Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Solubilization of Elemental Sulfur By Surfactants Promotes Reduction to H_2S by Thiols

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Experimental details

Materials and Methods. Chemicals were used as received from Sigma Aldrich, ThermoFisher Scientific, Acros Organics, and TCI. PBS Buffer solutions were made using 1 PBS Tablet (EMD Millipore) dissolved in 1.00 L of Millipore water to provide a pH=7.4 buffered solution with 10 mM phosphate, 140 mM NaCl, and 3 mM KCl. Buffered solutions were sparged with N_2 to remove dissolved oxygen and stored in an N_2 filled glovebox. UV-vis spectra were recorded on an Agilent Cary 60 UV-vis spectrometer equipped with a Quantum Northwest TC-1 temperature controller set at 25 ± 0.005 ºC. H_2S measurements were performed using a SULF-500 Type 1 Unisense electrode (extended tip - 12 cm) connected to a Unisense H_2S UniAmp.

Solubilization of S_8 by Surfactants. Scintillation vials containing a 10-20 mL solution of surfactant (100 mM) in pH 7.4 PBS buffer was stirred with excess S_8 (200 mg, 0.008 mmol) for 1 hour. After stirring, the heterogeneous mixture was filtered using 0.1 µm Whatman syringe filters to remove excess S_8. Solubilized S_8 was quantified by UV-vis spectroscopy by using the absorbance wavelength and extinction coefficient for S_8 (λ_{max} = 263 nm, ε = 6730 M^{-1} or λ_{max} = 325 nm, ε = 1040 M^{-1} for Triton-X100)

General Procedure for H_2S Calibration. NaSH (5.6 mg, 0.10 mmol) was degassed with N_2 for three 1-minute cycles and dissolved with 1 mL N_2 sparged PBS buffer to generate a 10 mM NaSH solution, which was then diluted to 1 mM. The Unisense SULF-500 electrode tip was placed in a 20 mL solution of PBS buffer and allowed to stabilize. With a stable signal, the tip was placed through a rubber septa cap in a 20 mL solution of N_2-degassed PBS buffer containing 100 mM surfactant containing 1 mM thiol (Cys, GSH, Hcy, or NAC) and allowed to stabilize prior to additions of 1 mM NaSH (5, 10, 20, 40, 60, 80, 100 µL). Calibration curves were performed daily for all H_2S measurements.

General Procedure for H_2S Measurements. A Unisense electrode was connected to a Unisense H_2S UniAmp and allowed the electrode to stabilize. The electrode tip is then submerged into the desired solution until the response stabilized (<15 mV), which was typically less than 15 minutes. Once the electrode had stabilized, a solution of desired surfactant and solubilized S_8 was prepared was again allowed to stabilize. With a stable signal the desired thiol (50-1000 µM) was injected and H_2S release was monitored. Each trial was repeated in triplicate.

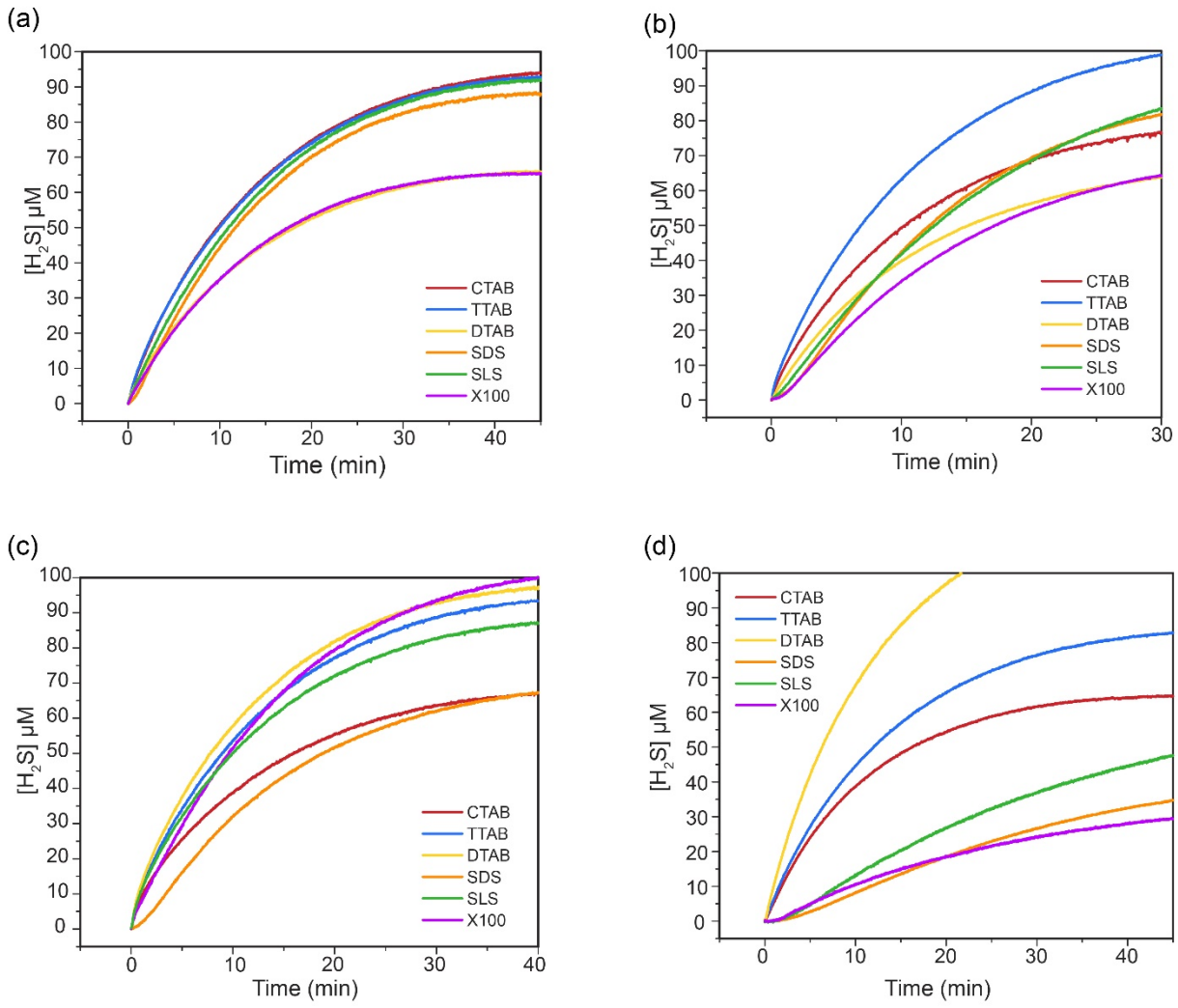

Figure S1. H_2S release of (80 µM) S^0 from thiol (1 mM, 12.5 equiv.) in each surfactant (100 mM) a) cysteine b) glutathione c) homocysteine and d) N-acetyl cysteine

Surfactant	Carbon Chain Length	[S_8] Avg. mM + Std. Dev.
CTAB	16	0.15 ± 0.0020
TTAB	14	0.099 ± 0.0037
DTAB	12	0.044 ± 0.0052
SDS	12	0.065 ± 0.0050
SLS	11	0.053 ± 0.0015
Triton-X100	27-30	0.250 ± .032

Table S1. Solubilized S_8 by surfactant (100 mM) in PBS Buffer (pH=7.4). UV-Vis spectra were baselined to stock solutions of respective surfactant and then S_8 was quantified. (S_8 measured at λ_{max} at 263 nm (at 295 nm for Triton-X100 due to absorbance overlap)).

	Thiol – Avg. H_2S Release + Std. Dev. (±)			
Surfactant	**Cys**	**Hcy**	**GSH**	**NAC**
CTAB	78 ± 10	67 ± 1.8	78 ± 4.4	73 ± 2.2
TTAB	92 ± 1.7	94 ± 3.0	101 ± 1.5	82 ± 2.1
DTAB	66 ± 2.2	98 ± 4.9	73 ± 9.0	112 ± 5.5
SDS	88 ± 2.7	69 ± 0.7	86 ± 9.6	42 ± 3.2
SLS	92 ± 5.8	105 ± 3.4	91 ± 5.8	61 ± 2.9
Triton -X100	65 ± 4.9	101 ± 1.1	68 ± 5.8	35 ± 2.9

Table S2. H_2S release from surfactant/S_8 + thiols

	$k_{obs}(s^{-1})$			
Surfactant	**Cys**	**Hcy**	**GSH**	**NAC**
CTAB	7.01×10^{-3}	3.76×10^{-3}	5.67×10^{-3}	6.71×10^{-3}
TTAB	6.07×10^{-3}	4.84×10^{-3}	4.30×10^{-3}	6.76×10^{-3}
DTAB	6.36×10^{-3}	4.13×10^{-3}	4.07×10^{-3}	5.69×10^{-3}
SDS	8.51×10^{-3}	4.70×10^{-3}	4.10×10^{-3}	8.37×10^{-3}
SLS	6.65×10^{-3}	4.59×10^{-3}	5.70×10^{-3}	2.24×10^{-3}
Triton -X100	8.42×10^{-3}	4.09×10^{-3}	2.83×10^{-3}	1.35×10^{-3}

Table S3. Rate of H_2S formation from surfactant (100 mM)/S_8 (10 μM S_8, 80 μM S^0) with added thiol (100 equiv.)