Supporting informations

Behavior of wormlike micellar solutions formed without any additives from semi-fluorinated quaternary ammonium salts

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I- Chemical characterizations of the synthesized products

Tertiary Amines (A_{n,m})

A8,1

Yield 95 %

spectral data: MS m/z (rel. ab. %): 521 ([M]+●, 5 %); 506 ([M-CH3]+, 20 %), 88 ([M-CF3(CF2)7,-CH2]+, 10 %), 58 ([M-CF3(CF2)8CHOHCH2]+, 100 %);

1H NMR (CD3OD): δ = 2.39 (m, CH2(a), 2H); 2.6 (m, CH(b), 1H); 2.49 (d, CH2(c), 2H); 2.29 (t, CH3(d), 6H); 4.2 (d, OH(e), 1H).

19F NMR (CD3OD): δ = -80.9 (t, CF3(a), 3F); -111.7 (m, CF2CH2(b), 2F); -126.2 (m, CF2(c), 2F); -123.3 (m, CF2(d), 2F); -122.8 (m, CF2(e), 2F); -121.9 (m, CF2(f), 2F); -121.6 (m, CF2(g,h), 4F).
A8,2

Yield 84 %

spectral data: MS m/z (rel. ab. %): 549 ([M]+●, 3 %), 116 ([M-CF₃(CF₂)₇, -CH₂]+, 30 %), 86 ([M-CF₃(CF₂)₈CHOHCH₂]+, 100 %), 69 [CF₃]+ 15 %;

¹H NMR (CD₃OD): δ = 2.18 (m, CH₂(a), 1H); 2.49 (m, CH₂(a), 1H); 4.2 (d-d, CH(b), 1H); 2.49 (m, CH₂(c,d), 6H); 1.04 (t, CH₃(e), 6H); 4.1 (d-d, OH(f), 1H).

¹⁹F NMR (CD₃OD): δ = -80.9 (t, CF₃(a), 3F); -111.7 (m, CF₂CH₂(b), 2F); -126.2 (m, CF₂(c), 2F); -123.3 (m, CF₂(d), 2F); -122.8 (m, CF₂(e), 2F); -121.9 (m, CF₂(f), 2F); -121.6 (m, CF₂(g,h), 4F).

A6,1

Yield 94 %

spectral data: MS m/z (rel. ab. %): 421 ([M]+●, 5 %); 406 ([M-CH₃]+, 20 %), 88 ([M-CF₃(CF₂)₇, -CH₂]+, 100 %), 58 ([M-CF₃(CF₂)₈CHOHCH₂]+, 100 %);

¹H NMR (CD₃OD): δ = 2.39 (m, CH₂(a), 2H); 2.6 (m, CH(b), 1H); 2.49 (d, CH₂(c), 2H); 2.29 (t, CH₃(d), 6H); 4.2 (d, OH(e), 1H).

¹⁹F NMR (CD₃OD): δ = -80.9 (t, CF₃(a), 3F); -111.7 (m, CF₂CH₂(b), 2F); -126.2 (m, CF₂(c), 2F); -123.3 (m, CF₂(d), 2F); -122.8 (m, CF₂(e), 2F); -121.8 (m, CF₂(f), 2F).

A6,2

Yield 89 %

spectral data: MS m/z (rel. ab. %): 449 ([M]+●, 5 %); 116 ([M-CF₃(CF₂)₇, -CH₂]+, 30 %), 86 ([M-CF₃(CF₂)₈CHOHCH₂]+, 100 %);

¹H NMR (CD₃OD): δ = 2.18 (m, CH₂(a), 1H); 2.49 (m, CH₂(a), 1H); 4.2 (d-d, CH(b), 1H); 2.49 (m, CH₂(c,d), 6H); 1.04 (t, CH₃(e), 6H); 4.1 (d-d, OH(f), 1H).

¹⁹F NMR (CD₃OD): δ = -80.9 (t, CF₃(a), 3F); -111.7 (m, CF₂CH₂(b), 2F); -126.2 (m, CF₂(c), 2F); -123.3 (m, CF₂(d), 2F); -122.8 (m, CF₂(e), 2F); -121.8 (m, CF₂(f), 2F).

A4,1

Yield 93 %

spectral data: MS m/z (rel. ab. %): 321 ([M]+●, 5 %); 306 ([M-CH₃]+, 20 %), 88 ([M-CF₃(CF₂)₇, -CH₂]+, 100 %), 58 ([M-CF₃(CF₂)₈CHOHCH₂]+, 100 %);

¹H NMR (CD₃OD): δ = 2.39 (m, CH₂(a), 2H); 2.6 (m, CH(b), 1H); 2.49 (d, CH₂(c), 2H); 2.29 (t, CH₃(d), 6H); 4.2 (d, OH(e), 1H).

¹⁹F NMR (CD₃OD): δ = -80.9 (t, CF₃(a), 3F); -111.7 (m, CF₂CH₂(b), 2F); -126.2 (m, CF₂(c), 2F); -123.3 (m, CF₂(d), 2F); -122.8 (m, CF₂(e), 2F); -121.8 (m, CF₂(f), 2F).
A_{4,2}

Yield 80 %

spectral data: MS m/z (rel. ab. %): 349 ([M]+●, 10 %), 116 ([M-CF_{3}(CF_{2})_{7}, -CH_{2}]^{+}, 30 %), 86 ([M-CF_{3}(CF_{2})_{8}CH_{2}OHCH_{2}]^{+}, 100 %);

^{1}H NMR (CD_{3}OD): \delta = 2.18 (m, CH_{2}(a), 1H); 2.49 (m, CH_{2}(a), 1H); 4.2 (d-d, CH(b), 1H); 2.49 (m, CH_{2}(c,d), 6H); 1.04 (t, CH_{3}(e), 6H); 4.1 (d-d, OH(f), 1H).

^{19}F NMR (CD_{3}OD): \delta = -80.9 (t, CF_{3}(a), 3F); -111.7 (m, CF_{2}CH_{2}(b), 2F); -126.2 (m, CF_{2}(c), 2F); -123.3 (m, CF_{2}(d), 2F).

Quaternary ammonium salts (F_{n}H_{m})

F_{8}H_{1}

Yield 91 % from A_{8,1}

^{1}H NMR (CD_{3}OD): \delta = 2.24 (m, CH_{2}(a), 2H); 4.6 (m, CH(b), 1H); 3.51 (t, CH_{2}(c), 2H); 3.26 (m, CH_{3}(d), 9H); 4.7 (m, OH(e), 1H).

^{19}F NMR (CD_{3}OD): \delta = -80.9 (t, CF_{3}(a), 3F); -111.7 (m, CF_{2}CH_{2}(b), 2F); -126.2 (m, CF_{2}(c), 2F); -123.3 (m, CF_{2}(d), 2F).

F_{8}H_{2}

Yield 88 % from A_{8,2}

^{1}H NMR (CD_{3}OD): \delta = 2.46 (m, CH_{2}(a), 2H); 4.6 (m, CH(b), 1H); 3.52 (m, CH_{2}(c,d), 6H); 3.14 (s, CH_{3}(e), 3H); 4.7 (m, CH(f), 1H); 1.37 (t, CH_{3}(g), 6H).

^{19}F NMR (CD_{3}OD): \delta = -80.9 (t, CF_{3}(a), 3F); -111.7 (m, CF_{2}CH_{2}(b), 2F); -126.2 (m, CF_{2}(c), 2F); -123.3 (m, CF_{2}(d), 2F); -122.8 (m, CF_{2}(e), 2F); -121.9 (m, CF_{2}(f), 2F); -121.6 (m, CF_{2}(g,h), 4F).

F_{6}H_{1}

Yield 94 % from A_{6,1}

^{1}H NMR (CD_{3}OD): \delta = 2.24 (m, CH_{2}(a), 2H); 4.6 (m, CH(b), 1H); 3.51 (t, CH_{2}(c), 2H); 3.26 (m, CH_{3}(d), 9H); 4.7 (m, OH(e), 1H).

^{19}F NMR (CD_{3}OD): \delta = -80.9 (t, CF_{3}(a), 3F); -111.7 (m, CF_{2}CH_{2}(b), 2F); -126.2 (m, CF_{2}(c), 2F); -123.3 (m, CF_{2}(d), 2F); -122.8 (m, CF_{2}(e), 2F); -121.8 (m, CF_{2}(f), 2F).

F_{6}H_{2}

Yield 89 % from A_{6,2}

^{1}H NMR (CD_{3}OD): \delta = 2.46 (m, CH_{2}(a), 2H); 4.6 (m, CH(b), 1H); 3.52 (m, CH_{2}(c,d), 6H); 3.14 (s, CH_{3}(e), 3H); 4.7 (m, CH(f), 1H); 1.37 (t, CH_{3}(g), 6H).

^{19}F NMR (CD_{3}OD): \delta = -80.9 (t, CF_{3}(a), 3F); -111.7 (m, CF_{2}CH_{2}(b), 2F); -126.2 (m, CF_{2}(c), 2F); -123.3 (m, CF_{2}(d), 2F); -122.8 (m, CF_{2}(e), 2F); -121.8 (m, CF_{2}(f), 2F).
**F₄H₁**

**Yield 93 % from A₄₁**

**¹H NMR** (CD₃OD): δ = 2.24 (m, CH₂(a), 2H); 4.6 (m, CH(b), 1H); 3.51 (t, CH₂(c), 2H); 3.26 (m, CH₃(d), 9H); 4.7 (m, OH(e), 1H).

**¹⁹F NMR** (CD₃OD): δ = -80.9 (t, CF₃(a), 3F); -111.7 (m, CF₂CH₂(b), 2F); -126.2 (m, CF₂(c), 2F); -123.3 (m, CF₂(d), 2F).

**F₄H₂**

**Yield 73 % from A₄₂**

**¹H NMR** (CD₃OD): δ = 2.46 (m, CH₂(a), 2H); 4.6 (m, CH(b), 1H); 3.52 (m, CH₂(c,d), 6H); 3.14 (s, CH₃(e), 3H); 4.7 (m, CH(f), 1H); 1.37 (t, CH₃(g), 6H).

**¹⁹F NMR** (CD₃OD): δ = -80.9 (t, CF₃(a), 3F); -111.7 (m, CF₂CH₂(b), 2F); -126.2 (m, CF₂(c), 2F); -123.3 (m, CF₂(d), 2F).

**II- Surfactant properties**

The surface tensions of the aqueous solutions of the fluorinated surfactants were measured using a Kruss K100 tensiometer by the Wilhelmy plate technique [N.R. Pallas, B.A. Pethica, Colloids Surf. 36 (1989) 369]. All of the measurements were performed at 25 °C.

**Table 1**: surface tension at the critical micellar concentration cmc (γcmc) and cmc measured for the synthesized surfactants

<table>
<thead>
<tr>
<th>surfactants</th>
<th>γcmc [mN/m]</th>
<th>cmc [mmol/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₄H₁</td>
<td>15.7</td>
<td>0.840</td>
</tr>
<tr>
<td>F₆H₁</td>
<td>16.6</td>
<td>1.280</td>
</tr>
<tr>
<td>F₄H₂</td>
<td>19.0</td>
<td>1.470</td>
</tr>
<tr>
<td>F₄H₂</td>
<td>17.5</td>
<td>0.756</td>
</tr>
<tr>
<td>F₆H₂</td>
<td>20.2</td>
<td>1.200</td>
</tr>
<tr>
<td>F₄H₂</td>
<td>22.9</td>
<td>1.360</td>
</tr>
</tbody>
</table>
III- DLS measurements

Figure 1. Zeta potential for F₈H₁. Red at C₁=20xcmc, blue F₈H₁ at C₂=30xcmc.

Figure 2. Zeta potential for F₈H₂. Red at C₁=20xcmc, blue F₈H₂ at C₂=30xcmc, green F₈H₂ at C₃=40xcmc.

Figure 3. Variation in diameter as a function of fluorinated chain. Blue line for F₈H₁, green line for F₆H₁, red line for F₄H₁.
Figure 4. Variation in diameter as function of the fluorinated chain. Blue line for F₈H₂, Red line for F₆H₂, green line for F₄H₂.

IV-Rheological curves

Figure 5. Storage and loss modulus at C₁=20xcmc as function of temperature for F₈H₂

Figure 6. Storage and loss modulus at C₁=20xcmc as function of temperature for F₆H₁.
Figure 7. $G'$ and $G''$ as function of frequency for $F_8H_2$ at $C_2=30\text{cmc}$

Figure 8. Correlation between viscosity and relaxation time for $F_8H_1$ at $C_2=30\text{cmc}$

Figure 9. Correlation between viscosity and relaxation time for $F_8H_2$ at $C_2=30\text{cmc}$