Viscoelastic micellar solution formed by Se-based ionic liquid surfactant and its response to redox changes

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1. Synthesis of N-selenium-containing alkyl-N-methylpyrrolidinium bromide

(1) **1,2-ditetradecyldiselane ($DC_{14}DSe$):**

Under N_2 flow, 15 g selenium power, 10 g NaOH and 150 mL THF were mixed in a 500 mL flask, and a black suspension was obtained. 3.3 mL $NH_2NH_2{\cdot}H_2O$ (85 wt%) was added drop by drop at 0 °C, resulting in a reddish brown solution. After that a solution of 56.9 g 1-bromotetradecane in 100 mL THF was injected into it under and the mixture was stirred for ca. 18 h at 25 °C. A yellow needle-like crystals, $DC_{14}DSe$ (40.6 g, yield 78%), was collected by the recrystallization with ethyl acetate, and directly used in the next synthesis. ^{1}H NMR of $DC_{14}DSe$ (400 MHz, $CDCl_3$), δ/ppm: 0.89-0.92 (t, J=6 Hz, 6H), 1.28-1.42 (m, 44H), 1.71-1.78 (m, 4H), 2.92-2.95 (t, J=6 Hz, 4H).

(2) **N-bromoethyl-N-methylpyrrolidinium bromide (BrC_mMPB)**

50 mL of acetonitrile solution of 8.2 g N-methylpyrrolidine was slowly added into 250 mL of acetonitrile solution of 1,2-dibromoethane under stirring. The mixture was continuously reacted at room temperature for 24 h. The solvent was removed by distillation under the reduced pressure, and the crude product was recrystallized with isopropanol. BrC_2MPB was obtained as yellow solid (20.8 g, yield 80%). ^{1}H NMR of BrC_2MPB (400 MHz, D_2O), δ/ppm: 2.15 (s, 4H), 3.03 (s, 3H), 3.51 (m, 4H), 3.74-3.78 (m, 4H).

(3) **N-(3-selanylcetyl)-N-methylpyrrolidinium bromide ($C_{14}SeC_2MPB$)**

Under N_2 flow, 50 mL of aqueous solution of 21 g sodium borohydride was added into 200 mL THF solution of 15 g $DC_{14}DSe$. After 1 h, 50 mL of aqueous solution of 14.5 g BrC_2MPB was slowly added into the above white suspension. The mixture was continuously reacted for 15 h at room temperature, and the collect the THF phase. The crude product after removing the solvent was dissolved in hot isopropanol, and filtered to remove the residual inorganic salt. A designed mount of petroleum ether was added into the filtrate, and white solid was collected as product (15.5 g, yield 63%). $C_{12}SeC_4MPB$ and $C_{10}SeC_6MPB$ were synthesized following the similar procedure.

^{1}H NMR of $C_{14}SeC_2MPB$ (400 MHz, D_2O), δ/ppm: 0.90-0.94 (t, J=8 Hz, 3H), 1.31-1.46 (m, 22H), 1.68-1.76 (m, 2H), 2.26 (s, 4H), 2.74-2.77 (t, J=6 Hz, 2H), 2.93-2.98 (m, 2H), 3.13 (s, 3H), 3.60 (s, 4H), 3.67-3.69 (m, 2H).

^{1}H NMR of $C_{12}SeC_4MPB$ (400 MHz, D_2O), δ/ppm: 0.90-0.94 (t, J=8 Hz, 3H), 1.31-1.44 (m, 18H), 1.64-1.70 (m, 2H), 1.74-1.80 (m, 2H), 1.91-1.99 (m, 2H), 2.25 (s, 4H), 2.59-2.68 (m, 4H), 3.09 (s, 3H), 3.37-3.42 (m, 2H), 3.49-3.59 (m, 4H).

^{1}H NMR of $C_{10}SeC_6MPB$ (400 MHz, D_2O), δ/ppm: 0.90-0.94 (t, J=8 Hz, 3H), 1.32-1.55 (m, 18H), 1.65-1.72 (m, 4H), 1.84 (m, 2H), 2.25 (s, 4H), 2.56-2.62 (m, 4H), 3.10 (d, 3H), 3.37-3.40 (m, 2H), 3.54-3.56 (m, 4H).

2. Additional results

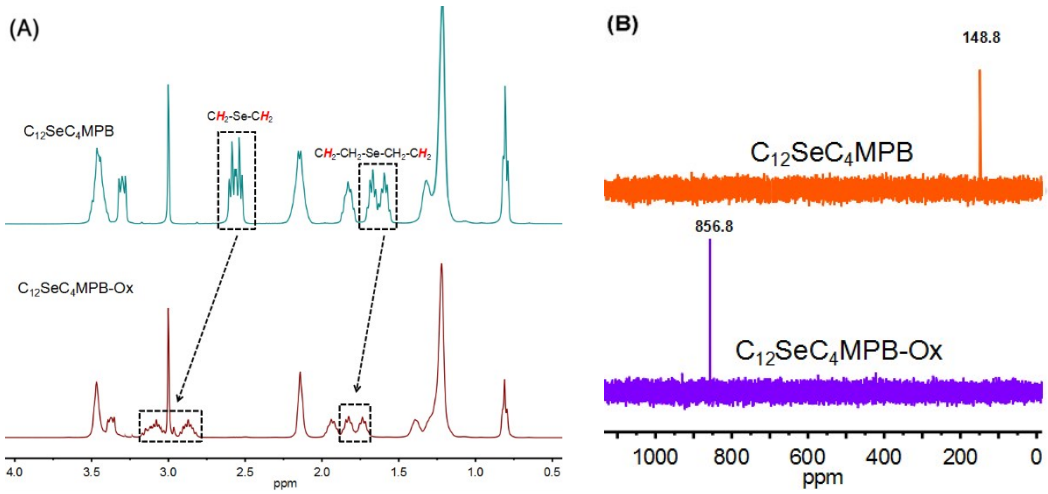


Figure S1. Evidences at the molecular level for the redox response of $C_{12}SeC_4MPB$. (A) ^1H NMR spectra using D_2O as solvent (B) ^{77}Se NMR spectra using D_2O as solvent.

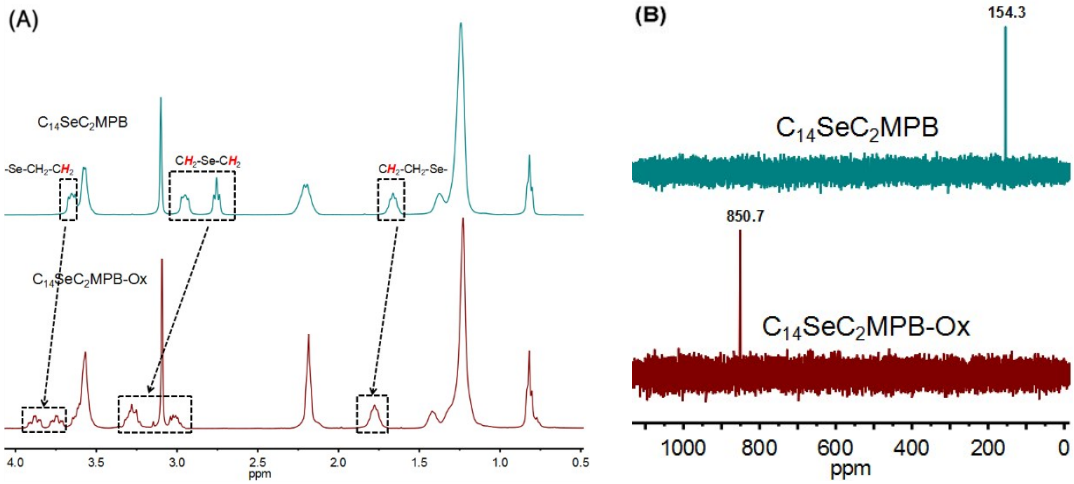


Figure S2. Evidences at the molecular level for the redox response of $C_{14}SeC_2MPB$. (A) ^1H NMR spectra using D_2O as solvent (B) ^{77}Se NMR spectra using D_2O as solvent.

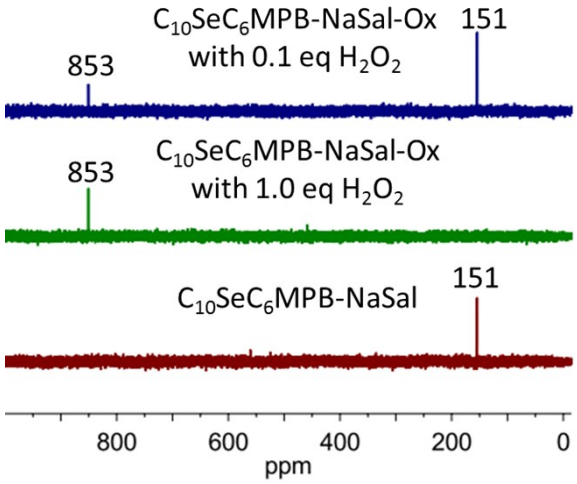


Figure S3. ^{77}Se NMR spectra of $C_{10}SeC_6MPB$-NaSal

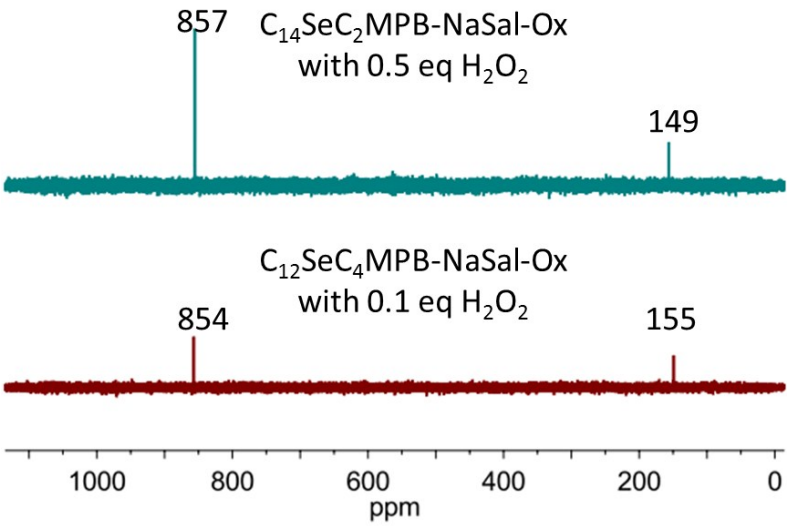


Figure S4. ^{77}Se NMR spectra of $C_{14}SeC_2MPB$-NaSal and $C_{12}SeC_4MPB$-NaSal after oxidation.

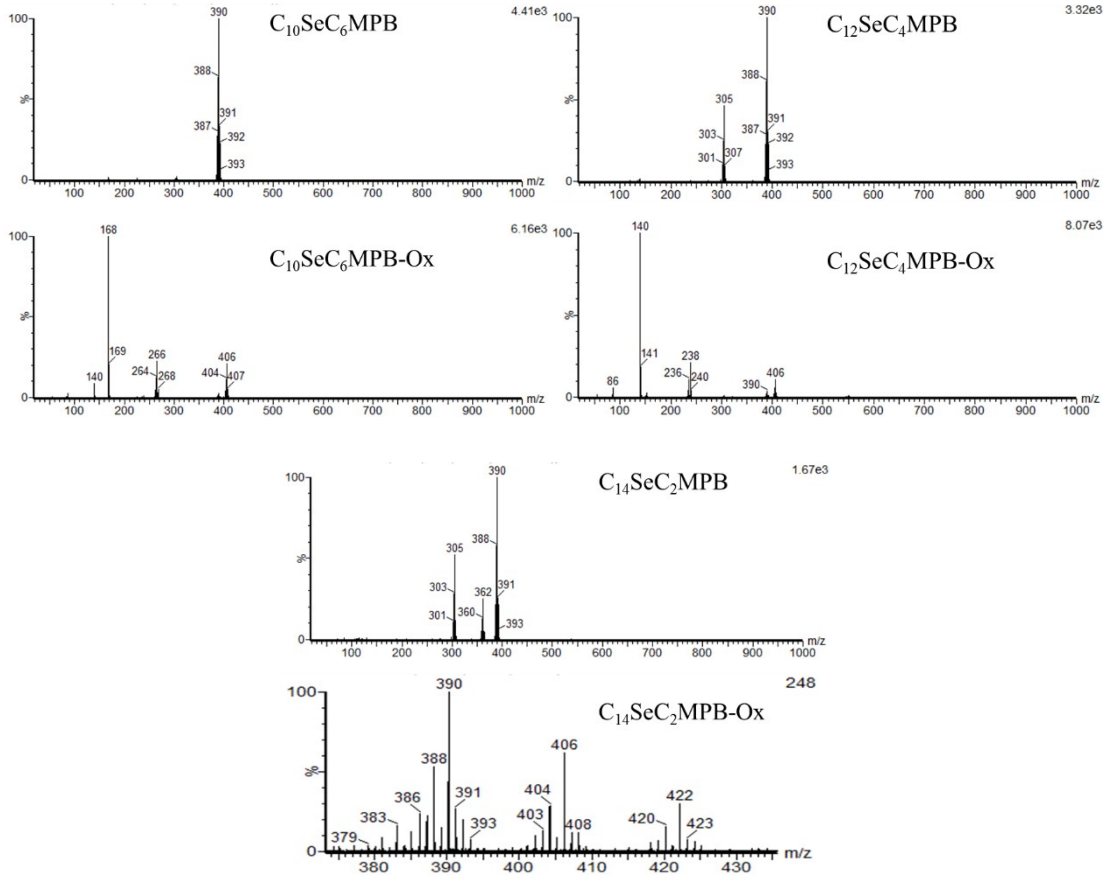


Figure S5. ESI MS spectra of selenium-containing surfactants.

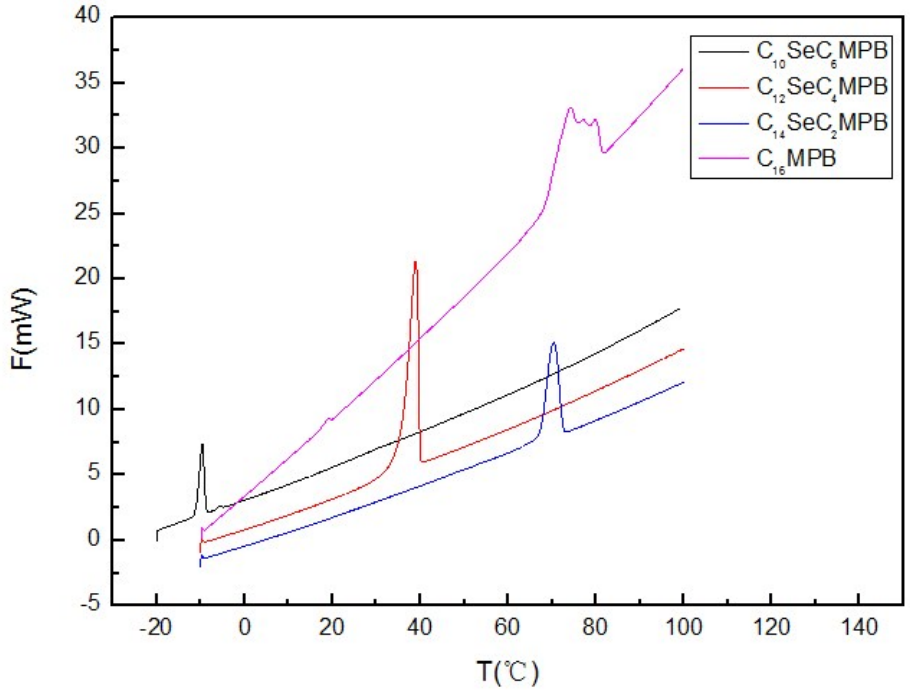


Figure S6. DSC thermograms of selenium-containing surfactants.

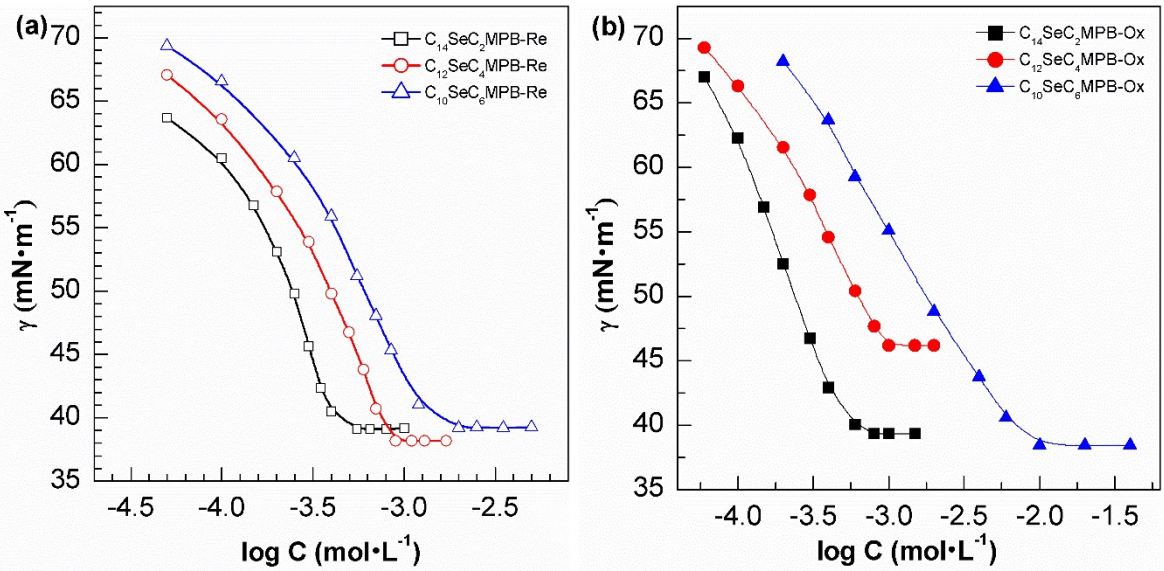


Figure S7. Variations of surface tension with surfactant concentration at 25 ºC.

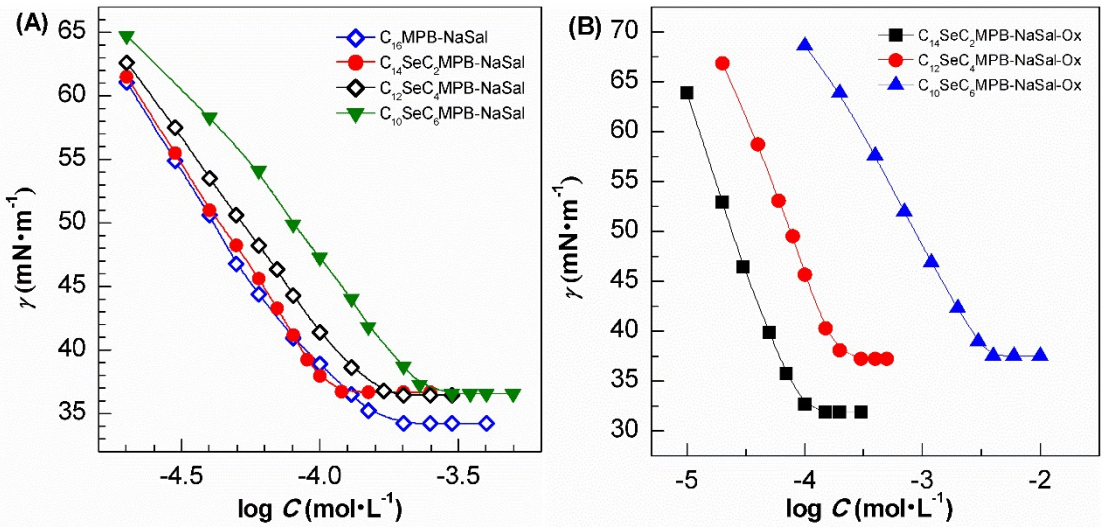


Figure S8. Variations of surface tension with surfactant concentration at 25 °C. The mole ratio of surfactant and NaSal was fixed at 1:1.

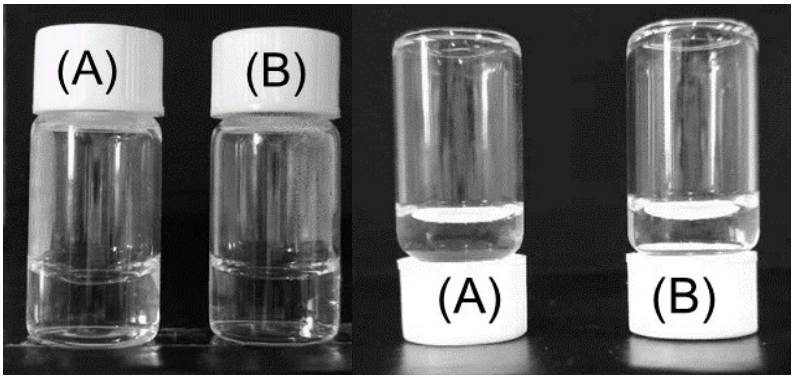
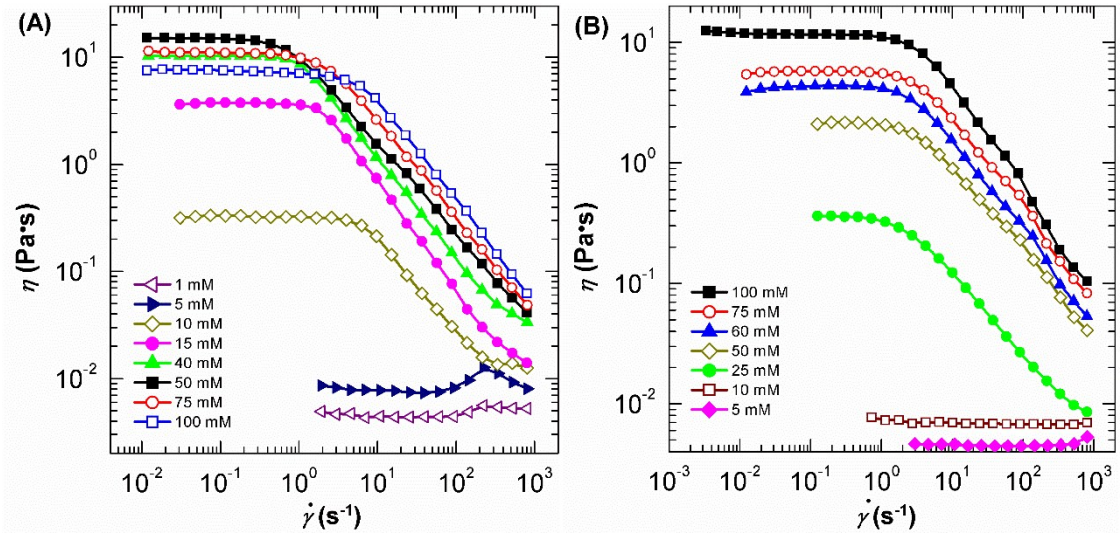


Figure S9. Snapshots of (A) 50 mM $C_{14}SeC_2$MPB solution and (B) 50 mM NaSal solution at room temperature.



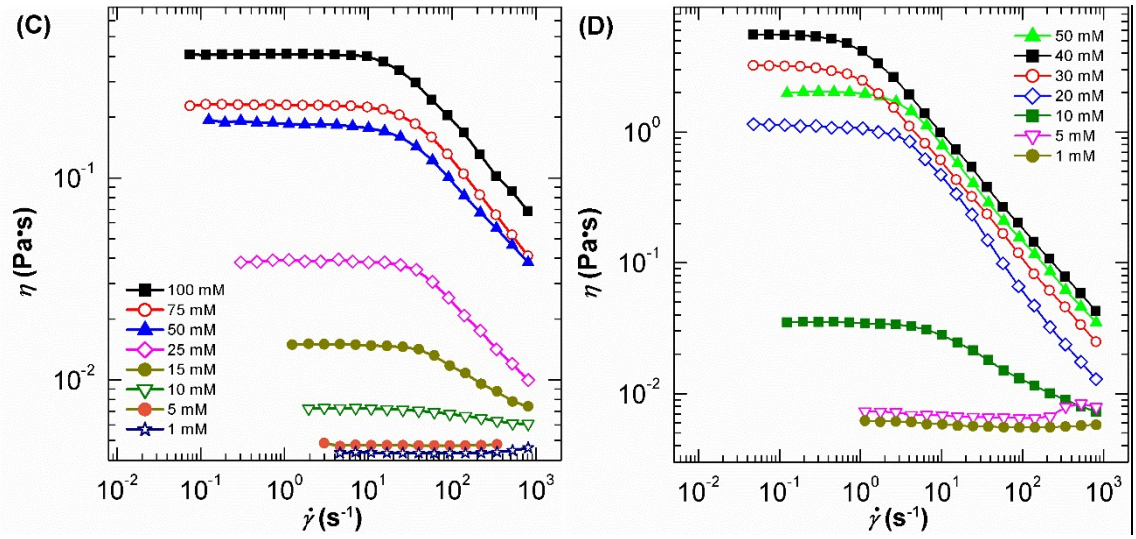


Figure S10. Steady rheological spectra of surfactant solutions at 25 °C. (A) $C_{14}SeC_2MPB$-NaSal, (B) $C_{12}SeC_4MPB$-NaSal, (C) $C_{10}SeC_6MPB$-NaSal, and (D) $C_{16}MPB$-NaSal. The molar ratio of CMPB and NaSal was fixed at 1:1 for all the systems.

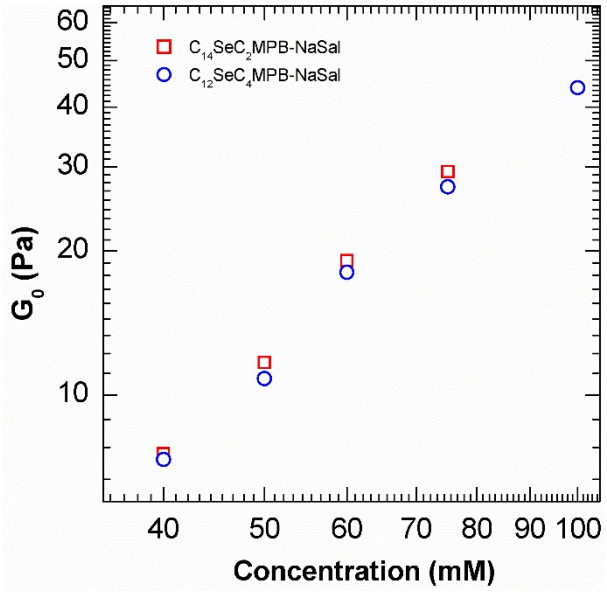


Figure S11. Variations of the plateau modulus G_0 with concentration.

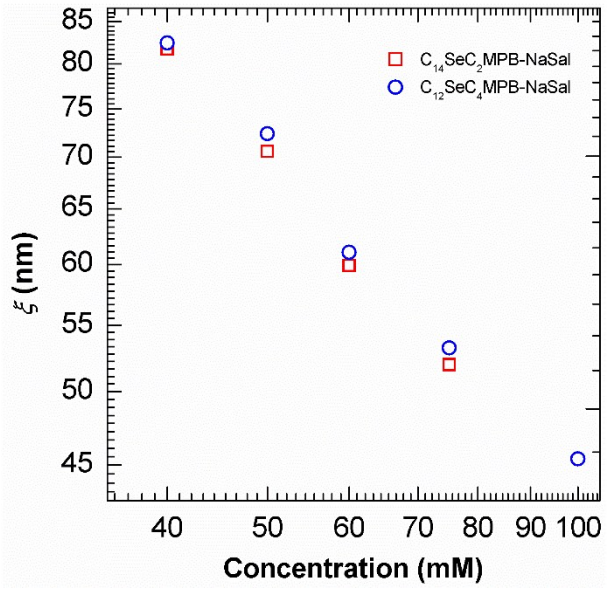


Figure S12. Variations of the mesh size of wormlike micellar network with concentration.

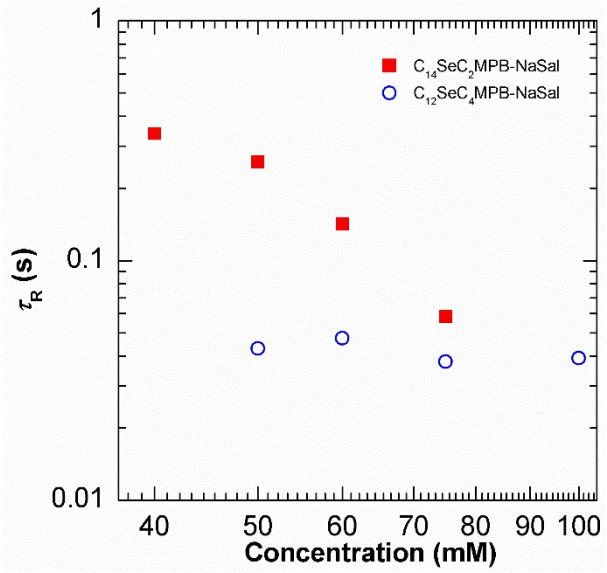


Figure S13. Variations of the relaxation time of CMPB-NaSal worms with concentration.

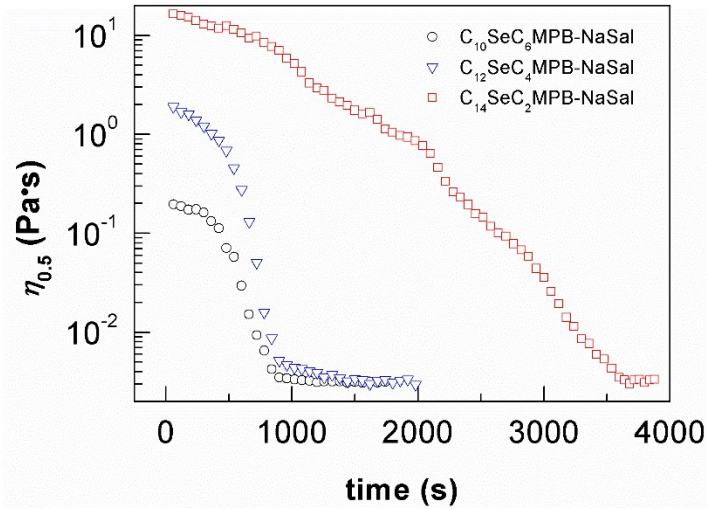


Figure S14. Real-time variations of viscosity at 0.5 s^{-1} with the addition of H_2O_2. (A) $C_{14}SeC_2MPB$-NaSal and 0.5 eq H_2O_2, (B) $C_{12}SeC_4MPB$-NaSal and 0.1 eq H_2O_2, (C) $C_{10}SeC_6MPB$-NaSal and 0.1 eq H_2O_2.

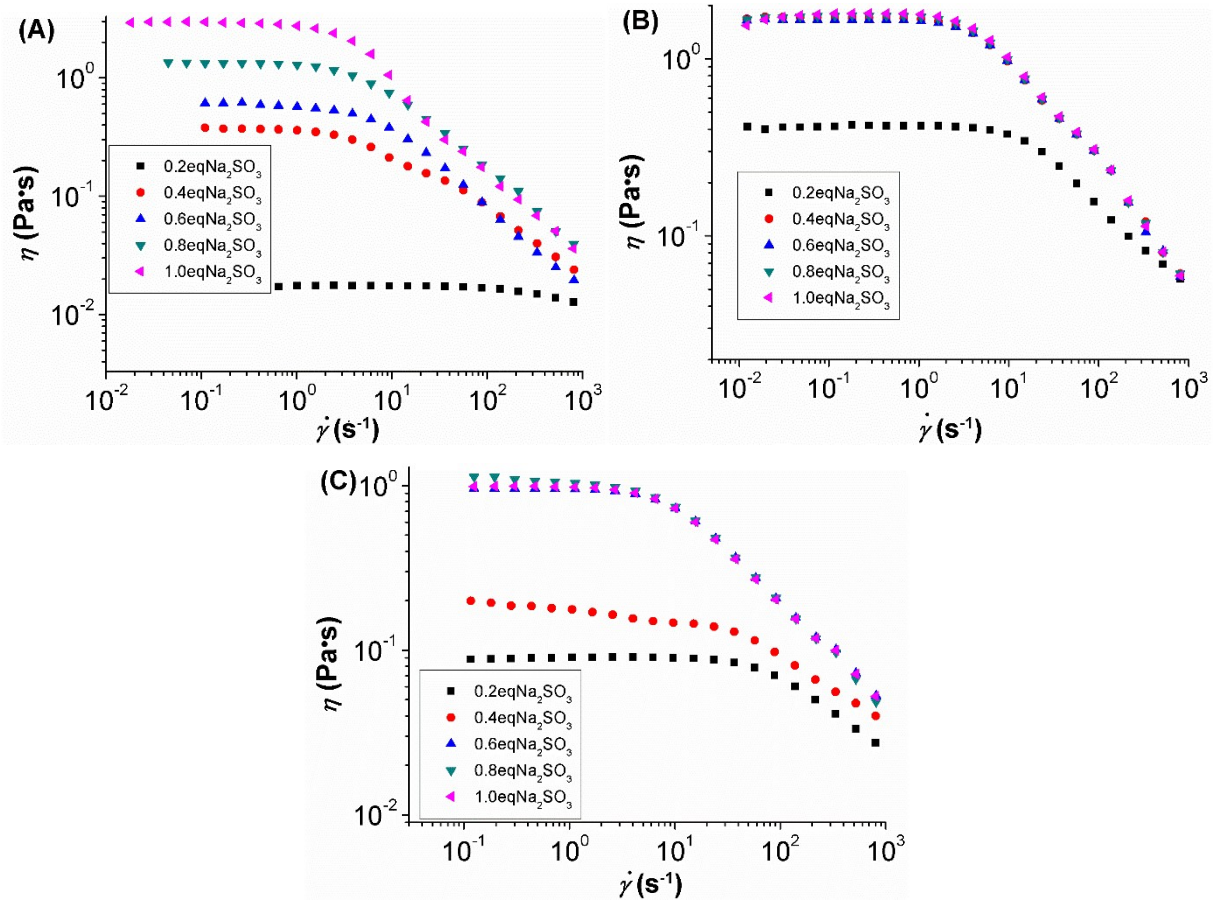


Figure S15. Steady rheology of wormlike micellar solution. The solution was first oxidized with H_2O_2, and then added Na_2SO_3. (A) $C_{14}SeC_2MPB$-NaSal and 0.5 eq H_2O_2, (B) $C_{12}SeC_4MPB$-NaSal and 0.1 eq H_2O_2, (C) $C_{10}SeC_6MPB$-NaSal and 0.1 eq H_2O_2. The concentration was fixed at 50 mM.

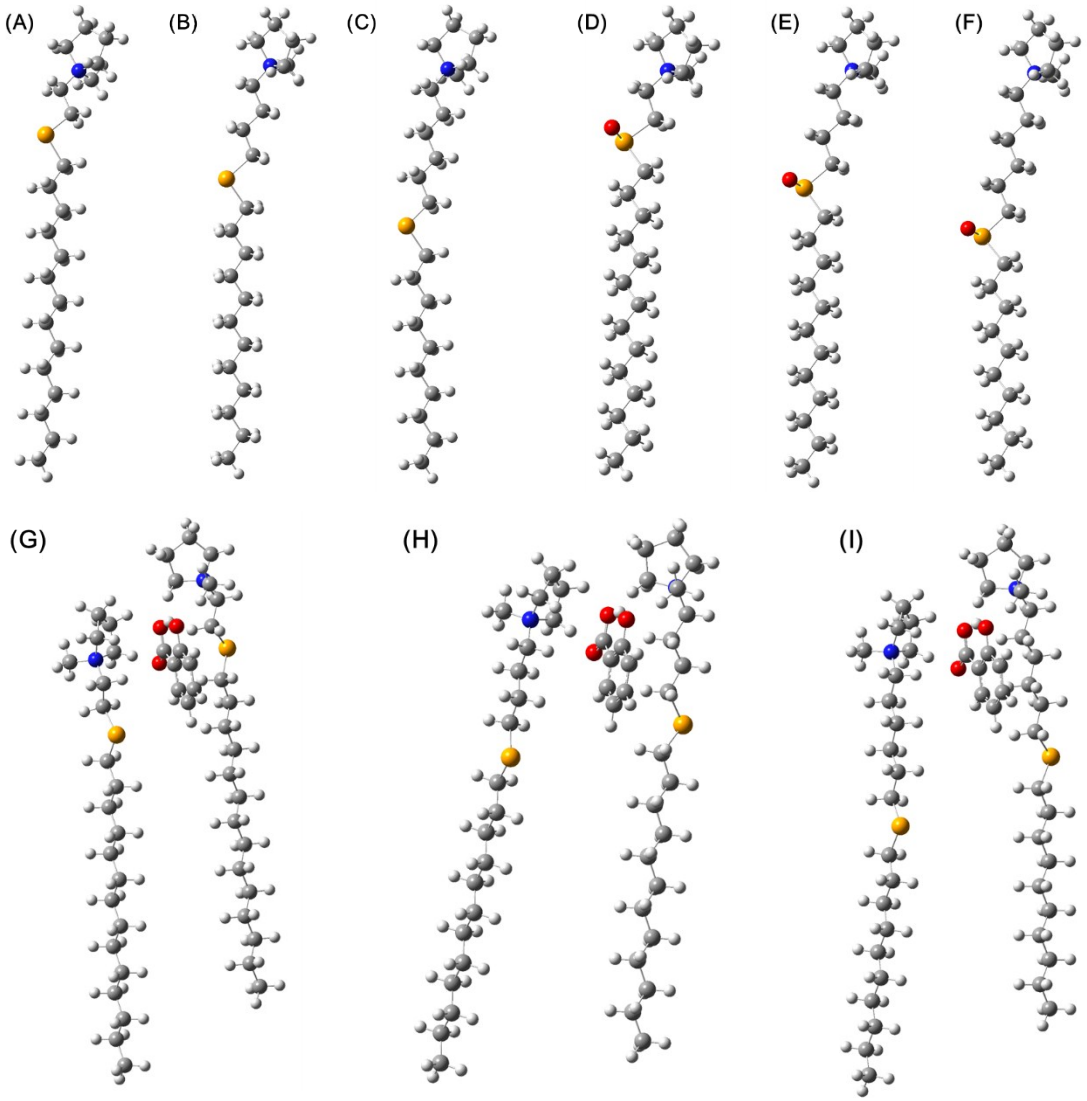


Figure S16. The optimized molecular structure using Density functional theory (DFT). Gray ball, C atom; white ball, H atom; yellow ball, Se atom; blue ball, N atom; red ball, O atom.

1. M. Zhao and L. Zheng, Micelle formation by N-alkyl-N-methylpyrrolidinium bromide in aqueous solution. *Phys. Chem. Chem. Phys.*, 2011, **13**, 1332-1337.