DOI: 10.1002/anie.200901543

Micellar Modifiers

Tri-Chain Hydrocarbon Surfactants as Designed Micellar Modifiers for Supercritical CO_2**

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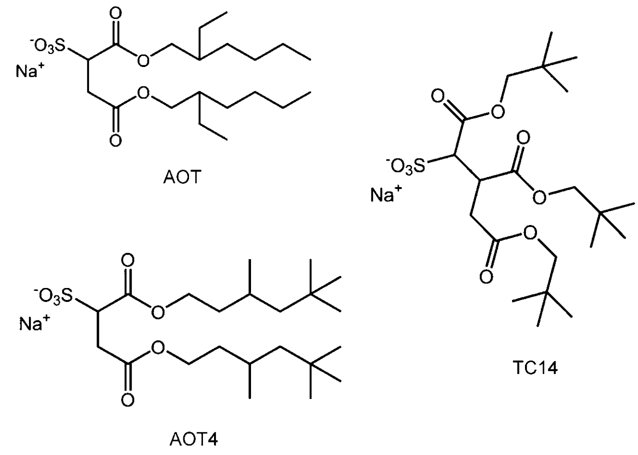
Herein, we present the first unambiguous evidence for hydrated reverse micelles (RMs) in dense or supercritical carbon dioxide ($scCO_2$). These RMs are formed with a low-cost designer triple hydrocarbon chain surfactant, sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulfonate (TC14; Scheme 1). This triple-chain surfactant has been designed to be specifically CO_2-philic. Although some specialized oxygenated surfactants are CO_2-philic,[1] the results described herein are a significant step forward, as the compounds can be readily synthesized from commercially available precursors. This is a unique approach, as surfactants for pure $scCO_2$ have previously been restricted to traditional hydrophilic or oleophilic classes, which were designed for other applications only in aqueous or organic media. TC14, bearing three CO_2-philic chains, efficiently forms hydrated RMs in $scCO_2$, whereas conventional twin-tailed surfactant analogues do not. This work is a proof-of-concept that low-cost hydrocarbon surfactants are now truly viable as fluid modifiers for $scCO_2$. The water-swollen RMs of TC14 generate internal nanostructured polar and interfacial domains, which affect the essential fluid properties of $scCO_2$, such as polarity, surface tension, wettability, and potentially viscosity. Given the known, well-documented benefits of $scCO_2$,[2] this finding can improve the cost, efficiency, and scope of $scCO_2$ applications, such as catalysis, cleaning, and enhanced oil recovery and carbon capture.



Scheme 1. Chemical structures di-chain and tri-chain surfactants.

Despite over 20 years of intense research, only custom-made perfluorinated amphiphiles[3,4] and polymers[5,6] have been shown to have high $scCO_2$ compatibility, thus altering $scCO_2$ properties by aggregation, stabilization of water-in-$scCO_2$ microemulsions,[5,7] gelation,[8] and dispersion of inorganic species.[9,10] Unfortunately, these fluorinated additives suffer from many disadvantages, including high cost and environmental persistence.[11] To unlock the vast potential of $scCO_2$-based technologies in sustainable and greener chemistry, new hydrocarbon $scCO_2$-active replacements are sorely needed. To date, non-fluorinated hydrocarbon surfactants[12–15] and polymers[16] have been reported with high solubility in $scCO_2$, and dispersion of nanoparticles has been achieved in both pure $scCO_2$[17] and heptane/$scCO_2$ mixtures.[18] However, there have been few reports of surfactant aggregation,[13] and certainly no unambiguous confirmation[3] by high-pressure small-angle neutron scattering (HP-SANS) of the formation of hydrated RMs stabilized by any purely hydrocarbon surfactant in neat $scCO_2$. HP-SANS[19,20] is a key diagnostic technique for detecting solute self-assembly and aggregation in $scCO_2$, and provides irrefutable evidence for the presence (or lack of) dispersed nanodomains of surfactant and water.[3]

Scheme 1 shows the chemical structures of the hydrocarbon surfactant TC14 synthesized for this work, along with commercially available AOT, which is commonly used for reversed micelle formation in organic solvents,[21] but is insoluble in $scCO_2$.[13] In recent years, the chain chemistry of AOT has been adapted to improve $scCO_2$ compatibility.[3,22] The twin-tailed structure of normal AOT was initially optimized by designing the *tert*-butyl-tipped AOT4, which forms dry RMs in pure $scCO_2$, albeit at quite extreme conditions (500 bar, 33 °C).[13,14] AOT4 also efficiently stabilizes water/CO_2 macro- and mini-emulsions;[23] disappointingly however, addition of water results in phase separation.[14] The

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[**] K.T., M.J.H., S.C., R.F.T., S.G., A.M., and O.M. thank EPSRC, Kodak, Infineum, HEFCE, the Malaysian government and the School of Chemistry at the University of Bristol for the provision of PhD scholarships. The ISIS-STFC Neutron Scattering Facility (formerly CCLRC) is thanked for the provision of beamtime and grants towards consumables and travel. The EPSRC is thanked for provision of funding under grants EP/C523105/1 and EP/F020686.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200901543.

next step is to add a third CO_2-philic chain, which has the effect of dramatically enhancing $scCO_2$ compatibility. From a family of custom-synthesized tri-chain surfactants,[15] TC14 is the most effective, for example, in conferring stability on nanoparticles in mixed heptane/CO_2 solvents,[18] but RMs of TC14 have not previously been observed in pure CO_2. The rationale behind TC14 is to increase the density of CO_2-philic terminal methyl groups in the region of the molecule that comes into contact with $scCO_2$ (the surfactant chains), whilst still maintaining a bulky hydrocarbon region. This should favor RM formation and the inevitable stabilization of internal polar domains that may act as sites for incorporation of water. The methyl groups lower the surface energy and boost compatibility in $scCO_2$,[13–15] which is consistent with the fractional free volume approach proposed by Johnston et al.,[24] and supported by other indices, such as the electron-density[25] or solvent-quality[26] approaches to surfactant design for specific solvents.

Samples of TC14 were prepared in a pressure cell sited on the LOQ SANS beamline at ISIS (UK). Dry (w0) and hydrated TC14 formulations (w5; $[\text{water}]_{\text{added}} = 5 \times [\text{surfactant}]$) in pure $scCO_2$ were prepared and analyzed by examination of phase behavior and HP-SANS profiles. Both dry and hydrated systems were visibly clear at 360 bar and 25 °C. These pressure and temperature conditions locate the $scCO_2$ in the near critical region ($P_c = 72.8$ bar, $T_c = 31.1$ °C). Under isothermal, moderately stirred conditions, the $w5$ sample showed a distinct clear-to-cloudy transition at $P_{\text{cloud}} = 280$ bar (Figure 1). This cloud point is indicative of a change from a stable to an unstable, biphasic system. Below P_{cloud}, halting the stirring resulted in a macroscopic phase separation; above P_{cloud}, the sample remained visibly clear regardless of whether the sample was stirred or not. HP-SANS was therefore used to probe the structures present in the clear, stable region.

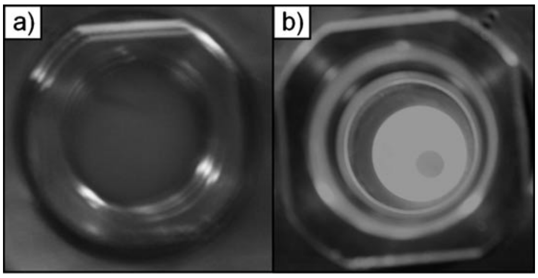

Figure 1. The appearance of stirred samples of TC14-stabilized hydrated micelles at a) 105 bar ($< P_{\text{cloud}}$; cloudy, two phases), and b) 360 bar ($> P_{\text{cloud}}$; clear, one phase). $P_{\text{cloud}} = 280$ bar. Photographs were taken in-situ with the pressure cell in the neutron beamline. In image (b), the beamline aperture is visible through the pressure cell windows.

SANS profiles obtained for dry and hydrated tri-chain TC14 RMs are compared in Figure 2 with signals from analogous twin-tailed AOT having formulations under the same conditions. The SANS from w0 micelles of AOT4 may be found elsewhere.[16] The SANS for both TC14 systems is clearly indicative of RMs, whereas the lack of scattering with either AOT4 or AOT is consistent with an absence of any aggregation. In addition, the increase in SANS intensity from dry to hydrated RMs is important, showing added water to either increase the micellar contrast, or volume fraction, or both; the signal increase is therefore consistent with hydration of the RMs. No effect of stirring on SANS was noticed (see the Supporting Information, Figure S3).

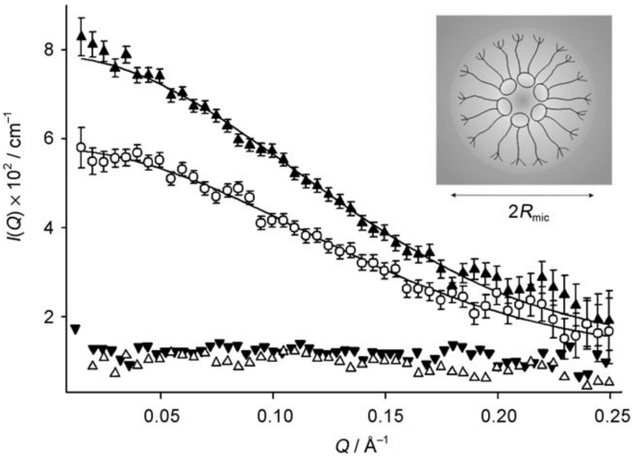

Figure 2. SANS profiles of TC14-stabilized dry (w0; ○) and hydrated micelles (w5; ▲) obtained in liquid CO_2 at 360 bar and 25 °C. The scattering obtained from formulated AOT4 w5 (▼) and dry AOT w0 systems (△) is also shown for comparison. The cell and CO_2 background have been subtracted for all the data presented. Smooth lines: model fits to the data (see the Supporting Information). Fitted radii R_{mic} (±10%) for both TC14-stabilized samples are 11 Å.

Data analysis to extract reversed micelle dimensions was performed using a standard model to account for spherical aggregates (see the Supporting Information). By using a precalculated fixed scale factor from known values for cell volume, water solubility in CO_2, RM volume fraction ϕ, and neutron contrast $\Delta\rho = \rho_{CO_2} - \rho_{RM}$ (including water where necessary), values for the mean RM radius R_{mic} were obtained. The output values were 11 Å for both dry and hydrated RMs, with typical uncertainties in the order of 10%. This similarity is not surprising given that the volume of water inside RMs is only sufficient to hydrate the ionic headgroups rather than generate nanosized droplets of free water. The number N_{agg} of surfactant molecules per RM calculated for the dry aggregates is 8 (i.e. 24 chains), which is lower than that of normal AOT in alkane solvents ($N_{\text{agg}} \approx 20$, or 40 chains).[21] However, reduced aggregation numbers are to be expected on increasing the hydrocarbon bulk from two to three chains.

Based on its molecular structure, TC14 is also expected to form RMs in heptane. Therefore, to check on the form and function of the SANS data given in Figure 2, parallel experiments were conducted on TC14 RMs dispersed in liquid deuterated heptane (Supporting Information, Figure S4). The SANS profiles in deuterated heptane and $scCO_2$ are similar; however, the deuterated solvent gave stronger SANS signals than $scCO_2$, by virtue of higher volume fraction, neutron contrast $\Delta\rho = (\rho_{\text{d-hept}} > \rho_{CO_2})$, and the lower background solubility of water in heptane (see the Supporting Information).

Costs for surfactant synthesis are estimated and presented in Table 1; diCF4 represents the currently leading short-chain fluorinated surfactant in $scCO_2$.[3] Even disregarding additional environmental benefits, the triple-chain TC14, loaded with terminal methyl groups, is much cheaper than compounds such as di-CF4. Clearly, cost is of great importance for applications involving high volumes of $scCO_2$. The presence of TC14 RMs increases water solubility in $scCO_2$ by about 150 % above the background level for water-saturated $scCO_2$ at 360 bar and 25 °C.[27] This significant conceptual advance demonstrates the importance of tri-chain surfactants, a widely under-studied class of compounds, for applications using $scCO_2$.

Table 1: Estimated economic costs of designer CO_2-philes.

Surfactant	Cost[a] [US$ g^{-1}]
AOT	0.5
AOT4	1.0
TC14	6.0
diCF4[b]	220.0

[a] Based on precursor prices at current rates from UK-based chemical suppliers and 50% yields. [b] The leading fluorinated AOT-derivative CO_2-phile. diCF4 = sodium bis(1H,1H-perfluoropentyl)-2-sulfosuccinate.[3]

Received: March 20, 2009

Keywords: carbon dioxide · reverse micelles · small-angle neutron scattering · surfactants · sustainable chemistry

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