Come Together: Molecular Details into the Synergistic Effects of Polymer-Surfactant Adsorption at the Oil/Water Interface – *Supplemental Information*

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Supplemental information

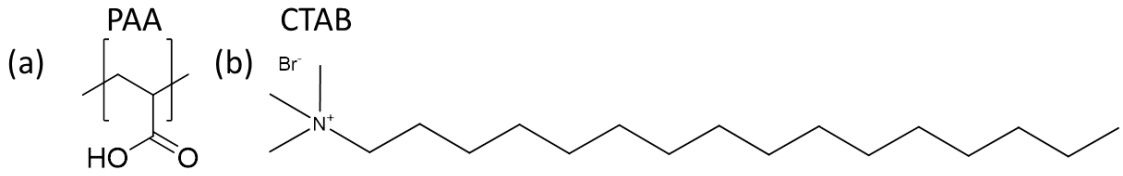

Figure S1. Molecular structures of PAA (a) and CTAB (b).

Table S1. Bulk data for the concentration range studied in this system.

[PAA monomer] (μM)	[PAA] (ppm)	pH	Fractional ionization	$[Na^+]$ (μM)	$[Na^+]$ + $[Br^-]$ (μM, with CTAB)	Ratio PAA/CTAB	$[COO^-]$ / $[CTA^+]$
0	0	5.77	0.15	0	15	0.00	0.00
1.4	0.1	5.75	0.15	0.4	15	0.09	0.01
4.2	0.3	5.73	0.15	1.2	16	0.28	0.04
14	1.0	5.57	0.13	3.9	19	0.93	0.12
28	2.0	5.55	0.13	7.7	23	1.9	0.24
42	3.0	5.29	0.10	11	26	2.8	0.29
83	6.0	5.83	0.16	22	37	5.6	0.90
139	10	5.54	0.13	44	59	9.3	1.2
417	30	5.36	0.11	107	122	28	3.1
1389	100	5.78	0.17	422	437	93	16
4167	300	6.08	0.26	1288	1303	278	72

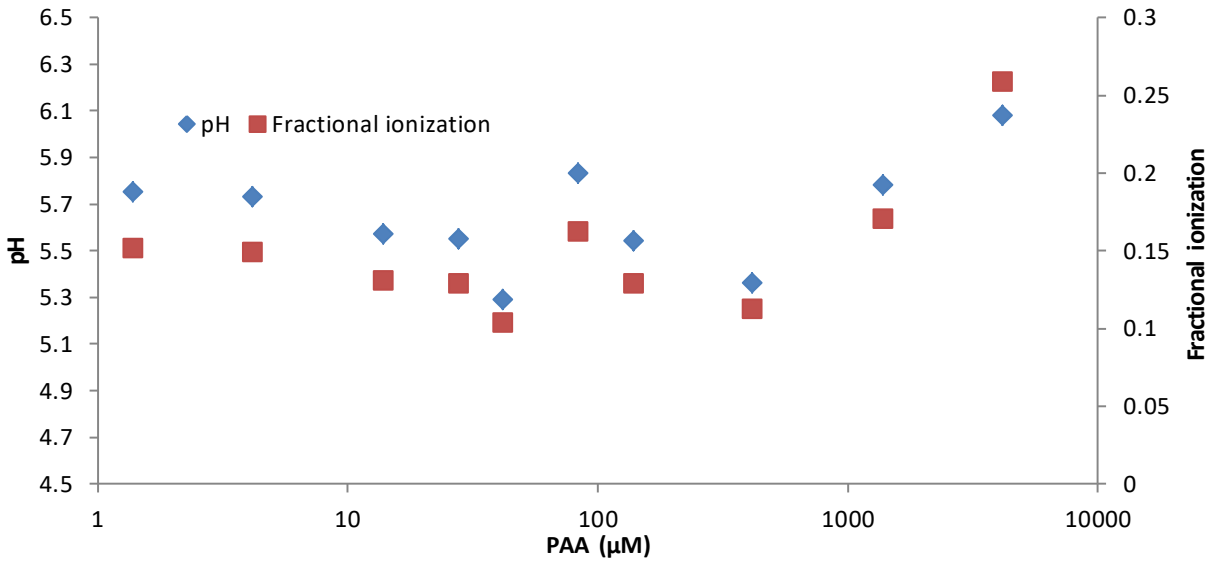

Figure S2. Solution pH (blue diamonds) and bulk PAA fractional ionization (red squares) for the PAA concentrations used in this study, prepared by the mixing protocol described in the text.

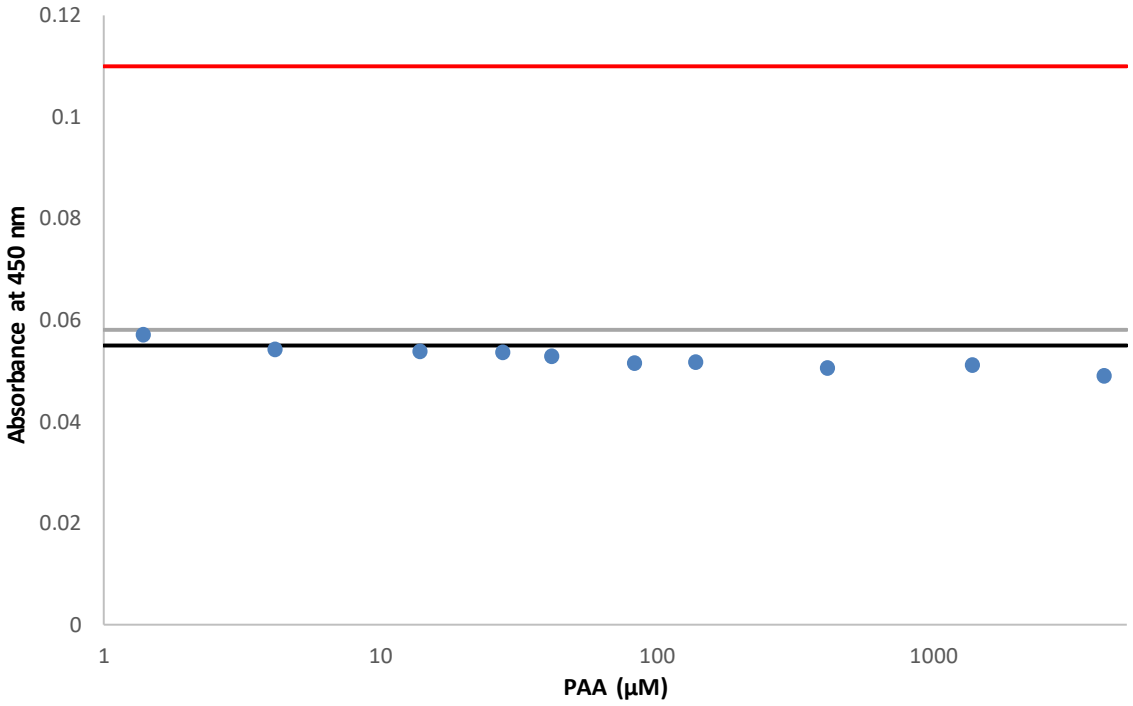

Figure S3. UV/Vis extinction data for PAA/CTAB solutions at 450 nm. Solutions have no chemical absorbance at 450 nm, so any increase in absorbance over that of pure water is caused by the scattering from large (greater than ~400 nm) aggregates. CTAB concentration is fixed at 15 μM, and PAA concentration varies as indicated on the bottom axis. The grey and black lines represent the absorbance of water and 15 μM CTAB solutions used as a control, respectively. The red line is used for reference of a chemically similar solution with known colloidal instability: 100 μM CTAB with 97 μM poly(styrene sulfonate) exhibits UV-Vis absorbance of 0.11 at 450 nm. These data were taken 1 day after mixing to match the age of solutions used in spectroscopy, however, no changes were observed over 5 days, even after mechanical perturbation.

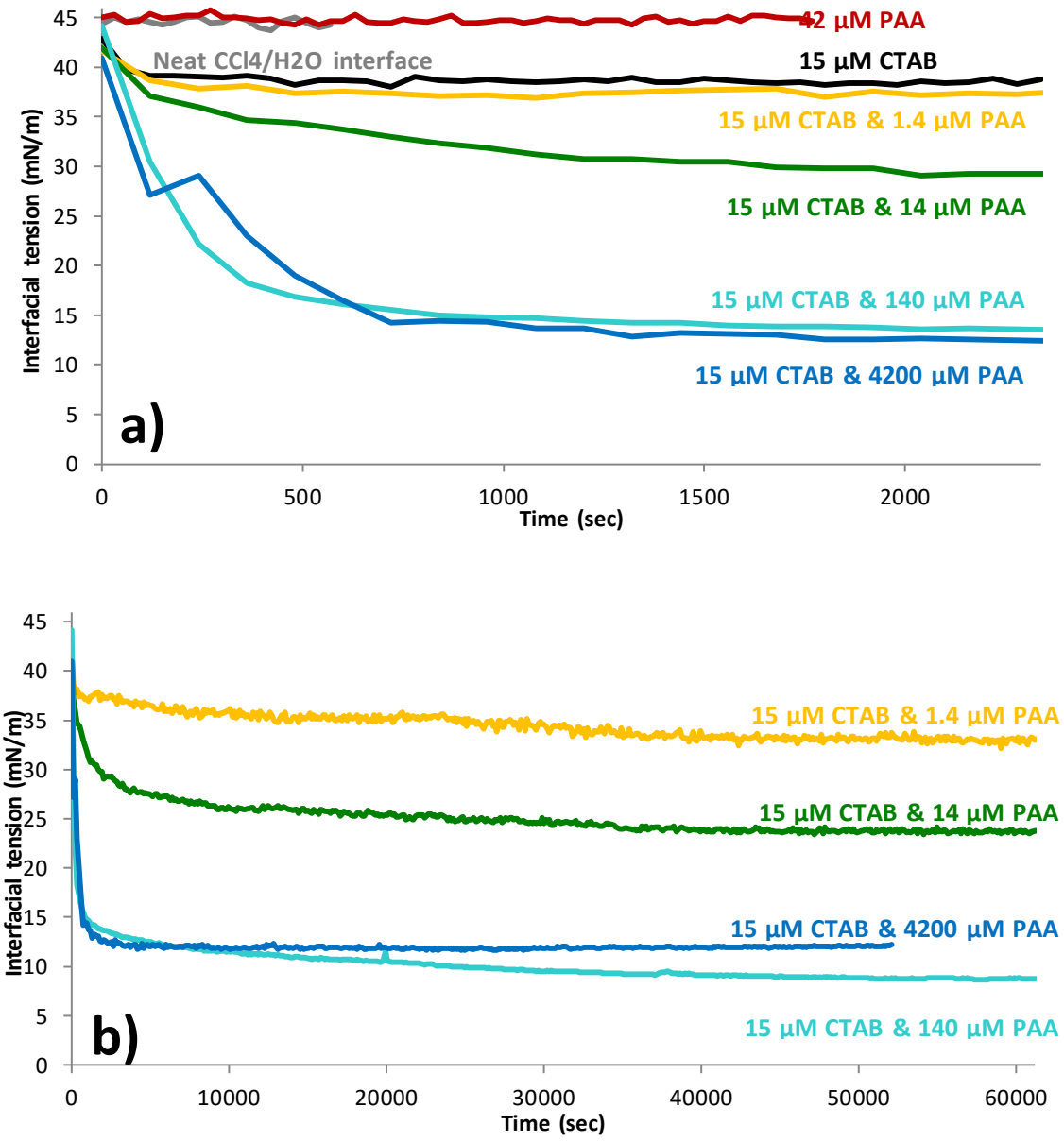

Figure S4. Dynamic surface tension for representative concentrations of CTAB and PAA. The first 2500 seconds of all samples are shown in a). PAA/CTAB mixtures have longer equilibration times, shown in b). Conversion to surface pressure was performed by subtracting the equilibrium surface tension value from that day's neat CCl_4/H_2O surface tension value.

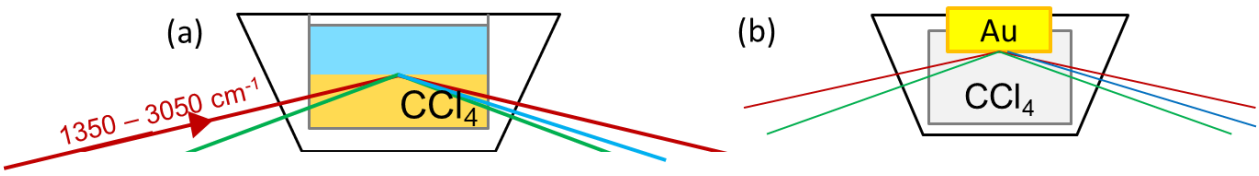

Figure S5. Total internal reflection sample (a) and gold normalization (b) setup utilizing a trapezoidal cell. Red, green, and blue beams symbolize tunable infrared, fixed visible, and resultant sum frequency signal, respectively. The reflected visible and IR beams are blocked or filtered out, and the generated sum-frequency signal is detected by a photomultiplier tube.

$$|\chi^{(2)}(\omega_{SF})|^2 = \left|\chi_{NR}^{(2)} e^{i\phi_{NR}} + \sum_{v} \int_{-\infty}^{\infty} \frac{A_v e^{i\varphi_v} e^{-[(\omega_L-\omega_v)/\Gamma_v]^2}}{\omega_L - \omega_{IR} - i\Gamma_L} d\omega_L\right|^2$$

Equation S1. Equation used for fits to experimental data. Each individual peak is fit to five parameters: amplitude (A), phase (φ), Lorentzian linewidth (Γ_L), frequency (ω_v), and Gaussian width (Γ_v). Additionally, fitting takes into account non-resonant contribution of constant amplitude, $\chi_{NR}^{(2)}$, and phase, ϕ_{NR}.

Table S2. Fitting parameters used for fits to experimental spectra, all with 15 µM d-CTAB. The COO^- region (a) is fit to one peak (Figure 3a), the COOH region (b) is fit to two peaks (Figure 3b), the C-D region (c) is fit to four peaks (Figure 2a), and the C-H region (d) is fit to four peaks (Figure 3c). In a – c, the broad low-frequency signal from D_2O vibrations is approximated as a nonresonant background.

a) COO^- region	[PAA]	14 µM	140 µM	4200 µM
Peak 1	Amplitude	0.45856	0.503074	0.538078
	Phase	0	0	0
	Linewidth	5	5	5
	Center	1409	1409	1409
	FWHM	9.02838	9.81718	8.73215
Nonresonant contribution	Amplitude	0.07853	0.072987	0.046144
	Phase	3.14159	3.14159	3.14159

b) COOH region	[PAA]	14 µM	140 µM	4200 µM
Peak 1	Amplitude	0.269634	0.352819	0.288496
	Phase	3.14159	3.14159	3.14159
	Linewidth	5	5	5
	Center	1732	1732	1732
	FWHM	55.0159	37.5275	33.2619
Peak 2	Amplitude	0.249177	0.464955	0.333523
	Phase	0	0	0
	Linewidth	5	5	5
	Center	1743	1743	1743
	FWHM	18.9063	17.1409	18.4119
Nonresonant contribution	Amplitude	0.249177	0.464955	0.333523
	Phase	0	0	0

c) C-D region	[PAA]	0 µM	1.4 µM	14 µM	140 µM	4200 µM
Peak 1	Amplitude	0.518809	0.621887	2.97394	6.13607	5.44081
	Phase	0	0	0	0	0
	Linewidth	11	11	11	11	11
	Center	2073	2073	2073	2073	2073
	FWHM	14.6113	9.57934	2.13457	0.949172	0.847897
Peak 2	Amplitude	0.805822	0.83829	1.1808	1.11743	0.78805
	Phase	0	0	0	0	0
	Linewidth	11	11	11	11	11
	Center	2105	2105	2105	2105	2105
	FWHM	8.95979	11.2443	6.38715	5.69247	7.71354
Peak 3	Amplitude	0.432064	0.54671	0.457171	0.515417	0.347735
	Phase	0	0	0	0	0
	Linewidth	11	11	11	11	11
	Center	2134	2134	2134	2134	2134
	FWHM	12.5727	14.294	19.4849	22.8616	23.8023
Peak 4	Amplitude	0.975983	0.689617	1.34454	0.604481	0.481493
	Phase	0	0	0	0	0
	Linewidth	11	11	11	11	11
	Center	2180	2180	2180	2180	2180
	FWHM	2.20034	21.5374	1.30492	7.35035	5.7122
Nonresonant contribution	NR amp	1.08558	0.324633	0.270618	0.071594	0.042873
	NR phase	0	0	0	0	3.14159

d) C-H region	[PAA]	14 μM	140 μM	4200 μM
Peak 1	Amplitude	0.082601	0.182938	0.093172
	Phase	0	0	0
	Linewidth	10.5	10.5	10.5
	Center	2852	2852	2852
	FWHM	26.9311	29.9821	34.9642
Peak 2	Amplitude	0.097799	0.091314	0.116393
	Phase	0	0	0
	Linewidth	10.5	10.5	10.5
	Center	2900	2900	2900
	FWHM	71.2899	48.1379	122.477
Peak 3	Amplitude	0.622554	1.09603	0.965758
	Phase	0	0	0
	Linewidth	10.5	10.5	10.5
	Center	2933	2933	2933
	FWHM	26.6659	26.1373	25.6431
Peak 4	Amplitude	0.873687	1.42803	1.17452
	Phase	3.14159	3.14159	3.14159
	Linewidth	12	12	12
	Center	2942	2942	2942
	FWHM	19.1555	17.4171	21.1573
Nonresonant contribution	NR amp	0	0	0
	NR phase	0	0	0