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Side Chain Effect on Micellarly Catalyzed Hydrolysis of Hydroxamic Acids in Perfluorooctanoic Acid Environment

A.C. Menik Fernando

SIDE CHAIN EFFECT ON MICELLARLY CATALYZED HYDROLYSIS OF HYDROXAMIC ACIDS IN PERFLUOROOCTANOIC ACID ENVIRONMENT

by

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Dedicated to my wife and my parents

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The side chain effect on micellar catalysis of hydroxamic acids with perfluorooctanoic acid as the reactive counterion surfactant in aqueous acetonitrile solution has been demonstrated in this thesis.

The rate constant-surfactant concentration profiles were used to estimate the critical micelle concentration and the second order rate constant for hydrolysis in the aqueous bulk phase.

The pseudo-phase ion exchange model satisfactorily explains the surfactant effect. The second order rate constants in the aqueous bulk phase show a direct relationship with steric substituent constants. The major influence of the change in micellar catalysis is the location in the micelle where the substrate is bound.

Further investigation regarding the location in the micelle where hydroxamic acids are bound is suggested.

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CHAPTER I

INTRODUCTION

During the past several years, interest in micelles has been tremendously expanded. This interest was awakened by the discovery of some similarities between micelles and cell membranes and also by the use of micelles as models for enzyme catalyzed reactions.[1-3]

From a practical standpoint, micelles play a very important role in the fields of Chemistry, Physics, Biology, Medicine, Material Engineering and Paper Science. As examples, micelle forming surfactants are extensively employed in industrial processes such as enhanced oil recovery, detergency, flotation and microemulsions.[4-6] In addition there are some potential applications in novel separation and reaction schemes such as catalysis[1] and solar energy conversions.[7]

Micelles can be defined as colloidal particles formed from the molecules of surfactants under appropriate conditions. When a surfactant is dissolved in water, four fundamental processes result (Figure 1): (1) Dissolution of surfactants, (2) Adsorption of dissolved surfactants at the solid-water interface, (3) Spreading of surfactants from their bulk phase directly to the air-water interface, (4) Aggregation of dissolved surfactants.

The molecules of surfactants have a strong affinity for the interface because they contain both hydrophilic and hydrophobic portions. These hydrophobic portions have a great tendency to keep away from water to

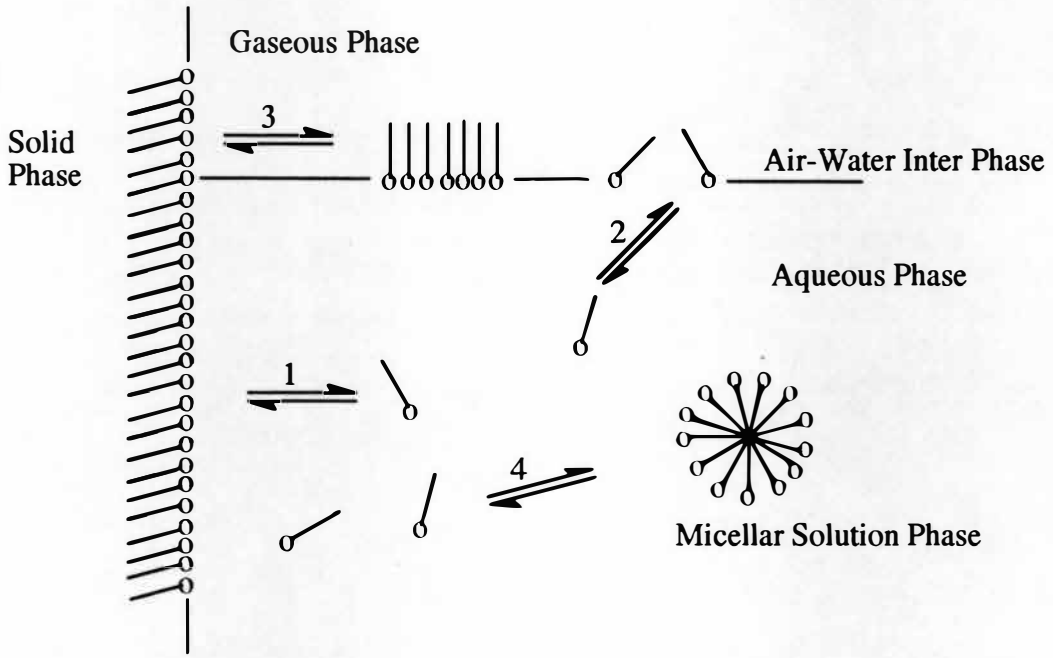


Figure 1. Fundamental Processes for Thermodynamical Equilibria in Aqueous Surfactant Solution.

reduce the surface free energy by decreasing the hydrophobic-water interphase. Among these four processes only surfactant aggregation is purely a concentration dependent process and a very important phenomena in surfactant chemistry. When the concentration of the surfactant reaches a specific value it undergoes aggregation. This concentration is called the critical micelle concentration (cmc). It has been documented that the cmc can be experimentally obtained by plotting some physico-chemical properties versus surfactant concentration. These properties includs osmotic pressure, turbidity, surface tension, equivalent conductivity, self diffusion as well as others.[8-9]

Some of the important factors known to affect the cmc in aqueous solution are: (a) structure of the surfactant, (b) presence of added electrolyte in solution, (c) presence in the solution of various organic additives, and (d) temperature of the solution.

In aqueous medium, the cmc decreases with increasing hydrophobicity of the hydrocarbon chain of the surfactant. When the number of carbon atoms in the hydrocarbon chain exceeds 16, however, cmc no longer decreases so rapidly as the number of carbons increases. Once it exceeds 18 carbons it may remain substantially unchanged with further increase in the chain length. This may be due to the coiling of these long chains in an aqueous medium.[10]

The presence of added electrolytes to ionic surfactants causes a decrease in the cmc. In other words, electrolytes favor the process of micellization. This is due to the decrease in the electrical repulsion of the ionic "head groups" surrounded bymore counterions.

For the understanding of the effect of organic additives on cmc, it is necessary to consider them in two categories. Class I (e.g. polar organic compounds, alcohols and amides) compounds decrease the cmc by being incorporated into the micelle. Class II (e.g. urea, formamide, guanidinium salts) compounds are believed to increase the cmc by disrupting the water structure.[11]

The effect of temperature on the cmc in aqueous medium is quite complex, first appearing to decrease with the temperature to a minimum and then increase.[11]

In general the aggregation number is in the range of 10-100 monomers[1]. The aggregation number of micelles is governed by the incompatibility between surfactant and solvents. The greater the incompatibility the greater is the aggregation number. Thus in aqueous solutions the aggregation number appears to increase as the length of the hydrophobic groups increases. An increase in the temperature causes a considerable decrease in the aggregation number in aqueous medium. The addition of neutral electrolytes to an aqueous solution seems to be to increase the aggregation number.

The shape of micelles has been described by several authors.[12-17] They have found that the shapes of micelles are dependent on surfactant concentration, temperature and the presence of other compounds in the medium. The shape of the micelle is roughly spherical.[1,13,17,18,] In more concentrated surfactant solutions it changes to an elongated shape.[19] The physical appearance of the micelle is like a "loose ball."[12] The dynamic roughness of the micelle surface is due to the uneven aggregation of the monomers.

Several models have been proposed to describe the catalytic effect of micelles. The spherical model (Figure 2) is the most commonly accepted one.

The average radii of micelles is 12 - 30 A^0 and is approximately equal to the length of the hydrocarbon chain ("tail") of the surfactant molecules. These "tails" are oriented in somewhat regular fashion into the center of the micelle structure by "sticking" to each other due to the hydrophobic-hydrophobic interactions. This interior volume is called the

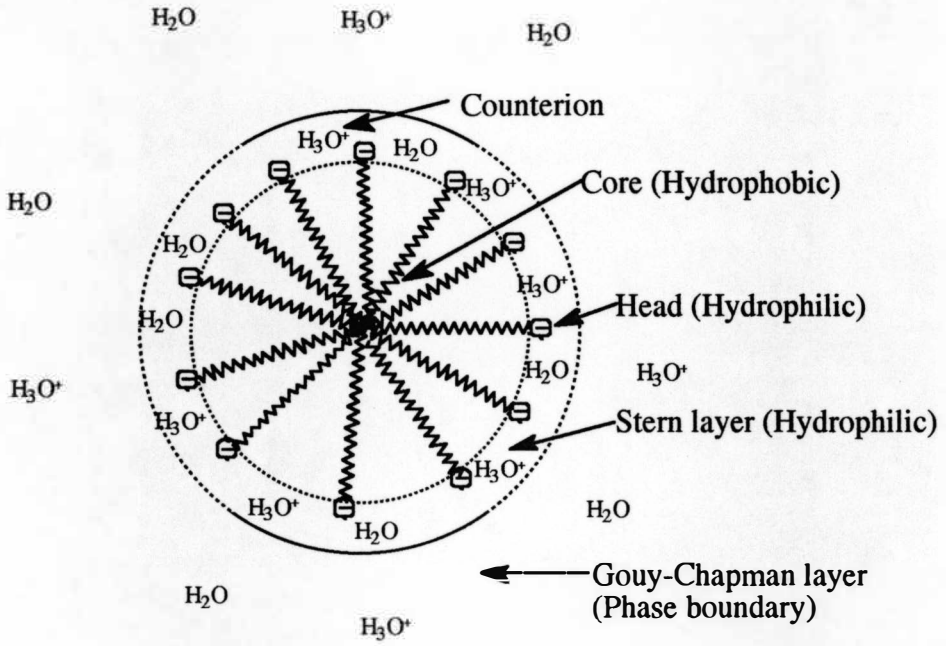


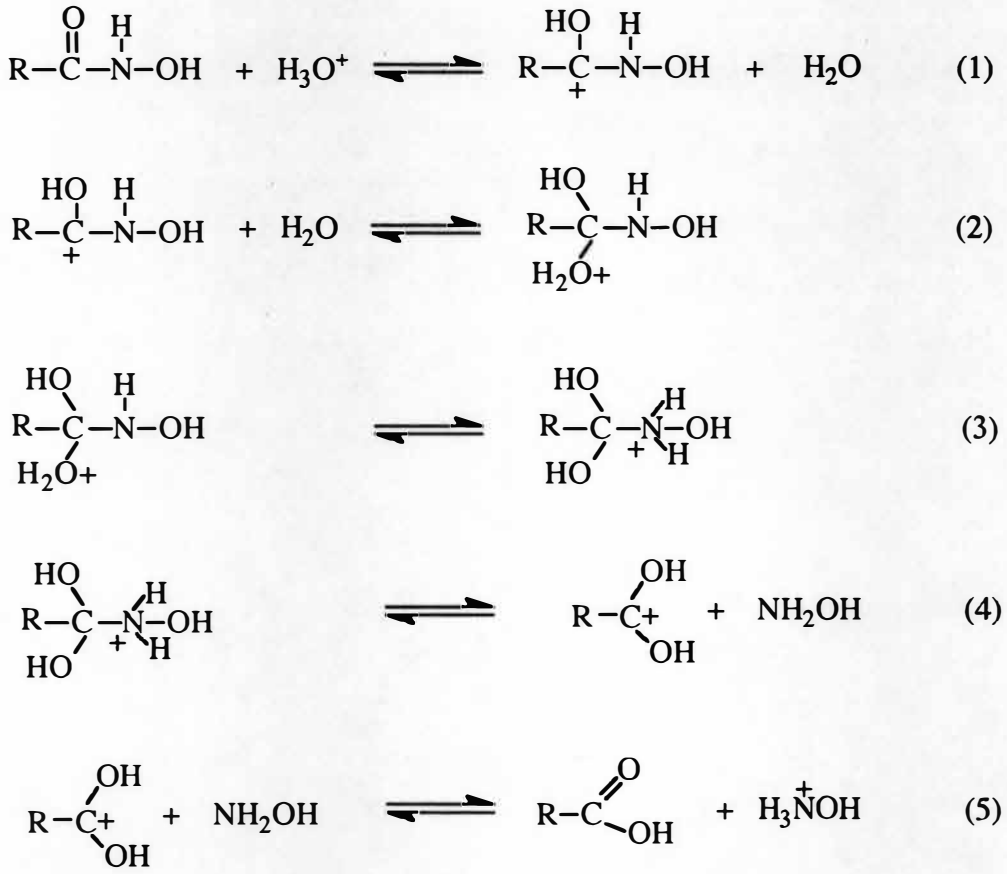
Figure 2. Model of Hypothetical Anionic Micelle in Aqueous Medium.

"core" of the micelle. The hydrophilic "head" groups are located at the micelle-water interface and may be hydrated with water molecules. About 80% of the counterions are tightly bound in the Stern layer to minimize the polar-polar "head" groups repulsion. Some of the remaining counterions reside in the Gouy-Chapman electrical double layer that extends further into the aqueous phase (see Figure 2), and exist in equilibrium with the outside bulk aqueous phase.

Micellar catalysis on amide-like compounds has been of interest because of the relationship to peptides. Considerable modification of the leaving group in the hydrolysis reaction results from the substitution of a

hydroxamic acid group for an amide group. The mechanism of the acid catalysed hydrolysis of hydroxamic acids has been proposed as follows.[19]

Mechanism of the Acid Catalyzed Hydrolysis of Hydroxamic Acids



Micellar Catalysis and Kinetics

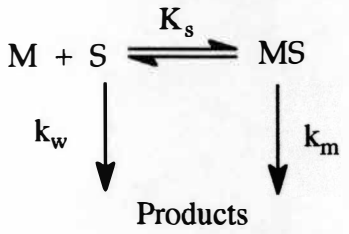
The substantial rate enhancement of a chemical reaction in a micellar solution is called micellar catalysis. Micellar catalysis in an aqueous environment can be explained by using the following two effects: (1) Concentrating the reagents into a smaller reactant volume, and

(2) Stabilizing the transition state compared to the aqueous phase with a charged micelle.

The micellar enhancement of reaction rates could result from one or both of these two effects.[20,21] D.C. Berndt and co-workers have reported that the second effect has a significant role in the micellar catalysis of substituted benzhydroxamic acids.[22]

From the microscopic point of view, the micellar solution is considered to consist of separate phases or pseudophases. So, a hydrophobic substrate that has a low solubility in the bulk aqueous phase and will have a higher solubility in the micellar phase. The solubility of the substrate is governed by its hydrophilic and hydrophobic moieties. The higher the hydrophobicity, the greater is the solubility of the substrate in the micellar phase. This is reflected in the binding of the substrate to the micelle. In general a substrate which has a greater hydrophobicity shows a higher affinity of binding to the micelle. As a result all the reactants (including H^+ in an anionic micelle) are brought into close proximity in the micellar phase. When the carbon equivalent ("number of carbons") of the substrate increases, it shows a larger effect in micellar rate enhancement due to the increase of the hydrophobicity.

The following standard kinetic scheme illustrates the pseudophase model for reactions in the micellar solution.



M and S are micelle and substrate, respectively, and k_w and k_m are the rate constant for the product formation outside and within the micelle respectively. K_s is the substrate micelle association constant (binding constant). Equation (6) has been derived from the pseudo phase ion exchange model (PPIE) for reactive counterion surfactants[23] for bimolecular reactions.

$$k_\psi = \frac{k_w[N_t]+\beta(k_m K_s - k_w)(C_t - cmc)}{K_s(C_t - cmc) + 1} \qquad (6)$$

k_ψ, k_w and k_m are the observed pseudo first order, aqueous phase and micellar phase rate constants, respectively. β is the degree of counterion binding to the micelle. C_t is the total surfactant concentration. N_t is the total concentration of surfactant counterion and is equal to C_t with no added salts.

Equation (6) can be rewritten and rearranged to equations (7) and (8). With $b = \beta (k_m K_s - k_w)/K_s$ the following transformation leads to a form useful for finding the constants K_s and k_m.

$$k_\psi = \frac{k_w C_t + bK_s(C_t - cmc)}{K_s(C_t - cmc) + 1} \qquad (7)$$

$$k_\psi = \frac{k_w C_t - k_\psi}{K_s (C_t - cmc)} + b \qquad (8)$$

Regression of k_ψ vs. $(k_w C_t - k_\psi)/(C_t - cmc)$ yields values for b and K_s. By rearranging $b = \beta (k_m K_s - k_w)/K_s$, equation (9) was obtained.

$$k_m = (bK_s + \beta k_w)/\beta K_s \qquad (9)$$

The value of β is in the range of 0.6-0.9, and it has been assumed as 0.8 for this work as in previous reports.[24,25]

In recent years much interest has been shown for the application of perfluorocarboxylic acid as a surfactant in micellar solutions.[8,9,26,27,30] Perfluorocarboxylic acids are strong acids which ionize almost completely due to the stronger electron withdrawing power of fluorine atoms compared to hydrogen atoms. It has been reported that perfluoroheptanoic acid behaves like HCl in aqueous solutions.[9] With the substitution of fluorine for hydrogen atoms, these surfactants have some distinct properties compared to normal hydrocarbon carboxylic acids. Since fluorine atoms are electron rich compared to hydrogen atoms, fluorocarbon chains have much stronger Van der Waals interactions with the solute than do hydrocarbon chains. Because of the greater hydrophobicity of the fluorocarbon chain, micellization is enhanced. In addition to the other two factors, the fluorocarbon chain is more rigid than a hydrocarbon chain due to the large size of the fluorine atoms.[9,26] This structural rigidity of the fluorocarbon chain has great influence on the micelle formation. It has been estimated that the effect of each CF_2 group towards micelle formation is roughly equivalent to 1.6 CH_2 groups.[11]

Previous Work and the Purpose of This Work

The study reported in this thesis is to get a better understanding for the interpretation of the previous experimental data.[25,28,29] Table 1 shows the previous studies for the variation of the k_ψ with the concentration of perfluorooctanoic acid for the hydrolysis of different hydroxamic acids.[30] Table 2 contains experimental data, k_w, cmc, b, k_m and K_s changes for different hydroxamic acids.[30]

The micelle exerts its largest effect by acting to "concentrate" the reagents into a smaller reactant volume. This is seen in the K_s values, larger K_s values lead to larger surfactant catalysis and k_ψ increases rapidly as surfactant concentration increases above the cmc. For interpretation of the data in the previous studies, the carbon equivalent (C_{eq}) was taken as equal to the number of carbon atoms present in aliphatic or alicyclic compounds[31]. But for aromatic compounds it is different. Solubility data[31] indicate that phenyl groups are less "soluble" in perfluoro solvents than in hydrocarbon solvents compared to alkyl groups. So the phenyl group was considered as 1.5 C, not 6 C, for C_{eq} calculations in perfluoromicellar solutions. It is considered as 3.5 C in hydrocarbon micellar solutions.[31] Thus one set of compounds, Ph-$(CH_2)_n$-CONHOH and RCONHOH have K_s values in order of carbon equivalent number (see Table 2).

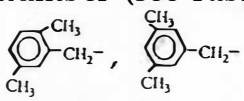
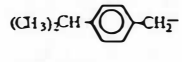
For another set with R groups  , and  K_s values are about the same but greater than for $Ph(CH_2)_n$- type of compounds of the same carbon equivalent. This set of compounds has alkyl groups on the periphery of the aromatic ring.

Table 1

Variation of the Observed Pseudo First Order Rate Constant (k_ψ) With the Concentration of Perfluorooctanoic Acid for the Hydrolysis of Different Hydroxamic Acids From Previous Studies

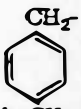
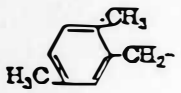
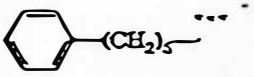
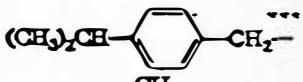
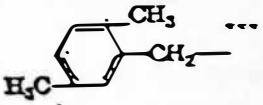
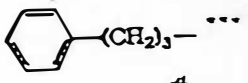
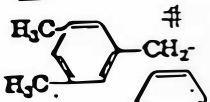
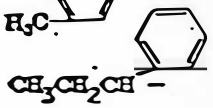
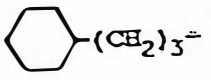
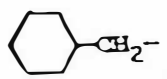
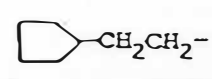
	$10^4 k_\psi$, min^{-1}					
	R =					
$10^2 C_c$, M	$CH_3(CH_2)_6$	$CH_3(CH_2)_6$				
			$CH_2(CH_2)_4$	$(CH_3)_2CH$	$CH_2(CH_2)_2$	
0.190	1.93					0.221
0.286			1.45	1.47	1.35	
0.476	3.03					
0.619			3.32			
0.667				2.60	3.28	0.7
0.762		4.43				
0.952	6.94	5.74		4.01	4.55	1.0
1.14			6.67			
1.34		11.0				
1.42	36.3					
1.90	54.8	29.0		16.1	11.8	2.3
2.38		38.2	26.9			
2.86		63.8		30.4	18.9	4.7
3.81	118.0	70.5		36.1	27.0	7.6
4.44			52.6			
4.76	133.0		58.4	51.7	32.1	10.4
5.00		81.0				
5.71	146.0		66.5	57.2	37.8	11.1
6.20		102.0				
6.67			72.1	58.1	44.0	12.5

Table 1 --- Continued

	$10^4 k_\psi$, min^{-1}			
$10^2 C_t$, M	R= $CH_3CH_2\overset{\phi}{C}H$	$-(CH_2)_3-$	$-CH_2-$	$-CH_2CH_2-$
0.286		1.84	0.387	1.58
0.476	0.225			
0.667		4.18	0.861	4.38
0.767	0.374			
0.952	0.449	6.06	1.45	5.89
1.33		9.77		
1.52				11.9
1.62		21.0		
1.90	0.985	28.5	3.75	16.2
2.86	2.10	50.6	6.70	26.1
3.81		63.6	9.55	33.1
4.76	2.90	79.3		
5.24				43.7
5.71		93.9	15.0	
6.67	3.38			

Table 2

Comparison of the Reaction Rates as Well as Binding Constants for Different Hydroxamic Compounds

R in R-CONHOH	C_{eq}*	k_w L/mol min.	k_m** $min.^{-1}$	K_s** L/mol	k_w^{rel}	k_m^{rel}	K_s^{rel}
$CH_3(CH_2)_8$-***	10.0	0.0700	0.0258	40.1	1.00	1.00	1.00
$CH_3(CH_2)_6$-***	8.0	0.0594	0.0250	17.0	0.85	0.97	0.42
 ***	7.5	0.0588	0.0183	15.0	0.84	0.71	0.37
 ***	6.5	0.0404	0.0121	24.4	0.58	0.47	0.61
 ***	5.5	0.0110	0.00240	26.4	0.16	0.093	0.66
 ***	5.5	0.0482	0.0191	5.38	0.69	0.74	0.13
 #	5.5	0.0434	0.00581	23.63	0.62	0.23	0.59
	5.5	0.00473	0.000549	42.4	0.068	0.021	1.10
	10.0	0.0635	0.0213	20.8	0.91	0.83	0.52
	8.0	0.0149	0.0241	1.52	0.21	0.93	0.038
	8.0	0.0636	0.0113	15.6	0.91	0 44	0.39

* C_{eq} = Carbon equivalent, see text

** The derived values usually good only to one or two significant figures.

*** Data for these compounds are from references 25 and 29.

\# D. C. Berndt and William R. Horton, unpublished results.

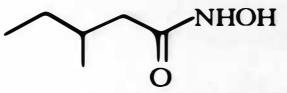
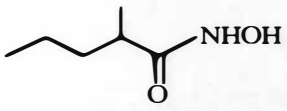
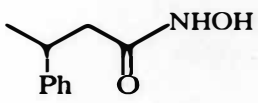
The reference compound is R = $CH_3(CH_2)_8$-

CH_3-CH_2-CH(Ph)-CONHOH #(1)

#(2)

The above two compounds have some K_s (#1, α branched) and k_m^{rel} (#2, β branched) values which are different from most of the others. Thus the following four compounds with α, β and γ branching were selected to investigate these differences to give complete α, β, γ substitutions in two series of compounds.

Selected Compounds for Further Investigation

Compound	Branching	Name
	γ	4-Methylpentanohydroxamic acid
	β	3-Methylpentanohydroxamic acid
	α	2-Methylpentanohydroxamic acid
	β	3-Phenylbutanohydroxamic acid

CHAPTER II

EXPERIMENTAL SECTION

Purification of Perfluorooctanoic Acid

Perfluorooctanoic acid was purchased from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin and purified by two successive recrystallizations in carbon tetrachloride (CCl_4, ACS). The recrystallizations were carried out by dissolving twenty five grams of perfluorooctanoic acid in 400 mL of CCl_4 (ACS) by heating on a steam bath. The resulting solution was allowed to cool and stand overnight. The crystals were separated by vacuum filtration and washed with ice cold CCl_4. The melting point was measured using a capillary melting point apparatus (Thomas Hoover Company, Ltd), and found to be 57 - 58^{0}C (literature mp[27] 56.4 - 57.9^0 C).

Preparation of Hydroxamic Acids

Hydroxamic acids were prepared, by adaptation of standard procedures[32] from the appropriate carboxylic acids using the following two steps.

$$RCOOH + CH_3OH \xrightarrow{H_2SO_4} RCOOCH_3 + H_2O \qquad (10)$$

$$RCOOCH_3 + H_2NOH \longrightarrow RCONHOH + CH_3OH \qquad (11)$$

Step 1: For each mole of carboxylic acid 10 moles of methanol were added into a boiling flask. Conc. H_2SO_4 (1 mL H_2SO_4 for 0.12 moles of carboxylic acid) was added, the mixture was swirled then refluxed for 5 hours. After the mixture was cooled to room temperature 125 mL of water were added for each 0.1 mole of carboxylic acid used. The resulting methyl ester was extracted into an equal volume of CH_2Cl_2. The CH_2Cl_2 layer was washed with an equal volume of 10% aq. NaOH to get rid of unreacted acids. The aqueous layer was checked with pH paper to make sure it was still alkaline. Then the CH_2Cl_2 layer was washed with distilled water. Finally the CH_2Cl_2 was boiled off on a steam bath in the hood. The residue was the ester.

Step 2: Two solutions for the conversion of ester to hydroxamic acid were prepared. One, for each 1/3 mole of ester, 1 mole of KOH was dissolved in 140 mL of CH_3OH and two, 2/3 mole of $H_2NOH.HCl$ was dissolved in 240 mL of CH_3OH. The KOH solution was first prepared by heating the solution on a steam bath to its boiling point. The $H_2NHOH.HCl$ solution was prepared by heating the solution to the boiling point and cooled to 40^0 C. The KOH solution was added slowly with cooling to the hydroxylamine hydrochloride solution. This new mixture was cooled to 10^0 C and the precipitated KCl was removed by suction filtration. Then the ester was added to the filtrate and the mixture refluxed for 2.5 hours. The solution was cooled and acidified with conc. HCl to pH=6 (pH paper as indicator). The solution was concentrated as much as possible to get solids by letting air from a hose blow on it. The compounds were recrystallized from different solvent systems until a

constant melting point was obtained. 4-Methylpentanohydroxamic acid, 3-methylpentanohydroxamic acid and 2-methylpentanohydroxamic acid were recrystallized from toluene several times.

3- Phenylbutanohydroxamic acid was first recrystallized from water three times and then from H_2O-CH_3OH (3 : 2 v/v) two times.

Elemental analyses were done by Midwest Microlab, Indianapolis IN. The results are in Table 3.

Table 3

Results of Elemental Analysis and Melting Points of Hydroxamic Acids

Compound	M.P. (^{0}C)	Theoretical composition	Actual composition
4-Methylpentanohydroxamic acid	54.5 - 55.0	C = 54.94% H = 9.99% N = 10.68%	C = 54.89% H = 9.93% N = 10.79%
3-Methylpentanohydroxamic acid	71.5 - 72.2	C = 54.94% H = 9.99% N = 10.68%	C = 55.45% H = 10.17% N = 10.77%
2-Methylpentanohydroxamic acid	99.0 - 99.6	C = 54.94% H = 9.99% N = 10.68%	C = 55.02% H = 10.10% N = 10.63%
3-Phenylbutanohydroxamic acid	126.0 - 126.4	C = 67.04% H = 7.26% N = 7.82%	C = 66.86% H = 6.99% N = 7.85%

Among these four compounds only 3-phenylbutanohydroxamic acid has been reported[33] in literature for melting point. There appear to be typographical errors in the reported

melting points for 2- and 3-phenylbutanohydroxamic acids. IR data are shown in Table 4 for these compounds.[36,37] (see the Apendix for spectra)

Table 4

IR Data for Hydroxamic Acids

Compound	Frequency, cm^{-1}	Remarks
4-Methylpentano-hydroxamic acid	1620	C=O stretching, conjugated and H-bonded
	3200, 3350	O-H and N-H stretching, overlaped
	1390 - 1350	CH_3 bending (doublet) for gem-dimethyl groups
3-Methylpentano-hydroxamic acid	1615	C=O stretching, conjugated and H-bonded
	3200, 3360	O-H and N-H stretching, overlaped
2-Methylpentano-hydroxamic acid	1620	C=O stretching, conjugated and H-bonded
	3200, 3360	O-H and N-H stretching, overlaped
3-Phenylbutano-hydroxamic acid	1620	C=O stretching, conjugated and H-bonded
	3030	Aromatic C-H stretching
	3200, 3360	O-H and N-H stretching, overlaped

Preparation of Reagents

Preparation of Ferric Chloride Solution

The solution was prepared according to the following ratio.

H_2O (mL) : conc.HCl (mL) : $FeCl_3.6H_2O$ (g) = 100 : 10 : 1

This solution was used as a indicator because it forms a maroon colored complex with hydroxamic acids. It was also used as a test reagent for the preparation of hydroxamic acid.

Preparation of 2.106 M Acetonitrile Solution

Aqueous CH_3CN solution was prepared by mixing 220 mL of CH_3CN (Aldrich Chemical Compony, Inc., HPLC grade) with Milli-Q™ water (reverse osmosis treated water passed through a carbon filter, two mixed bed DI columns, an organic scavenger column and a 0.2 micron capsule filter) in 2000 mL volumetric flask. This solution was used as the reaction medium and also as a solvent for the surfactant and hydroxamic acids.

Preparation of 0.0105 M Hydroxamic Acid Solutions

Prepared with 2.106 M acetonitrile solution.

Preparation of Surfactant Solutions

Perfluorooctanoic acid (surfactant) solutions (see table 7) were freshly prepared just before the start of the rate determination experiments.

Kinetic Procedure

1. Ten mL of the $FeCl_3$ solution were pipeted into each of seventeen 50 mL volumetric flasks. One of them was used as the blank which contained 4 mL of surfactant solution, 10 mL of $FeCl_3$ solution and diluted to the mark with a 1:1 (v/v) t-butyl alcohol/water mixture.

2. The Gilford-Beckman spectrophotometer was zeroed with the blank solution in the light beam. For all measurements, the same 10 mL sample cell was used and the wavelength was set at 520 nm. The sample cell was calibrated versus the blank cell using distilled water.

3. Forty mL of freshly prepared surfactant solution were pipeted into a 50 mL plastic reaction vessel (duplicate runs were carried out for all reactions). The reaction vessels were stoppered and placed in a stirred constant temperature oil bath (70 ± 0.2^0 C) for about 15 minutes to achieve thermal equilibrium. Two mL of 0.0105 M hydroxamic acid solution were pipeted into each vessel and the mixture swirled to get the solution well mixed.

4. After about 3 minutes a 4 mL sample was withdrawn (pipeted) from the reaction vessel and the initial time was recorded. The pipet was drained into the 50 mL volumetric flask which contained 10 mL of $FeCl_3$

indicator solution. The flask was diluted to the mark with the t-butanol/water (1:1, v/v) mixture and inverted at least twenty times.

Part of this solution was placed into the sample cell for absorbance measurements.

5. Further samples (4 mL) were withdrawn for absorbance measurements from time to time until the final absorbance measurement taken decreased to 1/3 of the initial absorbance. Eight measurements were done for each kinetic run.

6. To minimize error, all samples were taken with the same 4 mL pipet, which was rinsed twice with distilled water and then twice with 95% ethanol and dried with an air aspirator before each sample was taken.

In kinetic runs, the rate of hydrolysis was dependent upon the concentration of surfactant. The observed pseudo first order rate constant (k_ψ) was measured over the range of concentration 0.0050 - 0.060M surfactant.

Calculation of k_ψ

To calculate k_ψ the first order rate law was used.[34]

$$\ln(A_t - A_\infty) = -k_\psi t + \ln(A_0 - A_\infty) \qquad (12)$$

Since $A_\infty = 0$ in this experiment the equation used is

$$\ln A_t = -k_\psi t + \ln A_0 \qquad (13)$$

where A_t is the absorbance at time t, A_0 is the absorbance at initial time 0, A_∞ is the absorbance at complete reaction and k_ψ is the observed pseudo first order rate constant.

A plot of ln A_t vs time gives a nice straight line for the entire experiment. The least squares treatment fit of the data k_ψ was calculated from the slope of the graph. The average value for k_ψ was calculated from the duplicated measurement. The R^2 (R, correlation coefficient) value for all the experiments is above 0.98. The difference between the k_ψ values for each pair of runs is less than 1%.

Sample data for the determination of k_ψ for two runs of 4-methylpentanohydroxamic acid is shown in Table 5 and Table 6. The graphs of ln A_t versus time of sample data for the first and second kinetic runs of the same compound are shown in Figures 3 and 4.

The slope of the graph (Figure 3) for 4-methylpentanohydroxamic acid is -0.00314. Therefore the observed pseudofirst order rate constant, k_ψ is 0.00314 min^{-1}. The data from the duplicate run is 0.00315 min^{-1}. The average value for k_ψ is 0.003145 min^{-1}.

Table 5

Sample Data for the Determination of k_{ψ} for 4-Methylpentanohydroxamic Acid in 0.0476M Perfluorooctanoic Acid at 70 ± 0.2 ^{0}C

No.	Clock Time	t (min.)	A	ln A
1	10:08	0	0.2645	-1.3299
2	10:42	34	0.2360	-1.4439
3	11:27	79	0.2075	-1.5726
4	12:10	122	0.1820	-1.7038
5	12:46	158	0.1605	-1.8295
6	13:30	202	0.1405	-1.9626
7	14:19	251	0.1205	-2.1161
8	15:28	320	0.0965	-2.3382

Regression Output :

Constant	-1.3292
Std Err of Y Est	-0.00570
R Squared	0.9998
No. of Observations	8
Degree of Freedom	6
X Coefficient	-0.00314
Std Err of Coef.	1.973E-05

Table 6

Sample Data for the Determination of k_{ψ} for 4-Methylpentanohydroxamic Acid in 0.0381M Perfluorooctanoic Acid at 70 ± 0.2 °C

No.	Clock Time	t(min.)	A	ln A
1	10:35	0	0.2755	-1.3022
2	11:20	45	0.2355	-1.4264
3	12:01	86	0.2165	-1.5395
4	12:53	138	0.1845	-1.6830
5	14:02	207	0.1535	-1.8735
6	16:52	257	0.1345	-2.0115
7	20:54	379	0.0955	-2.3482
8	26:24	469	0.0745	-2.5966

Regression Output:

Constant	-1.3022
Std Err of Y Est	0.0109
R Squared	0.9995
No. of Observations	8
Degree of Freedom	6
X Coefficient(s)	-0.002760
Std Err of Coef.	2.527E-05

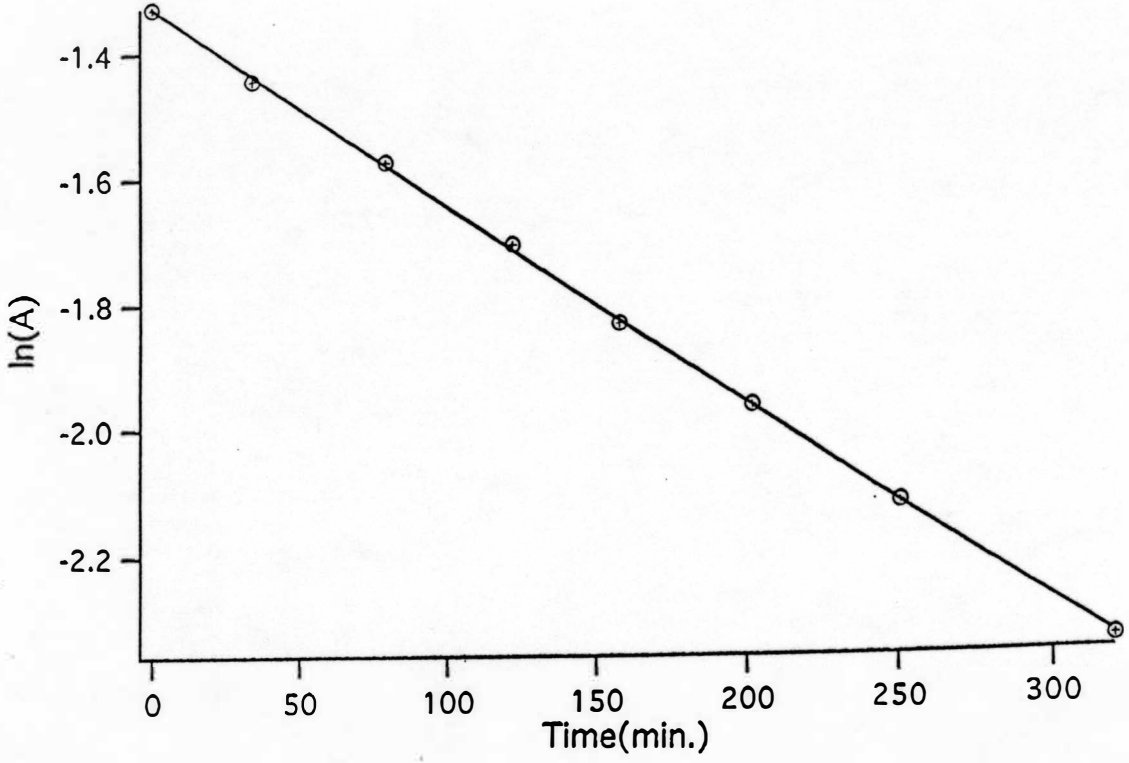


Figure 3. The Graph of ln A_t Versus Time for 4-Methylpentanohydroxamic Acid for the First Kinetic Run at 70 ± 0.2° C (Table 5).

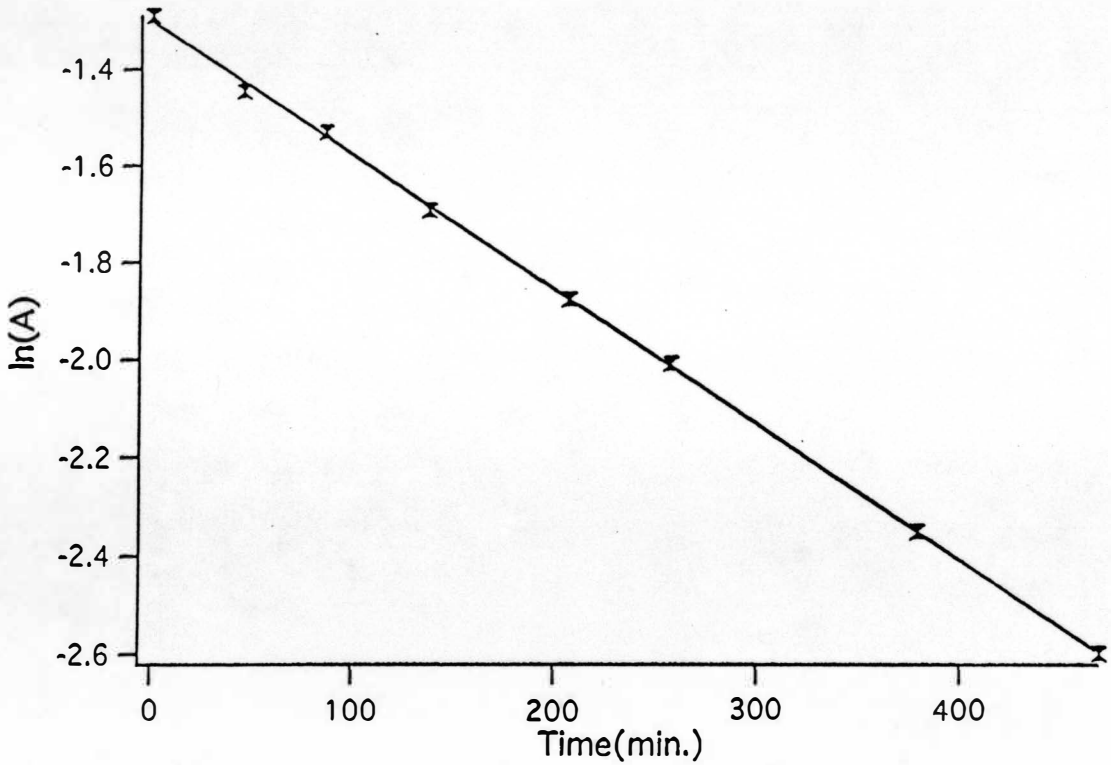


Figure 4. The Graph of ln A_t Versus Time for 4-Methylpentanohydroxamic Acid for the Second Kinetic Run at 70 ± 0.2° C (Table 6).

CHAPTER III

RESULTS AND DISCUSSION

The acidic hydrolysis of hydroxamic acids is represented by the following equation.

$$RCONHOH + H_3O^+ \longrightarrow RCO_2H + H_3N^+OH \qquad (14)$$

The rate of reaction increases with increasing perfluorooctanoic acid concentration both above and below the cmc. The rate enhancement above the cmc however is significantly larger compared to that below the cmc.

Perfluorooctanoic acid is a reactive counterion surfactant. It behaves as a normal acid catalyst below the cmc. Above the cmc it serves as a source of hydrogen ion as well as provides micelles to enhance the rate of hydrolysis of hydroxamic acids. In other words, above the cmc micellar catalysis occurs. In the micellar environment all the reactants, H_3O^+ and hydroxamic molecules are brought into a smaller reactant volume. The carbocation transition state is stabilized by the anionic perfluoro micelle during the process of hydrolysis. Micellar catalysis occurs because of these two important effects.

The experimental kinetic data for the hydrolysis of 4-methylpentanohydroxamic acid, 3-methylpentanohydroxamic acid, 2-methylpentanohydroxamic acid and 3-phenylbutanohydroxamic acid are

in Table 7. The rate constant-surfactant concentration profiles for the four compounds are shown in Figures 5, 6, 7 and 8.

Table 7

Variation of k_ψ With the Concentration of Perfluorooctanoic Acid for the Hydrolysis of Different Hydroxamic Acids in the Current Studies

	$10^4\ k_\psi$ (min.)			
$10^2\ C_t$, M	R= $CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-CH_2-$	$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-$	$CH_3-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-$	$CH_3-\underset{\displaystyle \bigcirc}{\underset{\vert}{CH}}-CH_2-$
0.238	1.96	---	---	---
0.450	---	0.517	---	---
0.476	3.51	---	---	0.634
0.700	4.56	---	---	---
0.714	---	0.753	0.322	0.830
0.952	5.81	0.966	0.422	1.11
1.14	---	1.14	---	---
1.40	9.37	---	---	---
1.43	---	---	0.599	---
1.57	11.0	---	---	---
1.91	14.9	2.22	1.00	2.22
2.21	---	---	1.29	3.10
2.86	21.1	3.74	1.89	4.06
3.81	27.7	5.05	2.52	5.65
4.76	31.45	6.10	3.10	6.61
5.71	---	7.52	---	---

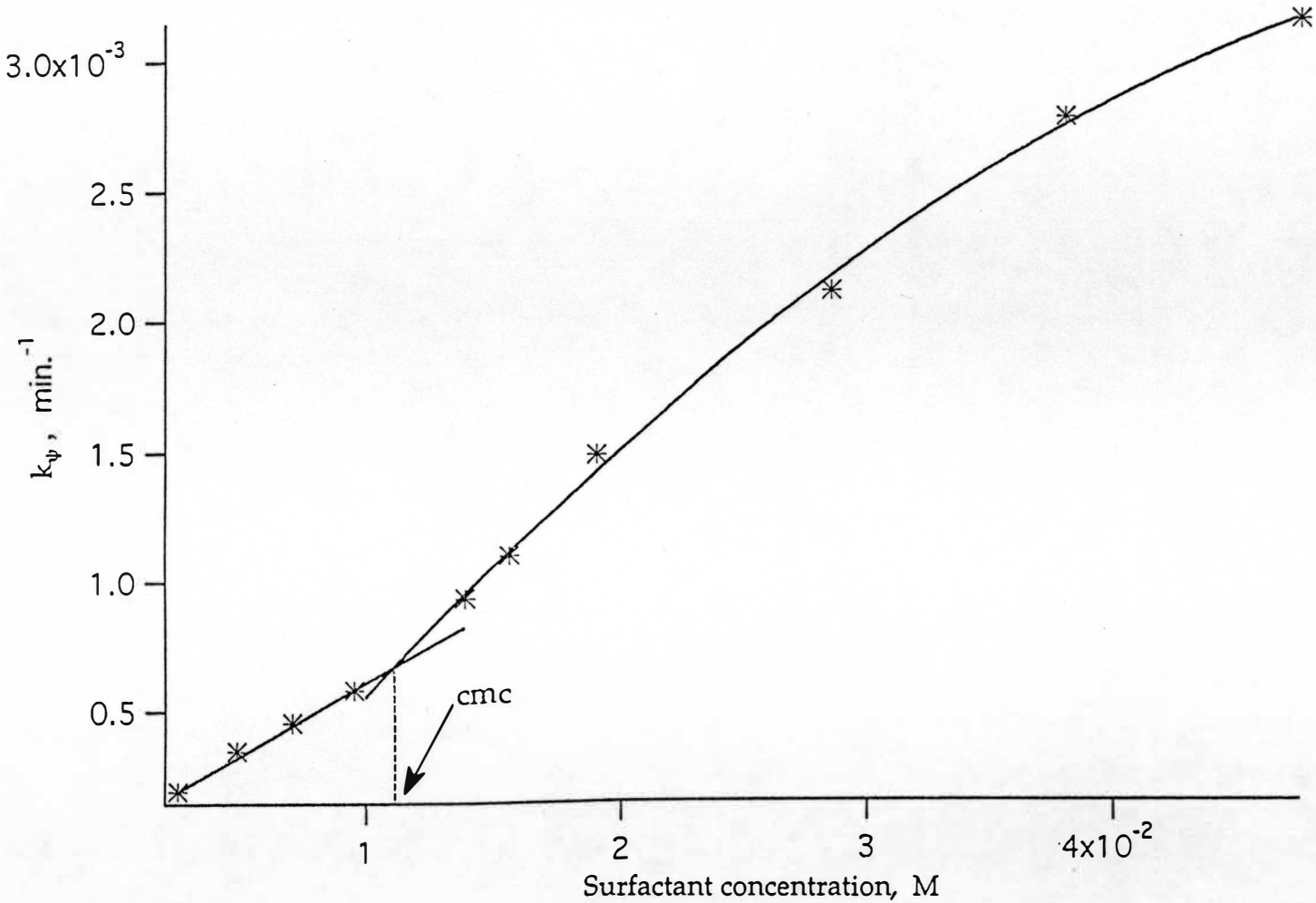


Figure 5. Rate Constant-Surfactant Concentration Profile for 4-Methylpentanohydroxamic Acid.

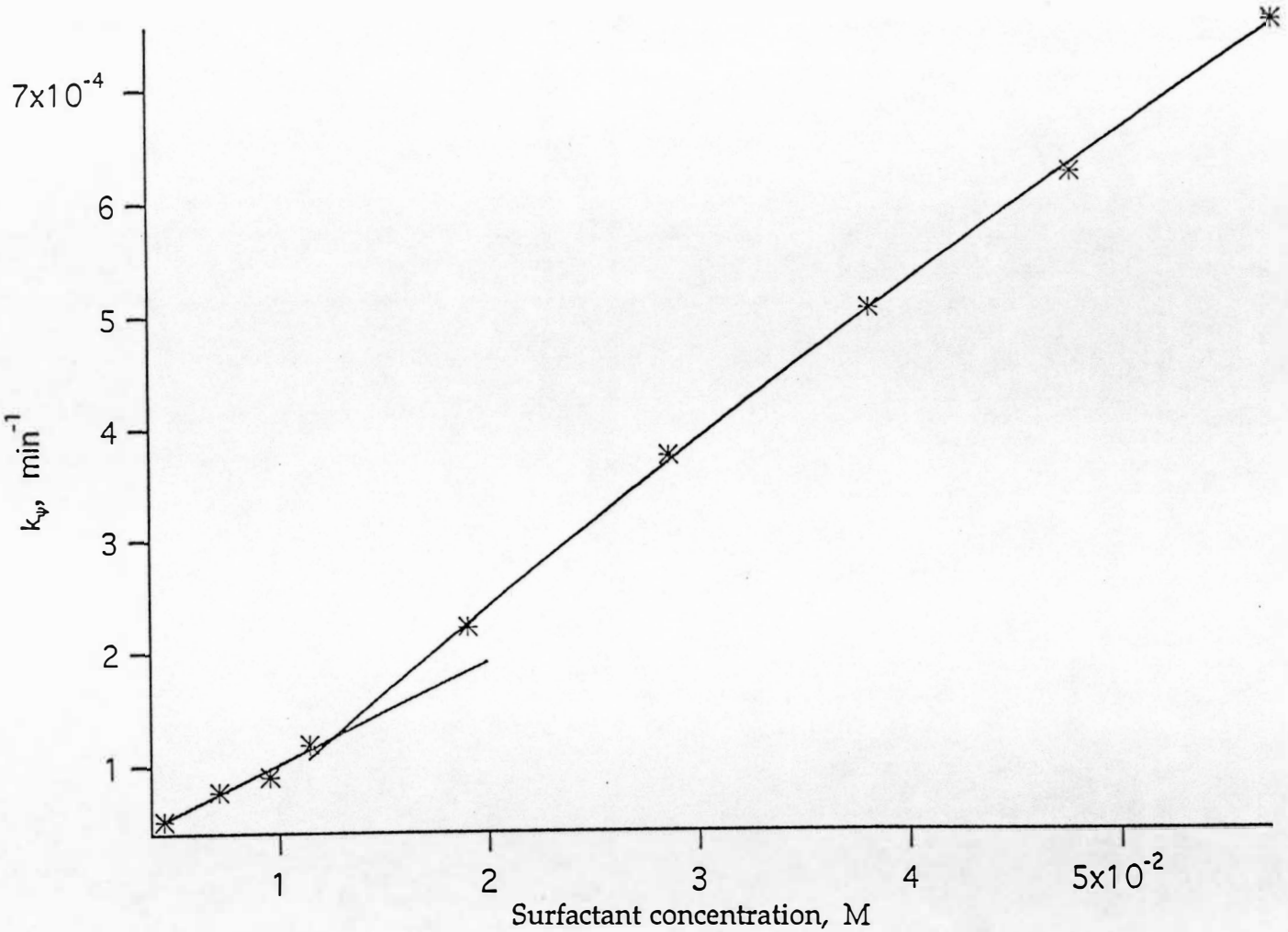


Figure 6. Rate Constant-Surfactant Concentration Profile for 3-Methylpentanohydroxamic Acid.

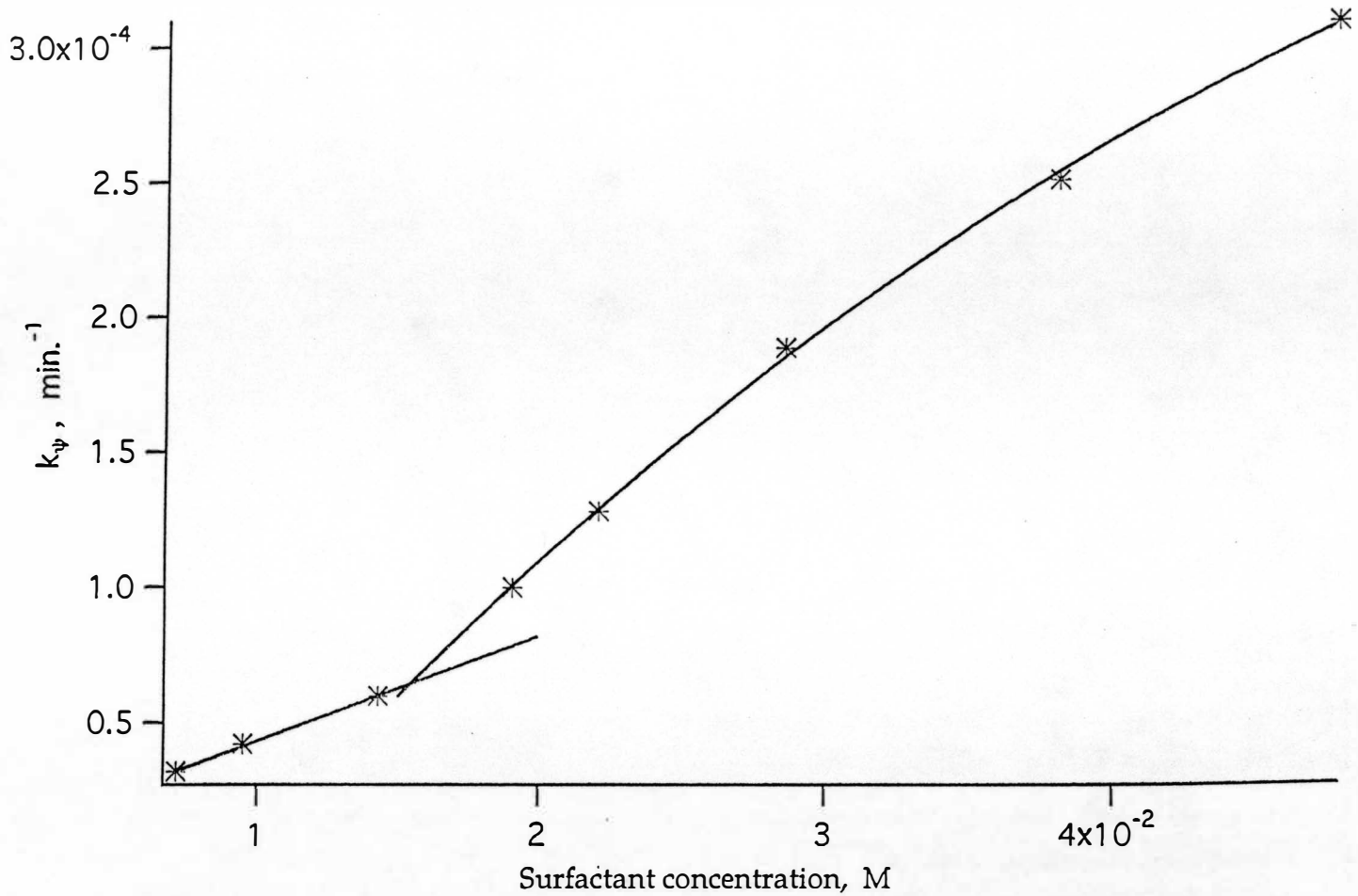


Figure 7. Rate Constant-Surfactant Concentration Profile for 2-Methylpentanohydroxamic Acid.

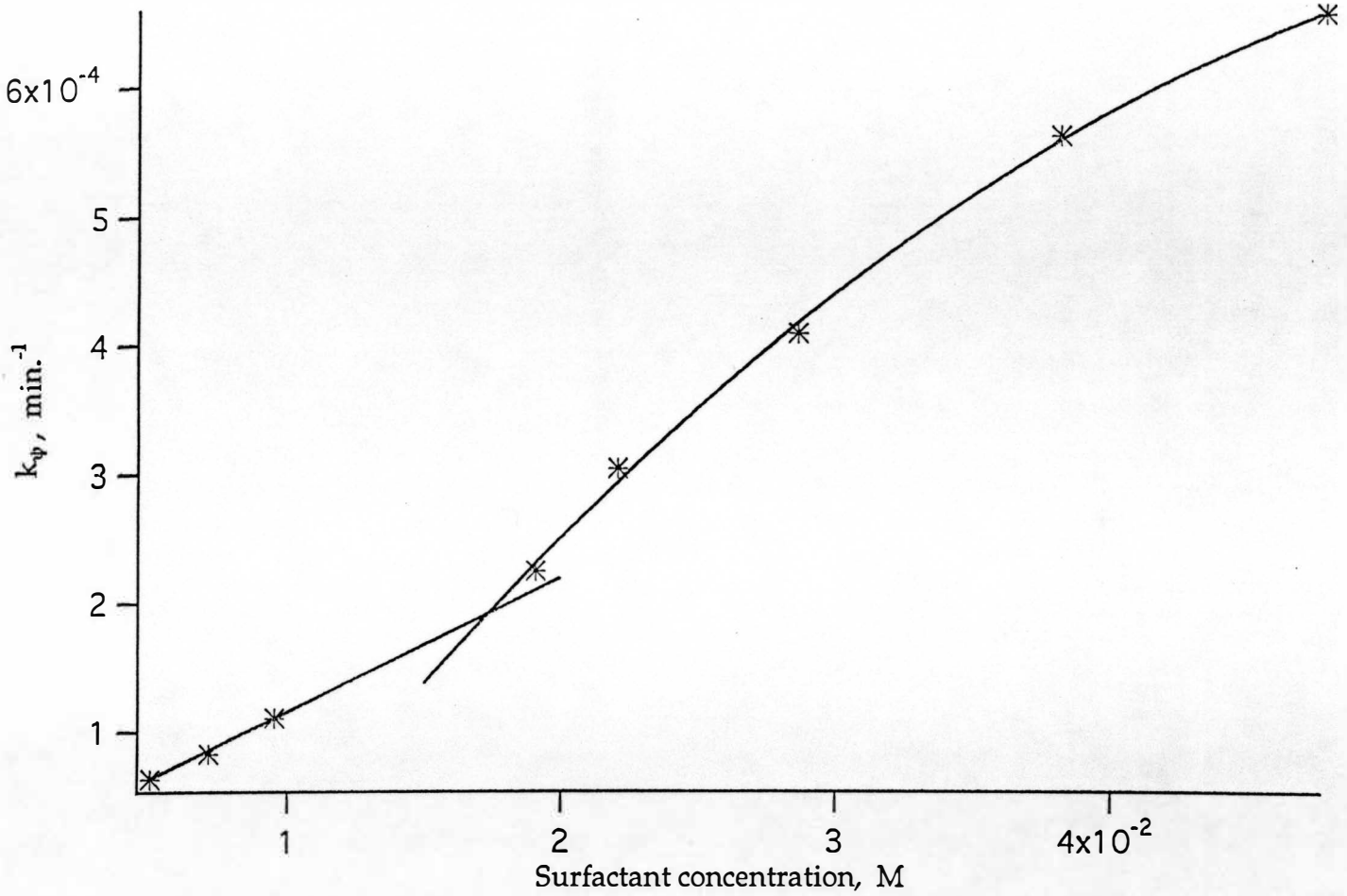


Figure 8. Rate Constant-Surfactant Concentration Profile for 3-Phenylbutanohydroxamic Acid.

These graphs were plotted using the Igor Pro computer program and the solid lines were extrapolated by using a linear function and a polynomial function to obtain the cmc. In these curves, intersections in the region of 0.01 to 0.02M of perfluorooctanoic acid were found for all the hydroxamic acids tested. These intersections of the two curves should approximately indicate the kinetic cmc of perfluorooctanoic acid under the actual experimental conditions. In this project, the cmc of the surfactant was estimated from the intersection of the extrapolations of the lines as shown in Figure 5.

There is no micelle formation in solution below the cmc. In this region, the acidic hydrolysis of hydroxamic acids follow the equation (15).[25]

$$k_{\psi} = k_w[H^+] \qquad (15)$$

where k_w is the second-order rate constant in the aqueous bulk phase. Since perfluorooctanoic acid is a strong acid, the $[H^+]$ is equal to the total surfactant concentration, C_t, below the cmc. Therefore a linear relationship passing through or near the origin was observed below the cmc. The value of k_w was determined using the least squares regression analysis, below the cmc. k_w is the slope of the k_{ψ} versus C_t linear plot.

The experimental data were further investigated by the application of the PPIE model above the cmc. Good linear relationships were obtained for plots of k_{ψ} versus $(k_w C_t - k_{\psi})/(C_t - \text{cmc})$ for all the hydroxamic acids (see Figures 9, 10, 11 and 12). The results of a sample calculation are shown in

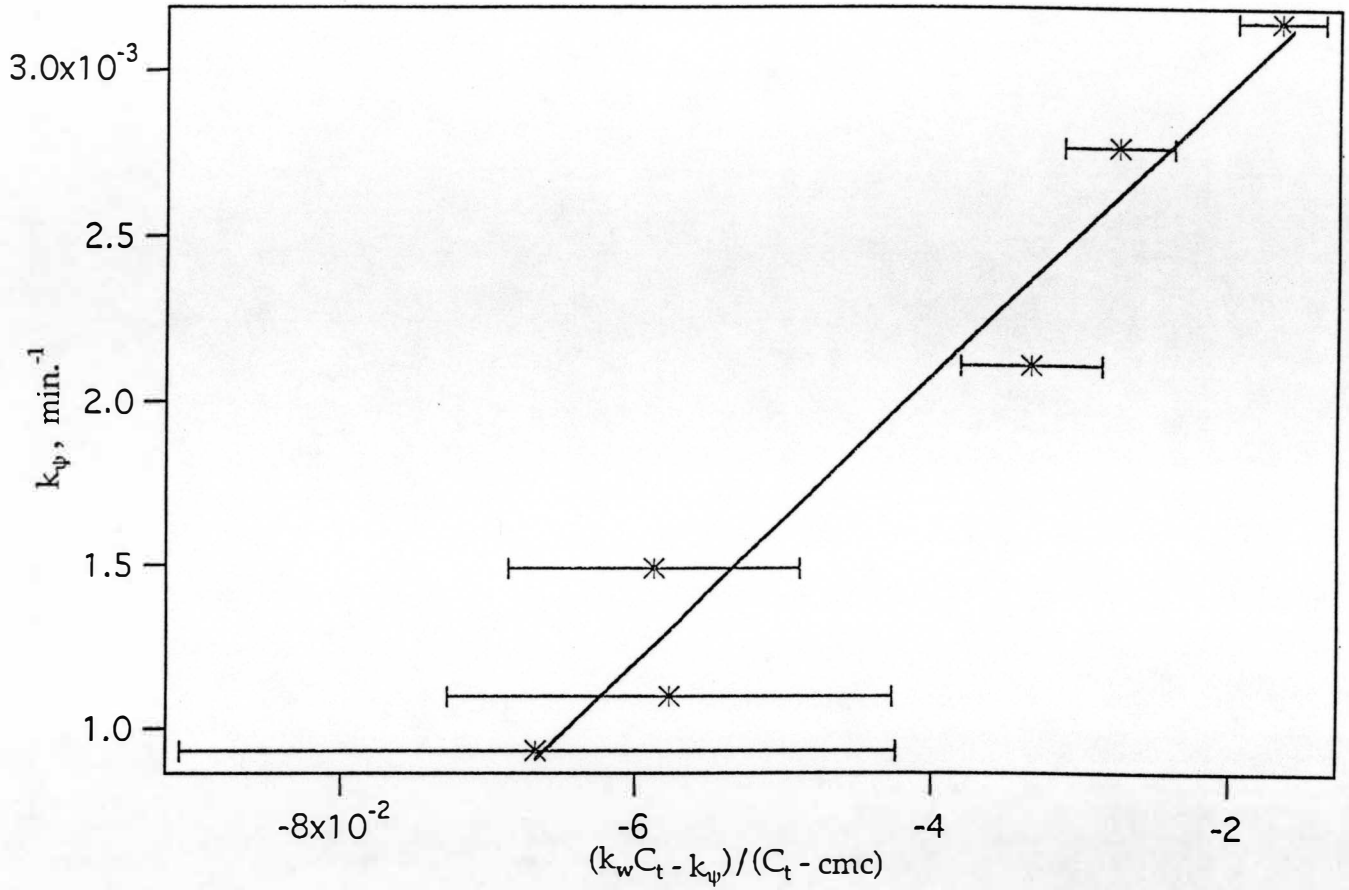


Figure 9. The Graph of k_ψ Versus $(k_w C_t - k_\psi)/(C_t - cmc)$ for 4-Methylpentanohydroxamic Acid.

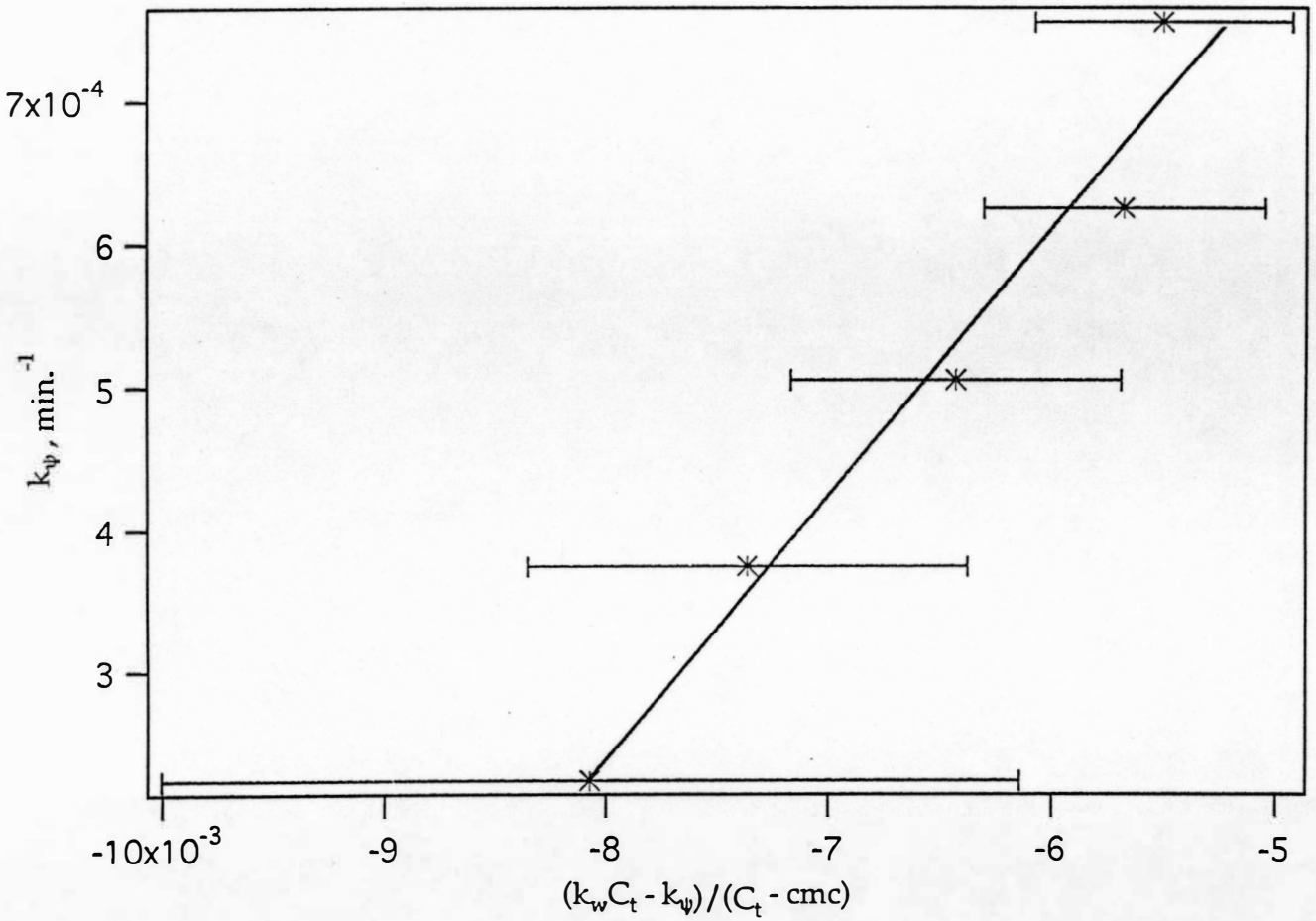
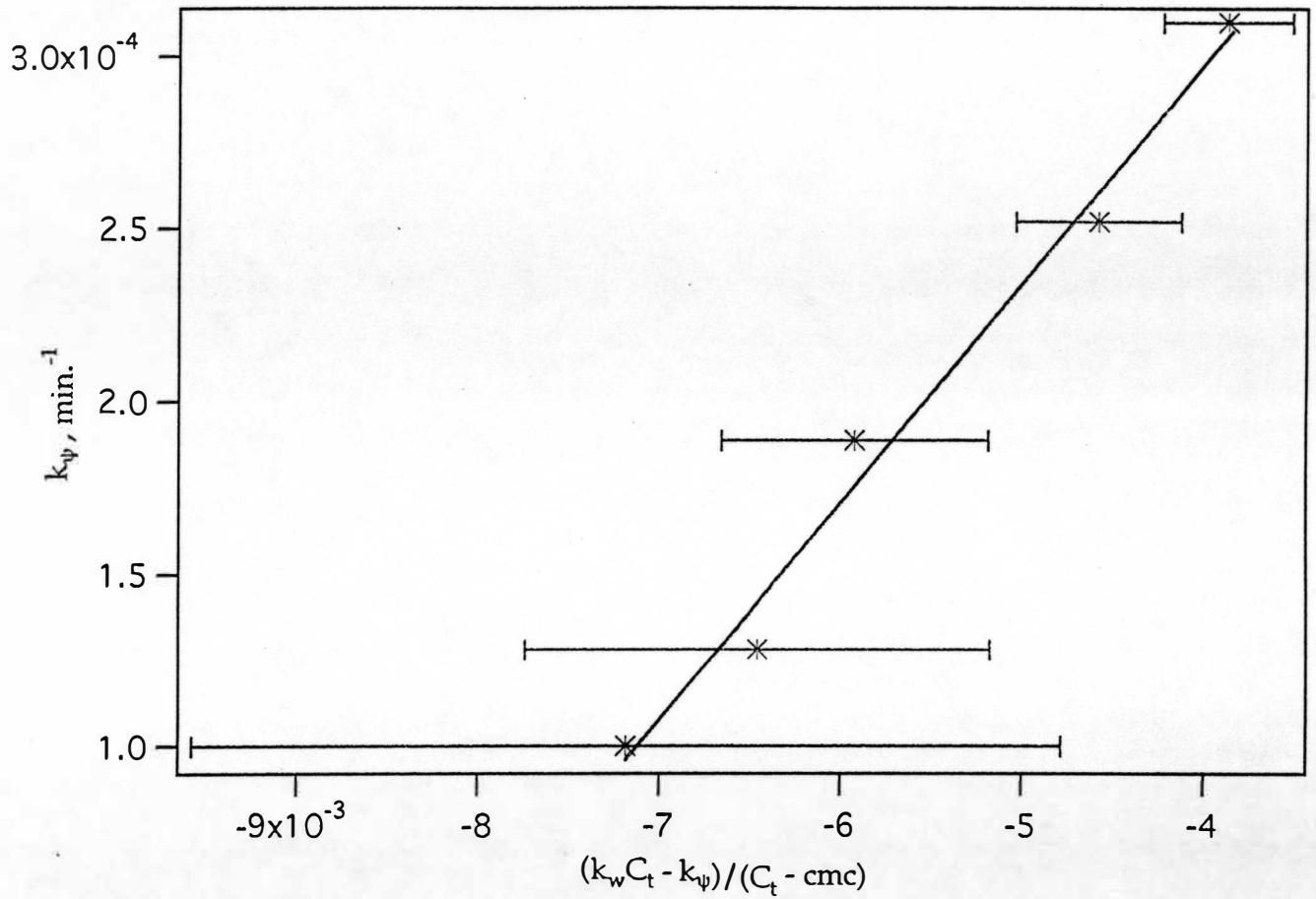


Figure 10. The Graph of k_ψ Versus $(k_w C_t - k_\psi)/(C_t - cmc)$ for 3-Methylpentanohydroxamic Acid.



✳ = Experiment data; ⊢——⊣ = Estimated error range

Figure 11. The Graph of k_ψ Versus $(k_w C_t - k_\psi)/(C_t - cmc)$ for 2-Methylpentanohydroxamic Acid.

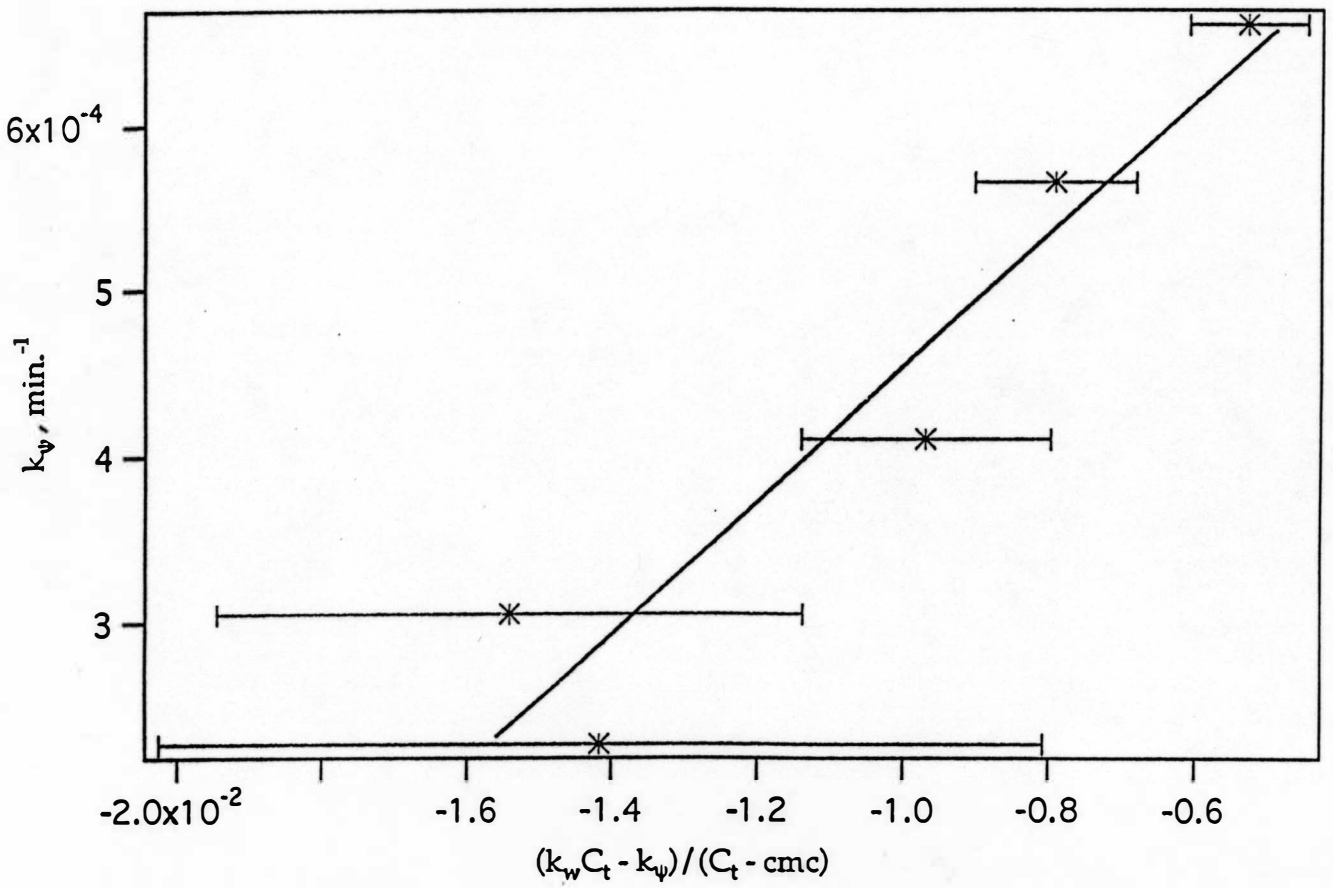


Figure 12. The Graph of k_ψ Versus $(k_w C_t - k_\psi)/(C_t - cmc)$ for 3-Phenylbutanohydroxamic Acid.

Table 8. The following equation (16) was used to calculate the relative errors for different experimental points for $(K_w C_t - k_\psi)/(C_t - cmc)$.

Table 8

Kinetic Parameters in PPIE Model for
4-Methylpentanohydroxamic Acid

$10^2 C_t$ (M)	$10^3 k_\psi$ (min^{-1})	$(k_w C_t - k_\psi)/(C_t - cmc)$
4.76	3.15	-0.0167
3.81	2.77	-0.0275
2.86	2.11	-0.0333
1.91	1.49	-0.0587
1.57	1.10	-0.0577
1.40	0.935	-0.0667

$$Z = (k_w C_t - k_\psi)/(C_t - cmc) \qquad (16)$$

Equation (17) was obtained from equation (16) by the use of partial differentials for the estimation of errors.

$$\Delta Z = \frac{C_t\,(\Delta k_w)}{(C_t - cmc)} + \frac{(k_\psi - k_w\,cmc)\,(\Delta C_t)}{(C_t - cmc)^2} - \frac{\Delta k_\psi}{(C_t - cmc)} + \frac{(k_w C_t - k_\psi)\,(\Delta cmc)}{(C_t - cmc)^2} \qquad (17)$$

The average values of % error for k_ψ and k_w were 1% and 2% respectively. The error in k_w was determined from the error in k_ψ by used the relationship in 15. The error for concentration was less than 0.5% based on the weighing and reading error of a 40 mL pipet. The error for cmc was 5% of its value (the cmc was 0.01113 for this experiment). The estimated errors for the expression $(k_w C_t - k_\psi)/(C_t - cmc)$ for different experimental points for the sample data are shown in Table 9 and also in Figure 9.

Table 9

The Estimated Errors for $(k_w C_t - k_\psi)/(C_t - cmc)$

C_t (M)	± Error	± Error %
0.0476	0.00297	17.8
0.0381	0.00367	13.4
0.0286	0.00472	14.2
0.0191	0.00985	16.8
0.0157	0.0150	26.0
0.014	0.0243	36.4

The estimated error (± Error %) is greater near the cmc, because the differences in the numerator and denominator in the quantity $(k_w C_t - k_\psi)/(C_t - cmc)$ are small near the cmc.

The calculated parameters for 4-methylpentanohydroxamic acid, 3-methylpentanohydroxamic acid and 2-methylpentanohydroxamic acid using the PPIE model are shown in Table 10.

Table 10

The Results From the Application of PPIE Model for Some Aliphatic Substrates

R	$CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-CH_2-$	$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-$	$CH_3-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-$	$CH_3-(CH_2)_8-$ * *
Branching	γ	β	α	none
k_w (L mol^{-1} $min.^{-1}$)	0.0533	0.00896	0.00386	0.0700
cmc (M)	0.0111	0.0126	0.0154	0.0103
b ($min.^{-1}$)	0.00382 ± 16% [a]	0.00173 ± 8% [a]	0.000550 ± 7% [a]	0.0192
K_s (L mol^{-1})	22.9 ± 30% [a]	5.36 ± 34% [a]	15.8 ± 28% [a]	40.1
k_m ($min.^{-1}$)	0.00710	0.00383	0.000932	0.0258
* R^2	0.95	0.97	0.98	---

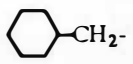
* R^2 is for the regression of k_ψ vs. $(k_w C_t - k_\psi)/(C_t - cmc)$.
* * Data for this compound is from reference 25.
[a] 95% confidence limit.

As shown in the Table 10, k_w decreases from γ branched to α branched compounds because of the steric hindrance. The value of k_w dropped from γ branching to β branching significantly greater than for the

change from β branching to α branching. So β branched compounds can be considered to have considerable steric hindrance compared to γ or unbranched compounds. This can be seen in the table (Table 11) of steric substituent constants (E_s). The larger the negative value of E_s the greater is the steric hindrance.

Table 11

Steric Substituent Constants for Some Selected Compounds

Substituent	Branching	E_s
n-alkyl	none	-0.33 to -0.40
CH_3 CH_3-CH-CH_2-CH_2-	γ	-0.35
CH_3 CH_3-CH-CH_2	β	-0.93
CH_3 CH_3-CH_2-CH-	α	-1.13
 Ph CH_3-CH_2-CH-	β α	-0.98 -1.5

The steric substituent constants found from the literature[33] in Table 11 are for some groups which are not exactly the same groups that have been investigated. In Table 10 the second group corresponds exactly to 4-methylpentanohydroxamic acid. Although the third and fourth compounds are one CH_2 group short in the main alkyl chain still these E_s

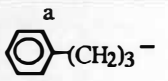
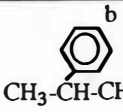
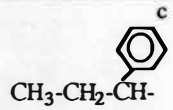
values can be used to compare the steric effect. The cmc for perfluorooctanoic acid in the presence of these three compounds is in the range of 0.011 - 0.015. The K_s values are not in a definite pattern for these three compounds. The K_s value for 3-methylpentanohydroxamic acid is relatively low compared to 2-methylpentano- and 4-methylpentano-hydroxamic acids. R^2 values (R = correlation coefficient) for these three compounds are above 0.95. The statistical F test for $R^2 = 0.95$ and six data points shows the correlation to be significant at the 99.9% level.

The kinetic data from the application of the PPIE model for three aromatic compounds are shown in Table 12. As explained for the results in Table 10, k_w decreases from γ-branched compounds to α-branched compounds. Similarly k_w dropped from γ-branched to β-branched compounds significantly greater than for the change from β-branched to α-branched compounds. For these three compounds the K_s value increases from γ-branched to α-branched compounds. 2-Phenylbutanohydroxamic acid shows the highest K_s relative value compared to other compounds.

By comparing the kinetic data for hydrolysis in a perfluoro environment for all the compounds (Table 13, from Tables 2, 7, 10, 12) which have been studied in our laboratory, the compounds can be arranged into several sets. In Table 13, one set of compounds consists of those with straight chains $CH_3(CH_2)_nCONHOH$, $R\text{-}(CH_2)_nCONHOH$ (R=cyclo hexyl or cyclo pentyl, $n \geq 2$) and $Ph(CH_2)_nCONHOH$ and these have K_s values in the order of the carbon equivalent (C_{eq}, see Chapter I).

Table 12

The Results From the Application of PPIE Model for Some Aromatic Substrates

R	a 	b 	c 
Phenyl substitution	γ	β	α
k_w (L mol^{-1} min^{-1})	0.0482	0.0116	0.00473
cmc (M)	0.0118	0.0173	0.0182
b (min^{-1})	0.00812	0.000856 ± 25% [d]	0.000350
K_s (L mol^{-1})	5.38	24.9 ± 60% [d]	42.4
k_m (min^{-1})	0.0191	0.00154	0.000549
* R^2	0.87	0.90	0.96

[a] Reference 25
[b] This work
[c] Reference 30
[d] 95% confidence limit

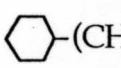
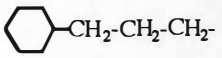
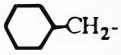
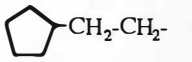
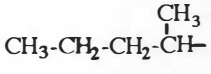
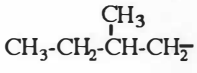
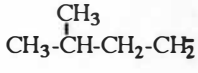
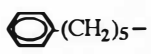
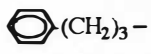
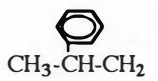
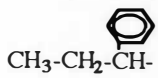
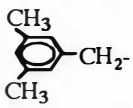
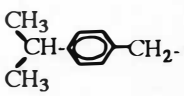
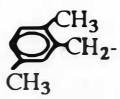
This result is expected for similarly constituted compounds. For further K_s values compare $Ph(CH_2)_3CONHOH$ to  $-(CH_2)_3CONHOH$ and compare $Ph(CH_2)_5CONHOH$ to alkyl substituted phenylacetohydroxamic acids, non-terminal phenyl substituted compounds and to octanohydroxamic acid. As discussed in Chapter I, the alkyl substituted phenyl groups present alkyl groups on their periphery which are somewhat different in their interactions

Table 13

Comparison of the C_{eq}, Reaction Rate Constants and Binding Constants for All the Hydroxamic Acids Investigated in Perfluoro Environment

R	C_{eq}	k_w^{rel}	k_m^{rel}	K_s^{rel}	k_w/k_m
$CH_3\text{-}(CH_2)_8\text{-}$	10	1	1	1	2.7
$CH_3\text{-}(CH_2)_6\text{-}$	8	0.85	0.97	0.42	2.4
	10	0.91	0.83	0.52	3.0
	8	0.21	0.93	0.038	0.62
	8	0.91	0.44	0.39	5.6
	6	0.055	0.027	0.39	5.6
	6	0.13	0.084	0.13	4.1
	6	0.76	0.18	0.57	11
	7.5	0.84	0.71	0.37	3.2
	5.5	0.69	0.74	0.13	2.5
	5.5	0.17	0.041	0.62	11
	5.5	0.068	0.021	1.1	8.6
	5.5	0.62	0.23	0.59	7.5
	6.5	0.58	0.47	0.61	3.3
	5.5	0.16	0.093	0.66	4.6

towards the perfluoro environment than are the exposed phenyl groups at the end of the alkyl chain. Compounds with non-terminal phenyl groups appear to behave more like the alkyl substituted phenyl group series than like the compounds with terminal phenyl groups.

k_m^{rel} values cannot be directly compared since some compounds (α- and β-substituted) exhibit considerable steric hindrance (Table 11). For these compounds smaller k_w values should correspond to smaller k_m values. If the only significant variable were steric hindrance then the k_w/k_m values should all be about the same. This is clearly not the case. For decano-, octano-, cyclohexylaceto-, 4-cyclohexylbutanohydroxamic acids as well as for some of the compounds with aryl groups, the k_w/k_m ratio is relatively low. The k_w/k_m value is relatively higher for 3-cyclopentylpropanohydroxamic acid, 2- and 3-methylpentanohydroxamic acids and 2,5-dimethylphenylacetohydroxamic acid. The highest k_w/k_m values occur for 4-methylpentanohydroxamic acid, 2- and 3-phenylbutanohydroxamic acids and 3,5-dimethylphenylacetohydroxamic acid. The considerable variation of k_w/k_m values thus indicates that there are specific micellar effects upon the reaction rate within the micelle (k_m).

Tables 10 and 12 present data for two α, β and γ substitution series, the former for methyl and the latter for phenyl groups. Both k_w and k_m increase with decreasing steric hindrance in both series; however, the k_w/k_m ratios and the K_s^{rel} values vary in a dissimilar fashion in the two series. The α and β substituted compounds in both series have about the same k_w/k_m ratios within experimental error, but for the methyl series the γ substituted compound has a higher value than the α and β analogs;

whereas, in the phenyl series the γ substituted compound has a lower k_w/k_m ratio than its α and β analogs.

One of the purposes of this work was to try to learn more about the anomalous behavior of 2-phenybutano- and cyclohexylacetohydroxamic acids in previous work in this laboratory. Thus 2-, 3-, and 4-methylpentanohydroxamic acids and 3-phenylbutanohydroxamic acid were studied in the present work. 2-Phenylbutanohydroxamic acid still appears to be anomalous with respect to K_s^{rel} and cyclohexylacetohydroxamic acid with respect to both k_w/k_m and K_s^{rel}.

The relative binding constant, K_s^{rel}, does not reflect the micellar catalysis for all the compounds. Different compounds have different binding abilities to the different locations of the micelle. The compounds which bind closer to the Stern layer might have higher micellar rates of reaction because the Stern layer provides a higher concentration of protons (H^+) and more stabilizing effect for the carbocationic transition states and intermediates than the less polar interior of the micelle. The compounds which bind somewhat away from the Stern layer may give low micellar rates, even though those compounds have higher K_s^{rel} values. The last three compounds in Table 13 plus 3-phenylbutanohydroxamic acid show similar binding constants but the micellar rates are not the same (k_w/k_m). Since structural features of the substrate greatly influence the micellar catalysis, there must be some specific micellar effects on the catalysis in the hydrolysis of hydroxamic acids in the perfluoro micellar environment.

CHAPTER IV

CONCLUSION

The rate of hydrolysis of hydroxamic acids can be enhanced in perfluorooctanoic acid medium compared to no acid catalyst and no surfactant. The rate enhancement is considerably greater above the cmc due to the micellar catalysis. Below the cmc, perfluorooctanoic acid acts as just a proton source, resulting in normal acid catalysis.

The side chain effect (steric effect) in normal acid catalysis can be explained by using the second order rate constant in the aqueous bulk phase, k_w. The value of k_w is smaller for α-branched compounds compared to β and γ-branched compounds. But the value of k_w dropped from γ to β-branched compounds more than from β to α-branched compounds.

The value of K_s somewhat parallels the value of C_{eq} for straight chain aliphatic compounds and for R-$(CH_2)_n$-CONHOH ($n \geq 2$, R = alicyclic or Ph) type compounds. Because of the low solubility of the compounds having Ph groups in perfluoro micellar solutions as discussed in chapter I, Ph is considered as 1.5 C not 6 C for the calculation of C_{eq}. The K_s values for 2-phenylbutanohydroxamic and cyclohexylacetohydroxamic acids seem particularly out of line compared to the other compounds as is the k_w/k_m ratio for the latter compound. The reason for this significant difference cannot be explained using the available data. The value of k_m^{rel} for branched (α, β) compounds cannot be directly compared with unbranched compounds because of the steric hindrance. So it is more reasonable to

compare the ratio of k_w/k_m. The smaller the ratio of k_w/k_m the greater is the micellar catalysis. Even though some of the compounds have higher binding constants to the micelle (K_s^{rel}), there may be lower micellar catalysis. (The micellar catalytic effect is a combination of k_m and K_s). This might be due to the structurally different hydroxamic acids binding at different locations in the micelle. The rate of reaction is determined by where the substrate binds to the micelle. If the substrate binds closer to the Stern layer, greater micellar catalysis can result due to the higher concentration of protons and the relative stabilization of the carbocationic transition states and intermediates. Similarly the compounds which bind away from the Stern layer may show lower micellar catalysis even though those compounds have higher binding constants to the micelle. The variations in K_s and k_w/k_m support the interpretation that there are specific micellar effects for the hydrolysis of hydroxamic acids in the perfluoro environment.

For a better understanding of this specific micellar catalysis on different hydroxamic acids, further investigations regarding the locations in the micelle where hydroxamic acids are bound is suggested. The difference in behavior with respect to α, β and γ substitution effects on the k_w/k_m ratios needs further exploration. Perhaps these compounds are solubilized in different locations within the micelles and/or the shape and volume of the methyl versus the phenyl group is an important factor in the substituent effects.

APPENDICES

Appendix A

IR Spectra of Hydroxamic Acids
(KBr Pellet)

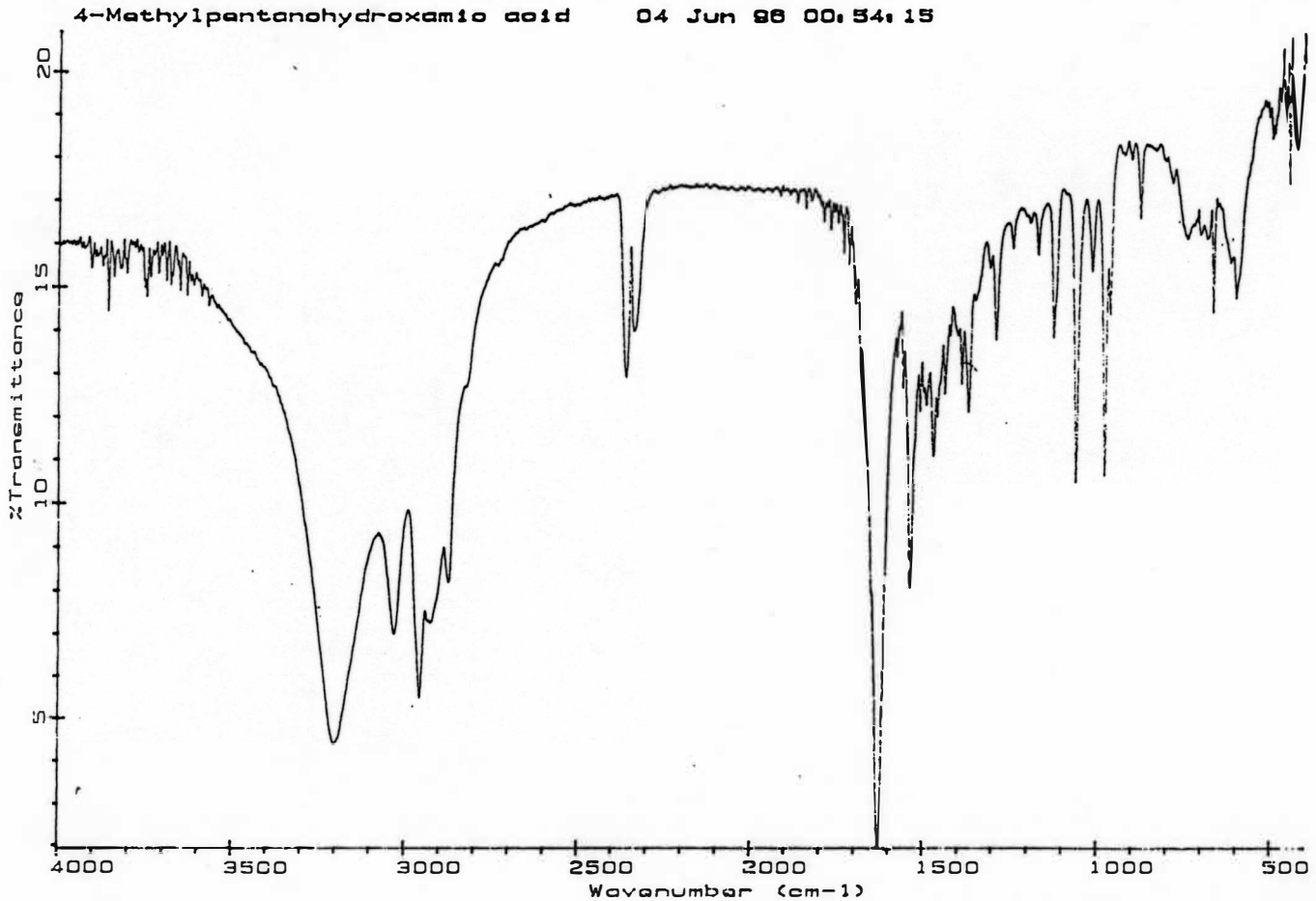


Figure 13. The IR Spectrum of 4-Methylpentanohydroxamic Acid (KBr pellet)

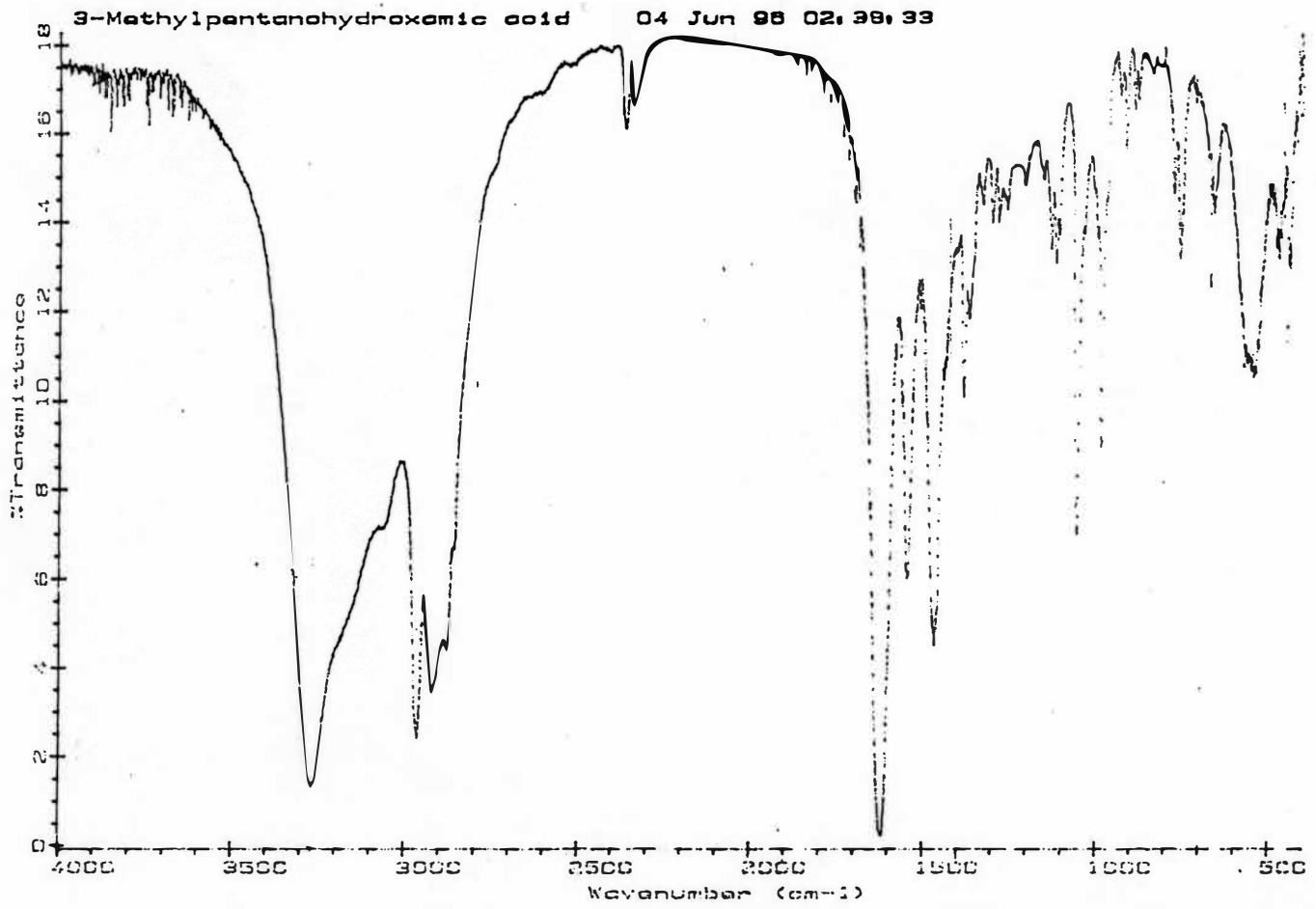


Figure 14. The IR Spectrum of 3-Methylpentanohydroxamic Acid (KBr pellet)

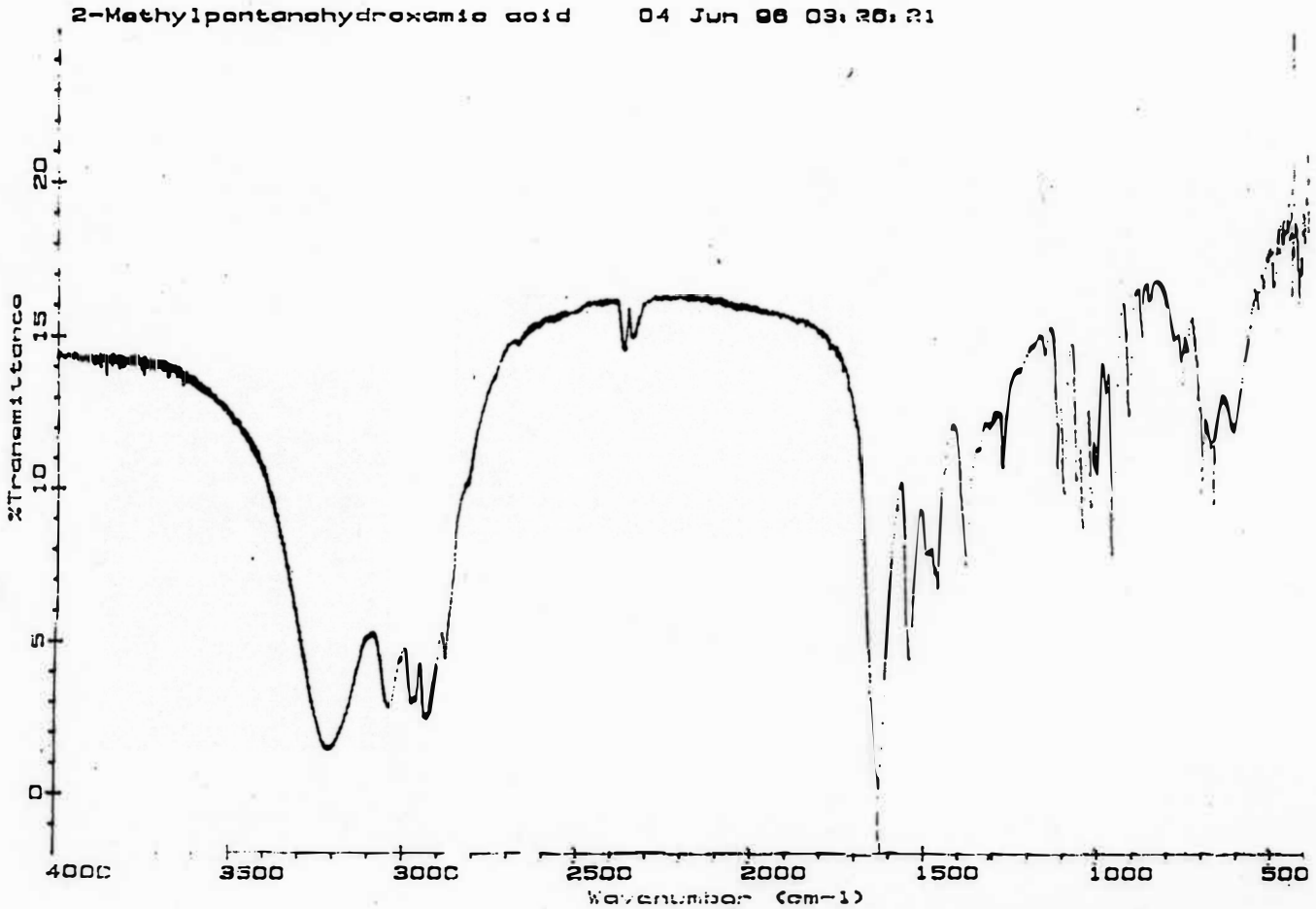


Figure 15. The IR Spectrum of 2-Methylpentanohydroxamic Acid (KBr pellet)

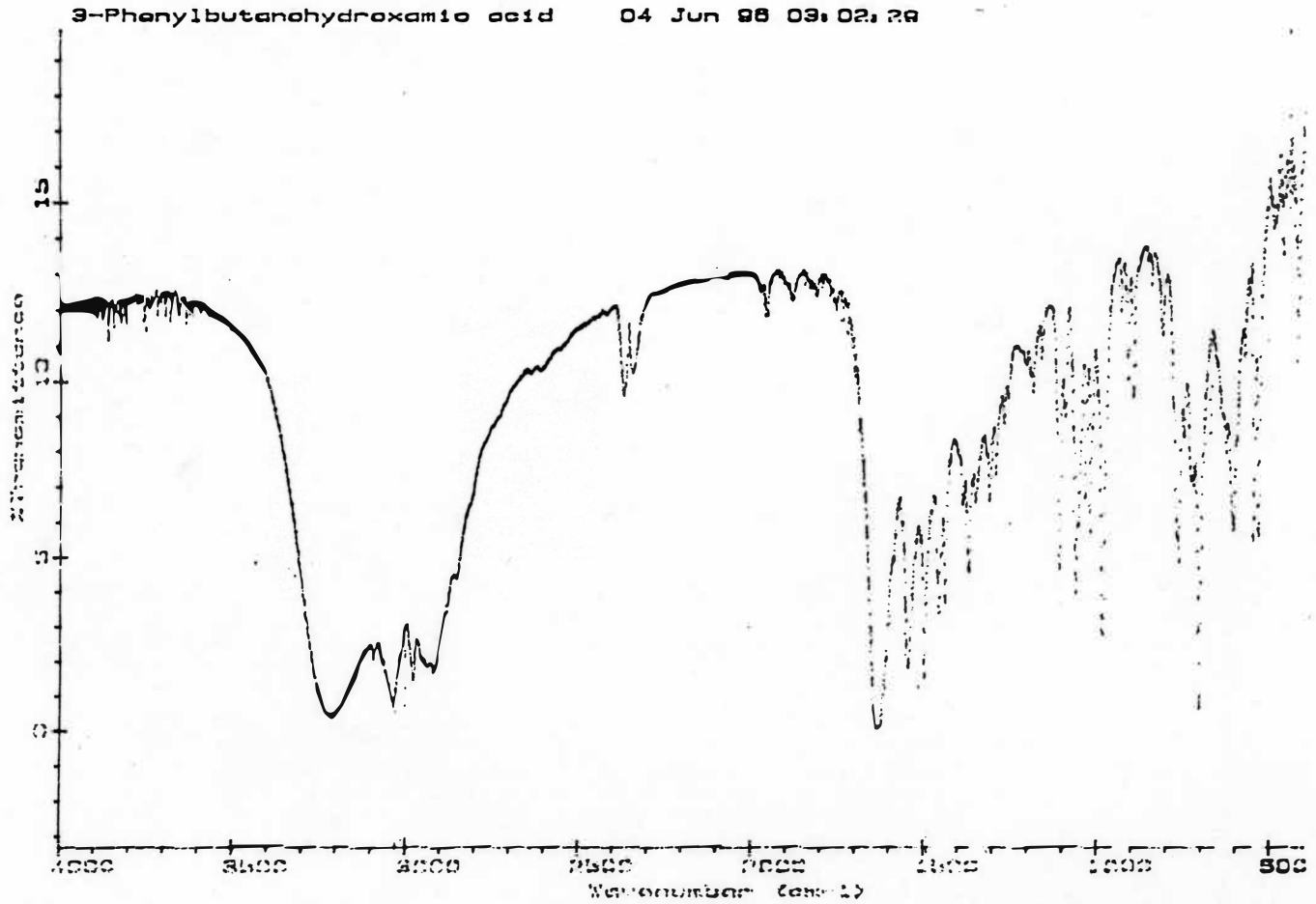


Figure 16. The IR Spectrum of 3-PhenylbutanohydroxamicAcid (KBr pellet)

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