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BIREFRINGENCE MEASUREMENTS IN LYOTROPIC NEMATIC PHASES

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ABSTRACT

Birefringence measurements have been made on lyotropic nematic phases prepared from the detergent tetradecyltrimethylammonium bromide. Assignments for the sign of the birefringence of the nematic disk and cylindrical phases of both positive and negative diamagnetic anisotropy have been made. It is suggested the classification of lyotropic nematic phases, based on the sign of the diamagnetic anisotropy or any other physical parameter, should be dropped. Classification should be in terms of thermodynamic properties, i.e. micelle structure.

Lyotropic nematic liquid crystals have been classified by means of the sign of the diamagnetic anisotropy from nmr measurements; and the observation of birefringence under a polarizing microscope[1,2]. Later nmr measurements showed that there were two types I and II of lyotropic nematics assigned from the signs of the diamagnetic anisotropy, positive and negative respectively[3]. These two types I and II of nematic phases were found by means of X-ray investigations to have two different micellar structures, cylinders and disks respectively[4,5]. It was later shown that the sign of the diamagnetic anisotropy could be changed by the inclusion of fluorocarbon or aromatics into the micellar structure, without inducing a phase change[6,7]. This lead to the classification of lyotropic nematics into four types $N_C^{\pm}$ $N_D^{\pm}$, where D and C represents a thermodynamic phase structural change from disks to cylinders and + and - signifies a change in the sign of the physical parameter, diamagnetic anisotropy, not necessarily involving a thermodynamic phase change[8].

In this communication preliminary birefringence measurements will be reported on all four types of lyotropic nematics. The present measurements were made on samples of lyotropic nematics derived from the detergents tetradecyl-trimethylammonium bromide and tetradecyl-trimethylammonium phenylsulphonate. The N_D^- and N_C^+ samples of nematic phases had the following composition weight: 28.38% detergent, 4.05% decanol, 6.76% CsCl and 60.81% D_2O; and 36% detergent and 64% D_2O respectively. The other samples, including N_C^- and N_D^- phase samples, were made by molar substitution of the phenyl sulphonate detergent into the first two. The samples of the various lyotropic nematic phases were prepared by weighing out the components carefully into a test tube with a constriction in the middle. The mixtures were then centrifuged and the tubes were flame sealed. After which the mixtures were homogeneously mixed by heating and centrifuging the mixture back and forth through the constriction. The N_D^- and N_D^+ lyotropic nematic phase samples align between glass plates to give pseudo isotropic textures. Their birefringence was measured by introducing the samples between the prisms of an Abbe refractometer. This method has been previously described[9]. The N_C^- and N_C^+ lyotropic nematic samples align parallel to the surface of glass plates and consequently the birefringence of these samples could not be measured by the above method. The birefringence in the cylindrical samples was measured using a polarizing microscope. This technique was first described by Sénarmont in 1840[10] and was adapted later for a polarizing microscope[11]. The technique involves the determination of the phase retardation between the ordinary and extraordinary vector of polarized light. This method is one order of magnitude more sensitive than the Abbe refractometer. By combining the two methods it was possible to assign the sign of the birefringence of each type of lyotropic nematic sample consistently.

The preliminary results are shown in the diagram. The full and open circles signify mesophases of positive and negative diamagnetic anisotropy, respectively. It can be clearly seen that, when aromatic ions are introduced into the micellar structure, which would change the sign of the diamagnetic anisotropy, that the magnitude of the birefringence increases with no sign change.

In the lyotropic nematic samples used here, the sign of the birefringence was found to be concomitant with the micellar structure; i.e. cylinders and disks for negative and positive birefringence respectively. It might then be expected that the measurement of the sign of the birefringence would provide an indication of the micellar structure. Caution should be advised because it has been shown in some lamellar phases that the sign of the birefringence is a function of water content[12]; however this phenomenon has not been observed for nematic materials.

It is preferable that the designation of the sign of the magnetic anisotropy be dropped as a means of classifying lyotropic nematic phase. The designation N_C and N_D should be kept, as this assignment is based on thermodynamic properties. Knowledge of the sign of the diamagnetic anisotropy was important to nmr spectroscopists using iron magnets but with the introduction of superconducting nmr systems, mesophase designation according to the sign of the diamagnetic anisotropy loses much of its significance to the modern nmr spectroscopist, because homogeneous alignment of samples is obtained in superconducting magnet systems independent of the sign of the diamagnetic anisotropy, i.e. samples with either diamagnetic anisotropy sign can be spun in a superconducting magnet. If the classification was maintained and more subgroups introduced when other physical parameters, such as birefringence, were measured, the number of mesophase designations would become numerous and the classification system would become unwieldly and ambiguous.

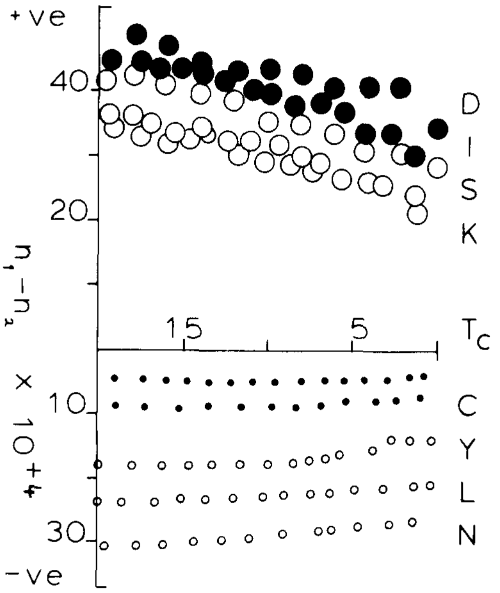

FIGURE I - variation of birefringence n_1-n_2 with temperature in lyotropic nematics, where $T_c = 0$ is the upper temperature for the onset of the nematic phase. The disk phases DISK were found to have positive +ve birefringence while the cylindrical phases CYLN were found to have negative -ve birefringence. The numerical birefringence values for both cylinders and disks increases with increasing % molarity of tetradecylammonium phenyl sulphonate detergent (0, 15, 30, 45, 60% M).

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