PRF# 58379-UNI10

A Deeper Look into Dendrimer Oil Demulsification and Recovery: The Importance of Dendrimer Generation and Surface Properties

Casey Ann Dougherty, Department of Chemistry, Iona College

Progress of Research

The goal of this grant proposal is to utilize commercially available dendrimers to provide a comprehensive study on the molecular weight and functionalization dependence of an effective oil and water demulsification reagent. These studies will aide us in developing future demulsification materials and oil recovering dendrimer materials.

Project 1. Light Crude Oil Demulsification with G3-G5 PAMAM dendrimer

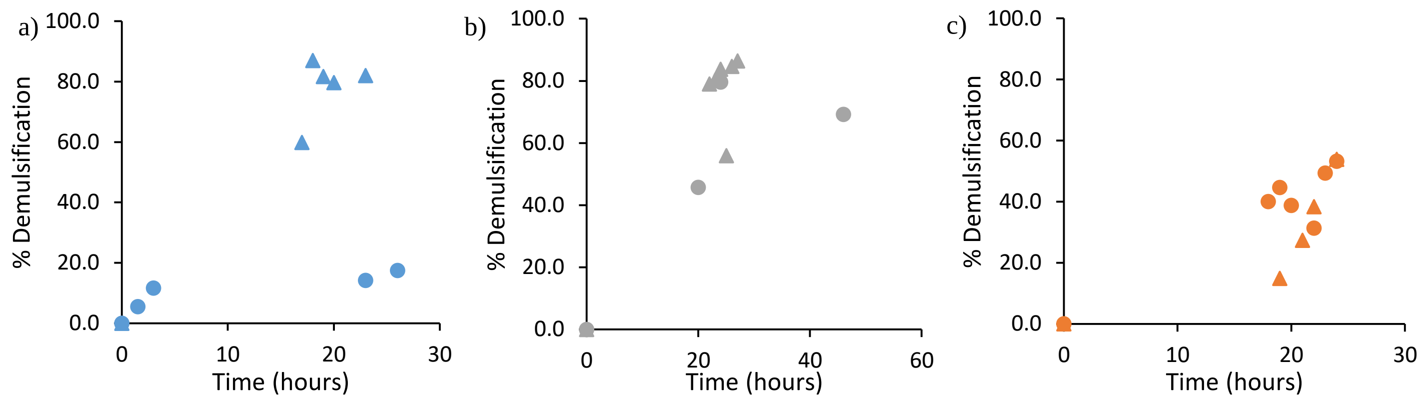

Figure 1. Percent demulsification of a) G3 PAMAM, b) G4 PAMAM, and c) G5 PAMAM at 90 mg/mL over time at 25 °C (circle) and 40 °C (triangle)

These studies have been conducted to better understand and investigate the trends found in light crude petroleum oil demulsification using high molecular weight PAMAM dendrimer materials. Previous studies have yet to determine the demulsification effects of dendrimers beyond G3 and many studies focus on the demulsification of heavy crude diesel oil rather than light petroleum oil. The first set of materials used in this project were amine terminated generation 3-5 PAMAM dendrimers. The dendrimers were exposed to 5% light petroleum crude oil in water emulsions and monitored over time using Ultraviolet-Visible Spectroscopy to determine oil content remaining in the water layer. Initial studies show there is trend in both generation and temperature dependence on oil and water separation efficiency (Figure 1). It can be noted that Figure 1c shows G5 PAMAM dendrimer has the least amount of demulsification efficiency at 53% of light crude oil at heated temperatures but produces a more efficient demulsification of 63% oil removel at room temperature. The initial conclusions show the largest polymer, the G5 PAMAM dendrimer (28,000 g/mol), has less temperature dependence for demulsification efficiency compared to the smallest polymer, the G3 PAMAM dendrimer (6,909 g/mol). As shown in Figure 1a, the G3 PAMAM dendrimer has the most efficient demulsification of crude light oil in water at 40ºC at 82%, but the efficiency dramatically reduces to 17% at room temperature. G3-5 PAMAM dendrimers were also functionalized with acetyl groups in order to minimally alter molecular weight but change surface charge dramatically. In aqueous solution, the dendrimers now have an overall neutral charge whereas the amine terminated dendrimers have an overall positive charge. The results show a significant drop in demulsification efficiency to less than 5% for all generations of dendrimer at both room temperature and 40ºC when the surface functionality becomes neutral (results not shown). This is in agreement with previous studies that acetylated dendrimer is less efficient at oil and water demulsification, but no studies have ever shown this result for dendrimers as large as the G5 PAMAM dendrimer, nor have the studies shown the demulsification with light crude oil.

In relation to the crude petroleum oil demulsification studies with dendrimer, we have begun a collaboration with the Sunghee Lee research lab in the Iona College chemistry department to conduct surface tension experiments on the light crude petroleum oil in water emulsions when exposed to the G3-5 PAMAM dendrimer materials. A comparison of the interfacial surface tension was conducted for the amine terminated G3-5 PAMAM dendrimers at both room temperature and 40ºC. It can be concluded the G4 PAMAM dendrimer has the lowest interfacial tension at both temperatures and G3 PAMAM dendrimer has the highest interfacial tension at both temperatures (Figure 2a and b). This conclusion deviates from any molecular weight trend conclusion and does not agree with the initial crude petroleum demulsification data. At this time, no mechanism has been proposed, but these results plan to be studied further.

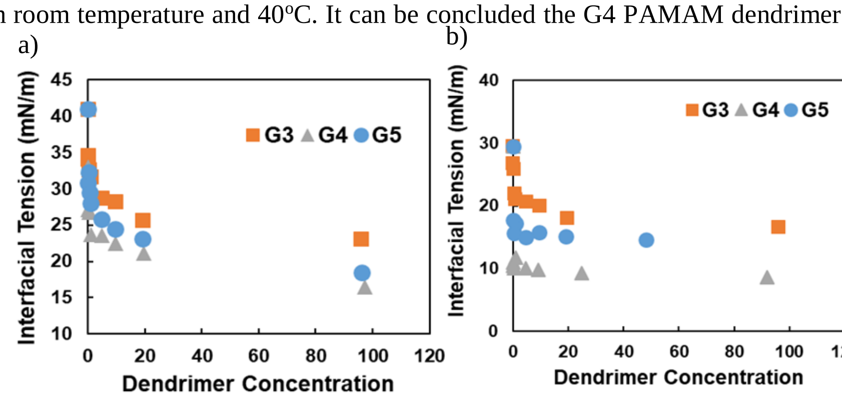

Figure 2. Interfacial tension experiments for G3-G5 PAMAM dendrimers at a) 25 °C and b) 40 °C.

Project 2. Oil Control Demulsification with G3-G5 PAMAM dendrimer

As the first project began to materialize initial results with the crude oil, it became apparent that the understanding of the crude oil composition was not well known nor well studied. In order to better understand the initial demulsification results from crude petroleum oil, we began to create our own oil mixture using a combination of phenanthrene and hexadecane as our model aromatic and hydrocarbon compounds. The known oil composition mixture of phenanthrene and hexadecane was then used in making the 5% oil in water emulsions for dendrimer demulsification studies. G3-G5 PAMAM dendrimers were exposure to 8% phenanthrene in hexadecane and 16% phenanthrene in hexadecane at both room temperature and 40ºC to help better understand the interactions of the PAMAM dendrimer with the different oil components (Figure 3). Interestingly, the G5 PAMAM dendrimer conclusions for the 16% phenanthrene/hexadecane demulsification results can be compared to the crude petroleum oil demulsification (Figure 3a). There is little temperature dependence with the percent demulsification levels at 69% for room temperature and 54% for 40ºC. This is consistent with the data from Figure 1c. The large temperature dependence of G3 PAMAM dendrimer as seen in Figure 1a is also seen in the 16% phenanthrene/hexadecane demulsification, with a decrease of percent demulsification from 87% to 4%. Overall, this project has shed light on the potential behavior of our PAMAM dendrimers and their potential interactions with aromatics in the oil/water emulsion using crude petroleum oil. Further studies need to be conducted to increase reproducibility and better understand the mechanism of demulsification using the known mixtures of oil.

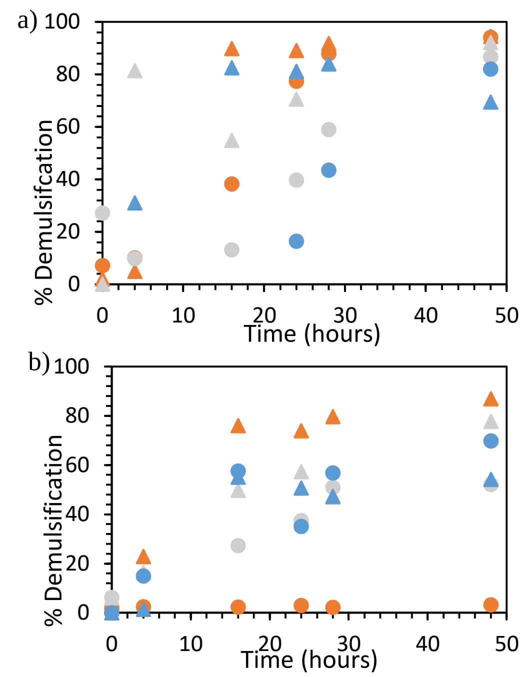

Figure 3. Percent demulsification of G3 (orange), G4 (grey), and G5 (blue) PAMAM dendrimer at 90 mg/mL over time at 27 °C (circles) and 40 °C (triangles) with a) 8% phenanthrene and b)16% phenanthrene in hexadecane oil composition.

<u>Project 3. G3-G5 PAMAM dendrimer interactions with amphiphilic molecules</u>

In addition to conducting demulsification experiments using known components for the oil, we have also begun to look at the interactions of dendrimers with known compositions of amphiphilic molecules. G3-5 PAMAM dendrimers were used with amine terminated surface functionalization and with fluorescein isothiocyanate (FITC) and poly(ethylene glycol) (PEG) modification in order to determine how altering the degree of hydrophobicity/hydrophilicity on a macromolecule impacts the interaction of the polymer with amphiphilic molecules. Water permeability was measured on an assembled bilayer of amphiphilic molecules. The assembly of the amphiphilic molecules was created using the Droplet Interface Bilayer method of the Sunghee Lee lab. Combined with Confocal Raman Microspectroscopic and Differential Scanning Calorimetric studies, this project has helped provide insight on the nature and extent of the interaction between PAMAM dendrimer and amphiphilic molecules. Initial results show there is more interaction between all PAMAM dendrimer generations and an assembly of DOPC:DOPS at 20%mol compared to an assembly of pure DOPC (Figure 4). This initial result indicates partial negative charge is imperative for extensive PAMAM dendrimer interaction with amphiphilic molecules since there is a significant decrease in water permeability with the addition of a negatively charged molecule into the lipid assembly.

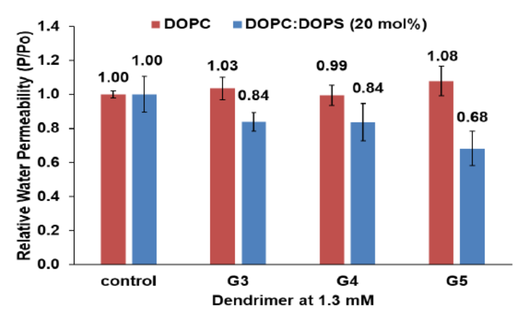

Figure 6. Water Permeability of G3-G5 PAMAM dendrimer through assembly of DOPC (red) and DOPC:DOPS at 20mol% (blue).

Impact of Research

The ACS PRF-UNI grant has provided significant support for supplies and student stipends to an institution with limited resources. Having the ability to fully setup a research laboratory space with the chemicals and supplies needed has helped produce very interesting and innovative experimental results in a short time at Iona College. More importantly, the grant has allowed for a newly hired professor to attract students and produce undergraduate driven research results. Multiple students have been able to be mentored on completely new research projects to Iona College. With the help of the ACS PRF-UNI grant, two publications should be produced by the end of this upcoming academic year with undergraduate students as lead authors from a primarily undergraduate institution. Overall, the most important impact of the grant has been to the students of Iona College. The students funded through the ACS PRF-UNI grant have gained extensive hands on research experience and exposure to professional presentation settings at local, regional, and national conferences. A student presenting her research on the interactions of dendrimers with amphiphilic molecules won a Poster Award recognizing posters prepared with a logical flow, clarity, and organization at a local, on campus research symposium. This same student was also able to attend the National American Chemical Society (ACS) Conference in San Diego, CA, in August 2019. Another student received 1st Place in Environmental & Earth Science II at The Collegiate Science & Technology Entry Program (CSTEP) 27th Annual Statewide Student Conference Poster Competition for her surface tension research on dendrimer demulsification in Spring 2019. This conference is specifically focused on engaging and recruiting underrepresented minorities in STEM research in the state of New York. An additional two students were also able to attend and present a poster at the National Conference on Undergraduate Research (NCUR) at Kennesaw State University in Kennesaw, GA, in Spring 2019 on their crude petroleum oil demulsification experiments. In total, 4 undergraduate students were able to get exposure to a variety of research conferences throughout the first year of the grant period, with even some excelling in their research and scholarly presentations so much so they were awarded for their scientific accomplishments.