Elaboration of Micelle Formation in Aqueous

and Two Phase Solutions by Surface Active Phosphines

by

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MASTERS OF SCIENCE

IN

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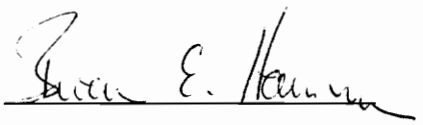

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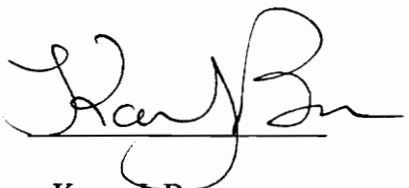

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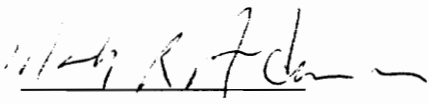

Mark R. Anderson

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ELABORATION OF MICELLE FORMATION IN AQUEOUS

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Chemistry

ABSTRACT

The surface active phosphine $P((C_6H_4)C_3H_6(C_6H_4)SO_3^-Na^+)_3$,**1**, aggregates in aqueous solution to form micelles. Light scattering experiments were used to determine the hydrodynamic radius of the aggregates. Fluorescence, conductivity, and surface tension experiments were used to measure the critical micelle concentration of these aggregates. Fluorescence experiments, using a quencher and probe analysis, show the number of particles per aggregate. Nuclear Magnetic Resonance (NMR) shows that these micelles are able to incorporate olefin within the hydrophobic region and are acting as phase transfer agents.

ACKNOWLEDGMENTS

In life people struggle to achieve goals both great and small. These goals are sought after with great effort and hopefully with great enthusiasm. Rarely, however, are these endeavors faced alone. It is important that each individual be assisted along his/her journey in order do ensure the greatest amount of success. I am unsure if this thesis demonstrates "the greatest amount success", but it is not because of a lack of support.

My advisor, Dr. Brian Hanson, has not only been a source of direction but also a source of inspiration. Without Dr. Hanson's guidance and support this work would not at all be possible. I am grateful for his patience, guidance, and most of all his understanding. The simple yet direct way in which he guided this project to its completion helped improve both my effort and my enthusiasm.

Another source of effort came from Dr. Hao Ding in his way of making sure I did the work I needed to do. Dr. Ding helped me and pushed me when I got stuck. At times I got frustrated and perhaps at these times was when Dr. Ding helped me the most.

I also received guidance and inspiration, especially when the chemistry was not going well, from the entire Hanson group. They supported me through both success and especially failure. To them, to Dr. Hanson, and to Dr. Ding I express great gratitude and my sincere wishes for your own successes.

I would like to thank my committee members Dr. Brewer and Dr. Wightman for their guidance and support. The project, however, would not have been completed if not for the following people who allowed me the use of their instrumentation and those individuals who showed me the proper techniques in using this instrumentation. First there is Dr. William

Velander and Art Degener who assisted with both the dynamic light scattering experiments and the surface tension experiments. Second is Dr. Gandour and Chris Curfman who assisted me with the conductivity measurements.

The greatest debt of gratitude is to my family. Being very different people and expecting very different things from life has not prevented my family from continuing to give me there unwavering support. The support of my family has been both a driving force and a resting place. I thank them for not only supporting me at Tech but also for their continuing support as I endeavor to live a good life.

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Chapter 1

Introduction

1.1 Introduction to Two Phase Catalysis

A catalyst is a substance that increases the speed of a reaction. The catalyst interacts with the reactants in order to improve the reaction rate yet is unchanged by the overall reaction. Industry uses catalysts to improve reaction activity to increase productivity while maintaining a low overhead. Thus, there is much industrial interest in finding ways of improving existing catalytic systems and to develop new catalysts. As catalytic processes improve industry saves money because it can produce more product at lower costs.

The chemistry investigated here is relevant to hydroformylation catalysis in water. Hydroformylation is the process that converts an olefin to an aldehyde by the addition of CO and H_2. Aldehyde synthesis is a large scale industrial process; most use either cobalt or rhodium complexes as catalysts. Current methods of hydroformylation are mainly homogeneous, one phase catalysis. In one phase systems the entire catalytic cycle occurs within a single phase. The substrate, starting material, and the catalyst begin in the organic phase and upon completion of the reaction the product is also in the organic phase. Advantages to homogeneous

catalysis include high activity and selectivity even under mild reaction conditions.[1] The most prevalent disadvantages are product separation and catalyst recovery.

The products of a one phase system have to be separated from both unreacted starting material and the catalyst. Some separation processes can be very harsh, for example distillation at high temperatures and/or high pressures. The conditions of separation might actually destroy the catalyst. In industry a large amount of catalyst is used and even a small percentage of loss can be very expensive; therefore, it is important to maximize catalyst recovery.

In two phase hydroformylation of higher olefins, such as 1-octene, the substrate is the organic phase while the catalyst is in the aqueous phase. The substrate, or olefin, is converted to an aldehyde by direct interaction with the catalyst. The reaction occurs in the aqueous phase and the product leaves the aqueous phase and enters the organic phase. One benefit of this type of two phase system is product separation. Separation of the product is as simple as removing the organic layer after the reaction is complete, leaving the catalyst unharmed and completely recovered in the aqueous phase. The industrial application of this type of system has been demonstrated by the "Shell Higher Olefin Process"(SHOP).[2] The products, oligomers, of this process are immiscible with

the polar phase, 1,4-butanediol. This allows for easy product separation as the substrate, ethylene, is catalytically oligomerized by an organonickel catalyst which remains in the polar phase. Another example of two phase hydroformylation catalysis used industrially is the production of butyraldehyde by the "Ruhrchemie/Rhone Poulenc Process" which uses a rhodium based hydroformylation system with water soluble phosphines.[3]

The focus of our research group is two phase hydroformylation in which the second phase is water. By using water for catalysis there is an added advantage in that water is environmentally safe. Thus, in the case of this two phase hydroformylation, the advantages are easy product separation, complete catalyst recovery, and environmental safety. These advantages have sparked a great deal of research in two phase systems.

In two phase homogeneous catalysis it is very important for the substrate to move into the aqueous phase in order to interact with the catalyst. Because of the importance of the substrate interacting directly with the catalyst in the aqueous phase, two phase systems have been designed to optimize the transfer of substrate into the aqueous phase. The substrate has to come into direct contact with the catalyst. The catalyst remains in the aqueous phase while the substrate must move from the organic phase into the aqueous

phase. This transfer of the substrate limits the reaction rate of the two phase hydroformylation. Therefore, by increasing the solubility of the substrate in the aqueous phase reaction rate is increased.

One very important issue has been the specific ligands used to form the catalyst. The catalyst is generally a transition metal complex with various ligands. These ligands interact with the metal modifying its coordination sphere electronically and sterically in order to improve reactivity and selectivity. In order to make these complexes water soluble polar functional groups are added to the ligands. Extensive research has been done on water soluble ligands and information can be found in several review articles.[4-7]

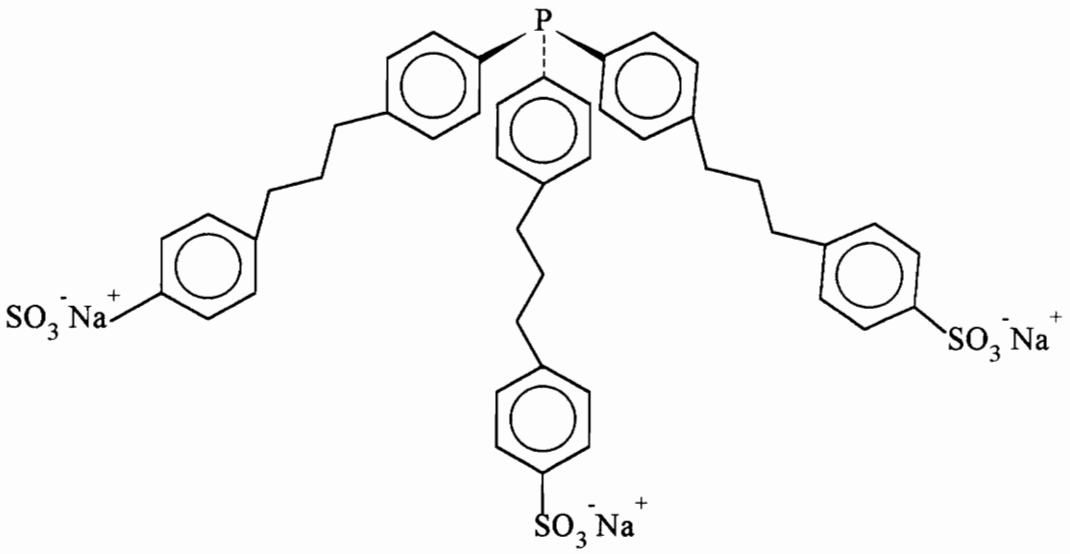
Research conducted in our laboratory has focused mainly on water soluble phosphines, specifically sulfonated arylphosphines. This focus began with the successful synthesis of *m, m,* m-trisulfonated triphenylphosphine(TPPTS).[8] Since the successful sulfonation of triphenylphosphine other arylphosphines have been synthesized. Fell and co-workers prepared sulfonated tris(2-pyridyl)phosphines by reaction with alkyl-1, 2-sultone(C_3-C_{14}). These phosphines have long alkyl chains and are surface active. The surface activity of these ligands makes it possible to satisfactorily hydroformylate higher olefins, such as 1-tetradecene although these ligands

have limited use since they formed stable emulsions.[9] Other surface active phosphines have also been made.

Two series of water soluble surface active phosphines have been synthesized in Dr. Brian Hanson's lab. The first series, $P[(CH_2)_n(C_6H_4\text{-}p\text{-}SO_3Na)]_3$ (n=1, 2, 3,6), was prepared by direct sulfonation.[10] Where n = 1 or 2 the sulfonation was done with oleum (18-24% SO_3) and where n = 3 or 6 the sulfonation could be done with concentrated sulfuric acid. The second series, $P[(C_6H_4)(CH_2)_n(C_6H_4\text{-}p\text{-}SO_3Na)]_3$ (n=3 or 6) is also prepared by direct sulfonation with concentrated sulfuric acid.[11] These ligands can be used to form complexes with rhodium. The rhodium based complexes made exhibit catalytic activity.

Complexes of the type $HRh(CO)(L)_3$ have been shown to be hydroformylation catalysts in two phase systems, where L = $P((C_6H_4)SO_3^-Na^+)_3$ [TPPTS] or $P((C_6H_4)C_3H_6(C_6H_4)SO_3^-Na^+)_3$ [PC3].[11] Figure 1 shows the molecular structure of both TPPTS and PC3. It can be seen that both ligands are water soluble, and that the PC3 has a longer "hydrocarbon arms" thus making it potentially surface active. The catalytic studies on rhodium complexes of both TPPTS and PC3 were done by Dr. Hao Ding. The following comparisons of TPPTS versus PC3 were also prepared by Dr. Ding. It can be seen from Figure 2 that

A)



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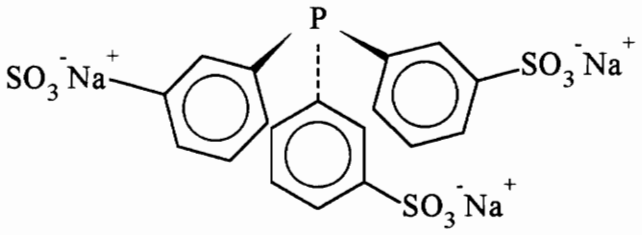

Figure 1: A) Structure of $P((C_6H_4)C_3H_6(C_6H_4)SO_3^-Na^+)_3$ [PC3]

B) Structure of $P((C_6H_4)SO_3^-Na^+)_3$ [TPPTS]

catalytic activity for the hydroformylation of 1-octene is higher when L = PC3 then when L = TPPTS.[12] It is observed in Table 1 that catalytic activity when L = PC3 is greater at higher solution ionic strength which is accomplished by the addition of salt.

The increased activity of PC3 over TPPTS has sparked research into discovering what added advantages surface active phosphines actually incur. Two phase homogeneous hydroformylation can be improved by the use of surface active phosphines.[11,12]

1.2 Introduction to Micelles

A micelle in water is an aggregation of particles that have both a hydrophobic and a hydrophilic end. These aggregates form spheres, or other three dimensional shapes, within the aqueous phase. The stability of these aggregates depends on many factors. At higher temperatures the aggregates do not hold together as micelles but rather break apart sometimes forming smaller micelles or no micelles at all. When the concentration of surfactant is too low micelles are unable to form. At high ionic strength, however, the micelles are stabilized and form at lower concentrations and can show an increase in size.[14-17] Figure 3a shows a simple model of a micelle in water, while in figure 3b a possible

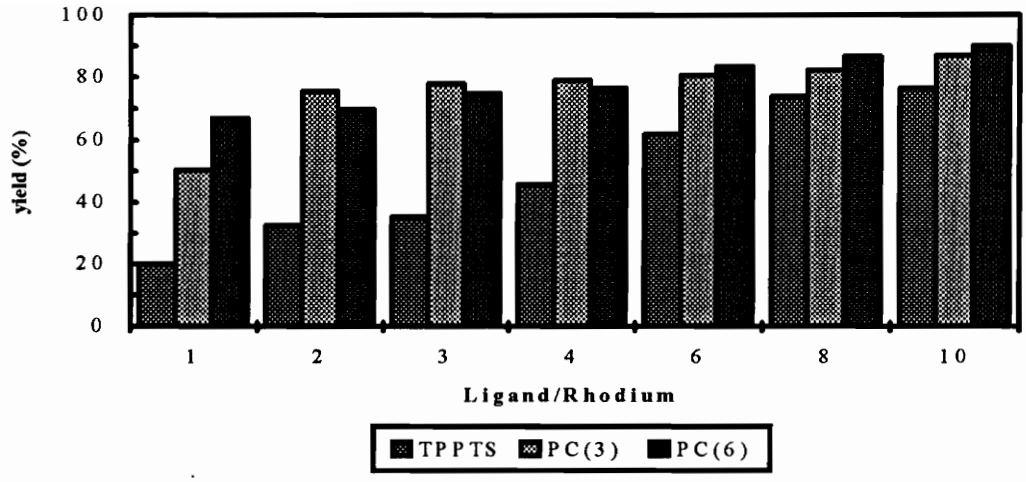

Figure 2: A) Reaction activity as a function of L/Rh(acac)$(CO)_2$ ratio for the ligands TPPTS, PC(3), PC(6) in the rhodium catalyzed hydroformylation of 1-octene. (Conditions: reaction time, 5h; reaction temperature, 120°C; initial pressure, 19.5 atm; [Rh] = 0.0005 M; stirring rate, 260 rpm.)[13]

Table 1: The effect of salt on the activity and selectivity of 1-octene hydroformylation with $P[C_6H_4(CH_2)_3C_6H_4SO_3Na]_3$.

	L/Rh = 3		L/Rh = 10		L/Rh = 20	
	Yield (%)	*n/b*	Yield (%)	*n/b*	Yield (%)	*n/b*
no salt	12.8	3.6	15.3	9.7	14.9	12.7
0.5 M Na_2HPO_4	14.6	9.8	22.3	12.2	23.2	16.8
0.5 M Na_2SO_4	14.2	10.1	23.4	13.3	22.6	17.0

(L = $P[C_6H_4(CH_2)_3C_6H_4SO_3Na]_3$, Reaction temperature = 120°C, Pressure at 120°C = 19.5 atm, Reaction time = 24 h, Rh/1-octene = 500. [Rh] = 0.005 M.)[13]

model for the solubilization of oil in an aqueous phase by a micelle is shown.[18-20]

Micelles form in both aqueous and organic phases. Micelles that form in water are generally referred to as oil in water micelles, while micelles in oil are referred to as water in oil micelles or reverse micelles. The more common micelle is the one in water as opposed to the micelle in oil. Both types of micelles form three dimensional shapes and solubilize material in the solvent. Both types of micelles consist of a hydrophobic and hydrophilic region. In the case of water in oil micelles, the solvent is non-polar, and the micelle has its hydrophobic region in contact with the solvent and its hydrophilic region buried within the micelle. The opposite is true for oil in water micelles. Water in oil micelles are commonly called reverse micelles as they have essentially exchanged the positions of the hydrophobic and hydrophilic regions of their micelles as compared to oil in water micelles. Similarities between different types of micelles include not only having hydrophobic and hydrophilic regions, but also being surface active within the appropriate solvent. The micelles are able to solubilize material in the solvent that would not normally be soluble. This is done by the micelle interacting with both the solute and the solvent simultaneously.

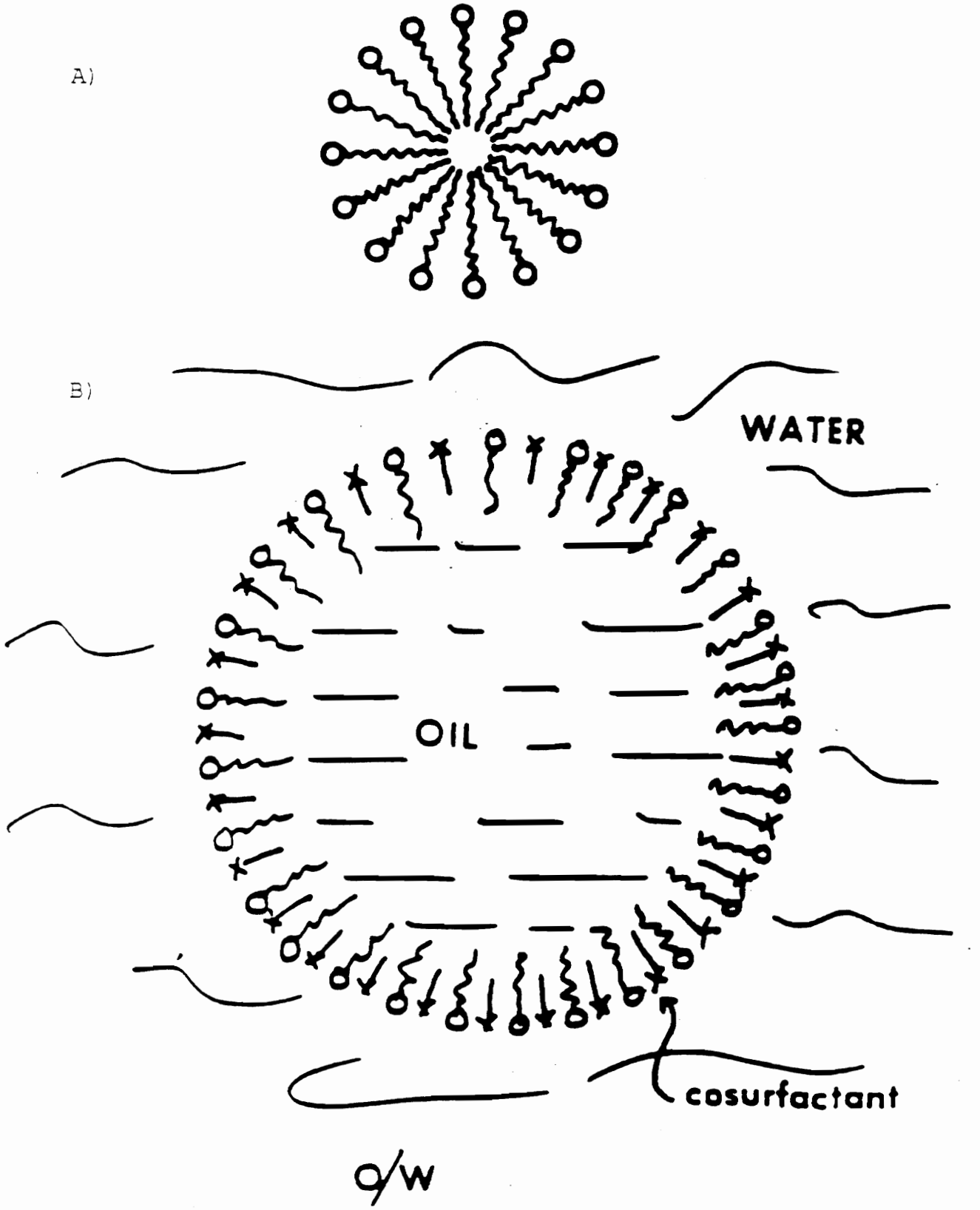

Figure 3: A) One possible model of a micelle. B) One model of a micelle bringing oil into water.[20]

In the case of oil in water micelles solubilization can be understood by realizing that micelles are actually surfactants. When oil is placed on the surface of water little oil beads can be seen floating on the water. If a surfactant is added to the water the oil drops disappear from the surface as they are dissolved in the aqueous phase. The surfactant forms micelles in water and solubilizes the organic material. Due to the nature of the micelle being both hydrophobic, organic, and hydrophilic, aqueous, it is able to hold the oil in its hydrophobic region while its hydrophilic region continues to interact with water. Basically, micelles are able to solubilize otherwise immiscible solutes into solution by simultaneously interacting with both the solute and solvent. This unique ability seems directly related to the independent polar and non-polar regions of all micelles.

Because of the special properties of micelles, research has been done to increase the surface activity of the ligands used to form the catalysts in two phase reaction systems. It is hoped this will improve reaction rates by increasing the amount of substrate that actually comes into contact with the catalyst. If the ligands or complexes in question form micelles then an increase in catalytic activity should be observed. This increased activity could be attributable to the solubilization of the substrate into the aqueous phase.

In fact it has been seen that the PC3 ligand does have improved catalytic activity over TPPTS under most reaction conditions.[12] The improved activity may be attributable to the micelles formed by the excess PC3 in the aqueous phase. Thus, the formation of micelles may help to solubilize the substrate in the aqueous phase increasing both the transfer of substrate into the aqueous phase and the amount of substrate that comes into contact with the catalyst; therefore, increasing the catalytic activity.

1.3 Direction of Research

This project was done in order to determine if, and what kind of micelles are formed by the PC3 ligand. Being able to determine the critical micelle concentration, the micelle size, and the aggregation number of the PC3 would prove that the PC3 ligand does indeed form micelles. Being able to determine if the free PC3 ligand forms micelles is one more step in elucidating the exact chemistry that occurs during two phase hydroformylation catalysis.

It is also important to determine the solubilizing property of the PC3 micelles. Determining if and how much substrate can be solubilized in the aqueous phase would help explain the increased activity when the hydroformylation is done with surface active phosphines. It will be important to

discover what exactly is happening within the catalysis reaction in order to pinpoint the exact reason PC3 shows increased catalytic activity over TPPTS.

Given the determination of what kind of micelles the PC3 forms it is our hope that we can elaborate on what type of ligand would be most effective for hydroformylation catalysis and perhaps discover why such a ligand would be so effective. The better we are able to explain what is happening; the better we can make the system operate.

Chapter 2

Determination of Critical Micelle Concentration

2.1 Introduction to Techniques

Critical micelle concentration (CMC) is the minimum concentration of molecules needed to form micelles. The CMC is determined in order to show that micelles are forming and at what concentration these micelles actually begin to aggregate.

Fluorescence experiments use fluorescence probes, such as Pyrene and Pyrenecarboxaldehyde to determine CMC. The reason these probes are used is because the solution environment affects the spectra of these probes. A large number of micelle systems have been studied by fluorescence spectroscopy with Pyrene as the probe, most of these were done to determine a CMC.[21-26]

The solution environment affects the emission spectrum of Pyrene. Specifically, the intensities if peaks 1 and 3, I_1 and I_3, are environmentally dependent.[27-29] The excitation wavelength is 332 nm while the maximum wavelength ($\lambda_{max.}$) of I_1 is at 358.5 nm and $\lambda_{max.}$ of I_3 is at 368.5 nm. If the solution is polar then I_1 is greater than I_3, as is the case in figure 4 with Pyrene in water. As the environment of the

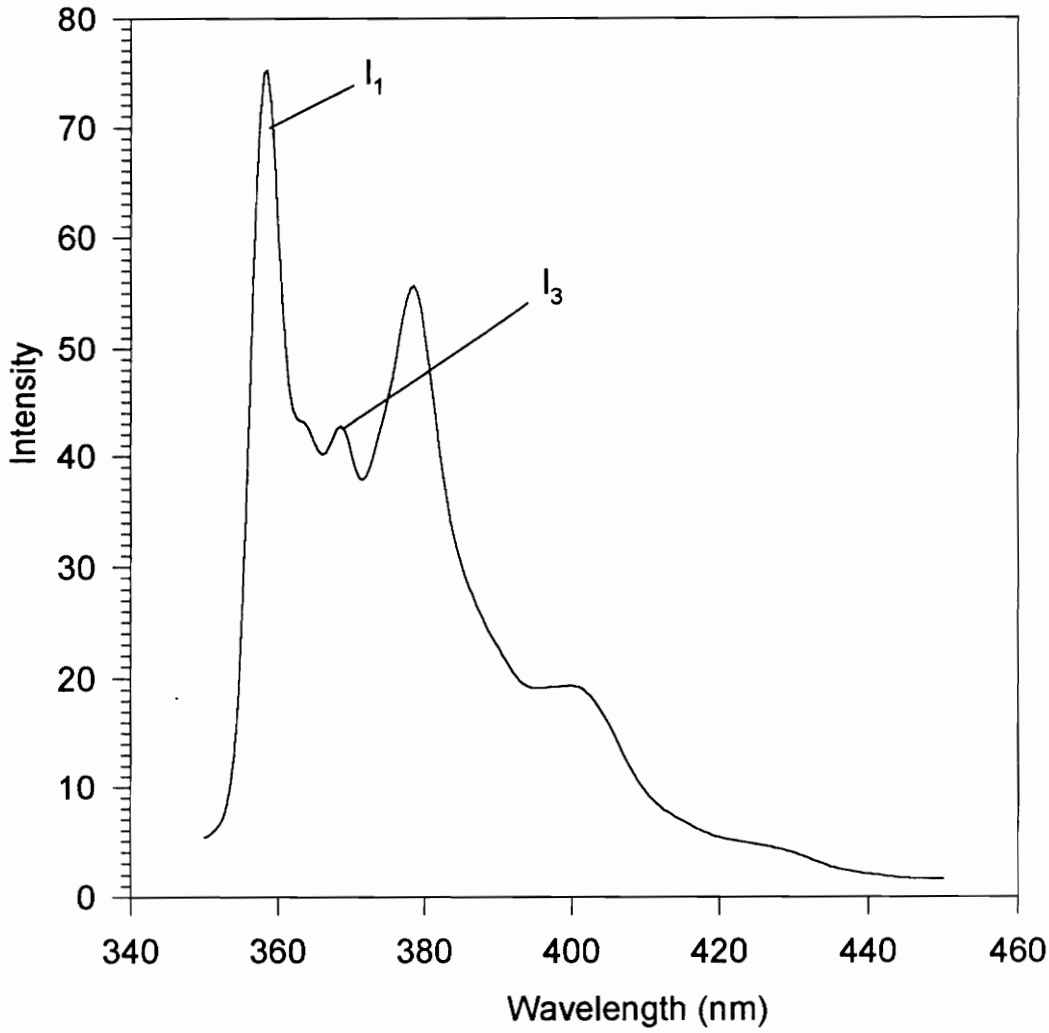

Figure 4: Fluorescence spectrum of Pyrene in water.

[Pyrene] = $<10^{-6}$, $\lambda_{excitation}$ = 332 nm, $\lambda_{emission}$ = 340-460 nm.

Pyrene becomes less polar I_3 grows while I_1 shrinks. This effect can is seen as Pyrene enters a micelle. Because Pyrene's interactions with micelles affect its fluorescence spectrum, it is used as a probe to determine CMC.[30,31] Pyrene is hydrophobic and favors entering into the micelle and thus as the CMC is approached the I_1/I_3 ratio will decrease until all the Pyrene is in the micelle at which time I_1/I_3 will become relatively constant. Therefore, a graph of I_1/I_3 versus concentration of the micelle solution will show the CMC. As can be seen from the sodium dodecyl sulfate (SDS) example, figure 5, the CMC is determined to be the point just before all the Pyrene is found within the micelles. In the SDS example the CMC was determined to be 0.006 M.

Literature values for SDS CMC range from 0.03 M to 0.0082 M.[32,35] It can be seen that SDS has a very large range for its CMC; the value obtained here is just beyond the lower limit of reported values. It is important to note that many factors effect CMC values. As was mentioned earlier the specific temperature, the presence of salt, sample purity and the solvent all affect the CMC. Further experiments, vide infra, the same sample of SDS confirm the CMC obtained by Pyrene. The SDS was used as a model system to help understand the use of Pyrene to determine CMC. SDS is used as a model in several cases as it is similar in behavior to the PC3 as both

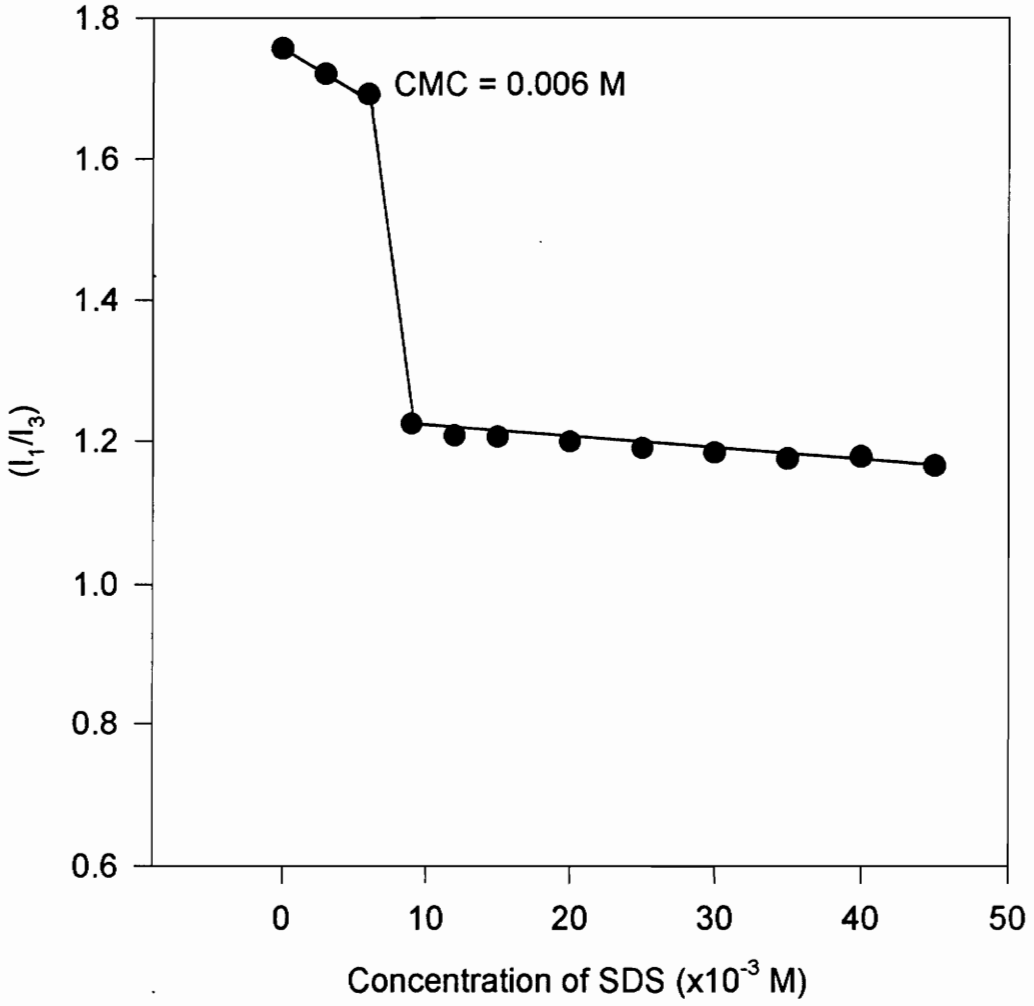

Figure 5: CMC of SDS determined using the fluorescence probe Pyrene. The CMC is determined to be the point just before all the Pyrene is within the micelles.

compounds have carbon backbones and sulfonate groups. Thus, their micelles have similar hydrophobic and hydrophilic regions. The PC3 ligand, however, contains three sulfonate groups per molecule.

The solution environment also affects the fluorescence spectrum of pyrenecarboxaldehyde by changing the position of $\lambda_{max.}$[31] The excitation wavelength is 380 nm giving an emission spectra whose $\lambda_{max.}$ is between 400 and 480 nm depending on the micelle concentration. The $\lambda_{max.}$ shifts to lower wavelengths when the pyrenecarboxaldehyde moves into the more hydrophobic region of the micelle. The nature of the results are similar to Pyrene. By plotting the $\lambda_{max.}$ versus the micelle concentration a sharp break is detected and the CMC can then be determined, as seen in figure 6. The CMC is the point at which the break initially occurs. This is the point just before all the probe is consumed by the micelle.[31]

It was observed that both fluorescence probes can be effective in measuring the CMC of micelle solutions. Having been able to make measurements with the fluorescence probes using SDS as a model system was essential; however, it was also important to confirm that the fluorescence experiments were also accurate. Therefore, surface tension was also done in order to determine CMC.

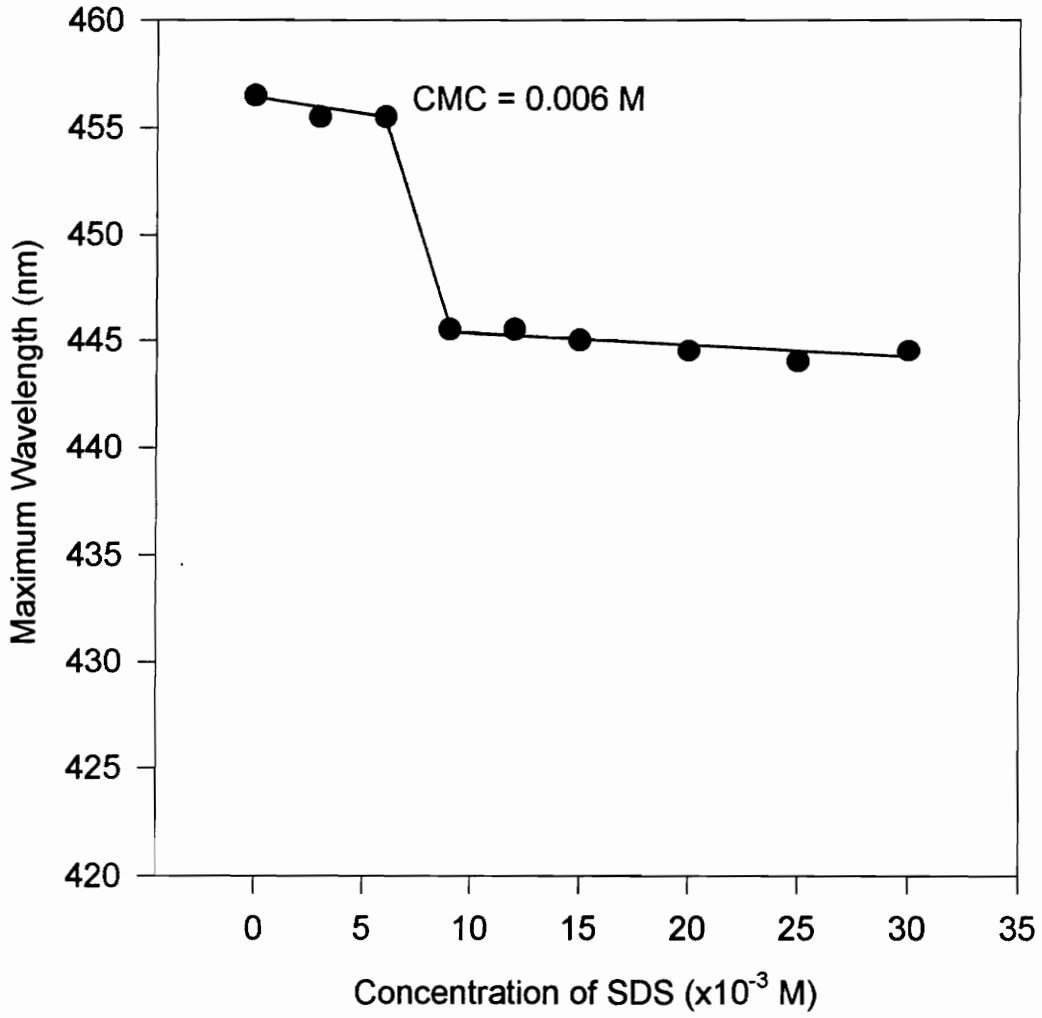

Figure 6: CMC of SDS determined by the fluorescence probe pyrenecarboxaldehyde.

Surface tension is a measure of how well a liquid holds together at its surface. A pure liquid has a given surface tension and the addition of foreign agents will effect this surface tension. For water, a polar substance, the addition of salt increases the cohesion between water molecules and thus increases the surface tension. The opposite is true when a surfactant, a compound that forms micelles, is added. The surface tension will decrease steadily as the concentration of micelles increases until the CMC is reached at which time the surface tension becomes constant.[31] It can be seen from figure 7 that surface tension can be used to determine the CMC by plotting surface tension versus concentration. The CMC is the point at which the surface tension becomes fairly constant. The concentration at which the surface tension no longer decreases is considered to be the CMC. In figure 7 the initial point at which the curve becomes flat is taken to be the CMC. Again it was determined that the CMC of SDS was 0.006 M.

Conductivity is a measure of the electric potential of a solution. The importance it has in determining CMC is in how the conductivity changes as micelle concentration changes. The rate of change for conductivity is higher before the CMC is reached then for after. This is because the micelles form large anionic spheres past the CMC which effectively hamper

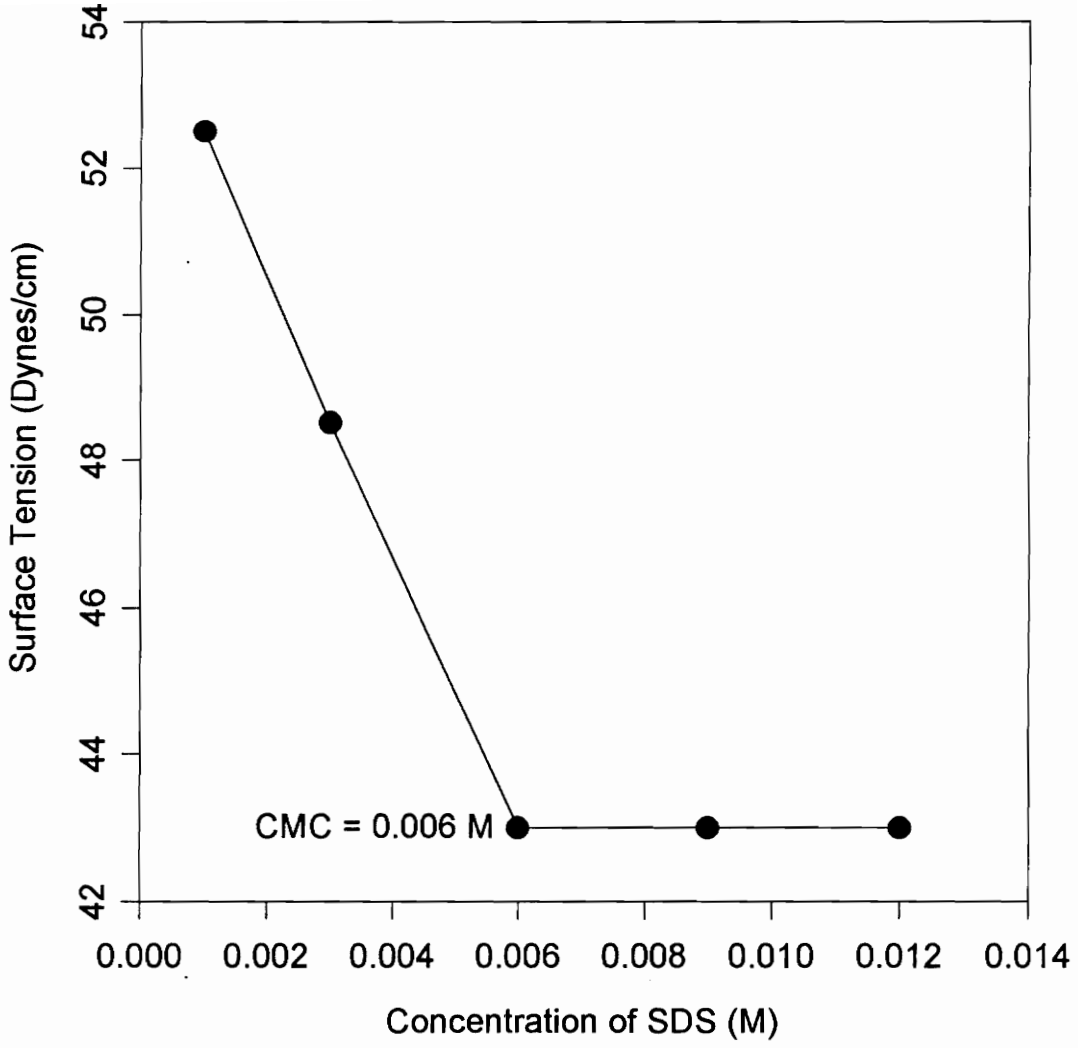

Figure 7: CMC of SDS determined by surface tension.

the increase in conductivity. Basically as the concentration increases more cations are bound to the micelles decreasing the amount of interaction with free anions. This phenomenon makes it possible to measure CMC using conductivity.

2.2 Experimental

Sodium dodecyl sulfate(SDS) was purchased from Aldrich and recrystallized from methanol. Pyrene and Pyrenecarboxaldehyde were purchased from Aldrich and recrystallized twice from ethanol. Sodium sulfate was purchased from Aldrich and used as received. PC3 was made in our laboratory following the procedure given by Dr. Ding.[13]

Both the SDS samples and the PC3 samples were prepared in the same way. In all cases the solutions were kept under nitrogen. Standard solutions were made in order to prevent weighing of very small amounts of solid.

2.2a Fluorescence Probes

A standard solution of probe, both Pyrene and pyrenecarboxaldehyde, was made by supersaturating deionized water, free of molecular oxygen, to give a probe concentration of $<10^{-6}$ M. This solution is prepared by stirring the probe in deionized water overnight and then filtering the excess probe from the solution.

A standard solution of PC3 or SDS at a concentration of 0.0200 M was made. When necessary the standard solutions were made with Na_2SO_4 present at a concentration of 0.250 M.

The standard solutions were added together directly in the fluorescence cells. The concentration of the PC3 or SDS was varied by adding different amounts to each cell using micropipetters. Once the samples were placed in the fluorescence cells they were taken to the fluorometer and emission spectra were obtained.

The instrument used was a Perkin Elmer Luminescence Spectrometer LS50 and the data was collected and analyzed with an IBM personal computer.

2.2b Surface Tension

The solutions were made with varying amounts of PC3 or SDS in nitrogen purged vials. The surface tension was measured with a surface tensiometer, in this case a FISHER Surface Tensiomat, Model 21 equipped with a 6 cm circumference platinum ring, that measures the surface tension directly in dynes/cm.

2.2c Conductivity

Measurements were made by adding successive amounts of a standard PC3 solution to the solution being measured. This is done in order to measure conductivity as concentration

increases. The additions should be made in order to give at least ten points above and ten points below the CMC.

2.3 Results

Figure 8 is a graph of I_1/I_3, from fluorescence spectra of Pyrene and PC3 in water, versus concentration of PC3. The graph does not have a sharp drop in relative intensity, but rather a smooth curve. Instead of being able to see a CMC clearly it appears that Pyrene interacts to some extent with PC3 at nearly all concentrations. Ultimately, however, the Pyrene is in a completely hydrophobic region which is consistent with incorporation within a micelle. The curve flattens out at a concentration of 1.0×10^{-3} M. It is observable that the micelles do interact with the Pyrene and a relatively constant ratio of intensities is reached. Therefore, it is possible that beyond a certain concentration of PC3 the CMC has been surpassed. This concentration is taken as the point at which the curve becomes flat, 1.0×10^{-3} M, as this indicates that all of the Pyrene has interacted with the micelles. The same type of curve seen in figure 8 is observed in figure 9. In the case of figure 9 the measurements were made in the presence of salt. Given the same type of analysis the CMC is seen to occur earlier in the presence of salt. With added salt, increased solution ionic

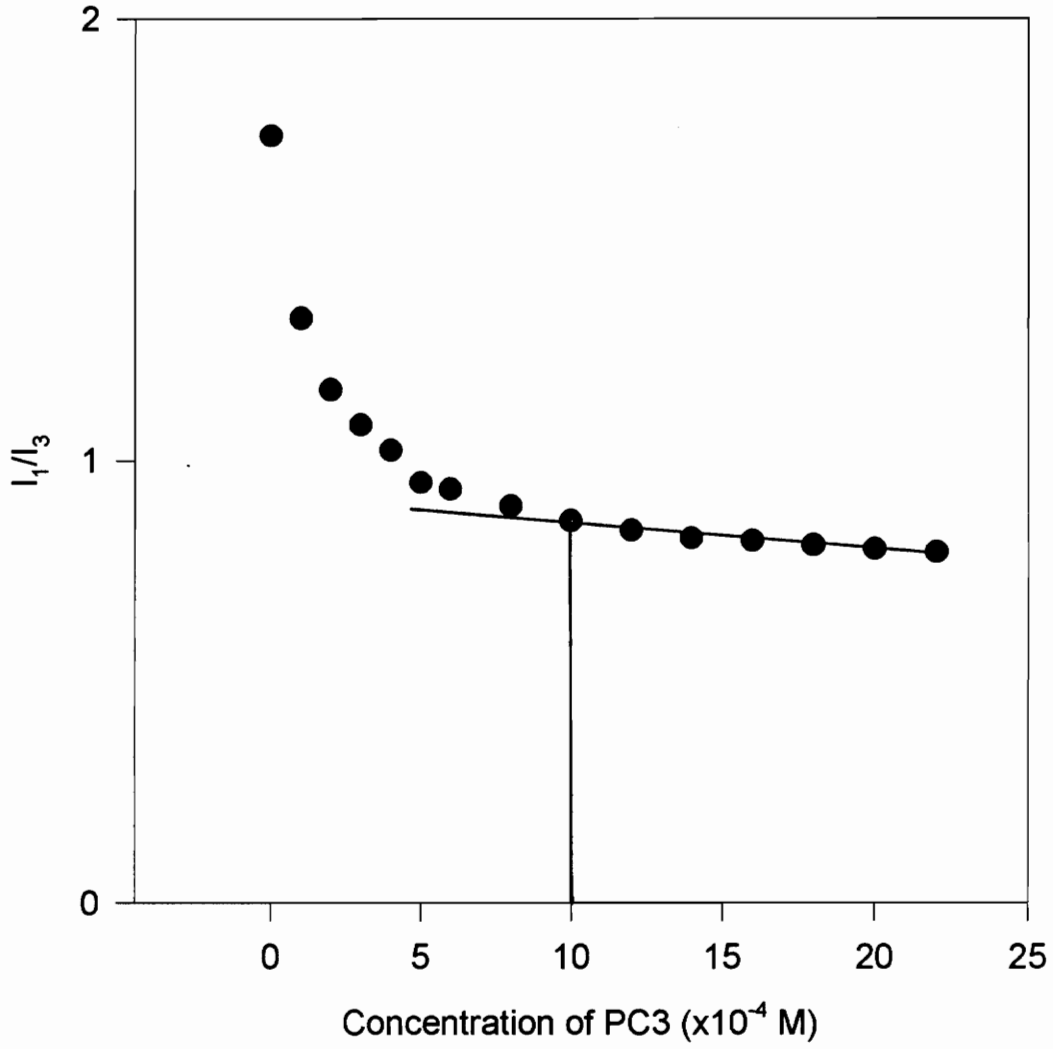

Figure 8: Relative intensity of Pyrene in the presence of PC3. A single CMC is not evident however it appears that micelles are formed at a [PC3] concentration >1.0 x10^{-3} M.

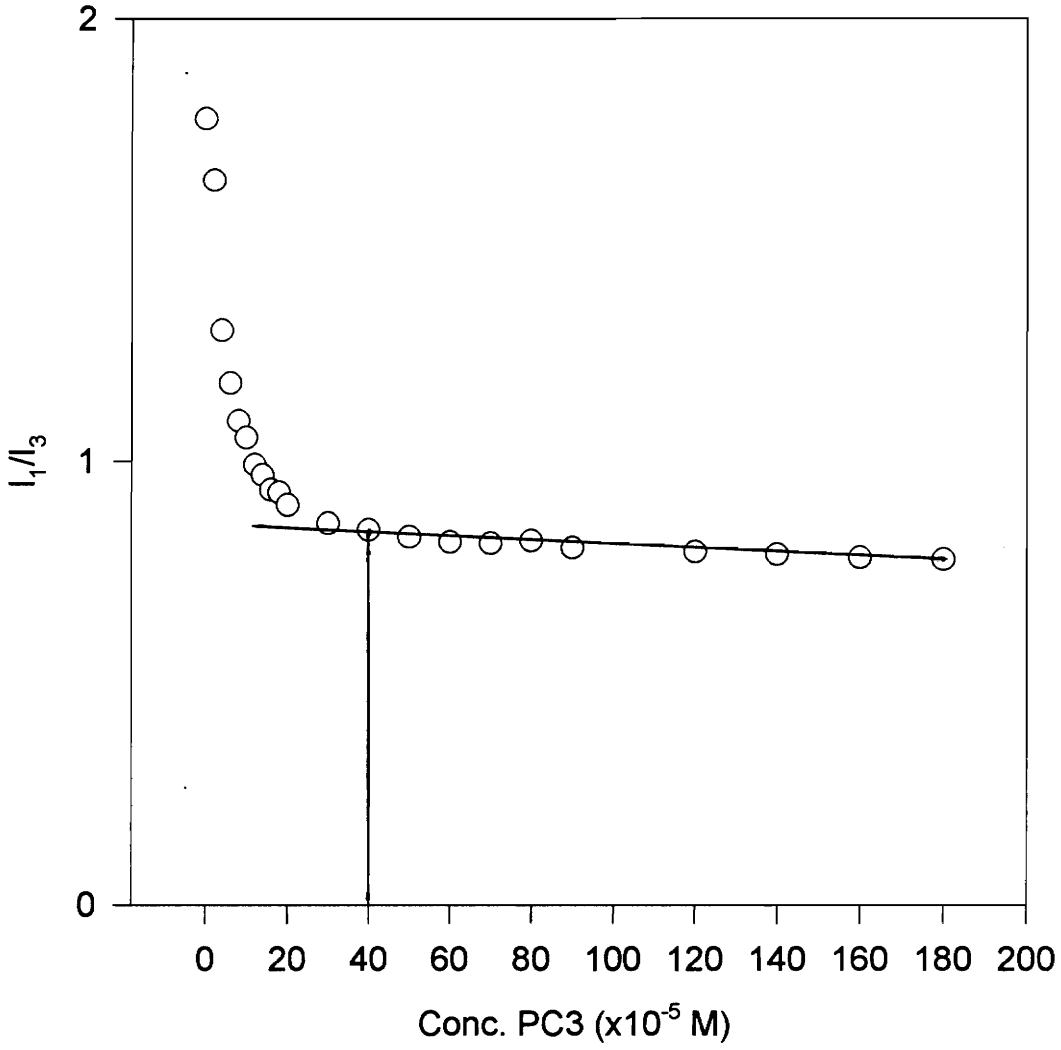

Figure 9: Relative intensity of I_1/I_3 of Pyrene in the presence of PC3 and salt (0.25 M Na_2SO_4). Uniform micelles appear to be formed at [PC3] > 4.0 x10^{-4} M.

strength, the CMC is <4.0 x10^{-4} M and without salt it is <1.0 x10^{-3} M, when using Pyrene as the fluorescence probe.

Figure 10 shows where the pyrenecarboxaldehyde has fully interacted with the micelles. By plotting the position of $\lambda_{max.}$ versus concentration, the CMC is seen to be passed at a concentration of 5.0 x10^{-4} M. Again the CMC is not clearly outlined by the plot and it is necessary to settle for knowing at what concentration the CMC has been passed. The same type of curve is seen in figure 11 when the experiment is done in the presence of salt. It is observed that the salt reduces the CMC to <1.2 x10^{-4} M as opposed to <5.0 x10^{-4} M.

Surface tension experiments offer the same kind of evidence seen by the fluorescence probes for the CMC. Figure 12 shows the CMC to be <6.0 x10^{-4} M with out salt and figure 13 shows the CMC to be <1.6 x10^{-4} M with added salt. These values are determined by taking the initial point at which the surface tension becomes relatively constant.

The conductivity experiment requires a computer analysis of the curve to determine the exact CMC. The curve is split into two separate lines. One line being below the CMC and the other line being above the CMC. Starting with the first ten points a slope and y-intercept are determined by the computer using linear regression. Then using the last ten points another slope and y-intercept are determined in the same way.

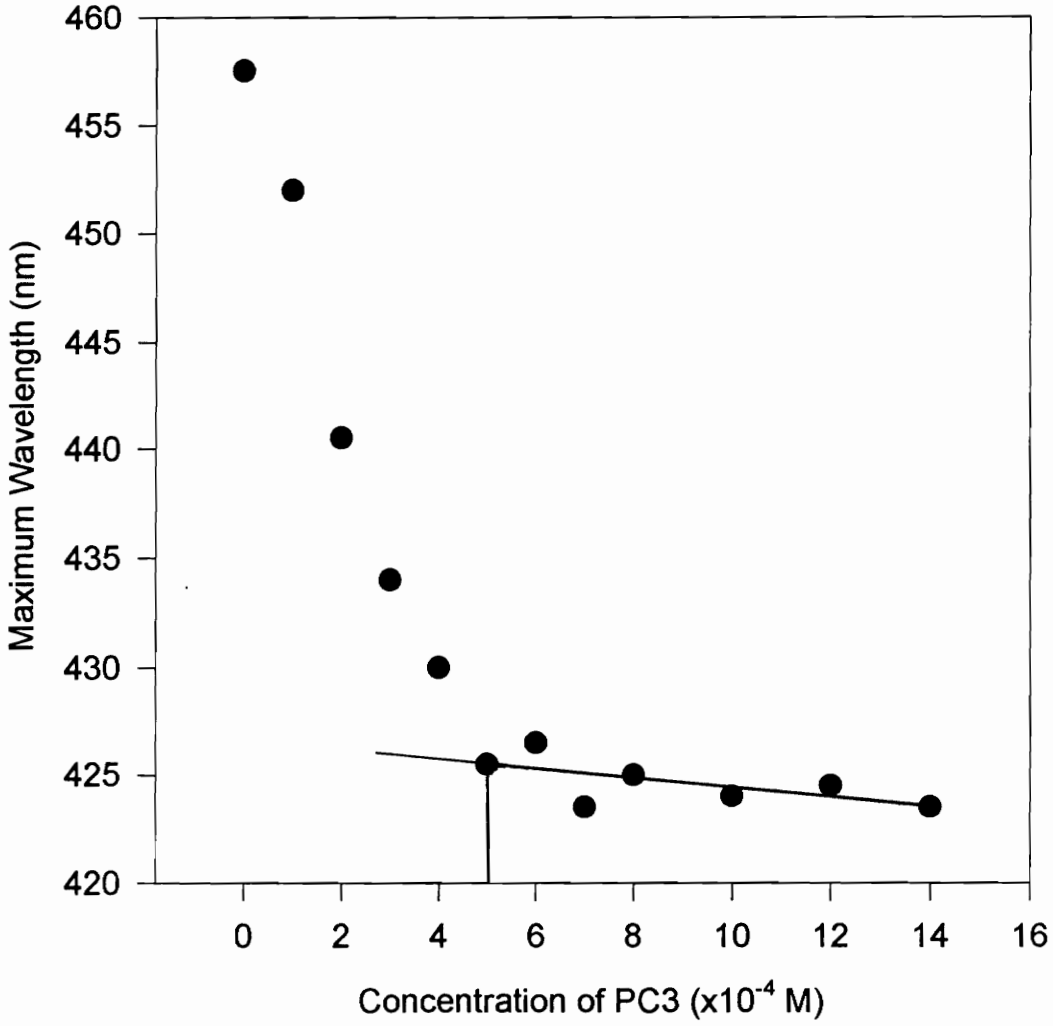

Figure 10: Position of $\lambda_{max.}$ of pyrenecarboxaldehyde in the presence of PC3. The CMC is exceeded at [PC3] <5.0 x10^{-4} M.

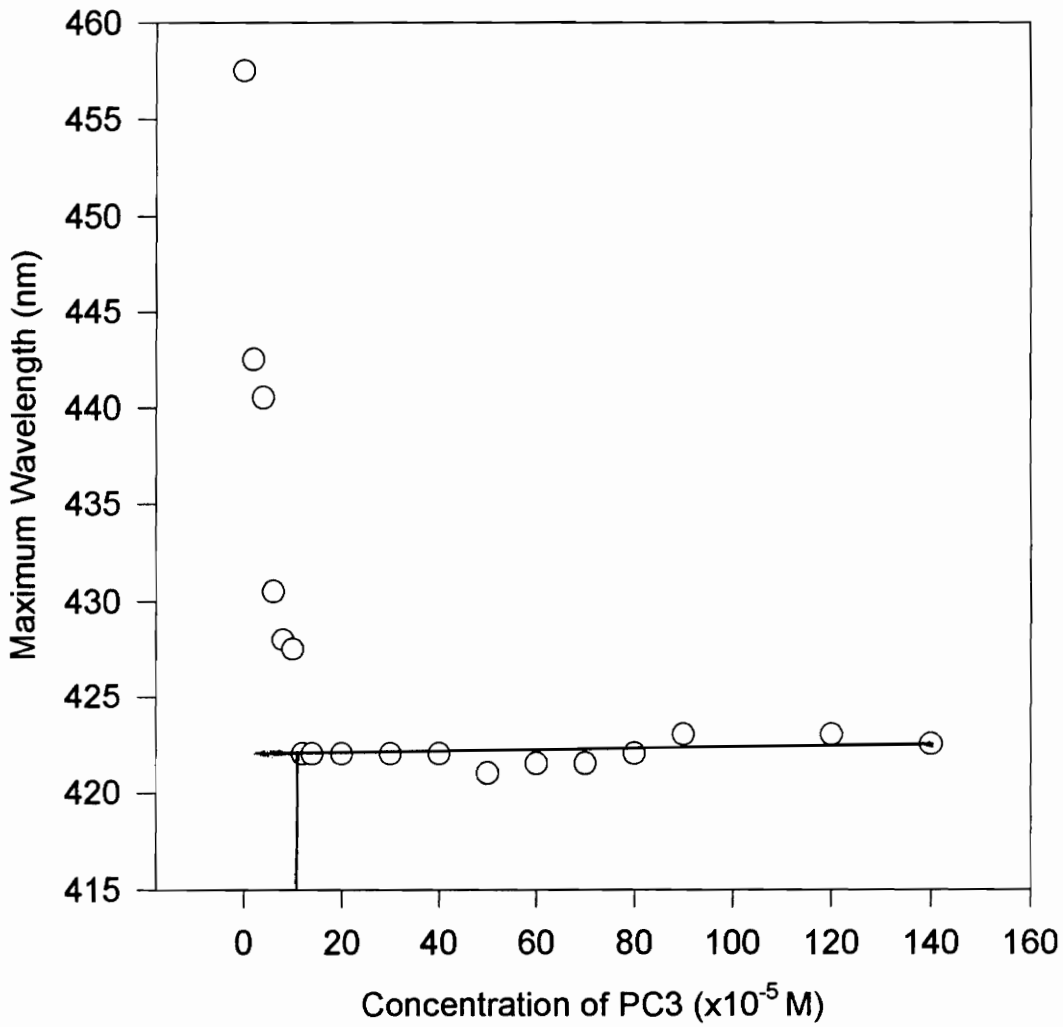

Figure 11: Position of $\lambda_{max.}$ of pyrenecarboxaldehyde in the presence of PC3 and salt (0.25 M Na_2SO_4). The CMC is exceeded at [PC3]< 1.2 $x10^{-4}$ M.

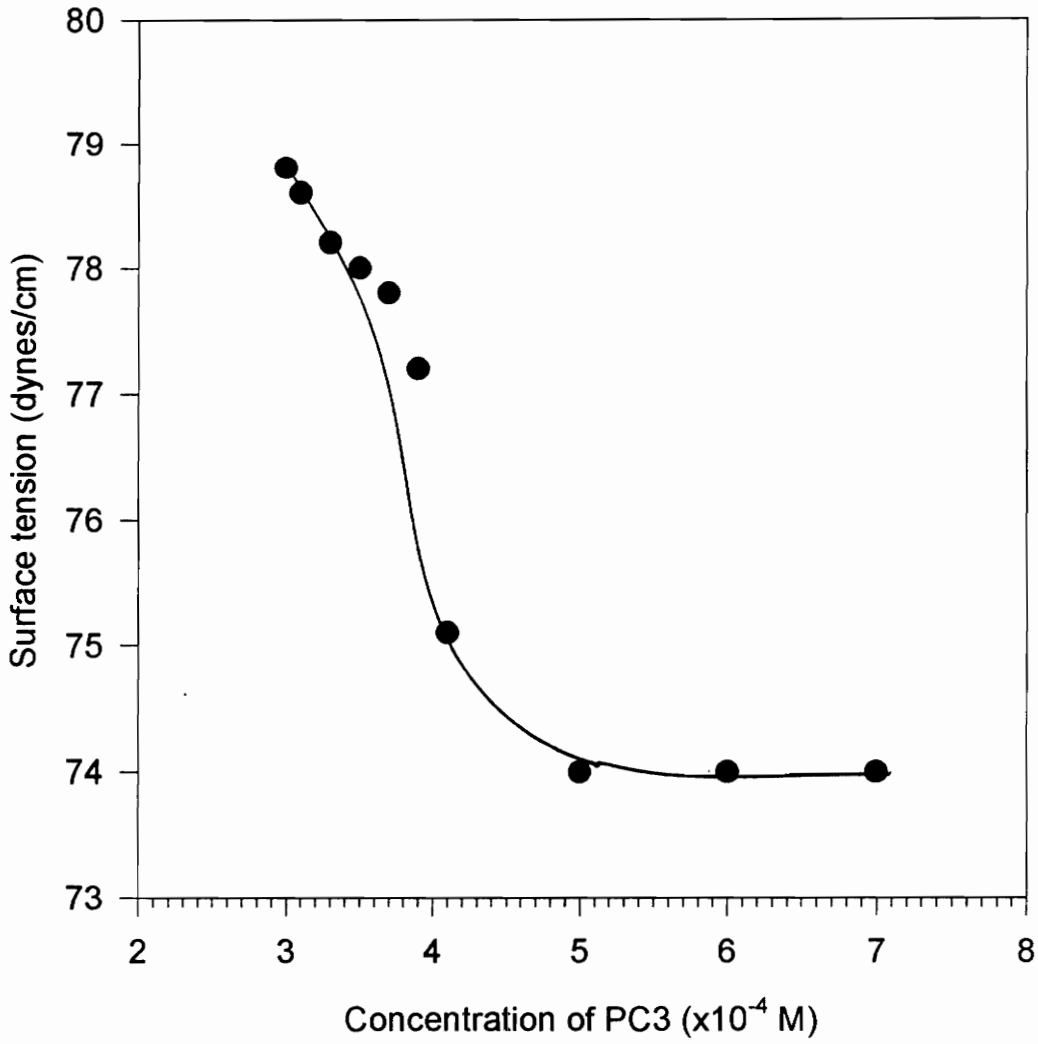

Figure 12: Surface tension measurements of PC3 solutions, without added salt.

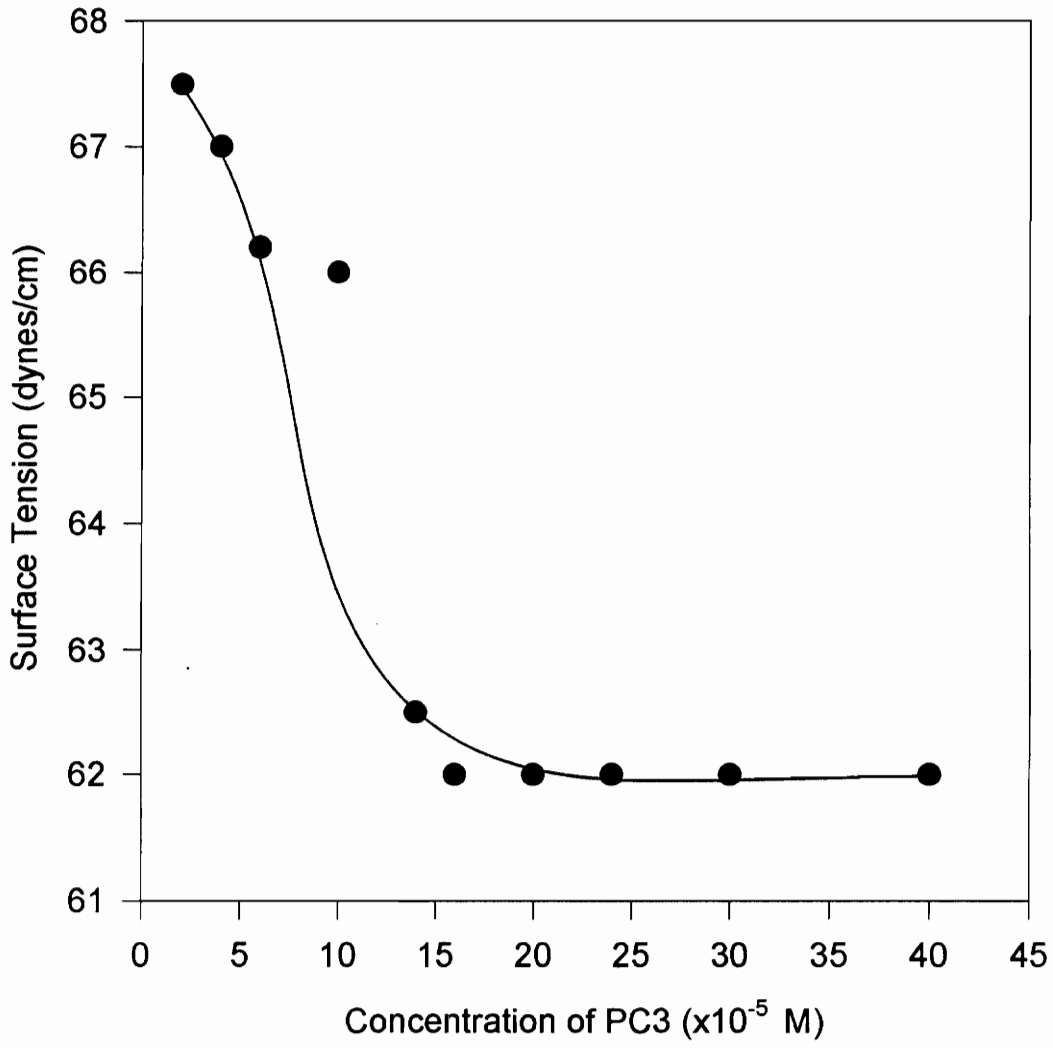

Figure 13: Surface tension measurements of PC3 in the presence of salt (0.25 M Na_2SO_4).

These two lines have the following equation

$$y = mx + b$$

where m is the slope and b is the y-intercept. The difference of the two lines gives the intersection of the lines, x.

$$y_1 - y_2 = (m_1 - m_2)x + (b_1 - b_2)$$

$$0 = m_f x + b_f$$

$$x = b_f/m_f$$

where m_f is the difference in the slopes and b_f is the difference in y-intercepts. Solving for x, the intersection of the two lines, one divides b_f by m_f (b_f/m_f). The x value is the intersection of the two lines and the CMC. By increasing the amount of points first to eleven below and eleven above then to twelve and so on the CMC can then be determined by averaging all the values of x.

In the case of figure 14, a distinct intersection is not very visible. The graph is of conductivity (Mhos) versus concentration (M) giving a fairly straight line. This line should, however, show a distinct bend, but due perhaps to the small size of the PC3 micelles the bend is simply hard to see. In fact after computer analysis the average CMC for this experiment was determined to be 4.7×10^{-4} M $\pm$ $.3 \times 10^{-4}$ M.

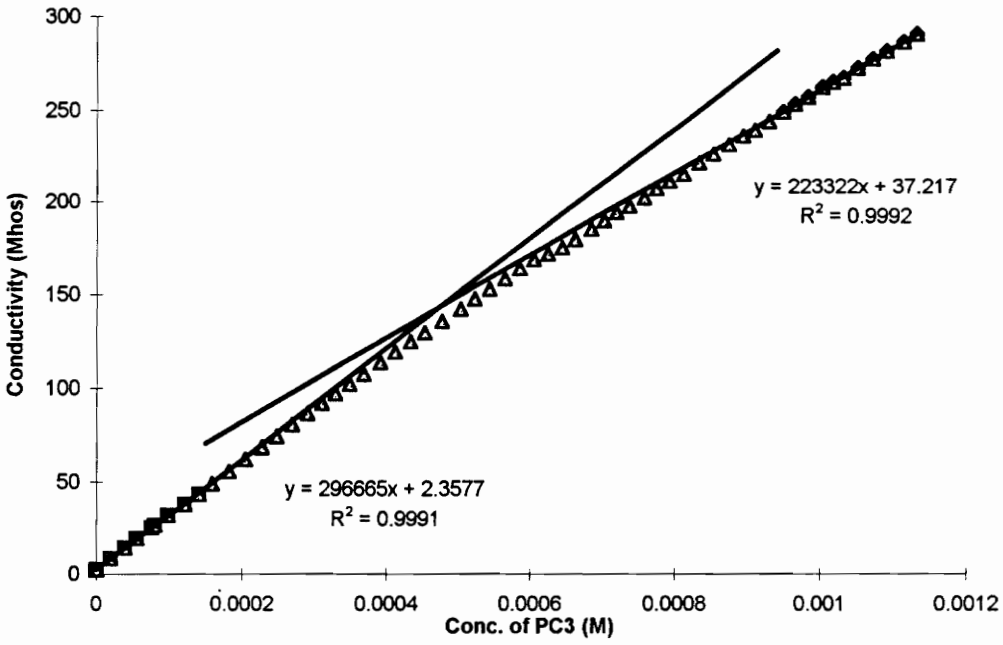

Figure 14: CMC of PC3 determined by conductivity. The CMC was determined to be 4.7 $x10^{-4}$ M ± 0.3 $x10^{-5}$ M.

2.4 Discussion

Results indicate that the CMC for the PC3 ligand can not be clearly ascertained. However, it can be concluded that after a given point the fluorescence probes have interacted completely with the micelles and thus the CMC has been exceeded. It can also be concluded that after a given point the surface tension no longer changes and thus the CMC has again been exceeded. The conductivity experiment may indicate a CMC and is consistent with the other experiments performed.

The SDS experiments gave definitive results while the PC3 experiments were less cooperative. The PC3 may not be as similar to SDS as previously thought. The SDS has a higher CMC then the PC3 which isn't surprising as the PC3 is a much larger molecule. However, the SDS and PC3 had very different interactions with the fluorescence probes. The PC3 has a much more gradual behavior as it approaches a possible CMC, instead of a very abrupt change. This gradual rather than abrupt change does demonstrate interaction with the probe but does not allow for direct evidence of a specific CMC. Therefore, what is reported is the point at which the CMC has been exceeded.

The results in table 2 shows a good agreement among the experiments done to determine CMC. The Pyrene experiments do

Table 2: Summary of CMC results found for SDS, PC3, and PC3 with added salt.

	SDS	PC3	PC3 with Na_2SO_4
Pyrene	0.006 M	< 1.0×10^{-3} M	< 4.0×10^{-4} M
Pyrene carboxaldehyde	0.006 M	< 5.0×10^{-4} M	< 1.2×10^{-4} M
Conductivity		4.7×10^{-4} M	
Surface Tension	0.006 M	< 6.0×10^{-4} M	< 1.6×10^{-4} M

not agree as well as with the other experiments; however, all the experiments do agree on an upper limit of the CMC.

It can be concluded for PC3 without added salt that the CMC is approximately 4.7×10^{-4} M. The CMC of PC3 with added salt can be said to be $< 1.4 \times 10^{-4}$ M.

The reported values for PC3 and PC3 with salt do show a trend. Even though an exact value was not yet ascertained, it is clear that the CMC of PC3 with salt is at least three times lower than without salt. It has been observed in many micelle systems that the addition of salt increases ionic strength and thus improves micelle stability.[15-18] The improved micelle stability leads to lower CMC as the micelles are able to form stable aggregates at lower concentrations. This has been observed with the PC3 as was expected.

Even though the PC3 behaves a little differently than SDS it seems clear that PC3 has properties similar to other micelles in that it has a CMC and that it's CMC is less with added salt. It follows then that PC3 does in fact form micelles.

Also, it is important to note again that the CMC with salt is lower then without salt. By increasing the amount of salt in the aqueous phase of the two phase hydroformylation catalysis the activity was increased. This increase could be due to stronger micelles being formed by the excess PC3

ligand. These stabilized micelles will increase the amount of 1-octene that enters into the aqueous phase; therefore increasing catalytic activity. The increased micelle stability upon addition of salt might be the reason $HRh(CO)(PC3)_3$ has increased catalytic activity when solution ionic strength is increased.

Chapter 3

Determination of Micelle Size

3.1 Introduction to Dynamic Light Scattering

The development of light scattering begins with Lord Rayleigh and receives its present form for colloids in solution by Debye.[32] Dynamic light scattering is actually a measure of static light scattering recorded at given time intervals. The light source, usually a LASER, sends light to the sample. The light is scattered towards the detector, a photomultiplier tube, which counts how many photons are being scattered. A computer then stores this information until the next count is made. Less then a second later the next count is made and compared to the last count. These counts can be analyzed by comparing neighboring time intervals or by comparing time intervals separated by a longer time delay.[33] The comparisons made make it possible to determine the translational diffusion coefficient, D_t.[34] Under the assumption of Brownian motion the diffusion coefficient, D_t, is converted to the hydrodynamic radius, R_h, of the particles using the Stokes-Einstein equation.[35]

$$R_h = (k_b T)/6\pi\eta D_t$$

Where k_b is Boltzman's constant, T is the temperature in Kelvin, and η is the solvent viscosity.

The hydrodynamic radius is determined by the computer program. Thus the data actually gives micelle size. Dynamic light scattering can be done on a variety of systems to determine solution dynamics, colloidal properties, and micelle size.[34,36] The studies done here were only done to determine micelle size. By using the molecular size detector we were able to determine the size of the micelles in various solutions.

3.2 Experimental

Methanol was purchased from Aldrich and used as received. Water was deionized and then distilled under nitrogen. 1-Octene and sodium sulfate were purchased from Aldrich and used as received. PC3 was made in the laboratory following Dr. Ding's procedure.[13]

The samples were prepared simply by adding PC3, water, salt, and or methanol to various solutions. The addition of different components was done in order to vary the solution environment of the PC3 to observe how the solvent affects the micelle size.

Water is present in all solutions. Methanol, when added, is at 50% by volume with water. Na_2SO_4 is added in each case with salt, at a concentration of 0.25 M. The Na_2SO_4 and the PC3 were added as solids. The water and the methanol

were added by micropipette. The samples were prepared in nitrogen purged vials with a 2.0 ml aqueous phase.

1-Octene was added to the solutions in different amounts to determine how it effects the micelle size. These amounts are .5 ml, 1.0 ml, and 3.0 ml to each type of solution in order to determine if the amount of 1-octene effects the micelles' size. The samples with 1-octene were measured after one day and then again after one week in both cases simply sitting without agitation for the given period of time.

A Biotag dp-801 molecular size detector was used to determine the hydrodynamic radius. This instrument has a 30 MW, 780 nm wavelength solid state laser and a solid state avalanche photodiode (APD).

3.3 Results

Table 3 shows the micelle diameter of PC3 micelles at a concentration of 0.005 M. It can be seen that as solution ionic strength increases, the micelle diameter also increases.

1-Octene also affects the micelle diameter. It can be seen in table 4 that the 1-octene actually reduces the micelle diameter after resting only one day. This is most likely due to 1-octene reducing the solution ionic strength. However, over time the micelle diameter increases. Given the same concentration of PC3 and resting for one week the micelle diameter was seen to increase, as shown in table 5.

Table 3: Micelle diameter of PC3 determined by dynamic light scattering.

Solution	Micelle Diameter (Å)
Water	24 ± 1.4
Water, Salt	40 ± 0.90
Water, Salt, Methanol	29 ± 2.9
Water, Methanol	22 ± 0.93

(Concentration of PC3 in all samples was 0.005 M. In cases with salt, 0.25 M Na_2SO_4 was added. Methanol was added at 50% by volume with water.)

Table 4: The effect of 1-octene on micelle diameter.

	Water, Salt, 1-Octene	Water, Salt, Methanol, 1-Octene	Water, Methanol, 1-Octene	Water, 1-Octene
PC3 (.005 M)	33 ± 1.0	27 ± 2.4	31 ± 5.6	19 ± 1.1
.50 ml Octene	34 ± 1.0	24 ± 1.4	33 ± 7.0	22 ± 4.6
3.0 ml Octene	34 ± 0.6	26 ± 1.4	26 ± 3.9	20 ± 3.8

(Samples left undisturbed for one day, micelle diameter reported in Å, salt = 0.25 M Na_2SO_4, methanol = 50% by volume, [PC3] = 0.005 M).

Table 5: Effect of 1-Octene on Micelle Diameter after one week.

Volume of 1-Octene (ml)	Diameter (Å) after one day	Diameter (Å) after one week
0.0	24 ± 1.4	24 ± 1.4
0.5	22 ± 4.6	45 ± 4.4
1.0	19 ± 1.1	34 ± 2.0
3.0	20 ± 3.8	30 ± 1.6

(Samples left undisturbed for one week, micelle diameter reported in Å, salt = .25 M Na_2SO_4, methanol = 50% by volume, [PC3] = 0.005 M).

3.4 Discussion

It can be seen that the micelle diameter is influenced by the solvent. The trend depends on the solution ionic strength. As the solution's ionic strength increases the diameter of the micelles increase. This increase in micelle size is an expected result since increased ionic strength stabilizes micelles. Thus, the micelle diameter in water alone is 24 Å, while the micelle diameter with added salt is 40 Å. The increase in micelle size upon addition of salt is also supported by the lower CMC for solutions with added salt. It is observed that added salt stabilizes and increases the size of micelles formed by PC3.

The addition of 1-octene has the effect of reducing micelle size after resting for only one day. This decrease in size may be attributed to lower ionic strength of the solutions or simply an unforeseen interaction of the 1-octene with the micelles. However, after resting for one week the micelles with the 1-octene increased in size.

It is speculated that the increase in size is due to the PC3 micelles solubilizing the 1-octene in the aqueous phase. By bringing 1-octene into the hydrophobic region of the micelle the micelle increases in size. Much like other surfactants bringing oil into water the PC3 forms micelles capable of bringing 1-octene into the aqueous phase.

Therefore, it is concluded that the PC3 ligand acts as a phase transfer agent transporting 1-octene into the aqueous phase. This is one reason for increased catalytic activity as more substrate would come into contact with the catalyst due to being solubilized in the aqueous phase.

Because the micelles are able to solubilize 1-octene in water, an increase in micelle stability and size should increase the amount of 1-octene brought into the aqueous phase. The addition of salt does indeed increase micelle stability and size; therefore, it follows that increased salt should improve catalytic activity. Results obtained by Dr. Ding can be seen in figure 3.[13] The results do show that the addition of salt does increase catalytic activity as expected.

Chapter 4

Determination of Aggregation Number

4.1 Introduction to the Quencher/Probe Experiment

The quencher/probe experiment uses a fluorescence probe (tris(2,2-bipyridine)ruthenium(II)-chloride) that has a distinct $\lambda_{max.}$ (maximum wavelength). The probe interacts with the micelles but does not change its fluorescence character in any way. The quencher (9-methylanthracene) is added to the solution through its interaction with the micelles. The quencher associates with the probe that shares the same micelle. The quencher interacts with the probe in such a way that it prevents the probe from emitting an observable fluorescence signal. Thus, each micelle has either both probe and quencher associated with it or just the probe. The only fluorescence seen then is that of micelles associated only with probe. Therefore, the fluorescence intensity of $\lambda_{max.}$ depends on the amount of probe (tris(2,2-bipyridine)ruthenium(II)-chloride) and quencher (9-methylanthracene) present in each sample.[37-39] In practice it is assumed that the distribution of probe and quencher on the micelles is a Poisson distribution. This makes it possible to determine the aggregation number, a, by measuring the total intensity of fluorescence with and without quencher.

The relationship between intensity, I, and quencher concentration is given by the following equation

$$I = I_0 \exp\{-[Q]/[M]\}, \quad [1]$$

where [M] is the mean concentration of micellar aggregates, [Q] is the quencher concentration, I_0 is the intensity without quencher. [M] is related to "a" by the following relationship

$$[M] = \{[surf_0] - [surf_{free}]\}/a, \quad [2]$$

where "a" is equal to the aggregation number, $[surf_0]$ is the concentration of surfactant, and $[surf_{free}]$ is the CMC of the surfactant. According to equation [1], ln I_0/I is proportional to [Q], and "a" can be calculated from the slope of this straight line {1/[M]}.[38,39]

An example of how this experiment works can be seen in figure 15 with SDS as a model. The slope was found to be 1558 M^{-1} making [M] = 6.418 $x10^{-4}$ M. Thus, from the known concentration of SDS, 0.034 M, the CMC of SDS, 0.006 M, and [M] the aggregation number can be determined:

$$a = ([surf_0] - [surf_{free}])/[M].$$

In the case of SDS a = 43, which agrees well with literature values. Depending on sample purity, values in the range of 40-60 have been reported.[37-39]

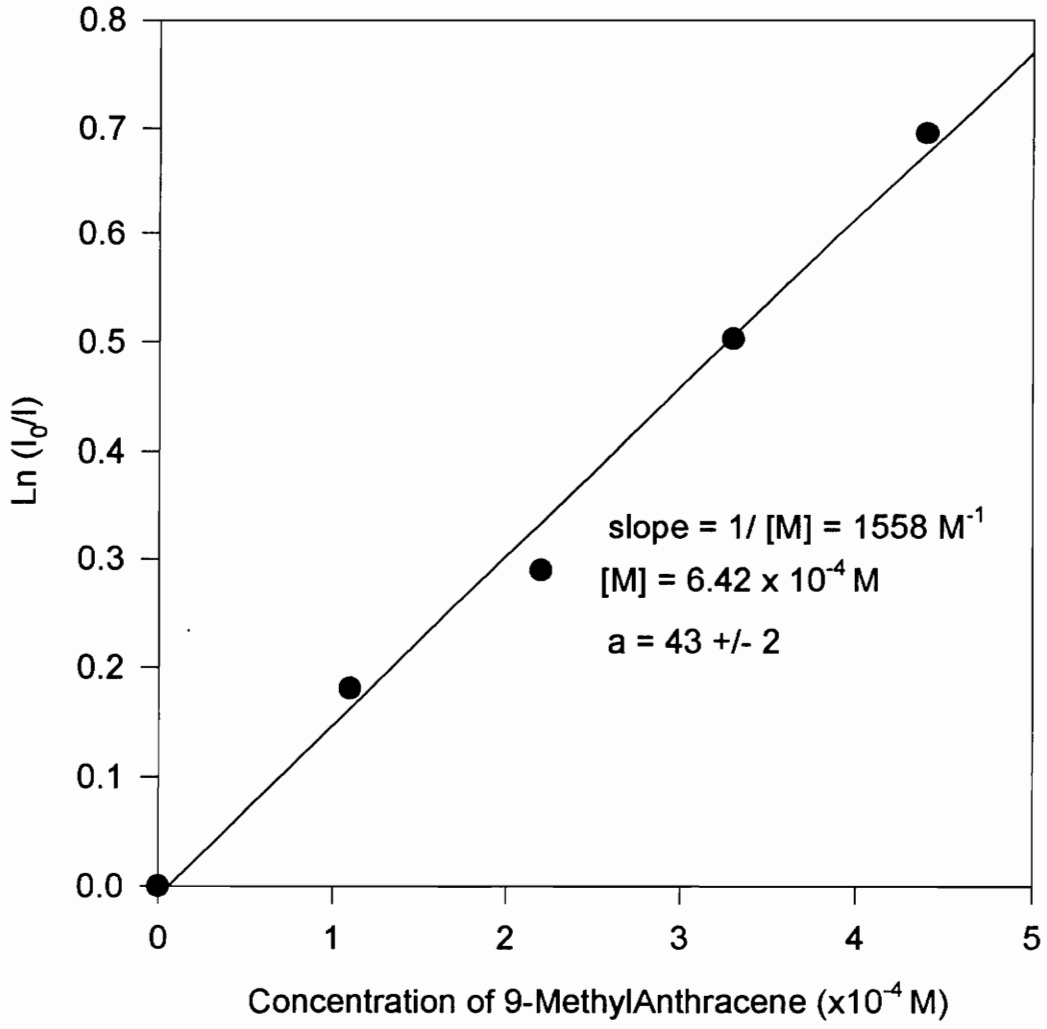

Figure 15: Determination of the aggregation number of SDS using quencher/probe experiment.

4.2 Experimental

The instrument used for this experiment was the same Perkin Elmer Luminescence Spectrometer model LS50 described earlier in Chapter 2. The wavelength of excitation was 453 nm, the maximum wavelength was 587.50 nm.

The samples for both SDS and PC3 were prepared in the same manner. All samples were kept under nitrogen. SDS was purchased from Aldrich and recrystallized from methanol. PC3 was synthesized in our laboratory following Dr. Ding's procedure.[13] The (tris(2,2-bipyridine)ruthenium(II)-chloride) was provided by Dr. Karen Brewer. The 9-methylanthracene was purchased from Aldrich and used as received. All solutions were made with house deionized water that was distilled under nitrogen.

The first step was to prepare stock solutions of the probe (tris(2,2-bipyridine)ruthenium(II) chloride) in water, the PC3 or SDS in water, and the quencher (9-methylanthracene) in diethylether. The standards were mixed to give a final volume of 2.0 ml of water at probe concentration of 5.3×10^{-5} M and PC3 concentration of 0.0050 M or SDS concentration of 0.034 M. The quencher concentration varied from 0.0 M to 6.25×10^{-4} M. The quencher was introduced into the sample by phase transfer.

The stock solution of quencher in ether was placed on top of the samples, already having probe and micelles, and nitrogen was blown over the samples while they were stirred. The ether evaporated as the quencher was brought into the aqueous phase by the micelles. Once in the aqueous phase the quencher interacted with the probe and thus lowered the fluorescence intensity. The solutions were stirred overnight to ensure complete evaporation of the ether and total interaction of the quencher with the probe. Emission spectra were then taken and the data was used to determine the aggregation number.

4.3 Results

It can be seen from figures 16 and 17 that the aggregation number for PC3 in two experiments was determined to be 3.2 and 3.6(when the CMC is taken to be 4.7 $x10^{-4}$ M).

4.4 Discussion

The aggregation number is the average number of particles present in each micelle formed by a given surfactant. The aggregation number for SDS was determined to be 43 which, as shown earlier, agrees with literature values.[38] However, the quencher/probe experiment with PC3 demonstrates that the phosphine has a very small aggregation

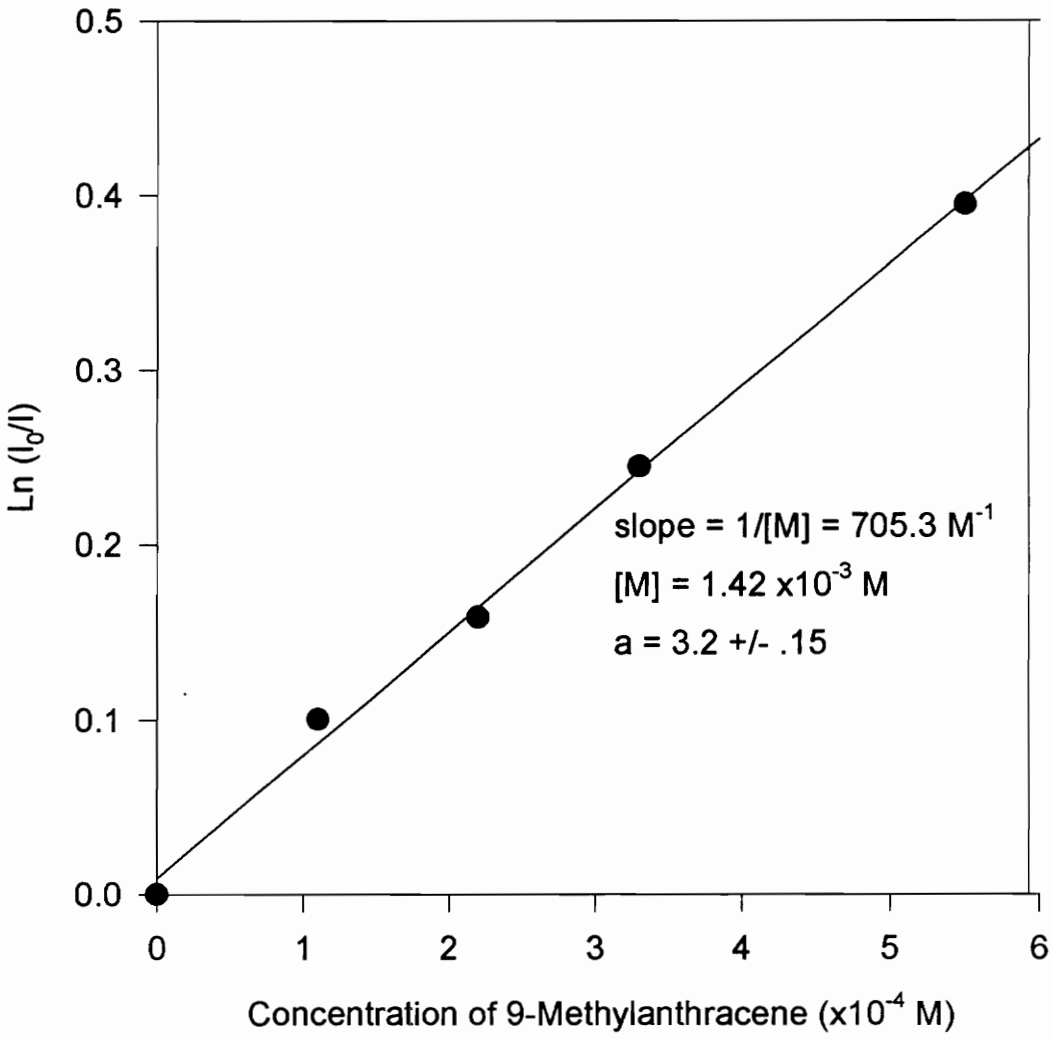

Figure 16: Aggregation number determined for PC3 using quencher/probe experiment. This experiment gives an aggregation number of 3.2 ± .15.

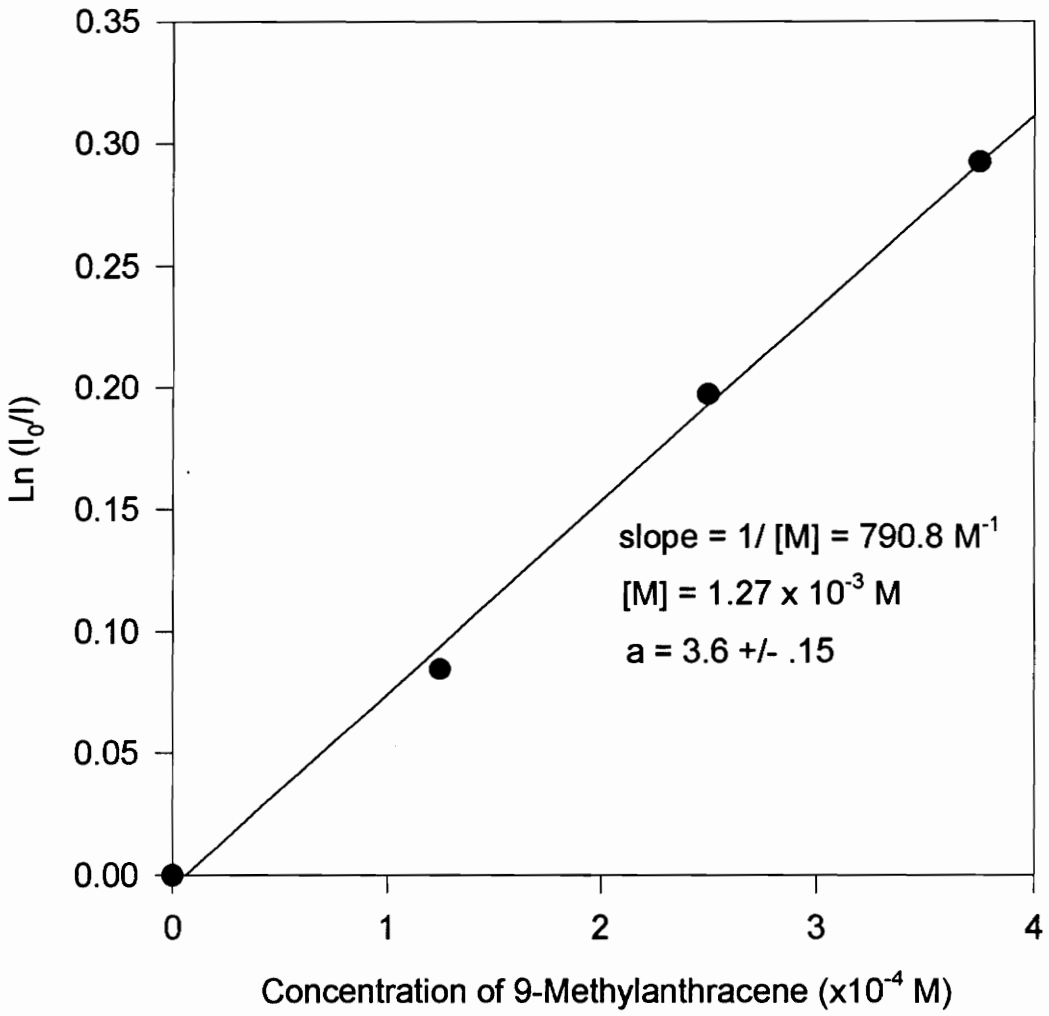

Figure 17: Aggregation number of PC3 determined by quencher/probe experiment. The aggregation number determined in this experiment was 3.6 ±.15.

number. The value obtained suggests an aggregation number for PC3 of 3 or 4, in the absence of salt.

If the aggregation number is taken to be 4 particles per aggregate then figure 18 could be a representation of a PC3 micelle. Figure 18 is a computer model of what a PC3 micelle might look like if it had an aggregation number of four. The model is done with the phosphorus atoms fixed at a distance of 6.5 Å in a tetrahedral arrangement. The diameter of the micelle in figure 18 is approximately 32 Å to 34 Å which is actually larger then the size seen with the light scattering instrument. This could be due to the fact that the aggregation number is less than four or that the molecular modeling parameters do not take into account all of the factors involved in determining aggregation size. It is possible that the phosphorous atoms are closer than 6.5 Å, just as it is possible that the aggregation number is smaller.

Salt does indeed increase micelle size, which in doing so may increase aggregation number as it does in the case of SDS.[18] Therefore, figure 19 is another computer model in this case postulating what a micelle of PC3 having an aggregation number of six might look like. The phosphorous atoms in figure 19 are also at a distance of 6.5 Å, but are in an octahedral arrangement. In the case of figure 19 the computer

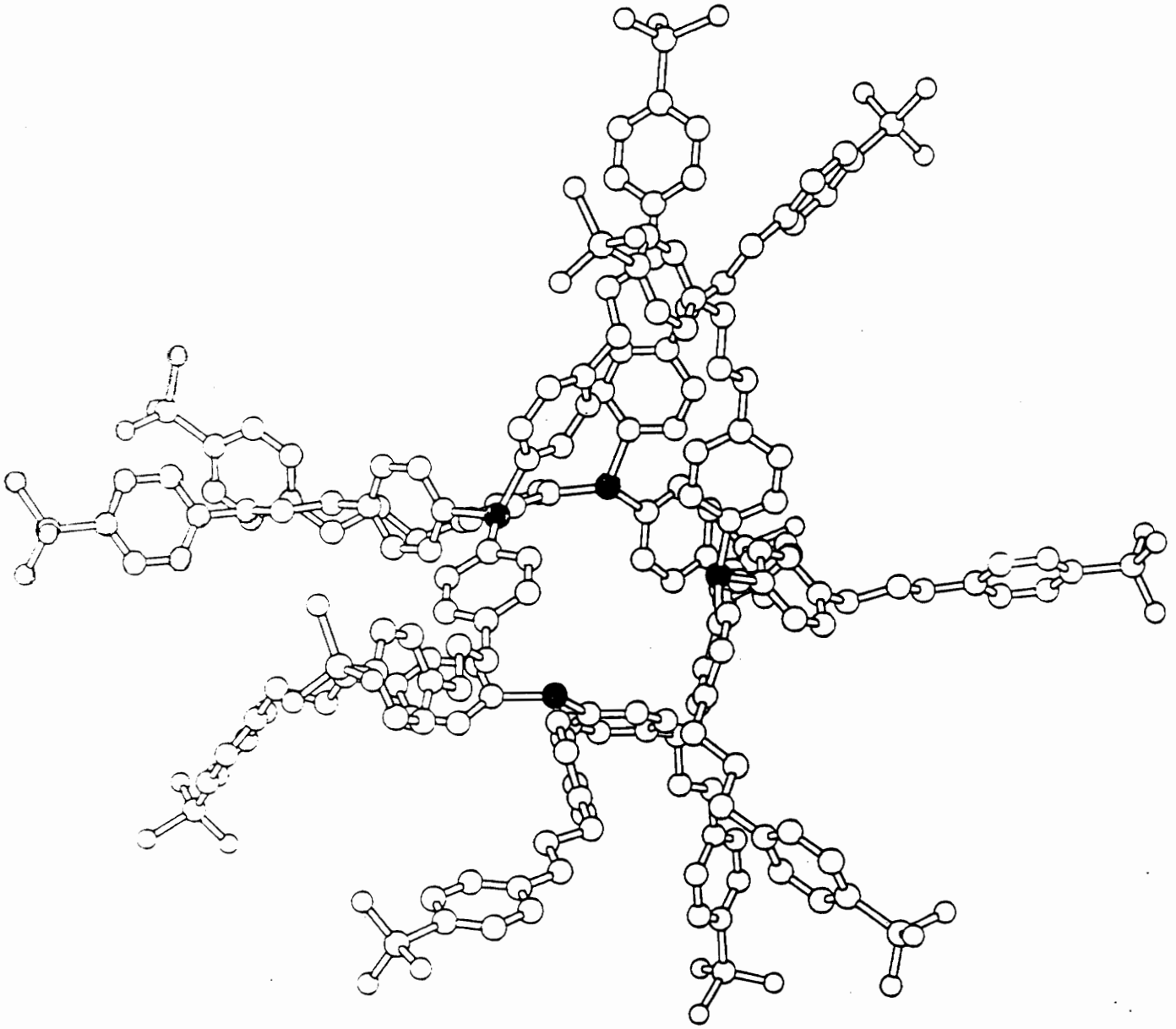

Figure 18: Computer model showing possible arrangement of four PC3 molecules in a micelle. Phosphorous atoms are in a tetrahedral arrangement at a fixed P-P diameter of 6.5 Å. The structure is locally minimized, ignoring electrostatic repulsion's of the SO_3^- groups. This particular model has a diameter of approximately 32-34 Å.

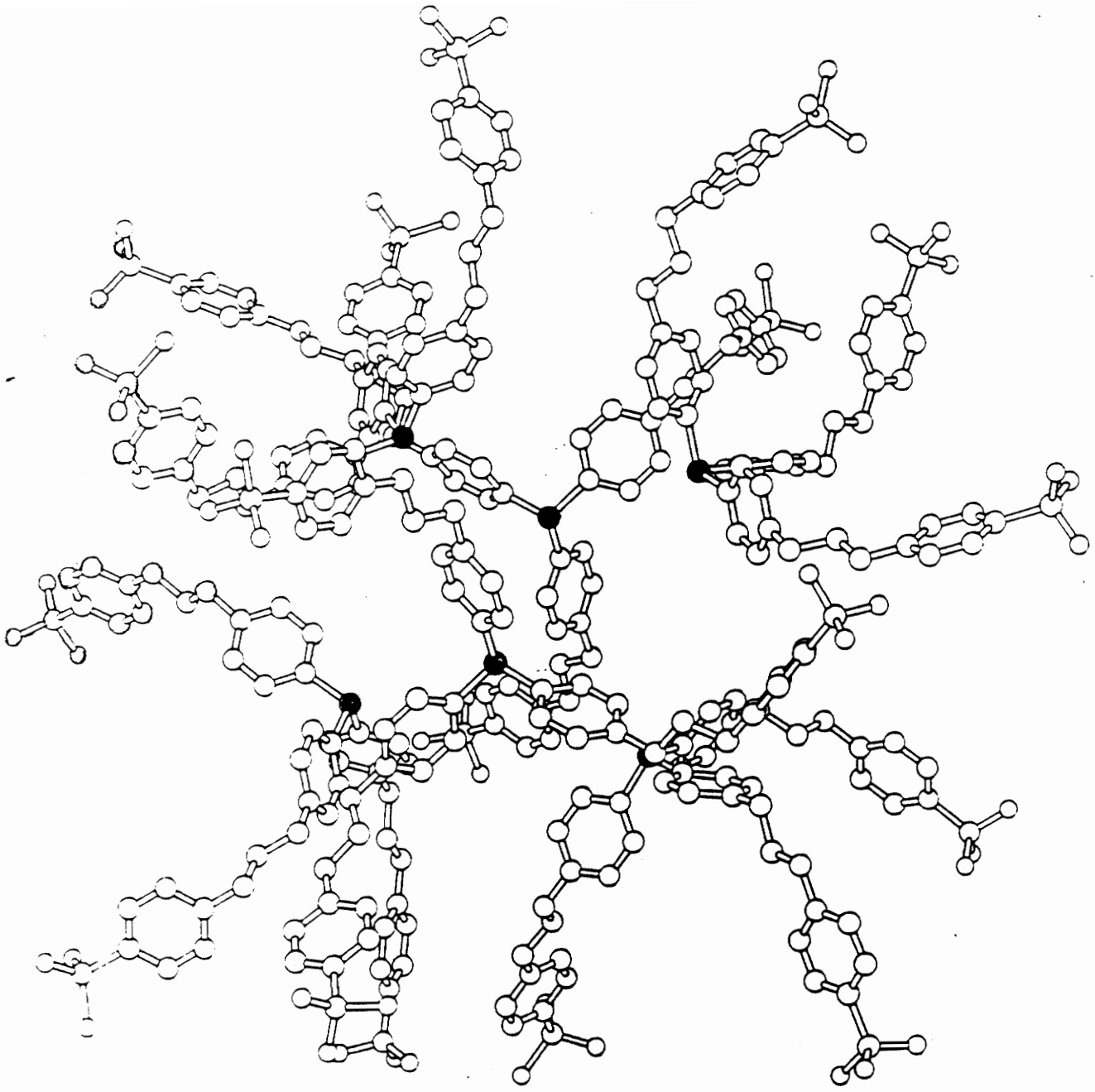

Figure 19: Molecular model of a PC3 micelle if aggregation number was taken to be 6. The P-P distance has been fixed at 6.5 Å, and the structure has been minimized as was done in figure 17. The diameter is approximately 38-40 Å which is much closer to the light scattering data when salt was present in solution.

model's diameter agrees well with the light scattering data with added salt at 38 Å to 40 Å. This is not evidence of an aggregation number but rather a postulated model for PC3 micelles based on the data at hand. It is still possible that the model does not take into account all factors affecting micelle size. In both cases the local minima are obtained in order to bring the methylene groups as close as possible while ignoring electrostatic repulsion's between the sulfonate groups. It may be possible to understand these micelle systems more in the future and at that time perhaps more precise techniques can be used to confirm or deny the models postulated in the text.

Chapter 5

Conclusions

It was determined that the PC3 ligand forms micelles in aqueous solutions. The micelle diameter was determined to be 24 Å without salt and 40 Å with added salt. The CMC was estimated to be 4.7 $x10^{-4}$ M without salt and < 1.2 $x10^{-4}$ M with added salt. The aggregation number was determined to be 3 or 4. It was determined that the PC3 micelles behave much like other micellar systems; therefore, the surface activity of PC3 may be attributable to its micelle character.

It has been postulated that the increase in activity seen in hydroformylation of 1-octene with the ligand PC3 over TPPTS is due in part to the surface activity of the PC3 ligand. It has been shown here that the PC3 ligand does in fact form micelles, and these micelles do indeed help solubilize 1-octene in water. Because the PC3 is able to solubilize the 1-octene in the aqueous phase this could account for the increased catalytic activity. Also, the activity increases as solution ionic strength increase. This is supported by the lower CMC of the PC3 and the increased micelle size as the solution ionic strength increases. Therefore, it is very possible that the increased catalytic activity is because the PC3 forms micelles and these micelles act as phase transfer agents by moving the 1-octene into the

aqueous phase where more 1-octene can interact with the catalyst and thus form more product.

The PC3 ligand is a better ligand for 1-octene hydroformylation than is TPPTS in solutions of low ionic strength, yet there could be an even better ligand than PC3. The reason PC3 is a good ligand may be due to its ability to form micelles. Perhaps further studies on the catalytic system using PC3 as the ligand may give even more evidence as to how the system actually works. Thus far we have but a piece of the puzzle. However, this piece fits very well and with continuing research the best possible catalytic system may be found. As our understanding of two phase hydroformylation catalysis increases, we will be better able to improve the system.

In the future it might be possible to determine how much 1-octene is actually solubilized by each PC3 molecule. Attempts were made; however, only qualitative results were obtained and further study needs to be done. Also, it may be possible to determine if the actual complex, $HRh(CO)(PC3)_3$, itself forms micelles. A complex that does not need excess ligand is another source of savings.

More studies on CMC and aggregation number might better elucidate the exact behavior of the PC3. Techniques such as

SANS, small angle neutron scattering, may be more appropriate for the small micelles formed by the PC3 ligand.

Much more work has to be done, and hopefully some day soon the optimal system will be in use.

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Appendix A-1

Table 6: Data for figure 8

[PC3] ($x10^{-4}$ M)	I_1	I_3	I_1/I_3
0.0000	68.7500	39.7280	1.7305
1.0000	69.8140	52.9010	1.3197
2.0000	75.3770	65.0020	1.1596
3.0000	82.0250	75.8520	1.0814
4.0000	91.0930	88.9870	1.0237
5.0000	96.0320	101.1050	0.9498
6.0000	107.2000	114.6950	0.9347
8.0000	117.6740	131.3690	0.8958
10.0000	124.4330	144.3240	0.8622
12.0000	137.8270	163.8260	0.8413
14.0000	149.5280	181.4770	0.8240
16.0000	178.7560	218.7230	0.8173
18.0000	184.6060	228.3830	0.8083
20.0000	191.3030	239.5080	0.7987
22.0000	197.6740	249.7490	0.7915

Appendix A-2

Table 7: Data for figure 9

Conc. PC3 ($x10^{-5}$ M)	I_1	I_3	I_1/I_3	Conc. PC3 ($x10^{-5}$ M)	I_1	I_3	I_1/I_3
0.0000	39.4570	22.2120	1.7764	30.0000	82.3550	95.6910	0.8606
2.0000	36.7720	22.4730	1.6363	40.0000	95.6450	113.0110	0.8463
4.0000	30.3070	23.4130	1.2945	50.0000	99.4030	119.6490	0.8308
6.0000	34.4540	29.3120	1.1754	60.0000	108.7870	132.8090	0.8191
8.0000	32.8410	30.1130	1.0906	70.0000	111.1740	136.1540	0.8165
10.0000	38.4320	36.5230	1.0523	80.0000	123.6090	150.5160	0.8212
12.0000	41.7740	42.1250	0.9917	90.0000	149.1440	185.1400	0.8056
14.0000	45.2150	46.6570	0.9691	120.0000	164.9950	206.8920	0.7975
16.0000	45.8580	49.0730	0.9345	140.0000	179.4050	226.6130	0.7917
18.0000	47.0430	50.6490	0.9288	160.0000	192.1540	244.9290	0.7845
20.0000	69.1670	76.6520	0.9024	180.0000	201.1190	257.6990	0.7804

Appendix A-3

Table 8: Data for figure 10

Conc. PC3 ($x10^{-4}$ M)	$\lambda_{max.}$
0.0000	457.5000
1.0000	452.0000
2.0000	440.5000
3.0000	434.0000
4.0000	430.0000
5.0000	425.5000
6.0000	426.5000
7.0000	423.5000
8.0000	425.0000
10.0000	424.0000
12.0000	424.5000
14.0000	423.5000

Appendix A-4

Table 9: Data for figure 11

Conc. PC3 ($x10^{-5}$ M)	$\lambda_{max.}$	Conc. PC3 ($x10^{-5}$ M)	$\lambda_{max.}$
0.0000	457.5000	30.0000	422.0000
2.0000	442.5000	40.0000	422.0000
4.0000	440.5000	50.0000	421.0000
6.0000	430.5000	60.0000	421.5000
8.0000	428.0000	70.0000	421.5000
10.0000	427.5000	80.0000	422.0000
12.0000	422.0000	90.0000	423.0000
14.0000	422.0000	120.0000	423.0000
20.0000	422.0000	140.0000	422.5000

Appendix A-5

Table 12: Data for figure 12

Conc. PC3 ($x10^{-4}$ M)	Surface Tension (dynes/cm)
3.0000	78.8000
3.1000	78.6000
3.3000	78.2000
3.5000	78.0000
3.7000	77.8000
3.9000	77.2000
4.1000	75.1000
5.0000	74.0000
6.0000	74.0000
7.0000	74.0000

Appendix A-6

Table 11: Data for figure 13

Conc. PC3 ($x10^{-4}$ M)	Surface Tension (dynes/cm)
2.0000	67.5000
4.0000	67.0000
6.0000	66.2000
10.0000	66.0000
14.0000	62.5000
16.0000	62.0000
20.0000	62.0000
24.0000	62.0000
30.0000	62.0000
40.0000	62.0000

Appendix A-7

Table 12: Data for figure 14

Conc. PC3	Conductivity	Conc. PC3	Conductivity	Conc. PC3	Conductivity
0	1.95	0.0003686	107.2	0.0007751	207
1.2E-06	2.31	0.0003918	113.4	0.0007929	211
1.982E-05	8.17	0.0004129	119	0.0008129	215
3.894E-05	14.17	0.0004335	124.5	0.0008343	221
5.561E-05	19.26	0.0004538	129.3	0.0008535	226
7.601E-05	25.3	0.0004777	135.5	0.0008748	231
7.998E-05	26.5	0.0005033	142	0.0008947	236
9.836E-05	32	0.0005237	147.3	0.0009104	239
0.0001214	37.9	0.0005441	152.6	0.0009305	244
0.0001407	43.5	0.0005656	158.2	0.00095	249
0.0001592	48.9	0.0005861	163.5	0.0009661	253
0.0001817	55.4	0.0006052	168.4	0.0009839	257
0.0002049	62	0.000625	171.6	0.001004	262
0.0002273	68.3	0.0006449	175	0.0010179	265
0.0002274	68.4	0.0006623	179.4	0.0010326	267
0.0002479	74.2	0.0006848	185.1	0.0010518	272
0.0002693	80.2	0.0007025	189.4	0.0010726	277
0.000291	86.2	0.0007196	193.8	0.001091	281
0.0003105	91.6	0.0007373	197.4	0.0011144	286
0.0003299	96.8	0.0007581	202	0.0011325	290
0.0003494	102				

(Concentration in Molarity and Conductivity in Mhos)

Appendix A-8

Table 13: Data for figure 16

Concentration of 9-methyl-anthracene ($x10^{-4}$ M)	I	ln I_0/I
0.0000	9.9940 (I_0)	0.0000
1.1000	9.0390	0.1004
2.2000	8.5290	0.1585
3.3000	7.8280	0.2443
5.5000	6.7350	0.3947

Appendix A-9

Table 14: Data for figure 17

Conc. of 9-methylanthracene ($x10^{-4}$ M)	ln I_0/I
0.0000	0.0000
1.2500	0.0849
2.5000	0.1971
3.7500	0.2921