Impact of Urea on Size and Red-Edge Emission Spectroscopy of Reverse Micelles

Tran Nguyen[1], Nancy E. Levinger[2], Bridget L. Gourley[1]

[1]*Department of Chemistry and BioChemistry, DePauw University*

[2]*Department of Chemistry, Colorado State University*

Abstract

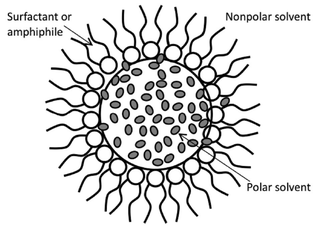
We use reverse micelles (RMs) as our model system to study the impact of osmolytes on water at the nanoscale. Reverse micelles are characterized by w_0 = [polar component]/[surfactant]. In our experiment, we focus on 5 different w_0 (w_0 = 1, 5, 10, 20, 40) and 3 concentrations of urea (0.5M, 1M, 2M). The Dynamic Light Scattering (DLS) illustrates a linear relationship between reverse w_0 (the ratio) and size. Additionally, the DLS data indicates that the impact of osmolytes on size for small reverse micelles is not significant. Furthermore, Red-Edge Emission Spectroscopy shows a bigger impact on emission for smaller reverse micelles compared to the larger w_0 samples.

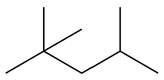
Introduction

Reverse micelles are formed by the presence of water and surfactant in nonpolar solvents. Because of its polarity, water interacts with amphiphilic surfactant and constructs reverse micelles. In this project, we used sodium diotylsufosuccinate (AOT) as the surfactant. AOT is commonly used as a surfactant because it readily forms reverse micelles when a small amount of a polar solvent is added to a non-polar solvent. Furthermore, AOT tends to form reverse micelles that are more homogeneous.

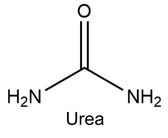
In reverse micelles, sizes of micelles are determined by the ratio of water to surfactant. The equation for w_0 is

$$w_0 = \frac{[H2O]}{[surfactant]}$$

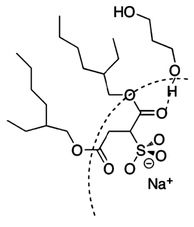




Isooctane (solvent)



Urea



AOT (Surfactant)

Methodology

Reverse Micelles preparation:
- Polar phase: Water, Urea solution in water (0.5M, 1M, 2M).
- Non-polar phase: Isooctane (solvent).
- Surfactant: AOT.

Sample size: w^0 = 1, 5, 10, 20, and 40.

Sample preparation:
- Sonicating 15 minutes 0.1M AOT in isooctane.
- Sonicating appropriate concentration of urea in water.
- Sonicating AOT solution and urea solution.

Instruments

Dynamic Light Scattering (DLS)
- Calibrating at 25°C and equilibrating 180 seconds.
- 5 measurements per sample with 12 runs per measurements.
- Measuring size of nano-size samples.

Fluorescence spectroscopy
- Exciting at 450nm at 0.5 nm band width.
- Emitted at 600 nm at 1nm bandwidth.
- Sonicating reverse micelles in evaporated Coumarin-343 vials to insert probe molecule.

Red Edge Emission Spectroscopy
- Exciting samples from 400 to 450 nm, step of 10 nm.
- Samples emitted from 460 to 560 nm, step of 1 nm.
- 5 scans per sample.

Results

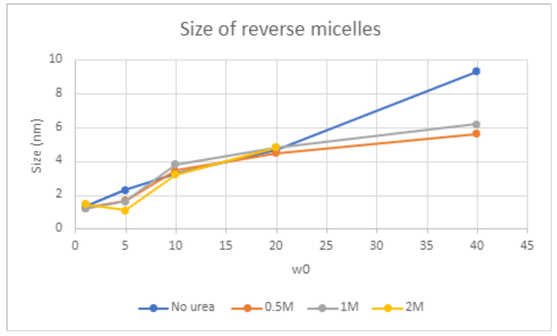


Figure 1: Size of reverse micelles at different urea concentrations

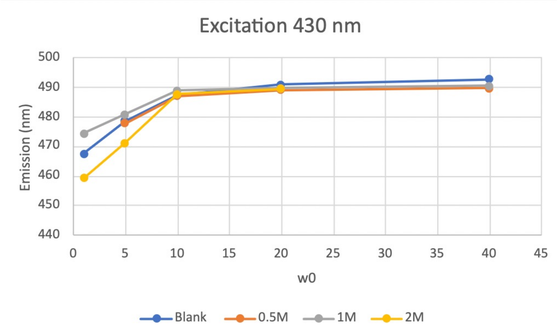


Figure 2: Emission of different w0 reverse micelles after exciting at 430nm

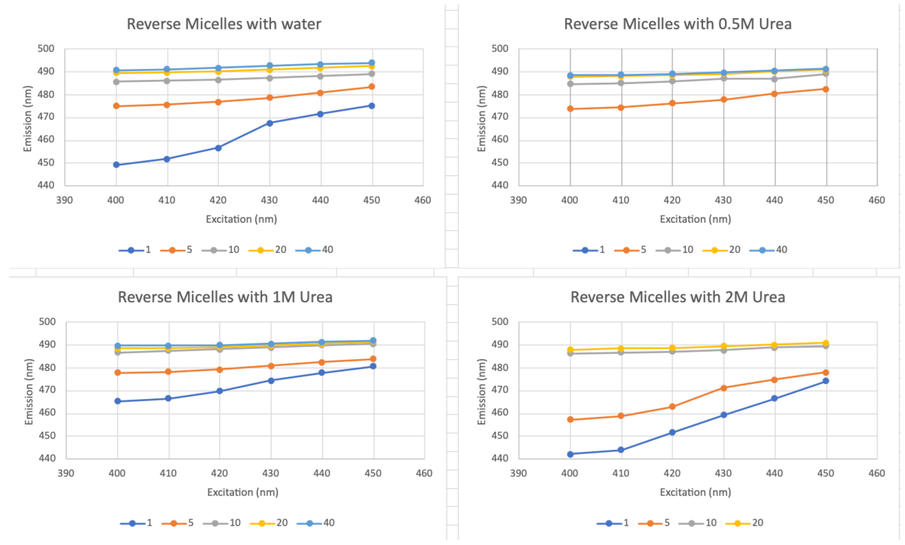


Figure 3: Emission of reverse micelles of different urea concentration

Discussion

Size Trend
- Size of reverse micelle model and w_0 has a linear relationship.
- For small w_0, under 20, size of samples with urea is similar to water reverse micelle samples, which indicates that the impact of osmolytes on size for small reverse micelles is not significant.
- For w_0 = 40, size of water reverse micelles is noticeably larger than urea reverse micelles. With larger reverse micelles, impact of urea on hydrogen bond is measurable.

Red-Edge Emission Spectroscopy
- When excitation is red-edge shifted, we see the bigger impact on emission for smaller reverse micelles.
- The emission is blue-shifted for small w_0 compared to large w_0.

Further Studies

- Perform fluorescence experiment using plate reader instrumentation (microscopic sample size) and compare to traditional fluorescence measurement (macroscopic sample size).
- Run NMR experiments to learn more about proton interaction between different molecules in a sample.
- Analyze Time-Resolved Emission Spectroscopy.

Acknowledgements

- This material is based upon work supported by the National Science Foundation under Grant No. 1956198 and 1956323. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.
- Thank you to Professor Bridget Gourley, PhD for her mentorship and support.
- Thank you to Professor Nancy Levinger, PhD, Colorado State University for her meaningful conversations and support.
- Thank you to Yayo Virgen, graduate student at Colorado State University, for his mentorship and guidance.
- Thank you to Department of Chemistry and BioChemistry, DePauw University and Department of Chemistry, Colorado State University for the use of facilities and materials.
- Thank you to the “DePauw University J. William Asher and Melanie J. Norton Endowed Fund in the Sciences”.

References

Nonaqueous Polar Solvents in Reverse Micelle Systems
N. Mariano Correa, Juana J. Silber, Ruth E. Riter, and Nancy E. Levinger
Chemical Reviews **2012** *112* (8), 4569-4602
DOI: 10.1021/cr200254q