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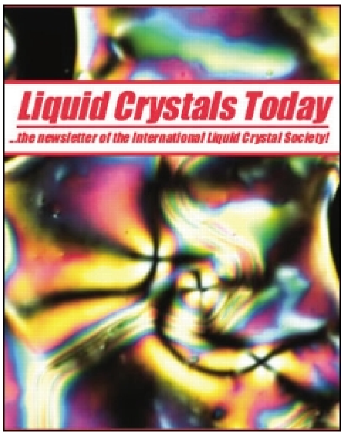

Liquid Crystals Today

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

65th Bunsen-Kolloquium, "Lyotropic Liquid Crystals" held at Pederborn, Germany, 14-15 October 1996

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To cite this Article Hiltrop, K. and Stegemeyer, H.(1997) '65th Bunsen-Kolloquium, "Lyotropic Liquid Crystals" held at Pederborn, Germany, 14-15 October 1996', Liquid Crystals Today, 7: 1, 9 — 11
To link to this Article: DOI: 10.1080/13583149708047663
URL: http://dx.doi.org/10.1080/13583149708047663

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65th Bunsen-Kolloquium

'Lyotropic Liquid Crystals'

held at Paderborn, Germany, 14–15 October 1996

Report by K. Hiltrop and H. Stegemeyer, Institute of Physical Chemistry, University of Paderborn, D-33095 Paderborn, Germany

Lyotropic liquid crystals (LLC) run through their phase sequence by variation of the composition of a mesogenic mixture of at least two components, one of them being water in most cases. The building blocks (structural units) of their long-range orientational order are either aggregates of amphiphilic molecules (micellar LLC) or macromolecules (polymeric LLC). A third species of LLC has been called 'chromonic' because they were first discovered in dye solutions; their mesogenic structure elements are aggregates as well. However, they are formed due to attractive van der Waals forces between the polycyclic dye molecules, in contrast to the micellar LLC which are believed to arise by the hydrophobicity of the amphiphiles expelling these moieties out of the water. In a certain sense LLC are related to their thermotropic analogues, but on the other hand there are distinct differences because the mesogenic unit of LLC is subjected to changes of size and shape depending on the thermodynamic parameters of the system. Structures of aggregates and their interrelation in different phases are objects of actual LLC research.

Figure 1. Logo of the 65th Bunsen-Kolloquium. Three randomly running hares aggregate to an ordered structure (with only three ears but two for every hare): tracery in the cloister of the Paderborn Cathedral (courtesy of M. Schumacher, Paderborn).

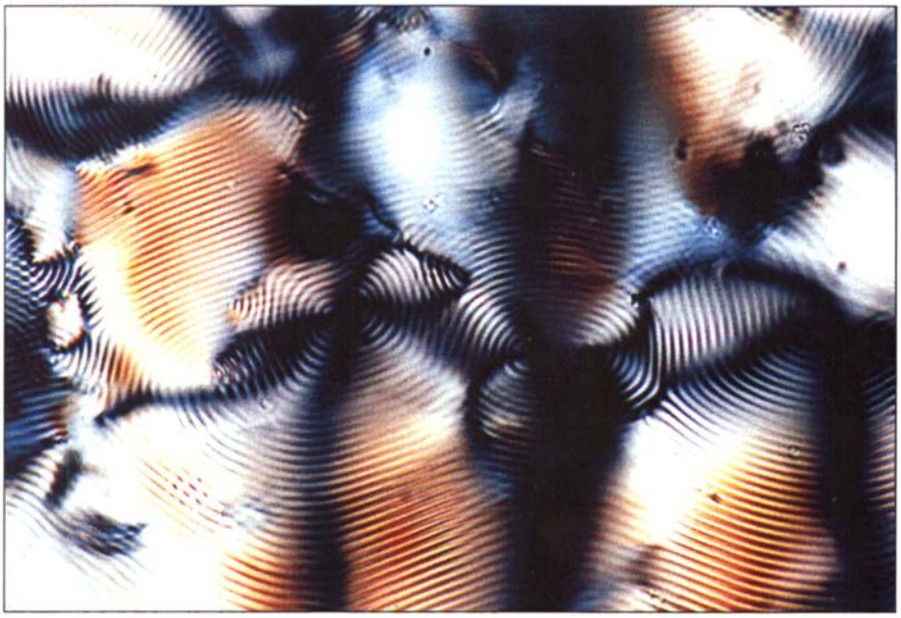

Figure 2. Fingerprint texture of a chiral nematic phase as seen in the polarizing microscope; the stripe distance corresponds to half of the helical pitch.

In contrast to thermotropic liquid crystals there is a lack of conferences especially devoted to lyotropics. Consequently leading scientists in the field were invited to present their results at the 65th Bunsen-Kolloquium which took place on 14–15 October in Paderborn, Germany, organized by H. Stegemeyer (Paderborn) H. Finkelmann (Freiburg) and W. v. Rybinski (Dusseldorf). The logo of the colloquium (Fig. 1) symbolizes the aggregation of independent units to an ordered structure.

The scientific part of the Bunsen colloquium consisted of four plenary lectures and ten invited lectures. In the following the most important contributions are briefly reviewed.

Phase behaviour of disc-like micellar systems

In his plenary lecture Neville Boden (University of Leeds, UK) reported on the properties of perfluorinated surfactants in binary mixtures with water. These systems exhibit a rather unusual phase diagram which made them very popular for study. The most extensively investigated example of these compounds is the caesium pentadecafluorooctanoate. One feature of these perfluoro LLC is the nematic phase of disc-like micelles existing over a wide range of temperature and concentration. Furthermore, the phase transition between the nematic and a lamellar phase can be induced by temperature variation which is also not often found with LLC. It was emphasized that the phase transition isotropic/nematic occurs at a well defined aspect ratio of the disc-like micelles, independent of the chain length and the headgroup of the surfactant. The transition nematic/lamellar was characterized as merely of the disorder/order type with unchanged aggregates. The disappearance of a two-phase region below a certain surfactant concentration was interpreted as a tri-critical point where the order of the phase transition changes from 1 to 2. In the lamellar phase consisting of discrete micelles at lower surfactant concentration the aggregates presumably develop into continuous bilayers at higher concentration. Obviously these perfluoro surfactant LLC behave in quite a similar manner to corresponding thermotropic mesophases.

Chiral lyotropic liquid crystals

Karl Hiltrop (University of Paderborn) dealt with the induction of phase chirality in nematic host phases of perfluorinated and 'normal' surfactants; moreover the observation of the phase transition nematic/lamellar by means of the phase chirality was discussed. It was shown that the above mentioned change of the phase transition order (i.e. the tricritical point) does not exist in the chiral samples; possibly it has been obscured by restricted resolution of the experimental method or instrument. In order to explain the still unknown mechanism of the phase chirality formation, a model of intramicellar chirality was proposed which postulates that the local orientational order of surfactant molecules within a disc-like micelle becomes chiral by the interaction with solubilized chiral dopants (double twist).

Keith Radley (University of Huddersfield, UK) was concerned with the occurrence of different chiral conformers of amino acid derivatives and their influence on the phase chirality. He found additivity of the chiral contributons of the *cis*- and *trans*-rotamers.

Intermediate structures between the classical mesophases

Recent work of Mike Holmes (University of Central Lancashire, UK) investigated liquid crystalline structures that are traversed by a system during a phase transition, e.g. lamellar to hexagonal. It became clear that there are thermodynamically stable intermediates which can be birefringent and of low viscosity. Up to now only optically isotropic and very viscous intermediate phases of cubic symmetry had been found. Enforced by inter-aggregate interaction, the new phases adopt non-uniform surface curvatures of their aggregates. An example of a rhombohedral mesh intermediate phase was dicussed in detail.

Brigitte Pansu (Université Paris Sud, France) described results on an intermediate phase with cubic symmetry existing between the hexagonal and the lamellar phase of a well known lyotropic mixture, namely sodium dodecylsulphate/octanol/water. However in this case the generally assumed structure of interpenetrating cylindrical aggregates is not compatible with the composition of the lyotropic mixture. Instead, a similar arrangement of ribbons fits the experimental data (space group Im3). The X-ray measurements were performed by scanning the beam through a concentration gradient sample.

Klaus Berger (Université Louis Pasteur, Strasbourg, France, formerly University of Paderborn) studied several sodium dodecylsulphate/co-surfactant/water systems and reported especially on the case of dodecanol. In a certain dodecanol concentration range his data could be explained by the assumption of a defective lamellar phase consisting of bilayers pierced by water filled holes. By polarizing microscopy a Schlieren texture was seen in a 'nematic' phase directly adjacent to the defective lamellar one. It was speculated that the structures of both phases might be strongly correlated. But what is the criterium for the classification of a phase ? Is it texture, is it alignability in electric or magnetic fields, or is it X-ray data?

Applications of lyotropic liquid crystals

Thomas Engels (Henkel KGaA, Dusseldorf, Germany) reviewed the wide range of technical applications of LLC. He demonstrated quite a lot of examples where the know-how of LLC is essential for the handling of processes during surfactant production as well as for the optimization of the efficiency of commercial surfactant products.

Christel Müller-Goymann (Technical University of Braunschweig, Germany) gave an introduction into lyotropic mesomorphism in pharmacy. Some non-steroidal anti-inflammatory drugs are capable of interactions with, e.g. phospholipids, thus forming structures ranging from liposomes via isotropic liquid crystalline gels to micellar solutions. Enhanced effectiveness by the application of certain drugs in a liquid crystalline state was emphasized, e.g. to enable sustained drug release and furthermore control skin permeation.

Structure/property relations of monomeric and polymeric amphiphiles

In a fervent presentation Avi Halperin (Institut de Chemie des Surfaces et Interfaces, Mulhouse, France) pointed out two main strategies for the design of polymeric amphiphiles. Amphiphilic monomers may be incorporated into the backbone of the polymeric chain, or non-amphiphilic monomers can be grouped into blocks. Three design parameters play an important role: (i) the number of incompatible units and their relative size, (ii) the chemical identity, rigidity etc. of the incompatible units, (iii) the topology of the chain. It became clear that flexible diblock copolymers of the type AB exhibit a close relationship to classical amphiphiles; on the other hand, more complex architectures give rise to specific polymeric properties.

Peter Fischer (University of Freiburg, Germany) reported on lyomesophases of side-chain polymer networks. By mechanical stress during the synthesis of the elastomers, anisotropy of the polymer coils can be induced and fixed in the system by further polymerization. Similar to corresponding thermotropic elastomers, uniformly aligned lamellar phases arise. Preliminary results showed a macroscopically anisotropic swelling behaviour of the lamellar phase on addition of water.

Chromonic lyotropic liquid crystals

Whilst the majority of the contributions were concerned with aqueous systems of surfactants, in the final section chromonic LLC were discussed. John Lydon (University of Leeds, UK) characterized this class of LLC by its structural unit: columns of molecules play the role of micelles in micellar LLC. Suited molecules often consist of extended, flat, rigid and aromatic systems which can be thought of as insoluble in one dimension. Besides the nematic and hexagonal phase of such columnar aggregates, also a more-ordered phase with an orthorhombic unit cell has been found. Furthermore, the existence of a lamellar structure, built up like a brick wall, has been demonstrated.

William Harrison (Kodak Limited, Harrow, UK) talked about so-called J-aggregates of certain cyanine dyes which had already been detected via their electronic spectra in the thirties by the late Gunter Scheibe (Munchen). These kind of dyes are used as additives to photographic suspensions with the aim of sensitization of silver halogenides. The planar, polycyclic dye molecules can associate by attractive van der Waals forces to form the J-aggregates which in turn can make up a liquid crystalline order. These LLC are extremely unusual systems because they can form at only 0.5 wt% dye. However, their phase behaviour is relatively simple as compared to that of micellar LLC due to order/disorder transitions of topologically invariant J-aggregates. The orientational order presumably arises mainly from long-range electrostatic repulsion between the aggregates of the ionic cyanine dyes.

During stimulating discussions the analogy of LLC to thermotropic systems was displayed as well as the necessity for different definitions. The colloquium was the first one of this kind within the Western hemisphere and has been sponsored by the Volkswagen-Stiftung and by the Henkel KGaA.