# SUPPORTING INFORMATION Dynamic effect of polymers at the surfactant-water interface: An ultrafast study

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## **S1: Sample Preparation**

Deuterium oxide (D<sub>2</sub>O, 99.9 atom% D), sorbitan monostearate (Span-60), acrylamide (AM) monomer, and polyacrylamide (PAM, average MW 40,000 Da) was purchased from Sigma Aldrich and n-octane (98+%) was purchased from Alfa Aesar. Reverse micelles (RMs) with a 20:1 water:surfactant ratio were prepared following as described previously.<sup>1</sup> The RMs containing AM monomer and PAM were prepared following the same procedure, using a 5wt% D<sub>2</sub>O solution containing either monomer or polymer. Dynamic light scattering (DLS) was performed to characterize the particle size and ensure no additional monomer/polymer in the oil phase. The DLS results showed that the RMs did not change their size drastically when encapsulating the monomer/polymer units (Table S1).

Table S1: Reverse Micelle (RM) diameters and polydispersity index (PDI) at 65 °C

	Micelle	
Sample	diameter (nm)	PDI
Pure RM	158	0.153
5wt% Acrylamide	155	0.156
5wt% Polyacrylamide	151	0.173

#### **S2: FTIR SPECTROSCOPY**

FTIR spectra were measured at 1 cm<sup>-1</sup> resolution using a Bruker Vertex 70 FTIR spectrometer. Each spectrum is an average of 32 scans from 400 to 4000 cm<sup>-1</sup>. The sample temperature was controlled using a recirculating chiller with accuracy of 0.1 °C. The temperature at the sample window was calibrated using a type K-type thermocouple. Spectra were measured from 15 to 27 °C in 2 °C increments and 27 to 72 °C in 3 °C increments. Additional spectra were taken at 25 °C at the start and end of each temperature series to confirm that spectral changes were fully reversible. The sample temperature was allowed to equilibrate for three minutes before each spectrum was acquired. Each spectrum was background-subtracted using spectra of the pure octane solvent measured under the same conditions. To analyze the measured FTIR data, the ester C=O stretching spectra are fit to a sum of three Gaussians (Figure 1, main text):

$$A(\omega) = \sum_{n=1}^{3} \frac{a_n}{\sqrt{2\pi c_n}} e^{\frac{-(\omega - b_n)^2}{2c_n}}$$

Where a, b, and c represent the peak amplitude, center frequency, and width respectively. Peak area correlates to the population of the individual hydrogen-bond (H-bond) species. The fit is repeated 10 times while randomly varying the starting point for each variable in order to ensure the fits converge to a global minimum. Representative spectra are shown in Figure 1 (main text). Peak 1 (highest frequency) is the 0 H-bond population, peak 2 (middle) is the 1 H-bond population, and peak 3 (lowest frequency) is the 2 H-bond population. These parameters were fit using a nonlinear least squares method with a bisquare robust convergence. Replicate fits give the temperature-dependent populations shown in Figures S1, 3, and 5. These populations were used to extract H-bond thermodynamics, shown in Figures S2, 4, and 6. All FTIR and 2D IR data analysis was performed using the MATLAB R2021b package of programs. In order to verify the quality of our results, we plot the total fit, the original spectrum, and their second derivatives. The second derivative plots help determine whether the fitted peak positions are correct. A representative fit is included below (Figure S7) from the high-temperature regime. The high-temperature (reverse-micelle) fits show excellent agreement to experimental second derivative spectra. The changes in populations observed around 35 °C occur as the surfactants transition from

the microemulsion phase (not analyzed here) towards the reverse-micelle phase. Enthalpies of Hbond formation are extracted from the temperature-dependent H-bond populations above this temperature.



Figure S1: RM with  $D_2O$ . The red line represents the 0 H-bond population as a function of temperature, the green represents the 1 H-bond population, and the blue represents the 2 H-bond population.



Figure S2: Van't Hoff plot of a RM. H-bond thermodynamics calculated from the log of the non-hydrogen bond populations vs the H-bonded populations. The values were taken from the temperature dependent FTIR measurements.



Figure S3: Reverse micelle with 5wt% acrylamide in D<sub>2</sub>O. The red line represents the 0 H-bond population as a function of temperature, the green represents the 1 H-bond population, and the blue represents the 2 H-bond population.



Figure S4: Van't Hoff plot of a RM with 5wt% AM encapsulated. H-bond thermodynamics calculated from the log of the non-Hbond populations vs the H-bond populations. The values were taken from the temperature dependent FTIR measurements.



Figure S5: Reverse micelle with 5wt% polyacrylamide in D<sub>2</sub>O. The red line represents the 0 H-Bond population as a function of temperature, the green represents the 1 H-Bond population, and the blue represents the 2 H-Bond population.



Figure S6: Van't Hoff plot of a RM with 5wt% PAM encapsulated. H-bond thermodynamics calculated from the log of the non-H-bond populations vs the H-bond populations. The values were taken from the temperature dependent FTIR measurements.



Figure S7: Sample fit (A) and the corresponding second derivative (B) for a reverse micelle containing 5wt% PAM at 45 °C. In the top panel the original FTIR spectrum is shown in blue dots, the sum of the three-gaussian equation is shown in red, the 0, 1, and 2 H-bond populations are shown in tan, purple, and green respectively. The bottom panel displays the original FTIR spectrum second derivative in blue and the fitted spectrum is represented in orange.

## S3: 2D IR Spectroscopy

Two-dimensional infrared (2D IR) measurements were performed on a spectrometer that has been described in detail previously.<sup>2</sup> In Brief, 800 nm pulses (~ 100 fs) were generated by a Ti:Sapphire laser (Astrella, Coherent Inc), then converted to mid-infrared frequencies using an optical parametric amplifier and a difference frequency generator (TOPAS Prime, Light Conversion). The generated pulses were split into pump and probe beams using a CaF<sub>2</sub> beamsplitter. The pump pulse was converted into two sequential excitation pulses using a Ge-based pulse shaper (QuickShape, PhaseTech Spectroscopy, Inc). The time delay between the second pump pulse and the probe pulse was controlled through a delay stage. The pump and probe pulses were polarized perpendicularly to suppress scatter contributions. The 2D IR signal was detected using a spectrometer and a 128x128 pixel magnesium cadmium telluride (MCT) array detector (Catalina, Teledyne). The

detector array was used to resolve the detection frequencies ( $\omega_3$ ) and a numerical Fourier Transform of the excitation pulse pairs from the pulse shaper was used to resolve the excitation frequencies ( $\omega_1$ ). The waiting time delay between pump and probe pulses was scanned from 150 fs to 3 ps. Spectra were collected at 65 °C, ensuring that the samples are in the reverse micelle phase.

Center line slope (CLS) fits to each spectrum was done to analyze the dynamics of the surfactant ester carbonyl. The CLS was calculated through measuring the 0 H-Bond peak for each sample, which is located at ~1750 cm<sup>-1</sup>, at different waiting times ( $t_2$ ) as shown in the main text. The only data points that were used to calculate the CLS decay were the points equal to or greater than 75% of the maximum peak intensity. The error bars reported in the main text are derived from performing the CLS fit with 10 replicate fits. The CLS was fit to a monoexponential decay with an offset:

$$\tau(t_2) = ae^{-\left(\frac{t_2}{b}\right)} + c$$

The exponential decay time (b) is reported in Table 1 (main text). The amplitude an offset constants are not analyzed since the values can be affected by partial overlap with other peaks, as reported previously.<sup>1</sup>



Figure S8: 2D IR spectra of ethyl acetate at 25°C.



Figure S9: 2D IR spectra of ethyl acetate with 5wt% polyacrylamide at 25°C.







Figure S11: 2D IR spectra of reverse micelles with 5wt% acrylamide at 65°C.



Figure S12: 2D IR spectra of reverse micelles with 5wt% polyacrylamide at 65°C.

# S4: Bulk Water Contribution to Interfacial Trends

The H-bond enthalpies that were shown in Figure S1-S6 only measure perturbations at the interface. To demonstrate that the addition of polymer alters the interfacial H-bond properties only in the presence of an interface, temperature dependent FTIR measurements were performed on

5wt% AM and 5wt% PAM using the ester C=O stretching mode of ethyl acetate, a fully soluble molecule, as a vibrational probe. The H-bond enthalpies ethyl acetate solutions did not show any change in the presence of the AM and PAM at the concentrations tested (Figures S13-S18). These results demonstrate that effects on the H-bond enthalpies and solvation dynamics are only present in the RM. In bulk solutions, there is no change in the H-bond enthalpies (shown below) as well as in H-bond dynamics (Figure 3, main text).

![](_page_15_Figure_1.jpeg)

Figure S13: Sample fit (A) and the corresponding second derivative (B) for 20 mg/mL ethyl acetate in  $D_2O$ . In the top panel the original FTIR spectrum is shown in light blue, the sum of the three-gaussian equation is shown in orange, the 1 and 2 H-bond populations are shown in blue and purple, respectively. The bottom panel displays the original FTIR spectrum second derivative in blue and the fitted spectrum.

![](_page_16_Figure_0.jpeg)

Figure S14: Van't Hoff plot of the 20 mg/mL ethyl acetate in  $D_2O$  solution. H-bond thermodynamics calculated from the log of the non-H-bond populations vs the H-bond populations. The values were taken from the temperature dependent FTIR measurements.

![](_page_17_Figure_0.jpeg)

Figure S15: Sample fit (A) and the corresponding second derivative (B) for 20 mg/mL ethyl acetate in 5wt% AM D<sub>2</sub>O solution. In the top panel the original FTIR spectrum is shown in light blue, the sum of the three-gaussian equation is shown in orange, the 1 and 2 H-bond populations are shown in blue and purple, respectively. The bottom panel displays the original FTIR spectrum second derivative in blue and the fitted spectrum.

![](_page_18_Figure_0.jpeg)

Figure S16: Van't Hoff plot of the 20 mg/mL ethyl acetate in 5wt% AM in D<sub>2</sub>O solution. H-bond thermodynamics calculated from the log of the non-H-bond populations vs the H-bond populations. The values were taken from the temperature dependent FTIR measurements.

![](_page_19_Figure_0.jpeg)

Figure S17: Sample fit (A) and the corresponding second derivative (B) for 20 mg/mL ethyl acetate in 5wt% PAM D<sub>2</sub>O solution. In the top panel the original FTIR spectrum is shown in light blue, the sum of the three-gaussian equation is shown in orange, the 1 and 2 H-bond populations are shown in blue and purple, respectively. The bottom panel displays the original FTIR spectrum second derivative in blue and the fitted spectrum.

![](_page_20_Figure_0.jpeg)

Figure S18: Van't Hoff plot of the 20 mg/mL ethyl acetate in 5wt% PAM in D<sub>2</sub>O solution. H-bond thermodynamics calculated from the log of the non-hydrogen bond populations vs the hydrogen bonded populations. The values were taken from the temperature dependent FTIR measurements.

#### **S5: Molecular Dynamics Box Composition and Protocol**

The simulation box was constructed using a singular surfactant species (Span-60), this was to ensure any effect to the interfacial dynamics was due to the incorporation of the encapsulants only and not from surfactant heterogeneity, as reported previously.<sup>1</sup> The box was then assembled using the same method described previously.<sup>1</sup> In brief, the surfactants were placed into two leaflets with a water pool between the two leaflets to account for the symmetry induced by the periodic boundary conditions of the simulations. The AM monomer and PAM were then placed in the center water pool during box construction.

After the initial box configuration was created and energy minimized, an NVT ensemble equilibration was performed for 20 ns followed by a 20 ns equilibration in an NPT ensemble, then a 20 ns NPT production run, all using a 2fs time step with a snapshot stored every 1 ps. The production runs were used for the analysis of H-bond populations, tetrahedral order parameters (Figure S19), water mean-squared displacement (Figure S20). Shorter 500 ps trajectories sampled at 20 fs intervals were used to calculate frequency-frequency autocorrelations, which were

computed using a frequency map as described in Section S6.<sup>3</sup> Bonds were constrained with a LINCS algorithm, temperature was set to 300 K, pressure was set to 1.0 bar using a Parrienllo-Rahman barostat all performed through GROMACS 2019.4 implementations. The CHARMM36 force field was used for the surfactants, monomers, polymers, as implemented in the CHARMM-GUI modeler program, and the TIP3P model was used for water.<sup>4,5</sup> The Texas Advanced Computing Center (TACC) was used to perform all simulations. The hardware used for one the TACC "Frontera" system is: Intel Xeon Platinum 8280 ("Cascade Lake") processor with 28 cores per socket and 56 per node at a clock rate of 2.7 GHz base frequency, and 192 GB of DDR-4 RAM per node, 480 GB SSD hard drives.

The H-bond populations to water to the surfactant ester C=O and surfactant headgroups, water to the monomer/polymer C=O, monomer/polymer C=O to the surfactant headgroup and C=O were extracted using the GROMACS 2019.4 "gmx hbond" tool using the default cutoff distance of 3.5 Å and a donor-hydrogen-acceptor angle of 35°. The data retrieved from the simulations was plotted and analyzed using the MATLAB version 2021b.

### **S6: Simulation Frequency-Frequency Correlation Functions**

An electrostatic map developed by Edington et. al. was used to computed the frequency-frequency correlation functions (FFCF).<sup>3</sup> The use of electrostatic maps, to allow for direct MD to experiment comparisons of molecular dynamics. The map computes the electric fields at the carbon atom C, terminal oxygen,  $O_T$ , and bridging oxygen,  $O_B$ . the fields are then translated to frequencies using the positions computed from the MD box and using electrostatic parameters. The 500 ps trajectories sampled at 20 fs intervals were used to calculate the frequency trajectories. Autocorrelations are then computed for each individual carbonyl oscillator and then averaged together to compute the entire frequency autocorrelation of the carbonyl ensemble. The result decay is a sum of three exponentials. Each exponential component represents a different timescale, one on the order of tens of femtoseconds that corresponds to the motion of water and motions of other molecules around the oscillator, an intermediate picosecond timescale that corresponds to the H-bond fluctuations, and a long timescale >10 ps that is attributed to the global rearrangement of the surfactant molecules. Our experiment is only able to capture the intermediate timescales through CLS analysis, therefore, the second exponential in the computed FFCF is the only computed quantity directly compared to experiment.

#### S7: Determining the Origin of the Interfacial affects from the Monomer and Polymer

Section S5 describes the MD simulation protocol, in addition to this each trajectory was analyzed to quantify the H-bond populations and the H-bond network structure. The H-bond populations are reported in the main text and the analysis parameters described in Section S5. Determining the H-bond network structure was done through a the tetrahedral order parameter (q) as postulated by Debenedetti and coworkers.<sup>6</sup> A detailed interpretation of this parameter, as related to interfaces, can be found in previous publications.<sup>7,8</sup> In brief, the tetrahedral order parameter is the projection of a water molecule's H-bond geometry onto a perfect tetrahedron. The higher the value of q is interpreted as that H-bond geometry matches more closely with a perfect tetrahedron, such as the structure found in ice. Figure S19 below shows the average value of the parameter as a function of distance from the interface. This analysis demonstrates that the inclusion of both the monomer and the polymer disrupt the H-bond network of the interfacial water. The tetrahedral order parameter analysis also gives insight to the long-range effects of the encapsulants, displaying a convergence past the first solvation shell  $\sim 0.3$  nm. The higher q parameter of the AM trajectories suggests that the monomer stabilizes the H-bond network of the interfacial water when compared to the PAM and the RM with no encapsulants. AM has the ability to donate and accept H-bonds allowing it to stabilize the H-bond network.

![](_page_23_Figure_0.jpeg)

Figure S19: The average q value as a function of water's distance to the SPAN60 ester carbonyl.

In addition, we compute the mean squared displacement (MSD) of the water molecules as a function of their initial distance to the interface (Figure S20), grouped as interfacial (<.35 nm), intermediate (.35-.60 nm) or bulk (>.60 nm). This analysis displays a similar trend to that of the q parameter analysis (Figure S19). The diffusion rate is the highest with the inclusion of the monomer (AM) and slowest with the inclusion of the polymer with the intermediate being the RM with no encapsulants. Both the MSD and the q analysis demonstrate the monomer system supports a more disordered interface. The diffusion and the q parameters adapt more bulk like characteristics than the other two systems studied. The polymer system displays a more ordered interface with the inclusion of the polymer which matches with experimental observations. The results of the AM analysis do not correspond to the experimental observations, but this could be due to an over estimation of the monomer's affect due to the nature of the MD box composition being a small system used to approximate the much larger system used in experiment, as discussed in the main text.

![](_page_24_Figure_0.jpeg)

Figure S20: Mean square displacement (MSD) was calculated from each trajectory using a 5 ps restart time with 20 fs spacing between frames.

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