Correlating the Structure and Rheology of Liquid Crystalline Phases in Emulsions

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ABSTRACT: *This paper describes the correlation between the structure of liquid crystalline phases in emulsions and their rheological characteristics. An oleosome/lipophilic liquid crystalline-forming system and hydrosome/hydrophilic liquid crystalline-forming system were investigated. At the same high shear rate viscosity, the oleosome-system showed less thixotropy and rapid recovery when compared with the hydrosome-system.*

In dilute solutions, surfactants form spherical micelles with aggregation numbers in the region of 50–100 units.[1,2] These micellar solutions are isotropic with low viscosity. At higher surfactant concentrations, the spherical micelles tend to form cylindrical structures, which show flow birefringence. At even higher surfactant concentrations, a series of mesophases referred to as liquid crystalline phases[3] appear, whose structure depends on the nature and concentration of the surfactant solution.

Three main types of liquid crystalline structures can be identified, as illustrated in **Figure 1**: hexagonal (H_1), micellar cubic (I_1) and lamellar (L_α) phase. These liquid crystalline phases can be identified using polarizing microscopy, X-ray diffraction, nuclear magnetic resonance (NMR) and various rheological techniques. Using polarizing microscopy, rheology and NMR, the liquid crystalline phases of a series of nonionic surfactants are investigated here, namely trideceth-7,9,11 and 20 (synthetic primary $C_{13–15}$ alcohol with 7, 9, 11 and 20 mol ethylene oxide).[4,5] The transition from isotropic micellar to hexagonal, cubic and lamellar phases were investigated using viscoelastic measurements. The results clearly showed that the structure of the liquid crystalline phases could be related to their rheological characteristics.

Many cosmetic o/w emulsions contain some of the surfactant assembly structures (liquid crystalline phases) in the continuous phase. These are produced using surfactant mixtures with a different hydrophilic-lipophilic balance (HLB).

The driving force for the formation of these liquid crystalline structures is the critical packing parameter P, shown by the following expression:[1,2]

$$P = \frac{v}{l_c a}$$

where v is the volume of the hydrocarbon tail with extended length l_c and a is the cross-sectional area of the head group.

For spherical units, such as cubic phases, P<1/3; for cylindrical units, such as the hexagonal phase, 1/3<P<½; for lamellar structures, P≈1. The most important liquid crystalline structures in o/w emulsions are those of the lamellar phase that are formed from several surfactant bilayers with the polar head groups pointing toward the aqueous phase. These bilayers can surround the oil droplets, thus producing a barrier against coalescence.[6] They also can extend in bulk solution, forming gel networks and hence they act as rheology modifiers. The volume of the hydrocarbon tail can be influenced by the nature of the molecules of the emollient, whereas the cross-sectional area of the head group is determined by the number of ethylene oxide units as well as the electrolyte concentration and nature.

Using the above concepts, two main types of lamellar liquid crystalline structures in emulsion systems have been developed: oleosomes and hydrosomes. A schematic of the two types of lamellar liquid crystalline structures in emulsion systems is shown in **Figure 2**.

As it is clear from **Figure 2**, the lamellar liquid crystals in the oleosome system surround the oil droplets, forming several surfactant bilayers. The latter produce a strong barrier against coalescence, since the bilayers have to be removed two-by-two before close approach of the oil droplets.[4] This results in shift of the potential energy to larger distances, thus counteracting the van der Waals attraction.

With the hydrosome system on the other hand, the surfactant bilayers form a three-dimensional gel network and

the oil droplets become entrapped in the holes of the network. This prevents close approach of the oil droplets, thus preventing coalescence.

The main objective of the present paper is to correlate the structure of the lamellar liquid crystalline phases in emulsions to their rheological characteristics. Two main types of structures, an oleosome system structure and a hydrosome system structure, were investigated. Two main rheological techniques, steady state and constant stress (creep), were applied. The steady state measurements produced the shear stress-shear rate curves as well as the viscosity as a function of shear rate. This method allows the study of time effects, i.e., the thixotropy. The constant stress or creep measurements allow one to obtain the critical stress, above which the liquid crystalline structure starts to undergo deformation (partial destruction).

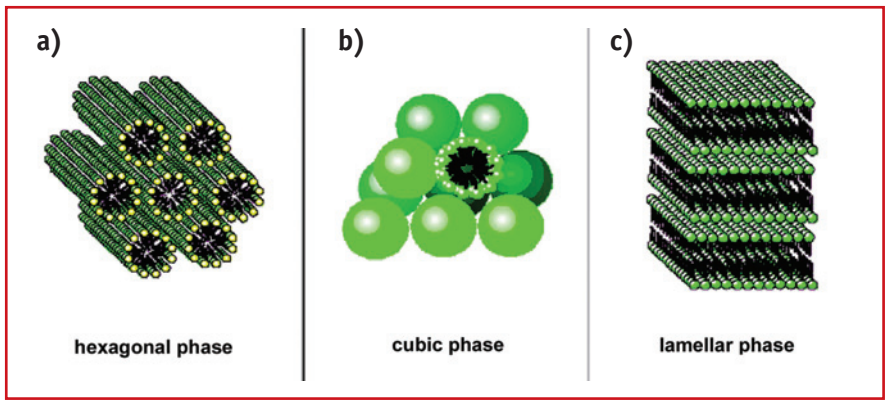

Figure 1. Schematic representation of the liquid crystalline phases: a) hexagonal phase, b) cubic phase, and c) lamellar phase

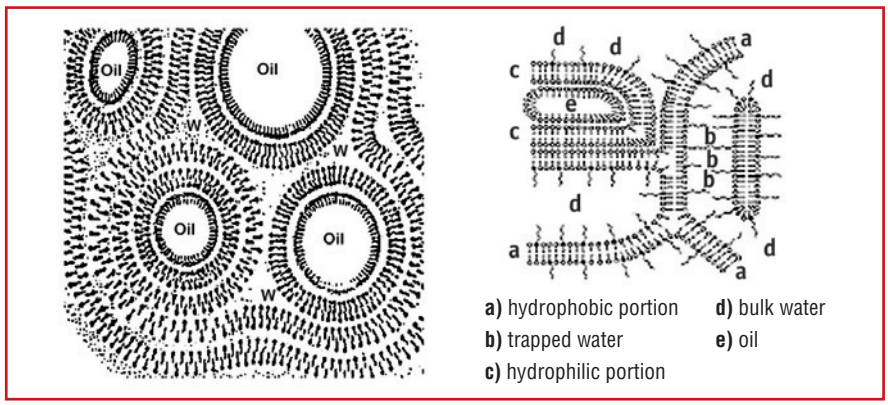

Figure 2. Schematic representation of oleosomes (left) and hydrosomes (right)

Experimental

Materials: The surfactants used for the preparation of the oleosome system-based emulsion were ethoxylated stearyl alcohols, such as steareth-2 and steareth-21, in combination with a polar emollient PPG-15 stearyl ether. The surfactant used for preparation of the hydrosome system was a blend of sorbitan stearate and sucrose cocoate.

Preparation of the emulsions: The oleosome systems were prepared by a direct emulsification technique, whereby the oil/emulsifier phase is added to the water phase at a temperature of 75°C while stirring. This is followed by a homogenization step using a high shear mixer[a] at a temperature >50°C. The emulsion then is cooled to room temperature under gentle stirring.

The hydrosome system is prepared by first creating the gel network of the surfactant liquid crystals. This is obtained by addition of the emulsifier system to water at 80°C, followed by swelling for 20 min. The oil phase is added while stirring and the whole system is homogenized for 1 min using a high shear mixer at 8000 rpm. The emulsion then is cooled to room temperature with gentle stirring.

Rheological measurements: Rheological measurements were conducted using a spectrometer[b] and the samples were placed in the gap between a cone and plate (cone angle 2°).

All flow measurements were carried out at 29°C and all creep measurements were carried out at 25°C using solvent trap to prevent evaporation.

In steady state measurements, a controlled shear rate, γ, was applied and the stress, σ, was measured. The shear rate was increased from 0 to 500 s^{-1} in 4 min and then reduced from 500 to 0 s^{-1} after another 4 min, which allows the observation of time effects (the thixotropic loop).[7]

In constant stress or creep measurements, various increments of stress are applied starting from the lowest value, and each time the strain γ is measured as a function of time for a period of 120 sec. At the end of this period, the stress is removed and the strain (which reverses the sign) is then measured for another 120 sec to obtain the creep recovery of the sample.

Results and Discussion

Figure 3 shows the shear stress-shear rate curves for an oleosome liquid crystalline system, whereas **Figure 4** shows the results for a hydrosome liquid crystalline system.

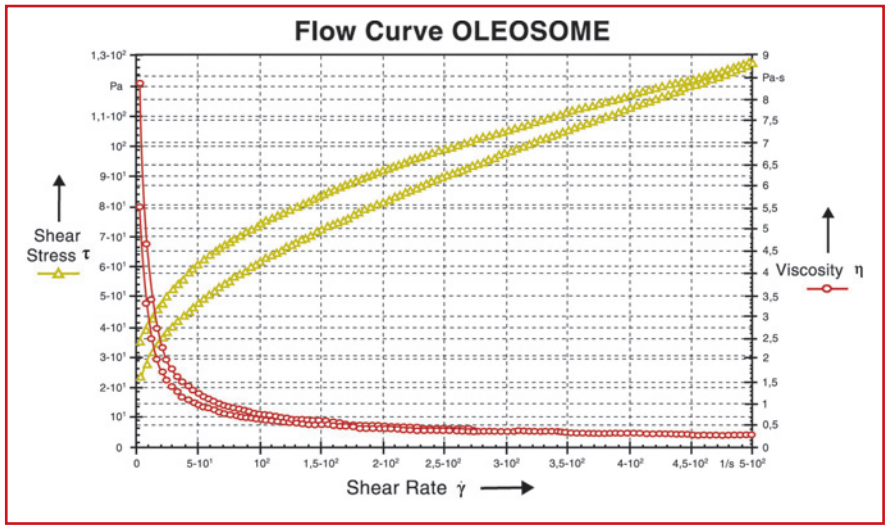

Figure 3. Shear stress-shear rate curves and viscosity-shear rate curves for an oleosome system

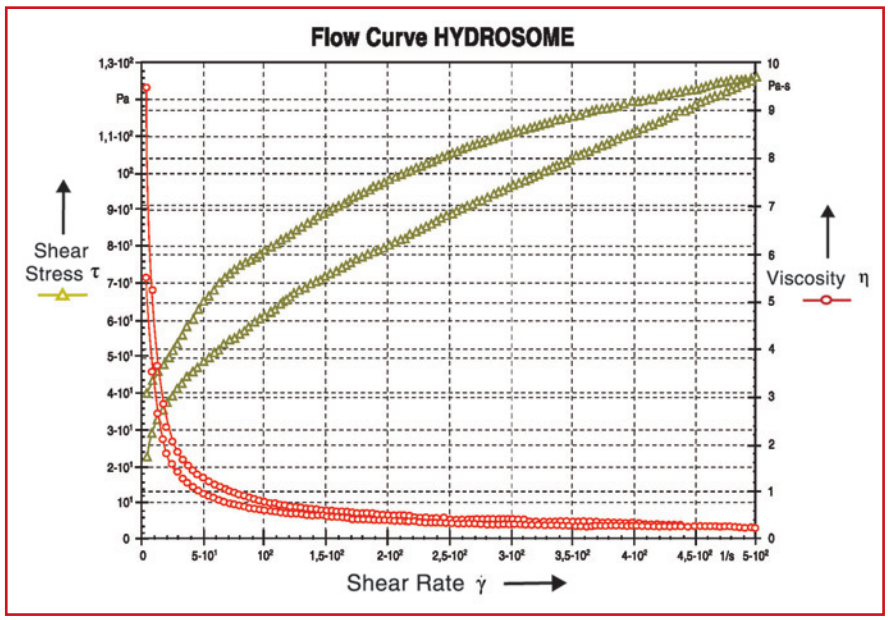

Figure 4. Shear stress-shear rate curves and viscosity-shear rate curves for a hydrosome system

At constant high shear viscosity the thixotropic index is higher for hydrosome systems when compared with the oleosome systems.

In both cases, the down curve (reducing the shear rate) is below the up curve. Also, the viscosity calculated from the down curve is lower than that calculated from the up curve. This is typical for systems that are sensitive to shear and hence they show time effects or thixotropy.

On application of shear (the up curve), the sample structure is partially destroyed and hence the shear thinning behavior. When the shear is removed (the down curve), the structure partially is recovered since the time applied (4 min) is not sufficient for complete recovery of the structure. This is reflected in the measured viscosity from the down curve, which is always lower than that calculated from the up curve. Thus the up and down curves show hysteresis and the area under the loop is a measure of thixotropy.

In general, at the same high shear rate viscosity, the hydrosome system shows greater thixotropy (as measured by the area under the loop) when compared with oleosome system. In addition, the variability in the thixotropic index (as measured by the ratio of the thixotropic loop area obtained with 4 min to the area obtained with 45 sec) between the various hydrosome system samples was much greater than that of the oleosome systems. Several other samples were measured to illustrate how the thixotropic index changes with the high shear viscosity of the samples. The results are shown in **Figure 5**.

At constant high shear viscosity the thixotropic index is higher for hydrosome systems when compared with the oleosome systems. Also, the highest value of high shear viscosity

[a] *The Ultra Turrax is manufactured by IKA Works, Inc., Wilmington, NC, USA.*
[b] *The Universal Dynamic Spectrometer, Physica UDS 200, is manufactured by Paar Physica, Germany.*

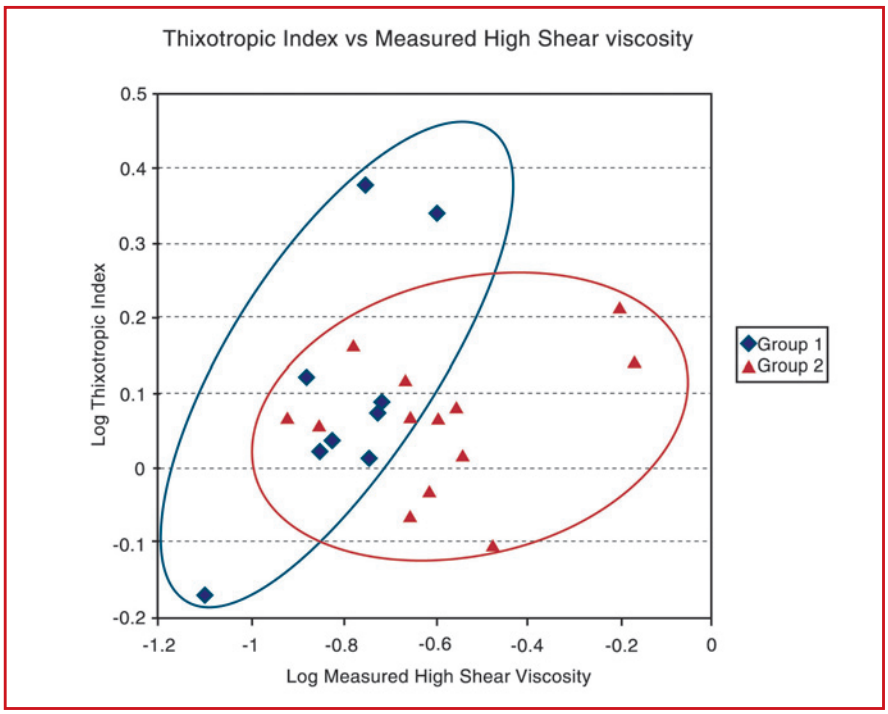

Figure 5. Thixotropic index versus high shear rate viscosity for various oleosome systems (group 2) and hydrosome systems (group 1)

was for oleosome system samples when compared with hydrosome system samples. Thus these steady state measurements correlate with the structure of the system.

Oleosome systems that contain several surfactant bilayers that are wrapped around the oil droplets are less susceptible to applied shear when compared with hydrosome systems that consist of a network structure of lamellar liquid crystals. This also is reflected in the recovery of the structure with the oleosome systems showing faster recovery when compared with the hydrosome systems.

Further evidence for the correlation between structure and rheology of liquid crystals in emulsions was obtained from constant stress (creep) measurements. **Figures 6** and **7** show typical results for oleosome and hydrosome system-based emulsions, respectively.

On application of a small stress value (well below the yield stress), a small deformation occurs and this increases slowly with time during the period of application (120 sec). When the stress is removed after this period, the deformation changes sign and the system recovers completely. As the stress gradually is increased, the deformation increases and the recovery becomes less and less complete. However, above a critical stress (to be denoted the yield stress), the deformation increases rapidly with time and only partial recovery occurs. In this way, one can establish the critical stress above which the structure is destroyed. Several other samples were measured to obtain the general trend of how the critical stress changes with the structure of the liquid crystalline phase. The results are shown in **Figure 8**.

These samples generally show a more rapid increase in the critical stress with increase in the high shear viscosity for the hydrosome systems when compared to the oleosome systems. In other words, at a given high shear rate viscosity, the critical stress is higher for hydrosome systems compared to oleosome systems. This reflects the three-dimensional gel network structure (with a higher number of contact points) of the hydrosome systems, compared to the multilayer structure of oleosome systems.

Conclusions

The present paper shows that rheological techniques can be applied to study the structure of liquid

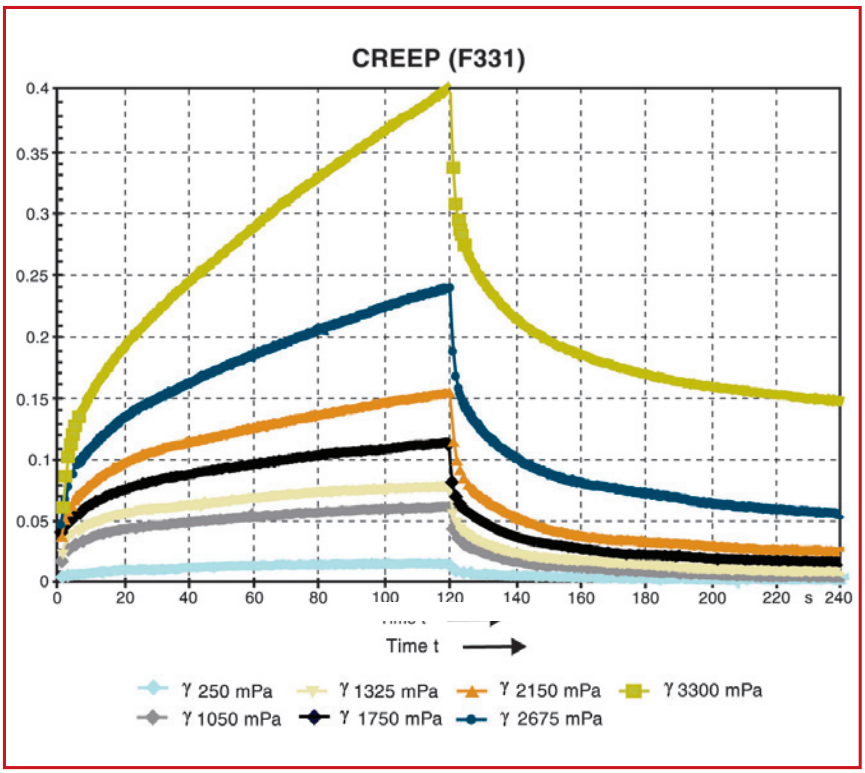

Figure 6. Creep curves for an oleosome system-based emulsion

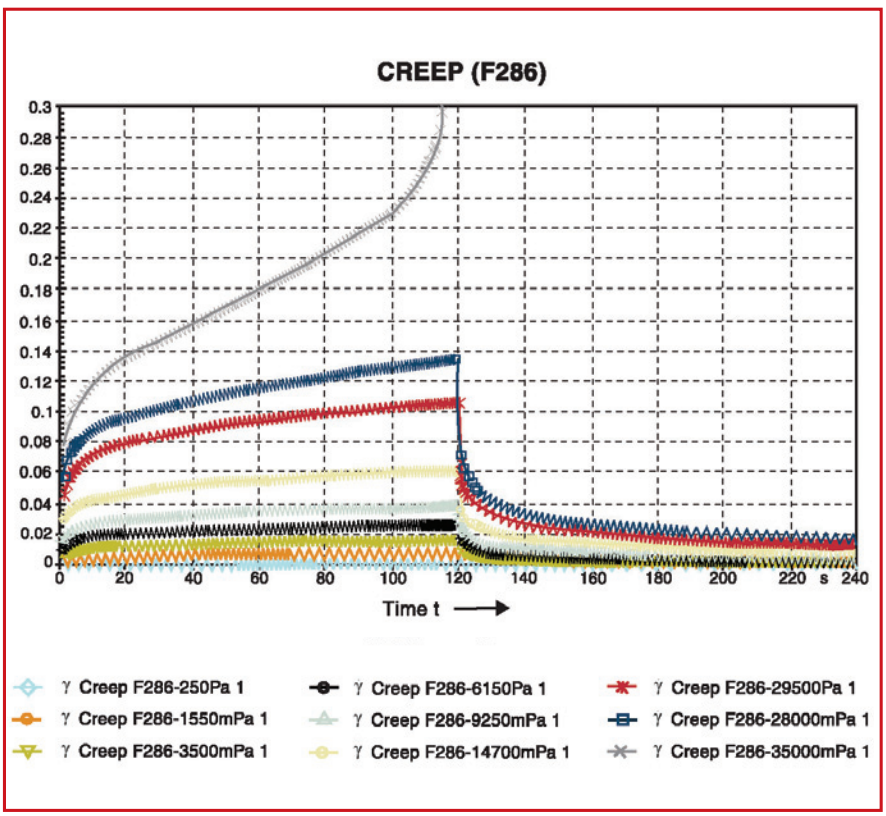

Figure 7. Creep curves for a hydrosome system-based emulsion

crystalline phases in emulsions. These measurements showed different rheological behavior for oleosome systems compared to hydrosome systems. The former, consisting of several bilayers of surfactant films around the oil droplets, are less susceptible to shear and show rapid recovery when compared with the gel network structure of the hydrosome systems. This was

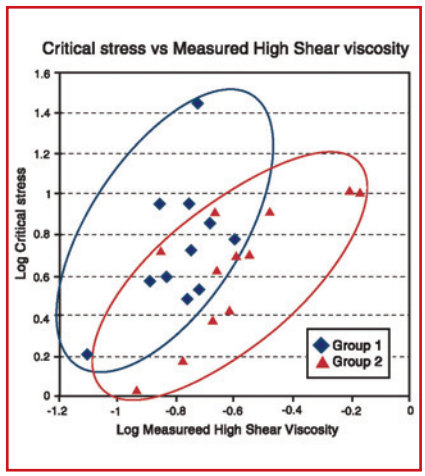

Figure 8. Variation of critical stress with high shear rate viscosity for various hydrosome systems (group 1) and oleosome systems (group 2)

reflected in the thixotropic index measurements. At a constant high shear rate viscosity the thixotropic index is higher for hydrosome systems than oleosome systems.

Constant stress (creep) measurements also showed that at constant high shear rate viscosity, the critical stress is higher for hydrosome systems than oleosome systems. This reflects the three-dimensional gel network structure of the hydrosome systems, which requires a higher stress for deformation than the multilayer structure of the oleosome systems.

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