Fluorinated Microemulsions as Reaction Media for Fluorous Nanoparticles

Electronic Supporting Information

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SANS data fitting

The form factor for polydisperse spheres each with radius $R$ is defined as follows:¹

$$P(Q) = \frac{\pi}{2} \int_0^\infty |G(Q,R)|^2 g(R) dR$$

(1)

$$G(Q,R) = \left( \frac{4\pi}{3} \right) R^3 \Delta \rho \left[ \frac{3j_1(QR)}{QR} \right]$$

(2)

Where $j_1(QR)$ is a first order spherical Bessel function and $g(R)$ in this case defines a Schultz distribution of homogeneous spheres:

$$g(R) = \frac{\left( \frac{Z+1}{R} \right)^{Z+1} R^Z \exp \left[-\left( \frac{Z+1}{R} \right)R \right]}{\Gamma(Z+1)}$$

(3)

Where the width parameter, $Z > -1$, $\bar{R}$ is the mean of the distribution and polydispersity defined by an RMS deviation $\sigma = \bar{R} / (Z+1)^{1/2}$.

Fits to diHCF4-stabilised w/fc microemulsions included an attractive Ornstein-Zernike structure factor (OZ $S(Q)$), as given in equation 4.

$$S(Q, \zeta) = 1 + \left[ \frac{\kappa}{1 + (Q\zeta)^2} \right]$$

(4)

This describes a decaying distribution, where $\zeta$ is a correlation length, and $\kappa$ is related to the strength of interactions via the isothermal compressibility.²
Droplet polydispersity

Compared to normal H-AOT-based hydrocarbon microemulsions (polydispersity ~ 0.20), the fitted polydispersity of the F-microemulsions (F-MEs) may seem quite high at 0.28 or above. Polydispersity, $p$, has been linked to interfacial rigidity, $2K + K_{BAR}$ as follows:

$$2K + K_{BAR} = \frac{k_B T}{8\pi \rho^2} - \frac{k_B T}{4\pi} f(\phi)$$

(5)

Interfacial rigidity has been shown to be strongly dependent on the total carbon number of the surfactant tails ($C_{surf}$), and also on the concentration of surface-active co-solvents (discussed in the main paper). The systems studied here consist of surfactants with $C_{surf} = 8$ (2 × 4 carbons in diCF3) or $C_{surf} = 10$ (2 × 5 C in diHCF4). Studies have been done using homologous twin-tailed di-C$_n$-PC surfactants, showing $2K + K_{BAR}$ to be related to roughly the square of $C_{surf}$ (actually, $2K + K_{BAR} \sim C_{surf}^{-2.4}$). This would imply that polydispersity should be approximately proportional to $C_{surf}^{-1}$. Using data reported therein, the dependence of $\ln (C_{surf})$ vs $\ln (p)$ is shown in figure S1 below. The calculated gradient is -1.16; from this it can be predicted that for $C_{surf} = 10$ diHCF4, polydispersity = 0.48. On this basis a polydispersity range of 0.28 – 0.49 as found for the F-microemulsions is entirely reasonable.

In addition, it is worth comparing the value found here of 0.28 with that found by Nave for a di-chain sulfosuccinate hydrocarbon based system, comparable to the F-MEs studies here: H$_2$O / diC$_6$SS / n-hexanol / hexane (10 vol% alcohol co-solvent). This system was studied by SANS and data fitted to a polydispersity of 0.26 (Note $C_{surf} = 12$ for diC$_6$SS). If the same inverse relationship can be assumed as for di-C$_n$-PC surfactants (a reasonable assumption) one would expect a polydispersity of 0.32 for $C_{surf} = 10$, which again agrees with the value of 0.28 typically found here.
Figure S1: Dependence of polydispersity on surfactant chain length for twin-tailed phosphocholine di-
C\textsubscript{n}-PC surfactants studied previously.\textsuperscript{4} Solid line shows a linear fit, with gradient -1.16.

Table S1: Calculated scattering length densities (s.l.d, \(\rho\)) for chemicals used in this study.

<table>
<thead>
<tr>
<th>Compound</th>
<th>s.l.d. (\times 10^{10}) / cm(^2)</th>
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<tbody>
<tr>
<td>H(_2)O</td>
<td>-0.56</td>
</tr>
<tr>
<td>D(_2)O (99%)</td>
<td>6.33</td>
</tr>
<tr>
<td>diHCF4</td>
<td>3.11</td>
</tr>
<tr>
<td>diCF3</td>
<td>3.15</td>
</tr>
<tr>
<td>1H,1H,5H-octafluoropentan-ol (OFP)</td>
<td>2.98</td>
</tr>
<tr>
<td>2H,3H-perfluoropentane (HPFP)</td>
<td>3.11</td>
</tr>
<tr>
<td>1H-perfluorohexane (HPFH)</td>
<td>3.42</td>
</tr>
</tbody>
</table>
D$_2$O vs H$_2$O contrast in the F-MEs

In an attempt to gain additional structural information available by SANS, some samples were studied with D$_2$O instead of H$_2$O (Figure S2). As can be seen, apart from a difference in the absolute value of $I(Q)$ (due to changes in contrast) there is little or no difference in the forms of the plots, implying that H$_2$O or D$_2$O can be used interchangeably in these systems without affecting largely the fit parameters.

Figure S2: Comparison of core contrast SANS data from water / diCF3 / OFP / HPFH microemulsions at $w = 40$ using either H$_2$O or D$_2$O nanodroplets to generate contrast. Solid lines represent form factor fits to the Shultz polydisperse spheres model. [diCF3] = 100 mM, OFP : HPFH = 1 : 9 (v:v), $T = 40^\circ$C. D$_2$O data and calculated fit has been multiplied by a constant value of 2.3 to overlay onto the H$_2$O data.
Additional SANS data and Repeats

Figure S3: Core contrast SANS data from H₂O / diCF₃ / OFP / HPFH microemulsions at different w = [H₂O] / [diCF₃] as indicated. Solid lines represent form factor fits to the Shultz polydisperse spheres model. [diCF₃] = 100 mM, OFP : HPFH = 1 : 9 (v:v), T = 40°C.

Figure S4: Core contrast SANS data from H₂O / diCF₃ / OFP / HPFP microemulsion systems at different w = [H₂O] / [diCF₃] values indicated. Solid lines represent form factor fits to the Shultz polydisperse spheres model. [diCF₃] = 100 mM, OFP : HPFH = 1 : 9 (v:v), T = 40°C. Note for w 20 and
40 SANS measurements were repeated using freshly made samples. Good agreement was seen between these repeats.

Figure S5: Core contrast SANS data from D$_2$O / diCF3 / OFP / HPFP microemulsions at high w = [D$_2$O] / [diCF3] values indicated. Solid lines represent form factor fits to the Shultz polydisperse spheres model. [diCF3] = 100 mM, OFP : HPFH = 1 : 9 (v:v), T = 40°C
Figure S6: Core contrast SANS data from H₂O / diCF₃ / OFP / HPFP microemulsions at different [diCF₃] values indicated. Solid lines represent form factor fits to the Shultz polydisperse spheres model. w = 40, OFP : HPFH = 1 : 9 (v:v), T = 40°C.
Figure S7 Core contrast SANS data from H₂O / diHCF4 / OFP / HPFP microemulsions at different w values as indicated. Solid lines represent form factor fits to the Shultz polydisperse spheres model with an attractive OZ S(Q) where necessary. [diHCF4] = 100 mM, OFP : HPFH = 1 : 9 (v:v), T = 40°C

Figure S8: Water droplet radius R vs w for diCF3 – stabilized water / OFP / HPFH microemulsions. R values are calculated from SANS analysis of core contrasts (Table 2) corrected for polydispersity via $R = a(p).R_{bar}$, as in equations 1, 2. Example error bars are shown. Linear fits from these data are also shown (gradient = 0.877).
Figure S9: Example SAED patterns for diCF3- (left) and AOT-coated (right) Ag-NPs. Patterns were very faint, consisting of diffraction spots, so dashed-line circles have been added to the patterns to highlight important d-spacings. In increasing distance from the centre of each pattern, these rings represent (111), (200), (220) and (222) Ag cubic crystal planes (also see Table S1)

<table>
<thead>
<tr>
<th>Ag cubic d-spacings [Å]</th>
<th>diCF3 coated Ag-NPs</th>
<th>AOT-coated Ag-NPs</th>
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</thead>
<tbody>
<tr>
<td>2.36 (111)</td>
<td>2.24</td>
<td>2.34</td>
</tr>
<tr>
<td>2.04 (200)</td>
<td>1.92</td>
<td>1.94</td>
</tr>
<tr>
<td>1.44 (220)</td>
<td>1.35</td>
<td>1.61</td>
</tr>
<tr>
<td>1.18 (222)</td>
<td>1.16</td>
<td>1.19</td>
</tr>
</tbody>
</table>

Table S2: Comparison of d-spacing values obtained by SAED analysis and theoretical values for the cubic structure of silver for both diCF3 and AOT coated Ag-NPs.
Figure S10. UV spectra of Ag nanoparticles redispersed in OFP / HPFP.

References