

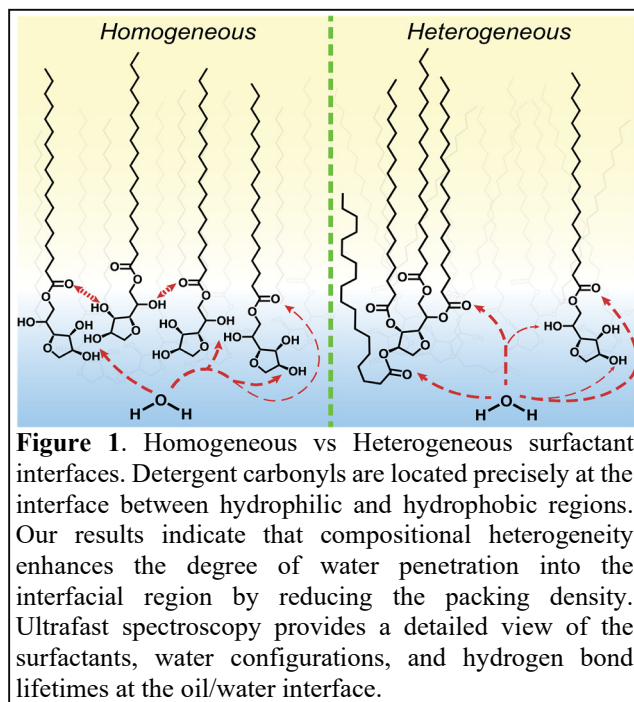
## Interfacial Solvation in Reverse Micelles: Ultrafast 2D IR Spectroscopy of Surfactants

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## 1. Research Progress

Surfactant structures are extremely diverse, from simple organic sulfates to highly-structured biological glycolipids. Despite everyday use, as chemists, we lack a fundamental understanding of how molecular properties correlate to surfactant activity. Indeed, current models are based on simple geometric parameters such as surface areas, which lack molecular information, and are crude by modern chemical standards.

**Surfactant structure, composition, and heterogeneity:** Our project seeks to quantify interfacial solvation by characterizing the hydrogen-bond (HB) populations at the surfactant/water interface. We have used ultrafast two-dimensional infrared (2D IR) spectroscopy to specifically probe the dynamics of the carbonyl vibrations in sorbitan surfactants. Therefore, while this technique probes the bulk solution, the inherent location of the probes, positioned precisely at the 1 nm interface between the hydrophobic and hydrophilic regions of the interface, enable for interface-selective measurements.



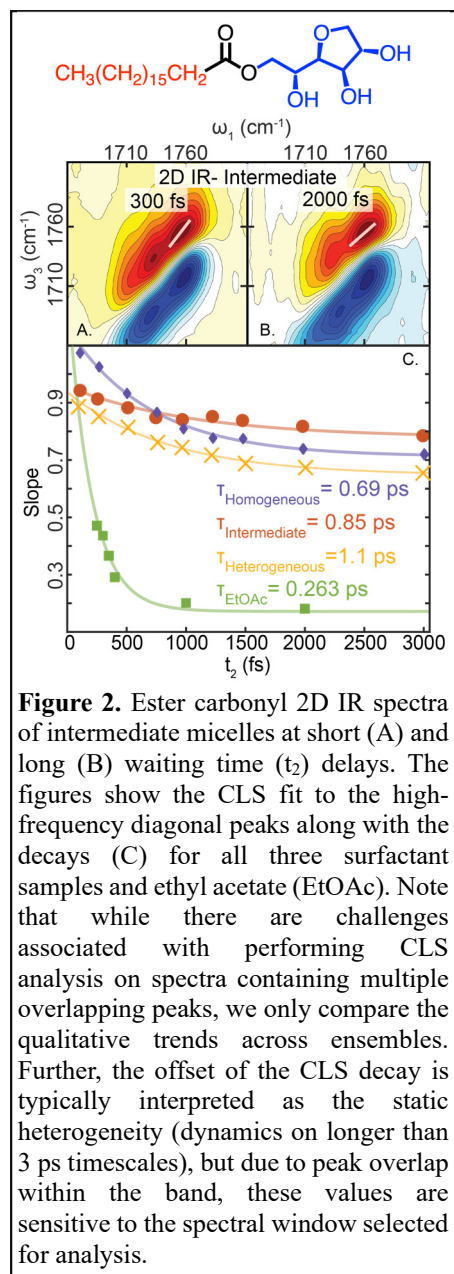
**Figure 1.** Homogeneous vs Heterogeneous surfactant interfaces. Detergent carbonyls are located precisely at the interface between hydrophilic and hydrophobic regions. Our results indicate that compositional heterogeneity enhances the degree of water penetration into the interfacial region by reducing the packing density. Ultrafast spectroscopy provides a detailed view of the surfactants, water configurations, and hydrogen bond lifetimes at the oil/water interface.

Our initial studies have focused on characterizing the effect of surfactant heterogeneity in sorbitan surfactants. Industrial compositions contain hundreds of surfactants, as such it is important to understand how a heterogeneous composition affects the interface. We have found that commercial supplies of “sorbitan monostearate” contain the compound only in single-digit purity, the composition includes di- tri- and tetra-sterates, as shown in Table 1, along with a distribution of tail lengths (not shown). We have tested the effect of heterogeneity by purifying the mixtures to contain primarily the singly-substituted sorbitan (Figure 1, left), and compared the C=O HB populations with the heterogeneous composition (Figure 1, right). Our results show that heterogeneity reduces the packing efficiency of the surfactants, producing a more hydrated headgroup. In other words, the increased area per surfactant causes water to penetrate further into the otherwise hydrophobic region of the micelle.

**Table 1:** Composition of sorbitan samples by degree of fatty acid (FA) substitution. 1 FA groups contain a single substitution, whereas 2, 3, 4 groups have the corresponding number of FA chains. The homogeneous composition consists primarily of 1FA substitutions.

Sample	Composition (%)			
	1FA	2FA	3FA	4FA
Homogeneous	82	11	6	1
Intermediate	41	40	13	7
Heterogeneous	36	22	24	18

Ultrafast 2D IR measurements of the HB dynamics at the carbonyl positions (Figure 2) indicate that the increased hydration is accompanied by a slowdown of water dynamics, suggesting that interfacial water is confined by the surfactants, making for stronger interactions and longer-lived carbonyl H-bonds. The relationship between surfactant heterogeneity and interfacial H-bonding originates primarily from differences in surfactant packing density. Area-per-surfactant values extracted from MD simulations show that heterogeneous mixtures are more loosely packed compared to their homogeneous analogs. These effects are a combination of two different contributions: **1.** An increased number of hydrocarbon tails lowers the packing efficiency in the hydrophobic region, increasing the conformational entropy



**Figure 2.** Ester carbonyl 2D IR spectra of intermediate micelles at short (A) and long (B) waiting time ( $t_2$ ) delays. The figures show the CLS fit to the high-frequency diagonal peaks along with the decays (C) for all three surfactant samples and ethyl acetate (EtOAc). Note that while there are challenges associated with performing CLS analysis on spectra containing multiple overlapping peaks, we only compare the qualitative trends across ensembles. Further, the offset of the CLS decay is typically interpreted as the static heterogeneity (dynamics on longer than 3 ps timescales), but due to peak overlap within the band, these values are sensitive to the spectral window selected for analysis.

surfactants and has carried out FTIR measurements to characterize the hydrogen bond populations at the interface. This project has helped Morgan gain technical lab and instrumentation skills. Morgan is a co-author in our recent publication in Langmuir.

**Jennifer Sormberger (Sophomore Undergraduate, UT-Austin)** – Jennifer is performing experiments of reverse micelles with different components in the oil phase to better understand how aromatic vs aliphatic compounds affect the hydration and dynamics of sorbitan surfactants.

**David Castro (High School Student, Welch Summer Scholar)** – David spent the summer of 2019 in the Baiz group developing protocols and performing chromatography to purify different surfactant mixtures.

of the surfactants and reducing their average order parameters; **2.** An increase in FA substitutions also reduces the number of hydroxyls available for surfactant-surfactant H-bonding. Indeed, we observe fewer of these HBs in simulations of the heterogeneous mixture when compared to a uniform sorbitan monostearate micelle. This suggests that hydroxyl groups promote surfactant-surfactant interactions, and consequently reduce the area-per-surfactant.

**Dynamical coupling across the surfactant-water interface:** Our current efforts are directed at understanding the effect of the oil phase viscosity. To this end, we are carrying out 2D IR spectroscopy to quantify the surfactant-water H-bond dynamics while varying the composition of the oil phase. Squalene is used as a high viscosity (15 cP) oil phase component, in mixtures with octane (0.4 cP). Preliminary results indicate a 60% slowdown of dynamics at the oil water interface in squalene compared to octane. The H-bond populations remain largely unchanged, which suggests that the oil phase composition does not affect the H-bond strengths in the aqueous phase, implying that surfactant packing is also unaffected. These preliminary results are interesting because measured C=O dynamics are typically considered to be driven by the H-bond networks of water, and by consequence, larger molecules are “slaved” to the dynamics of their solvation shell. Given the separation of timescales between picosecond H-bond dynamics and long-timescale reorientation of surfactants, we would expect that water dynamics adapt to the “static” configurations of the surfactants. If this is the case, the H-bond dynamics should not change with oil-phase composition. However, our results indicate that the dynamics of the aqueous and the oil components are coupled through the interface.

#### Students Participating in the Project:

**Christopher P. Baryames (Fourth year, Graduate Student, UT-Austin)** – Chris has carried out all the ultrafast experiments and simulations of the mixed surfactants as well as the oil phase viscosity experiments. Chris has presented his results at the ACS National Meeting (2018) in New Orleans, LA as well as the ACS National Meeting (2019) in San Diego, CA.

**Morgan Teel (Junior Undergraduate, UT-Austin)** – Morgan has performed purification to generate homogeneous compositions of