamellar phase, which becomes swollen with water between the bilayers. The oil is then emulsified and the droplets become entrapped in the “holes” of the “gel” network. The viscoelastic nature of the “gel” prevents close approach of the oil droplets. The hydrosomes can be obtained using **Arlatone 2121** (sorbitan stearate and sucrose cocoate) or **Arlatone LC** (sorbitan stearate and sorbityl laurate). A schematic representation of hydrosomes is shown in Figure 6.2.

#### 6.5

#### Emulsion Stabilization Using Lamellar Liquid Crystals

The lamellar liquid crystals produce several bilayers that “wrap” the droplets. This produces an energy barrier preventing coalescence. This is similar to the process of steric stabilization produced by polymeric surfactants [6]. As a result of the presence of these multilayers, the potential drop between two droplets is shifted to longer distances, thus preventing any coalescence [7]. For coalescence to occur, these multilayers have to be removed “two-by-two” and this produces an effective barrier against emulsion coalescence. The liquid crystalline structure can also prevent Ostwald ripening by providing a high elasticity at the O/W interface.

One of the most useful techniques to study liquid crystalline structures is dynamic (oscillatory) measurements. The storage modulus  $G'$  (the elastic component) and the loss modulus  $G''$  (the viscous component) are measured as a function of strain amplitude at a constant frequency of 1 Hz.

With **Arlatone LC** (sorbitan stearate and sorbityl stearate) at 5%,  $G'$  and  $G''$  remain constant up to a strain amplitude of 0.015 (long linear viscoelastic region). This is consistent with the formation of a coherent "gel" structure that is important for application and stabilization of the emulsion. In contrast, if the sorbityl laurate is removed from the system, i.e. using sorbitan stearate alone at the same concentration (5%),  $G'$  starts to decrease rapidly with increase in applied strain. In this case no liquid crystalline structure is produced and only reversed micelles ( $L_2$  phase) are formed. With the latter system, emulsion stabilization is not possible.

## 6.6

### Materials and Methods

The surfactants used for the preparation of the oleosome-based emulsions are ethoxylated stearyl alcohol in combination with an emollient (such as isohexadecane or PPG-15 stearyl ether). For the hydrosome-based emulsions a blend of sorbitan stearate and sucrose cocoate (or sorbityl laurate) was used. The oleosome emulsions were prepared by the direct emulsification technique with the emulsifiers dissolved in the oil phase. For hydrosome emulsions the gel network of the surfactant system was first prepared by heating and swelling the mixture in the water phase followed by addition of the oil while stirring.

The rheological measurements were carried out using a Physica USD 200 universal dynamic spectrometer (Paar Physica, Germany) and a cone-plate geometry device (50 mm radius,  $2^\circ$  angle). Two rheological tests were performed: constant stress (creep test) and dynamic measurements (frequency sweep test) (Figure 6.3).

In the creep measurements, a constant stress was applied on the system and the deformation (strain)  $\gamma$  was followed as a function of time for 2 min. The compliance  $J$  calculated is simply the strain divided by the applied stress for each

