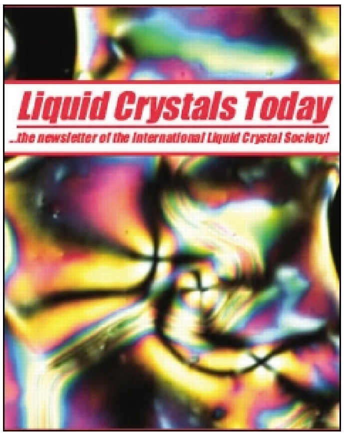
This article was downloaded by:
On: *16 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals Today

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713681230

A new hexatic phase observed in biomembrane-like films

C. Y. Chao[a]; W. J. Hsieh[a]; M. T. Hsu[a]; J. T. Ho[b]; I. J. B. Lin[c]
[a] Department of Physics, National Taiwan University, Taipei 10617, Taiwan, ROC [b] Department of Physics, University at Buffalo, The State University of New York, Buffalo, NY 14260, USA [c] Department of Chemistry, National Dong Hwa University, Hualien 97441, Taiwan, ROC

To cite this Article Chao, C. Y. , Hsieh, W. J. , Hsu, M. T. , Ho, J. T. and Lin, I. J. B.(2005) 'A new hexatic phase observed in biomembrane-like films', Liquid Crystals Today, 14: 3, 1 — 3
To link to this Article: DOI: 10.1080/14645180500358835
URL: http://dx.doi.org/10.1080/14645180500358835

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Liquid Crystals Today, Vol. 14, No. 3, September 2005, 1–3

Taylor & Francis
Taylor & Francis Group

A new hexatic phase observed in biomembrane-like films

C.Y. CHAO*†, W.J. HSIEH†, M.T. HSU†, J.T. HO‡ and I.J.B. LIN§

†Department of Physics, National Taiwan University, Taipei 10617, Taiwan, ROC
‡Department of Physics, University at Buffalo, The State University of New York, Buffalo, NY 14260, USA
§Department of Chemistry, National Dong Hwa University, Hualien 97441, Taiwan, ROC

(*Received 13 July 2005; in final form 1 September 2005*)

An intermediate surface hexatic phase between the liquid and the crystalline phases has been found for the first time in a lyotropic lamellar liquid–crystal (LC) system. This phase is highly unusual in that it has long-range six-fold bond-orientational order but liquid-like nearest-neighbor positional correlations, and could represent a significant departure from our current understanding of defect-mediated melting in two dimensions. Our result represents the first report of an in-plane hydration force that is due to the existence of at least two water molecules situated between a hydrated nitrate functionality and an imidazolium-based core in adjacent molecules.

It is commonly known that there are three states of matter – solid, liquid and gas. In three dimensions, the crystalline solid melts directly into the liquid via a first-order transition. What processes are involved when two-dimensional (2D) systems melt? Theories of 2D melting [1–3] suggest a mechanism in which a 2D solid could melt through the dissociation of topological defect pairs. In particular, Halperin and Nelson [2] predicted the existence of an intermediate hexatic phase, with long-range bond-orientational order (BOO) but short-range positional order, between the 2D solid and the isotropic liquid. Such a hexatic phase has been found in free-standing thin films of several liquid-crystal (LC) materials and in other 2D systems [4, 5]. This intermediate hexatic phase has also been seen on the surface of materials that do not exhibit bulk hexatic behavior [6], and therefore may not be all that rare in nature.

It is generally expected theoretically [2] and observed experimentally [5] that, the hexatic phase has long-range BOO, and its positional correlations, while short-range, should be much stronger than those in an ordinary liquid. It has long been suspected but never demonstrated that lyotropic lamellar bilayers that are common in biological membranes, because of their intrinsic 2D nature, should exhibit hexatic behavior. Employing a unique transmission electron microscope (TEM) with an environmental sample chamber, we have recently discovered a new type of hexatic phase in hydrated free-standing LC thin films [7]. This phase is highly unusual in that it has only liquid-like nearest-neighbor positional correlations but nevertheless exhibits well-developed BOO. The only previous suggestion to date of possible hexatic behavior in a lyotropic system [8] lacked direct evidence for the existence of BOO. Our unexpected finding of this new hexatic phase stimulates further investigations.

An amphiphilic 1-dodecylimidazolium nitrate salt ([$C_{12}H_{25}$–imH][NO_3]), which is known to exhibit lyotropic LC properties in water [9], is used in our study. The nitrate salt was first mixed with about 30% distilled water to form a thin paste, which was then used for film spreading. The films are typically a few bilayers, and their thickness was determined using optical reflectivity [10]. Films with thickness of up to ten bilayers were drawn for electron-diffraction (ED) measurements, but most of the results here refer to a four-bilayer film only. The relative humidity (RH) inside the hydrated specimen chamber was maintained at over 90% and held unchanged, because the films easily ruptured when RH was reduced to below 90%. Above 25°C, the film was in the smectic-*A*-like L_α phase. Its ED pattern showed a diffuse ring of constant intensity, indicating the liquid nature of this phase. When the film was cooled to below 25°C, six symmetric diffuse arcs coexisting with the diffuse ring appeared, as shown in figure 1, signifying the occurrence of long-range BOO on the surface bilayers while the interior remained in the L_α phase. This is very similar to the smectic-*A*–hexatic-*B* surface-freezing transition observed in thermotropic LC thin films [11–13], in which a more ordered surface phase is found to grow onto a less ordered interior in a layer-by-layer manner. Subsequently, upon further cooling, the entire film

---

*Corresponding author. Email: cychao@ntu.edu.tw

Liquid Crystals Today
ISSN 1358-314X print/ISSN 1464-5181 online © 2005 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/14645180500358835

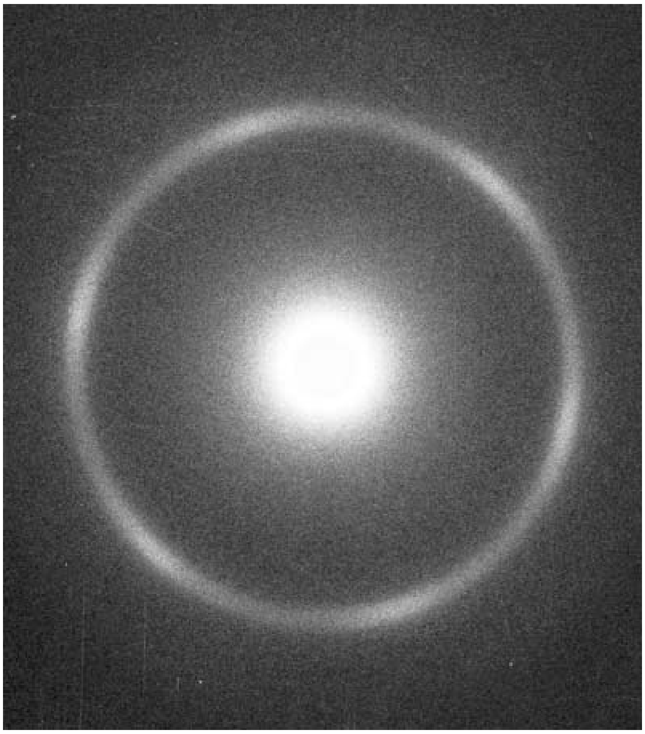


Figure 1. Electron diffraction pattern from a four-bilayer lyotropic LC film at 21°C under 90% RH.

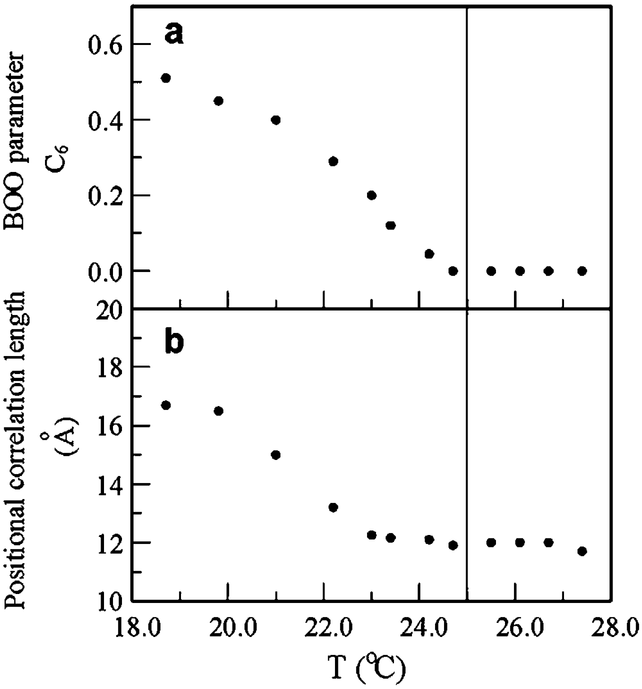


Figure 2. Temperature dependence of (a) the BOO parameter C_6 and (b) the in-plane positional correlation length ξ of the surface L_{hex} phase.

underwent another transition at about 18.5°C to an orthorhombic crystalline phase [7].

The intermediate surface phase, which we call the lamellar hexatic liquid (L_{hex}), appears to be a novel lyotropic LC phase. Its integrated ED intensity suggests that the surface hexatic phase always has a thickness of one bilayer in films of different thickness. The six-fold azimuthal intensity modulation of this L_{hex} phase denotes long-range BOO and can be analyzed to extract the BOO parameter C_6 [14]. The temperature dependence of C_6 at 90% RH is shown in figure 2(a). The radial width of the L_{hex} phase is quite unusual in that the six arcs due to the surface phase appear to be as diffuse in the radial direction as the uniform ring due to the interior liquid, suggesting a close similarity in their positional correlations. In fitting the radial intensity across the six arcs, we have found that a liquid-like Lorentzian function was significantly superior to the square-root Lorentzian (SRL) function. This is in contrast to previous experiments on hexatic LC phase [5], in which it was necessary to use the SRL fit as suggested theoretically by the coupling between the hexatic and positional orders [15]. Figure 3 shows the radial scans and Lorentzian fits across the surface L_{hex} arcs and the interior L_α ring at 21°C, yielding comparable positional correlation lengths ξ of 15.1 and 11.9 Å, respectively. The temperature dependence of ξ in the L_{hex} phase is seen in figure 2(b), showing that, even when C_6 has reached a significant value of 0.5, ξ increases only slightly (to <17 Å) from its value of 12 Å in the liquid phase. The values of ξ in the L_{hex} phase are

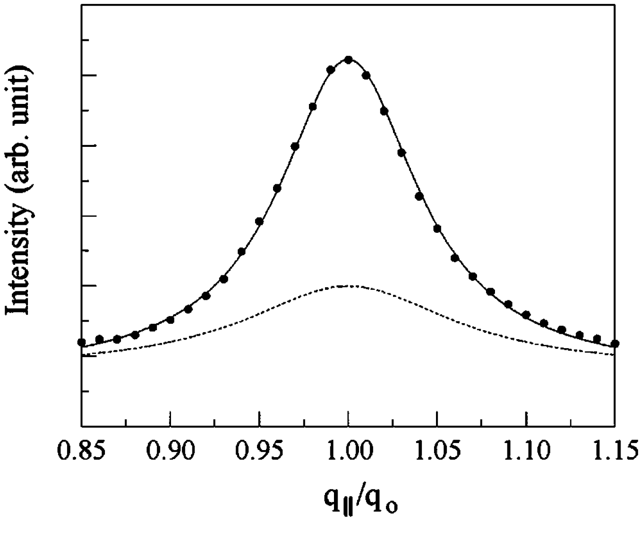


Figure 3. Radial scan (solid circles) and Lorentzian fit (solid line) across the surface L_{hex} arcs at 21°C, yielding a positional correlation length ξ of 15.1 Å. The fit (dotted line) across the interior smectic-*A* L_α ring at the same temperature with a ξ of 11.9 Å is shown for comparison. The in-plane wave vector $q_{\|}$ is normalized with respect to the intermolecular wave vector q_o.

significantly less than those found in other hexatic LC phases [5]. Since our ED data indicate an average intermolecular distance of 10.1 Å, which remains unchanged with decreasing temperature, the positional correlations in the L_{hex} phase appear to never extend appreciably beyond nearest neighbors and are decidedly liquid-like.

The L_{hex} phase seen here appears to be quite different from the hexatic phases that have been observed experimentally [4, 5] or predicted in the theory of 2D melting. According to the defect-mediated mechanism of 2D melting [2], the occurrence of a relatively small number of free dislocations in the hexatic phase destroys long-range translational order but not long-range BOO. The positional correlation length ξ is thus related to the density of defects. It is generally expected and also found experimentally in colloidal systems [16] that the density of defects deep in the hexatic phase is rather low, resulting in ξ being significantly larger than that in an ordinary liquid. In contrast, the L_{hex} phase we reported here exhibits the unexpected coexistence of well-developed BOO and liquidlike positional correlations (or a high density of defects).

The fact that this discovery occurs in a lyotropic system with a lamellar bilayer structure whose alkyl chains have an interdigitated arrangement in the bulk [9] leads us to speculate a possible role played by the hydration force [17]. Since the diameter of the head group of the nitrate salt molecule is about 5 Å while the actual in-plane distance between molecules is twice that, there could be at least two water molecules intercalated in between the hydrated nitrate ion and imidazole core on the two ends of adjacent molecules, resulting in an additional in-plane short-range repulsive hydration force, which has been estimated in other lyotropic systems to have a range of about one water molecule (~2.5Å) beyond the primary water shell [18]. Such repulsive hydration force results in much weaker correlations between the molecules of the lamellar bilayer films, causing a liquid-like radial correlations found in the L_{hex} phase. Our discovery also represents the first report of *in-plane* hydration force in lyotropic lamellar bilayer systems. In addition, our experimental results also suggest that the water molecules possessing larger kinetic energy in between those bilayers could have the chance of passing through the membrane-like bilayer films via the osmosis process, which is directly related to the hydration force [4, 19]. In lyotropic and biological systems, water is always viewed as important part of the entire system and also a necessary component which interacts with those bilayers or other biological materials at all times and thus easily affects the structural arrangement of the bilayer films. Our experimental results suggest that the intercalated water molecules or the plausible passage [17, 18] of water molecules through the membrane-like bilayers weakens the interaction force between the molecules of these bilayer films, and the resulting dynamic balance causes the surface of these lamellar bilayer films to exist in a state (see figure 1) qualitatively similar but quantitatively different from the conventional 2D hexatic and 2D liquid states reported previously in many other LC films [5].

Our discovery not only reinforces the existence of surface hexatic liquid in nature, but also further provides important information about the composition and organization of bilayers which are model systems for biological membranes. Besides, it provides new food for thought in regard to the location of the water molecules in these bilayer membrane films. Moreover, our unique environmental TEM can also open the door to new research areas linking the disciplines of physics, chemistry, biology, and medicine.

References

[1] J.M. Kosterlitz, D.J. Thouless. *J. Phys. C*, **6**, 1181 (1973).
[2] B.I. Halperin, D.R. Nelson. *Phys. Rev. Lett.*, **41**, 121 (1978); D.R. Nelson, B.I. Halperin. *Phys. Rev. B*, **19,** 2457 (1979).
[3] A.P. Young. *Phys. Rev. B*, **19**, 1855 (1979).
[4] W.H. de Jeu, B.I. Ostrovskii, A.N. Shalaginov. *Rev. Mod. Phys.*, **75**, 181 (2003).
[5] C.F. Chou, A.J. Jin, S.W. Hui, C.C. Huang, J.T. Ho. *Science*, **280**, 1424 (1998).
[6] C.Y. Chao, C.F. Chou, J.T. Ho, S.W. Hui, A.J. Jin, C.C. Huang. *Phys. Rev. Lett.*, **77**, 2750 (1996).
[7] C.Y. Chao, M.T. Hsu, W.J. Hsieh, J.T. Ho, I.J.B. Lin. *Phys. Rev. Lett.*, **93**, 247801 (2004).
[8] G.S. Smith, E.B. Sirota, C.R. Safimya, R.J. Plano, N.A. Clark. *J. Chem. Phys.*, **92**, 4519 (1990).
[9] C.K. Lee, H.W. Huang, I.J.B. Lin. *Chem. Commun.*, **19**, 1911 (2000).
[10] H.T. Chiang, V.S. Chenwhite, R. Pindak, M. Seul. *J. Phys. II (France)*, **5**, 835 (1995).
[11] R. Geer, T. Stoebe, C.C. Huang, R. Pindak, J.W. Goodby, M. Cheng, J.T. Ho, S.W. Hui. *Nature*, **355**, 152 (1992).
[12] A.J. Jin, M. Veum, T. Stoebe, C.F. Chou, J.T. Ho, S.W. Hui, V. Surendranath, C.C. Huang. *Phys. Rev. Lett.*, **74**, 4863 (1995).
[13] C.Y. Chao, C.R. Lo, P.J. Wu, T.C. Pan, M. Veum, C.C. Huang, V. Surendranath, J.T. Ho. *Phys. Rev. Lett.*, **88**, 085507 (2002).
[14] C.F. Chou, J.T. Ho, S.W. Hui, V. Surendranath. *Phys. Rev. Lett.*, **76**, 4556 (1996).
[15] G. Aeppli, R. Bruinsma. *Phys. Rev. Lett.*, **53**, 2133 (1984).
[16] C.A. Murray. in *Bond-Orientational Order in Condensed Matter Systems*, edited by K.J. Strandburg (Springer-Verlag, New York, 1992).
[17] J.N. Israelachvile. *Intermolecular and Surface Forces* (Academic Press, London, 1992).
[18] T.J. Mclntosh, S.A. Simon *Biochemistry*, **32**, 8374 (1993).
[19] H.I. Petrache, N. Gouliaev, S. Tristram-Nagle, R. Zhang, R.M. Suter, J.F. Nagle. *Phys. Rev. E*, **57**, 7014 (1998).