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## Branched trichain sulfosuccinates as novel water in CO<sub>2</sub> dispersants

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**Abstract** A series of highly branched trichain sulfosuccinate surfactants have been synthesized and studied in condensed CO<sub>2</sub> and aqueous environments. Aqueous critical micelle concentrations (CMCs) showed a general trend of increasing CMC with decreasing chain length, whereas increased branching appeared to increase solubility in CO<sub>2</sub> and aid the dispersion of water. Near infrared spectra confirmed observed cloud

with a large increase in solubility above the cloud pressures in this solvent.

**Keywords** CO<sub>2</sub> · Active surfactants · Tri-chain surfactants · Near infrared spectroscopy

### Introduction

Condensed carbon dioxide has the potential to become the solvent of choice for a wide range of industrial processes. CO<sub>2</sub> is essentially environmentally benign, and this combined with its low price and toxicity provides the driving force for seeking to improve the solvent power of CO<sub>2</sub>.

Without additives, CO<sub>2</sub> is generally regarded as a poor solvent—being unable to solubilize polar or high molecular weight moieties. The addition of surfactants can greatly improve the solvent strength of carbon dioxide illustrated by the already established applications in, for example, precision cleaning of machine parts and dry cleaning of materials, replacing harmful halogenated solvents such as perchloroethane (perc) [1].

Even with these advances, CO<sub>2</sub> cannot find widespread use as a reaction medium unless surfactants can be obtained, which can incorporate high polarity solvents (such as water) into the CO<sub>2</sub> continuous phase. To achieve this goal, it is important to understand which chemical features are required to increase surfactant activity in CO<sub>2</sub>. Much work has already been carried out in this field and it

is well known that highly fluorinated surfactants are capable of solubilizing significant amounts of water inside reverse micelle nanodomains [1–3]. Unfortunately, fluorosurfactants do not present the ideal solution to this problem, being both expensive and harmful to the environment leading to the search for nonfluorous alternatives [4].

Recent research has shown that chain tip branching can dramatically increase the miscibility of double hydrocarbon chain ionic surfactants in CO<sub>2</sub> [5]—the first step in the search for water solubilizing agents. Work outlined in this study continues to explore the effects of chain tip branching using trichain sulfosuccinate (TCS) surfactants—a class of compound not used before in CO<sub>2</sub> research. The compound AOT 14, which is a dichain analogue, most closely related to TCS 14<sup>1</sup>, was also investigated to establish the importance of the number of hydrocarbon chains on compatibility with CO<sub>2</sub>.

The structures of the four compounds investigated are shown in Table 1; TCS 11, 13, and 14 all have the same molecular weight, and vary only in the type of chain

<sup>1</sup>Nomenclature has been chosen to be consistent with other surfactants previously synthesized in this group.

**Table 1** Chemical structures of trichain sulfosuccinate surfactants

Name	TCS 11	TCS 12	TCS 13	TCS 14
Structure				

branching. Aqueous critical micelle concentrations (CMCs) were investigated using conductivity, and the general trends as a function of chain length and branching compare with those seen for standard single and double chain anionic surfactants.

The performance of TCS surfactants in carbon dioxide has also been investigated via visual determination of cloud points both as binary mixtures and ternary mixtures using water. To provide a more quantitative measure of CO<sub>2</sub> compatibility, Near infrared (NIR) spectroscopy was used: in the region 2,200–2,400 nm, NIR is sensitive to the presence of CH groups from the CO<sub>2</sub> solubilized surfactants.

## Experimental

### Synthesis

All TCS surfactants were obtained from following the route in Scheme 1.

Synthesis of TCS 14 is given as an example.

#### *Synthesis of (E)-3-(2,2-dimethyl-propoxycarbonyl)-pent-2-enedioic acid bis-(2,2-dimethyl-propyl) ester (1)*

Transaconitic acid (5 g, 28.75 mmol) and neopentyl alcohol (3.2 eq., 8.07 g, 92 mmol) was dissolved in toluene (100 ml) and *p*-toluene sulfonic acid (0.99 g, 5.75 mmol) added. The reaction mixture was heated to 110 °C for 12 h and the water generated removed via Dean and Stark apparatus. The reaction mixture was washed repeatedly with saturated NaHCO<sub>3</sub> (aq) solution, the organic phase dried over

MgSO<sub>4</sub> and solvent removed to give an off-white oil. Purification was achieved via flash column chromatography over SiO<sub>2</sub> using 10% Et<sub>2</sub>O/petroleum ether.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): (δ=0.97) C(CH<sub>3</sub>)<sub>3</sub>, (δ=3.77,3.88,3.90) CO<sub>2</sub>CH<sub>2</sub>, (δ=4.02) CH<sub>2</sub>CO<sub>2</sub>, (δ=6.99) C=CH–  
Yield: 78%

#### *Synthesis of sodium; 1,2,3-tris-(2,2-dimethyl-propoxycarbonyl)-propane-1-sulfonate*

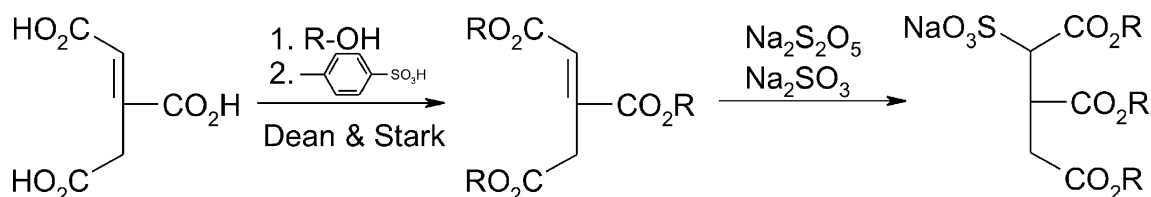
Triester (1) (8.3 g, 22.4 mmol), was dissolved in ethanol (100 ml) and water added up to saturation. Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (2.2 eq., 9.37 g, 49.3 mmol), Na<sub>2</sub>SO<sub>3</sub> (1.8 eq., 5 g, 40.3 mmol) was then added and the mixture was allowed to heat under reflux for 6 h. Solvent was completely removed to give white solid product which underwent crude purification via sohxlet extraction using dry distilled AcOEt. Further purification was achieved by dissolving in the minimum amount of dry MeOH and centrifuging at 6,000 rpm for 30 min. The supernatant solution was decanted from residual salts and solvent removed to yield white solid.

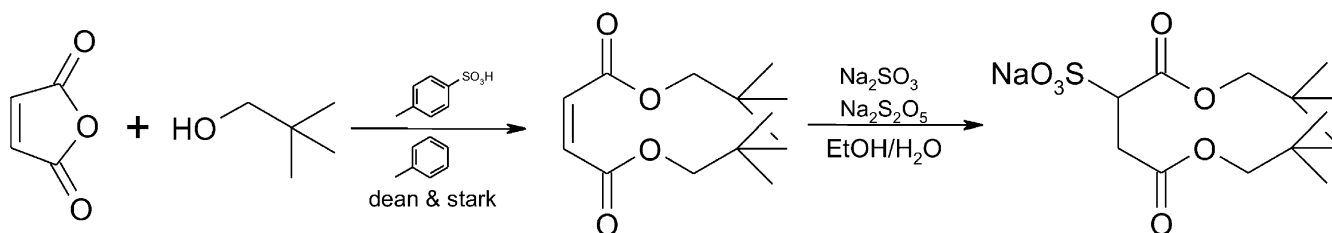
<sup>1</sup>H NMR: (δ=0.97) C(CH<sub>3</sub>)<sub>3</sub>, (δ=3.68–3.90) CO<sub>2</sub>CH<sub>2</sub>, (δ=3.95) CH<sub>2</sub>CO<sub>2</sub>, (δ=3.22) CH–, (δ=4.49) NaO<sub>3</sub>S–CH–  
Yield: 56%

Dichain surfactant (AOT 14) was synthesized following Scheme 2.

#### *Synthesis of (Z)-but-2-enedioic acid bis-(2,2-dimethyl-propyl) ester (2)*

Maleic anhydride (5 g, 51 mmol) and neopentyl alcohol (3 eq., 13 g, 153 mmol) was dissolved in toluene (100 ml) and

**Scheme 1** General synthesis of TCS surfactants



**Scheme 2** Synthesis of AOT 14

*p*-toluene sulfonic acid (0.99 g, 5.75 mmol) added. The reaction mixture was heated to 110 °C for 12 h and water generated removed via Dean and Stark apparatus. The reaction mixture was washed repeatedly with saturated NaHCO<sub>3</sub> (aq) solution, the organic phase dried over MgSO<sub>4</sub> and solvent removed to give an off-white oil. Purification was achieved via flash column chromatography over SiO<sub>2</sub> using 10–20% Et<sub>2</sub>O/petroleum ether solvent gradient.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): (δ=0.97) C(CH<sub>3</sub>)<sub>3</sub>, (δ=3.89) CO<sub>2</sub>CH<sub>2</sub>, (δ=6.27) C=CH–  
Yield: 78%

#### Synthesis of sodium; 1,2-bis-(2,2-dimethyl-propoxycarbonyl)-ethanesulfonate (AOT 14)

Diester (2) (5.5 g, 21.5 mmol), was dissolved in ethanol (100 ml) and water added up to saturation. Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (2.2 eq., 9.37 g, 49.3 mmol), Na<sub>2</sub>SO<sub>3</sub> (1.8 eq., 5 g, 40.3 mmol) was then added and the mixture was allowed to heat under reflux for 6 h. Solvent was completely removed to give a white solid product, which underwent crude purification via sohxlet extraction using dry distilled AcOEt. Further purification was achieved by dissolving in the minimum amount of dry distilled acetone and centrifuging at 6,000 rpm for 30 min.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): (δ=0.91) C(CH<sub>3</sub>)<sub>3</sub>, (δ=3.86) CO<sub>2</sub>CH<sub>2</sub>, (δ=3.23) CH<sub>2</sub>CO<sub>2</sub>, (δ=4.43) CHCO<sub>2</sub>  
Yield: 63%

#### CMC measurements

Aqueous CMCs were determined via conductivity measurements using a Jenway 3410 electrochemistry analyzer. Deionized water (18.2 Ω cm) was obtained from an Option 3 Elga purification system. Each set of CMC measurements was repeated with individually prepared solutions.

#### CO<sub>2</sub> phase behavior

Phase behavior of surfactants in CO<sub>2</sub> was carried out using a custom manufactured high pressure cell equipped with

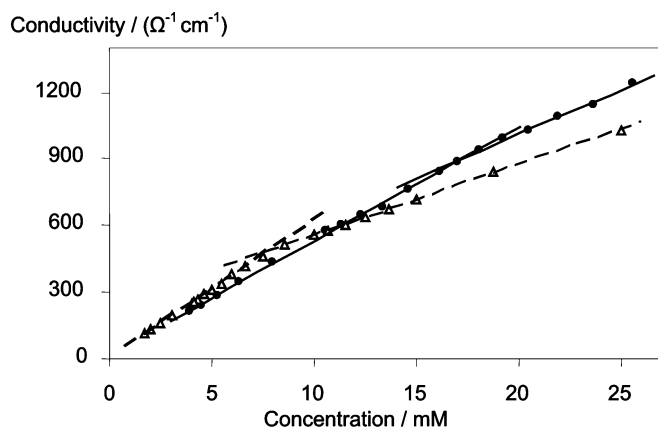
three sapphire windows and two magnetic stirrer bars (a detailed description can be found elsewhere [6]). In a typical experiment, surfactant was placed in the cell which was then sealed. The cell was then placed on a magnetic stirrer plate and cooled to 15 °C via a recirculating water bath (Grant LTG 6G). Liquid CO<sub>2</sub> was then distilled into the cell from a cylinder via a valve near the bottom of the cell and residual air bled out from a valve in near the top of the cell. The temperature was raised as required using the recirculating water bath and the pressure controlled using a hydraulic pump and measured using a pressure transducer. All cloud point measurements were made by increasing pressure until the stirred mixture was optically transparent, and then manually lowering pressure until a cloud point was noted by visual inspection (rapid onset of a clear-to-cloudy transition).

#### Near infrared spectroscopy

NIR spectra of binary surfactant/CO<sub>2</sub> mixtures were obtained using a Thermo-Nicolet Nexus spectrometer comprising a DTGS detector and a tungsten lamp. In a typical experiment, excess surfactant was placed in a custom made gauze attached to the piston inside the pressure cell. The cell was filled with CO<sub>2</sub>, placed on a magnetic stirring plate and allowed to equilibrate. The cell was then removed from the stirring plate and placed in the FT-IR instrument and aligned with the beam using a custom made x/y/z plate. The spectrum was recorded after any solids in the fluid had settled. Spectral data handling and CO<sub>2</sub> background subtraction were carried out using OMNIC version 5.12 Software.

**Table 2** CMCs of TCS surfactants, with total carbon numbers and effective chain lengths

Name	TCS 11	TCS 12	TCS 13	TCS 14
Total carbon number	15	18	15	15
Effective chain length	4	5	4	3
CMC/mM	7.5	7.8	8.3	17.5



**Fig. 1** Conductivity measurements TCS 12 (triangles) and TCS 14 (circles) to determine CMCs

## Results and discussion

### Aqueous CMCs

Direct comparison between surfactants within a branched series is not always straightforward, owing to the effects of branch length and position within the chain. In similar previous studies of dichain sulfosuccinates (AOTs), the approach taken was to focus on the effective chain length, i.e., the length of the longest linear portion of the chain only [7]. Using this approach with the TCS surfactants reveals a general trend of decreasing CMC with increasing chain length (Table 2) and it is clear from the conductivity data in Fig. 1 that these compounds undergo classical behavior, displaying a clearly defined critical micelle concentration.

Closer investigation of the aqueous CMCs shows deviation from behavior observed in standard single chain surfactant systems. There appears to be little linear dependence of  $\log(\text{CMC})$  on the chain length, and indeed the CMC for TCS 12 (with an effective chain length of

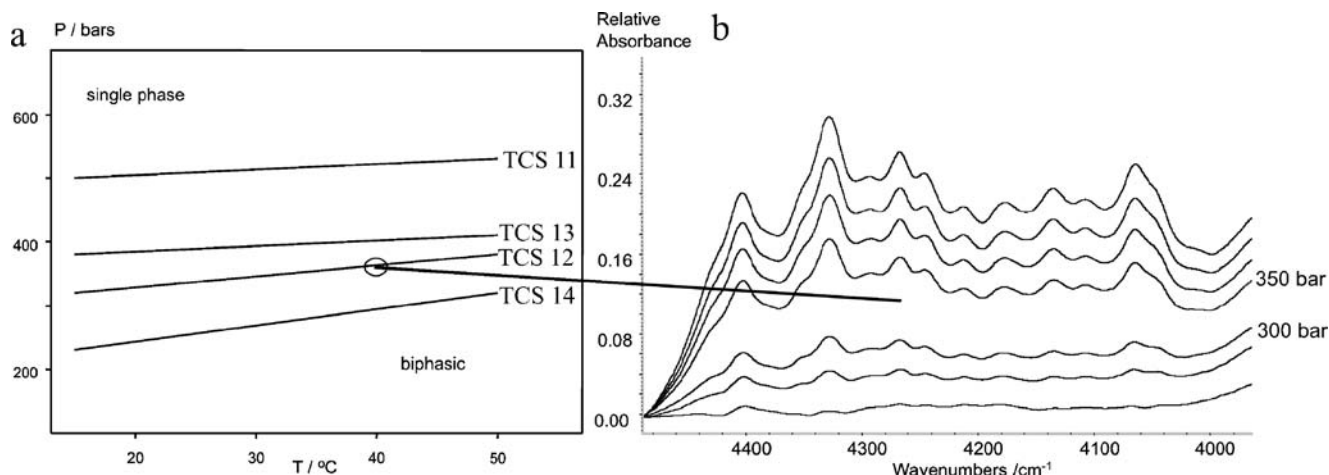
five) is very similar to those of TCS 11 and 13 (both with effective chain lengths of four) especially when considering the experimental resolution. It may be possible that the effects of chain branching obscure the trends due to short chain lengths, and that these effects may be enhanced in this series of surfactants because of the additional chain. It is unlikely, however, that chain branching could lead to such large deviations from expected trends and further investigations into the aqueous behavior of these unusual compounds is required to determine general behavior of trichain surfactants.

### Solubility in CO<sub>2</sub>

All the TCS surfactants exhibited good solubility in CO<sub>2</sub> at 0.025 M, resulting in homogeneous optically transparent solutions, above fully reversible cloud transition points. Figure 2a shows the pressure–temperature phase diagram of binary CO<sub>2</sub>/surfactant mixtures. Solubility was confirmed by NIR which showed that all surfactants have increased miscibility with CO<sub>2</sub> on increasing temperature and pressure. Jumps in solubility were also seen above the observed cloud point pressures. A typical example of which is shown in Fig. 2b.

CO<sub>2</sub> affinity seemed to show a strong dependence on chain tip branching with the trimethyl capped TCS 14 having significantly lower cloud points than dimethyl capped chains (TCS 13 and TCS 12), which in turn were far more soluble in CO<sub>2</sub> than TCS 11—where branching occurs along the chains and not at the chain tips. Again this mirrors the results seen within dichain sulfosuccinates where it was observed that only surfactants comprising highly branched chain tips (e.g., AOT 3 and 4) showed any affinity for CO<sub>2</sub> [5].

As well as having lower cloud points at 0.25 M, TCS 14 was also soluble at higher concentrations than the other



**Fig. 2** a Cloud points for TCS surfactants in CO<sub>2</sub> at surfactant concentrations of 0.025 M. b NIR data demonstrating the solubility of TCS 12 at 40 °C as a function of pressure (each spectrum corresponds to a 50-bar jump in pressure)

surfactants studied. The compound dissolved completely at 0.05 M above 250 bar at 50 °C and no upper solubility was found making it possibly the most CO<sub>2</sub> soluble hydrocarbon anionic surfactant discovered to date. It is interesting to note that even the lowest branched TCS surfactant showed high CO<sub>2</sub> compatibility relative to hydrocarbon dichain surfactants—higher in fact, than that seen for AOT 4, the most soluble of the hydrocarbon dichain AOT analogues [5].

Comparing the behavior of the TCS 12 and TCS 13 suggests that chain length also plays a role in CO<sub>2</sub> solubility—albeit a more subtle one than tip branching. It is probable that an optimum chain length exists, as seen for dichain fluoro-AOT like surfactants in carbon dioxide, for which it has been shown that chain lengths of between four and seven carbons long perform better than much longer or shorter chains [8–11].

All these TCS surfactants were also able to disperse water in CO<sub>2</sub> at 50 °C, stabilizing water loadings of  $w=5$  (where  $w = [\text{water}]/[\text{surfactant}]$ ) with the same trends in cloud points to those seen in the binary mixtures (Fig. 2). TCS 14 was the only surfactant able to solubilize water loadings of  $w=10$  at surfactant concentrations of 0.025 and 0.050 M (both with cloud points at 500 bar and 50 °C) a performance which approaches that of the most efficient fluorinated dichain AOT analogues [8–11].

The AOT 14 surfactant is an analogue, most closely related to the trichain TCS 14. Compatibility studies with AOT 14 showed little solubility in CO<sub>2</sub> and no ability to disperse water above background solubility. This indicates that a third chain dramatically increases surfactant solubility in CO<sub>2</sub>, pointing to new avenues for design of CO<sub>2</sub>-philic surfactants bearing three chains.

## Conclusions

Building on past work in this field [5], new cheap, easily synthesizable surfactants, bearing high methyl group densities in the chain-tip region have been studied as novel CO<sub>2</sub>-philes. The addition of a third chain to sulphosuccinate surfactants has been proven to dramatically enhance activity in CO<sub>2</sub>. All TCS surfactants studied have been shown to be soluble in condensed carbon dioxide, some at concentrations higher than any other ionic surfactants previously reported. The surfactants exhibit standard cloud point behavior, with positive dP/dT gradients defining fully reversible and cycleable phase transitions. NIR confirms this and shows step changes in solubility at the cloud point. The surfactants also efficiently entrain water into the system, again at higher levels than those reported previously for charged surfactants. Importantly, a clear link has been shown between chain-tip structure and CO<sub>2</sub>-philicity; the surfactant with the most chain-tip branching exhibited the lowest cloud point pressures at any given temperature, whereas the surfactant with the least branching at the chain tips had the highest cloud point pressures. This is promising for the design of new surfactants, where incorporation of a third chain and the focus of extra CO<sub>2</sub>-philic groups at the chain-tips could lead to super surfactants for carbon dioxide.

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