Electronic Supplementary Information

Switchable Viscosity Triggered by CO_2 Using Smart Worm-like Micelles

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Experimental

Materials. Sodium stearate ($C_{18}CNa$), n-octadecanol, chlorosulfonic acid, 2-(dimethylamino)ethanol (DMAE), N,N,N',N'-tetramethyl-1,4-butanediamine (TMDAB), sodium nitrate ($NaNO_3$) and tetrabutylammonium bromide (TBAB) were purchased from Sigma-Aldrich. CO_2 (Praxair, Medical grade) and N_2 (Praxair, 99.998%) were used as received. Deionized water with a resistivity of 18.2 MΩ cm (Synergy-UV, Millipore) was used throughout this study.

The aqueous solutions of surfactants were prepared by dissolving known amounts of surfactant and additives in deionized water with gentle agitation.

Synthesis of Octadecyl Sulfate Sodium Salt ($C_{18}SNa$). The compound was prepared following a literature method.[1] n-Octadecanol, 10.0 g (0.037 mol) was dissolved in 50 mL of chloroform at 40 °C and then cooled to 5 °C. An excess chlorosulfonic acid (4.7 g, 0.04 mol) was added dropwise with constant stirring for about 20 min at 5 °C. Stirring was continued for 3 h at 40 °C and the mixture was allowed to settle overnight at room temperature. The mixture was filtered at 5 °C and the solid product was dried under vacuum for 24 h and crystallized at 0 °C from a basic ethanolic solution with 5.0 w.t.% sodium hydroxide. The white powder was again recrystallized using anhydrous ethanol and vacuum-dried for another 24 h (Yield, 65%). ^{1}H NMR (Bruker 400 MHz, $CDCl_3$, TMS) for $C_{18}SNa$: δ 0.952 [t, 3H, $\boldsymbol{CH_3}(CH_2)_{15}CH_2CH_2$], 1.188–1.347 [m, 30H, $CH_3\boldsymbol{(CH_2)_{15}}CH_2CH_2$], 1.53 [t, 2H, $CH_3(CH_2)_{15}\boldsymbol{CH_2}CH_2$], 3.55 [t, 2H,$CH_3(CH_2)_{15}CH_2\boldsymbol{CH_2}$].

Measurement of Viscosity. Samples with required amounts of reagents in vials were homogenized and kept in a water bath at a specified temperature for at least 24 h to ensure equilibration before performing rheological measurements. The viscosity of the sample solutions was measured on a capillary rheometer (RH-2200, Bohlin Instruments), whose bore diameter is 15 mm and barrel bore length is 250 mm. There was a constant and controlled temperature around the capillary tubes containing the sample, so that the sample viscosity could be measured at a controlled temperature (15-80 °C). The system was sealed to reduce water evaporation during the measurements. The barrel was completely filled with the sample before every experiment. The ram forces the viscous sample to flow with a volumetric rate through the barrel. Capillaries were attached to the bottom of the barrel and the ram was moved downward. All samples were extruded from capillary rheometer at a wide shear rate range. The shear viscosity of samples as a function of shear rate was measured. Each measurement was repeated three times using the samples with the same concentration; therefore, the calculated value is the average of three measurements. At low shear rate, the shear viscosity is independent of shear rate and a viscosity plateau is obtained, demonstrating a Newtonian fluid behaviour. Upon extrapoloating the plateau values to zero shear rate, the zero-shear viscosity can be obtained.

Measurement of Particle Size and Zeta-Potential. Particle size and zeta-potential were determined using a Zetasizer Nano ZS (size range from 0.6 nm to 8.9 μm). All aqueous solutions of DMAE and $C_{18}SNa$ were filtered with a 0.2 μm membrane filter before the measurements to avoid interference from dust for testing via dynamic light scattering (DLS).

Switching the Viscosity Triggered by CO_2. The aqueous solution of DMAE (200 mM) and $C_{18}SNa$ (200 mM): 7.45 g sodium octadecyl sulfate was added to 100 mL deionized water followed by mechanical agitation for several minutes at 60 ºC, and the viscosity was measured. After adding 1.78 g DMAE, the viscosity was measured again. After CO_2 was sparged through the solution for 15 min at 60 ºC, the solution became a gel and the viscosity was measured again. After N_2 was sparged through the solution for 50 min at 60 ºC, the solution viscosity dropped back to water-like and was measured again. Because the Krafft point of octadecyl sulfate sodium salt ($C_{18}SNa$) is 56 ºC,[1] the viscosity was always measured at 60 ºC.

The aqueous solution of 30.65 g $C_{18}CNa$ (200 mM) with 32.2 g TBAB (200 mM) or 8.5 g $NaNO_3$ (200 mM) was prepared in 500 mL deionized water followed by mechanical agitation for 6 h at 80 ºC and became a transparent and viscous solution; the viscosity was measured. After CO_2 was sparged through the solution for 10 min at 60 or 80 ºC, the solution became a milky suspension; the viscosity, zeta-potential and particle size were measured. After N_2 was sparged through the solution for 30 min at 60 or 80 ºC, the solution viscosity increased and was measured again. Sodium stearate ($C_{18}CNa$) has a Krafft point of 71 ºC.[2]

Cryo-TEM. The solution (5 μL) at ambient temperature was located on a carbon-coated film with a copper grid, and slightly printed with filter papers and got a thin liquid film (20−400 nm) on the grid surface. The grid was thrust quickly into liquid ethane at -180 °C and then delivered into liquid nitrogen at -190 °C for storage. Then the vitrified samples stored in liquid nitrogen was delivered into a JEOL 2011 scanning transmission electron microscope via a Gatan Cryo-transfer and cooling holder. The working temperature was kept below -170 °C.[3]

Additional Results

Table S1 Zero-shear viscosity of aqueous solutions of either $C_{18}SNa$ or DMAE under CO_2 or N_2 at 60 ºC.

	Surfactant $C_{18}SNa$ (200 mM)		DMAE (200 mM)	
	Under CO_2	Under N_2	Under CO_2	Under N_2
Viscosity (mPa·s)	1.2	1.1	1.3	1.2

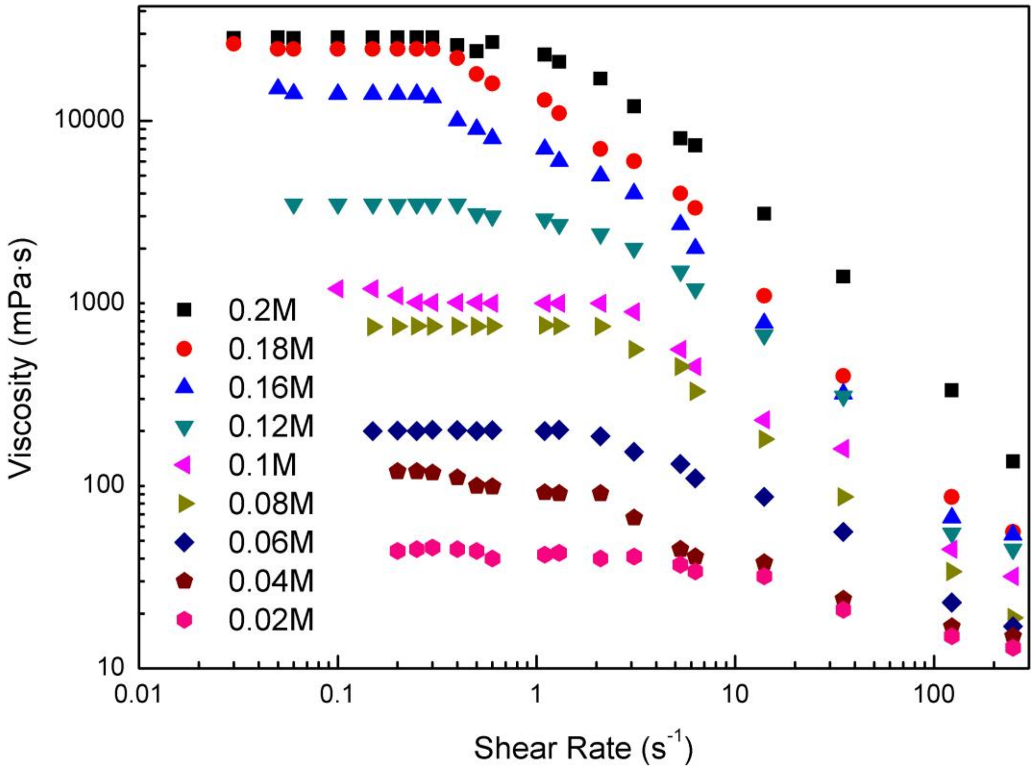

Fig. S1 The effect of surfactant $C_{18}SNa$ concentration and the shear rate on the solution viscosity in the presence of DMAE (200 mM) and 1 bar of CO_2 at 60 ºC.

Table S2 Zero-Shear viscosity of the mixture of surfactant C_{18}CNa (200 mM) and $NaNO_3$ (200 mM) in water solution under CO_2 or N_2 at 80 ºC.

	Process	Viscosity (mPa·s)
1	After stirring 10 min	12400
2	After bubbling CO_2 10 min	2.1
3	After bubbling N_2 40 min	12100

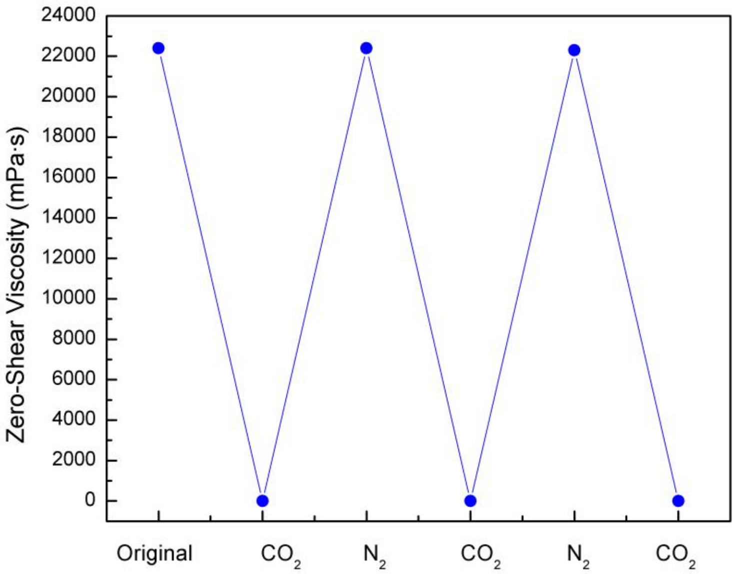

Fig. S2 The switchable viscosity of C_{18}CNa (200 mM) and TBAB (200 mM) in water solution controlled by CO_2 at 60 ºC.

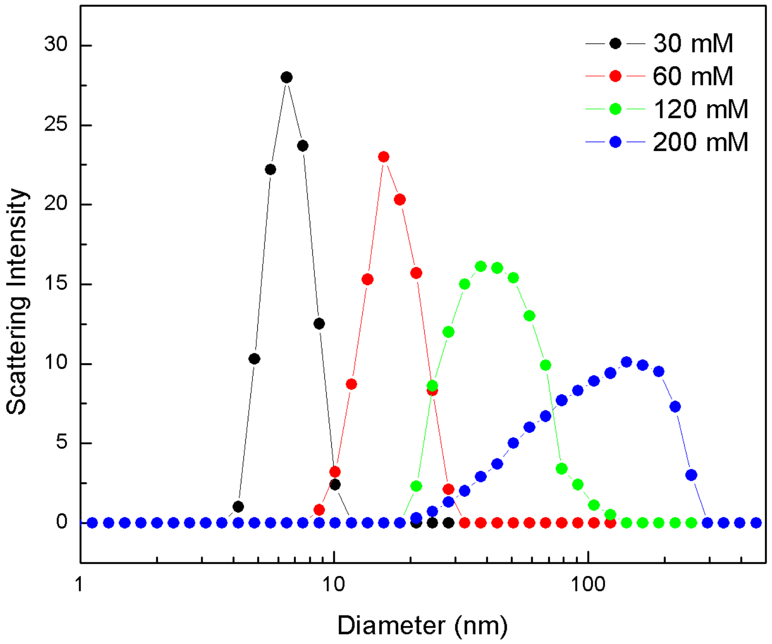

Fig. S3 Intensity weighted distribution of apparent hydrodynamic diameter of micellar solutions as a function of increasing C_{18}SNa concentration from 30 to 200 mM in the presence of 200 mM DMAE and 1 bar of CO_2 at 60 °C.

We took advantage of DLS to test the hydrodynamic properties and radius of the microstructures (Fig. S3). When the concentration of the DMAE is fixed and that of C_{18}SNa is increased, the equivalent hydrodynamic diameter is enhanced. The diameter of the sample containing 200 mM DMAE and 200 mM C_{18}SNa tested via DLS is 107 nm, which shows the entanglement length, i.e., the average contour length between two entanglement points, and it should demonstrate the formation of elongated wormlike micelles. Thus the DLS data suggest the structures in the microscopic view grow from small and separated forms into elongated wormlike micelles.[4]

References

1 A. Verma and M. K. Purkait. *Indian J. Chem. Technol.* 2010, **17**, 233.

2 R. Klein, D. Touraud and W. Kunz. *Green Chem.*, 2008, **10**, 433.

3 Z. Chu, Y. Feng, X. Su and Y. Han. *Langmuir*, 2010, **26**, 7783.

4 H.Yin, Y. Lin and J. Huang. *J. Colloid Interface Sci.*, 2009, **338**, 177.