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LYOTROPIC MESOMORPHISM IN MICELLAR LIQUID  
CRYSTALS FORMED FROM AQUEOUS SOLUTIONS OF THE  
SALTS OF PENTADECAFLUOROCTANOIC ACID.

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A thesis presented in accordance

with the requirements for the degree of Doctor of Philosophy.

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## ABSTRACT

High resolution phase diagrams for the caesium pentadecafluorooctanoate (CsPFO)/water and the ammonium pentadecafluorooctanoate (APFO)/heavy water systems have been determined, together with a partial phase diagram, in the liquid crystal phase transition regime, for the APFO/water system. In all three systems a discoidal nematic ( $N_D^+$ ) phase occurs over an extensive concentration and temperature range. This phase is intermediate to an isotropic micellar solution phase (I), to higher temperatures/lower concentrations and a micellar lamellar phase ( $L_D$ ) to lower temperatures/higher concentrations. The distinctions between the phase diagrams lies in the temperature and composition of the phase transitions. A variety of techniques have been used to delineate these temperatures including  $^2H$ ,  $^{14}N$  and  $^{133}Cs$  NMR spectroscopy, DSC and electrical conductivity. The NMR method is the main technique and  $^{133}Cs$  NMR in particular has proved to be an excellent nucleus for the precise detection of phase transition temperatures. It is the first time  $^{133}Cs$  NMR has been used for this purpose. The NMR measurements show a preference for counterion binding to sites of lowest surface curvature.

Isotope effects are shown by both the CsPFO and the APFO systems. The overall effect on substituting heavy water for water is to raise the phase transition temperatures, by about 3 K at a volume fraction amphiphile  $\phi = 0.1$  and by about 1 K at  $\phi = 0.4$ . The isotope effect is caused by an increase in micelle size in heavy water as a result of an enhanced hydrophobic effect. Isotope effects are also shown in a study undertaken on the thermodynamics of micellization in the CsPFO/water system. The cmc's in heavy water at a given temperature occur at higher concentrations than those in water, a result which is opposite to the isotope effect in hydrocarbon surfactant systems. It is shown that small changes in both the fraction of bound ions and the aggregation numbers between the two systems have a profound effect on the calculated thermodynamic parameters. A full understanding of the thermodynamics of micellization would require precise determinations of these quantities.

The effect of substituting  $\text{Cs}^+$  ions for  $\text{NH}_4^+$  ions is to raise the temperature of the liquid crystal phase transitions by about 23 K at a given volume fraction. The reason for this is that the micelles in the APFO/water system are smaller than those in the CsPFO/water system for any given volume fraction and temperature. This is probably due to the greater ability of the  $\text{Cs}^+$  ions to reduce the electrostatic repulsion between the anionic head groups in the micelle which leads to a reduction in micelle surface curvature and an increase in micelle size.

$^2\text{H}$  NMR has been used to monitor magnetic-field induced order in an isotropic solution of discoidal micelles of CsPFO on approaching a transition to a nematic phase. The field induced order is revealed as a quadrupole splitting of the isotropic signal which is first observed, at the field strength of the experiment (6.34 T), at a temperature approximately 80 mK higher than the upper boundary to the transition ( $T_{\text{IN}}$ ). The splitting increases rapidly with decreasing temperature and diverges as a hypothetical second-order transition to the nematic phase is approached at  $T^*$ . The divergence follows a  $(T_{\text{IN}}-T^*)^{-1}$  dependence as predicted by molecular field theory. At  $T_{\text{IN}}$  the divergence is quenched and in the biphasic region the quadrupole splitting is constant. This facilitates the precise determination of  $T_{\text{IN}}$  and  $(T_{\text{IN}}-T^*)$ . This latter quantity, which was measured over the surfactant weight fraction  $w$  range of  $w = 0.15$  to  $w = 0.35$ , approaches zero (i.e becomes second order) only at infinite dilution.  $T_{\text{IN}}-T_{\text{NI}}$ , which is more easily measured than  $T_{\text{IN}}-T^*$  is shown to be an alternative measure of the strength of the isotropic to nematic transition.

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Abbreviation used in this Thesis

<b>B</b>	magnetic field
$\beta_A$	fraction of ammonium ions bound to the surface
$\beta_{Cs}$	fraction of $Cs^+$ ions bound to the surface of the micelle
$\chi$	nuclear quadrupole coupling constant
cmc	critical micelle concentration
CsPFN	caesium heptadecafluorononanoate (perfluorononanoate)
CsPFO	caesium pentadecafluorooctanoate (perfluorooctanoate)
$\delta_{\alpha\beta}$	Kronecker delta
DACl	decylammonium chloride
$\Delta\chi$	diamagnetic susceptibility anisotropy
$\Delta\tilde{\nu}$	quadrupole splitting
$\Delta\nu_{1/2}$	linewidth at half height
DSC	differential scanning calorimetry
DSCG	disodium cromoglycate
e	electronic charge
FID	free induction decay
$\gamma$	magnetogyric ratio
$g_N$	nuclear g factor
$\eta$	asymmetry parameter
I	nuclear spin quantum number
$\kappa_{\perp}$	conductivity perpendicular to the director
$\kappa_{\parallel}$	conductivity parallel to the director
$\mu_N$	nuclear magneton
MTAB	tetradecyltrimethylammonium (myristyltrimethylammonium) bromide
<b>n</b>	mesophase director
n or $\tilde{n}$	micellar aggregation number
$N(CH_3)_4PFN$	tetramethylammonium heptadecafluorononanoate
$n_{\alpha}$	direction cosines of the nematic symmetry axis

NH <sub>4</sub> PFN	ammonium heptadecafluorononanoate
NH <sub>4</sub> PFO	Ammonium pentadecafluorooctanoate
P	spin angular momentum
$\langle P_2(\cos\alpha) \rangle_s$	shape factor
Q	nuclear electric quadrupole moment
q	electric field gradient at the nucleus
q <sub>zz</sub>	component of the nuclear quadrupole-electric field coupling parallel to the magr
S <sub>αβ</sub>	lowest rank orientational ordering tensor
SDS	sodium decyl sulphate
σ <sub>γγ</sub>	components of the chemical shift tensor
σ <sub>I</sub>	chemical shift of the isotropic phase
S <sub>O-D</sub>	order parameter relating the average orientation of the O- <sup>2</sup> H bond
T <sub>2</sub> <sup>*</sup>	apparent value of T <sub>2</sub>
T <sub>1</sub>	longitudinal or spin-lattice relaxation time
T <sub>2</sub>	transverse or spin-spin relaxation time
x <sub>A</sub>	mole fraction of amphiphile
x <sub>W</sub>	mole fraction of water

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Nana Donald

who passed away this year before the completion of my

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