

Research Progress

Asphaltenes, represent the most polar and aromatic components of petroleum and are specifically defined by their solubility in benzene and toluene and insolubility in n-heptane and n-pentane. The presence of asphaltenes in petroleum can substantially reduce oil performance and refining yields due to their high viscosities and propensity to aggregate and phase separate. Typically, asphaltene inhibitors are employed during the extraction process in order to disrupt aggregation and prevent flocculation. While a variety of inhibitor designs exist, the basic structure can be divided into a polar head group to specifically target the asphaltenes and a nonpolar tail group to stabilize the complexed asphaltene-inhibitor structure in the surrounding nonpolar oil medium. Thus, inhibitor performance is critically linked to the affinity of asphaltenes towards the inhibitor head group. However, the complex and wide variety of asphaltene structures (island and archipelago) and heteroatoms (N, S, O) presents a substantial challenge to developing a comprehensive assessment of inhibitor performance. This research investigates the chemistry of asphaltene-inhibitor interactions through the use self-assembled nonaqueous reverse micelle (RM) structures. Specifically, we aim to: 1) determine inhibitor affinities and binding mechanisms using heteroatom proxies of asphaltene molecules, 2) investigate the influence of asphaltene architecture on inhibitor affinity, 3) and quantify the impact of resin fractions on asphaltene stabilization.

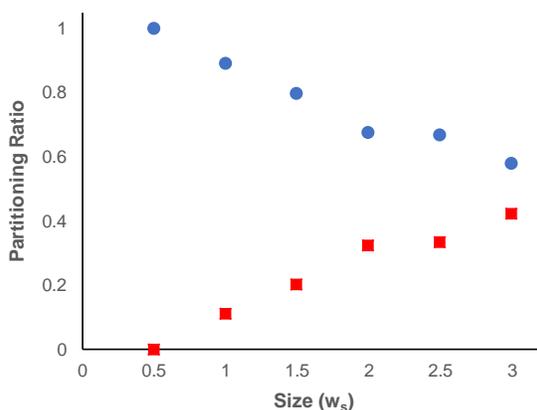


Figure 2. Interfacial and core partitioning ratios of EG with AOT RMs. Interfacial EG (blue circles) represent those EG molecules interacting with the surrounding AOT surfactant, while core EG (red squares) represent EG molecules with bulk-like characteristics.

pyridines located within the RMs gradually increases from 0.37 for $w_s = 0.5$ to 0.44 in a $w_s = 3$ RM. For the larger sizes, the fraction of pyridines within the RM drastically increases to over 0.70, making hydrogen-bound pyridines the dominate species in solution. To investigate the origins of this shift at $w_s > 3$, we examined the properties of EG within the nonaqueous interior. Previously we observed that the O-H stretch of EG in a $w_s = 0.5$ RM was blue shifted and narrow relative to neat EG. As the w_s ratio increased the IR spectra gradually red shifted and broadened, converging toward neat EG. Using the MCR-ALS method we were able to fit the O-H stretch region of EG to a

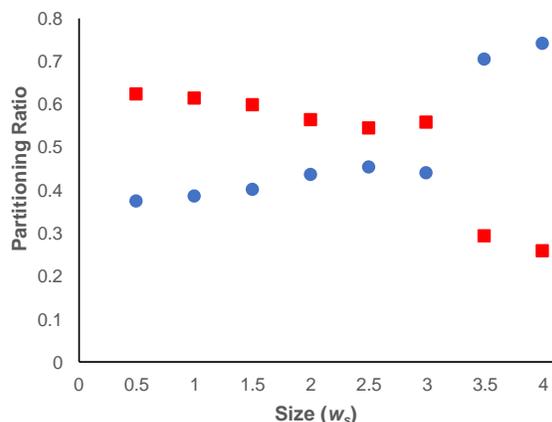


Figure 1. Partitioning ratios of pyridine located inside (blue circles) in interior of EG/AOT RMs and outside (red squares) in the surrounding heptane solvent.

Our previous studies focused on the properties of pyridine. Pyridine possesses a conjugated, cyclic structure along with a nitrogen heteroatom, making it an ideal proxy of a heteroatom site within a larger asphaltene structure. In the course of our studies we observed that the IR absorption transition frequencies of pyridine in protic solvents are distinct from those in aprotic solvents. With the ability to distinguish between hydrogen-bound and unbound species of pyridine we examined the IR spectra of pyridine-doped EG (ethylene glycol)/AOT (dioctyl sulfosuccinate sodium salt) RMs prepared at various sizes based on the $w_s = [EG]/[AOT]$ ratio. The IR spectra show peaks in the 1592 cm^{-1} region, which we assign as pyridine located within the RMs, while a second peak at 1580 cm^{-1} , is assigned as indicative of unbound pyridine localized in the nonpolar heptane solvent. To quantify the ratios of hydrogen-bound and unbound pyridine we used a multivariate curve resolution alternating least squares algorithm (MRC-ALS) to deconvolve the spectral contributions from each species. Partitioning ratios as a function of w_s are displayed in Figure 1. The fraction of

combination of interfacial ($w_s = 0.5$) and core (neat) EG. Partitioning ratios as a function of w_s are displayed in Figure 2. The interfacial fraction decreases as the w_s ratio increases, similar to observations for H₂O in aqueous AOT RMs, while the core fraction increases. By $w_s = 3$ 0.42 of the EG. We hypothesize that the incorporation of pyridine into the EG/AOT RMs is mediated by the core EG molecules and that a fractional threshold of core EG must be reached in order to solvate pyridine in the nonaqueous interior. We plan to further examine the onset of pyridine solvation within the RM interior to evaluate our hypothesis.

Many heteroatoms within asphaltenes possess the potential for hydrogen bonding interactions. While the nitrogen lone pair has the potential act as a hydrogen bonding acceptor site, we wanted to extend our studies to hydrogen bond donors, so we began studies focusing on the hydrogen bond donor, pyrrole, and the nonhydrogen bond donating analog, 1-methylpyrrole. Similar to our observations for pyridine, the IR spectrum of pyrrole is sensitive to the hydrogen bonding capacity of the solvent. In particular, the C=C asymmetric stretch of pyrrole in EG appears at 1537 cm⁻¹, while in both heptane and neat pyrrole the C=C is located at 1529 cm⁻¹. The overall peak is substantially broadened in protic EG, compared to aprotic heptane. To examine how pyrrole is localized into RMs we examine the IR spectra of a series of pyrrole-doped EG/AOT RMs, displayed in Figure 3. For all sizes of RM, the C=C asymmetric stretch of pyrrole appears at 1535 cm⁻¹, between both the frequencies observed for pyrrole in EG and heptane. The overall band shape, broad and asymmetric, is more consistent with pyrrole in hydrogen bonding environments, than aprotic environments. Based on these observations we believe that pyrrole has been incorporated into the RM interior. In contrast, studies of methylpyrrole showed very modest frequency shifts in response to solvent environment, shifting from 1509 cm⁻¹ in EG to 1507 cm⁻¹ in heptane. When prepared with EG/AOT RMs, methylpyrrole failed to incorporate into the EG interior, instead exhibiting peaks consistent with solvation in the surrounding heptane. These observations suggest that hydrogen bonding plays a fundamental role in dictating incorporation of molecular species into the nonaqueous interior. While these studies have provided insights into the role hydrogen bonding interactions play in localizing pyrrole within RMs, we were unable to monitor the impact at the point of the interaction, the N-H stretch, due to overlapping signal from the O-H stretch of EG. In order to examine the N-H stretch of pyrrole we have embarked on studies focusing on pyrrole doped in DMF/AOT RMs. The combination of pyrrole and DMF will allow us to observe the N-H stretch of pyrrole while still maintaining favorable hydrogen bonding interactions between the N-H of pyrrole and the carbonyl of DMF.

In addition to our IR-based studies we have been working towards quantifying asphaltene-inhibitor distances in our RMs using nuclear Overhauser effect (NOE) experiments. A critical first step in these experiments was optimizing pulse setting and validating the method. While initial attempts proved successful in quantifying proton distances within an oxygen heterocycle, THF, extending this technique to RMs has proven challenging due to overlapping proton signals from the AOT surfactant and the EG polar interior. We are still investigating the optimal pulse settings in this more complex experiment to selectively target either surfactant or heterocycle protons to measure asphaltene-inhibitor distances.

Career Development

Financial support from ACS PRF has been used to provide research opportunities for 4 undergraduate students at CNU. Beyond supporting research through the purchase of materials, this grant also provided 2 paid summer research opportunities (Rana Fadah and Kathrine Routon). Mackenzie Lindholm and Mason Tucker, summer research students from 2018, continued to work on their projects throughout the academic year, including as part of their senior capstone research course. Mason presented our research at the 2018 Southeastern Regional Meeting of the ACS (SERMACS). The poster featured work from all 3 summer 2018 research students (Mason, Mackenzie, and Rana) as well as ACS Project SEED student, Zaaheem McCall. Both Mackenzie and Mason graduated in Spring 2019 with degrees in biochemistry and chemistry, respectively. Mackenzie received a job offer at Pharmaceutical Product Development (PPD) Inc., and I have received multiple inquiries regarding Mason for lab technician positions.

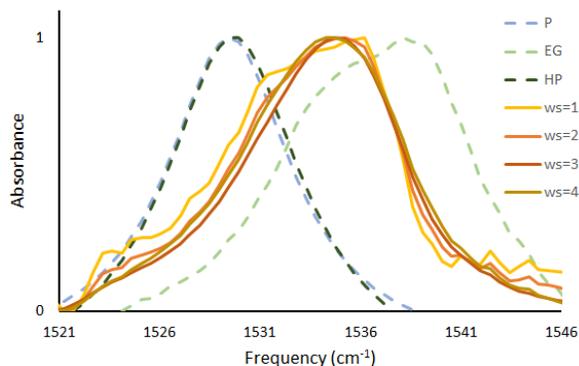


Figure 3. Normalized infrared absorption spectra of pyrrole in EG/AOT RMs. Spectra are denoted as follows: $w_s = 1.0$ (yellow), $w_s = 2.0$ (orange), $w_s = 3.0$ (red), $w_s = 4.0$ (brown), EG (green dashed), Heptane (dark blue dashed), and neat pyrrole (light blue dashed).

