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Probe Location within Interfacial Layer of CTAB Reverse Micelle System

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Probe Location within Interfacial Layer of CTAB Reverse Micelle System

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Abstract

To understand the chemistry of the interfacial region of reverse micelles (RM), we studied RM system made with the cationic surfactant cetyltrimethylammonium bromide (CTAB), alkanol co-surfactants dissolved in cyclohexane with water core. Spectroscopic methods, specifically UV-Vis absorption of Coumarin 343 (C343) as a probe molecule, were used to determine basic properties of RM systems. However, the probe location was difficult to determine because the spectrum (absorbance), when dissolved in RM solution, didn't match the spectra in any of the pure components. Our data suggests that the interfacial layer of RM cannot be thought of behaving only the characteristic of single one of the components; rather, it behaves as a mixture of multiple components with unique characteristics. The interfacial layer appears to have roughly three distinct regions. By combining two components at a time, our data shows that C343 is most likely to reside in the middle or outer interfacial regions, which is surprising because C343 is polar enough that it would be expect to preferentially migrate into the water core.

CTAB Reverse Micelle

- Polar Core: water
- Surfactant: Cetyltrimethylammonium Bromide (CTAB)
- Co-surfactant: alkanol
- Probe (dye): Coumarin 343
  - Shows λ_{max} at 426nm in water
  - Shows λ_{max} at 444nm in 1-hexanol
  - Shows λ_{max} at 447nm in 1-octanol
  - Shows λ_{max} at 445nm in 1-decanol
  - Shows λ_{max} at 430nm in cyclohexane
- Nonpolar solvent: cyclohexane/isooctane
  - Monomer C343 in cyclohexane absorbs at 405nm while dimer C343 in cyclohexane absorbs at 425nm (Correa 13052).

Topic Focus

- How does w_0 value (size of reverse micelle) affect the wavelength of maximum absorption in CTAB RM

$$w_0 = \frac{[\text{water}]}{[\text{surfactant}]}$$

- How does co-surfactants affect the wavelength of maximum absorption in CTAB RM
- How does solvents affect the wavelength of maximum absorption in CTAB RM
- The exact probe location in CTAB RM

Methods

- **Sample preparation:** 25 mL samples were made volumetrically with 0.1 M CTAB in cyclohexane, a co-surfactant to surfactant ratio of 5 to 1 and enough water to achieve the desired w_0. CTAB, co-surfactant, water and half of the cyclohexane were sonicated until the solution was clear. The rest of the needed cyclohexane was added. The final solution was sonicated for at least 30 minutes until visually clear.
- **UV-Vis Spectroscopy:** UV-vis absorption of Coumarin 343 was specifically used in the experiments. C343 shows different absorbance in different environments (solvents). Measuring absorbance of C343 in CTAB reverse micelle system could indicate the location of the C343, but also demonstrated a new perspective of interfacial layer of reverse micelle.

Results

The figures below represent the absorbance of C343 in a variety of CTAB RM systems (Figure 1, 2 and 3).

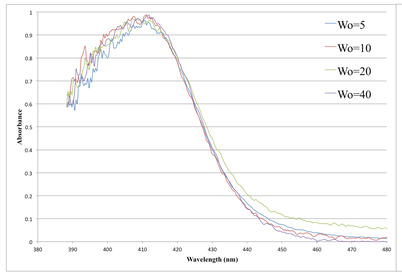

Figure 1. Normalized Absorbance of C343 in RM with 1-hexanol as Co-Surfactant in Different w_0 Values

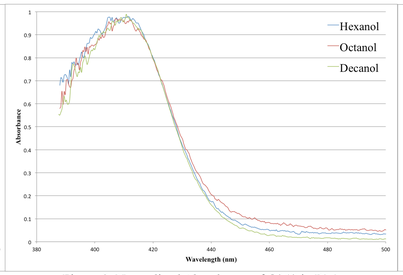

Figure 2. Normalized Absorbance of C343 in RM Cyclohexane as Solvent with Different Co-Surfactants (w_0=20)

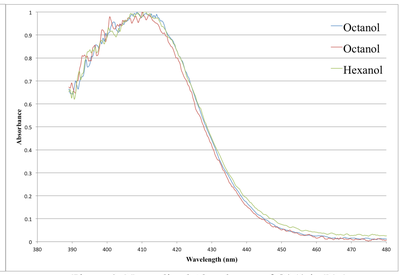

Figure 3. Normalized Absorbance of C343 in RM Isooctane as Solvent with Different Co-surfactants (W_0=20)

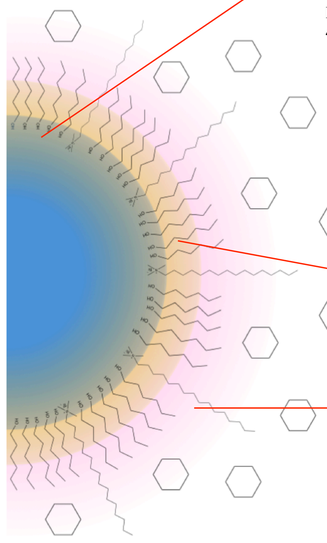

Figure 4. CTAB Reverse Micelle Interfacial Layers

Inner Region: contains water, surfactant, and co-surfactant. To mimic the isolated inner region, solutions with the absorbance of C343 was measured in a solution with only water, surfactant and co-surfactant in the same ratios as found in the RM, shown in Figure 5 below. C343 demonstrates an absorbance λ_{max} value at 421nm.

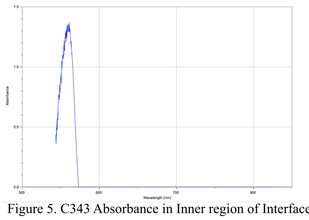

Figure 5. C343 Absorbance in Inner region of Interface

Middle Region: contains mainly surfactant and co-surfactant. The absorption spectrum of C343 dissolved in a solution of exclusive surfactant and co-surfactant in the same ratio found in RM is show in Figure 6. It demonstrates an absorbance λ_{max} value at 408nm.

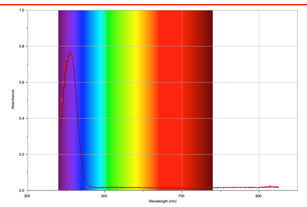

Figure 6. C343 Absorbance in Middle Region of Interface

Interesting fact: The λ_{max} value for C343 shows a hypochromic shift when comparing the absorbance between water and RM. The RM solutions were made by first dissolving C343 water and then adding that solution to the other materials. Because C343 is polar, we anticipated it would stay in the water. However, the spectrum of C343 in RM shifts and shows absorbance λ_{max} value at 407nm, which suggests C343 migrates from water core to middle or outer region of interfacial layer, spectra shown below in Figure 8.

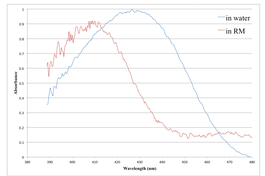

Figure 8. Normalized C343 Absorbance in Water then RM

Outer Region: contains surfactant, so-surfactant, and cyclohexane. The absorption spectrum of C343 dissolved in a solution of surfactant, co-surfactant and cyclohexane in similar proportion to those found in RM is shown in Figure 7. C343 shows an absorbance λ_{max} value at 408nm

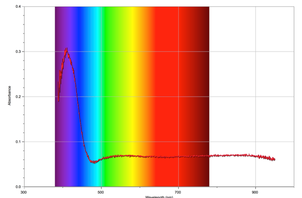

Figure 7. C343 Absorbance in Outer Region of Interface

Conclusions

- w_0 value doesn't affect the absorbance of C343 in CTAB reverse micelle system.
- Co-surfactant, alkanols with different length chain, don't affect the absorbance of the C343 in CTAB reverse micelle system.
- Solvent doesn't affect the absorbance of C343 in CTAB reverse micelle system
- Our data supports a conclusion that the probe molecule, C343, more likely resides in middle and outer regions of the interface despite anticipating it would prefer to remain in the water layer because of the similar polarity
- Cholesterol doesn't dissolve in cyclohexane after 30 minutes of sonication at room temperature.

Future Works

- Find a way to isolate and store the interfacial layer of CTAB RM system.
- Test the basic properties of isolated interface.
  - How and why the interfacial layer of reverse micelle behaves differently to pure components?
  - How different ratios of [surfactant] to [co-surfactant] alter the property of interface?
- Use other potential probe molecules to investigate the interfacial layer.
  - Reichardt's Dye (B30) seems like a potential candidate because its absorbance spectra is highly sensitive to solvent polarity.
- As the major component in on cellular membranes, cholesterol presents an interesting a co-surfactant in CTAB reverse micelle to investigate.

Acknowledgement

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