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_S° 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, $s_{\mathrm{n,app}}$ should read $s_{\mathrm{w,app}}$.

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/H_2O 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 D_2O for H_2O, and ethylene glycol (EG) for H_2O, 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/H_2O mixtures for H_2O 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)/D_2O have been investigated using ^{133}Cs and ^{2}H 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 ^{2}H quadrupole splittings of D_2O 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/H_2O 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.

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 *surfactant only*
x	mole fraction
ξ	meshsize

List of Abbreviations

12-2-12	ethanediyl-α,ω-bis(dodecyldimethylammonium bromide)
CTAB	cetyltrimethylammonium bromide
DMA	*N*,*N*-dimethylacetamide
DMF	*N*,*N*-dimethylformamide
DTAB	dodecyltrimethylammonium bromide
EG	ethylene glycol
FA	formamide
HFN	heptadecafluorononanoate ion
NMF	*N*-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_2O)

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