

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

$$P(Q) = \int_0^{\frac{\pi}{2}} |G(Q, R)|^2 g(R) dR \quad (1)$$

$$G(Q, R) = \left(\frac{4\pi}{3}\right) R^3 \Delta\rho \left[\frac{3j_1(QR)}{QR} \right] \quad (2)$$

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

$$g(R) = \frac{\left(\frac{Z+1}{\bar{R}}\right)^{z+1} R^z \exp\left[-\left(\frac{Z+1}{\bar{R}}\right)R\right]}{\Gamma(Z+1)} \quad (3)$$

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.

$$S(Q, \zeta) = 1 + \left[\frac{\kappa}{1 + (Q\zeta)^2} \right] \quad (4)$$

This describes a decaying distribution, where ζ is a correlation length, and κ 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)^{2,3}, 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:^{3,4}

$$2K + K_{BAR} = \frac{k_B T}{8\pi\eta^2} - \frac{k_B T}{4\pi} f(\phi) \quad (5)$$

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).⁵ The systems studied here consist of surfactants with $C_{surf} = 8$ ($= 2 \times 4$ carbons in diCF3) or $C_{surf} = 10$ (2×5 C in diHCF4). Studies have been done using homologous twin-tailed di- C_n -PC surfactants⁴, 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,⁴ 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 Nave⁶ for a di-chain sulfosuccinate hydrocarbon based system, comparable to the F-MEs studies here: H₂O / diC6SS / 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 diC6SS). 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.

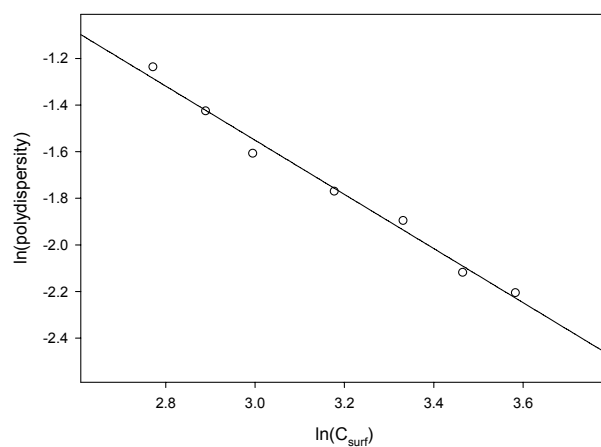


Figure S1: Dependence of polydispersity on surfactant chain length for twin-tailed phosphocholine di- C_n -PC surfactants studied previously.⁴ Solid line shows a linear fit, with gradient -1.16.

Compound	s.l.d. x 10^{-10} / cm^{-2}
H ₂ O	-0.56
D ₂ O (99%)	6.33
diHCF ₄	3.11
diCF ₃	3.15
1H,1H,5H-octafluoropentan-ol (OFP)	2.98
2H,3H-perfluoropentane (HPFP)	3.11
1H-perfluorohexane (HPFH)	3.42

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

D₂O vs H₂O contrast in the F-MEs

In an attempt to gain additional structural information available by SANS, some samples were studied with D₂O instead of H₂O (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 H₂O or D₂O can be used interchangeably in these systems without affecting largely the fit parameters.

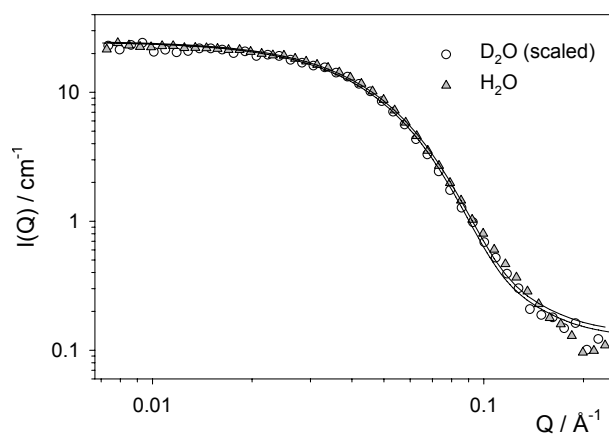


Figure S2: Comparison of core contrast SANS data from water / diCF₃ / OFP / HPFH microemulsions at $w = 40$ using either H₂O or D₂O nanodroplets to generate contrast. Solid lines represent form factor fits to the Schultz polydisperse spheres model. [diCF₃] = 100 mM, OFP : HPFH = 1 : 9 (v:v), T = 40°C. D₂O data and calculated fit has been multiplied by a constant value of 2.3 to overlay onto the H₂O data.

Additional SANS data and Repeats

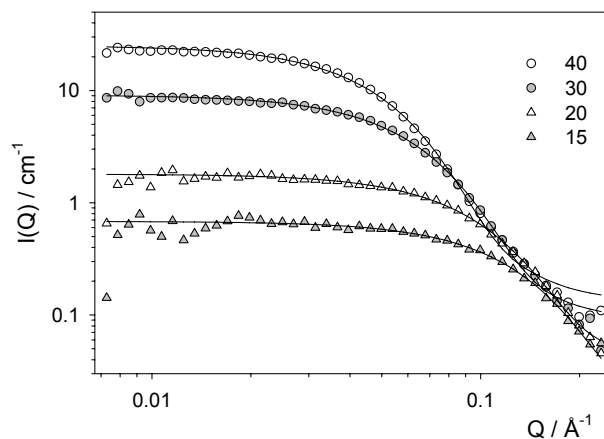


Figure S3: Core contrast SANS data from H₂O / diCF₃ / OFP / HPFH microemulsions at different $w = [\text{H}_2\text{O}] / [\text{diCF}_3]$ as indicated. Solid lines represent form factor fits to the Schultz polydisperse spheres model. $[\text{diCF}_3] = 100 \text{ mM}$, OFP : HPFH = 1 : 9 (v:v), $T = 40^\circ\text{C}$

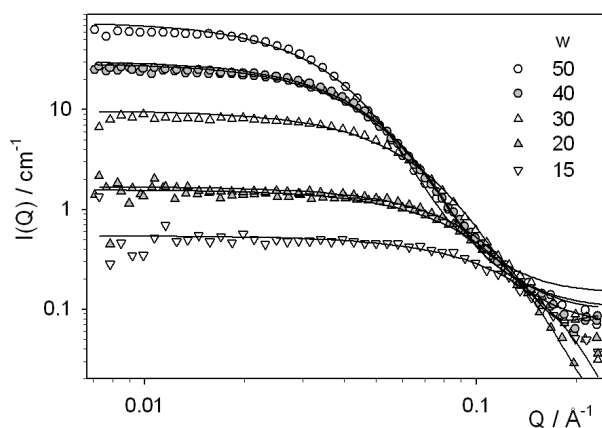


Figure S4: Core contrast SANS data from H₂O / diCF₃ / OFP / HPFP microemulsion systems at different $w = [\text{H}_2\text{O}] / [\text{diCF}_3]$ values indicated. Solid lines represent form factor fits to the Schultz polydisperse spheres model. $[\text{diCF}_3] = 100 \text{ mM}$, OFP : HPFH = 1 : 9 (v:v), $T = 40^\circ\text{C}$. Note for $w = 20$ and

w 40 SANS measurements were repeated using freshly made samples. Good agreement was seen between these repeats.

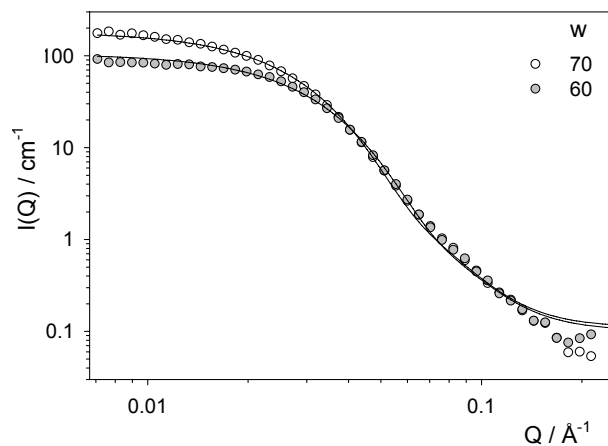


Figure S5: Core contrast SANS data from D_2O / diCF3 / OFP / HPFH microemulsions at high $w = [\text{D}_2\text{O}] / [\text{diCF}_3]$ values indicated. Solid lines represent form factor fits to the Schultz polydisperse spheres model. $[\text{diCF}_3] = 100 \text{ mM}$, OFP : HPFH = 1 : 9 (v:v), $T = 40^\circ\text{C}$

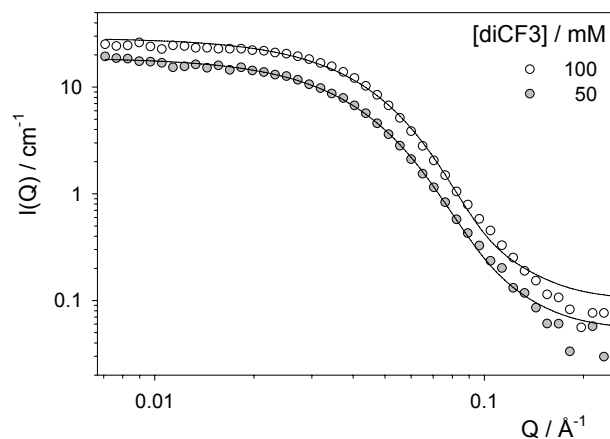


Figure S6: Core contrast SANS data from H₂O / diCF₃ / OFP / HPFP microemulsions at different [diCF₃] values indicated. Solid lines represent form factor fits to the Shultz polydisperse spheres model. $w = 40$, OFP : HPFH = 1 : 9 (v:v), T = 40°C.

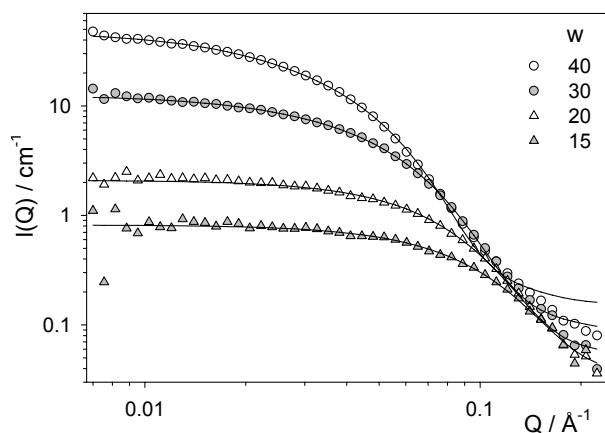


Figure S7 Core contrast SANS data from H₂O / diHCF4 / OFP / HPFP microemulsions at different w values as indicated. Solid lines represent form factor fits to the Schultz polydisperse spheres model with an attractive OZ S(Q) where necessary. [diHCF4] = 100 mM, OFP : HPFH = 1 : 9 (v:v), T = 40°C

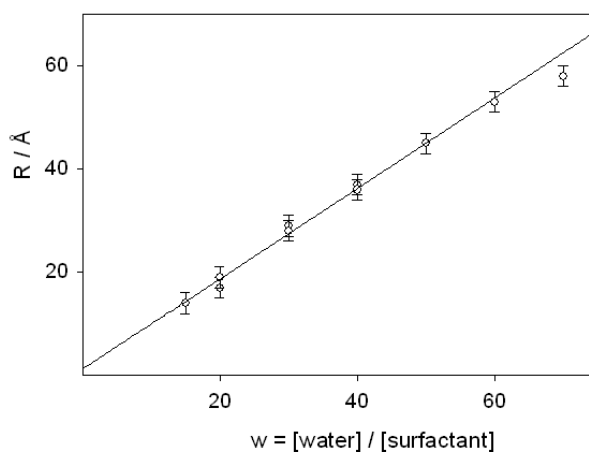


Figure S8: Water droplet radius R vs w for diCF3 – stabilized water / OFP / HPFH microemulsions. R values are calculated from SANS analysis of core contrasts (Table 2) corrected for polydispersity via $R = \alpha(p) \cdot R_{bar}$, as in equations 1, 2. Example error bars are shown. Linear fits from these data are also shown (gradient = 0.877).

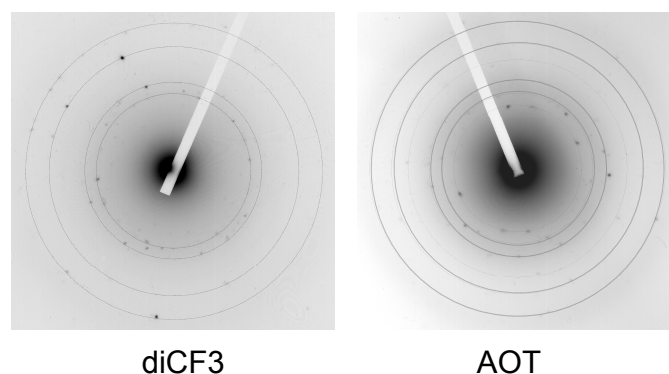


Figure S9: Example SAED patterns for diCF3- (left) and AOT-coated (right) Ag-NPs. Patterns were very faint, consisting of diffraction spots, so dashed-line circles have been added to the patterns to highlight important d-spacings. In increasing distance from the centre of each pattern, these rings represent (111), (200), (220) and (222) Ag cubic crystal planes (also see Table S1)

Ag cubic d-spacings [7]	diCF3 coated Ag-NPs	AOT-coated Ag-NPs
2.36 (111)	2.24	2.34
2.04 (200)	1.92	1.94
1.44 (220)	1.35	1.61
1.18 (222)	1.16	1.19

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.

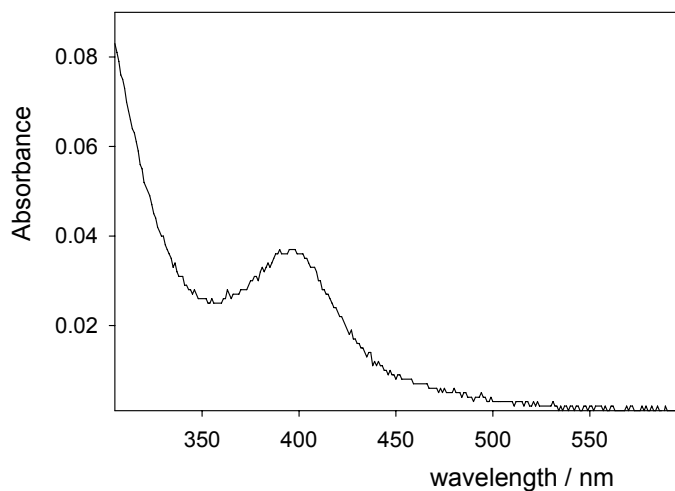


Figure S10. UV spectra of Ag nanoparticles redispersed in OFP / HPFP.

References

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