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Shape Transitions in Supercritical CO_2 Microemulsions Induced by Hydrotropes

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Abstract

The ability to induce morphological transitions in water-in-oil (w/o) and water-in-CO_2 (w/c) microemulsions stabilized by a tri-chain anionic surfactant 1,4-bis(neopentyloxy)-3-(neo-pentyloxycarbonyl)-1,4-dioxobutane-2-sulfonate (TC14) with simple hydrotrope additives has been investigated. High pressure small-angle neutron scattering (SANS) has revealed the addition of a small mole fraction of hydrotrope can yield a significant elongation in the microemulsion water droplets. For w/o systems, the degree of droplet growth was shown to be dependent on the water content, the hydrotrope mole fraction and chemical structure; whereas for w/c microemulsions a similar, but less significant effect was seen. The expected CO_2 viscosity increase from such systems has been calculated and compared to related literature using fluorocarbon chain surfactants. This represents the first report of hydrotrope induced morphology

changes in w/c microemulsions, and is a significant step forward towards the formation of hydrocarbon worm-like micellar assemblies in this industrially relevant solvent.

Introduction

Over the last 30 years there has been a drive to design additives able to modify the properties of supercritical carbon dioxide ($scCO_2$) to render it more suitable for industrial applications[1-3]. Whether trying to improve surface tension, wettability or viscosity, the ability to optimize the physico-chemical properties of $scCO_2$ is of great interest.

One particular application that would benefit from further development is the use of $scCO_2$ for enhanced oil recovery (CO_2-EOR) from porous rocks[4, 5]. The main disadvantage of using CO_2 in EOR is the very low viscosity, which does not readily facilitate transport over oil bearing reservoirs, but rather through porous media (fingering) which occurs to make a pathway of least resistance[6]. There is therefore a need to develop systems that can enhance CO_2 viscosity[7-11].

Numerous surfactants and co-solutes are known to generate viscous phases in both aqueous and organic media[12-14] but due to limited solvency of CO_2, they are unsuitable for use in that solvent. Fluorinated surfactants, many based on the classic anionic surfactant Aerosol-OT (AOT), have been designed for CO_2 and are able to form water-in-CO_2 (w/c) microemulsions[15-21] as has been highlighted in numerous reviews[6]. It has been shown that by counterion modification of these surfactants, the formation of rod-like micelles[22] can be induced leading to viscosity increases of up to 90 %[6, 23]: the importance of counterion choice in the design of CO_2-philic surfactants has been the focus of a recent review[24]. Unfortunately, these surfactants are highly fluorinated and therefore expensive and environmentally unfriendly[25, 26]. To overcome this problem, low fluorine/hydrocarbon replacements have recently been developed[27-29].

One of the first hydrocarbon surfactants compatible enough with CO_2 to form microemulsions is the tri-chain hydrocarbon TC14 (Figure 1)[30]. As for the fluorinated surfactants, TC14 has also been studied with a series of different counterions, but whereas similar rod-like micelles were formed in hydrocarbon solvents, the same effects were not observed in CO_2 showing that counterion exchange cannot be used as a strategy to enhance viscosity for this surfactant class[31].

Another approach to form rod-like micelles in alkane solvents is using surfactant/hydrotrope mixtures[32-35]. Hydrotropes are small amphiphilic molecules which have hydrophilic character, and the ability to increase solubility of organic compounds in water[36-38]. They have been shown to induce both aqueous micellar and w/o microemulsion growth [32, 34]. Recently, Hatzopoulos et al. found that when AOT was mixed with a series of simple carboxylic acid salt hydrotropes (Table 1b-e), depending on the structure of the additive and the amount of water present, either spherical or rod-like nanodroplet microemulsions could be formed [33]. In this new paper the same series of hydrotropes has been studied but using the promising CO_2-philic surfactant TC14 in both w/o and w/c microemulsions.

Here it has been demonstrated that similar spherical to rod-like transitions can be obtained using TC14 in both w/o and w/c microemulsions. For w/o alkane systems, significant elongations could be obtained, with rod-shaped nanodroplets having aspect ratios over 100. In CO_2, the effects were less pronounced, but still significant with microemulsion aspect ratios over 2 for the prolate ellipsoids formed. The $scCO_2$ viscosity increases which would be expected from the presence of these ellipsoidal micelles has been estimated and results comparable to enhancements seen in similar *w*-value microemulsions of counterion modified, fluorinated

surfactants [NEEDS A REF]. This represents a significant step in the ability to form rod-like micelles in $scCO_2$. So far the only viable method of obtaining this has been through modification of the counterion of fluorocarbon surfactants, which requires lengthy and expensive, synthesis. Here, similar results have been obtained by taking a hydrocarbon surfactant with a single counterion and cheap, readily available additives.

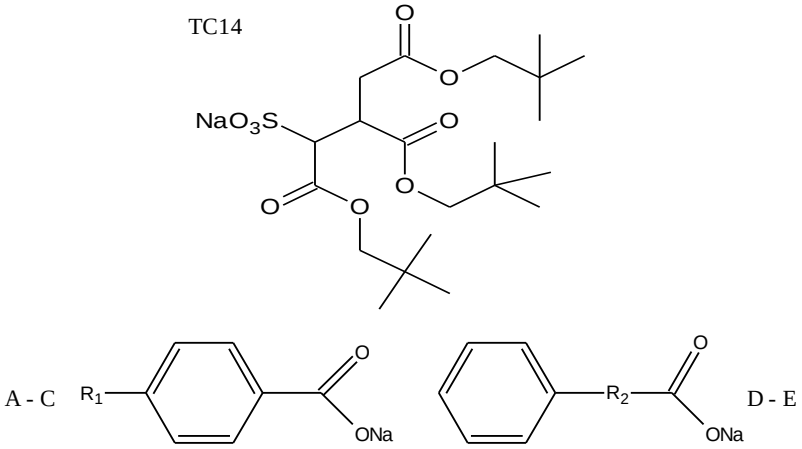


Figure 1. The surfactant, TC14, and hydrotropes studied here where: (A) is C_2Benz where R_1 = CH_3CH_2, (B) is C_4Benz where R_1 = $CH_3(CH_2)_3$, (C) is C_8Benz where R_1 = $CH_3(CH_2)_7$ (D) is PhenC_3 where R_2 = CH_2CH_2 and (E) is PhenC_5 where R_2=$(CH_2)_4$.

Experimental

Materials

Details describing the synthesis and purifications of TC14 and the hydrotropes have been published previously[37, 39]. Microemulsions were prepared at a fixed surfactant concentration of 0.05 mol dm^{-3} and hydrotrope mole fraction, *X*, of 0.10 and 0.20 (where *X* = [moles of hydrotrope]/ [moles of hydrotrope]+[moles of surfactant]). Water was added until the desired water to surfactant ratio (the *w* value = [water]/[surfactant][40]) was reached.

Small-Angle Neutron Scattering (SANS)

SANS measurements were performed using the time-of-flight instruments LOQ[41] and SANS2D[42] at the ISIS spallation source, Rutherford Appleton Laboratory, Oxfordshire, UK. LOQ spans a scattering vector, Q, range of $0.008 < Q < 0.25$ $Å^{-1}$ by using neutron wavelengths of 2.2 – 10 Å and SANS2D spans $0.002 < Q < 1$ $Å^{-1}$ using neutron wavelengths of 2 – 14 $Å^{-1}$. Q is defined as:

$$Q = \frac{4\pi}{\lambda}\sin\frac{\theta}{2} \quad (1)$$

Where θ is the scattering angle and λ the incident neutron wavelength. Samples in alkane solvents were run in quartz cells (Hellma) with a pathlength of 1 mm at 25 °C. High-pressure SANS was performed using a Thar pressure cell as described previously[23] with a 10 mm pathlength at 45 °C and 400 bar. All scattering data were normalised for the sample transmission,

empty cell, and solvent background and put on an absolute intensity scale using standard procedures for each instrument given errors in scattering intensity of within 5 %[43].

The neutron scattering intensity as a function of scattering vector, I(Q), is dependent on the number of scattering bodies, *Np*; the particle volume, *Vp*; the difference in scattering length density between the scattering body and the solvent ($\Delta\rho$); the form factor, P(Q); which describes particle size and shape; the structure factor, S(Q), which describes interactions between different scattering bodies; and the background incoherent scattering as defined by[44]:

$$I(Q) = N_p V_p^2 (\Delta\rho)^2 P(Q) S(Q) + B_{inc} \quad (2)$$

The neutron scattering contrast in this study arises primarily between the deuterated microemulsion water core and the carbon dioxide. Numerous models have been developed to describe both P(Q) and S(Q) and can be combined manually or in fitting programs with parameters in those models adjusted until a fit is obtained. Here the fitting program SANSview has been used to analyse the data[29]. The equations describing the three scattering laws used, Schultz polydisperse spheres[45, 46], ellipsoidal[47] and rod[45] form factor and more detail on scattering contrast, can be found in the supporting information. As noted in other CO_2 high pressure SANS studies, due to the low surfactant concentration and low-dielectric constant of supercritical CO_2, no structure factor has been needed in the data fitting

Results and Discussion

water-in-oil microemulsions

Scattering data for TC14 stabilised water-in-heptane microemulsions of varying *w* value are shown in Figure 2. As with data previously seen for water-in-cyclohexane microemulsions[31], the nanodroplets formed are best described by a polydisperse sphere form factor and solid lines in Figure 2 show the fits obtained with the radii values presented in Table 1.

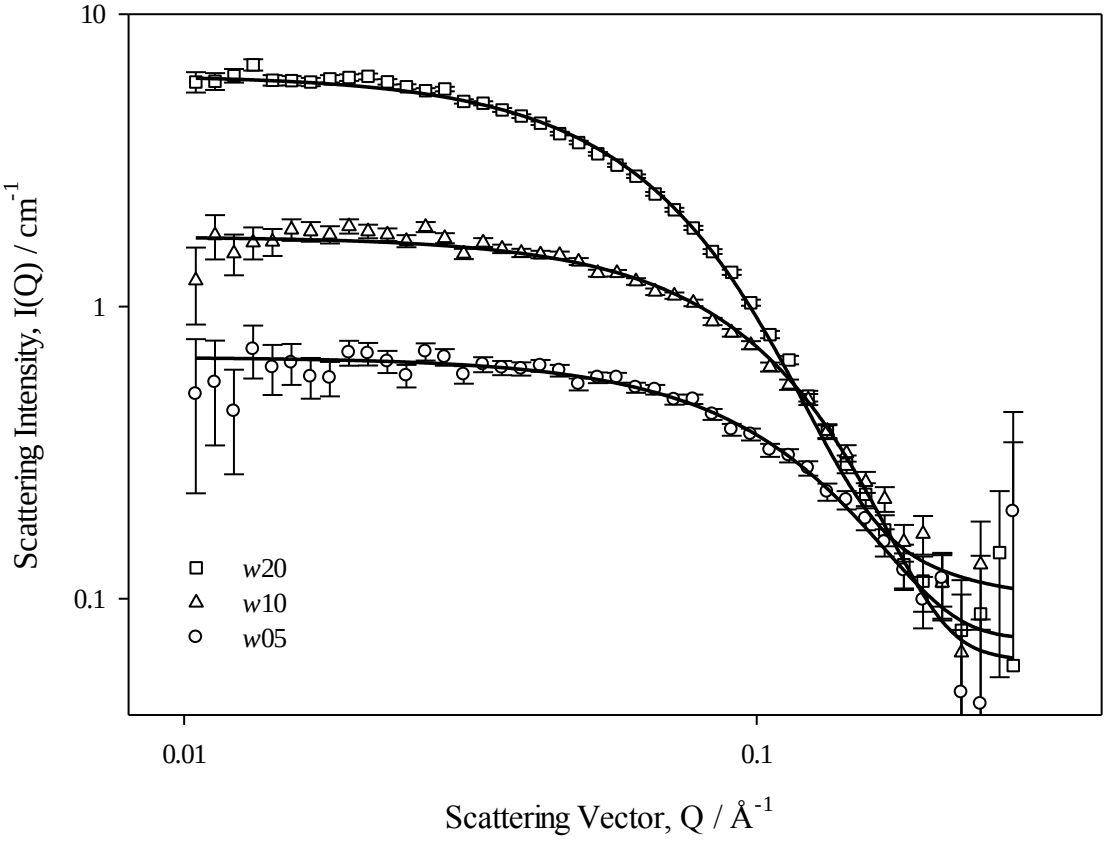


Figure 2. Scattering data for microemulsions of TC14/water/heptane at *w*5, 10 and 20. Solid lines show fits to a polydisperse sphere form factor.

Table 1. Fit parameters obtained for water-in-oil microemulsions of heptane and TC14.

w	Polydisperse spheres fit parameters	
	R / ± 1Å	σ^a ± 0.1
5	15.0	0.20
10	16.5	0.20
20	25.0	0.20

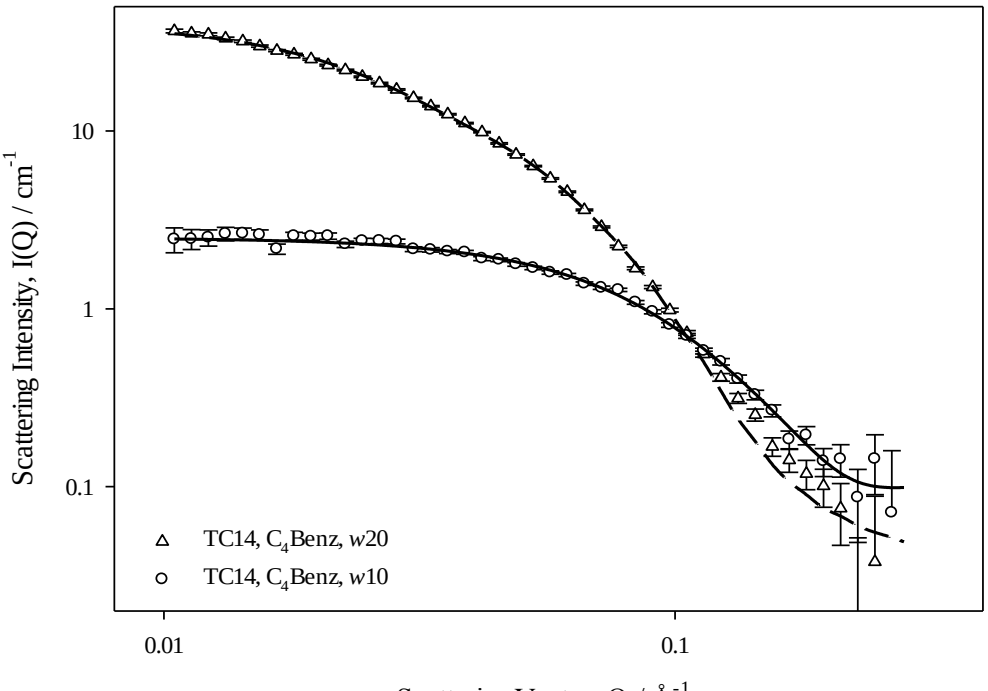
[a]Where σ is the Schultz distribution of radius as described in the model (Supporting information).

When hydrotropes were added to these triple-chain TC14 water-in-oil microemulsions, trends comparable with those seen previously for double-chain AOT microemulsions[33] were observed; that is, an elongation of the microemulsion droplets where the extent of distortion was dependent upon the *w* value, structure (such has hydrocarbon chain length), and in this case, mole fraction of the added hydrotrope.

Effect of w value

Data and fits for *w*10 and *w*20 microemulsions of TC14 in the presence of C_4Benz are presented in Figure 3 and are typical of the scattering data for all the systems (*w*5 microemulsions in the presence of hydrotrope were not stable and phase separated). All data and fits can be found in the supporting information. The addition of 0.10 mole fraction of hydrotrope to a *w*10 TC14 microemulsion induced a shape transition from a sphere to ellipsoidal droplets. The addition of more water to form a *w*20 system was shown to cause further elongation, so much so that in the case of C_4Benz (Figure 3) and C_8Benz the scattering data are better described by a rod form factor. As the length obtained from the C_8Benz rod fit is larger than the resolution

of the SANS instrument, the absolute length is uncertain although it is clear the microemulsion rod lengths are at least 1000 Å. Fit parameters are presented in Table 2 and further model limit explanations in the supporting information. In the previous work by Hatzopoulos et al.[33], in the presence of hydrotropes, microemulsions with AOT were shown to have maximum elongation at the lowest *w* values studied (*w*10). On increasing the water content the droplets became more spherical until at high water content spheres were formed. This was explained by the fact that as the water content increases the aqueous concentration of the hydrotrope decreases towards the critical aggregation concentration, *cac*. At this effectively lower hydrotrope concentration, less adsorption into the microemulsion interface occurs and therefore less elongation. When the concentration falls below that of the *cac* spherical droplets were once again seen to form. Here the opposite effect is observed and the elongation of the microemulsion increases as the *w* value increases. As TC14 is unable to stabilise *w* values as high as those obtainable in microemulsions of AOT [CRAIG GIVE A REF HERE PERHAPS TO ONE OF SANDRINES PAPERS – THEN UPDATE THE REF LIST], the aqueous concentration of the hydrotrope never goes below the critical aggregation concentration, and the spherical form factor was never recovered. For TC14, *w*20 is near the water solubility limit which may explain the different effect of water addition.



Hydrotrope	Fit parameters using ellipsoidal form factor			
	*w*10		*w20*	
	0.10 mole fraction of hydrotrope	0.20 mole fraction of hydrotrope	0.10 mole fraction of hydrotrope	0.20 mole fraction of hydrotrope

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Figure 3. Scattering data for microemulsions of TC14/water/heptane with 0.10 mole fraction of C_4Benz at *w*10 (open Circles) and *w*20 (open triangles). Fits are to an ellipsoidal form factor (solid lines) and rod form factor (dashed line).

Table 2. Fit parameters obtained from fitting SANS data of water-in-oil microemulsions of TC14 in the presence of 0.10 and 0.20 mole fraction of hydrotrope.

	R_a/Å[a]	R_b/Å	R_a/R_b	R_a/Å	R_b/Å	R_a/R_b		R_a/Å	R_b/Å	R_a/R_b	R_a/Å	R_b/Å	R_a/R_b
C_2Benz	70.0	17.0	4.1	85.5	14.5	5.9		80.0	22.5	3.5	115.5	22.0	5.3
C_4Benz	38.5	15.0	2.5	75.0	15.5	4.8		147.0*	28.5	5.2	-	-	-
C_8Benz	57.0	16.5	3.5	124.0	16.5	7.5		4000.0*	29.0	138	-	-	-
PhenC_3	53.5	17.0	3.2	62.0	18.0	3.4		53.0	18.0	3.0	69.0	20.0	3.5
PhenC_5	45.0	16.0	2.8	73.0	15.5	4.7		111.0	27.0	4.1	-	-	-

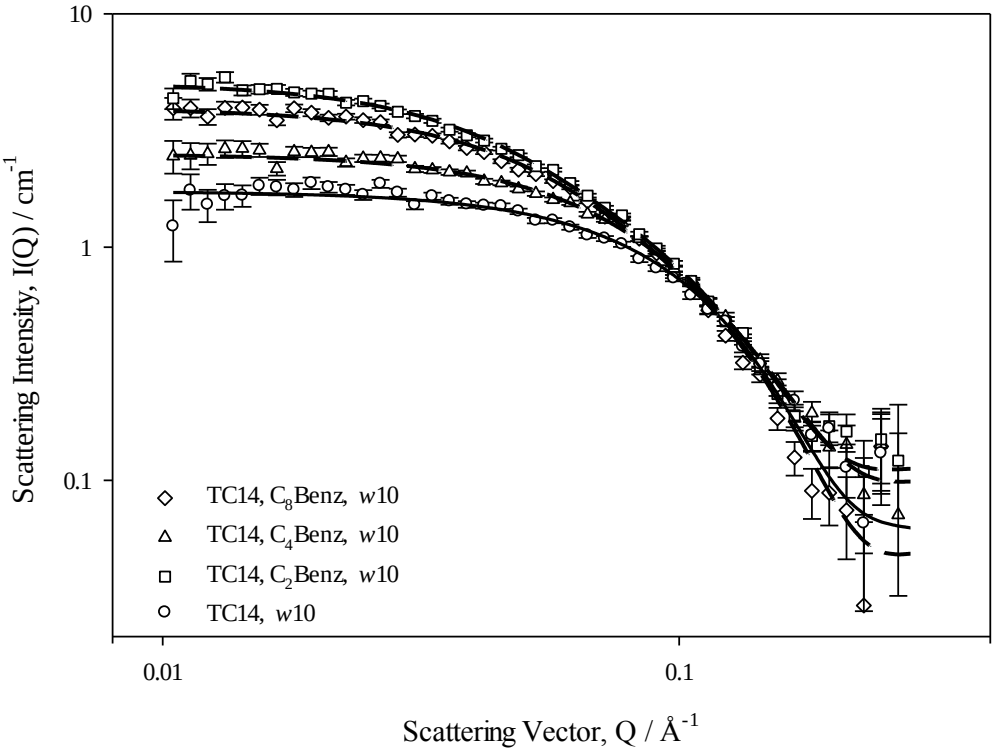
[a]Where R_a/R_b is the ellipticity and when equal to 1, the form factor is for that of a sphere, if greater than one, a prolate ellipsoid and if less than one, an oblate ellipsoid (see supporting information for model details). [b]When the ellipticity is greater than 5 the form factor can be well approximated by a rod model. Systems where this occurs have been marked with an asterisk. See supporting information further explanation. [c] Although this was the fit value obtained, due to the resolution of the instrument used, the value is clearly greater than 1000 Å. See text for more information. Errors in R_a are $\pm$ 2Å and R_b $\pm$1 Å.

Effect of hydrotrope mole fraction

Increasing the mole fraction of hydrotrope from 0.10 to 0.20 caused further growth in the microemulsions at both *w* values studied, although, for the longer chain C_4Benz and C_8Benz hydrotropes, the systems were no longer stable at X = 0.20 and *w*20. The fact increasing hydrotrope concentration leads to more elongation supports the previously found trends[33] that higher concentration causes greater adsorption of the hydrotrope into the microemulsion interface. However, the further elongation with increasing *w* value suggests that this cannot be the whole story, and the nature of the surfactant must have some effect.

Effect of hydrotrope structure

As well as hydrotrope mole fraction and microemulsion *w* value, the length of the hydrotrope chain and structure of the "head" group was also shown to have a notable effect on the transitions. Figure 4 shows scattering data for the three different C_nBenz hydrotropes at 0.10 mole fraction for *w*10 [CRAIG CHECK w IS ITALICIZED THROUGHOUT] and 20 microemulsions with fit parameters presented in Table 2. Given the ± 1 Å error in the radii, the spherical radius (R_b) of the microemulsion is not affected by the hydrotrope when compared to the pure TC14 microemulsions. This is in agreement with results seen with AOT[33], however, as also noted with AOT systems, there is no obvious trend visible regarding the magnitude of elongation and the structure of hydrotrope used. It is clear though that hydrotropes can be used to generate elongation in w/o microemulsions of TC14, which suggests the approach could be applied to water-in-CO_2 microemulsions.


10
1
0.1
Scattering Intensity, I(Q) / cm-1
TC14, C8Benz, w10
TC14, C4Benz, w10
TC14, C2Benz, w10
TC14, w10
0.01
0.1
Scattering Vector, Q / Å-1

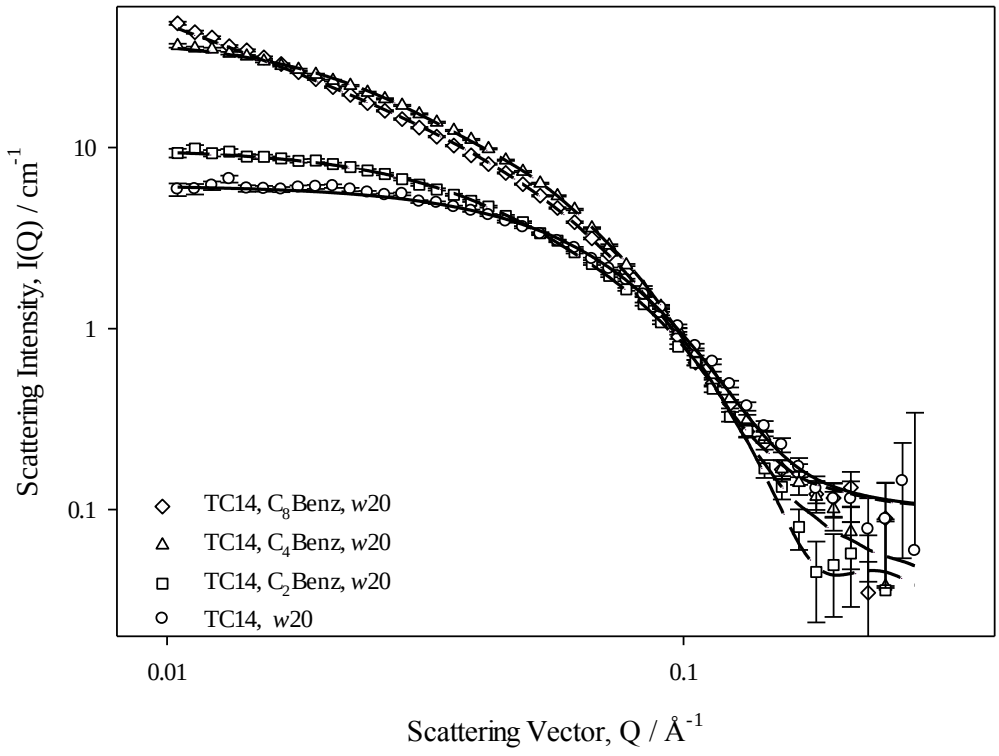

10
1
0.1
Scattering Intensity, I(Q) / cm-1
TC14, C8Benz, w20
TC14, C4Benz, w20
TC14, C2Benz, w20
TC14, w20
0.01
0.1
Scattering Vector, Q / Å-1

Figure 4. Scattering data for *w*10 (top) and *w*20 (bottom) microemulsions of TC14/water/heptane with either no hydrotrope (open circles) or 0.10 mole fraction of C_2Benz (open squares), C_4Benz (open triangles) or C_8Benz (open triangles). Fits are to polydisperse spheres (solid lines), ellipsoids (long dashed lines) and rods (short dashed lines).

Water-in-CO_2 microemulsions

TC14 is known to form spherical water-in-CO_2 (w/c) microemulsion droplets with radii of 10 Å[30] (Table 3, Figure 5). After the addition of hydrotropes, as with w/o systems, the w/c droplet aspect ratios were seen to increase (from R_a:R_b 1 to ~2.5) showing a substantial elongation. Unfortunately, the maximum aspect ratios are lower than those for w/o systems, most likely due to the fact that suitably high *w* values are not stable in CO_2, and this is where the greatest growth was observed in the w/o systems. Unlike in w/o systems, the structure of the hydrotrope was shown to have very little effect on the microemulsion morphology. All C_nBenz and PhenC_n hydrotropes where shown to form comparable microemulsion domains with a slightly larger polar radius than the hydrotrope free systems and with an elongation of ~2.5. The effect of hydrotrope concentration was also studied for the C_nBenz hydrotropes with 0.20 mole fraction also investigated. As with the w/o analogues, larger elongation was observed at higher

Hydrotrope	Ellipsoid/ Sphere parameters					
	0.10 mole fraction of hydrotrope			0.20 mole fraction of hydrotrope		
	R_a /±2Å	R_b /±1Å	R_a/R_b	R_a /±2Å	R_b /±1Å	R_a/R_b
None	10.0	10.0	1.00	-	-	-
C_2Benz	29.0	12.5	2.30	25.0	11.5	2.20
C_4Benz	31.0	13.0	2.40	33.0	12.0	2.75
C_8Benz	30.0	12.0	2.50	34.0	12.0	2.80
PhenC_3	30.0	13.0	2.30	-	-	-
PhenC_5	30.0	12.0	2.50	-	-	-

hydrotrope concentration, however the effect was much less significant in w/c systems.

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Table 3. Fit parameters obtained from fitting SANS data for water-in-CO_2 microemulsions of TC14 in the presence of 0.10 and 0.20 mole fraction of hydrotrope.

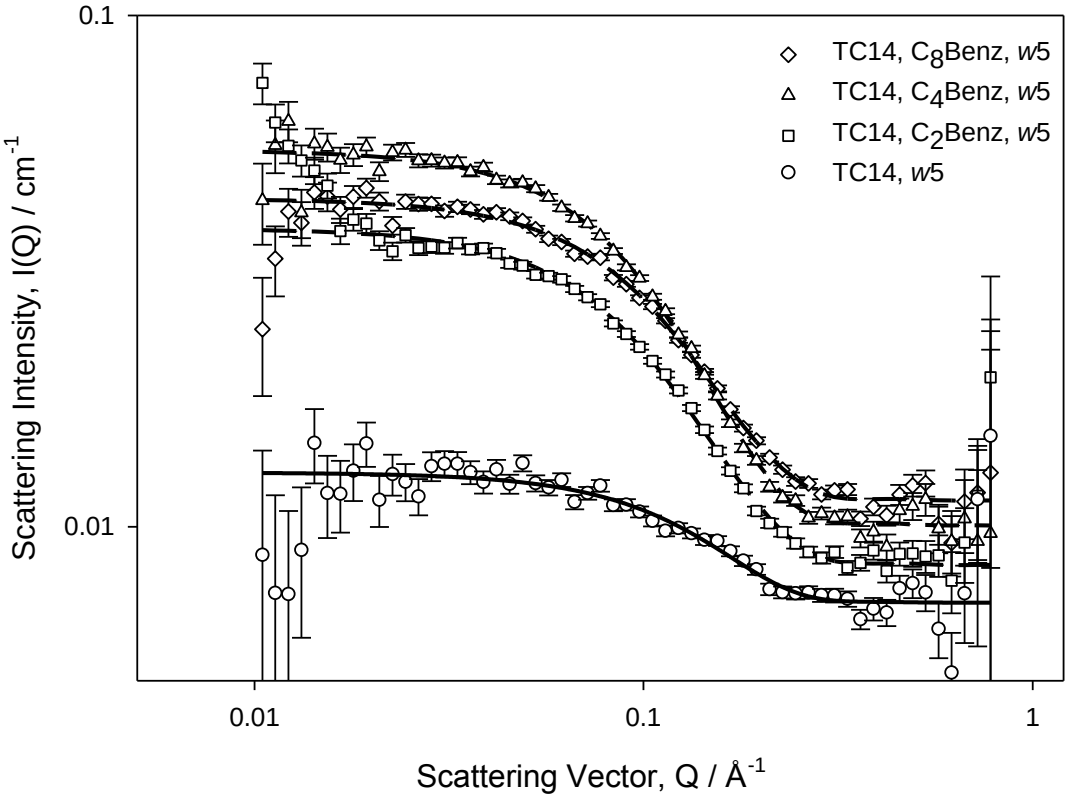

Figure 5. Scattering data and fits for *w*5 water-in-supercritical CO_2 microemulsions of TC14 with either no hydrotrope (open circles) or 0.10 mole fraction of C_8Benz (open diamonds), C_4Benz (open triangles) and C_2Benz (open squares). Fits are to spheres (solid line) and ellipsoids (dashed lines). Data were collected at 400 bar and 45 °C.

Supercritical CO_2 viscosity enhancement calculations

In a previous study, Cummings et al.[48] synthesised a series of fluorinated surfactants with different counterions which micellized to generate elongated rod-like w/c microemulsions. Using results from SANS and high pressure viscosity measurements, a relationship was found between microemulsion aspect ratio and viscosity enhancement of the CO_2 continuous microemulsions.

Using equations 3[49] and 4[48, 50] below, the viscosity enhancement expected from the TC14/hydrotrope systems has been estimated[49].

$$[\eta] \cong 2.5 + 0.4075(X_{mic} - 1)^{1.508} \quad (3)$$

$$\frac{\eta_{mic}}{\eta_{co_2}} \cong \eta_{rel} \cong 1 + [\eta]\varphi_p + K_H[\eta]^2{\varphi_p}^2 \quad (4)$$

Where: $[\eta]$ is the intrinsic viscosity; X_{mic} the microemulsion aspect ratio [CRAIG ELLIPTICITY MAY GET CONFUSED WITH THE PARAMETER DETERMINED USING ELLIPSOMETRY] (R_a/R_b); $\eta_{rel}$the relative viscosity which is the ratio of the micellar solution viscosity, η_{mic} and the viscosity of neat scCO$_2$, η_{CO_2}; φ, the volume fraction of the

microemulsion droplets and K_H, the Huggins coefficient for rods (in this case 0.40 [NEEDS A REF]). More information can be found in supporting information.

Using equations 3 and 4 and the SANS determined aspect ratios from Table 3, the relative viscosity enhancements predicted for *w*5, w/c microemulsions containing TC14 and C_nBenz hydrotropes at 0.20 mole fraction have been calculated and the results presented in Table 4.

Table 4. Relative viscosity, η_{rel}, values calculated using equations 3 and 4.

Hydrotrope	**R_a /Å**	**R_b /Å**	**R_a/R_b**	$[\eta]$	η_{rel} (ϕ = 0.018)	η_{rel} (ϕ = 0.044)
C_2Benz	25.0	11.5	2.20	3.03	1.056	1.14
C_4Benz	33.0	12.0	2.75	3.45	1.063	1.16
C_8Benz	34.0	12.0	2.80	3.49	1.064	1.16

It can be seen that even at the low volume fraction used in this study (0.018) the increase in $scCO_2$ viscosity expected would be 6 %. Expected viscosity increases have also been calculated for systems at the same volume fraction used by Cummings et al. [48] so comparisons can be made. It is worth nothing that this higher volume fraction is readily accessible using TC14. At this higher volume fraction, a 16 % increase in viscosity could be expected; Cummings et al. observed increases between 18 – 100 %.

Conclusions

The formation of rod-like, water-in-oil and water-in-CO_2 microemulsions stabilized by TC14 by the addition of small mole fractions of hydrotrope has been investigated. This has built on previous work showing that hydrotropes can cause micellar growth in both aqueous systems[32, 34] and in w/o microemulsions with AOT[33]. For water-in-oil microemulsions, *w* value and hydrotrope mole fraction were shown to affect the degree of elongation and enhanced anisotropy of the microemulsion nano-domains. The nature of the hydrotrope structure ("head group" and chain length) were also shown to affect the morphology of the microemulsion droplets formed but the trends are still unclear.

For water-in-CO_2 systems, higher mole fractions of hydrotrope gave rise to more elongated microemulsion assemblies, however, the effects were much less pronounced than those seen in heptane. The hydrotrope chemical structure seems to have little effect on the microemulsion shape and, due to the relatively poor stabilising power of TC14, higher *w* values > 20 could not be studied. Using methodology developed by Cummings et al.[48], the relative viscosity increase expected for these elongated micromulsions in CO_2 has been calculated: the surfactant-hydrotrope mixtures used in this new work are chemically simpler than the fluorinated surfactants used by Cummings et al[48] .

This ability to form, all-hydrocarbon, elongated microemulsions in CO_2 easily and cheaply is so far unheard of. Promoting microemulsion growth without the use of fluorinated surfactants or counterion ion exchange[6, 23], which requires additional synthetic steps, is a significant advance in the formation of self-assembling viscosity modifiers for applications in CO_2.

Acknowledgements

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Supporting Information Available

Additional details of SANS model fitting and relative viscosity calculations can be found in the supporting information. This material is available free of charge via the Internet at http://pubs.acs.org.

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