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Reactive Counterion Surfactant Catalysis of Hydroxamic Acid Hydrolysis with Perfluorooctanoic Acid

Mohamed El-Sayed Ayoub

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**REACTIVE COUNTERION SURFACTANT CATALYSIS OF HYDROXAMIC ACID
HYDROLYSIS WITH PERFLUOROOCTANOIC ACID**

by

Mohamed El-Sayed Ayoub

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

**Western Michigan University
Kalamazoo, Michigan
August 1986**

REACTIVE COUNTERION SURFACTANT CATALYSIS OF HYDROXAMIC ACID
HYDROLYSIS WITH PERFLUOROOCTANOIC ACID

Mohamed El-Sayed Ayoub, M.A.

Western Michigan University, 1986

A micellar effect upon the rate of hydrolysis of hydroxamic acids in aqueous perfluorooctanoic acid has been demonstrated for hydroxamic acids with chain lengths of six, eight, and ten carbons. In this system the counterion, hydrogen ion, is a catalyst. Typical rate constant-surfactant concentration profiles for micellar catalysis were obtained. The results for these hydrolyses are consistent with the pseudo-phase model for micellar effects.

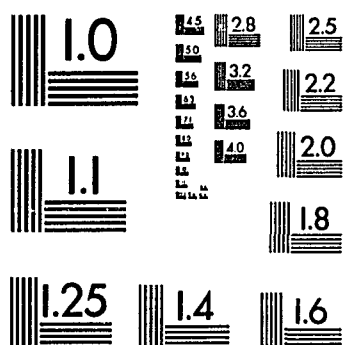
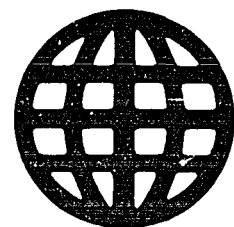
In addition the Arrhenius activation energies were determined for the reaction of octanohydroxamic acid at surfactant concentrations above and below the critical micelle concentration of the surfactant. The activation energy is lower for reaction in the micellar solutions than it is for the non-micellar solutions. This also indicates the micellar effect upon the reaction rate.

ACKNOWLEDGEMENTS

I am very grateful to Professor Donald Berndt who guided and encouraged me during this work and also in preparation of this paper. I would also like to thank all the faculty members in the Chemistry Department for their helpful advice. I am certain that I enjoyed my stay here at Western because of that.

Mohamed El-Sayed Ayoub

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Western Michigan University

M.Sc. 1986

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**To My Father's Soul
and My Family**

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INTRODUCTION

$$\underbrace{\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2}_{\text{hydrophobic}}-\underbrace{\text{OSO}_3^-\text{Na}^+}_{\text{hydrophilic}}$$

1

as:

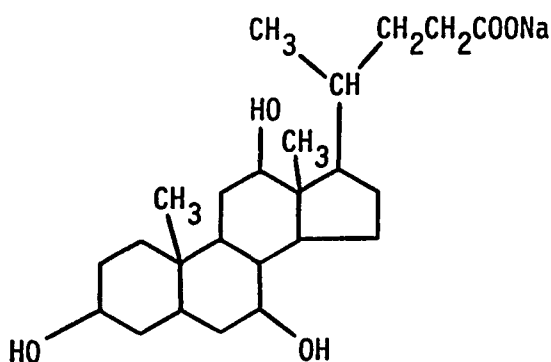
1. Anionic: the hydrophilic moiety is anionic, e.g., potassium laurate $\text{CH}_3(\text{CH}_2)_{10}\text{COO}^-\text{K}^+$, sodium lauryl sulfate $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$.

2. Cationic: the hydrophilic moiety is cationic, e.g., hexadecyltrimethylammonium bromide $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$, dodecylpyridinium chloride $\text{C}_{12}\text{H}_{25}\text{N}^+\text{Cl}^-$.

3. Ampholytic: this type can behave as either an anionic, nonionic or cationic species depending upon the pH of solution, e.g., the zwitterionic form of N-dodecyl-N,N-dimethylbetaine, $\text{C}_{12}\text{H}_{25}\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$.

4. Nonionic: the hydrophilic moiety of this type can contain hydroxyl groups or a polyoxyethylene chain, e.g., polyoxyethylene p-tert-octylphenyl ether, $\text{C}_8\text{H}_{17}\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{H}$ and polyoxyethylenemonohehexadecyl ether, $\text{CH}_3-(\text{CH}_2)_{15}(\text{OCH}_2\text{CH}_2)_{21}\text{OH}$.

5. Naturally occurring compounds: e.g., cholic acid and desoxycholic acid, and their salts.



Sodium Cholate

When an ionic detergent is added to water at very low concentrations, the detergent behaves like any other strong

electrolyte, it is completely dissociated. With respect to the effect of the structure of solutions, there is a large interfacial energy¹ between the hydrocarbon chain and water which will be minimized as far as possible by curling up the chain. There are two ways in which the free energy can be reduced:

1. Adsorption at the interface between air and solution with the hydrocarbon chain remote from the water, so that the high energy of hydrocarbon/water interface is lost.

2. Dimerization or formation of small aggregates containing a small number of soap monomers. Dimerization has been reported by Mysels et al.⁴ for sodium dodecylsulfate. However, neither of these processes can prevent the increase of free energy with further increase in the concentration of the surfactant. A concentration is reached at which micelle formation begins in the solution. This concentration is the critical micelle concentration (cmc). Accurate experimental work shows that it is not a single sharp concentration but rather a narrow range.⁵ The cmc is usually determined experimentally by plotting some property as a function of concentration and extrapolating the results at low and high concentrations to an intersection point. A large number of experimental techniques^{5,6} can be utilized to determine cmc values, the most popular ones being investigations of electrical conductance and surface tension. The factors affecting the critical micelle concentrations are:

1. Hydrocarbon chain length and structures: In all cases the cmc decreases as hydrocarbon chain length increases. For the same head group, compounds containing longer hydrocarbon chains

form micelles at lower concentrations than those containing short chains. The position of the head group in the hydrocarbon chain also affects the cmc.⁷ The closer the head group to the center of the chain, the higher the cmc due to the two branches of the chain partially shielding one another. Also the presence of a double bond in the chain causes an increase in the cmc, eg., for potassium stearate at 55°C the cmc is 4.5×10^{-4} M while for potassium oleate the cmc is 1.2×10^{-3} M.

2. Nature of the polar head group: For ionized detergents the cmc values are fairly similar, i.e., the effect of different ionized groupings on the cmc is not large. The number of ionic groups also affects the cmc, the more ionized groups present in the surfactant, the higher the cmc due to increase in electrical work to form the micelles as the number of groups increases. For the nonionic type of surfactant, increase in the length of the polyoxyethylene chain causes an increase in the cmc and decreases micelle size. Also the nature of the counterion in the case of ionized detergents has some effect on the cmc; it was found that the cmc decreases⁹ as the solvation of the counterion decreases.

3. Effect of additives: Addition of salts decreases the cmc for ionized detergents because the screening action¹⁰ of simple electrolytes lowers the repulsion forces between the polar head groups and less electrical work is required in micelle formation. The micelle size increases with increased salt concentration due to reduction in electrical repulsions affecting the balance of forces upon which the size of the micelle depends.

4. Effect of temperature: The effect of temperature¹¹ on

the cmc varies over certain ranges for ionized detergents, e.g., sodium dodecylsulfate gives a minimum in the cmc-temperature curve at 25°C; for the nonionic detergent, $\text{CH}_3-(\text{CH}_2)_9(\text{OCH}_2\text{CH}_2)_5\text{OH}$, a decrease in the cmc with increasing temperature¹² is observed.

It should be realized that micelles, when formed, are not indestructible. Several studies have been made of micellar breakdown following the change spectrophotometrically¹³ or by following it conductimetrically.¹⁴ There is rapid exchange of monomer units between micelles and bulk solution. It is correct to think of micelles as spheres¹⁵ (Figure 1) in which the hydrophobic portion occupies a volume known as the core and the hydrophilic portion forms the surface layer which is called the Stern layer which contains tightly bound counterions that move with the micellar aggregate. The Gouy-Chapman layer contains the remaining counterions loosely arranged according to a Boltzmann distribution extending radially into the aqueous phase. Most of the counterions are associated with the Stern layer. The micelle may take other shapes depending upon the surfactant concentration,¹⁶ temperature,¹⁷ and other compounds¹⁸ in solution. Other aggregate shapes¹⁹ are ellipsoid, rod-like and lamellar.

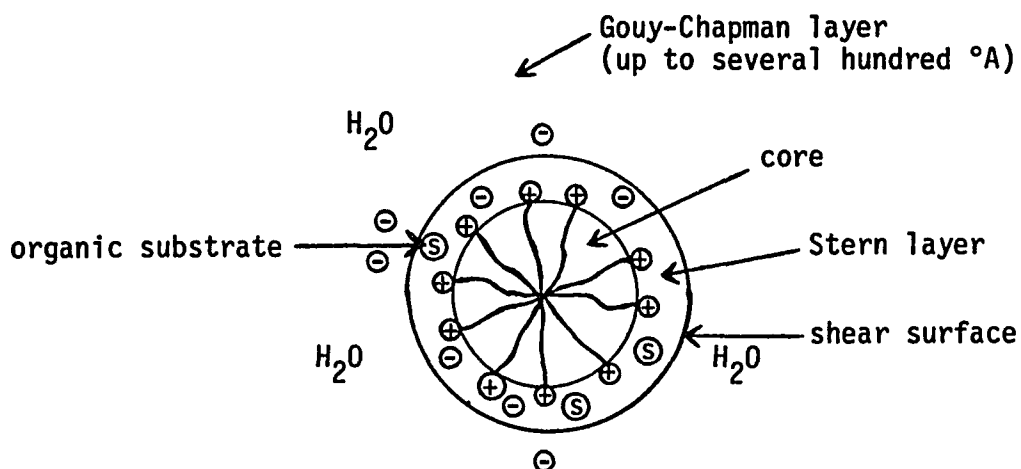


Figure 1. Model of Hypothetical Cationic Micelle Showing the Locations of Headgroups, Surfactant chains and Counterions.

Micellar Catalysis and Kinetics

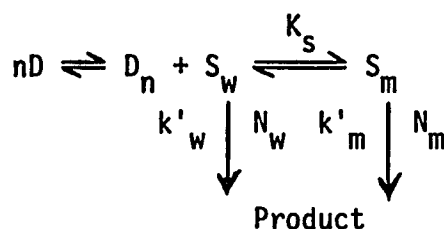
Micellar catalysis in water is generally rationalized in terms of reaction in the micellar and in the aqueous pseudo phase.³ Most models of micellarly catalyzed reactions assume that the overall rate of reaction is the sum of rates in each pseudo phase and that changes in the rate with increasing surfactant concentration or added reagents reflect changes in the distribution of reactants between the pseudo phase. Other models also consider the effects of the micellar surface charge on the initial and transition state free energies in the micellar pseudo phase²⁰ relative to the aqueous phase. Pseudo phase formation occurs above the cmc, and all additional surfactant above the cmc forms micelles with the monomer concentration remaining constant and equal to the cmc. Quantitative treatments of micellar effects on reaction rates and equilibria generally fit the data very well at high surfactant concentration, but sometimes fail near the

cmc. The model explicitly assumes that changes in micelle size and shape²¹ as the surfactant concentration changes are not very important, so that only those factors which control the distribution of reactants will significantly affect the observed rate. Buffer effects are particularly difficult to interpret also. The presence of both reactive and unreactive counterions must be accounted for in the distribution of the counterions between the micellar and aqueous pseudo phases.

Micelles are assumed to have a "hydrocarbon like" interior surrounded by the Stern layer containing hydrated head groups partially neutralized by counterions in the case of ionic surfactants. It is assumed that the degree of water penetration into the core does not significantly affect the interpretation of micellar effects on the rate. The reaction site within the micellar pseudo phase is assumed to be the Stern layer.²¹ A number of studies indicate that the micellar-bound substrates, usually polar organic molecules, are in an environment of moderate polarity similar to that of ethanol and not the nonpolar environment of the hydrocarbon core.^{22,23} Also the distribution of all reactants between the two phases is always in equilibrium because their diffusion rate is orders of magnitude faster than the rate of the reaction.³ The binding of a neutral organic substrate is dominated by the hydrophobic effect mediated to varying degrees by dipole and hydrogen bonding interactions and binding occurs regardless of surfactant charge type.²²

Scheme I illustrates the pseudo phase model for reactions in the micellar solution, assuming that the distribution of

substrates(s) is described by a simple binding constant (K_s)



Scheme I

where S_w and S_m are substrate concentrations in the bulk water phase and in the micellar pseudo phase.

D_n = concentration of micellized surfactant with aggregation number n .

N_w and N_m are reactive counterion concentrations in the water and micelle phases. $[N]$ is always in large excess over substrate concentration, which will establish a pseudo order condition so that:

$$k'_w = k_w[N_w] \quad \text{and} \quad k'_m = k_m m_N^S$$

where k'_w = pseudo first-order rate constant in water phase

k'_m = pseudo first-order rate constant in the micellar phase.

m_N^S = mole ratio of micellar bound reactive ion (N_m) to micellized surfactant D_n with aggregation number n . m_N^S is equal to β which is defined as the degree of counterion binding because of the absence of any nonreactive counterion for reactive counterion surfactants. Values of β are independent surfactant concentration and are always within the range of 0.6-0.9.²⁴

The kinetic equation derived,²⁵ based on the above scheme

for a reactive counterion surfactant (N) is:

$$k_{\psi} = \frac{k_w[N_T] + \beta S(k_m K_s - k_w)[D_n]}{1 + K_s[D_n]} \quad (1)$$

where k_{ψ} = observed rate constant

k_w and k_m = second-order rate constant in water and in micellar phase.

$[N_T] = C_t$ = stoichiometric concentration of reactive counterion

S = molar density of micellar phase expressed in moles of surfactant per liter of micellar phase.

In most cases: $K_s k_m \gg k_w$ ²⁵

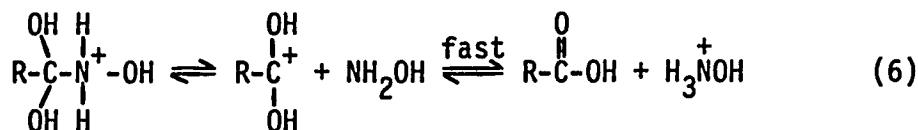
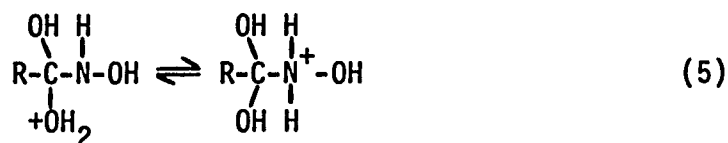
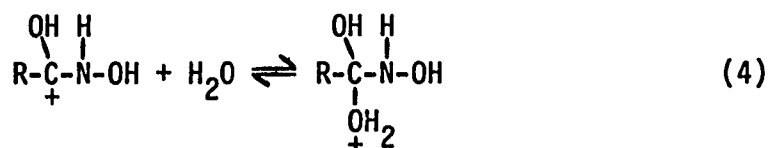
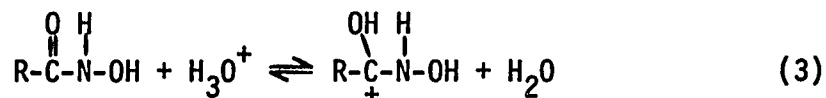
$$k_{\psi} = \frac{k_w[N_T] + k_m K_s \beta S[D_n]}{1 + K_s[D_n]} \quad (2)$$

The derivation of the previous equation assumes that micellized surfactant is in excess over substrate. $[D_n] \gg [S_m]$ and that the micellar pseudo phase occupies only a small fraction of the total solution volume. The former assumption fails only near the cmc and binding constants are usually determined well above the cmc.²⁵ Equation (2) fits a few cases, for example: The long chain sulfonic acid catalyzed hydrolysis of acetals including the effect of added HCl,²¹ the addition of CN^- to N-alkyl-3-carbamoylpyridinium ion in cetyltrimethylammonium cyanide,²⁶ and the reaction of azide ion with 2,4-dinitrochlorobenzene and 2,4-dinitrochloronaphthalene in cetyltrimethylammonium azide.²⁷ However equation (2) fails for some reactions, but not all reactions in cationic surfactants.

Several explanations are possible; all require substantial modification of the pseudo phase model.²⁰

Hydrolysis of Hydroxamic acids

Hydroxamic acid hydrolysis²⁸ and the mechanism²⁹ for hydrolysis using anionic surfactants has been reported as follows:



The purpose of this thesis is to study the substrate effect on the rate of hydrolysis of hydroxamic acids using perfluorooctanoic acid as surfactant. This surfactant is of the reactive counterion type. Previous studies of micellarly catalyzed hydroxamic acid hydrolysis employed nonreactive counterion surfactants with added reactive ions. The acid catalyzed hydrolysis reactions³⁰ followed the equation derived by Romsted¹⁹ appropriate for such cases:

$$k_2 = \frac{k'_m \beta S K_s (C_t - \text{cmc})}{[K_s (C_t - \text{cmc}) + 1][I_t + X_t K_I]} + \frac{k'_w}{K_s (C_t - \text{cmc}) + 1} \quad (7)$$

where k_2 = overall second-order rate constant.

k'_w and k'_m are rate constants in the aqueous and micellar pseudo phases.

I_t = the total concentration of the hydrophilic reactant ion.

X_t = the total concentration of the surfactant counterion.

K_I = the ion exchange constant.

Perfluorosurfactants have been little studied for their effect on reaction kinetics. Recently a study of the rate of hydrolysis of n-octanohydroxamic acid as an example of an aliphatic substrate in addition to two other aromatic substrates with perfluorooctanoic acid was made.³¹ The results are in agreement with what will be reported in the Results and Discussion sections of this thesis.

The second purpose of this study was to investigate the influence of temperature on the reaction above and below the cmc by evaluation of Arrhenius activation energies.

CHAPTER II

PREPARATION OF COMPOUNDS AND KINETIC PROCEDURES

Purification of Perfluorooctanoic Acid ($\text{CF}_3-(\text{CF}_2)_6\text{COOH}$)

The compound was purchased from Aldrich Chemical Company. Purification was accomplished by two successive crystallizations. Nine grams of the compound were dissolved in 300 ML of CCl_4 (ACS) on the steam bath, the hot mixture was filtered and allowed to cool in a refrigerator. The crystals were separated by use of suction filtration and were washed with a minimum amount of solvent. The melting point was measured using a Thomas Hoover melting point apparatus and was found to be $56.5\text{--}58^\circ\text{C}$ (literature $56.4\text{--}57.9^\circ\text{C}$).³² Also the purity was tested by titration of the surfactant against standardized NaOH, calculated molecular weight was 408.2 g/mol (theoretical = 414.1 g/mol).

Preparation of Hydroxamic Acids

Hexanohydroxamic, octanohydroxamic and decanohydroxamic acids were prepared and purified by Professor Donald Berndt.

Preparation of Ferric Chloride Solution

The solution was prepared according to the following ratio:

H_2O (mL): concentrated HCl (mL): FeCl_3 (g) = 100:10:1

The ferric chloride solution is used as an indicator, it forms a maroon complex with unreacted hydroxamic acid.

Verification of Beer's Law

A 0.007 M surfactant solution was prepared using 1:1 (v/v) t-butylalcohol:H₂O. Also a 5.0×10^{-4} M solution of octanohydroxamic acid was prepared using 1:1 (v/v) t-butylalcohol:H₂O. Into 50 mL volumetric flask (A), the following amounts were pipeted: 25 mL of surfactant solution, 10 mL of FeCl₃ solution and 3 mL of octanohydroxamic acid solution. Then the solution in the flask was diluted to the mark with 1:1 (v/v) t-butylalcohol:H₂O. Into another 50 mL flask (B) were pipeted all the previous solutions as in flask (A) except that 6.0 mL of the hydroxamic acid was used instead of 3.0 mL and then the solution diluted to the mark with 1:1 (v/v) t-butylalcohol:H₂O. Into a third 50 mL volumetric flask (Blank) were pipeted 25 mL of surfactant solution, 10 mL of FeCl₃ solution, and the solution was diluted with 1:1 (v/v) t-butylalcohol:H₂O to the mark. The absorbance of solutions A and B versus the Blank at 520 nm using a Gilford-Beckman spectrophotometer were determined. The results indicated the applicability of Beer's Law, Table 1.

Table 1
Verification of Beer's Law

Compound	Solution	Abs
n-octanohydroxamic acid	A (3 mL)	0.140
	B (6 mL)	0.289

Preparation of Reactions, Solutions and Kinetic Procedures

1. The surfactant solution of the desired surfactant concentration was prepared using double distilled water as solvent.

2. 40 mL of surfactant solution were pipeted into each reaction vessel (plastic test tubes or bottles). The reaction tubes were placed in an oil bath for about 10-15 minutes to allow equilibration with the oil bath temperature.

3. The initial concentration of hexanohydroxamic acid in the kinetic runs was 5.0×10^{-4} M but for decanohydroxamic acid was 2.22×10^{-4} M (because of its low solubility in water).

4. For hexanohydroxamic acid 1 mL and for decanohydroxamic acid 5 mL of the solution were pipeted into each reaction tube containing the surfactant solution.

5. Ferric chloride solution (10 mL) was pipeted into each of eight 50 mL volumetric flasks. One of these was the Blank which contained 10 mL of FeCl_3 solution, 3 mL of surfactant solution for the hexanohydroxamic acid (5 mL instead of 3 mL, in the case of decanohydroxamic acid) and diluted to the mark with 1:1 (v/v) t-butylalcohol: H_2O . Samples of the reaction mixture were taken with a 3 mL pipet for hexanohydroxamic acid and a 5 mL pipet for

decanohydroxamic acid. The time of the sample was recorded as the time at which the pipet finished draining into the FeCl_3 solution in the 50 mL volumetric flask which was then diluted with 1:1 (v/v) t-butylalcohol: H_2O to the mark and inverted twenty times.

6. The absorbance of the solutions versus the blank was taken two times and the average reading was recorded. The wave length was 520 nm and 10 cm uv cells were used. The sample cell was calibrated versus the blank cell using distilled water.

For each of the hydroxamic acids the rate constants were determined over the surfactant concentration range of 0.005-0.035 M. The observed rate constants are pseudo first-order since the surfactant concentration is in excess compared to the hydroxamic acid concentration.

The following derivation³⁴ illustrates the relationship between the observed rate constant and measured absorbances.

$$\ln a/(a - x) = k_{\text{obs}}t \quad (8)$$

where a = initial concentration of hydroxamic acid

x = concentration of reacted hydroxamic acid

k_{obs} = pseudo first-order rate constant.

Since the concentration of hydroxamic acid is proportional to absorbance

$$\therefore \ln a/(a - x) = \ln(A_{\infty} - A_0)/(A_{\infty} - A_t) \quad (9)$$

where A_{∞} = measured absorbance at time infinity

A_0 = measured absorbance at time = 0

A_t = measured absorbance at time t

Assuming that the reaction will go to completion, $A_{\infty} = 0$.

$$\ln A_t = -k_{\text{obs}}t + \ln A_0 \quad (10)$$

A plot of $\ln A_t$ versus time yields a straight line with slope equal to $-k_{\text{obs}}$. A least-squares treatment of $\ln A_t$ versus time was used to determine pseudo first-order rate constants. A typical example of rate data is in Table 2 below.

Table 2

Sample Data for the Determination of k_{obs} of
 5.0×10^{-4} M Hexanohydroxamic Acid and
 2.44×10^{-2} M Surfactant at $70 \pm 0.1^\circ\text{C}$

Sample Number	Clock Time	Time (min)	AVE Abs
1	10:41	0	0.220
2	11:21	41	0.186
3	12:11	90	0.161
4	14:04	203	0.124
5	15:05	264	0.101
6	16:20	339	0.082

The least squares result yields:

$$\text{correlation coefficient} = -0.997$$

$$\text{slope} = -0.00281 \text{ min}^{-1}$$

The data are shown in Figure 2 and for the duplicate, and the average rate constant was calculated.

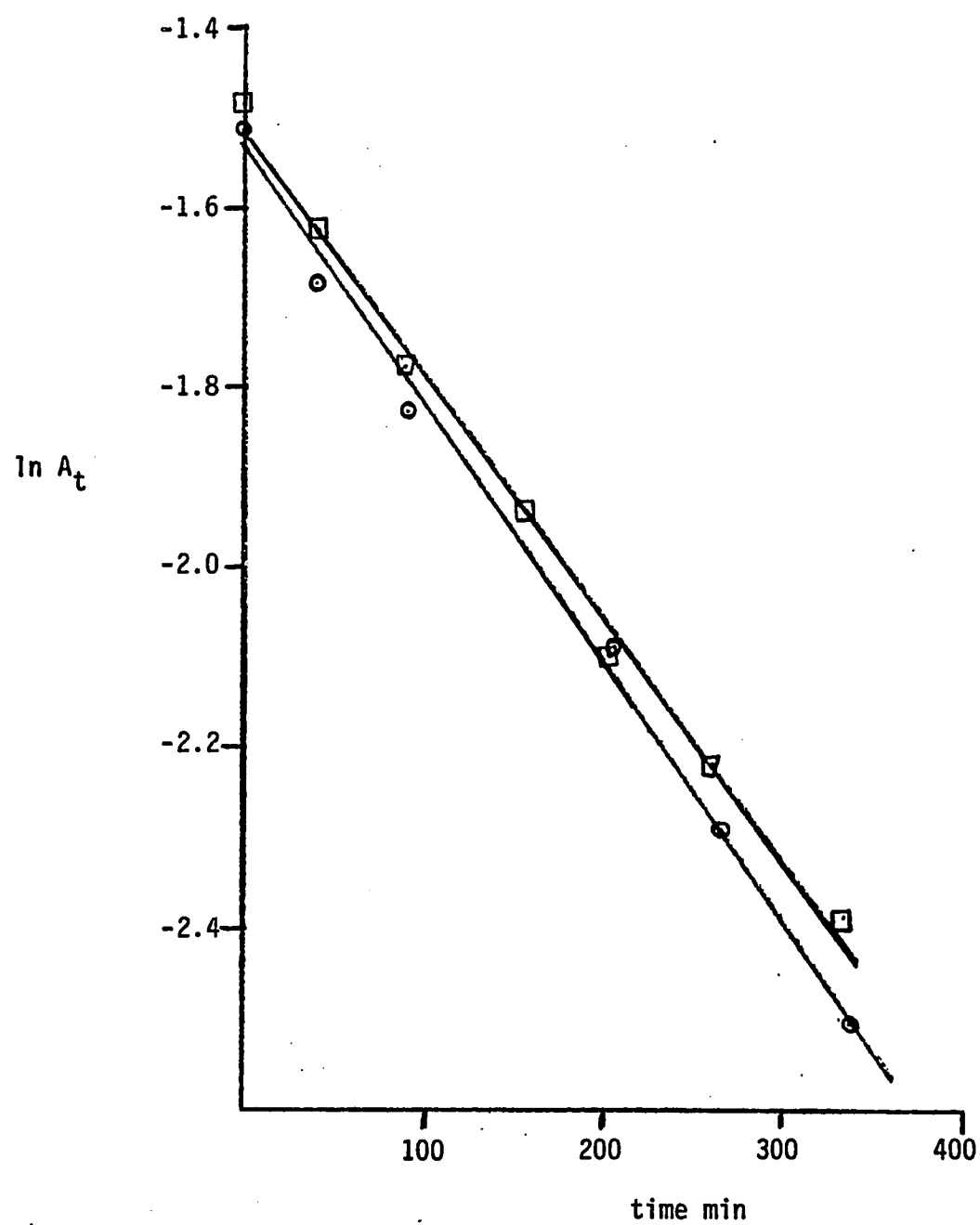


Figure 2. The Graph of Log Versus Time

CHAPTER III

RESULTS AND DISCUSSION

Kinetic studies of the rate of acid catalyzed hydrolysis of hexanohydroxamic and decanohydroxamic acids have been carried out with the surfactant, perfluorooctanoic acid. The surfactant provides the acid catalyst as well as the formation of micelles. Micellar catalysis is observed. See Table 3.

The data indicate micellar rate enhancement as shown by comparison of rate constants above and below the cmc. The results are consistent with known factors which affect the rate constant of reaction in the micellar phase. The ratio depends upon the nature of the substrate; it increases from 3.9 for aromatic substrates up to 40 for the aliphatic substrates. The ratio increases more for longer aliphatic chains. Perhaps there is no micellar effect, but only acidic catalysis for the aromatic substrates.

The kinetic data obtained for n-hexanohydroxamic and n-decanohydroxamic acids are given in Tables 4 and 5.

For both hydroxamic acids, the rate constant (k_{obs}) versus surfactant concentration profiles (Figures 3 and 4) show typical micellar catalysis with a sharp break in the curve at the cmc. The cmc is usually defined operationally²⁵ from such graphs, since the actual value varies somewhat with temperature and the presence

Table 3
Data for Rate of Hydrolysis of Some Hydroxamic Acids
Below and Above the cmc at $70 \pm 0.1^\circ\text{C}$

Hydroxamic Acids	$k_{\text{obs}} \text{ sec}^{-1}$		Ratio
	$C_t^a = 0.00750 \text{ M}$	$C_t^a = 0.0342 \text{ M}$	
	No Micelle	Micelle Present	
$\text{H}-\text{C}_6\text{H}_4-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{NHOH}$	0.69×10^{-5b}	2.70×10^{-5b}	3.9
$\text{Br}-\text{C}_6\text{H}_4-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{NHOH}$	0.73×10^{-5b}	2.80×10^{-5b}	3.8
$\text{CH}_3-(\text{CH}_2)_4-\overset{\text{O}}{\parallel}\text{C}-\text{NHOH}$	0.58×10^{-5}	6.90×10^{-5}	12
$\text{CH}_3-(\text{CH}_2)_6-\overset{\text{O}}{\parallel}\text{C}-\text{NHOH}$	0.90×10^{-6b}	29.61×10^{-5b}	33
$\text{CH}_3-(\text{CH}_2)_8-\overset{\text{O}}{\parallel}\text{C}-\text{NHOH}$	1.04×10^{-5}	4.17×10^{-4}	40

^aTotal surfactant concentration. ^bH. Akhavan-Tafti, Western Michigan University, unpublished results.

of other additives. A "kinetic" cmc was estimated from the intersection of the extrapolations of the lines as shown in Figure 4. The value of the cmc is estimated to be 0.010 M for perfluorooctanoic acid at $70 \pm 0.1^\circ\text{C}$ from kinetic data for the reaction of decanohydroxamic acid. The literature value is in the range of 0.0080-0.0091 M at 25°C as determined by a solubility method.³²

Table 4
Kinetic Data for Hydrolysis of n-Hexanohydroxamic Acid
as a Function of Perfluorooctanoic Acid as
Surfactant at $70 \pm 0.1^\circ\text{C}$

$C_t \times 10^2 \text{ M}$	ave. $k_{\text{obs}} \times 10^3 \text{ min}^{-1}$
3.42	4.14
2.93	3.49
2.44	2.85
1.95	1.42
1.46	0.481
0.976	0.442
0.488	0.254

Note. ave. k_{obs} are average of 2 or 3 values. Percent differences in k_{obs} of duplicate runs did not exceed 5%.

Equation (2) can be rearranged to equation (11) as follows:

$$k_{\text{obs}} = k' + \frac{k_w C_t - k_{\text{obs}}}{K_s (C_t - \text{cmc})} \quad (11)$$

where $k_\psi = k_{\text{obs}} =$ pseudo first-order rate constant

$$k' = k_m \beta S$$

$$[D_n] = C_t - \text{cmc}$$

$$[N_T] \cong C_t$$

Equation (11), based upon the pseudo phase model, fails²⁶ near the cmc because of specific interactions between surfactant and reactants and also for reasons not currently understood. For

Table 5

Kinetic data for Hydrolysis of n-Decanohydroxamic Acid
as a Function of Perfluorooctanoic Acid as
Surfactant at $70 \pm 0.1^\circ\text{C}$

$C_t \times 10^2, \text{M}$	ave. $k_{\text{obs}} \times 10^2, \text{min}^{-1}$
3.11	2.46
2.67	2.28
2.22	2.13
1.78	1.81
1.33	1.50
1.20	0.869
1.06	0.223
0.889	0.0671
0.444	0.0290

Note. ave. k_{obs} are average of 2 or 3 values; percent differences in k_{obs} of duplicate runs did not exceed 5%.

example for reactive counterion surfactants having very hydrophilic counterions such as hydroxide and fluoride ions the model fails.³⁵

The right hand term of equation (11) is subject to considerable error at surfactant concentrations near the cmc, thus equation (11) should be tested over a significant concentration range of the surfactant considerably above the cmc.

An error analysis indicates that the overall error in the term $(k_w C_t - k_{\text{obs}})/(C_t - \text{cmc})$ decreases from 23% to 9% as the total surfactant concentration increases. This overall error is calculated assuming a 5% error in k_{obs} , k_w , and cmc.

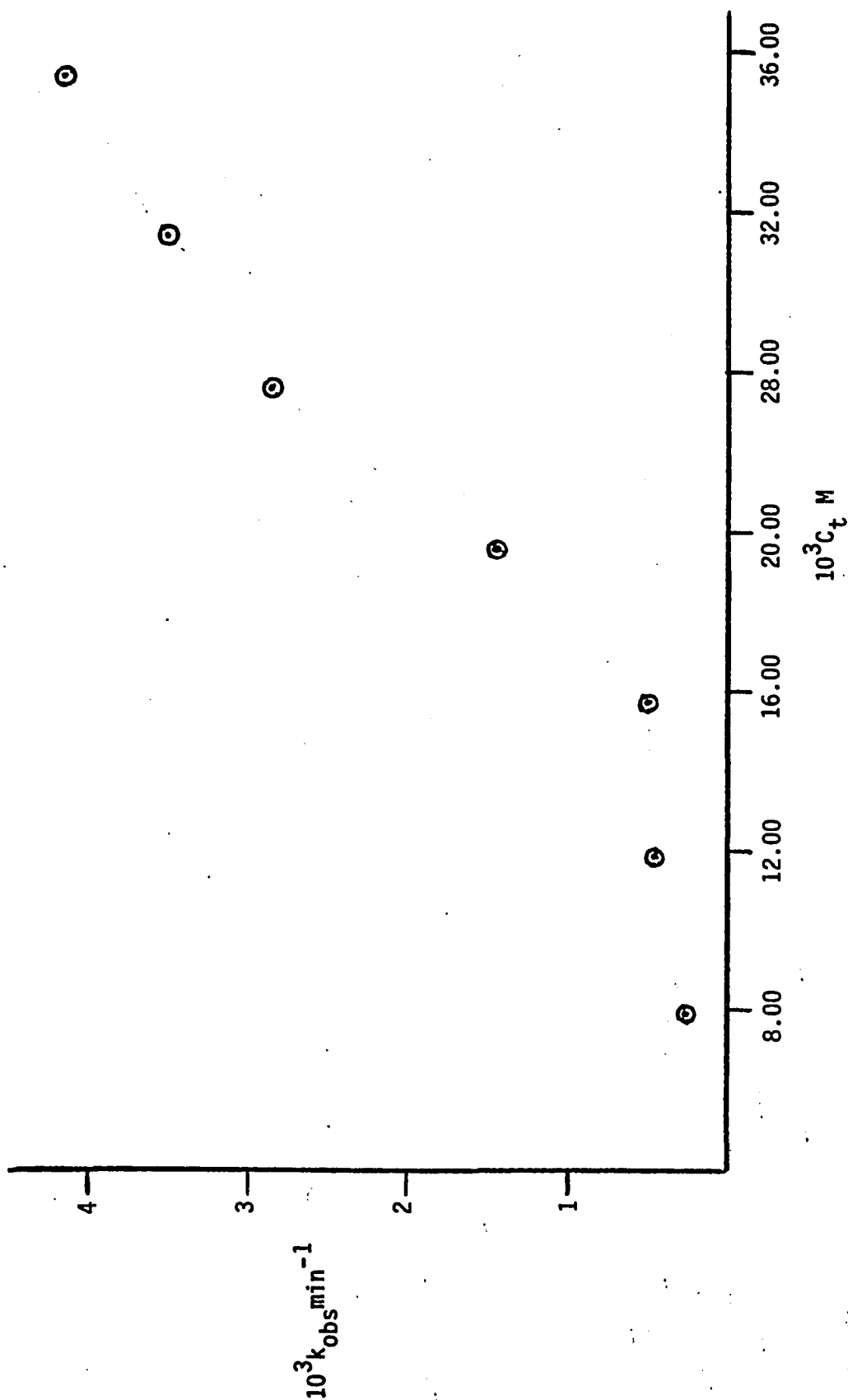


Figure 3. Rate Constant Surfactant Concentration Profile for Hydrolysis of Hexanohydroxamic Acid

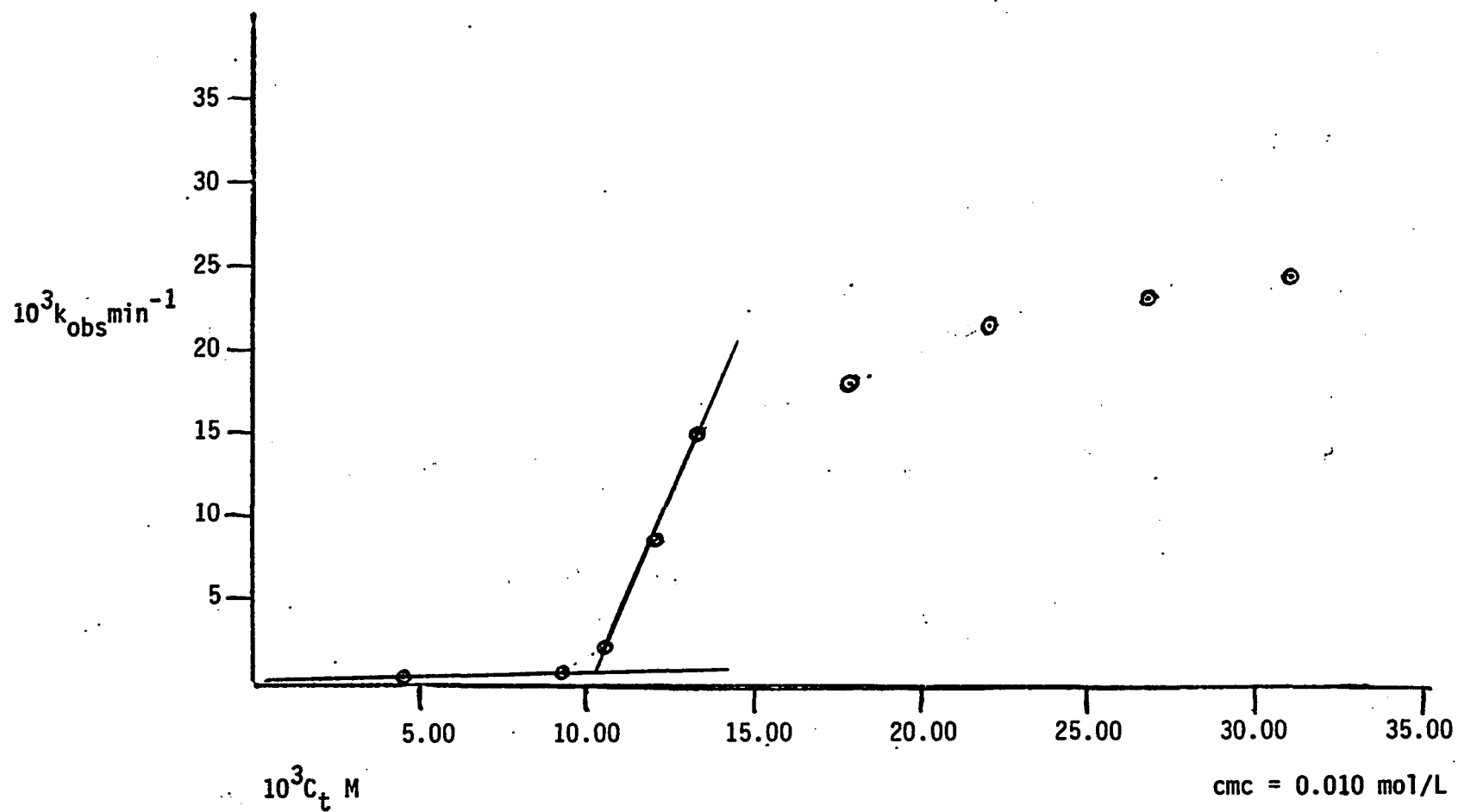


Figure 4. Determination of cmc From Rate Constant-Surfactant Concentration Profile Obtained for Hydrolysis of Decanohydroxamic Acid

Table 6
Parameters for Equation (11) for
Decanohydroxamic Acid Above the cmc

$C_t \times 10^2 \text{ M}$	$(C_t - \text{cmc}) \times 10^2$	$k_{\text{obs}} \times 10^2 \text{ min}^{-1}$	$\frac{k_w C_t - k_{\text{obs}}}{C_t - \text{cmc}}$
3.11	2.07	2.46	-1.08
2.67	1.63	2.28	-1.29
2.22	1.18	2.13	-1.67
1.78	0.0738	1.81	-2.28
1.33	0.0293	1.50	-4.80
1.20	0.0160	0.869	-4.91

A plot of k_{obs} (pseudo first-order rate constant) versus $(k_w C_t - k_{\text{obs}})/(C_t - \text{cmc})$, Figure 5 shows a somewhat linear relationship for decanohydroxamic acid. Notice that there will be also some error in $k_w C_t$ since the perfluorooctanoic acid does not completely ionize and may have a different fraction ionized at significantly different total surfactant concentration (C_t). In addition the extent of ionization may be influenced by micelle formation above the cmc.

The value of k_w was evaluated for surfactant concentrations below the cmc, i.e., in the region in which there are no micelles, the average $k_w = 4.34 \times 10^{-2} \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ for hexanohydroxamic acid and $7.04 \times 10^{-2} \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ for decanohydroxamic acid.

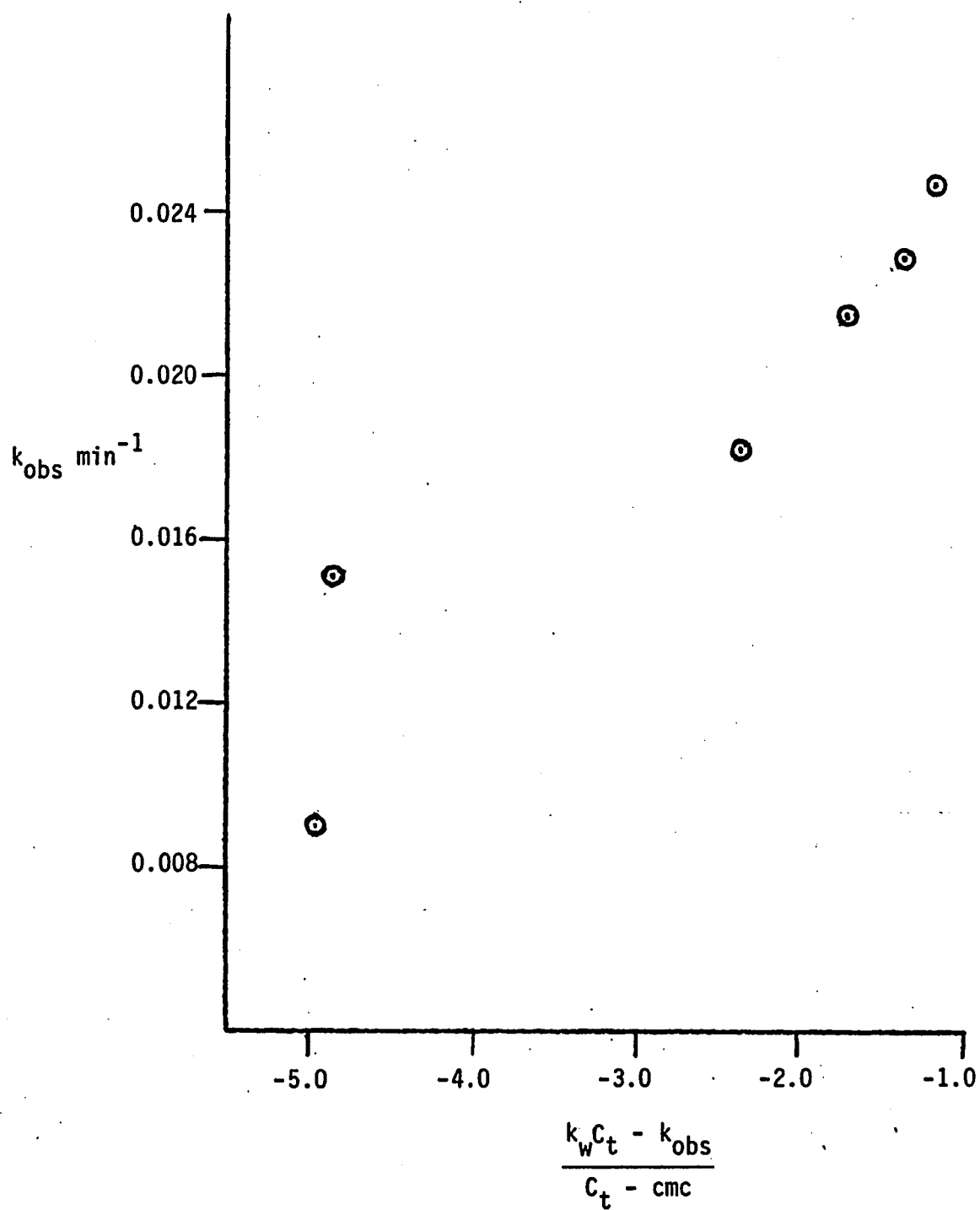


Figure 5. Plot Equation 11 for Hydrolysis of Decanohydroxamic Acid

A previous study³¹ which used octanohydroxamic acid (5×10^{-4} M) as organic substrate and perfluorooctanoic acid as surfactant indicated that equation (11) might be applicable. However equation (11) failed for phenylacetohydroxamic and 4-bromophenylacetohydroxamic acids investigated in that study. In fact there may be very little micellar effect for these two acids.

Thus the applicability of equation (11) to the studies with perfluorooctanoic acid in water solution cannot be evaluated at this time. The solubility of the surfactant in water is too low to permit a sufficiently wide range of surfactant concentration to be used for an adequate test of the equation. As an example, the perfluorinated compounds have much lower cmc's, i.e., less solubility, than the corresponding hydrocarbon surfactants; the cmc's for sodium perfluorooctanoate and sodium octanoate are 0.030 and 0.38 M, respectively.

Another purpose of this thesis is to calculate Arrhenius activation energies (E_a) for reactions in the micellar and non-micellar solutions. The reaction which was investigated is the hydrolysis of n-octanohydroxamic acid using perfluorooctanoic acid as surfactant.

The rate constant (k_{obs}) was evaluated at concentrations (C_t) above the cmc, i.e., concentrations at which micelles form, at temperatures 60.3, 70.0, and 79.1°C. Also k_{obs} was determined below the cmc at these temperatures and at 90.1°C. The validity of the Arrhenius equation (12) was confirmed by plotting the logarithm of the rate constant against the reciprocal of absolute

temperature. Straight lines were obtained, e.g., Figure 6 (F-test³⁶ shows significance within 1-5% level except for the 0.0293 M surfactant case in which it is almost within the 5% level).

$$k = Ae^{-E_a/RT} \quad (12)$$

$$\ln k = \ln A - E_a/RT \quad (13)$$

The Arrhenius equation (12) indicates that molecules must acquire a certain critical energy (E_a) before they can react, the Boltzmann factor $e^{-E_a/RT}$ being the fraction of molecules that contain the necessary energy. Variation of temperature allows one to vary the average energy of reactants in accord with a Maxwell-Boltzmann distribution function.

Table 7 summarizes the results obtained from the Arrhenius equation. However one should remember that the Arrhenius equation is only a good approximate representation of the temperature dependence of k . The influence of micelles upon the rate of reaction can be seen by comparison of the E_a values at surfactant concentrations in the range 2.44×10^{-2} to 3.42×10^{-2} M, i.e., above the cmc and at 0.750×10^{-2} M, i.e., below the cmc. The E_a values are lower for solutions with micelles than the E_a for solutions without micelles for the reaction under investigation. The same result was obtained for the condensation of 4,4'-diaminodiphenyl ether with furfural using sodium dodecylsulfate as surfactant at pH = 10.5³⁷. The activation energy for the case with no micelles is 7.4 kcal/mol and it is 1.2 kcal/mol in the micellar case. Also there are cases in which E_a is not

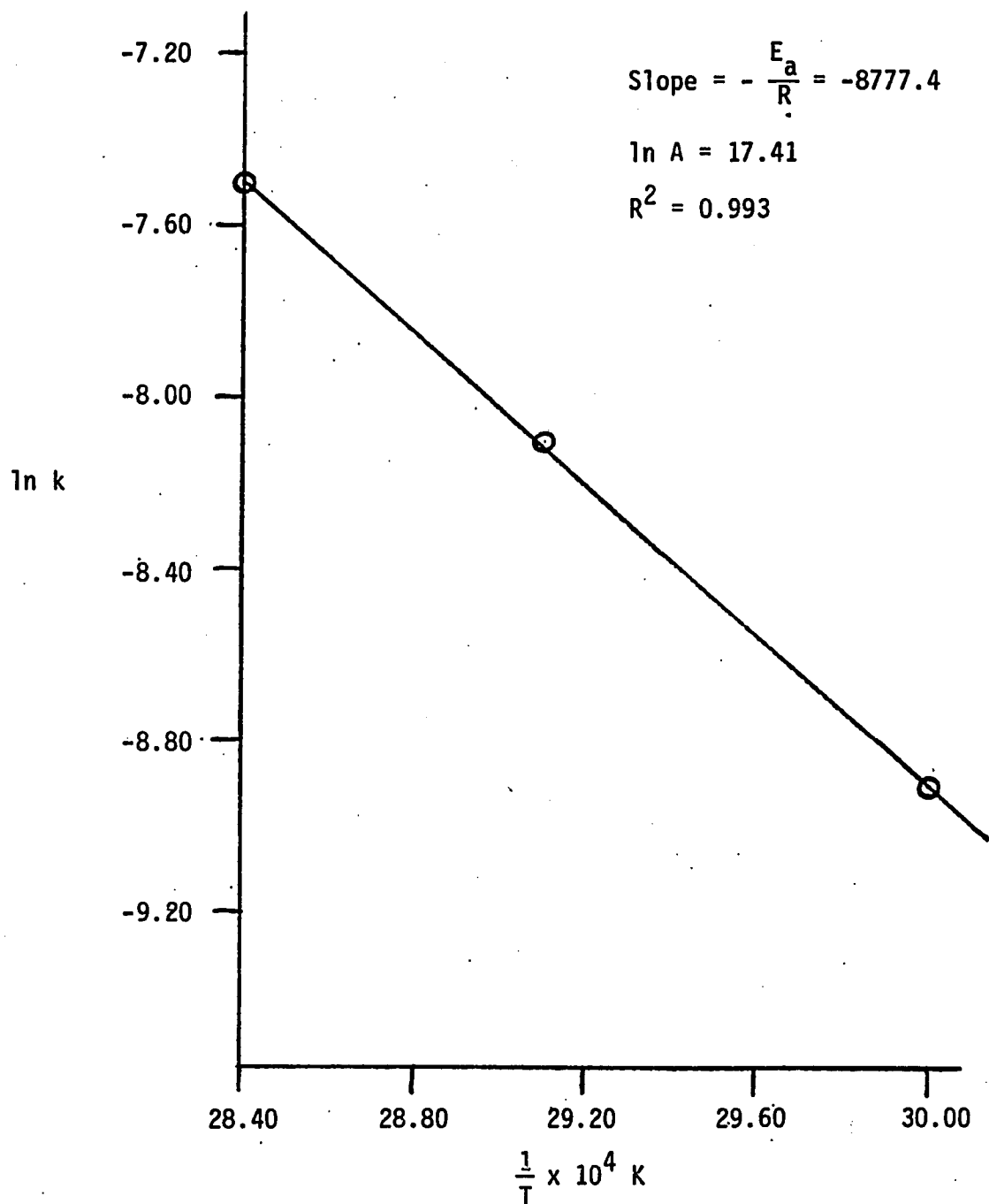


Figure 6. Dependence of Natural Logarithm of Observed Rate Constant for the Hydrolysis of Octanohydroxamic Acid, on the Temperature for $3.42 \times 10^{-2} \text{ M}$ Perfluorooctanoic Acid

Table 7

Summary for the Results Obtained by Plotting Equation (13) for
 Surfactant Concentration Range 0.750×10^{-2} - 3.42×10^{-2} M
 for Hydrolysis of Octanohydroxamic Acid

$C_t \times 10^2$ (M)	T (K)	$k \times 10^4$ (sec ⁻¹)	E_a (kcal/mol)	$\ln A^a$
3.42	352.25	5.32	17.4	17.4
	343.15 ^b	2.96		
	333.45	1.31		
2.93	352.25	4.42	16.2	15.40
	343.15 ^b	2.72		
	333.45	1.21		
2.44	352.25	3.50	14.5	12.79
	343.15 ^b	2.11		
	333.45	1.09		
0.750	363.45	0.28	18.4	15.08
	352.25	0.15		
	343.15 ^b	0.090		
	333.45	0.027		

^aA is not a true frequency factor, because k is pseudo rate constant. ^bH. Akhavan-Tafti, Western Michigan University, unpublished results.

significantly different for the micellar and non-micellar cases, e.g., the oxidation of diethyl sulfide with the surfactant sodium dodecylsulfate has essentially constant enthalpy, but different entropies of activation above and below the cmc.³⁸ In a similar

way the increase in concentration of cetyltrimethylammonium bromide from 0.004-0.1 M is accompanied by no change in E_a although a considerable change in entropy of activation occurs³⁹ for the base catalyzed oxidative cleavage of the C-C bond in 1,1-bis(p-chlorophenyl)-2,2,2-trichloroethanol. For the basic hydrolysis of N-methyl-p-toluanilides with cetyltrimethylammonium bromide, a change in E_a but not in the entropy of activation was observed for one compound and changes in both E_a and entropy of activation occurred for a second compound.⁴⁰

The error in the activation energies may be determined as follows as described by Wiberg.⁴¹ Since three temperatures are used in the case of surfactant concentrations above the cmc, the slope is primarily determined by the first and third points and the middle point partially controls the value of the intercept. Even when four temperatures are used (case below the cmc), the slope is almost entirely controlled by the first and fourth points. Let α be the maximum fractional error in the rate constant ($\alpha = 0.05$) and δ the error in the activation energies

$$\% \quad \delta = \frac{2RTT'\alpha}{T' - T} \quad (14)$$

where T and T' are the lowest and highest temperatures, respectively.

The magnitude of the error in kcal/mol which results from this treatment indicates that $\delta = 1$ for calculated activation energies for reactions above the cmc and 0.8 for activation energy for reaction below the cmc.

Conclusions

A micellar effect upon the rate of hydrolysis of hydroxamic acids in aqueous perfluorooctanoic acid has been demonstrated for aliphatic hydroxamic acids with chain lengths of six, eight, and ten carbons. Typical rate constant-surfactant concentration profiles for micellar catalysis were obtained. In addition, the Arrhenius activation energies determined for reaction of octanohydroxamic acid at surfactant concentrations above the cmc were lower than the activation energies for reactions below the cmc, thus indicating the effect of micellization on the rate of reaction.

The low solubility of perfluorooctanoic acid in water prevented the use of a sufficiently wide range of surfactant concentrations necessary to test the theoretical equation (based on the pseudo phase model) appropriate for this surfactant type. Thus it is recommended that a search for a solvent system which would provide a greater solubility range for perfluorooctanoic acid be sought so that an adequate test of the model equation for micellar effects can be made.

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