

Coming to order: Adsorption and structure of nonionic polymer at the oil/water interface as influenced by cationic and anionic surfactants

Supporting Information

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SUPPLEMENTAL INFORMATION:

Variables in the following tables correspond to the VSF fit equation given in Equation 3.

FIGURE 3 Spectral fits:

PAM + 0.015 mM d-DTAB (SSP)		0.015 mM PAM	4.2 mM PAM	21 mM PAM
Peak 1 (C-H stretch)	Amplitude	0.06 ± 0.01	0.096 ± 0.009	0.11 ± 0.01
	Phase	0	0	0
	Lorentzian	2	2	2
	Peak Position	2875 ± 3	2872 ± 2	2871 ± 2
	Gaussian	15 ± 4	15 ± 2	15 ± 3
Peak 2 (CH ₂ symmetric stretch)	Amplitude	0.319 ± 0.003	0.450 ± 0.003	0.458 ± 0.004
	Phase	0	0	0
	Lorentzian	2	2	2
	Peak Position	2935.5 ± 0.3	2935.7 ± 0.2	2935.2 ± 0.2
	Gaussian	14.4 ± 0.3	14.1 ± 0.2	14.0 ± 0.3

Table S1: Fit parameters for mixed system traces in Figure 3a. All solutions consisted of PAM (0.015, 4.2, and 21 mM) with 0.015 mM d-DTAB in D₂O. Peaks 1 and 2 correspond to the alpha carbon CH stretch and the CH₂ symmetric stretch (d+) from the PAM backbone, respectively.

0.015 mM d-DTAB (SSP)		
Peak 1 (Coordinated D ₂ O peak 1)	Amplitude	0.92 ± 0.02
	Phase	3.14
	Lorentzian	2
	Peak Position	2576 ± 4
	Gaussian	47 ± 3
Peak 2 (Coordinated D ₂ O peak 2)	Amplitude	0.42 ± 0.02
	Phase	0
	Lorentzian	2
	Peak Position	2719 ± 1
	Gaussian	18 ± 1
Peak 3 (Free OD)	Amplitude	0.11 ± 0.02
	Phase	0
	Lorentzian	2
	Peak Position	2682 ± 1
	Gaussian	15 ± 3

Table S2: Fit parameters for the d-DTAB in D₂O (grey) trace in Figure 3a. Peaks 1 and 2 correspond to coordinated water modes and Peak 3 corresponds to the free OD mode.

PAM + 0.015 mM d-DTAB (SPS)		0.015 mM PAM	4.2 mM PAM	21 mM PAM
Peak 1 (C-H stretch)	Amplitude	1.71 ± 0.09	1.60 ± 0.09	1.47 ± 0.08
	Phase	0	0	0
	Lorentzian	2	2	2
	Peak Position	2875 ± 3	2873 ± 3	2870 ± 3
	Gaussian	63 ± 14	63 ± 13	52 ± 7
Peak 2 (CH ₂ symmetric stretch)	Amplitude	0.12 ± 0.2	1.2 ± 0.2	1.07 ± 0.07
	Phase	0	0	0
	Lorentzian	2	2	2
	Peak Position	2959 ± 2	2957 ± 2	2957 ± 1
	Gaussian	32 ± 3	30 ± 3	28 ± 2
Nonresonant	Amplitude	1.09 ± 0.05	1.07 ± 0.05	1.08 ± 0.04
	Phase	3.14	3.14	3.14

Table S3: Fit parameters for mixed system traces in Figure 3b. All solutions consisted of PAM (0.015, 4.2, and 21 mM) with 0.015 mM d-DTAB in D₂O. Peaks 1 and 2 correspond to the alpha carbon CH stretch and the CH₂ asymmetric stretch (d-) from the PAM backbone, respectively. The elevated background in the spectra is fit to a nonresonant signal.

FIGURE 5 Spectral fits:

PAM + 0.015 mM d-DTAB (SSP)		0.015 mM PAM	4.2 mM PAM	21 mM PAM
C=O peak	Amplitude	1.51 ± 0.09	2.2 ± 0.1	1.85 ± 0.08
	Phase	0	0	0
	Lorentzian	5	5	5
	Peak Position	1650.4 ± 0.8	1651.1 ± 0.6	1649.6 ± 0.5
	Gaussian	12 ± 1	10.3 ± 0.8	10.0 ± 0.7

Table S4: Fit parameters for mixed system traces of the carbonyl region in Figure 5. All solutions consisted of PAM (0.015mM, 4.2, and 21 mM) with 0.015 mM d-DTAB in D₂O.**FIGURE 6 Spectral fits:**

PAM + 0.001 mM d-CTAB (SSP)		0.015 mM PAM	4.2 mM PAM	21 mM PAM
Peak 1 (C-H stretch)	Amplitude	0.051 ± 0.007	0.07 ± 0.008	0.12 ± 0.01
	Phase	0	0	0
	Lorentzian	2	2	2
	Peak Position	2879 ± 3	2875 ± 2	2873 ± 2
	Gaussian	20 ± 4	15 ± 2	12 ± 2
Peak 2 (CH ₂ symmetric stretch)	Amplitude	0.266 ± 0.002	0.413 ± 0.002	0.396 ± 0.004
	Phase	0	0	0
	Lorentzian	2	2	2
	Peak Position	2937.2 ± 0.3	2937.1 ± 0.2	2934.0 ± 0.3
	Gaussian	15.7 ± 0.3	15.4 ± 0.2	15.4 ± 0.3

Table S5: Fit parameters for mixed system traces in Figure 6. All solutions consisted of PAM (0.015, 4.2, and 21 mM) with 0.001 mM d-CTAB in D₂O. Peaks 1 and 2 correspond to the alpha carbon CH stretch and the CH₂ symmetric stretch (d+) from the PAM backbone, respectively.

FIGURE 7 Spectral fits:

4.2mM PAM + 0.015 mM d-DTAB (SSP)		@ t = t _o	@ t > t _{eq}
Peak 1 (C-H stretch)	Amplitude	0.07 ± 0.008	0.07 ± 0.008
	Phase	0	0
	Lorentzian	2	2
	Peak Position	2875 ± 2	2874 ± 2
	Gaussian	17 ± 3	16 ± 2
Peak 2 (CH ₂ symmetric stretch)	Amplitude	0.357 ± 0.002	0.363 ± 0.002
	Phase	0	0
	Lorentzian	2	2
	Peak Position	2936.4 ± 0.2	2936.0 ± 0.2
	Gaussian	14.6 ± 0.2	14.1 ± 0.2

Table S6: Fit parameters for the mixed system spectral insets in Figure 7. All solutions consisted of 4.2 mM PAM with 0.015 mM d-DTAB in D₂O. Peaks 1 and 2 correspond to the alpha carbon CH stretch and the CH₂ symmetric stretch (d+) from the PAM backbone, respectively. Comparison of the VSF peak fit intensities from t_o to t_{eq} show the spectra of polyacrylamide is unchanging over time.

FIGURE 8 Spectral Fits:

PAM + 0.015 mM d-SDS (SSP)		0.015 mM PAM	4.2 mM PAM	21 mM PAM
Peak 1 (Coordinated D ₂ O)	Amplitude	0.9 ± 0.1	0.7 ± 0.1	0.7 ± 0.2
	Phase	0	0	0
	Lorentzian	5	5	5
	Peak Position	2485 ± 6	2484 ± 25	2486 ± 48
	Gaussian	80 ± 6	96 ± 4	110 ± 7
Peak 2 (Free OD)	Amplitude	0.5 ± 0.1	0.42 ± 0.08	0.5 ± 0.2
	Phase	0	0	0
	Lorentzian	12	12	12
	Peak Position	2716 ± 1	2717 ± 2	2719 ± 2
	Gaussian	8 ± 2	10 ± 2	8 ± 3
Peak 3 (Background peak 1)	Amplitude	0.09 ± 0.03	0.1 ± 0.04	0.10 ± 0.04
	Phase	0	0	0
	Lorentzian	5	5	5
	Peak Position	2789 ± 2	2790 ± 3	2791 ± 3
	Gaussian	40 ± 8	43 ± 10	44 ± 10
Peak 4 (Background peak 2)	Amplitude	0.067 ± 0.009	0.07 ± 0.02	0.08 ± 0.03
	Phase	0	0	0
	Lorentzian	5	5	5
	Peak Position	2871 ± 31	2872 ± 47	2878 ± 43
	Gaussian	111 ± 31	112 ± 46	115 ± 46
Peak 5 (CH ₂ symmetric stretch)	Amplitude	0.08 ± 0.01	0.09 ± 0.01	0.07 ± 0.01
	Phase	3.14	3.14	3.14
	Lorentzian	2	2	2
	Peak Position	2932 ± 2	2931 ± 2	2928 ± 3
	Gaussian	13 ± 3	16 ± 3	20 ± 5

Table S7: Fit parameters for mixed system traces in Figure 8a. All solutions consisted of PAM (0.015, 4.2, and 21 mM) with 0.015 mM d-SDS in D₂O. Peaks 1 and 2 correspond to the coordinated water and free OD modes, respectively. Peaks 3 and 4 fit the broad signal from ~2750-3050 cm⁻¹, characterizing the background signal from the sulfate headgroup of d-SDS. Peak 5 is assigned to the d+ stretch from the PAM backbone.

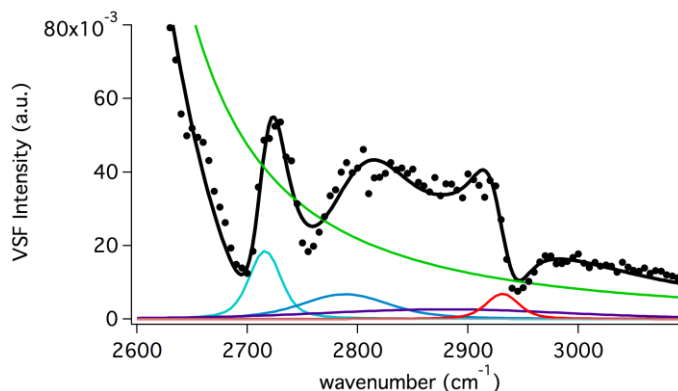


Figure S1: The underlying five peaks that contribute the full fit for 4.2 mM PAM with 0.015 mM d-SDS in D₂O in Figure 8a (black trace shown here). The coordinated D₂O, Free OD, and two background peaks are displayed as the green, light blue, and dark blue and purple traces, respectively. The red peak is the PAM asymmetric CH₂ stretch (also shown in Figure 8a), which is responsible for the interference feature observed in all the mixed system spectra in Figure 8a.

0.015 mM d-SDS (SSP)		
Peak 1 (Coordinated D ₂ O)	Amplitude	0.9 ± 0.2
	Phase	0
	Lorentzian	5
	Peak Position	2480 ± 30
	Gaussian	100 ± 4
Peak 2 (Free OD)	Amplitude	0.62 ± 0.06
	Phase	0
	Lorentzian	12
	Peak Position	2719 ± 2
	Gaussian	11 ± 1
Peak 3 (Background peak 1)	Amplitude	0.10 ± 0.01
	Phase	0
	Lorentzian	5
	Peak Position	2781 ± 3
	Gaussian	40 ± 8
Peak 4 (Background peak 2)	Amplitude	0.14 ± 0.02
	Phase	0
	Lorentzian	5
	Peak Position	2880 ± 9
	Gaussian	112 ± 14

Table S8: Fit parameters for the d-SDS in D₂O (grey) trace in Figure 8a. Peaks 1 and 2 correspond to the coordinated water and free OD modes, respectively. Peaks 3 and 4 fit the broad signal from ~2750-3050 cm⁻¹, characterizing the background signal from the sulfate headgroup of SDS.

0.015 mM d-SDS + 1 M NaCl (SSP)		0 mM PAM	4.2 mM PAM
Peak 1 (Coordinated D ₂ O peak 1)	Amplitude	0.07 ± 0.01	0.080 ± 0.007
	Phase	0	0
	Lorentzian	5	5
	Peak Position	2646 ± 4	2640 ± 8
	Gaussian	60 ± 10	75 ± 22
Peak 2 (Coordinated D ₂ O peak 2)	Amplitude	0.27 ± 0.01	0.38 ± 0.01
	Phase	0	0
	Lorentzian	5	5
	Peak Position	2488 ± 12	2490 ± 8
	Gaussian	88 ± 11	66 ± 8
Peak 3 (Free OD)	Amplitude	0.11 ± 0.03	0.1 ± 0.1
	Phase	0	0
	Lorentzian	12	12
	Peak Position	2720 ± 2	2719 ± 4
	Gaussian	11 ± 5	8 ± 11
Peak 4 (Background peak 1)	Amplitude	0.03 ± 0.01	0.04 ± 0.02
	Phase	0	0
	Lorentzian	5	5
	Peak Position	2785 ± 8	2790 ± 9
	Gaussian	53 ± 18	43 ± 19
Peak 5 (Background peak 2)	Amplitude	0.067 ± 0.004	0.056 ± 0.004
	Phase	0	0
	Lorentzian	5	5
	Peak Position	2906 ± 18	2909 ± 21
	Gaussian	174 ± 35	123 ± 37

Table S9: Fit parameters for mixed system traces in Figure 8b. All solutions contain 0.015 mM d-SDS and 1 M NaCl in D₂O, with either 0mM or 4.2 mM PAM. Peaks 1 and 2 correspond to the two coordinated water modes, and Peak 3 corresponds to the Free OD mode. Peaks 4 and 5 are two background peaks, fitting the broad signal from ~ 2750 - 3050 cm⁻¹ to characterize the background signal from the sulfate headgroup of d-SDS.

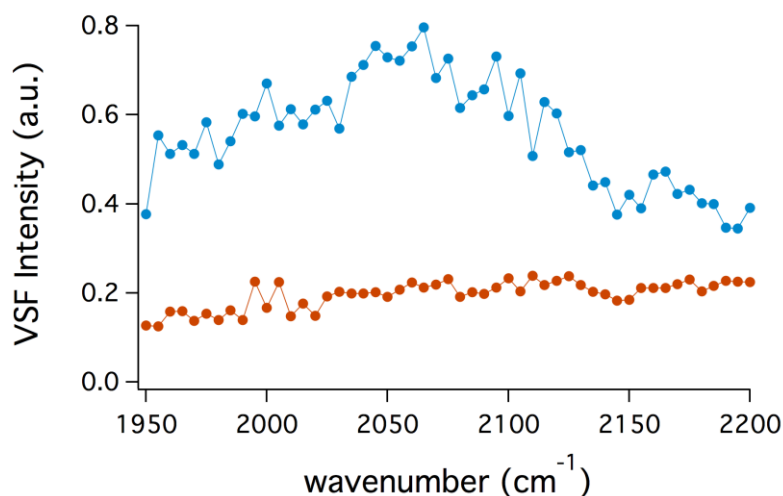
SUPPLEMENTARY VSF SPECTRA:

Figure S2: Spectra in SSP polarization combination of 0.015 mM d-DTAB in solvents H₂O (orange trace) and D₂O (blue trace). Lines are guides to the eye. No C-D peaks from d-DTAB are observed around 2100 cm⁻¹ in either spectra. At this concentration of surfactant, the C-D modes of the d-DTAB are hidden under the VSF signal from coordinated water molecules, which is induced by the surfactant's interfacial charge. Because D₂O modes are redshifted to lower wavenumbers from the H₂O modes, the surfactant solution containing D₂O as the solvent (blue trace) has a higher VSF intensity. In either solvent, C-D modes of surfactant are not observed.