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Action of hydrotrpores in water-in-CO$_2$

microemulsions

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Abstract
The effects of a homologous series of sodium p-n-alkylbenzoate hydrotrpores in water-in-supercritical CO$_2$ (w/c) microemulsions have been investigated, by comparing the phase behaviour and droplet structures obtained using small-angle neutron scattering (SANS). The w/c microemulsions appeared to be generally stable upon addition of hydrotrpores, however, on increasing the alkyl chain length of the hydrocarbon and fluorocarbon moieties of the surfactants, different effects on stability were observed. Using high-pressure SANS (HP-SANS), the effects of hydrotrpore type on the structures of microemulsion droplets were studied. Interestingly, evidence was found for multiple shell structures with a hydrotrpore rich layer between the water cores and the surfactant films. Such findings are significant to the understanding of self-assembly of co-adsorbed species in supercritical CO$_2$ (scCO$_2$), as the hydrotrpore layers potentially have significant effects on surfactant packing, and can modify the physico-chemical properties of scCO$_2$ through formation of worm-like micellar assemblies.

Keywords: microemulsions, supercritical CO$_2$, hydrotrpores, fluorinated surfactants, shape transition, small-angle neutron scattering
1. Introduction

Being nontoxic, non-flammable, and inexpensive, supercritical CO$_2$ (scCO$_2$) has received considerable attention as an attractive substitute to normal petrochemical solvents; one of the potential applications of scCO$_2$ is enhanced oil recovery (CO$_2$-EOR) of crude oil from porous rock.$^{1,2}$ However, due to the low viscosity liquid CO$_2$ does not readily facilitate transport to oil bearing rock, but rather through surrounding porous media which offers pathways of least resistance.$^{3,4,5}$ To overcome such limitations, different techniques have been investigated to improve the CO$_2$ mobility and conformance such as CO$_2$ thickeners,$^{6,7}$ conformance control gels and in depth mobility control of CO$_2$ foams assisted by various stabilizers.$^{8,9,10}$

One of the great challenges in the field is addressing the fact that scCO$_2$ is a poor medium for most commercially available surfactants which have been developed for alkane solvent (e.g. AOT).$^{11}$ And even for those specifically designed surfactants that effectively stabilise water-in-CO$_2$ (w/c) microemulsions, modification of the self-assembled structures, which has been well-established as an effective method to enhance the viscosity in alkane solvent, is generally inhibited in scCO$_2$.

In one of the very few reports on anisotropic self-assembled structures in scCO$_2$, it was found that by exchanging the surfactant counter ion Na$^+$ with divalent species such as Co$^{2+}$ and Ni$^{2+}$, a sphere-rod shape transition can be obtained for the micelles formed not only in alkane solvents with hydrocarbon surfactants,$^{12}$ but also in scCO$_2$. However, the shape transitions were only observed at very low water content with water: surfactant molar ratio ($W = [\text{water}] / [\text{surf}]$) $\leq 10$, and furthermore, micelles formulated by the counter-ion exchanged surfactants generally require a relatively high pressures (~300 bar) to be
stabilised in scCO$_2$. These factors have largely limited practical applications to modify scCO$_2$

viscosity using this approach.

Hydrotropes are small amphiphilic molecules with hydrophilic character, having the ability
to increase solubility of organic compounds in water. Hydrotropes have attracted great
industrial interest as additives, especially for boosting efficiencies of surfactants in both
aqueous and oil phases.$^{13,14}$ Hatzopoulos et al. have conducted a series of studies to
investigate the links between the properties of hydrotropes and surfactants with a
systematic variation of the molecular structures.$^{15,16}$ Interesting shape transitions between
spherical-cylindrical structures have been reported for a number of AOT stabilised water-in-
oil (w/o) microemulsions on addition of certain hydrotropes. In recent work,$^{17}$ effects of
such hydrotrope additives have been investigated with a custom-made tri-chain
hydrocarbon CO$_2$-active surfactant (TC14), and using High-Pressure Small-angle neutron
scattering (HP-SANS) elliptical micelles were confirmed for microemulsions in both alkane
solvents and scCO$_2$. That initial study is significant in the development of viscosity modifiers
for applications in scCO$_2$, not only because it represents a new approach to promote
micellar growth, but also because the same general effects of hydrotropes are found in both
water-in-oil (w/o) and water-in-CO$_2$ (w/c) microemulsions.

In this paper, effects of hydrotropes in w/c microemulsions were further investigated by in-
depth SANS studies using selective contrast variation to reveal core-shell internal micellar
structures. Although hydrocarbon surfactants are more economically viable and
environmental friendly,$^{18,19}$ fluorocarbon surfactants have been applied here to formulate
w/c microemulsions, owing to following considerations: firstly, fluorocarbon surfactants
offer a much higher stabilisation of w/c microemulsions, which allows the behaviour of
hydrotrope molecules to be studied in a well-defined aqueous core structures;$^{20}$ secondly,
core-shell SANS contrast can be enhanced when a fluorocarbon surfactant shell is present.

Lastly, by employing the hydrocarbon-fluorocarbon mixed systems, the generality for the behavior of hydrotropes with CO₂-philic surfactants can be further tested.

2. Experimental

2.1 Materials and compositions: The structures of surfactants and hydrotropes studied here can be found in Table 1. The details of surfactant synthesis, purification and characterization have been described elsewhere.\textsuperscript{21, 22} The surfactants were used at constant molarity (0.017 mol L\textsuperscript{-1} in a 0.02 L cell), the hydrotropes were dissolved in water with mixed H\textsubscript{2}O and D\textsubscript{2}O at fixed concentrations of [hydrotrope]=0.23 mol L\textsuperscript{-1} and 0.46 mol L\textsuperscript{-1}. An appropriate aqueous solution of the hydrotrope was then introduced to the cell with a fixed water: surfactant ratio W = [water]/[surf] = 15.
<table>
<thead>
<tr>
<th>Compounds</th>
<th>Structure</th>
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<tbody>
<tr>
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</tr>
<tr>
<td>nFG(EO)$_2$</td>
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</tr>
<tr>
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<tr>
<td>BenzC$_n$</td>
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</table>

Table 1. Structures of the surfactants and hydrotropes used in this study.

For experiments as a function of CO$_2$ bulk density, the volume fraction (vol. %) of the microemulsions may be slightly different as the cell volume is also varied to achieve different pressures: vol. % = 0.017 at P=350 bar, vol. % = 0.015 at P=200 bar, and vol. % = 0.014 at P=160 bar, with the temperature remaining as constant T=45°C, the resulting CO$_2$ density can be calculated using Span-Wagner equation of state and varies within the range $\rho_{CO_2} = 0.91 ~ 0.71 \text{ g cm}^{-3}$.  

2.2 Pressure cell: All samples were studied in a stainless steel cell with variable volume (12-20 mL) controlled by a piston with an external hydraulic pump. Once filled with CO$_2$, the pressure was measured by a built-in pressure transducer with accuracy $\pm 1$ bar. Two sapphire
windows fitted in parallel allow for visual observations of phase behavior. Temperature was controlled at 45 °C by a water bath flowing around a heating circuit in the cell body. In order to obtain w/c microemulsions, the appropriate amount of pre-weighed surfactant and hydro trope solution in D₂O/H₂O was fed into the cell to establish the W (= [water]/[surf]) of interest. Subsequently, the cell was sealed and liquid CO₂ was introduced at relatively low temperature ~5°C and re-equilibrated at 45°C in the cell under magnetic stirring. The inlet line was closed once the pressure reached 120 bar, and under these conditions CO₂ is in the supercritical state. The pressure could be further increased using a hydraulic pump, up to a maximum of 450 (±5) bar, which allowed stable w/c microemulsions to be formulated.

2.3 SANS: SANS experiments were carried on the SANS2D instrument at the ISIS spallation source, Rutherford Laboratory, UK. SANS2D spans a Q range of 0.002 < Q < 1 Å⁻¹ with neutron wavelength λ of 2.2-10 Å⁻¹.

The transfer of momentum, or scattering vector Q is defined as

\[ Q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \]  

where θ is the scattering angle and λ the incident neutron wavelength.

The scattering data were normalized for the sample transmission, empty cell and solvent background and put on an absolute intensity I(Q)/cm⁻¹ scale using standard procedures, the errors in intensity I(Q) are expected to be lower than 5%. The scattering intensity I(Q) is plotted as a function of Q, which can be broadly described by:
I(Q) \propto P(Q)S(Q) + B_{\text{inc}} \quad (2)

$B_{\text{inc}}$ is the background incoherent scattering, $S(Q)$ is the structure factor related to interparticle interactions. In this study, the systems were at low concentration in a non-polar medium, therefore, to a first approximation $S(Q)$ can be neglected (~1).

$P(Q)$ is the form factor which describes the internal structure of scattering particles. It should be noted that, by varying the scattering contrast which arises from the difference in scattering length density (SLD) between adjacent phases, the scattering profile can be altered depending on which region is ‘highlighted’. In order to study the effect of hydrocarbon additives on fluorocarbon surfactant films in w/c microemulsions, a core-shell contrast was employed to highlight the different local domains, as described in ref. 20.

The data have been analysed by the fitting program SASview using a built-in spherical core-shell form factor model. The scattering laws used can be found in Supporting information, the SLD of the water core and CO$_2$ bulk were calculated from their compositions and constrained for the purposes of fitting (with 30 wt% D$_2$O and 70 wt% H$_2$O, SLD$_{\text{core}}$=1.5×10$^{-6}$ Å$^{-2}$; SLD$_{\text{CO2}}$=1.8×10$^{-6}$Å$^{-2}$ when $\rho_{\text{CO2}}$ =0.71 g cm$^{-3}$, and 2.3×10$^{-6}$Å$^{-2}$ when $\rho_{\text{CO2}}$ =0.92 g cm$^{-3}$). The SLDs of different hydrotropes are: SLD$_{\text{C0Benz}}$=1.5×10$^{-6}$Å$^{-2}$, SLD$_{\text{C2Benz}}$=1.3×10$^{-6}$Å$^{-2}$, and SLD$_{\text{C8Benz}}$=0.85×10$^{-6}$Å$^{-2}$, which are relatively close that for the mixed D-H water core.

In addition, the maximum concentration of additives in the aqueous cores is < 0.5 mol L$^{-1}$, which should have no notable effect on the “volume fraction”. Therefore, addition of hydrotropes should not have any significant impact on the value of SLD$_{\text{core}}$. On the other hand, due to the unknown influence of hydrotropes on surfactant packing, the SLD of surfactant layer, or the shell, is difficult to predict. However, the surfactant chain length (or the shell thickness) is expected to be unaffected by the presence of these additives, and can
be treated as a constrained parameter. For this study, the shell thickness for each surfactant was correspondingly obtained from the hydrotrope free w/c microemulsions, with the SLD value calculated from the structure and density of an equivalent fluoroalcohol with same number of CF₂ units (SLD_{shell}~3.5×10^{-6} Å⁻²), the results show essentially identical shell thicknesses for 6FG(EO)₂ and 6FS(EO)₂ ~ 8 Å, whereas for 4FG(EO)₂, the shell thickness is ~6 Å. These parameters were then fixed in the analyses of systems with added hydrotropes, with the SLD_{shell} being allowed to adjust within a sensible range (3×10^{-6} to 4×10^{-6} Å⁻²).
3. Results and discussion

3.1 Phase behaviour: The phase behaviour of the w/c microemulsions at W15 with C$_n$Benz additives has been studied via visual observation at as a function of temperature and pressure, and the results are summarised in Figure 1. In general, turbid-transparent phase transitions have been observed for all the samples, however, for two of the mixtures: 4FG(EO)$_2$+C$_0$Benz and 6FS(EO)$_2$+C$_8$Benz, although such phase transitions were still observed, the systems appeared to coexist with significant amount of undissolved droplets, even at the highest pressure up to 400 bar. Nevertheless, the results (Figure 1a, 1b, 1c) have clearly revealed that the CO$_2$ density at the phase boundary decreases linearly with temperature.
Figure 1 Phase behaviour of w/c microemulsions at W15 stabilised by 4FG(EO)$_2$, 6FS(EO)$_2$ and 6FG(EO)$_2$ surfactants (in figure a, b and c respectively) after mixing with different hydrotropes. The measured phase transition pressures-temperatures have been converted to the corresponding CO$_2$ densities. In Figure 1d, the effect of hydrotrope chainlength are compared for each surfactant at 45 °C by plotting the alkyl carbon number $N$ against the CO$_2$ density at the phase transition point. It should be noted again that, for the circled data points, the system actually appeared to be transparent but coexisted with droplets, instead of a clear single phase as the others.

In Figure 1d, the stability of the w/c microemulsions have been cross compared at 45 °C, and all three surfactants appeared to exhibit very different behaviour as a function of hydrotrope chain length N. For the systems with 6FG(EO)$_2$, the effect of hydrotrope
additives appeared to be relatively mild, whereas a more significant destabilisation, as indicated by the increasing CO$_2$ density at the phase transition point is seen for 6FS(EO)$_2$ stabilised systems as N increases. Interestingly, for 4FG(EO)$_2$ stabilised systems, variation of N also appeared to give significant effects, but with the opposite trend compared to 6FS(EO)$_2$: as shown in the figure, with a long chain hydrotrope, C$_8$Benz, the stabilisation point for 4FG(EO)$_2$ system was obtained at much lower CO$_2$ density, but with a more hydrophilic additive (i.e. C$_0$Benz or C$_2$Benz), the stabilisation pressure/density increases, hence, the system become less stable.

3.2 Hydrotropes with 6FG(EO)$_2$ and 6FS(EO)$_2$: Studies based on water-in-oil (w/o) microemulsions have demonstrated that the effect on the structure of microemulsion droplets varies with the chain length N of hydrotrope additives.$^{15,16}$ In Figure 2a, the SANS from 6FS(EO)$_2$ stabilised microemulsions with short chain C$_n$Benz additives (n=0, 2) at 350 bar are compared, and the main fitting parameters are listed in Table 2. The shift of scattering profiles for both C$_0$ and C$_2$Benz added systems clearly indicates a small reduction in the core radius ($R_{\text{core}}$), from 18 Å for a hydrotrope free microemulsion, to ~15 Å on average as C$_0$Benz and C$_2$Benz hydrotropes were added. Moreover, an interesting dependence between the size polydispersity of microemulsion droplets and hydrotrope concentration was also observed: at lower hydrotrope molar concentration (M=0.23 mol L$^{-1}$, $M_{\text{hydrotrope}}: M_{\text{surfactant}}$ ~ 1:16), the polydispersities were found ~25%. With increased hydrotrope concentration (0.46 mol L$^{-1}$, $M_{\text{hydrotrope}}: M_{\text{surfactant}}$ ~1:8), however, the polydispersity dropped to 18%, which was equivalent to the hydrotrope free microemulsion. As suggested by a number of studies,$^{29,30}$ variation in the microemulsion size polydispersity can be interpreted in the framework of film bending energy theory: details of the
correlation between polydispersity and film bending energies can be found in the
Supporting Information for this paper.

The reduction in microemulsion radius found in these systems could be explained by the
effect of increased charge screening at the headgroups, and increased entropy of mixing
due to addition of hydrotopes, the film bending energy initially decreases, as indicated by
the increase of the size polydispersity compared to hydrotrope free system. As the charge
screening becomes more significant with increasing hydrotrope concentration, surfactant
films appear to become more rigid, and the polydispersity decreases.

On the other hand, once a longer chain hydrotrope, C8Benz, was introduced at
concentration 0.23 mol L−1 to the aqueous core, both the structure and stability of w/c
microemulsion were found be significantly different: instead of stable single phase
microemulsions, the systems appear to coexist with an extra phase, which can be seen by
SANS from the sharply increased intensity at low Q range. More importantly, a significant
enhancement of intensity was also found for the mid-Q range the peak, and the scattering
profile is not consistent with the core-shell model as seen for the 6FS(EO)2 stabilised w/c
microemulsions (See Supporting Information). In a previous contrast variation SANS study of
w/c microemulsions, it was demonstrated that such enhancement could be obtained as a
result of increased definition of the core-shell boundary, such as a reduction in SLDcore.

Although in an earlier section, it was noted that the hydrotopes dispersed in the aqueous
cores should not have any significant effects on the value of SLDcore. However, as an
amphiphilic molecule, C8Benz is very likely to accumulate at the water/CO2 interface. The
SANS results seem to suggest that, instead of mixing towards the fluorocarbon shell which
would should result in a reduction in core-shell contrast, a hydrocarbon-rich layer has been
formed, which causes a change at the core-shell interface. Hence, a core multi-shell model has been applied to analyse these data, with a hydro trope rich layers as extra shells between the H$_2$O/D$_2$O cores and the fluorocarbon shells. The SLD$_{\text{hydro trope-layer}}$ was set to 0.95 × 10^{-6} \text{Å}^2$, based on the SLD of C$_8$Benz with assumptions that the hydro trope layer coexists with 20 wt% H$_2$O/D$_2$O of the aqueous core. Good agreement was obtained between the multi-shell model and the scattering profile as shown in Figure 2b, and the fitting parameters are listed in Table 2.

It should be noted that, although a hydrocarbon moiety is also found in 6FS(EO)$_2$ surfactant itself, interestingly, a multiple-shell scattering profile has never been observed in any other w/c microemulsions reported. This is possibly due to hydration of the headgroups, and also the weak contrast in such systems.
Figure 2a (upper) shows the SANS results for 6FS(EO)₂ and 6FG(EO)₂ stabilised microemulsions with short chain hydrotropes (C₀ and C₂Benz). The datasets have been multiplied by factors of 1.5× for 6FS+C₀Benz at 8:1, 3× for 6FS+C₂Benz at 16:1 and 4× for 6FS+C₂Benz at 8:1. Figure 2b (lower) compares the effect of a longer chain hydrotrope (C₈Benz) on w/c microemulsions with 6FS and FG(EO)₂, in comparison to the w/c microemulsions without hydrotropes. The datasets for 6FG+C₈Benz have been multiplied by 3×, and 6FG(EO)₂-only system by 4×.

The interactions between the hydrocarbon moieties of surfactant and hydrotropes was further investigated in w/c microemulsions stabilised by 6FG(EO)₂. As shown in Table 1, the surfactant has the same fluorocarbon chain as 6FS(EO)₂, but with an extra methylene unit.
next to the headgroup, such modification on structure has been reported to enhance the water loading capacity effectively stabilize w/c microemulsions.32

For the system with added C₈Benz, despite the enhanced stabilities compared to 6FS(EO)₂ systems, SANS results have also shown that thickness of the hydrocarbon-rich layer was reduced by ~45% (from 11 Å to 6 Å) in 6FG(EO)₂ stabilised microemulsions. Such a difference between 6FG(EO)₂ and 6FS(EO)₂ stabilised systems should be attributed to the additional methylene group in the hydrophilic region of the surfactant, as suggested by Sagisaka et.al,32 this introduces extra flexibility for surfactant packing at the interface.

<table>
<thead>
<tr>
<th>System</th>
<th>Shell SLD / (10⁻⁶ Å⁻²)</th>
<th>R_core/Å (±1 Å)</th>
<th>Thickness Shell /Å (±1 Å)</th>
<th>σ / R_core</th>
<th>[hydrotrope] / (mol L⁻¹)</th>
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<tr>
<td>6FS(EO)₂</td>
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<td>8</td>
<td>0.18</td>
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<td>8</td>
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<td>6</td>
<td>0.35</td>
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Table 2. Important fitting parameters for hydrotrope free and different hydrotrope mixed w/c microemulsions with surfactants 6FS(EO)₂, 6FG(EO)₂ and 4FG(EO)₂. Data were obtained at 350 bar, 45°C.

*The system was turbid at stirring, the data were analysed for the clear phase with the stirrer stopped.
In summary, the results have clearly indicated that, despite being expelled from the 
fluorocarbon shell, long chain hydrotropes tend to mix with the hydrocarbon moiety of the 
surfactant. But with a relatively constrained structures at the interface as obtained in the 
6FS(EO)₂ stabilised systems, the hydrotropes suffer a greater entropy penalty, and therefore 
is located further from the surfactant layer. As unfavourable interactions increase between 
the hydrotrope alkyl chains and the sulfosuccinate groups in the surfactant, the systems also 
become relatively unstable.

3.3 Hydrotropes with 4FG(EO)₂: As compared in the previous section, reduction of 
surfactant chain length with only two CF₂ units on each tail appeared to result in significant 
effects on the stabilisation of w/c microemulsions with CₙBenz additives. SANS on 4FG(EO)₂ 
systems has shown that a sharp rise of low Q intensity was obtained for the microemulsions 
mixed with C₀Benz, consistent with the visual observation of large droplets even at the 
highest pressure (350 bar). However, the peak at medium Q corresponding to the core-shell 
interference was still obtained for both stirred and non-stirred (thus, a clear single phase) 
systems, which confirmed formation of a Winsor II type microemulsion.

With increased hydrotrope chain length, C₂Benz and C₈Benz formed stable mixtures with 
4FG(EO)₂ stabilised w/c microemulsions. SANS results also showed similar behaviour for 
4FG(EO)₂, 6FG(EO)₂ and 6FS(EO)₂ stabilised systems with C₂Benz hydrotrope. For the system 
with the long chain C₈Benz additive, however, SANS did not show strong evidence for the 
multi-shell structure as found in 6FS/FG(EO)₂+C₈Benz systems. Although by using the core 
multi-shell model, good fits could still be obtained, the hydrotrope layer thickness, however, 
cannot be determined with any precision. Moreover, the multi-shell model fitting cannot be
so readily distinguished from a single shell model (see Supporting information) as clearly as found with the 6FS/FG(EO)₂ + C₈Benz systems.

Nevertheless, the scattering from the 4FG+C₈Benz system showed a notable increase of background intensity compared with the hydrotrope free systems, which should be attributed to increasing incoherent scattering from the hydrocarbon additives. Therefore, the hydrotrope molecules might be held within the microemulsion droplets, otherwise the ¹H containing compounds would be too dilute in the bulk phase (≈7.5×10⁻⁴ mol L⁻¹) to give such a significant effect on incoherent scattering. Moreover, Hatzopoulos et al.¹⁸ have demonstrated that the critical aggregation concentration (cac) of C₈Benz in aqueous solution is 0.011 mol L⁻¹, whereas in this study, the concentration of hydrotrope in the aqueous core was ~0.23 mol L⁻¹, thus, about 20×cac. At this concentration, such amphiphilic molecules can be hardly dispersed in the aqueous core as normal solutes. Therefore, it is reasonable to believe that the long chain hydrotrope C₈Benz should behave in the same way regardless to the surfactant chain length.
Figure 3. SANS results for 4FG(EO)$_2$ stabilised microemulsions with C$_0$, C$_2$ and C$_8$Benz. It should be noted that C$_0$Benz gives a turbid mixture with 4FG(EO)$_2$, SANS studies were performed while the system was being stirred and steady, and the results are compared. The systems with C$_2$ and C$_8$ hydrotropes have been multiplied by 3×.

From a series of w/c microemulsions with a similar contrast as applied in this study, Yan et al. have demonstrated that by either increasing the core size or decreasing surfactant chain length, the scattering from the core become more significant and the core-shell features become less apparent. Furthermore, the SLD of the hydrotrope is very close to that for the core, and in 4FG(EO)$_2$ stabilised systems where the core-shell structure appears to be less pronounced, and therefore, to distinguish such a subtle structural feature is very difficult, especially within ~ 5Å.
3.4 Effect of CO₂ density: The systems discussed in above sections were all obtained at 350 bar with the bulk density ρCO₂=0.917 g cm⁻³. In previous studies, it has also been revealed that variation of bulk density can result in significant effects on the film properties in w/c microemulsions and could even drive droplet shape transitions.²⁰ Herein, the structures of microemulsion droplets in the hydrotrope mixed systems, in particular, for those obtained from stable and clear phases, are compared at reduced pressure using SANS.
Figure 4a (upper) compares the SANS from w/c microemulsions with two short chain hydrotropes (C0 and C2) at reduced CO₂ density ($\rho_{CO₂}=0.812$ g cm⁻³, $P=200$ bar at 45°C).

The datasets for 6FS+C₂Benz and 6FG+C₂Benz systems have been multiplied by a factor of 3×. In 3b (lower), the structure has been compared between the 4FG and 6FG(EO)₂ stabilised microemulsions with C8 hydrotrope at reduced CO₂ density ($\rho_{CO₂}=0.812$ g cm⁻³, $P=200$ bar at 45°C; and $\rho_{CO₂}=0.759$ g cm⁻³, $P=160$ bar at 45°C), datasets for 4FG+C₈Benz at 160 bar has been multiplied by 4×, and the system at 200 bar by 5×.

For a bulk density $\rho_{CO₂}=0.917$ g cm⁻³ at 350 bar, 6FS and 6FG(EO)₂ stabilised w/c microemulsions with added short chain hydrotropes (C₀ and C₂Benz) appear to have similar structures. However, as pressure is reduced to 200 bar ($\rho_{CO₂}=0.812$ g cm⁻³), a notable
difference is obtained for the two systems: as shown in Figure 4a, the definition of primary and secondary peaks diminished with 6FS(EO)$_2$, consistent with a significant increase in polydispersity. Whereas in 6FG(EO)$_2$ stabilised microemulsions, the core-shell features were more clearly distinguished and little differences in structure are noted compared to the 350 bar case. On the other hand, for systems stabilised by 4FG(EO)$_2$, pressure variation appears to affect the polydispersity, which increased from 26% to 32% as CO$_2$ density was reduced from 0.812 g cm$^{-3}$ to 0.759 g cm$^{-3}$.

Once a longer chain hydrotrope (C$_8$Benz) was introduced to 4 and 6FG(EO)$_2$ stabilised microemulsions, however, the effect of bulk density appears to be quite the opposite compared short chain hydrotropes. Most notable is for the 6FG(EO)$_2$ system from 200 and 160 bar ($p$CO$_2$=0.812 and 0.759 g cm$^{-3}$ respectively), the scattering profiles interpreted in terms of the core multi-shell model indicate increasing hydrotrope layer thickness, reducing core radius and increasing polydispersity. Whereas for 4FG(EO)$_2$ stabilised systems, such effects on the hydrotrope layer were not observed. It should be noted that the core multi-shell model applied in these systems is based on a constant composition assuming 80%wt hydrotrope coexists with 20%wt H$_2$O/D$_2$O in the hydrotrope layer, and the layer-thickness is treated as a variable. Alternatively, if the hydrotrope layer thickness was set as a fixed parameter, a decreased SLD$_{hydrotrope layer}$ will be obtained corresponding to increasing hydrotrope concentration in the co-existing water droplet phase. Nevertheless, results have clearly revealed that the effect of bulk density on the adsorption of hydrotropes is more significant in 6FG(EO)$_2$ stabilised microemulsions comparing to systems with 4FG(EO)$_2$, which can be attributed to increasing effect of de-mixing between hydrotropes and fluorocarbon surfactants. Comparison of the behaviour of C$_8$Benz in 4 and 6FG(EO)$_2$ seems
to suggest that, despite the similarity of structures at the headgroup, the surfactant with reduced CF$_2$ units is more miscible with the hydrotrope, which may be attributed to the reduced antipathy for the hydrocarbon species as the number of CF$_2$ units is reduced.

<table>
<thead>
<tr>
<th>System</th>
<th>Shell SLD /10^6 Å$^{-2}$</th>
<th>$R_{core}$/Å ($\pm 1$ Å)</th>
<th>Thickness Shell /Å ($\pm 1$ Å)</th>
<th>$\sigma / R_{core}$</th>
<th>P CO$_2$ / (g cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6FS(EO)$_2$+C$_6$Benz</td>
<td>3.6</td>
<td>16</td>
<td>8</td>
<td>0.27</td>
<td>0.812</td>
</tr>
<tr>
<td>6FS(EO)$_2$+C$_2$Benz</td>
<td>3.2</td>
<td>13</td>
<td>8</td>
<td>0.34</td>
<td>0.759</td>
</tr>
<tr>
<td>6FG(EO)$_2$+C$_6$Benz</td>
<td>3.2</td>
<td>17</td>
<td>8</td>
<td>0.20</td>
<td>0.812</td>
</tr>
<tr>
<td>6FG(EO)$_2$+C$_2$Benz</td>
<td>3.4</td>
<td>19</td>
<td>8</td>
<td>0.23</td>
<td>0.759</td>
</tr>
<tr>
<td>4FG(EO)$_2$+C$_2$Benz</td>
<td>3.3</td>
<td>14</td>
<td>6</td>
<td>0.33</td>
<td>0.812</td>
</tr>
<tr>
<td>6FG(EO)$_2$+C$_6$Benz</td>
<td>3.5</td>
<td>11</td>
<td>8</td>
<td>0.30</td>
<td>0.812</td>
</tr>
<tr>
<td>6FG(EO)$_2$+C$_4$Benz</td>
<td>3.7</td>
<td>12</td>
<td>6</td>
<td>0.32</td>
<td>0.812</td>
</tr>
<tr>
<td>6FG(EO)$_2$+C$_6$Benz</td>
<td>3.5</td>
<td>7</td>
<td>15 (hydrotrope layer)</td>
<td>0.35</td>
<td>0.759</td>
</tr>
<tr>
<td>4FG(EO)$_2$+C$_8$Benz</td>
<td>3.8</td>
<td>16</td>
<td>6 (hydrotrope layer)</td>
<td>0.26</td>
<td>0.759</td>
</tr>
</tbody>
</table>

Table 3 Important fitting parameters for different hydrotrope mixed w/c microemulsions with surfactants 6FS(EO)$_2$, 6FG(EO)$_2$ and 4FG(EO)$_2$ at reduced pressure with constant temperature 45°C.

Although it has been suggested in a previous section that, the less apparent core-shell structures in 4FG(EO)$_2$ may result in difficulty in distinguishing the hydrotrope rich layer in such systems. However, if the hydrotrope molecules accumulate with a similar behaviour as in 6FG(EO)$_2$ systems, an effect should be eventually obtained, but that was observed for neither of the systems stabilised by 4FG(EO)$_2$ at reduced bulk densities.
4. Conclusions

The behaviour of hydrotropes have been investigated systematically in water-in-scCO$_2$ (w/c) microemulsions stabilised by a series of fluorocarbon surfactants: 6FS(EO)$_2$, 6FG(EO)$_2$ and 4FG(EO)$_2$.

In summary, w/c microemulsions can be influenced by hydrotrope additives in two ways: firstly, the electrostatic interaction arising from hydrotrope ionization in the water pool, which in general will tend to destabilise microemulsions; and secondly, adsorption of hydrotrope molecules towards the water/surfactant/CO$_2$ interface. It should be noted that, consistent with a number of studies on hydrotropic behaviour in aqueous phases, instead of an ‘on-off’ association switch seen with most classical surfactant systems, a stepwise association is preferred for hydrotropes over a range of concentration. In other words, even at concentrations above the cac, the effect of hydrotropes could be very different as the adsorption continues to increase at higher concentrations: this is expected to be achieved by longer chain hydrotropes. However, as the hydrotrope becomes more ‘surfactant-like’ with increasing hydrophobicity, the mixture becomes less stable with increasing counteraction from the fluorocarbon moieties in the surfactant layer. Although contrast variation SANS has shown evidence for interfacial segregation of the surfactants and hydrotropes, the resolution of this technique is not high enough to enable further speculation regarding the relative orientations and distributions of the two components in the films.

Although only certain hydrotrope: surfactant ratios were considered, higher levels are more likely to induce elongated micellar structures, the results have clearly revealed the generality of the action of hydrotropes with microemulsions, both water-in-CO$_2$(here) and
water-in-hydrocarbon $^{15,16}$ systems. Furthermore, the packing of hydrotropes into the surfactant films has also emphasised the significance of surfactant headgroup structure. Interactions between the hydrotropes and hydrocarbon moieties of the surfactants appear to be key for affecting stability, and possibly structure, of the microemulsion droplets. Such effects may not be limited to surfactant-hydrotrope systems as discussed in this study, but can also be expanded to other additives, such as para-substituted phenols,\textsuperscript{35,36,37} which have been demonstrated as effective viscosity modifiers in hydrocarbon systems through formation of extended elongated micelles. By highlighting the similarities between self-assembly of these surfactant-hydrotrope mixtures in scCO\textsubscript{2} and hydrocarbon solvents, effective methods could be developed to improve the physicochemical properties of scCO\textsubscript{2}, which allows potential applications to be practically achievable.

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