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A NEW LYOTROPIC LIQUID CRYSTAL PHASE

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ABSTRACT

A new lyotropic liquid crystal phase type has been identified using the polarizing microscope. The phase lies in a region between the nematic and the classical hexagonal. It is suggested the structure of the phase is related to the thermotropic smectic-A mesophase.

Amphiphiles which form lyotropic liquid crystals upon solvation give rise to a regular sequence of mesophases. In a detergent system with decreasing water and increasing decanol, the sequence is usually:- isotropic micellar, viscous isotropic, middle soap, cubic, lamellar, reverse cubic, reverse viscous isotropic and reverse micellar[1]. No binary system gives rise to all phase types although the solvation sequence is always maintained. It is well known that simple organic mesogens upon heating give rise to liquid crystals with various types of order.

the lower temperature liquid crystals usually have dimensional order and are generally known as smectics, while at high temperatures liquid crystals with only orientational order are known as nematics[2]. In thermotropic liquid crystals, from symmetry and order arguments, fourteen different smectic phase types can be predicted of which at least ten smectic phases types have been reported[3]. Recently it has been found that in the two binary systems cesium perfluorooctanate/heavy water (CsPFO/D_2O) and tetradecyltrimethylammonium benzenesulfonate/heavy water (MTABS/D_2O) the dimensionally ordered liquid crystals lamellar and middle soap phases, respectively, gave rise upon heating and solvation to the orientational ordered nematic phase[4]. A reassessment of the results in the MTABS/D_2O system with further experimental evidence will be discussed in this paper.

The detergent was prepared by dissolving commercial tetradecyltrimethylammonium bromide in methanol and adding excess silver oxide. After filtering, the methanol solution was neutralized with benzenesulphonic acid. The solution was evaporated to dryness and recrystallized several times from ethyl acetate and ethanol. A sample was made with the following composition 40% MTABS and 60% D_2O. The ingredients were weighed out into a test tube with a constriction in the middle. After the tube was heat sealed, the ingredients were homogeneously mixed by continuous heating and centrifuging. The phase retardation between the ordinary and extraordinary light ray was measured using a technique first described by Sénarmont in 1840[5] and later adapted for the polarizing microscope[6]. The method has been extended to measure birefringence[7] where the

sign of the retardation infers the sign of the birefringence. The sample was viewed using a polarizing microscope while subjected to the influence of a magnetic field as previously described[8]. The temperature here was controlled using a brass block sample holder through which water was circulated from a calora. The temperature was measured using a digital thermometer with an accuracy of ± 0.1°C.

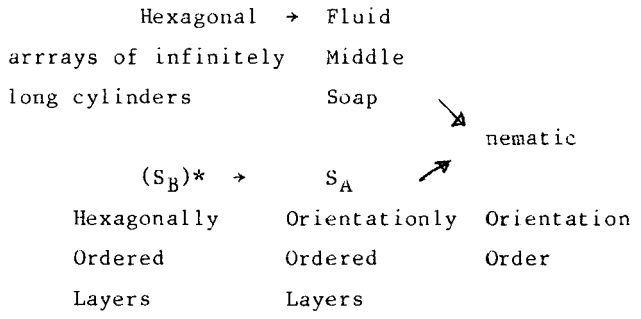
The figure 1 shows phase retardation in the sample as a function of temperature. The measurements were made by decreasing the temperature of the sample from the high temperature isotropic region with the magnetic field switched on. When the slope of the line is considered, eight different regions are signified. Regions I, II, III and IV were homogeneous phases whereas the regions between were assumed to be heterogeneous two phases regions. Region I is fluid and optically isotropic and presumably is an isotropic micellar solution. Region II was assigned as nematic. It was fluid and was oriented by the magnetic field in such a way as to indicate negative diamagnetic anisotropy. Region IV was assigned as the classical hexagonal where the phase structure is hexagonal arrays of infinitely long cylinders. The sample was rigid and did not flow, and was not oriented by the magnetic field. Region III could not be given a classical lyotropic structure. It was fluid similar to Region II but it was not oriented in the moderate magnetic field of 1 K gauss used here. It could well be oriented by a bigger magnetic field such as that of an nmr cryogenic magnet but such investigations were not made. The regions between the I, II, III and IV regions were designated as

heterogeneous two phase regions. The slopes were steep and presumably the retardation measurements were weighted averages. When thermostated at the appropriate temperature the samples overnight separated out into two layers. The liquid crystal regions II, III and IV all gave indications of being optically uniaxial and from the sign of the retardation, the sign of the birefringences was indicated in every case to be negative. The planar micrographic textures which were observed indicate a cylindrical micellar or closely related structure.

^2H_2O nmr over the liquid crystal region does not give any clear indication about structure. Upon cooling the sample from the isotropic region, a super imposed singlet and doublet spectrum was obtained which clearly indicates a heterogeneous two phase region. In the liquid crystal region the spectra are oriented indicating firstly a transition to a nematic phase. Presumably the macro orientation is maintained but not enhanced when cooled to the dimensional order phases. The slope of the increasing quadrupolar splitting is gradual and does not indicate where the onset of dimensional order liquid crystals occurs, or the onset of any two phase regions. The figure 2 shows a polar micrograph of a sample 20% MTABS/80% D_2O where the D_2O has dried out forming a concentration gradient. There are three main regions. The dark one is presumably isotropic micellar. The region with strongest briefringence has a textures characteristic of a hexagonal phase. There is only one region between the hexagonal and the isotropic region. The retardation measurements indicate this region is probably Region III. This would indicate nematics are not formed in

this binary system at room temperature contrary to the original report (4). The results indicate that Region III has a phase structure somewhere between a nematic and a hexagonal. The structure might be layers of orientational ordered cylinders of finite length. It is possible that there is a parallellism between this phase type and the smectic-A(S_A) in thermotropic liquid crystals.

In the MTABS/D_2O system a sequence of mesophase is encountered which has similarities to those found in thermotropic liquid crystals.



( )* indicates that although the hexagonal and S_B have some similarities such as optically uniaxiallily and rigidity, the two structures are not necessarily equivalent.

The investigation of lyotropic liquid crystals in respect to dimensional order is a very important field of research which warrants intensive investigation.

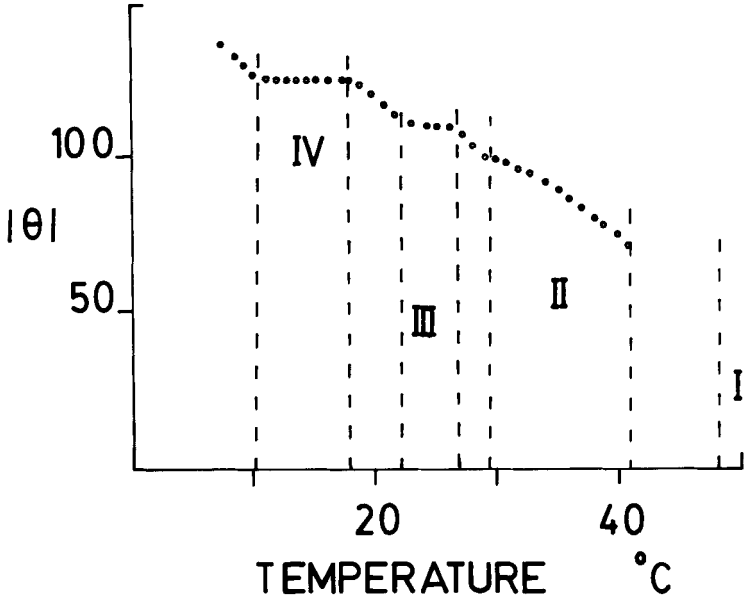


Figure 1 - Variation of $|\theta|$ the phase retardation between the ordinary and extra-ordinary ray of polarized light as a function of temperature. $|\theta|$ Represents the magnitude of the retardation where the sign was found negative, a result of negative birefringence. Sample composition was 40% MTABS and 60% D_2O.

Figure II - Photomicrograph of a concentration gradient, set up by allowing D_2O to evaporate from the edges of a 20% MTABS 80% D_2O sample held between a microscope slide and a cover slip. Temperature 22°C. The dark isotropic area has the highest D_2O concentration.

REFERENCES

1. P.A. Winsor, Chem. Rev., 68, 1 (1968).
2. G.H. Brown, J.W. Doane and V.D. Neff, "A Review of the Structure and Physical Properties of Liquid Crystals", C.R.C. pub., Cleveland (1971).
3. A. deVries, Mol. Cryst. Liq. Cryst., 63, 215 (1981).
4. N. Boden, K. Radley and M.C. Holmes, Mol. Phys., 42, 493 (1981).
5. H. de Sénarmont, Ann. chim. et phys. (2), 73, 337 (1840).
6. D.J. Goldstein, J. Microscopy, 91, 19 (1970).
7. K. Radley, Mol. Cryst. Liq. Cryst. Lett., in press.
8. M. Holmes, N. Boden and K. Radley, Mol. Cryst. Liq. Cryst., 100, 93 (1983).