Lyotropic liquid crystals – from cubosomes to small monocrystals

Abstract

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The goal of this work was the investigation of the monocrystals and nanoparticles of the bicontinuous lyotropic liquid crystalline phases. This work consists of two parts: experimental part and theoretical one.

The **experimental part** of our work had two aims: 1 - investigation of the phase diagram of the lyotropic system used for production of cubosomes, 2 - production of cubosomes and their observation by means of a transmission electron microscope (TEM).

The starting point of our experimental research was the phase diagram of the phytantriol/water/ethanol ternary system established previously by R. Sheshka and P.Faye (students on M1 practice in the LPS lab). We reexamined this phase diagram in much more details using a new experimental setup tailored for an automated and accurate control of the ethanol concentration. This new investigation of the phytantriol/water/ethanol phase diagram led to several discoveries:

1 - we have found that the addition of ethanol in adequate concentrations to the L1 phase surrounding our samples (droplets of phytantriol) induces the L3 (sponge) and Lα (lamellar) phases beside the already known L2, Pn3m and H1 phases;

2 - the corrected phase diagram Temperature-vs-ethanol concentration has several remarkable features such as the line of phase coexistence of three isotropic phases (L1+L2+L3) limited by two quadruple points (L1+L2+L3+H1 and L1+L2+L3+Pn3m). To the best of our knowledge the existence of the quadruple points was not reported in the literature so far. Moreover the phase coexistence of three isotropic phases is a unique result presented only in our work;

3 - the phenomenon of the nucleation of L1 inclusions in the Pn3m phase was reported in previous studies [70] but only in our work the explanation of this phenomenon was given;

4 - the sequence of phase transition Pn3m+L1 $\rightarrow$L3+L1$\rightarrow$ Lα+L1$\rightarrow$ L1+L2 was detected for the first time (Fig. 27).

We attempted also to elaborate a novel method of preparation of dispersed nanoparticles of the liquid crystalline Pn3m phase. Our aim was to prepare cubosomes in a more controlled way than it was done in all known methods used previously. Unfortunately, our attempts to generate nanoparticles of the liquid crystalline phase without using any stabilizing agent was unsuccessful: as expected the nanoparticles were generated but their dispersion was unstable : nanoparticles of the Pn3m phase quickly stuck together. We concluded that the role of stabilizing agent was crucial in preparation of cubosomes. Since our main goal was the investigation of the structure of cubosomes we prepared them by the ultrasonication method. We obtained many well shaped nanoparticles of Pn3m phase. In the images we can clearly see the internal either cubic or hexagonal structure [92]. We have discovered that smaller particles have spherical shapes and those with the larger sizes are polyhedral.

In the **theoretical part** of the work we were interested in the geometry and stability of interfaces formed when the Pn3m phase is surrounded by an isotropic phase. In particular, we examined the geometry of the facets formed at the droplet of the Pn3m phase. The calculations within the framework of Landau-Brazovskii model with one scalar order parameter related to the local concentration of water were performed. These calculations were done for infinitely large facets built of identical elements. Such approximation works very well for the case of the monocrystals or an interface between two phases. The calculations performed in the continuous Landau-Brazovskii model enabled detailed determination of the structure of the bicontinuous phase. In the continuous model it is much easier to study the facets formed in different directions since the structure of the lattice does not have to be taken into account.

We obtained and investigated small cubosomes by minimization of the Landau-Brazovskii functional. The size of the cubosomes obtained by mathematical modeling was smaller than the size of the cubosomes observed in transmission electron microscope. Nevertheless, these structures may be usefull in understanding the internal structure of the interwoven channels inside the particles especially in the layer close to the facet. The existence of cubosomes with the same symmetries, very similar shapes but different internal structure was observed. These cubosomes have four open channels on each facet and without knowing their internal structure one could incorrectly guess that they are the same. In fact, each cubosome is substantially different from other cubosomes.

We hope that our investigation will be useful in designing new experiment. A significant improvement can be obtained when cubosomes are built of diblock copolymer [93]. These cubosomes will be larger than those built of phytantriol. Thus, it should be much easier to investigate them for example by AFM.