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THE EFFECT OF ADDED ELECTROLYTE ON THE PHASE BEHAVIOUR OF THE MICELLAR LIQUID CRYSTAL SYSTEM CAESIUM PENTADECAFLUOROOCTANOATE / WATER.

A thesis presented in the partial fulfilment
of the requirements for the degree
of Master of Science
in Chemistry at
Massy University

Ashok Neil Parbhu

1990

ABSTRACT

This thesis is a study of the effects of added electrolyte (CsCl) on the aggregate structure and hence on the macroscopic phase behaviour of the micellar liquid crystal system caesium pentadecafluorooctanoate / heavy water. The techniques used were ^{2}H, ^{133}Cs and ^{35}Cl N.M.R. spectroscopy. The relationship between the quadrupole splittings of these nuclei and the structure and order of the liquid crystal mesophase is discussed in detail. A partial phase diagram for the CsPFO / CsCl / $^{2}H_2O$ system at a fixed 1 : 1 weight ratio of CsPFO to $^{2}H_2O$ is presented. The phase behaviour has been compared with that for a hydrocarbon surfactant. The changes in phase transition temperatures with added salt has been shown to be due to an increase in the micellar size. This increases with added electrolyte but is constant along the lamellar to nematic transition line. It is shown that there is a strong coupling between micelle size and the micellar fractional surface charge.

Specifically the effect of caesium chloride on the CsPFO / $^{2}H_2O$ system was investigated using ^{2}H, ^{133}Cs and ^{35}Cl N.M.R. spectroscopy to probe the micellar structure and identify the phase transitions. A full description of the N.M.R theory pertaining to this work is presented.

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1. INTRODUCTION

Lyotropic liquid crystals were known to the ancient world in the form of concentrated soap solutions. These viscous solutions are now refered to as smectic (Greek: σμῆγμα = soap) phases. Until recently however scientists have paid little attention to them other than to "rough out" phase diagrams for mainly the commercial purposes of soap and detergent manufacturing.

Lyotropic liquid crystals are composed of two or more components, where one of the components is a an amphiphile and the other essential component is a solvent (usually water). An amphiphile is a molecule which consists of a polar head group and non-polar hydrophobic chain. Examples of amphiphile molecules are soaps, phospholipids, synthetic detergents and some proteins. Other components of lyotropic liquid crystals system can be alcohols and/or inorganic salts. Phase transitions in these systems can be brought about by both temperature and composition changes.

Historically the general belief was that amphiphiles on dissolution in water, would form small discrete micelles in dilute solutions [1], and liquid crystals with extended aggregate structures in concentrated solutions [2,3,4]. The small discrete micelles can be spherical, disc or rod shaped, while the extended aggregate structures are cylinders or bimolecular layers of indefinite size. As a result of this artificial separation research into micellar solutions and lyotropic liquid crystals has evolved as separate fields of endeavour.

Another type of liquid crystal which was only discovered in 1888 [5] are the thermotropic liquid crystals, which typically consist of long lathe-like molecules or disk shaped molecules. These systems can be single components, or mixtures of similar types of molecules. As their name suggests phase changes are brought about by temperature changes. The long thin molecules undergo a sequence of phase transitions from isotropic where there is no long range orientational order to nematic (Greek: νῆμα = thread) where there is long range orientational order, to smectic where there is long range orientational and translational order of the symmetry axes of the molecules, on decreasing the temperature. The corresponding sequence for disk shaped molecules is isotropic to nematic to columnar. The commercially exploitable phase is the nematic phase, and the closely related cholesteric phase formed from molecules with chiral centres. The useful property of these phases is that they can be aligned in a magnetic or electric field as a consequence of anisotropy in their diamagnetic or dielectric susceptibilities. The molecules therefore align themselves in the force field so as to minimize their energy by aligning along (+ve susceptibility) or at 90^0 to (-ve susceptibility) the direction of the field. This property has resulted in massive commercial exploitation of thermotropic liquid crystals starting in the early 70's .

At the end of the 60's a magnetically orientatable lyotropic phase was discovered [6] which by analogy with the thermotropic liquid crystals was given the title nematic phase. This discovery has lead (albeit slowly at first) to renewed interest in lyotropic liquid crystals. Several more lyotropic nematic phases have now been discovered.

The early reported nematic phases were located over narrow concentration ranges in complex mixtures of amphiphile, solvent and salts or alcohols such as the sodium decyl sulfate/decanol/water system which exhibits a nematic phase, for a fixed weight fraction of decanol of 0.07, over an amphiphile weight fraction range w from 0.34 to 0.39 [7]. For a long time it was thought that a third component (salt or alcohol) was essential for the production of stable nematic phases. However, several binary systems which exhibit nematic phases have now been observed. The decylammonium chloride(DACl)/water system for example, which was long thought to require salts to form a stable nematic phase, exhibits such a phase over the range w = 0.42 to 0.49 [8]. The disodium cromoglycate/water system also exhibits a nematic phase from w = 0.10 to 0.15 [9]. These are examples of hydrocarbon amphiphiles where the nematic range is typically limited to very small concentration ranges. On the other hand fluorocarbon amphiphiles have been observed to exhibit nematic phase regions over large temperature and concentration ranges in aqueous solutions. These include the caesium , ammonium and tetramethylammonium salts of pentadecafluorooctanoic [10,11,12] and heptadecafluorononononoic acids [12,13]. To date the only system for which a high resolution phase diagram has been published is the caesium pentadecafluorooctanoate (CsPFO) / water system [10,14]. It is likely that other soaps of the perfluorinated carboxylic acids will produce nematic phases but solubility limitations can prevent these from being observed [12].

The obvious question is, what is the molecular property which allows the phase to become oriented in a magnetic field? Thermotropics become orientated in the nematic phase as a result of the diamagnetic anisotropy of the molecules. In lyotropic liquid crystals, in the nematic phase, it has been shown that the structural unit consists of anisotropic micelles. The first report of a micellar nematic phase [15,16] has been followed by many more and it is now clear that uniaxial nematic micellar phases can be prepared from both ionic [17] and non-ionic [18] amphiphiles.

Nematic micellar mesophase are classified in terms of the micellar structure. There are three distinct structural varieties of anisotropic micelle: rod shaped, disc shaped, or biaxial micelles. Rod shaped micelles, maybe actual rods with semi-spherical end caps or prolate ellipsoids, form a nematic mesophase designated as 'canonic' (Greek : κανῶν = rod) and denoted N_C. The disc shaped micelles, maybe flat discs, discs with hemispherical rims or oblate ellipsoids, form a nematic mesophase designated as discotic

(Greek : δισχοξ = quoit) and denoted N_D. There are also biaxial micelles, maybe asymmetric ellipsoids or biaxial platelets, which form biaxial nematic mesophases denoted as N_B [19]. These classifications can be sub-classified as either + or - depending upon the diamagnetic susceptibility anisotropy of the aggregate, defined by $\Delta\chi = \chi_{//} - \chi_{\perp}$. $\chi_{//}$ and $\chi_{\perp}$ are respectively the components of the aggregate diamagnetic susceptibility parallel and perpendicular to the director. A micelle with a positive diamagnetic susceptibility anisotropy will align with its symmetry axis parallel to a magnetic field and one with a negative anisotropy will align perpendicular to the field.

Recently the CsPFO / water system has been shown to undergo a series of order-disorder transitions analogous to the isotropic to nematic to smectic A series of transitions in thermotropic liquid crystals. Other systems also exhibit this behaviour [20]. In all of these systems there exists a concentration regime where the nematic to lamellar transition simply involves the imposition of translational order on decreasing the temperature. There is no reason to suppose that this behaviour is unique to the above systems and it is quite possible that there is universal behaviour in both thermotropic and lyotropic liquid crystals.

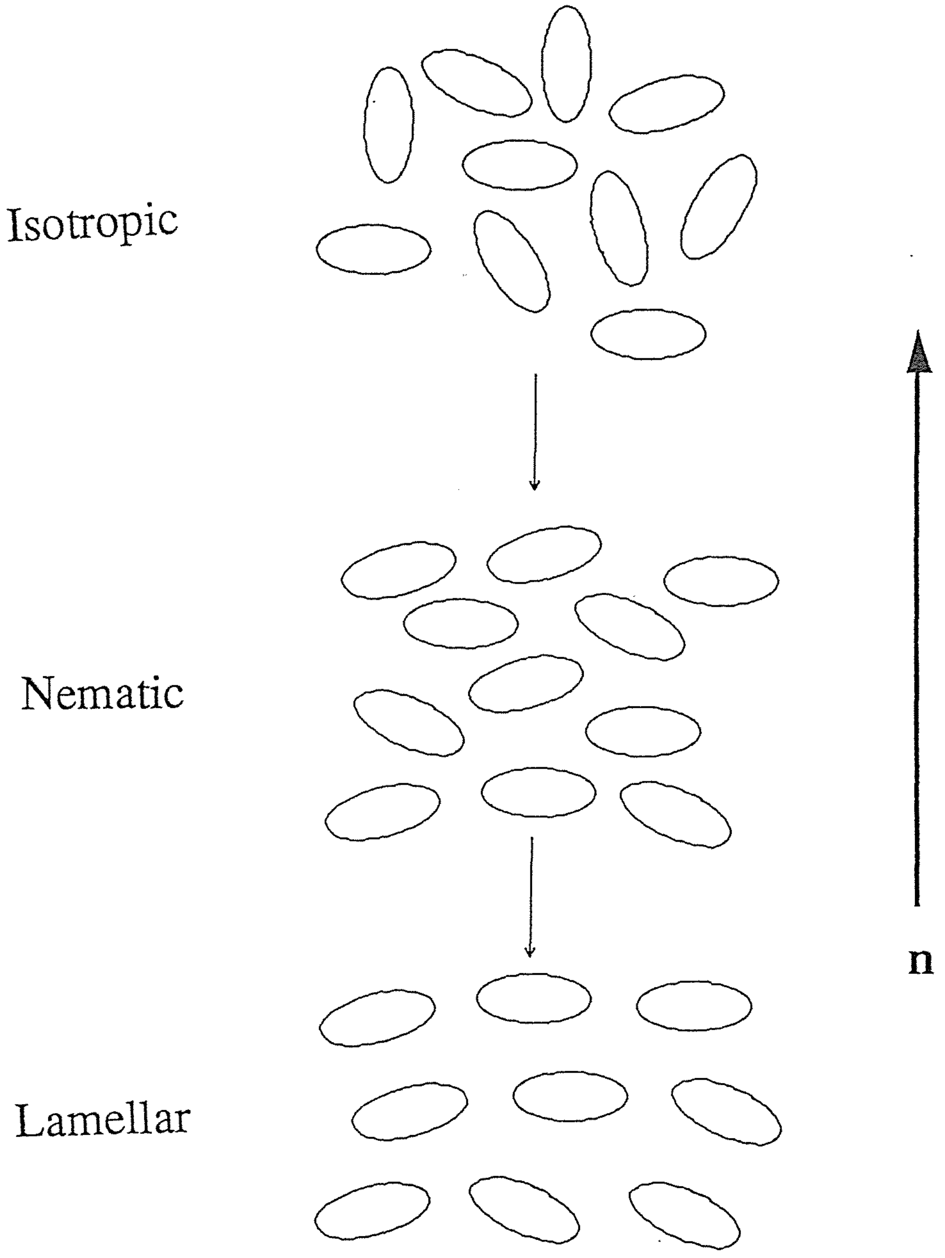
The nature of the interaggregate interactions which drive the phase transitions must however be different as the fundamental structural unit in thermotropics is an anisotropic molecule while in lyotropics it is an anisotropic charged aggregate. The driving force of thermotropic organization is attraction between cores of lathe-like or disc-shaped molecules while for lyotropics it is the repulsive interaction between charged aggregates that dominates (+ve or -ve depending on the nature of the head group) [21] , although there is evidence that long range attractive potentials are also involved [22]. Another complication in lyotropic liquid crystals is that the size and shape of the aggregate varies with temperature and composition, i.e. it does not have fixed dimensions, and the packing fraction of the micelles is relatively low compared with that for thermotropics. By modifying the shape and size of the micelle (aggregate) it should be possible to produce liquid crystals with "designer" properties, and in particular nematic phases with exploitable qualities. One possible way to effect micelle size and shape is to alter the counter-ion binding at the micellar surface. This will alter the charge density at the surface and will also moderate the intermicellar interactions.

The aim of this study was to examine the effect of added salt on the phase behaviour of the CsPFO / ^2H_2O system. In addition it was hoped to relate the phase behaviour to the changes in the size and/or shape of the micelles, and to see if these changes could be related to the degree of counter-ion binding.

The CsPFO/CsCl/^2H_2O system was chosen for this study because as a system it has many attractive features. Firstly, the CsPFO/^2H_2O system exhibits an N_D^+ phase over a wide range of both concentration (0.225 to 0.632 weight fraction, w, of CsPFO) and temperature (285.3 to 351.2 K) [10] . This phase lies between an isotropic micellar solution phase I to higher temperatures and a lamellar phase to lower temperatures. There is no detectable change in the size of the discoid micelle at the transition from N_D^+ to lamellar phase [21,23] which suggests that in the lamellar phase the small discoid micelle is stable with respect to the classical bilayer, i.e. it is an L_D phase. Secondly, because it is a simple two component system the effect of added salt will be clear and thirdly, the phase transitions are a simple series of order-disorder transitions as demonstrated in figure 1 .

Another advantage of the system is that because the nematics phase has positive diamagnetic susceptibility the local director will align along the director of a magnetic field to give a macroscopically aligned uniaxial mesophase. This is a particularly useful

Figure 1. Schematic representation of order-disorder transitions in a system of discoidal micelles. The director **n** represents the preferred orientation of the micelle symmetry axis. In the nematic phase there is the imposition of orientational ordering of the symmetry axes and in the lamellar phase positional ordering of the centre of masses is also present.


Isotropic
Nematic
Lamellar
n

property for the detection of phase transition temperatures. These features have obviously appealed to many other researchers as the CsPFO/^2H_2O system and some of its analogs have been extensively investigated. The main reason for its popularity is the published high resolution phase diagram of the system which is the only one so far published [10]. In particular the system has attracted the attention of physicists who have studied the effect of the counter-ion, alcohols, salts, and mixed amphiphiles on the pretransitional behaviour at the I to N_D^+ transition [24,25,26]. The N_D^+ to L_D transition on the other hand has received little attention to date. The concentration chosen to study the effects of added salt was w = 0.5, at this concentration the N_D^+ to L_D transition is first order. In the binary system the transition becomes second order on decreasing w at a tricritical point Tcp (w = 0.43, T = 304.80 K). We have chosen CsCl as the salt to examine the effect of an electrolyte, because in having a common cation for the salt and the amphiphile, there are no complications from the effects of competitive (selective) ion binding at the micellar surface.

All investigations into both the mesophase behaviour and the micellar structure were conducted by examining the NMR of quadrupole nuclei, of which there are three useful ones in the CsPFO/^2H_2O/CsCl system. The ^2H quadrupole splittings of ^2H_2O have been shown to reflect mesophase order as well as aggregate shape and size [10] and ^{133}Cs quadrupole splittings in addition to the above depend also on the degree of counter-ion binding [14]. The ^{35}Cl quadrupole splittings will reflect the degree of coion binding.

A major part of this work involved the elucidation of a precise phase diagram. A strong criticism of previous work on lyotropic liquid crystals is that they have been done on poorly defined systems with inadequate (at best) phase diagrams. In this report the phase diagram for the system CsPFO/^2H_2O/CsCl will be presented first. The weight ratio of CsPFO to ^2H_2O is held constant at 0.5 (which represents a mole ratio of 1 to 27.3) and the phase transition temperatures are plotted against the weight fraction of CsCl (w_e). Samples will be identified in the text according to their w_e values. The techniques used to define the phase diagram will follow its presentation.