ESRF	**Experiment title:** **Formation of Inverted Columnar Hexagonal Lyotropic Liquid Crystalline Phases in Mixtures Containing Amine-Metal Hydroxides**	**Experiment number**: 26-02-294
Beamline: **BM26B**	**Date of experiment**: from: 4.09 to:8.09.2005	**Date of report**: 22.03.2005
Shifts: 3	**Local contact(s)**: Florian Meneau Wim Bras	*Received at ESRF:* *Raluca Gearba* *Denis Anokhin* *Dimitri Ivanov*

Names and affiliations of applicants (* indicates experimentalists):

R.I. Gearba[1*], D. V. Anokhin[1], A.I. Bondar[2], Oliver Weichold[3], Shou-Chian Hsu[3], Martin Möller[3], D.A. Ivanov[1,2*]

[1] Institut de Chimie des Surfaces et Interfaces, CNRS UPR9069, 15, rue Jean Starcky, BP 2488, 68057 Mulhouse CEDEX, France.
[2] Laboratoire de Physique des Polymères, CP-223, Université Libre de Bruxelles, Bld. du Triomphe, B-1050, Brussels, Belgium.
[3] DWI an der RWTH Aachen e.V.Pauwelsstrasse 8, 52056 Aachen, Germany.

Report:

One-dimensional (1D) nanostructures, such as nanorods and nanowires, is an interesting and increasingly important class of materials with diverse applications in organic electronic devices[1] and medicine.[2,3] In recent years, many approaches have been developed for the preparation of 1D nanostructures, including vapor-phase transport process[4a], arc-discharge[4b] , laser ablation[4c], wet chemical routes[4d] and template-based methods[4e]. The most common template-based methods include the use of lyotropic liquid crystals (LC)[5] forming inverted hexagonal (H_I) phases. Generally, the H_I is formed by long mutually parallel aqueous cylinders, surrounded by a continuous oil phase. Many reports on the preparation of H_I phases have been published to date[6]. However, *in situ* preparation of 1D nanomaterials in H_I phases is still rare and include the use of ternary mixtures. The major reason is that they are generally formed by tiny relative amount of components and covers a small area in the phase diagram. In addition, the order of H_I phases is easely disrupted when dopped with metallic ions.

Here we report on the structure and phase behavior of an oleic acid/1-decanol/ammonium hydroxide ternary systems. The phase structure was studied by X-ray diffraction and revealed that the H_I phases are formed at ambient temperature in a wide compositional range of the ternary solutions. The results are summarized in Table 1. A typical X-ray diffraction pattern (fig.1) shows three peaks in the small-angle region with the corresponding s-values obeying the ratio 1:√3:2. This indicates the formation of a hexagonal columnar phase. In was found that the lattice parameter **a** increases from 39.7 to 44.2 Å with incresing the concentration of oleic acid. In addition, a braod peak (halo) situated at 4.3 Å was detected and can be assigned to the disordered hydrocarbon chains. Fig. 2 is a schematic representation of the proposed H_I phase. The columns with the hydrocarbon chains of the amphiphiles are pointing

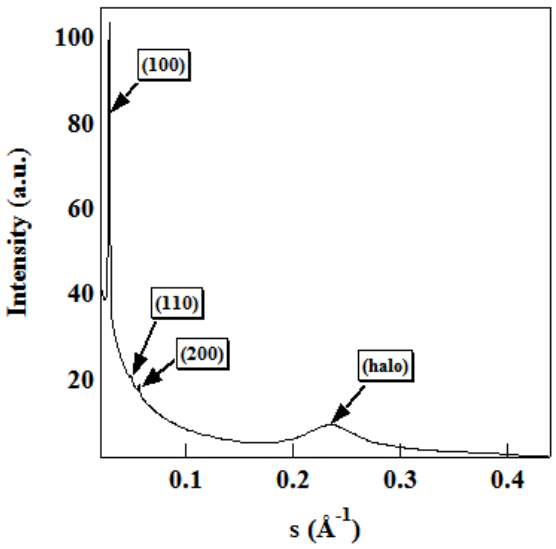

Fig.1 *X-ray diffraction of oleic acid/1-decanol/ ammonium hydroxide solution (52/15/33) recorded at 25 °C.*

outwards. The inverted character of the hexagonal phase can be therefore easely checked by miscibility tests by adding small amounts of water or hexane to the ternary solution. It was determined that hexane was absorbed by the sample, while water persists even under violent shaking. From the model, the water channel radius (R_w) and the hydrophobic tail length (L) were estimated and they found to vary between 10.8 and 14.1 Å and 7.1 to 9.2 Å, respectively.

Furthermore, polarized optical microscopy observations of the oleic acid/1-decanol/ammonium hydroxide ternary system dopped with 0.1 M Ag^+ and Cu^{2+} ions shows the presence of a fan-shaped texture consistent with the existance of a columnar hexagonal mesophase. These observations show that ion doping does not disrupt the H_I phase. Therefore, we expect that the studied systems can serve as easy route in the preparation of nanorods and nanowires.

Note that the use of synchrotron radiation was required for these studies. The ternary mixtures are very weak scatterers and therefore long acquisition times would be necessary for X-ray measurements using laboratory sources of X-rays, which would result in a partial evaporation of solvents and a compositional variation.

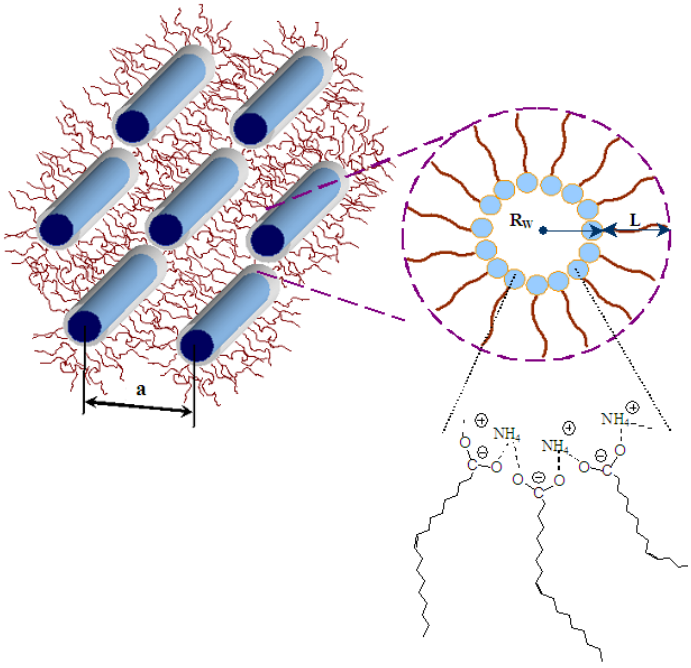

Fig.2. *Schematic representation of a three-dimensional network of the H_I phase: a- interchannel distance, R_w- water channel radius and L- hydrophobic tail length.*

Table 1: X-ray diffraction data

No	Composition (wt %) oleic acid/1-decanol/amonium hydroxide	hkl	$d_{hkl\ exp}$, Å	$d_{hkl\ calc}$, Å	a, Å	R_w^*, Å	L^{**}, Å
1	25/48/27	100 110 200	34.39 19.73 17.11	34.39 19.85 17.19	39.7	10.8	9.0
2	35/38/27	100 110 200	35.0 20.33 17.60	35.0 20.2 17.5	40.4	11.0	9.2
3	30/30/40	100 110 200	36.73 21.28 18.58	36.73 20.20 18.36	42.4	14.1	7.1
4	37/25/38	100 110 200	37.37 21.58 18.65	37.37 21.27 18.68	43.2	14.0	7.6
5	52/15/33	100 110 200	38.27 22.06 19.01	38.27 22.09 19.13	44.2	13.3	8.8

* R_w-water channel radius, $R_w^2 = \frac{\sqrt{3}\phi_A a^2}{2\pi}$, where **a** is the lattice parameter and ϕ_A - the fractional volume of the ammonium hydroxide solution, L^{**} is the hydrophobic chain length

References

1. Terabe, K., Hasegawa1, T., Nakayama, T., Aono, M., 2005, *Nature*, **433**, 47-50.
2. Salem, A., Searson, P. C., Leong, K. W., 2003, *Nature Mater.,* **2**, 668-671.
3. Nagesha, D. K., Whitehead, M. A., Coffer, J. L., 2005, *Adv. Mater*., **17**, 921-924.
4. a)Chattopadhyay, S., Shi, S. C., Lan, Z. H., Chen, C. F., Chen, K. H., Chen, L. C., 2005, *J. Am. Chem. Soc*., **127**, 2820-2821; b) Zhou, Y., Yu, S. H., Cui, X. P., Wang, C. Y., Chen, Z. Y., 1999, *Chem. Mater*., **11**, 545-546; c) Morales, A. M., Lieber, C. M., 1998, *Science*, **279**, 208-211; d) Murphy, C. J., Jana, N. R., 2002, *Adv. Mater.*, **14**, 80-82; e) Nyamjav, D., Kinsella, J. M., Ivanisevic, A., 2005, *Appl. Phys. Lett.*, **86**, 093107-1-093107-3.
5. a) Stupp, S. I., Braun, P. V., Osenar, P., 1996, *Science*, **380**, 325-328 ; b)Stupp, S. I., Braun, P. V., Osenar, P., Tohver, V., Kennedy, S. B., 1999, *J. Am. Chem. Soc.*, **121**, 7302-7309 ; c)Huang, N. M., Shahidan, R., Khiew, P. S., Peter, L., Kan, C. S., 2004, *Colloids Surf. A*., **247**, 55-60 ; d) Jiang, X., Xie, Y., Lu, J., Zhu, L., He, W., Qian, Y., 2001, *J. Mater, Chem.*, **11**, 1775-1777.
6. Ekwall, P., Mandell, L., Fontell, K., 1968, *Acta Chem. Scand*., **22**, 373-375; b) Brown, G. H., 1968, *Proc. Int. Liq. Cryst. Conf*., Part 1, pp. 346-364; c) David, H., Gin, D. L., 1998, *Chem. Mater.*, **10**, 1827-1832; d) Reppy, M. A., Gary, D. H., Pindzola, B. A., Smithers, J. L., Gin, D. L., 2001, *J. Am. Chem. Soc*., **123**, 363-371.

.