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The Polarizing Effects of Inhibitors upon the Reaction of Iron with Hydrochloric Acid

Duane L. Mickelson

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THE POLARIZING EFFECTS OF INHIBITORS UPON
THE REACTION OF IRON WITH HYDROCHLORIC ACID

by-

Duane L. Mickelson

A thesis presented to the
Faculty of the School of Graduate
Studies in partial fulfillment
of the
Degree of Master of Arts

Western Michigan University
Kalamazoo, Michigan
July, 1965

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Duane L. Mickelson

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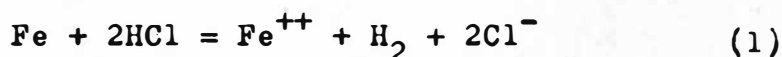
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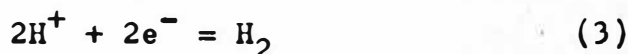
INTRODUCTION

Corrosion inhibitors have been widely studied. Electrical methods of study have been utilized (7) (10) (24) and polarization curves (2) (6) (18) (26) have been plotted by many observers in studying different aspects of corrosion. In this research the measured polarizing currents are used strictly in an effort to find out how the corrosion inhibitors affect the anodic and the cathodic reactions.

The overall reaction taking place is the following:



This consists of the following two half-reactions,



At the anodic areas the reaction is an oxidation (Eq. 2), the iron being oxidized to the ferrous state. At the cathodic areas the reaction is a reduction (Eq. 3), hydrogen ions being reduced to hydrogen gas. These two reactions take place spontaneously when iron is immersed in hydrochloric acid.

A corrosion inhibitor is defined as a substance that will effectively decrease the rate of a corrosion reaction when present in small amounts in the reaction environment. If the inhibitor is effective in reducing the rate of the

anodic reaction (Eq. 2) it is called an anodic inhibitor. If it is effective in reducing the rate of the cathodic reaction (Eq. 3) it is called a cathodic inhibitor.

It is also possible for some substances to increase the rate of the anodic and/or cathodic reaction. Such substances are called accelerators. If the rate of the anodic reaction is increased the substance is called an anodic accelerator, and if the rate of the cathodic reaction is increased it is called a cathodic accelerator.

As can be seen from Equation (1), both the anodic and the cathodic reactions are taking place simultaneously. Therefore, in order to find out which reaction is being altered, it is necessary to "separate" the two reactions in some way. One way is to measure the rate of iron dissolution and the rate of hydrogen evolution (5) (9) (16). This method is possible, but it is complicated by the fact that some of the hydrogen is absorbed by the metal. Another way is to pass a polarizing current between the iron and a counter electrode (24). If the iron is made highly positive with respect to the counter electrode, the cathodic reaction, which consumes electrons, is transferred to the counter electrode (Figure 1). Therefore, the iron behaves as a pure anode, and the only reaction taking place is the dissolution of iron, Equation (2). If the iron is made negative

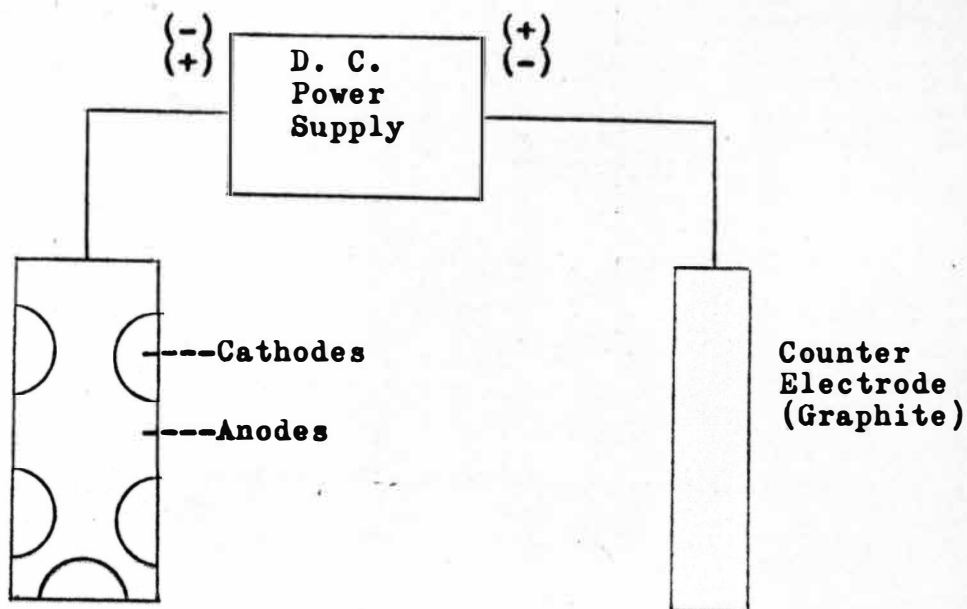


Figure 1. When a polarizing current is passed between the iron and the counter electrode either the anodic or cathodic reaction is made negligible, depending upon the polarity of the polarizing current.

with respect to the counter electrode, the anodic reaction is made negligible by the large supply of electrons coming from the counter electrode system. Therefore, the iron now behaves as a pure cathode, and the only reaction taking place on its surface is the evolution of hydrogen.

To measure any changes which the inhibitor or accelerator is producing, the potential of the iron electrode is monitored with respect to a silver-silver chloride (Ag-AgCl) reference electrode. The potential is first measured in

hydrochloric acid at the current density (milliamperes per square centimeter of exposed electrode surface, ma/cm^2) being used. It is then measured at the same current density in an acid solution which contains an inhibitor. The difference in the two potentials is taken to be the effect produced by the inhibitor.

When a positive polarizing current is passed between the iron and the counter electrode the substance is an inhibitor if the change in potential, ΔE , is positive. If the change in potential is in the negative direction the substance is an anodic accelerator. When a negative polarizing current is passed between the iron and the counter electrode (the cathodic reaction is now being studied), the substance is an inhibitor if the change in potential is negative, and it is an accelerator if the change is in the positive direction.

Another method for expressing the effects of inhibitors is by means of the Tafel equation (22) (25),

$$\eta = a + b \log i \quad (4)$$

where η is the overpotential in volts and i is the current density in $\text{amperes}/\text{cm}^2$. a and b are constants. In this method, which will be used to interpret the potentiostatic measurements, the logarithm of the current density is plotted against the overpotential. The value of a is read from the graph at the point where $i = 1$ ($\log i = 0$). The value of b is determined from the slope of the line.

When the anodic reaction is being studied, it will be shown that the substance is an inhibitor if the value of a is more positive in the inhibited solution than in the plain acid (Figure 2). It will also be shown that the substance is an accelerator if a is more negative. When the cathodic reaction is being studied, it will be shown that the substance is an inhibitor if a is more negative in the inhibited solution than in the plain acid, and that it is an accelerator if a is more positive.

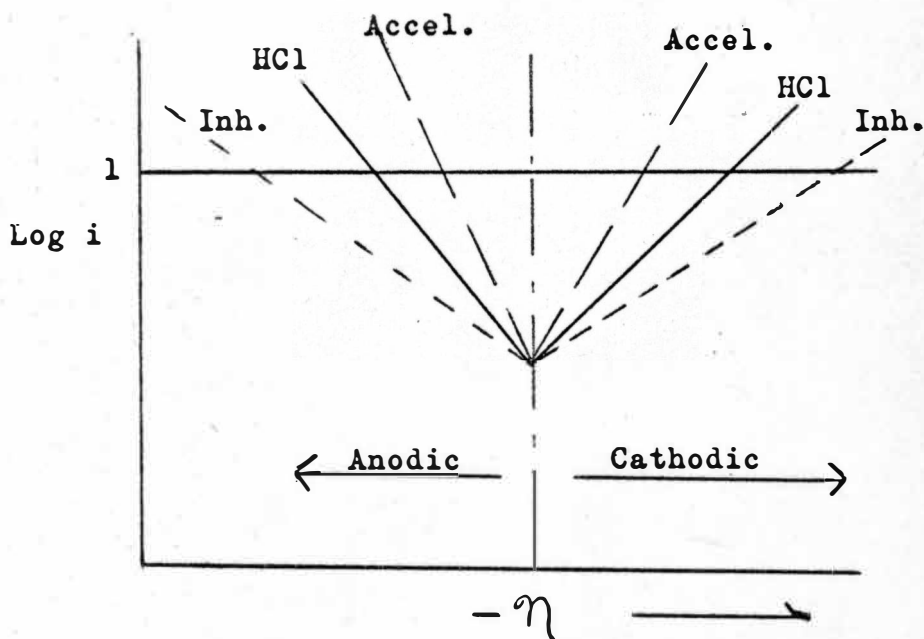


Figure 2. Tafel plot. This figure shows how a is used to determine the nature of the inhibitor.

EXPERIMENTAL

The iron electrodes used in these experiments were Armco pure iron rods, one-eighth inch in diameter and twelve feet long. These rods were cut into short segments, each being approximately six inches long. The segments were stored in a dessicator jar over calcium chloride to keep them from oxidizing. Before use the electrodes were polished by rotating them in a drill press chuck and sanding them with #400-J emery paper. This was done to remove any superficial oxide film, and also to smooth the surface and therefore remove any sharp points, which would react more readily than other parts of the surface. After polishing, the rods were rinsed several times with absolute ethanol (to remove moisture and also grease and salt picked up in handling the electrodes), dried, and stored in a dessicator until ready for use.

In some of the experiments (all of the later ones) the Armco iron rods were annealed to remove strains. The annealing was accomplished by heating the iron rods in a tube furnace in an atmosphere of helium (to prevent oxidation) at 900 degrees centigrade for an hour and a half. The furnace temperature was then gradually reduced over a period of several hours. After annealing, the electrodes were stored in a dessicator until ready for use.

The reproducibility of the potential (23) of the annealed electrodes is somewhat better than that for the

unannealed ones. This can be attributed to a decrease in local cell action. There are sites on the electrode that would react faster than others due to strains in the metal. Since the number of active sites changes the potential from rod to rod, removing the strains makes the potentials more uniform.

Immediately before use the end of the iron rod and all but one inch of the sides were coated with paraffin. First the rod was coated to within one and one-quarter inch of the polished end. The coated end was then placed in the electrode holder (See Figure 3).

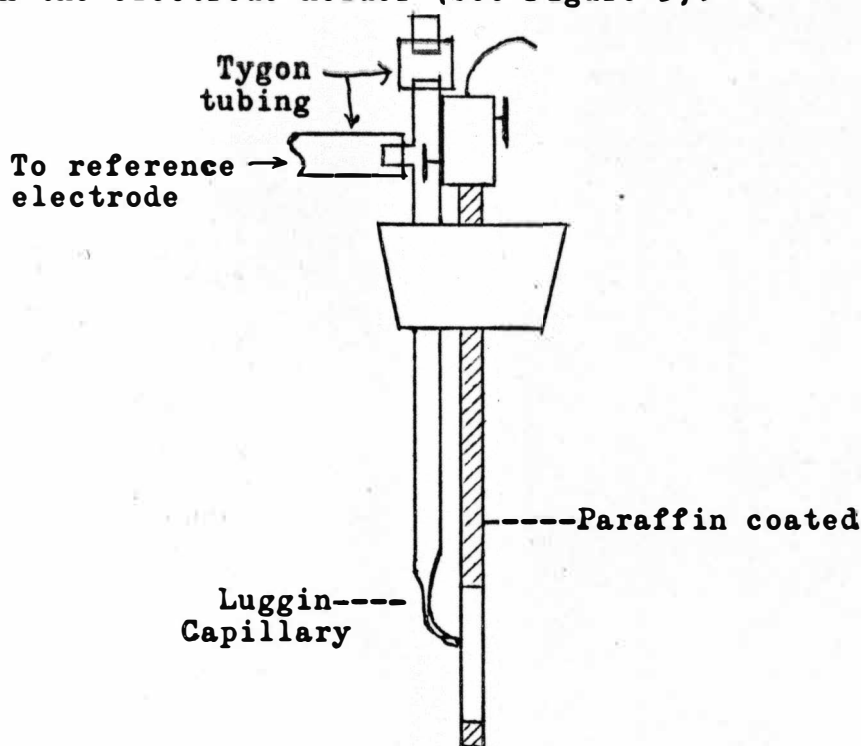


Figure 3. Electrode assembly. The iron electrode and the Luggin capillary were mounted in a rubber stopper to keep them in place.

The exposed end was then dipped into the paraffin until only one inch of the bare rod was left exposed. This was done to insure uniform area in all experiments.

The Luggin capillary from the reference electrode was then adjusted until its tip just touched the side of the iron electrode. The electrode assembly was then placed in the reaction vessel and the acid bridge was placed in a tube of 4.8 N hydrochloric acid containing the reference electrode (Figure 4). The acid bridge was then filled by suction and stoppered. The counter electrode (1/4 inch graphite rod, 6 inches long) was placed in the proper tube of 4.8 N hydrochloric acid, and its acid bridge was also filled. Electrical connections were then made to the counter electrode, working electrode and reference electrode.

The Ag-AgCl reference electrodes used in this research were especially prepared so as to eliminate any liquid junction potential. They were prepared in a solution of 4.8 N hydrochloric acid. Since this was the solvent that was being used, no liquid junction potential could occur.

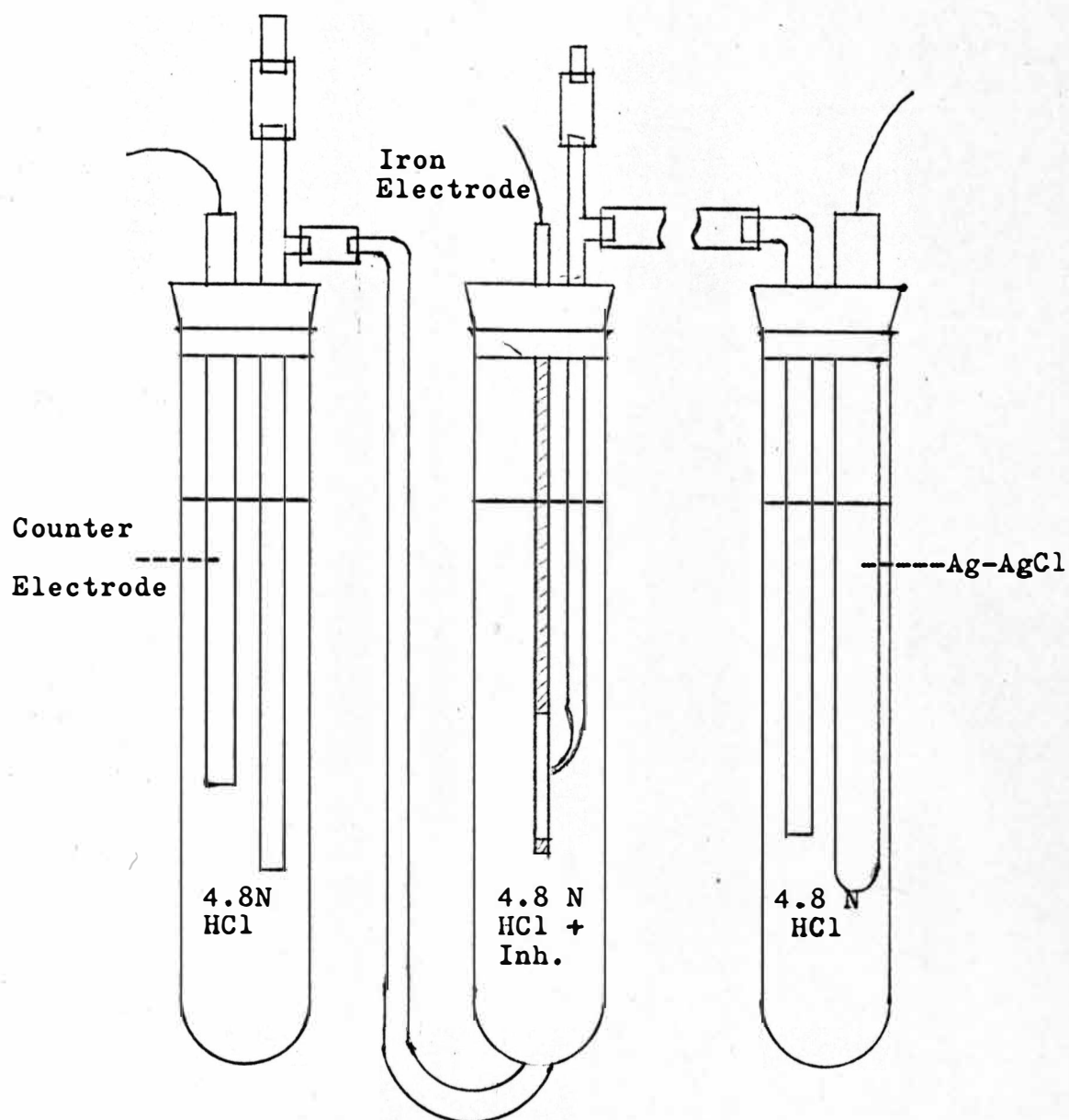
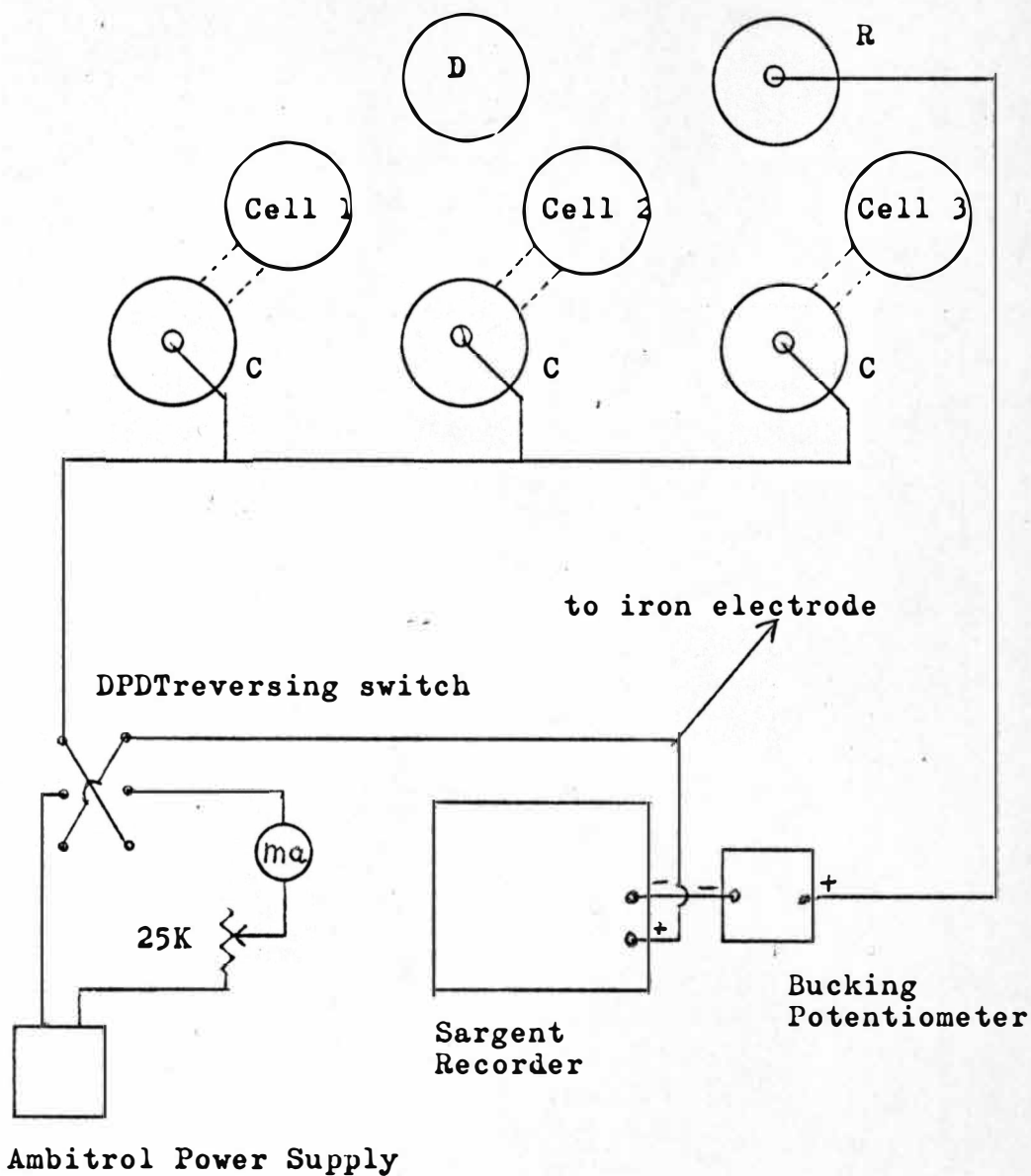


Figure 4. Apparatus used for measuring electrode potentials at different polarizing current densities. The apparatus was immersed in a constant temperature water bath at 30°C.

Galvanostatic Measurements

The circuit used for the galvanostatic (constant current) measurements is shown in Figure 5. All of the cells were immersed in a constant temperature bath at 30° C. Cell number 1 contained 4.8 N hydrochloric acid. The experiments were always started with the electrode assembly in this cell. The current density was adjusted to - 10 ma/cm², and the potential was recorded for thirty minutes. After this time the Tygon tubing between the reference electrode cell and the Luggin capillary was pinched off, and the assembly was removed from cell 1 and placed in cell 2. Cell 2 contained a solution of 4.8 N hydrochloric acid plus an inhibitor. It was left here for ten minutes, during which the potential was again recorded. The acid bridge was then pinched off again and the electrode assembly was removed. This time the electrode was rinsed in a tube of 4.8 N hydrochloric acid which was contained in the water bath. The reason for rinsing the electrode was to remove any adhering solution and inhibitor. The assembly was then placed in cell 1 again for ten minutes. In this way the sample is bracketed with two controls. The assembly is then removed from cell 1 and placed in cell 3 using the same procedure. Cell 3 contained either the same inhibitor at a different concentration or another inhibitor. The



C--Counter electrode
 D--Rinse tube (4.8 N HCl)
 R--Ag-AgCl reference electrode

Figure 5. Circuit diagram used for galvanostatic measurements. The 25K potentiometer was used to make current adjustments below 25 ma. All of the cells were immersed in the constant temperature bath at 30° C.

potential recording took the form shown in Figure 6.

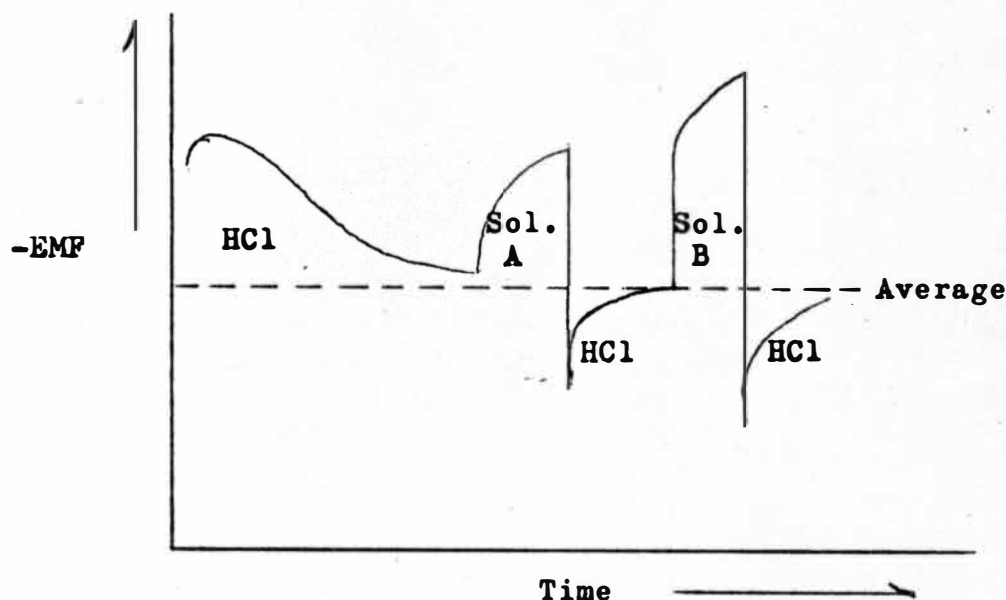


Figure 6. This is an example of what the recorded potential curves look like. The reference point is found by averaging the two control runs in 4.8 N HCl which lie on either side of a particular sample.

The initial rise in - EMF is due to the rapid reaction of the reactive sites. When the electrode is placed in the cell containing the solution under study there is a change in EMF. This change may be either positive or negative, depending upon whether the substance is an inhibitor or an accelerator. When the electrode is returned to the 4.8 N hydrochloric acid it is seen that the potential is not quite the same as it was before. The two potentials for the electrode on either side of a particular inhibited solution are averaged, and the change in potential due to

the inhibitor is measured from this average value as a reference point. In this way each inhibited solution has its own reference point at a given current density.

Potentiostatic Measurements

It is also possible to obtain the same information which we have received from the above galvanostatic measurements by fixing the potential at certain values and measuring the changes in current (potentiostatic method). The two methods should give the same results, and do, as will be seen later. The advantage of the potentiostatic method is that the operator has some control over the electrode processes taking place in the solution. No such control is realized with the galvanostatic method.

One disadvantage with the particular circuit used here was that the operational amplifier which was available for use (Heath model EUW-19A) had a low current output, 20 ma maximum. This limited the current densities to about 7.5 ma/cm². Operational amplifiers of higher output currents are made, but they were not available for this study.

The circuit diagram used for the potentiostatic measurements is shown in Figure 7 (19) (27). The cell arrangement is shown in Figure 4. The desired potential is set on the bucking potentiometer. The operational amplifier then adjusts the counter electrode current so that the working electrode assumes an equal but opposite potential to that

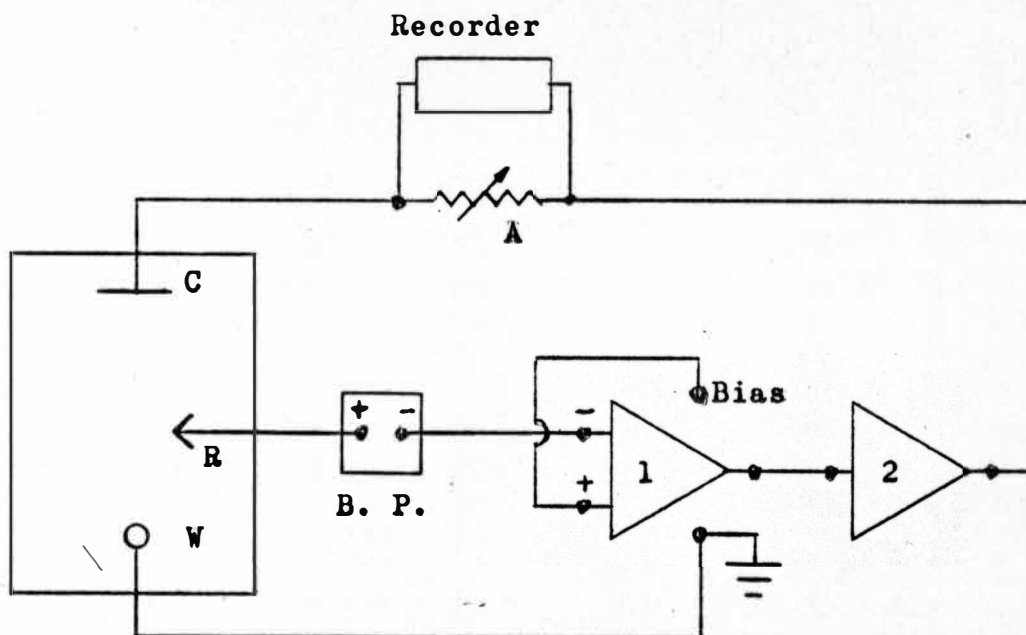
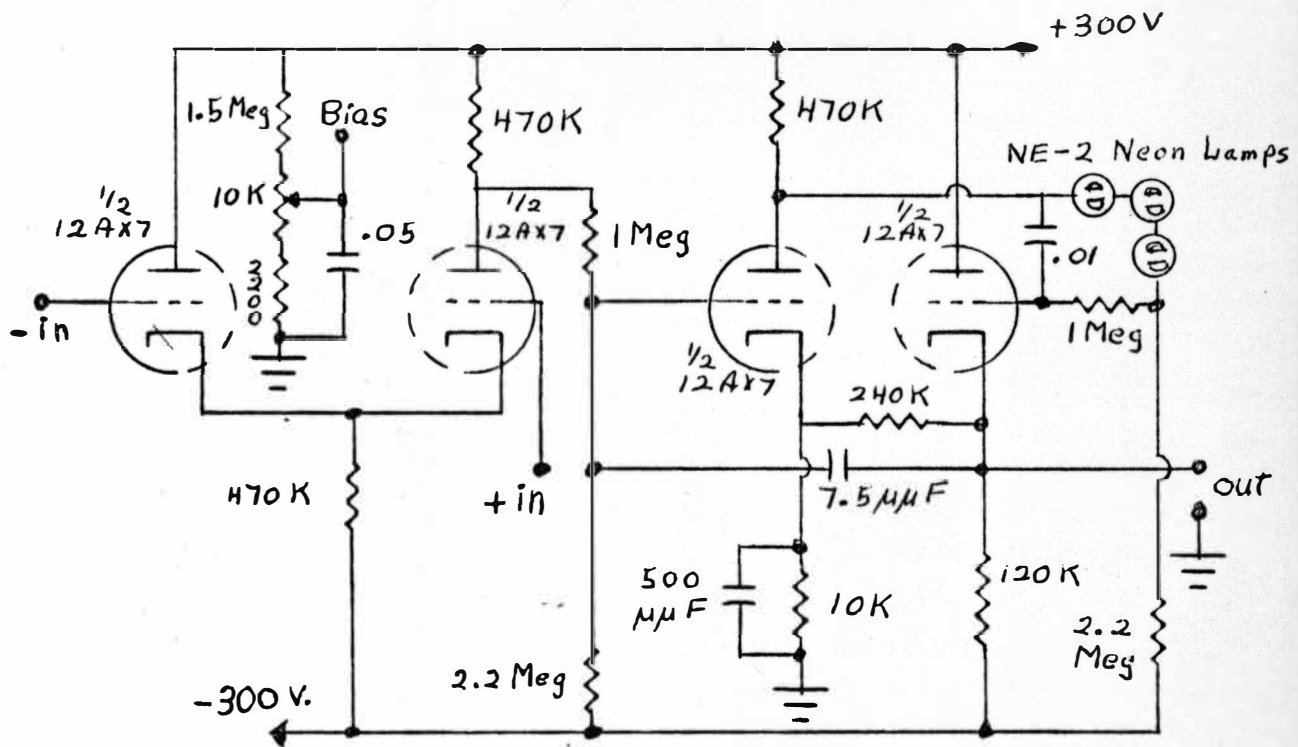
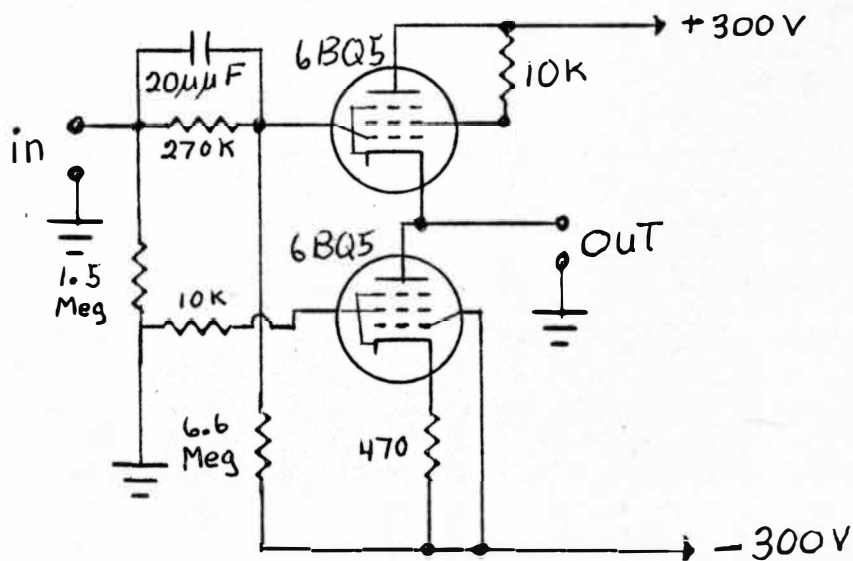


Figure 7. Circuit used for potentiostatic measurements. The operational amplifier adjusts its output current in such a way as to keep the potential at its negative input at ground potential. The desired potential is set on the bucking potentiometer.

- C--Counter electrode, graphite
- R--Reference electrode, Ag-AgCl
- W--Working electrode, iron
- B. P.--Bucking potentiometer
- A--Decade resistance box
- 1--Operational amplifier (See Figure 7a)
- 2--Booster amplifier (See Figure 7a)



(1)



(2)

Figure 7a. Circuit diagram for operational amplifier (1) and booster amplifier (2)

set on the bucking potentiometer (with respect to the Ag-AgCl). After the current has become constant, the potential is changed to another value and the current is again allowed to become constant. The potential at the input of the operational amplifier with respect to ground was continuously monitored using a Beckman Zeromatic pH meter. The scale on this meter was expanded so as to read 140 mv full scale. This was accomplished by placing the proper resistance (784 ohms) across the Thermo Compensator jacks. The measured potential should be zero during operation. If it did drift, it could be adjusted back to zero by use of the bias control on the amplifier.

The current flowing through the counter electrode circuit was measured by monitoring the potential drop across a known resistance. A Bausch and Lomb VOM 5 strip-chart recorder was used for this potential measurement.

The bucking potentiometer was especially prepared for this research study. It consists mainly of a ten-turn, 10,000 ohm helipot and a mercury cell (Figure 8). The slidewire was calibrated in two ranges, 1 volt full scale and 0.1 volt full scale. Once calibrated, exact voltage settings could be read from the microdial.

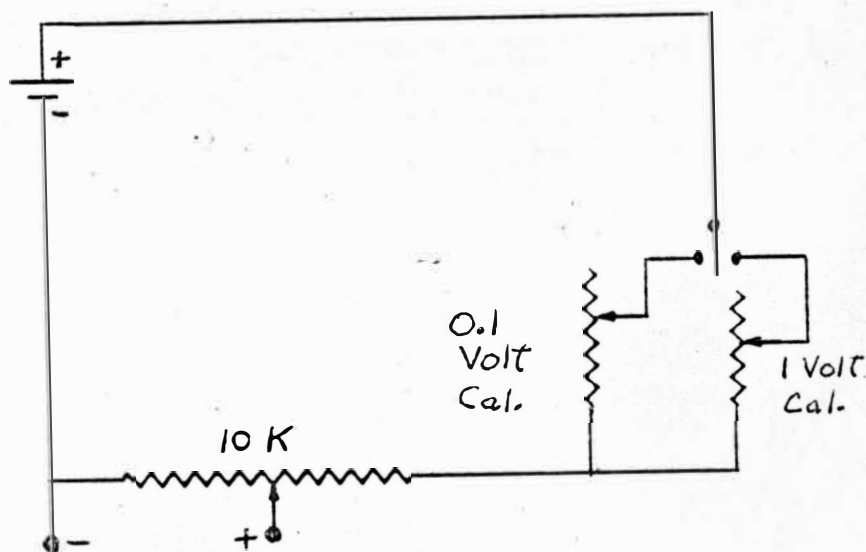


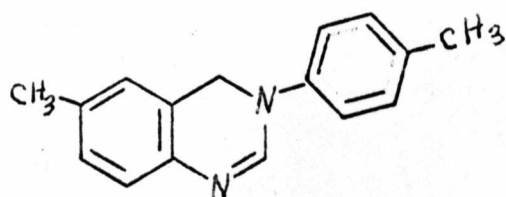
Figure 8. Bucking potentiometer. On the 1 volt scale the accuracy was 1 mv. On the 0.1 volt scale it was 0.1 mv.

DISCUSSION OF RESULTS

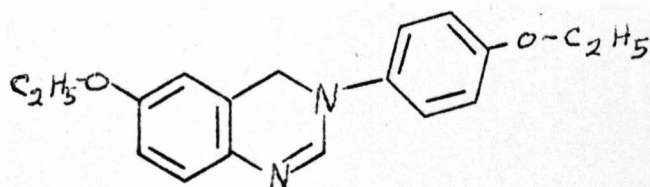
Galvanostatic Measurements

The DHQ series

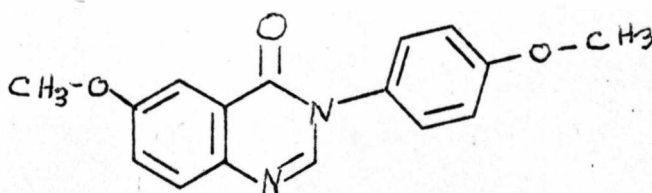
The data shown in Table I were acquired using the galvanostatic method. This series of compounds includes DHQ (1) (6-methyl-3-p-tolyl-3,4-dihydroquinazoline), ethoxy-DHQ and methoxy-DHQ-one. They have the following structures:



DHQ



ethoxy-DHQ



methoxy-DHQ-one

Table I. Effect of inhibitor concentration upon the anodic and the cathodic reactions

Compound	Conc. in M	Cathodic ΔE	Anodic ΔE
DHQ	0.005	-150 mv	+225 mv
"	0.0005	- 85	+194
"	0.0002	- 41	+177
"	0.0001	- 23	+108
"	0.00007	- 17	+ 69
"	0.00005	- 14	+ 19
"	0.000005	- 8	+ 15
"	0.0000005	- 3	- 1
Ethoxy-DHQ	Sat'd	-110	+ 89
	0.0005	- 99	+ 66
Methoxy-DHQ-one	0.005	- 98	+170
	0.001	- 35	+ 90
"	0.0005	- 21	+ 44
"	0.0001	- 5	+ 8
"	0.00005	- 3	+ 4
"	0.000005	0	0

Note: In Tables I thru VII the cathodic ΔE 's were measured at a current density of -10 ma/cm^2 , and the anodic ΔE 's were measured at a current density of $+10 \text{ ma/cm}^2$.

It can be seen from the data that DHQ is a stronger anodic inhibitor than ethoxy-DHQ, and that ethoxy-DHQ is stronger than methoxy-DHQ-one. These compounds affect the cathodic reaction as follows,

ethoxy-DHQ \approx DHQ $>$ methoxy-DHQ-one (all at 0.0005 M).

It can also be seen from the data that the amount of inhibition increases with concentration. In Tables I thru VII the error in the value of ΔE does not exceed $\pm 10\%$ or 1 mv, whichever is greater.

The aniline series

The next series of compounds studied included aniline, N-methylaniline and N,N-dimethylaniline (13). (See Table II).

Table II. Effect of inhibitor concentration upon the anodic and the cathodic reactions

Compound	Conc. in M	Cathodic ΔE	Anodic ΔE
Aniline	0.05	- 12 mv	+ 12 mv
"	0.005	- 5	0
"	0.0005	- 3	0
"	0.00005	- 1	- 1
N-methyl- aniline	0.05	- 19	+ 19
"	0.005	- 4	+ 3
"	0.0005	- 2	+ 1
"	0.00005	- 4	0
N,N-dimethyl aniline	0.05	- 30	+ 28
	0.005	- 15	+ 6

Both the anodic and the cathodic inhibition is increased by adding methyl groups to aniline. The dimethylaniline is a stronger inhibitor than methylaniline which is turn is stronger than aniline. This can be explained in the following way: alkyl groups are electron releasing groups, therefore, the methyl groups release electrons to the nitrogen causing an increase in electron density there. This increase causes the compound to be adsorbed more strongly on the iron. Therefore, it would be expected that the inhibition strength should decrease in the following order; dimethylaniline > methylaniline > aniline. This is in agreement with the data.

The amine series

Another series of compounds studied included ethylamine, n-butylamine, n-amylamine, n-hexylamine, diethylamine, dibutylamine and diamylamine (11) (12) (21). The data in Table III show that the inhibition strength of the primary amines decreases in the order hexyl > amyl > butyl. The inhibition strength of the dialkyl amines also decreases in this order, diamyl > dibutyl > diethyl. The increased inhibition with increasing chain length has been explained (20) by proposing that the chains at least partially lay flat on the surface. It is also possible that the increase is due to increasing base strength. No explanation is proposed as to why ethylamine and n-butylamine are cathodic accelerators.

Methyl ketones

A series of methyl ketones was also studied. The data from these compounds are shown in Table IV. At first it appeared as if they were all cathodic inhibitors. All of the compounds studied except 2-pentanone gave a negative change in potential when the cathodic reaction was being studied. The 2-pentanone was then distilled, but the distillate gave essentially the same results as the original solution. Attempts were then made to purify the other ketones by making bisulfite addition products. After this procedure the 2-butanone and the 2-heptanone agreed with

Table III. Effect of alkyl amines upon the cathodic and anodic reactions

Compound	Conc. in M	Cathodic ΔE	Anodic ΔE
Ethyl-amine	0.05	+ 10 mv	+ 2 mv
n-Butyl-amine	0.1	+ 16	+ 17
"	0.05	- 10	+ 6
"	0.005	- 4	+ 2
n-Amyl-amine	0.05	- 20	+ 10
n-Hexyl-amine	0.05	- 56	+ 16
Diethyl-amine	0.05	- 10	+ 2
Dibutyl-amine	0.05	- 21	+ 16
Diamyl-amine	0.05	- 36	+ 46

Table IV. Effect of methyl ketones upon the cathodic and anodic reactions

Compound	Conc. in M	Cathodic ΔE	Anodic ΔE
Acetone	0.05	- 7 mv	+ 10 mv
"(dist.)	0.05	- 4	- 4
"	0.05	- 4 *	0 *
"(reag.)	0.05	- 7	0
2-Butanone	0.05	- 6	+ 2
"	0.05	+ 16*	- 1*
2-Pentanone	0.05	+ 21	+ 2
"	0.05	+ 18	+ 10
2-Heptanone	0.05	- 16	+ 12
"	0.05	+ 10*	+ 4*

* After purification by bisulfite addition

the 2-pentanone. Acetone could not be made to agree with these. It was first distilled, but this gave the same results. It was then purified by making a bisulfite addition product. This purified substance also gave the same result. A sample from a bottle of reagent grade acetone was also tried, but this also gave similar results. No explanation for this has been found.

Ketones are oxidizing agents, so it would be expected that they should accelerate the cathodic reaction. Electrons and water could react directly with the ketones to give alcohols. This reduction would take place at the cathodic areas.

Nitroethane

Another very interesting compound studied was nitroethane (Table V). No explanation has been offered for the change from cathodic inhibitor to cathodic accelerator with increasing concentration. It acts as an anodic inhibitor at all of the concentrations studied.

Table V. Effect of nitroethane concentration upon the cathodic and the anodic reactions

Compound	Conc. in M	Cathodic ΔE	Anodic ΔE
Nitroethane	0.060	+ 31 mv	+ 12 mv
"	0.045	+ 33	+ 10
"	0.025	+ 3	+ 7
"	0.012	- 18	+ 8
"	0.005	- 20	+ 2
"	0.0005	- 13	+ 2

Formaldehyde

Another compound which gives results similar to this is formaldehyde (4) (14) (15). (See Table VI). It also seems to change from a cathodic inhibitor to a cathodic accelerator between a concentration of 0.0005 M and 0.001 M. The change here is not as large as it was in the previous case. The reason for the cathodic acceleration is similar to that for ketones as explained on page 24.

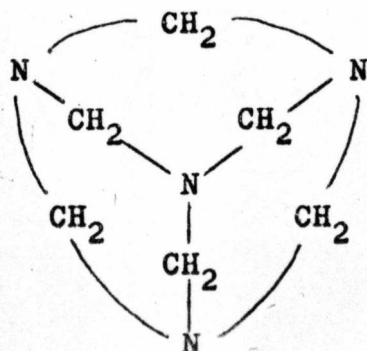
Table VI. Effect of formaldehyde concentration upon the cathodic and the anodic reactions

Compound	Conc. in M	Cathodic ΔE	Anodic ΔE
Formaldehyde	0.05	+ 28 mv	+ 28 mv
"	0.01	+ 31	+ 10
"	0.005	+ 13	+ 6
"	0.001	+ 11	+ 2
"	0.0005	- 3	0
"	0.00005	- 4	+ 1

Hexamine, ethanol and n-propanol

Another compound studied was hexamine (17). (See Table VII).

It has the following structure:



Hexamine

Table VII. Data for hexamethylenetetramine (hexamine), ethanol and n-propanol

Compound	Conc. in M	Cathodic ΔE	Anodic ΔE
Hexamine	0.05	+ 54 mv	+ 31 mv
Ethanol	0.05	- 2	0
n-Propanol	0.05	- 4	0

It is a cathodic accelerator and an anodic inhibitor.

Hexamine breaks down into formaldehyde and ammonia in acid solution, and this formaldehyde accounts for its ability to accelerate the cathodic reaction.

Two alcohols were also studied, ethanol and n-propanol. These compounds produced such a small change in potential that it was concluded that alcohols have no effect upon the reaction between iron and hydrochloric acid.

Potentiostatic Measurements

The data acquired from the potentiostatic measurements are shown graphically in Figures 9 through 13. The values of a and b (Tafel constants) which were computed from these plots are tabulated in Table VIII. The error in these measurements is about $\pm 10\%$. The Tafel plot for the uninhibited acid has been superimposed upon each of the Tafel plots for the individual inhibitors. This makes the comparison much clearer. A short horizontal line will be noticed on each plot near the intersection of the cathodic and the anodic curves. This is the value of the corrosion current as determined by the weight loss method (Table IX). Ideally, it should coincide with the intersection of the anodic and the cathodic line. The error in these measurements is about $\pm 10\%$.

DHQ

Figure 9 gives a comparison of the Tafel plot for 0.005 M DHQ with that for the uninhibited acid. Referring back to Figure 2, it is seen that both the anodic and the cathodic reactions are inhibited. This agrees completely with the results found using the galvanostatic method. The slopes (values of b) of the lines for the inhibited and the uninhibited solutions are almost identical. The values of a , however, are quite different, as can be seen from Table VIII.

Table VIII. The values of the Tafel constants a and b are given for both the anodic and the cathodic reactions for each compound studied. Each value given is the average of at least two individual determinations.

Solution	Anodic		Cathodic	
	a mv	b V	a mv	b V
4.8 N HCl	-308	0.093	-480	0.162
0.05 M DHQ	-127	0.109	-638	0.160
0.00125 M Methoxy-DHQ	-142	0.118	-595	0.153
0.005 M Hexamine	-266	0.085	-465	0.124
0.05 M Nitroethane	-296	0.060	-392	0.262
0.005 M Nitroethane	-307	0.220	-493	0.204

Table IX. Corrosion currents in inhibited and uninhibited solutions as determined by the weight-loss method

Solution	Wt. Loss	grams	Corrosion current
		cm ² -sec	
4.8 N HCl	0.0146 g	6.76 x 10 ⁻⁸	0.233 $\frac{\text{ma}}{\text{cm}^2}$
0.005 M DHQ	0.0015	0.708 x 10 ⁻⁸	0.0242
0.00125 M Methoxy-DHQ	0.0014	0.645 x 10 ⁻⁸	0.0222
0.005 M Hexamine	0.0046	2.17 x 10 ⁻⁸	0.0747
0.05 M Nitroethane	0.0221	10.43 x 10 ⁻⁸	0.360
0.005 M Nitroethane	0.0140	6.60 x 10 ⁻⁸	0.228

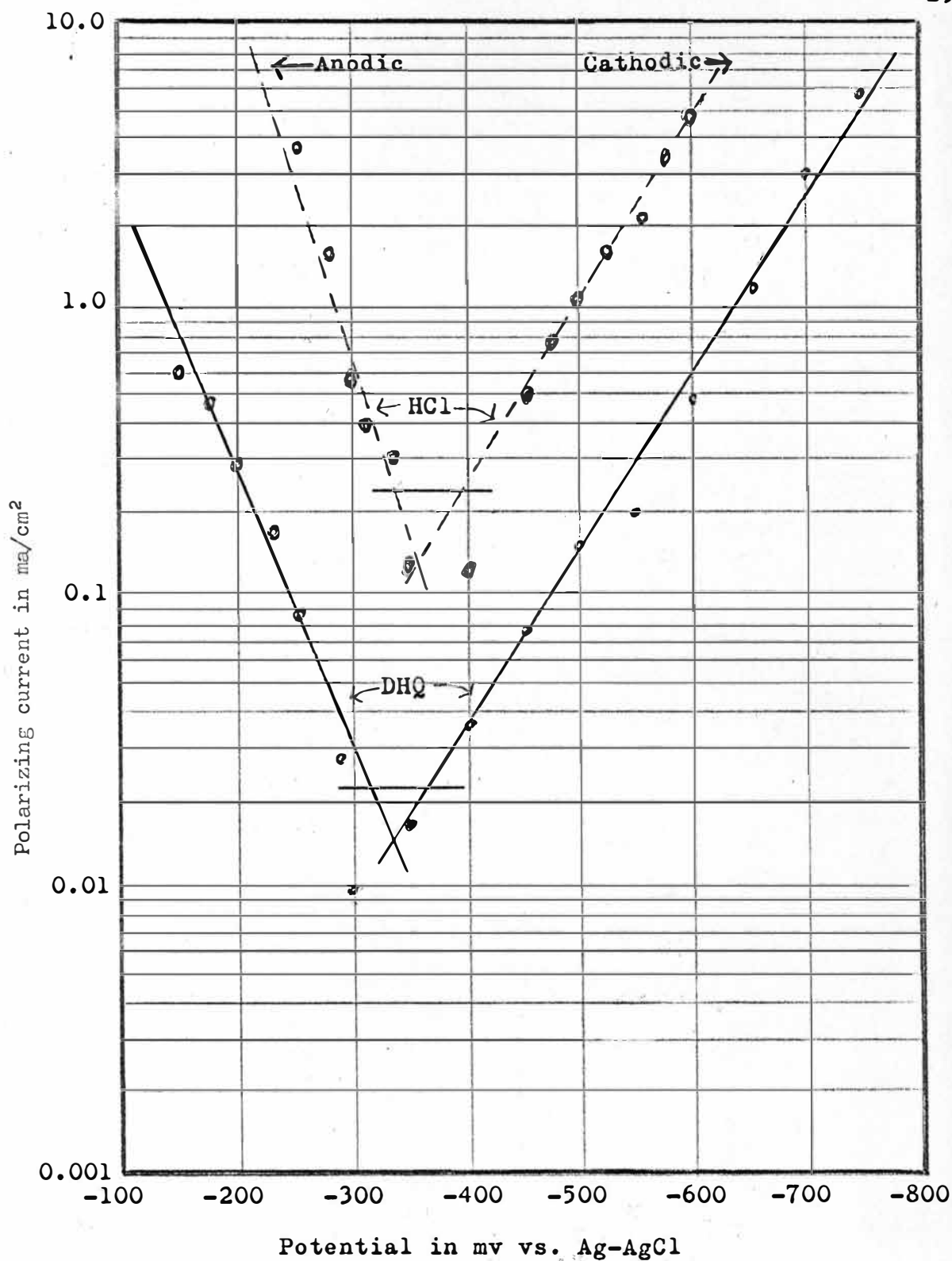


Figure 9. The Tafel plot for DHQ is compared with that for the uninhibited acid.

For the cathodic reaction the value of a is about 160 mv more negative, and for the anodic reaction it is about 180 mv more positive.

Methoxy-DHQ

Figure 10 is a comparison of the 0.00125 M methoxy-DHQ solution and the plain acid. The Tafel plot for this compound looks very similar to that for DHQ. From this plot it can readily be seen that methoxy-DHQ inhibits both the anodic and the cathodic reactions. Again, the values of b are very close for the inhibited and the uninhibited solutions, while the values of a are quite different. For the anodic reaction a is about 170 mv more positive for the inhibited solution, and for the cathodic reaction it is 115 mv more negative.

Hexamine

Figure 11 is a Tafel plot for 0.05 M hexamine. This graph shows that hexamine has only a small effect on the anodic reaction, and that it is a cathodic accelerator. However, if one looks at the average of several experiments, (Table VIII), it is seen that hexamine does inhibit the anodic reaction. These data agree with those obtained by the galvanostatic measurements.

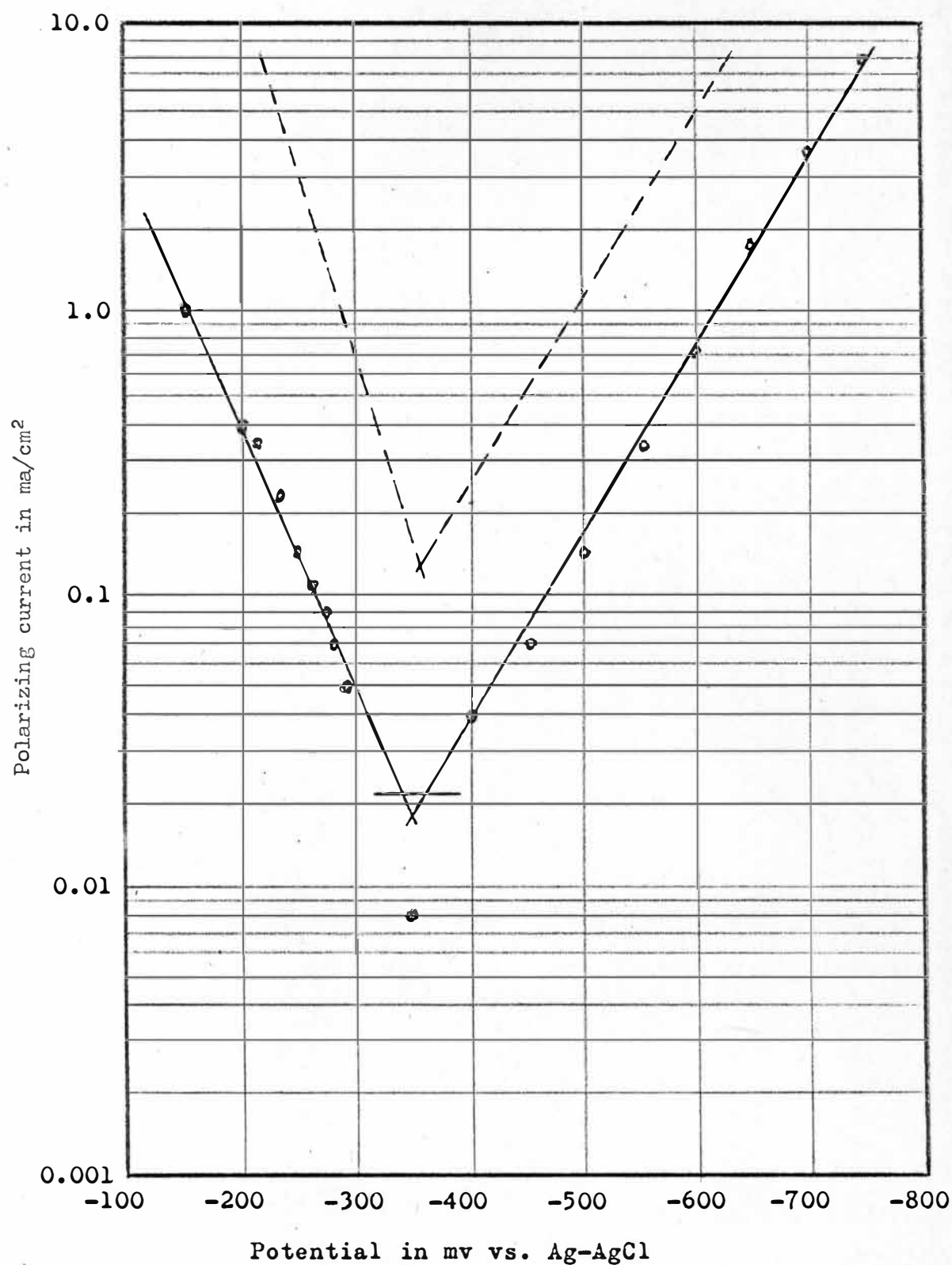


Figure 10. The Tafel plot for Methoxy-DHQ is compared with that for the uninhibited acid.

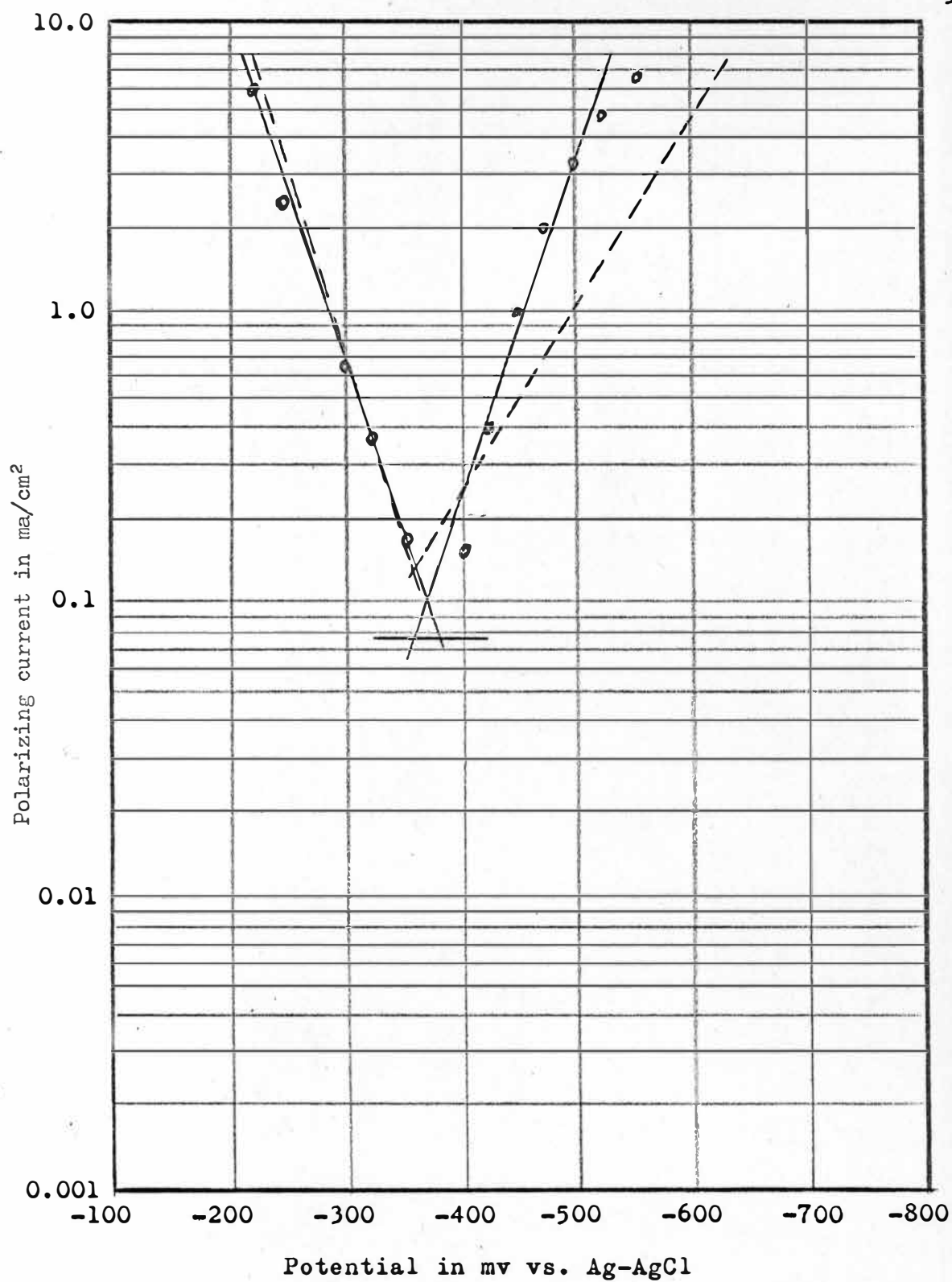


Figure 11. The Tafel plot for Hexamine is compared with that for the uninhibited acid.

Nitroethane

In Figure 12 the logarithm of the current density is plotted against the measured potential for a solution 0.05 M in nitroethane. It can be seen from the graph that at this concentration nitroethane is a cathodic accelerator and possibly a very weak anodic accelerator. The average values from Table VIII show that it is a very weak anodic inhibitor. These data also agree reasonably well with the galvanostatic measurements.

Figure 13 gives the Tafel plot for 0.005 M nitroethane. At this concentration it is seen that nitroethane is a cathodic inhibitor and an anodic accelerator. Both reactions are only slightly affected.

From Figures 11, 12, and 13 it can be seen that the value of b for the cathodic reaction of the inhibited solution does not coincide with those for the uninhibited 4.8 N hydrochloric acid. No explanation has been found for this difference in the value of b .

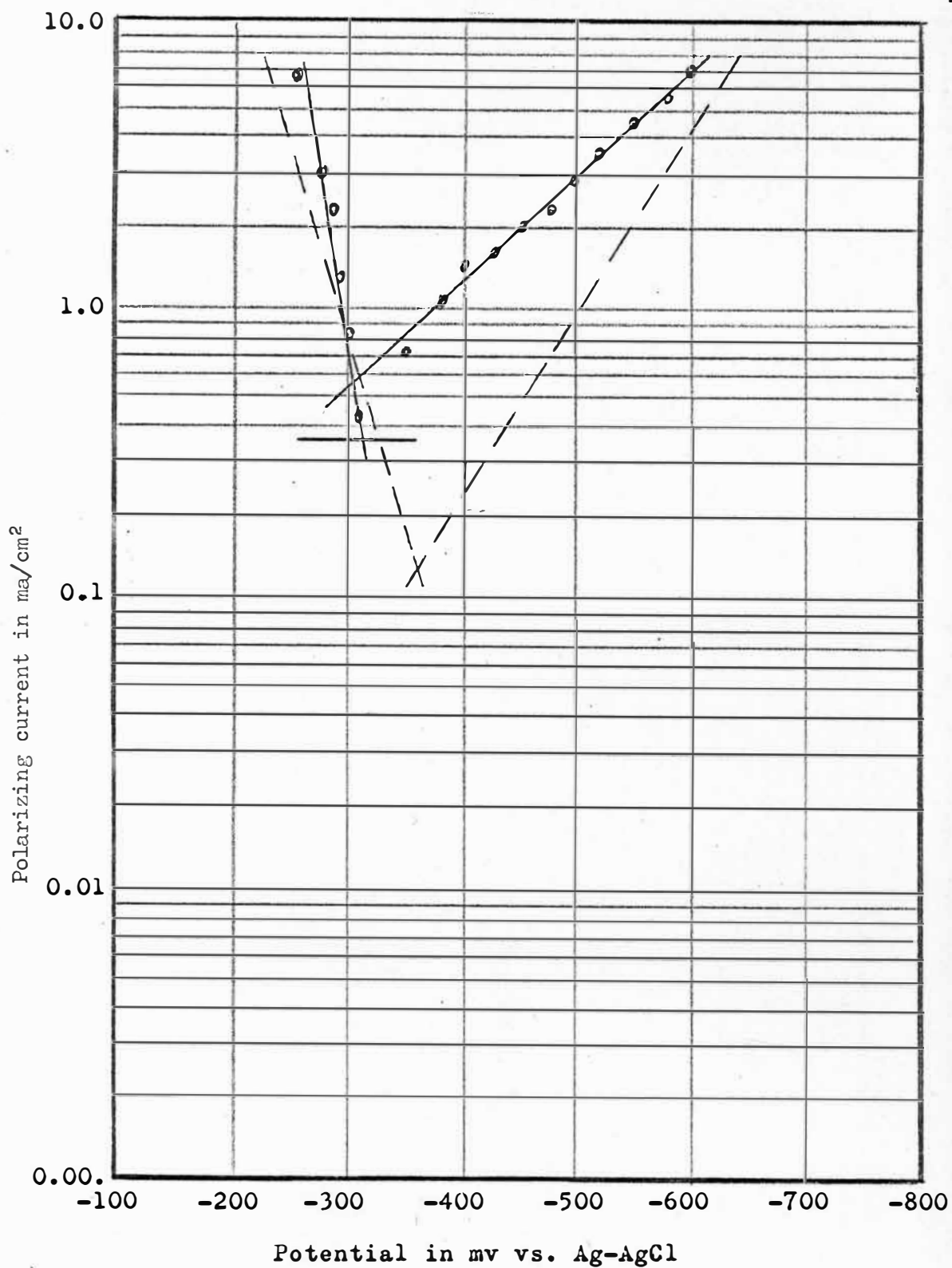


Figure 12. The Tafel plot for 0.05 M Nitroethane is compared with that for the uninhibited acid.

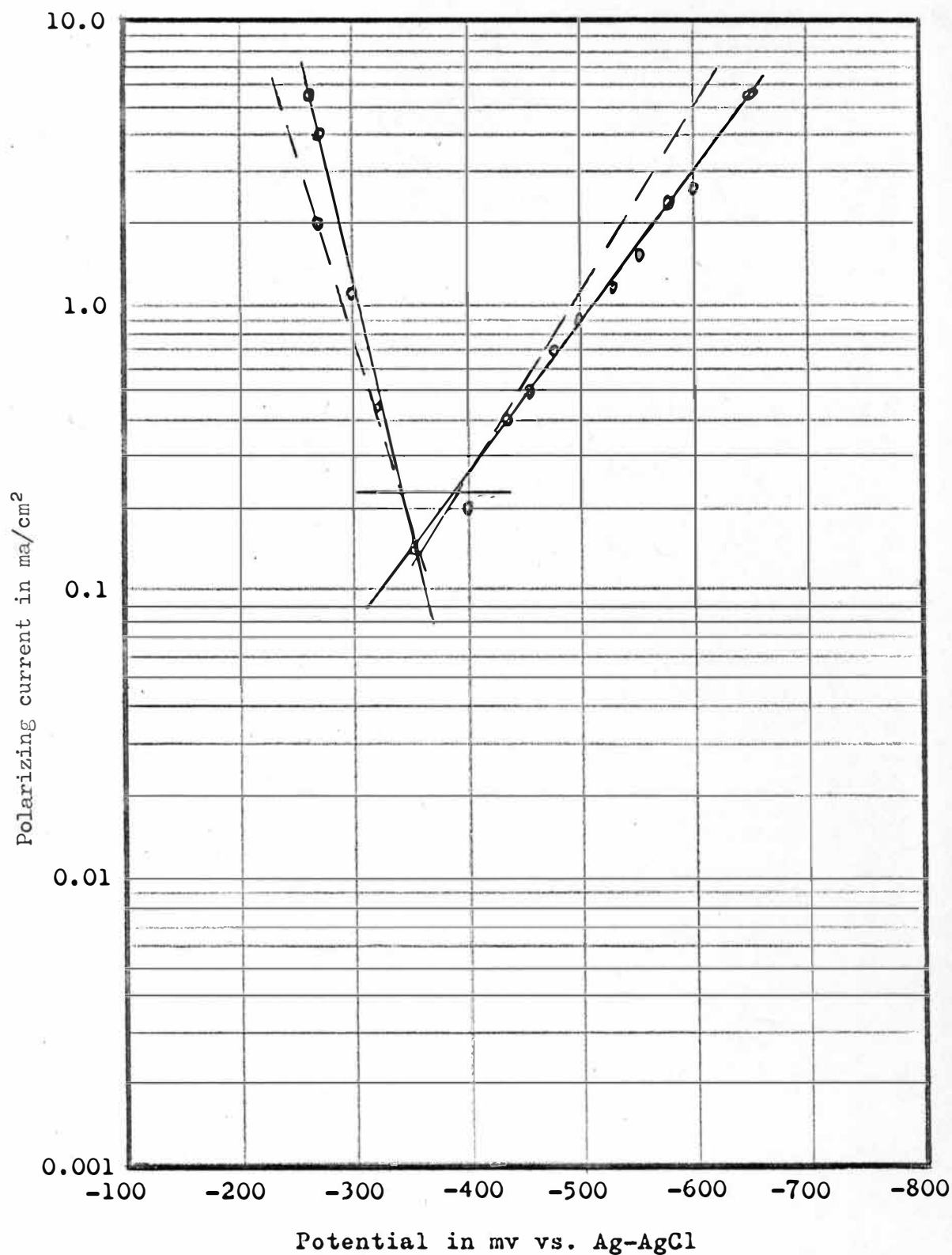


Figure 13. The Tafel plot for 0.005 M Nitroethane is compared with that for the uninhibited acid.

SUMMARY AND CONCLUSIONS

In this study it has been shown how some specific types of corrosion inhibitors affect the anodic and the cathodic reactions which take place when iron is immersed in hydrochloric acid. Both formaldehyde and nitroethane show a dramatic change in inhibition properties with changes in concentration. No explanation has been postulated for this phenomenon. This would be a good problem for further study.

It has been shown that either the galvanostatic or the potentiostatic method may be used in the classification of corrosion inhibitors with exactly the same results. The potentiostatic method is the preferred one, however, since the reaction taking place at the electrode can be controlled. The use of the potentiostatic method in this research was made possible through the exploitation of the operational amplifier. The rapid response to minute changes in the cell could not have been realized by conventional potentiostats.

BIBLIOGRAPHY

- (1) Anderson, R. H., E. R. Allen and P. A. van der Meulen, *Corrosion* 17, 437t-440t (1961).
- (2) Anoshchenko, I. P., *Zhur. Priklad. Khim.* 30, 393-400 (1957). *Chem. Abstr.* 51, 11970d (1957).
- (3) Ayers, R. C., and N. Hackerman, *J. Electrochem. Soc.* 110, 507-13 (1963).
- (4) Balezin, S. A., and V. S. Kemkhadze, *Zhur. Abshchei. Khim.* 22, 1848-55 (1952). *Chem. Abstr.* 47, 1026f (1953).
- (5) Cavallaro, L., and G. Bolognesi, *Atti Acad. Sci. Ferrara* 24, No. 1, 10 (1946-47). *Chem. Abstr.* 43, 547i (1949).
- (6) Cavallaro, L., L. Felloni, G. TrabANELLI and F. Pulidori, *Electrochim. Acta* 8, 521-7 (1963). *Chem. Abstr.* 59, 4788a (1963).
- (7) Ch'iao, Shih-Jen, and C.A. Mann, *Ind. Eng. Chem.* 39, 910-919 (1947).
- (8) Evans, U. R., "The Corrosion and Oxidation of Metals," Edward Arnold Ltd., London, 1961.
- (9) Felloni, L., and G. Bolognesi, *Ann. Chim.* 47, 985-95 (1957). *Chem. Abstr.* 52, 852h (1958).
- (10) Fischer, H. and H. Yamaoka, *Naturwissenschaften* 48, 70 (1961). *Chem. Abstr.* 55, 18529f (1961).
- (11) Fujii, S., and K. Aramaki, *Boshoku Gijutsu* 7, 161-5 (1958). *Chem. Abstr.* 53, 2054d (1959).
- (12) Hackerman, N., R. M. Hurd and R. R. Annand, *Corrosion* 18, 37t-42t (1962).
- (13) Hisamatsu, Y., and M. Kanno, *Nippon Kinzoku Gakkai-Shi* 17, 149-52 (1953). *Chem. Abstr.* 49, 10155e (1955).
- (14) Hoar, T. P., and R. P. Khera, *Ann. Univ. Ferrara Sez.* 5, Suppl. No. 3, 73-97 (1960). *Chem. Abstr.* 56, 9817i (1962).

- (15) Hugel, G., Ann. Univ. Ferrara, Sez. 5, Suppl. (1960), 229-38 (1961). Chem. Abstr. 56, 9869a (1962).
- (16) Jaudon, E., Metaux, corrosion, usure 19, 12-17 (1944). Chem. Abstr. 41, 7277e (1947).
- (17) Khitrov, V. A., and V. F. Khmel'kov, Izv. Voronezhsk. Gos. Pedagog. Inst. 29, 91-9 (1960). Chem. Abstr. 57, 3136h (1962).
- (18) Legault, R. A., and M. S. Walker, Corrosion 19, 222t-226t (1963).
- (19) Malmstadt, H. V., C. G. Enke and E. C. Toren, "Electronics for Scientists," Benjamin, New York, 1963. P. 341.
- (20) Mann, C. A., B. E. Lauer and C. T. Hultin, Ind. Eng. Chem. 28, 159-63 (1936).
- (21) Meakins, R. G., J. Appl. Chem. 13, 339-45 (1963).
- (22) Milazzo, G., "Electrochemistry," Elsevier Publishing Co., London, 1963. p. 192.
- (23) Nathan, C. C., and E. Eisner, Corrosion 14, 193t-199t (1958).
- (24) Phelps, E. H., Corrosion 18, 239t-246t (1962).
- (25) Potter, E. C., "Electrochemistry," Cleaver-Hume Press Ltd., London, 1956. p. 128.
- (26) Prazak, M., Corrosion 18, 449t (1962).
- (27) Schwarz, W. M., and I. Shain, Anal. Chem. 35, 1770-78 (1963).

VITA

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