Micellization of Hydrocarbon Surfactants in Supercritical Carbon Dioxide

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Supercritical carbon dioxide (sc-CO_2) could be viewed as the ideal chemical processing solvent; it is cheap, nontoxic, volatile, inert, nonflammable, and recyclable.[1] Unfortunately, weak intermolecular interactions are a limiting factor especially for polar solutes. Surfactants could overcome this but, very few commercial materials dissolve in CO_2.[2] Certain fluorocarbons are CO_2-soluble,[3−10] and fluoro-surfactants do stabilize reversed micellar[4,6−9] and CO_2-water dispersions, which have been used as media for various reactions.[8−10] Furthermore, a new "green" dry-cleaning technology is based on CO_2.[11] Owing to the high cost of fluorous chemicals efforts have been made to obtain CO_2-soluble hydrocarbon polymers.[12,13] With hydrocarbon surfactants there is some indirect spectroscopic evidence for aggregation in CO_2.[14,15] Here we show that anionic hydrocarbon surfactants can be custom-designed to form reversed micelles in sc-CO_2, without the need for other additives. These are related to common Aerosol-OT, which alone does not aggregate,[15] and a trimethyl functional group renders the new surfactants CO_2-soluble. Direct structural evidence from small-angle neutron scattering (SANS) indicates micellar radii ∼14−15 Å. UV−vis measurements show the micelles also disperse a polar dye which is otherwise insoluble. These results establish principles for designing other low-cost CO_2-philic hydrocarbon surfactants.

Recently it has been demonstrated that fluorinated analogues of Aerosol-OT (sodium bis-2-ethyl-1-hexyl sulfosuccinate, AOT,
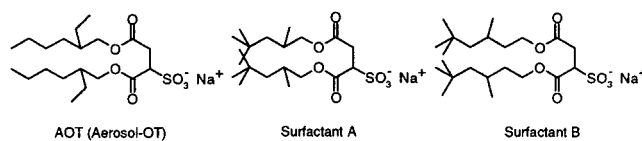

Figure 1. Surfactants used in this work. AOT (Aerosol-OT) sodium bis-(2-ethyl-1-hexyl)sulfosuccinate, surfactant **A** (sodium bis(2,4,4-trimethyl-1-pentyl)sulfosuccinate) and surfactant **B** (sodium bis(3,5,5-trimethyl-1-hexyl) sulfosuccinate.

see Figure 1) are very effective stabilizers for water-in-carbon dioxide (w/c) microemulsions.[7,16] Limiting air−water surface tensions at the critical micelle concentration, γ_{cmc}, for these fluoro-surfactants lie between 27.8 and 17.7 mN m^{-1}, and this has been used as a guide to design hydrocarbon surfactants with enhanced CO_2 solubility. For hydrocarbons it is known that γ_{cmc} decreases with the extent of methylation in the hydrophobic chain tip region.[17,18] Hence, a series of AOT analogues with various degrees of chain branching were synthesized, and their aqueous phase behavior investigated.[18] Of six different surfactants the highly methyl-branched compounds **A** and **B** (Figure 1) showed the lowest γ_{cmc}; 27 and 28 mN m^{-1} respectively compared with 31 mN m^{-1} for AOT itself.

Surfactants **A** and **B** both dissolved in stirred sc-CO_2: at 33 °C and 250 bar the solid was initially insoluble; however, after around 10 min the surfactant began to melt, and after 20 min a single-phase transparent solution was formed. Under identical conditions AOT did not dissolve.

Scattering length density calculations[19] indicate sufficient neutron contrast between hydrocarbon surfactant and CO_2 ($\Delta\rho \approx 2 \times 10^{10}$ cm^{-2}). The solutions were therefore studied by high-pressure SANS in a stirred cell, as described elsewhere.[7,16,20] The $I(Q)$ data for surfactant **A**, AOT, and CO_2 alone are shown in Figure 2, from which the empty cell scattering has been subtracted. For AOT and CO_2 the results are consistent with an incoherent background signal, and no significant aggregation of AOT in sc-CO_2. On the other hand, for surfactant **A** the enhanced intensity and smooth decay indicates micelle formation. A similar curve was obtained for surfactant **B**, and the scattering did not change after 1 day, suggesting the micelles are relatively stable under these conditions. Subtracting the cell + CO_2 signal gave curves such as those shown in Figure 3. The intensities essentially scale with concentration, although agreement is not perfect, perhaps owing to the difficulties of accurate absolute normalization of high-pressure SANS data.[7] These data were fitted by the scattering law for a Schultz distribution of spherical particles,[21] yielding values for an average radius R_{av} and polydispersity factor σ/R_{av}. Fitted parameters for the lines shown in Figure 3, and also data with surfactant **B**, were $R_{av} = 14 \pm 1$ Å and $\sigma/R_{av} = 0.20$. The radii are consistent with "dry" reversed micelles, as observed with these surfactants in n-heptane.[18] As a further check data for **A** and **B** micelles, at 0.10 mol dm^{-3} in sc-CO_2 at 33 °C and 500

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(20) High-pressure SANS experiments were performed on LOQ at ISIS, UK, to measure scattering cross-sections $I(Q)$ (cm^{-1}) as a function of momentum transfer Q (Å^{-1}) = $(4\pi/\lambda) \sin(\theta/2)$: λ is the incident neutron wavelength ($2.2 \rightarrow 10$ Å) and θ the scattering angle ($<7°$). The high-pressure cell, and corrections to the raw data to account for both pressure-induced sample volume changes, and the path-length, were as described before.[7,16]
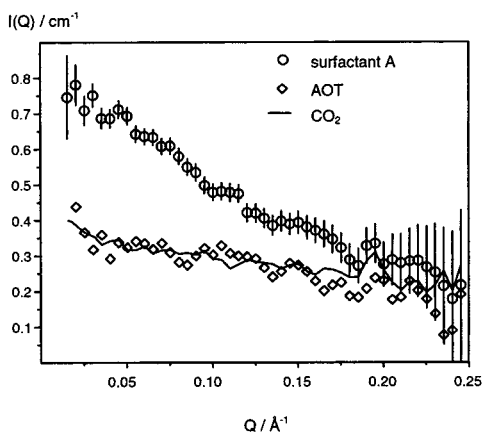
Figure 2. SANS signals obtained at 33 °C and 500 bar after subtraction of the empty cell. The effective surfactant concentration is 0.10 mol dm^{-3}. Error bars are shown for surfactant **A** data only.

bar were analyzed in terms of the Guinier approximation[22] to provide another estimate for the radii, as shown in the inset to Figure 3. Values generated from the fitted lines were slightly higher than those obtained by model fitting (18 and 16, both ± 2 Å, respectively for surfactants **A** and **B**). However, both types of analysis are consistent with spherical micelles.

UV−vis dye solubilization measurements were also made.[23] If reversed micelles were present the positively charged chromophore, dimidium bromide ($\lambda_{max} \approx 550$ nm), should be incorporated owing to favorable interactions with the surfactant anionic headgroups. No dimidium bromide absorbance could be detected in pure CO_2, consistent with an insoluble dye. With added Aerosol-OT (0.025 mol dm^{-3}) no dye uptake was observed, consistent with no aggregation.[15] However, with the CO_2-soluble surfactant **B** as dispersant a spectrum characteristic of dimidium bromide in reversed micelles was obtained (Figure 4).

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(21) $I(Q)$ data were analysed using the multi-model FISH program as described before.[7,16] From a range of possible models a Schultz distribution of spherical particles gave the best fits and most physically reasonable parameters. This scattering law may be written

$$I(Q) = \left(\frac{\phi(\rho_{micelle} - \rho_{CO_2})^2}{\sum_i V_i X(R_i)} \right) \sum_i [V_i^2 P(Q,R_i) X(R_i)]$$

where ϕ, R, and V are the particle volume fraction, radius, and volume, respectively, and ρ_i denotes a scattering length density. The spherical form factor is $P(Q,R_i)$, and $X(R_i)$ is the Schultz function, which is characterized by an average radius R_{av} and rms deviation $\sigma = R_{av}/(Z + 1)^{1/2}$, where Z is a width parameter. For CO_2 the neutron scattering length density may be taken as ρ_{CO_2} = (mass density × 2.498 × 10^{10} cm^{-2})[19] hence effects of P and T on ρ_{CO_2} were taken into account. Calculated scale factors were ±15% of those expected owing to sample compositions, indicating the model is physically reasonable.

(22) For dilute aggregated systems estimates for the micelle radii R were obtained using the Guinier law which is valid at low $Q (QR < 1)$

$$\ln[I(Q)] = \ln[I(0)] - \frac{(QR_g)^2}{3} \quad R = \sqrt{5R_g/3}$$

In the above R_g is a radius of gyration and $I(0)$ is an intensity factor related to concentration and contrast.

(23) UV−vis spectra were recorded using a single-beam Hewlett-Packard HP-8452 diode-array spectrometer, which had been modified to accept samples in the pressure cell (path-length 1.5 cm). Samples were prepared as for SANS, but with the addition of a weighed amount of the cationic dye dimidium bromide (Aldrich). The systems were stirred at 40 °C and 500 bar for 30 min before recording the absorbance spectra, for which the background was the cell + CO_2 alone.
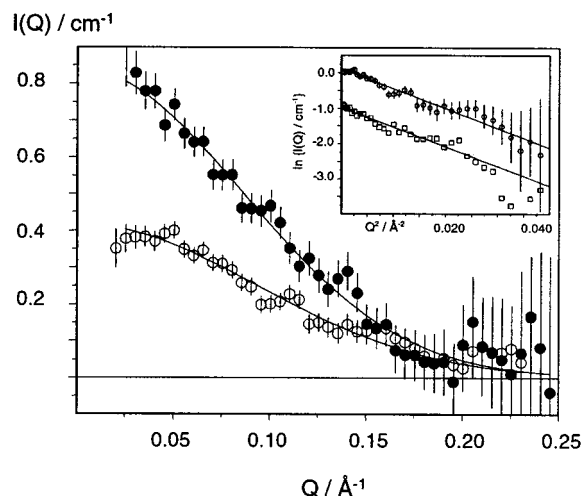

Figure 3. SANS data obtained after subtracting the cell + *sc*-CO_2 background for surfactant **A** as a function of concentration at 0.15 (●) and 0.10 (○) mol dm^{-3}. $T = 33$ °C and 500 bar. The fits are to a polydisperse sphere model[21] with $R_{av} = 14 ± 1$ Å and $\sigma/R_{av} = 0.20$. Inset shows Guinier plots for surfactant micelles of A (open circle) and B (open square) both at 0.10 mol dm^{-3}, and under the same conditions as the main figure. Gradients of the least-squares linear fits, shown as lines, were used to calculate micellar radii.[22] For presentation purposes the surfactant **A** data have been shifted vertically by a factor of e.
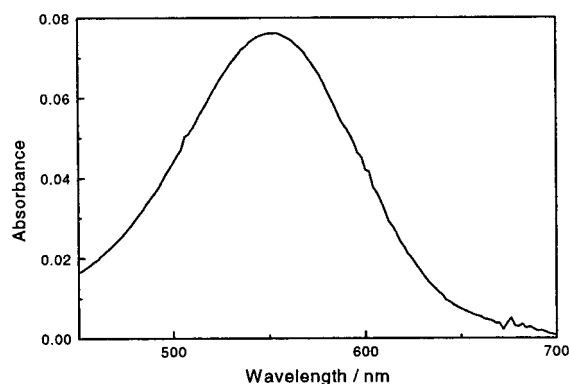

Figure 4. UV-vis spectrum of dimidium bromide dispersed in *sc*-CO_2 with reversed micelles of surfactant **B** at 40 °C and 500 bar. The surfactant concentration is 0.025 mol dm^{-3}.

To conclude, while the common anionic hydrocarbon surfactant Aerosol-OT does not aggregate, two related compounds, each possessing a high degree of chain tip methylation, do form reversed micelles in *sc*-CO_2. These principles may be helpful for designing a wider range of low-cost "CO_2-philic" hydrocarbon surfactants, especially for stabilizing bio- and food-compatible water-CO_2 emulsions and microemulsions.