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## Micellar Catalyzed Hydrolysis of Hydroxamic Acids by Perfluorooctanoic Acid

Mohammad Hashem Akhavan Tafti

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**MICELLAR CATALYZED HYDROLYSIS OF HYDROXAMIC ACIDS BY  
PERFLUOROOCTANOIC ACID**

by

**MOHAMMAD HASHEM AKHAVAN-TAFTI**

**A Thesis  
Submitted to the  
Faculty of The Graduate College  
in partial fulfillment of the  
requirements of the  
Degree of Master of Arts  
Department of Chemistry**

**Western Michigan University  
Kalamazoo, Michigan  
December 1988**

## MICELLAR CATALYZED HYDROLYSIS OF HYDROXAMIC ACIDS BY PERFLUOROOCTANOIC ACID

Mohammad Hashem Akhavan Tafti, M. A.

Western Michigan University, 1988

The work reported herein demonstrated that a perfluorocarboxylic acid does indeed behave as a reactive counterion surfactant exhibiting micellar catalysis, this conclusion was further verified by subsequent experimentation.

Rates of acidic hydrolysis of octano-, phenylaceto-, and 4-bromo phenylaceto-hydroxamic acid have been determined in aqueous perfluorooctanoic acid - a reactive counterion surfactant system. Typical micellar catalysis was observed for the hydrolysis of octanohydroxamic acid but not for the arylacetohydroxamic acids.

Further investigation into finding a more water soluble surfactant which has reactive counter ions is suggested in order to test the theoretical equation (based on the pseudo phase model) appropriate for this surfactant type.

## ACKNOWLEDGMENTS

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A special debt of gratitude is owed to Professor Nagler who believed in me and always encouraged me to pursue new ideas.

Financial support in the form of a research assistantship and teaching assistantship from Western Michigan University is gratefully acknowledged.

Special thanks; to Cheryl McCoy for her help in preparing this thesis.

I wish to express my deepest appreciation to my wife Zahra for her infinite love and support during this work and her tolerance of the often lonely life of the wife of a graduate student.

Last, but certainly far from least, I wish to thank my parents who truly sacrificed their livelihood so I could come to the U.S.A. for higher education.

Mohammad Hashem Akhavan-Tafti

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**Micellar catalyzed hydrolysis of hydroxamic acids by  
perfluorooctanoic acid**

**Akhavan-Tafti, Mohammad Hashem, M.A.**

**Western Michigan University, 1988**

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**Dedication**

**To Zahra and Mariam, the hopes of my life,  
and to my parents**

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## CHAPTER I

### INTRODUCTION

Recently there has been considerable interest in the structure of micelles<sup>1,2</sup> as well as their effect in catalyzing certain reactions.<sup>2,3</sup> Interest in this topic has continued to develop although in the early stages the concept of micelles met extreme resistance.

(So novel was this finding that in 1925 when some of the evidence for it was presented to the colloid committee for the advancement of science in London, it was dismissed by the chairman, a leading international authority, with the words, "Nonsense McBain!" )

Current activities and interests in micelles range from soaps and detergents, to "model" systems<sup>5</sup> for a variety of problems related to monolayers, colloidal systems in general, proteins, emulsion polymerization, enhanced oil recovery, and mimicking enzyme catalysis.<sup>6</sup> The latter interest has caused increased research to aid in understanding the mechanisms of micellar catalyzed reactions.

Even though micelles mimic enzyme catalysis, they differ sharply in structure. The fundamental behavior of micelle forming monomers is their amphiphilicity or amphipathicity, i.e. the presence in the same molecule or ion of polar and nonpolar

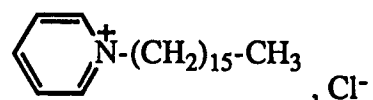
A great variety of amphipathic monomers are in existence. The most common of these is sodium lauryl sulfate,  $\text{CH}_3(\text{CH}_2)_{11}\text{-OSO}_3^-\text{Na}^+$ , found in mouth wash. These amphipathic monomers can be classified as non-ionic, anionic, cationic and zwitterionic surfactants.<sup>7</sup>

1. Non-ionic: the hydrophilic portion of this kind of surfactant more often consists of hydroxyl groups or a polyoxyethylene chain, e.g., brij 30 [polyoxyethylene (4) lauryl ether],  $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_{44}\text{OH}$ , and tween 20[polyoxy

ethylene(20)sorbitanmonolaurate].

2. Anionic: the hydrophilic portion is an anion, e.g., sodium lauryl sulfate,  $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$ ).

3. Cationic: the hydrophilic portion is a cation, e.g, hexadecyl trimethyl ammonium chloride,  $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Cl}^-$ , and hexadecyl pyridinium chloride:



4. Zwitterionic: these surfactants possess both anionic and cationic groups on the hydrophilic moiety and, depending on the pH of the solution and the structure, can behave as either anionic, cationic or neutral species. The more common zwitterionic surfactants include N-alkyl and C-alkyl betaines and sultaine, 3-(dimethyldodecylammonio)propane-1-sulfonate,  $\text{CH}_3(\text{CH}_2)_{11}\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3^-$ .

As shown above, this classification depends upon the nature of the head groups. The ionic surfactants are of course always associated with counter ions and their properties are often modified significantly by different counterions.

The amphipathic molecules have a tendency to collect at any interface where the hydrophobic groups are partially or completely protected from exposure to water while their hydrophilic groups can remain wetted. These general tendencies account for their surface activity, the ability to adsorb to air-water or oil-water interfaces and to surfaces of hydrophobic solids such as carbon or to macromolecules such as proteins.

Although ionic surfactants at low concentration in aqueous medium behave like solution electrolytes,<sup>7</sup> above a certain surfactant concentration micelle formation by amphipaths results due to the dual tendencies of the molecules mentioned above. This concentration is known as the critical micelle concentration (cmc). Careful experimentation has shown that the cmc is not a single sharp concentration but rather a narrow range of concentrations.<sup>8</sup> A more exact definition of the cmc is that

which includes the cmc is narrow enough that with proper care it can be determined with 1% accuracy. The cmc is usually obtained experimentally by plotting the change in some physical or chemical property as a function of surfactant concentration and extrapolating the results both at low and high concentrations to an intersection point. A variety of methods have been used to determine the cmc values, the most common ones being the utilization of electrical conductance, ultrasound, and surface tension.<sup>10</sup>

The value of the cmc is governed by a large number of parameters. Usually, the more surface active the amphiphilic monomer, the greater the affinity for micelle formation, and, as a result, the lower the cmc of the micelle produced. Accordingly, in all cases the cmc decreases as hydrocarbon chain length increases, even though the nature of the hydrophilic head group has little effect on the cmc value. The position of the head group in the hydrocarbon chain has a large effect on the cmc. The closer the head group to the center of the chain, the higher the cmc. The presence of polar groups, C = C double bonds, and chain branching results in an increase in the cmc value. Addition of strong electrolytes decreases the cmc of ionic surfactants due to the

Temperature also has an effect on the cmc value; however, the effects of temperature on the cmc of ionic surfactants are considerably more complex than those for non-ionic surfactants.<sup>13</sup>

Ionic micelles (shown in Figure 1) can be described as roughly spherical, however, recent experiments have shown ellipsoidal shapes for the most common small micelles.<sup>14,15</sup> The average radii of micelles is 12-30 Å. The hydrophobic part of the aggregate forms the "core" of the micelle while the hydrophilic head groups are located at the micelle-water interface in contact with and wetted by a number of water molecules. The charged head groups and counter ions of the ionic micelles are located in a compact region, known as the "Stern layer." The close association of the counter ions and the ionic head groups is responsible for the reduction of the net charge on the



micelles. Most of the counter ions are located in the so-called "Gouy-Chapman electrical double-layer" where they are completely dissociated from the charged aggregate and are able to exchange with ions in the bulk of the solution. A dynamic equilibrium exists between the monomer in solution and the micelle.<sup>16</sup> Some monomers leave while others combine, while still others protrude from the micelle. This means that micelles, when formed, are not sharply defined entities. Micelle shape is dependent on the concentration of the surfactant. Other aggregate shapes are rod-like, and lamellar. Micelle size is described by the aggregation number (N), which is the number of monomers per micelle, and the length of the aliphatic chain of the surfactant. Typical values for the aggregation numbers of ionic surfactants in aqueous medium range from 10 to 100, e.g, the aggregation number for dodecyl pyridinium iodide is 87.<sup>17</sup> Like the cmc, aggregation numbers are dependent on the concentration of surfactant, the presence of inorganic and organic additives and on the temperature. Increasing the concentration of the surfactant well above the cmc usually results in an increase in the micellar size. Similarly, the decrease in cmc caused by additives is paralleled by an increase in the aggregation number. Since the effectiveness of micellar catalysis can subtly depend on micellar size and geometry,<sup>18</sup> knowledge of these and other factors on aggregation behavior is clearly required for meaningful interpretation of the kinetic data.

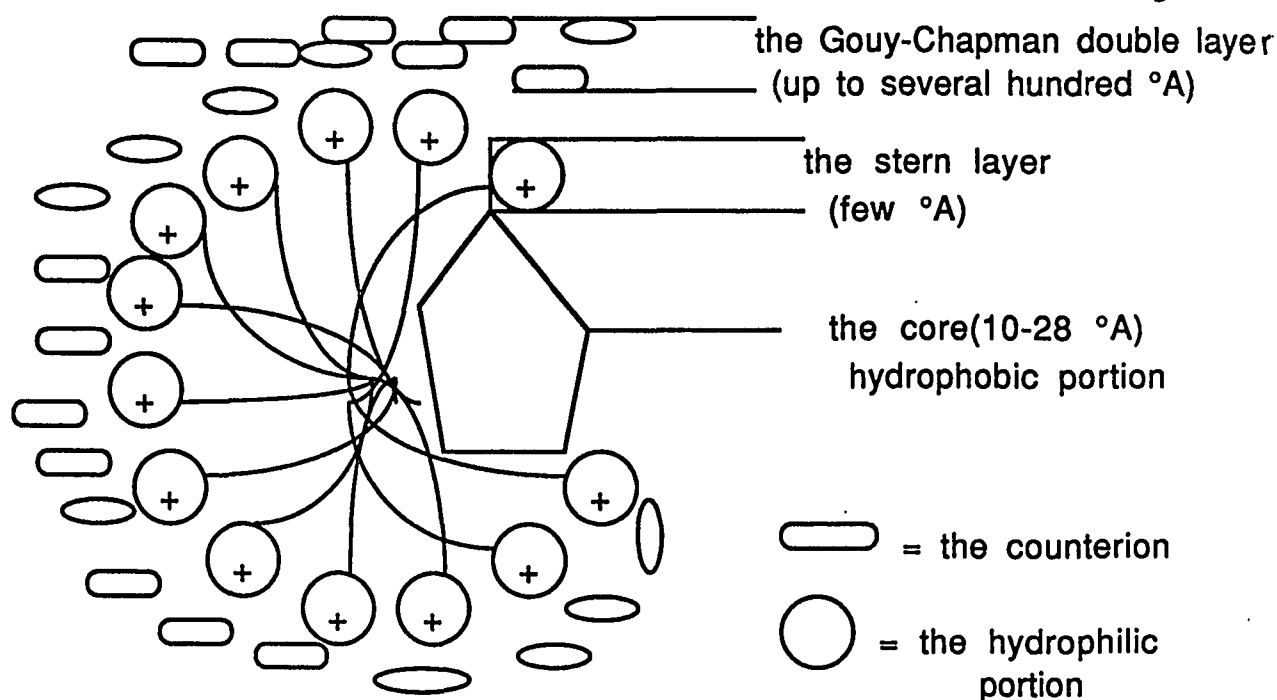


Figure 1. Model of Hypothetical Cationic Micelle Showing the Locations of Headgroup, Surfactant Chains, and Counterions.

### Micellar Catalysis and Kinetics

Catalysis occurs when micelles are present. Micellar catalysis in water is best explained in terms of reactions in the micellar and in the aqueous pseudo phase.<sup>7</sup> The reactant is usually of low solubility in water and, therefore, more soluble in the micellar phase. Solubilization of the reactant is similar to an extraction in that the reactant is distributed between two phases: the bulk solution and the micelle.

A knowledge of the location of solubilization can aid in the understanding of the catalysis. Most models of micellar catalyzed reactions assume that the overall rate of reaction is the sum of rates in each pseudo phase and that changes in the rate with increasing surfactant concentration or added reagents reflects the change in the distribution of reactants between the two pseudo phases. Another explanation for the

concentration of reactants in the micellar micro-environment results in a rate enhancement with no increase in the rate constant.<sup>7</sup> Other models also consider the transition state stabilization that occurs when the charge in the transition state is stabilized relative to the reactant state in the micellar pseudo phase relative to the bulk phase by the charge in the Stern layer (if the transition state is destabilized, inhibition of the reaction occurs). Rate acceleration now occurs due to an increase in the rate constant.<sup>19</sup> These models assume that changes in micelle size and shape<sup>20</sup> as the surfactant concentration changes are not significant, so that only those factors which control the distribution of reactants between the two pseudo phases will play an important role on the observed rates.

As described earlier, micelles have been considered to contain a hydrophobic core and a polar surface.<sup>20</sup> Actually, the water penetration, viscosity, and polarity of the different regions of micellar structure are matters of current investigation and discussion<sup>21</sup>. As a result micelles are able to solubilize organic molecules. The site of solubilization varies with the nature of the solubilized species and of course the surfactant. Information on the sites of solubilization is usually obtained from studies on the solubilizate before and after solubilization (by such techniques as u.v., n.m.r., e.s.r., and fluorescence). Based on these investigations, the following three models of incorporation have been suggested: (1) adsorption on the surface of the micelle, at the micelle/solvent interface, (2) in the case of polyoxy-ethylene groups (non-ionic surfactants) between the hydrophilic head groups, and (3) in the inner core of the micelle. The most likely solubilization sites are, however, the interface and the Stern layer. Therefore, the reaction site within the micellar pseudo phase is believed to be in the Stern layer.<sup>20</sup>

The solubilization process is a dynamic one, and the solubilizate is in dynamic equilibrium between the micelle and the aqueous phase (residence time  $10^{-3}$  -  $10^{-5}$

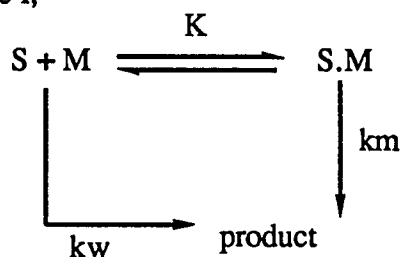
sec.). The more hydrophobic a solute molecule, the longer is the residence time.<sup>21 22</sup>

The tendency of a solute to interact with micelles is generally expressed through the binding constant,  $K$ ; for the reaction:  $S + M \xrightleftharpoons{K} S.M$ , where  $S$  and  $M$  are the substrate and the micellar aggregate, respectively. Thus,

$$K = [SM] / ([S][M]) \quad (1)$$

$M$  is generally expressed as the concentration of micellized surfactant,  $M$  (i.e., analytical concentration of surfactant,  $C_D$ , less  $cmc$ ).

An approximate pseudo phase model for unimolecular reactions catalyzed by micelles is shown in scheme I,<sup>7</sup>



Scheme I

where  $k_m$  and  $k_w$  are rate constants for product formation within and outside the micelle respectively. This model leads to the following relationship:

$$\frac{1}{k_w - k_{obs}} = \frac{1}{k_w - k_m} + \left( \frac{1}{k_w - k_m} \right) \left( \frac{N}{K (C_D - cmc)} \right) \quad (2)$$

where  $k_{obs}$  is the observed pseudo first order rate constant, and  $N$  is the micelle aggregation number. There are many limitations when equation (2) is applied to bimolecular reactions<sup>23</sup>, namely that:

1. It has been assumed that the substrate does not associate with the monomeric surfactant.
2. The substrate association has 1:1 stoichiometry with micelle.

3. The substrate does not significantly alter the micellization and cmc.

4. The rate of reaction of many bimolecular reactions goes through a maximum with increasing M, however, most reactions exhibiting micellar catalysis are inhibited by counterions, and the larger the ion, the greater the effect. This behavior has been explained by the fact that an electrolyte exists for a "binding site" on the Stern layer of the micelle, and the ability to alter the micellar structure.

5. In the acid hydrolysis, the hydronium ions themselves can be partitioned between the two pseudo phases. But, equation (2) only deals with partitioning of the substrate, S, between the two pseudo phases and ignores the partitioning of the other reactant.

6. It is also assumed that there is no change in the micellar structure when the surfactant concentration is changed.

In order to overcome some of these limitations, equations are developed from bimolecular reaction theories.<sup>24</sup> These equations take into account the partitioning of the other reactant between the water and micellar pseudo phases. Equation (3), derived by Romsted,<sup>25</sup> is for application to bimolecular reactions.

$$k_2 = \frac{k_m \beta s K (C_D - \text{cmc})}{[K (C_D - \text{cmc}) + 1] [I_t + \chi_t K_I]} + \frac{k_w}{[K (C_D - \text{cmc}) + 1]} \quad (3)$$

In equation (3),  $I_t$  is the total concentration of the reactive hydrophilic ion,  $\chi_t$  is the total concentration of the surfactant counter ion,  $\beta$  is the degree of counter ion binding to the Stern layer, and  $s$  is the molar density of the micellar phase.  $K_I$  is the ion exchange constant for the hydrophilic reactant and surfactant counter ions. Values of  $\beta$  are independent of the surfactant concentration and are always within the range of 0.6 - 0.9.<sup>26</sup>

For bimolecular reactions, where the other reactant is the counter ion of the surfactant, the kinetic equation derived is:

$$k_{\psi} = \frac{k_w [C_D] + \beta s (k_m K - k_w) (C_D - cmc)}{1 + K (C_D - cmc)} \quad (4)$$

where  $k_{\psi}$  is the observed rate constant and  $C_D$  is the stoichiometric concentration of the reactive counter ions. However, equation (4) under certain circumstances ( $K k_m \gg k_w$ )<sup>27</sup> is reduced to:

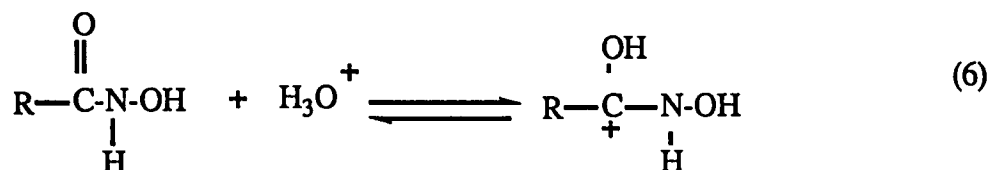
$$k_{\psi} = \frac{k_w [C_D] + k_m K \beta s (C_D - cmc)}{1 + K (C_D - cmc)} \quad (5)$$

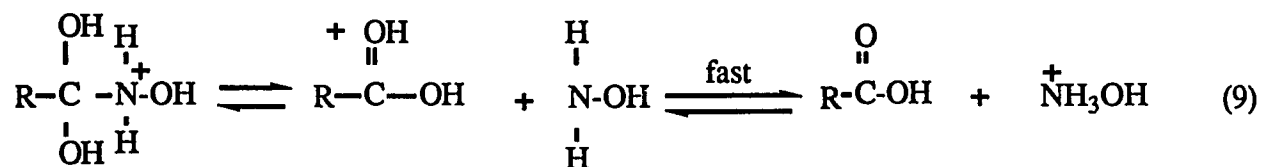
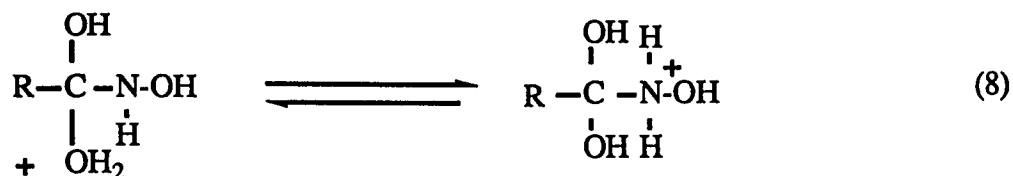
For the simplification of equation (4) to equation (5), the following assumptions have been made:

1. Micellar concentration is far greater than the substrate.
2. Micellar pseudo phase occupies only a small fraction of the total solution volume.

### Hydrolysis of Hydroxamic Acids

The proposed mechanism for the hydrolysis of hydroxamic acids using anionic surfactant is as follows<sup>6,28</sup>:





The present work focuses on the kinetic evaluation of a model surfactant, perfluorooctanoic acid, possessing a reactive counter ion, on the rate of hydrolysis of several hydroxamic acids. Previous studies of micellarly catalyzed hydrolysis of hydroxamic acids have successfully employed nonreactive counter ion surfactants with added reactive ions. Perfluoro surfactants have not been fully explored. This work will provide the first example of the effect of perfluorooctanoic acid on the rate of hydrolysis of several hydroxamic acids.

## CHAPTER II

### PREPARATION OF COMPOUNDS AND KINETIC PROCEDURES

#### Purification of Perfluorooctanoic Acid ( $\text{CF}_3(\text{CF}_2)_6\text{CO}_2\text{H}$ )

Perfluorooctanoic acid was purchased from Aldrich Chemical company, Milwaukee, Wisconsin. Further purification<sup>29</sup> was done by recrystallization three times from  $\text{CCl}_4$  (ACS). Fifteen grams of the surfactant was dissolved in a minimum amount of hot  $\text{CCl}_4$  (ACS) and the hot mixture was filtered and the clear colorless filtrate was refrigerated over night; the crystals were separated by use of suction filtration and washed several times with cold solvent. The melting point was measured using a Thomas Hoover melting point apparatus and was found to be  $56.5 - 58.0\text{ }^\circ\text{C}$  (literature  $56.4 - 57.9\text{ }^\circ\text{C}$ ).<sup>29</sup> To further test the purity of the surfactant, it was standardized against a sodium hydroxide solution, the secondary standard, which was standardized against potassium hydrogen phthalate (KHP), the primary standard. KHP was dried at  $110\text{ }^\circ\text{C}$  for 24 hours before use. Phenolphthalein was used as the indicator. The results of the standardization are in Table 1 and Table 2. The calculated molecular weight was found to be  $414.24\text{ g/mole}$  (theoretical =  $414.1\text{ g/mole}$ ).

#### Preparation of Hydroxamic Acids

Octanohydroxamic acid m.p.  $77.8 - 78.1\text{ }^\circ\text{C}$  (literature  $78 - 79\text{ }^\circ\text{C}$ ),<sup>31</sup> phenylacetohydroxamic acid m.p.  $142.5 - 144.0\text{ }^\circ\text{C}$  (literature  $143 - 133\text{ }^\circ\text{C}$ ),<sup>31</sup> and 4-bromophenylacetohydroxamic acid m.p.  $157.1 - 158\text{ }^\circ\text{C}$  (literature  $157 - 158\text{ }^\circ\text{C}$ )<sup>31</sup>



were prepared and purified by Professor D.C. Berndt W.M.U., Kalamazoo, Michigan and they were used as received.

### Preparation of the Ferric Chloride Solution

The ferric chloride solution was prepared according to the following ratio:

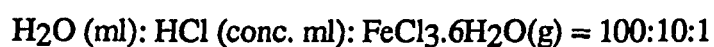


Table 1

### Standardization of NaOH Stock Solution

Measurement Trial	1	2	3	4	N
KHP (grams)	0.2063	0.2064	0.2065	0.2066	
					0.0878
NaOH (ml)	11.40	11.50	11.55	11.56	

Table 2

## Molecular Weight Determination of Perfluorooctanoic Acid

Trial	NaOH(ml) <sup>a</sup>	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>6</sub> COOH(g)	Molecular wt <sup>b</sup>
1	4.06	0.1478	414
2	4.20	0.1523	413
3	4.28	0.1550	412
4	4.44	0.1625	416

a: [NaOH]=0.0878 N

b: Molecular wt. was calculated using the following relationship:

$$\text{M.W. of CF}_3(\text{CF}_2)_6\text{COOH} = \frac{[\text{CF}_3(\text{CF}_2)_6\text{COOH}]}{(\text{M}_{\text{NaOH}})(\text{V}_{\text{NaOH}}(\text{L}))} \quad (10)$$

Ave. molecular weight for CF<sub>3</sub>(CF<sub>2</sub>)<sub>6</sub>COOH = 414 g/mole.

This solution was used as a quencher and an indicator. Ferric ion forms a maroon or violet color complex with hydroxamic acids.<sup>30</sup>

Calibration of Oil Bath Thermometer

The oil bath thermometer was calibrated against a thermometer previously standardized by Professor D.C. Berndt against a National Bureau of Standards thermometer. Equations (11) - (13) are used to arrive at the corrected temperature of the reaction.

Previous thermometer:

$$T_{\text{previous}} + 0.06 \text{ } ^\circ\text{C} = \text{True temperature} \quad (11)$$

Oil bath thermometer:

$$T_{\text{oil bath}} - 0.12 \text{ } ^\circ\text{C} = T_{\text{previous}} \quad (12)$$

However the corrected oil bath temperature is:

The oil bath -  $0.06^{\circ}\text{C}$  = True Temperature

(13)

The oil bath thermometer was calibrated at  $70.0^{\circ}\text{C}$ .

### Verification of Beer's Law

Previously in our laboratory, the spectrophotometric method which was used for the analysis of hydroxamic acids, in the presence of anionic and cationic surfactants,<sup>28,31</sup> was as follows: twenty-five millileter (pipet) of a  $0.01199\text{ M}$  aqueous surfactant solution;  $10\text{ mL}$  (pipet) of the ferric chloride solution; and  $3\text{ mL}$  or  $6\text{ mL}$  (pipet) of a  $5 \times 10^{-4}$  aqueous solution of the hydroxamic acid were mixed in a  $50\text{ mL}$  volumetric flask, and the contents were diluted to the mark using double distilled water. However, when we applied the same procedure using perfluorooctanoic acid as the surfactant it resulted in a water insoluble maroon colored precipitate. In order to overcome this solubility problem the following procedure was adopted: a  $0.01\text{ M}$  surfactant solution was prepared using  $1:1\text{ (v/v)}$  glacial acetic acid (gold label purchased from Aldrich Chemical company): double distilled water. Also, a  $5.0 \times 10^{-4}\text{ M}$  solution of octanohydroxamic acid was prepared using  $1:1\text{ (v/v)}$  of glacial acetic acid:  $\text{H}_2\text{O}$ . Into a  $50\text{ mL}$  volumetric flask (A), the following amounts were pipetted:  $25\text{ mL}$  of surfactant solution,  $10\text{ mL}$  of ferric chloride solution and  $3\text{ mL}$  of octanohydroxamic acid solution. Then the solution in the flask was diluted to the mark with  $1:1\text{ (v/v)}$  glacial acetic acid: double distilled water. Into another  $50\text{ mL}$  volumetric flask (B) were pipetted all of the previous solutions that were in flask (A) except that  $6.0\text{ mL}$  of octanohydroxamic acid was pipetted. Into the last flask (C) were pipetted  $25\text{ mL}$  of surfactant solution,  $10\text{ mL}$  of  $\text{FeCl}_3$  solution, and the contents were diluted to the mark using  $1:1\text{ (v/v)}$  glacial

acetic acid: double distilled water. The absorbance of solutions (A) and (B) versus the blank solution (C) were determined at 520 nm using a Gilford-Beckman spectrophotometer. The results verify the applicability of Beer's Law (Table 3).

#### Preparation of Stock Reactants and Surfactant Solutions

Stock reactant solutions of  $2.05 \times 10^{-2}$  M of octanohydroxamic acid, phenylacetohydroxamic acid, and p-bromophenylacetohydroxamic acid were prepared in double distilled water. These solutions were used for all kinetic runs. Surfactant solution was freshly made prior to each kinetic run. The surfactant solution of the desired surfactant concentration was prepared using double distilled water as solvent.

Table 3

#### Verification of Beer's Law

Compound	Solution	Absorbance
Octanohydroxamic acid	A (3 ml)	0.183
	B (6 ml)	0.368

#### Kinetic Procedure

Forty milliliters (pipet) of the freshly prepared surfactant solution was placed in

each reaction vessel (duplicate runs were performed for all reactions). Glass tubes and stoppers were used for all runs. The reaction vessels were stoppered and placed in a stirred constant temperature oil bath ( $70.0 \pm 0.5$  °C corrected) for approximately 20 minutes. During the equilibration time the blank was prepared. Three milliliters (pipet) of the freshly prepared surfactant solution was placed in a 50 mL volumetric flask, which contained 10 mL (pipet) of the ferric chloride solution and diluted to the mark with 1:1 (v/v) glacial acetic acid: H<sub>2</sub>O. The flask was inverted and shaken (gently to avoid foaming) 12 times and the blank was placed in a 10 cm UV cell.

One milliliter of the stock reactant solution was added to the equilibrated reaction vessels. This addition resulted in a final reactant concentration of  $5 \times 10^{-4}$  M. The tubes were stoppered, inverted 6 times, and allowed to equilibrate for at least ten minutes in the constant temperature bath. At various times a 3 mL sample was removed and added to a 50 mL volumetric flask which contained 10 mL of the ferric chloride indicator solution. Formation of the complex and the temperature reduction quenched the reaction. The mixture was diluted to the mark with 1:1 (v/v) glacial acetic acid: H<sub>2</sub>O, inverted and shaken 12 times, and placed in a 10 cm UV cell. The absorbance was immediately taken against the appropriate blank and recorded.

Rates of reaction were measured in duplicate. Duplicate runs of both compounds were carried out concurrently. Sample time was taken to be the time at which the 3 mL pipet started to drain. All samples, including preparation of the blank, were taken with the same 3 mL pipet, which was rinsed with 95% ethanol and blown dry with an aspirator. The same 40 mL pipet was used for surfactant solution and the same 1 mL pipet was used for the reactant solutions which were rinsed and dried as described. All absorbances were measured with 10 cm UV cells in a Gilford spectrophotometer at 520 nm. Two readings were taken and averaged, however, most readings were within instrumental error ( $\pm 0.002$  A)<sup>32</sup>.

The reactions were followed for at least two half-lives. For octanohydroxamic acid, the rate constants were determined over the surfactant concentration range of 0.005 - 0.035M.

However, for phenylaceto-, and 4-bromophenylacetohydroxamic acids, the rate constants were determined over the surfactant concentration range of 0.0075 - 0.035 M. The observed rate constants were pseudo first-order since the surfactant concentration was in great excess compared to the hydroxamic acid concentration.

The following derivation<sup>33,34</sup> depicted in equation (14) illustrates the relationship between the observed rate constants and the measured absorbances.

$$\ln A_0/A = k_{\text{obs}}t \quad (14)$$

where  $A_0$  is the initial hydroxamic acid concentration,  $A$  is the concentration of the hydroxamic acid at time ( $t$ ), and  $k_{\text{obs}}$  is the psuedo first order rate constant. The relationship of the hydroxamic acid concentration to the absorbance of the complex leads to the following equation:

$$\ln(A_t - A_\infty) = -k_{\text{obs}}t + \ln(A_0 - A_\infty) \quad (15)$$

where  $A_t$  is the absorbance of the complex at time ( $t$ ), and  $A_0$  is the absorbance of the complex at time zero. The absorbance at infinity,  $A_\infty$ , i.e., complete reation, is zero. Therefore, equation (15) can be reduced to:

$$\ln A_t = -k_{\text{obs}}t + \ln A_0 \quad (16)$$

The pseudo first order rate constant,  $k_{\text{obs}}$ , is determined by a least squares treatment of the  $\ln A_t$  versus time data. The calculated slope is  $-k_{\text{obs}}$ . Table 4 contains the raw data for one run of the acid catalyzed hydrolysis of octanohydroxamic acid in the presence of perfluorooctanoic acid.

Table 4

Sample Data for the Determination of  $k_{\text{obs}}$  for  $5 \times 10^{-4}$  M  
Octanohydroxamic Acid and  $1.95 \times 10^{-2}$  M  
Surfactant at  $70.0 \pm 0.5^\circ\text{C}$

Sample#	Clock Time	Time (min)	Ave. Abs.
1	11:33	0	0.275
2	12:00	27.7	0.212
3	12:29	55.9	0.161
4	12:52	79.0	0.130
5	13:12	99.5	0.107
6	13:40	126	0.0820
7	14:06	152	0.0640

The least squares treatment of the data by equation (16) gave the following results: slope = -0.0096, intercept = -1.29, and the correlation coefficient = -0.99997. Therefore,  $k_{\text{obs}} = -(-0.0096) \text{ min}^{-1} = 0.0096 \text{ min}^{-1}$ . Data from the duplicate run gave  $k_{\text{obs}} = 0.0095 \text{ min}^{-1}$  and the average  $k_{\text{obs}} = 9.55 \times 10^{-3} \text{ min}^{-1}$  or  $1.59 \times 10^{-4} \text{ sec}^{-1}$ . The percent difference in  $k_{\text{obs}}$  of the duplicate run was  $[(0.0096 - 0.0095)/0.0095] \times 100 = 1.05\%$ . The plot of  $\ln(A_t)$  versus time is shown in Figure (2).

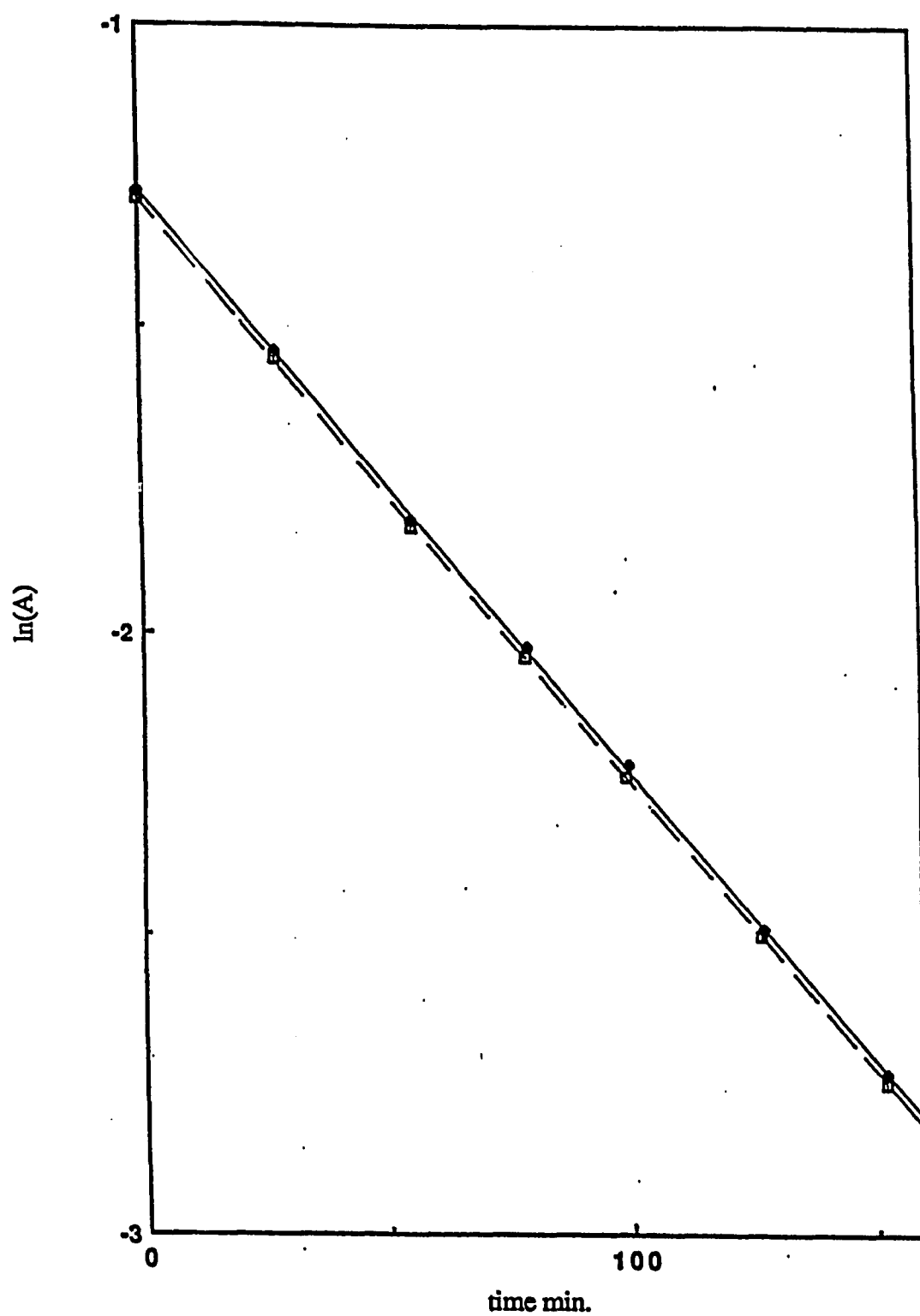


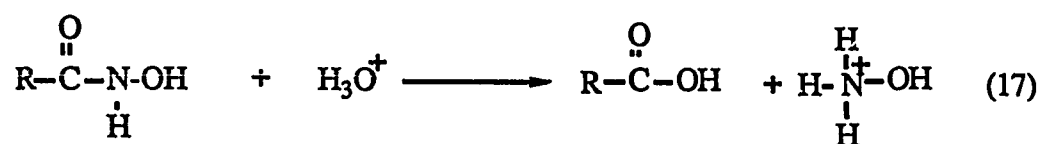
Figure 2. The Graph of  $\ln(A_t)$  Versus Time



## CHAPTER III

### RESULTS AND DISCUSSION

The net reaction for the acidic hydrolysis of hydroxamic acids is:



The surfactant, perfluorooctanoic acid used in this study is both the acid catalyst and the micellar catalyst. Since the surfactant is a reactive counterion type, in order to make the overall reaction pseudo first order (hydroxamic acid being the rate limiting reactant) the surfactant was used in excess. The rate constants were determined over the surfactant concentration range of 0.005 - 0.035 M (which was in great excess compared to hydroxamic acid concentration of  $5 \times 10^{-4}\text{M}$ ).

The pseudo first order rate constant,  $k_{\text{obs}}$ , commonly increases with increasing surfactant concentration above the cmc until a maximum occurs.<sup>7</sup> The data indicate micellarly catalyzed rate enhancement. This result is seen by comparison of the rate constants above and below the cmc (see Table 5).

Tables 6, 7, and 8 summarize the results of the least squares treatment of the kinetic data for octanohydroxamic acid, phenylacetohydroxamic acid, and 4-bromophenylacetohydroxamic acid respectively.

The data were further treated by equation 5 (discussed in Chapter I). In order to use equation 5, the cmc needed to be determined. An experimental cmc was found from the rate-surfactant profile, a plot of rate versus  $C_D$ . The intersection of the extrapolation of the lines at low surfactant concentration of the sigmoid curve was the experimental cmc. A sample determination is shown in Figure 3. The kinetic cmc was determined to

be  $1.17 \times 10^{-3}$  M for perfluorooctanoic acid at  $70.0 \pm 0.5$  °C from kinetic data for the hydrolysis of octanohydroxamic acid. The literature value is in the range of  $8.0 \times 10^{-3}$  to  $9.1 \times 10^{-3}$  M at 25 °C as determined by a solubility method.<sup>29</sup>

Table 5

Data for Rate of Hydrolysis of Some Hydroxamic Acids  
Below and Above the cmc  
at  $70.0 \pm 0.5$  °C.

Compound	$k_{\text{obs}} \text{ sec}^{-1}$		Ratio
	$C_D = 0.0073 \text{ M}^a$	$C_D = 0.0342 \text{ M}^a$	
	Micelle not present	Micelle present	
$\text{C}_6\text{H}_5\text{—CH}_2\text{—C}(=\text{O})\text{—N—OH}$	$6.9 \times 10^{-6}$	$2.7 \times 10^{-5}$	3.9
$\text{Br—C}_6\text{H}_4\text{—CH}_2\text{—C}(=\text{O})\text{—N—OH}$	$7.3 \times 10^{-6}$	$2.8 \times 10^{-5}$	3.8
$\text{CH}_3\text{—(CH}_2)_4\text{—C}(=\text{O})\text{—N—OH}$	$5.8 \times 10^{-6b}$	$6.9 \times 10^{-5b}$	12.0
$\text{CH}_3\text{—(CH}_2)_6\text{—C}(=\text{O})\text{—N—OH}$	$9.0 \times 10^{-6}$	$2.9 \times 10^{-4}$	33.0
$\text{CH}_3\text{—(CH}_2)_8\text{—C}(=\text{O})\text{—N—OH}$	$1.0 \times 10^{-5b}$	$4.2 \times 10^{-4b}$	40.0

<sup>a</sup>Total surfactant concentration. <sup>b</sup>Ayoub, M.E., M.A. Thesis, Western Michigan University, 1986.<sup>37</sup>

For the arylhydroxamic acids see Figures 4 and 5.

Equation (5) can be rearranged as follows:

$$k\psi K (C_D - \text{cmc}) + k\psi = k'_m K (C_D - \text{cmc}) + k_w C_D \quad (18)$$

where  $k'_m = k_m \beta S$

Table 6

Kinetic Data for the Hydrolysis of Octanohydroxamic Acid  
as a Function of Perfluorooctanoic Acid  
as Surfactant at  $70.0 \pm 0.5^\circ\text{C}$

$C_D \times 10^2 \text{ M}$	Ave. $k_{\text{obs}} \times 10^2 \text{ min}^{-1}$
3.4	1.8
2.9	1.6
2.4	1.3
1.9	0.95
1.5	0.58
1.2	0.22
0.98	0.070
0.73	0.050
0.49	0.035

Note: Ave.  $k_{\text{obs}}$  are average of 2 values. percent difference in  $k_{\text{obs}}$  of duplicate runs did not exceed 2%.

$$k\psi K (C_D - \text{cmc}) - k'_m K (C_D - \text{cmc}) = k_w C_D - k\psi \quad (19)$$

$$(k_{\psi} - k'_m) (K) (C_D - \text{cmc}) = k_w C_D - k_{\psi} \quad (20)$$

$$k_{\psi} - k'_m = \frac{k_w C_D - k_{\psi}}{K (C_D - \text{cmc})} \quad (21)$$

by simple rearrangement of equation (21) we arrive at equation (22).

$$k_{\psi} = k'_m + \frac{k_w C_D - k_{\psi}}{K (C_D - \text{cmc})} \quad (22)$$

Table 7

Kinetic Data for Hydrolysis of Phenylacetohydroxamic Acid  
as a Function of Perfluorooctanoic Acid  
as Surfactant at  $70.0 \pm 0.5^{\circ}\text{C}$

$C_D \times 10^2$	Ave. $k_{\text{obs}} \times 10^3 \text{ min}^{-1}$
3.4	1.6
2.9	1.4
2.4	1.2
1.9	0.99
1.5	0.67
0.73	0.42

Note: Ave.  $k_{\text{obs}}$  are average of 2 values. Percent difference in  $k_{\text{obs}}$  of duplicate runs did not exceed 2%.

Equation (22), based upon the pseudo phase model, fails<sup>35</sup> near the cmc because of specific interaction between surfactant and reactants and also for reasons not currently understood. For example for reactive counterion surfactants which possess

The  $k_w C_D$  has been evaluated for each  $(k_{\psi}, C_D)$  point from the  $k_w$  determined

below the cmc. There is some error in the  $k_w C_D$  term since the perfluorooctanoic acid does not completely ionize and may have a different fraction ionized at significantly different total surfactant concentrations. In addition, the extent of ionization may be influenced by micelles above the cmc. The average  $k_w = 1.21 \times 10^{-3} \text{ L} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$  for octanohydroxamic acid,  $k_w = 9.28 \times 10^{-4} \text{ L} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$  (single value) for phenylacetohydroxamic acid, and  $k_w = 9.76 \times 10^{-4} \text{ L} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$  (single value) for 4-bromophenylacetohydroxamic acid.

Table 8

Kinetic Data for Hydrolysis of 4-Bromophenylacetohydroxamic Acid  
as a Function of Perfluorooctanoic Acid  
as Surfactant at  $70.0 \pm 0.5^\circ \text{C}$ .

$C_D \times 10^2 \text{ M}$	Ave. $k_{\text{obs}} \times 10^3 \text{ min}^{-1}$
3.4	1.7
2.9	1.5
2.4	1.3
1.9	0.93
1.5	0.66
0.73	0.44

Note: Ave.  $k_{\text{obs}}$  are average of 2 values. Percent difference in  $k_{\text{obs}}$  of duplicate runs did not exceed 2%.

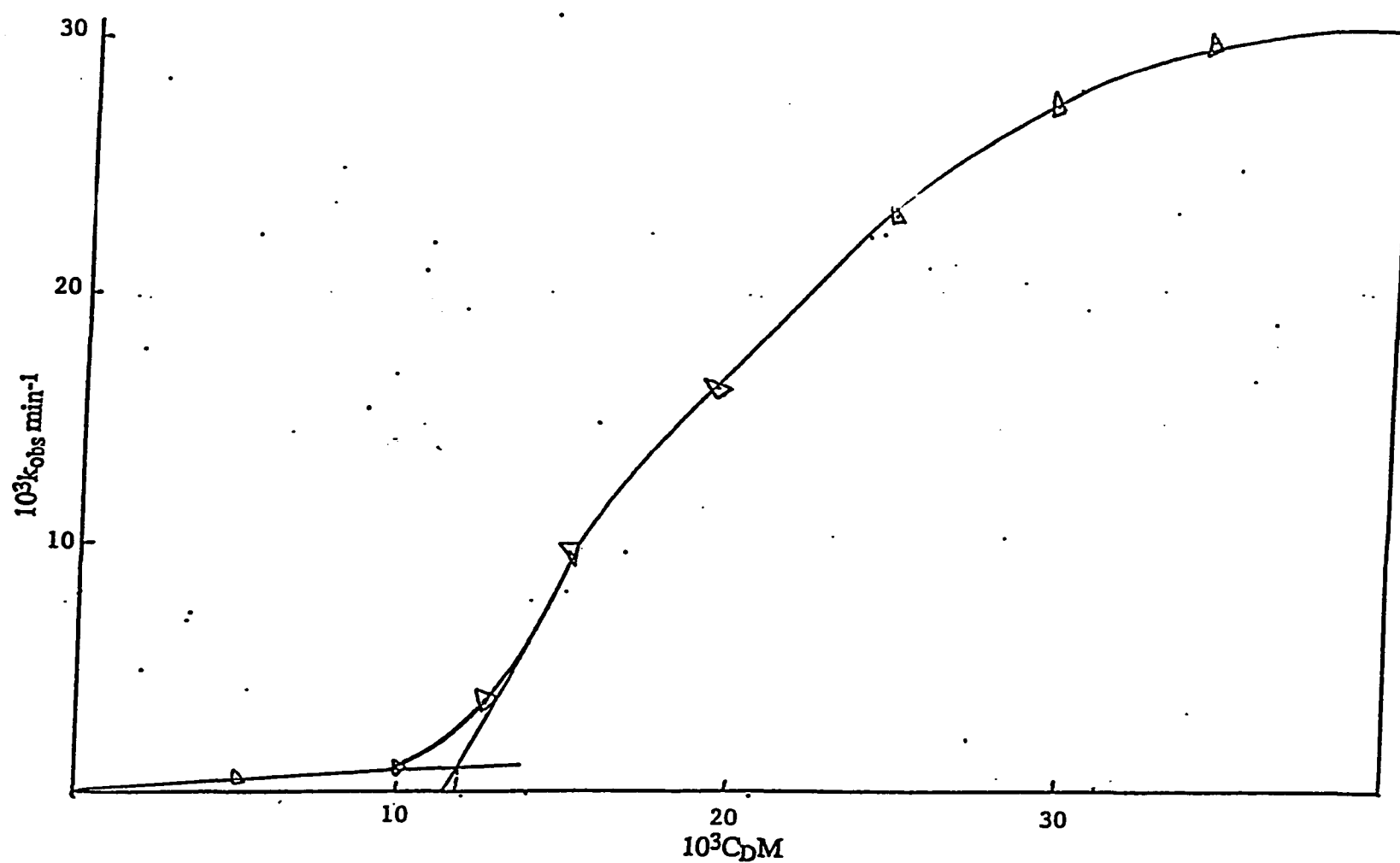


Figure 3. Determination of cmc From Rate Constant - Surfactant Concentration Profile Obtained for Hydrolysis of Octanohydroxamic Acid.

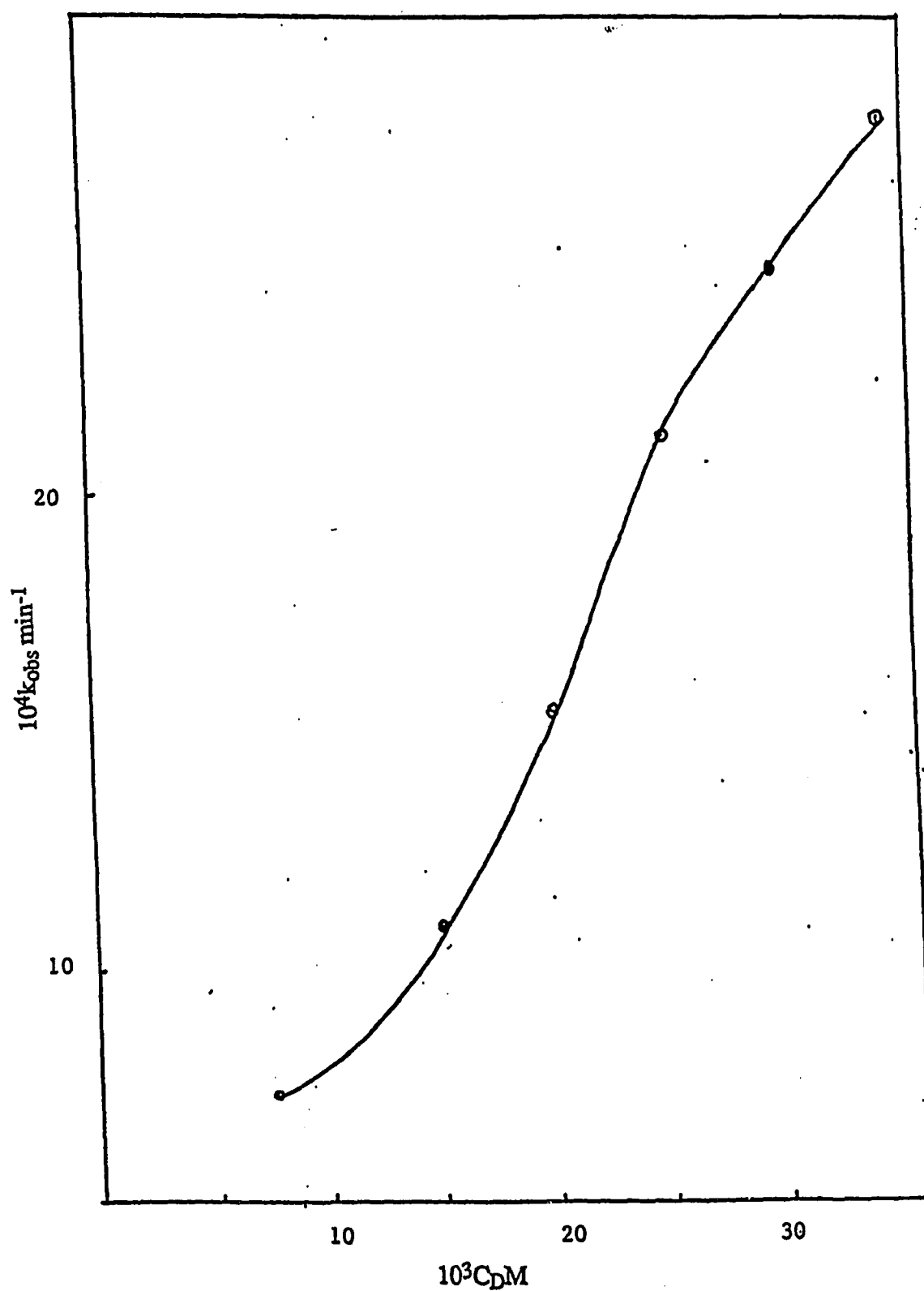


Figure 4. Rate Constant Surfactant Concentration Profile for Hydrolysis of Phenylacetohydroxamic Acid.



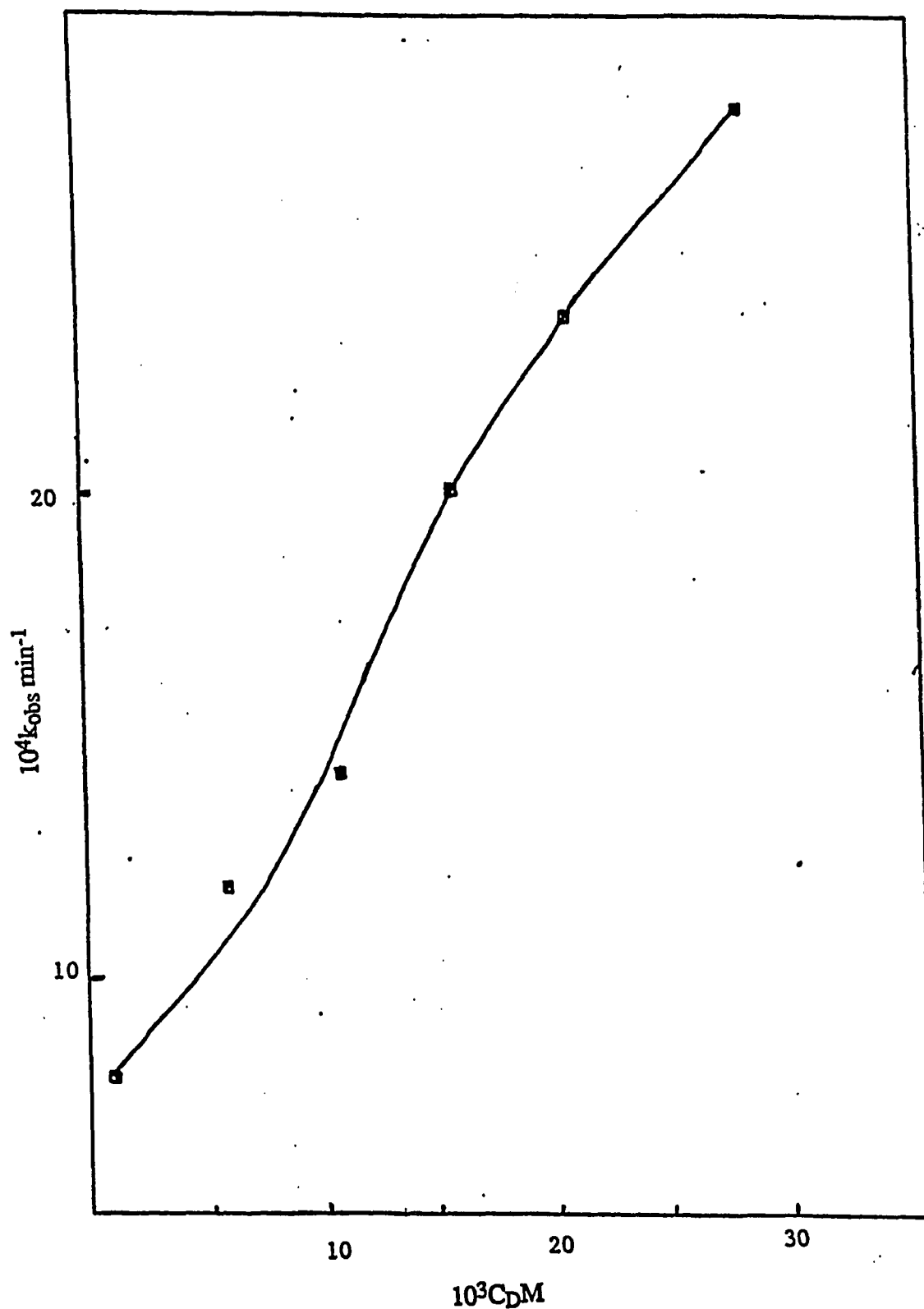


Figure 5. Rate Constant Surfactant Concentration Profile for Hydrolysis of 4-Bromophenylacetohydroxamic Acid.

A plot of  $k_{obs}$  (pseudo first-order rate constant) versus  $(k_w C_D - k_{obs}) / (C_D - cmc)$  is shown in Figure 6 for octanohydroxamic acid.

For  $k_{obs}$  versus  $(k_w C_D - k_{obs}) / (C_D - cmc)$  corresponding to octanohydroxamic acid, phenylacetohydroxamic acid and 4-bromophenylacetohydroxamic acid, see Tables 9, 10, and 11.

Table 9

Parameters for Equation (22) for Octanohydroxamic Acid Above cmc

$C_D \times 10^2 \text{ M}$	$(C_D - cmc) \times 10^2 \text{ M}$	$k_{obs} \times 10^2 \text{ min}^{-1}$	$\frac{k_w C_D - k_{obs}}{C_D - cmc}$
3.4	2.2	1.8	-0.68
2.9	1.8	1.6	-0.81
2.4	1.3	1.3	-0.86
1.9	0.78	0.95	-1.0
1.5	0.33	0.58	-1.4
1.3	0.080	0.22	-1.6

Note: Ave.  $k$  are average of 2 values. Percent difference in  $k_{obs}$  of duplicate runs did not exceed 2%.

All of the values of the kinetic ratio,  $k_m/k_0$ , listed in Table 5 are greater than one. The indication, according to the standard kinetic scheme is that the reaction within the micelle,  $k_m$ , is more predominant than the reaction in the bulk solution,  $k_0$ . The increased micellar rate can be understood by the proximity effect.<sup>19</sup> The reactant is more soluble in the micelle. The acid concentration (those of the surfactant) is exclusively surrounding the micelle: perfluorooctanoic acid is the reactive counterion

Table 10

Parameters for Equation (22) for  
Phenylacetohydroxamic Acid  
Above cmc

$C_D \times 10^2 \text{ M}$	$(C_D - \text{cmc}) \times 10^2 \text{ M}$	$k_{\text{obs}} \times 10^2 \text{ min}^{-1}$	$k_{C_D} - k_{\text{obs}}$
			$C_D - \text{cmc}$
3.4	2.3	1.6	0.014
2.9	1.8	1.4	0.016
2.4	1.3	1.2	0.011
1.9	0.83	0.90	0.026
1.5	0.33	0.67	0.049

Note: Ave.  $k_{\text{obs}}$  are average of 2 values. Percent difference in  $k_{\text{obs}}$  of duplicate runs did not exceed 2%.

The outcome is determined by the micellar rate constant,  $k_m$ , which is greater than the bulk rate constant,  $k_0$ , due to the increase in the concentration of the reactants in the micellar pseudo phase compared to the bulk solution.

Table 11

Parameters for Equation (22) for  
4-Bromophenylacetohydroxamic Acid  
Above cmc

$C_D \times 10^2 \text{ M}$	$(C_D - \text{cmc}) \times 10^2 \text{ M}$	$k_{\text{obs}} \times 10^2 \text{ min}^{-1}$	$k_w C_D - k_{\text{obs}}$
			$C_D - \text{cmc}$
3.4	2.3	1.7	0.016
2.9	1.8	1.5	0.015
2.4	1.3	1.3	0.015
1.9	0.83	0.93	0.030
1.5	0.33	0.65	0.068

Note: Ave.  $k_{\text{obs}}$  are average of 2 values. Percent difference in  $k_{\text{obs}}$  of duplicate runs did not exceed 2%.

Based on the results from this study and a subsequent study<sup>37</sup> which used hexanohydroxamic acid, and decanohydroxamic acid as the organic substrates and perfluorooctanoic acid as the surfactant, it appears that equation (22) might be applicable to the acid hydrolysis of aliphatic hydroxamic acids. However, equation (22) failed

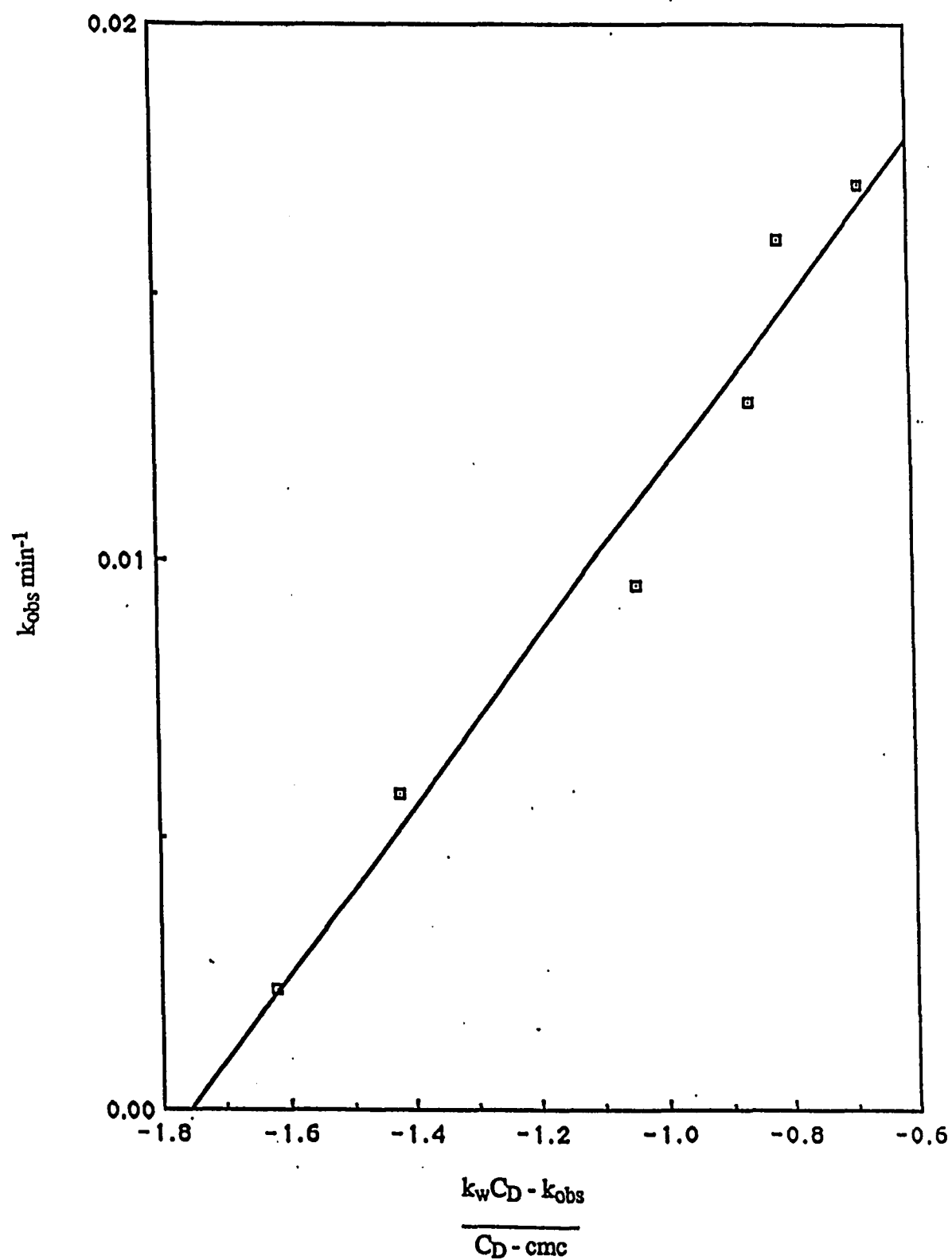


Figure 6. Plot of Equation (22) for Hydrolysis of Octanohydroxamic Acid.

## CHAPTER IV

### CONCLUSION

The work reported herein demonstrated that a perfluorocarboxylic acid does indeed behave as a reactive counterion surfactant exhibiting micellar catalysis, this conclusion was further verified by subsequent experimentation.<sup>37</sup>

The standard kinetic scheme, and equation (22) work some what to describe the micellar catalyzed acid hydrolysis of aliphatic hydroxamic acids with chain lengths of six, eight, and ten<sup>37</sup> carbons. However, when applied to micellar catalyzed hydrolysis of arylacetohydroxamic acids equation (22) failed. The low solubility of perfluorooctanoic acid in water precluded the use of a wide range of surfactant concentrations In order to test the applicability of equation 22 to reactive counterion type surfactant.<sup>37</sup>

Further investigation into finding a more water soluble surfactant which has reactive counterions is suggested in order to test the theoretical equation (based on the pseudo phase model) appropriate for this surfactant type.

## REFERENCES

1. Menger, F. M., Acc. Chem. Res. **12**, 111 (1979).
2. Bunton, C. A. In: Techniques in Chemistry, Academic Press, New York, vol **10**, chap. 4, (1976).
3. Cordes, E. H., Pure and Applied Chem. **50**, 617 (1978).
4. J. W. McBain In: Colloid Chemistry, J. Alexander, (Edi), vol. 5, pp. 102-103, Reinhold Publishing Corp., New York, (1944).
5. P. Mukerjee, Adv. Colloid Interface Sci., **1**, 241 (1967).
6. Berndt, D. C., Sendelback, L. E. Micellar-catalyzed reaction of hydroxamic acids, J. Org. Chem., **42**, 3305-3306, (1977).
7. J. H. Fendler and E. J. Fendler, Catalysis in Micellar and Macromolecular Systems, Academic Press, New York, (1975).
8. Ref. 4. chap. 2, pp. 18-41.
9. Williams, R. J., Phillips, J. M., and Mysels, K., J. Faraday Soc., **51**, 728, (1955).
10. Paland, D. C., & Suherage, H. A., Hydrophobic bonding and micelle stability. The influence of ionic head groups., J. Colloid Interface Sci., **21**, 273 ,(1966) .
11. Mittal, K. L., and Mukerjee, P. The wide world of micelles. In: Micellization, Solubilization and Microemulsions K. L. Mittal (Ed.), vol **1**, Plenum Press, New York, (1977).
12. Ernst, J. R., Sudholter, and Engberts, B. F. Salt effects on the critical micellar concentration, Iodide counterion binding and surface micro-polarity of 1-methyl-4-dodecylpyridinium iodide micelles, J. Phys. Chem., **83**, 1855 , (1979).
13. Osugi, J., Sato, M., and Ifaky, N., Rev. Phys. Chems. Jap., **38**, 58, (1968).
14. C. Tanford, J. Phys. Chem., **76**, 3020, (1972).
15. C. Tanford, Proc. Nat. Acad. Sci. U.S. A., **71**, 1911, (1974).
16. Ref. 7, 14, and 15.

## REFERENCES

1. Menger, F. M., Acc. Chem. Res. **12**, 111 (1979).
2. Bunton, C. A. In: Techniques in Chemistry, Academic Press, New York, vol 10, chap. 4, (1976).
3. Cordes, E. H., Pure and Applied Chem. **50**, 617 (1978).
4. J. W. McBain In: Colloid Chemistry, J. Alexander, (Edi), vol. 5, pp. 102-103, Reinhold Publishing Corp., New York, (1944).
5. P. Mukerjee, Adv. Colloid Interface Sci., **1**, 241 (1967).
6. Berndt, D. C., Sendelback, L. E. Micellar-catalyzed reaction of hydroxamic acids, J. Org. Chem., **42**, 3305-3306, (1977).
7. J. H. Fendler and E. J. Fendler, Catalysis in Micellar and Macromolecular Systems, Academic Press, New York, (1975).
8. Ref. 4. chap. 2, pp. 18-41.
9. Williams, R. J., Phillips, J. M., and Mysels, K., J. Faraday Soc., **51**, 728, (1955).
10. Paland, D. C., & Suherage, H. A., Hydrophobic bonding and micelle stability. The influence of ionic head groups., J. Colloid Interface Sci., **21**, 273 ,(1966) .
11. Mittal, K. L., and Mukerjee, P. The wide world of micelles. In: Micellization, Solubilization and Microemulsions K. L. Mittal (Ed.), vol 1, Plenum Press, New York, (1977).
12. Ernst, J. R., Sudholter, and Engberts, B. F. Salt effects on the critical micellar concentration, Iodide counterion binding and surface micro-polarity of 1-methyl-4-dodecylpyridinium iodide micelles, J. Phys. Chem., **83**, 1855 , (1979).
13. Osugi, J., Sato, M., and Ifaky, N., Rev. Phys. Chems. Jap., **38**, 58, (1968).
14. C. Tanford, J. Phys. Chem., **76**, 3020, (1972).
15. C. Tanford, Proc. Nat. Acad. Sci. U.S. A., **71**, 1911, (1974).
16. Ref. 7, 14, and 15.



17. Krescheck, G. C. Hamor, E., Davenport, G., and Scheraga, H. A., J. Amer. Chem. Soc., **88**, 246, (1966).
18. Bunton, C. A., In: Reaction Kinetics in Micelles, E. H. Cordes, (Ed.) p. 73, Plenum Press, New York, (1973).
19. Baumrucker, J., Calzadilla, M., and Cordes, E. H., Micellar catalysis for carbonium ion reactions. In: Reaction Kinetics in Micelles, E. Cordes (Ed.), pp. 25-52, Plenum Press, New York, (1975).
20. Bunton, C. A., Romsted, L. S. and Sanelli, G. Tests for pseudo phase model of micellar catalysis: its partial failure. J. Am. Chem. Soc., **101**, 1253, (1979).
21. Fendler, J. H., Membrane Mimetic Chemistry, Wiley-Interscience, New York, (1982).
22. Cordes, E. H., and Gitler, C., Prog. Biorg. Chem., **2**, 1, (1973).
23. Bunton, C. A. Ohmenzetter, L. K. and Sepulveda, L., J. Phys. Chem., **81**, 2000 (1977).
24. Berezin, I. V., Martinek, K., and Yatsimirski, A. K., Physiochemical foundations of micellar catalysis, Russ. Chem. Rev., **42**, 787-802, (1973).
25. Romsted, L. A. General kinetic theory of rate enhancements for reactions between organic substrates and hydrophilic ions in micellar systems. In: K.L., Micellization, Solubilization, and Microemulsion Mittal (Ed.), vol **2**, pp. 509-530, Plenum Press, New York, (1977).
26. Romsted, L. S. Ph.D. thesis, Indiana University, (1975).
27. Romsted, L. S., Micellar effects on reaction rates and equilibria, In: Surfactants in Solution, Mittal, K. L. and Lindman, B. (Eds.), vol. 2, Plenum Press, New York, (1984).
28. Berndt, D. C., and Ward, I. E., Kinetics and Mechanism of Acidic and Alkaline Hydrolysis of Hindered N-methyl arylhydroxamic acids, J. Org. Chem., **41**, 3297, ( 1976).
29. Shindo, K., Hato, M., and Hayashi, T., The physicochemical properties of aqueous solutions of fluorinated surfactants, J. Phys. Chem., **76**, 909, (1972).
30. Christian, R. V., Jr., Leffler, I. D., and Dagler, J.S., Iron (III)-benzohydroxamate complex ions, Anal. Chem., **26**, 1666, ( 1954).
31. Berndt, D. C. and Sendelbach, L. E., Micellar-catalyzed reaction of hydroxamic acids, J. Org. Chem., **42**, 3305, (1977).
32. Gilford Instrument Laboratories, Inc., Gilford Photometer 525 Operator's Manual, Oberlin, Ohio, (1978).

33. Moore, J.W., and Pearson, R. G., Kinetics and Mechanism, 3rd ed., chap. 3, pp. 47-54, John Wiley and Sons, Inc., New York, (1981).
34. Daniels, F. and Alberty, R. A. Physical Chemistry, 3rd ed., Chap. 10, pp. 325-380, John Wiley and Sons, Inc., New York, (1966).
35. Bunton, C. A., Romsted, L. S. and Thamvit, C., The pseudophase model of micellar catalysis, Addition of Cyanide ion to N-alkyl pyridinium ion, J. Am. Chem. Soc., **102**, 3900, (1980).
36. Bunton, C. A., Ceridelle, G., Hara and Sepulveda, L., MicellarCatalysis and reactant incorporation in dephosphorylation and nucleophilic substitution, J. Am. Chem. Soc., **101**, 2429, (1979).
37. Berndt, D. C., Ayoub, M.E., and Akhavan-Tafti, H., Micellarcatalysis by perfluorooctanoic acid, International Journal of Chemical Kinetics, **19**, 513, (1987).

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