

## Aromatic pentafluoro- $\lambda^6$ -sulfanyl ( $\text{SF}_5$ ) surfactants: $m\text{-SF}_5(\text{CF}_2)_n\text{C}_6\text{H}_4\text{SO}_3\text{K}$

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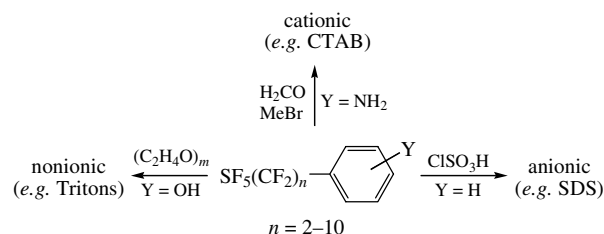
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The synthesis and characterization of new fluorinated surfactants based on  $\text{SF}_5$ -aromatic system are presented for the first time.

For over 40 years,<sup>1</sup> the only known  $\text{SF}_5$ -aromatic systems contained the  $\text{SF}_5\text{C}_6\text{H}_4$  moiety. The new synthetic strategy that we have recently developed<sup>2</sup> has opened the floodgate for preparing a large assortment of *o*, *m*, *p*- $\text{SF}_5(\text{CF}_2)_n\text{C}_6\text{H}_4\text{X}$  and chiral *o*, *m*, *p*- $\text{SF}_5\text{CF}_2\text{CFYC}_6\text{H}_4\text{X}$  derivatives that have technologically important applications in lithium batteries, fuel cells and ion-exchange resins.<sup>3–8</sup> More readily degradable than  $\text{CF}_3$ -terminated molecules, the  $\text{SF}_5$ -aromatic structural motif is readily integrated into fluorinated polymers,<sup>2</sup> liquid crystals<sup>9</sup> and surfactants. In this paper, we focus on sulfonate surfactants, showing below (Scheme 1) how other classic analogues of cationic (CTAB: hexadecyltrimethylammonium bromide), anionic (SDS, sodium dodecyl sulfonate), and nonionics (Tritons: *t*-octylphenoxypolyoxyethanols) may be synthesised.

A number of surface active  $\text{SF}_5$ -fluoroalkyl sulfonic acids and salts are known.<sup>3,4,7,8,10,11</sup> 3M researchers first demonstrated that the polar, yet weakly hydrophobic  $\text{SF}_5$ -terminated alkyl group exhibits surface activity greater than  $\text{CF}_3$ -terminated compounds.<sup>10,11</sup> They observed a lower surface tension for the



**Scheme 1** Synthetic approach.

shorter chain  $\text{SF}_5$ -ammonium carboxylate than the longer chain  $\text{CF}_3(\text{CF}_2)_6\text{C}(\text{O})\text{ONH}_4$ .<sup>10,11</sup> While little is known concerning the surface tension of aqueous solutions of organic  $\text{SF}_5$ -carboxylate salts; to our knowledge, nothing is known about organic  $\text{SF}_5$ -sulfonate salts. Since some of the lowest air–water surface tensions ( $15\text{--}20\text{ mN m}^{-1}$ ) are reported for *para*-fluorocarbon aryl sulfonates,<sup>12–15</sup> we explored a new homologous series containing  $\text{CF}_2$  groups as a spacer between the  $\text{SF}_5$  group and

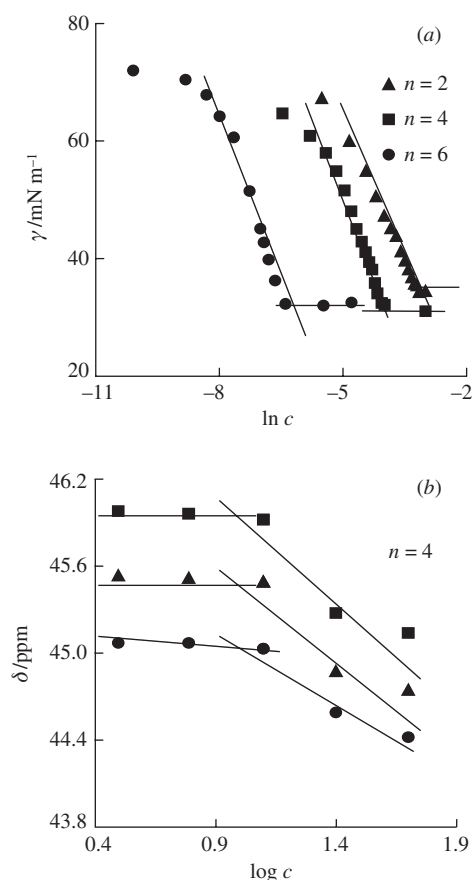
**Table 1** Summary of thermodynamic parameters. C<sub>10</sub>(H) and C<sub>8</sub>(F) refer to C<sub>10</sub>H<sub>21</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Na and C<sub>8</sub>F<sub>17</sub>SO<sub>3</sub>Li, respectively. The numbers in parentheses for *a* and *b* indicate the uncertainty. The numbers in parentheses for CMC and Δ*G* correspond to values evaluated by NMR.

(CF <sub>2</sub> ) <sub><i>n</i></sub>	<i>a</i>	<i>b</i>	CMC/ 10 <sup>−3</sup> mol dm <sup>−3</sup>	Γ/10 <sup>−3</sup> mol per 1000 m <sup>2</sup>	σ/Å <sup>2</sup> molec <sup>−1</sup>	CMC/C <sub>20</sub>	Π <sub>CMC</sub> / mN m <sup>−1</sup>	−Δ <i>G</i> <sub>micelle</sub> / kJ mol <sup>−1</sup>	−Δ <i>G</i> <sub>ads</sub> / kJ mol <sup>−1</sup>
2	20(1)	0.50(3)	37.6 (58.2)	3.0	55.8	2.1	38.2	17.8 (17.0)	29.7 (30.7)
4	7(1)	0.45(5)	18.1 (10.7)	3.5	46.4	2.7	41.0	19.6 (21.2)	31.1 (32.4)
6	0.77(1)	0.45(1)	1.9	4.1	41.0	2.5	40.3	25.2	35.2
C <sub>10</sub> (H)	—	—	3.1	3.9	43.0	1.4	25.8	26.3	33.0
C <sub>8</sub> (F)	—	—	6.3	3.0	55.0	10	42	22.3	36.2

aromatic sulfonic acid/salt. Remarkably, we find evidence of aggregation and interfacial adsorption (hence surface tension reduction) even in *meta*-SF<sub>5</sub>(CF<sub>2</sub>)<sub>*n*</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>K (*n* = 2, 4, 6).

The acids and salts *m*-SF<sub>5</sub>(CF<sub>2</sub>)<sub>*n*</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H and *m*-SF<sub>5</sub>(CF<sub>2</sub>)<sub>*n*</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>K (*n* = 2, 4, 6), were synthesised (see Scheme 1) by sulfonating SF<sub>5</sub>(CF<sub>2</sub>)<sub>*n*</sub>Ph with chlorosulfonic acid followed by a base hydrolysis to yield the sulfonate salts. Removing K<sup>+</sup> ions by ion-exchange chromatography gave the corresponding acid (see Supplementary Materials for synthetic and structural details, which are available free *via* <http://www.turpion.org/suppl/mc/2315/suppl2315.pdf>).

Surface tension,  $\gamma$ , of these compounds [Figure 1(a)] decreases with sub-phase surfactant concentration, *c*, exhibiting a distinct leveling after a certain critical concentration that depends on the fluorocarbon chain length. The minimum surface tension is approximately 32 mN m<sup>−1</sup>, higher than the *para*-fluorocarbon aryl sulfonates. The concentration dependence of surface tension is consistent with an interfacial adsorption punctuated either by micellization or by exceeding the solubility limit, *i.e.*, when the Krafft temperature is > 23 °C. To distinguish between the two possibilities, NMR chemical shift studies were conducted. Micellization leads to a continuous variation of chemical shift with concentration.<sup>16</sup> Exceeding the solubility limit, however,



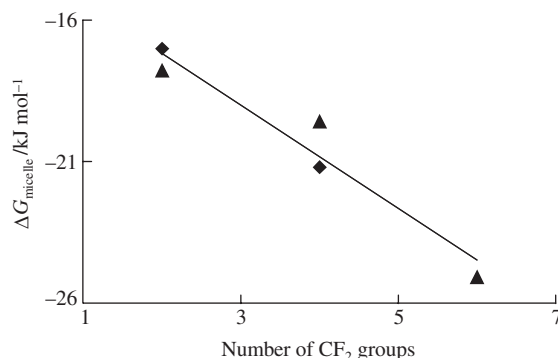
**Figure 1** Semi-log plots of (a) surface tension and (b) fluorine chemical shift vs. surfactant concentration for varying numbers of CF<sub>2</sub> groups. In (b) from bottom to top, we present (CF<sub>2</sub>)<sub>*n*</sub> and equatorial (doublet) fluorine from the SF<sub>5</sub> group, respectively. The chemical shift of the CF<sub>2</sub> group has been shifted by an additive constant (154.7 ppm) and the chemical shift of the equatorial SF<sub>5</sub>, by 1.4 ppm for clarity of presentation.

results in a two-component NMR spectrum arising from solid-liquid coexistence due to slow (on the time scale of NMR) molecular exchange between the phases. The chemical shifts for axial SF<sub>5</sub> and CF<sub>2</sub> groups shown in Figure 1(b) display a smooth variation with surfactant concentration. From the bend in the slopes of surface tension and chemical shift data, we estimated the critical micelle concentrations (CMCs).

The surface pressure at the CMC,  $\Pi_{\text{CMC}}$  ( $= \gamma_w - \gamma_{\text{CMC}}$ ),<sup>17</sup> measures the surfactant effectiveness in reducing surface tension. Present surfactants display significantly higher (lower)  $\Pi_{\text{CMC}}$  than the protonated alkyl-aryl sulfonates (*p*-fluoroaryl sulfonates). The ratios of adsorption to micellization efficiencies, CMC/C<sub>20</sub>, (where C<sub>20</sub> is a surfactant concentration needed to reduce  $\gamma_w$  by 20 mN m<sup>−1</sup>) are greater (smaller) than the protonated (fluorinated) surfactants. This may be due to inefficient interfacial packing resulting from the *meta*-placement of the hydrophilic sulfonate group off the long molecular axis, rectifiable in *para*-derivatives.

To gain further insight into the self-assembly process, interfacial packing parameters were determined using Langmuir-Szyszkowski (LS) and Gibbs models.<sup>18</sup> The LS model predicts that  $\gamma = \gamma_0[1 - b \ln(1 + c/a)]$ , where  $\gamma_0$  is the surface tension of water. The coefficient  $b = RT\Gamma_{\infty}/\gamma_0$ , where  $\Gamma_{\infty}$  is the maximum possible adsorption, is a characteristic constant of a homologous series while *a* is compound-specific. Nonlinear least squares fits to the  $\gamma$  vs. *c* data (Table 1) show a constant *b* ( $\Gamma_{\infty} \approx 7 \times 10^{-3}$  mol/1000 m<sup>2</sup>) and a systematic decrease in *a* with number of CF<sub>2</sub> groups. The Gibbs interfacial excess,<sup>19</sup>  $\Gamma = (0.5RT)d\gamma/d \ln c$ ,<sup>†</sup> and molecular area  $\sigma$  ( $= 10^{23}/(N_A \Gamma$  in units of nm<sup>2</sup>) were also computed using the semi-log plot of  $\gamma$  vs.  $\ln c$  [Figure 1(a)]. Note that  $\Gamma/\Gamma_{\infty}$  ( $\approx 0.5$ ) verifies loose interfacial packing, which depends on the fluorocarbon chain length. Longer chains, perhaps due to favourable fluorocarbon–fluorocarbon interactions, pack more closely.

The micellization and adsorption free energies,  $\Delta G_{\text{mic}} \approx RT \ln(c_{\text{CMC}}/55.5)$  and  $\Delta G_{\text{ads}} = \Delta G_{\text{micelle}} - \Pi_{\text{CMC}}\sigma$ , respectively, are presented in Table 1. These free energies, cross-sectional areas and surface excesses are comparable to C<sub>7</sub>F<sub>15</sub>SO<sub>3</sub>Li and equivalent (using 1.5CH<sub>2</sub>≡1CF<sub>2</sub> rule<sup>19</sup>) protonated *p*-C<sub>10</sub>H<sub>21</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Na surfactants. Figure 2 indicates that the decrease in  $\Delta G_{\text{micelle}}$



**Figure 2** Plot of  $\Delta G_{\text{micelle}}$  vs. the number of CF<sub>2</sub> groups attached. The fitted line gives the slope and intercept of −1.9 kJ per CF<sub>2</sub> group and −13 kJ mol<sup>−1</sup>, respectively.

<sup>†</sup> The factor of 2 accounts for a complete ionization of the potassium salt. When this ionization is not considered, the extracted values of  $\Gamma > \Gamma_{\infty}$  are physically impossible. Resonance structures of SF<sub>5</sub> and CF<sub>2</sub> groups attached to phenyl rings predict an electron deficiency at *o*- and *p*-positions, stabilising the ionised sulfonate group.<sup>20</sup>

per  $\text{CF}_2$  group is considerably smaller ( $\sim 2 \text{ kJ mol}^{-1}$ ) than for typical fluorinated surfactants,<sup>19</sup> but comparable to values for  $\text{CH}_2$  groups.<sup>21</sup> Parallel free energy reduction is observed in  $\text{RCOO}(\text{CH}_2)_n\text{SO}_3\text{Na}$  and mixed fluorohydrocarbon nonionics where the presence of two highly polar opposing groups reduces the  $\Delta G_{\text{micelle}}(\text{CH}_2)$  by half.<sup>18</sup>

Structurally similar bolaamphiphiles<sup>22</sup> containing two terminal polar hydrophilic groups form vesicles rather than micelles. The polar hydrophobic  $\text{SF}_5$  terminus, however, appears to suppress vesicular structures, but it may permit microemulsions of polar oils such as asphaltenes, amphiphatic proteins and lyotropic liquid crystals, which are valuable templates for the synthesis of nanostructured material.

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