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

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Submitted in accordance with the requirements
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 ^2H and ^{133}Cs NMR. All the systems exhibited an isotropic micellar solution phase which underwent transitions to first a micellar nematic N_D^+ and then a micellar lamellar L_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 ^2H_2O. A comparison with the caesium pentadecafluorooctanoate (CsPFO)/^2H_2O 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 ^2H quadrupole splittings of ^2H_2O. 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 CsPFO/CsCl/^2H_2O and ammonium pentadecafluorooctanoate (APFO)/NH_4Cl/^2H_2O systems. The addition of electrolyte has the effect of increasing the phase transition temperatures in both systems. ^2H 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}Cs and ^{35}Cl NMR. The effect of counter-ion has been investigated by progressively substituting APFO for CsPFO on a mole for mole basis. The Cs^+ ions are shown to be preferentially "bound" over 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 Cl^- ions with F^-, Br^-, and I^- ions. It has been shown that the co-ion has no significant effect on the phase behaviour.

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List of Symbols

a	(1) head group area (2) length of the minor axis
a/b	micelle axial ratio
α'	contribution of a monomer in the toroidal, semicylindrical rim to the excess free energy
$\boldsymbol{B}$	magnetic field
b	length of the major axis
β	$1/k_BT$
β^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
β_{Cl}	bound fraction of chloride ions
β_{Cs}	bound fraction of caesium ions
c	electrostatic energy
χ_{Cl}	nuclear quadrupole coupling constant of the ^{35}Cl nucleus.
χ_{Cs}	nuclear quadrupole coupling constant of the ^{133}Cs nucleus
χ_D	nuclear quadrupole coupling constant for ^{2}H in heavy water
Cep	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
ε_0	permittivity in a vacuum
ε	relative permittivity

ϕ	volume fraction of amphiphile
ϕ_p	total particle volume fraction
γ	magnetogyric ratio
γ_I	interfacial tension
$g_i(a)$	bulk energy and entropy effects associated with the packing of the hydrophobic tails
g_N	nuclear *g* factor
η	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
$\mathrm{L_D}$	lamellar phase
μ	magnetic moment
$\bar{\mu}^0$	chemical potential
μ_N	nuclear magneton
$\boldsymbol{n}$	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
$\mathrm{N_D^+}$	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
σ	chemical shift shielding tensor.
$S_{O\text{-}D}$	order parameter relating the average orientation of the O-^{2}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
Tcp	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
Tp(I,N,L)	triple point
ν	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_{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
ψ_0	electrostatic potential at the surface
z	the charge

List of Abbreviations

APFO	Ammonium pentadecafluorooctanoate
C10	CsNFD/^2H_2O system
C7	CsTFH/^2H_2O system
C8	CsPFO/^2H_2O system
C9	CsHFN/^2H_2O 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.