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Cationic and Anionic Micellar Catalyzed Hydrolysis of Hydroxamic Acids

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CATIONIC AND ANIONIC MICELLAR CATALYZED HYDROLYSIS OF HYDROXAMIC ACIDS

by

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The hydrolysis of octanohydroxamic and N-methyloctanohydroxamic acids in the presence of cationic and anionic micelles was investigated. Rate constants were determined for the hydrolyses in cetyltrimethylammonium bromide (ctab), the cationic surfactant, with 0.1111 N NaOH and in sodium 1-dodecanesulfonate, the anionic surfactant, with 0.09270 N HCl at 50.01 ± 0.11°C. The acid hydrolysis and the base hydrolysis of N-methyloctanohydroxamic acid followed the standard model for micellar catalysis:

$$\text{Micelle} + \text{Substrate} \underset{}{\overset{K}{\rightleftharpoons}} \text{Micelle}\cdot\text{Substrate}$$

$$\text{Substrate} \xrightarrow{k_o} \text{Product} \qquad \text{Micelle}\cdot\text{Substrate} \xrightarrow{k_m} \text{Product}$$

where k_o and k_m were the rates outside and in the micelle, respectively. The base hydrolysis of octanohydroxamic acid followed pseudo zero-order kinetics above 4.92×10^{-4} M ctab and pseudo first-order kinetics below this surfactant concentration.

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Douglas Eugene Conran

CONRAN, DOUGLAS EUGENE

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CHAPTER I

A BRIEF REVIEW

Micelles

Within recent years, interest in micelles has expanded. Fostered by improved[1] or new techniques,[2] the understanding of micellar phenomena has grown. Additional impetus has come from the many applications of micelles. Development has ranged from initial use as cleansing agents, i.e., soaps and detergents, to emulsion polymerization,[3] enhanced oil recovery,[4] and possible fuel production from photochemical splitting of water.[5] In addition, similarities between surfactant monolayers, micelles,[3] and vesicles[6] to phospholipid regions in biological systems and, primarily, enzymes have suggested micelles as a model for cell walls[7] and enzyme catalysis.[8] The latter suggestion has led to increased interest in examination of mechanisms of micellarly catalyzed reactions.

Although micelles may mimic enzyme catalysis,[8] structurally few similarities exist between enzymes and micelles. The basic structural unit of a micelle, the surfactant, belongs to the general class of compounds called amphiphiles,[9] which are characterized by possessing distinctive hydrophobic and hydrophilic portions. A commonly encountered surfactant, sodium lauryl sulfate ($CH_3(CH_2)_{11}$-OSO_3^- Na^+), is found in many shampoos. Further classifications, according to the hydrophobic portion, are ionic--anionic and

cationic--and non-ionic--zwitterionic and polar.[10] The example is anionic.

Micellarly catalyzed reactions are most often carried out in aqueous solution, and at low concentrations ionic surfactants behave like solution electrolytes.[11] Above a certain surfactant concentration the monomers (surfactants) undergo cooperative aggregation and form micelles. This concentration is the critical micelle concentration (cmc).[3,11] Ionic micelles (shown in Figure 1) can

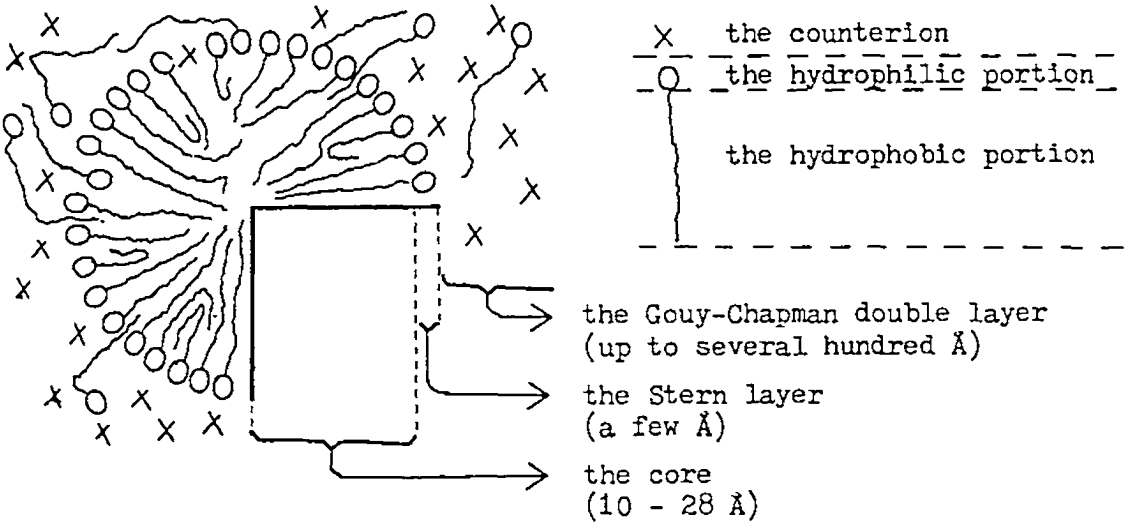


Figure 1. A Spherical Ionic Micelle in Cross Section

be described as spheres with the hydrophobic portion composing the volume, known as the core; the hydrophilic portion forming the surface area, called the Stern layer; and counterions surrounding the sphere.[9,11] A dynamic equilibrium exists between the monomer in solution and in the micelle.[3,8,12] Monomers leave while others combine while still others protrude from the micelle. This means

the Stern layer, which has a net charge, is not sharply defined. Micelle shape is dependent on the surfactant concentration,[11,13] temperature,[11,12] and other compounds in solution,[11,12] i.e., electrolytes as well as non-electrolytes. Other aggregate shapes are elipsoid,[3,11] rod-like,[3] and lamellar.[3] Micelle size is described by the aggregation number[11] (N), which is the number of monomers per micelle, and the length of the aliphatic chain of the surfactant.[13]

Catalysis occurs when micelles are present. Micelle formation begins at the cmc, which is experimentally determined by a change in a physical or spectroscopic property with a variation in surfactant concentration. The cmc is dependent on many factors, such as: alkyl chain length, unsaturation, and chain branching of the surfactant.[14]

The cmc is affected by external influences, like electrolytes, which decrease the cmc.[14] Solution electrolytes exist in equilibrium with the surfactant counterions. Sixty to seventy percent of surfactant counterions are "bound" to the micelle.[13] Counterion "binding" is not like enzyme binding, but is a decreasing concentration of counterions with increasing distance from the micelle.[13]

The reactant is usually of low solubility in water and, therefore, more soluble in the micellar core. Solubilization of the reactant is similar to an extraction in that the reactant is distributed between two phases: the bulk solution and the micelle.[15] Knowing the location of solubilization can aid in the interpretation of the catalysis.[15] Polar reactants are expected to be located near

the surface, amphiphilic compounds have the polar portion on the surface and the alkyl chain towards the interior, and hydrocarbons are solubilized in the core.[13]

One explanation for the observed catalytic effect is that the reactants are brought into close proximity. A higher concentration of reactants in the micellar micro-environment results in a rate enhancement with no increase in the rate constant.[16] Another view, transition state stabilization, occurs when the charge in the transition state is stabilized relative to the reactant state compared to the bulk phase by the charge in the Stern layer. (If the transition state is destabilized, inhibition of the reaction occurs.) Rate enhancement now occurs because of an increase in the rate constant.[17] Rate increases can also be a result of both the above effects.

For unimolecular reactions the standard kinetic scheme is shown in Figure 2,

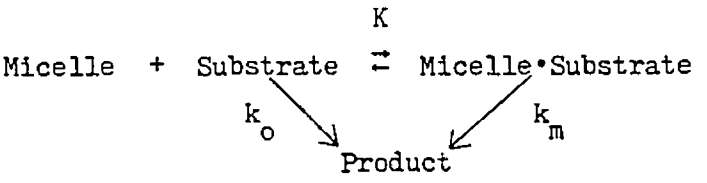


Figure 2. Standard Kinetic Scheme for Micellar Catalysis

where k_o and k_m are the rate constants in bulk solution and in the micelle, respectively, and K is an equilibrium constant.[8] This scheme leads to the relationship in Equation 1, where k_o, k_m, and K are the same as above, C_D is the bulk surfactant concentration, and N is the aggregation number.[8]

$$\frac{1}{k_o - k_{obs}} = \frac{1}{k_o - k_m} + \frac{1}{k_o - k_m}\left(\frac{N}{K\,(C_D - cmc)}\right) \qquad (1)$$

Equations developed from bimolecular reaction theories,[18-21] which also take into account the partitioning of the second reactant between bulk and micellar phases, are more difficult to use than Equation 1. Equation 2, derived by Romsted[19] for bimolecular reactions, is one such equation. In Equation 2, I_t is the total

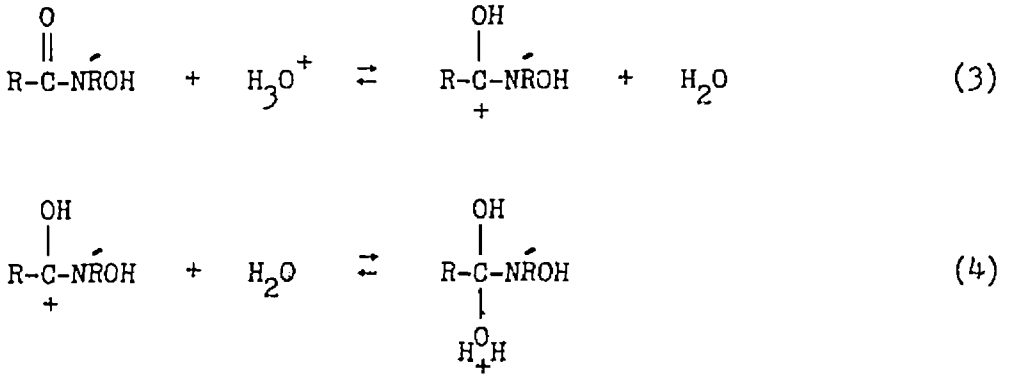
$$k_2 = \frac{k_m \beta S K_a (C_t - cmc)}{[K_a\,(C_t - cmc) + 1][I_t + X_t K_I]} + \frac{k_\omega}{[K_a\,(C_t - cmc) + 1]} \qquad (2)$$

concentration of the reactive hydrophilic ion, X_t is the total concentration of the surfactant counterion, C_t is the total surfactant concentration, β is the degree of counterion binding to the Stern layer, and S is the molar density of the micellar phase. K_a is the equilibrium constant for the organic substrate, K_I is the ion exchange constant for the hydrophilic reactant and surfactant ions, and k_2, k_m, and k_ω are the second order rate constants overall, and in micellar and bulk phases, respectively. However, these theories also lead to equations similar to Equation 1 under certain circumstances ($I_t \gg X_t K_I$ and I_t = constant) and treatment by the standard kinetic scheme and Equation 1 has been successfully done.[17,22]

More detailed and thorough discussion of micelles can be found in references 8 and 10.

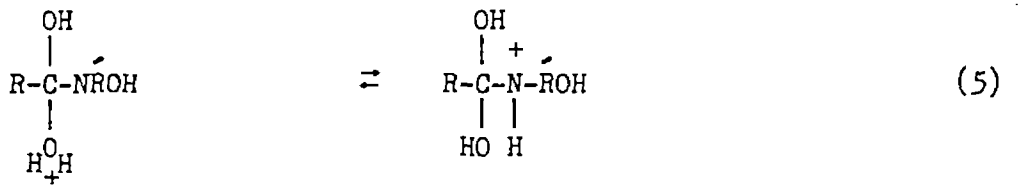
Acid Hydrolysis

Hydroxamic acid hydrolysis with anionic surfactants has been reported[23] and the mechanism [24] is shown below.

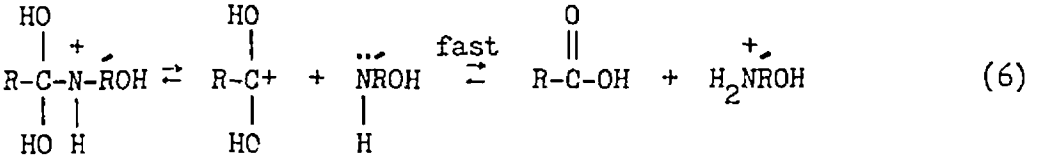


(3)

(4)



(5)



(6)

These studies investigated substituent effects with phenylacetohydroxamic acids.[25] Hydrolysis of an alkylhydroxamic acid, octanohydroxamic acid, with sodium dodecylsulfate has been reported.[23] The hydrolysis in 0.203 N HCl at 50.7°C and in a C_D range of 0.01-0.06 M found $k_m = 44.8 \times 10^{-3}$ sec^{-1}, K/N = 119, and $k_m/k_o = 9.74$. No reports of N-substituted alkylhydroxamic acids were found; however, the N-substituted arylhydroxamic acid hydrolysis has been studied.[24]

One purpose of this thesis is to study the acid hydrolysis of a N-substituted alkylhydroxamic acid.

Base Hydrolysis

Base hydrolysis of hydroxamic acids in bulk solution has been reported.[26] It was noted in these reports that the hydroxamic acid can be in one of three forms (Equation 7) under basic conditions.

$$\underset{\text{A}}{R\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH\text{-}O^-} \rightleftarrows \underset{\text{B}}{R\text{-}\overset{\overset{O}{\|}}{C}\text{-}N\text{-}OH} \rightleftarrows \underset{\text{C}}{R\text{-}\overset{\overset{HO}{|}}{C}\text{=}N\text{-}O^-} \qquad (7)$$

Form B predominates and form C is in minute amounts.[27] Both forms A and B can react with water and base; therefore, a more complicated interpretation may be expected.[28-30]

The second purpose of this thesis is to measure the rate of hydrolysis of octanohydroxamic and N-methyloctanohydroxamic acids in base with a cationic surfactant, cetyltrimethylammonium bromide.

CHAPTER II

EXPERIMENTAL PREPARATIONS AND KINETICS

Compounds

Preparation of Sodium 1-Dodecanesulfonate Surfactant

The sulfonate surfactant was prepared by the general reaction[31]

$$R\text{-}CH_2\text{-}Br + SO_3^{=} \rightarrow R\text{-}CH_2\text{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}\text{-}O^- + Br^- . \qquad (8)$$

Sodium sulfite (51.5 g, 0.408 mol) was dissolved in 150 mL of distilled water. To the clear aqueous solution 1-bromododecane (82 mL, 0.31 mol) was added. The two-phase system was carefully refluxed with added boiling chips to avoid bumping and foaming. When the organic layer was no longer apparent (144 hrs.), the reaction was stopped. Upon cooling a large mass of white precipitate was formed. It was broken and dislodged from the reaction flask, and water (250 mL) was used to wash the flask. The resulting slurry was filtered. The solid was crushed (mortar and pestle), suspended in water (250 mL), cooled (≈ 2°C), filtered, and air dried. The dried solid was crushed and then was extracted two times with hot petroleum ether (65 - 110°C) to remove any dodecanol or dodecyl bromide. Lastly, it was filtered and air dried. Methanol (1.4 L) was used to crystallize the crude product. It was twice recrystallized from 95% ethanol. The yield was 43% (based on 1-bromododecane). IR, NMR (Table 1), and elemental analysis (Galbraith Labs, Inc., Table 2) of the product

TABLE 1

Spectral Analysis of Sodium 1-Dodecanesulfonate

Section[a] of Molecule	IR[b] Frequency (cm^{-1})	IR[b] Remarks	^{1}H-NMR[c] Chemical Shift [δ(ppm)]	^{1}H-NMR[c] Ratio
α			0.9 (b)	3.3
β			1.34 (s)	20.0
γ			3.19 (t)	1.9
ϵ	1200	ν_{SO_2} Symmetrical		
ϵ	1465	ν_{SO_2} Antisymmetrical		

a $\underbrace{CH_3}_{\alpha} - \underbrace{(CH_2)_{10}}_{\beta} - \underbrace{CH_2}_{\gamma} - \underbrace{SO_3^-Na^+}_{\epsilon}$

b KBr pellet.

c Trifluoroacetic acid as solvent.

TABLE 2

Elemental Analysis of Sodium 1-Dodecanesulfonate

Analysis	% C	% H	% S
Observed	52.84	9.17	11.82
Calculated	51.91	9.25	11.77

corresponded to those of the desired substance.[32,33] The surfactant was stored in a desiccator over solid potassium hydroxide.

Purification of Cetyltrimethylammonium Bromide, $[CH_3(CH_2)_{15}N(CH_3)_3^+ Br^-]$

Cetyltrimethylammonium bromide (ctab) was purchased from Eastman Kodak Co. Further purification[34] was done by recrystallization: three times from an acetone:95% ethanol (20:1, v/v) mixture and once from methanol:ether (ether was the non-solvent).[35] Oven drying at 110°C caused some decomposition of the compound; therefore, the crystals were air dried at room temperature. The IR and NMR of the compound were compared to published spectra.[36,37] The elemental analysis (Galbraith Labs, Inc., Table 3) and the spectra were satisfactory.

TABLE 3

Elemental Analysis of Cetyltrimethylammonium Bromide

Analysis	% C	% H	% N
Observed	62.43	11.66	4.03
Calculated	62.61	11.62	3.84

Preparation of Octanohydroxamic Acid, $[CH_3(CH_2)_6CONHOH]$

Octanohydroxamic acid was supplied by Dr. D. C. Berndt. The observed melting point, determined with a Thomas Hoover melting point apparatus, was 77.5 - 78.0°C (literature, 78 - 79°C).[38]

Preparation of N-Methyloctanohydroxamic Acid, $[CH_3(CH_2)_6CON(CH_3)OH]$

The N-methyloctanohydroxamic acid was prepared according to the procedure of Berndt and Ward,[39] and the acid chloride according to Fieser and Fieser.[40] A mixture of octanoic acid (37.5 mL, 0.236 mol) and methylene chloride in a 1:2 ratio (v/v) was slowly added to constantly stirred thionyl chloride (0.7 mol). When the evolution of gas stopped, the mixture was refluxed until no additional gas evolved (6 hrs.). Unreacted thionyl chloride and solvent were removed by distillation (room temperature, approx. 30 mmHg) and the residue was distilled (45.5 - 46.8°C, 1.7 - 1.2 mmHg) to yield the clear octanoyl chloride (36.1 g, 0.222 mol, 94% yield based on the acid) which was used without further purification.

N-Methylhydroxylamine hydrochloride (25.2 g, 0.302 mol) was dissolved in methanol (240 mL, ACS grade). Sodium carbonate monohydrate (37.5 g, 0.303 mol) was added to the methanol solution and stirred. Octanoyl chloride (52 mL, 0.305 mol) was slowly added to the constantly stirred ice-water-bath-cooled mixture over a period of one hour. The pH was frequently checked (pHydrion paper, pH range = 6.0 - 8.0) to maintain a pH $\geq$ 7. Sodium carbonate was added when needed to maintain a neutral or basic condition. Filtration of the solution yielded a clear yellow filtrate. The residue was washed three times with methanol and the washings were added to the filtrate. Removal of the solvent was accomplished by evaporation with an air stream. The resulting yellow oil gave a positive ferric chloride test (see "Preparation of the Ferric Chloride Solution").

Crystallization of the crude product was accomplished from a water:95% ethanol (2:1, v/v) mixture. The mixture was placed in a freezer (≈ -2°C), seeded, and allowed to stand for several weeks. Filtration of the white crystals was done very quickly by suction through an ice cold Büchner funnel. This procedure was done three times. The wet product was dried in a loosely covered crystallizing dish in the refrigerator for several months. The product was further dried in a desiccator (drying agent, Drierite) in the refrigerator, and, finally, stored in a desiccator with fresh drying agent (Drierite) in the refrigerator. The recovered yield of N-methyl-octanohydroxamic acid was 9.63 g (18.4% yield based on N-methyl-hydroxylamine). The melting point was 15.0 - 17.3°C, which was determined in a cooled oil bath allowed to warm to room temperature. IR, NMR spectra (Table 4) and elemental analysis (Galbraith Labs, Inc., Table 5) corresponded to those of the desired product.[33,41]

Acid and Base

Standardization of 0.1854 N Stock Hydrochloric Acid Solution

Preparation and standardization of the hydrochloric acid solution followed the procedure in Skoog and West.[42] Double distilled water was used for all solutions. The hydrochloric acid was standardized against a sodium hydroxide solution, the secondary standard, which was standardized against potassium hydrogen phthalate (KHP), the primary standard. KHP was dried at 110°C for 24 hours before use. Phenolphthalein was the indicator. The results of the

TABLE 4

Spectral Analysis of N-Methyloctanohydroxamic Acid

Section[a] of Molecule	IR		^{1}H-NMR[b]	
	Frequency (cm^{-1})	Remarks	Chemical Shift [δ(ppm)]	Ratio
α			0.9 (t)	2.96
β			1.3 (b)	10.6
γ			2.44 (t)	2.05
ϵ	1620	$\nu_{C=O}$ conjugated and H-bonded		
π			3.25 (s)	2.87
μ	3190	ν_{OH} H-bonded		
ϵ-μ	1390	ν_{C-N}		

a $\underbrace{CH_3}_{\alpha} - \underbrace{(CH_2)_5}_{\beta} - \underbrace{CH_2}_{\gamma} - \underbrace{CO}_{\epsilon} - \underbrace{NOH}_{\mu} - \underbrace{CH_3}_{\pi}$

b Carbon tetrachloride as solvent.

TABLE 5

Elemental Analysis of N-Methyloctanohydroxamic Acid

Analysis	% C	% H	% N
Observed	62.46	11.09	8.32
Calculated	62.40	11.05	8.08

standardization are in Table 6.

Table 6

Standardization of 0.1854 N HCl Stock Solution

Measurement	Trial 1	2	3	4	$\bar{N}$	s^a
Secondary Standard, 0.1035 N NaOH						
KHP, grams	0.6186	0.6735	0.7254	0.8531		
NaOH, mL	29.27	31.84	34.28	40.38	0.1035	0.00008
Stock Solution, 0.1854 N HCl						
NaOH, mL	44.70	44.79	44.77	44.89	0.1854	0.0003

Note. Twenty-five milliliter of the stock HCl solution was used for all trials in the standardization of 0.1854 N HCl stock solution.

a The experimentally computed standard deviation with N-1 degrees of freedom was s.

Preparation and Standardization of 0.2222 N, 0.3659 N, and 0.09078 N Carbon Dioxide Free Stock Sodium Hydroxide Solutions

Carbon dioxide free sodium hydroxide solution was prepared according to the procedure provided by Dr. R. Steinhaus (Western Michigan University). A 50% sodium hydroxide solution was prepared in a polyethylene jar and allowed to stand undisturbed for at least 48 hours. During this time a crust had formed on the top of the

solution and any insoluble carbonate salts would have settled to the bottom. The clear middle solution was removed by inserting a pipet, with positive pressure on the pipet bulb, through the crust. This procedure prevented solid from being traped in or on the tip of the pipet. Approximately 24 mL of the solution was removed and added to 2 liters of freshly boiled double distilled water and the solution was stored in a tightly sealed polyethylene bottle. This stock solution was standardized by the procedure in Skoog and West.[42] KHP was the standard and phenolphthalein was the indicator. The results are contained in Table 7. Two other solutions at approximately half and double the stock solution concentration were made and standardized by the same methods. The results of those standardizations are also listed in Table 7.

Additional Preparations

Preparation of the Ferric Chloride Solution

A ferric chloride solution was prepared according to the following ratio:

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

The ferric chloride solution was used as a quencher and indicator. Ferric ion and hydroxamic acids form complexes which have a violet or maroon color.[43]

Calibration of Oil Bath Thermometer

The oil bath thermometer was calibrated against a thermometer

TABLE 7

Standardization of 0.2222 N, 0.3659 N, and 0.09078 N Carbon Dioxide Free NaOH Stock Solutions

Measurement	Trial 1	2	3	4	$\bar{N}$	s^a
			0.2222 N NaOH			
KHP, grams	1.1516	1.0155	0.9226			
NaOH, mL	25.37	22.38	20.32		0.2222	0.00007
			0.3659 N HCl			
KHP, grams	1.9278	1.3874	1.0393	1.2316		
NaOH, mL	25.77	18.57	13.91	16.49	0.3659	0.0003
			0.09078 N NaOH			
KHP, grams	0.7661	1.1799	0.9066	0.8169		
NaOH, mL	41.33	63.66	48.88	44.06	0.09078	0.00005

a The experimentally computed standard deviation with N-1 degrees of freedom is s.

previously calibrated by Dr. D. C. Berndt against a National Bureau of Standards thermometer. The results are in Equations 9, 10, and 11.

Previous Thermometer : $T_{previous} + 0.06°C = \text{True Temperature}$ (9)

Oil Bath Thermometer : $T_{oil\ bath} + 0.10°C = T_{previous}$ (10)

Therefore the correction for the oil bath thermometer was

$$T_{\text{oil bath}} + 0.16°C = \text{True Temperature} \qquad (11)$$

The calibration was done at approximately 50°C.

Verification of Beer's Law

The spectrophotometric method for the analysis of hydroxamic acids, in the presence of surfactant, was verified as follows: Twenty-five milliliter (pipet) of a 0.01199 M aqueous surfactant solution; 10 mL (pipet) of the ferric chloride solution; and 3 mL or 6 mL (pipet) of a 5×10^{-4} M aqueous solution of the hydroxamic acid were mixed in a 50 mL volumetric flask. Absorbances were taken versus the blank (contained no hydroxamic acid) with a Gilford spectrophotometer at 520 nm in matched 10 cm UV cells. If Beer's law applies, the absorbance of the solution with 6 mL of the hydroxamic acid will be twice the absorbance of the solution with 3 mL. The absorbances of the solutions and the percent difference between twice the absorbance of the 3 mL solution and the absorbance of the 6 mL solution are reported in Table 8. Beer's law appears to apply.

Kinetic Solutions

Preparation of Stock Reactant and Surfactant Solutions

Stock reactant solutions of 1×10^{-3} M of octanohydroxamic acid and N-methyloctanohydroxamic acid were prepared in double distilled water. These solutions were used for all kinetic runs. Surfactant solutions were freshly prepared for each kinetic run. Seventy

TABLE 8

Verification of Beer's Law

Compound[a]	Absorbance with 3 mL of compound	Absorbance with 6 mL of compound	% difference in absorbance
In Sodium 1-Dodecanesulfonate			
N-M[b]	0.535	1.075	0.47
N-H	0.447	0.890	0.45
In CTAB			
N-M	0.256	0.427[c]	0.078
N-H	0.260	0.521	0.19

Note. Surfactant concentration = 0.01199 M, compound concentration = 5×10^{-4} M.

a N-M refers to N-methyloctanohydroxamic acid and N-H refers to octanohydroxamic acid.

b Concentration = 8×10^{-4} M.

c Five milliliter used.

milliliter (pipet) of the surfactant solution at double the desired reaction surfactant concentration was made with sodium 1-dodecanesulfonate in 0.1854 N HCl or with ctab in 0.2222 N NaOH.

Kinetic Procedure

Fifteen milliliter (pipet) of the freshly prepared surfactant

solution was placed in each of four reaction tubes (duplicate runs for both reactants). Glass tubes and stoppers were used for the acid runs and polyethylene tubes and stoppers were used for the base runs. The reaction tubes were stoppered and placed in a stirred constant temperature oil bath (50.01 ± 0.11°C corrected) for approximately 20 minutes.

During the equilibration time the blank was prepared. Three milliliter (pipet) of the freshly prepared surfactant solution and 3 mL of double distilled water were placed in a 10 mL Erlenmeyer flask and swirled. Three milliliter of this diluted solution (50% dilution of the surfactant solution) was placed in a 50 mL volumetric flask, which contained 10 mL (pipet) of the ferric chloride solution and diluted to the mark with double distilled water. The flask was inverted and shaken ten times and the blank was placed in a 10 cm UV cell.

Fifteen milliliter of the stock reactant solution was added to the equilibrated reaction tubes. This addition resulted in a reactant concentration of 5×10^{-4} M and the surfactant concentration half of that prepared. The tubes were stoppered, inverted three times, and allowed to equilibrate for at least ten minutes in the oil bath.

At various times a 3-mL sample was removed and added to a 50 mL volumetric flask which contained 10 mL of the ferric chloride indicator solution. Formation of the complex and the temperature reduction quenched the reaction. The mixture was diluted with double distilled water, inverted and shaken ten times, and placed in a 10

cm UV cell. The absorbance was immediately taken against the appropriate blank and recorded.

Rates of reaction were measured in duplicate. Duplicate runs of both compounds were carried out concurrently, except for a few acid runs, which were too fast, and, for these, the compounds, in duplicate, were measured sequentially. Sample time was taken to be the time at which the 3 mL pipet started to drain. All samples, including preparation of the blank, were taken with the same 3 mL pipet, which was rinsed with 95% ethanol and blown dry with an air stream which was dried by passing through a Drierite packed tube. The same 15 mL pipet was used for both surfactant solution and reactant solution and rinsed and dried as described. All absorbances were taken with 10 cm UV cells in a Gilford spectrophotometer at 520 nm. Two readings were taken and averaged, however, most readings were within instrumental error (± 0.002 A).[44]

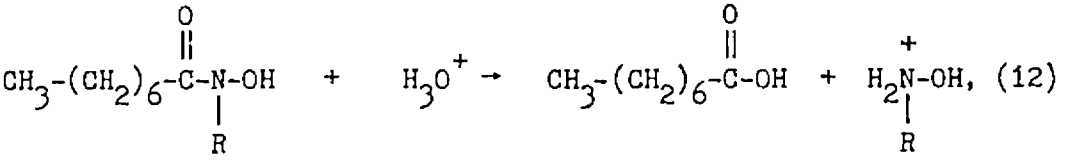
The reactions were followed for at least two half-lives, except when the reactions took four or five days to reach one half-life. The rates without surfactant were followed for at least two half-lives regardless of the length of reaction.

CHAPTER III

RESULTS

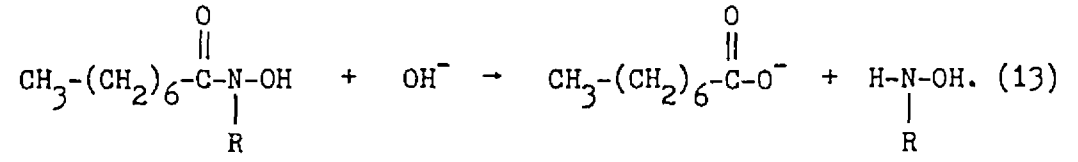
Analysis by Standard Kinetic Scheme

The overall reaction for the acid hydrolysis was



$$CH_3\text{-}(CH_2)_6\text{-}C(=O)\text{-}N(R)\text{-}OH + H_3O^+ \rightarrow CH_3\text{-}(CH_2)_6\text{-}C(=O)\text{-}OH + H_2N^+(R)\text{-}OH, \quad (12)$$

and for the base hydrolysis the overall reaction was



$$CH_3\text{-}(CH_2)_6\text{-}C(=O)\text{-}N(R)\text{-}OH + OH^- \rightarrow CH_3\text{-}(CH_2)_6\text{-}C(=O)\text{-}O^- + H\text{-}N(R)\text{-}OH. \quad (13)$$

In both cases, the acid or the base was in great excess compared to the hydroxamic acid, and the observed rate was pseudo first-order. Under this condition the observed rate would be proportional to the concentration of the hydroxamic acid, which was related to the absorbance of the iron:hydroxamic acid complex.

The integrated rate equation for the reaction is

$$\ln (a_o/a) = kt \quad (14)$$

where a_o is the initial hydroxamic acid concentration, a is the concentration of the hydroxamic acid at time t, and k is the first order rate constant.[45] The relationship of the hydroxamic acid concentration to the absorbance of the complex leads to the equation

$$\ln (A_t - A_\infty) = -k_{obs}t + \ln (A_o - A_\infty) \quad (15)$$

or

$$\ln A_t = -k_{obs}t + \ln A_o \qquad (16)$$

where A_t is the absorbance of the complex at time t and A_o is the absorbance of the complex at zero time. The absorbance at infinite time, A_∞, i.e., complete reaction, is zero. The pseudo first-order rate constant, k_{obs}, is determined by a least squares treatment of the ln A_t versus time data. The calculated slope is $-k_{obs}$.

Table 9 contains the raw data for one run of the acid catalyzed hydrolysis of N-methyloctanohydroxamic acid in the presence of sodium 1-dodecanesulfonate. The least squares treatment of the data by Equation 16 gave the following results: slope = -1.25, intercept = -1.12, and the correlation coefficent = -0.99997. Therefore, k_{obs} = -(-1.25) = 1.25 hr^{-1}. Data from the duplicate run gave k_{obs} = 1.23 hr^{-1} and the average k_{obs} = 1.24 hr^{-1} or 34.4 x 10^{-5} sec^{-1}. The percent difference in k_{obs} of duplicate runs is [(1.25 - 1.23)/1.23]·100 = 1.63%.

Table 10 summarizes the results of the least squares treatment of the kinetic data, the range of the correlation coefficent (r), and the range of the percent difference in the duplicate runs for the acid catalyzed hydrolysis of N-methyloctanohydroxamic acid and octanohydroxamic acid in sodium 1-dodecanesulfonate. Table 11 summarizes the results for both compounds in base with ctab as surfactant.

The data was further treated by Equation 1 (discussed in Chapter I "A Brief Review: Micelles"). In order to use Equation 1 the cmc needed to be determined. A "kinetic" cmc was found from the rate-surfactant profile, a plot of rate versus C_D. The intersection of the extrapolation of the lines at low surfactant concentration of the

TABLE 9

Sample Data for the Determination of k_{obs} of N-Methyloctanohydroxamic Acid in 0.09270 N HCl at 50.01 ± 0.11°C

Sample number	Clock time	Elapsed time (hr)	Absorbance	Average absorbance
1	13:01	0	0.324 0.324	0.324
2	13:11	0.167	0.262 0.264	0.263
3	13:25	0.400	0.195 0.195	0.195
4	13:40	0.650	0.143 0.144	0.143
5	13:55	0.90	0.105 0.106	0.105
6	14:10	1.15	0.076 0.076	0.076

Note. Sodium 1-dodecanesulfonate concentration was 0.009990 M.

sigmoid curve was the kinetic cmc. A sample determination is shown in Figure 3. The kinetic cmcs were determined to be 2×10^{-3} M for sodium 1-dodecanesulfonate in 0.09270 N HCl and 2×10^{-4} M for ctab in 0.1111 N NaOH. Equation 1 did not apply over the total range of surfactant concentrations for bimolecular reactions. The limits were that C_D must be above the cmc and C_D must be less than the concentration at which k_{obs} was a maximum. A sample determination using Equation 1 for the acid catalyzed hydrolysis of N-methyloctanohydrox-

TABLE 10

Kinetic Data for the Acid Hydrolysis in 0.09270 N HCl at 50.01 ± 0.11°C as a Function of Sodium 1-Dodecanesulfonate Concentration

	N-H[a]		N-M[a]	
$C_D \times 10^3$ (M)	ave. $k_{obs} \times 10^5$ (sec^{-1})	$t_{1/2}$ (hr)	ave. $k_{obs} \times 10^5$ (sec^{-1})	$t_{1/2}$ (hr)
0.0	2.07	9.30	4.94	3.89
0.060	1.99	9.65	4.85	3.97
0.485	2.06	9.34	4.99	3.86
3.01	5.69	3.38	12.5	1.55
4.996	11.5	1.67	22.0	0.874
7.996	17.4	1.11	31.0	0.622
9.990	21.9	0.877	34.4	0.559
11.99	23.3	0.827	37.1	0.519
15.00	26.2	0.736	39.2	0.492
20.40	29.6	0.650	42.6	0.452
30.01	32.5	0.592	44.4	0.433
40.00	34.7	0.555	44.3	0.435
60.07	34.2	0.564	44.2	0.436

Note. The value of r ranged from -0.9967 to -0.9999. Percent difference in k_{obs} of duplicate runs did not exceed 3.0%.

a See Table 8 for explanation of symbols.

TABLE 11

Kinetic Data for the Base Hydrolysis in 0.1111 N NaOH at 50.01 ± 0.11°C as a Function of Cetyltrimethylammonium Bromide Concentration

	N-H[a]		N-M[a]	
$C_D \times 10^4$ (M)	ave. $k_{obs}^b \times 10^6$ (sec^{-1})	$t_{1/2}$ (hr)	ave. $k_{obs} \times 10^6$ (sec^{-1})	$t_{1/2}$ (hr)
0.0	1.96	98.2	1.84	105
0.27	2.20	87.5	1.84	105
1.5	2.78	69.3	1.87	103
4.92	(0.731)	(58.9)	2.80	68.8
10.0	(1.06)	(37.9)	3.67	52.5
12.0	(1.28)	(31.9)	4.19	46.0
30.04	(2.14)	(18.5)	4.83	39.9
50.02	(2.53)	(16.3)	7.80	24.7
201.9	(2.89)	(13.6)	8.08	23.8
399.9	(3.15)	(12.2)	6.92	27.8
600.1	(3.16)	(11.4)	7.07	27.2

Note. The value of r ranged from -0.9956 to -0.9996. Percent difference in k_{obs} of duplicate runs did not exceed 5.3%.

a See Table 8 for explanation of symbols.

b Numbers in parentheses were determined by use of pseudo-zero order equations and are ave. $k_{obs} \times 10^{10}$ mol L^{-1} sec^{-1}.

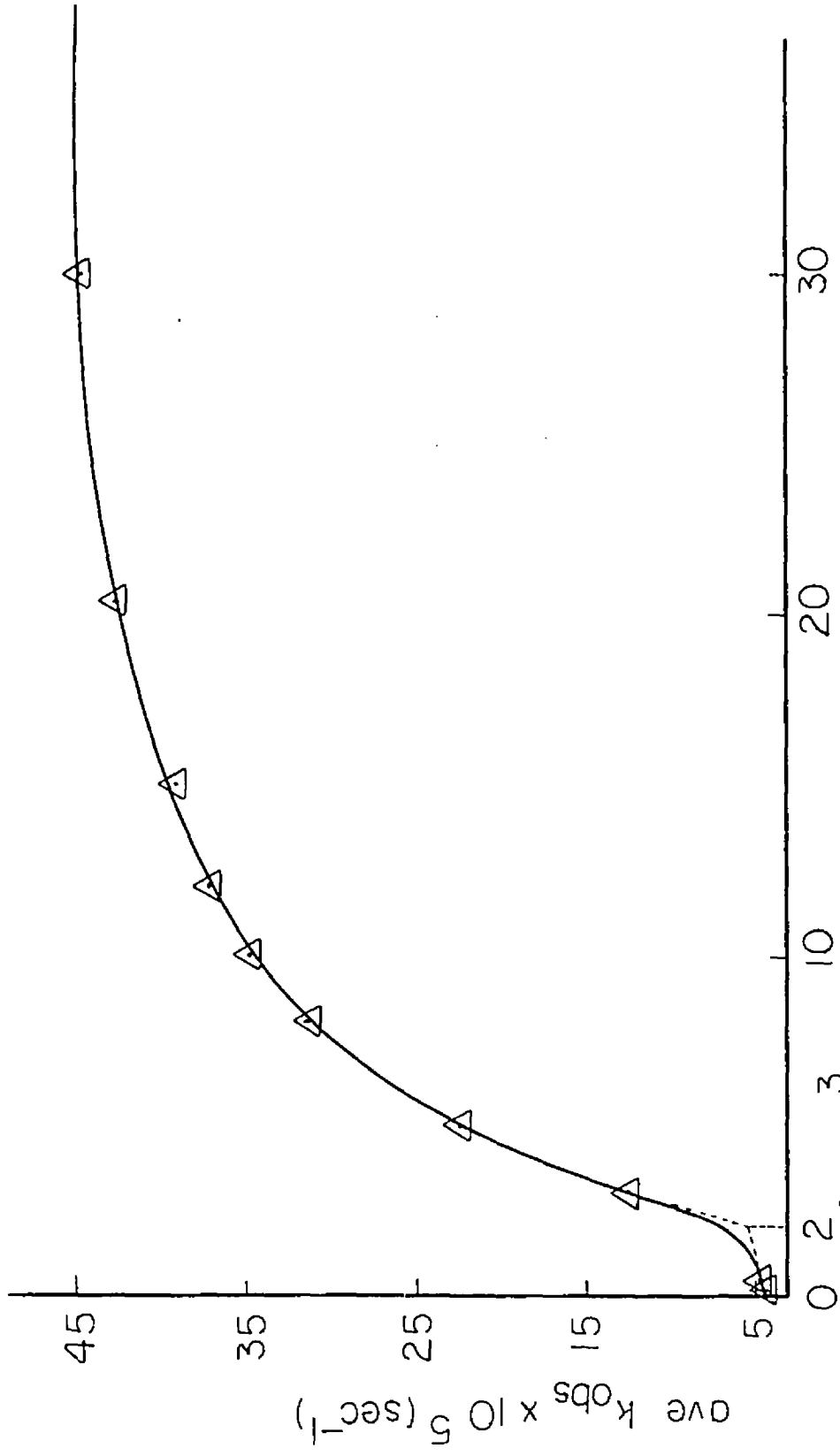


Figure 3. Determination of Kinetic Cmc from a Rate-Surfactant Profile.

amic acid in sodium 1-dodecanesulfonate is contained in Table 12.

TABLE 12

Calculation of Sample Data by Equation 1 for Acid Hydrolysis of N-Methyloctanohydroxamic Acid in Sodium 1-Dodecanesulfonate

$C_D \times 10^3$ (M)	$1/(C_D - cmc)$ (M^{-1})	ave. $k_{obs} \times 10^5$ (sec^{-1})	$1/(k_o - k_{obs})$ (sec)
7.996	166.8	31.0	-3840
9.990	125.2	34.4	-3390
11.99	100.1	37.2	-3100
15.00	76.92	39.2	-2920
20.40	54.35	42.6	-2660
30.01	35.70	44.4	-2530

Note. Cmc = 2×10^{-3} M and $k_o = 4.94 \times 10^{-5}$ sec^{-1}.

The least squares treatment of the data in Table 12 by Equation 1 resulted in the following values: intercept, $1/(k_o - k_m)$, = -2135; slope, $[1/(k_o - k_m)] \cdot (N/K)$, = -10.07; and the correlation coefficent (r) = -0.9981. These values lead to $k_m = 51.8 \times 10^{-5}$ sec^{-1}, K/N = 212, and F(1,5) = 1049[46] which shows significance at the 0.1% level.[47] Table 13 shows the results of the least squares treatment of the data by Equation 1 and the range of the correlation coefficent for the acid hydrolysis of both compounds with sodium 1-dodecanesulfonate and the base hydrolysis of N-methyloctanohydroxamic acid with ctab. Figure 4 shows the plot of Equation 1 for the acid hydrolysis of both compounds and Figure 5 the base hydrolysis of N-methyloctanohydrox-

TABLE 13

Results of Data Correlation for the Acid and Base Hydrolysis by Equation 1

Compound	K/N	$k_m \times 10^5$ (sec^{-1})	$k_o \times 10^5$ (sec^{-1})	k_m/k_o	$C_D \times 10^3$ range (M)
Acid Hydrolysis					
N-H[a]	101	40.2	2.07	19.5	7.996 - 40.00
N-M[a]	212	51.8	4.94	10.5	7.996 - 30.1
Base Hydrolysis					
N-M[a]	1001	0.612	0.184	3.32	0.492 - 3.004

Note. Correlation coefficent ranged from -0.9918 to -0.9981.

a See Table 8 for explanation of symbols.

amic acid in ctab. Evaluation of the data for the base hydrolysis of octanohydroxamic acid by Equation 1 was not possible because the reaction was pseudo zero-order above the cmc (determined from N -methyloctanohydroxamic acid data).

Table 14 contains the raw data for one run of the base catalyzed hydrolysis of octanohydroxamic acid in 0.1111 N NaOH and 30.04×10^{-4} M ctab. Figure 6 shows the absorbance versus time plot of the data in Table 14. The straight line indicates that the reaction is pseudo zero-order in hydroxamic acid. Also, the reaction order, determined by the Noyes equation, is -0.72 ± 0.2 which is close to zero-order.

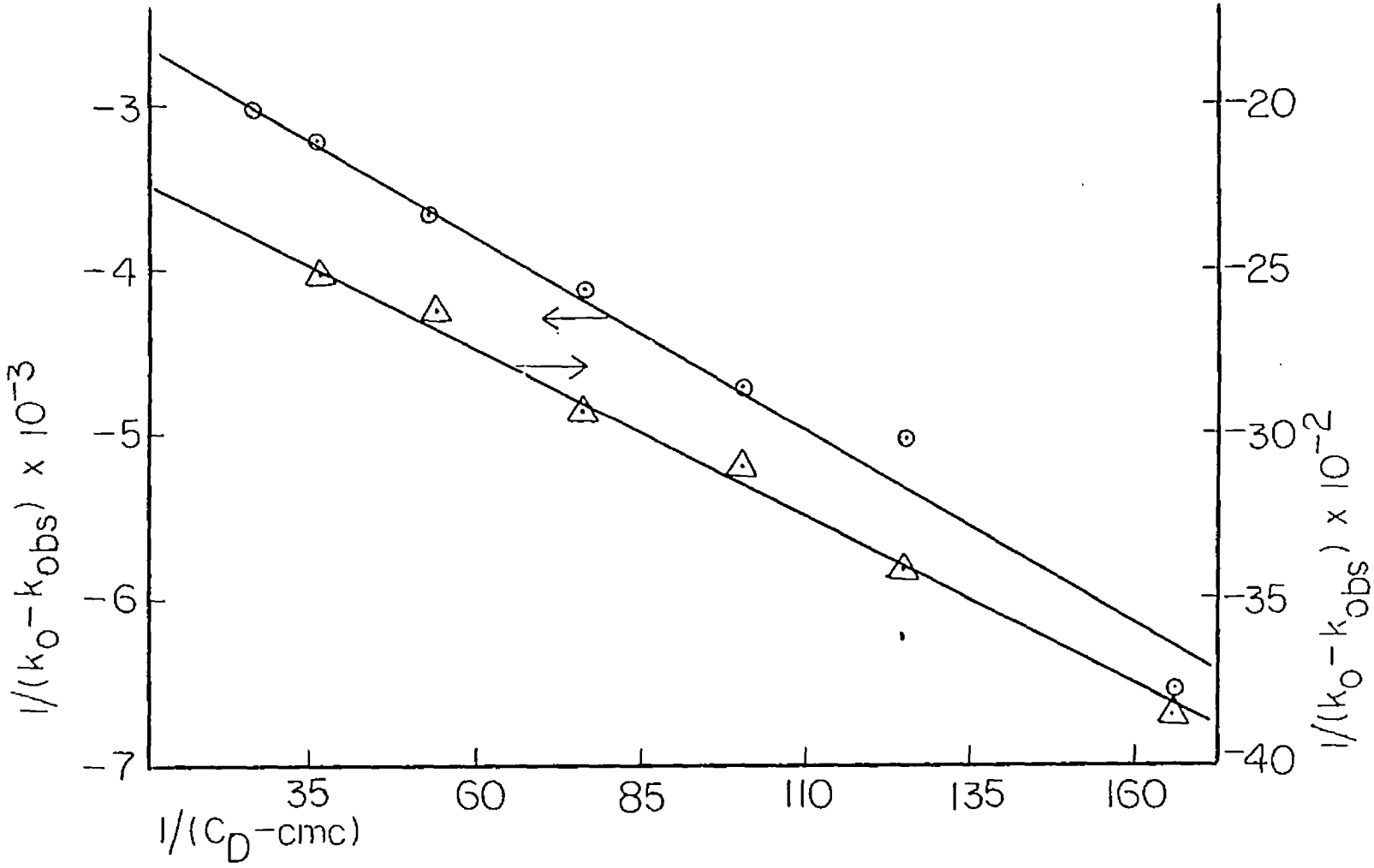


Figure 4. Plot of Equation 1 for the Acid Hydrolysis of Octanohydroxamic Acid (⊙ , left hand axis) and N-Methyloctanohydroxamic Acid (△ , right hand axis).

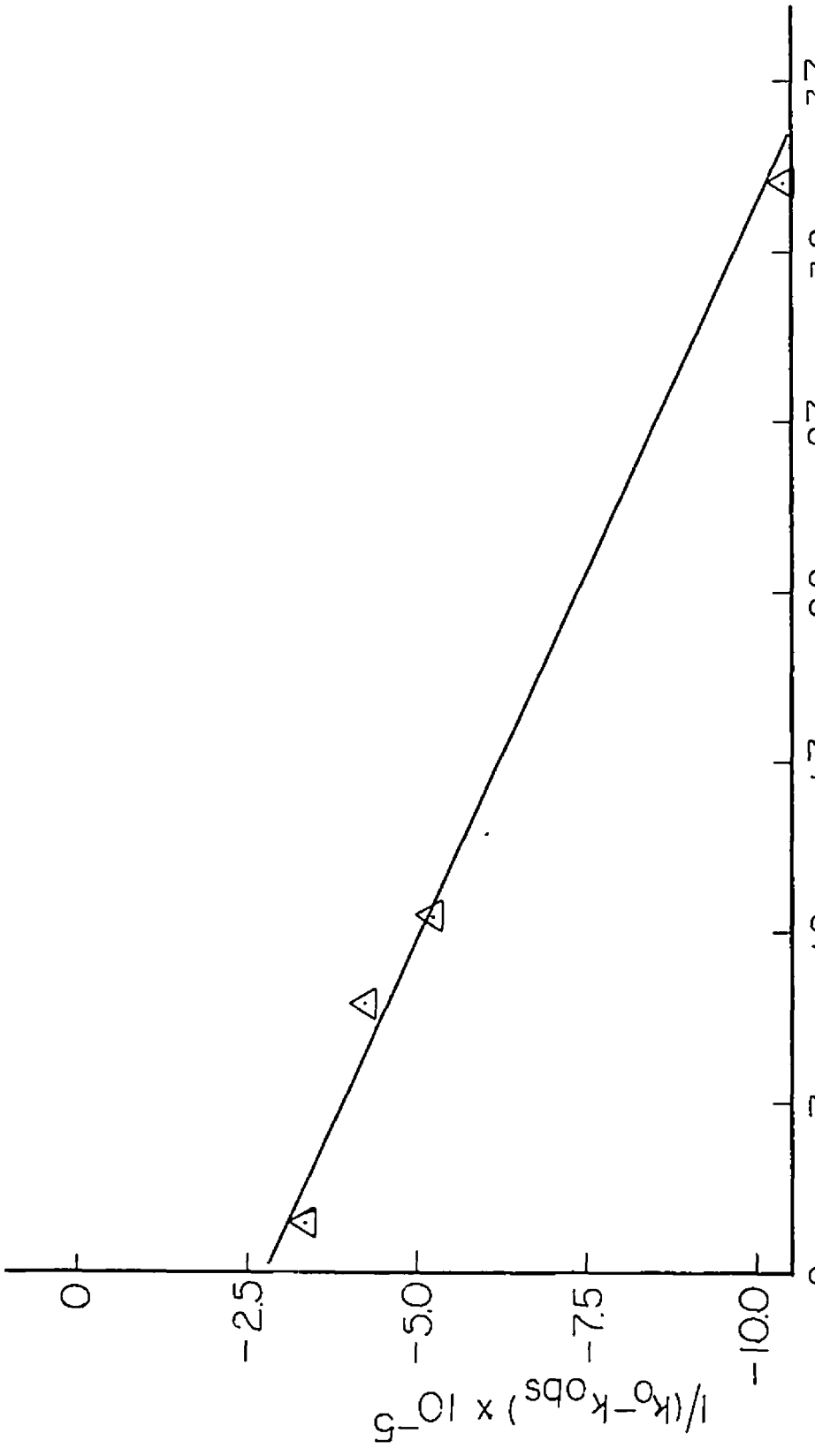


Figure 5. Plot of Equation 1 for the Base Hydrolysis of N-Methyloctanohydroxamic Acid.

TABLE 14

Sample Data for the Determination of k_{obs} for Octanohydroxamic Acid in 0.1111 N NaOH at 50.01 ± 0.11°C

Sample number	Clock time	Elapsed time (hr)	Absorbance	Average absorbance
1	09:11	0	0.248 0.248	0.248
2	14:00	4.81	0.217 0.217	0.217
3	18:18	9.12	0.190 0.189	0.190
4	22:04	12.88	0.164 0.165	0.165
5	04:37	19.43	0.119 0.120	0.120
6	09:32	24.36	0.084 0.087	0.086
7	12:27	27.26	0.070 0.072	0.071
8	15:05	29.90	0.054 0.052	0.053

Note. Ctab concentration = 30.04×10^{-4} M.

(See "Determination of Reaction Order by Use of the Noyes Equation" for explanation of the Noyes equation.) The least squares treatment of the data for a zero order equation,

$$A_t = -\epsilon bkt + A_o, \qquad (17)$$

(see Appendix A for derivation of equation) gives the following

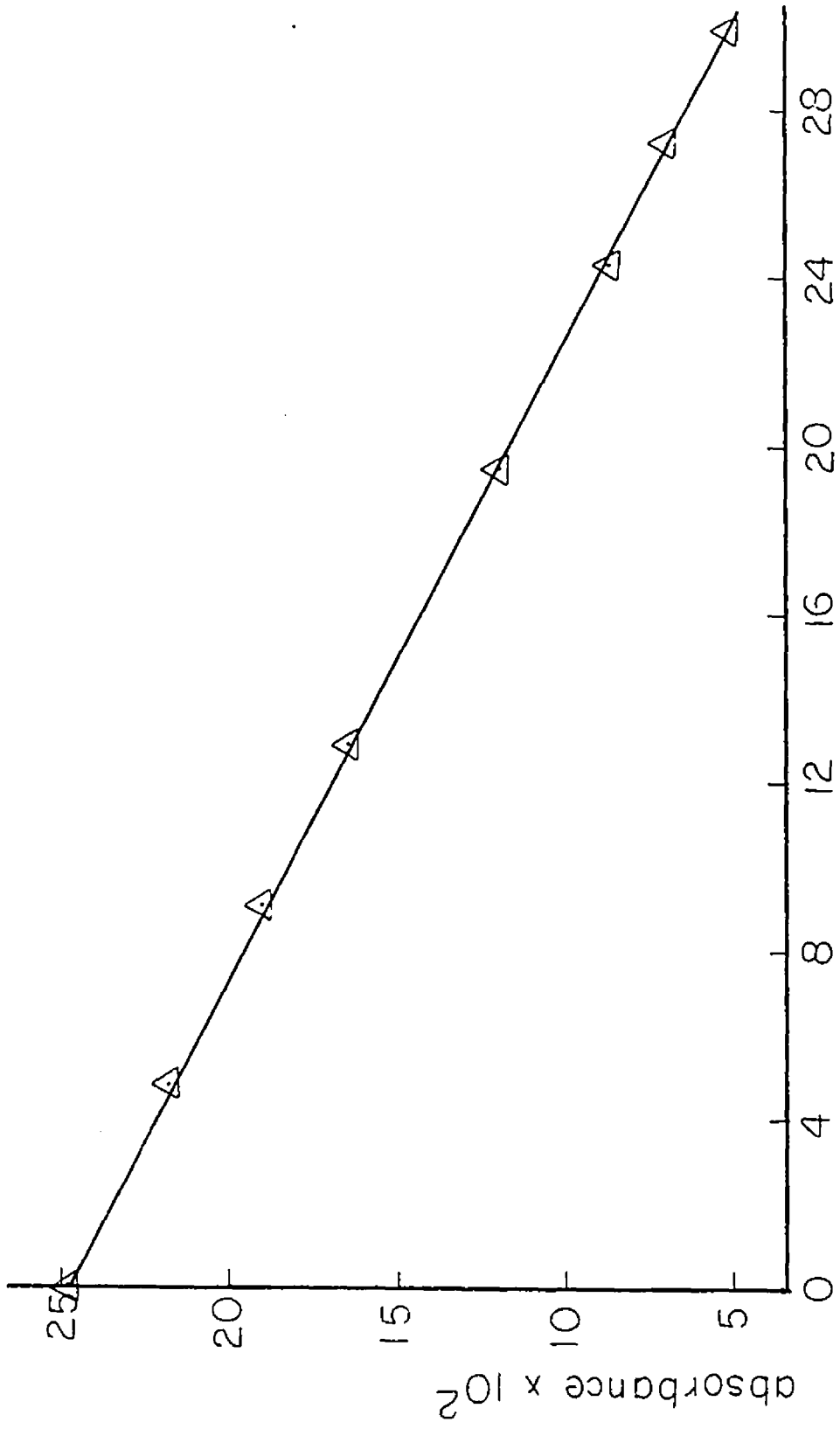


Figure 6. Plot of Absorbance Versus Time Data for the Base Hydrolysis of Octanohydroxamic Acid in 0.1111 N NaOH and 30.04×10^{-4} M CTAB.

results: slope, $-\epsilon bk$, = -6.57×10^{-3} A hr^{-1}; intercept, A_o, = 0.249 A; and the correlation coefficent = -0.9998. Therefore, $k = -(-6.57 \times 10^{-3})/\epsilon b$ or 2.10×10^{-10} mol L^{-1} sec^{-1} (the molar absorptivity, ϵ, = 8.67×10^{2} A cm^{-1} M^{-1}, from Table 8 and b = 10 cm). The duplicate run gives $k = 2.18 \times 10^{-10}$ mol L^{-1} sec^{-1} and the average $k = 2.14 \times 10^{-10}$ mol L^{-1} sec^{-1}. Figure 7 shows the plot of rate versus C_D for the pseudo zero-order points of the base hydrolysis of octanohydroxamic acid, which is similar to a rate-surfactant profile, Figure 3.

Determination of Δk_m and $\Delta K/N$

The accuracy of the values derived from Equation 1, k_m and K/N, listed in Table 13, can be estimated if the uncertainty in k_{obs} (Δk_{obs}) is known. The error in k_m (Δk_m) and K/N [$\Delta (K/N)$] can be calculated relative to Δk_{obs}, since

$$\frac{\Delta k_m}{\Delta k_{obs}} \approx \frac{\partial k_m}{\partial k_{obs}} \text{ when } \Delta k_{obs} \rightarrow 0.$$

This leads to

$$\Delta k_m = \frac{\partial k_m}{\partial k_{obs}} \cdot \Delta k_{obs}. \qquad (18)$$

Solving Equation 1 for k_m gives

$$k_m = \frac{k_{obs} \cdot [1 + (K/N) \cdot (C_D - cmc)] - k_o}{(K/N) \cdot (C_D - cmc)}. \qquad (19)$$

Using Equations 18 and 19 yields

$$\Delta k_m = \frac{\partial}{\partial k_{obs}} \frac{k_{obs} \cdot [1 + (K/N) \cdot (C_D - cmc)] - k_o}{(K/N) \cdot (C_D - cmc)} \cdot \Delta k_{obs}. \qquad (20)$$

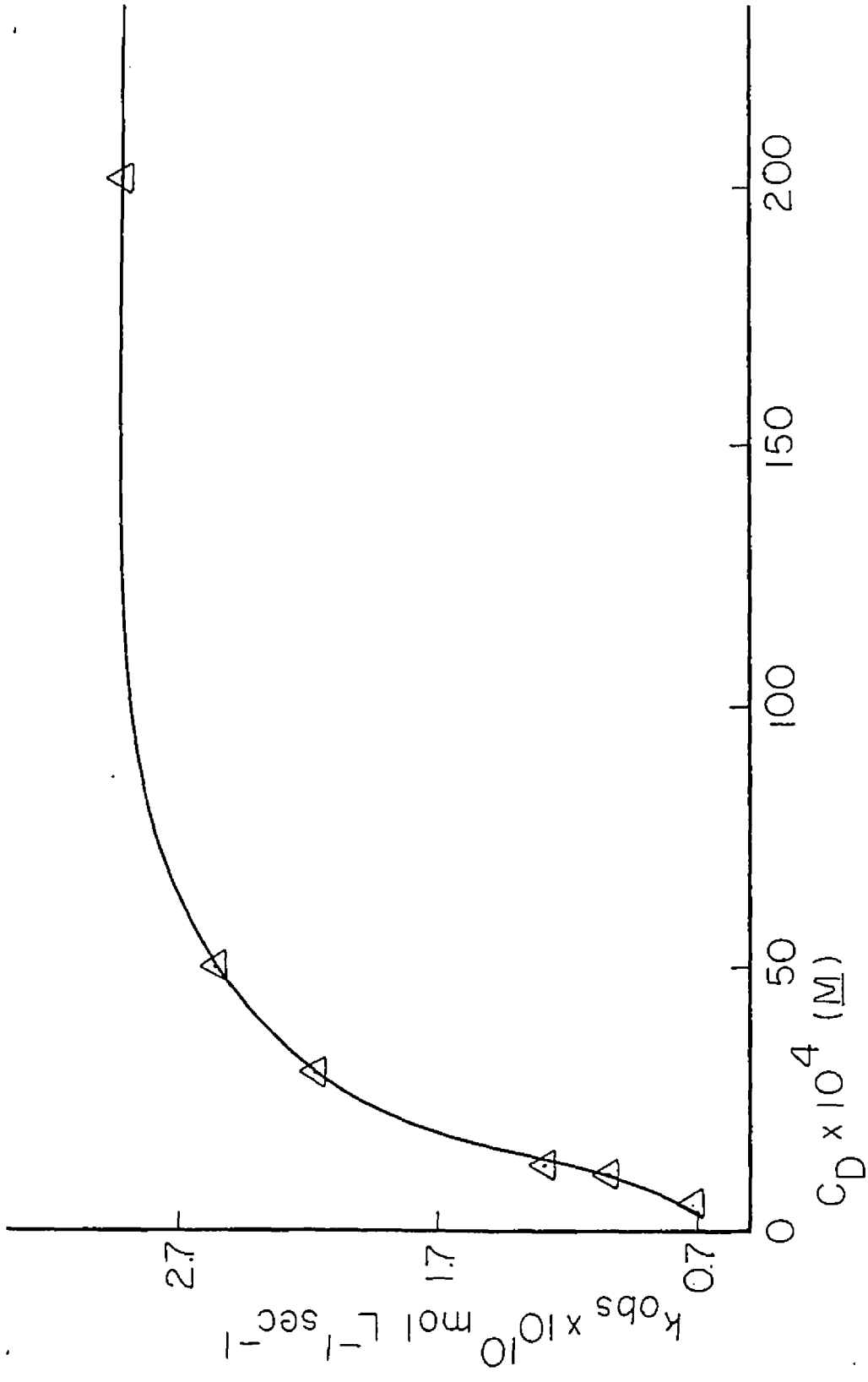


Figure 7. Plot of the Pseudo Zero-Order Rate Versus C_D for the Base Hydrolysis of Octanohydroxamic Acid in CTAB.

When K/N, C_D, cmc, and k_m are constant,

$$\Delta k_m = \frac{1 + (K/N) \cdot (C_D - cmc)}{(K/N) \cdot (C_D - cmc)} \cdot \Delta k_{obs}. \quad (21)$$

Applying the same procedure, $\Delta (K/N)$ can be determined when Equation 1 is rearranged to Equation 22.

$$K/N = \frac{k_{obs} - k_o}{(k_m - k_{obs}) \cdot (C_D - cmc)} \quad (22)$$

Therefore,

$$\Delta (K/N) = \frac{\partial (K/N)}{\partial k_{obs}} \cdot \Delta k_{obs} \quad (23)$$

or

$$\Delta(K/N) = \frac{\partial}{\partial k_{obs}} \frac{k_{obs} - k_o}{(k_m - k_{obs}) \cdot (C_D - cmc)} \cdot \Delta k_{obs}. \quad (24)$$

When k_o, C_D, cmc, and k_m are constant,

$$\Delta(K/N) = \frac{1 + (K/N) \cdot (C_D - cmc)}{(k_m - k_{obs}) \cdot (C_D - cmc)} \cdot \Delta k_{obs}. \quad (25)$$

An example is the acid hydrolysis of N-methyloctanohydroxamic acid in sodium 1-dodecanesulfonate. In this example, $C_D = 7.996 \times 10^{-3}$ M, $k_{obs} = 31.0 \times 10^{-5}$ sec^{-1}, K/N = 212, $k_m = 51.8 \times 10^{-5}$ sec^{-1}, cmc = 2×10^{-3} M, and k_{obs} = 3% of k_{obs} = 9.3×10^{-6} sec^{-1}. From Equation 21,

$$\Delta k_m = \frac{1 + 212 \cdot (7.996 \times 10^{-3} - 2 \times 10^{-3})}{212 \cdot (7.996 \times 10^{-3} - 2 \times 10^{-3})} \cdot 9.3 \times 10^{-6}$$

$$= 1.66 \times 10^{-5} \text{ sec}^{-1}.$$

The percent error is

$$\frac{\Delta k_m}{k_m} = \frac{1.66 \times 10^{-5}\ sec^{-1}}{51.8 \times 10^{-5}\ sec^{-1}} \cdot 100 = 3.2\%.$$

From Equation 25

$$\Delta(K/N) = \frac{1 + 212 \cdot (7.996 \times 10^{-3} - 2 \times 10^{-3})}{(51.8 - 31.0) \times 10^{-5} \quad (7.996 - 2) \times 10^{-3}} \cdot 9.3 \times 10^{-6}$$

$$= 16.9$$

and the percent error is

$$\frac{\Delta(K/N)}{K/N} = \frac{16.9}{212} \cdot 100 = 7.99\%.$$

By this procedure, the error in k_m and K/N, for the acid hydrolysis of N-methyloctanohydroxamic acid, ranged from 3.0 - 3.2% and 8.0 - 21.0%, respectively. The error in k_m and K/N for octanohydroxamic acid in acid ranged from 3.0 - 3.7% and 6.1 - 23.9%, respectively, and for N-methyloctanohydroxamic acid in base the errors ranged from 3.2 - 6.1% and 10.1 - 15.2%, respectively.

Determination of Reaction Order by Use of the Noyes Equation

A change from pseudo first-order to pseudo zero-order was observed in the base hydrolysis of octanohydroxamic acid. This can be seen by comparison of Figure 6, a plot of absorbance versus time data for octanohydroxamic acid with its straight line indicating pseudo zero-order kinetics, and Figure 8, the same type of plot for N-methyloctanohydroxamic acid and its curved line showing pseudo first-order kinetics. Pseudo first-order kinetics was observed below 4.92×10^{-4} M ctab and above this concentration the reaction was pseudo zero-

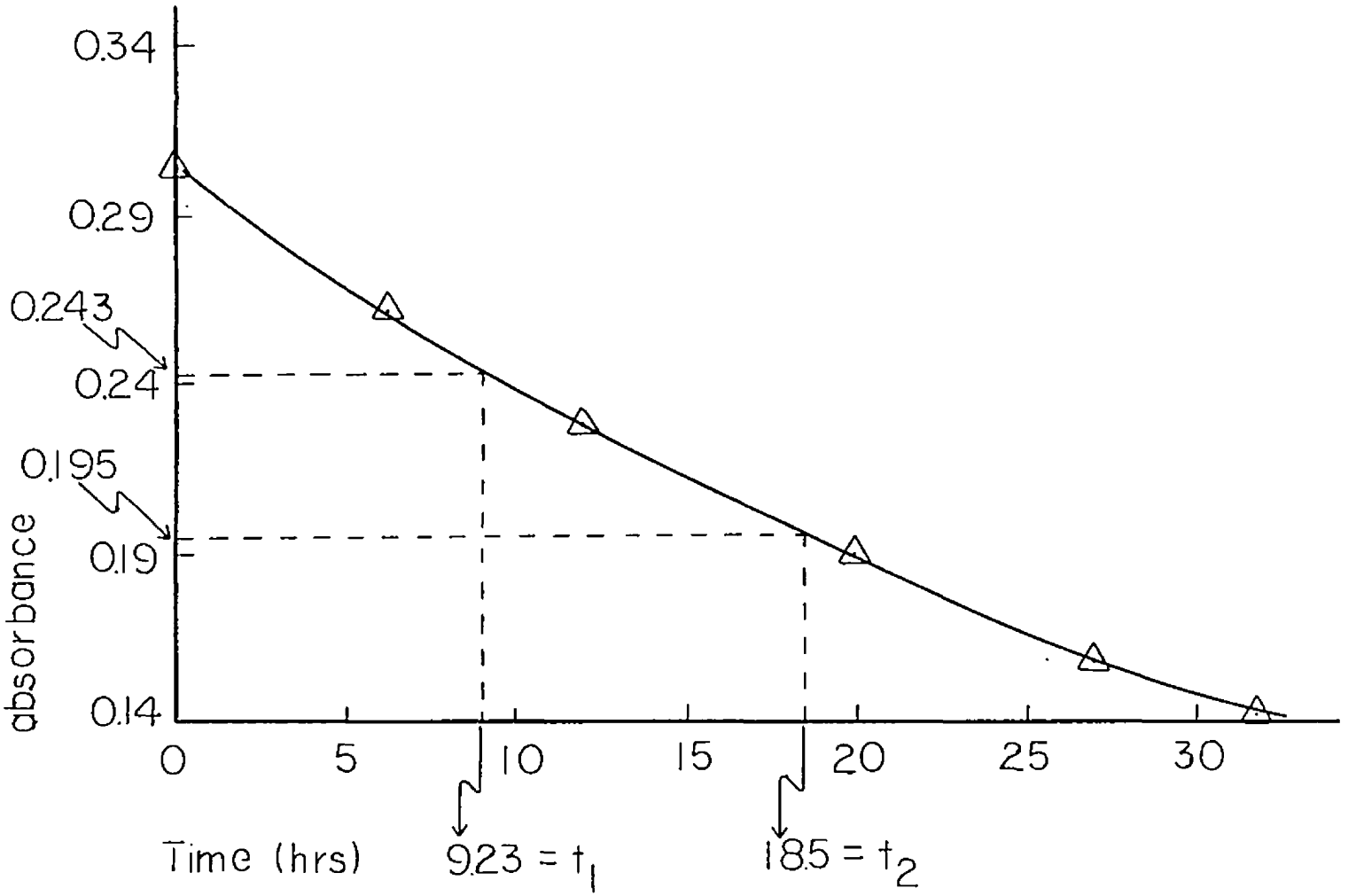


Figure 8. Example of a Determination of Reaction Order by the Use of Two Successive Fractional-Life Periods.

order. To investigate this change in order, additional base hydrolyses were done at higher (0.1829 N) and lower (0.04539 N) NaOH concentrations.

The order of these reactions was determined by a fractional-life method. The order of a reaction can be determined by use of the Noyes equation,[48]

$$n = 1 + \frac{\log t'_{1/2} - \log t_{1/2}}{\log a - \log a'} \qquad (26)$$

where $t_{1/2}$ is the half-life of one reaction with initial concentration a and $t'_{1/2}$ is the half-life of another reaction with initial concentration a'. The Noyes equation is valid if the rate expression is of the form

$$\frac{dx}{dt} = k(a - x)^n \qquad (27)$$

where a is the initial concentration, x is the amount reacted, and n is the reaction order. Although the Noyes equation was derived for two separate runs with different initial concentrations, two successive time intervals in a single run may be used. In this case, the concentration at the end of one time interval becomes the initial concentration for the new time interval. Furthermore, the Noyes equation can be applied to any t_y, the time for the fraction reacted to be equal to y. The equation in this case is

$$n = 1 + \frac{\log [(t_2/t_1) - 1]}{\log [1/(1 - y)]} \qquad (28)$$

where y is some fractional-life, t_1 is the time at the y fraction of

the initial concentration (absorbance) to have reacted, and t_2 is the time the y fraction of the concentration (absorbance) of the new time interval of a single run to have reacted; that is, $t_1 = a(1 - y)$ and $t_2 = a(1 - y)^2$.

An example of the use of Equation 28 is shown in Figure 8. The run shown is the base hydrolysis of N-methyloctanohydroxamic acid in 0.04539 N NaOH and 0.039981 M ctab. y was chosen to be 0.2 because data at the beginning of the reaction may be more accurate.[48] Therefore, t_1 and t_2 would be the times when the absorbance had fallen to 0.8 and 0.64, respectively, of the initial value. The initial absorbance was 0.304 and the absorbances are 0.243 and 0.195. From Figure 8, t_1 = 9.23 hrs. and t_2 = 18.5 hrs. Using t_1, t_2, and Equation 28 gives n = 1.02. The duplicate run gave n = 1.03 and the average n = 1.03. This value indicates that the reaction was pseudo first-order; therefore, pseudo first-order equations were used to determine k. The results for the octanohydroxamic acid hydrolysis in 0.1111 N NaOH are listed in Table 15. The additional base runs at 0.1829 N and 0.04539 N NaOH are listed in Table 16. The order determined by the Noyes equation quantitatively followed what was qualitatively observed in plots of absorbance versus time data.

Approximation of Error in Calculation of Reaction Order

The accuracy of the values derived from Equation 28, n, listed in Tables 15 and 16, can be estimated if the uncertainty in t_1 (Δt_1) and t_2 (Δt_2) are known. The error in n (Δn) can be calculated relative to Δt_1 and Δt_2, since

TABLE 15

Reaction Order of Base Hydrolysis of Octanohydroxamic Acid by Use of Equation 28

$C_D \times 10^4$ (M)	Order	$C_D \times 10^4$ (M)	Order
0.0	1.06 ± 0.2	30.04	-0.072 ± 0.2
0.27	1.04 ± 0.1	50.01	0.043 ± 0.2
1.5	1.04 ± 0.2	201.9	0.026 ± 0.1
4.92	-0.059 ± 0.1	399.9	0.012 ± 0.2
10.0	-0.077 ± 0.1	600.1	-0.078 ± 0.2
12.00	-0.072 ± 0.1		

$$|\Delta n| = \left|\frac{\partial n}{\partial t_1}\right| |\Delta t_1| + \left|\frac{\partial n}{\partial t_2}\right| |\Delta t_2| . \qquad (29)$$

From Equation 28

$$|\Delta n| = \left|\frac{\partial}{\partial t_1}\left(1 + \frac{\ln[(t_2/t_1) - 1]}{\ln[1/(1 - y)]}\right)\right| |\Delta t_1|$$

$$+ \left|\frac{\partial}{\partial t_2}\left(1 + \frac{\ln[(t_2/t_1) - 1]}{\ln[1/(1 - y)]}\right)\right| |\Delta t_2| \qquad (30)$$

when y and t_1 or t_2 are appropriately held constant

$$|\Delta n| = \left|\frac{-t_2}{t_1(t_2 - t_1) \cdot \ln[1/(1 - y)]}\right| |\Delta t_1|$$

$$+ \left|\frac{1}{t_2 - t_1 \circ \ln[1/(1 - y)]}\right| |\Delta t_2| . \qquad (31)$$

TABLE 16

Kinetic Data for the Base Hydrolysis in 0.1829 N and 0.04539 N NaOH at 50.01 ± 0.11°C

NaOH (N)	$C_D \times 10^4$ (M)	Order	Ave. k	$t_{1/2}$ (hr)
Hydrolysis of Octanohydroxamic Acid				
0.04539	50.05	0.024 ± 0.1	2.97[a]	13.5
0.1829	20.1	0.105 ± 0.1	2.51[a]	16.7
Hydrolysis of N-Methyloctanohydroxamic Acid				
0.04539	399.8	1.03 ± 0.2	6.20[b]	31.1
0.1829	200.1	0.915 ± 0.2	8.13[b]	32.7

Note. The value of r ranged from -0.9975 to -0.9998. Percent difference in k for duplicate runs did not exceed 2.5%.

a Pseudo zero-order equations were used to determine k and are ave. k x 10^{10} mol L^{-1} sec^{-1}.

b Pseudo first-order equations were used to determine k and are ave. k x 10^6 sec^{-1}.

Δt_1 and Δt_2 are related to the average observed error in the absorbance, ± 0.001 A, and are determined graphically from a plot of absorbance versus time data, such as, Figure 6. From Figure 8, Δt_1 = 0.1 hr and Δt_2 = 0.2 hr. In this example, the base hydrolysis of N-methyloctanohydroxamic acid, y = 0.2, therefore, Equation 31 is

$$|\Delta n| = \left|\frac{-18.5}{9.23 \cdot 9.27 \cdot \ln(1.25)}\right| 0.1| + \left|\frac{1}{9.27 \cdot \ln(1.25}\right| 0.2|$$

$$= 0.19 \approx 0.2$$

and for the duplicate run $\Delta n \approx 0.2$ for an average Δn of 0.2. Tables 15 and 16 show the calculated orders and the associated average Δn values. The large Δn values are a consequence of the low absorbances. The requirement that the reactant concentration be less than C_D[8] and the method of analysis are contributors to the low absorbances.

CHAPTER IV

DISCUSSION

Experimental Conditions

All reactions were carried out at 50.01 ± 0.11°C. The initial concentration of the reactants, octanohydroxamic acid and N-methyl-octanohydroxamic acid, was 5×10^{-4} M. The hydrolysis was run without surfactant to determine the rate in bulk solution, k_o. The surfactant concentration ranged from below the kinetic cmc and increased until the rate reached a plateau. The standard kinetic scheme, Figure 2, was used to interpret the rate data. Equation 1 allowed determination of k_m, the micellar rate, and K/N, which is related to how well the reactant is bound to the micelle.

Reaction Order

Equation 12, the overall reaction for the acid hydrolysis, indicates that if the acid concentration is large relative to the hydroxamic acid concentration the observed rate will be pseudo first-order. Previous work [23-26] and the results of this study show that an acid concentration of 0.09270 N HCl results in pseudo first-order kinetics, as expected.

The base hydrolysis is also expected to show pseudo first-order kinetics based on previous studies [24,26] of related compounds, N-methyl-benzohydroxamic acids, and the overall reaction for the base hydrolysis, Equation 13. N-Methyloctanohydroxamic acid shows pseudo

first-order kinetics and, therefore, fits the typical pattern of micellar catalysis. However, octanohydroxamic acid exhibits pseudo first-order behavior below 4.92×10^{-4} M ctab. Without surfactant and below the kinetic cmc pseudo first-order kinetics is observed, as would be expected from previous work without surfactant[24] and the behavior of surfactants below the cmc.[11] At 4.92×10^{-4} M ctab and above pseudo zero-order kinetics, qualitatively seen in the absorbance versus time data and determined by the Noyes equation, is observed. Therefore, further interpretation by Equation 1 would be invalid since Equation 1 is based on the standard kinetic scheme, which is first order in substrate.

Acid Hydrolysis

The pseudo first-order rate constant, k_{obs}, commonly increases with increasing surfactant concentration above the cmc until a maximum occurs.[8] The data for the acid hydrolysis shows this behavior, which can be seen in Figure 3, the rate-surfactant profile, Table 10, and the correlation by Equation 1 over a limited surfactant concentration range ($r \approx -0.9918$ to -0.9981, F test[46] shows significance within the 0.1% level[47]) as shown in Figure 4. Examination of k_{obs} and $t_{1/2}$ for the acid hydrolysis, Table 10, reveals that the surfactant has a significant effect on the rate of hydrolysis above the kinetic cmc, 2×10^{-3} M sodium 1-dodecanesulfonate. k_{obs} increases and $t_{1/2}$ decreases as the surfactant concentration increases. The maximum rate occurs at 30.01×10^{-3} M sodium 1-dodecanesulfonate for N-methyloctanohydroxamic acid and at 40.00×10^{-3} M for octanohydrox-

amic acid. An increase in surfactant concentration above these maximums exhibits a decrease in the reaction rate (Table 10). Presence of a maximum in the rate-surfactant profile occurs frequently. The decrease has been interpreted to occur from an increase in the number and size of micelles resulting in a dilution of the reactant and of the hydrophilic ionic reactant in the micelles[8] which brings about a decrease in the micellar rate constant, k_m, therefore, decreasing k_{obs}, which is a combination of k_m and k_o.

N-Methyloctanohydroxamic acid is hydrolyzed faster than octanohydroxamic acid (Table 10). The reaction is most likely similar to an amide hydrolysis. As such, the relative rate depends on many factors, and if loss of the leaving group is the rate-limiting step, then the reactant with the leaving group that can best accommodate the developing negative charge would be the faster reactant.[49,50] Comparison of the leaving groups, finds that $CH_3\text{-}\overset{+}{N}H_2OH$ can best accommodate the electrons and, therefore, N-methyloctanohydroxamic acid would be expected to react faster. The presence of the micelles did not significantly affect the behavior of the leaving group since the order of the relative rate did not change; that is, N-methyloctanohydroxamic acid is faster with and without surfactant.

All the values of the kinetic ratio, k_m/k_o, listed in Table 13, are greater than one. The indication, according to the standard kinetic scheme, Figure 2, is that the reaction within the micelle, k_m, is more predominant than the reaction in bulk solution, k_o. The increased micellar rate can be understood by the proximity effect.[16] The reactants are more soluble in the micelle. The acid concen-

tration surrounding the micelle is increased by the electrostatic attraction: The micelle is composed of negatively charged surfactant molecules, i.e., 1-dodecanesulfonate anion. The outcome is the determined micellar rate constant, k_m, is greater than the bulk rate constant, k_o, due to the increase in the concentration of the reactants compared to bulk. This does not indicate whether or not the micellar rate constant, corrected to the micellar phase volume, is greater than the bulk rate constant.[8, 16]

In the standard kinetic scheme, Figure 2, K is an equilibrium constant between the free reactant and the micellarly bound reactant. Table 13 lists the K/N values, which are related to K, assuming that N does not significantly change over the surfactant range used. K/N gives an indication of the position of the equilibrium. N-Methyloctanohydroxamic acid, K/N = 212, would be expected to be bound tighter to the micelle than octanohydroxamic acid, K/N = 101. The kinetic ratio, discussed above, follows an inverse relationship to K/N; that is, the larger K/N becomes the smaller the kinetic ratio. This has been interpreted to indicate that the larger K/N the deeper the reactant is solubilized in the micelle; therefore, the reactant is in the hydrocarbon core of the micelle.[22] Less contact with the acid occurs bringing about a smaller k_m relative to the bulk rate. This effect is seen in a smaller kinetic ratio.

Base Hydrolysis

For N-methyloctanohydroxamic acid, the base hydrolysis follows the standard kinetic scheme: The rate increases with increasing

surfactant concentration and pseudo first-order kinetics is observed. A maximum occurs at 201.9 x 10^{-4} M ctab and at larger surfactant concentrations the rate decreases to a plateau at $\approx$ 7 x 10^{-6} sec^{-1}. The presence of a maximum in the rate-surfactant profile is described above ("Acid Hydrolysis").[8] Table 13 and Figure 5 show the results of the interpretation by Equation 1 (r = -0.9959, F test[46] shows significance within the 1.0% level[47]). The kinetic ratio = 3.32 and K/N = 1001. The low kinetic ratio would be expected from the large K/N as discussed above ("Acid Hydrolysis").[22]

The half-life, $t_{1/2}$, listed in Table 11, for N-methyloctanohydroxamic acid and octanohydroxamic acid, shows that the hydrolysis is faster for octanohydroxamic acid with and without ctab. The base hydrolysis is probably like an amide hydrolysis. The relative rate for such reactions is dependent upon many factors; however, the major differences in these two reactants are the leaving group and the location of the negative charge on the reactant, which would be expected to be in the anionic form under the experimental conditions. If the loss of the leaving group is the rate-determining step, then the faster reaction would be expected to be the one with the leaving group that can best accommodate the negative charge, that is, the weaker Lewis base.[49,50] In this case, N-methylhydroxylamine is the stronger base, and, therefore, octanohydroxamic acid would be expected to react faster. Again the order of the relative rate did not change with the introduction of micelles which implies that the micelles did not produce a large change in mechanism.

Octanohydroxamic acid must not follow the standard kinetic

scheme because above the kinetic cmc, 2×10^{-4} M ctab (assumed to be the same as that of N-methyloctanohydroxamic acid) pseudo zero-order kinetics is observed (Table 11). This result is not expected since the reaction is pseudo first-order below the kinetic cmc and without surfactant. To investigate this unexpected observation, hydrolyses in 0.04539 N and 0.1829 N NaOH were done. In both cases, octanohydroxamic acid shows pseudo zero-order kinetics. N-Methyloctanohydroxamic acid was also run at these base concentrations and resulted in pseudo first-order kinetics (Table 16). Therefore, the base concentration from 0.04539 to 0.1829 N does not play an important role in the change in order for octanohydroxamic acid. Further investigation into how octanohydroxamic acid is solubilized in ctab micelles and the effect the micelles have on the equilibrium between the free acid and its salt may help in understanding this unanticipated observation.

Conclusion

The standard kinetic scheme, Figure 2, and Equation 1 work well to describe the micellarly catalyzed acid hydrolysis of N-methyloctanohydroxamic and octanohydroxamic acids in sodium 1-dodecanesulfonate. The rate of hydrolysis for N-methyloctanohydroxamic acid is faster with and without surfactant.[49,50] The kinetic ratio, k_m/k_o, and K/N show an inverse relationship due to solubility factors.[24]

The cationic micelles, formed with ctab, catalyze the base hydrolysis of N-methyloctanohydroxamic acid, and the use of the standard kinetic scheme and Equation 1 work well in interpreting the data.

A large K/N, 1001, and a small kinetic ratio, 3.32, were found. Octanohydroxamic acid shows pseudo zero-order kinetics above the kinetic cmc. Apparently, the base concentration does not play a significant role in the change in the order of the reaction, since no change in the order is observed at half and double the base concentration for both compounds.

Further investigation into how octanohydroxamic acid is solubilized in ctab micelles and what form, free acid or salt, the compound is in in the micellar micro-environment, which is where most of the compound is expected to be found, may help in understanding the observed change in order. In addition, studies with other N-substituted alkylhydroxamic acids should be done to help understand the solubility, lipophilic, and electronic effects on the micellarly catalyzed hydrolysis of these compounds.

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APPENDIX A

DERIVATION OF ZERO ORDER RATE EQUATION

The rate expression for a zero order reation is

$$\frac{-dC}{dt} = k \tag{32}$$

where C is the reactant concentration, t is the time, and k is the zero order rate constant. Integration of the rate expression results in Equation 33

$$C_t = kt + C_o \tag{33}$$

where C_t is the reactant concentration at time t and C_o is the reactant concentration at zero time. When a_o = the initial reactant concentration at zero time and x = the amount reacted at time t, then Equation 33 becomes

$$(a_o - x) = -kt + a_o \tag{34}$$

and dividing by a_o gives

$$\frac{(a_o - x)}{a_o} = \frac{-kt}{a_o} + 1. \tag{35}$$

$$\frac{(a_o - x)}{a_o} = \frac{A_t - A_\infty}{A_o - A_\infty} = \frac{A_t}{A_o} \quad \text{since } A_\infty = 0 \tag{36}$$

where A_t = absorbance at time t, A_o = initial absorbance at t = 0, and A_∞ = absorbance at infinite time, i.e., complete reaction, is zero. Substituting Equation 36 into Equation 35 gives

$$\frac{A_t}{A_o} = \frac{-kt}{a_o} + 1$$

or

$$A_t = \frac{-A_o kt}{a_o} + A_o. \qquad (37)$$

Beer's law for the initial absorbance and concentration states is

$$A_o = \epsilon b a_o \qquad (38)$$

where ϵ = molar absorptivity and b = path length in cm. Using Equations 37 and 38 gives

$$A_t = \frac{-\epsilon b A_o kt}{A_o} + A_o$$

or

$$A_t = -\epsilon bkt + A_o. \qquad (17)$$

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