PRF# 57575-DNI5

Fundamental Studies on Nanocrystal Stabilized CO_2 Foams and Emulsions

Esteban E. Urena-Benavides, The University of Mississippi

This project is aimed at investigating fundamental interfacial effects affecting the properties of CO_2/brine Pickering foams and emulsions stabilized by cellulose nanocrystals (CNC). It is expected that success on this project will lead to dry, CO_2 based, fracking fluids to improve the sustainability of traditional fossil fuels. The CO_2 based fluid would trap the greenhouse gas underground while allowing extraction of natural gas and oil.

The work during the second year of study continued inconclusive work from the first year on assessing the ability of CNC to stabilized highly non-polar organic fluids like dodecane, heptane and perfluorooctane in American Petroleum Institute (API) brine. These fluids are being used as model compounds to mimic the solvent properties of high pressure CO_2. In addition the synergistic effect of surfactants like dodecyltrimethylammonium bromide (DTAB), octyl-β-D-glucopyranoside (OGP) and bis(2-hydroxyethyl) cocoalkylamine (CAA), and the thickener guar gum has been investigated.

Surface tension measurements were used to confirm the adsorption of CNC onto the dodecane/brine interface and the adsorption of surfactants on the CNC surface. In addition Raman spectroscopy measurements were done with Dr. Nathan hammer from the Department of Chemistry and Biochemistry to study the functional groups involved on the interactions. It was determined that hydroxyl groups on the CNC surface interact with OGP, DTAB and CAA, all of which adsorb onto the surface of the CNC in synthetic seawater and API brine. The results also suggest that ionic interactions still play a role during adsorption even at high ionic strengths, although non-ionic interactions like hydrogen bonding also become important. Interestingly, adsorption of surfactants onto the CNC did not lead to an increased surface tension of DTAB solutions suggesting that the CNC coated DTAB particles have a larger tendency to remain at the interface.

As part of this research Dr. Urena-Benavides's group developed an equation for the adsorption energy of rod-like particles on an interface and used it to estimate the adsorption energy of CNC at the oil/brine interface. It was found that CNC have desorption energies on the dodecane/brine interface in the range of 400kT – 650kT. Addition of DTAB lowers the energy to 170kT – 250kT, although a lower interfacial tension of only 5-14 mN/m maintains significant emulsion stability. In the case of CAA, the desorption energy is only 80kT – 87kT, while the surface tension is 14-18 mN/m. Emulsions prepared with CAA and CNC are not stable mainly due to the low desorption energy and moderate surface tension.

The high pressure apparatus to test CO_2 foam stability and viscosity was finished towards the end of the second year of the project. However unexpected delays in the construction of the setup prevented the PI's lab to conduct significant experiments with. This led to the PI requesting a no-cost extension of 1 year, which has already been granted. A high pressure cell has is being setup to measure interfacial tension and contact angles in supercritical CO_2. Work for the third year will focus on continuing stabilization experiments of high oil to water ratio emulsions using CNC and surfactants at elevated temperatures. The goal initial goal was to achieve stable 90% to 95% oil/brine emulsions of heptane and perfluorooctane in API brine and in CO_2/brine foams. Foams with

There have been five undergraduate students and one graduate student involved on this project from the beginning. After the first year, one of the undergraduate students graduated and found a job as a Mud Engineer at Halliburton. Another undergraduate student worked in the group for 1 year and then decided to focus more on her classes; however was able to get an internship. She has since graduated and found a job at a battery company Hankook AtlasBX. A third student graduated in May 2018 after two years in Dr. Urena-Benavides's lab, he started a Ph.D. in polymer science at the University of Southern Mississippi. Two more undergraduate students joined this project a year ago and are still working on it; they are expected to graduate in May 2020.

So far, one manuscript has been published with the graduate student as the first author, and one of the undergraduates as a co-author. Two more publications are in preparation. [1] The same graduate student also presented a poster at the 93rd ACS Colloid & Surface Science Symposium. Receiving this grant has helped our research group to establish collaborations with researchers inside and outside the University of Mississippi which resulted in two externally funded research grants, one from the National Science Foundation and the other from the

National Institute of Food and Agriculture. It has also helped the PI gain recognition in the field of nanoparticles stabilized Pickering emulsions. In addition, the high pressure systems built as a result to this project has created research infrastructure at the University of Mississippi that is not available in any other institution in the state.

References

(1) Parajuli, S.; Dorris, A.; Middleton, C.; Rodriguez, A.; O'Haver, M.; Hammer, N.; Ureña-Benavides, E. E. Surface and Interfacial Interactions in Dodecane/Brine Pickering Emulsions Stabilized by Combination of Cellulose Nanocrystals and Emulsifiers. *Langmuir* **2019**, *35* (37), 12061–12070. https://doi.org/10.1021/acs.langmuir.9b01218.