Ultra-stable N_2/water foams stabilized by dilute nanoparticles and surfactant at high salinity and high pressure

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This paper generated an ultra-stable foams stabilized by surface modified silica nanoparticles referred as SNP and cationic surfactant in high salinity brine. The evaluation of foam performance and the corresponding stabilization mechanism by SNP were investigated in terms of phase behavior, bulk shear rheology of the aqueous phase, the elastic dilational modulus of the gas-brine interface, and the foam stability both at atmospheric and high pressure.

Table S1 shows the phase behavior of different cationic surfactants with SNPs in 22% TDS brine at 50 °C. It can be seen that increasing the concentration of Arquad 12-50 from 0.01 to 0.02% led to the precipitation of SNPs after 5 days as it made the particles too hydrophobic.

Table S1. Phase behavior of various cationic surfactants with SNPs in 22% TDS brine at 50 °C and a low pH of 6.4: O represents clear aqueous phase, X represents slightly turbid phase that does not settle, and XX represents precipitation

Surfactant and concentration wt%	Nanoparticle	NP Concentration wt%	Initial State	Final State (5 days)
0.01% Arquad 12-50	SNP	0	O	O
		0.05	X	XX
		0.1	X	X
		0.2	X	X
		0.3	X	X
		0.5	X	X
0.02% Arquad 12-50	SNP	0	O	O
		0.05	X	XX
		0.1	X	XX
		0.2	X	XX
		0.3	X	XX
		0.5	X	XX
		0.5	X	XX
0.01% Arquad C-27	SNP	0.3	X	X
0.01% Arquad T-27		0.3	X	X
0.01% Arquad SV-50		0.3	X	X

In Fig. S1, both the concentrations of Arquad 12-50 and SNP were increased by 10 fold to further investigate the weak-gel formation behavior. Relative to more dilute SNP concentrations in Fig. 1b, the G' values of modulus were higher than G″ from 0.2 to 600 Hz, indicating modestly stronger gelation. The G' increased for 0.5% SNPs and then did not change much with a further

increase in SNP concentration.

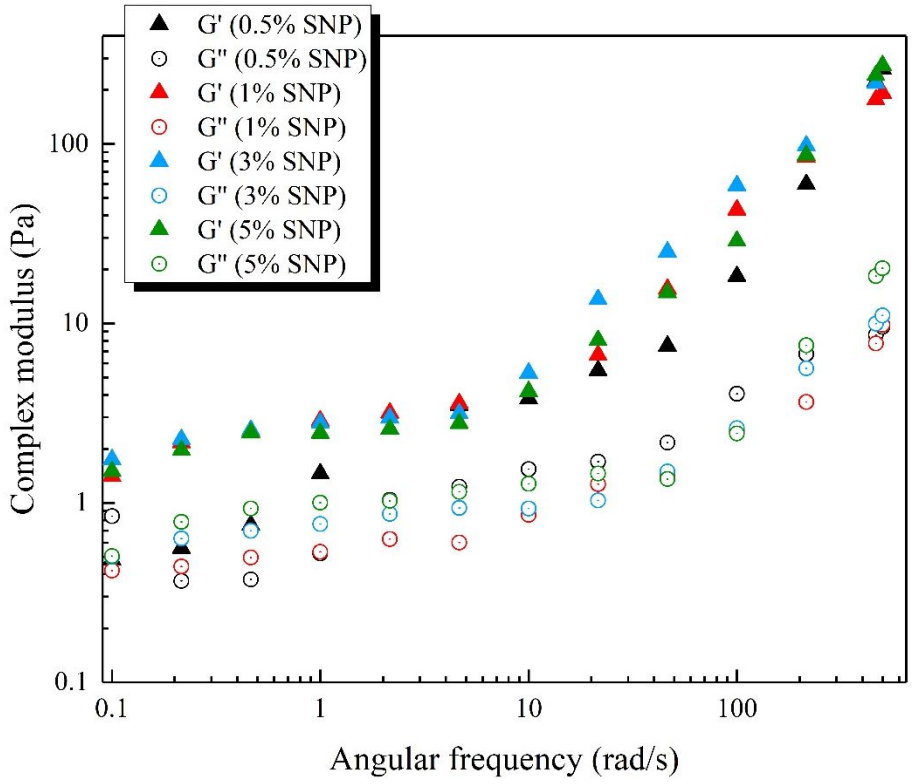

Fig. S1. Complex modulus of 0.1% Arquad 12-50 with different concentration of SNP.

Fig. S2 shows the equilibrium surface tension curves of Aqruad 12-50 solutions with and without SNPs. As seen, when Arquad 12-50 concentration is above CMC, its corresponding surface tension is close to 30 mN/m. When SNPs were mixed with 0.01 wt% Arquad 12-50 solution, the surface tension of the mixture increased. Furthermore, increasing SNP concentration caused a higher increase in the surface tension. Here we believe that the Arquad 12-50 molecules leave the bulk phase and absorb onto the surface of SNPs, thus leading to the increase in the surface tension. On the other hand, the modification of the SNP surface with cationic surfactant Arquad 12-50 makes the SNP more hydrophobic, making it easier for them irreversibly absorb on the gas-liquid interface. Therefore, the mixture solution was made up of partially hydrophobic SNP and surfactant Arquad 12-50 which is below the CMC. Finally, the gas-liquid interface is likely to be stabilized by a greater concentration SNP, to favor more stable foams.

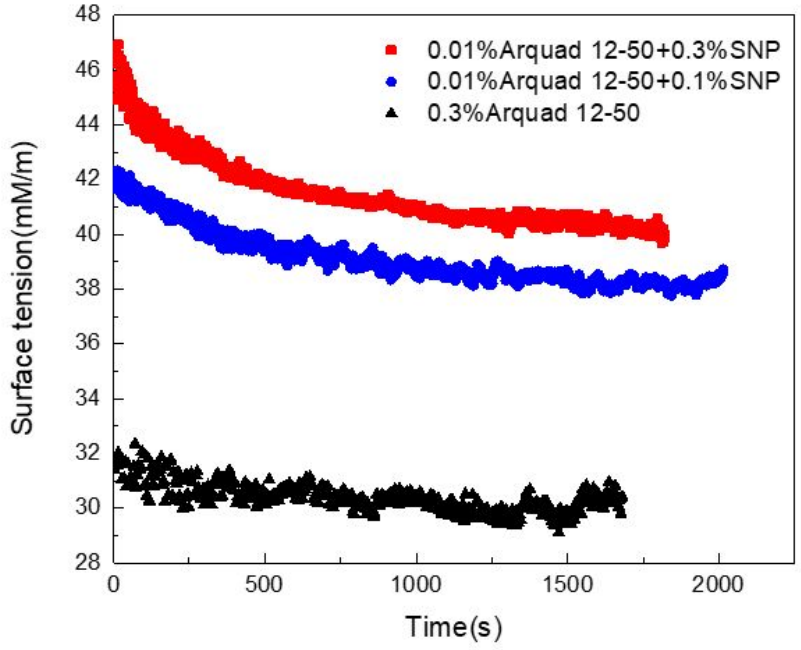

Fig. S2. The effect of SNP on the dynamic and steady state surface tension in 22% TDS brine at atmospheric pressure and room temperature

Fig. S3 shows the foam height at 50 °C for different foam systems. The most stable foam was with 0.01% Arquad 12-50 with 0.3% SNP, the height of which was maintained after 4 days. However, the texture became coarse as the bubble size increased.

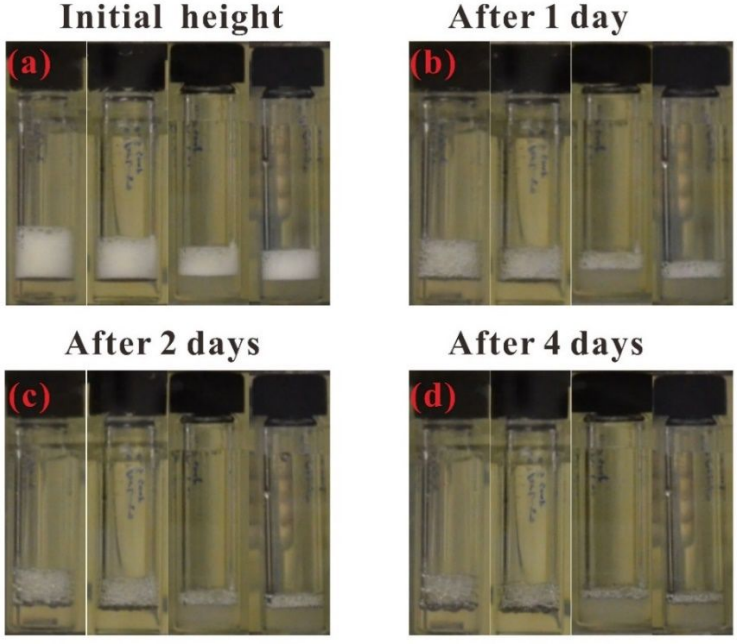

Fig. S3. Camera images for foam height at 50 °C water bath with 0.01 wt% cationic surfactant and 0.3 wt% SNP:

Arquad 12-50, Arquad C-50, Arquad T-27, Arquad SV-50 from left to right: (a) initial foam height, (b) foam height after 1 day, (c) foam height after 2 days and (d) foam height after 4 days.

Fig. S4 shows the foam stability in terms of bubble size evolution at 25 ℃ and atmospheric pressure. It can be seen than the existence of SNP highly improved the foam stability with smaller bubble size and more bubble number.

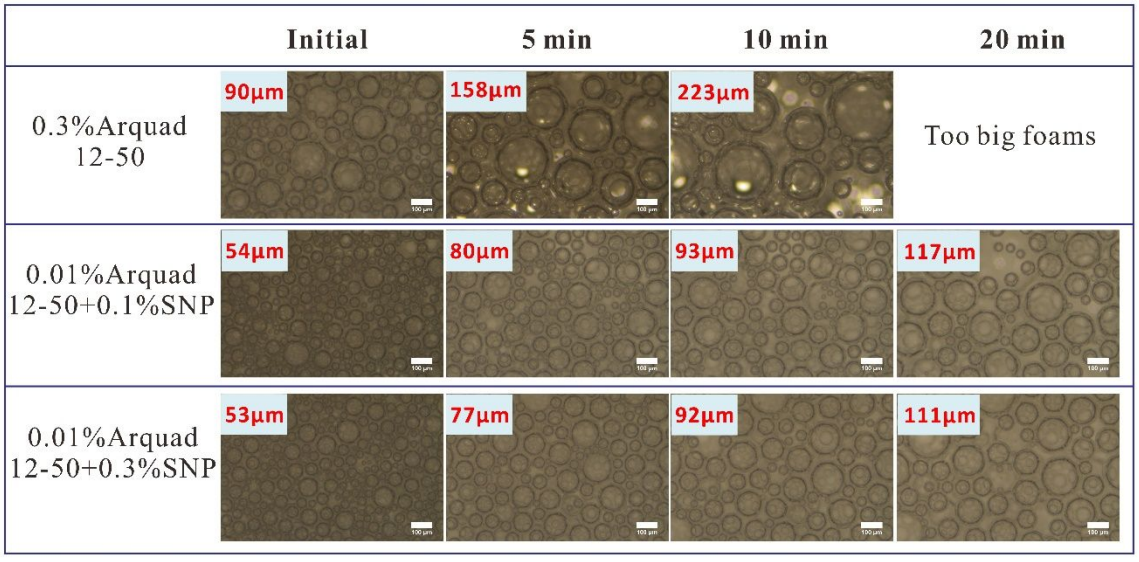

Fig. S4. Bubble size evolution of foams generated at 25 ℃ and atmospheric pressure with and without SNP; white scale bar on lower right corner of each panel indicates 100 μm.

Fig. S5 shows the initial bubble size at different foams quality at 208 bar and 50 °C. For 0.3% Arquad 12-50, 90% foam quality led to an uneven bubble size distribution, demonstrating unstable foams at such high quality. Moreover, when adding 0.1% SNP into 0.01% Arquad 12-50, strong foams with fine texture were not observed at 90% foam quality. However, when increasing the concentration of SNP to 0.3%, the combined system had small bubbles at all the foam qualities.

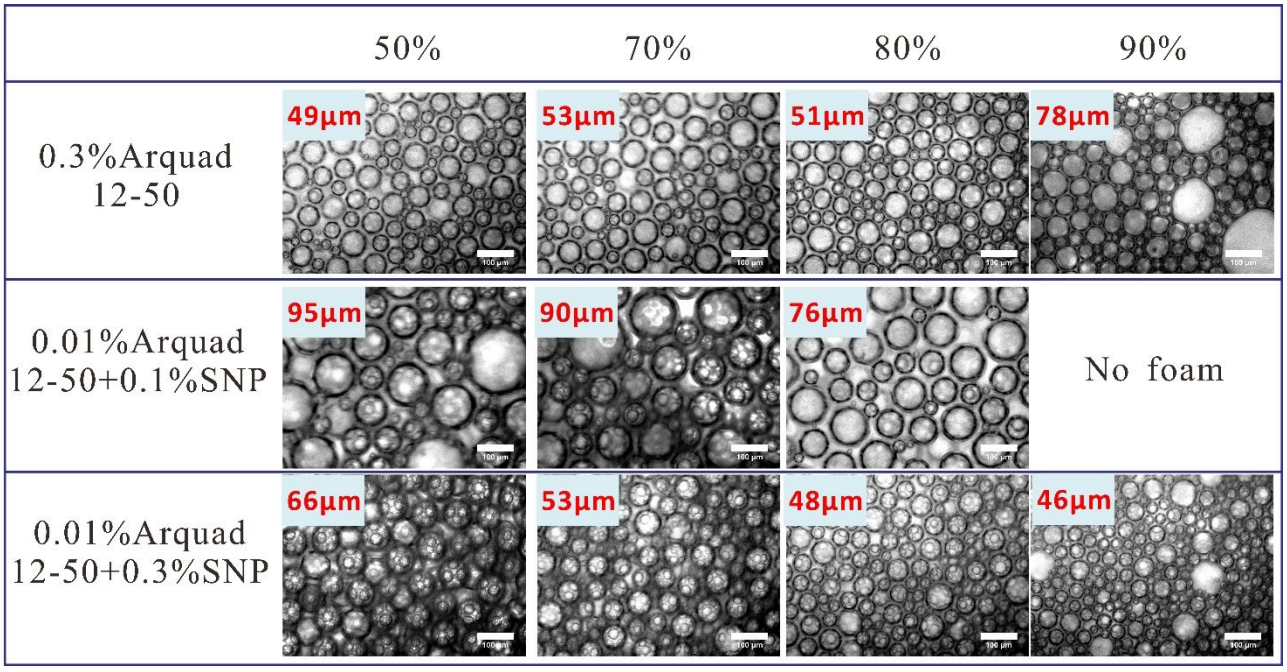

Fig. S5. Initial images of N_2 foam at different foam quality at 50 ℃ and 208 bar.

Table S2 summarizes the foam stability in terms of long-term foam height and bubble size evolution of surfactant-only system and the mixture system with surfactant and SNP.

Table S2. Bulk foam height H at 50 °C, foam Sauter mean diameter D_{sm} at 208 bar and 50 °C, dD^3_{sm}/dt, bulk foam apparent viscosity in bead-pack (η_{app}) at a quality of 80% at 208 bar and 50 °C.

System	H after 24h (mm)	Initial D_{sm} (μm)	dD^3_{sm}/dt at RT	dD^3_{sm}/dt at 50 °C	η_{app} (cP)
0.3% Arquad 12-50	0	50.5	0.026	0.68	86.4
0.01%Arquad 12-50+0.1%SNP	8.24	75.7	0.0039	0.0049	65.9
0.01%Arquad 12-50+0.3%SNP	9.24	47.6	0.0019	0.0028	91.2