EUROPEAN SYNCHROTRON RADIATION FACILITY

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Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Time Resolved Studies of the Lyotropic Phase Transitions of the Inverse Bicontinuous Cubic Phases Using the Pressure Jump Technique	**Experiment number**: SC-1962
Beamline: ID02	**Date of experiment**: from: 21st to: 24th April 2006	**Date of report**: 28/02/08
Shifts: 9	**Local contact(s)**: Stephanie Finet	*Received at ESRF:*

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Report:

During previous ESRF beamtime sessions we have introduced the pressure jump technique with a view to studying lyotropic phase transitions involving bicontinuous cubic phases. The pressure technique has several advantages over other trigger mechanisms: 1) it does not significantly alter the solvent properties 2) pressure propagates rapidly so that equilibrium is achieved rapidly and, 3) pressure-jumps can be bidirectional, i.e. in the pressurization and depressurization direction. We were able to attain reproducible dynamics for this process by generating samples composed of topologically distinct, physically separated domains with a narrow size distribution. The fact that dynamical reproducibility is dependent on uniform domain size provided strong evidence for structural changes at the scale of the unit cell being topologically and geometrically coupled to structural constraints at the nano-scale, such as changes in molecular shape. During SC-1962 we wished to build on our earlier measurements where we measured the rate of transition as a function of the pressure difference, and look at the effect of domain size. The rate of transition was found to be strongly dependent upon the difference between the final pressure of the system and the pressure at the phase transition boundary. In contrast to temperature jumps, these experiments showed that the reduction in lamellar spacing is not linear, instead each curve appears to consist of an initial linear decrease, which is a result of the final thermodynamic pressure-dependent state, followed by a portion that is approximated by a mono-exponential decay and is a consequence of stalk formation. We wished to further investigate the kinetics of this process in detail so as to allow us to deconvolute these two dynamic processes and obtain reliable measurements for the rate of transition as a function of pressure. These measurements are vital to the development of our activation energy model for this complex and collective process.

We studied a number of systems including monoolein / 20 wt% H_2O and looked at the kinetics of the L_α-Q_{II}^D transition as a function of pressure-jump amplitude and temperature. To this effect relevant p-T phase diagrams were constructed thereby allowing us to plan our p-jumps (example shown in figure 1).

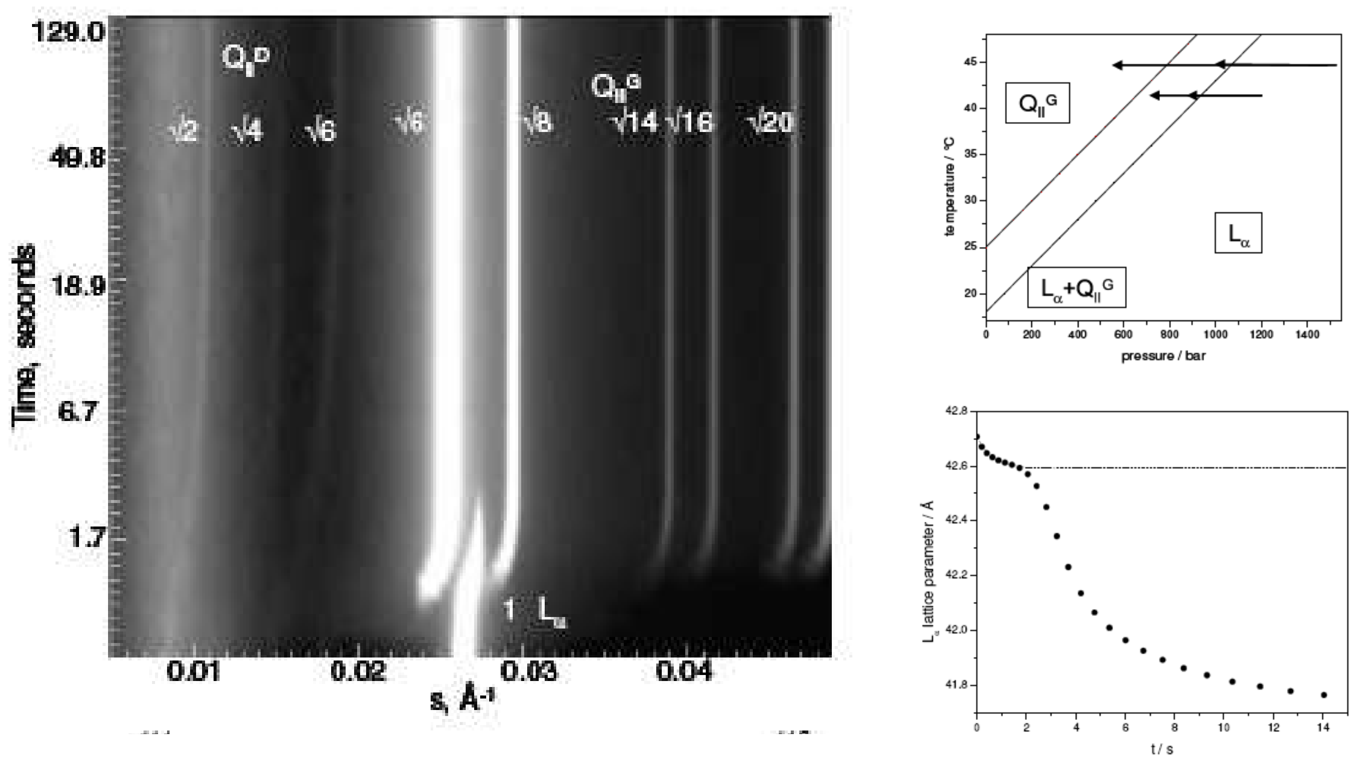

Figure 1 (a) (left) 'Stacked' plots following pressure-jumps from 1520 to 840 bar for MO 20 wt% H_2O; **(b) (top right)** the p-T phase diagram for MO / 20wt% H_2O; **(c) (bottom right)** the mono-exponential decay decrease in L_α lattice parameter during Stage I following a pressure-jump from 1200 to 870 bar.

The transformation shown in figure 1 (a) and (c) may be divided into two stages. From our measurements we can see that Stage I both the lattice parameter and intensity of the fluid lamellar phase change by only a small amount. The half-width of the fluid lamellar phase remains constant throughout this stage. Such behaviour may be contrasted with that of ME 30 wt% H_2O in previous studies where a similar division into two stages was observed but the half-width displayed a pronounced increase during Stage I reaching a maximum value at the end of this stage. The second stage occurs immediately after the formation of the cubic gyroid (Q_{II}^G) phase and is characterised by a pronounced decrease in the intensity of the L_α peaks and concomitant increase in peak intensity of the growing Q_{II}^G phase. At this point a pronounced increase in disorder is noted in the remaining fluid lamellar phase. The half-width of the L_α first-order reflection increases sharply towards a maximum halfwidth between 1.5 and 2 times that seen initially. The emergent cubic phase is also initially disordered displaying broad peaks which sharpen with time. As for all lamellar to cubic transitions the forming cubic phase is more hydrated than expected from equilibrium data and dehydrates with time. However overall changes in lattice parameter for this phase are much smaller than those observed for the forming cubic phase in ME both in excess water and under limited hydration conditions. Such behaviour may reflect the overall reduced water content of this system. The presence of a swollen Q_{II}^D cubic phase coexisting with the fluid lamellar phase is seen in these measurements. However, uniquely to this system, the cubic phase appears unaffected by the transition itself, existing throughout the transformation and merely relaxing under the effect of pressure.

The decrease in lattice parameter of both the L_α and Q_{II}^G phases with time throughout the transformations we measured appear to be structural features of all transitions from a fluid lamellar to an inverse bicontinuous cubic phase. The L_α decrease begins immediately following the pressure-jump and, as for both ME samples, may be divided into two distinct stages. During Stage I the lattice parameter and intensity of the L_α phase change by only a small amount. For this sample the overall speed of transition is relatively fast and Stage I occurs over an extremely short timescale (< 1s for most jumps). This initial stage is attributed to the effect of a large decrease in pressure on the acyl chains. The appearance of the Q_{II}^G phase at the end of Stage I indicates that formation of significant numbers of stalks in the system must have already occurred. For ME under limited hydration conditions the formation of stalks during Stage I is associated with a considerable increase in planar disorder and attributed to the inhomogeneous formation of stalks between the bilayers. We suggested that this could be due to difficulties with sufficient membrane undulations towards the centre of the onion vesicles with stalk formation occurring preferentially towards the surface of each domain. Such behaviour is consistent with the experimental observations seen during SC-1962; the large region of co-existence of the L_α and Q_{II}^G phases and the inability of the centrally located swollen Q_{II}^D phase to act as a seed for the transition. However no increase in disorder of the L_α phase for MO was noted during Stage I with the half-width of the first-order lamellar reflection constant throughout this stage. This could indicate that the effect of stalk formation on the L_α bilayer spacing is much less pronounced for MO than for ME. It should be noted that the molecular structure of MO is identical to that of ME except that the double bond at the 9-carbon position is cis rather than trans. The removal of the kink in the acyl chain introduced by the presence of the trans double bond allows more efficient chain packing in ME compared to MO. This will affect structural parameters such as the bilayer rigidity which will affect the process of stalk formation and the ease with which such formation occurs. Therefore an inhomogeneous distribution of stalks between the lamellar bilayers will not lead to a significant variation in bilayer spacing and hence no increase in planar disorder.

The large increase in disorder of the L_α phase at the beginning of Stage II, along with a correspondingly disordered appearing Q_{II}^G phase, may reflect difficulties in transporting water throughout the system. Unlike planar disorder, this should give rise to uniformly broad diffraction peaks which do not show an increase in half-width with scattering vector, s. If the effect of stalk formation on the bilayer spacing is indeed negligible for this system then the pronounced decrease in lattice parameter of the L_α phase observed during Stage II must be solely related to dehydration of the L_α phase. In fact, an analysis of the water content of each phase throughout the transformation indicates that the decrease in L_α lattice parameter is accounted for by a transfer of water from the L_α phase to the more highly hydrated Q_{II}^G phase.

This work alongside that of SC-1838 contributed to two publications in Langmuir:

Shearman, G.C. et al, **Calculations of and evidence for chain packing stress in inverse lyotropic bicontinuous cubic phases**, LANGMUIR, 2007, Vol: 23, Pages: 7276 - 7285, ISSN: 0743-7463

Conn, C.E. et al, **A Pressure-Jump Time-Resolved X-ray Diffraction Study of Cubic-Cubic Transition Kinetics in Monoolein** (2008), Langmuir, *in press*