

Supporting Information

Influence of a CO₂-switchable additive on the surface and foaming properties of a cationic non-switchable surfactant

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S1 Purification of C₁₄TAB

Surface tension measurements of the purchased tetradecyltrimethylammonium bromide (C₁₄TAB) (*Acros Organics*, purity 99 %) showed a distinct minimum around the CMC in the σ - c -curve (Figure S1.1). This indicates the contamination of the surfactant with surface active impurities.^{1,2} The surfactant was therefore recrystallized twice from an acetone/ethanol mixture. An amount of 20 g of the purchased C₁₄TAB was mixed with 300 mL acetone and heated up to 65 °C. Afterwards, 15 mL ethanol was added drop wise to the dispersion until all of the C₁₄TAB was dissolved. The solution was cooled to room temperature and stored in the fridge over night. The white crystalline solid was separated from the acetone/ethanol mixture and dried under high vacuum. After the second recrystallization 18 g of the purified C₁₄TAB were obtained. In the σ - c -curve of the purified C₁₄TAB no minimum is visible, confirming the purity of the surfactant (Figure S1.1).

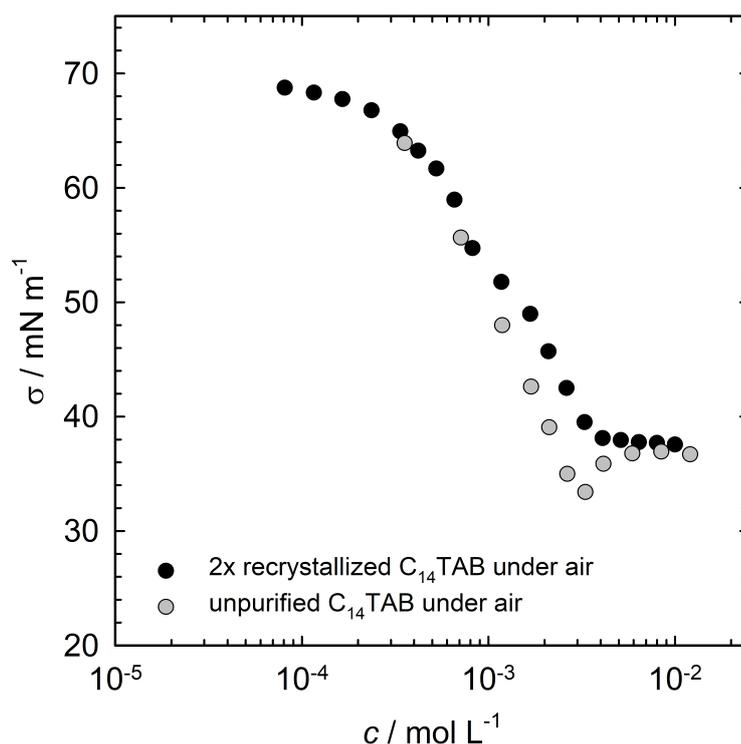


Figure S1.1: Surface tension as a function of the surfactant concentration of an aqueous solution of unpurified and 2x recrystallized C₁₄TAB at 23 ± 1 °C. Former one shows a distinct minimum, indicating the contamination with surface active impurities, which are not present in the purified surfactant.^{1,2}

S2 Purity of TMBDA

The CO₂-switchable additive TMBDA (*N,N,N,N*-tetramethyl-1,4-butanediamine, 98 %) was bought from *abc*r and was used without further purification. The purity of TMBDA was confirmed by ¹H NMR spectroscopy (Figure S2.1).

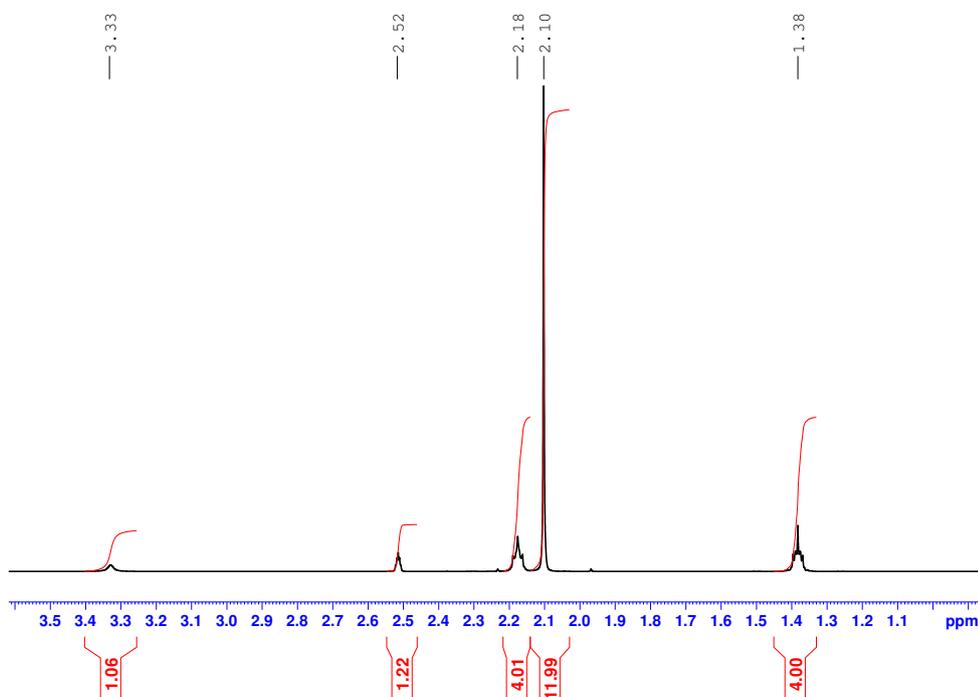


Figure S2.1: ¹H NMR spectrum of the additive TMBDA (*N,N,N,N*-tetramethyl-1,4-butanediamine), ¹H NMR (500 MHz, DMSO-d₆): 1.38 (dd, 4H, CH₂), 2.1 (s, 12H, NCH₃), 2.18 (t, 4H, CH₂N).

S3 Protonation of TMBDA

Taking a look at the protonation of TMBDA in aqueous solutions, one has to distinguish between three coexisting species, i.e. the neutral and the mono- and diprotonated TMBDA.^{3,4} The simplified reaction scheme looks as follows



with

$$K_{a1} = \frac{[\text{B}]_{\text{aq}}[\text{H}_3\text{O}^+]_{\text{aq}}}{[\text{BH}^+]_{\text{aq}}}, \quad (\text{S3.2})$$

$$K_{a2} = \frac{[\text{BH}^+]_{\text{aq}}[\text{H}_3\text{O}^+]_{\text{aq}}}{[\text{BH}_2^{2+}]_{\text{aq}}}, \quad (\text{S3.3})$$

and

$$[\text{B}]_0 = [\text{B}]_{\text{aq}} + [\text{BH}^+]_{\text{aq}} + [\text{BH}_2^{2+}]_{\text{aq}}, \quad (\text{S3.4})$$

where $K_{a1} = 5.012 \cdot 10^{-11} \text{ mol L}^{-1}$ and $K_{a2} = 1.698 \cdot 10^{-9} \text{ mol L}^{-1}$.^{3,5} With Equation S3.2 - Equation S3.4 one can derive three equations for the ratio of the neutral $[\text{B}]_{\text{aq}}/[\text{B}]_0$, the monoprotated $[\text{BH}^+]_{\text{aq}}/[\text{B}]_0$, and the diprotated TMBDA $[\text{BH}_2^{2+}]_{\text{aq}}/[\text{B}]_0$ in the solution as a function of the pH (Figure S3.1), namely

$$\frac{[\text{B}]_{\text{aq}}}{[\text{B}]_0} = \frac{K_{a1}K_{a2}}{M} \quad (\text{S3.5})$$

$$\frac{[\text{BH}^+]_{\text{aq}}}{[\text{B}]_0} = \frac{K_{a2}[\text{H}_3\text{O}^+]_{\text{aq}}}{M} \quad (\text{S3.6})$$

$$\frac{[\text{BH}_2^{2+}]_{\text{aq}}}{[\text{B}]_0} = \frac{[\text{H}_3\text{O}^+]_{\text{aq}}^2}{M} \quad (\text{S3.7})$$

with

$$M = K_{a1}K_{a2} + K_{a2}[\text{H}_3\text{O}^+]_{\text{aq}} + [\text{H}_3\text{O}^+]_{\text{aq}}^2. \quad (\text{S3.8})$$

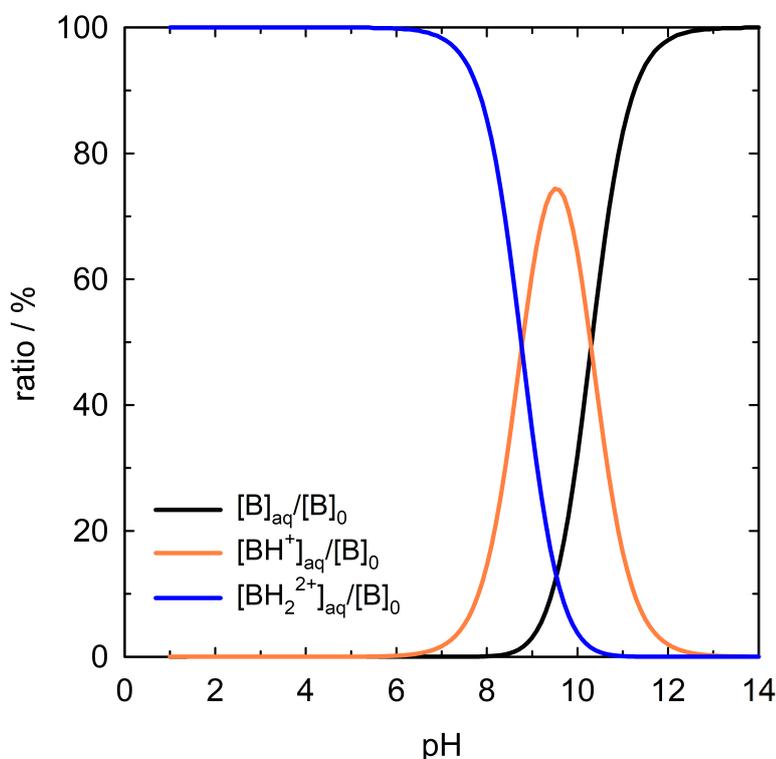


Figure S3.1: The calculated ratio of the neutral $[\text{B}]_{\text{aq}}/[\text{B}]_0$, the monoprotated $[\text{BH}^+]_{\text{aq}}/[\text{B}]_0$, and the diprotated TMBDA $[\text{BH}_2^{2+}]_{\text{aq}}/[\text{B}]_0$ as a function of the pH.

S4 Derivation of the Gibbs adsorption isotherm for systems containing C₁₄TAB and TMBDA

The following derivations were kindly provided by Volodymyr Kovalchuk from the Institute of Biocolloid Chemistry of the National Academy of Sciences of Ukraine, Kiev, Ukraine.

S4.1 Same-charge surfactant mixture

For a mixture of two same-charge surfactants, namely C₁₄TAB and diprotonated TMBDA, the following adsorption isotherm and equation of state can be used^{6,7}

$$b_1\gamma_{\pm}(c_{R1}c_X)^{\frac{1}{2}} = \frac{(\theta_1(\theta_1 + \theta_2))^{\frac{1}{2}}}{1 - (\theta_1 + \theta_2)} \exp(-2a_1\theta_1 - 2a_{12}\theta_2) \quad (\text{S4.1})$$

$$b_2\gamma_{\pm}(c_{R2}c_X)^{\frac{1}{2}} = \frac{(\theta_2(\theta_1 + \theta_2))^{\frac{1}{2}}}{1 - (\theta_1 + \theta_2)} \exp(-2a_2\theta_2 - 2a_{12}\theta_1) \quad (\text{S4.2})$$

$$\Pi = -RT\Gamma_{\infty} [\ln(1 - \theta_1 - \theta_2) + a_1\theta_1^2 + a_2\theta_2^2 + 2a_{12}\theta_1\theta_2] \quad (\text{S4.3})$$

where c_{R1} and c_{R2} are the surfactants bulk concentrations, c_X is the counterions concentration ($c_X = c_{R1} + c_{R2}$), b_1 and b_2 are the surfactants surface-to-bulk distribution coefficients, θ_1 and θ_2 are the partial surface coverages, γ_{\pm} is the activity coefficient for the ions in the bulk, a_i are the Frumkin interaction parameters, and Γ_{∞} is the limiting adsorption.

Considering the most simple case, we will assume $\gamma_{\pm} = 1$ (because the ions concentrations are below 0.01 mol dm⁻³) and neglect interactions between the surfactants ($a_i = 0$). Then, from Equation S4.1 and Equation S4.2, we obtain

$$b_1^2 c_{R1} c_X + b_2^2 c_{R2} c_X = \frac{(\theta_1 + \theta_2)^2}{(1 - (\theta_1 + \theta_2))^2} \quad (\text{S4.4})$$

If the surfactants concentrations c_{R1} and c_{R2} change proportionally (preserving the same ratio $r = c_{R2}/c_{R1}$ by dilution), then $c_X = (1 + r)c_{R1}$ and Equation S4.4 turns to

$$b_{ef} c_{R1} = \frac{\theta}{1 - \theta} \quad (\text{S4.5})$$

where $b_{ef} = (b_1^2(1 + r) + b_2^2 r(1 + r))^{\frac{1}{2}}$ is the effective adsorption constant and $\theta = \theta_1 + \theta_2$ is the total surface coverage. With Equation S4.3 and Equation S4.5 it is not difficult to check that

$$\frac{1}{2RT} \frac{d\Pi}{d \ln c_{R1}} = \Gamma_{\infty} \theta \quad (\text{S4.6})$$

For high concentrations $\theta \rightarrow 1$ and

$$\frac{1}{2RT} \frac{d\Pi}{d \ln c_{R1}} \rightarrow \Gamma_{\infty} \quad (\text{S4.7})$$

S4.2 Ionic an non-ionic surfactant mixture

For ionic and non-ionic surfactant mixture, namely C₁₄TAB and neutral TMBDA, the set of equations can be used⁸

$$b_1 c_1 = \frac{\theta_1}{1 - \theta_1 - \theta_2} \exp(-2a_1 \theta_1 - 2a_{12} \theta_2) \quad (\text{S4.8})$$

$$b_2 c_2 = \frac{\theta_2}{1 - \theta_1 - \theta_2} \exp(-2a_2 \theta_2 - 2a_{12} \theta_1) \quad (\text{S4.9})$$

$$\Pi = -\frac{RT}{\omega_0} [\ln(1 - \theta_1 - \theta_2) + a_1 \theta_1^2 + a_2 \theta_2^2 + 2a_{12} \theta_1 \theta_2] \quad (\text{S4.10})$$

where ω_0 is the partial molar surface area. Again, neglecting interactions between the surfactants ($a_i = 0$) from Equation S4.8 and Equation S4.9, one obtains

$$b_1 c_1 + b_2 c_2 = \frac{\theta_1 + \theta_2}{1 - \theta_1 - \theta_2} \quad (\text{S4.11})$$

For the surfactants concentrations c_1 and c_2 changing proportionally ($c_{R2} = r c_{R1}$) Equation S4.11 turns to

$$b_{ef} c_1 = \frac{\theta}{1 - \theta} \quad (\text{S4.12})$$

where $b_{ef} = b_1 + b_2 r$ is the effective adsorption constant and $\theta = \theta_1 + \theta_2$ is the total surface coverage. Proceeding similarly to the previous case, one can show that for high concentrations $\theta \rightarrow 1$ and

$$\frac{1}{RT} \frac{d\Pi}{d \ln c_1} \rightarrow \frac{1}{\omega_0} \quad (\text{S4.13})$$

Note that in Equation S4.6-S3.13 Γ_{∞} is equal to $(2\omega_0)^{-1}$, where ω_0 is the molar surface area of ions.⁸ This sets equivalence between the equations S3.7 and S3.13.

S5 Time evolution of the liquid fraction and of the foam bubble sizes

In Figure S5.1 the time evolution of the liquid fraction ε of foams generated with aqueous 35 mM (10x CMC) C₁₄TAB, C₁₄TAB:TMBDA 1:1, and 1:5 solutions can be seen.

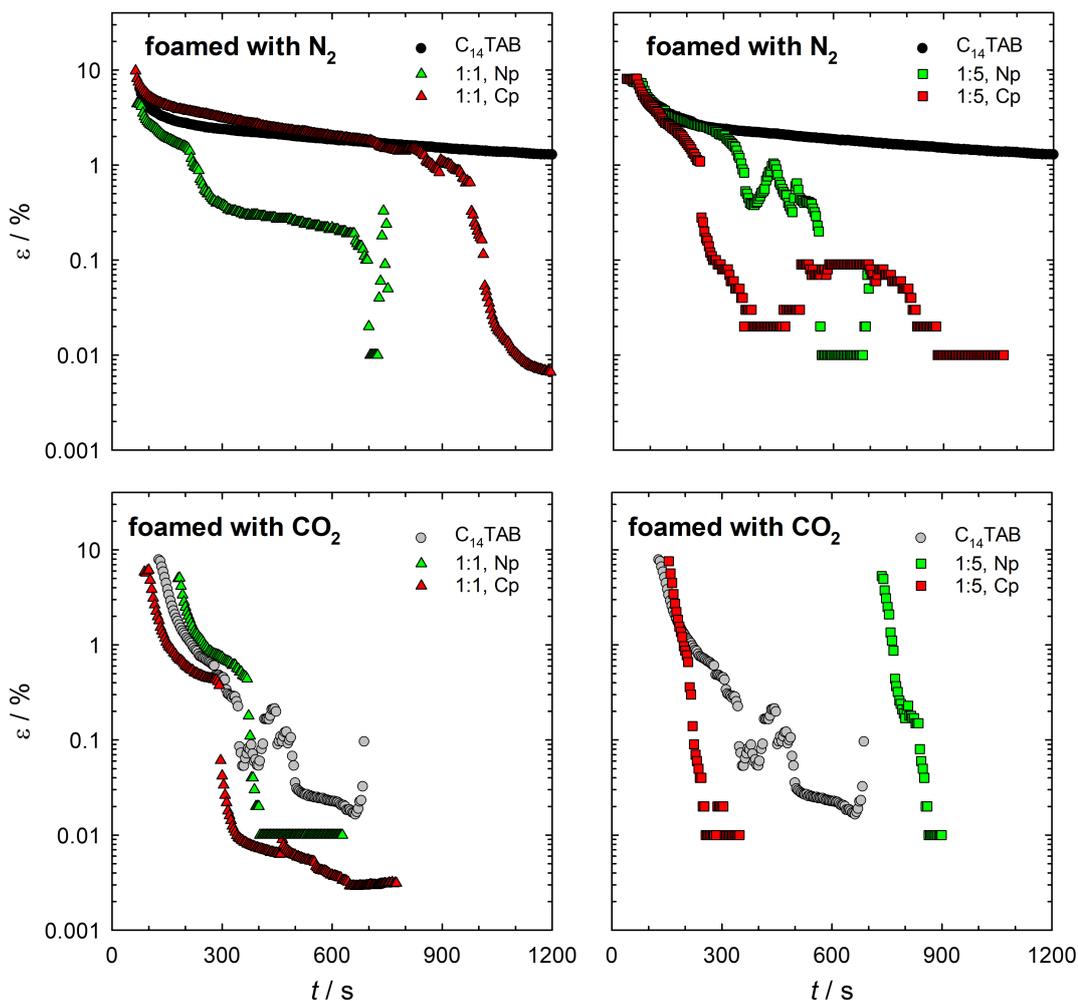


Figure S5.1: Time evolution of the liquid fraction ϵ for foams stabilized with aqueous 35 mM (10x CMC) $C_{14}TAB$, $C_{14}TAB:TMBDA$ 1:1 and 1:5 solutions. The solutions were pre-sparged with either N_2 (Np, green) or CO_2 (Cp, red). (top) foamed with N_2 ($Q = 84 \text{ mL min}^{-1}$). (bottom) foamed with CO_2 ($Q = 84 \text{ mL min}^{-1}$).

In Table S5.1 the time evolution of the arithmetic mean radius $\langle r \rangle$ and polydispersity index PI of the foam bubbles after generation of foams stabilized with aqueous 35 mM (10x CMC) $C_{14}TAB$, $C_{14}TAB:TMBDA$ 1:1, and 1:5 solutions can be seen. For foams generated with N_2 images were taken at 0 s, 100 s, and 200 s after foam generation and for foams generated with CO_2 images were taken at 0 s, 10 s, and 20 s after foam generation. The bubble images, used for the determination of the arithmetic mean radius $\langle r \rangle$ and polydispersity index PI , as well as their distribution can be seen in Figure S5.2 - Figure S5.7.

Table S5.1: Time evolution of the arithmetic mean radius $\langle r \rangle$ and polydispersity index PI of the foam bubbles after generation of foams stabilized with aqueous 35 mM (10x CMC) $C_{14}TAB$, $C_{14}TAB:TMBDA$ 1:1, and 1:5 solutions. The solutions containing TMBDA were pre-sparged with either N_2 (Np) or CO_2 (Cp) before foaming with N_2 or CO_2

		t / s		
solution foamed with N_2		0	100	200
$C_{14}TAB$	$\langle r \rangle / mm$	0.34	0.34	0.33
	PI	0.16	0.17	0.22
$C_{14}TAB:TMBDA$ 1:1, Np	$\langle r \rangle / mm$	0.32	0.30	0.33
	PI	0.29	0.40	0.53
$C_{14}TAB:TMBDA$ 1:1, Cp	$\langle r \rangle / mm$	0.31	0.29	0.29
	PI	0.21	0.34	0.50
$C_{14}TAB:TMBDA$ 1:5, Np	$\langle r \rangle / mm$	0.30	0.30	0.29
	PI	0.25	0.33	0.49
$C_{14}TAB:TMBDA$ 1:5, Cp	$\langle r \rangle / mm$	0.33	0.32	0.38
	PI	0.17	0.34	0.57
solution foamed with CO_2		0	10	20
$C_{14}TAB$	$\langle r \rangle / mm$	0.35	0.39	0.44
	PI	0.38	0.41	0.46
$C_{14}TAB:TMBDA$ 1:1, Np	$\langle r \rangle / mm$	0.67	0.74	0.66
	PI	0.32	0.25	0.49
$C_{14}TAB:TMBDA$ 1:1, Cp	$\langle r \rangle / mm$	0.41	0.54	0.75
	PI	0.50	0.56	0.29
$C_{14}TAB:TMBDA$ 1:5, Np	$\langle r \rangle / mm$	0.62	0.67	-
	PI	0.54	0.62	-
$C_{14}TAB:TMBDA$ 1:5, Cp	$\langle r \rangle / mm$	0.49	0.80	-
	PI	0.52	0.42	-

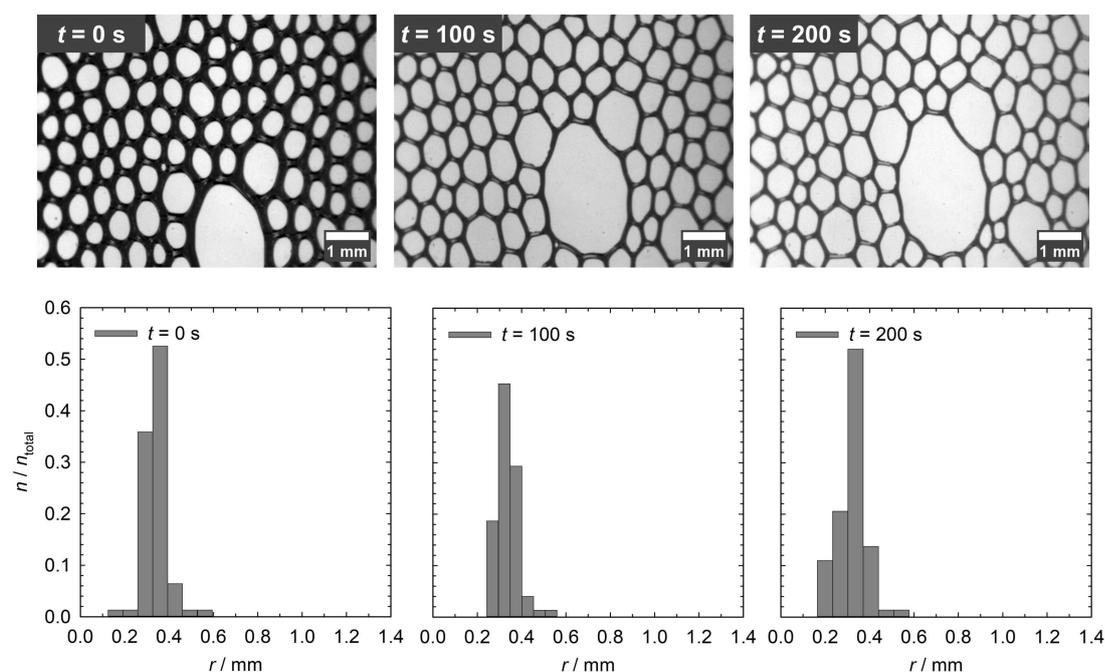


Figure S5.2: Cell size analysis pictures and bubble size distributions n/n_{total} plotted versus the bubble radius r for foams stabilized with an aqueous 35 mM (10x CMC) $C_{14}TAB$ solution foamed with N_2 . Photos were taken 0 s, 100 s, and 200 s after foam generation stopped.

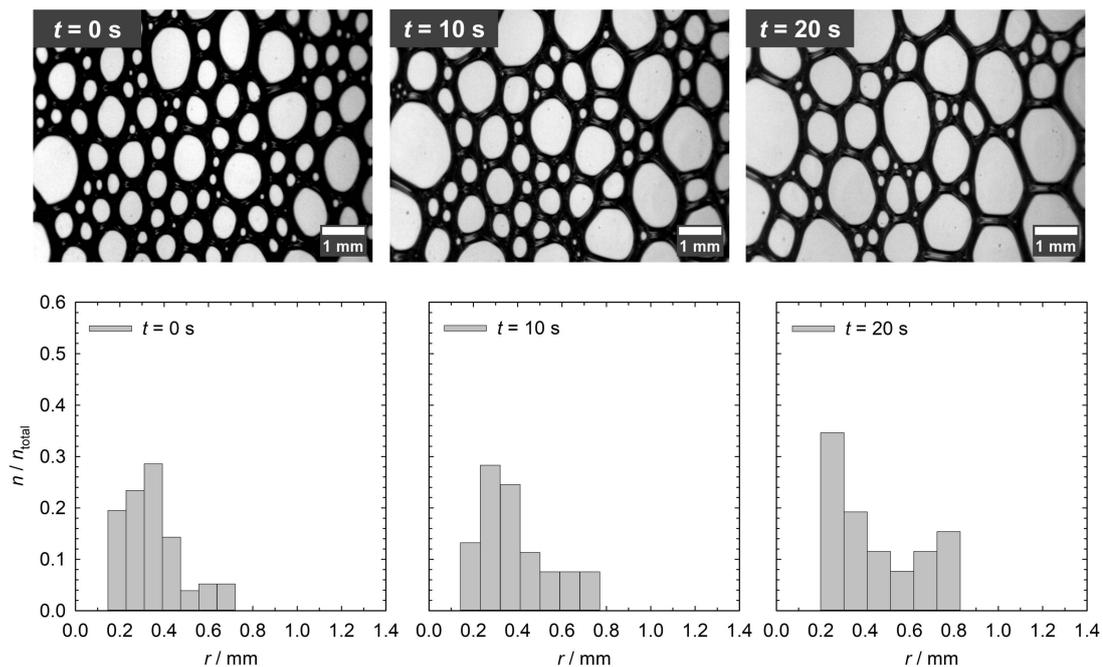


Figure S5.3: Cell size analysis pictures and bubble size distributions n/n_{total} plotted versus the bubble radius r for foams stabilized with an aqueous 35 mM (10x CMC) C_{14} TAB solution foamed with CO_2 . Photos were taken 0 s, 10 s, and 20 s after foam generation stopped.

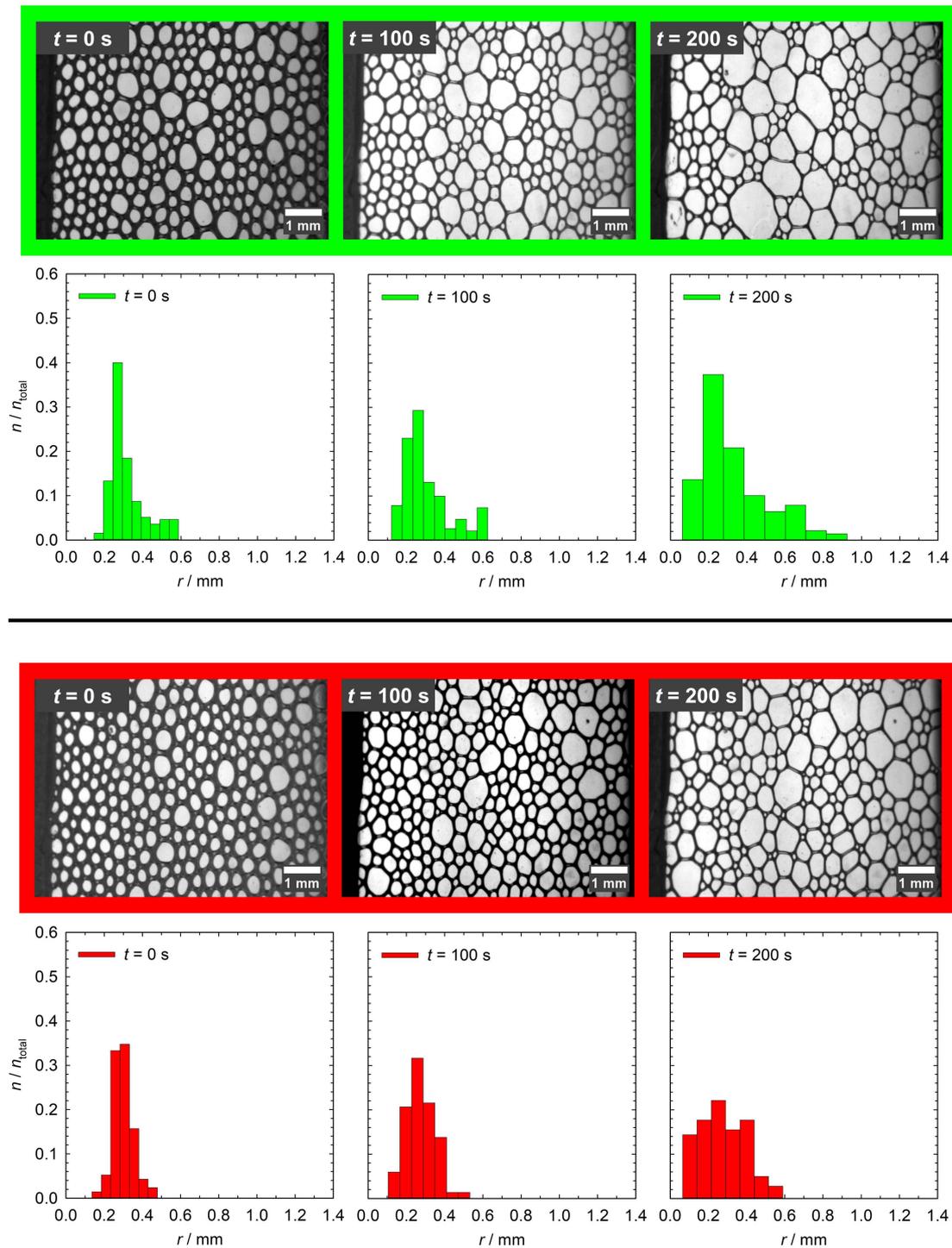


Figure S5.4: Cell size analysis pictures and bubble size distributions n/n_{total} plotted versus the bubble radius r for foams stabilized with aqueous 35 mM (10x CMC) $C_{14}TAB:TMBDA$ 1:1 solutions, i.e. the solutions contained 35 mM (10x CMC) surfactant and 35 mM TMBDA, foamed with N_2 . Photos were taken 0 s, 100 s, and 200 s after foam generation stopped. (top) the surfactant solution was pre-sparged with N_2 (Np, green). (bottom) the surfactant solution was pre-sparged with CO_2 (Cp, red).

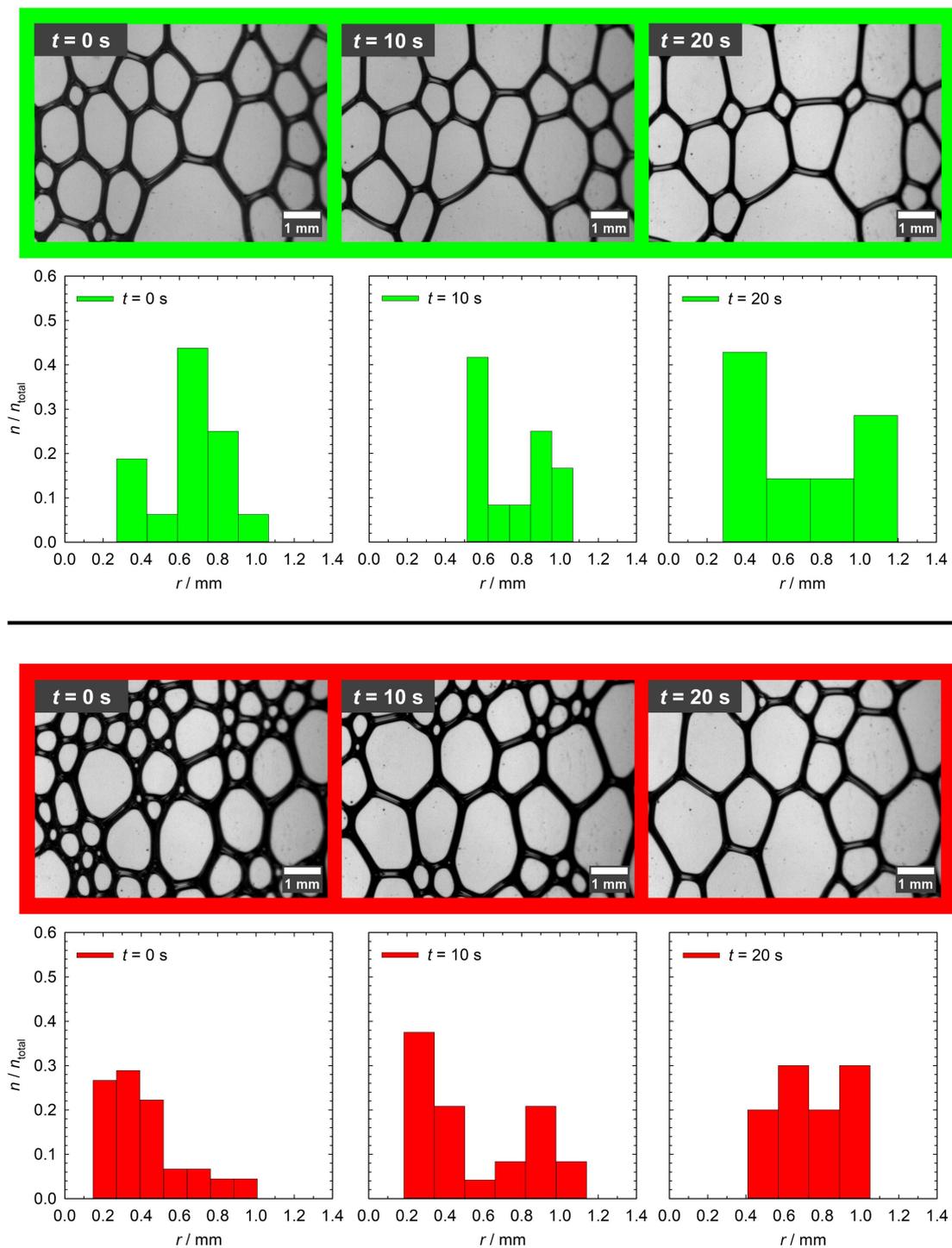


Figure S5.5: Cell size analysis pictures and bubble size distributions n/n_{total} plotted versus the bubble radius r for foams stabilized with aqueous 35 mM (10x CMC) $C_{14}TAB:TMBDA$ 1:1 solutions, i.e. the solutions contained 35 mM (10x CMC) surfactant and 35 mM TMBDA, foamed with CO_2 . Photos were taken 0 s, 10 s, and 20 s after foam generation stopped. (top) the surfactant solution was pre-sparged with N_2 (Np, green). (bottom) the surfactant solution was pre-sparged with CO_2 (Cp, red).

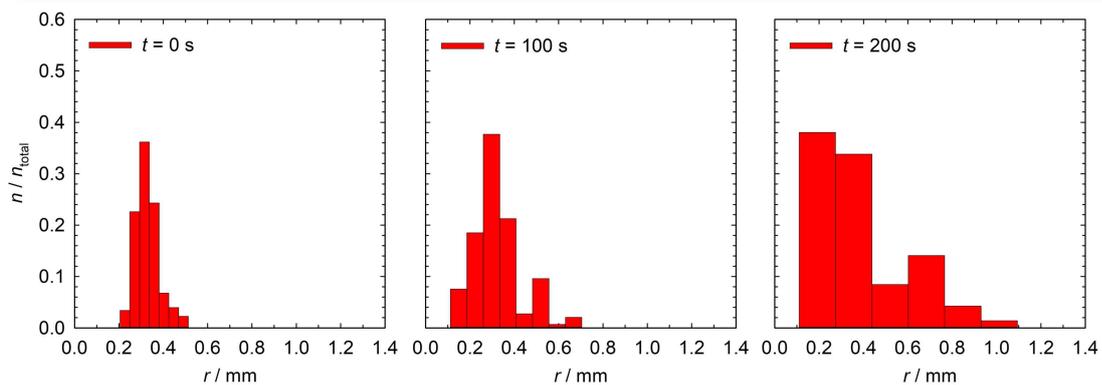
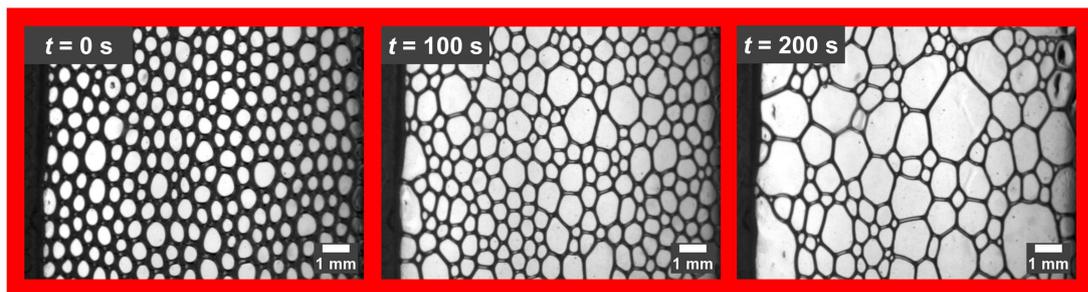
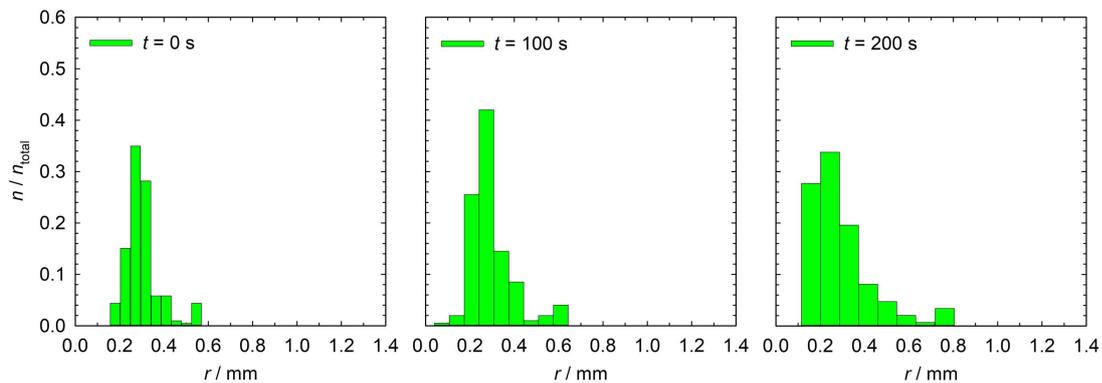
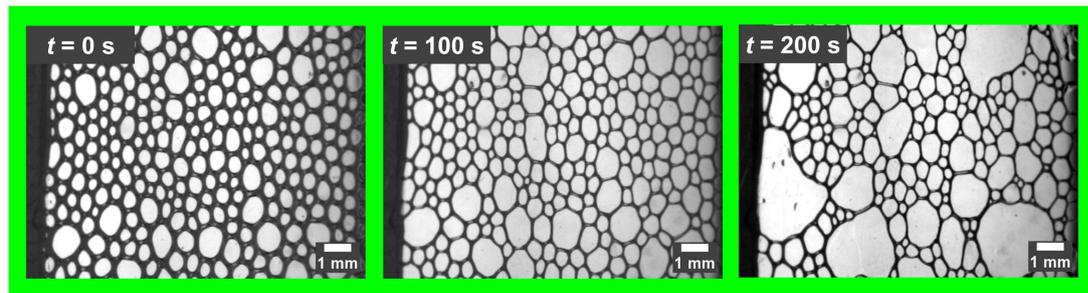


Figure S5.6: Cell size analysis pictures and bubble size distributions n/n_{total} plotted versus the bubble radius r for foams stabilized with aqueous 35 mM (10x CMC) $\text{C}_{14}\text{TAB}:\text{TMBDA}$ 1:5 solutions, i.e. the solutions contained 35 mM (10x CMC) surfactant and 175 mM TMBDA, foamed with N_2 . Photos were taken 0 s, 100 s, and 200 s after foam generation stopped. (top) the surfactant solution was pre-sparged with N_2 (Np, green). (bottom) the surfactant solution was pre-sparged with CO_2 (Cp, red).

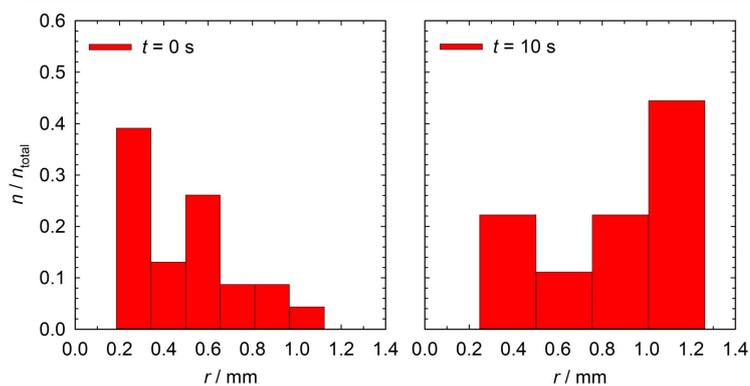
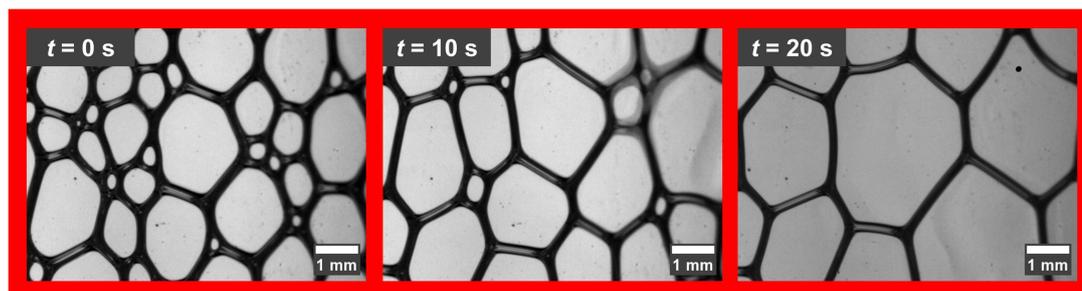
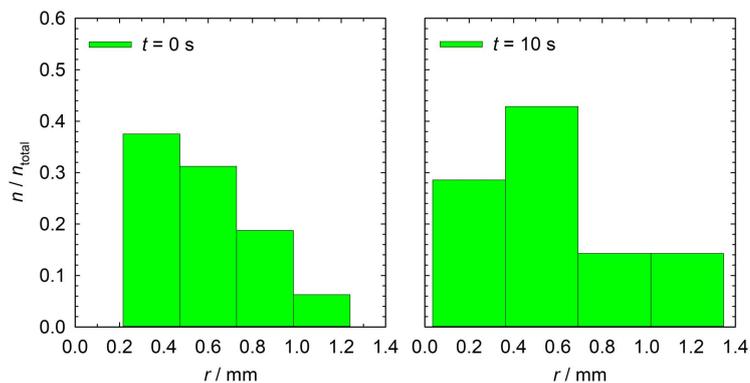
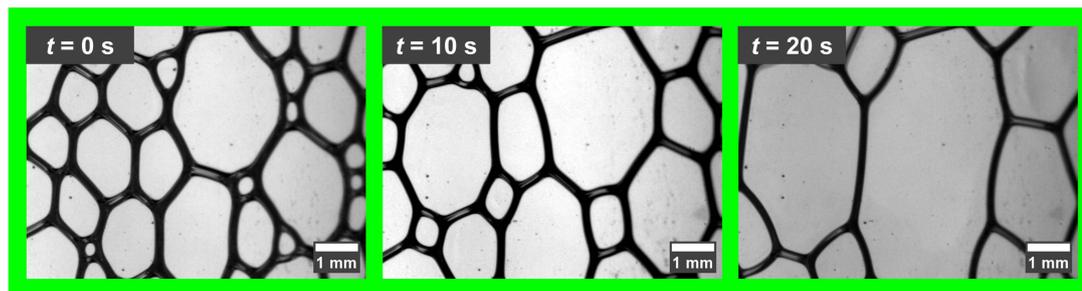


Figure S5.7: Cell size analysis pictures and bubble size distributions n/n_{total} plotted versus the bubble radius r for foams stabilized with aqueous 35 mM (10x CMC) C₁₄TAB:TMBDA 1:5 solutions, i.e. the solutions contained 35 mM (10x CMC) surfactant and 175 mM TMBDA, foamed with CO₂. Photos were taken 0 s, 10 s, and 20 s after foam generation stopped. (top) the surfactant solution was pre-sparged with N₂ (Np, green). (bottom) the surfactant solution was pre-sparged with CO₂ (Cp, red).

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