Structural and rheological investigation of Fd3m inverse micellar cubic phases.

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ABSTRACT

In the present study we demonstrate that Fd3m inverse micellar cubic phase can be obtained by adding a hydrophobic component, such as the food grade limonene, to the binary system monolinolein / water.

At full hydration of Fd3m phase ($12.68\%_{wt}$), SAXS measurements and topological models have shown that this phase is formed by 16 smaller micelles and 8 larger micelles per cubic lattice cell (Q^{227} group), with radii of the micellar polar cores with average size of 2.3nm, and 170 monolinolein molecules per micelle. Investigation of the viscoelastic properties of Fd3m discrete micellar phase revealed a rheological signature similar to the bicontinuous Pn3m and Ia3d cubic phases but with a shift in the relaxation spectrum related to a complex set of slower relaxation mechanisms. Fd3m phase at $11.2\%_{wt}$ water begins melting in an inverse microemulsion (L_2 phase) coexisting with water above 28.5°C with complete melting obtained at 40-45°C, as evidenced by SAXS and rheology.

Keywords: liquid crystals, micellar cubic phases, self-assembly, shear rheology, phase transition.

1 INTRODUCTION

Lipid-based lyotropic Liquid crystalline (LC) phases in bulk are of technological relevance for food, cosmetics and pharmaceutics applications through formation of dispersed nanoparticles with internal self assembled LC structures that are proposed as nanovehicules for controlled delivery of drugs and bioactives ingredients, or as nanoreactors for the increased yield of flavouring compounds synthesis [1].

Aqueous system of monolinolein with two unsaturations have been described by small angle X-ray scattering (SAXS) and detailed rheology characterization has also been reported [2]. This system is characterized by the formation of inverse bicontinuous cubic phases such as Pn3m and Ia3d.

The same monolinolein-water system, upon oil addition (i.e. ternary mix of monolinolein / tetradecane oil / water) was shown to exhibit an additional LC phase, not present in the binary mix monolinolein/water: an inverse discrete micellar cubic phase of Fd3m type (Q^{227} group), as revealed by SAXS measurement [3].

In the present study, by combining SAXS and rheology we investigate the structure and viscoelastic properties of an inverse discrete micellar cubic phase of Fd3m type obtained in the bulk from the ternary system monolinolein / limonene oil / water.

2 MATERIAL AND METHODS

2.1 Sample preparation

Dimodan U is a commercial–grade form of monolinolein containing more than $98\%_{wt}$ monoglyceride. The hydrocarbon tail consists predominantly of di-unsaturated C18 chains.

Samples were prepared at constant weight ratio between limonene and lipid. This was expressed by α, defined as:

$$\alpha = \frac{mass_{\text{limonene oil}}}{mass_{\text{limonene oil}} + mass_{\text{monolinolein}}} \qquad (1)$$

α, was maintained to the fixed value of $40\%_{wt}$ in all experiments. Demineralised water was then added to this mixture of monolinolein / limonene oil, at different volume fractions.

2.2 Small Angle X-ray Scattering (SAXS)

Small angle X-rays scattering (SAXS) experiments were performed using a SAXSess instrument (Anton Paar) with a line collimation set-up. The measurements were carried out in the q-range of 7.7×10^{-2} nm^{-1} to 28,5 nm^{-1} . The system used a Cu Ka radiation source in a sealed tube (λ=1,542 nm). Formation of the Fd3m phase at 23°C was followed by SAXS by acquiring diffractograms at different times (t= 0 and 5days). Temperature evolution of the mesophase ($11.2\%_{wt}$) has also been investigated on the range 23°C to 80°C.

Values given for the lattice parameters ($a_{lattice}$) of the various Fd3m cubic mesophases were extracted using the most intense reflection (311) by using the following expression [3]:

$$\left(\frac{a_{lattice}}{d_{311}}\right) = \sqrt{(3^2 + 1^2 + 1^2)} \qquad (2)$$

2.3 Shear rheology

The rheological study of the Fd3m phase was carried out using a Anton Paar Physica MCR 500 rheometer in a strain-controlled mode (direct strain oscillation / DSO). The measurement geometry used was a DIN concentric cylinder (CC 17, Couette cell), with inner cylinder of 17 mm.
The frequency-dependence of G', G'' and tan(δ) on the range of frequencies $\omega = 2.10^{-3} - 628$ rad.s^{-1} was studied on Fd3m phases obtained at $\alpha = 40\%$wt and 11.2%wt water after t = 0, t = 5 days and t = 7 days equilibration at constant temperature of 23°C. The spectrum of relaxation times was extracted by inverse Laplace transformation of frequency scans of (G'), (G''), as described elsewhere for binary system monolinolein (Dimodan U) / water [2].
The temperature dependence of G' and G'' at frequency $\omega = 1$ rad.s^{-1} and for low strain = 10^{-2} % using a constant heating or cooling rate of 0.2 °C.min^{-1} has been measured in the range 20°C to 80°C.

3 RESULTS

3.1 Structure of Fd3m micellar cubic phase

Immediately after mixing the phase formed by the ternary system: monolinolein / limonene oil / water is turbid but evolves into a hard transparent phase in 5 days.
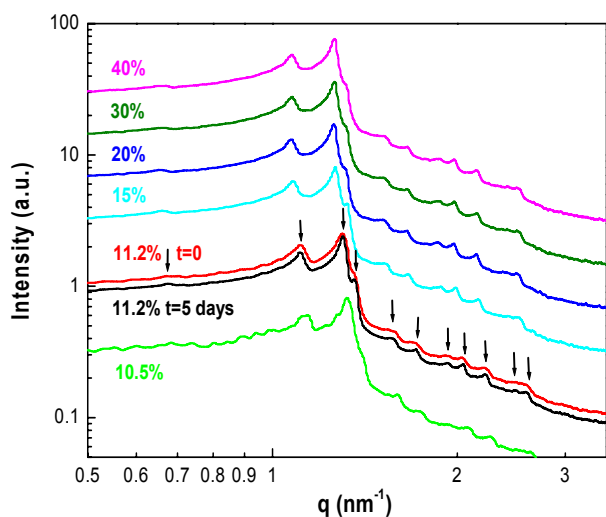

Figure 1: SAXS diffractograms of lipid/water/limonene mixtures at different level of hydration (from 10.5%$_{wt}$ to 40%$_{wt}$) equilibrated at 23°C for five days.

SAXS measurements were carried out at t = 0 and t = 5days on ternary mixture for different amount of water (see Fig. 1) show eleven typical reflections of the Q^{227} group space, independently of the elapsed time.
Lattice parameter calculated from SAXS measurements (see Fig. 2) demonstrates an increase with the hydration level, of the lattice parameter of Fd3m cubic cell up to 16.51nm corresponding to full hydration (12.68%$_{wt}$ water).
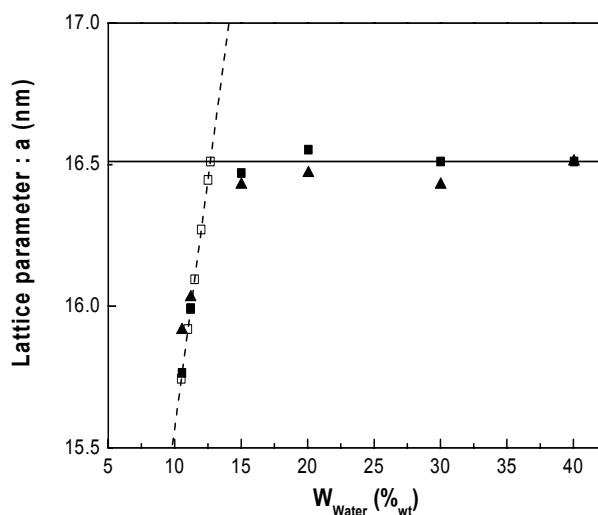.

Figure 2: Evolution of the lattice parameter (a) with hydration level (W_{water}) for samples just after formation (t=0, filled triangles) and after five days equilibration at 23°C (t = 5days, filled squares). Open squares symbols correspond to values of a, interpolated by linear regression

A topological model [4] has been proposed to describe Fd3m structure in ternary systems formed by amphiphiles / water / oil. It allows calculating the micelle size (r), the number of amphiphile molecules per micelle (N_L) and the specific average surface area occupied by each amphiphilic molecules at the micelle surface (a_s), once the lattice parameter ($a_{lattice}$) of the inverse Fd3m cubic phase and the volume fraction of the polar (i.e. water plus hydrophilic heads of amphiphiles: ϕ_{polar}) and apolar phase (i.e. oil plus alkyl tails of amphiphiles: ϕ_{apolar}) are known.
In our case we calculated these two volume fractions (ϕ) as:

$$\Phi_{apolar} = \left(\Phi_{limonene} + \Phi_{monolinonein\,alkyl\,tails}\right) \qquad (3)$$

$$\Phi_{polar} = \left(\Phi_{water} + \Phi_{head}\right) = \left(1 - \Phi_{apolar}\right) \qquad (4)$$

Using the model of Uddin et al.[4] for Fd3m that accounts for existence of only one monodisperse type of micelles in the system with size, r we defined :

$$r = \left(\frac{3}{4 \cdot \pi \cdot n_{micelles}} \right)^{1/3} \cdot \left[1 - \left(\Phi_{alkyl\,tails} + \Phi_{lim} \right) \right]^{1/3} \cdot a_{latt} \quad (5)$$

$$a_S = \left(\frac{3 \cdot \dfrac{M_{mono} - M_{head}}{\rho_{mono}} \cdot \dfrac{1}{N_a}}{r} \right) \cdot \left[\frac{1 - \left(\Phi_{alkyl\,tails} + \Phi_{lim} \right)}{\Phi_{alkyl\,tails}} \right] \quad (6)$$

$$N_L = \frac{\Phi_{mono\,alkyl\,tails} \cdot a_{lattice}^3}{\left(\dfrac{M_{mono} - M_{head}}{\rho_{mono}} \cdot \dfrac{1}{N_a} \right)} \cdot \frac{1}{n_{micelles}} \quad (7)$$
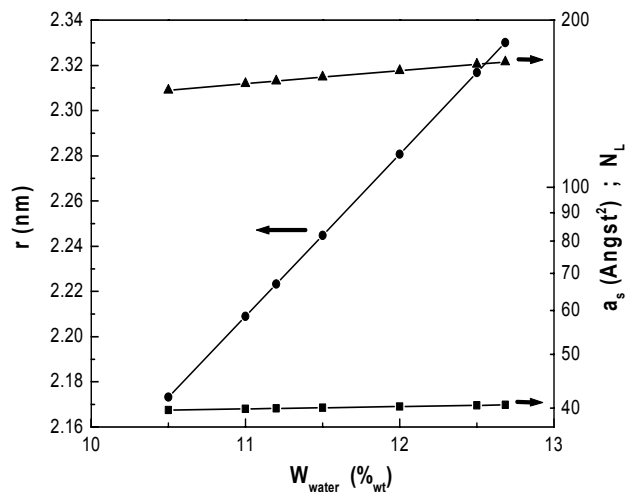

Figure 3: Topological parameters of Fd3m bulk structure at different water amount ranging from 10.5%$_{wt}$ to 12.68%$_{wt}$ (full hydration).

At full hydration the Fd3m is composed of micelles with average radius of 2.3nm and 170 monolinolein molecules per micelle occupying each an area of 40.6 Å^2.

3.2 Rheological properties of Fd3m phase

The frequency scan for Fd3m phase measured at different times (see Fig. 5) demonstrate an ageing of the phase during 5 days with increase of the storage modulus in the order of 10^5 Pa, comparable to that found for bicontinuous cubic phases : Pn3m and Ia3d [2].
However the relaxation spectrum of Fd3m presents a dominating time ($\approx$ 100s) that is shifted by a decade compared to such bicontinuous phases (see Fig.6). For both type of LC structures this time can be attributed to the relaxation of hydrophilic / hydrophobic interface as reported previously [2].
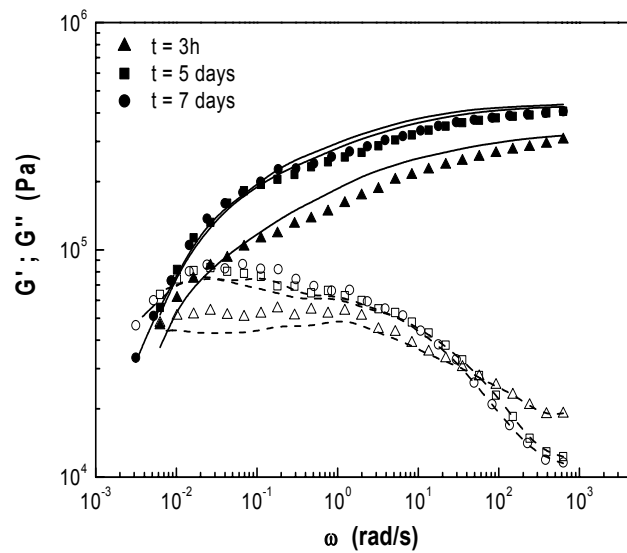

Figure 5: Frequency dependence of the storage modulus (G', filled symbols) and loss modulus (G'', open symbols) for bulk Fd3m mesophase with α = 40%$_{wt}$ 11.2%$_{wt}$ water at 23°C after various time of equilibration : t = 3h, t = 5 days and t = 7 days.
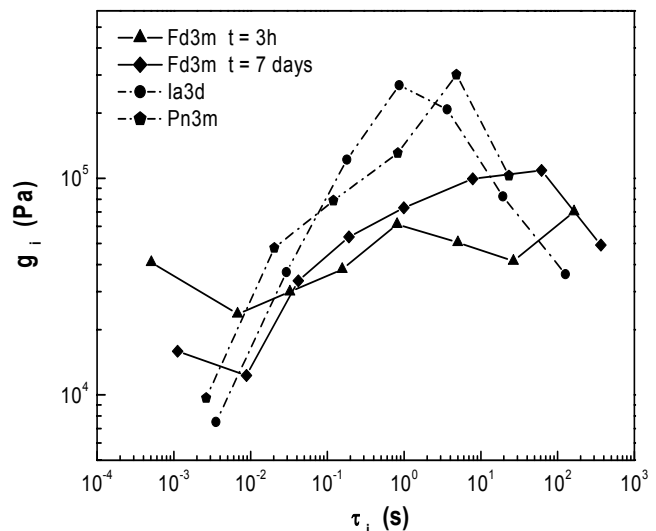

Figure 6: Relaxation spectrum (g_i, τ_i) calculated from storage and loss moduli displayed in Figure 5 using Laplace inversion method. For comparison at α=0%: Pn3m with 20%$_{wt}$ water at 55°C and Ia3d with 20%$_{wt}$ water at 40°C.

Its increase in the case of Fd3m could be related to slower kinetic phenomena of structural equilibrium restoration associated to: (i) diffusion of water from micelles of distinct sizes due to the differential Laplace pressure gradient existing among them, (ii) rearrangement of the deformed interfaces into the dodecahedral and hexakaidecahedral structures (iii) packing back the perturbed micellar structure into the Q^{227} lattice.

This could also arise from the lower hydration level (11.2%$_{wt}$ water) and lower temperature (23°C) at which Fd3m exists. In this respect, previous study on bicontinuous cubic phases [2] indicated that decreasing water content or temperature, leads to increase of τ_{max}.
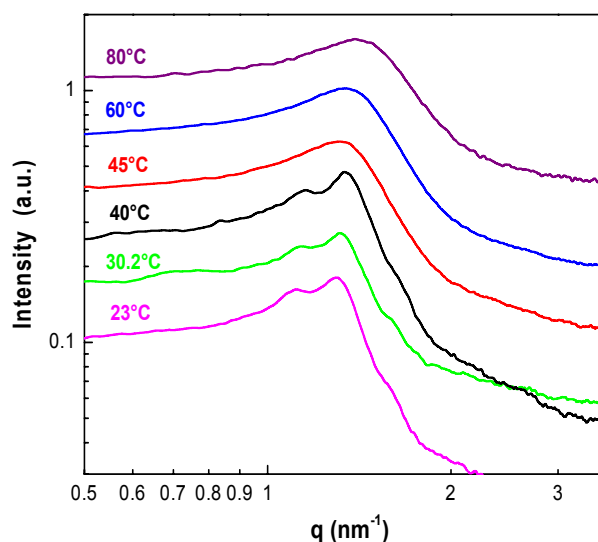
3.3   Thermal behaviour of Fd3m phase

Figure 7: Temperature dependence of the structure of Fd3m at $\alpha = 40\%_{wt}$ and 11.2%$_{wt}$ water measured by SAXS after equilibration of five days at 23°C.
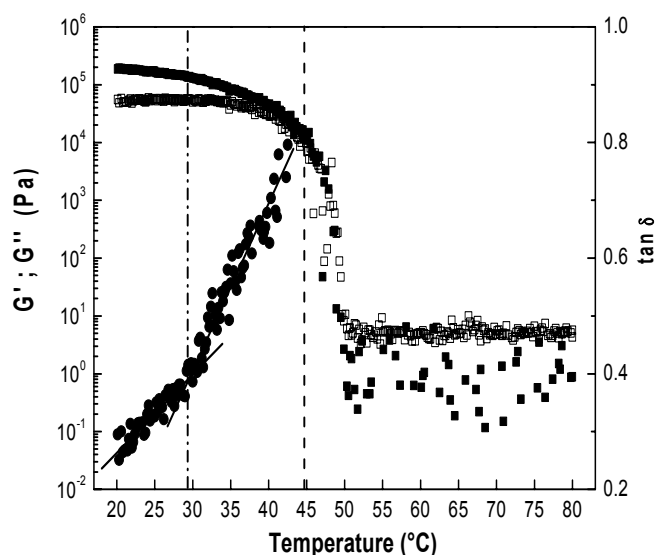

Figure 8: Temperature evolution of the storage modulus (G', filled squares), loss modulus (G'', open squares) and tan(δ) (filled circles) for Fd3m phase at $\alpha = 40\%_{wt}$ 11.2%$_{wt}$ water after five days equilibration at 23°C.

SAXS diffractograms of the structural evolution of the phase with temperature (see Fig.7) show that bulk Fd3m is completely melted into a L_2 phase above 40°C-45°C as evidenced by disappearance of its multiple reflections yielding a single broad peak centered at 1.35nm^{-1}.
However the onset of Fd3m melting with apparition of water in excess should happens around 29°C as supposed from the sharp increase of turbidity in the sample.

Two major phase transitions are clearly observable from the rheological measurements (see Fig.8). The first corresponds to the onset of the melting of the highly rigid Fd3m phase to yield a coexistence region of L_2 + water + Fd3m. This transition is clearly indicated by an increase in the slope of tan(δ) at ca. 29°C.
The second phase transition is illustrated by the sharp drop in G' and G'' observed between 40°C-45°C. This drop is associated with the complete loss of the rigidity associated with the viscoelastic Fd3m phase, to yield a viscous L_2 + water mixture.

4   CONCLUSIONS

Inverse discrete micellar cubic phase Fd3m (Q^{227} group) can be formed from addition of an hydrophobic component such as limonene oil ($\alpha = 40\%_{wt}$) to monolinolein / water system which normally leads only to the bicontinuous LC phases Pn3m and Ia3d. Fd3m structure at full hydration (12.68%$_{wt}$) is composed of micelles with average radius of 2.3nm and 170 monolinolein molecules per micelle occupying each an area of 40.6 Å^2.
Above 29°C Fd3m phase begins to melt into a mixture coexisting of an inverse micro emulsion (L_2) and water. Complete melting of the Fd3m phase is achieved at 40-45°C.
Rheological signature of Fd3m is similar to that observed for the bicontinuous cubic phases Pn3m and Ia3d in homologue binary systems. However, it presents a complex set of slower relaxation mechanisms which lead, compared to inverse bicontinuous cubic phases, to a shift by one order of magnitude of the whole relaxation spectrum due to multiple relaxation mechanisms that micelles undergo upon shear deformation, small hydration level and low temperature of the Fd3m phase.

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