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Micellar Catalysis of Hydrolysis of Substituted Hydroxamic Acids with Perfluorooctanoic Acid

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MICELLAR CATALYSIS OF HYDROLYSIS OF SUBSTITUTED HYDROXAMIC ACIDS WITH PERFLUOROOCTANOIC ACID

by

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MICELLAR CATALYSIS OF HYDROLYSIS OF SUBSTITUTED HYDROXAMIC ACIDS WITH PERFLUOROOCTANOIC ACID

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The work demonstrated the effects of differently located and substituted phenyl groups, as well as aliphatic groups in the hydroxamic acids, on micellar catalysis with perfluorooctanoic acid as the reactive counterion surfactant in aqueous acetonitrile solution.

Kinetic rate constant-surfactant concentration profiles for the decano-, 2,5-dimethylphenylaceto-, 4-isopropylphenylaceto-, 4-phenylbutano-, and 6-phenyl-hexanohydroxamic acids were examined and analysis on the data obtained were reported.

The pseudo-phase ion exchange (PPIE) model has been satisfactorily applied to explain the observed micellar effects.

Further investigation into more appropriately substituted hydroxamic acids is suggested in order to obtain a more complete set of data and further evaluation.

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CHAPTER I

INTRODUCTION

A surfactant (a contraction of the more explicit term of surface active agent) is a type of organic compound characterized by possessing two regions in the molecular structure. In the molecule of a surfactant, one region has little affinity for the solvent, known as a *lyophobic* region, while the other has strong affinity for the solvent, called the *lyophilic* region. Hence, surfactants are amphipathic substances and the dual nature is called amphipathy[1].

When the surfactant is dissolved in water, the presence of the hydrophobic region causes distortion of the water liquid structure and increases in the free energy and entropy of the system. It is thus spontaneous that surfactant molecules tend to leave the aqueous solution by absorbing at the surface. On the other hand, the hydrophilic region is responsible for the solubility of the surfactant. The presence of hydrophilic groups prevents the surfactant from being expelled completely from the water as a separate phase.

The hydrophobic region of a surfactant is usually a long-chain hydrocarbon residue, and less often a

halogenated or oxygenated hydrocarbon or siloxane chain. Conversely, the hydrophilic region is an ionic or highly polar nonionic group.

Surfactants are widely employed for many purposes such as chemical emulsion polymerization, ore refining, agricultural sprays, cosmetics, inks, foods, textiles, pharmaceuticals, etc. Microemulsions are also prepared from surfactants[2].

Conventionally, surfactants are often classified on the basis of the chemical nature of the hydrophilic group. These categories are:

1. Anionic: the surface active portion is an anion, e.g., sodium stearate, $CH_3(CH_2)_{16}COO^-Na^+$.

2. Cationic: the surface active portion is a cation, e.g., dodecylamine hydrobromide, $CH_3(CH_2)_{11}{}^+NH_3Br^-$.

3. Ampholytic: both anion and cation may be present in the surface active portion, depending upon the pH value of the solution, e.g., the zwitterionic form of 3-(dimethyldodecylammonio)-propane-1-sulfonate, $CH_3(CH_2)_{11}N^+(CH_3)_2CH_2CH_2CH_2SO_3^-$. It bears a positive charge in an acidic media while in basic media it behaves like an anionic surfactant.

4. Nonionic: the hydrophilic portion of this type of surfactant consists of hydroxyl groups or a polyoxyethylene chain, which bears no ionic charge, e.g., polyoxyethylene monohexadecyl ether, $CH_3(CH_2)_{15}(OCH_2CH_2)_{21}OH$.

According to their applications, surfactants are also named as wetting, emulsifying, dispersing and foaming agents, or simply detergents in general.

Surfactant molecules have the tendency to concentrate at the interface between air and the solution characteristically with the hydrophobic portion remote from the water to reduce the free energy by minimizing the hydrocarbon-water interface. The physico-chemical properties of surfactant solutions, in fact, show a peculiar concentration dependence[3,4]. When the concentration reaches a certain value, an extensive association of surfactant molecules occurs to form large aggregates, i.e. micelles. This is the concept of critical micelle concentration, or cmc for short. Numerous experiments have shown that the cmc is a narrow range of concentration instead of a simple sharp point[5]. Micelle formation is a phase separation model[6]. It should be realized that the micellization is an alternative mechanism for removing hydrophobic groups from contact with the water[7], which makes the water-surfactant system more stable thermodynamically.

The determination of the cmc is usually carried out by plotting some changes in physical or chemical properties as a function of surfactant concentration and extrapolating the results both at low and high concentration to an intersection point. For example, the break in electrical

conductance, surface tension, and the solubilization of a compound having a low solubility against surfactant concentration curves are commonly used for this purpose[7]. Spectral techniques, such as ultraviolet and NMR methods have also been utilized to determine the cmc[8,9].

The critical micellar concentration may be affected by a number of factors. Among them, influence of surfactant structure, additives to the solution and the ambient temperature are most pronounced.

1. As a rule, the cmc in aqueous media decreases as the hydrophobic character of the surfactant increases. Increase of the hydrocarbon chain length, which causes a higher hydrophobicity, will lower the cmc. Similarly, hydrocarbon chain branching, introduction of carbon-carbon double bonds, or polar groups such as -O-, -OH into the hydrocarbon chain will decrease the hydrophobic property, and a higher cmc is expected.

2. Addition of an electrolyte to an ionic surfactant solution decreases the cmc. This depression is mainly due to the decrease in the thickness of the ionic atmosphere surrounding the ionic head groups, and consequently decreased electrical repulsion between them in the micelles.

Some organic materials may either be incorporated into the micelle or modify the solvent-micelle interactions. Their effect on the cmc is variable.

3. Elevation of temperature has a complex effect on the cmc of ionic surfactants. However, a tendency to increase the cmc of nonionic surfactants is more or less observed.

Several models have been put forward to describe the shape, size and features of the micelle. The most commonly accepted one is a spherical structure (Figure.1).

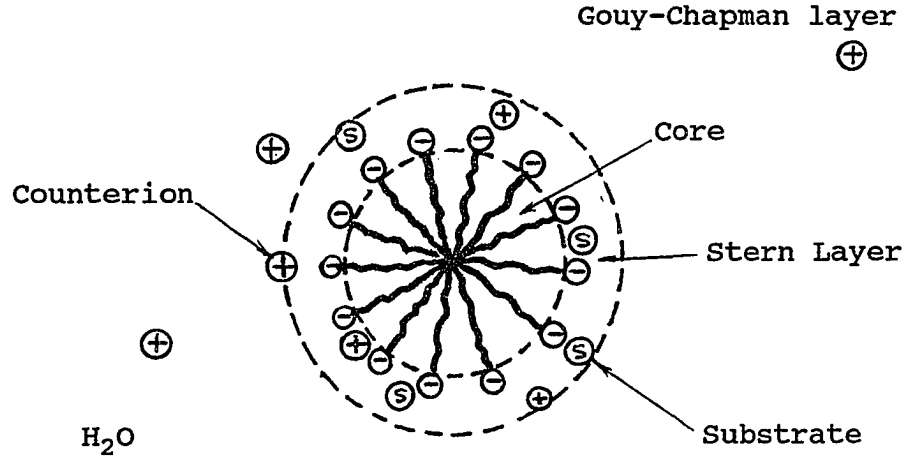


Figure 1. Model of Hypothetical Anionic Micelle in Aqueous Media.

In the sphere of a micelle, the surfactant molecules are oriented with their polar heads towards the aqueous phase and form the so-called Stern layer. In ionic micelles, most of the counterions are tightly bound in the Stern layer and this is responsible for the reduction of the net charge on the micelle surface and the compactness

of the Stern layer itself. Outside the micelle, there exists a "Gouy-Chapman electrical double-layer" which extends further into the aqueous phase, where the remaining counterions are loosely contained.

The interior region, or core of the micelle, is occupied by the hydrophobic portion of the surfactant. The radius of a micelle is approximately equal to the length of the fully extended hydrocarbon chain. The average micellar radii is about 12-30Å.

Other possible micelle types like rodlike, lamellar, etc., have also been well documented[7].

The shapes and sizes of micelles are dependent upon the nature and concentration of the surfactant and other environmental factors. For example, addition of electrolyte to ionic surfactants or raising the temperature for nonionic ones often leads to the development of asymmetric micellar shapes[7].

At higher concentrations, surfactant micelles can further aggregate to form a variety of different liquid crystalline phases such as lamellar, hexagonal, and cubic[10]. As the concentration of a surfactant increases, rodlike micelles are likely to transform into a cubic phase and then a hexagonal phase[11].

Models for various cubic phases have been presented[12], and their possible relevance to biological systems has been discussed[13].

Micellar Catalysis and Kinetics

It often happens that the rate of a chemical reaction can be substantially enhanced in micellar solution. This phenomenon is called micellar catalysis. Micellar catalysis in water is generally rationalized in terms of reaction in micellar and in aqueous pseudo phases[14]. It is assumed that the overall rate of most micellarly catalyzed reactions is the sum of the rates in each pseudo phase and that changes in the overall rate with increasing surfactant concentration reflect changes in the distribution of reactants between the two pseudo phases. The enhanced reaction of the solubilized substrate occurs within or near the Stern layer[15].

In an aqueous micellar solution, water molecules penetrate beyond the polar headgroups, but only part way into the micelle. In this connection, the microenvironment of the Stern layer shows a polarity, as measured by dielectric constants[16] similar to that of an alcohol or an aqueous alcohol mixture and is comparable to that of the surface of simple globular proteins[17]. A solute or substrate in the pseudo micellar phase may interact with both the nonpolar chain of the individual surfactant molecules and with the polar head groups without penetrating into the nonpolar micellar core[18].

The catalytic effect of micelles on chemical reactions can be attributed to both electrostatic

interactions and concentration effects. An electrostatic interaction may affect the rate of a reaction by its effect on differential charges of the transition state and reactant state of the reaction relative to the aqueous phase. Micelles may also serve to concentrate the reagents of a bimolecular reaction and thereby increase the rate of reaction[18].

There is always a rapid exchange of monomer units of the surfactant between the micellar and the bulk solution[9]. It is assumed that the individual surfactant molecules do not complex with the substrate except when they are in the form of a micelle.

The scheme below illustrates the pseudo phase model for reactions in the micellar solution:

$$nD \rightleftharpoons D_n$$

$$D_n + S_w \overset{K_s}{\rightleftharpoons} S_m$$

$$k_w' \downarrow N_w \qquad k_m' \downarrow N_m$$

products

In this scheme, D_n is the concentration of micellized surfactant with an aggregation number of n which is in kinetic equilibrium with surfactant monomer D. k_w' and k_m' are the first-order rate constants in the bulk water phase and in the micellar pseudo phase with substrate concentrations of S_w and S_m, respectively. N_w and N_m are reactive ion concentrations and K_s is the constant for the

binding of the substrate to the micelle; its value can be expressed as

$$K_s = [S_m]/[D_n][S_w] \qquad (1)$$

For bimolecular reactions, in which the other reactant is the counterion of the surfactant, the kinetic equation derived[19] is

$$k_\psi = \frac{k_w[N_t] + ß(k_m K_s - k_w)(C_t - cmc)}{K_s(C_t - cmc) + 1} \qquad (2)$$

where k_ψ is the observed overall pseudo first-order rate constant; k_w is the second-order rate constant in the aqueous phase; k_m is a pseudo first-order rate constant in the micellar phase; C_t is the total surfactant concentration; cmc is the critical micelle concentration; N_t is the total concentration of surfactant counterion and is equal to C_t if there are no added salts; ß is the degree of counterion binding to the Stern layer, which has a value within the range of 0.6-0.9[20].

In most circumstances, $K_s k_m >> k_w$[19]

then

$$k_\psi = \frac{k_w C_t + ßk_m K_s(C_t - cmc)}{K_s(C_t - cmc) + 1} \qquad (3)$$

In the derivation of equations (2) and (3), it has been assumed that the micellized surfactant concentration

is much greater than the substrate concentration and that the micellar pseudo phase occupies only a small fraction of the total solution volume. Accordingly, reactive counterion concentrations are also always in large excess.

For simplification, a rearrangement of (3) yields

$$k_\psi = \frac{k_w C_t - k_\psi}{K_s(C_t - cmc)} + k_m' \qquad (4)$$

In practical application, regression of k_ψ versus $(k_w C_t - k_\psi)/(C_t - cmc)$ allows the evaluation of k_m' ($k_m' = \beta k_m$) and K_s. However, the differences in the numerator and denominator of the latter quantity make this term sensitive to experimental error[21].

Perfluorocarboxylic Acids and Their Micelles

Perfluorocarboxylic acids are very surface active in solution. Because of the substitution of fluorine for hydrogen atoms, this type of surfactant has some distinct properties different from those of normal hydrocarbon ones.

Perfluorocarboxylic acids are strong acids which essentially ionize completely due to the strong electron withdrawing property of fluorine atoms. The strength of the acid is related to the length of the perfluorocarbon chain. It has been found that the dissociation constants of the fluorocarboxylic acids increase significantly between perfluoroacetic acid and perfluorobutyric acid[22].

In the case of perfluoroheptanoic acid, it behaves like HCl[9], a typical strong inorganic acid, at low concentration.

For the perfluorocarboxylic acid above the cmc, there is so strong a counterion binding to the micelles that hydrogen bonding between hydronium counterions and carboxylate ions is likely. Since the fluorine atoms are electron rich compared to hydrogen atoms, fluorocarbon chains would have much larger intermolecular Van der Waals interactions than hydrocarbon chains. Thus the reduction of the net charge in the micelles and appreciable intermolecular interactions between the fluorocarbon chains leads to a larger tendency to aggregate than for hydrocarbon surfactants. For these reasons, fluorocarbon surfactants are more likely to form rodlike rather than spherical micelles[23]. Recent studies[9] indicate that perfluoroheptanoic acid above its cmc in water solution at room temperature forms aggregates much larger than normal micelles. It was suggested that the micelles aggregate to form larger aggregates which are dispersed in the solution and may exist in a cubic phase.

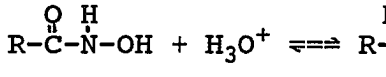
In addition, due to the larger size of fluorine atoms, a fluorocarbon chain is more rigid than a hydrocarbon chain[24,25]. It has been estimated that the effect of each CF_2 group toward micelle formation is roughly equivalent to 1.6 CH_2 groups[26]. Solutions of

fluorocarbon surfactants above the cmc have much lower surface tensions than those of hydrocarbon surfactants if other conditions are the same[27].

Hydrolysis of Hydroxamic Acids in Micellar Solution

The purpose of this thesis is to present more information on the effect of perfluorooctanoic acid on the rates of hydrolysis of hydroxamic acids[2] with different chemical structures.

The mechanism of hydroxamic acid[2] hydrolysis in acidic media has been proposed as follows[28]:



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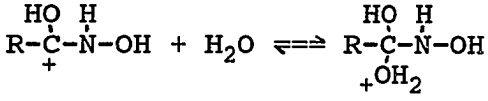

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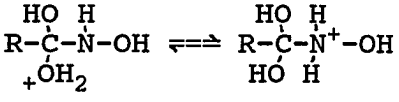

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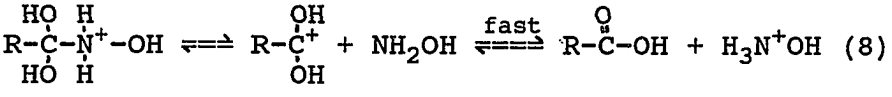


(8)

Both a reactive counterion surfactant and nonreactive counterion surfactants with added reactive ions have been successfully employed in the micellar catalysis of the hydrolysis of the hydroxamic acids[21].

Particularly, it has been found that the pseudo-phase ion exchange (PPIE) model is satisfactory for hydrogen ion with the perfluorooctanoic acid as the reactive counterion surfactant in the acidic hydrolysis of hydroxamic acids in water and in aqueous acetonitrile as solvent[21]. Aqueous acetonitrile as opposed to strictly water solutions have been employed to improve the solubility of substrates and surfactant.

In previous studies in water solution, normal micellar catalysis was observed with variously substituted phenylacetohydroxamic acids with sodium 1-dodecanesulfonate as surfactant with added hydrochloric acid. In this hydrocarbon based surfactant system, 4-bromophenylaceto-hydroxamic acid reacted nearly three times faster than phenylacetohydroxamic acid in micellar solutions[29], but at essentially the same rate as the phenylacetohydroxamic acid below the cmc. With perfluorooctanoic acid as surfactant in water, there was little difference in rate constants for the two compounds either above or below the cmc, and little if any micellar effect. Thus it was decided to explore the effect on micellar catalysis of different "chains" in the hydroxamic acids; that is, to explore the effect of differently located and substituted phenyl groups, as well as aliphatic groups, on micellar catalysis with perfluorooctanoic acid.

CHAPTER II

PREPARATION OF COMPOUNDS AND KINETIC PROCEDURES

Purification of Perfluorooctanoic Acid (CF_3-$(CF_2)_6COOH$)

Perfluorooctanoic acid was purchased from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin. Purification was accomplished by two successive recrystallizations[30]. Twenty-five grams of the compound were added to 400 mL of CCl_4 (ACS) and heated on the steam bath to dissolve the acid completely. The mixture was allowed to cool and stand overnight. The crystals formed were separated through filtration and washed with cold CCl_4 solvent. The melting point of the crystallized acid was measured using a Thomas Hoover capillary melting point apparatus and was found to be 56.3-58°C (literature 56.4-57.9°C)[31].

Preparation of Hydroxamic Acids

Hydroxamic acids were prepared from the appropriate carboxylic acids. The preparation included the following two steps:

$$RCOOH + CH_3OH \xrightarrow[\text{reflux}]{H_2SO_4} RCOOCH_3 + H_2O \qquad (9)$$

$$RCOOCH_3 + H_2NOH \xrightarrow{CH_3OH} RCONHOH + CH_3OH \qquad (10)$$

Laboratory procedures:

1. Ten moles of CH_3OH and one mole of RCOOH were placed in a round-bottom flask. Then, 8.3 mL of concentrated H_2SO_4 were slowly added to the mixture with stirring followed by a reflux of about 5 hours. After cooling to room temperature, 250 mL of H_2O for each mole of RCOOH used and an equal volume of CH_2Cl_2 were added to the mixture. The mixture was poured into a separatary funnel and shaken well. The bottom CH_2Cl_2 layer was drained and extracted with an equal volume of 10% aqueous NaOH. The aqueous layer was checked with pH paper to make sure it was still alkaline after extraction. If not, the CH_2Cl_2 layer was extracted again with fresh 10% NaOH. Finally, the CH_2Cl_2 layer was extracted with distilled water. The CH_2Cl_2 was boiled off on a steam bath in the hood. The residue left was the ester.

2. Approximately 3.3 moles of KOH dissolved in 460 mL of CH_3OH and 2.2 moles $NH_2OH \cdot HCl$ in 790 mL of CH_3OH were required for each mole of ester.

The KOH solution was prepared by dissolving KOH in hot CH_3OH on a steam bath.

The $H_2NOH \cdot HCl$ solution was next prepared at the boiling point of CH_3OH (64.5°C), then cooled to about 40°C. The KOH solution previously prepared was added slowly to

the $H_2NOH.HCl$ solution with cooling. The new mixture was cooled to 10°C in an ice bath. The precipitate of KCl was removed by suction filtration.

This filtrate was added to the ester obtained before, the flask was stoppered and allowed to stand for a day.

The mixture was acidified with glacial acetic acid to pH=6. The solution was concentrated as much as possible by blowing air on it. Then water equal to four times the volume of the residue was added to the mixture to precipitate the hydroxamic acid.

Prior to use, the product was crystallized several times using suitable solvents until the melting point became constant.

4-phenylbutanohydroxamic acid, mp 72.1-74°C (literature[32] mp 85°C), was crystallized from an ethanol-water solvent. Spectroscopic and chemical methods were applied to confirm the compound. Both the IR spectrum of the ester intermediate and the ^1H NMR spectrum of the final product were all consistent with the expected structures. Furthermore, the product formed a maroon colored solution with acidic $FeCl_3$ test reagent, which characteristically indicates a complex formation reaction between $FeCl_3$ and hydroxamic acids. Thus, the literature melting point value may be a misprint.

6-phenylhexanohydroxamic acid, mp 79.0-80.2°C, was crystallized from toluene. The analysis of this compound

was performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. The calculated compositions were: C,69.54%; H,8.27%; N,6.77%, and found were: C,69.50%; H,8.19%; N,6.76%.

Decanohydroxamic (mp 85.0-86.3°C), 4-isopropylphenylacetohydroxamic (mp 138-140.5°C), and 2,5-dimethylphenylacetohydroxamic acids (mp 154-155°C) were supplied by Professor Donald C. Berndt.

Preparation of Ferric Chloride ($FeCl_3$) Solution

The solution was prepared in the following ratio:

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

This solution is used as an indicator. It forms a maroon complex with unreacted hydroxamic acid in kinetic runs. It was also used as a test reagent in the preparation of hydroxamic acids.

Preparation of Stock Reactant Solutions

The aqueous acetonitrile solution (2.106M) was prepared by mixing 220 mL of acetonitrile ($CH_3C{\equiv}N$, Aldrich Chemical Company, Inc. HPLC) with double distilled water in a 2000 mL volumetric flask. This solution is used as the solvent for the surfactant and hydroxamic acids.

Hydroxamic acid solutions (0.0105M) were prepared with the above aqueous acetonitrile solution.

Surfactant (perfluorooctanoic acid) solutions were prepared freshly before use.

Kinetic Procedures

1. Ten mL of the ferric chloride 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 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 UV 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 needed for all reactions). The reaction vessels were stoppered and placed in a stirred constant temperature oil bath ($70\pm0.2^{o}C$) for about 15 minutes to achieve thermal equilibrium. Two mL of 0.0105M hydroxamic acid solution were pipeted into each vessel and swirled to get the solution well mixed. This resulted in an initial reactant concentration of $5\times10^{-4}M$ for the hydroxamic acid.

4. After about 3 minutes, a 4 mL (pipet) sample was withdrawn from the 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 mixture and inverted for 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 measurement from time to time until the final absorbance taken decreased to 1/3 of the initial one. Usually, eight measurements were required for one 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, rates of hydrolysis were dependent upon the concentration of surfactant. For the hydroxamic acids tested in this thesis, the observed rate constants were determined over a surfactant concentration range of 0.002-0.07M.

The surfactant concentration is considered to be constant since it is in large excess in comparison with that of hydroxamic acid (5×10^{-4}M). The relationship between the observed rate constant and absorbance (proportional to concentration) can therefore be depicted on the basis of the pseudo first-order concept[33,34], i.e.,

$$-dA/dt=k_{\psi}A \qquad (11)$$

or the integral form,

$$\ln A_t=-k_{\psi}t+\ln A_o \qquad (12)$$

where A_t is the absorbance of sample at time t, A_o is the absorbance at initial time 0, k_{ψ} is the observed pseudo first-order rate constant.

Equation (12) gives a straight line if $\ln A_t$ is plotted against t. From the graph, $-k_{\psi}$ and $\ln A_o$ which are the slope and intercept on the Y axis, respectively, can be found. In this thesis, a least-squares treatment of $\ln A_t$ versus time was used to determine the pseudo first-order rate constants. An example is given in Table 1.

The least squares regression equation had the following form:

$$\ln A_t = -1.20-0.00379t$$

where the slope is -0.00379. Therefore, the observed pseudo first-order rate constant, i.e. k_{ψ}, was $0.00379 min^{-1}$.

Data from the duplicate run gave $k_{\psi}= 0.00377 min^{-1}$. The average observed pseudo first-order rate constant was $0.00378 min^{-1}$.

Usually, it was required that the percent difference in k_{ψ} of duplicate runs did not exceed 5%.

Table 1

Sample Data for the Determination of k_ψ for 5×10^{-4}M 4-phenylbutanohydroxamic Acid and 0.0571M Surfactant at 70±0.2°C

Sample Number	Clock Time	Time(min)	Absorbance
1	10:12	0	0.294
2	10:49	37	0.256
3	11:32	80	0.217
4	12:26	134	0.178
5	13.00	168	0.156
6	14:11	239	0.114
7	14:57	285	0.099
8	15:22	310	0.088

The graph of $\ln A_t$ versus time of sample is shown in Figure 2.

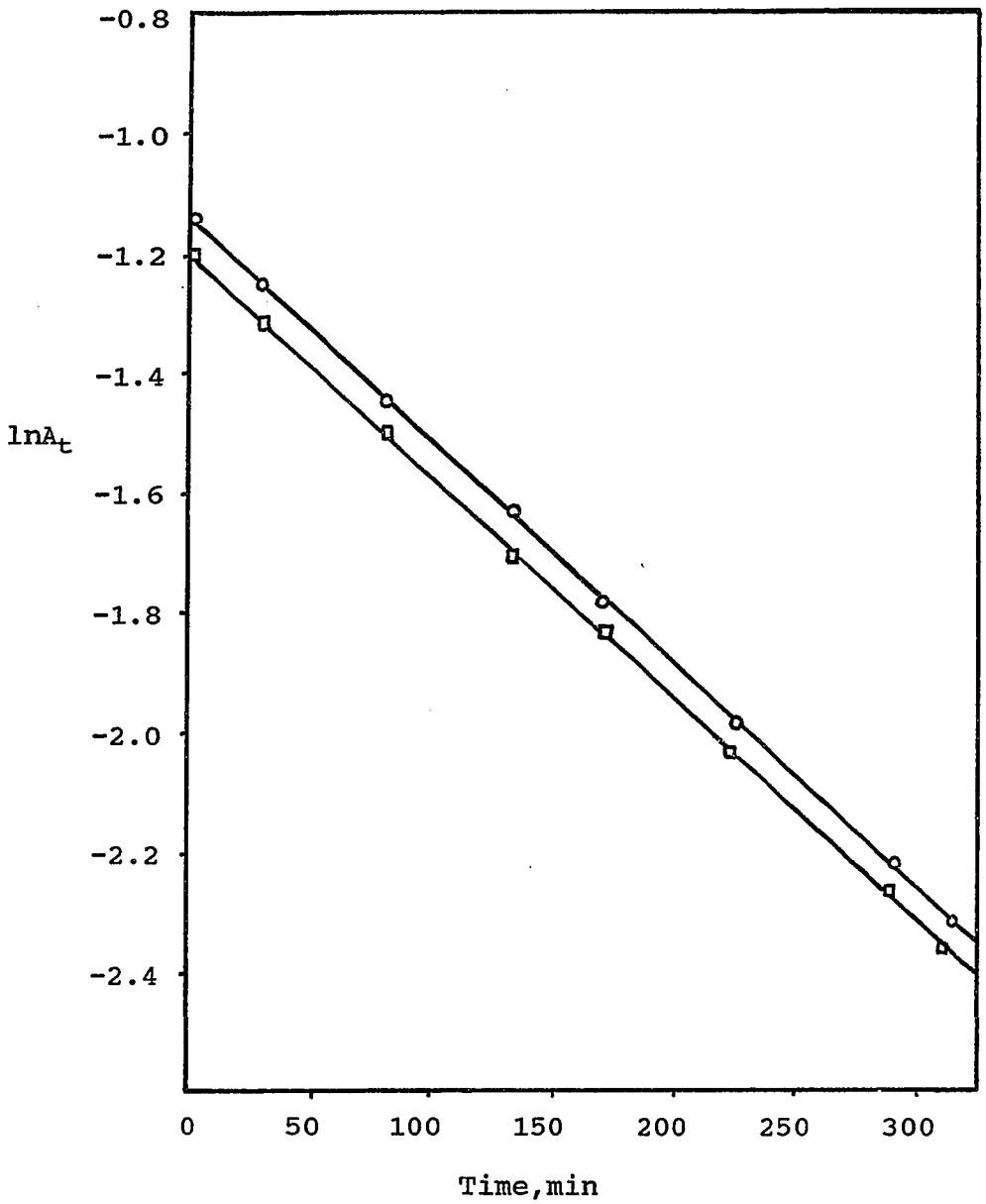


Figure 2. The Graph of lnA$_t$ Versus Time.

CHAPTER III

RESULTS AND DISCUSSION

The acidic hydrolysis reaction of hydroxamic acids is given in equation (13).

$$RCH_2CONHOH + H_3O^+ \text{---> } RCH_2COOH + H_3N^+OH \qquad (13)$$

The reaction rate of hydrolysis increases with increases in the concentration of perfluorooctanoic acid both above and below the cmc.

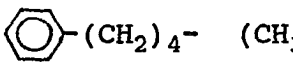
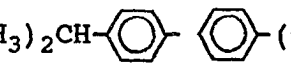
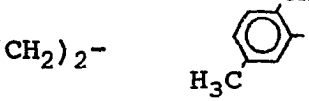
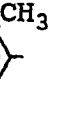
Perfluorooctanoic acid is a reactive counterion surfactant. It behaves as a normal acid catalyst below the cmc, while at concentrations above the cmc, it serves as a source of hydrogen ion as well as providing micelles to enhance the hydrolysis reaction. In other words, micellar catalysis occurs.

The experimental kinetic data for decano-, 6-phenylhexano-, 4-isopropylphenylaceto-, 4-phenylbutano-, and 2,5-dimethylphenylacetohydroxamic acids are reported in Table 2.

The surfactant concentration dependence profiles of the observed rate constant k_ψ are given in Figures 3, 4, and 5.

Table 2

Kinetic Data for Hydrolysis of $RCH_2CONHOH$ as a Function of Perfluorooctanoic Acid in Aqueous Acetonitrile at 70±0.2°C

	$k\psi \times 10^4 min^{-1}$				
$C_t \times 10^2 M$	R= $CH_3(CH_2)_7-$				
0.190	1.68				0.23
0.286		1.45	1.53	1.40	
0.476	3.03				
0.619		3.32			
0.667			2.74	3.32	0.71
0.952	6.93		4.01	4.58	1.06
1.14		6.67			
1.42	36.4				
1.90	54.9		13.1	11.8	2.38
2.38		26.9			
2.86	83.0		30.8	19.0	5.50
3.33		41.0			6.80
3.81	118		42.0	27.0	7.99
4.44		52.6			
4.76	132	58.4	51.7	32.1	10.4
5.71	135	66.5	57.1	37.8	11.1
6.67		72.1	58.1	44.0	12.5

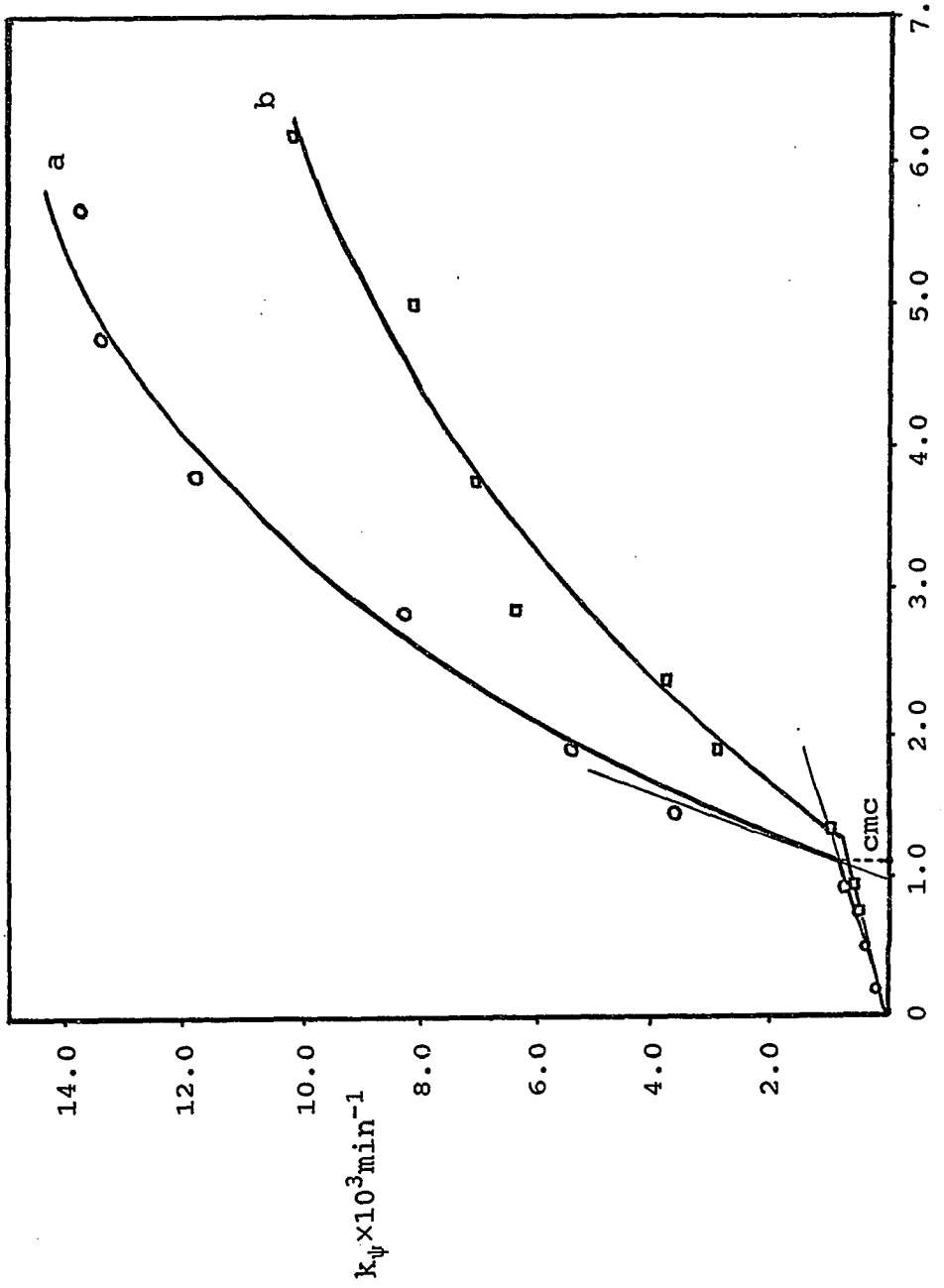


Figure 3. Rate Constant Surfactant Concentration Profiles for [a]decano- and [b]octanohydroxamic[21] Acids. (The solid lines are the calculated curves.)

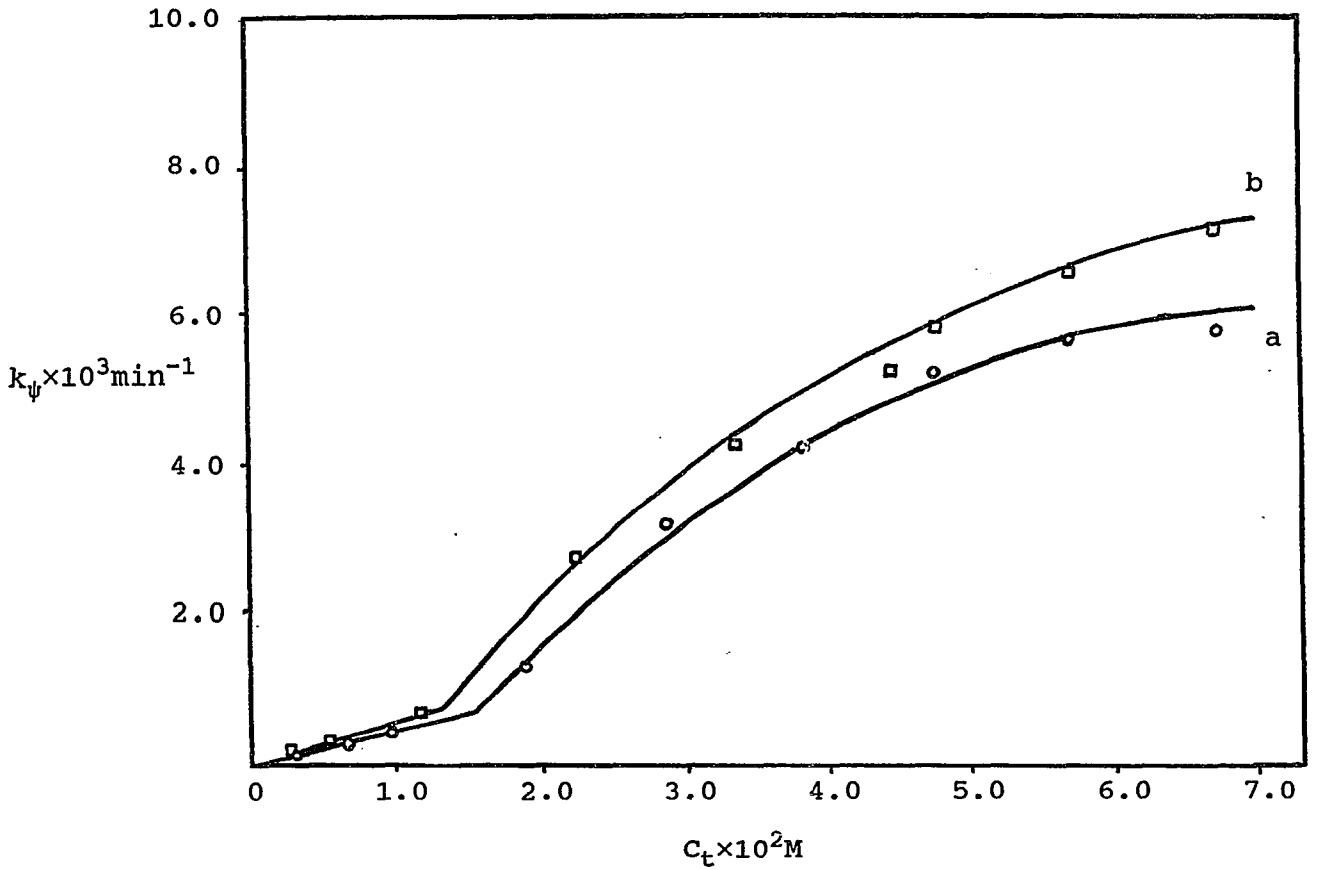


Figure 4. Rate Constant-Surfactant Concentration Profiles for [a]4-isopropylphenylaceto- and [b]6-phenylhexanohydroxamic Acids. (The solid lines are the calculated curves.)

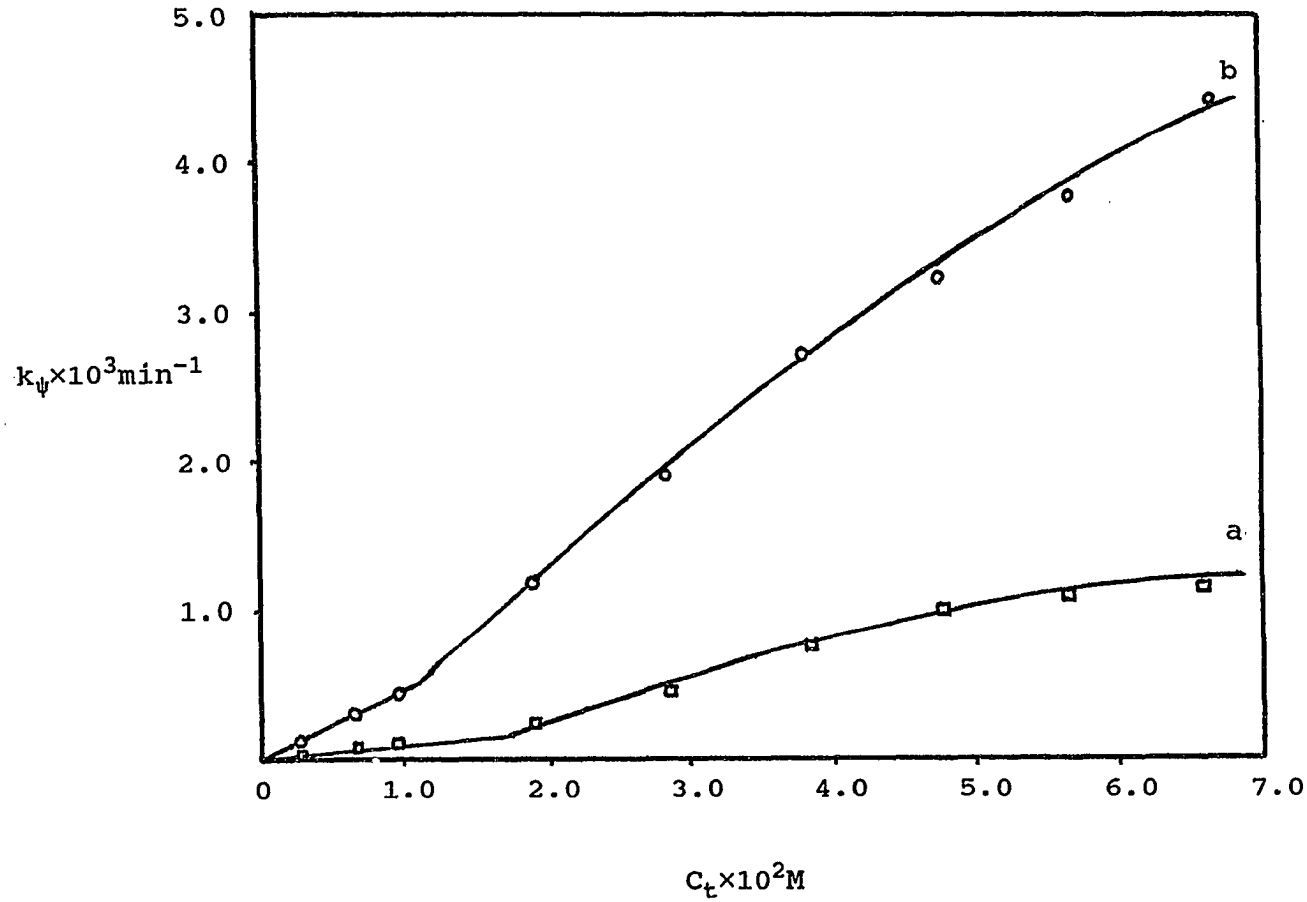


Figure 5. Rate Constant-Surfactant Concentration Profiles for [a]2,5-dimethylphenylaceto- and [b]4-phenylbutanohydroxamic Acids. (The solid lines are the calculated curves.)

In the above curves, breaks in the region of 0.01 to 0.02M of surfactant concentration were found for all the hydroxamic acids tested. These breaks should approximately indicate the kinetic cmc of perfluorooctanoic acid under the actual experimental conditions. The literature cmc value of perfluorooctanoic acid in water solution at 25°C is 0.0096M[35]. Obviously, a comprehensive effect of solvent, additive, and higher temperature increased, more or less, the cmc of the surfactant in these cases.

In this thesis, the cmc of the surfactant was estimated from the intersection of the extrapolations of the lines as shown in Figure 3.

There is no micelle formation in solution below the cmc. In the low to moderate acidity range in the absence of micelles, the acidic hydrolysis of hydroxamic acids follows equation[36] (14)

$$K_{\psi}=k_{w}[H^{+}] \qquad (14)$$

where k_w is a second-order rate constant in water. For perfluorooctanoic acid below the cmc, $[H^+]$ is the hydrogen counterion concentration which is equal to C_t, the total surfactant concentration. Therefore, a linear relationship passing through or near the origin was observed below the cmc.

The value of k_w was determined through the least-squares regression treatment of kinetic data in the region

in which there are no micelles. k_w is the slope of the $k\psi$ versus C_t linear plot.

Further information was obtained through equation (4) using the kinetic data above the cmc. In the regression equation of k_ψ versus $(k_wC_t-k_\psi)/(C_t-cmc)$, k_m' is the intercept and the reciprocal of K_s is the slope. An example of data treatment is given in Table 3 and Figure 6.

Table 3

Parameters for equation (6) for 6-phenylhaxanohydroxamic acid above the cmc

$C_t \times 10^2 M$	$(C_t-cmc)\times 10^2$	$k_\psi \times 10^2$/min	$\frac{k_wC_t-k_\psi}{C_t-cmc}$
2.38	0.0100	26.9	-0.129
3.33	0.0195	41.0	-0.110
4.44	0.0306	52.6	-0.0866
4.76	0.0338	58.4	-0.0784
5.71	0.0433	66.5	-0.0760
6.67	0.0529	72.1	-0.0622

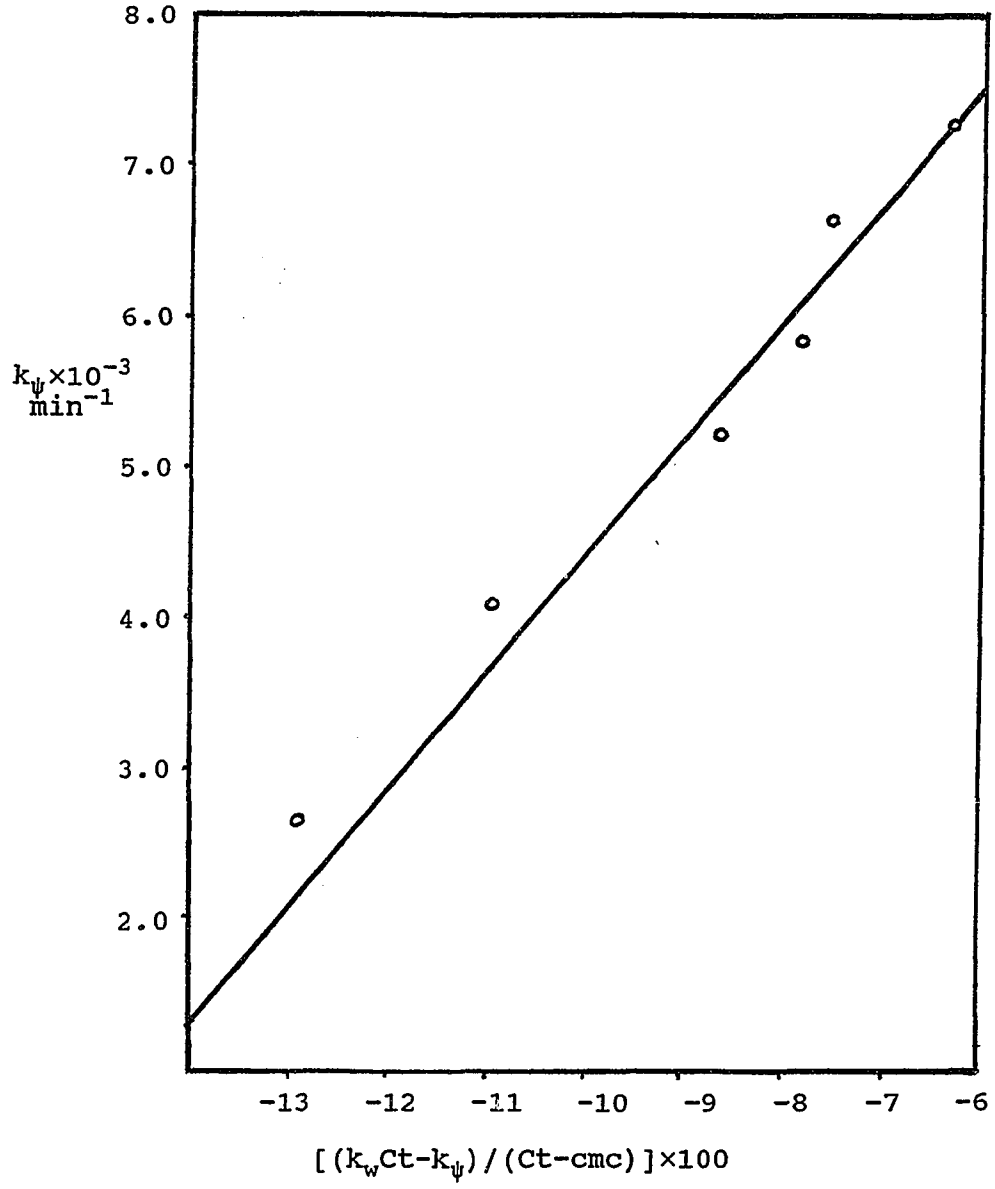


Figure 6. Plot of Equation (6) for Hydrolysis of 6-phenylhexanohydroxamic Acid.

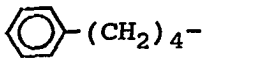
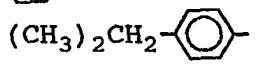
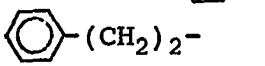
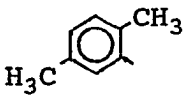
Good linear relationships were obtained for plots of k_ψ versus $(k_wC_t-k_\psi)/(C_t-cmc)$ for all the hydroxamic acids tested. The quality of the regression treatment results were evaluated with the statistical R^2 and F test. For example, with six data points for analysis, R^2 values of 0.863 and 0.977 lead to significance at 99 and 99.9% levels, respectively. The R^2 values and other kinetic parameters discussed are listed in Table 4. The standard deviations for k_m' values obtained are also listed.

To determine the reliability of the data of the kinetic runs and applicability of equation (6), calculated curves were obtained from equation (2) with $k_mK_s-k_w \approx k_mK_s$. See solid lines in Figures 3, 4, and 5. The calculated curves fit the data quite well. Thus the PPIE model for reactive counterion surfactant with perfluoroctanoic acid again explains the data for hydrolysis of the hydroxamic acids tested in aqueous acetonitrile solution satisfactorily.

As noted in the introduction, there are recent data suggesting that perfluoroheptanoic acid forms microemulsions in water above the cmc. The experimental conditions in this thesis are different from those in which microemulsions were found for perfluoroheptanoic acid; nevertheless, it is possible that microemulsions exist in the present system. PPIE has been successfully used with microemulsion systems also.

Table 4

Parameters for Calculation of Theoretical k_ψ Versus Surfactant Concentration Curves for $RCH_2CONHOH$

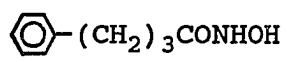
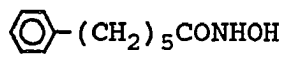
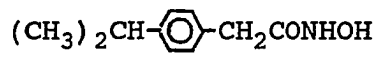
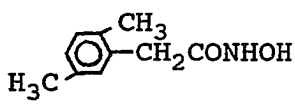
Substrate	k_w, $\frac{mol}{L.min}$	cmc, M	k_m', $\frac{1}{min}$	K_s[b], $\frac{L}{mol}$	R^2, %	St-dev
R=						
$CH_3(CH_2)_7-$	0.071	0.0104	0.018	40.5	89.0	0.0016
$CH_3(CH_2)_5-$ [a]	0.059	0.0122	0.017	17.0		
	0.059	0.0135	0.012	13.8	97.7	0.0048
	0.041	0.0157	0.009	23.5	91.4	0.00078
	0.048	0.0114	0.009	4.78	86.3	0.0012
	0.011	0.0183	0.002	19.0	91.8	0.00013

[a] In 2.19M aqueous acetonitrile solution[21].
[b] These K_s values are the ones used to calculate the solid curves in Figures 3,4 and 5; but the K_s values have only one or two significant figures.

Several relative comparisons were made using the kinetic parameters obtained to study the micellar catalytic behavior of perfluorooctanoic acid in the hydrolysis of the hydroxamic acids. These attempts were to correlate the effects of the substituted chain of hydroxamic acids to micellar catalysis. The results are given in Table 5.

Table 5

Relative Kinetic Parameter Ratios of Hydroxamic Acids

Hydroxamic Acid	K_s/K_s'	k_ψ/k_wC_t	k_m'/k_w
$CH_3(CH_2)_8CONHOH$	8.4	3.33	0.26
$CH_3(CH_2)_6CONHOH$[a]	3.5	2.76	0.29
	1.0	1.38	0.18
	2.9	1.97	0.20
	4.9	2.44	0.22
	3.9	1.77	0.17

[a] In 2.19M aqueous acetonitrile solution[21]

In Table 5, k_ψ/k_wC_t is the ratio of the observed rate constant k_ψ at 0.0571M to an extrapolated rate constant assuming only reaction in the water phase at the same concentration using equation (14). A greater ratio value

effect. Generally, an increase of k_ψ/k_wC_t value is expected as the hydrophobic portion of the hydroxamic acid molecule increases. An empirical rule states that the effect of a phenyl group on the solubility in water is approximately equal to a straight four carbon hydrocarbon chain[37]. However, according to our observation, this rule did not explain the kinetic data in a predictable way. In fact, steric hindrance of a more substituted phenyl group may also have an influence on the catalytic effect in case of 2,5-dimethylphenylacetohydroxamic acid.

K_s/K_s' is the ratio of K_s of different hydroxamic acids relative to that of 4-phenylbutanohydroxamic acid. Solubilization of a substrate in the micelles relative to its solubility in water is directly related to the hydrophobicity of the nonpolar chain in the substrate. Hence, the magnitude of K_s/K_s' provides a relative order of micellar catalytic potential. In previous work, it seemed that phenyl groups have lower binding to perfluorocarbon micelles than to hydrocarbon micelles compared to the binding of aliphatic chains[38]. A tentative conclusion drawn from the data in Table 5 is that more substitution on the benzene ring leads to an increase in binding to the micelle as reflected in K_s values.

The k_m'/k_w values are rather similar (the units of k_m' and k_w are not the same, but comparison of the ratios is valid). This indicates that most of the micellar catalytic

effect results from the binding of the substrate to the micelle in the presence of hydrogen ion and water and effectively increases their concentrations, and hence the reaction rate.

A comprehensive overview of the data in Table 5 leads to the following deductions. A more hydrophobic chain in the hydroxamic acid leads to more catalysis by a micellar effect. Substitution of a phenyl group in the chain increases the hydrophobicity of the substrate as the total number of carbons increases, but does not affect the micellar effect in a constant manner. A more substituted phenyl group seems to have a more pronounced influence on the hydrolysis rate (through the K_s values).

Because of the limited data at this time, the above interpretations need to be examined further when more data are available.

CHAPTER IV

CONCLUSIONS

The work demonstrated the effects of differently located and substituted phenyl groups, as well as aliphatic groups in the hydroxamic acids, on micellar catalysis with perfluorooctanoic acid as the reactive counterion surfactant in aqueous acetonitrile solution.

Kinetic rate constant-surfactant concentration profiles for the hydroxamic acids was examined and analysis on the data obtained were reported. Typical micellar catalysis was observed for the hydrolysis of decano-, 6-phenylhexano-, 2,5-dimethylphenylaceto-, and 4-isopropylphenylacetohydroxamic acids, and to a less extent for 4-phenylbutanohydroxamic acid.

A more hydrophobic chain in the hydroxamic acid leads to more catalysis by a micellar effect. Substitution of a phenyl group in the chain increases the hydrophobicity of the substrate as the total number of carbons increases, but does not affect the micellar effect in a constant manner. A more substituted phenyl group seems to have a more pronounced influence on the hydrolysis than a less substituted one.

The pseudo-phase ion exchange (PPIE) model has been again applied to explain the observed micellar effects satisfactorily.

Further study to test more appropriately substituted hydroxamic acids is suggested in order to obtain a more complete set of data and further evaluation.

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