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The Effect of Pyridine and Some 4-Substituted Pyridines on Corrosion Inhibition

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UNION COLLEGE - GRADUATE STUDIES

Schenectady, New York

THE EFFECT OF PYRIDINE AND SOME 4-SUBSTITUTED
PYRIDINES ON CORROSION INHIBITION

A thesis presented to the Committee on Graduate Studies
and the Department of Chemistry of Union College, Schenectady,
New York, in partial fulfillment of the requirements for the
degree of Master of Science.

By Eugene Andrew Grossi MS 1967

By Eugene Andrew Grossi

Approved by William B. Martin, Jr.
Thesis advisor

Approved by Wm. C. G. L.
Committee on Graduate Studies

Date 6/17/67



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To Joyce, Michael and Andrew

ACKNOWLEDGEMENTS

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ABSTRACT

A study of the corrosion inhibition activity of pyridine and eight of its 4-substituted derivatives was undertaken. The effect of these compounds on the corrosion of carbon steel in deoxygenated aqueous ammonium citrate solution at room temperature was studied.

The rate of corrosion is found to be diffusion controlled under these experimental conditions. The rate of diffusion of hydrogen ions through a ferrous mono hydrogen citrate corrosion film is believed to be rate-limiting.

A mechanism for the inhibition of the corrosion of carbon steel in this system is proposed. The pyridine derivatives are believed to adsorb at cathodic sites and to create an additional diffusion barrier.

Pyridine derivatives which are strongly associated with protons as pyridinium ions in solution adsorb normal to the surface. The interaction is assumed to be primarily coulombic between the positive pyridinium ion and the excess electron density at the cathodic sites. Pyridine derivatives which have an electron deficient ring system apparently adsorb chemically parallel to the surface. This bonding would involve the overlap of d orbitals of iron and vacant or electron deficient orbitals of the pyridine ring.

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I INTRODUCTION

A study of the effect of structure on the ability of 4-substituted pyridine derivatives to inhibit metallic corrosion has been undertaken. The metal-environment system chosen for study was carbon steel in deoxygenated aqueous ammonium citrate at room temperature. Pyridine and eight of its derivatives were investigated.

The pyridine derivatives were selected for study, since the previous studies reported in the literature has demonstrated that these compounds act as corrosion inhibitors in various acidic media, although a systematic study of the effect of structure on inhibitive properties has not been reported. While aqueous solutions of ammonium citrate have been shown to be exceedingly corrosive to carbon steel at elevated temperatures, such as those encountered in chemical cleaning applications, very little work has been undertaken at lower temperatures.

Our purpose, then, was to study the structural effects of substitution on pyridine's properties as a corrosion inhibitor, and to determine if a linear free energy relationship, as expressed by a Hammett sigma-rho equation, could be found to exist between inhibitor activity and substituent parameters; or, as Hackerman and Hurd¹ demonstrated for 4-substituted, N-methylanilines in hydrochloric acid, that the activities could be correlated with the pi orbital

I INTRODUCTION (CONTINUED)

character of the bond between the adsorbed amine and the metallic surface.

The art of inhibiting corrosion through the use of organic substances dates to the Middle Ages. The master-armourers added flour, yeast, and other products to their acids when pickling metal articles to retard dissolution of the metal and to prevent its embrittlement.² The science of corrosion inhibition of organic compounds was put on a firmer basis by the work performed in the late 1920's, which were early attempts to understand the role of inhibitor adsorption in the inhibition process.^{3,4} Since that time the application of electrochemical methods, such as electrode polarization, double layer capacitance, and electrocapillarity measurements, and surface chemical investigations have increased our understanding of the fundamental nature of inhibition. However, a better understanding of the interaction between adsorbed molecules and metallic surfaces must be developed.

The first large scale systematic investigation of the effect of the structure of an organic molecule on its ability to inhibit corrosion was performed by Mann and coworkers⁵ in the 1930's. These workers investigated more than one hundred and fifty compounds in 5% sulfuric acid at room temperature. Their studies showed alkyl sulfides and thioureas to be superior to the other compounds tested. These compounds included alkylamines, anilines, ketones, aldehydes, esters, and a few pyridines. A recent study⁶ of several types of organic inhibitors in 10% hydrochloric acid at room temperature confirmed that the protective value of sulfur-containing compounds is generally superior to that of their nitrogen

analogs. In spite of this fact, nitrogen-containing organic inhibitors have been the subject of considerable investigation, especially for non-ferrous metals such as aluminum.⁷

A study of the structural effects in a number of polymethylenamines, piperidine, pyrrolidine, and di-n-amylamine on the corrosion inhibition efficiency of these compounds in 6 N hydrochloric acid, led Hackerman and coworkers⁸ to conclude: (1) that there is little direct dependence of inhibitor efficiency on the surface area covered by the amine, (2) that there is no direct dependence of inhibitor efficiency on the number of methylene groups, or its related parameters such as solubility, (3) that the base strength alone can not be used to postulate the strength of the adsorbate-metal bond, and (4) that the marked differences in efficiency for molecules of different structure are not caused by differences in the free amine concentration. Mann et.al.⁹ had previously found that differences in inhibitor efficiency could be related to the area covered by a molecule within groups of similar methyl- and dimethylanilines. These authors also reported that in sulfuric acid the inhibitor activity of propylamine is greater than that of ethylamine, which in turn is greater than that of methylamine.

The studies on the inhibitor activity of pyridine and its derivatives which have been reported in the literature have been quite limited in scope. The order of decreasing inhibitor activity in 5% sulfuric acid was found to be: 3-butylpyridine, quinoline, 2,4-dimethylpyridine, 3-propylpyridine, 2-ethyl-4-methylpyridine, 4-methylpyridine,

3-ethylpyridine, and lastly, pyridine.⁵ The only definite conclusion which can be drawn is that the corrosion inhibiting properties of 3-substituted pyridines increases with increasing length of the alkyl chain. Every and Riggs⁶ found the order of efficiency in 10% hydrochloric acid to depend on inhibitor concentration. At an inhibitor concentration of one percent the order was found to be 2-ethylpyridine less than pyridine, less than picolinic acid, 2-hexylpyridine, and 4-n-propylpyridine, the last three of which were equal in activity.

A number of studies of the adsorption of pyridine on metallic surfaces, notably iron and mercury, have been reported in the literature. Parfenov and Cherryakov¹⁰ determined the amount of pyridine adsorbed on an iron plate from a solution of pyridine in sulfuric acid by measuring the surface tension of mercury in this solution at the maximum electrocapillarity potential before and after immersion of the plate. Their results indicated that 1.4×10^{-5} moles of pyridine were adsorbed per sq. cm. of iron surface from a 10^{-3} molar pyridine solution. Conway and Barradas,¹¹ on the basis of electrocapillarity measurements in solutions of pyridine, concluded that the specific pi orbital interactions determine the orientation of the pyridine molecules at a mercury electrode surface. Also employing electrocapillarity measurements, together with differential capacitance measurements, Klyukina and Damaskan¹² reported that pyridine is adsorbed from neutral potassium chloride

solutions onto a negatively charged mercury electrode in a vertical orientation (adsorbed through nitrogen-metal interaction). But as the negative charge is diminished the molecules reorient themselves to a position in which the pyridine ring is parallel to the surface. This parallel orientation was also noted by Annard and co-workers¹³ for the adsorption of 4-ethylpyridine onto iron from hydrochloric acid, and by Yu Yao¹⁴ for the adsorption of pyridine vapor onto iron.

II EXPERIMENTAL PROCEDURES

A-Specimen Preparation

The steel specimens used in this study were of American Iron and Steel Institute type 1020 carbon steel. These specimens were sheared from 0.17 cm. thick cold rolled sheet stock; its vender analysis shown in Table 1. The dimensions of the specimens were 5.1 cm. x 2.5 cm. x 0.17 cm., and each specimen weighed approximately 18 grams after preparation. The geometric surface area was 28.1 cm^2 .

The specimens were initially ground on 400 grit garnet paper, moistened with methanol. Methanol was used rather than water because wetting with water led to rapid deterioration of the grinding paper. After a brief rinse in distilled water, the specimens were polished on 600 grit silicon carbide paper, which had been wet with water. The polished specimen was then exposed to a water jet in order to dislodge particles of abrasive which might have imbedded in the surface.

The specimens were then degreased in boiling benzene for ten minutes, rinsed in flowing distilled water, and etched in 15% sulfuric acid for ten minutes. After etching the surface possessed a slightly matte appearance and was free of visible scale and discoloration. The etching treatment was followed by a rinse in flowing distilled water and then a rinse in

TABLE I

CHEMICAL ANALYSIS OF STEEL SPECIMENS

Element	Weight Percent Present
Carbon	0.18
Managanese	0.38
Phosphorus	0.016
Sulfur	0.028
Nickel	0.002
Chromium	0.002
Copper	0.08
Vanadium	0.05
Molybdenum	0.04
Iron	Remainder

acetone. The specimens were placed in a desiccator containing anhydrous calcium sulfate until they were to be weighed.

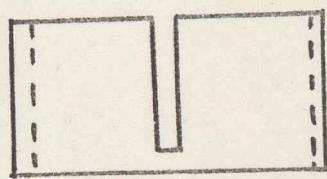
The samples were weighed to the nearest 0.1 mg. using a Ainsworth and Sons Type DLB double-pan analytical balance. After they had been weighed, the specimens were mounted in a polyethylene holder and placed in a glass test container with a screw-on closure cap. The holder and test container are shown in Figure 1. The closure cap remained in place until the test container was to be filled with the test solution.

B-Test Solution Preparation and Transfer

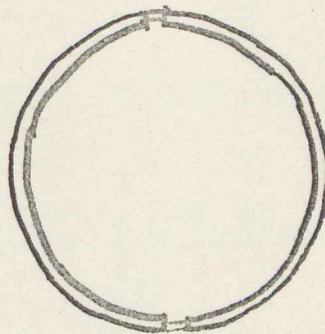
Since it was desired to study the effect of inhibitor structure on the corrosion of carbon steel in ammonium citrate solutions with a low residual oxygen concentration (0.5 ppm.), it was necessary to construct an apparatus in which the test solutions could be prepared and transferred to the test containers without exposing them to the atmosphere. The apparatus shown in Figure 2 was used for this purpose.

The system consisted of four liter polyethylene reservoir, glass valves and tubing, and a syringe and stainless steel tube for introducing the liquid pyridine derivatives into the reservoir. The procedure employed to prepare and transfer the test solutions was as follows:

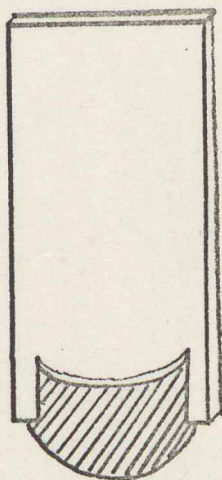
If the pyridine derivative was a solid (as 4-cyano, 4-amino-, 4nitro-, or 4-hydroxypyridine) or if no inhibitor was being added, then weighed amounts of the ammonium citrate and the solid pyridine derivative were added to the solution reservoir and approximately 3000 ml. of deionized water was



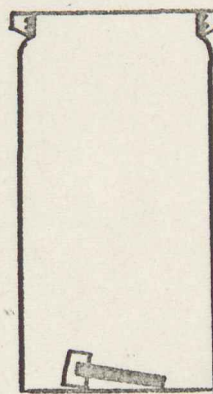
a



b



c



d

Figure 1. Specimen Holder and Container
 a- Side view of holder (twice scale)
 b- Top view of holder (twice scale)
 c- Face view of specimen in holder (to scale)
 d- Specimen orientation in container

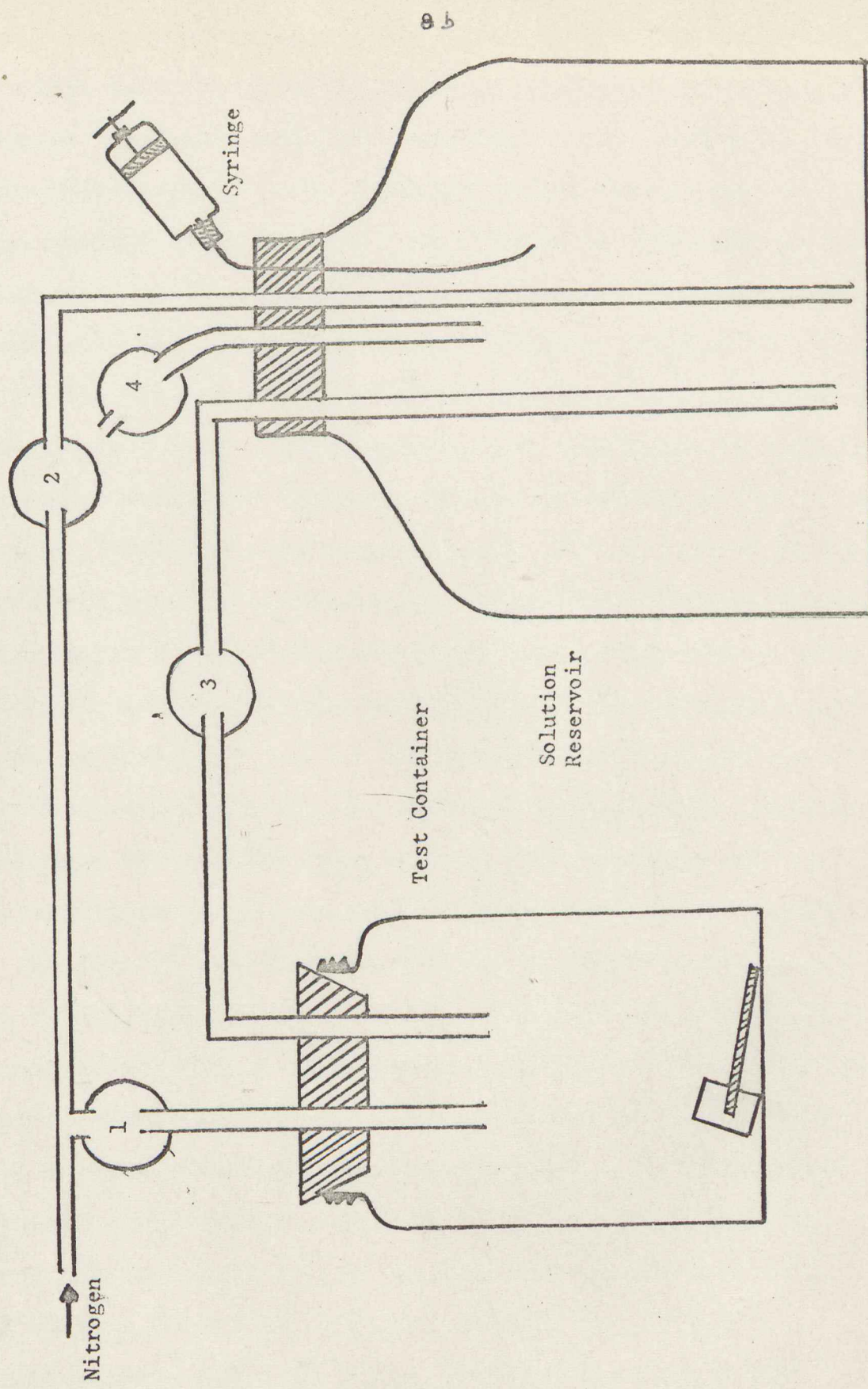


Figure 2. Test Solution Preparation and Transfer Apparatus

added. The rubber stopper, through which the glass and stainless steel tubes entered the reservoir, was put in place. The deionized water was prepared by passing steam condensate through a Illco-Way Research Model Dionizer (mixed bed). This water had an average resistivity of ten megohm-cm. The resistivity was measured using a Industrial Instruments, Inc. flow through conductivity cell, having a cell constant of 0.01 cm^{-1} .

If the pyridine derivative was a liquid (as pyridine, or its 4-chloro-, 4-methyl-, 4-ethyl-, and 4-methoxy- derivatives), the weighed amount of ammonium citrate was added to the reservoir, together with approximately 3000 ml. of deionized water and a syringe containing the liquid pyridine derivative was connected to the stainless steel tube. The liquids were degassed in a vacuum desiccator for 30 minutes at approximately 100 mm. Hg pressure, and the correct volume of liquid was loaded into the syringe in a dry box having a dry nitrogen atmosphere. The syringe size varied from 0.1 cc. for preparing 10^{-4} molar solutions to 100 cc. for preparing 10^{-1} molar solutions.

In those experiments, in which a pyridine derivative was added to the test solution, a weighed amount of solid citric acid was added at the same time as the ammonium citrate. The amount of citric acid needed was calculated from the volume of 0.1 molar citric acid required to bring the pH of a 250 ml. volume of 0.5 molar ammonium citrate solution plus the desired concentration of the pyridine derivative back to a value of 4.5 ± 0.05 . For example, 250 ml. of 0.5 molar ammonium citrate and 0.01 molar pyridine solution required 1.2 ml. of 0.1 molar citric acid to bring the pH back to 4.5, the pH of 0.5 molar ammonium citrate without added pyridine.

Therefore, from this value, it was calculated that 0.176 g. of citric acid should be added to a 3000 ml. volume of 0.5 molar ammonium citrate and 0.01 molar pyridine solution to establish a pH of approximately 4.5. This procedure was performed for each inhibitor and concentration. Spot checks revealed that this method usually gave a pH of $4.5 \pm .05$, a value which was considered satisfactory. The pH measurements were made with a Beckman Model G pH meter, using a general purpose glass electrode, and a fiber type calomel reference electrode. The pH meter was calibrated with Coleman Certified Buffers at pH 4.0 and 6.0.

When the rubber stopper was in place in the reservoir, nitrogen gas (Linde H.P., dry grade) was bubbled through the solution in the reservoir by opening valves 2 and 4. The bubbling was continued for 30 minutes to deoxygenate the solution and to insure a uniform concentration throughout the solution. If the pyridine derivative was a solid, the solution was now ready to be transferred to the test containers.

If the pyridine derivative was a liquid, it was injected into the reservoir and bubbling continued for 3-5 minutes to insure that thorough mixing had taken place. The liquid inhibitors were not added with the ammonium citrate and citric acid since it was feared that the prolonged bubbling necessary to deoxygenate the solution would carry significant amounts of these liquids out of the solution.

When the solution was ready to be transferred to the test container, valves 2 and 4 were closed and valve 1 was open. The test container was purged as the nitrogen gas flowed through the container and out of it under the loose fitting rubber

stopper resting in the container neck. The container was purged for 15 minutes. When the purge was completed, valves 2 and 3 were opened, and the solution allowed to flow into the container until its level in the container reached a calibrated line. The volume of solution, corrected for the specimen and holder volumes, was 500 ± 20 ml. at 21°C . After closing valve 3, gas was allowed to flow through valve 1 for an additional 5 minutes. The stopper was then removed from the container neck, and the screw-on closure cap immediately put in place.

The test containers were placed in a water thermostat at $21 \pm 2^{\circ}\text{C}$ for the desired exposure time. The temperature was maintained by a 1000 watt immersion heater, regulated by a H-B Instrument Company Type Tr-50 Thermoregulator. Five test specimens, each in a separate container, were exposed at each test condition, since preliminary experiments showed that the scatter in the weight loss data was usually 10 to 15%, and as high as 30 to 40% for short time exposures.

C-Chemical Materials

Ammonium Citrate- Mallinckrodt Analytical Reagent dibasic ammonium citrate ($(\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7$) was used in preparation of the test solutions. The limits of impurities in this material are given in Table 2.

Citric Acid- The citric acid used to adjust the hydrogen ion concentration in the solutions containing pyridine derivatives was Matheson, Coleman and Bell A.C.S. Reagent grade, and was used without further purification. The maximum limits of impurities are given in Table 2.

TABLE 2

MAXIMUM IMPURITY LIMITS OF AMMONIUM
CITRATE AND CITRIC ACID USED IN THIS STUDY

<u>Impurity</u>	<u>Ammonium Citrate</u>	<u>Citric Acid</u>
Heavy Metals	0.0005%	0.0005%
Iron	0.001	0.005
Oxalate	0.05	0.05
Phosphate	0.005	0.001
Sulfate	0.005	0.002
Chloride	0.001	-
Insoluble Matter	0.005	0.005
Residue After		
Ignition	0.010	0.020

Pyridine- Fisher Certified Reagent pyridine was distilled under nitrogen and the 115-116°C fraction collected and stored in a tightly stoppered container until it was used.

4-Aminopyridine- The 4-aminopyridine was obtained from the Reilly Tar and Chemical Corp. and recrystallized from benzene before use. The melting point of the recrystallized product was 155°C. (Literature, 158°C)

4-Chloropyridine- Beacon Chemical Industries 4-Chloropyridine was used without further purification. The boiling point of this material was 145-6°C. (Literature, 148°C)

4-Cyanopyridine- Reilly Tar and Chemical Corp. 4-cyanopyridine was used without further purification, and had a melting range of 75-8°C. (Literature, 80°C)

4-Ethylpyridine- The 4-ethylpyridine was obtained from Distillation Products Industries, and was distilled under nitrogen. The 166-8°C fraction was collected. (Literature, 166°C)

4-Hydroxypyridine- Aldrich Chemicals Company 4-hydroxypyridine was recrystallized from ethyl ether. This recrystallized product had a melting point of 148°C. (Literature, 148.5°C.)

4-Methoxypyridine- The 4-methoxypyridine was obtained from Aldrich Chemicals Company and was used without further purification. This product had a boiling point of 188-190°C, taken under nitrogen. (Literature, 191°C.)

4-Methylpyridine- Reilly Tar and Chemical Corp. 4-methylpyridine was distilled under nitrogen and the 142-4°C fraction collected and stored in a stoppered container until it was used. (Literature, 141°C)

4-Nitropyridine- The 4-nitropyridine was obtained from Beacon Chemical Industries, and was recrystallized from aqueous ethyl alcohol. The melting point of the recrystallized product was 49°C. (Literature, 50°C)

D-Weight Loss Determinations

At the conclusion of the desired exposure time, the test containers were removed from the water bath. The specimens were removed from the solutions by gripping the specimens' holders with a crucible tongs. After a wash in flowing distilled water and a rinse in acetone the specimens were placed in a desicator until they were weighed. The weight measured at this time was called the pre-defilming weight, and the difference between this value and the initial weight was called the pre-defilming weight loss.

Since an adherent gray corrosion film was found to form on the specimens during their exposure to ammonium citrate solutions, with and without inhibitor, it was necessary to remove this film to obtain a true metal loss value. A method, which proved to be satisfactory, was to rub the surface of the specimens with a slurry of Cameo Copper Cleaner, using a stiff-bristle nylon brush. The rubbing time was standardized at 30 seconds per side. To determine the amount of metal which was being removed along with the film, twenty specimens, which had been prepared according to the procedure in part A, but not exposed to ammonium citrate solutions, were subjected to this treatment. These specimens were weighed before and after the defilming process. The weight loss distribution is shown

in Figure 3. The mean weight loss calculated from these data was 1.5 mg. The average deviation was approximately ± 0.14 mg. Thus, 1.5 mg. was added to the weight obtained after the defilming process had been performed on the test specimen. The difference between this corrected post-defilm weight and the initial specimen weight will heretherto be referred to as the net weight loss.

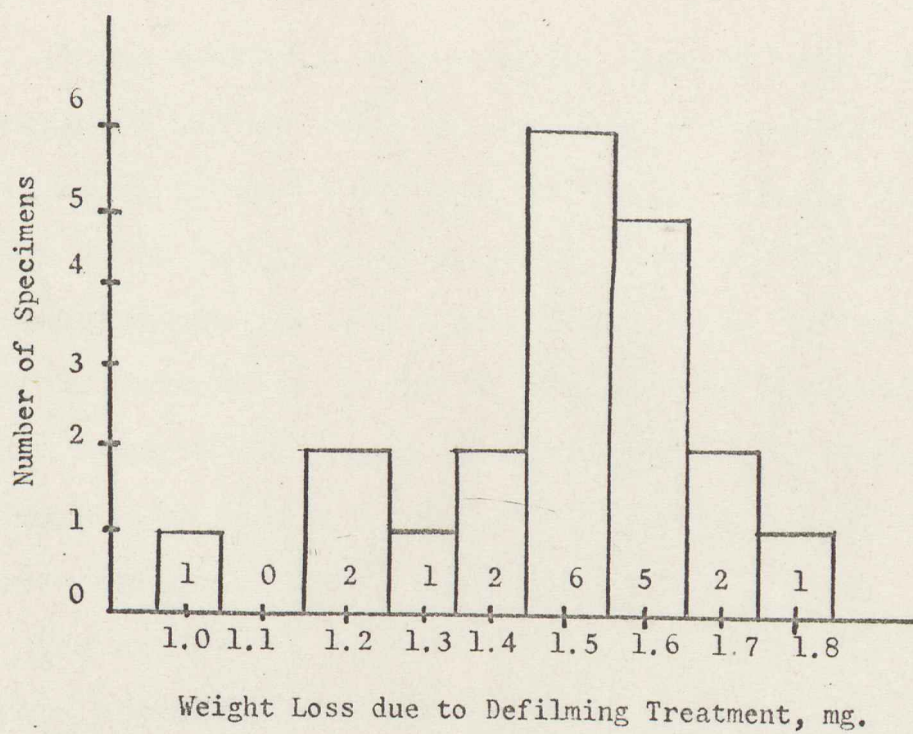


Figure 3. Weight Loss Distribution of Blank Specimens Exposed to the Defilming Treatment.

III RESULTS

A-The Effect of Ammonium Citrate Concentration on the Corrosion of Carbon Steel

It was desirable to determine the corrosion versus time behavior of carbon steel at a number of ammonium citrate concentrations in order to (1) gain a feeling for the degree of precision to be expected in the data to be collected, (2) determine an ammonium citrate concentration at which the scatter in the observed data would be 10% or less of the magnitude of the net weight loss, and (3) gain at least qualitative information about the mechanism of the corrosion reaction from the relationship between weight loss and exposure time.

The net weight loss versus time data for three ammonium citrate concentrations are given in Table 3 and presented graphically in Figure 4. The scatter in the data, as represented by the average deviation, is quite large, especially at the shorter time exposures where it represented 5 to 40% of the observed net weight loss. It was therefore decided to conduct the inhibitor experiments at a combination of solution concentration and exposure time, such that the ratio of the data scatter to the magnitude of the net weight loss would be 10% or less. The conditions of 25 hours' of exposure in a 0.5 Molar ammonium citrate solution were chosen for the inhibitor experiments.

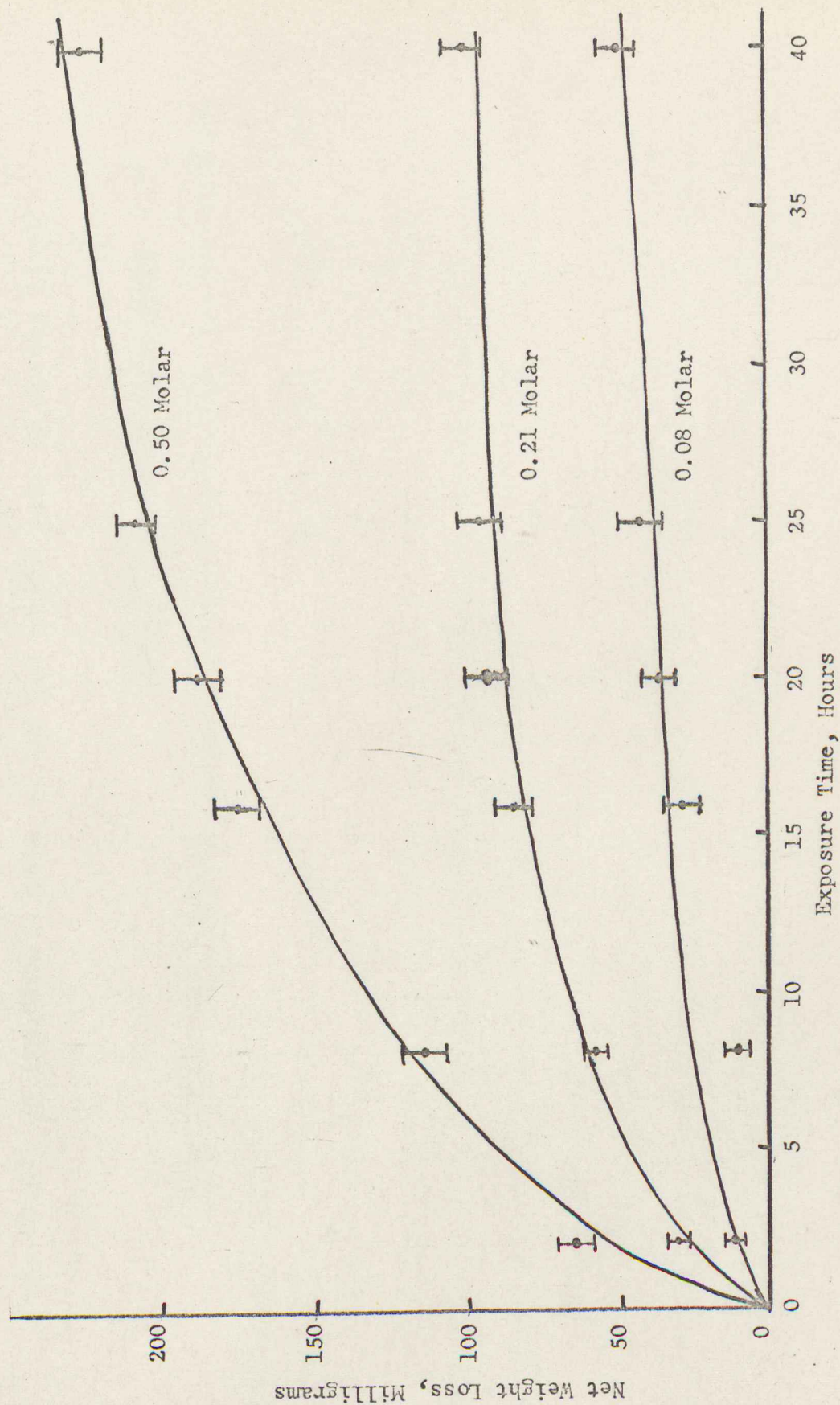


Figure 4. Net Weight Loss vs. Exposure Time in Ammonium Citrate Solutions.

TABLE 3

The Effect of Ammonium Citrate on the Net Weight Loss of Carbon Steel

Ammonium Citrate Concentration	Time, hours						Net Weight Loss, milligrams					
							2	8	16	20	25	40
0.08 Molar:	Mean.....	12	10	28	36	42	48					
	Average Deviation.....	3	4	5	5	6	6					
	Maximum Deviation.....	6	8	7	10	9	10					
0.21 Molar:	Mean.....	30	57	83	91	94	98					
	Average Deviation.....	3	3	6	7	7	6					
	Maximum Deviation.....	5	5	9	10	11	9					
0.50 Molar:	Mean.....	63	112	173	186	206	222					
	Average Deviation.....	6	7	7	7	6	7					
	Maximum Deviation.....	8	10	9	8	10	11					

The parabolic nature of the curves in Figure 4 suggested that it might be useful to plot the square of the net weight loss data as a function of the exposure time. Such a plot is shown in Figure 5. The relationships appear to be linear except for long exposure times, when the net weight loss is less than that predicted by a parabolic equation. This decrease in corrosion rate may be explained by the decrease in hydrogen ion concentration which occurred during the course of an experiment.

For example, during the 0.50 molar ammonium citrate tests it was noted that the pH would rise from an initial value of 4.5 to a final value of about 4.7. This change represents a decrease from a concentration of 3.2×10^{-5} to 2.0×10^{-5} moles/liter of hydrogen ions or a 40% change.

The parabolic relationship between net weight loss and time, at least at short exposure times, together with the visual observation of the formation of a corrosion film on the specimen surfaces, after one to two hours' exposure, suggest that diffusion of active species through this film may be a rate controlling step in the overall corrosion mechanism.

The solution was observed to become more intensely yellow in color with increasing exposure time. This color is characteristic of the ferrous ion in solutions containing the citrate ion.¹⁵ The aforementioned observations will be considered in more detail in the discussion.

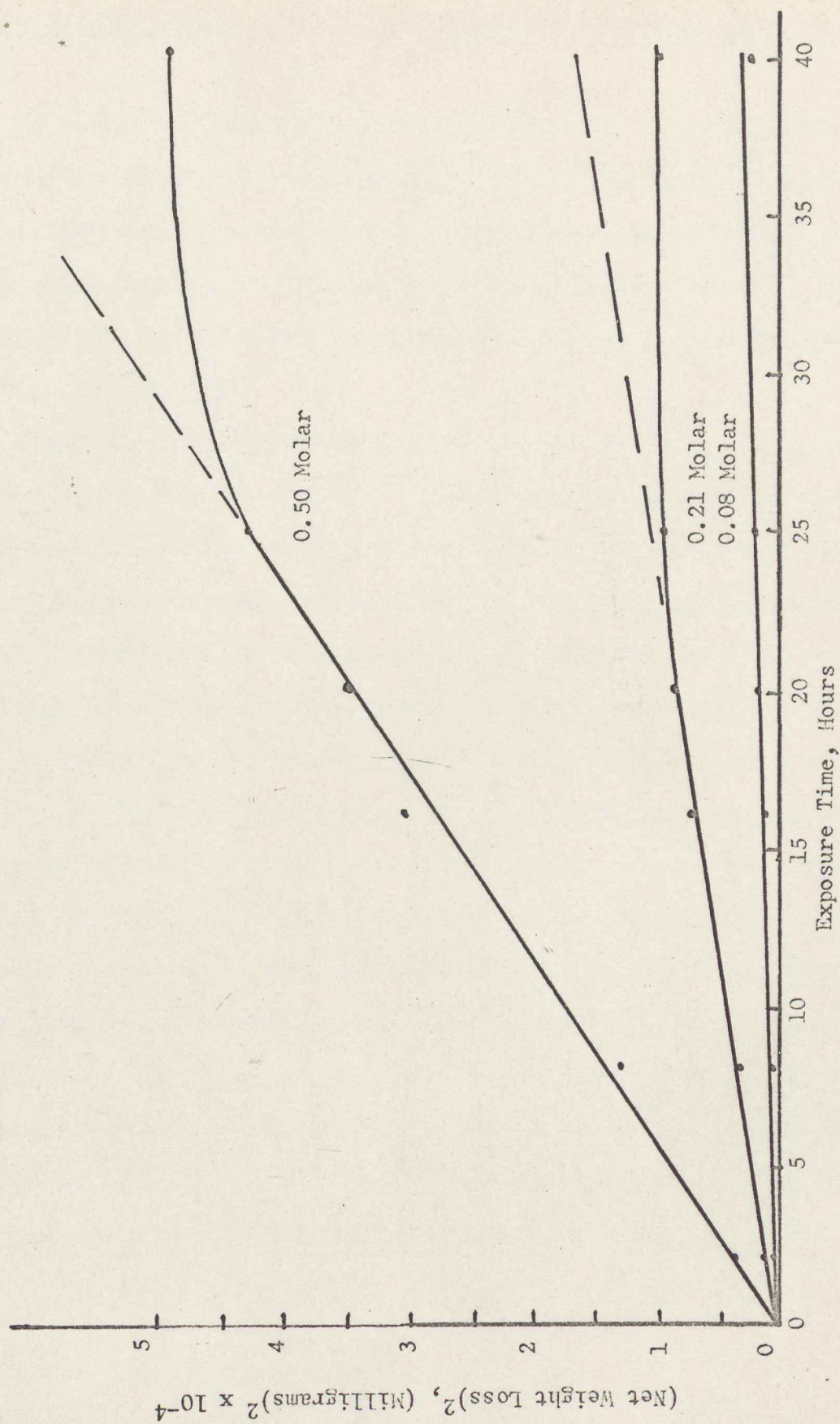


Figure 5. $(\text{Net Weight Loss})^2$ vs. Exposure Time in Ammonium Citrate Solutions.

B-The Effect of Pyridine Concentration on the Net Weight Loss Versus Exposure Time Relationship in 0.50 Molar Ammonium Citrate Solutions

In order to determine the concentration at which the pyridine derivatives should be studied to obtain data which would be significant with respect to the expected scatter in the data, exposure tests were conducted at pyridine concentrations of 10^{-4} to 10^{-1} molar in 0.5 molar ammonium citrate solutions. The results are shown in Table 4.

When one considers the precision of the data, it is doubtful if the values at zero and 10^{-3} molar pyridines concentrations are significantly different. However, the net weight loss values at 10^{-4} molar are uniformly greater than the zero pyridine values, and this increased corrosion in the dilute inhibitor solution is probably significant. This point will be discussed later.

In Figure 6 the net weight loss data for zero and 10^{-1} molar pyridine in 0.5 molar ammonium citrate solution are plotted as the square of the net weight loss versus time. While the curves are similar in that they both exhibit a lower net weight loss at long exposure times than would be predicted from the linear portion of the curves, a least squares analysis of these data showed the intercept of the zero pyridine curve to be very near to the origin, ($b=0.003 \text{ mg.}^2$), whereas the intercept calculated for the 10^{-1} molar solution is -17 mg.^2 . The importance of the difference in these intercepts will be taken up in the discussion.

TABLE 4 (Continued)

		<u>Net Weight Loss, milligrams</u>						
		Time, hours	2	8	16	20	25	40
<u>Pyridine Concentration</u>								
10^{-3} Molar:	Mean.....	60	115	178	180	204	228	
	Average Deviation.....	4	5	6	5	6	6	
	Maximum Deviation.....	6	8	9	9	10	9	
<hr/>								
10^{-2} Molar:	Mean.....	47	100	155	163	183	201	
	Average Deviation.....	3	5	4	5	5	6	
<hr/>								
10^{-1} Molar:	Mean.....	38	80	122	142	166	175	
	Average Deviation.....	4	4	3	5	4	6	
	Maximum Deviation.....	6	7	7	10	8	10	

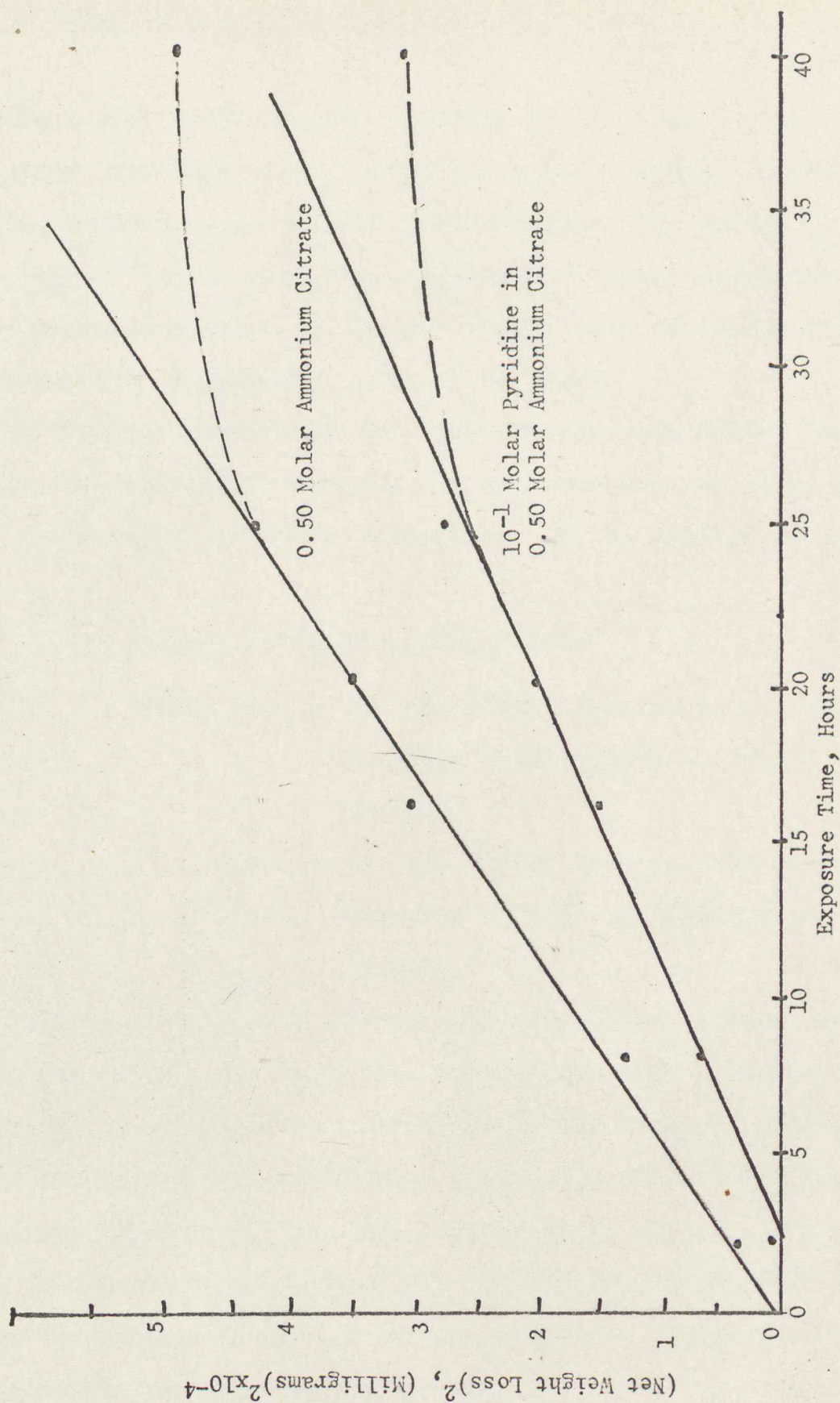


Figure 6. (Net Weight Loss)² vs. Exposure Time for 0 and 10⁻¹ Molar Pyridine in 0.50 Molar Ammonium Citrate Solution.

C-The Effect of 4-Substituted Pyridines on the Net Weight Loss
in 0.50 Molar Ammonium Citrate Solutions

The eight 4-substituted pyridine derivatives investigated in this study were the amino-, chloro-, cyano-, ethyl-, hydroxy-, methyl-, methoxy-, and nitro-, derivatives. The effect of 10^{-3} , 10^{-2} , and 10^{-1} mole per liter solutions of these compounds in 0.50 molar ammonium citrate on the net weight loss of carbon steel was determined for an exposure time of 25 hours.

In Table 5 are listed the observed mean net weight losses, the average and maximum deviations for pyridine and its eight derivatives.

The Percent Corrosion Inhibition, %I, is defined as follows:

$$\%I = ((NWL_0 - NWL_I) / NWL_0) \times 100\%$$

Where NWL_0 = the net weight loss in 0.50 molar ammonium citrate with no inhibitor present.

NWL_I = the net weight loss in 0.50 molar ammonium citrate with inhibitor present.

Figures 7 through 9 present the calculated Percent Corrosion Inhibition versus the logarithm of the inhibitor concentration in 0.50 molar ammonium citrate solution for 25 hours of exposure. The inhibitors have been arbitrarily grouped on the three plots in such a way as to make the curves most easily read. As can be seen, there is a considerable variation in the magnitude of the inhibition and in the slopes of the percentage corrosion inhibition versus the logarithm of the inhibitor concentration curves. In Table 6

are listed these calculated slopes for the various inhibitors. As interpretation of these results will be presented in the discussion.

TABLE 5

Net Weight Losses in 0.50 Molar Ammonium Citrate Containing
Various Pyridine Derivatives for 25 hours' Exposure Time

<u>Compound</u>	<u>Concentration</u> <u>Moles/liter</u>	<u>Net Weight Loss</u> <u>milligrams</u>	<u>Average</u> <u>Deviation</u>	<u>Maximum</u> <u>Deviation</u>
None	0	206	6	9
Pyridine	10^{-4}	218	5	8
	10^{-3}	204	6	10
	10^{-2}	183	5	7
	10^{-1}	166	4	8
4-Aminopyridine	10^{-3}	175	3	6
	10^{-2}	138	4	9
	10^{-1}	72	4	10
4-Chloropyridine	10^{-3}	179	5	8
	10^{-2}	152	4	6
	10^{-1}	113	4	7
4-Cyanopyridine	10^{-3}	173	4	7
	10^{-2}	113	3	8
	10^{-1}	68	5	8

TABLE 5 (Continued)

<u>Compound</u>	<u>Concentration</u> <u>Moles/liter</u>	<u>Net Weight Loss</u> <u>milligrams</u>	<u>Average</u> <u>Deviation</u>	<u>Maximum</u> <u>Deviation</u>
4-Ethylpyridine	10^{-3}	196	6	8
	10^{-2}	161	3	7
	10^{-1}	134	4	9
4-Hydroxypyridine	10^{-3}	163	5	9
	10^{-2}	122	5	9
	10^{-1}	93	4	7
4-Methoxypyridine	10^{-3}	167	4	9
	10^{-2}	138	4	8
	10^{-1}	103	5	8
4-Methylpyridine	10^{-3}	190	4	8
	10^{-2}	171	4	6
	10^{-1}	159	6	8
4-Nitropyridine	10^{-3}	190	6	8
	10^{-2}	99	4	9
	10^{-1}	23	4	7

TABLE 6

The Slopes of the Percent Corrosion Inhibition-
the Logarithm of the Inhibitor Concentration Plots

<u>Inhibitor</u>	<u>Slope of Line (Percent/decade)</u>
Pyridine	8.5
4-Aminopyridine	25
4-Chloropyridine	16
4-Cyanopyridine	25
4-Ethylpyridine	15
4-Hydroxypyridine	17
4-Methoxypyridine	20
4-Methylpyridine	7.5
4-Nitropyridine	40

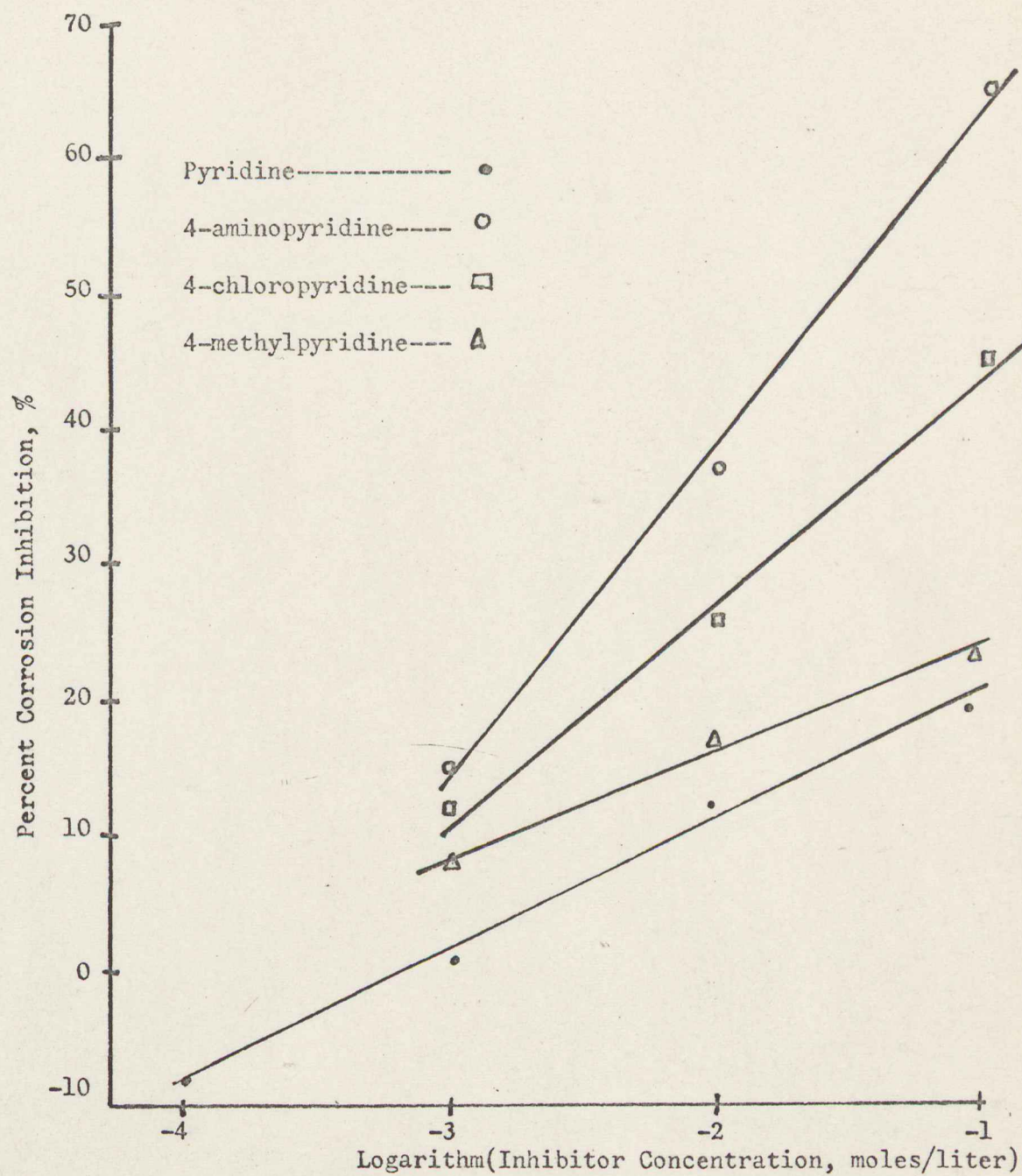


Figure 7. Percent Corrosion Inhibition vs. Logarithm of the Inhibitor Concentration. Pyridine and 4-amino-, 4-chloro-, and 4-methyl- pyridine.

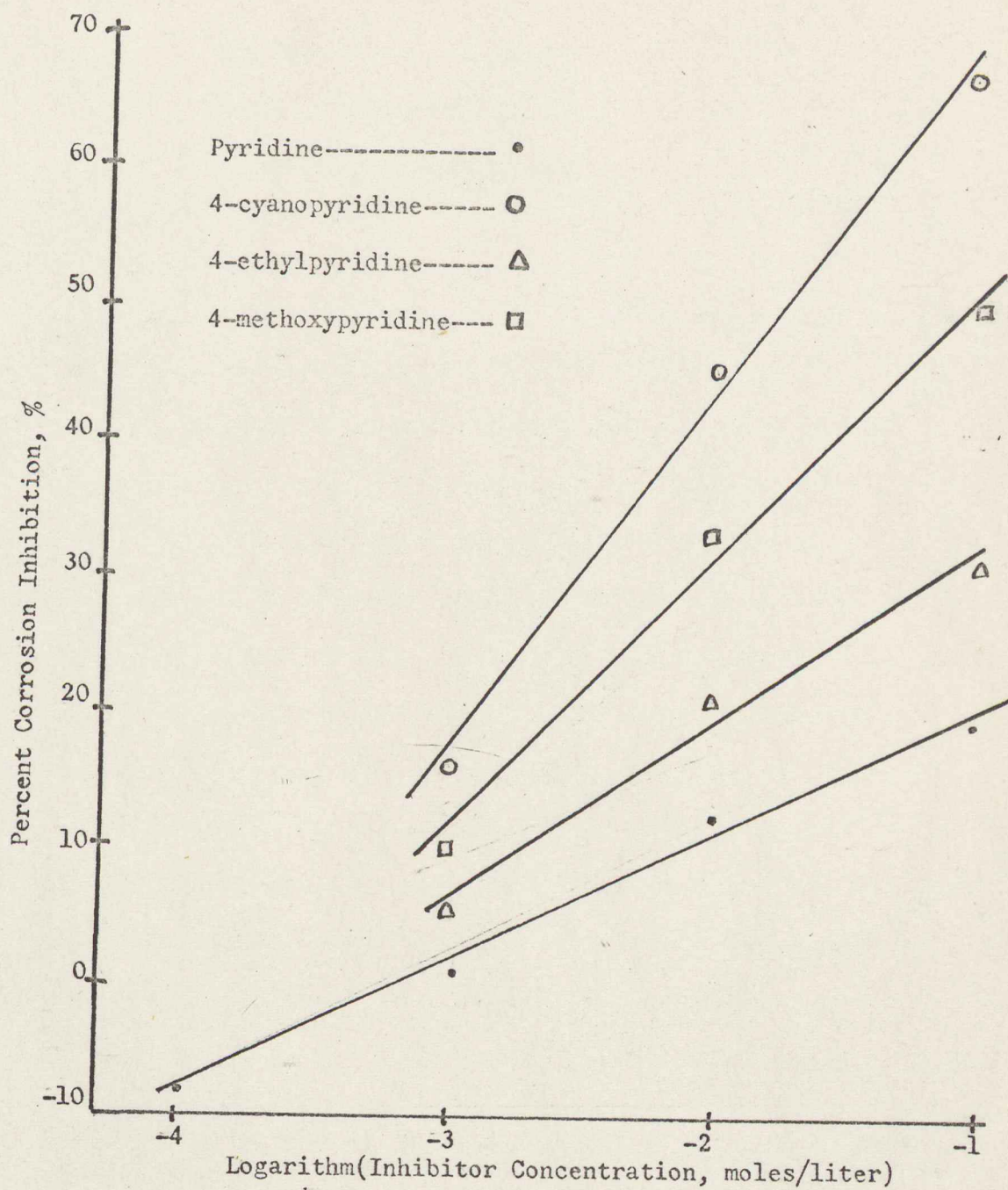


Figure 8. Percent Corrosion Inhibition vs. Logarithm of the Inhibitor Concentration. Pyridine and 4-cyano-, 4-ethyl-, and 4-methoxy- pyridine.

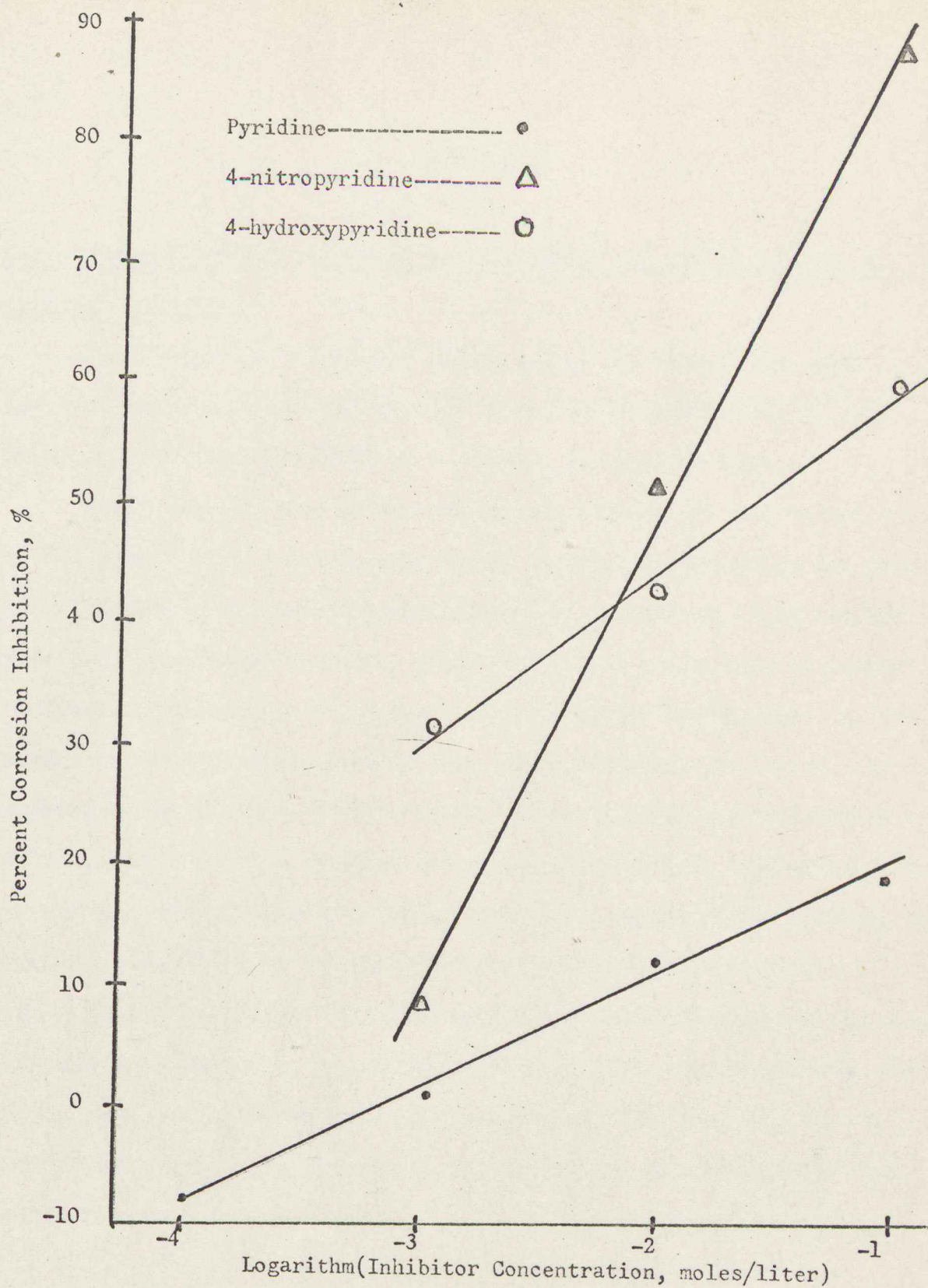


Figure 9. Percent Corrosion Inhibition vs. Logarithm of the Inhibitor Concentration. Pyridine and 4-hydroxy- and 4-nitropyridine.

IV DISCUSSION

A-A Proposed Mechanism for the Corrosion of Carbon Steel in Ammonium Citrate Solution

Any proposed mechanism which might be suggested here must account, at least qualitatively for the formation of a corrosion film and for the observed net weight loss with time.

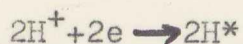
According to the electrochemical theory of corrosion developed by Whitney¹⁶ and others, the total corrosion reaction is comprised of oxidation, or anodic reactions, and reduction, the number of chemical equivalents being reduced. Thus in an electrochemical corrosion reaction, the number of electrons being lost to the anodic areas of the metal by the species being oxidized must be equal to the number of electrons being lost by the cathodic areas of the metal to the species being reduced.. The rate of the total reaction, as expressed by the electron current flowing from the anodic areas to the cathodic areas, is controlled by the individual reaction, be it an anodic, a cathodic, or a diffusion reaction, which has the slowest rate. Thus one might say that a given corrosion reaction may be under anodic control, cathodic control or diffusion control, depending on which step in the total process is controlling the over-all rate of reaction.

Consider first the anode process. In the absence of strong oxidizing agents, the predominant anodic reaction of iron is its oxidation to the ferrous state:



Polarization studies have shown this reaction to be rapid in most media.¹⁷

At the cathode, the reduction of hydrogen ions to atomic hydrogen is the predominant reaction. The atoms subsequently combine to form molecular hydrogen.



Where H^* represents adsorbed hydrogen atoms on the metallic surface.

These reactions are rapid in acidic solutions but are slow in neutral or alkaline media.

The principle electrochemical reactions appear to be the oxidation of iron and the reduction of hydrogen ions. What other chemical or diffusion reactions might be taking part in the total corrosion reaction? Consider the observation of the formation of a corrosion film in this work and the development of a yellow color in solution.

The formation of a corrosion product film on the test specimens, one to two hours after exposure began, is indicative of a substance which is of limited solubility in the test solutions. Bell¹⁸ has found that this product is ferrous monohydrogen citrate, $\text{FeHC}_6\text{H}_5\text{O}_7$, which does not readily dissolve in citrate solution at low pH. The amorphous character of this film

may be indicative of a polymetic material with hydrogen citrate ions being linked together by ferrous ions. The yellow coloration of the test solutions has been found to be the result of the presence of the $\text{Fe}(\text{HC}_6\text{H}_5\text{O}_7)^{\bar{2}}$ and $\text{Fe}(\text{H}_2\text{C}_6\text{H}_5\text{O}_7)^{\bar{4}}$ species in solution. The absence of oxygen apparently prevents the formation of the ferric oxidation state. It is noted that, if at the conclusion of an experiment, the test solutions containing the yellow ferrous citrate complexes are allowed to stand in the air for a number of hours, the solutions gradually change to a reddish-brown color. This color is characteristic of ferric citrate complexes.¹⁵

These observations allow postulation of a mechanism by which the corrosion of carbon steel in aqueous ammonium citrate proceeds.

(1) The oxidation of iron takes place at anodic areas on the steel surface. These anodic areas may be created by differences in crystal orientation distribution of impurities, or surface deformations.

(2) The concentration of ferrous ions, created in step (1), increases until the solubility limit of the ferrous monohydrogen citrate is exceeded near the steel surface, and deposition occurs. The formation of a deposit which adheres to the steel surface creates a barrier to the diffusion of species to and from the steel surface.

(3) At the cathodic areas hydrogen ions are reduced to adsorbed hydrogen atoms which, in turn, combine to form molecular hydrogen.

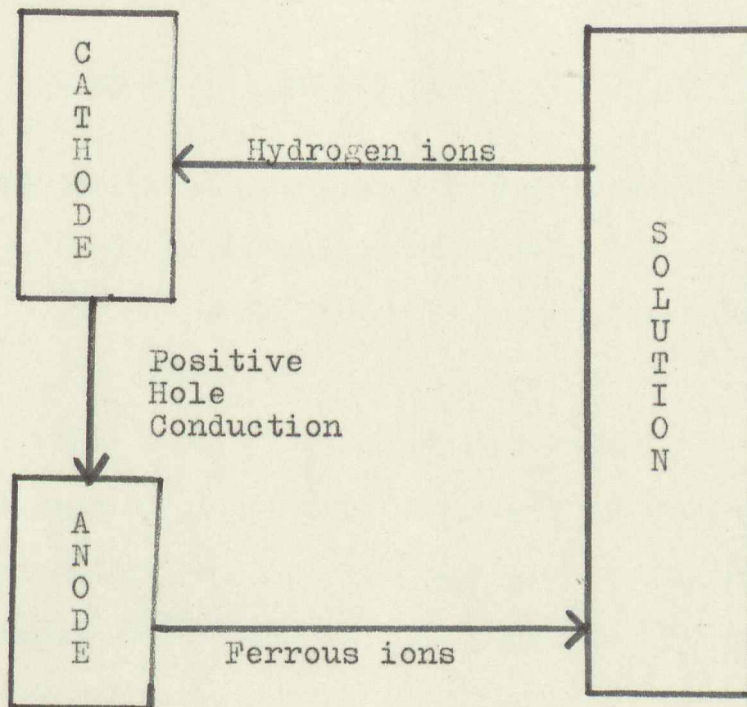
(4) Hydrogen ions from the bulk of solution diffuse to the cathodic surfaces preventing concentration polarization of these areas, and a resulting decrease in cathodic reaction

rate.

(4) Hydrogen ions from the bulk of solution diffuse to the cathodic surfaces preventing concentration polarization of these areas, and a resulting decrease in cathodic reaction rate.

(5) Ferrous ions diffuse from the vicinity of the anodic areas, again preventing concentration polarization of these areas, and a consequent decrease in anodic reaction rate.

Thus a complete circuit is established for the flow of positive charge from the anode to cathode, as represented below:



At the Cathode reduction takes place and positive charge leaves the solution.

At the Anode oxidation takes place and positive charge enters the solution.

The net weight loss with time presented in Table 3 and Figures 4 and 5 will aid in a determination of which reactions may be rate controlling. It will presently be shown that the parabolic relationship which was observed is consistent with a reaction in which the diffusional resistance of a solid corrosion product controls the rate. The mathematical approach used below is that presented by Gardner.¹⁹

Beginning with the Nerst²⁰ relationship which expresses the velocity of diffusion- controlled reactions between solids and fluids:

$$-(dm/dt) = (AD/r_1)(m/V) \quad (1)$$

Where m = gram moles of reactant present at time t in solution.

D = the diffusion constant

r_1 = the diffusion resistance offered by the "Nerst film"

V = the total volume of solution

A = area of the phase boundary

This equation expresses the rate of transfer to a phase boundary at which the rate of reaction of the transferred species is more rapid than the rate of transfer. It can also express the rate of transfer from a phase boundary at which the rate of production of the transferred species is more rapid than the rate of transfer away. The first statement expresses a possible situation for hydrogen ions diffusing to the cathodes and the second, a possible situation for the ferrous ions diffusing from the anodes.

If a solid reaction product is being formed on the surface, the total resistance to the diffusion of species to or from the phase boundary is the sum of the resistance of the Nerst film and the corrosion product film. Thus equation (1) may be re-written as:

$$-(dm/dt) = (AD/(r_1+r_2))(m/V) \quad (2)$$

Where r_2 = resistance offered by the solid corrosion products to diffusion. Let the value of r_2 be proportional to the thickness of the corrosion film, y or

$$r_2 = k_2 y \quad (3)$$

Also let the time rate of growth of the corrosion film (dy/dt) be proportional to the rate of reaction of the reactant where concentration is expressed by m/V , or

$$k_1 (dy/dt) = - (dm/dt) \quad (4)$$

If equations (3) and (4) are substituted into equation (2) one obtains:

$$dy/dt = (AD/k_1)(m/V)(1/r_1+k_2y) \quad (5)$$

Rearranging yields:

$$(r_1+k_2y)dy = (AD/k_1)(m/V)dt \quad (6)$$

Integrating from $t = 0$, to $t = t$ and $y = 0$, to $y = y$ and assuming that r_1 is independent of y ,

$$\int_0^y r_1 dy + \int_0^y k_2 y dy = (AD/k_1)(m/V) \int_0^t dt \quad (7)$$

$$\text{Or, } r_1 y + (k_2 y^2)/2 = (AD/k_1)(m/V)t$$

If r_1 is small compared to r_2 (or k_2y) than equation (8) may be written as

$$y^2 = (2AD/k_1k_2)(m/V)t \quad (9)$$

Equation 9 describes a straight line relationship between the square of the thickness of the corrosion film and exposure time.

The relationship in equation (9) was derived assuming that m/V , the concentration of the reactive species, which was here assumed to be protons, did not change with time. Measurement of hydrogen ion concentration versus exposure time showed that no appreciable change in hydrogen ion concentration took place until thirty to thirty-five hours exposure, at which time the concentration was observed to decrease moderately rapidly. If one calculates the change in pH that would be expected from the corrosion of 226 mg. of iron in a 0.5 molar ammonium citrate solution one finds the pH should change from 4.50 to 4.57. The observed change observed was from 4.50 to 4.68. In the calculation the amount of citrate species co-ordinated with iron in the corrosion film and iron in solution was not considered. However the calculation does point out that a loss of buffering action was to be expected and predicts the direction in which the pH would occur.

It may be shown that the observed net weight loss with time is a function of hydrogen ion concentration and that decreases in hydrogen ion concentration during long time exposures gives a net weight loss in over 25 hours less than that predicted by equation (9). If the data for 20 hours of exposure for the three ammonium citrate solutions is plotted

against the observed hydrogen ion concentration, Figure 10 is obtained. The 20 hours exposure time was chosen because no deviation in the pH values from the initial values was observed for this time of exposure. The decreases in net weight loss with decreases in hydrogen ion concentration shown in Figure 10 confirms the plausibility of the hypothesis that the decreases in net weight loss at long exposure times is due to a loss of buffering action in the solutions with a consequent decrease in hydrogen ion concentration.

It must be realized that the net weight loss discussed in this study is not truly equivalent to the "y," or the weight equivalent of the thickness of the corrosion product film. The net weight loss is equal to the weight of iron in the corrosion film plus the weight dissolved in solution. Spectrophotometric analysis of the test solutions after steel specimens have been exposed in them for up to 25 hours, indicate that less than five percent of the iron is present in solution. The extinction coefficient data presented by Hamm et.al.¹⁵ was used to calculate these percentages. It thus appears that over ninety-five percent of the iron remained in the corrosion film and therefore as a first approximation, the measured weight loss may be considered to be directly proportional to the corrosion film thickness.

On the basis of the dependence of net weight loss on the hydrogen ion concentration and the fit of the observed data to an equation describing a reaction rate controlled by diffusion of an active species through a corrosion product film, it is proposed that a possible rate controlling step in the corrosion of carbon steel in deoxygenated aqueous ammonium citrate is the

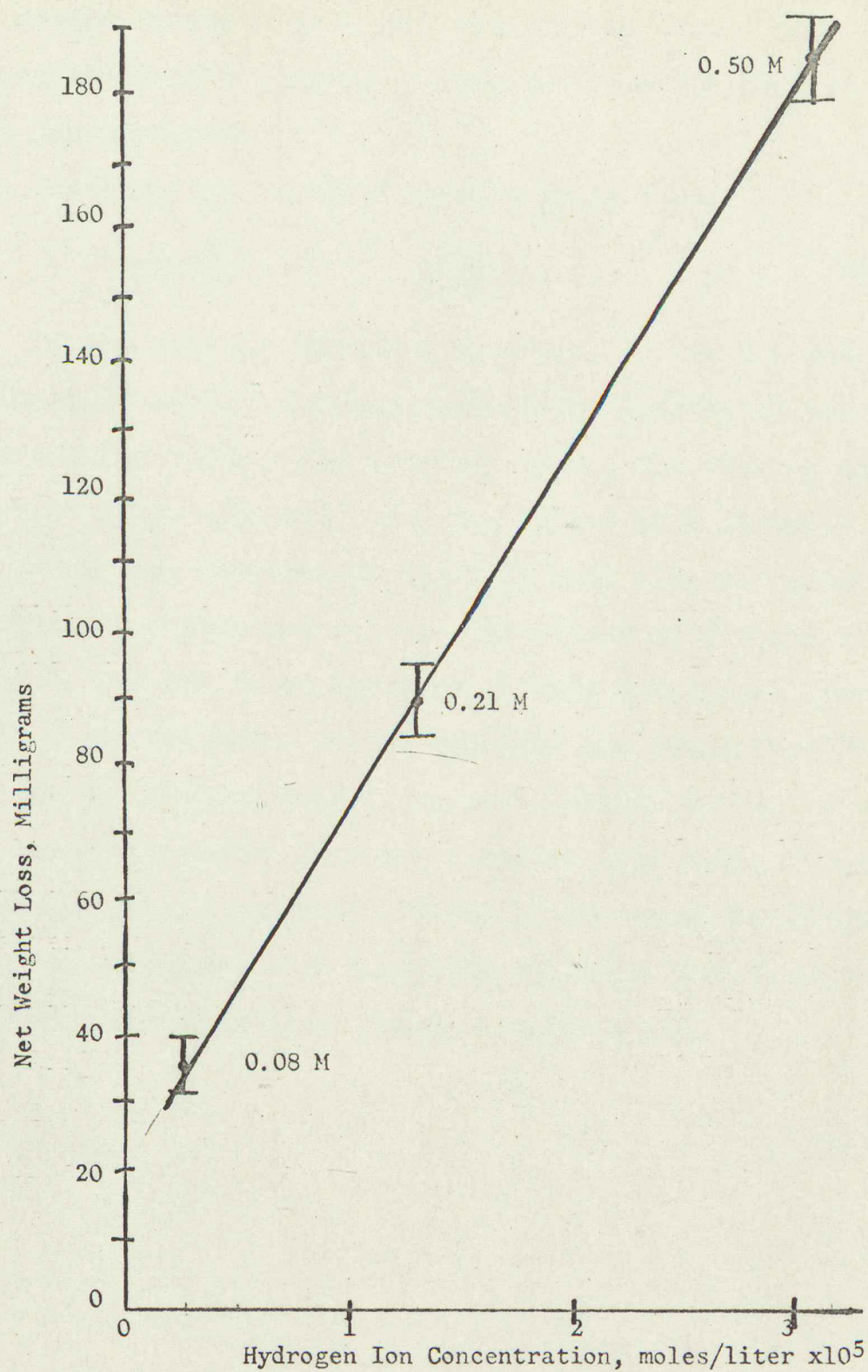


Figure 10. Net Weight Loss after 20 Hours of Exposure vs. Hydrogen Ion Concentration.

diffusion of hydrogen ions to the cathodic surfaces. It is also possible that the rate of diffusion of ferrous ions away from the anodic surfaces is a rate controlling step. Unfortunately, the experiments necessary to define the mechanism more clearly were not performed.

Equation (9) may be rewritten as follows:

$$\frac{y^2}{(m/V)t} = \frac{2AD}{k_1 k_2} = K \quad (10)$$

If the area of the phase boundary, A , and the diffusion constant, D remain constant, and if the density of the corrosion film remains essentially constant during the time of exposure (so that k_2 is constant) then the values of K obtained by performing the division on the left hand side of equation (10) should have a constant value. The values of K are given in Table 7, for the three ammonium citrate solutions. The value of (m/v) is the value of the hydrogen ion concentration.

At the present time it is not possible for us to explain the non-constancy of K within a set of data taken at the same concentration of ammonium citrate or the large difference in magnitude between the K values at 0.5 molar and those at 0.08 and 0.21 molar ammonium citrate concentration.

TABLE 7

Calculate Values of K from Equation (10)
for Three Ammonium Citrate Concentrations

<u>Time, Hours</u>	<u>k, mg²-liter/mole/hour x10⁻⁷</u>		
	<u>0.08 M.</u>	<u>0.21 M.</u>	<u>0.50 M.</u>
2	2.9	3.3	6.2
8	0.5	3.0	4.9
16	2.0	3.2	5.9
20	2.6	3.0	5.3
25	2.8	2.6	5.3

B-A Proposed Mechanism for Corrosion Inhibition by Pyridine and Its Derivatives

It was pointed out earlier in the results that, whereas the plot of the square of the net weight loss vs. time for carbon steel in 0.50 molar ammonium citrate passed essentially through the origin, the same plot for a solution containing 0.1 moles/liter of pyridine intercepted the ordinate axis significantly far from the origin. Equation (8) states

$$r_1 y + k_2 y^2 / 2 = (AD/k_1)(m/V)t \quad (8)$$

If r_1 , the Nernst film resistance, is much less than $k_2 y$, the resistance of the corrosion product then $k_2 y^2 / 2 + r_1 y \approx k_2 y^2 / 2$ and when $t=0$, $y^2 = 0$ will hold, This appears to be the situation in the uninhibited solution. If in inhibited solutions we consider r_1 to be the Nerst film resistance plus an inhibitor film resistance, then when $t=0$, y does not equal zero but equals $-2r_1/k_2$. Since r_1 and k_2 are both positive values, the observed intercept is a negative quantity as predicted by equation (8).

The concept of an inhibitor adsorbing on a metallic surface and forming a diffusion barrier to the ingress of reactive species (or the egress of species produced by reaction) is quite useful and will serve as the basis for the mechanism which will be proposed in this discussion.

As a beginning the Hammett sigma-rho linear free energy relationship will be briefly described as it pertains to the adsorption of inhibitors. If one views the adsorption of molecules onto a surface as an equilibrium between these

adsorbed molecules and solvated molecules in solution, than an equilibrium constant exists for this adsorption process. In a series of molecules which are similar in structure and in size, such as the 4 - substituted pyridines, the more strongly adsorbed members of the series should possess the largest equilibrium constants, and should show the best inhibitive qualities. The Hammett sigma-rho equation expresses this idea in a quantitative way:

$$\text{Log}(K/K_0) = \rho \sigma$$

Where K = the adsorption equilibrium constant for a given substituted pyridine

K_0 = the adsorption equilibrium constant for pyridine

σ = the substituent constant which is determined by the nature of the substituent. Pyridine = 0

ρ = reaction constant which determines how sensitive the value of K is to changes in σ

As a first approximation it will be assumed that the percent of corrosion inhibition is directly proportional to the equilibrium constant, K ,

$$\%I = C_1 K \quad (13)$$

and therefore that the net weight loss must be inversely proportional to K or

$$NWL = c_2 / K \quad (14)$$

$$\log(NWL_p / NWL_I) = \rho \sigma \quad (12)$$

where NWL_p percent corrosion inhibition for a pyridine derivatives

NWL_I percent corrosion inhibition for pyridine

In Figure 11, the $\log(NWL_p / NWL_I)$ for 10^{-1} molar inhibitor concentrations in 0.50 molar ammonium citrate has been plotted against the sigma values reported by Fischer et. al.²¹ These values were derived from basicity studies of pyridine derivatives, and are probably more appropriate for use as substituent constants than are those derived from benzene ring studies. A number of features can be noted in Figure 11. A minimum in the curve can be noted in the region of sigma approximately equal to zero. The branch of the curve in the direction of increasing positive sigma values has a much greater slope than does the branch in the direction of increasing negative values of sigma. There appears to be more reason to assign a linear relationship between the log term and sigma in the left hand branch of the curve than in the right hand branch.

One might speculate on the implications of these data with

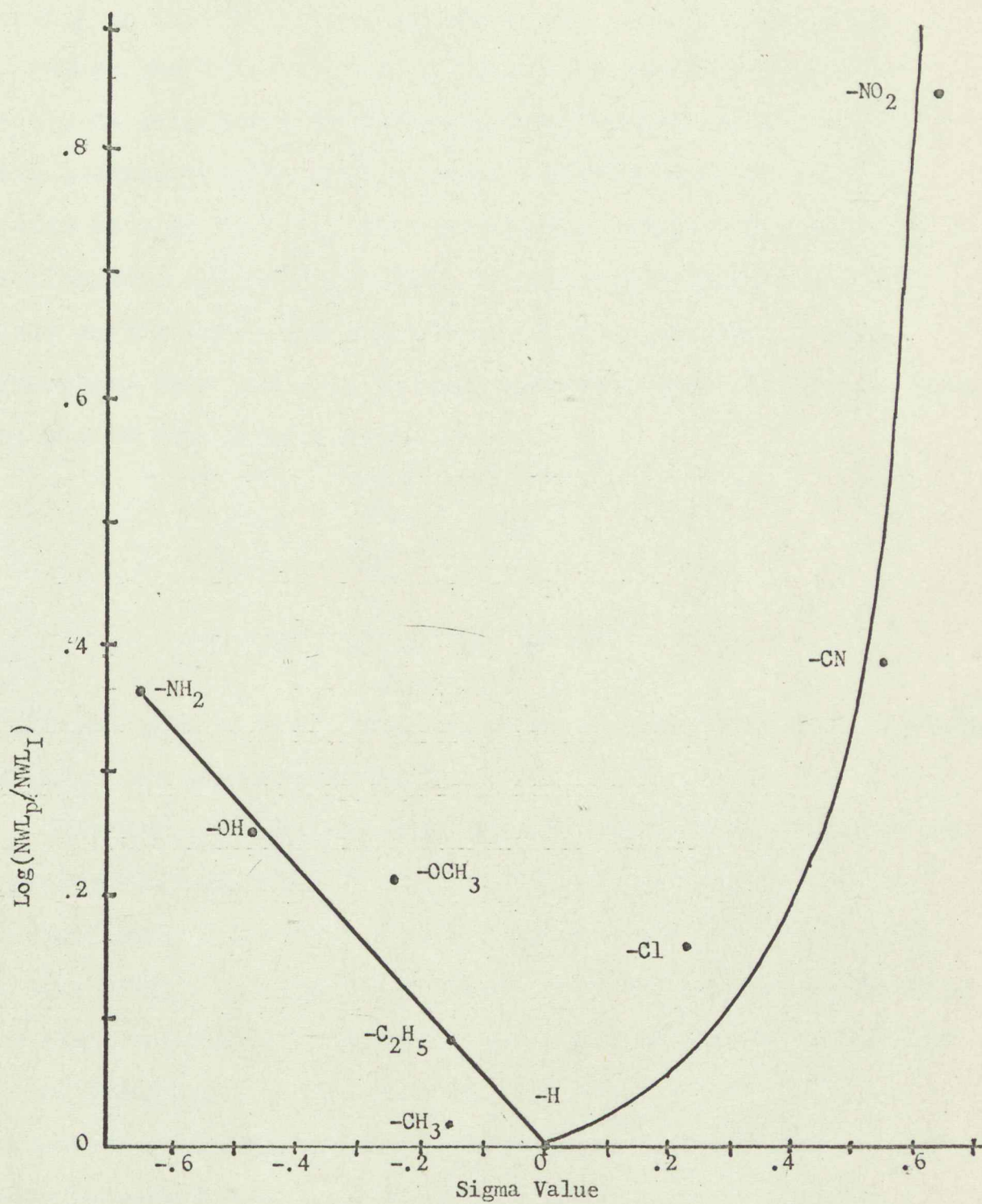
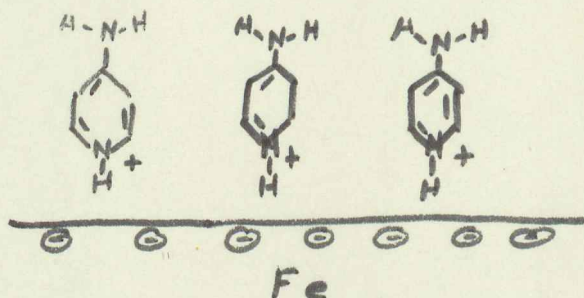


Figure 11. $\text{Log}(\text{NWL}_p/\text{NWL}_l)$ vs. Sigma Value.

respect to a possible inhibition mechanism. In the left hand branch the inhibitor activity increases with increasing negative values of sigma. This implies that an increasing electron density on the pyridine ring and on the ring nitrogen atom increases the inhibitor activity of the pyridine molecule. It can be calculated from the reported dissociation constant²¹, that 4-aminopyridine exists almost entirely as a protonated cation at a pH of 4.5. This positively charged species would be attracted electrostatically to negatively charged cathodic sites on the steel and might be physically adsorbed. This adsorption does not lead to true adsorbate-metal bond formation, and may be represented as below:



A similar type of adsorption may also be postulated for 4-hydroxypyridine and 4-methoxypyridine.

However, 4-ethylpyridine has been shown to adsorb with its pyridine ring parallel to an iron surface in acid solutions having higher hydrogen ion concentrations than those existing in this study. As the value sigma increases in a positive sense the electron density in the ring is decreased and the pi orbitals on the pyridine ring may be said to become better electron acceptors. One might then postulate the formation of surface bonds between occupied d orbitals of the iron and electron deficient pi orbitals of the pyridine molecule. This would lead to chemical adsorption of the pyridine molecule with the

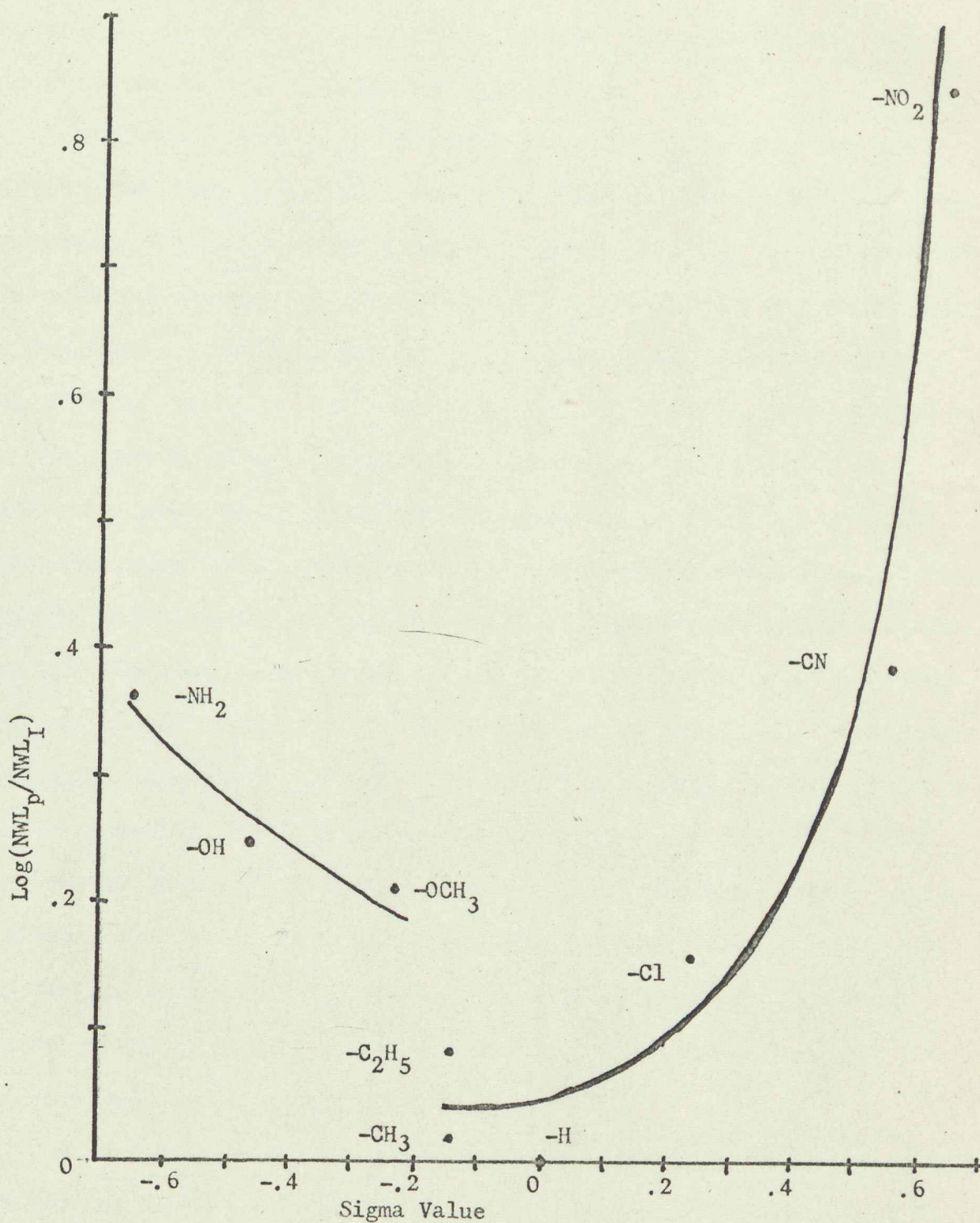


Figure 12. $\text{Log}(\text{NWL}_p/\text{NWL}_I)$ vs. Sigma Value. Grouping According to Proposed Adsorption Modes is Shown.

ring oriented parallel to the iron surface. This implies that the pyridine would be most readily adsorbed on an iron surface with an excess electron density. Thus, as in the case of the physically adsorbed pyridinium cations, these molecules would be adsorbed on cathodic sites on the steel.

It might be well to redraw the curves in Figure 11 to reflect the two types of adsorption mechanisms which have been proposed. This has been done in Figure 12. The difference in the rate of change of the slopes of these curves may be explained as follows: the interaction of a chemically adsorbed species and a metal surface would be expected to be much more sensitive to the structure of a molecule than would the interaction between a physically adsorbed species and a metallic surface. Physical adsorption involves only coulombic interactions between adsorbate and metal, whereas chemical adsorption requires overlap of orbitals, the character of which is sensitive to electron density distribution in the molecule being adsorbed. Therefore one would expect the chemical adsorption branch in Figure 12 to show a greater sensitivity to changes in sigma values, which represents changes in electron density in the ring, than would the physical adsorption branch. The degree of association of the pyridinium ions taking part in physical adsorption will depend greatly on the sigma values, but once formed these cations will undergo similar interactions.

It was noted in the results that 0.50 molar ammonium citrate containing 10^{-4} moles/liter pyridine gave a higher net weight loss than did the same solution without pyridine. It is possible that insufficient pyridine was adsorbed at this

concentration to form a protective monomolecular layer on the cathodic areas. The flow of current would then shift to these uncovered areas and give rise to increased hydrogen evolution in local areas. The evolution of increased hydrogen at small areas might disrupt the corrosion film in places and result in an increased corrosion rate. The increased rate would result from the freer access which the hydrogen ion would have to diffuse to the metal surface. The 10^{-3} molar pyridine solution showed essentially the same net weight loss as the uninhibited solution. One might picture the surface as now being almost covered by a monolayer. The inhibition due to the adsorbed pyridine might be in balance with the increased corrosion due to the high local hydrogen evolution. The net result would be seen as the total amount of corrosion, but that most of the weight loss would be concentrated in a small area associated with film rupture.

The inhibition of corrosion of steel specimens at 25 hours of exposure shows a linear relationship with the logarithm of the inhibitor concentration. This was found to be true for all the inhibitors studied. With the exception of 4-hydroxy- and 4-methoxy- pyridine, the plots all intercepted zero percent inhibition at a concentration value in the region of 5×10^{-4} moles/liter. This may indicate that a monolayer may be forming at solution concentrations in this range.

The best inhibitors, 4-nitro-, 4-cyano-, and 4-amino-, were characterized by the lines with the greatest slopes. This is probably a reflection of the bond strength of the adsorbate-metal interaction.

V Conclusions

The results of this study have led to the postulation of the following conclusions:

- (1) The rate determining step in the corrosion of carbon steel in deoxygenated aqueous ammonium citrate is the diffusion of a species, thought to be the hydrogen ion, through a corrosion product film. This film has been identified by others as a ferrous monohydrogen citrate.
- (2) The net weight losses observed after a constant time of exposure are linearly proportional to the hydrogen ion concentration, in the range of pH 4.5 to 5.6.
- (3) The inhibition of the corrosion steel by pyridine derivatives in deoxygenated ammonium citrate solutions is related to the adsorption of the pyridine molecule or the pyridinium cation onto cathodic areas. These adsorbed species form a barrier to the diffusion of hydrogen ion to the cathodic surfaces.
- (4) the 4-amino-, 4-hydroxy-, and 4-methoxypyridines are believed to physically adsorb on cathodic areas by a coulombic interaction between the positively charge pyridinium ions and the excess electron density at the cathodes.
- (5) Pyridine and its 4-nitro-, 4-cyano-, 4-chloro-,

4-ethyl-, and 4-methyl- derivatives are believed to adsorb as neutral molecules. Their interaction is through overlap of electron deficient or vacant pi orbitals with filled d orbitals of iron. This may be considered to be chemical adsorption.

- (6) The interaction between the chemically adsorbed molecules appears to be much more sensitive to structural changes than the physical adsorption interaction.

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