

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

**Self-Assembly and Self-Organisation of Discotic  
Micelles formed in Aqueous Solutions of the Salts  
of Fluorinated Carboxylic Acids**

**Ashok Neil Parbhu**

**Department of Chemistry and Biochemistry**

**Massey University**

**New Zealand**

*Submitted in accordance with the requirements*

MASSEY UNIVERSITY



1061646438

*degree Doctor of Philosophy*

**March 1994**

## Abstract

The phase behaviour of a series of discotic micellar liquid crystal systems found in aqueous solutions of perfluorinated carboxylic acids has been determined mainly by the use of  $^2\text{H}$  and  $^{133}\text{Cs}$  NMR. All the systems exhibited an isotropic micellar solution phase which underwent transitions to first a micellar nematic  $\text{N}_\text{D}^*$  and then a micellar lamellar  $\text{L}_\text{D}$  phase on decreasing temperature or increasing the surfactant concentration. It was found that the self-organisation could be understood within the framework of a hard particle interaction and the changes in the phase transition temperatures on the addition of salt, change of counter-ion, and substitution of different chain length fluorocarbons were the result of changes in the micellar self-assembly.

The effect of amphiphile chain length was investigated by studying the caesium salts of perfluorinated carboxylic acids with chain lengths of 7, 9 and 10 carbons, in  $^2\text{H}_2\text{O}$ . A comparison with the caesium pentadecafluorooctanoate ( $\text{CsPFO}$ )/ $^2\text{H}_2\text{O}$  system shows the four systems exhibit universal phase behaviour with the phase transition temperatures at any given volume fraction of surfactant being simply displaced in temperature. In addition, the variation in the axial ratio of the discotic micelles along the transition lines has been established from the magnitudes of the  $^2\text{H}$  quadrupole splittings of  $^2\text{H}_2\text{O}$ . It has been shown that for any given thermodynamic state of the system axial ratios of the discotic micelles decrease with increasing chain length, *i.e.*: the micelle aggregation number increases. At the phase transition temperatures, however, the micelles have the same axial ratio irrespective of the length of the fluorocarbon chain.

The influence of inorganic electrolyte on the mesophase behaviour has been studied in the  $\text{CsPFO}/\text{CsCl}/^2\text{H}_2\text{O}$  and ammonium pentadecafluorooctanoate ( $\text{APFO}$ )/ $\text{NH}_4\text{Cl}/^2\text{H}_2\text{O}$  systems. The addition of electrolyte has the effect of increasing the phase transition temperatures in both systems.  $^2\text{H}$  NMR has been used in conjunction with low angle x-ray scattering to probe changes in the micelle structure as a function of electrolyte. It has been shown that electrolyte promotes growth of the micelle, *i.e.* a decrease in the axial ratio. But, as in the case of changing the chain length, the axial ratio of the discotic micelle is the same at the phase transition temperatures for any given volume fraction of amphiphile.

The role of the counter-ion and co-ion have also been established by  $^{133}\text{Cs}$  and  $^{35}\text{Cl}$  NMR. The effect of counter-ion has been investigated by progressively substituting APFO for CsPFO on a mole for mole basis. The  $\text{Cs}^+$  ions are shown to be preferentially "bound" over  $\text{NH}_4^+$  ions, but the micelle size is the same at the phase transition temperatures. Co-ion effects on the phase behaviour of the added salt systems has been probed by substitution of  $\text{Cl}^-$  ions with  $\text{F}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  ions. It has been shown that the co-ion has no significant effect on the phase behaviour.

# Table of Contents

List of Symbols	vi
List of Abbreviations	x
Acknowledgments	xi
<b>Chapter 1</b>	
Introduction.....	1
References.....	8
<b>Chapter 2</b>	
Materials and Methods.....	10
2.1 Chemicals.....	10
2.2 Preparation Of Samples.....	11
2.2.1 NMR Sample Preparation.....	11
2.2.2 Polarizing Optical Microscopy Sample Preparation.....	13
2.2.3 Densitometer Sample Preparation.....	13
2.2.4 Qualitative Phase Detection Sample Preparation.....	14
2.3 Instrumentation.....	14
2.3.1 Nuclear Magnetic Resonance ...	14
2.3.1.1 NMR Temperature Control and Measurement.....	15
2.3.2 Polarising Microscopy.....	17
2.3.2.1 Polarising Microscopy Temperature Control and Measurement.....	17
2.3.3 Density Measurements.....	17
2.3.3.1 Density Temperature Control and Measurement.....	19
2.3.4 Qualitative Phase Detection.....	19
2.3.4.1 Qualitative Phase Detection Temperature Control and Measurement.....	19
References.....	19
<b>Chapter 3</b>	
NMR.....	20
3.1 The Zeeman Interaction.....	20
3.2 Quadrupole Splitting.....	21
3.2.1 Deuterium Quadrupole Splitting.....	24
3.2.2 Caesium Quadrupole Splitting.....	25
3.2.3 Chlorine Quadrupole Splitting.....	25

3.3 $^{133}\text{Cs}$ Chemical Shift Anisotropies.....	26
3.4 Appearance of NMR Spectra.....	27
3.5 Determination of Liquid Crystal Phase Boundaries .....	31
3.5.1 Isotropic-to-Nematic Phase Transition.....	31
3.5.2 Lamellar-to-Nematic phase transition boundary .....	36
3.5.3 Lamellar-to-Isotropic phase transition boundary .....	40
References.....	42

## Chapter 4

Theories of Self-Assembly and Self-Organisation .....	43
4.1 Self-Assembly Models.....	44
4.1.1 Phenomenological Approach to Self-Assembly .....	44
4.1.2 Free Energy Approach to Self-Assembly.....	46
4.2 Self-Organisation Model.....	51
4.2.1 Self-Organisation in Reversibly Assembling Lyotropic Systems .....	51
References.....	55

## Chapter 5

### Effect of Amphiphile Chain Length on the Self-Assembly and Self-Organisation of Micelles of the Caesium Salts of Perfluorocarboxylic Acids in Aqueous

Solutions .....	56
5.1 Introduction .....	56
5.2 The Phase Behaviour.....	56
5.3 Aggregate Size Along Phase Transition Boundaries .....	60
5.4. Comparison of Phase Behaviour with Hard Particle Models.....	66
5.4.1. Effect of Changing Chain Length on Micelle Size.....	68
5.4.2 Effect of Temperature on Micelle Size .....	70
5.5 Concluding comments .....	73
References.....	74

## Chapter 6

### Effect of Added Electrolyte on the Self-Assembly and Self-Organization in the

APFO/ $^2\text{H}_2\text{O}$ and CsPFO/ $^2\text{H}_2\text{O}$ Systems .....	76
6.1 The NMR Model to Probe Aggregate Structure.....	76
6.2 Ternary Systems.....	81
6.2.1 APFO/ $\text{NH}_4\text{Cl}/^2\text{H}_2\text{O}$ System.....	81
6.2.2 CsPFO/ $\text{CsCl}/^2\text{H}_2\text{O}$ System .....	91

6.2.2.1 CsPFO/CsCl/ <sup>2</sup> H <sub>2</sub> O System at a fixed mass ratio of CsPFO to <sup>2</sup> H <sub>2</sub> O of 1 : 1 .....	91
6.2.2.2 CsPFO/CsCl/ <sup>2</sup> H <sub>2</sub> O System at a fixed mass ratio of CsPFO to <sup>2</sup> H <sub>2</sub> O of 1 : 4.....	98
6.2.2.3. Effect of Electrolyte on the First Order Nematic-to- Lamellar Transition .....	102
6.2.2.4 CsPFO/CsCl/ <sup>2</sup> H <sub>2</sub> O Triangular Phase Diagrams .....	102
6.3 Discussion.....	111
6.3.1 Effect of Electrolyte on Self-Assembling Systems.....	111
6.3.2 Influence of Electrolyte on T <sub>cp</sub> .....	116
6.3.3 The Influence of Co-ions on the Phase Behaviour.....	118
6.3.4 Field Induced Order.....	121
References.....	127

## Chapter 7

Effect of Counter-Ion Identity on the Self-Organisation and Self-Assembly .....	129
7.1 Phase Behaviour of the APFO/CsPFO/ <sup>2</sup> H <sub>2</sub> O system.....	129
7.2 Micelle Size at the T <sub>NI</sub> and T <sub>LN</sub> Transitions.....	132
7.4 Counter-Ion Binding .....	132
7.5 Conclusion .....	134
References.....	135

## Appendix A

Phase Transition Temperatures.....	136
------------------------------------	-----

## Appendix B

Quadrupole Splittings at the Phase Transitions.....	141
---	-----

## Appendix C

Density Measurements.....	149
References.....	150

## List of Symbols

$a$	(1) head group area (2) length of the minor axis
$a/b$	micelle axial ratio
$\alpha'$	contribution of a monomer in the toroidal, semicylindrical rim to the excess free energy
$B$	magnetic field
$b$	length of the major axis
$\beta$	$1/k_B T$
$\beta^b$	free energy difference corresponding to the work needed per monomer to form part of an infinite bilayer out of surfactant ions present in solution
$\beta_{Cl}$	bound fraction of chloride ions
$\beta_{Cs}$	bound fraction of caesium ions
$c$	electrostatic energy
$\chi_{Cl}$	nuclear quadrupole coupling constant of the $^{35}Cl$ nucleus.
$\chi_{Cs}$	nuclear quadrupole coupling constant of the $^{133}Cs$ nucleus
$\chi_D$	nuclear quadrupole coupling constant for $^2H$ in heavy water
$C_{ep}$	critical end point
$\Delta\bar{\nu}$	quadrupole splitting,
$\Delta\chi$	anisotropy in the magnetic susceptibility
$\Delta\chi_a$	anisotropy in the magnetic susceptibility of an amphiphile
$e$	elementary charge
$\epsilon_0$	permittivity in a vacuum
$\epsilon$	relative permittivity

$\phi$	volume fraction of amphiphile
$\phi_p$	total particle volume fraction
$\gamma$	magnetogyric ratio
$\gamma_i$	interfacial tension
$g_i(a)$	bulk energy and entropy effects associated with the packing of the hydrophobic tails
$g_N$	nuclear $g$ factor
$\eta$	asymmetry parameter
$h_i(a)$	interfacial tension and electrostatic energy contributions to chemical potential
I	isotropic micellar solution phase
$I$	nuclear spin quantum number
$i$	surfactant environment
LC	liquid crystal region
$L_D$	lamellar phase
$\mu$	magnetic moment
$\bar{\mu}^0$	chemical potential
$\mu_N$	nuclear magneton
$n$	mesophase director
$n_a$	number of moles of amphiphile
$n_b$	number of bound water molecules per amphiphile
$n_e$	number of moles of electrolyte
$N_D^+$	nematic phase
$\langle P_2(\cos \alpha) \rangle_s$	shape factor

$P$	spin angular momentum
$Q$	nuclear quadrupole moment
$q_{zz}$	component of the nuclear quadrupole-electric field gradient coupling parallel to the direction of the magnetic field,
$S$	order parameter
$s$	aggregation number
$\sigma$	chemical shift shielding tensor.
$S_{O-D}$	order parameter relating the average orientation of the O- <sup>2</sup> H bond of a water molecule with respect to the micelle surface
$S_{rim}$	number of surfactants in the rim
$T^*$	temperature of the theoretical second order transition
$T_{cp}$	tricritical point
$T_{IL}$	temperature of the upper boundary to the isotropic-to-lamellar transition
$T_{IN}$	temperature of the upper boundary to the isotropic-to-nematic transition
$T_{LI}$	temperature of the lower boundary to the isotropic-to-lamellar transition
$T_{LN}$	temperature of the lower boundary to the nematic-to-lamellar transition
$T_{NI}$	temperature of the lower boundary to the isotropic-to-nematic transition
$T_{NL}$	temperature of the upper boundary to the nematic-to-lamellar transition
$T_p(I,N,L)$	triple point
$v$	space filling volume associated with each molecule
$W$	monomer solution phase
$w_a$	mass fraction of amphiphile
$w_c$	mass fraction of electrolyte
$x_a$	mole fraction of amphiphile

$X_{\text{APFO}}$	mole fraction of APFO of the total mole fraction of amphiphile
$x_e$	mole fraction of electrolyte
$x_w$	mole fraction of amphiphile heavy water
$y$	relative stability parameter
$\psi_0$	electrostatic potential at the surface
$z$	the charge

## List of Abbreviations

APFO	Ammonium pentadecafluorooctanoate
C10	CsNFD/ $^2$ H <sub>2</sub> O system
C7	CsTFH/ $^2$ H <sub>2</sub> O system
C8	CsPFO/ $^2$ H <sub>2</sub> O system
C9	CsHFN/ $^2$ H <sub>2</sub> O system
cmc	critical micelle concentration
CsNFD	caesium nonadecafluorodecanoate
CsHFN	caesium heptadecafluorononanoate
CsPFO	caesium pentadecafluorooctanoate
CsTFH	caesium tridecafluoroheptanoate
EL	Eriksson and Ljunggren model
MBG	McMullen, Ben-Shaul, and Gelbart model
o.d.	outer diameter
RbPFO	rubidium pentadecafluorooctanoate
TH	Taylor and Herzfeld model

## Acknowledgments

I am grateful to Associate Professor Ken Jolley for his support throughout my postgraduate studies. I am indebted to him for many things; his encouragement, confidence in my work, and his friendship, but primarily it is his patience for which I am most appreciative.

I would like to express appreciation to Associate Professor Gavin Hedwig for his guidance and encouragement.

I am grateful to my colleagues at Massey University, Dr David Parker, Dr Mark Smith, Dr Pat Edwards, and Mr Scott Thomsen, and for their assistance and encouragement. I also would like to thank my colleagues at Leeds University Dr Johnathan Clements and Dr Gerson Orquies for providing me with x-ray and conductivity data. Thankyou to Professor Neville Boden for helpful discussions.

Thankyou to the technical staff of the science faculty for their assistance.

I am grateful for the financial assistance granted for travel to Leeds by both the New Zealand Royal Society and the British Council. The research experience that I gained has proved to be invaluable. Thankyou to the Massey University Vice Chancellors Committee for my Ph.D. scholarship

I am truly indebted to Karen Morgan for her support to the very end.

Finally I would like to acknowledge (again) my appreciation to my family; Mum, Dad, Bharat, and Ramila, for their continued encouragement.