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Effect of Counterion and Solvent on the Self-Assembly of Perfluorocarbon Surfactants.

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Addenda

- p 57 The rod charge density ν is the effective charge per unit length of cylindrical micelle.
- p 77 In equation [4-1] the square brackets [] denote the concentration in moles per litre of solution. In equilibrium constant expressions, *e.g.* equation [4-9] the square brackets denote a dimensionless number which is the molar concentration divided by the standard state concentration of 1 mole per litre.
- p 77 Figure 5.5 should read Figure 4.5
- p 86 In equation [4-11] and thereafter, the free energy ΔG_3° represents the free energy change with respect to a standard state in which concentrations are expressed as mole fractions
- p 97 10 lines from bottom, $s_{n,app}$ should read $s_{w,app}$.
- p 136 Figure 5.1 should read Figure 5.8

Abstract.

This work investigates the effects of changing the counterion and the solvent on the self-assembly and self-organisation of anionic perfluorocarbon surfactants. Specifically, the following investigations were carried out:

- The concentration dependence of the rheological behaviour of tetraethyl- and tetramethylammonium perfluorononanoate/H₂O has been examined. The behaviour at intermediate concentrations is consistent with solutions of very long and entangled self-assembled rodlike micelles which is not observed in systems with unalkylated ammonium ions as counterions. At higher surfactant concentrations their rheological behaviour suggests that the rodlengths go through a maximum. At higher concentrations still the systems exhibit liquid crystalline phase behaviour which is consistent with the presence of discotic micelles i.e. a rod-to-disk transition must occur.

- The effects of substituting D₂O for H₂O, and ethylene glycol (EG) for H₂O, on the self-assembly of ammonium perfluorooctanoate (APFO) has been examined by variations in the electrical conductivity of their solutions as functions of temperature and surfactant concentration. The effect of substituting EG/H₂O mixtures for H₂O on APFO micellisation at 298 K was also examined. The results were interpreted within a phenomenological statistical thermodynamic model which showed that differences in self-assembly arise largely from modification of the solution/fluorocarbon interfacial tension.

- The effects of changing the solvent from water to mixtures of water and the cosolvents formamide (FA), ethylene glycol (EG), *N*-methylformamide (NMF), *N,N*-dimethylformamide (DMF), and *N,N*-dimethylacetamide (DMA) on the phase behaviour of the micellar liquid crystal caesium perfluorooctanoate (CsPFO)/D₂O have been investigated using ¹³³Cs and ²H NMR. With increasing concentration of cosolvent the isotropic *I* - to - discotic nematic *N_D* and *N_D* - to - smectic *L* sequences of transitions are displaced to lower temperatures, but the general phase behaviour is conserved. The efficacy of the cosolvents in depressing the phase transition temperatures parallels the order of their effect on the solution/fluorocarbon interfacial tension i.e. DMA>DMF>NMF>EG>FA. Measurement of the ²H quadrupole splittings of D₂O reveal that increasing the cosolvent concentration at constant temperature results in a concomitant decrease in micelle size but the axial ratios of the discotic micelles have essentially singular values at both the *I* - to - *N_D* and *N_D* - to - *L* transitions. The effect of cosolvent on the phase transition temperatures can be qualitatively understood in terms of phase transitions driven by hard particle interactions and, separately, modifications in the micelle self assembly as a consequence

of changes in the solution/fluorocarbon interfacial tension with the addition of cosolvent.

- The effects of the cosolvents on the micellar size of APFO/H₂O at high surfactant concentration have been investigated by small angle x-ray diffraction (SAXS) and have also been shown to arise from changes in the solution/fluorocarbon interfacial tension.

Contents.

<i>List of Symbols</i>	<i>vi</i>
<i>List of Abbreviations</i>	<i>vii</i>
<i>Acknowledgements</i>	<i>viii</i>
1. INTRODUCTION	1
1.1 REFERENCES.....	11
2. MATERIALS AND METHODS	15
2.1 CHEMICALS, PURIFICATION AND GENERAL SAMPLE PREPARATION.....	15
2.1.1 <i>Chemicals used and surfactant synthesis</i>	15
2.1.2 <i>Purification of surfactants</i>	15
2.1.3 <i>General sample preparation</i>	15
2.2 TEMPERATURE CONTROL AND MEASUREMENT.....	16
2.2.1 <i>Temperature control</i>	17
2.2.2 <i>Temperature measurement</i>	18
2.2.3 <i>The water triple-point cell</i>	18
2.2.3.1 <i>Construction of the cell</i>	19
2.2.3.2 <i>Priming and using the cell</i>	20
2.2.3.3 <i>Testing the cell</i>	21
2.3 CONDUCTIVITY.....	23
2.3.1 <i>Sample preparation</i>	23
2.3.2 <i>Conductivity measurement</i>	23
2.4 NMR.....	23
2.4.1 <i>Sample preparation</i>	23
2.4.2 <i>NMR measurement</i>	24
2.5 OPTICAL MICROSCOPY.....	24
2.6 RHEOLOGY.....	25
2.6.1 <i>Sample preparation</i>	25
2.6.2 <i>Temperature control and measurement</i>	25
2.6.3 <i>Rheology Measurements</i>	25
2.6.4 <i>Data analysis: extracting η_0, G_0 and τ</i>	27
2.7 SURFACE TENSION OF BINARY SOLVENT MIXTURES.....	27
2.8 SMALL-ANGLE X-RAY DIFFRACTION (SAXS).....	29
2.8.1 <i>Sample preparation</i>	29
2.8.2 <i>Temperature control and measurement</i>	29
2.8.3 <i>X-ray measurement</i>	29
2.8.4 <i>Data analysis: micelle size from SAXS</i>	30
2.9 AUTOMATED DATA COLLECTION.....	32
2.10 REFERENCES.....	34
3. RHEOLOGY OF AQUEOUS PHASES OF TEAHFN AND TMAHFN	35
3.1 INTRODUCTION.....	35
3.2 RHEOLOGY THEORY.....	35
3.2.1 <i>Shear Stress σ and shear strain γ</i>	36
3.2.1.1 <i>Shear between rectangular parallel plates</i>	36
3.2.1.2 <i>Linear viscoelasticity</i>	36
3.2.1.3 <i>Shear between a cone and plate</i>	37
3.2.2 <i>Oscillating shear experiments</i>	38
3.2.3 <i>Modelling linear viscoelasticity</i>	40
3.2.4 <i>Cole-Cole representation</i>	42

3.3	CATES' MODEL FOR EQUILIBRIUM POLYMER DYNAMICS.....	43
3.3.1	<i>Stress relaxation mechanisms</i>	44
3.3.1.1	Reptation.....	44
3.3.1.2	Chain scission.....	45
3.3.1.3	Bond interchange.....	46
3.3.1.4	End interchange.....	46
3.3.1.5	End evaporation.....	46
3.3.1.6	Rouse and breathing modes.....	46
3.3.2	<i>Cates' model predictions</i>	47
3.3.2.1	Dilute regime ($\phi < \phi^*$).....	48
3.3.2.2	Semidilute regime ($\phi > \phi^*$).....	48
3.4	APPLICATION OF CATES' MODEL TO TEAHFN AND TMAHFN/WATER.....	49
3.4.1	<i>The TEAHFN/water system</i>	49
3.4.2	<i>The TMAHFN/water system</i>	50
3.4.3	<i>Comparison of scaling laws between experiment and theory</i>	52
3.4.3.1	The zero-shear viscosity η_0	52
3.4.3.2	The zero-shear modulus G_0	54
3.4.3.3	The terminal relaxation time τ	56
3.4.4	<i>Mean rodlengths from rheology</i>	57
3.4.5	<i>General summary of results and comparison of systems with and without salt</i>	59
3.5	MODIFIED PREDICTION OF GROWTH OF CHARGED RODLIKE MICELLES.....	59
3.5.1	<i>Application of the modified growth model to TEAHFN and TMAHFN/water systems</i>	62
3.6	BEHAVIOUR OF TMAHFN/WATER OVER THE LIQUID CRYSTAL PHASE TRANSITIONS.....	63
3.7	DISCUSSION OF RESULTS FROM RHEOLOGICAL MEASUREMENTS.....	64
3.8	UNUSUAL TMA ⁺ AND TEA ⁺ COUNTERION EFFECTS.....	67
3.8.1	<i>Evidence from cmc determination</i>	67
3.8.2	<i>Evidence from kinetic measurements</i>	68
3.8.3	<i>Evidence from light scattering</i>	69
3.8.4	<i>The case for ion-specific interactions</i>	69
3.9	REFERENCES.....	71
4.	SOLVENT EFFECTS ON MICELLISATION.....	73
4.1	EXPERIMENTAL DETERMINATION OF CMC'S.....	74
4.1.1	<i>Obtaining the temperature-dependence of the conductance</i>	74
4.1.2	<i>Extraction of cmc's</i>	77
4.1.3	<i>Experimental cmc results</i>	80
4.1.3.1	APFO/H ₂ O and APFO/D ₂ O systems.....	80
4.1.3.2	APFO/EG system.....	82
4.1.3.3	APFO/EG/H ₂ O systems.....	83
4.2	THEORETICAL TREATMENTS OF THE MICELLISATION.....	84
4.3	THERMODYNAMICS OF MICELLISATION.....	85
4.3.1	<i>Obtaining the free ion fraction from conductivity</i>	87
4.3.2	<i>Experimentally determined free ion fractions α</i>	89
4.4	PHENOMENOLOGICAL STATISTICAL THERMODYNAMIC MODELS.....	91
4.4.1	<i>Nagarajan's model</i>	92
4.4.1.1	Transfer free energy.....	93
4.4.1.2	Electrostatic headgroup repulsion.....	95
4.4.1.3	Fluorocarbon/solvent interfacial free energy.....	95
4.4.1.4	Steric headgroup repulsion.....	96
4.4.2	<i>Calculations using Nagarajan's model</i>	96
4.4.3	<i>Results of calculations and comparison with experiment</i>	97
4.4.4	<i>Solvent-dependent micellisation free energies</i>	99
4.4.4.1	Application to H ₂ O/EG mixtures.....	102
4.4.4.2	Calculation of solvent-dependent free energy contributions.....	103

4.4.4.3 Results of calculations.....	105
4.4.5 <i>The effect of temperature in Nagarajan's model</i>	106
4.4.6 <i>Summary of Nagarajan's model predictions</i>	106
4.4.6.1 Effect on cmc.....	106
4.4.6.2 Effect on average aggregation number s	107
4.5 DISCUSSION OF EXPERIMENTAL CMC RESULTS.....	107
4.5.1 <i>The isotope effect on micellisation</i>	107
4.5.1.1 The isotope effect on cmc's.....	107
4.5.1.2 The isotope effect on the cmc minimum.....	112
4.5.1.3 Experimental thermodynamic parameters of aqueous APFO micellisation.....	112
4.5.2 <i>Surfactant aggregation in ethylene glycol - does a cmc exist?</i>	115
4.5.2.1 Experimental thermodynamic parameters of APFO/EG micellisation.....	116
4.5.2.2 Surfactant aggregation in solvent/water mixtures.....	117
4.6 REFERENCES.....	119
5. EFFECT OF SOLVENT AT HIGH SURFACTANT CONCENTRATION.....	121
5.1 NMR INVESTIGATION OF $w = 0.5$ CsPFO/D ₂ O/COSOLVENTS.....	122
5.1.1 <i>Determining T_{IN} by NMR</i>	122
5.1.2 <i>The effect of cosolvent on T_{IN}</i>	122
5.1.3 <i>Obtaining micelle sizes from NMR</i>	123
5.1.4 <i>Variation of micelle size with temperature and cosolvent concentration from NMR</i>	126
5.1.5 <i>2H quadrupole splittings of DMF-d_7</i>	128
5.2 SAXS INVESTIGATION OF $w = 0.5$ APFO/H ₂ O/COSOLVENTS.....	129
5.2.1 <i>Deriving micellar structural parameters from SAXS</i>	129
5.2.2 <i>Variation of micelle size with temperature and cosolvent concentration from SAXS</i>	132
5.2.3 <i>Calculation of γ_{int} from SAXS</i>	134
5.3 SUMMARY.....	140
5.4 REFERENCES.....	141
6. CALCULATION OF INTERFACIAL TENSIONS IN TERNARY SYSTEMS..	142
6.1 A PHENOMENOLOGICAL METHOD FOR CALCULATING INTERFACIAL TENSION.....	143
6.1.1 <i>Numerical calculations of interfacial tension and comparison with experimental data</i>	145
6.1.2 DISCUSSION AND APPLICATION TO THE MICELLAR INTERFACE.....	147
CONCLUSIONS.....	150
APPENDIX A: POLYNOMIALS FROM CONDUCTANCE MEASUREMENTS ..	151
APPENDIX B: DATA EXTRACTED FROM CONDUCTANCE	
MEASUREMENTS	153

List of Symbols.

a	average headgroup area
α	free counterion fraction
A	area
β	bound ion ion fraction
c	molar concentration
χ	nuclear quadrupole coupling constant (or Flory interaction parameter)
δ	surfactant headgroup radius
ε	relative permittivity
ϕ	volume fraction
γ	surface or interfacial tension (or strain in Chapter 3 only)
G	electrical conductance (or stress relaxation modulus in Chapter 3 only)
η	viscosity
κ	conductivity
λ	ionic conductivity at infinite dilution
L	micelle long-axis length scale
Λ	molar ionic conductivity
m	molal concentration (or dipole moment)
r	radius
R	hydrophobic chainlength
s	surfactant aggregation number
σ	stress
t	time
τ	terminal relaxation time
u	electrophoretic mobility
v, V	volume
w	weight fraction of <i>surfactant only</i>
x	mole fraction
ξ	meshsize

List of Abbreviations

12-2-12	ethanediyl- α,ω -bis(dodecyldimethylammonium bromide)
CTAB	cetyltrimethylammonium bromide
DMA	<i>N,N</i> -dimethylacetamide
DMF	<i>N,N</i> -dimethylformamide
DTAB	dodecyltrimethylammonium bromide
EG	ethylene glycol
FA	formamide
HFN	heptadecafluorononanoate ion
NMF	<i>N</i> -methylformamide
NMR	nuclear magnetic resonance
PFO	pentadecafluorooctanoate ion
POS	perfluorooctanesulphonate ion
SAM	self-assembled perfluorocarbon monolayer
SANS	small-angle neutron scattering
SAXS	small-angle x-ray scattering
SDS	sodium dodecylsulphate
TAA	tetraalkylammonium ion
TEA	tetraethylammonium ion
TMA	tetramethylammonium ion
TPA	tetrapropylammonium ion
W	water (H ₂ O)

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