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

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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 $N_0^r$ 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 $^2\text{H}_2\text{O}$. A comparison with the caesium pentadecafluorooctanoate (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 CsPFO/CsCl/$^2\text{H}_2\text{O}$ and ammonium pentadecafluorooctanoate (APFO)/NH$_4$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 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
- $\alpha'$ 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 $^2$H in heavy water
- $C_{ep}$ critical end point
- $\Delta \tilde{v}$ quadrupole splitting,
- $\Delta \chi$ anisotropy in the magnetic susceptibility
- $\Delta \chi_a$ anisotropy in the magnetic susceptibility of an amphiphile
- $e$ elementary charge
- $\varepsilon_0$, permitivity in a vacuum
- $\varepsilon$, relative permitivity
\( \phi \) volume fraction of amphiphile

\( \phi_p \) total particle volume fraction

\( \gamma \) magnetogyric ratio

\( \gamma_1 \) 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

\( \mu^0 \) 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 \( O-\^{}2H \) 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

\( T_{LU} \) 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

\( \nu \) space filling volume associated with each molecule

\( W \) monomer solution phase

\( w_a \) mass fraction of amphiphile

\( w_e \) 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

$\psi_0$  electrostatic potential at the surface

$z$  the charge
### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>APFO</td>
<td>Ammonium pentadecafluorooctanoate</td>
</tr>
<tr>
<td>C10</td>
<td>CsNFD/H₂O system</td>
</tr>
<tr>
<td>C7</td>
<td>CsTFH/H₂O system</td>
</tr>
<tr>
<td>C8</td>
<td>CsPFO/H₂O system</td>
</tr>
<tr>
<td>C9</td>
<td>CsHFN/H₂O system</td>
</tr>
<tr>
<td>cmc</td>
<td>critical micelle concentration</td>
</tr>
<tr>
<td>CsNFD</td>
<td>caesium nonadecafluorodecanoate</td>
</tr>
<tr>
<td>CsHFN</td>
<td>caesium heptadecafluorononanoate</td>
</tr>
<tr>
<td>CsPFO</td>
<td>caesium pentadecafluorooctanoate</td>
</tr>
<tr>
<td>CsTFH</td>
<td>caesium tridecafluoroheptanoate</td>
</tr>
<tr>
<td>EL</td>
<td>Eriksson and Ljunggren model</td>
</tr>
<tr>
<td>MBG</td>
<td>McMullen, Ben-Shaul. and Gelbart model</td>
</tr>
<tr>
<td>o.d.</td>
<td>outer diameter</td>
</tr>
<tr>
<td>RbPFO</td>
<td>rubidium pentadecafluorooctanoate</td>
</tr>
<tr>
<td>TH</td>
<td>Taylor and Herzfeld model</td>
</tr>
</tbody>
</table>
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