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Structural Effects on Micellar Catalyzed Reaction of Hydroxamic Acids

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STRUCTURAL EFFECTS ON MICELLAR CATALYZED REACTION OF HYDROXAMIC ACIDS

by

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Nop Utrapiromsuk

To

my mother and father

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INTRODUCTION

For many years scientists have tried to find a model which resembles a biological system, so that they can use this model for studying biological systems in human and in living organisms. Micelle systems provide the environment to mimic enzyme systems to some degree.[1]

Soaps and detergents generate micelles. Soaps and detergents have been used as cleansing agents for a long time. Their cleansing properties are related to micelle formation. Actually, soap is simply a mixture of sodium salts of long chain fatty acids, $R\text{-}COO^{-}\ Na^{+}$, and some detergents are general sodium salts of straight chain alkyl hydrogen sulfates, for example

$$n\text{-}C_{11}H_{23}CH_2OH \xrightarrow{H_2SO_4} n\text{-}C_{11}H_{23}CH_2OSO_3H \xrightarrow{NaOH}$$

$$n\text{-}C_{11}H_{23}CH_2O\overset{\ominus\ \oplus}{SO_3}Na$$

Soaps and detergents, in general, are called "surfactants", which when dissolved in water will form or be dispersed in spherical clusters (or at some concentrations, ellipsoid[1]) called "Micelles", which is "like an air bubble in water environment"[2]. So in fact the surfactants are not really all dissolved in water but partially dissolved. That is so because a surfactant molecule has a polar end such as

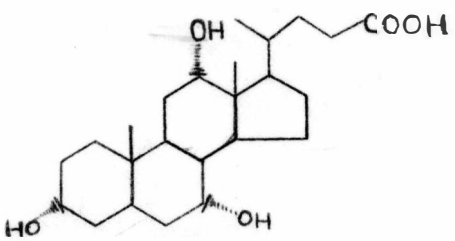
$$\overset{O}{\overset{\|}{C}}\text{-}O^{\ominus}\ Na^{\oplus} \quad \text{or} \quad -SO_3^{\ominus}Na^{\oplus}$$

and also a nonpolar end, mainly, the long hydrocarbon chain,

such as an alkyl group. The polar end, related to water-soluble substances, is said to be hydrophilic. The nonpolar end, related to water-insoluble substances, is said to be hydrophobic. Therefore, the surfactant is an amphipathic compound.

Surfactants may be classified[1], depending on the chemical structure of the hydrophilic moiety bound to the hydrophobic portion, as

1. Cationic, for example, dodecyl ammonium chloride ($CH_3(CH_2)_{11}NH_3Cl$)
2. Anionic, for example, sodium 1-dodecanesulfonate ($CH_3(CH_2)_{11}SO_3Na$)
3. Nonionic, for example, polyoxyethylene(3)decanol ($CH_3(CH_2)_9O\text{-}(CH_2CH_2O)_3H$)
4. Ampholytic (Zwitterionic), for example, C-dodecyl N,N,N-trimethyl glycine ($CH_3(CH_2)_{11}\text{-}CH(COO^{\ominus})N^{\oplus}(CH_3)_3$)
5. Naturally occurring surfactants, for example, cholic acid



When a surfactant is dissolved in water, in a certain concentration range, micelles will be formed. In general, micelles are aggregates of surfactant molecules. Therefore a micelle consists of several surfactant molecules with an aggregation number (N) which will vary depending upon the concentration of surfactant, the presence of inorganic and organic additives and also on the temperature.[1] Generally, the numbers (N) in aqueous solution are in the range 10 to 100.[1]

The structure of an ionic micelle is shown in cross section in Figure 1. The average radii of micelles is 12-30°A. Generally, micelles at concentrations close to their critical micelle concentrations

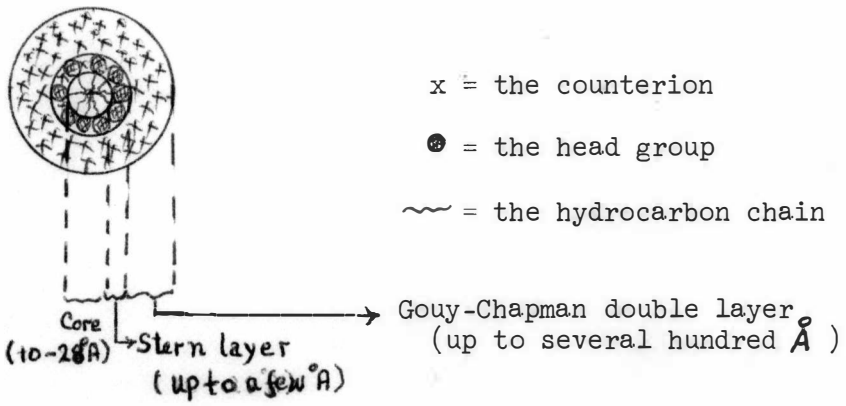


Figure 1. The Cross-Section of an Ionic Micelle

(CMC) are roughly spherical[1], however, recent calculations based on geometrical considerations indicated ellipsoidal shapes for the most common small micelles.[3,4] The hydrophobic part of the aggregate forms the "core" of the micelle while the polar head groups are located at the micelle-water interface in contact with and hydrated by a number of water molecules. The charged head groups and counterions of the ionic micelles are located in a compact region, known as the "Stern layer". The compactness of the Stern layer is responsible for the reduction of the net charge on the micelle. Most 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. The component parts of the micelle are in rapid equilibrium with individual surfactant molecules in the bulk solution.

As mentioned before, a minimum concentration of surfactant is

necessary in order to form micelles or to study the properties of micelles. The narrow range of concentration at which the micelles first become detectable is called the "critical micelle concentration" (CMC). For surfactants containing a long chain hydrocarbon group, the value of the CMC is between 10^{-4} to 10^{-2} M. The value of the CMC is dependent on:[1,2]

1. The size of hydrocarbon chain length, the longer the chain the lower the CMC.
2. Polar group, chain branching tends to increase CMC.
3. Temperature and
4. Any additional substances present.

For the study of micellar catalysis in acidic hydrolysis systems, the surfactants generally used are anionic ones which are alkali or alkaline earth-metal salts of mono- or poly- basic carboxylic acids and of sulfuric, sulfonic, or phosphoric acid containing a saturated or unsaturated hydrocarbon substituent. Some of the manufactured surfactants are obtained from hydrolysis of fats and oils followed by neutralization with the appropriate hydroxide when the salt is desired. However, commercially available surfactants are often not pure so purification is required before use in chemical studies.

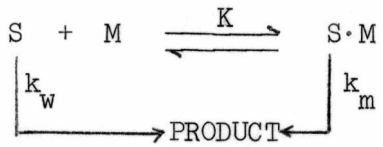
General Features of Micellar Catalysis and Investigation of Past Work

In a micellar catalysis study, the concentration of substrate and product are very low compared to the surfactant concentration. This is so because micelles are easily perturbed, highly mobile structures, so that the substrate concentration preferably should be much

lower than that of the surfactant in order to minimize perturbation of micellar structures.[2] In addition, the lower substrate concentration will allow the detection of partition of the substrate between the bulk phase and micellar phase. Specifically, for acidic hydrolysis in micellar systems, an anionic surfactant is chosen to provide micelles, for example, sodium lauryl sulfate (NaLS) or sodium 1-dodecanesulfonate. In that system both covalent and hydrogen bonding interactions between surfactant and all the reagents in the system could be important.[5]

An approximate model reaction scheme of micellar catalysis is shown in Scheme I,[1,2]

SCHEME I



where S is substrate, M is micelle, K is an equilibrium constant, k_w and k_m are rate constants for product formation outside and within the micelle respectively. This model leads to the relationship.[1]

$$1/(k_w - k_{obs.}) = 1/(k_w - k_m) + 1/(k_w - k_m)\ N/K(C_D - CMC) \qquad (1)$$

where $k_{obs.}$ is the observed pseudo first order-rate constant,[1] N is the micelle aggregation number, and C_D is the total surfactant concentration. Limitations of equation (1) have been discussed,[1,2,5] namely, that:

1. It has been assumed that the substrate does not complex with the monomeric surfactant.

2. The association has 1:1 stoichiometry.

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

4. The rate of reaction of many bimolecular reactions goes through a maximum with increasing C_D, however, most reactions exhibiting micellar catalysis are inhibited by counterion, and the larger the ion, the greater is the effect. This behavior has been rationalized by assuming a competition between the reactant and the electrolyte for a "binding site" on or in the micelle, also the ability to alter the micellar structure.[1,2]

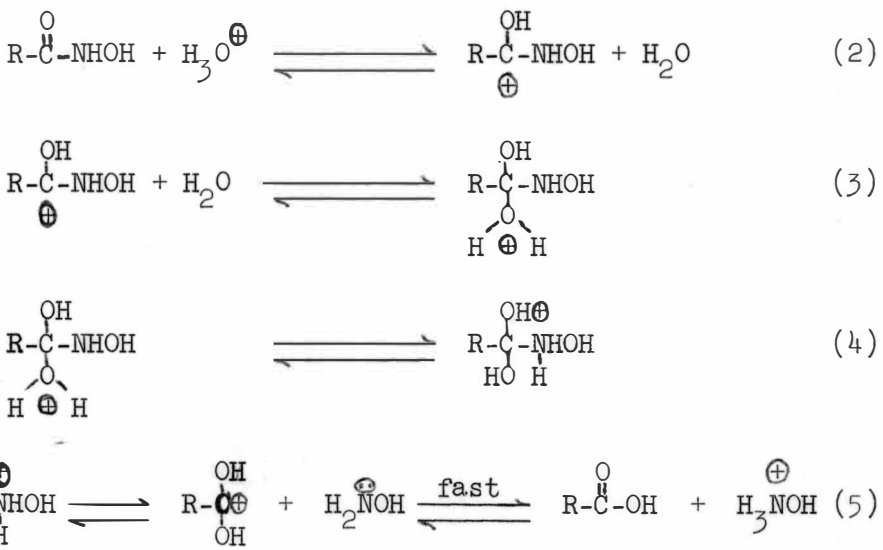
5. In the acid hydrolysis, the hydronium ions themselves can be partitioned between aqueous and micellar phases. But the way equation (1) is written only takes into account the partitioning of the reactant, the substrate S, between water and the micelle and ignores any partitioning of other reagents.[5]

6. Changes in micellar structure with change in surfactant concentration.

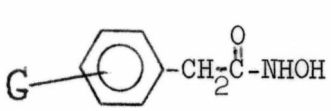
For micellar catalysis of amide hydrolysis, there seems to be only one report.[6] Mechanistic studies of the acidic hydrolysis of hydroxamic acids have been reported[7] and the mechanism is illustrated in Scheme II.

These studies showed first order dependence on hydronium ion and first order-rate dependence on hydroxamic acid and pseudo first-order rate dependence in the presence of excess hydrochloric acid. Recently, there is one report[8] of a micellar catalyzed reaction of a hydroxamic acid. The reaction studied was the acid catalyzed hydrolysis of octanohydroxamic acid and phenylacetohydroxamic acid in the presence of sodium lauryl sulfate. Making use of equation (1), a graph of $1/(k_w - k_{obs.})$ vs. $1/(C_D - CMC)$ using the data for octanohydroxamic

SCHEME II



acid in which the CMC was taken as 10^{-3} M and C_D was in the range 0.01-0.06 M in 0.203 N HCl at 50.7°C, yielded $k_m = 44.8 \times 10^{-5}$ sec.$^{-1}$, K/N = 119 and the catalytic ratio, k_m/k_w is 9.74. The report also noted that the hydrolysis mechanism in the micellar environment might be analogous to that in the absence of micelles. It was reported also that the micellar effect varies as a function of substrate groups in the hydroxamic acid. Due to that statement in the report above further investigation is required. Therefore the objective of this thesis is the study of micellar catalysis of acid hydrolysis of hydroxamic acids in a chosen surfactant with various substrates. The general structure of the hydroxamic acids studied is:



G is the substituent group. Possible correlation of k_m and K/N with

lipophilic substituent parameters which measure the tendency of a group to be attracted to an organic environment compared to a water environment was also to be investigated.

EXPERIMENTAL PART

Preparation of Methyl p-Methylphenylacetate ($H_3C-C_6H_4-CH_2-C(=O)-OCH_3$)

The general procedure given by Shriner et al[9] was used. The starting reagent, p-methylphenylacetic acid was checked for purity by determining the melting point: found 90-92°C (literature[10] 91-93°C). The acid (25 g, 0.166 mole) was refluxed with 134 ml (3.32 mole) of A.C.S. grade methanol and 8.00 ml of concentrated sulfuric acid (97%) for forty-two hours. The resulting solution was quenched with solid sodium carbonate and made basic (~pH 8, determined by pH paper) with aqueous 2M sodium hydroxide. The crude methyl ester was extracted with three 50 ml portions of diethyl ether. The ether solution was dried with calcium chloride (anh.), then with magnesium sulfate (anh.) over night. Evaporation of the ether solution with air yielded a white precipitate and a liquid. The layers were separated with dichloromethane and the organic layer was dried with magnesium sulfate (anh.) over night. Evaporation of excess dichloromethane with air yielded the solid yellow ester. The infra-red (IR) and proton nuclear magnetic resonance (NMR) spectra were obtained and were consistent with the structure of methyl p-methylphenylacetate, yield 26.5% (based on the acid); see Table 1 and Figure 2 for spectral results.

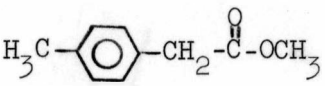
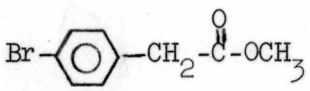
Preparation of Methyl p-Bromophenylacetate ($Br-C_6H_4-CH_2-C(=O)-OCH_3$)

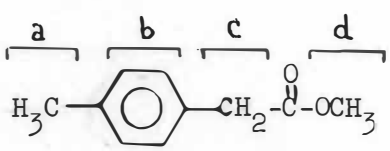
The method was the same as for the preparation of methyl

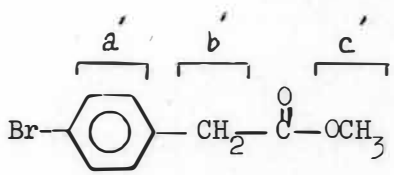
p-methylphenylacetate. p-Bromophenylacetic acid (25 g, 0.116 mole) was refluxed with 100 ml (2.47 mole) of A.C.S. grade methanol and 5.00 ml of concentrated sulfuric acid for forty-five hours. A deep yellow solid was obtained, yield 96.5% (based on the acid). The result as shown in Table I and Figure 2 are consistent with the structure for methyl p-bromophenylacetate.

TABLE I

INFRARED ANALYSIS OF PREPARED ESTERS

Compound	$V_{C=O}(cm^{-1})$	$V_{aromatic\ C-H\ str.}(cm^{-1})$
	1725	3000
	1727	3000





δ a : b : c : d = 2.30(S):7.07(S):3.48(S):3.60(S) δ a' : b' : c' = 7.25 : 3.49(S):3.63(S)

Integration ratios; a : b : c : d = 32:40:18:36 a' : b' : c' = 44:20:36

Figure 2. NMR analysis of prepared esters, using CCl_4 as solvent.

Preparation of Phenylacetohydroxamic acid ((I) or (p-H))

The compound was prepared by Dr. D. C. Berndt.

Preparation of N-Hydroxy-4-methylphenylacetamide (CH_3-⟨⬡⟩-CH_2-$\overset{O}{\overset{\|}{C}}$-NHOH) ((II) or (p-$CH_3$))

Potassium hydroxide (7.24 g, 0.129 mole) was dissolved in hot methanol (20 ml) to give solution 1. Hydroxylamine hydrochloride (6.0 g, 0.086 mole) was dissolved in hot methanol (32 ml) to give solution 2. Solution 1 and 2 were cooled to about 35°C, 1 was added to 2, and a white precipitate formed which was KCl. The mixture was cooled to 5°C. The KCl was removed by filtration. Methyl p-methylphenylacetate (7.06 g, 0.043 mole) was added to the filtrate, and the solution was swirled for a while. It was let stand for forty-two hours. The resulting solution was then buffered to pH-6 with acetic acid (against pH paper) and then concentrated via an air stream to yield crude crystals (A). The crystals were collected and gave an intensively positive ferric chloride test for hydroxamic acid. An IR spectrum of A was obtained. Further concentration and cooling of the mother liquor in a freezer yielded more crystals (B). The crystals were collected by filtration and an IR spectrum of B was obtained. Comparison of the spectra from A and B showed them to be identical. Further concentration and cooling yielded crystals (C). Crystals A, B, and C were combined and recrystallized with 1:2 (v:v) ethyl alcohol : water twice and air dried. During the determination of the melting point, it was noted that when the sample was inserted into

the temperature bath of the Thomas Hoover apparatus, it bubbled when the temperature was close to the melting point. The results are in Table II. Some decomposition appears to occur during melting. The pure product was structurally analyzed by IR, NMR and an elemental analysis by Galbraith Lab., Inc., as shown in Table III, Figure 3, and Table IV, respectively. The yield was 59.2% (based on the ester).

TABLE II

MELTING POINTS OF HYDROXAMIC ACIDS
DETERMINED WITH A THOMAS-HOOVER APPARATUS

Compound	Insert temperature at (°C)	mp°C	Note
II	145	155-156	Bubble
III	142	153-158	Bubble
II	150	158-159	No bubble
III	145	157-158	No bubble

Preparation of N-Hydroxy-4-bromophenylacetamide (Br--CH_2-C(=O)-NHOH) ((III) or (p-Br))

The same procedure was used as for the preparation of II, but the quantities used were different.

Solution 1: KOH (13.7 g, 0.244 mole) dissolved in 50 ml of hot methanol.

Solution 2: Hydroxylamine hydrochloride (11.4 g, 0.163 mole) dissolved in 65 ml of hot methanol.

Methyl p-bromophenylacetate (18.7 g, 0.0814 mole) was the ester

used. The crude crystals were recrystallized from ethylacetate first, then twice with 1:2 (v:v) ethyl alcohol:water. The melting point, IR and NMR spectra and elemental analysis were obtained and the results are given in Tables II and III, Figure 3, and Table IV, respectively. The yield was 78.1% (based on the ester).

TABLE III

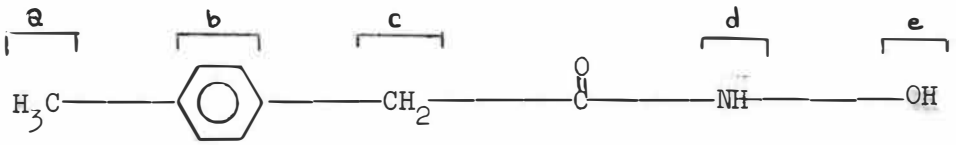
IR ANALYSIS OF HYDROXAMIC ACIDS

Compound	$\nu_{C=O}(cm^{-1})$	$\nu_{N-H}(cm^{-1})$
II	1618	3200
III	1625	3200

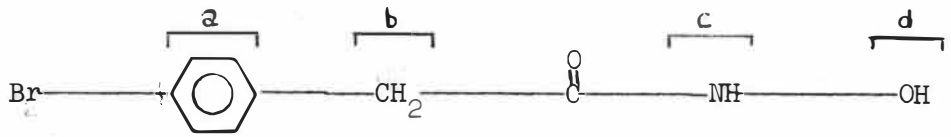
TABLE IV

ELEMENTAL ANALYSIS OF HYDROXAMIC ACIDS

Compound	Analysis	% C	% H	% N	Formula
II	Observed	64.87	6.85	8.30	$C_9H_{11}O_2N$
	Calculated	65.43	6.71	8.48	
III	Observed	41.67	3.76	5.79	$C_8H_8O_2NBr$
	Calculated	41.76	3.51	6.09	



δ a : b : c : d : e = 2.3(S):7.14(S):3.25(S):10.57(broad):8.73(broad)



δ a : b : c : d = 7.36(q):3.3(S):10.66(broad):8.84(broad)

Integration ratios: a : b : c : d = 52:33:12:12

Figure 3. NMR analysis of hydroxamic acids, using DMSO as solvent.

Preparation of Standard 0.101 N HCl

The procedure for preparation of the standard solution and the titration technique followed the method as indicated in Skoog and West.[11] The acid solution was prepared by using double distilled water. Standard sodium hydroxide solution, which was standardized against potassium hydrogen phthalate (KHP) as a primary standard, was used against HCl solution. Phenolphthalein was the indicator. The following Tables V and VI list the results of the standardization.

TABLE V

STANDARDIZATION OF NaOH AGAINST 0.100 M KHP

Trial	0.100 M KHP,ml	NaOH,ml	Ave.ml NaOH	S*	N NaOH
1	20	20.1			
2	20	20.2	20.2	0.0580	0.0990
3	20	20.2			

* s = standard deviation

TABLE VI

STANDARDIZATION OF HCl AGAINST 0.00990 N NaOH

Trial	HCl,ml	NaOH,ml	Ave.,ml	s*	N HCl
1	10	10.1			
2	10	10.2	10.2	0.0570	0.101
3	10	10.2			

* s = standard deviation

Preparation of Ferric Chloride Solution

The $FeCl_3$ solution was prepared as the following ratio:

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

$FeCl_3$ solution is the indicator for detecting hydroxamic acids which give a maroon or violet colored iron-hydroxamate complex.[12]

Purification of and Tests of the Surfactant

The surfactant, $CH_3(CH_2)_{11}SO_3^{\ominus}Na^{\oplus}$, sodium 1-dodecanesulfonate, was prepared by Dr. D. C. Berndt. It was further purified by two recrystallizations from 95% ethanol. The purity was checked by an elemental analysis (Galbraith Laboratories, Inc., Knoxville, TN) and by comparison of IR and NMR spectra with spectra reported in the literature.[13,14] The surfactant was stored in a desiccator with potassium hydroxide (solid) as drying agent.

TABLE VII

ELEMENTAL ANALYSIS OF SODIUM 1-DODECANESULFONATE

Compound	Analysis	% C	% H	% S
Sodium 1-dodecane-sulfonate	Observed	52.91	9.26	11.89
	Calculated	52.91	9.25	11.77

The pure sodium 1-dodecanesulfonate was tested for resistance to acidic hydrolysis by refluxing 0.00180 moles of the surfactant with 0.101 N HCl for eight hours, then all the liquid was removed over a two day period by using an air stream. IR and NMR spectra were obtained for the residue. The spectra were identical to those of the starting surfactant.

The spectrophotometric method for hydroxamic acid analysis used in earlier studies[7,8] was checked in the presence of the surfactant.

Beer's Law appears to apply--See Table VIII. Pipets were used to measure the aliquots with the final volume being 50 ml after dilution with distilled water.

Also the pH of pure surfactant in solution was measured with a pH meter[a] to check for presence of acids--see Table IX.

TABLE VIII

THE SPECTROPHOTOMETRIC METHOD FOR A HYDROXAMIC ACID IN THE PRESENCE OF THE SURFACTANT

Sample	ml of 0.0120M surfactant	ml of 0.0005M I	$FeCl_3$ solution	Ave. absorbance at 520 nm
A	25	3	10 ml	0.255
B	25	6	10 ml	0.521
Blank	25	0	10 ml	0.000

TABLE IX

pH OF SURFACTANT IN SOLUTION WITH THE pH METER[a]

Sample	Ave. pH
Distilled water	4.9
$1x10^{-2}$ M surfactant	5.2
$1x10^{-1}$ M surfactant	5.1

[a] "Coleman" metrion II pH meter

Compounds I, II, and III were tested for solubility at 0.000500 Molar in water, at room temperature and at 50°C. Dissolution occurred slowly at room temperature, more rapidly with shaking at 50°C.

Calibration of Thermometer

Dr. D. C. Berndt calibrated the thermometer against a standard one. Result: $T_{actual} = T_{observed} + 0.1°C$.

Preparation of Reaction Solution and Kinetic Procedures

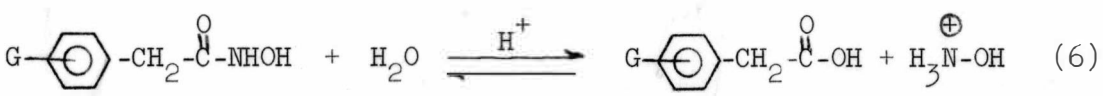
The reaction solutions were prepared as follows:

1. A solution of the surfactant at the desired concentration in 0.101 N HCl was prepared.
2. The soap solution (25 ml) was pipeted into a reaction vessel (a glass-stoppered test tube). The reaction vessel was then placed in a constant temperature oil bath for about 10-15 minutes (the temperature is set at 50.13±0.12°C) to get a uniform temperature.
3. The hydroxamic acid (pre-weighed to yield a concentration of 0.0005M) was added to the solution in the reaction vessel and shaken to get complete solution.
4. After the hydroxamic acid was completely dissolved, the solution was equilibrated in the temperature bath for 10-20 minutes.
5. A ferric chloride solution (10 ml) was pipeted into seven 50 ml volumetric flasks. One of these serve as a blank which contains 10 ml of $FeCl_3$ solution and 3 ml of the soap solution diluted with water to the mark.

Samples of the reaction mixture were taken with a 3 ml pipet from time to time. The time of the samples was recorded as that time when the 3 ml pipet had finished draining into the $FeCl_3$ indicator solution in the 50 ml volumetric flask. The flask was diluted with water to the mark, and inverted ten times. The absorbance of the solution vs.

the blank was taken two times with a Beckman D. U. spectrophotometer with the wave length set at 520 nm. The average absorbance value was recorded. Ten cm cells were used for the absorbance measurements. For each hydroxamic acid rate measurements in six different concentrations of surfactant (1.00×10^{-3}, 1.00×10^{-2}, 3.00×10^{-2}, 5.00×10^{-2}, 7.00×10^{-2}, and 0.100 M in 0.101 N HCl) and in 0.101 N HCl without surfactant were carried out.

Since these experiments involve the acidic hydrolysis of hydroxamic acids, the chemical reaction in the vessel is as indicated in equation (6):



(6)

The hydroxamic acid concentration is proportional to the absorbance of the ferric chloride-hydroxamic acid solution. The observed rate is pseudo first order since the hydrochloric acid concentration is in large excess compared to the hydroxamic acid concentration.

The pseudo first-order rate constants, k_{obs}, for all runs were determined via the relationship between measured absorbance and hydroxamic acid concentration. The following derivation illustrates this relationship between measured absorbance, k_{obs}, and hydroxamic acid concentration.[15] Since the hydrolysis rate is pseudo first-order,

$$\log \left[a/(a-x) \right] = kt/2.303 \qquad (7)$$

where a = initial hydroxamic acid concentration,
x = concentration of acid reacted in time t, and
k = first-order rate constant.

Concentration of the hydroxamic acid may be related to some physical property, λ , which is directly proportional to concentration. For the rate expression this may be illustrated as:

$$\log \left[a/(a-x) \right] = \log \left[(\lambda_{\infty} - \lambda_o)/(\lambda_{\infty} - \lambda) \right] \quad (8)$$

where λ_{∞} = measured property at time infinity, and

λ_o = measured property at time = 0.

Since absorbance (A) is directly proportional to the concentration of hydroxamic acid, equation (8) may be written as:

$$\log \left[a/(a-x) \right] = \log \left[(A_{\infty} - A_o)/(A_{\infty} - A_t) \right] \quad (9)$$

Since $A_{\infty} = 0$ for the hydroxamic acid-ferric ion complex, because at time infinity no hydroxamic acid remains, the rate expression is finally represented as:

$$\log A_t = -k_{obs} t/2.303 + \log A_o \quad (10)$$

A plot of the log of measured absorbance ($\log A_t$) versus time yields a slope of $-k_{obs}/2.303$. A least squares treatment of the log of absorbance versus time data was used for actual determination of the observed pseudo first-order rate constants. A typical example of rate data is as follows:

Compound: II, initial concentration 0.0005 M
Temperature: 50.13±0.12 C, solvent 0.101 N HCl
Wave length: 520 nm, slit 0.15 mm
Cell # I

	O'clock	Time (hr)	A	Ave. A
1	10:00 A.M	0	0.168 0.167	0.168
2	11:30 A.M.	1.5	0.153 0.153	0.153
3	1:00 P.M.	3	0.141 0.141	0.141
4	3:00 P.M.	5	0.121 0.122	0.122
5	5:00 P.M.	7	0.109 0.108	0.109
6	8:00 P.M.	10	0.089 0.0895	0.089

From equation (10) and the least squares result,

Correlation Coefficient (r) = -0.9995
Slope = -0.02746
Intercept = -0.7730

The data is shown graphically in Figure 4 and from the result yields, $k_{obs} = -2.303 \times (-0.02746) = 6.32 \times 10^{-2}$ hr^{-1}. Similarly data from reaction in cell # II yields $k_{obs} = 6.27 \times 10^{-2}$ hr^{-1}. So the average $k_{obs} = 6.30 \times 10^{-2}$ hr^{-1} or 1.66×10^{-5} sec^{-1}. Table X summarizes the kinetic data of the three compounds. An example calculation using equation (1) is given in Table XI.

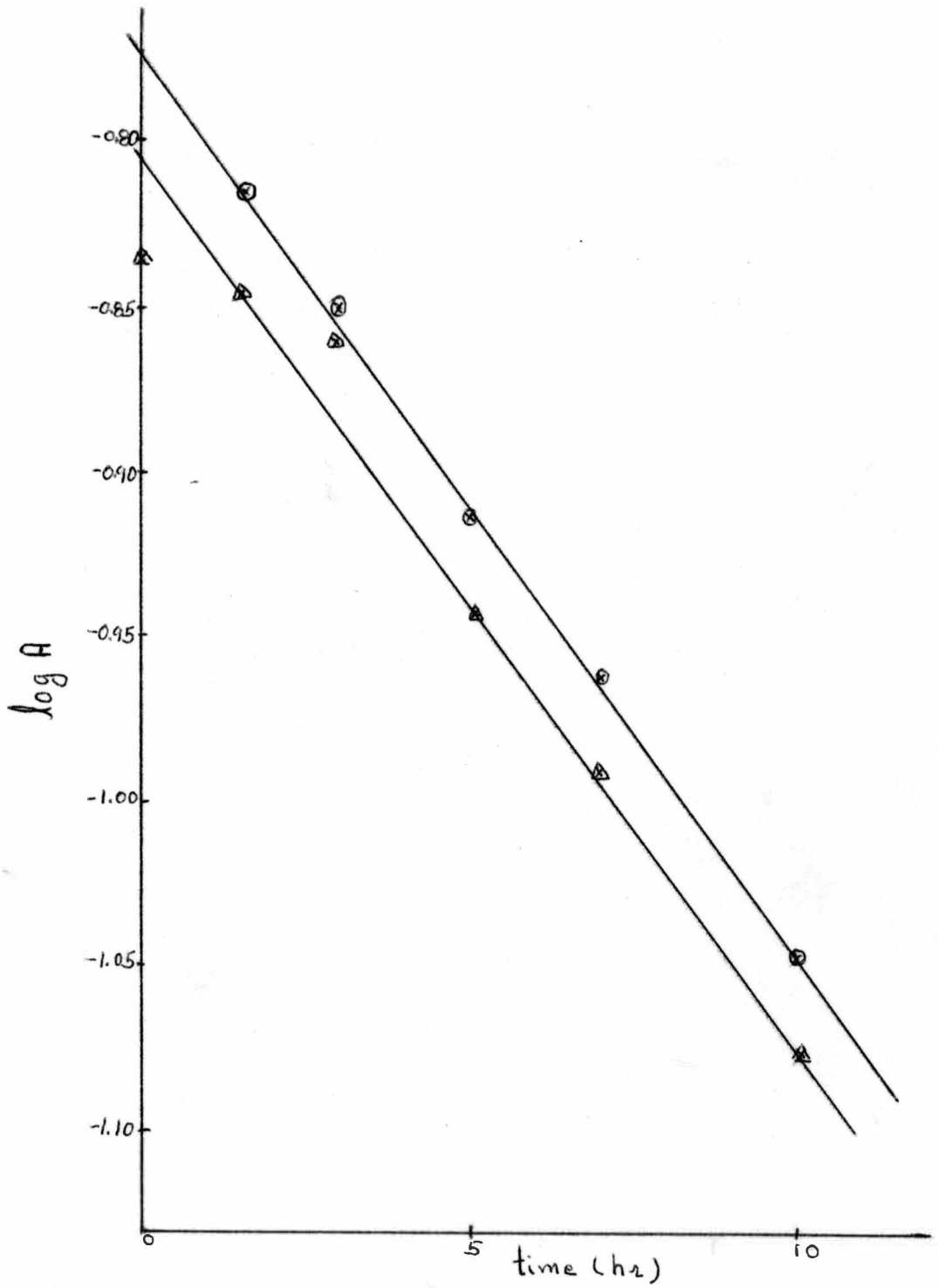


Figure 4. The graph of log A_t of II in 0.101 N HCl for cell # I (⊗) and cell # II (△).

TABLE X

KINETIC DATA FOR HYDROXAMIC ACID HYDROLYSES IN 0.101 N HCl
AT 50.1°C AS A FUNCTION OF SODIUM 1-DODECANESULFONATE CONCENTRATION

Compound	Ave. k_{obs} (sec^{-1}) and half-lives ($t_{1/2}$)(hr)													
	C_D	0		0.00100		0.0100		0.0300		0.0500		0.0700		0.100	
		$k \times 10^5$	$t_{1/2}$	$k \times 10^5$	$t_{1/2}$	$k \times 10^5$	$t_{1/2}$	$k \times 10^5$	$t_{1/2}$	$k \times 10^5$	$t_{1/2}$	$k \times 10^5$	$t_{1/2}$	$k \times 10^5$	$t_{1/2}$
I		1.66	11.6	1.58	12.2	2.71	7.09	5.03	3.83	6.30	3.06	7.63	2.52	8.62	2.23
II		1.75	11.0	1.84	10.5	5.16	3.73	10.2	1.88	13.0	1.49	14.2	1.35	15.4	1.25
III		1.51	12.8	1.50	12.8	7.60	2.52	15.5	1.24	18.3	1.05	19.6	.983	19.5	.987

TABLE XI

CALCULATION OF PARAMETERS FOR EQUATION (1)

$k_{obs}(sec^{-1})$	$1/(k_w-k_{obs})$	$C_D(\underline{M})$	$1/(C_D-CMC)$
$1.02x10^{-4}$	$-11.8x10^{3}$	0.03	50
$1.30x10^{-4}$	$-8.92x10^{3}$	0.05	25
$1.42x10^{-4}$	$-8.02x10^{3}$	0.07	16.7
$1.54x10^{-4}$	$-7.35x10^{3}$	0.10	11.1

Note: Compound is II, CMC = 0.01 M.

$k_w = 1.75x10^{-5}$ sec^{-1}

From least squares r is -0.9999, intercept, $1/(k_w-k_m)$ is $-6.09x10^{3}$ sec^{+1} and slope, $\left[1/(k_w-k_m)\right](N/K)$ is $-1.42x10^{-2}$. So

$$K/N = 53.3$$

$$k_m = 1.82x10^{-4} \text{ sec}^{-1}$$

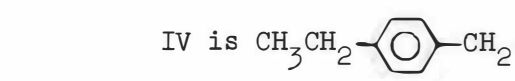
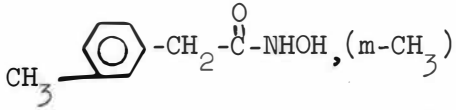
Figure V and Table XII are the example and summarizes the results for correlation of the data for five hydroxamic acids by equation (1). Equation (1), as discussed in the previous section, does not apply over the whole range of surfactant concentration for bimolecular reactions. First, C_D must be above the CMC and second, C_D must not be above the value for which k_{obs} is a maximum. The C_D ranges used in the calculations are given in Table XII.

TABLE XII

THE RESULTS FOR CORRELATION OF THE DATA FOR FIVE HYDROXAMIC ACIDS BY EQUATION (1)

Compound	K/N	k_m (sec^{-1})	k_w (sec^{-1})	k_m/k_w	C_D range (M)
I	27.0	1.11×10^{-4}	1.66×10^{-5}	6.72	0.03 - 0.1
II	53.3	1.82×10^{-4}	1.75×10^{-5}	10.4	0.03 - 0.1
III	98.4	2.26×10^{-4}	1.51×10^{-5}	15.0	0.03 - 0.07
IV[a,b]	129.	2.13×10^{-4}	1.79×10^{-5}	12.0	0.024 - 0.07
V[c,b]	60.0	1.55×10^{-4}	1.70×10^{-5}	9.15	0.02 - 0.07

[a, c] The hydroxamic acids were prepared and the kinetic studies were performed by S. S. Jaglan, where:

IV is  , (p-CH_3CH_2), V is  , (m-CH_3)

[b] S. S. Jaglan, Department of Chemistry, Western Michigan University, unpublished results.

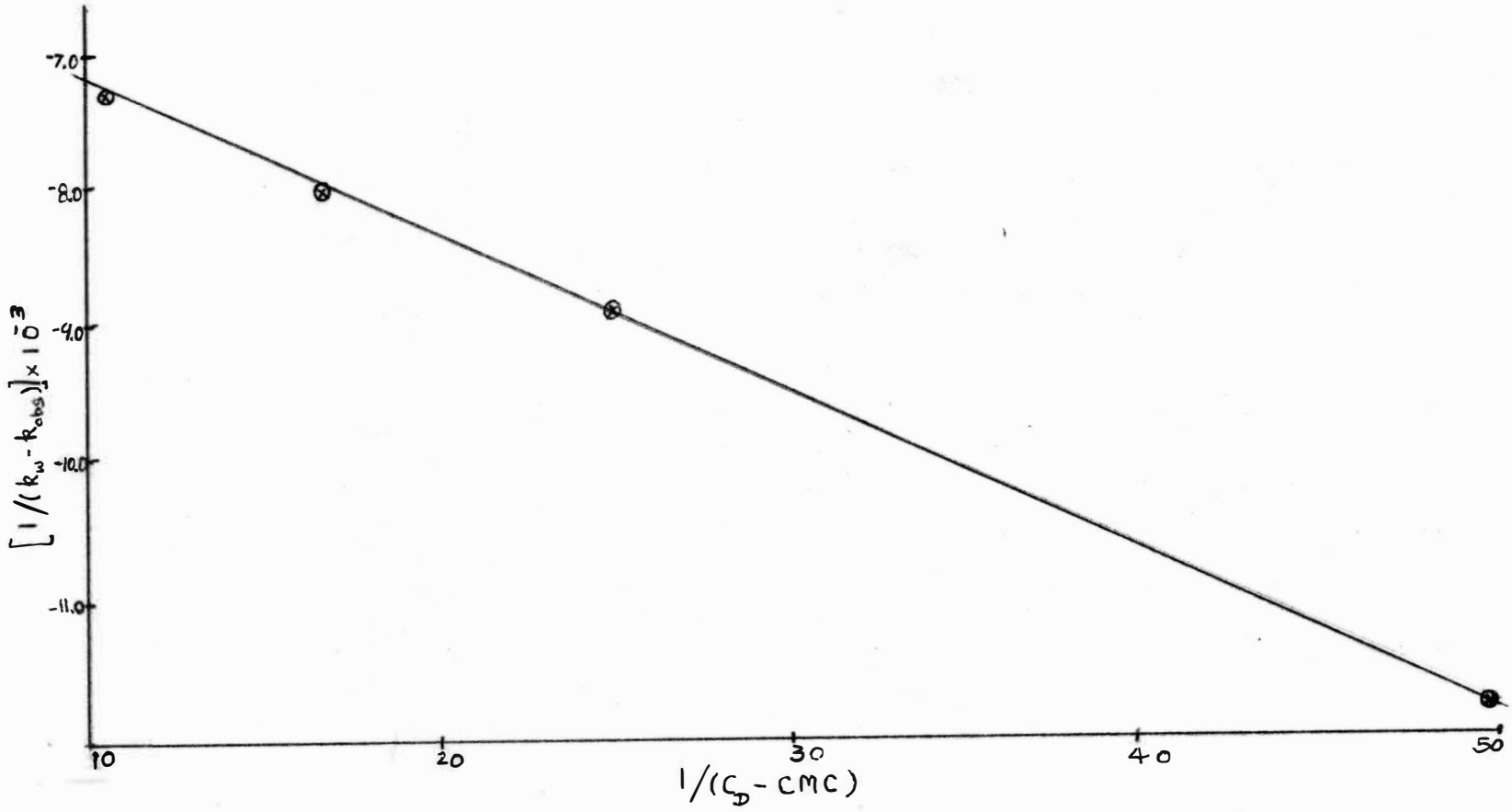


Figure 5. The graph of $1/(k_w - k_{obs})$ vs. $1/(C_D - CMC)$ of II, from the data in Table XI.

RESULTS AND DISCUSSION

In this experiment, the condition has been chosen, such as acid concentration of HCl is 0.101 N and the temperature is 50.13±0.12°C, because the rate of the reaction is pH dependent, and 0.1 M HCl at 50°C produces a reasonable reaction time. In addition, the temperature 50°C is higher than room temperature so by the time an aliquot of the reaction solution is pipeted into the $FeCl_3$ solution at room temperature, the rate of the reaction is considerably reduced.

Initially sodium dodecylsulfate was used as the surfactant but since it undergoes hydrolysis in aqueous acid solution,[1] there were some problems in using it. Therefore sodium 1-dodecane sulfonate was chosen as the surfactant.

From the results shown in Table X, it can be seen that the surfactant has a significant effect upon the hydrolysis rates above the CMC. Compare the $t_{1/2}$ in different concentrations of the surfactant, they decrease as the surfactant concentration increases. However, as mentioned before, micellar systems often reach a maximum catalytic effect. This type of behavior is illustrated in Figure 6 in which k_{obs} is given as a function of surfactant concentration. This shows that there is an optimum concentration of surfactant in a given set of conditions.

Table XII shows that the kinetic ratio, k_m/k_w, are all greater than one. That means in the model of Scheme I, that the reaction within the micelle is more predominant than outside the micelle;

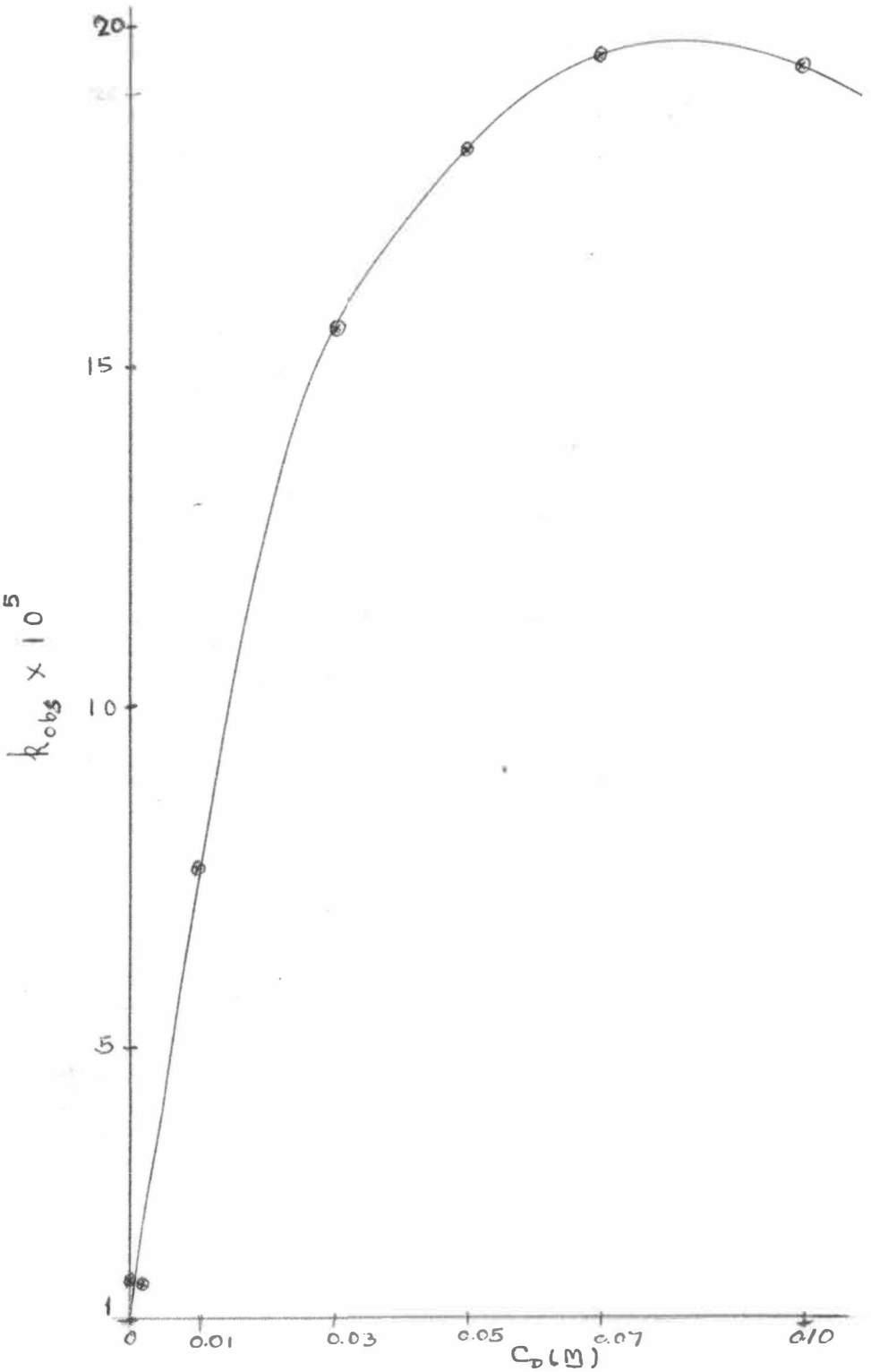


Figure 6. The graph of III by Plotting k_{obs} vs. C_D, the data are from Table X.

therefore, the competition between these two parameters, k_m and k_w, play major roles in the value of k_{obs}.

Comparison of the kinetic ratio of the substituted hydroxamic acids indicates that the order of the ratio, k_m/k_w, is p-Br> p-CH_3CH_2> p-CH_3> m-CH_3> p-H. This parallels the order of the k_m values.

The effect of structure on micellar catalysis can be examined by testing for possible correlations of log(K/N) and log k_m with certain structural parameters or substituent constants. One such parameter is the "lipophilicity" substituent constant, π, defined by:

$$\pi = \log P_x - \log P_H \qquad (11)$$

where P_x is the partition coefficient of the substituted benzene and P_H is the partition coefficient of benzene, and by definition

$$P = C_{octanol}/C_{water} \qquad (12)$$

where C is concentration. The aggregation number, N, although unknown, will be the same for all the compounds listed in Table XII since the reaction conditions were the same for each compound. Therefore K/N may be used as a measure of K. The presence of other compounds as well as temperature changes influence the value of N. N for sodium 1-dodecanesulfonate under one set of conditions has been reported as 54[1]. Therefore the K values for the compounds in the present study are large values. Figure 7 shows the linear correlation between log K/N and π ($r = 0.9924$, F-test[16] significant within 0.1% level). The correlation of log K/N shows dependence for K on hydrophobicity.

This is reasonable since the Stern layer of a micelle is less polar than water[17] and since the interior of the micelle is hydrophobic.

Also log k_w shows a good linear correlation with σ° which is the substituent constant analogous to the Hammett substituent constant except that it is derived for use with systems in which the reaction center is separated from the benzene ring by a saturated group--in the present case, a CH_2 group. Figure 8 shows the correlation ($r = -0.9820$, F-test shows significance within the 1% level)[16]. The reaction constant, ρ, has a value of -0.1746.* It should be noted, however, that the range of σ° values is small. This correlation would be expected since k_w is the rate constant in the aqueous environment only.

It is possible that log k_m might be a function of σ° (electrical or polar effect of the substituent group) and π (lipophilicity). By assuming that polar and lipophilicity effects are separable and can be treated as a sum, equation (13) results:

$$\log k_{m_G} = \rho\sigma^\circ_G + \kappa\pi_G + \log k_{m_H} \qquad (13)$$

in which α is a susceptibility constant. A least squares treatment yields:

$$\log k_{m_G} = 0.125\,\sigma^\circ_G + 0.299\pi_G - 3.94218 \qquad (14)$$

The coefficient of multiple correlation is 0.96996 but the F-test indicates that the correlation is not significant at the 5% level. Thus equation (13) does not yield a satisfactory correlation even though

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* Figure 8. The equation is:
$\log k_{w_G} = \sigma^\circ\rho + \log k_{w_H}$., ρ is the slope.

TABLE XIII[a]

THE LINEAR FUNCTION OF LOG K/N AND π

	K/N	log K/N	π[b]
p-H	27.0	1.43	0.
p-CH_3	53.3	1.73	0.56
p-CH_3CH_2	129.	2.11	1.02
p-Br	98.4	1.99	0.86
m-CH_3	60.0	1.78	0.56

[a] The data are for the Figure 7

[b] Lipophilicity constants, π, Reference 18

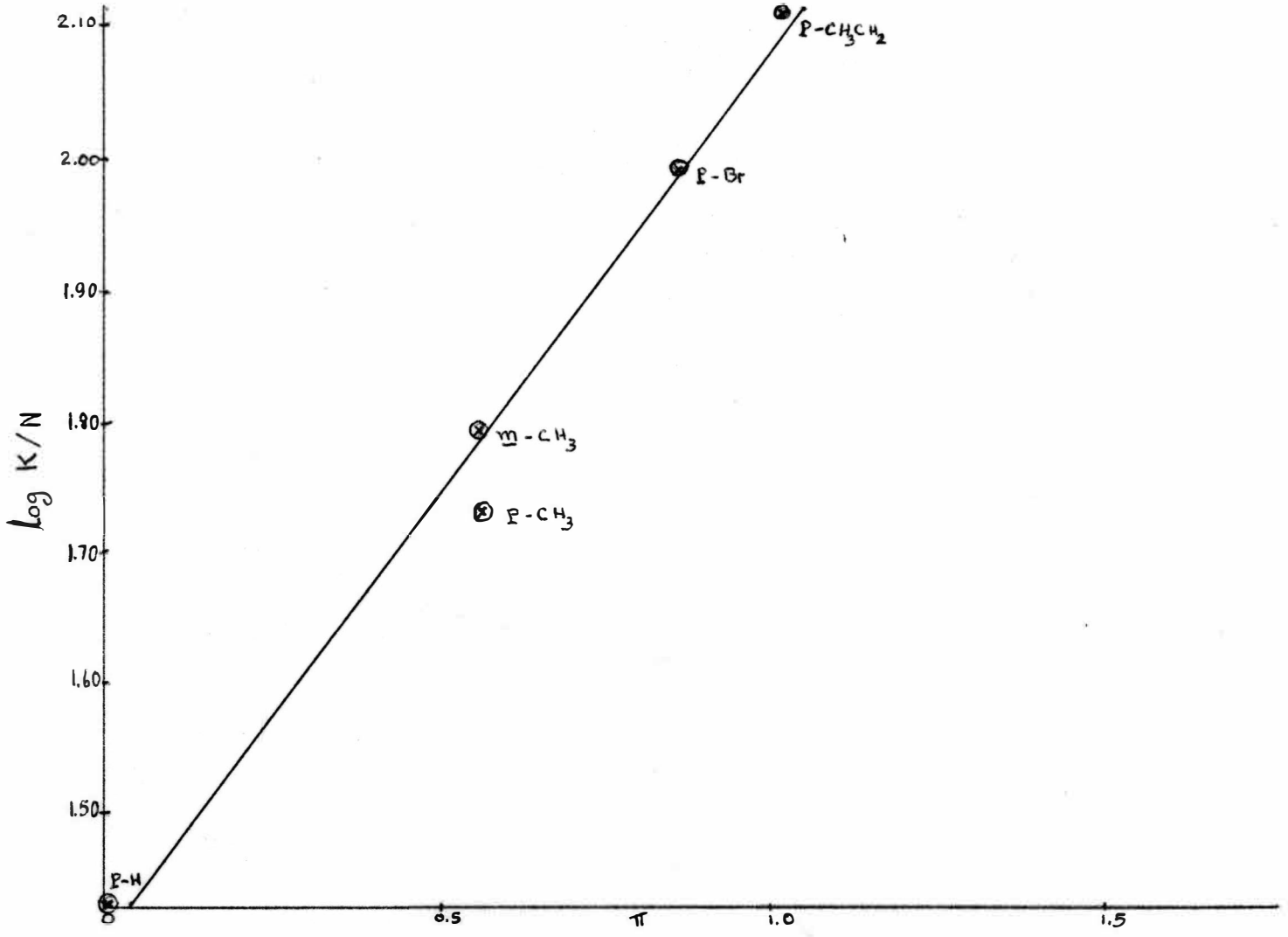


Figure 7. The graph of log K/N vs. π, the data are from Table XIII.

TABLE XIV[a]

THE LINEAR CORRELATION OF LOG k_w AND σ°[b]

	$k_w \times 10^5$	log k_w	σ°
p-H	1.66	-4.78	0.00
p-CH_3	1.75	-4.76	-0.12
p-CH_3CH_2	1.79	-4.75	-0.13
p-Br	1.51	-4.82	0.26
m-CH_3	1.69	-4.77	-0.07

[a] The data are for Figure 8

[b] The values are from Reference 19

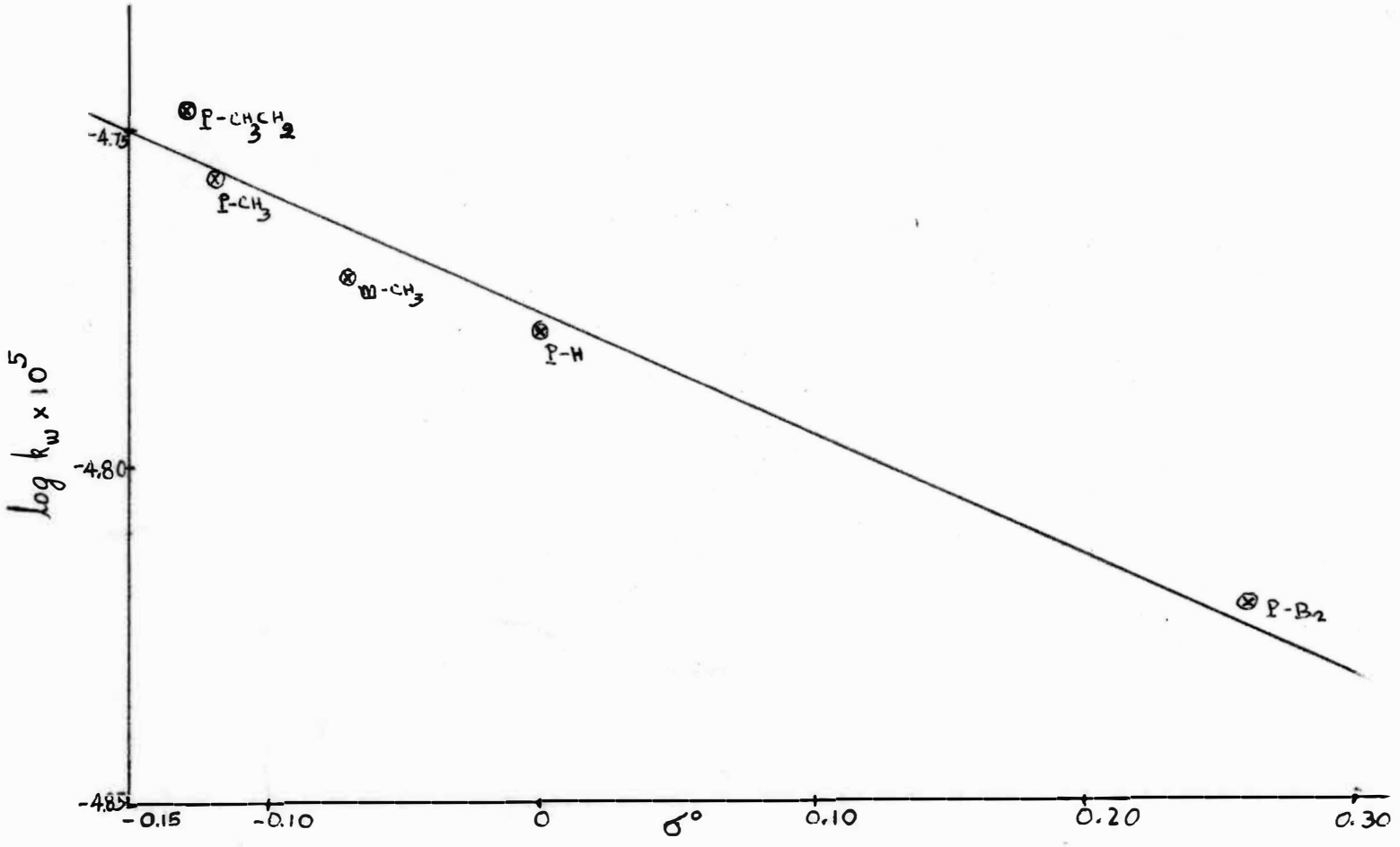


Figure 8. The graph of log k_w vs. σ°, the data are from Table XIV.

the log k_{m_H} = -3.942 from the calculation compares well to the log k_{m_H} = -3.955 from experiment.

If equation (13) is changed to equation (15) by omission of the σ° term, then

$$\log k_{m_G} = \alpha\pi_G + \log k_{m_H} \qquad (15)$$

A plot log km_G vs. π_G as in Figure 9 gave a better correlation ($r = 0.9559$) and the F-test is significant within 5% level. However considerable scatter remains in the graph and the correlation of log k_m with π alone is not very satisfactory. Therefore log k_m is not a simple function of either π or σ° although there appears to be some rough correlation with π and hence "lipophilicity". This result may be seen by taking account of the fact that the values of k_m are a lot different for the different G-groups, compared to the values for k_w which do not vary much, so roughly the statement in the equation (13) becomes as the equation (15).

Since in the calculation of K/N and k_m, the CMC of the surfactant was assumed to be 0.01 M,[1,20,21] the values for k_m and K/N would vary somewhat if a somewhat different value of the CMC were used. The CMC depends upon several factors as mentioned before, however, it will be the same for all the compounds in this study, since the conditions were identical for all of them.

In conclusion, the structural effect on the micellar catalysed reaction of hydroxamic acids does follow Scheme I over a limited range of surfactant concentration as shown in Figure 5 and Table XII.

TABLE XV[a]

THE LINEAR CORRELATION OF LOG k_m AND π

	$k_m \times 10^4$	log k_m	π[b]
p-H	1.11	-3.96	0
p-CH_3	1.82	-3.74	0.56
p-CH_3CH_2	2.13	-3.67	1.02
p-Br	2.26	-3.65	0.86
m-CH_3	1.55	-3.81	0.56

[a] The data are for Figure 9
[b] The values are from Reference 18

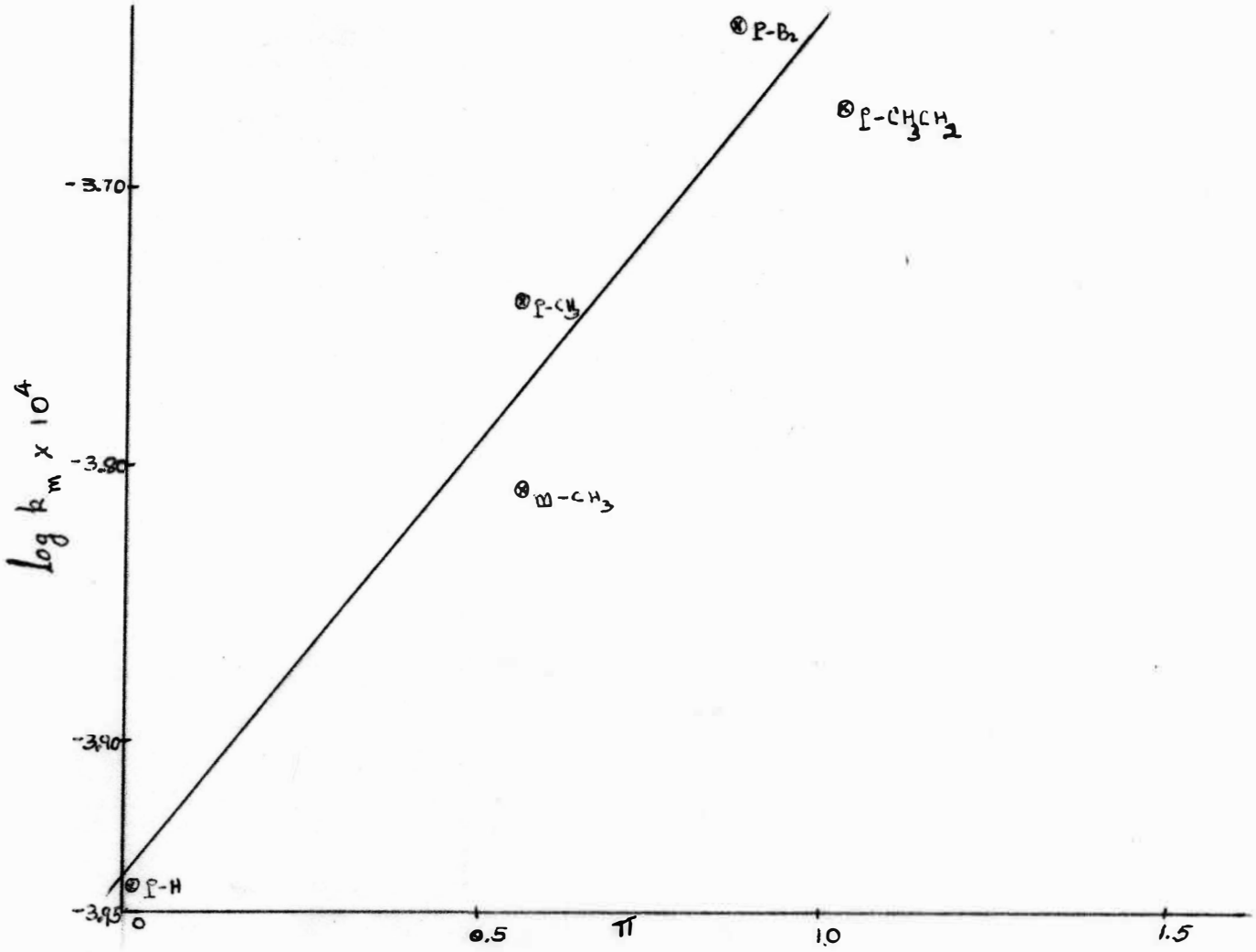


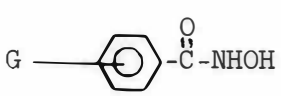
Figure 9. The graph of log k_m vs. π, the data are from Table XV.

The observed rate constant, K, and k_m depend on:

1. Structure of surfactant[1]
2. Structure of organic reactant[1]
3. Experimental conditions in the system: concentration of surfactant, temperature, solvent and the presence of any additives.

The study reported here investigated factor 2 above, and has shown that the micelle produces a significant effect on the rate of reaction and also that the substituent G-group influences the rate of the reaction. As the results shown in Table XII indicate, the rate of reaction in the micellar environment (k_m) does not appear to be influenced in the usual manner by electron withdrawing and releasing groups. In fact the withdrawing substituent (Br) and releasing substituents (alkyl) both increase k_m compared to H as substituent. It seems that the shape and size of the organic reactant which affects its fit in the micelle may be more important than the inductive effect in the total result of the reaction.

However, log K/N and π are very well correlated, but log k_m and π are only roughly correlated. Further investigation of more and different groups of hydroxamic acids, or perhaps a change in the structure of hydroxamic acid to



is required to elucidate substituent effects upon k_m and to further verify the correlation of log K/N by lipophilicity constants.

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