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New phenomena and a new lyotropic phase detected by isoplethal and hygroscopic methods

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Abstract

Several striking phenomena found recently by isoplethal and hygroscopic methods are reviewed briefly: rich and poor facetings at cubic/isotropic interfaces, growth by redistribution process in cubic crystals, faceting by the ratchet-like effect in a saw-tooth temperature cycling, asymmetric shapes of cubic crystals induced in thermal gradients by the Ludwig–Soret effect and anisotropic and facet-by-facet surface meltings. We also report on the discovery, by hygroscopy, of a new phase that has been so far missed by isoplethal methods. The constellation of facets of this ephemeral phase suggests a random hexagonal close packed structure similar to the one found recently in soft polymeric colloids.

1. Introduction

In lyotropic systems, the variety of phases occurring as a function of temperature and composition in at least binary mixtures is plethoric. Moreover, from the Gibbs phase rule it turns out that coexistence of phases is ubiquitous. For these reasons, structures and shapes of interfaces in lyotropic systems appear as a wide and attractive field of study. Let us emphasize that the subset of cubic/isotropic interfaces on which we focus here is wide on its own because several cubic lyotropic phases of different symmetries and/or topologies can coexist with at least four isotropic phases: two micellar phases L1 and L2, the sponge phase L3 and water vapour.

Interfaces of cubic phases with the liquid L1, L2 or L3 phases have been studied by the traditional *isoplethal* method in which, by definition [1], samples have fixed compositions. In figure 1(a) we show an example of a simple set-up well adapted for the isoplethal method that has been used recently in studies of shapes of interfaces, such as $Pn3m/L1$, in a C12EO2/H2O system with a miscibility gap [2, 3] (see section 2).

In order to study cubic/vapour interfaces, we have developed the simple set-up shown in figure 1(b) that allows us to observe, by microscopy, droplet-like samples surrounded by a gas atmosphere of controlled hygrometry (humidity). For obvious reasons, we propose to call this method *hygroscopy*.

Hygroscopy has some advantages when compared with the isoplethal method. For instance, phases with a very narrow concentration existence range Δc can be missed by the

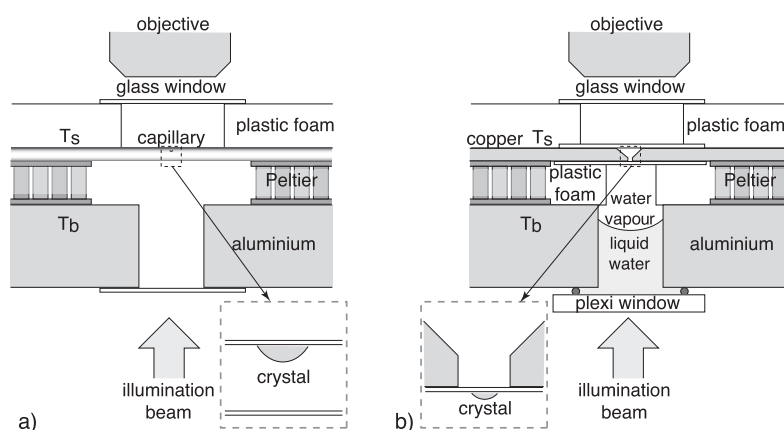


Figure 1. Set-ups for isoplethal and hygroscopic studies of lyotropic systems: (a) a flat capillary is filled with a surfactant/water mixture of a predetermined composition; (b) a droplet of the surfactant is surrounded by a humid atmosphere; the relative humidity at the crystal surface is determined by the temperature difference $T_s - T_b$.

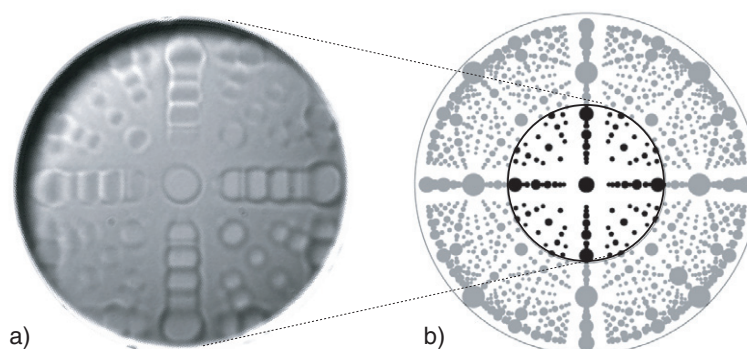


Figure 2. An example of the rich faceting at cubic/vapour interfaces: (a) DTACl/water system (for the phase diagram see figure 6). The photograph shows a $Pm3n$ crystal obtained from a droplet of the L2 micellar phase at $T = 70^\circ\text{C}$. (b) Simulation of the faceting of a spherical $Pm3n$ crystal.

isoplethal method. As a remedy, Laughlin and Munyon [4] developed the diffusive interfacial transport (DIT) method in which samples with concentration gradients are used. Unfortunately, in the DIT method, lyotropic systems are out of equilibrium, by definition. Hygroscopy is free of these drawbacks of the isoplethal and DIT methods. Using it, we have found a new lyotropic phase (see section 3).

2. New phenomena

2.1. Rich and poor facetings

The starting point of our studies of lyotropic interfaces was the discovery of the devil's-staircase-like faceting of $Ia3d$ crystals (C12EO6/water mixture) surrounded by a humid atmosphere [6, 7]. Today we know that such a *rich* faceting is a rule at all other cubic/vapour interfaces studied so far. As an example we show in figure 2(a) a photograph, obtained by means of the hygroscopic set-up from figure 1(b), of a $Pm3n$ crystal in the DTACl/water system.

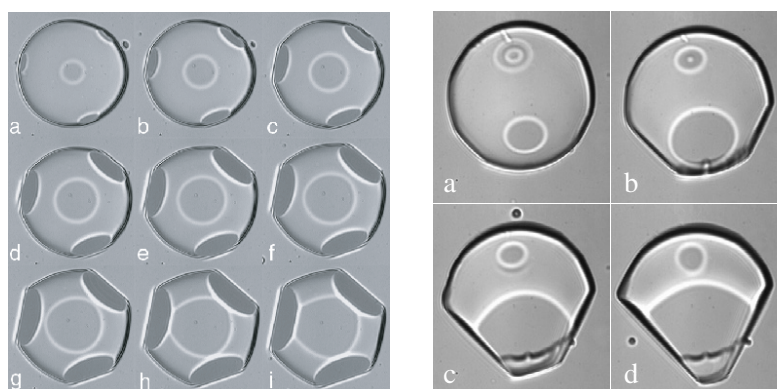


Figure 3. Out-of-equilibrium effects at the $Pn3m/L1$ interface in the C12EO2/water mixture. Left: the ratchet effect [3]. The series of photographs (a)–(i) shows the evolution of the shape of a $Pn3m$ -in-L1 crystal subjected to a saw-tooth temperature cycling. Right: the Ludwig–Soret effect. The series of photographs (a)–(d) shows the evolution of the shape of a $Pn3m$ -in-L1 crystal subjected to a temperature gradient.

Following to Nozières *et al* [5], such a rich faceting is due to a conjunction of a large size of unit cells (≈ 10 nm) with a large tension at the cubic/vapour interface (≈ 25 dyn cm $^{-1}$). The lyotropic systems provide us with an opportunity to test this theory because the interfacial cubic/isotropic tension can be varied in a large extent. Indeed, as mentioned above, cubic phases can coexist not only with the water vapour but also with isotropic liquid phases and in such a case the interfacial tension between two liquid phases is expected to be much smaller. In agreement with these considerations, observations of the $Pn3m/L1$ interface (C12EO2/water mixture) by means of the isoplethal set-up (figure 1(a)) have shown that its faceting is *poor* as shown in figures 3 and 4. In the C12EO2/water system, the cubic/isotropic tension can be lowered even more because the $Pn3m$ phase can coexist with the sponge phase L3 (see the phase diagram of Lynch *et al* [8] in figure 4). Experiments have shown that the $Pn3m/L3$ interface is *completely rough*.

2.2. Growth by redistribution and ratchet-like effects [3]

The number of molecules per unit cell n_{uc} is variable and depends on temperature. When temperature changes and n_{uc} , for example, decreases the molecules are removed from the already existing unit cells and are redistributed in new unit cells. In the case of $Pn3m$ -in-L1 crystals, these new unit cells are created at rough parts of the $Pn3m/L1$ interface. As a result, the size of facets is growing. This *growth by redistribution* phenomenon, which looks exactly the same as the growth of solid crystals from a solution, takes place at a constant number of surfactant molecules.

The growth by redistribution is in general not reversible. As a result, when cubic crystals are subjected to a saw-tooth temperature cycling, the size of facets is larger and larger from cycle to cycle as shown in figure 3 [3].

2.3. Asymmetric crystal shapes due to the Ludwig–Soret effect [9]

Being *organized solutions*, lyotropic cubic crystals display a beautiful Ludwig–Soret-like effect when they are subjected to temperature gradients. In the case of $Pn3m$ -in-L1 crystals, the temperature gradient induces the thermodiffusion of surfactant inside $Pn3m$ crystals. This

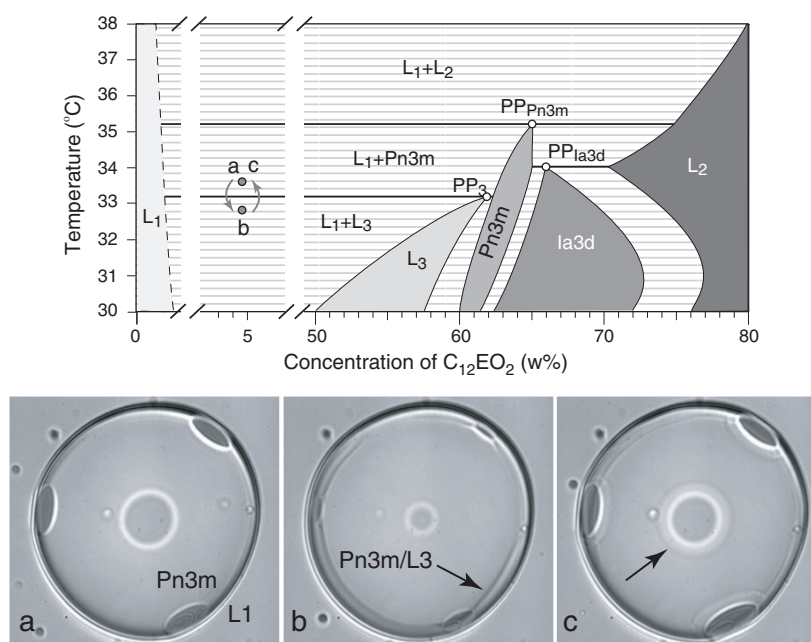


Figure 4. Direct demonstration of the anisotropic surface melting at the $Pn3m/L1$ interface. (a) Initial shape of the $Pn3m$ -in- $L1$ crystal at $T = T_{PP3} + 0.01$ K. (b) Crystal shape upon cooling to $T = T_{PP3} - 0.01$ K. A macroscopic layer of the sponge phase $L3$ covers rough parts of the $Pn3m/L1$; this is marked by the arrow. (c) Evolution of the crystal shape after return to $T = T_{PP3} + 0.01$ K. The arrow points to the contact line $Pn3m/L1/L3$.

transfer of surfactant inside the $Pn3m$ crystal is revealed by a spectacular change in its shape: the $Pn3m$ crystal seems to melt on its hot side and to grow on its cold side as shown in figure 3.

2.4. Anisotropic and facet-by-facet surface melting [10]

Crystals are known to melt partially on their surfaces at temperatures below their triple crystal/liquid/vapour point [11–13]. In the case of lyotropic systems, one has to choose phases which would be analogous respectively to the crystal, isotropic liquid and vapour phases. Cubic lyotropic phases are obviously analogous to crystals. The choice of the isotropic liquid-like phase is less obvious because lyotropic cubic phases can ‘melt’ into three isotropic phases $L1$, $L2$ and $L3$ with different topologies. The choice of the vapour-like phase is not evident at all. One possibility results from the occurrence, on the $C12EO2$ /water phase diagram, of the triple point at which the $Pn3m$ phase coexists with two isotropic phases, $L3$ and $L1$, playing respectively roles of the liquid and vapour phases. The series of photographs in figure 4 shows that upon cooling below the triple point $PP3$ rough parts of the $Pn3m/L1$ are wetted by a layer of the sponge phase while facets stay dry and only decrease their size.

Another possibility is offered by the hygroscopic method in which the vapour phase plays its own role. In the mono-olein/water system (see the T -versus- H phase diagram in figure 5), the $Ia3d$ crystals can melt into the $L2$ phase. The series of photographs in figure 5 shows that the *facet-by-facet melting* process occurs here: rough parts of the $Ia3d$ /vapour interface are wetted by the $L2$ phase and facets disappear, one after another, when $Ia3d \rightarrow L2$ is approached.

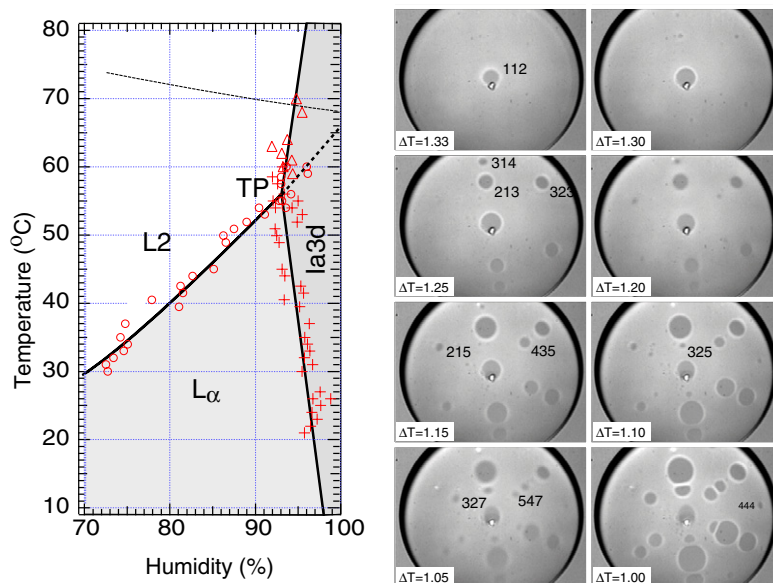


Figure 5. Hygroscopic study of the mono-olein/water system [10]. The T -versus- H phase diagram has been obtained by means of the set-up shown in figure 1(b). The series of photographs shows the phenomenon of the facet-by-facet melting at the $Ia3d$ /vapour interface. The distance, in terms of humidity, from the $L2$ - $Ia3d$ transition increases when the temperature difference ΔT between the reservoir of water and the sample is lowered.

(This figure is in colour only in the electronic version)

3. An ephemeral phase

The study of the facet-by-facet melting at lyotropic interfaces in the DTACI/water system lead us to the discovery of a new phase. In the search for an example of the melting from a cubic phase into the L1 phase, we focused on the DTACI/water system where a direct phase transition from the $Pm3n$ phase into the L1 phase was known to occur (see the T -versus- c phase diagram in figure 6 established by Balmbra *et al* [14]). Hygroscopic experiments have shown however that below 70 °C the transition from the L1 to $Pm3n$ phase is not direct. Indeed, in figure 6, pictures (a) and (d) correspond, as expected, to the L1 and $Pm3n$ phases but the texture of the sample in picture (b) is abnormal and clearly proves the existence of a new phase. We called this new phase *ephemeral* because its humidity range is very narrow, it does not appear on the way back from $Pm3n$ to L1 and it disappears completely in the presence of impurities.

What is the structure of this new phase? The initial polycrystalline texture does not provide any hints for its identification. Fortunately, after annealing for a few hours, a facet constellation with hexagonal symmetry appears as shown in figure 7. Beside its symmetry, this constellation has another remarkable feature: the distribution of facets on the crystal surface is very inhomogeneous. All facets are located on six meridians while all other parts of the crystal surface are rough.

In terms of the Donnay–Harker model, the selection rules for the occurrence of facets are similar to the selection rules for Bragg reflections. Therefore, the distribution of Bragg spots in the reciprocal space of the ephemeral phase should be very inhomogeneous as well. This feature is reminiscent of recent x-ray diffraction experiments with the so-called random

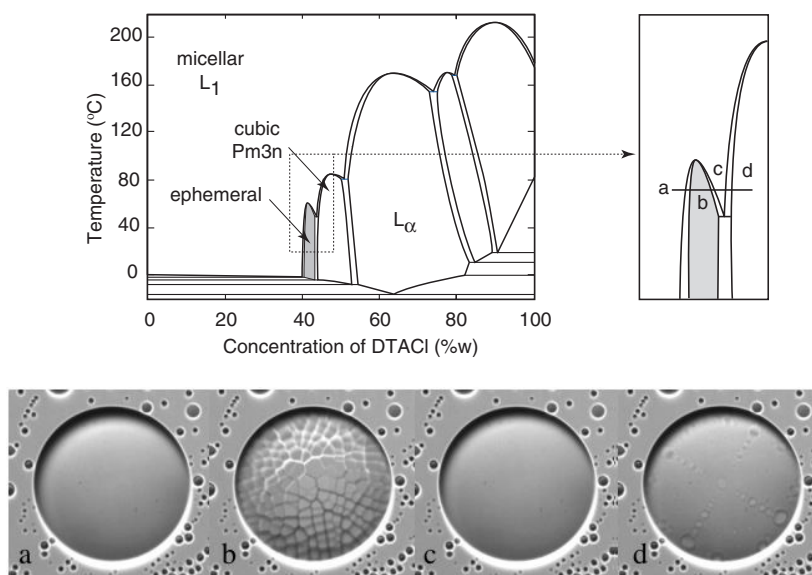


Figure 6. Experimental evidence for the ephemeral phase. The phase diagram of the DTACl/water mixture, established by Balmbra *et al* [14], has been completed here by the addition of the ephemeral phase. The series of photographs (a)–(d) shows indeed that at $T = 60^\circ\text{C}$ the transition from the micellar L_1 phase to the cubic $Pm3n$ phase is mediated by another unknown phase.

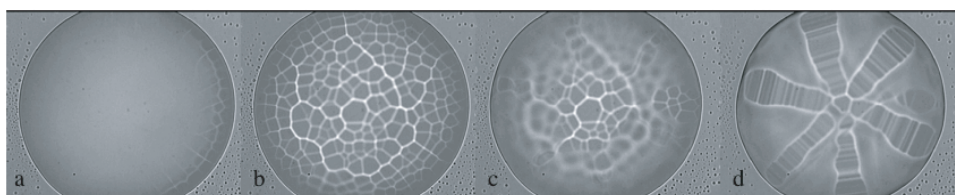


Figure 7. Faceting of the ephemeral phase in the DTACl/water system: (a) beginning of the $L_1 \rightarrow \text{rhcp}$ phase transition, (b) mosaic polycrystalline structure, (c) beginning of the annealing and (d) faceting after annealing.

hexagonal close packed (rhcp) structure in colloidal systems [15], where 2D hexagonal crystal planes form a random stack. Due to the disorder, two-thirds of the hcp Bragg spots are smeared out into diffuse rods while the other Bragg spots are preserved. In the DTACl/water system, the L_1 and $Pm3n$ phases are micellar. The intermediate ephemeral phase should therefore be micellar as well. By analogy with colloidal crystals, the order of micelles could be rhcp.

This hypothesis is reinforced by the theoretical predictions of Zihlerl and Kamien [16] concerning the phase sequence in a system of soft spheres such as polymer or surfactant micelles. Following this theory, when the density increases, the phase sequence can be liquid \rightarrow close packed (fcc, hcp or rhcp) \rightarrow bcc $\rightarrow Pm3n$.

In the DTACl/water system, the phase sequence is similar but the bcc phase seems to be missing. During the conference (poster P 7.25, ‘HCP-BCC-A15 transitions of spherical micelles in a nonionic surfactant/water system’), we have had the pleasure to learn that the complete theoretical phase sequence $L_1 \rightarrow \text{hcp} \rightarrow \text{bcc} \rightarrow Pm3n$ has been detected recently by Imai *et al* [17] in the C12EO8/water binary system. We intend to check in the near future whether this complete phase sequence can also be seen by hygroscopy.

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