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Adsorption studies of organic compounds on the hydrogen electrode using a microcoulometric technique

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ADSORPTION STUDIES OF ORGANIC COMPOUNDS
ON THE HYDROGEN ELECTRODE
USING A MICROCOULOMETRIC TECHNIQUE

BY

PHILIP LAMAR OGLESBY

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I wish also to thank my wife Sara for her generous efforts in the compilation of this work.

INTRODUCTION

This work was concerned with the adsorption of various organic compounds and their effect on the hydrogen electrode where adsorption is defined as the accumulation of a chemical substance at the boundary separating two phases. In this case, the two phases were the electrode and the ionic solution surrounding it.

This work was actually a continuation of work begun by T. C. Franklin and R. D. Sothern. Franklin and Sothern studied the competitive adsorption of hydrogen and nitriles on the platinized platinum electrode by means of a micro-coulometric technique which they developed. They noted: (1) that the active area of the hydrogen electrode was poisoned by nitriles; (2) that the log of the fraction of the active area poisoned by the nitriles was a straight line function of the log of the concentration of nitriles present in the solution around the hydrogen electrode; (3) that the Nernst potential of the hydrogen electrode in acid solution was a straight line function of the log of the amount of hydrogen adsorbed on the electrode; (4) that the integral heat of adsorption for hydrogen on platinum obtained was 4000 calories/mole; (5) that the active area of the hydrogen electrode increased with increasing hydrogen pressure above the system; and (6) that the poisoning effect of the nitrile increased with increase in molecular weight. However, some of the data collected by Franklin and Sothern showed much scatter when graphed. This was particularly true in the case of the data for the potential as a function of the hydrogen adsorbed. Therefore, the slope of the curve of the potential vs. the log of the amount of hydrogen adsorbed was not definitely established. It was also not definitely proven that data for two different electrodes could be superimposed. Therefore, this present investigation was a continuation of the work started by Franklin and Sothern using their microcoulometric technique.

The objectives of this work were: (1) to repeat the experiments of Franklin and Sothern on poisoning the hydrogen electrode with acetonitrile in 2 N sulphuric acid and to definitely establish the slope of the straight line of potential vs. log of the amount of hydrogen adsorbed on the electrode; (2) to determine whether the data for two different electrodes could be superimposed; (3) to extend the investigation to the study of the adsorption of amines on platinized platinum and the effect of this adsorption on the potential of and amount of hydrogen on the hydrogen electrode; (4) to determine how the molecular structure of the amines affected their adsorption properties on the hydrogen electrode; (5) to determine how the pH of the solution around the hydrogen electrode affected the adsorption of amines on the hydrogen electrode; and (6) to determine how pH affected the Nernst potential as a function of the amount of adsorbed hydrogen on the electrode.

HISTORICAL

The phenomena of adsorption has been known since the late 1700's when C. W. Scheele[1] studied the adsorption of materials by charcoal. As far as the relation of adsorption to electrochemistry and the electrode, this was not considered till much later; but the study of electrochemistry alone started about the same time that adsorption on charcoal was discovered, that is, in the late 1700's.

Galvanic electricity was discovered by Luigi Galvani in about 1780. The electric cell itself was not discovered until the early 1800's. It was not until after 1850 that the theory of electrochemistry and the galvanic cell were developed.

It was in 1889 that Nernst[2] put forward his theory concerning electrode potentials. He proposed that the potential difference between a material in a solution containing its ions was similar to the phenomena of solubility of neutral substances. In 1916, Langmuir[3] pointed out from discoveries that there was conclusive evidence to prove that the existence of

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[1] Glasstone, S., "Textbook of Physical Chemistry", D. Van Nostrand Co., Inc., New York, N. Y. (1946)
[2] Nernst, Z. physikal. Chem., 4, 129 (1889)
[3] Langmuir, Trans. Amer. Electrochem. Soc., 29, 125 (1916)

large potential differences at the material junctions of a galvanic cell were of the same order of magnitude as the electromotive force of the whole cell.

The earliest theory of significance concerning the electrical double layer was proposed by Helmholtz[4,5] between 1879 and 1881. The electrical double layer theory is an idea that the ions at the junction of the electrode in the solution will distribute themselves in such a manner as to achieve a state of equilibrium. In achieving this state, the ions dissolve into solution from the electrode and continue to dissolve until the forces of the electrical double layer are sufficient to prevent the dissolution of any more ions from the electrode, or when the work done by an ion passing across the double layer is sufficient to balance the tendency to dissolve because the solution pressure of the metal becomes equal to the osmotic pressure of the ions in solution[6]. The early picture of the double layer proposed by Helmholtz[4,5] was to consider the double layer as a simple condenser. This was not a true picture of the double layer and it was pointed out by Gouy[7,8,9] that the ions of a double layer could not be

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[4] Helmholtz, Wied. Ann., 7, 337 (1879)

[5] Helmholtz, Monats. Preuss. Akad. Sci. (Nov. 1881)

[6] Butler, J.A.V., "Electrical Phenomena at Interfaces", The MacMillan Co., New York, N. Y. (1951)

[7] Gouy, J. de physique (4), 9, 357 (1910)

[8] Gouy, Annales de phys., 7, 129 (1917)

[9] cf. Bikerman, Z. physikal. Chem., 163, 378 (1933)

concentrated at a definite distance from the surface of the electrode. He proposed a diffuse layer theory, but it was not until 1924 that a good picture of the double layer theory and phenomena pertaining thereto was brought out by Stern[10]. He suggested a type of double layer which is a combination of the Helmholtz fixed layer and the Gouy diffuse layer. It was after the development of these theories (the Stern theory of the double layer, the Nernst theory of the potential of a reversible electrode and other theories explaining the phenomena occurring at the junction of the metal in the solution which make up an electrode) that investigation of adsorption on the electrode began.

This history is primarily concerned with giving a review of the important articles previously written pertaining to these investigations and articles related thereto. Of particular concern, were studies made on the adsorption of material on the hydrogen electrode and the effect of these materials on the Nernst potential of the electrode. The other related fields of investigation which are of interest are: (1) adsorption studies on the surface of heterogeneous catalysts; (2) the effect of organic inhibitors on overpotential; and (3) the effects of the adsorption of polar organic inhibitors in acid dissolution of metal or in corrosion. In this historical review, the topics of interest

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[10] Stern, Z. Elektrochem., 30, 508 (1924)

will be reviewed in the following order: (1) the adsorption of a substance on the hydrogen electrode and its effect upon the Nernst potential of the electrode; (2) adsorption studies on the surface of heterogeneous catalysts; (3) the effect of organic inhibitors on overpotential; and (4) the effects of the adsorption of polar organic inhibitors in acid dissolution of metals in corrosion.

N. A. Isgarishev and E. Kolddaeva[11] studied the poisonous effects of potassium cyanide, arsenious oxide, hydrogen sulfide, quinine and brucine on the hydrogen electrode in both sulphuric acid solution and potassium hydroxide solution. They pointed out that these poisons lowered the Nernst potential of the reversible hydrogen electrode but they also noted that the Nernst potential returned to its original value after several hours. They concluded that the lowering of the equilibrium potential was due to the union of the platinum with the poisonous compounds. The unstableness of these compounds in acid solution resulted in their removal from the platinum after a period of time, causing the potential to rise again.

The use of ammonia, hydrogen sulfide, cyanides and mercury salts as poisons on the hydrogen electrode was investigated by A. H. Aten, et al[12,13]. These poisons were found to

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[11] Isgarishev, N.A. and Kolddaeva, E., Z. Electrochem. 30, 83-86 (1924)

[12] Aten, A.H., Bruin, P. and DeLange, W., Rec. Trav. Chim. 46, 417-429 (1927)

[13] Aten, A.H. and Zierren, M., Rec. Trav. Chim. 48, 944-948 (1929)

decrease the equilibrium potential of the electrode and their effects were found to be accelerated by the presence of oxygen. Two types of poisoning phenomena were discovered, one in which the electrode recovered after a short time and the other permanent. They also studied arsenious oxide as a poison and found that its poisoning effects depended on: (1) the surface conditions of the electrode; (2) the area of the electrode; (3) presence or absence of oxygen in the system; (4) the agitation of the solution; and (5) the nature of the electrolyte around the electrode. At a later date, further studies were conducted by this group[14] still using arsenious oxide as a poison. It was found that reactions proceeded very slowly at the poisoned hydrogen electrode and that the electrode recovered from poisoning by anodic polarization.

J. Lisiecki[15] investigated the effect of a dichlorochromium complex on the hydrogen electrode and found that the hydrogen electrode is de-polarized and permanently poisoned with the above compound.

Further studies of the adsorption of hydrogen sulfide on the hydrogen electrode were made by H. Jablczynska-Jedrzejowska[16,17,18]. The electrode was found to be

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14. Aten, A.H. and Zieren, H., Trans. Am. Electrochem. Soc. 58, 24 (1930)
15. Lisiecki, J., Roczniki Chem. 13, 552-560 (1933)
16. Jablczynska-Jedrzejowska, H., Roczniki Chem. 16, 306-312 (1936)
17. Jablczynska-Jedrzejowska, H., Roczniki Chem. 16, 574-581 (1936)
18. Jablczynska-Jedrzejowska, H., Roczniki Chem. 18, 550-555 (1938)

poisoned by the hydrogen sulfide even when it was in low concentration. The rate of poisoning increased with increasing concentration of hydrogen sulfide and decreased with increasing concentration of acid in the solution. The poisoning effect could not be destroyed by hydrogen or concentrated sulphuric acid and therefore was concluded to be permanent. While hydrogen sulfide was found to poison the hydrogen electrode in a stable manner, potassium cyanide and sulphur dioxide did not. In each case, the poisoning of the electrode was removed by the addition of oxygen to the system. The potential of the hydrogen electrode was investigated as a function of the concentration of hydrogen sulfide added and it was found to decrease with increasing concentration of hydrogen sulfide. Another fact which was determined was that the velocity of poisoning decreased with increasing thickness of platinum black.

Measurements were made by Slygin and Ershler[19] on the amount of hydrogen adsorbed for both smooth and platinized platinum electrodes using mercury and arsenic as the poisons. It was found that small amounts of mercury and arsenic were adsorbed on the most active spots of the platinum. The fact was noted that the number of atoms of hydrogen displaced by one molecule of arsenic, potassium cyanide and mercury are

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[19] Slygin, A. and Ershler, B., Acta. Physiochim. U.R.S.S. **11**, 45-58 (1939)

4, 10 and 40 in the case of a dilute solution. The effects were due not only to a blocking of the electrode surface but also to a specific interaction effect.

Studies were made on the adsorption of acetic acid on the platinum electrode by H. Oikawa and T. Mukaibo[20]. The amount of adsorbed acetic acid was measured as a function of the decreasing adsorbed hydrogen with the amount of adsorbed hydrogen being determined by means of an oscillographic potential - time curve. A Freundlich adsorption isotherm agreement was obtained.

The last article under topic (1) to be mentioned is that of Franklin and Sothern[21]. They studied the adsorption of nitriles on the hydrogen electrode and the resultant effect on the Nernst potential of the electrode, the results of which were discussed in the introduction to this thesis.

The work of F. H. Pollard[22] in the field of adsorption on heterogeneous catalysts was on the adsorption of carbon monoxide and hydrogen on platinized asbestos. It was found that carbon monoxide will displace hydrogen already adsorbed on platinized asbestos and it was concluded that this fact accounted for the poisoning effect of carbon monoxide on platinum used as a catalyst in hydrogenation.

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[20] Oikawa, H. and Mukaibo, T., J. Electrochem. Soc. Japan 20, 568-571 (1952)

[21] Franklin, T.C. and Sothern, R., J. Phys. Chem., 58, 1951 (1954)

[22] Pollard, F.H., J. Phys. Chem., 27, 356 (1923)

In catalytic poisoning, Maxted and coworkers have done some very outstanding work. One of Maxted's articles[23] was a study of the effect of lead and mercury salts on platinum. He found the adsorption of lead and mercury ions to be a linear function of their concentrations up to the point of saturation of the platinum where it then became constant. The catalytic activity of platinum was found to decrease as a linear function of the concentration of poison. In later investigations by Maxted[24,25], he noted that compounds containing elements which had a free pair of electrons which could be donated to form a coordinate covalent bond were catalytic poisons. He noted that those elements containing a free pair of electrons occurred in groups Vb and VIb of the periodic table. Compounds containing these elements were particularly effective on platinum and nickel catalysts. The compound (poison) was strongly chemisorbed on the metal catalyst and tied up the active sites of the catalyst. It was noted by him that metal catalysts that were poisoned by those compounds containing elements having a free electron pair were metals which had a d-shell which could utilize the electron pair from the compound; therefore, a bond could be formed between the metal catalysts and the toxic compound

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[23] Maxted, E.B., J. Chem. Soc., 127, 73-77 (1925)
[24] Maxted, E.B., J. Chem. Soc., 1949, 1987
[25] Maxted, E.B., and Moon, K.L., J. Chem. Soc. 1949, 2171

with the compound furnishing an electron pair to the d-shell of the metal catalyst. Compounds without a free electron pair showed little or no poisoning effect. Compounds with unsaturated bonds were noted to be poisons since they have a free electron pair to donate to the catalyst d-shell. The metal catalysts were found to be primarily elements of group VIII in the periodic table.

The relation of adsorption of compounds on an electrode to overpotential will now be reviewed, overpotential being defined as the difference in potential between an electrode across which passes a certain current and the same electrode acting reversibly in the same solution[26].

The effect of alkaloids on the hydrogen overpotential was investigated by J.O'M. Bockris and B. E. Conway[27]. While it is known that poisons such as arsenious oxide increase the hydrogen overpotential when added to a solution containing the hydrogen electrode, certain groups of alkaloids such as the quinoline group function as activators decreasing the hydrogen overvoltage. On platinized platinum, all the alkaloids were found to act as poisons.

Again referring to overpotential investigations, P. J. Hillson[28] investigated the strength of adsorption of hexyl

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26. Kortum, G. and Bockris, J.O'M., "Textbook of Electrochemistry", Vol. II, Elsevier Publishing Co., New York, N. Y. (1951)
27. Bockris, J.O'M. and Conway, B.E., Nature 159, 711-712 (1947)
28. Hillson, P.J., J. Chim. Phys. 49, 88-96 (1952)

alcohol and other compounds on various electrodes and their effects on the overvoltage of these electrodes. The overvoltage use of the electrode was considered to be due to the formation of an adsorbed film of the organic compound which inhibits the discharging of hydrogen ions on the electrode.

Further studies of hydrogen overvoltage were made by M. Bonnemay[29]. He studied platinized platinum electrodes poisoned while acting as anodes in the electrolysis of hydrochloric acid, under conditions evolving chlorine. He proposed that the mechanism of poisoning may be due to the occupation of adsorption sites on the platinum by chlorine so the discharge of hydrogen can only occur without adsorption.

In connection with corrosion, it is known that the adsorption of organic compounds on metals reduces or inhibits the rate of corrosion or solution of metals. Work by Speller and Chappell[30], Chappell, Roetheli and McCarthy[31], Forrest, Roberts and Roetheli[32] and Ardagh, Room and Owen[33] showed that organic bases or amines were very good inhibitors. It was

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29. Bonnemay, M., J. Chim. Phys., 49, 142-146 (1952)
30. Speller and Chappell, Chem. Met. Eng., 34, 421-423 (1927)
31. Chappell, Roetheli and McCarthy, Ind. Eng. Chem., 20, 582 (1928)
32. Forrest, Roberts and Roetheli, Ind. Eng. Chem., 20, 1369 (1928)
33. Ardagh, Room and Owen, Ind. Eng. Chem., 25, 1116 (1933)

noted that the higher the molecular weight of the amine, the stronger the inhibitor it was. It was found by Mann, Lauer and Hultin[34] that aliphatic amines were very good inhibitors, especially tri-butyl and tri-amyl amines. Recently, Gatos[35] studied the effect of various amines on polarographic maxima and found that maxima suppression resulted. He suggested that corrosion inhibitors might be evaluated by their effect on polarographic maxima. The article which is especially noteworthy in connection with the work included in this thesis is entitled "Action of Polar Organic Inhibitors in Acid Dissolution of Metals" by Norman Hackerman and A. C. Makrides[36]. Various theories of electrode corrosion inhibition are discussed in this article, the first of which was the theory of cathodic corrosion inhibition by organic compounds proposed by Mann[37]. The main features of this theory are: (1) the organic inhibitors exist in acid solution as cations; (2) these inhibitors are adsorbed by means of electrostatic attraction; and (3) the resultant adsorbed film of organic inhibitor on the cathode stops the hydrogen ions from reaching the surface of the cathode, thus increasing the interfacial resistance. It is assumed in this theory that the nature of the cathode does not

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[34] Mann, C.A., Lauer, B.E. and Hultin, C.T., Ind. Eng. Chem., 28, 159 (1936)

[35] Gatos, H.C., "Corrosion Inhibitors in the Polarographic Maxima", J. Electrochem. Soc., 101, 433-441 (1954)

[36] Hackerman, N. and Makrides, A.C., Ind. Eng. Chem., 46, 523-527 (1954)

[37] Mann, C.A., Trans. Electrochem. Soc., 69, 115 (1936)

change. Hackerman and Makrides pointed out many discrepancies in Mann's theory, such as the fact that his theory does not account for (1) phenomena occurring simultaneously at the cathode and anode; and (2) compound structural group effects such as the fact that sulphur containing compounds are better inhibitors than corresponding nitrogen compounds. The evidence available in this article from research which has been done indicates in the adsorption of organic compounds that there are other adsorption forces acting in the adsorption of these organic inhibitors besides the electrostatic forces, which are the only ones in Mann's theory. Hackerman and Makrides postulated that the adsorption of polar organic inhibitors is general and not restricted to the electrostatic type of adsorption of Mann's theory. This general adsorption of organic inhibitors is both physical and chemical in nature. The physical adsorption results from: (1) the van der Waals forces; and (2) the electrostatic interaction occurring at the cathode. The chemical adsorption is proposed to be the type postulated by Mexted[24,25] where there is a coordinate covalent bond formed between the metal electrode and the organic inhibitor with the organic inhibitor furnishing a free pair of electrons to the d-shell of the metal electrode. The chemisorption could cause inhibition by decreasing the dissolution tendency of the metal at the anode or by increasing the overpotential for hydrogen discharge at the cathode (poisoning the cathode). It might be noted that although residual valences at the surface of the metal electrode enter into the chemisorption, these alone are not sufficient for strong chemisorption and therefore the unfilled atomic orbits are required, principally the d-shells. From this chemisorption postulate of Hackerman and Makrides, they drew the conclusion that iron should adsorb the organic inhibitors more effectively than zinc. Indeed, this was found to be true. The mechanism of inhibition by aliphatic amine is considered by Hackerman and Makrides to be the following:

$$RNH_3^+ \text{ (sol.)} \rightleftharpoons RNH_2 + H^+ \rightleftharpoons RNH_2 - \text{iron}$$

where RNH_2—iron denotes chemisorbed amine.

Other facts presented in this article by Hackerman and Makrides were that aliphatic amines are better inhibitors than aromatic amines therefore piperidine is a better inhibitor than pyridine since piperidine is less aromatic than pyridine. It was also noted by them that the introduction of methyl groups onto the pyridine ring increased pyridine's inhibiting power. It therefore was concluded from this that α-picoline is a stronger inhibitor than pyridine. This completes the summary of facts of importance mentioned in the article by Hackerman and Makrides as related to this thesis.

EXPERIMENTAL METHODS

A. MATERIALS

The series of organic compounds studied on the hydrogen electrode as competitive adsorbates with hydrogen were acetonitrile, pyridine, n-ethyl amine, n-propyl amine, n-butyl amine, secondary butyl amine, allyl amine, piperidine, pyrrole and α-picoline. The adsorbents used in this research were micro-electrodes of platinized platinum wire which was number 20 gauge wire and about two centimeters in length. The electrodes were sealed into pyrex tubing 15 centimeters in length which were then filled with mercury to make contact with the platinum. The electrodes were next cleaned electrolytically. After cleaning, each of the electrodes was platinized for three minutes with an applied voltage of three volts in a solution of chloroplatinic acid which contained 0.3% lead acetate. The electrode was then removed and washed in distilled water, after which it was aged in a solution which would be the type used during the experiment for this electrode. The electrode was aged in this solution for one day. After aging, the electrode was removed from the aging solution and placed in the electrode sleeve (Figure A) of the cell.

The cell shown in Figure A is basically a hydrogen electrode connected by a salt bridge to a saturated calomel electrode (standard electrode). This cell (Figure A), consisting of the two electrodes mentioned above, was kept at a constant temperature by immersing it in a constant temperature water bath. All rubber parts used in this cell were boiled in sodium hydroxide to remove sulphur impurities. Experimental changes occurring in the cell were recorded by means of a Sargent, Model XXI, polarograph, which was used as a microcoulometer and a Leeds and Northrup Student Type potentiometer, which was used to measure the equilibrium potential of the cell. The solutions used in the hydrogen electrode during these experiments were the following for the various pH's: for pH's = 14.3 and 13.5, a solution of sodium hydroxide was used; for pH = 10.1, a solution of sodium hydroxide with potassium hydrogen phosphate was used; and for all acid pH's, sulphuric acid solutions were used. The salt bridge used between the hydrogen electrode and the saturated calomel electrode in the cell contained agar saturated with sodium chloride when the hydrogen electrode contained a basic solution and agar saturated with ammonium sulphate when acid solution was used in the hydrogen electrode. This was done to reduce transference error.

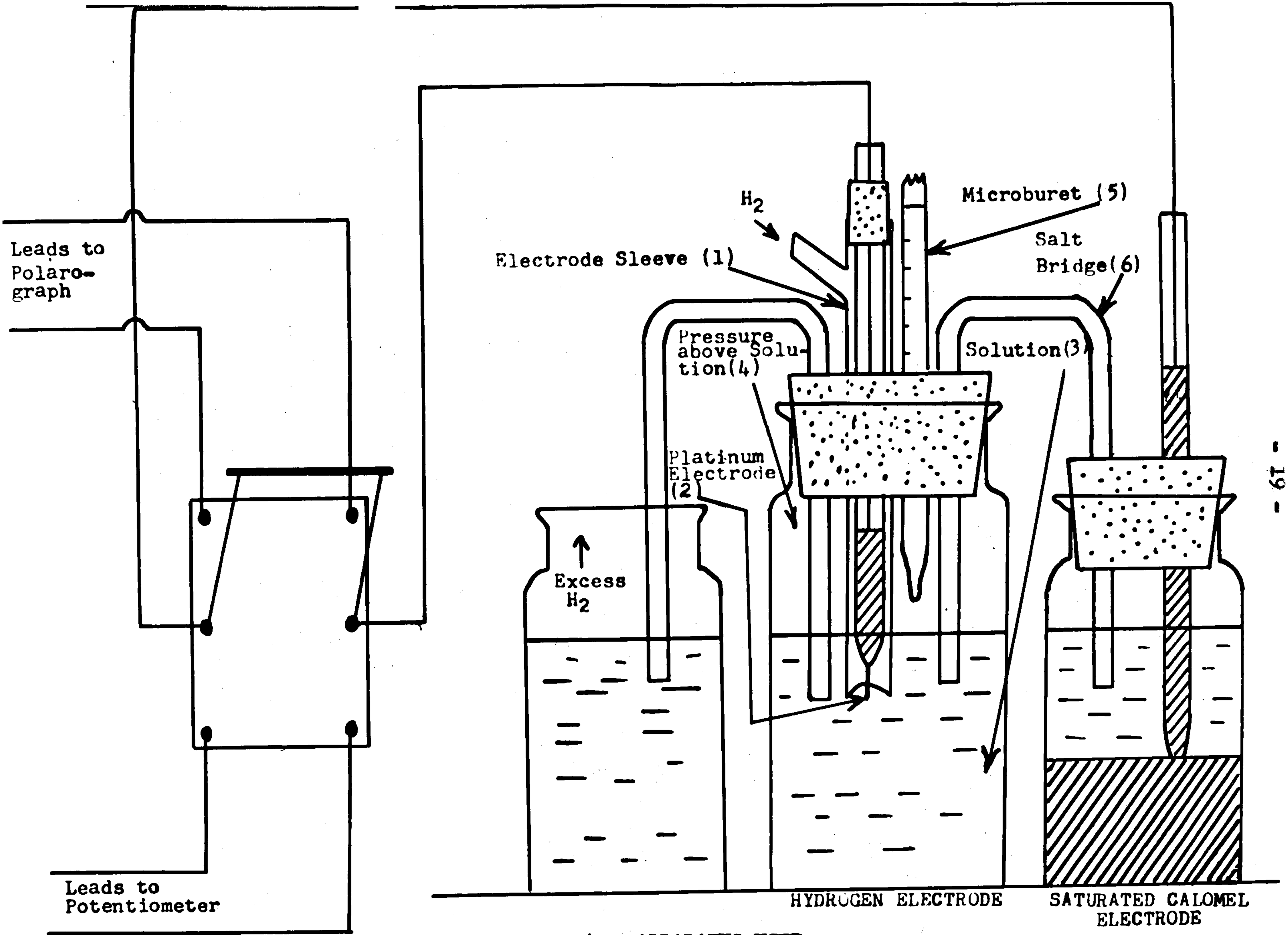


FIGURE A. APPARATUS USED

B. PROCEDURE

(Refer to Figure A.)

Hydrogen was passed through the electrode sleeve (1) and bubbled over the platinum electrode (2) for three minutes, then the hydrogen was cut off and the hydrogen pressure above (4) the solution (3) in the hydrogen electrode (5) was adjusted to one atmosphere. Sufficient time was allowed for the platinum electrode to come to equilibrium with its solution. The potential of the cell was then measured. After the potential measurements had been made, the polarograph was switched in and the hydrogen adsorbed on the platinum electrode (anode) was oxidized by the polarograph. The polarograph plotted a current time curve for the oxidation with the voltage increasing over a small range. The area under the curve was a measure of the quantity of electricity necessary to oxidize the adsorbed hydrogen. The procedure was repeated six to seven times. Then a weighed amount of the organic compound (approximately 1 milligram) was added from a microburet (5) to 250 milliliters of solution around the platinum electrode and the entire procedure above was repeated six to seven times. This procedure was repeated for about five more increasing concentrations of organic compound until the current time curve approached a limiting value.

The areas under the curves, representing the quantity of electricity necessary to oxidize the adsorbed hydrogen off, were measured by means of a Dietzgen No. 132 planimeter both for the curves before an organic compound was added and for the curves representing increasing amounts of organic compound added. These planimeter readings were recorded as shown in Tables I through XXII. Then, the initial mean planimeter reading Ao, that is, the planimeter reading representing the mean areas of the curves for the hydrogen adsorbed before an organic compound was added, had subtracted from it the mean planimeter reading A, representing the mean of the area under the curves for a given concentration of the organic compound. This difference between the two readings was divided by the initial mean planimeter reading Ao. This fractional quantity $\frac{Ao-A}{Ao}$ is analogous to Freundlich's x/m in the Freundlich equation written $\log x/m = \log k + (1/n) \log c$ where c is the concentration of adsorbed material. Since it is seen from this equation that $\log \frac{Ao-A}{Ao}$ vs. $\log c$ should be a straight line to obey this equation, it was decided to plot $\log \frac{Ao-A}{Ao}$ vs. the log of concentration of organic compound added. This was one of the graphical plots that was made. Plots of the changing potential readings vs. the logarithm of the corresponding microcoulombs necessary to remove the adsorbed hydrogen were made. The microcoulomb readings were obtained by putting the corresponding planimeter reading in the equation shown in Table XXIII.

DISCUSSION OF RESULTS

The results of the investigation of acetonitrile as a poison on the hydrogen electrode in sulphuric acid solution at pH = 0 are shown in Figures 1 and 2. Figure 1 shows the potential to be a straight line function of the log of the amount of hydrogen adsorbed (log microcoulombs) on the electrode in the case where acetonitrile was used to poison the active area of the electrode. Figure 2 shows the log of the fraction of the active area poisoned by acetonitrile to be a straight line function of the log of the concentration of acetonitrile present in the solution around the hydrogen electrode. These two facts are in agreement with the work previously reported by Franklin and Sothern[21]. The data in Figures 1 and 2 shows much less scatter than the earlier work of Franklin and Sothern[21] and the slopes of the curves were definitely established. The slope of the curve of Figure 1 was found to be 0.0587. This value is shown to equal $\frac{2.303\ RT}{nF}$ in the Nernst equation

$$E = E^{o} - \frac{2.303\ RT}{nF} \log \frac{a_{H^{+}}}{P_{H_2}^{1/2}}$$

where:

E^{o} = voltage of saturated calomel electrode against a hydrogen electrode in a solution of unit activity of hydrogen ions

$a_{H^{+}}$ = activity of the hydrogen ions

$P_{H_2}^{1/2}$ = pressure of the hydrogen

R = ideal gas law constant = 8.314 joules/degree mole

n = no. of electrons transferred = 1

F = a faraday = 96,500 coulombs

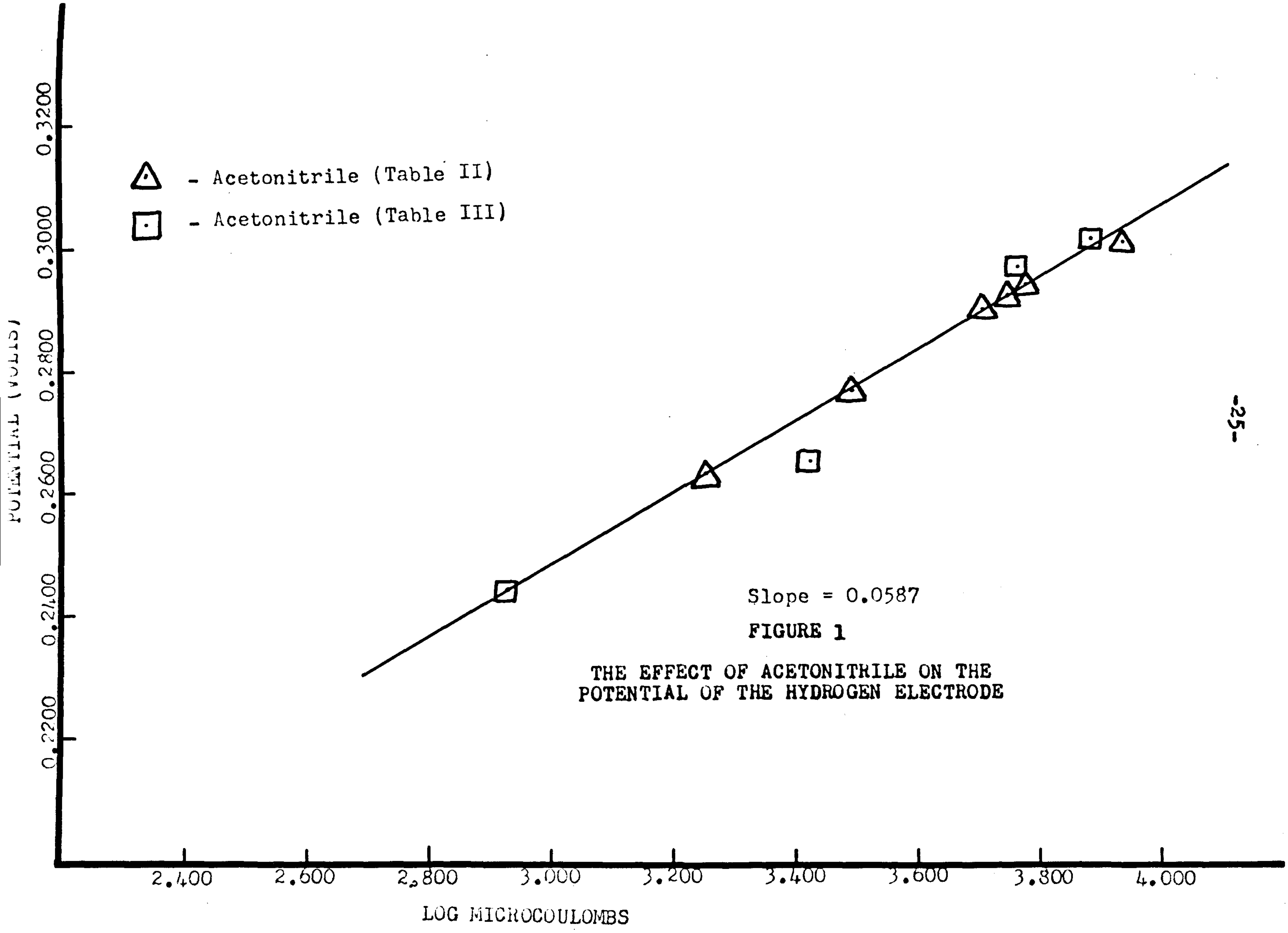
T = temperature = 295.2°K (22.74°C)

Calculated value of $\frac{2.303\ RT}{nF}$

$$\frac{2.303\ RT}{nF} = \frac{(2.303)(8.314\ \text{joules/degree mole})(295.2°K)}{(1)(96{,}500\ \text{coulombs})}$$

$$= 0.0587$$

Values of the slope of Figure 1 is 0.0587. The scatter was eliminated because the electrode was allowed to come to equilibrium with the solution containing the poison before the potential reading was taken. The erraticness noted by previous workers[21] in potential measurements on the hydrogen electrode with a poison in the solution around it was caused by the bubbling of the hydrogen over the electrode when the measurement was taken. Therefore, instantaneous pressure variation occurred over the system causing equilibrium not to be definitely established, the result being the potential measured was erratic and varied with the rate of bubbling. Figure 1 also shows that the data for two different electrodes (Runs 1 and 2) lie on the same straight line curve of potential vs. log of the fraction of the active area poisoned, indicating that the data for two different hydrogen electrodes are superimposable. It is noted that the slopes of the straight line curves of the log of the fraction of the active area poisoned by acetonitrile vs. the log of the concentration of acetonitrile present are seen to be the same in Figure 2 for three different temperatures and electrodes. This probably indicates the mechanism of adsorption to be the same since the slopes are the same. This would necessarily follow since the poison in each case is the same compound. It is likewise noted that the three curves shift to the left as temperature increases. It is probably true that the data for the three different curves would have been on one curve if the temperature had been constant.



Slope = 0.0587

FIGURE 1

THE EFFECT OF ACETONITRILE ON THE POTENTIAL OF THE HYDROGEN ELECTRODE

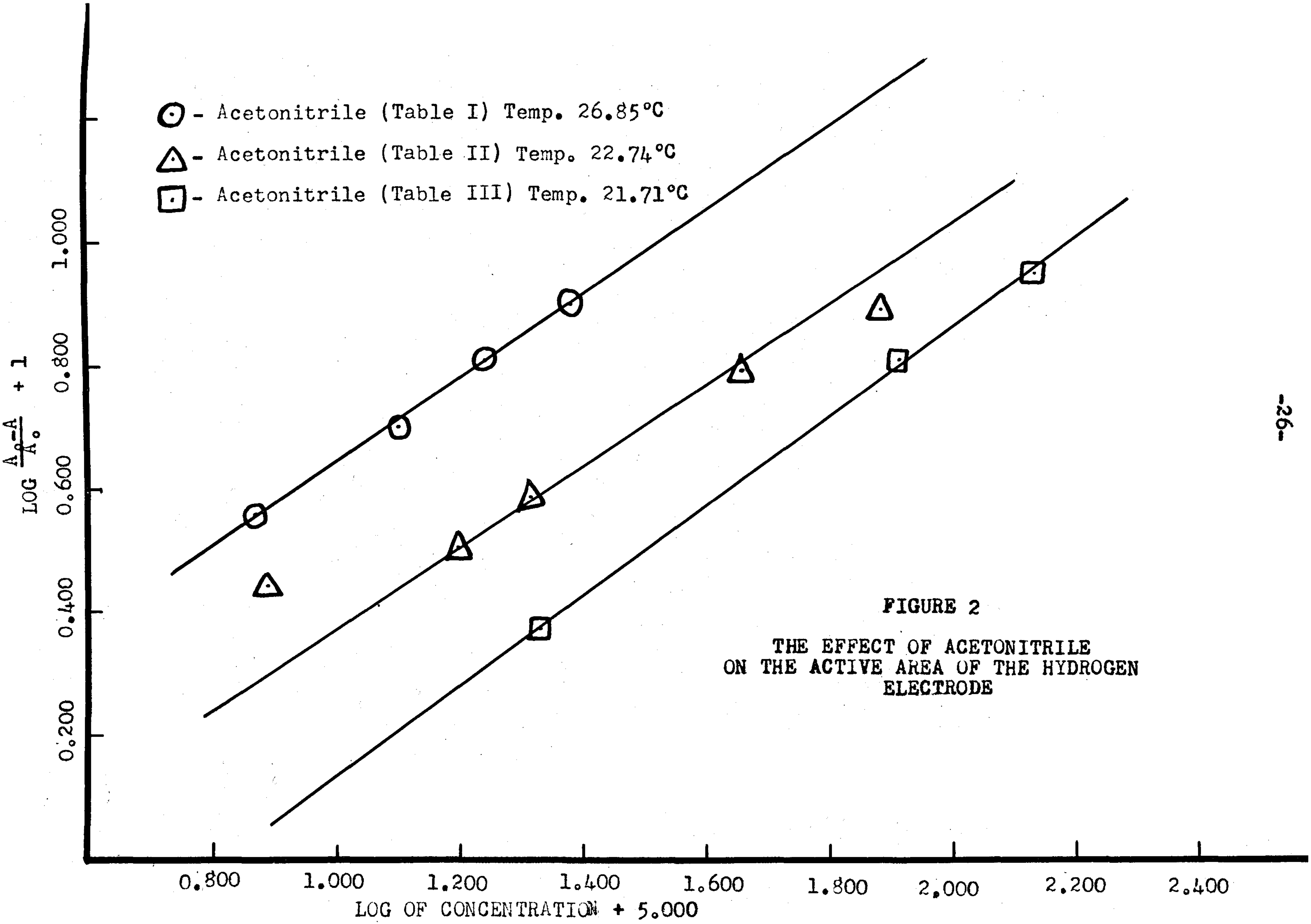


FIGURE 2

THE EFFECT OF ACETONITRILE ON THE ACTIVE AREA OF THE HYDROGEN ELECTRODE

Table I

The Effect of Acetonitrile as a Poison

Temperature = 26.85°C
Buffered at pH = 0
Electrode potential changed
with adsorption of poison

No.	Planimeter reading		Mean value	Micro-coulombs	Log-micro coulombs	Log $\frac{A^{o}-A}{A^{o}}$	Log of conc. of acetonitrile log millimoles/ml
1	1-A 1-B 1-C	2.50	2.50	3030.0	3.4814	------	--------------
2	2-A 2-B 2-C	1.62 1.59 1.60	1.60	1939.2	2.2876	0.5563-1	0.8675-5
3	3-A 3-B 3-C	1.25 1.26 1.17	1.23	1491.8	3.1734	0.7059-1	0.1004-4
4	4-A 4-B 4-C	0.90	0.88	1066.5	3.0280	0.8116-1	0.2399-4
5	5-A 5-B 5-C	0.52	0.49	593.9	2.7737	0.9053-1	0.3836-4

Table II

The Effect of Acetonitrile as a Poison

Temperature = 22.74°C
Buffered at pH = 0
Electrode potential changed
with adsorption of poison

No.	Planimeter reading	Mean value	Log-micro coulombs	Log $\frac{A^0-A}{A^0}$	Log of conc. of acetonitrile log millimoles/ ml	Mean potential measured in solution
1	1-A 8.20 1-B 8.90 1-C 8.30 1-D 8.65 1-E 8.00 1-F 8.24	9.38	3.9120			0.3018
2	2-A 5.91 2-B 5.90 2-C 6.15 2-D 6.30 2-E 6.00 2-F 6.00	6.08	3.7726	0.4385-1	0.8847-5	0.2951
3	3-A 5.30 3-B 5.25 3-C 5.70 3-D 5.70 3-E 5.70 3-F 5.70 3-G 5.70	5.70	3.7447	0.5049-1	0.1944-4	0.2930
4	4-A 5.05 4-B 5.40 4-C 5.20 4-D 4.86 4-E 5.22 4-F 5.08 4-G 5.15	5.15	3.7008	0.5860-1	0.3109-4	0.2910
5	5-A 3.20 5-B 3.16 5-C 3.20 5-D 2.96 5-E 3.25 5-F 3.35	3.19	3.4930	0.7920-1	0.1558-4	0.2768
6	6-A 1.80 6-B 1.85 6-C 1.83	1.83	3.2516	0.8930-1	0.8788-4	0.2639

Table III

The Effect of Acetonitrile as a Poison

Temperature = 21.71°C
Buffered at pH = 0
Electrode potential changed
with adsorption of poison

No.	Planimeter reading		Mean value	Log-micro coulombs	Log $\frac{A_o-A}{A_o}$	Log of conc. of acetonitrile log millimoles/ml	Mean potential measured in solution
1	1-A 1-B 1-C 1-D 1-E 1-F 1-G	11.50 11.77 11.56 11.75 11.68 11.65 11.40	11.61	3.8774			0.3021
2	2-A 2-B 2-C 2-D 2-E 2-F 2-G	8.34 8.89 9.02 9.00 9.15 9.10 8.60	8.87	3.7608	0.3718-1	0.2299-4	0.2978
3	3-A 3-B 3-C 3-D 3-E 3-F 3-G	4.05 4.36 3.58 3.98 3.99 3.94 4.30	4.03	3.4182	0.8146-1	0.9101-4	0.2654
4	4-A 4-B 4-C 4-D	1.45 1.33 1.20 1.20	1.30	2.9268	0.9484-1	0.1269-3	0.2445

It was decided to compare the poisoning effect of acetonitrile in acidic (sulphuric acid solution) and basic (sodium hydroxide solution) solutions. Figure 3, which is a plot of the log of the fraction of the active area poisoned by acetonitrile as a function of the log of the concentration of acetonitrile present in the solution around the hydrogen electrode, shows that the data for the hydrogen electrode in basic solution at pH = 14.3 poisoned by acetonitrile lies on the straight curve of the data for the electrode poisoning in acid solution at pH = 0. This shows that the poisoning ability of acetonitrile is unaffected by the hydrogen ion concentration in the solution around the electrode. It was noted that the poisoning by acetonitrile in acid solution at pH = 0 affected the potential of the electrode according to the relation established in Figure 1 but the poisoning in basic solution at pH = 14.3 had no effect on the potential of the hydrogen electrode, that is, the potential remained constant with the addition of acetonitrile when the hydrogen electrode was in basic solution at pH = 14.3.

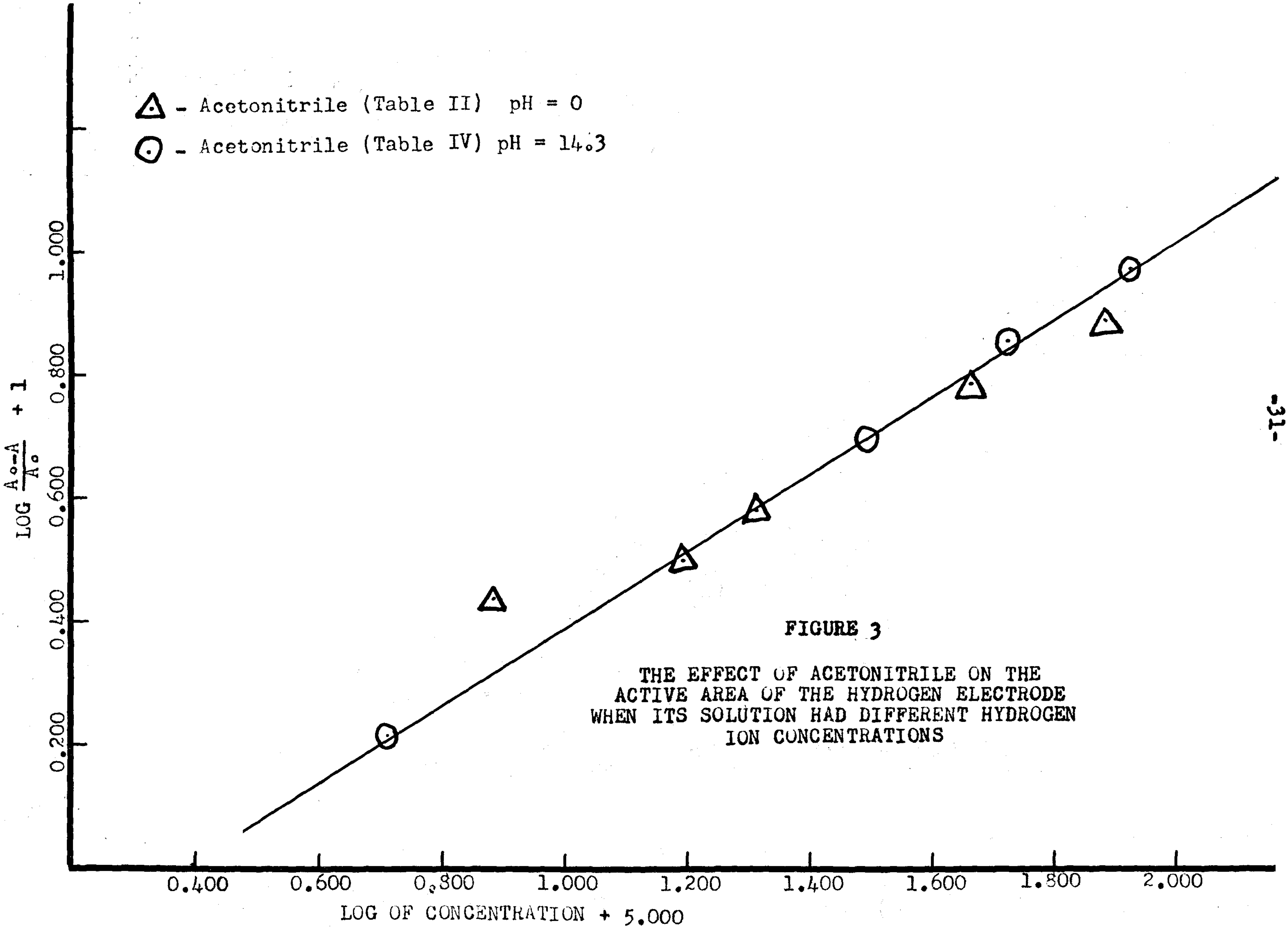


FIGURE 3

THE EFFECT OF ACETONITRILE ON THE ACTIVE AREA OF THE HYDROGEN ELECTRODE WHEN ITS SOLUTION HAD DIFFERENT HYDROGEN ION CONCENTRATIONS

Table IV

The Effect of Acetonitrile as a Poison

Temperature = 25°C
Buffered at pH = 14.3
Electrode potential remained
constant with adsorption of
poison

No.	Planimeter reading	Mean value	Log $\frac{Ao-A}{Ao}$	Log of conc. of acetonitrile log millimoles/ml
1	6.40	6.40		
2	5.35	5.35	0.2150-1	0.7095-5
3	3.20	3.20	0.6990-1	0.4956-4
4	1.75	1.75	0.8613-1	0.7181-4
5	0.35	0.35	0.9756-1	0.9194-4

The investigation was next carried to a series of amines. These amines were studied in a basic solution (sodium hydroxide solution) at pH = 14.3. Figure 4 shows that the slope of the curve of the log of the fraction of the active area poisoned by the amine vs. the log of the concentration of the amine is the same for the various amines considered, which were n-ethyl amine, n-propyl amine and n-butyl amine. The fact that the slopes of these curves for the three amines are the same probably indicates that the mechanism of poisoning for each of the three is the same. It is seen from Figure 4 that the curve for n-butyl amine is higher (further to the left) on the graph than the curve for n-propyl amine and likewise the curve for n-propyl amine is higher than the curve for n-ethyl amine, indicating that the poisoning effect of n-butyl amine is greater than that of n-propyl amine on the hydrogen electrode and also that n-propyl amine is a stronger poison than n-ethyl amine on the hydrogen electrode. This result led to Figure 5 which shows a plot of the millimoles of amine added to produce the same degree of poisoning vs. the molecular weight. Figure 5 indicates that the greater the molecular weight, the greater the poisoning effect of the amine. This result is noted to agree with the earlier work of Franklin and Sothern[21] in the case of nitriles. Likewise, it is noted that this result corresponds to results of earlier workers[30,31,32,33] with amines as corrosion inhibitors. Again returning to Figure

4, we see that the data for two hydrogen electrodes are superimposable since the data for n-propyl amine studied on two different electrodes lies on the same curve.

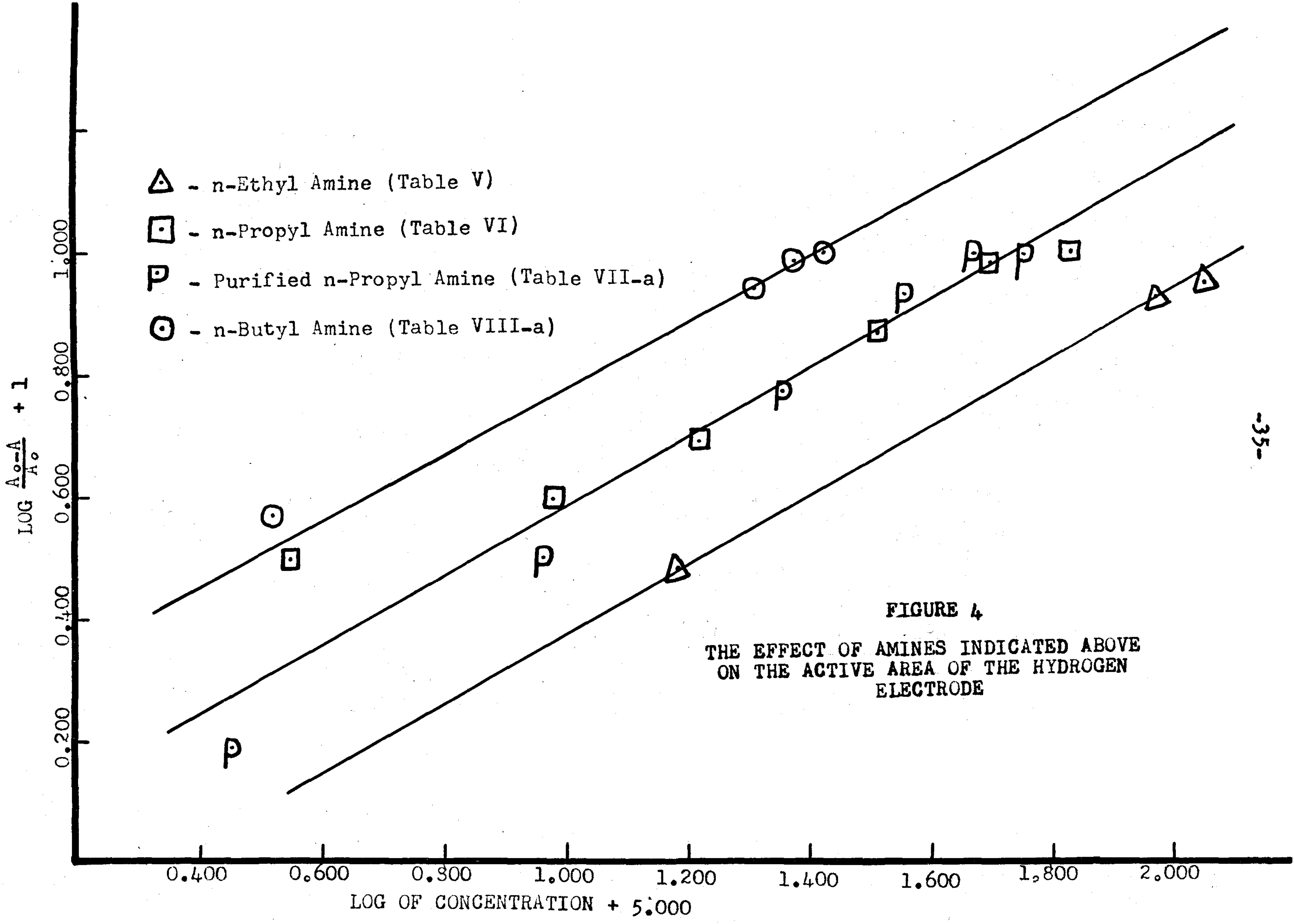


FIGURE 4

THE EFFECT OF AMINES INDICATED ABOVE ON THE ACTIVE AREA OF THE HYDROGEN ELECTRODE

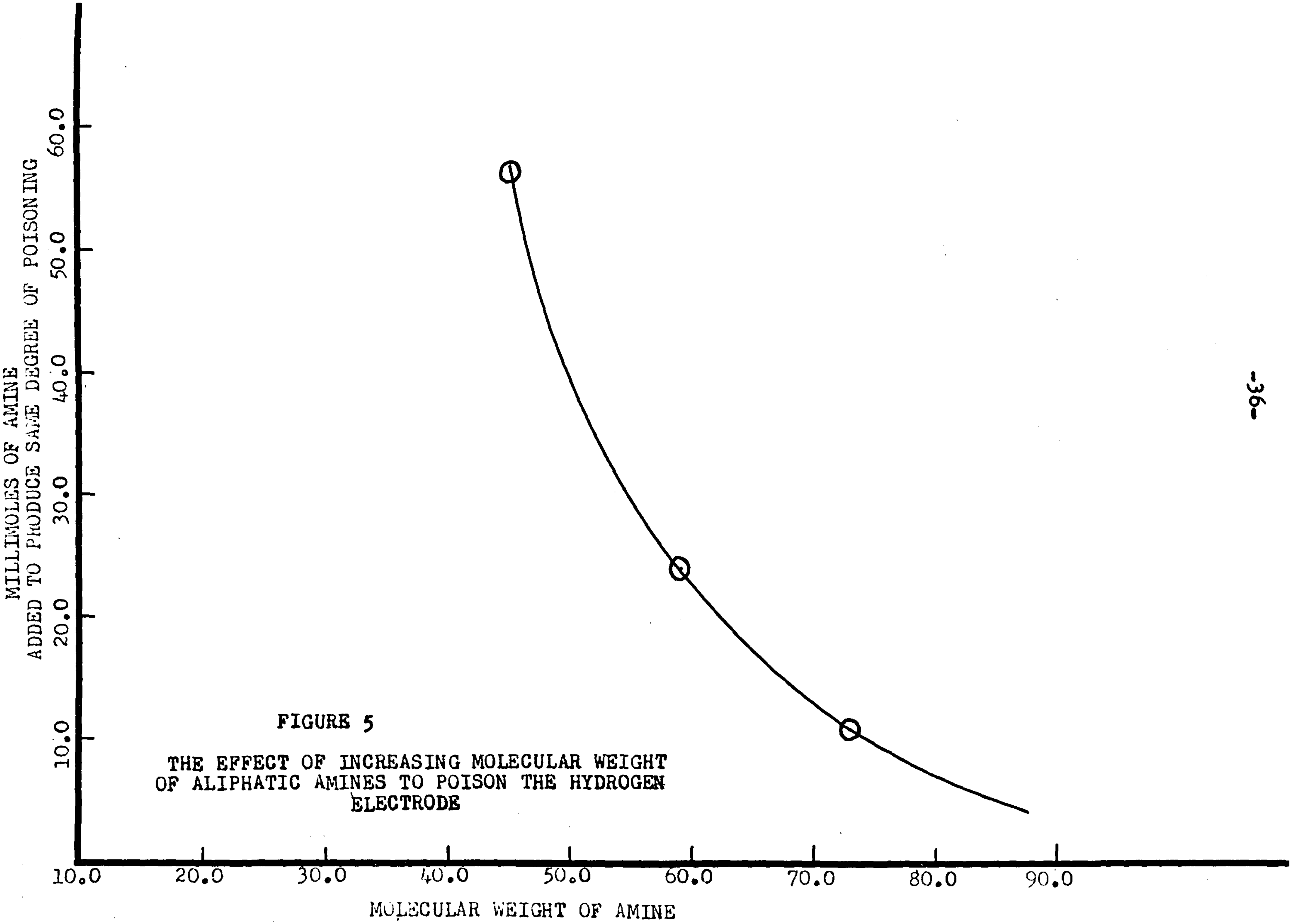


FIGURE 5

THE EFFECT OF INCREASING MOLECULAR WEIGHT OF ALIPHATIC AMINES TO POISON THE HYDROGEN ELECTRODE

Table V

The Effect of n-Ethyl Amine as a Poison

Temperature = 25°C
Buffered at pH = 14.3
Electrode potential remained constant with adsorption of poison

No.	Planimeter reading		Mean value	Log $\frac{Ao-A}{Ao}$	Log of conc. of n-Ethyl Amine log millimoles/ml
1	1-A	9.75	9.60		
	1-B	10.00			
	1-C	9.05			
	1-D	10.70			
	1-E	8.50			
2	2-A	6.45	6.68	0.4831-1	0.1936-4
	2-B	6.90			
3	3-A	2.00	1.53	0.9251-1	0.9718-4
	3-B	1.80			
	3-C	1.40			
	3-D	1.25			
	3-E	1.15			
4	4-A	0.95	0.92	0.9562-1	0.0514-3
	4-B	0.90			
	4-C	0.90			

Table VI

The Effect of n-Propyl Amine as a Poison

Temperature = 25°C
Buffered at pH = 14.3
Electrode potential remained constant with adsorption of poison

No.	Planimeter reading		Mean value	Log $\frac{Ao-A}{Ao}$	Log of conc. of n-Propyl Amine log millimoles/ml
1	1-A 1-B 1-C	10.90 10.90 10.70	10.83		
2	2-A 2-B 2-C	7.40 7.30 7.40	7.37	0.5044-1	0.5483-5
3	3-A 3-B 3-C	6.60 6.65 6.35	6.53	0.5988-1	0.9793-5
4	4-A 4-B 4-C	5.45 5.35 5.65	5.48	0.6937-1	0.2219-4
5	5-A 5-B 5-C	3.05 2.70 2.55	2.77	0.8717-1	0.5142-4
6	6-A 6-B 6-C	0.55 0.20 0.35	0.37	0.9849-1	0.6991-4
7	7-A 7-B	0.05	0.05	0.9990-1	0.8326-4

Table VII-a

The Effect of Purified n-Propyl Amine as a Poison

Temperature = 25°C
Buffered at pH = 14.3
Electrode potential remained
constant with adsorption of
poison

No.	Planimeter reading		Mean value	Micro-coulombs	Log $\frac{Ao-A}{Ao}$	Conc. X 10^4	Log of conc. of Purified n-Propyl Amine log millimoles/ml
1	1-A	13.00	13.00	6350			
	1-B	13.10					
	1-C	12.90					
2	2-A	11.20	11.03	5390	0.1810-1	0.28	0.4489-5
	2-B	11.90					
	2-C	10.00					
3	3-A	9.00	8.88	4340	0.5011-1	0.92	0.9634-5
	3-B	8.50					
	3-C	9.15					
4	4-A	5.00	5.26	2560	0.7748-1	2.27	0.3562-4
	4-B	5.65					
	4-C	4.90					
	4-D	5.50					
5	5-A	2.00	2.00	975	0.9274-1	3.58	0.5538-4
	5-B	2.00					
6	6-A	0.20	0.22	107	0.9926-1	4.69	0.6710-4
	6-B	0.25					
	6-C	0.20					
7	7-A	0.02	0.05	24.4	0.9983-1	5.68	0.7541-4
	7-B	0.08					

Table VIII-a

The Effect of n-Butyl Amine as a Poison

Temperature = 25°C
Buffered at pH = 13.5
Electrode potential remained
constant with adsorption of
poison

No.	Planimeter reading		Mean value	Micro-coulombs	Log $\frac{Ao-A}{Ao}$	Conc. X 10^4	Log of conc. of n-Butyl Amine log millimoles/ml
1	1-A 1-B	15.70 15.75	15.73	5110			
2	2-A 2-B 2-C	10.05 9.90 9.70	9.88	3220	0.5704-1	0.33	0.5202-5
3	3-A 3-B	2.00 1.95	1.98	644	0.9416-1	2.07	0.3152-4
4	4-A 4-B	0.45 0.30	0.45	145	0.9872-1	2.38	0.3770-4
5	5-A 5-B	0.05	0.05	62.5	0.9986-1	2.65	0.4224-4

After the investigation of the poisoning effect of the amines as a function of their molecular weight, it was decided to investigate an amine with the same molecular weight but having different structures. The amine chosen for this was n-butyl amine, the three forms of which were isobutyl amine, secondary butyl amine and n-butyl amine. The results of this investigation are shown in Figure 6. It is seen from Figure 6 that the slopes of the curves of the log of the fraction of the active area poisoned vs. the log of the concentration of the amine for each of the three forms of butyl amine are practically the same, indicating that the mechanism of adsorption for each of the three forms considered is identical; but it is noted from Figure 6 that the straight line curves of n-butyl amine and isobutyl amine lie almost on top of each other, indicating their poisoning ability to be approximately the same; but it is seen that the curve for secondary butyl amine is below that of isobutyl amine and n-butyl amine, showing it to be weaker in its poisoning effect than the other two. These results indicate that the variations in the positions of the carbons in the butyl chain, as in the case of isobutyl amine, has no effect on the ability of the amine to poison the electrode; but if the position of the amine group is changed from the primary position to the secondary position, as in the case of secondary butyl amine, then the ability of the amine group to poison is reduced.

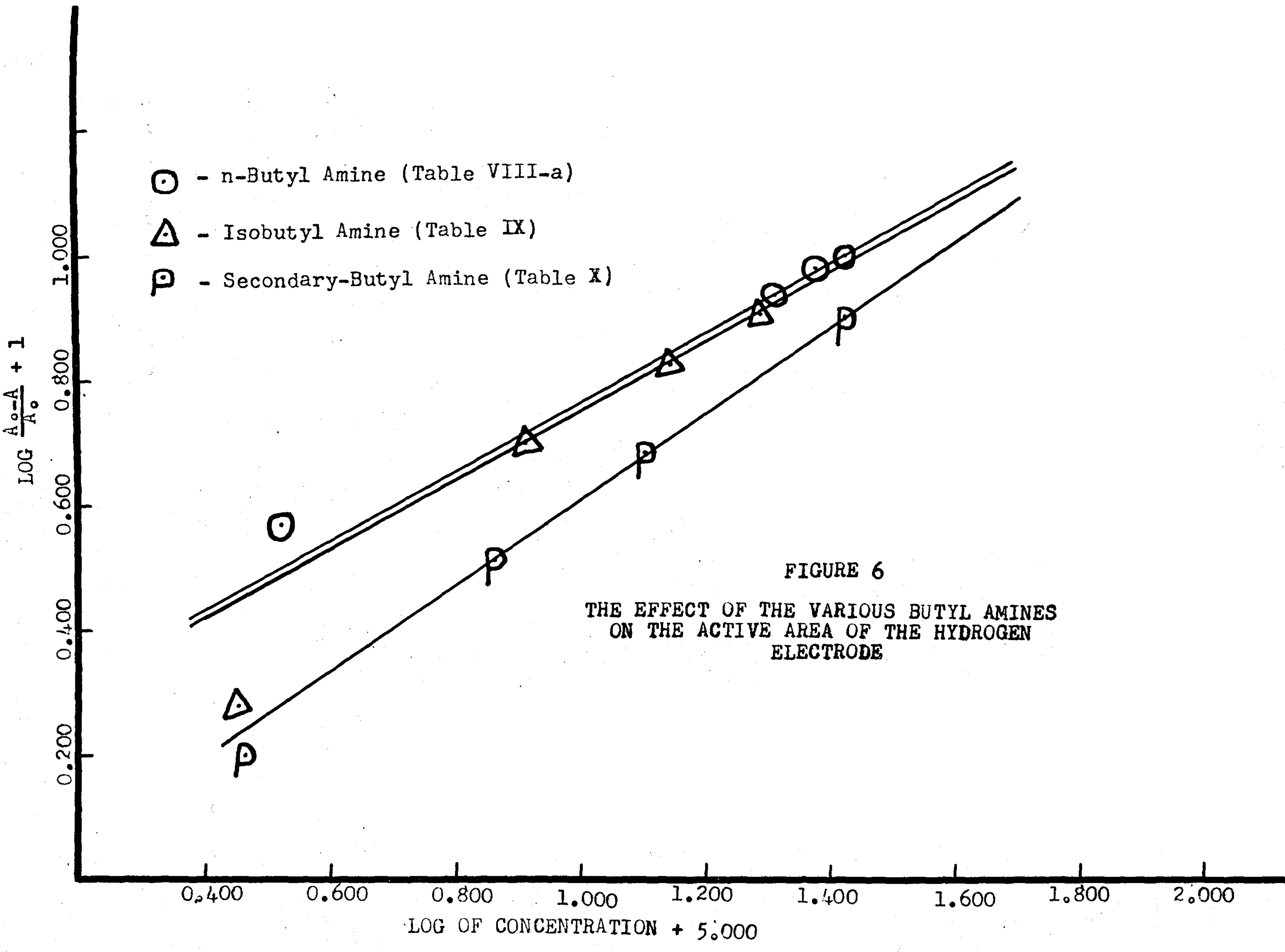


FIGURE 6

THE EFFECT OF THE VARIOUS BUTYL AMINES ON THE ACTIVE AREA OF THE HYDROGEN ELECTRODE

Table IX

The Effect of Isobutyl Amine as a Poison

Temperature = 25°C
Buffered at pH = 14.3
Electrode potential remained
constant with adsorption of
poison

No.	Planimeter reading		Mean value	Log $\frac{Ao-A}{Ao}$	Log of conc. Isobutyl Amine log millimoles/ml
1	1-A 1-B	9.90 9.75	9.83		
2	2-A 2-B	7.90 8.00	7.95	0.2816-1	0.4539-5
3	3-A 3-B	4.85 5.35	5.10	0.6823-1	0.9181-5
4	4-A	3.15	3.10	0.83223-1	0.1452-4
5	5-A 5-B	1.80 1.80	1.80	0.9122-1	0.2846-4

Table X

The Effect of Sec.-Butyl Amine as a Poison

Temperature = 25°C
Buffered at pH = 14.3
Electrode potential remained
constant with adsorption of
poison

No.	Planimeter reading		Mean value	Log $\frac{A_o-A}{A_o}$	Log of conc. Sec.-Butyl Amine log millimoles/ml
1	1-A 1-B 1-C	10.65 9.70 10.00	10.12		
2	2-A 2-B	8.40 8.60	8.50	0.2043-1	0.4612-5
3	3-A 3-B 3-C	6.95 6.65 6.85	6.85	0.5094-1	0.0645-5
4	4-A 4-B	4.95 5.50	5.23	0.6841-1	0.1021-4
5	5-A	1.95	1.95	0.9070-1	0.4258-4

Figure 7 shows that the slope of the curve for n-butyl amine is the same as that for piperidine, while the slope for allyl amine is less than that of the other two, indicating a possible difference in the mechanisms of adsorption for allyl amine and for the other two amines. It is likewise observed in Figure 7 that the straight line curve for piperidine is below that of n-butyl amine, indicating that piperidine is weaker in its poisoning ability than n-butyl amine. This is in agreement with the results discussed by Hackerman and Makrides[36] for corrosion inhibitors. They said that cyclic structural amines were weaker corrosion inhibitors than the aliphatic amines. The results shown in Figure 7 for piperidine and allyl amine should not be considered conclusive as only one experiment was carried out for each of these, while the other compounds mentioned thus far were investigated more extensively. It might also be mentioned that pyrrole was found to poison the hydrogen electrode in a sodium hydroxide solution at $pH = 14.3$.

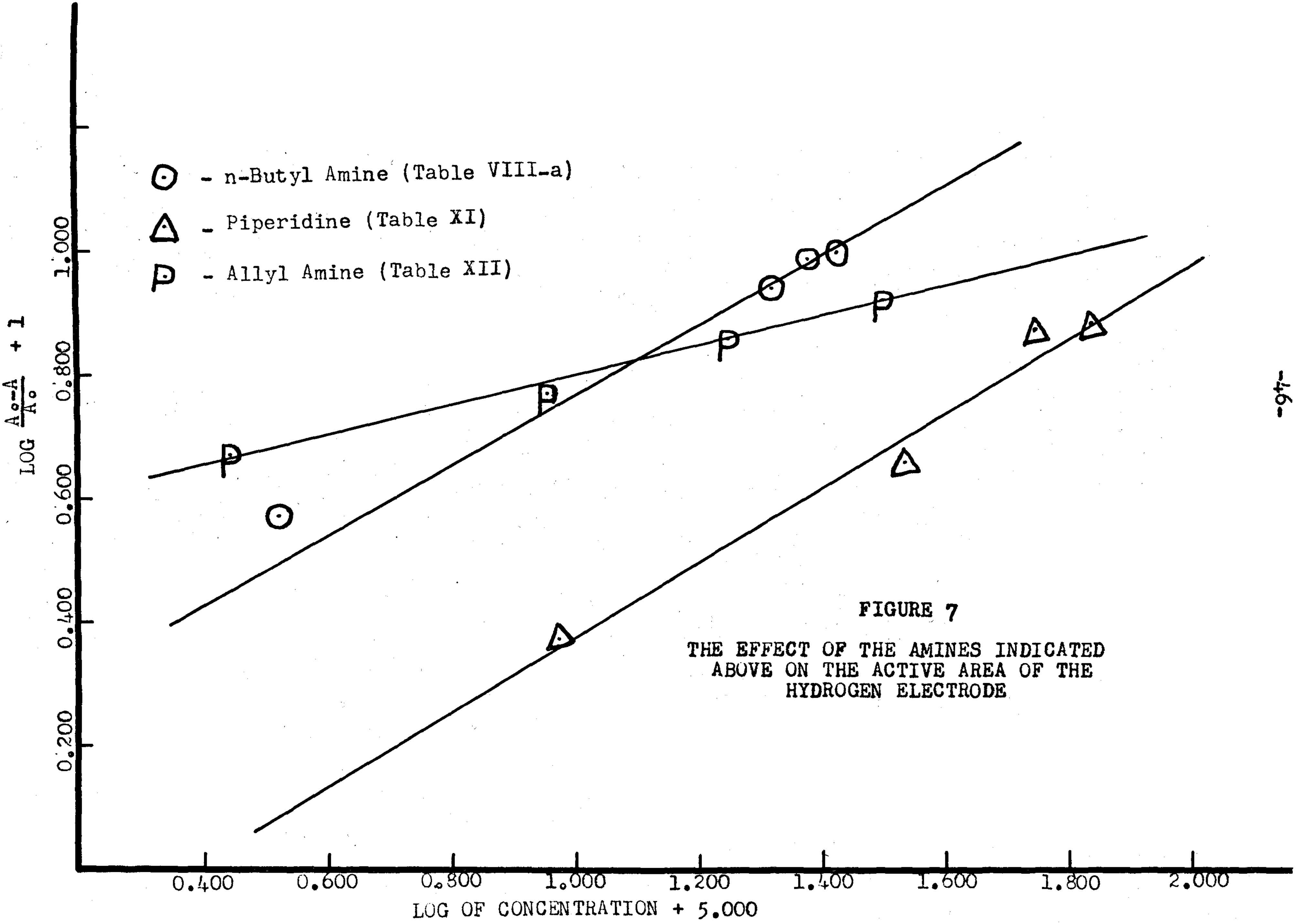


FIGURE 7

THE EFFECT OF THE AMINES INDICATED ABOVE ON THE ACTIVE AREA OF THE HYDROGEN ELECTRODE

Table XI

The Effect of Piperidine as a Poison

Temperature = 25°C
Buffered at pH = 14.3
Electrode potential remained constant with adsorption of poison

No.	Planimeter reading		Mean value	Log $\frac{Ao-A}{Ao}$	Log of conc. Piperidine log millimoles/ml
1	1-A 1-B 1-C	8.50 7.80 7.15	7.83		
2	2-A 2-B 2-C	6.70 6.70 7.00	6.80	0.1181-1	0.5663-5
3	3-A 3-B 3-C	6.00 6.00 6.00	6.00	0.3687-1	0.9698-5
4	4-A 4-B 4-C	4.05 4.50 4.25	4.26	0.6589-1	0.5315-4
5	5-A 5-B 5-C 5-D	1.40 2.00 2.50 1.95	1.96	0.8749-1	0.7367-4
6	6-A	1.85	1.85	0.8829-1	0.8307-4

Table XII

The Effect of Allyl Amine as a Poison

Temperature = 25°C
Buffered at pH = 14.3
Electrode potential remained constant with adsorption of poison

No.	Planimeter reading		Mean value	Log $\frac{Ao-A}{Ao}$	Log of conc. Allyl Amine log millimoles/ml
1	1-A 1-B 1-C 1-D	8.35 7.40 8.50 6.50	8.43		
2	2-A 2-B 2-C	5.80 3.85 4.30	4.50	0.6686-1	0.4404-5
3	3-A 3-B 3-C	4.05 4.40 3.50	3.50	0.7670-1	0.9358-5
4	4-A 4-B 4-C 4-D	4.60 3.25 2.50 2.10	2.30	0.8616-1	0.2468-4
5	5-A 5-B 5-C 5-D	2.00 2.00 1.20 1.35	1.28	0.9285-1	0.4944-4

Figure 8 shows an interesting result which occurred during this investigation. Upon adding n-propyl amine to an active hydrogen electrode, the active area of the electrode was completely poisoned out. Then, upon addition of pyridine to this poisoned electrode, there appears to be a reactivation of the electrode. Again, a new unpoisoned hydrogen electrode was taken and this time its active area was poisoned out with n-butyl amine and then pyridine was added and again there was found an apparent increase in active area upon the addition of pyridine to the poisoned system, as shown in Figure 9. This unusual phenomena of the apparent activation of the electrode by the addition of pyridine in basic solution at pH = 14.3 indicated a discreet difference between pyridine and the other amines investigated since all of the previous amines mentioned poisoned the electrode.

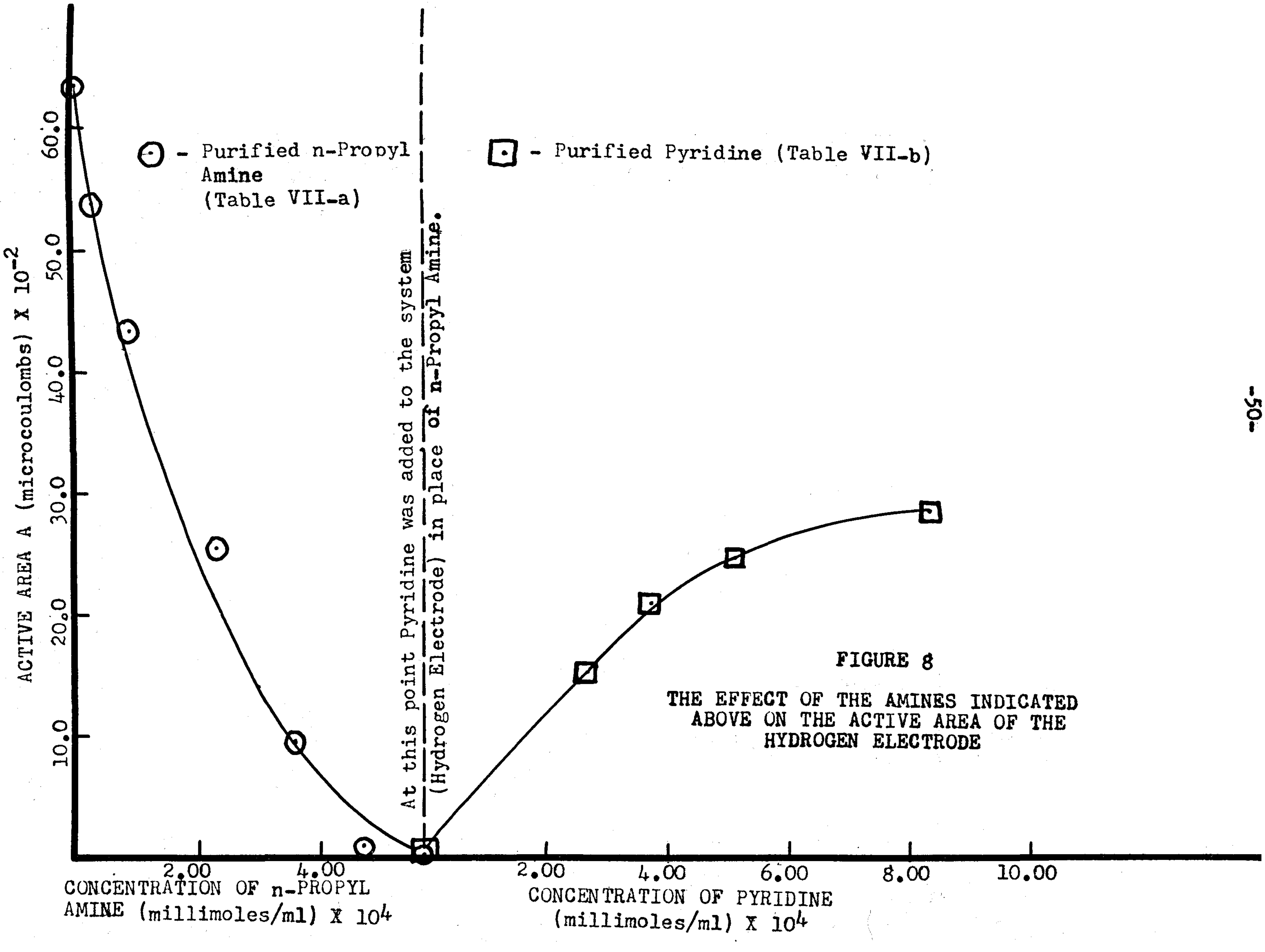


FIGURE 8

THE EFFECT OF THE AMINES INDICATED ABOVE ON THE ACTIVE AREA OF THE HYDROGEN ELECTRODE

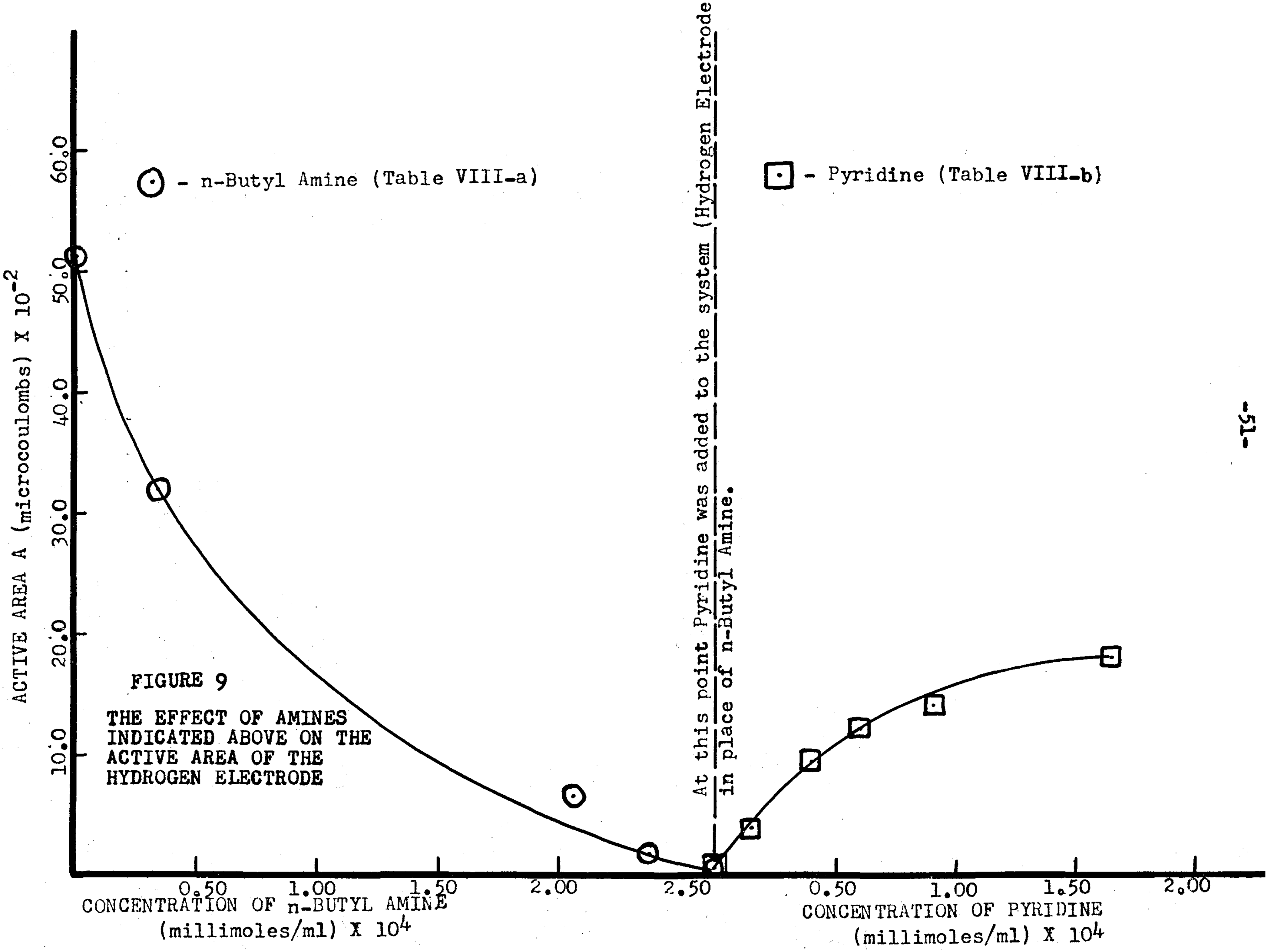


FIGURE 9

THE EFFECT OF AMINES INDICATED ABOVE ON THE ACTIVE AREA OF THE HYDROGEN ELECTRODE

Table VII-b

The Effect of Purified Pyridine as an Activator on the Platinized Platinum Electrode Which Has Been Poisoned by the Purified n-Propyl Amine (Refer to Table VII-a)

Temperature = 25°C
Buffered at pH = 14.3
Electrode potential remained constant with adsorption of poison

Planimeter reading	Mean value	Micro-coulombs	Log $\frac{Ao-A}{Ao}$	Conc. X 10^4	Log of conc. of Purified Pyridine log millimoles/ml
1-A 0.02 1-B 0.08	0.05	24.4	0.9983-1		
2-A 3.30 2-B 2.90 2-C 3.15	3.12	1520	0.8808-1	2.64	0.4208-4
3-A 4.30 3-B 4.40	4.35	2120	0.8231-1	3.74	0.5724-4
4-A 5.00 4-B 5.10 4-C 5.00	5.03	2460	0.7075-1	5.13	0.7098-4
5-A 5.80 5-B	5.80	2030	0.7434-1	8.32	0.92015-4

Table VIII-b

The Effect of Pyridine as an Activator on the Platinized Platinum Electrode Which Has Been Poisoned by the n-Butyl Amine (Refer to Table VIII-a)

Temperature = 25°C
Buffered at pH = 13.5
Electrode potential remained
constant with adsorption of
poison

No.	Planimeter reading	Mean value	Micro-coulombs	Log $\frac{Ao-A}{Ao}$	Conc. X 10^4	Log of conc. of Pyridine log millimoles/ml
1	1-A 0.05	0.05	62.5	0.9986-1		
2	2-A 1.20	1.20	390	0.9655-1	0.15	0.1812-5
3	3-A 2.80	2.80	910	0.9149-1	0.40	0.5975-5
4	4-A 3.70	3.70	1200	0.8835-1	0.60	0.7784-5
5	5-A 4.30	4.30	1400	0.8613-1	0.90	0.9529-5
6	6-A 5.50	5.50	1790	0.8131-1	1.65	0.2173-4

Upon finding this phenomena exhibited by pyridine, it was decided to investigate the adsorption of pyridine as a function of pH. Also, the adsorption of a normal amine (that is, one which poisoned the electrode rather than activated the electrode in basic solution) was investigated as a function of pH. Figure 10 shows a plot of the log of the fraction of the active area increase vs. the log of the concentration of pyridine. Three curves are shown in Figure 10, all having the same slope but determined at different pH's. Since all three curves have the same slope, it is concluded that the mechanism of activation adsorption of pyridine in basic solution is the same for all pH's on the basic side. The three curves were determined for the pH's indicated in Figure 10. It is seen from the curves in Figure 10 the greater the pH, or the more basic the solution in which adsorption occurred, the greater the apparent activation effect of pyridine. At a pH of 7, which is the neutral pH, that is, neither acid nor basic, it was found that pyridine neither activated nor poisoned the hydrogen electrode. Data showing this is found in Table XVI. Figure 11, having curves of log of the fraction of active area decrease vs. log of concentration of pyridine, shows that the slope of the curves are the same regardless of pH values on the acid side of the neutral pH (pH = 7) but shows that the height of the curve on the graph decreases as the solution becomes less acidic (pH increases). Figure 12 shows curves of log of fraction of active area decrease vs. log of concentration of n-butyl amine for various pH's in basic solution. It is noted that all these curves have the same slope, indicating that the mechanism of adsorption of n-butyl amine in basic solution is probably the same regardless of pH; but it is seen that these curves decrease in their height on the graph as the solution becomes less basic (pH decreases). Figure 13 shows the graphical results condensed from Figures 11 and 12. Curves are shown for pyridine and n-butyl amine of pH vs. percent fraction area change. The curve for pyridine shows that pyridine causes a fractional area increase in basic solution, that is, pH's greater than 7, and a fractional area decrease in acid solution (pH less than 7). It is seen from this curve that in basic solution the apparent activation effect of pyridine increases with increasing pH, while in acid solution, the apparent poisoning effect of pyridine decreases with increasing pH. The boundary (a point where there is no area change due to the addition of poison or activator) for pyridine occurs at a pH of 7. At this point, the mechanism of adsorption of pyridine changes from an apparent activation on the basic side of a pH of 7 to a poisoning effect on the acid side of the pH of 7. It is seen that the curve for n-butyl amine lies in Region 1 (Region of fraction of area decrease) indicating that n-butyl amine is a poison only. It is seen from this curve for n-butyl amine in Region 1 that the greater the pH (the more basic the solution) the stronger the poisoning effect of n-butyl amine. However, it is noted that n-butyl amine is still a poison at a pH of 7 and continues to be a poison into the acid pH range with decreasing poisoning ability. The fact that amines are poisons in the acid pH range was noted by Hackerman and Makrides[36] in their article on corrosion inhibitors.

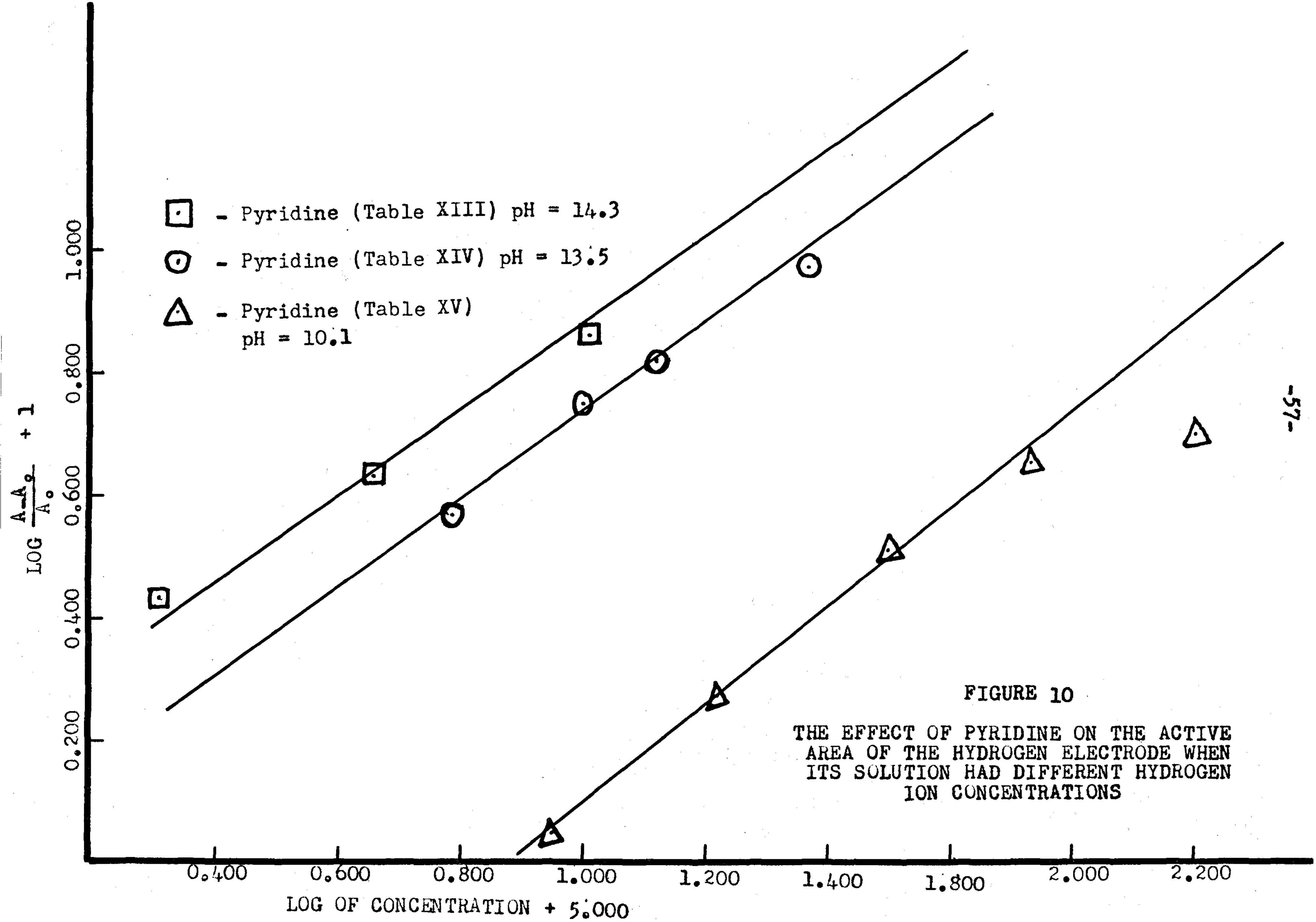


FIGURE 10

THE EFFECT OF PYRIDINE ON THE ACTIVE AREA OF THE HYDROGEN ELECTRODE WHEN ITS SOLUTION HAD DIFFERENT HYDROGEN ION CONCENTRATIONS

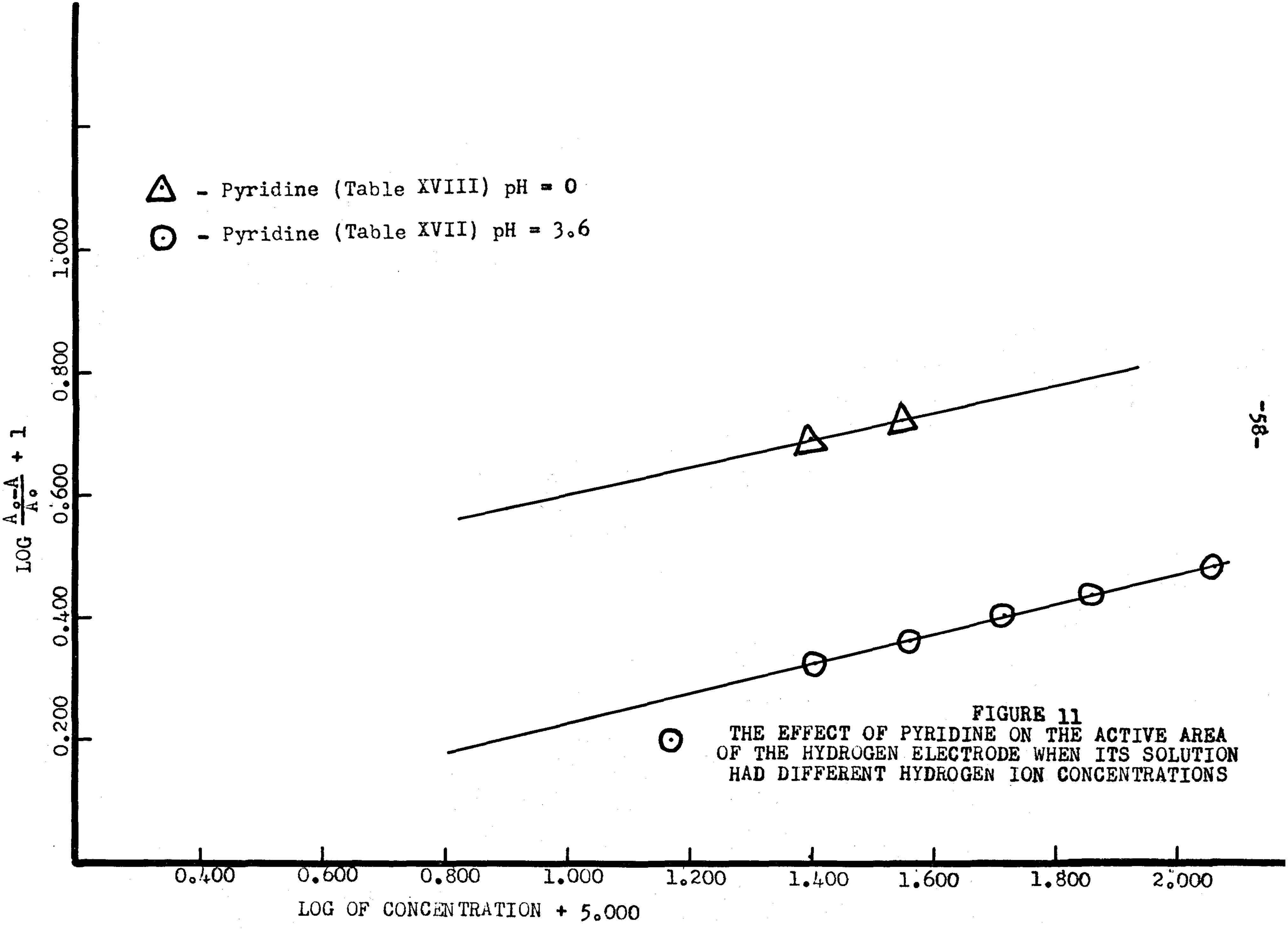


FIGURE 11
THE EFFECT OF PYRIDINE ON THE ACTIVE AREA OF THE HYDROGEN ELECTRODE WHEN ITS SOLUTION HAD DIFFERENT HYDROGEN ION CONCENTRATIONS

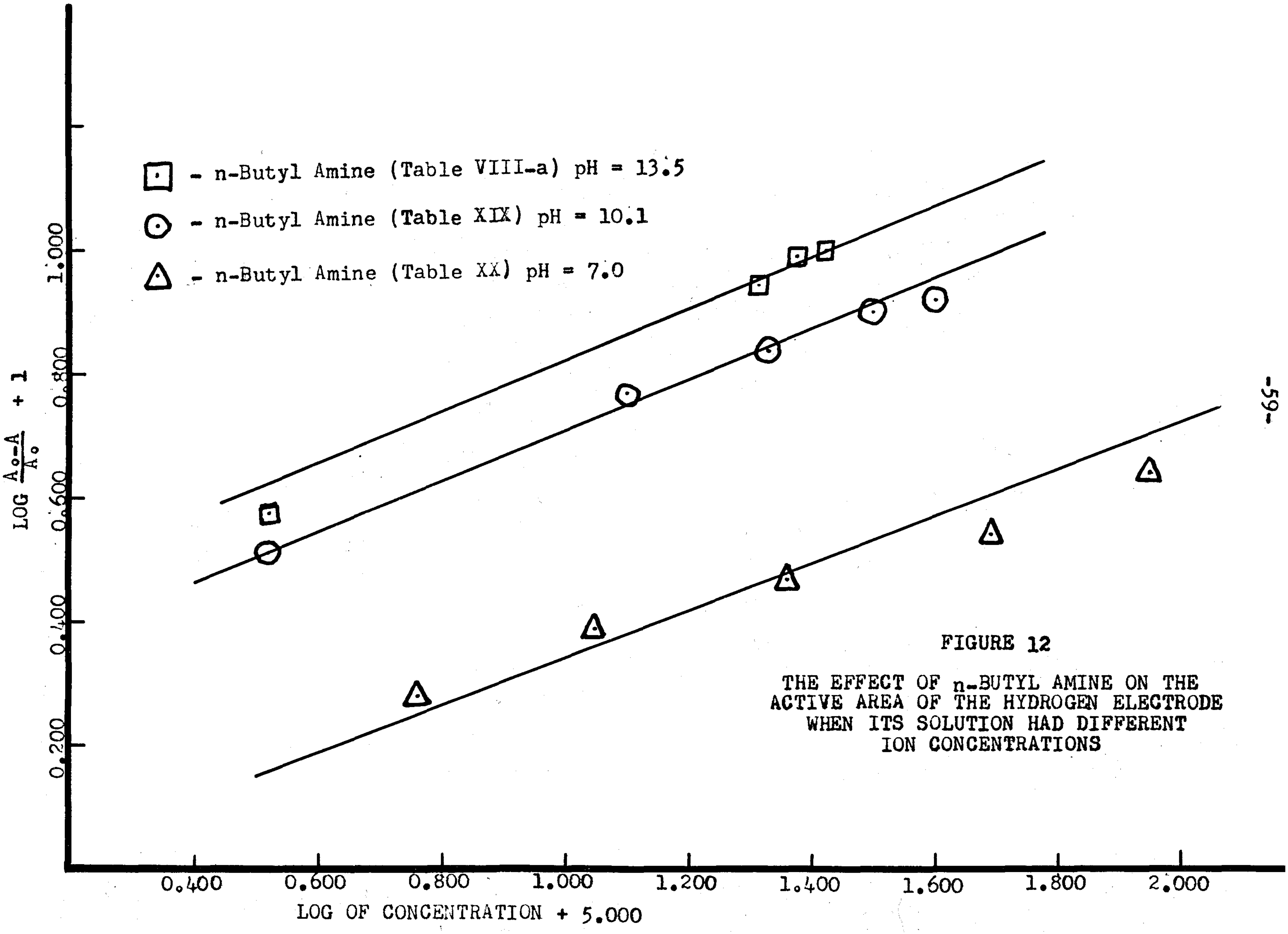


FIGURE 12

THE EFFECT OF n-BUTYL AMINE ON THE ACTIVE AREA OF THE HYDROGEN ELECTRODE WHEN ITS SOLUTION HAD DIFFERENT ION CONCENTRATIONS

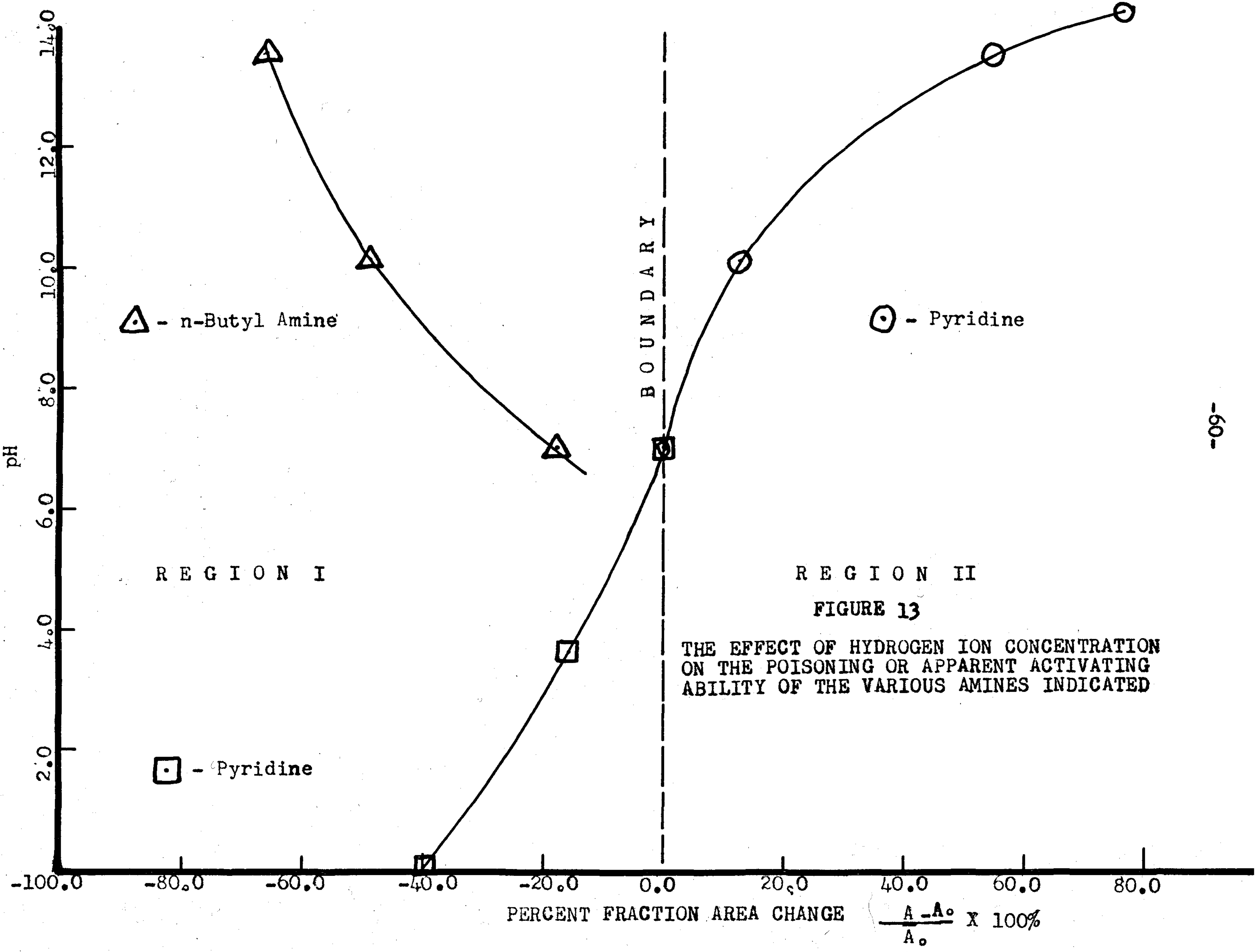


FIGURE 13

THE EFFECT OF HYDROGEN ION CONCENTRATION ON THE POISONING OR APPARENT ACTIVATING ABILITY OF THE VARIOUS AMINES INDICATED

Table XIII

The Effect of Pyridine as an Activator

Temperature = 25°C
Buffered at pH = 14.3
Electrode potential remained
constant with adsorption of
activator

No.	Planimeter reading	Mean value	Log $\frac{A-Ao}{Ao}$	Log of conc. Pyridine log millimoles/ml
1	1-A 6.85	6.85		
2	2-A 9.70 2-B 9.00 2-C 7.70 2-D 8.40	8.70	0.4315-1	0.3140-5
3	3-A 9.90 3-B 10.00 3-C 9.60	9.83	0.6385-1	0.6604-5
4	4-A 12.80 4-B 11.70 4-C 13.80 4-D 9.70 4-E 11.50	11.89	0.8667-1	0.0142-4

Table XIV

The Effect of Pyridine as an Activator

Temperature = 25°C
Buffered at pH = 13.5
Electrode potential remained constant with adsorption of activator

No.	Planimeter reading		Mean value	Log $\frac{A-Ao}{Ao}$	Log of conc. Pyridine log millimoles/ml
1	1-A	5.45	5.45		
2	2-A 2-B 2-C	7.45 7.20 7.75	7.47	0.5689-1	0.7904-5
3	3-A 3-B	8.40 8.60	8.50	0.74790-1	0.0178-4
4	4-A	9.05	9.05	0.81990-1	0.1222-4
5	5-A 5-B	10.50 10.70	10.60	0.9754-1	0.3700-4

Table XV

The Effect of Pyridine as an Activator

Temperature = 25°C
Buffered at pH = 10.1
Electrode potential remained
constant with adsorption of
activator

No.	Planimeter reading	Mean value	Log $\frac{A-Ao}{Ao}$	Log of conc. Pyridine log millimoles/ml
1	1-A 7.40 1-B 7.40 1-C 7.60	7.47		
2	2-A 7.95	7.95	0.8088-2	0.5903-5
3	3-A 8.30	8.30	0.0457-1	0.9697-5
4	4-A 8.85	8.85	0.2666-1	0.2181-4
5	5-A 9.90	9.90	0.5123-1	0.4959-4
6	6-A 10.75 6-B 10.85 6-C 10.95 6-D 10.85	10.85	0.6556-1	0.7357-4
7	7-A 11.25	11.25	0.7042-1	0.9986-4

Table XVI

The Effect of Pyridine

Temperature = 25°C
Buffered at pH = 7.0
Electrode potential remained constant with adsorption of pyridine

No.	Planimeter reading	Mean value	Log $\frac{A-Ao}{Ao}$	Log of conc. Pyridine log millimoles/ml
1	1-A 9.20			
2	2-A No Change			0.7407-5
3	3-A No Change			0.2878-4
4	4-A No Change			0.5162-4
5	5-A No Change			0.6620-4
6	6-A No Change			0.9021-4
7	7-A No Change			0.1571-3

Table XVII

The Effect of Pyridine as a Poison

Temperature = 25°C
Buffered at pH = 3.6
Electrode potential changed
with adsorption of poison

No.	Planimeter reading	Mean value	Log-micro coulombs	Log $\frac{Ao-A}{Ao}$	Log of conc. Pyridine log millimoles/ml
1	1-A 16.05 1-B 16.15	16.10	3.8806		
2	2-A 15.00 2-B 15.50	15.25	3.8651	0.7226-2	0.6521-5
3	3-A 13.50	13.50	3.8121	0.2081-1	0.1729-4
4	4-A 12.70 4-B 12.05 4-C 12.45	12.70	3.7856	0.32465-1	0.4084-4
5	5-A 12.35	12.35	3.7735	0.3672-1	0.5883-4
6	6-A 12.00	12.00	3.7610	0.4059-1	0.7161-4
7	7-A 11.70	11.70	3.7500	0.4366-1	0.8653-4
8	8-A 11.20	11.20	3.7310	0.4834-1	0.0621-3

Table XVIII

The Effect of Pyridine as a Poison

Temperature = 25°C
Buffered at pH = 0
Electrode potential changed
with adsorption of poison

No.	Planimeter reading	Mean value	Log micro-coulombs	Log $\frac{Ao-A}{Ao}$	Log of conc. Pyridine log millimoles/ml	Mean potential measured in solution
1	1-A 9.41 1-B 9.81 1-C 9.94 1-D 10.36 1-E 9.90 1-F 9.84	9.88	3.9838			0.2881
2	2-A 7.85 2-B 8.02 2-C 7.85 2-D 7.92 2-E 7.81 2-F 7.95	7.90	3.8866			0.2784
3	3-A 5.00 3-B 5.03 3-C 4.92 3-D 5.16	5.03	3.6906	0.6912-1	0.4065-4	0.1936
	4-A 4.80 4-B 4.72 4-C 4.68	4.73	3.6639	0.7171-1	0.5461-4	0.1885

Table XIX

The Effect of n-Butyl Amine as a Poison

Temperature = 25°C
Buffered at pH = 10.1
Electrode potential remained constant with adsorption of n-Butyl Amine

No.	Planimeter reading	Mean value	Log $\frac{Ao-A}{Ao}$	Log of conc. n-Butyl Amine log millimoles/ml
1	1-A 15.05 1-B 15.15 1-C 14.80	15.00		
2	2-A 10.10 2-B 10.20	10.15	0.5097-1	0.5218-5
3	3-A 6.10	6.10	0.7733-1	0.1056-4
4	4-A 4.40 4-B 4.10 4-C 4.70	4.40	0.8492-1	0.3342-4
5	5-A 3.10	3.10	0.89946-1	0.5004-4
6	6-A 2.40	2.40	0.9243-1	0.6044-4
7	7-A 2.00	2.00	0.9379-1	0.7480-4

Table XX

The Effect of n-Butyl Amine as a Poison

Temperature = 25°C
Buffered at pH = 7.0
Electrode potential remained
constant with adsorption of
n-Butyl Amine

No.	Planimeter reading	Mean value	Log $\frac{Ao-A}{Ao}$	Log of conc. n-Butyl Amine log millimoles/ml
1	1-A 9.35 1-B 9.20	9.28		
2	2-A 7.45 2-B 7.90 2-C 7.15	7.50	0.2829-1	0.7624-5
3	3-A 7.00	7.00	0.3904-1	0.0555-4
4	4-A 6.25 4-B 6.80	6.53	0.4718-1	0.3646-4
5	5-A 6.00 5-B 6.00 5-C 6.05	6.02	0.5457-1	0.6896-4
6	6-A 5.10 6-B 5.30	5.20	0.6431-1	0.9487-4
7	7-A 3.70	3.70	0.7791-1	0.3347-3

Since pyridine appeared to activate the electrode in basic solution, it was decided to study another compound with a similar structure to pyridine. The compound chosen was α-picoline. It is seen from Figure 14, showing log of the fraction of the area increase vs. the log of the concentration of amine, that α-picoline is also an apparent activator but does not appear to be as strong an activator as pyridine. Aniline was also investigated. From the data obtained, it could not be determined whether it was an activator or poison.

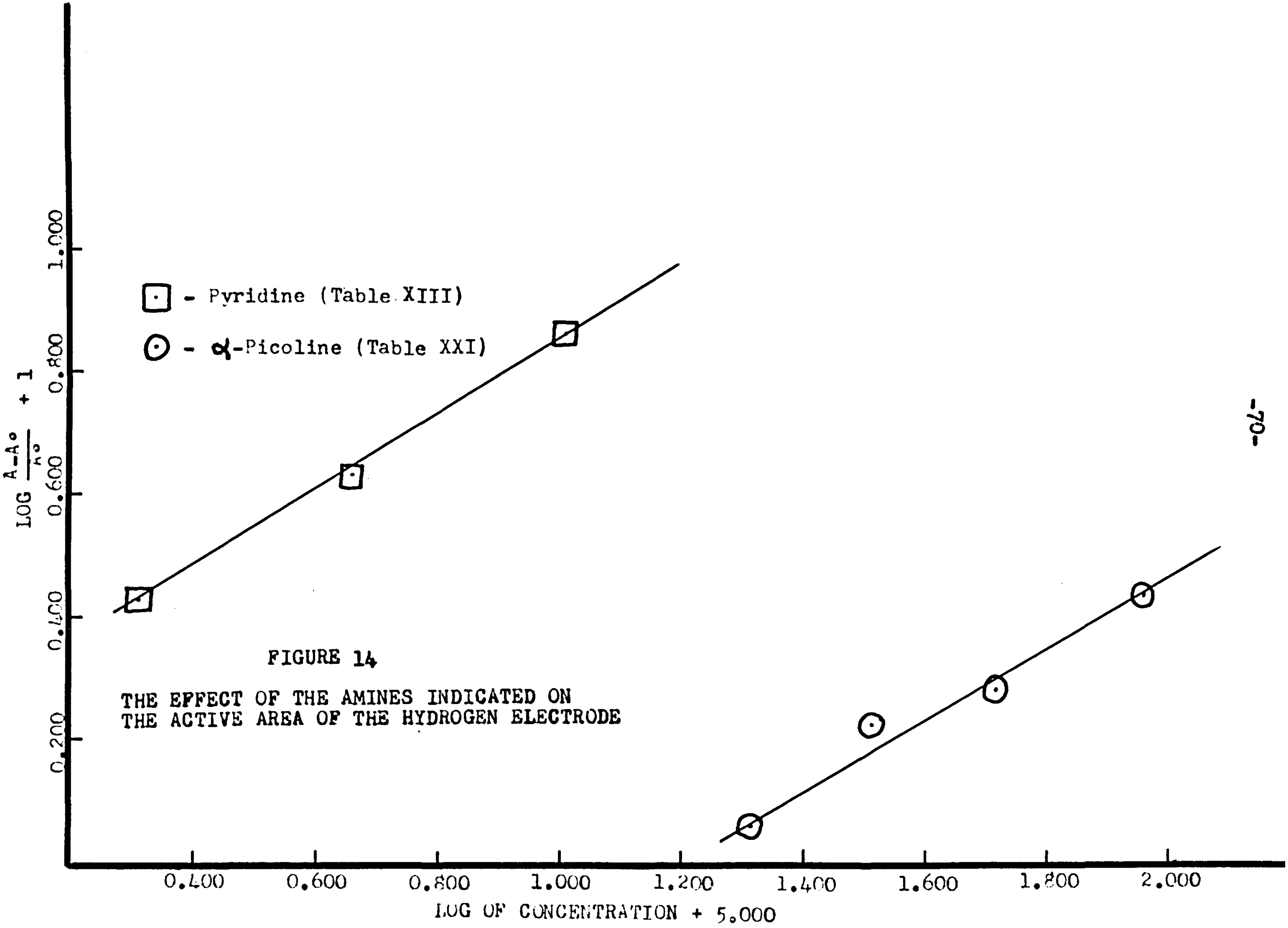


FIGURE 14

THE EFFECT OF THE AMINES INDICATED ON THE ACTIVE AREA OF THE HYDROGEN ELECTRODE

Table XXI

The Effect of α-Picoline as an Activator

Temperature = 25°C
Buffered at pH = 4.3
Electrode potential remained
constant with adsorption of
α-Picoline

No.	Planimeter reading	Mean value	Log $\frac{A-Ao}{Ao}$	Log of conc. α-Picoline log millimoles/ml
1	1-A 15.00	15.00		
2	2-A 15.25 2-B 15.35	15.30	0.3010-2	0.3010-5
3	3-A 16.60	16.60	0.0294-1	0.9085-5
4	4-A 17.10	17.10	0.0569-1	0.3160-4
5	5-A 17.50	17.50	0.2227-1	0.5145-4
6	6-A 17.85	17.85	0.2780-1	0.7185-4
7	7-A 19.05	19.05	0.4314-1	0.9605-4

It is noted that none of the amines studied, including pyridine, affected the Nernst potential of the hydrogen electrode in basic solution; however, pyridine did effect the Nernst potential in acid solution (pH = 0) as shown in Figure 15, where a potential is plotted against the log of the amount of hydrogen adsorbed (log microcoulombs). The slope of this straight line curve shown in Figure 15 is seen to be 0.3125 or approximately five times the constant in the Nernst equation. It was seen that the data for two different electrodes lies on this straight line in Figure 15 and, therefore, the data for two different electrodes in the case of pyridine is seen to be superimposable.

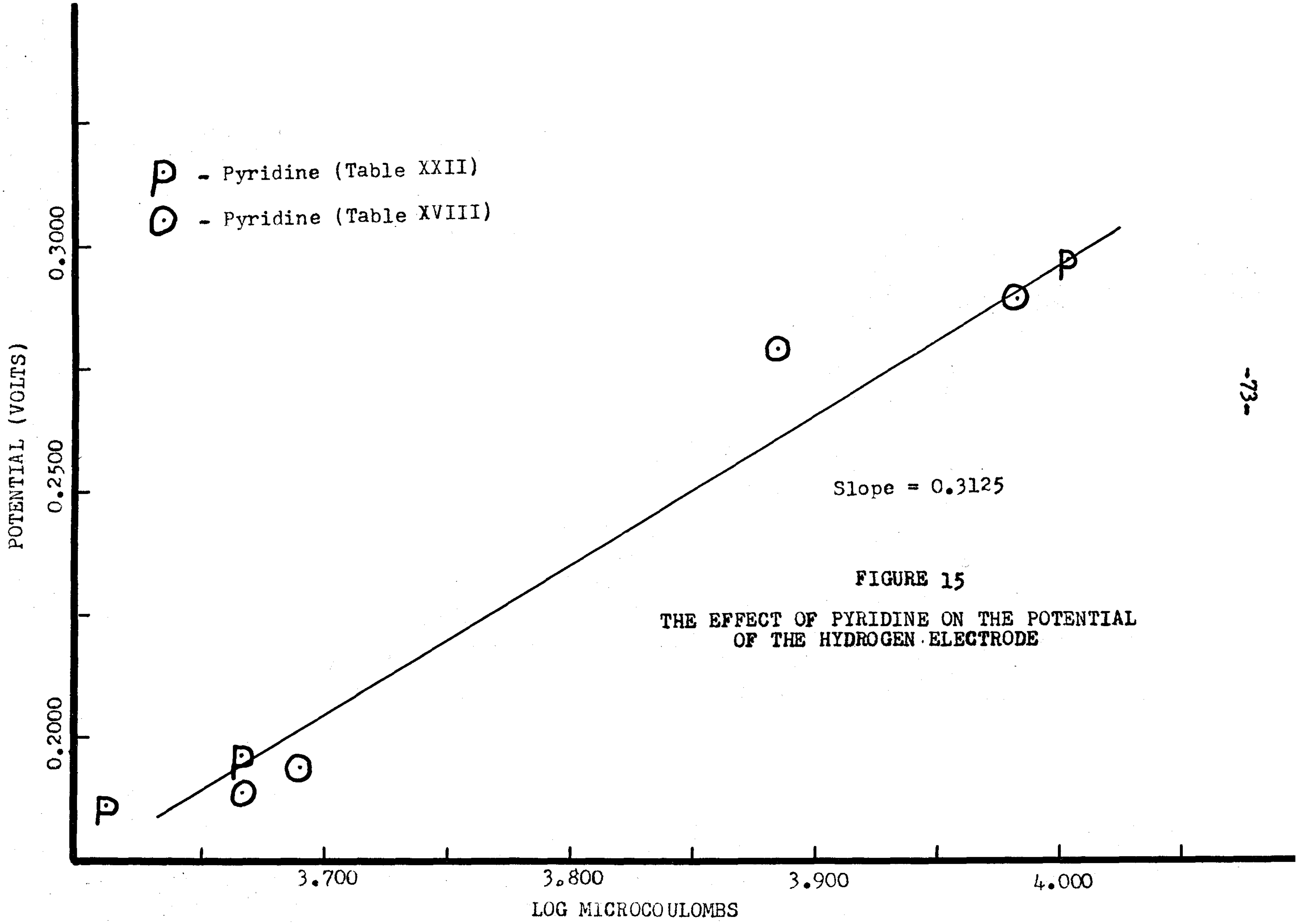


FIGURE 15

THE EFFECT OF PYRIDINE ON THE POTENTIAL OF THE HYDROGEN ELECTRODE

Table XXII

The Effect of Pyridine as a Poison

Temperature = 21.55°C
Buffered at pH = 0
Electrode potential changed
with adsorption of poison

No.	Planimeter reading	Mean value	Micro-coulombs	Log micro-coulombs	Mean potential measured in solution
1	1-A 11.11 1-B 11.81 1-C 11.14 1-D 11.36	11.25	10964	4.0399	0.2971
2	2-A 5.00 2-B 4.81 2-C 4.48 2-D 4.65	4.73	4609.8	3.6637	0.1960
3	3-A 4.35 3-B 4.00 3-C 4.25	4.20	4093	3.6122	0.1960

Finally, a comparison is made between the poisoning ability of a nitrile and an aliphatic amine with the nitrile being acetonitrile and the amine being n-ethyl amine. This result is shown in Figure 16 which shows that acetonitrile's poisoning ability is approximately the same as n-ethyl amine's poisoning ability in a basic solution at pH = 14.3.

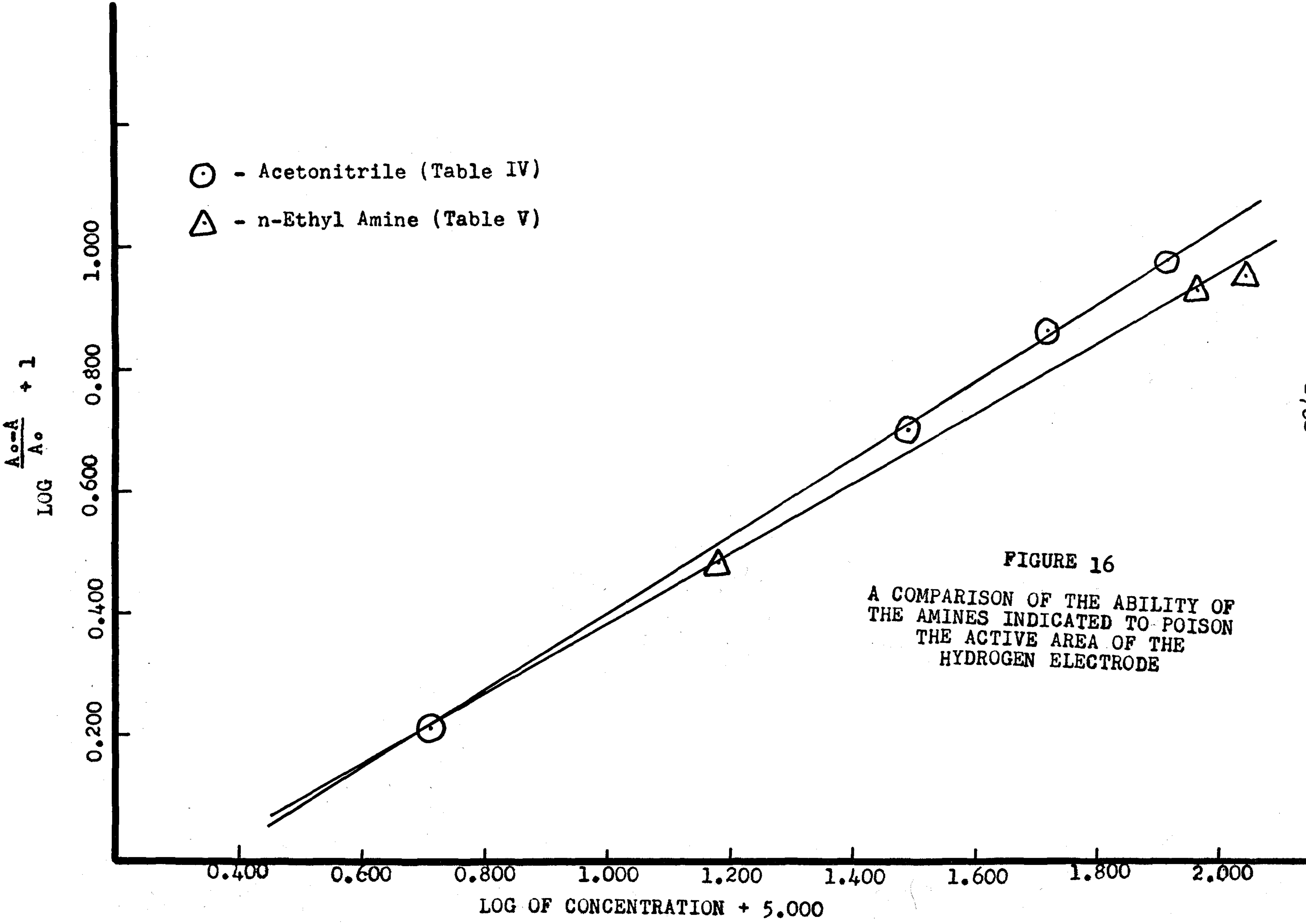


FIGURE 16

A COMPARISON OF THE ABILITY OF THE AMINES INDICATED TO POISON THE ACTIVE AREA OF THE HYDROGEN ELECTRODE

Table XXIII

This is a table of the sensitivity values for each of the previous tables in order to convert the planimeter readings in each of the tables to microcoulomb readings, which is a measure of the amount of hydrogen removed from the electrode in electrical units. The microcoulomb reading is obtained from the planimeter readings using the following equation:

Microcoulombs = 3249 (sensitivity value)(planimeter reading)

Sensitivity Value	Table Referred To
0.300	I
0.300	II
0.200	III
0.100	IV
0.150	V
0.150	VI
0.150	VII-a
0.150	VII-b
0.100	VIII-a
0.100	VIII-b
0.100	IX
0.100	X
0.150	XI
0.150	XII
0.150	XIII
0.100	XIV
0.100	XV
0.100	XVI
0.150	XVII
0.300	XVIII
0.100	XIX
0.100	XX
0.100	XXI
0.300	XXII

CONCLUSION

The results of this research can be interpreted as being in agreement with the general adsorption theory discussed by Hackerman and Makrides in their article[36], which utilizes the Marted theory[24,25] of chemisorption, since the adsorbent (platinum) is the Marted type, that is, one which can receive a pair of unshared electrons into its d-shell and the adsorbates (nitriles, amines) are the type which have a pair of electrons which can be furnished to the adsorbent. In the conclusions drawn from the results, the agreement of these results with the general adsorption theory will be noted. The fact that acetonitrile was noted to poison the hydrogen electrode in acid solution and basic solution is in agreement with the general adsorption theory. It is concluded therefore that acetonitrile furnishes a pair of electrons to the d-shell of the platinum electrode, displacing the hydrogen from the bond between it and the platinum. Noting the results that all the amines poisoned the hydrogen electrode in basic solution with the exception of α-picoline and pyridine, it is concluded that these amines, excepting α-picoline and pyridine, form the dative bond with platinum in agreement with the general adsorption theory.

It is concluded that pyridine and α-picoline disagree with the general adsorption theory since they appear to activate the electrode in basic solution. It is possible that pyridine forms a complex with hydrogen by utilizing certain catalytic properties of platinum, therefore giving an apparent increase in area of the electrode due to the fact that hydrogen is not only adsorbed on the hydrogen electrode but also binds with pyridine to form a weak bond. The fact that pyridine was found to poison the hydrogen electrode in an acid solution makes it appear that pyridine is acting in accordance with the general adsorption theory. The result that pyridine is a poisoner of the electrode in acid solution is indeed in agreement with the results pointed out by Hackerman and Makrides[36] on pyridine as an inhibitor in corrosion.

The result that the poisoning ability of the aliphatic amine increased with its molecular weight is in corresponding agreement with earlier works[30,31,32,33] on aliphatic amines as corrosion inhibitors. This result is also in agreement with the general adsorption theory. Since n-butyl amine was found to be a stronger poison than secondary butyl amine, it is concluded that primary amines have a greater poisoning ability than secondary amines. n-Butyl amine being a stronger poison in basic solution than piperidine, indicates that cyclic amines are weaker poisons than corresponding aliphatic amines. This result agrees with corrosion studies by Hackerman and

Makrides[36], which pointed out that aliphatic amines are stronger corrosion inhibitors than the cyclic amines and, likewise, cyclic amines are stronger than the aromatic amines.

The result that n-butyl amine decreased in its poisoning ability with increasing hydrogen ion concentration (decreasing pH) would appear to be in agreement with the general adsorption theory, since the free pair of electrons on the amine group would tend to be tied up by the hydrogen ions as the hydrogen ion concentration increased, therefore, decreasing the availability of the free pair of electrons to the platinum.

The fact that pyridine increased in its apparent activation effects with increasing pH's above pH = 7 and became a poison at pH's below pH = 7 with increasing poisoning ability with decreasing pH's below pH = 7, appears to completely disagree with the general adsorption theory since the general adsorption theory would predict that pyridine would be a strong poison at pH's above pH = 7 with increasing poisoning ability as the pH values increase. It is seen that pyridine does the exact opposite. It appears to agree with the general adsorption theory below pH's of 7 since it is a poison in this pH range but by the general adsorption theory, its poisoning ability should decrease with decreasing pH's below pH = 7 but pyridine does just the opposite, its poisoning ability increases in this direction.

Since the slopes of the straight line curve potential of the hydrogen electrode vs. the log microcoulombs has been shown to be the value of the Nernst equation constant when the hydrogen electrode was in acid solution and acetonitrile was used as a poison, it is concluded that the potential is not dependent on the pressure of the hydrogen ($P^{1/2}_{H_2}$) as is commonly written, but on the amount of hydrogen adsorbed on the hydrogen electrode when in acid solution. These two statements are mutually compatible since Franklin and Sothern[21] have shown that the amount of hydrogen adsorbed is linearly proportional to the pressure of the hydrogen. Since it was noted that the potential did not change with the amount of hydrogen adsorbed when the hydrogen electrode was in basic solution, it is concluded that the potential of the hydrogen electrode in basic solution is not governed by the amount of hydrogen adsorbed as in the case when the hydrogen electrode is in acid solution. The fact that the slope of the straight line curve of potential vs. log microcoulombs for the hydrogen electrode in acid solution when pyridine was used as a poison is approximately five times the value of the Nernst equation constant, points out that this tremendous increase in the constant is due to the unusual inter-mechanism between the platinum, hydrogen and pyridine, which has been shown to be confirmed by other results in connection with the adsorption of pyridine on the hydrogen electrode, indicating that pyridine does not act like the normal poisons.

SUMMARY

The adsorption on the hydrogen electrode of the organic compounds studied was found to agree with the Freundlich equation. It was noted that the data for two different electrodes was superimposable. The Nernst potential of the hydrogen electrode decreases with decreasing amounts of hydrogen adsorbed when the hydrogen electrode was in acid solution; while, on the other hand, the Nernst potential did not change with decreasing amounts of hydrogen adsorbed on the electrode when the hydrogen electrode was in basic solution. The slope of the straight line curve of decreasing potential vs. the log of the amount of hydrogen adsorbed (log microcoulombs) was found to be equal to 0.0587, which is the constant in the Nernst equation when acetonitrile was used as a poison. On the other hand, the slope was found to be approximately five times the above value when pyridine was used as a poison. All the amines that were studied were found to poison the hydrogen electrode in basic solution with the exception of pyridine and α-picoline, which appeared to activate the electrode. The poisoning ability of the aliphatic amines has been shown to decrease with decreasing molecular weight of the amine. n-Butyl amine was shown to

be a stronger poison in basic solution than secondary butyl amine, while isobutyl amine appeared to have the same poisoning strength as n-butyl amine. Piperidine was found to be a weaker poison than n-butyl amine. The poisoning ability of n-butyl amine was found to decrease with decreasing pH. It appears to remain a mild poison even in the acid pH range. Pyridine was noted to decrease in its apparent activating ability with decreasing pH until a pH of 7 has been reached, where at this pH, pyridine appears to act neither as an activator nor an inhibitor. Pyridine appears as a poison with increasing poisoning ability with decreasing pH values below the pH value of 7.

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AUTOBIOGRAPHY

I, Philip Lamar Oglesby, was born on January 15, 1931 in Chicago, Illinois. In September 1948, I graduated from Oceana High School, Oceana, Virginia. My college education began at William and Mary, Norfolk Division where I was a student until 1951, at which time I entered the University of Richmond, receiving a Bachelor of Science degree in Chemistry in June 1953. I then entered Graduate School in the Department of Chemistry at the University of Richmond and did graduate work there during 1953 and 1954. In September 1954, I entered the University of Maryland Graduate School to pursue studies in Physics.