Prelab 6: Determination of the Mean Aggregation Number of a Micellar System

Introduction
The purpose of this lab is to find the mean aggregation number, N, of sodium dodecyl sulfate within micelles in aqueous solution. Usually, hydrocarbons have low solubilities in water because they cannot undergo hydrogen bonding. If a molecule is amphiphilic like sodium dodecyl sulfate (SDS), then it has both hydrophilic and hydrophobic properties and can undergo hydrogen bonding. When enough SDS is dissolved in water surface tension decreases, and the solubility of the hydrocarbon increases. This occurs when the critical micelle concentration (CMC) is reached. The monomers undergo self-organization to form micelles, colloidal dispersion of organized surfactant molecules. Their interiors consist of a hydrocarbon chain structure, and their exteriors have polar, ionic structures. A micelle is constructed of a number of surfactant molecules, the aggregation number N. The value of N depends on the type of surfactant, temperature, and electrolyte concentration.

If the assumption that surfactant molecules are present as either monomeric units or micelles that have N monomers, there will be a concentration \([M]\) that is expressed as:

\[ [M] = ([S]_o - \text{CMC})/N \]

where CMC is the concentration of free monomers in solution, \(N\) is the mean aggregation number, and \([M]\) is the average micelle concentration. To find \(N\) using a fluorimeter, the following assumptions must be made: a luminescent probe molecule is added to the micellar system and that there are many more micelles present than probe molecules. If a luminescence quencher is added to the system the following assumptions must also be made: the quencher is associated with micelles only, the solubilized quencher occupy micelles randomly, and the probe will not luminesce if it shares a micelle with another quencher. Because the micelle is constantly exchanging monomers with solvent, the probe must determine the aggregate number at a time less than the time it takes for a micelle to undergo exchange. The ratio of the luminescence intensity, \(I\), of a quencher molecule to that with no quencher present, \(I^0\) is equal to the fraction of probe containing micelles that do not have a quencher molecule.

The randomness of a quencher to be placed in a micelle can be described by the following equation:

\[ P_n = \langle q^n \rangle \exp(-\langle q \rangle)/n! \]

And \(\langle q \rangle\) is the probability that a micelle has at least one quencher. On a larger scale, \(\langle q \rangle = [Q]/[M]\), with \([Q]\) as the bulk quencher and \([M]\) as the micelle concentration. The probability of a micelle with no quencher is described by this equation:

\[ P_n = \exp(-\langle q \rangle) = \exp(-[Q]/[M]) \]

Because luminescence is produced, then:

\[ I/I^0 = \exp(-[Q]/[M]) \]

And finally:

\[ \ln(I/I^0) = [Q]N/([S]_o - \text{CMC}) \]

This equation can be used to determine \(N\) and \(\text{CMC}\), depending on which variable (either \([Q]\) or \([S]\)) is fixed.

Experiment
A Perkin Elmer LS-5B fluorimeter will be used for this experiment. The probe molecule is Ru(bipy)$_2$Cl$_2$ and the quencher is 9-methyl anthracene. In the first part of the experiment, the surfactant concentration is fixed. The probe concentration should not exceed 7.2 * 10$^{-10}$ M. Two 50 ml solutions of 0.045 M in SDS should be made. Dissolve the solute in water. Fill one volumetric flask. Make 5 ml of 0.15 solution of the quencher and inject into the other SDS solution. Solutions will be prepared by varying the amounts of quencher in the experiment, from 0 to 100%. The luminescence will be measured by the fluorimeter at an excitation of 450 nm and a wavelength of 625 nm. The second part of the experiment is about the same except that the surfactant concentration is varied. For all solutions, the luminescence intensity is measured at 625 nm.

Error

If someone touches one of the optical faces, the fluorimeter will show that more light has been absorbed when this is not the case. Also error can arise from trying to measure such small concentrations. Too much ethanol might hinder the solubility of the quencher. All glassware should be clean so that no unwanted particles affect absorbance.
Experiment 6: Determination of the Mean Aggregation Number of a Micellar System

Abstract

The purpose of this lab is to find the critical micelle concentration (CMC), which is the concentration of bulk surfactant molecules that allows the bulk solution properties of amphiphilic molecules to change, and the aggregation number N, which is the definite number of surfactant molecules that comprise a micelle. This was done by making solutions that first varied in the concentration of quencher (9-methylanthracene) and then making solutions that varied in surfactant (sodium dodecyl sulfate, SDS) concentration. The probe in the experiment was (Ru(bipy)_3)_2^{2+}. Luminescence intensities I/T were measured with a Perkin-Elmer LS-5B luminescence spectrophotometer (fluorimeter). The values of N and CMC were found from the slope and intercept of a linear least squares fit.

Theory

Normally hydrocarbons are insoluble in water because they do not have the polarity to participate in hydrogen bonding. However, if these hydrocarbons are amphiphilic molecules then they can become soluble. These molecules can function as surfactants because they can change the properties of water. If enough of these surfactant molecules are dissolved in water they can change the properties of water greatly and increase the ability of hydrocarbons that dissolve in water. The concentration at this level is the critical micelle concentration (CMC). Micelles are aggregates of monomers that undergo self-organization to form these structures. The number of molecules that form the micelles is the aggregation number N.

The value of CMC and N are determined indirectly by use of the fluorimeter. In order for this technique to work, several assumptions must be made:
1) Because the luminescent probe is added to the micellar system, the luminescence intensity of the system is proportional to the fraction of “tagged” micelles
2) There are more micelles present than molecules with the luminescent probe.

When the quencher is added to the system, it removes photoexcitation energy from the probe so it does not luminesce after it absorbs light; therefore, it can also be assumed that the quencher is only associated with micelles, and that they occupy the micelles randomly. If a probe shares a micelle with a quencher, it will not luminesce.

The luminescence intensity is proportional to the number of micelles that are occupied by a probe molecule with no quencher. If the amount of quencher is increased, then it should be expected that intensity decreases, and if the amount of quencher is decreased, then the opposite effect would occur.

Experimental

A Perkin-Elmer LS-5B fluorimeter was used. The surfactant in this experiment was sodium dodecyl sulfate, or SDS. The probe in this experiment was Ru(bipy)_3^{2+} and
the quencher was 9-methylantracene. For the first part of the experiment, the concentration of the surfactant was fixed. Six samples were prepared with quencher concentrations that varied from 0 to 100%. The luminescence of each solution was measured by the fluorimeter at excitation and wavelengths of 450 and 625 respectively. In the second part of the experiment, the concentration of the surfactant was varied. With that exception only, the procedure for the first part was identical for the second. For both parts of the experiment, concentration of the probe remained at 7*10⁻⁵ M.

Data
Part I

<table>
<thead>
<tr>
<th>Amount of quencher (ml)</th>
<th>Concentration (M)</th>
<th>Intensity</th>
<th>Absorbance</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>82.0</td>
<td>1.2002</td>
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<tr>
<td></td>
<td></td>
<td>81.5</td>
<td></td>
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<tr>
<td>2 +/- 0.1</td>
<td>(1.2 +/- 0.02)*10⁻⁶</td>
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<td>69.8</td>
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<tr>
<td>4 +/- 0.1</td>
<td>(2.4 +/- 0.03)*10⁻⁶</td>
<td>63.9</td>
<td>1.1859</td>
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<td>64.5</td>
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<td>1.2800</td>
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<td>53.3</td>
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<tr>
<td>8 +/- 0.1</td>
<td>(4.8 +/- 0.6)*10⁻⁶</td>
<td>46.1</td>
<td>1.2805</td>
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<tr>
<td>10 +/- 1</td>
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<td>1.2805</td>
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Part II

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<th>Intensity</th>
<th>Absorbance</th>
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<td>1.2805</td>
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<td>41.0</td>
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<td>65.6</td>
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<td>74.8</td>
<td>0.8877</td>
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</table>

¹Mean Aggregation Number N: 66.2 ± 7
Standard Value: 60.2 +/- 2

Critical Micelle Concentration, CMC: \(5.2 \times 10^{-4}\)
Standard Value: \(8.2 \times 10^{-3}\)

Temperature: 298.15 K

Discussion and Conclusion
According to the data, it seems that was expected to happen actually happened. With the increase in quencher concentration, there was less intensity as there were more quenchers to share a micelle with a probe, thus decreasing luminescence. When the concentration of surfactant was increased, the opposite effect occurred because the number of micelles increased, thus reducing the possibility that a micelle would have both a probe and a quencher. When a micelle contains a nonpolar molecule, the concentration of that molecule in the micelle is much higher than its concentration in solution.

Several steps were taken to calculate the values for N and CMC. First, because the error from transferring 200 and 100 μl in the first and second parts of the lab was so small that it was decided that this was negligible. However, errors in transferring volumes in milliliters were calculated. Errors in concentrations that were constant were not considered. To determine N and CMC, the method of least squares fit was used. The values from the first part of the lab (fixed surfactant concentration) were used to determine the values. The concentration of 9-methylanthracene was made by diluting the solution from the first part of the lab with 2.5 ml of ethanol. By using the values from this part of the lab would have led to more error. The value for N was found by letting B = 1/N when using the least squares method. N was found to be 66.2. The standard value is 60 +/- 2. This value was used to CMC. This was done by choosing one of the trials and assigning values of [S] and [Q] with N. The value for CMC was found to be \(5.2 \times 10^{-4}\). The standard value is \(8.2 \times 10^{-3}\). The temperature of the micellar system was the same as normal room temperature. The graph was created by using the data from part 2 of the experiment. This was done to comply with the graph by Turro and Yejkla. The first value for the intensity was used.

Questions: At the end of the lab report

Error
Much of the error can definitely be attributed to the transference of solutions to vary concentrations. The concentrations can be altered if solutions of one concentration come in contact with solutions of other concentrations. If the concentrations are not correct, the experiment can give some seriously erroneous results. Errors also can arise when making the surfactant and quencher concentration (i.e. weighing the solutes or not adding the right amount of solvent).

\(^2\)Ibid.
Calculations

Quencher concentration varied (fixed substrate)

\[ 0.15 \text{ mol} \times 0.000003 = (\text{negligible error}) = 3 \times 10^{-7} \text{ mol} \]

\[ 3 \times 10^{-7} \text{ mol} \times 0.050 (\pm 0.001 \text{ L}) = 6 \times 10^{-6} \pm 0.001 \]

\[ \frac{0.083}{0.050} = 0.001 \]

\[ (6 \times 10^{-6})(0.050) = 1.2 \times 10^{-7} \]

\[ 6 \times 10^{-6} (\pm 0.1 \times 10^{-6} \text{ mol L}^{-1}) \]

\[ (0.08 \pm 0.01 \text{ L})\times (0.002 \pm 0.0001 \text{ L}) \text{ error in quencher addition} \]

\[ 1.2 \times 10^{-8} \text{ mol} \]

\[ \frac{0.1 \times 10^{-4}}{6 \times 10^{-6}} = 2\% \]

\[ \frac{0.001}{0.002} = 5\% \]

\[ 2\% + 5\% = 7\% \]

\[ 1.2 \times 10^{-8} \text{ mol L}^{-1} (0.071) = 8.4 \times 10^{-10} \]

\[ 1.2 \times 10^{-8} (\pm 0.08 \times 10^{-8} \text{ mol}) \]

\[ 0.010 (\pm 0.001) \text{ L} \]

\[ \frac{0.08 \times 10^{-8} \text{ mol L}^{-1}}{1.2 \times 10^{-8} \text{ mol}} = 6\% \]

\[ \frac{0.001}{0.010} = 10\% \]

\[ 1.8 \times 10^{-6} \pm 0.02 \times 10^{-6} \text{ mol L}^{-1} \]

\[ 1.2 \times 10^{-8} (0.016) = 14.2 \times 10^{-4} \]

4 mL Quencher

\[ (6 \times 10^{-6} \pm 0.1 \times 10^{-6} \text{ mol L}^{-1})(0.004 \pm 0.0001 \text{ L}) \]

\[ 2\% \]

\[ \frac{1000}{1000} = 3\% \]

\[ 2\% + 3\% = 5\% \]

\[ 2.4 \times 10^{-8} \text{ mol L}^{-1} (0.05) = 1.2 \times 10^{-10} \]

\[ 2.4 \times 10^{-8} \pm 0.05 \times 10^{-8} \text{ mol} \]

\[ 0.010 (\pm 0.001) \text{ L} \]

\[ 2.4 \times 10^{-8} \pm 0.05 \times 10^{-8} \text{ mol} \]

\[ 0.05 \times 0.001 \text{ L} = 2.4 \times 10^{-10} \]

\[ 0.05 \text{ L} \]

\[ 0.05 \times 10^{-8} \text{ mol} \]

\[ 0.05 \times 0.001 \text{ L} \]

\[ 2.4 \times 10^{-10} \pm 0.03 \times 10^{-10} \text{ mol L}^{-1} \]

6 mL Quencher

\[ (6 \times 10^{-6} \pm 0.1 \times 10^{-6} \text{ mol L}^{-1})(0.004 \pm 0.0001 \text{ L}) \]

\[ 3.6 \times 10^{-8} \text{ mol} \]

\[ 2\% \]

\[ \frac{0.001}{0.002} = 2\% \]

\[ 2\% + 4\% = 6\% \]

\[ 3.6 \times 10^{-8} \text{ mol L}^{-1} \]

\[ 0.010 (\pm 0.001 \text{ L}) \]

\[ 3.6 \times 10^{-8} \text{ mol} \]

\[ 0.010 (\pm 0.001 \text{ L}) \]

\[ 3.6 \times 10^{-8} \text{ mol} \]

\[ 0.010 (\pm 0.001 \text{ L}) \]

\[ 3.6 \times 10^{-8} \pm 0.05 \times 10^{-10} \text{ mol L}^{-1} \]

\[ (3.6 \times 10^{-8})(0.013) = 4.8 \times 10^{-8} \text{ mol} \]

\[ 2\% + 1\% = 3\% \]

\[ 3\% + 10\% = 13\% \]

8 mL Quencher

\[ (6 \times 10^{-6} \pm 0.1 \times 10^{-6} \text{ mol L}^{-1})(0.008 \pm 0.0001 \text{ L}) = 4.8 \times 10^{-6} \text{ mol} \]

\[ 2\% + (2\% \times 10^{-10} \text{ mol}) = 4.8 \times 10^{-6} \pm 0.1 \times 10^{-6} \text{ mol} \]

\[ 4.8 \times 10^{-6} \text{ mol L}^{-1} \]

\[ 0.010 (\pm 0.001 \text{ L}) \]

\[ 4.8 \times 10^{-6} \text{ mol L}^{-1} \]

\[ 0.010 (\pm 0.001 \text{ L}) \]

\[ 4.8 \times 10^{-6} \pm 0.0 \times 10^{-9} \text{ mol L}^{-1} \]
**Surfactant Concentration (Fixed [Q])**

\[ 1 \times 10^{-5} \text{ mol L}^{-1} (0.001 \pm 0.0001 \text{ mol L}^{-1}) \]

\[ 1 \times 10^{-5} + 0.0001 + 0.0001 = 3 \times 10^{-5} \text{ mol L}^{-1} \]

\[ 1 \times 10^{-5} + 0.2 \times 10^{-5} \text{ mol L}^{-1} \]

\[ 1 \times 10^{-3} \times 0.2 = 2 \times 10^{-3} \text{ mol L}^{-1} \]

\[ 1 \times 10^{-3} \pm 0.3 \times 10^{-5} \text{ mol L}^{-1} \]

2 mL Surfactant

\[ (0.001 \pm 0.0001 \text{ mol L}^{-1})(0.002 \pm 0.0001 \text{ L}) \]

\[ 2 \times 10^{-5} + 10 \% + 5 \% = 15 \% \]

\[ 2 \times 10^{-5} \times 0.15 = 3 \times 10^{-6} \text{ mol} \]

\[ 2 \times 10^{-5} \pm 0.3 \times 10^{-5} \text{ mol L}^{-1} \]

4 mL Surfactant

\[ (0.001 \pm 0.0001 \text{ mol L}^{-1})(0.004 \pm 0.0001 \text{ L}) \]

\[ 4 \times 10^{-5} \to 10 \% + 3 \% = 13 \% \]

\[ 4 \times 10^{-5} \times 0.13 = 5 \times 10^{-6} \text{ mol} \]

\[ 4 \times 10^{-5} \pm 0.5 \times 10^{-5} \text{ mol L}^{-1} \]

6 mL Surfactant

\[ (0.001 \pm 0.0001 \text{ mol L}^{-1})(0.006 \pm 0.0001 \text{ L}) \]

\[ 6 \times 10^{-5} \to 10 \% + 2 \% = 12 \% \]

\[ 6 \times 10^{-5} \pm 0.7 \times 10^{-5} \text{ mol L}^{-1} \]

\[ 0.010 \pm 0.001 \text{ L} \]

\[ 6 \times 10^{-5} \to 10 \% + 10 \% = 20 \% \]

\[ 6 \times 10^{-5} \pm 0.7 \times 10^{-5} \text{ mol L}^{-1} \]

8 mL Surfactant

\[ (0.001 \pm 0.0001 \text{ mol L}^{-1})(0.008 \pm 0.0001 \text{ L}) = 8 \times 10^{-5} \text{ mol L}^{-1} \]

\[ 8 \times 10^{-5} \pm 0.9 \times 10^{-5} \text{ mol L}^{-1} \]

\[ 8 \times 10^{-5} \pm 0.9 \times 10^{-5} \text{ mol L}^{-1} \]

\[ 8 \times 10^{-5} \pm 0.9 \times 10^{-5} \text{ mol L}^{-1} \]

Where are calculations for N77/2 relevant?
Calculations (continued)

Least squares fit using fixed surfactant concentration

\[ \ln \left( \frac{I_{0}/I}{1} \right) = (\text{[Q]} \text{N})^{-1} [S_0] - (\text{[Q]} \text{N})^{-1} \text{CMC} \]

**Trial**

1 (2 mL) 37500
2 (2 mL) 18600
3 (4 mL) 12500
4 (8 mL) 9400
5 (8 mL) 7500

\[ v = \frac{[S_0]}{[Q]} \]

**?**

\[ y = \left( \frac{\ln(10/2)}{0.037} \right) x = 0.927 \pm 0.02 \]

\[ 4.13 \pm 0.08 \rightarrow 4.1 \pm 0.1 \]

\[ 2.36 \pm 0.06 \]

1.74

\[ \text{not CS:1/2} \]

Plots:

\[ \text{CS:0.75, 1.44 \pm 0.05} \]

Intensity: 6.44 + 6.98 = 69.7

\[ \text{Error} = \sigma_x = \sigma_{x/NN} = 0.0244 \]

\[ \text{Intensity: } \frac{63.9 + 64.2}{2} = 64.1 \]

\[ \sum d_i = -0.3 = 0 \]

\[ \sigma_x = \sqrt{\frac{0.18}{5}} = 0.1877 \]

\[ \text{Intensity: } \frac{53.6 + 53.3}{2} = 53.5 \]

\[ \sum d_i = 0.25 (-0.25) \]

\[ \sigma_x = \frac{0.158}{5} = 0.06 \]

\[ \frac{\sigma_x}{\sqrt{ nn}} = 0.06 \]

\[ \text{Intensity: } \frac{40.6 + 41.0}{2} = 40.8 \]

\[ \sigma_x = 0.13 \pm 0.04 \]

\[ \frac{\sigma_x}{\sqrt{ nn}} = 0.05 \]
\[ y = A + Bx \]
\[ B = \frac{1}{N} \sum (x - \bar{x})^2 \]
\[ \Delta = N \sum x^2 - \sum x \]

\[ \sum xy = \frac{1235125 \pm 750}{2ml} \]
\[ (37500)(6.27) = (235125)(0.003) \]
\[ 235100 \pm 800 \]
\[ 77644 \pm 1893.75 \]
\[ 77644 \pm 2000 \]
\[ 78000 \pm 2000 \]
\[ \sum x = 85700 \]
\[ \sum y = 15.94 \]
\[ \sum dy = 0.23 \]
\[ 5018810000 \]
Finding CMC

Using trial 5 (8 mL)

\[ \ln \left( \frac{I^0/I} {I} \right) = \left( [Q] N \right)^2 \frac{[S_0]} {([Q] N)^{-1} CMC} \]

\[ 1.74 = \left( [4.8 \times 10^{-6} \pm 0.16 \times 10^{-6}] [64.20] \right)^{-1} [0.045] - \left( [4.8 \times 10^{-6} \pm 0.16 \times 10^{-6}] [64.20] \right)^{-1} CMC \]

\[ 0.00031776 \quad \frac{2.9}{4.8} = 2.0 \% \quad 0.0020 \quad 0.02 \quad \Rightarrow \]

\[ 1.74 = (0.03 \pm 0.01)(0.045) - (0.03 \pm 0.01)(MC) \]

\[ 1.74 = (0.00135 \pm 0.001483) \]

\[ 1.73845 \pm 0.001483 CMC \]

\[ 0.032159 \pm 0.001483 CMC \]

\[ 1.74 \] (OK)

Questions:

2) \[ [M] = ([S] - CMC) / N \]

\[ \left( 8 \times 10^{-2} M - 6 \times 10^{-3} M \right) / 70 \]

\[ [M] = 0.0010571 \mathrm{M} \] and \[ [M] = 1 \times 10^{-3} \mathrm{M} \] (check)

3) n-hexane

C-C-C-C-C-C, \[ \text{C}_{6} \text{H}_{14} \]

\[ 12(6) + 14 = 86 \]

\[ 0.39 \times 1 \text{ mol} / 86 \text{ g} = 0.0045 \text{ mol} \]

\[ 0.0045 \times 84.84 \text{ g/mol} = 0.3848844 \text{ mol} \]

\[ 0.005 \rightarrow 4.25 \text{ L} \text{ n-hexane} \]

The mean occupation \# of n-hexane is 3, because for every 0.005 mol of n-hexane, there is only 0.001 mol of micelle. For every micelle, either 1, 2, 3, 4 or 5 mol of n-hexane can fit inside. The probability for a micelle to have at least 1 mol of n-hexane is 108%.

\[ P_n = \frac{n^e}{n!} \rightarrow 1 = \frac{n^e}{n!} \]

\[ n! = e^e \]

\[ n! = .36787944 \]