Structural Effects on Micellar Catalyzed Hydrolysis of Hydroxamic Acids with Perfluorooctanoic Acid as Surfactant

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STRUCTURAL EFFECTS ON MICELLAR CATALYZED HYDROLYSIS
OF HYDROXAMIC ACIDS WITH PERFLUOROOCTANOIC ACID
AS SURFACTANT

by

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Xing Zhang

STRUCTURAL EFFECTS ON MICELLAR CATALYZED HYDROLYSIS
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AS SURFACTANT

Xing Zhang, M.A.

Western Michigan University, 1995

This thesis demonstrated the structural effects on micellar catalyzed hydrolysis of hydroxamic acids with prefluorooctanoic acid as the reactive counterion surfactant in aqueous acetonitrile solution.

For different hydroxamic acids, the observed pseudo-first order rate constant-surfactant concentration profiles were obtained and were used in the determination of critical micellar concentrations (cmc).

The micellar catalytic effect was satisfactorily explained by the pseudo-phase ion exchange (PPIE) model. The PPIE model was successfully applied in the determination of the reaction rate constants both in the water phase and in micellar pseudo-phase.

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

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CHAPTER I

INTRODUCTION

The rate of chemical reactions can often be substan-
tially enhanced in micellar solutions[1]. This kind of
phenomena is called micellar catalysis. In micellarly
catalyzed reactions, in addition to the reaction condi-
tions, the nature of the micelle and the structure of the
reactant (substrate) can also greatly influence the
reaction rate.

It is understood that the micellization of surfactant
is a thermodynamically stabilizing process for a given
water-surfactant system[2]. When surfactant is dissolved into
water, the hydrophobic portion of the surfactant molecules
have the tendency to be remote from the water to reduce the
free energy by minimizing the hydrocarbon-water interface.
When the concentration of the surfactant reaches a certain
value, an extensive association of surfactant molecules
occurs to form large aggregates, i.e., micelles. The
concentration at which micelles begin to form is called the
critical micelle concentration (cmc). Numerous experiments
have shown that the cmc is a narrow range of concentration
instead of a simple sharp point[3].

Micelle formation is apparently controlled by two opposing factors, the cohesive forces between hydrophobic surfactant tails and the affinity of the hydrophilic groups for water[4]. At a given temperature, the balance between these factors determines the size, shape, and charge of the micelle.

The shape of ionic micelles are often described as roughly spherical (Figure 1)[4].

Gouy-Chapman layer

Core

Counterion

Stern Layer

H₂O

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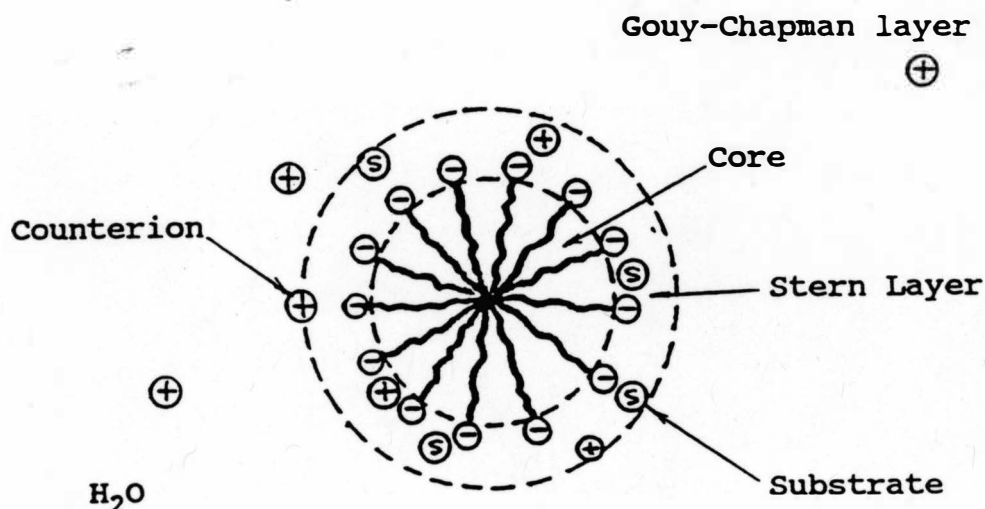
Figure 1. Model of Hypothetical Anionic Micelle in Aqueous Media.

In the sphere of a micelle, the hydrophobic portions of the surfactant molecules are oriented towards each other, forming a volume called the core, and the hydrophilic portions of the surfactant molecules point to the surface of the core, called the Stern layer. Most of the counterions are tightly bound in the Stern layer. This

close association of the counterions and the ionic head groups is responsible for the reduction of the net charge on the micelles. Some of the counterions are located in the so-called "Gouy-Chapman electrical double-layer" where they are completely dissociated from the charged aggregate and are able to exchange with ions in the bulk of the solution. A dynamic equilibrium exists between the monomer and micelle in solution[5]. Some monomers leave the micelle while others combine. This means that micelles, when formed, are not sharply defined entities. The shape of an actual micelle is concentration dependent[2]. The size of micelle is described by the aggregation number(N), which is the number of monomers per micelle, and the length of the hydrophobic group of the surfactant.

Since several physical properties of micellar solutions change abruptly at the cmc, the value of the cmc can be determined by measuring such properties as surface tension, electrical conductivity, osmotic pressure, light scatting, viscosity, dye solubilization, and other physical properties.[6,7]

In recent years, much interest has been shown toward the micellar solutions formed from perfluorocarboxylic acids. Because of the substitution of fluorine for hydrogen atoms, this type of surfactant is very surface active in solution.

The cmc of fluorinated or hydrocarbon surfactants

decreases with increasing number of carbon atoms[8]. The cmc for fluorinated surfactants in aqueous solution depends on the fluorocarbon chain length and the counterion and the cmc decreases with increasing hydrophobe chain length. The greater hydrophobicity of the fluorocarboxy chain enhances the amphiphilic character of the surfactant and increases surface activity compared to hydrocarbon chains, reflected in lower surface tensions and lower cmc values. At equal chain length the critical micelle concentrations of perfluorinated surfactant are lower than those of their hydrocarbon analogues. The cmc of a fluorinated surfactant also depends on the nature of the hydrophile but of a lesser effect than on the hydrophobic structure.

Micelles in surfactant solutions can incorporate in or upon themselves molecules of substances which are otherwise insoluble in the solvent, usually water.

A molecule solubilized by an ionic surfactant may be in the core of the micelle, between the hydrophobic chains in the layer formed by the counterions, or on the surface of the micelle. Since the micelle is in a dynamic state, the location of the solubilized molecule in a micelle can not be sharply defined. Like surfactant molecules or ions in the micelle, molecules of the solubilized substance are mobile and a rapid interchange between different sites may be possible[7]. It is believed, however, that the preferred location of the solubilized molecules in a given micelle

depends on the structure of the solubilized substance as well.

The amount of a substance which can be solubilized depends on several factors. The dominant variables are the structures of the surfactant and the solute. Both the structure of the hydrophobic chain and the nature of the counterion can affect solubilization[9,10].

For a chemical reaction which takes place in a micellar solution, the reactant is usually of low solubility in water and more soluble in the micellar phase. Solubilization of the reactant is similar to an extraction in that the reactant is distributed between two phases: the bulk solution and the micelle. The location of the reactant in the micelle can greatly affect the catalysis process. Polar reactants are expected to be located near the surface of the micelle, amphiphilic compounds have the polar portion on the surface and the alkyl chain towards the interior, and hydrocarbons are solubilized in the core[9,10].

Most models of micellarly catalyzed reactions assume that the overall rate of reaction is the sum of rates in each pseudo phase[5] and that changes in the rate with increasing surfactant concentration or added reagents reflects the change in the distribution of reactants between the two pseudo phases[5,10]. The site of solubilization varies with the nature of the solubilized species and

of course the surfactant.

The solubilization process is also a dynamic one, and the solubilized substance is in dynamic equilibrium between the micelle and the aqueous phase. The tendency of a solute to interact with micelles is generally expressed through the binding constant, K_s: for the reaction : S + M $\rightleftharpoons$ S.M, where S and M are the substrate and the micellar aggregate respectively. Thus,[5]

$$K_s = [SM] / ([S][M])\tag{1}$$

where M is generally expressed as the concentration of micellized surfactant.

The scheme below illustrates the pseudo phase model for reactions in micellar solution[5]:

$$nD \rightleftharpoons D_n$$

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

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

products
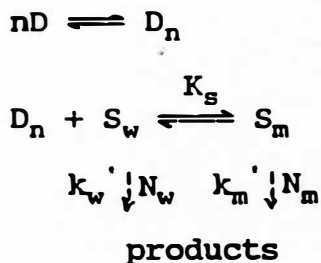
where D_n is the concentration of micellized surfactant with an aggregation number of n which is in kinetic equilibrium with surfactant monomer D. k_w' and k_m' are the rate constants in the bulk water phase and in the micellar pseudo phase with substrate concentrations of S_w and S_m, respectively. N_w and N_m are reactive ion concentrations and

K_s is the constant for the binding of the substrate to the micelle.

For bimolecular reactions, in which the other reactant is the counterion of the surfactant, the kinetic equation derived is[5]

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

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; β is the degree of counterion binding to the Stern layer, which has a value within the range of 0.6-0.9[5].

Equation (2), rewritten and rearranged, gives the following equations[11]:

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

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

where,

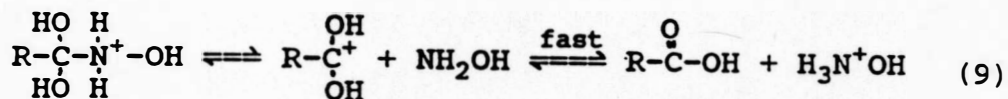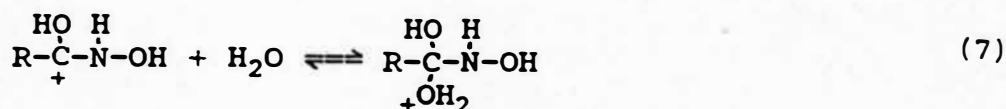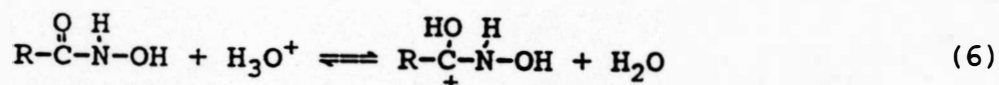$$b = \beta(k_m K_s - k_w)/K_s \qquad (5)$$

In practical applications, regression of k_ψ versus $(k_w C_t - k_\psi)/(C_t - cmc)$ allows the evaluation of k_m and K_s.

Hydrolysis of Hydroxamic Acids in Micellar Solution

The purpose of this work is to obtain more information on the influence of reactant structural effects on the micellarly catalyzed hydrolysis of hydroxamic acids with perfluorooctanoic acid as the reactive counterion surfactant in aqueous acetonitrile solution.

The mechanism of hydroxamic acid hydrolysis in acidic media has been proposed as follows[12]:

$$\text{R-C(=O)-N(H)-OH} + H_3O^+ \rightleftharpoons \text{R-C(OH)-N(H)-OH}^+ + H_2O \tag{6}$$

$$\text{R-C(OH)}^+\text{-N(H)-OH} + H_2O \rightleftharpoons \text{R-C(OH)-N(H)-OH with }^+OH_2 \tag{7}$$

$$\text{R-C(OH)(}^+OH_2)\text{-N(H)-OH} \rightleftharpoons \text{R-C(OH)-N}^+\text{(H)(OH)-OH} \tag{8}$$

$$\text{R-C(OH)(HO)H-N}^+\text{(H)-OH} \rightleftharpoons \text{R-C}^+\text{(OH)(OH)} + NH_2OH \xrightarrow{\text{fast}} \text{R-C(=O)-OH} + H_3N^+OH \tag{9}$$

The structural influence on the rates of hydrolysis of a series of hydroxamic acids in aqueous acetonitrile, with perfluorooctanoic acid serving as a reactive counterion surfactant, have been extensively studied pre-

viously[11,13,14]. Variation in the structure of the hydrophobic moiety of the hydroxamic acid substrate was obtained by the incorporation of different chain lengths and differently substituted aryl groups into the substrate. The major influence of the change in substrate structure is on the binding constant for binding of the substrate to the surfactant aggregate. The pseudophase ion exchange (PPIE) model for reactive counterion surfactant has been successfully applied in the previous studies[11,13,14].
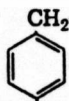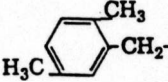
Table 1 and table 2 show the results from previous studies[11].

The previous studies show that a more hydrophobic chain in the hydroxamic acid leads to more catalysis by a micellar effect. Hence, generally speaking, the longer the hydrophobic chain a hydroxamic acid has, the more micellar effect will be expected.

The pseudo-phase ion exchange (PPIE) model has been satisfactorily applied in the explanation of the observed micellar effects in the previous studies[11,13,14].
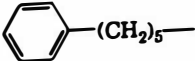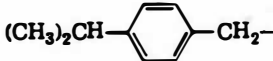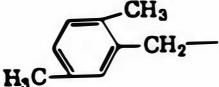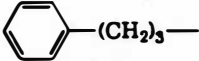
Based on the previous studies, we decided to choose the following compounds as our study object to further investigate the chain branching as well as chain length effects on the hydrolysis of hydroxamic acids with perfluorooctanoic acid as surfactant: cyclohexylacetohydroxamic acid, 3-cyclopentylpropanohydroxamic acid, 4-cyclohexylbutanohydroxamic acid, and 2-phenylbutanohydroxamic acid.

Table 1

Kinetic Data for Hydrolysis of RCO-NHOH as a Function of Perfluorooctanoic Acid Concentration at 70 ± 0.2°C in 2.11 M Acetonitrile

$10^4 k_\psi, min^{-1}$

$10^2 C_i, M$	$CH_3(CH_2)_8-$	$CH_3(CH_2)_6^*-$	$CH_2(CH_2)_4-$	$(CH_3)_2CH$	$CH_2(CH_2)_2-$	xylene
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

* The aqueous acetonitrile concentration is 2.19M.

Table 2

The Results of the Application of the PPIE Model for Previous Studies

| compound R	k_w,	cmc, M	b, min^{-1}	k_m, min^{-1}	K_s, L mol^{-1}
$CH_3(CH_2)_8-$	0.0700	0.0103	0.0192	0.0258	0.1
$CH_3(CH_2)_6-$	0.0594	0.0122	0.0171	0.0250	7.0
phenyl$-(CH_2)_5-$	0.0588	0.0140	0.0115	0.0183	5.0
$(CH_3)_2CH-$phenyl$-CH_2-$	0.0404	0.0138	0.00832	0.0121	4.4
H_3C-, CH_3-phenyl$-CH_2-$	0.0110	0.0182	0.00159	0.00240	6.4
phenyl$-(CH_2)_3-$	0.0482	0.0118	0.00812	0.0191	5.38

CHAPTER II

PREPARATION OF COMPOUNDS AND KINETIC PROCEDURES

Purification of Perfluorooctanoic Acid

Perfluorooctanoic acid was purchased from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin. Purification was accomplished by two successive recrystallizations. 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 56.2°C to 57.1°C (literature 56.4-57.9°C)[15].

Preparation of Hydroxamic Acids

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

$$RCOOH + CH_3OH \xrightarrow{H^+} RCOOCH_3 + H_2O$$

$$RCOOCH_3 + H_2NOH \longrightarrow RCONHOH + CH_3OH$$
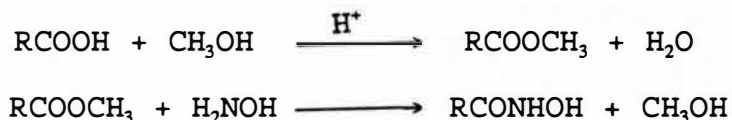
Lab procedures corresponded to the following:

Step 1: For each mole of the carboxylic acid, 10 moles of CH_3OH were added, followed by 1 mL of concentrated H_2SO_4. The mixture was refluxed 5 hours, then cooled to room temperature or below. For each 0.1 mole of the RCO_2H used, 25 mL of H_2O and an equal amount of CH_2Cl_2 were added to the cooled mixture. The mixture was shaken in a separatory funnel, and the layers separated. The CH_2Cl_2 layer was extracted with an equal volume of 10% aqueous NaOH; the aqueous layer was checked after the extraction with pH paper to make sure it was still alkaline. The CH_2Cl_2 layer was extracted with distilled water and the CH_2Cl_2 evaporated on a steam bath in the hood. The residue is the ester. Its structure was confirmed by an infrared spectrum.

Step 2: For each 1/3 mole of ester 1 mole of KOH was dissolved in 140 mL of CH_3OH and 2/3 mole of $NH_2OH.HCl$ (hydroxylamine hydrochloride) was dissolved in 240 mL of CH_3OH. The KOH solution was prepared first by heating on a steam bath to get all of the KOH in solution. Next the $H_2NOH.HCl$ solution was prepared at the b.p of CH_3OH. The solution was cooled to 40°C and the KOH solution was added slowly with cooling to the $H_2NOH.HCl$ solution. The new mixture was cooled to 10°C. The precipitate of KCl was removed by suction filtration. The ester was added to the filtrate and the mixture was let stand for a day. The mixture was acidified with glacial acetic acid to pH=6.

The solution was concentrated as much as possible by letting air from a hose blow on it to reduce the volume by approximately 1/2. Water (equivalent to three or four times the solution volume) was added which produced a precipitate of the hydroxamic acid. The product was collected by filtration, crystallized, and its melting point determined. Crystallization was repeated until the m.p. was constant.

Cyclohexylacetohydroxamic acid, mp 146.6-148.1°C, was crystallized from a water-methanol solution. The analysis of this compound was performed by MIDWEST MICROLAB, Indianapolis, IN. The calculated composition is: C, 61.12%; H, 9.62%; N, 8.91%, and found was: C, 61.07%; H, 9.67%; N, 8.96%.

3-Cyclopentylpropanohydroxamic acid, mp 92.8-93.7°C, was crystallized from a water-methanol solution. The analysis of this compound was performed by MIDWEST MICRO-LAB, Indianapolis, IN. The calculated composition is: C, 61.12%; H, 9.62%; N, 8.91%, and found was: C, 60.94%; H, 9.83%; N, 9.01%.

4-Cyclohexylbutanohydroxamic acid, mp 79.2-81.0°C was prepared by D.C. Berndt and 2-phenylbutanohydroxamic acid, mp 119-120°C (lit. 124-125°C)[16] was prepared by Wai Hoe Lock.

Preparation of Ferric Chloride (FeCl$_3$) Solution

The solution was prepared in the following ratio:

$$H_2O(mL):HCl(conc.,mL):FeCl_3.6H_2O(g)=100:10:1$$
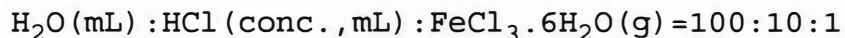
This solution is used as an indicator. It forms a maroon complex with unreacted hydroxamic acid in kinetic runs. It is also used as a test reagent in the preparation of hydroxamic acids.

Preparation of Stock Reactant Solutions

The aqueous acetonitrile solution (2.106M) was prepared by mixing 220 mL of acetonitrile (CH$_3$C≡N, HPLC, Aldrich Chemical Company, Inc. Milwaukee, WI) 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 (0.0105) 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 the 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 carried out for all reactions). The reaction vessels were stoppered and placed in a stirred constant temperature oil bath (70 $\pm$ 0.2°C) for about 10 minutes to achieve thermal equilibrium. Two mL of 0.0105 M hydroxamic acid solution were pipeted into each vessel and swirled to get the solution well mixed. This resulted in an initial reactant concentration of 5×10^{-4}M for the hydroxamic acid.

4. After 3 minutes, a 4 mL (pipet) sample was withdrawn from the reaction vessel and the initial time was recorded. The sample 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-butyl alcohol/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 measurements from time to time until not much solution was left (usually 8 measurements for each run).

6. Rates of reaction were measured in duplicate. Two

absorbance readings for each sample were taken and aver-aged. Most readings were within instrumental error $(\pm0.002A)$[17]. 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.

The reaction rates were measured over the surfactant concentration range of 0.002-0.067 M.

The first order rate law is[18,19]

$$\ln(A_t-A_\infty) = -k_\psi t + \ln(A_0 - A_\infty) \qquad (10)$$

Since $A_\infty = 0$ in the present study, the equation used is

$$\ln A_t = -k_\psi t + \ln A_0 \qquad (11)$$

where A_t is the absorbance of sample at time t, A_0 is the absorbance at initial time, 0, and k_ψ is the observed pseudo first-order rate constant.

From the above rate expression equation, a linear relationship should exist between time and $\ln A_t$. The slope of the straight line will give the observed first-order rate constant. In this work, a least-squares treatment of $\ln A_t$ versus time was used in the determination of the observed first-order rate constant. The R^2 value for all the least-squares is above 0.98. The Std Err of Coef. for all the data was less than 0.0001. Sample data and its treatment is shown in Table 3 and Table 4.

Therefore, the obtained k_ψ for 4-cyclohexylbutanohy-

droxamic acid and 0.0286 M Surfactant at 70 ± 0.2°C from the above two runs of measurements is 0.00506 min^{-1}. The relative error is ± 0.00003/0.00506 = 0.59% .

The graphs of $\ln A_t$ versus time of sample data are shown in Figures 2 and 3.

Table 3

Sample Data and Their Treatment for the Determination of k_ψ for 5×10^{-4} M of 4-cyclohexylbutanohydroxamic Acid and 0.0286 M Surfactant at 70 ± 0.2°C (First Run)

No.	Clock Time	t(min)	A	lnA
1	18:41	0	0.288	-1.245
2	19:00	19	0.266	-1.324
3	19:20	39	0.240	-1.427
4	19:50	69	0.206	-1.580
5	20:15	94	0.183	-1.698
6	20:35	114	0.164	-1.808
7	20:55	134	0.147	-1.917
8	21:15	154	0.132	-2.025

Regression Output:

Constant	-1.232
Std Err of Y Est	0.0088
R Squared	0.999
No. of Observations	8
Degrees of Freedom	6
X Coefficient	-0.00509
Std Err of Coef.	5.99E-05

Table 4

Sample Data and Their Treatment for the Determination of k_ψ for 5×10^{-4} M of 4-cyclohexylbutanohydro-xamic Acid and 0.0286 M Surfactant at $70 \pm 0.2°C$ (Second Run)

No.	Clock Time	t(min)	A	lnA
1	18:41	0	0.288	-1.245
2	19:10	29	0.253	-1.374
3	19:35	54	0.222	-1.505
4	20:05	83	0.192	-1.650
5	20:25	104	0.175	-1.743
6	20:45	124	0.156	-1.858
7	21:05	144	0.140	-1.966
8	21:25	164	0.127	-2.064

Regression Output:

Constant	-1.234
Std Err of Y Est	0.0088
R Squared	0.999
No. of Observations	8
Degrees of Freedom	6
X Coefficient	-0.00503
Std Err of Coef.	5.84E-05
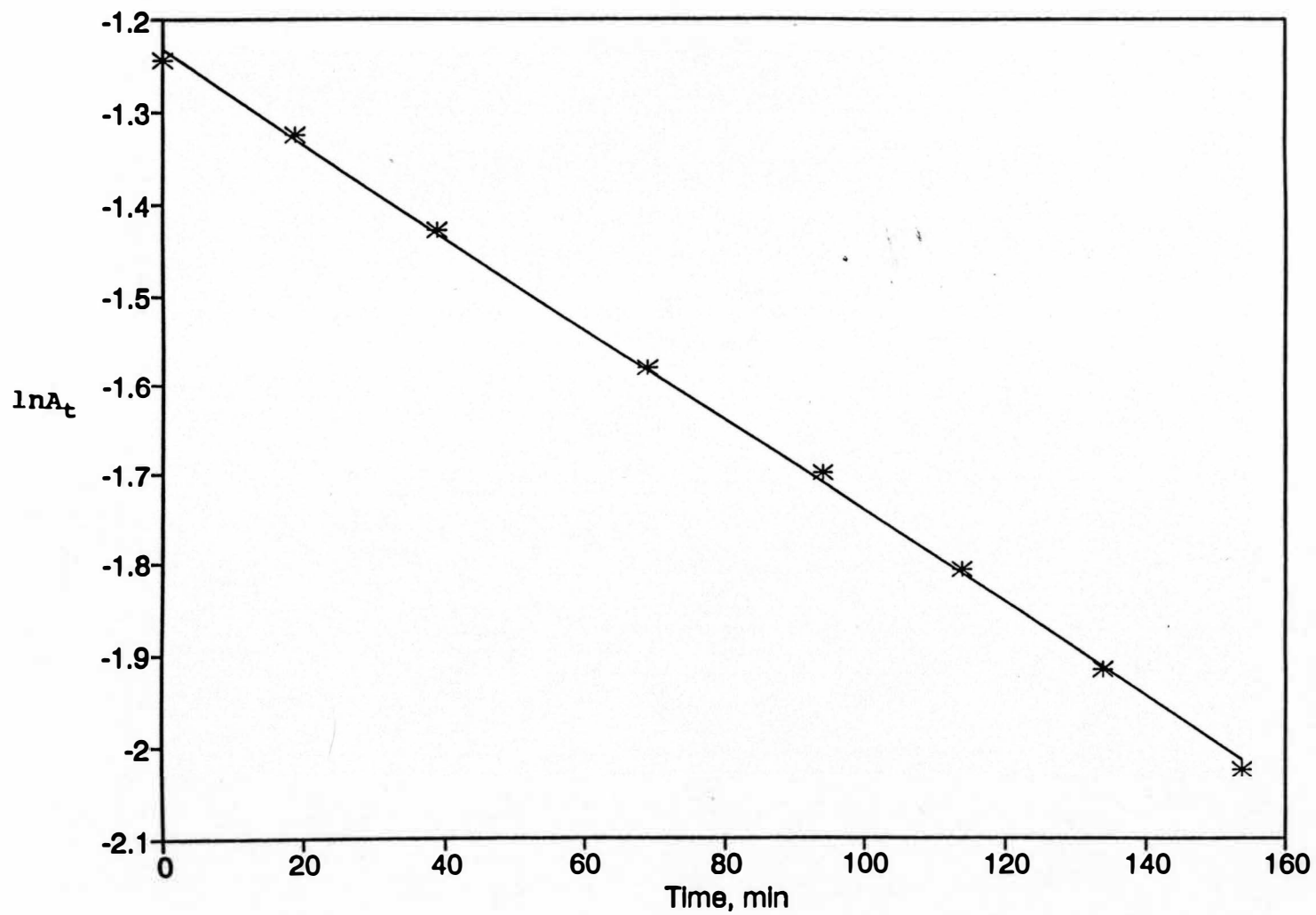
Figure 2. The Graph of $\ln A_t$ Versus Time for Run One.
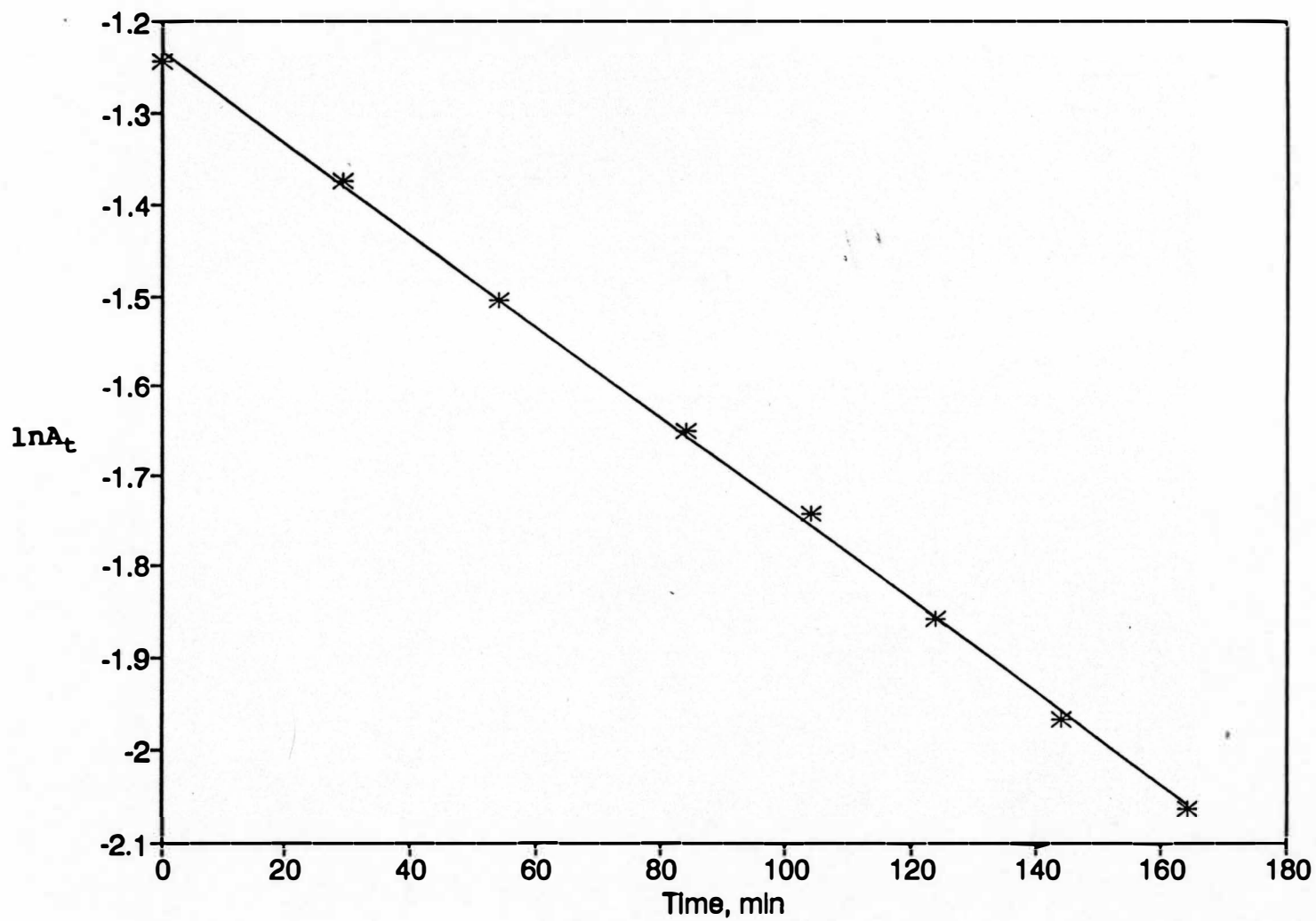
Figure 3. The Graph of $\ln A_t$ Versus Time for Run Two.

CHAPTER III

RESULTS AND DISCUSSION

The overall acidic hydrolysis reaction of hydroxamic acids is given in the following equation

$$RCH_2CONHOH + H_3O^+ \longrightarrow RCH_2COOH + H_3N^+OH$$

The reaction rate increases with an increase 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 above the cmc.

The experimental kinetic data for the hydroxamic acid hydrolyses are in Table 5.

The results of the application of the PPIE model is shown in Table 6.

The β value was assumed to be 0.8 in calculating k_m. The surfactant concentration dependence profiles of the observed rate constant k_ψ are given in Figures 4,5,6 and 7.

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Table 5

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

$10^4 k_\psi$, min^{-1}

	R=			
$10^2 C_t$, M	CH_3CH_2CH	⬡–$(CH_2)_3$–	⬡–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 6

The Results From the Application of the PPIE Model

Results	R= CH_3CH_2CH-	⬡ $-(CH_2)_3-$	⬡ CH_2-	⬠ CH_2CH_2-
k_w, L mol^{-1}min^{-1}	0.00473	0.0635	0.0149	0.0636
cmc, M	0.0182	0.0122	0.0135	0.0122
b, min^{-1}	0.000350	0.0146	0.0114	0.00575
K_s, L mol^{-1}	42.4	20.8	1.52	15.6
k_m, min^{-1}	0.000549	0.0213	0.0241	0.0113
R^2*	0.96	0.95	0.98	0.96

* R^2 is for the regression of k_ψ vs. $(k_w C_t - k_\psi)/(C_t - cmc)$.

In these curves, breaks in the region of 0.01 to 0.02 M 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 experiments show that different substrates have an influence on the cmc. Therefore, for the different hydroxamic acids employed, the cmc is slightly different.

In this study, the cmc of the surfactant was estimated from the intersection of the extrapolations of the lines as shown in Figure 6.
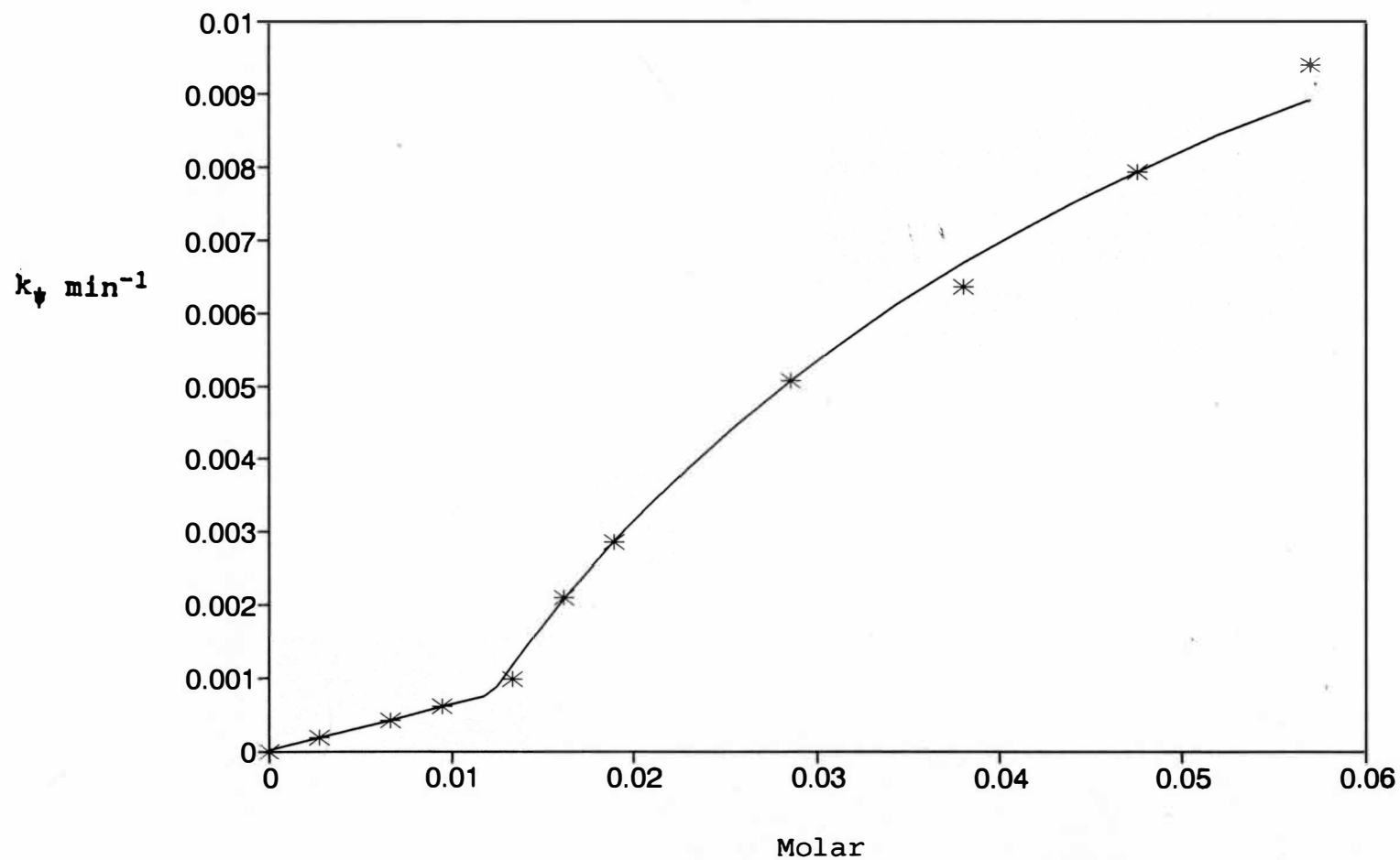
Figure 4. Rate Constant-Surfactant Concentration Profile
for 4-cyclohexylbutanohydroxamic Acid. (The
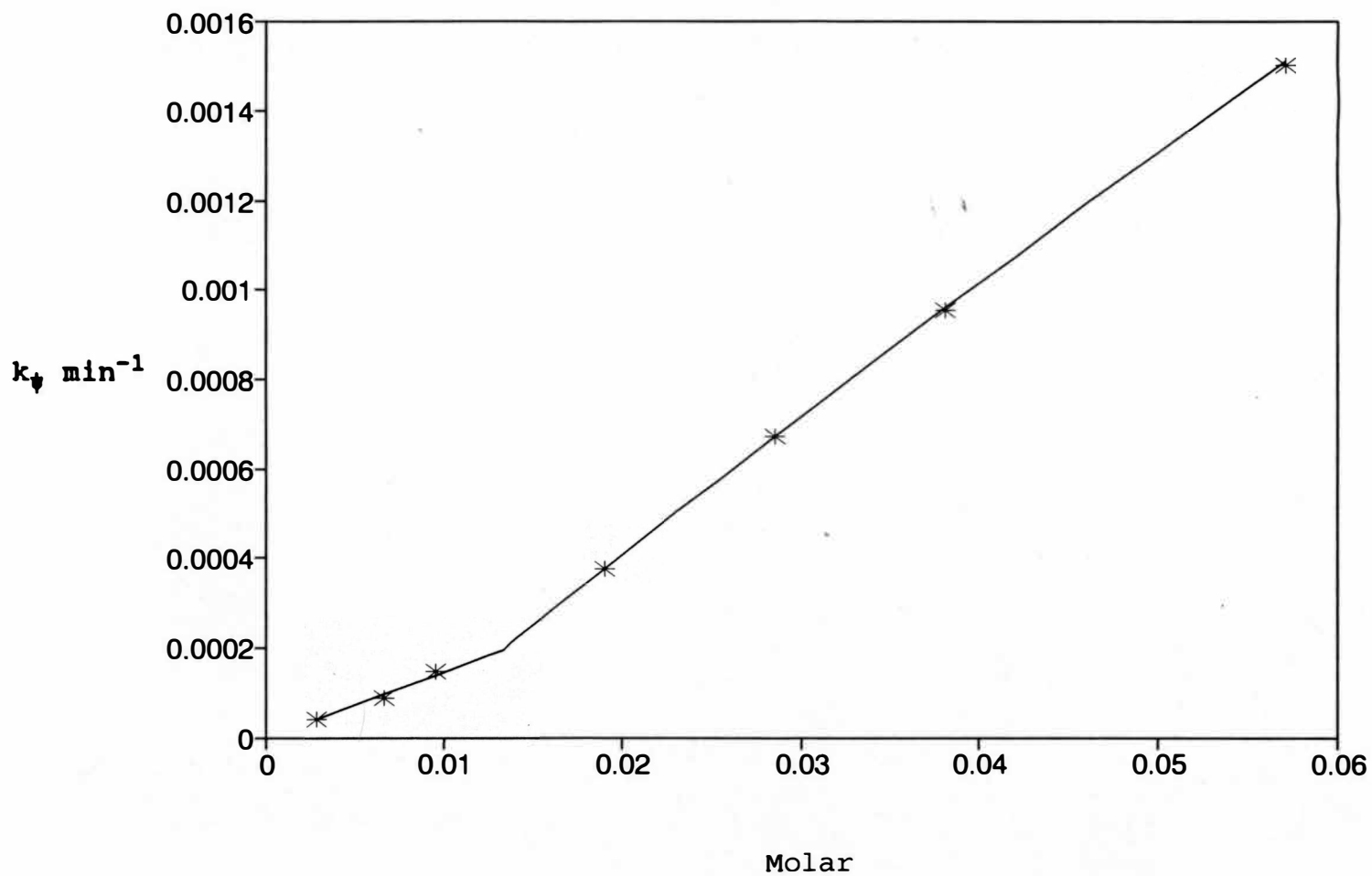solid line is the calculated curve.)

Figure 5. Rate Constant-Surfactant Concentration Profile
for Cyclohexylacetohydroxamic Acid. (The
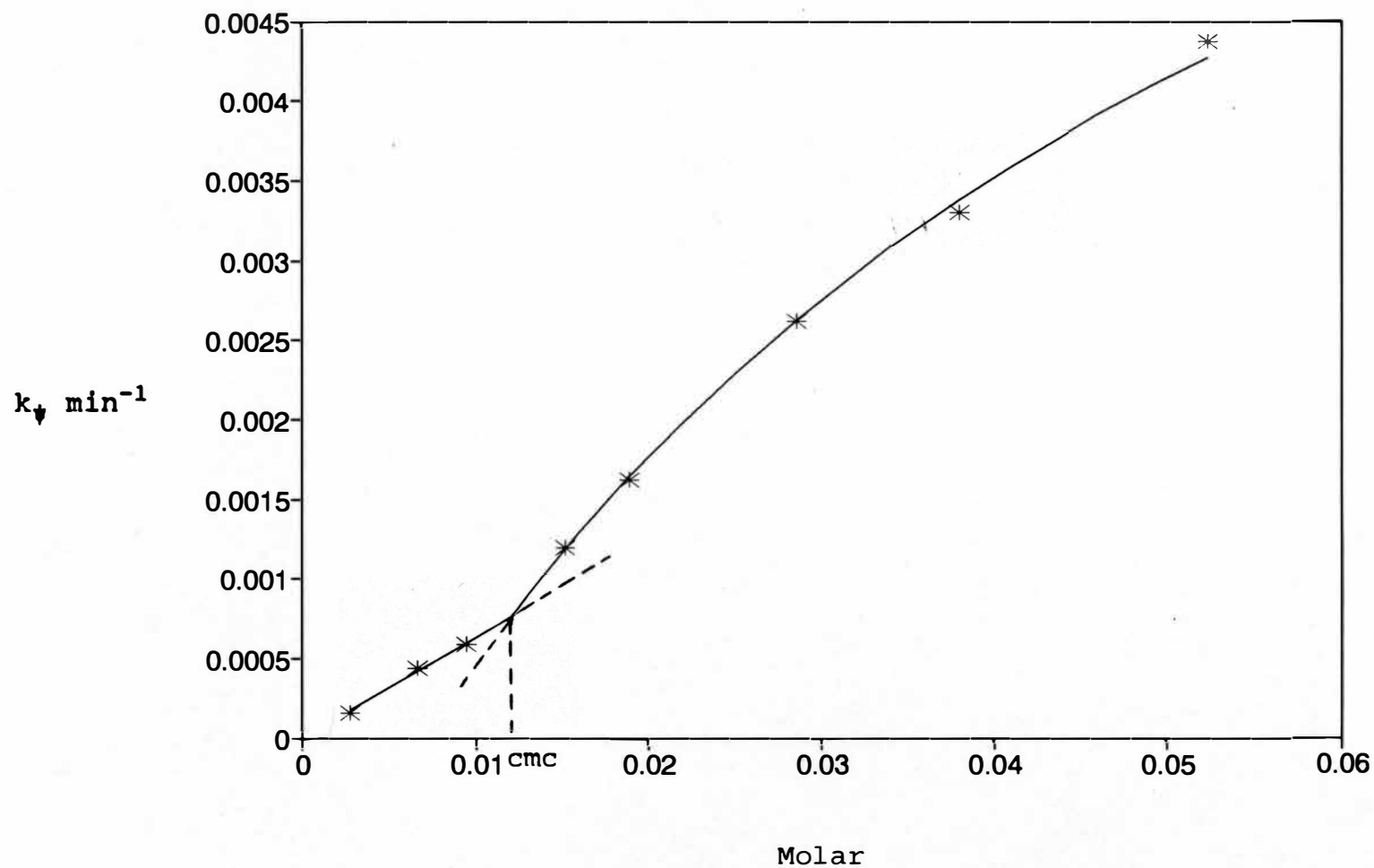solid line is the calculated curve.)

Figure 6. Rate Constant-Surfactant Concentration Profile
for 3-cyclopentylpropanohydroxamic Acid. (The
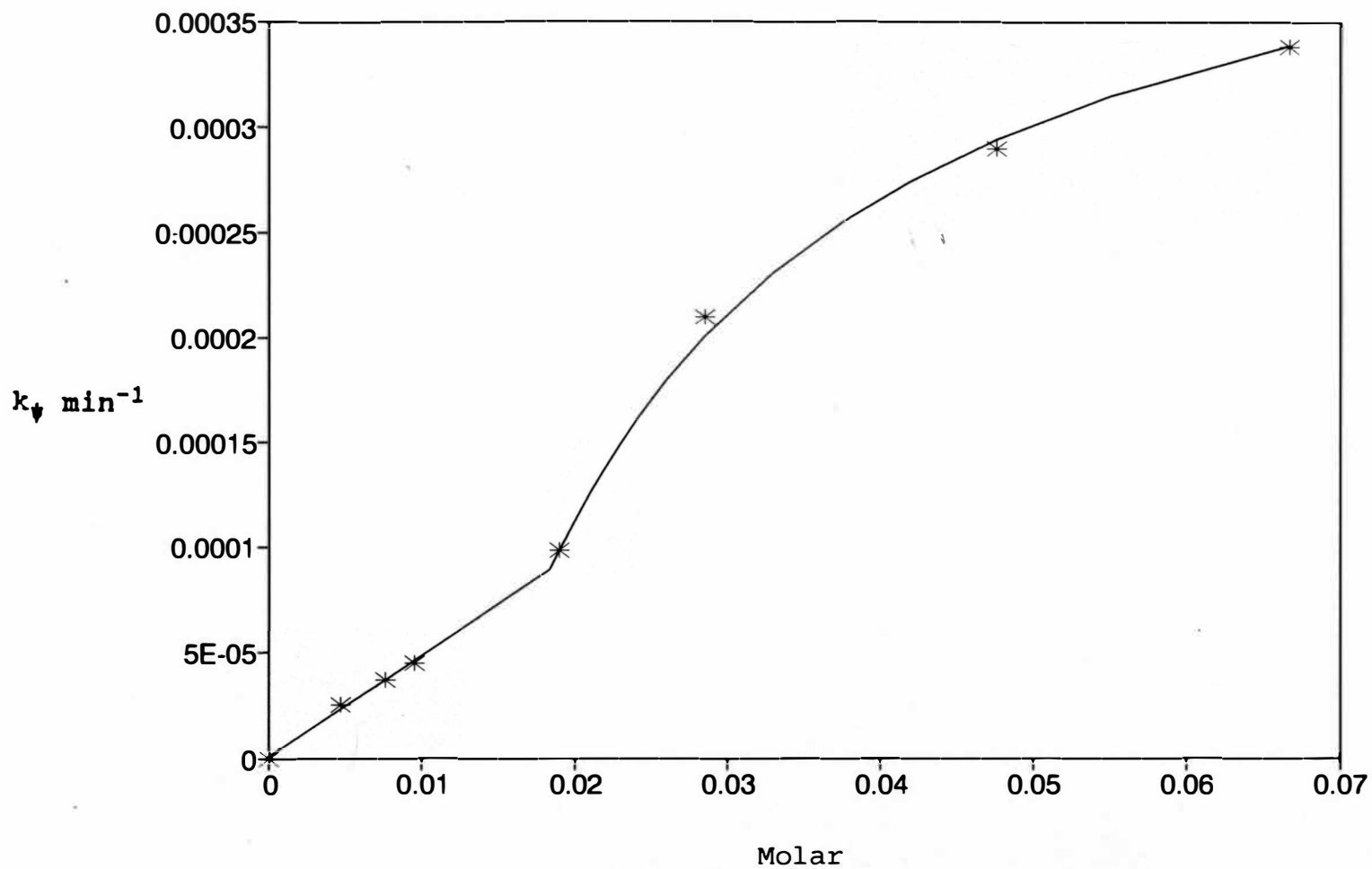solid line is the calculated curve.)

Figure 7. Rate Constant-Surfactant Concentration Profile for 2-phenylbutanohydroxamic Acid. (The solid line is the calculated curve.)

There is no micelle formation in the solution below the cmc. In the low to moderate acidity range in the absence of micelles, the acidic hydrolysis of hydroxamic acids follows equation[11]

$$k_\psi = k_w [H^+]$$

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 for the different hydroxamic acids was determined through the least-squares regression treatment of the kinetic data in the region below the cmc.

The experimental data were further examined by the application of the PPIE model above the cmc. From the mathematical expression for the PPIE model, we know that a good linear relationship should exist between k_ψ and $(k_w C_t - k_\psi)/(C_t - cmc)$. k_m, the reaction rate constant in the micellar pseudo phase, can be evaluated from the intercept, an assumed value for ß, and K_s, the binding constant for the binding of the organic substrate to the micelle; K_s is the reciprocal of the slope. The results of a sample calculation are shown in Table 7.

Table 7

Parameters in PPIE Model for 4-Cyclo-
Hexylbutanohydroxamic Acid

C_t*10^2M	$k_\psi*10^3/min$	
1.62	2.10	-0.269
1.90	2.85	-0.242
2.86	5.06	-0.198
3.81	6.36	-0.152
4.76	7.93	-0.139
5.70	9.39	-0.129

Figure 8 shows the graphic result.

From Figure 8 we can see a certain departure from the expected linear relationship. This is because the quantity $(k_wC_t-k_\psi)/(C_t-cmc)$ is very sensitive to experimental errors, especially near the cmc. The relative errors for different experimental points for $(k_wC_t-k_\psi)/(C_t-cmc)$ can be calculated based on the following mathematical expression:

let $\chi = (k_wC_t-k_\psi)/(C_t-cmc)$, then

$$\Delta\chi = \frac{\partial\chi}{\partial k_w}dk_w + \frac{\partial\chi}{\partial C_t}dC_t + \frac{\partial\chi}{\partial k_\psi}dk_\psi + \frac{\partial\chi}{\partial cmc}dcmc \qquad (13)$$

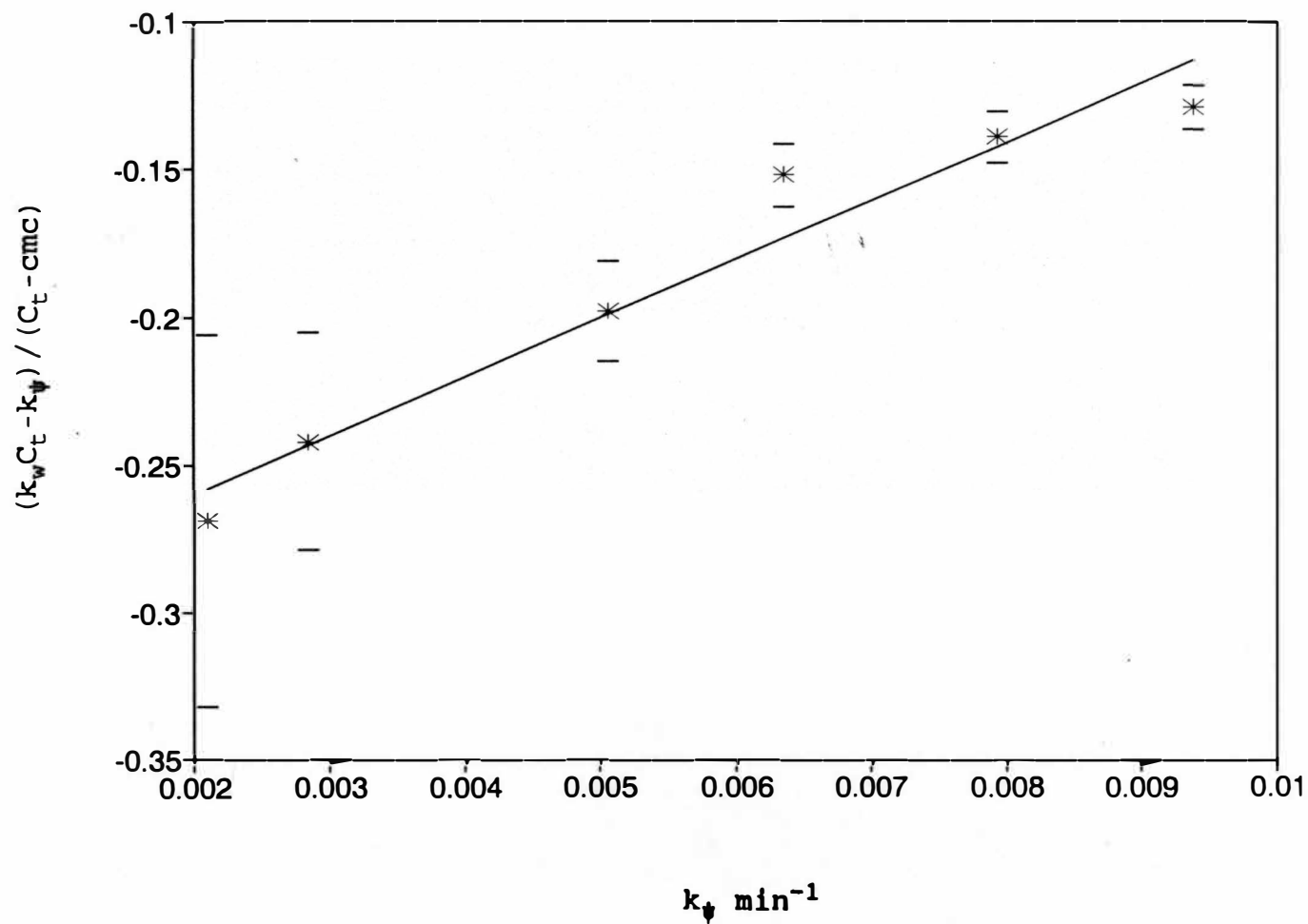From regressions of k_ψ and k_w we know that the relative

Figure 8. Plot of $(k_wC_t-k_\psi)/(C_t-cmc)$ Versus k_ψ for 4-cyclohexylbutanohydroxamic Acid. (* = Experimental data; - = Estimated error range.)

errors for k_ψ and k_w are 1.2% and 1% respectively. Let the errors for concentration be 1% of its actual value (based on the reading error of a 4 mL pipet), and the error for cmc be 5% of its value (the cmc is about 0.012 in this example, and the combined error in making and reading graph is about two-tenths of 0.003 which is one unit on the graphic paper). The estimated errors for item $(k_w C_t - k_\psi)/(C_t - cmc)$ for different experimental point for the sample data are shown in Table 8 and also in Figure 8.

Table 8

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

Concentration	±Err	±Err%
0.0162	0.0631	23.5
0.0190	0.0370	15.3
0.0286	0.0167	8.4
0.0381	0.0106	7.0
0.0476	0.0087	6.2
0.0571	0.0075	5.8

As proposed in the introduction, in addition to the reaction conditions, the surfactant concentration and the actual reactant structure also affect the hydrolysis of hydroxamic acids with perfluorooctanoic acid as the

reactive counterion surfactant in aqueous acetonitrile solution. From the above results, the influence of the surfactant concentration is obvious.
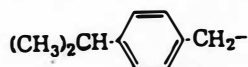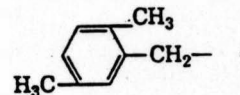
Experiments have shown that a phenyl group at the end of a straight chain alcohol, such as $Ph-(CH_2)_n-OH$, acted like 1.5 $-CH_2-$ units for solubilization in sodium perfluorooctanoate micelles and 3.5 CH_2 units in analogous hydrocarbon micellar media[20]. Therefore, a carbon equivalent for each of the compounds of our study is given using Ph=1.5C. Comparison of reaction rate constants k_w and k_m, as well as binding constants, K_s, were made for the different hydroxamic acids studied as well as for previously studied compounds and are shown in Table 9.

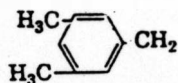From the table we can see that the K_s values increase for increasing $-CH_2-$ equivalent for unsubstituted phenyl (except the branched compound CH_3CH_2CH-). These compounds are $CH_3(CH_2)_8-$, $CH_3(CH_2)_6-$, $Ph(CH_2)_5-$ and $Ph(CH_2)_3-$. For the more substituted phenyl groups such as , and , the K_s values are essentially the same, but greater than $Ph(CH_2)_n-$ of same carbon equivalent. These compounds have more alkyl groups on the periphery of the ring than do the $Ph(CH_2)_n-$.
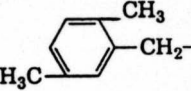
Table 9

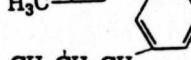### Comparison of the Reaction Rates as Well as Binding Constants for Different Hydroxamic Acids

R in R-CONHOH	Ceq^{*}	k_w L/mol min	k_m^{**} 1/min	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
[phenyl]-$(CH_2)_5$—***	7.5	0.0588	0.0183	15.0	0.84	0.71	0.37
$(CH_3)_2CH$-[phenyl]-CH_2—***	6.5	0.0404	0.0121	24.4	0.58	0.47	0.61
[CH_3,H_3C-phenyl]-CH_2—***	5.5	0.110	0.00240	26.4	0.16	0.093	0.66
[phenyl]-$(CH_2)_3$—***	5.5	0.0482	0.0191	5.38	0.69	0.74	0.13
[H_3C,H_3C-phenyl]-CH_2-#	5.5	0.0434	0.00581	23.63	0.62	0.23	0.59
$CH_3CH_2CH_2$-[phenyl]	5.5	0.00473	0.000549	42.4	0.068	0.021	1.10
[cyclohexyl]-$(CH_2)_3$-	10.0	0.0635	0.0213	20.8	0.91	0.83	0.52
[cyclohexyl]-CH_2-	8.0	0.0149	0.0241	1.52	0.21	0.93	0.038
[cyclopentyl]-CH_2CH_2-	8.0	0.0636	0.0113	15.6	0.91	0 44	0.39

*   Ceq = carbon equivalent, see text.
**   The derived values usually good only to one or two significant figures.
*** Data for these compounds are from references 11 and 14.
\#   D.C.Berndt and William R. Horton, unpublished results.

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

From Table 9 we can also find steric interference for the hydrolysis of branched hydroxamic acids. Steric interference is largest in CH_3CH_2CH- and also occurs in ⬡—CH_2- to some extent. The branching in ⬡—$(CH_2)_3-$ and ⬠—$(CH_2)_2$ appears to be removed far enough from $-CNHOH$ so that these two compounds fit the general pattern for K_s, k_w, k_m. Therefore, the reaction rates (see k_w and k_m) of 2-phenylbutanohydroxamic acid and cyclohexylacetohydroxamic acid are relatively slow although the first compound has a high binding constant and the second compound has $k_m > k_w$. In general, $k_w^{rel} > k_m^{rel}$ except for R = ⬡—CH_2-. Table 10 shows the steric effect of various groups in terms of Taft's E_s parameters derived from ester reactivities[21].

Here a larger negative E_s value means a larger steric effect. The reference compound has $R=CH_3$. Thus the E_s values show the order of steric effect to be

$$\underset{Ph-CH-}{\overset{CH_2CH_3}{|}} > \text{⬡}-CH_2 > \textit{n}\text{-ALKYL}$$
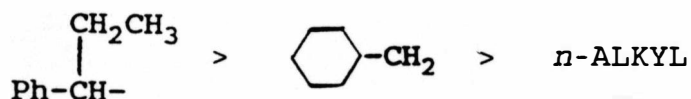
This steric hindrance order also matches our experimental results for the rate constants k_w. Also, the rate is lower for (2-methylbenzyl with CH₃ ortho) than for (3,5-dimethylbenzyl) due to a steric effect in the first compound.
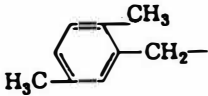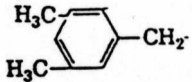
Table 10

Steric Effect Constants

R	E_s [21]
$n\text{-}C_3H_7$	-0.36
$n\text{-}C_4H_9$	-0.39
$n\text{-}C_5H_{11}$	-0.40
$n\text{-}C_8H_{17}$	-0.33
$Ph\text{-}CH_2$	-0.38
$Ph\text{-}CH_2CH_2\text{-}$	-0.38
$Ph\text{-}CH_2CH_2CH_2$	-0.45
⬡$\text{-}CH_2$	-0.98
$\overset{\displaystyle CH_2CH_3}{\underset{\displaystyle Ph\text{-}CH\text{-}}{\big|}}$	-1.5

CHAPTER IV

CONCLUSION

The hydrolysis rate of hydroxamic acids can be enhanced by micellar catalysis with perfluorooctanoic acid as the reactive counterion surfactant in aqueous acetonitrile solution. The extent of rate enhancement depends on the micellar concentration and the structure of the actual hydroxamic acid.

The hydrolysis of hydroxamic acids in micellar solution follows the pseudophase ion exchange model (PPIE). The mathematical expressions derived from the pseudophase ion exchange model can be satisfactorily applied in calculating the overall rate constant k_ψ, water phase reaction rate constant, k_w, micellar pseudophase rate constant k_m, and binding constant for the binding of the organic substrate to the micelle, K_s.

With the assumption that one phenyl ring is equivalent to 1.5 carbons, generally speaking, the more carbon or carbon equivalent a hydroxamic acid has, the more micellar catalysis effects there will be. This can be roughly reflected in the value of binding constant K_s. That is, the bigger the K_s value is, the bigger the micellar catalysis effect will be. This can be understood in the way that the

increase of carbon or carbon equivalent increases the hydrophobic character of a hydroxamic acid, making it more soluble in the micellar pseudophase, so that more micellar effects occur.

The steric effects, as reflected in E_s values, hold in the hydrolysis of hydroxamic acids with perfluorooctanoic acid as the reactive counterion surfactant in aqueous acetonitrile solution. That is, the steric effects are in the following order in the hydrolysis of hydroxamic acids:

$$\underset{\text{Ph-CH-}}{\overset{\text{CH}_2\text{CH}_3}{|}} \quad > \quad \bigcirc\text{-CH}_2 \quad > \quad n\text{-alkyl}$$
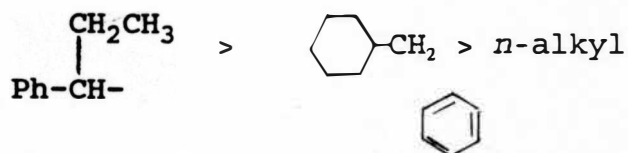
This can explain why CH_3CH_2CH- and $\bigcirc\text{-CH}_2-$ have low reaction rates although the first compound has a relatively high binding constant to the micelle.

The K_s value for R = CH_3CH_2CH-) is higher than expected compared to other compounds and the k_m for R = $\bigcirc\text{-CH}_2-$ is higher than its k_w which is also different from the general trend. Therefore, further study of hydroxamic acids with α- and β- branches is suggested in order to obtain a more complete set of data to further explore chain branching effects in the substrate on micellar catalysis.

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