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Prelab Experiment 6: Mean Aggregation Number of a Micellar System

Introduction

Hydrocarbons have low solubilities in water because they cannot disrupt and participate in the hydrogen bonding within the water. The incompatibility of hydrophobic and hydrophilic properties can be overcome if a molecule possesses both hydrophobic and hydrophilic properties. Such molecules can act as surfactants in that they change the bulk properties of water. One such molecule is sodium dodecyl sulfate (SDS, $\text{Na}^+ \text{OSO}_3\text{C}_{12}\text{H}_{25}$). The long hydrocarbon chain is the hydrophobic part and the OSO_3Na^+ is the ionic portion. The surface tension of the water decreases while the solubility of the hydrocarbons increases. These properties occur at a certain concentration of SDS, called the critical micelle concentration (CMC). A micelle is an organized cluster consisting of about 60-120 monomers for SDS. Micelles are spherical in shape and are a colloidal dispersion of organized surfactant molecules with an interior arrangement of the hydrocarbon chain structure and an exterior of the ionic portion. The mean aggregation number (N), i.e. the average number of SDS molecules per micelle, will be determined experimentally. The value of N is not only dependent on the nature of the surfactant but also on the temperature and electrolyte concentration in an aqueous solution.

The following expression can be written describing such a system:

$$\{M\} = (\{S\}_0 - \text{CMC}) / N$$

where $\{S\}_0$ is the surface concentration and is above the CMC, the CMC is the concentration of free monomers in solution, and $\{M\}$ is the concentration of micelles containing N monomers. It should be noted that micellar solutions are not static and that there is constant reorganization and monomer transfer between the solution and the micelles. Therefore N represents the mean aggregation number and $\{M\}$ represents an average micelle concentration.

In this experiment, the average value of N will be determined by the use of a luminescence quenching technique. A luminescent probe, $\text{Ru}(\text{bpy})_3^{2+}$ will be added to the solution. Each probe molecule is assumed to be associated with one and only one micelle. The concentration of $\text{Ru}(\text{bpy})_3^{2+}$ is much less than micelles. A luminescence quencher is added to the system at various concentrations. It is also assumed the quencher is only associated with micelles and not solvated in the aqueous solution. Micelle quenchers associate randomly whether they have a probe molecule or not. A micelle with a probe molecule and a quencher will not luminesce. The lifetime of $\text{Ru}(\text{bpy})_3^{2+}$ is $\sim 770\text{ns}$ which is much faster than the micelle reorganization time which is on the order of 1-10ms. The luminescence intensity is proportional to the number of micelles with a probe molecule and no quencher.

The statistics of the experiments is governed by the Poisson distribution. The probability of finding n quenchers (q) in a selected micelle (m) is given by

$$P_n = \frac{\langle q \rangle^n \exp(-\langle q \rangle)}{n!}$$

$$\text{where } \langle q \rangle = q/m = \{Q\}/\{M\}$$

The probability, then, that a micelle contains no quencher and a probe -- i.e. the luminescing micelle is equation 2 with $n=0$:

$$P_0 = \exp(-\langle q \rangle) = \exp(-\{Q\}/\{M\})$$

The ratio of the intensity of the luminescence with quencher and without quencher can then be related by

$$I/I^0 = \exp(-\{Q\}/\{M\})$$

Combining this equation with 1 gives the following expression with which we can determine N

$$\ln(I^0/I) = \{Q\}N / (\{S\}_0 - \text{CMC})$$

If Q is varied and S is constant, then a linear least squares fit can be used to obtain N. Also, if Q is constant and S is varied, we can find both N and the CMC values from a simple linear fit.

Experimental

The experiment will consist of two parts: the first will be with a fixed SDS concentration and the second part will be a fixed quencher concentration. The quencher will be 9-methylanthracene. Fluorescence measurements will be made with a Perkin-Elmer LS-5B luminescence spectrophotometer. The luminescence probe will be the water soluble Ru(bpy)₃Cl₂. 9-methyl anthracene is ordinarily not soluble in water but the SDS surfactant enables it to dissolve.

For the first part of the experiment, the SDS will remain at a constant concentration and the quencher will be varied for each sample. An aqueous solution of Ru(bpy)₃Cl₂ not to exceed 7.2 x 10⁻⁵ M will be prepared from a 7 x 10⁻³ M stock solution. Two 0.045 M SDS solutions and a 0.15 M 9-methylanthracene (in ethanol) solution will also be prepared. 200 μL of the quencher stock solution will be injected into one of the two SDS solutions. The two SDS solutions will be combined such that there are six solutions with quencher concentrations ranging from 0-100%, all with constant SDS concentrations. 100 μL of Ru(bpy)₃Cl₂ solution will then be added to all solutions.

The absorbance of every solution will be checked on a Cary 219 UV-Vis spectrophotometer, and it should be the same for each sample. Emission will then be monitored for each sample (λ_{ex} = 450 nm, λ_{em} = 625 nm). All spectroscopic measurements will be made using the same face of a polystyrene cuvette. The ambient temperature of the solutions should be noted.

The second part of the experiment will be similar to the first except now the quencher is constant and the SDS is varied. The quencher stock will be 0.050 M 9-methylanthracene in ethanol. One SDS stock will be 0.01 M and one will be 0.05 M. 100 μL of quencher stock will be injected into both SDS stock solutions. The two SDS solutions will be combined as before and 100 μL of Ru(bpy)₃²⁺ solution will be injected into each sample. Absorption and emission measurements on all samples will be taken as described.

Error Analysis

The most profound source of error in this experiment will likely come from human error in the making of the solutions. By using such equipment as correctly tared volumetric flasks and microliter pipettes, this error can be reduced. For all aqueous solutions, it will be important to use purified, deionized water. The use of ethanol in the quencher stock solution will provide a negligible, but present error. A change in absorbance from sample-to-sample of Ru(bpy)₃²⁺ will indicate the extent of the inconsistency of probe concentrations in the samples. When combined with the error in SDS and quencher concentrations, preparation will prove to be the most significant in the experimental error. Other systematic errors will include fluctuations in the fluorimeter light counts and Cary absorbance readings between identical samples. Using different sides of the cuvette may have an effect on absorbance so it will be important to mark a side of the cuvette and have that side in the same position in the Cary for all samples.

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Lab Experiment 6: Mean Aggregation Number of a Micellar System

I. Abstract

Aqueous solutions containing various concentrations of a surfactant, sodium dodecyl sulfate (SDS) and quencher, 9-methyl anthracene, were prepared. Equal amounts of $\text{Ru}(\text{bpy})_3^{2+}$ were injected into all solutions and the monochromatic absorbance ($\lambda = 450\text{nm}$) of each sample was measured. Steady state photoluminescence ($\lambda = 650\text{nm}$) measurements of $\text{Ru}(\text{bpy})_3^{2+}$ were recorded for all samples. One set of samples contained constant SDS concentration while the other contained constant quencher concentration. The concentration of free monomers in solution, CMC, and N , the mean aggregation number, were determined through graphical analysis. The experimental value for N was determined to be 1 and the value for CMC was found to be $0.007 \pm 0.001 \text{ M}$

35.5 ± 1.5 (pt. 1), 55 ± 6 (pt. 2)

II. Theory

The insolubility of hydrocarbons can be overcome with the addition of surfactants (surface-active agents). Surfactants such as SDS ($\text{NaOSO}_3\text{C}_{12}\text{H}_{25}$) act in a way to change the bulk properties of water. The long hydrocarbon chain is the hydrophobic part and the $\text{OSO}_3\text{-Na}^+$ is the ionic portion. The surface tension of the water decreases while the solubility of the hydrocarbons increases. These properties occur at a certain concentration of SDS, called the critical micelle concentration (CMC). A micelle is an organized cluster consisting of about 60-120 monomers for SDS. Micelles are spherical in shape and is a colloidal dispersion of organized surfactant molecules with an interior arrangement of the hydrocarbon chain structure and an exterior of the ionic portion. The mean aggregation number (N), is defined as the average number of SDS molecules per micelle. The value of N is not only dependent on the nature of the surfactant but also the temperature and electrolyte concentration in an aqueous solution.

III. Experimental

The experiment consisted of two parts: the first was with a fixed SDS concentration and the second part was a fixed quencher concentration. The quencher was 9-methylanthracene. Fluorescence measurements were made with a Perkin-Elmer LS-5B luminescence spectrophotometer. The luminescence probe was the water soluble $\text{Ru}(\text{bpy})_3\text{Cl}_2$. 9-methyl anthracene is ordinarily not soluble in water but the SDS surfactant enables it to dissolve.

For the first part of the experiment, the SDS remained at a constant concentration and the quencher was varied for each sample. An aqueous solution of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ at $7.2 \times 10^{-5} \text{ M}$ was prepared from a $7 \times 10^{-3} \text{ M}$ stock solution. Two 0.045 M SDS solutions and a 0.15 M 9-methylanthracene (in ethanol) solution were prepared. $200 \mu\text{L}$ of the quencher stock solution was injected into one of the two SDS solutions. The two SDS solutions were combined such that there were six solutions with quencher concentrations ranging from 0-100%, all with constant SDS concentrations. $100 \mu\text{L}$ of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ solution were added to all solutions.

The absorbance of every solution was checked on a Cary 219 UV-Vis spectrophotometer, and it was approximately the same for each sample. Emission was then monitored for each sample ($\lambda_{\text{ex}} = 450\text{nm}$, $\lambda_{\text{em}} = 625\text{nm}$). All spectroscopic measurements were made using the same face of a polystyrene cuvette. The ambient temperature of the solutions were noted at 298K .

The second part of the experiment is similar to the first except now the quencher is constant and the SDS is varied. The quencher stock was 0.050 M 9-methylanthracene in ethanol. One SDS stock was 0.01M and one was 0.05M. 100uL of quencher stock was injected into both SDS stock solutions. The two SDS solutions were combined as before and 100 uL of $\text{Ru}(\text{bpy})_3^{2+}$ solution was injected into each sample. Absorption and emission measurements on all samples were taken as described.

IV. Data (see attached charts and graphs)

V. Discussion/Conclusions

The mean aggregation number was found to be ~~35.5~~ ^{35.5} 1.5 in part one (constant {S}) and ~~34.9~~ ^{35.5} 1.5 in part two (constant {Q}) and the {CMC} was found to be .007 .001M. This is in good agreement with the values of Turro and Yekta. 85 ± 6

In part one, with the fixed surfactant concentration ($\{S\} = .045 \cdot 9.03 \times 10^{-4} \text{M}$), the quencher was varied and different emission spectra were taken. The quencher concentrations were plotted against the inverse natural logarithm of I_0/I and the plot was fitted to a straight line (see graphs). The plot did not follow the expected Stern-Volmer kinetics, in which a linear relation is observed when {Q} is plotted against I_0/I . The CMC was determined from part two and its value was used in part one to determine the mean aggregation number by the equation $N = m(\{S\} - \text{CMC})$, where m is the slope of the linear plot.

In part two, the quencher was fixed ($\{Q\} = 1.0 \cdot 11 \times 10^{-4}$), and the SDS concentration was varied. The {SDS} was plotted against $[\ln I_0/I] - 1$ as in part one and was fit linear. The slope and y-intercept of this graph was used in conjunction to find the CMC by the equation $\text{CMC} = -b/m$. The mean aggregation number for this run was determined by the equation $N = (1/\{Q\})m$.

Referring to question one, the local concentration should be the mols of benzene per unit volume of the spherical micelle. Conversion of units gives a value of .35M for the local concentration of benzene in the micelle (see attached calcs.)

For the second question, the concentration of micelles can be determined from the equation $\{M\} = (\{S\} - \text{CMC})/N$. The calculated value is .001M.

The mean occupation number can be determined simply by dividing the number of moles of n-hexane by the number of moles of micelles, based on the assumption that each n-hexane molecule is in a micelle. Using the .001M value from question 2 gives a value of 45 as the mean occupation number of n-hexane.

VI. Error Analysis

The most profound source of error in this experiment came from human error in the making of the solutions. By using such equipment as correctly tared volumetric flasks and microliter pipettes, this error was reduced. For all aqueous solutions, it was important to use purified, deionized water. The use of ethanol in the quencher stock solution will provide a negligible, but present error. A change in absorbance from sample-to-sample of $\text{Ru}(\text{bpy})_3^{2+}$ will indicate the extent of the inconsistency of probe concentrations in the samples. Combining the error in SDS and quencher concentrations, preparation was the most significant in the experimental error. Error calculations are included in the attached sheets. Other systematic errors included fluctuations in the fluorimeter light counts and Cary absorbance readings

not used

in the calculations

between identical samples. Using different sides of the cuvette may have an effect on absorbance so it was important to mark a side of the cuvette and have that side in the same position in the Cary for all samples.

CMC Calculations

Part I: Fixed ESS

$$I_0 = 75.5$$

$$\sigma_m = \sigma_y \sqrt{\frac{N}{\Delta}}$$

$$\sigma_y = \sqrt{\frac{1}{N-2} \sum_{i=1}^N (y_i - A - Bx_i)^2}$$

} using A and B from linear fit

$$\Delta = N \sum x^2 - (\sum x)^2$$

$$\begin{aligned} &= 6(3.24 \times 10^{-6}) - 3.24 \times 10^{-6} \\ &= 5.4 \times 10^{-6} \end{aligned}$$

$$\sigma_y = \sqrt{\frac{1}{4} \sum_{i=1}^6 (y_i - (-0.02296) - 9.28(x_i))^2}$$

$$\sigma_y = .02$$

$$\therefore \sigma_m = 21$$

see back
↓

Part I (cont'd)

$$M = \left(\frac{N}{S - CMC} \right) = \left(\frac{N}{.045M - .007M} \right)$$

~~$M = 3.3$~~ $N = 35$

Error in {S}:

$$\{S\} = \frac{.649g}{50mL} \left(\frac{1mol}{288.38g} \right) \left(\frac{1000mL}{L} \right)$$

$$\{S\} = .045M$$

$$\Delta M_{mass} = \pm .001g$$

$$\Delta Vol = \pm 1mL$$

$$.001g \left(\frac{1mol}{288.38g} \right) = 3.467 \times 10^{-6}$$

$$\therefore \frac{\Delta \{S\}}{\{S\}} = \sqrt{\left(\frac{\Delta mol}{mol} \right)^2 + \left(\frac{\Delta L}{L} \right)^2}$$

$$\Delta \{S\} = \{S\} \sqrt{\left(\frac{.001}{.649} \right)^2 + (.02)^2}$$

$$\Delta \{S\} = .045M (.02)$$

$$= 9.03 \times 10^{-4}M$$

Part I (cont'd)

$$\sigma_N = \sqrt{(\sigma_{cmc}^2 + \sigma_s^2) m^2 + \sigma_m^2 (cmc - s)^2}$$

$$\sigma_N = 1.5$$

you used
wrong slope.

graph not done
correctly.

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Part II (cont'd)

$$N = \frac{1}{Qm} = \boxed{54.9} \checkmark$$

$$\sigma_N = \sqrt{\frac{\sigma^2 m^2 + \sigma_m^2 Q^2}{m^4 Q^4}} = \boxed{6.1} \checkmark$$

Part II: Fixed {Q}

$$CMC = \frac{-b}{m} = \boxed{\frac{.007}{.002} = 3.5}$$

$$\sigma_b = \sigma_y \sqrt{\frac{\sum x^2}{n}}$$

$$\sigma_{CMC} = \sqrt{\frac{b^2 \sigma_m^2 + \sigma_b^2 m^2}{m^4}}$$

$$\boxed{\sigma_b = .2}$$

$$\sigma_m = \sigma_y \sqrt{\frac{N}{\Delta}}$$

$$\therefore \sigma_{CMC} = .0014$$

↑
0.004

$$\Delta = 5(.04992) - .027556$$

$$\Delta = .222044$$

$$\sigma_y = \sqrt{\frac{1}{4} \sum_{i=1}^5 (y_i - (-1.3972) - 182.21(x_i))^2}$$

$$= .42$$

$$\therefore \sigma_m = 2$$

Error in $\{Q\}$

$$\{Q\}_2 = 1 \times 10^{-4} M$$

$$\{Q\} = \frac{.05 M (.1 mL)}{50 mL}$$

$$\Delta_{\text{mass}} = \pm .001 g$$

$$\text{Mass} = \frac{.05 \text{ mol}}{L} \left(\frac{1 L}{1000 mL} \right)$$

$$\Delta_{\text{vol}} = \pm .5 mL$$

$$.005 mL \left(\frac{.05 \text{ mol}}{L} \right) = 2.5 \times 10^{-4} \text{ mol}$$

$$\text{mass}_i = .035 g$$

$$\frac{\Delta \{Q\}_1}{\{Q\}_1} = \sqrt{\left(\frac{.001 g}{.035 g} \right)^2 + \left(\frac{.5 mL}{5 mL} \right)^2}$$

error in step 1
of part II

$$\{Q\}_1 = .05 M$$

$$\Delta \{Q\}_1 = .0052 M$$

$$\{Q\}_2 = \frac{.05 M (.1 mL)}{50 mL} = \frac{\{Q\}_1 V_2}{V_3}$$

$$\Delta \{Q\}_1 = .0052 M \quad \{Q\}_1 = 1 \times 10^{-4} M$$

$$\Delta V_2 = 1 \mu L$$

$$\{V_2\} = 100 \mu L = .1 mL$$

$$\Delta V_3 = 1 mL$$

$$\{V_3\} = 50 mL$$

$$\frac{\Delta \{Q\}_2}{\{Q\}_2} = \sqrt{\left(\frac{\Delta \{Q\}_1}{\{Q\}_1} \right)^2 + \left(\frac{\Delta V_2}{V_2} \right)^2 + \left(\frac{\Delta V_3}{V_3} \right)^2}$$

$$\Delta \{Q\}_2 = 1.1 \times 10^{-5} M \rightarrow \text{error in } \{Q\}$$

Questions

① "Local Concentration" = $\frac{\text{mol} \text{ [O]}}{\text{unit Volume}} = \frac{\text{mol} \text{ [O]}}{L}$

$V_{\text{sphere}} = \frac{4}{3} \pi r^3$

$r = 1.5 \text{ nm}$

$V_{\text{sphere}} = 14.14 \text{ nm}^3 \left(\frac{1 \text{ m}}{10^9 \text{ nm}} \right)^3 = 1.4 \times 10^{-26} \text{ m}^3 \left(\frac{1 \text{ L}}{10^{-33} \text{ m}^3} \right)$

$3 \text{ mol [O]} \left(\frac{1 \text{ mol [O]}}{6.022 \times 10^{23} \text{ mol}} \right) = 4.98 \times 10^{-24} \text{ mol [O]} = 1.41 \times 10^{-23} \text{ L}$

Local Concentration = .35 M

② CMC = $6 \times 10^{-3} \text{ M}$

$N = 70$

$\{M\} = ? \quad \{S\}_0 = .08 \text{ M}$

$\{M\} = \left(\frac{\{S\}_0 - \text{CMC}}{N} \right) = \text{.001 M}$

③ $390 \text{ mg n-hexane} \left(\frac{1 \text{ mol n-hex}}{86 \text{ g}} \right) = .0045 \text{ mol n-hex}$

~~$\frac{390 \text{ mg n-hexane}}{86 \text{ g}} = .0045 \text{ mol n-hex}$~~

~~$\left(\frac{.0045 \text{ mol n-hex}}{1.14 \times 10^{-26} \text{ m}^3} \right) = .39 \text{ mol/L}$~~

~~$\left(\frac{.0045 \text{ mol n-hex}}{1.14 \times 10^{-26} \text{ m}^3} \right) = .39 \text{ mol/L}$~~

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rough sketch

rough sketch

rough sketch

rough sketch

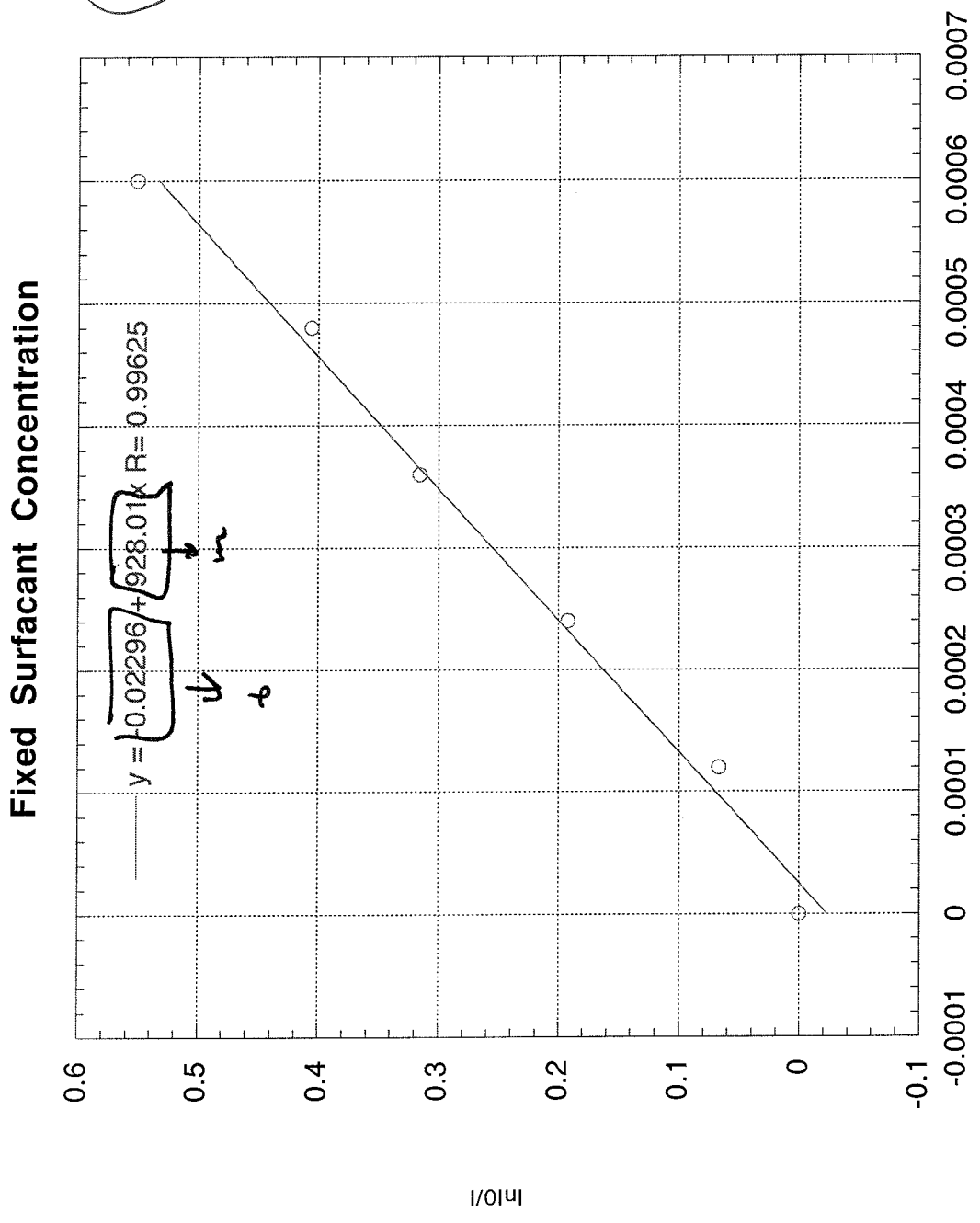
rough sketch

$$m = 928$$

$$\sigma_m = 21$$



$$\text{slope} = 1264 \pm 54$$
$$y_{\text{Int}} = -0.02 \pm 0.014$$

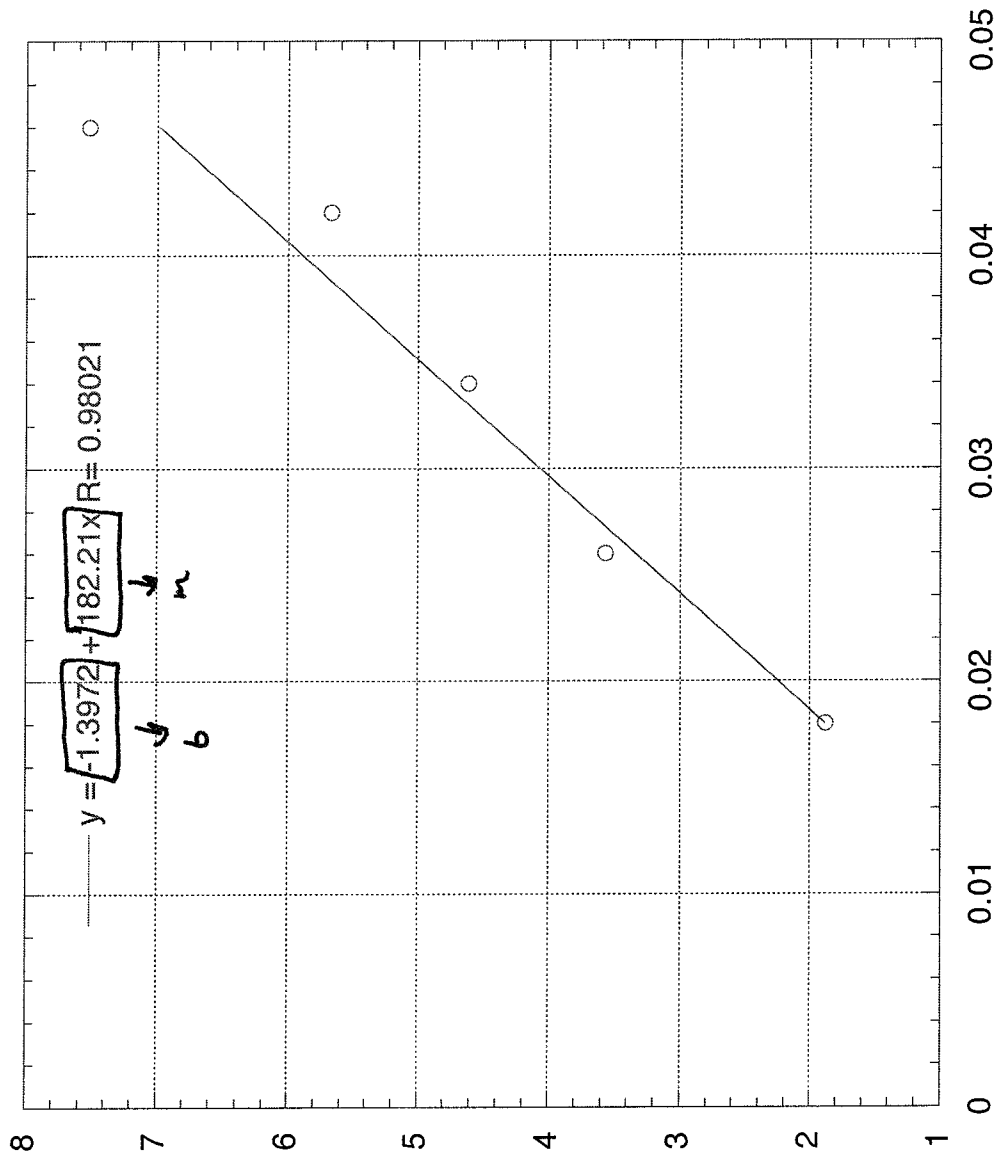


units

$$\sigma_m = 2$$

$$\sigma_b = .2$$

Fixed Quencher Concentration



$1/\ln(10/I)$

(s)
unit

units

	I(part I)	{Q}	I0/I	ln I0/I	{S}	I(part II)	1/ln(I2/I)	I0(part II)/I
0	75.500	0.0000	1.0000	0.0000	0.0000	75.500	n/a	1.0000
1	43.500	0.00060000	1.7356	0.55137	0.018000	66.100	1.8796	1.1422
2	50.300	0.00048000	1.5010	0.40613	0.026000	60.800	3.5688	1.2418
3	55.050	0.00036000	1.3715	0.31589	0.034000	63.300	4.6180	1.1927
4	62.300	0.00024000	1.2119	0.19217	0.042000	57.050	5.6738	1.3234
5	70.600	0.00012000	1.0694	0.067102	0.046000	44.350	7.5208	1.7024

Part I: $\{S\} = .045 \pm 9.0 \times 10^{-9} M$

$N = 35 \pm 2$

Part II: $\{Q\} = 1.0 \pm .11 \times 10^{-4} M$

$N = 55 \pm 6$

CMC = $.007 \pm .001 M$

Should have 2 tables.

is that a divider?!