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THE APPARENT ADSORPTION OF SOME ALIPHATIC COMPOUNDS FROM AQUEOUS SOLUTIONS AS INFERRED FROM HYDROGEN OVERVOLTAGE MEASUREMENTS

BY

Bert Howard Clampitt

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I. INTRODUCTION

There is voluminous literature on the subject of adsorption from solution. Many of the 6002 references in Deitz's extensive Bibliography of Solid Adsorbents (1) are devoted to articles in this field, and Cassidy's Adsorption and Chromotography (2) is largely devoted to solution adsorption.

An examination of this literature relating to adsorption from solution reveals that the major portion of the work has been done on charcoal, silica gel, and similar large surface area substances. There is a very noticeable lack of data reported for adsorbents with a small surface area, especially small metal surfaces.

The reason that most solution adsorption work has been done on large area adsorbents lies in the way adsorption from solution is usually measured. Adsorption from solution is usually calculated from the following formula

$$\frac{V\ (C_o - C_f)}{m} = A\Gamma$$

where V is the volume of solution equilibrated with m grams of adsorbent. C_o and C_f are the original and final concentrations respectively. A is the surface area, and Γ is the surface excess.

Unless the surface area A is very large the difference in concentration $(C_o - C_f)$ will be so small that it will be unmeasurable. With charcoal and silica gel the surface areas are of order of magnitude 500 m^2/gm., and so the measurements can easily be made and the equation applied. Common metal surfaces have areas of perhaps 0.1 m^2/gm. It, therefore, becomes evident that unless one can prepare a metal with a large surface area this method can not be employed.

Adsorption on metal surfaces has important bearing on many related phenomena. Metallic corrosion is one of the fields in which the results should prove very valuable. The electrochemical theory (3) is the commonly accepted explanation for the corrosion of metals in a water solution. In brief, the theory states that differential aeration of the metal surface causes galvantic cells to be formed whenever the metal is brought into contact with the electrolyte. That is, different portions of the metal act as positive and negative electrodes. The metal dissolves from the anodic portions, and hydrogen is evolved on the cathodic areas. Corrosion of the metal will be hindered by any process which alters the local galvantic cell action.

It has long been known that the addition of certain substances greatly reduces the corrosion rate. Marangoni and Stephanelli (4) first reported this effect in 1872. The mechanism by which these corrosion inhibitors reduce the rate of dissolution of the metal is still much debated. It is generally agreed, however, that the extent of inhibition is dependent on the adsorption of the inhibitor on the cathodic areas of the metals. The debate regarding mechanism centers around whether the adsorbed films act as mechanical protectors or not. Studies of adsorption from solution by metal surfaces would be of value in elucidating on the mechanism of corrosion and inhibition as well as in permitting prediction of better inhibitors.

Studies of adsorption from solution by metals should also prove of value in the field of heterogeneous catalysis. This field has become increasingly important in its application to hydrogenation of various organic compounds. The current opinion (5) is that the hydrogenation mechanism consists of adsorption of the unsaturated organic compound and or hydrogen, reaction at the surface, and desorption of products.

From the foregoing discussion, it can readily be seen that any impurity that is adsorbed irreversibly on the surface of the catalyst will greatly alter its effectiveness. The removal of these catalytic poisons constitutes a very considerable industrial cost. It is believed that catalytic poisons owe a great part of their effectiveness to the blocking of the surface so that the reactants are prevented from reaching the surface. Adsorption studies should throw light on the mechanism of catalytic poisoning as well as on catalysis itself.

Lubrication of metal surfaces is also believed to depend on adsorption. It is generally assumed that polar compounds are adsorbed on metal surfaces and that these adsorbed layers are responsible for the lubricating properties of these substances. There are many references in the literature which deal with lubrication of metals, but few which refer to a study of the adsorption process in this connection. Greenhill (6,7) in a recent series of articles has investigated both the lubricating and adsorption properties of certain substances from benzene solutions and has concluded that only a small number of adsorbed layers is needed to provide effective lubrication. Extension of this type of research to other solvents, especially water, would be of great value.

Wetting of metals is closely allied to lubrication of metals. This field has many practical applications, among them: adhesion of paints of metals, stablization of metal sols, separation of certain precious metals by the flotation process, adhesion of rubber to metals, etc. A more thorough understanding of the wetting of metals would be of great value to each of these applied fields. It is felt that adsorption studies are of fundamental importance if an adequate understanding of the wetting of metals is to be found.

A promising method for obtaining adsorption isotherms on small metal surfaces appears to be available from hydrogen overvoltage measurements. Hydrogen overvoltage is defined as the potential at which hydrogen is discharged on a particular metal surface minus the reversible hydrogen potential. This has a non zero value for all substances except platinized platinum.

The first important contribution to the field of hydrogen overvoltage was made in 1905 when Tafel (8) published his famous empirical equation

$$\eta = a + b \text{ Log } j$$

in which η is the overvoltage; j the current density; and a and b are constants. The surface area dependence of this equation and the effect of impurities on the overvoltage was noted by several early authors (9,10), but they failed to interpret these facts as due to adsorption. The earliest published quantitative inference of adsorption from steady state current-overvoltage measurements appears to be that of Ch'iao and Mann (11) in 1947.

Wetterholm (12) pointed out in 1949 that the addition of an organic compound would affect the hydrogen overvoltage in one or more of the following ways:

(1) A solvent effect on the overvoltage changing the over-all velocity of the hydrogen liberation reaction. This may result in either an increase or decrease in potential.

(2) A reduction effect resulting from an alternate hydrogen consumption process at the cathode. This can only lower the potential.

(3) An adsorption effect resulting from the concentration of the organic compound occurring at the metal-solution interface. This will increase the potential.

By proper choice of the organic compound, it is felt that the first two effects could be eliminated and reasonably accurate adsorption isotherms could be obtained.

A second method of obtaining adsorption data from overvoltage measurements results from the early work of Bowden and Rideal (13). They measured hydrogen overvoltage as a function of time and found that the initial portion of the curve was quite linear. They concluded that the slope of the line should be inversely proportional to the double layer capacity of the metal-solution interface, and they proceeded to find the proportionality constant.

Although Proskurnin and Frumkin (14) warned as early as 1935 of the marked effect of adsorbable contaminates on the double layer capacity, it was not until 1940 that Barclay and Butler (15) recognized a quantitative relation between alteration in double layer capacitance and adsorption.

Previously reported adsorption isotherms obtained by either method are very few and almost always the adsorption results were not the primary aim of the research. Ch'iao and Mann (11), although the first to realize that adsorption isotherms could be obtained from steady state current-overvoltage measurements, performed their experiments under conditions far from ideal as far as hydrogen overvoltage measurements are concerned. Their experimental procedure was open to criticism on several points. It is well known that dissolved oxygen greatly alters overvoltage results and no special care was taken to remove oxygen from the electrolyte, in fact the cell was opened to the atmosphere throughout the experiment. The electrolyte was also exposed to contamination from several rubber tubes, and it is expected this would greatly alter the results. For the current densities employed concentration polarization is an important factor; yet no special care was taken to eliminate it, in fact the solution was not even stirred.

A later article by Swearington and Schram (16) is a continuation of the method employed by Ch'iao and Mann. The apparatus was reported to be the same. Because of the experimental condition, it is felt that the results presented in both papers are not too accurate. In fairness it must be pointed out that the primary aim of each of these articles was not adsorption but rather measurement of inhibitor efficiency.

The experimental apparatus described by Wetterholm (12) appears to be carefully designed and adequate for accurate overvoltage measurements.

The experimental results are believed to be accurate; however, for the particular adsorbates used certain potential changes occur that are erroneously described as due to adsorption. (A more complete discussion of this paper appears in a later section.)

The work of Barclay and Butler (15) on double layer capacitance was done under very good experimental conditions; however, it was restricted to one metal, mercury, and one adsorbate, t-amyl alcohol. Subsequent work by this method is very scattered and none of it was done with the primary purpose of obtaining adsorption results.

The need for adsorption results on metal surfaces coupled with the scattered availability of such data in the literature makes this research seem warranted. It is felt that the experimental conditions under which most of the previous work has been done could be improved. By doing this, the accuracy of the results should correspondingly be increased, and a generally satisfactory technique made available.

II. THEORIES OF OVERVOLTAGE

A. Possible Reaction Paths

Bockris (17,18) lists the possible reaction paths of the hydrogen evolution as:

$$\begin{array}{ll} (1) & H_3O^+ + e \xrightarrow{\text{slow}} MH + H_2O \\ (2) & MH + MH \xrightarrow{\text{fast}} 2M + H_2 \end{array} \qquad (a)$$

$$\begin{array}{ll} (1) & H_3O^+ + e \xrightarrow{\text{fast}} MH + H_2O \\ (2) & MH + MH \xrightarrow{\text{slow}} 2M + H_2 \end{array} \qquad (b)$$

$$\begin{array}{ll} (1) & H_3O^+ + e \xrightarrow{\text{slow}} MH + H_2O \\ (2) & MH + H_3O^+ + e \xrightarrow{\text{fast}} H_2 + H_2O \end{array} \qquad (c)$$

$$\begin{array}{ll} (1) & H_3O^+ + e \xrightarrow{\text{fast}} MH + H_2O \\ (2) & MH + H_3O^+ + e \xrightarrow{\text{slow}} H_2 + H_2O \end{array} \qquad (d)$$

Each of these possible reaction paths will be considered now in some detail.

B. Summary of the Theories

1. Slow discharge theory

This theory assumes reaction path (a) is responsible for hydrogen overvoltage and was originally developed by Erdy-Gruz and Volmer (19,20).

The initial postulate is that the discharge of the hydrogen ion is a slow process requiring an energy of activation necessary for the transfer of an electron from the metal to the hydrogen ion. Then the number of neutralizations taking place per second is:

$$N_o = k_1' \; [H^+] \, e^{-\frac{U}{RT}} \tag{1}$$

where k_1' is a constant and $[H^+]$ is the activity of the hydrogen ions at the electrode surface; the subzero refers to the condition that the electrode is at zero potential. If, however, a potential difference E exists between the electrode and solution; then if the electrode is negatively charged with respect to the solution, neutralization of the protons by electrons requires less work by an amount EF per mole. Only part of this work, however, is realized before the transition state is reached. As work done on the system after the transition state does not affect the velocity of the reaction, only a fractional part of this work is effective in lowering the potential barrier; i.e. an amount αEF is effective, where $0 < \alpha < 1$. The number of neutralizations now becomes:

$$N_f = k_1' \; [H^+] \, e^{-\frac{(U-\alpha EF)}{RT}} = k_1 \; [H^+] \, e^{\frac{\alpha EF}{RT}} \tag{2}$$

The reverse process, namely the transfer of an electron from a neutral hydrogen atom to the metal, can be represented as:

$$N_b = K_2' \; [H] \, e^{-\frac{W}{RT}} \tag{3}$$

where W is the free energy of activation for the process, and $[H]$ is the activity of hydrogen atoms at the interface. If the electrode is negatively charged, the process will be hindered and consequently the free energy of activation raised by an amount βEF where $0 < \beta < 1$; therefore:

$$N_b = K_2' \, [H] e^{-\frac{W+\beta EF}{RT}} = k_2 [H] e^{\frac{-\beta EF}{RT}} \qquad (4)$$

At the equilibrium potential, E_R, the two rates must be equal, that is:

$$N_f = N_b = k_1 [H^+] e^{\frac{\alpha E_R F}{RT}} = k_2 [H] e^{\frac{-\beta E_R F}{RT}} \qquad (5)$$

One may rewrite this in the form:

$$[H] = k_3 [H^+] e^{\frac{(\alpha+\beta) E_R F}{RT}} \qquad (5)$$

If one neglects any change in the free energy of the system caused by alteration of the hydrogen ion activity in the double layer, then the total free energy change of the system caused by applying the potential E_R is $E_R F$. In which case $\alpha + \beta = 1$.

The assumption is now made that the energy barrier is symmetrical. In which case $\alpha = \beta = 0.5$.

If a potential E, different from E_R by an amount η, is applied then:

$$N_f - N_b = \frac{i}{F} = k_1 [H^+] e^{\frac{\alpha(E_R+\eta)F}{RT}} - k_2 [H] e^{\frac{-\beta(E_R+\eta)F}{RT}} \qquad (6)$$

or

$$i = k_3 [H^+] e^{\frac{\alpha \eta F}{RT}} - k_4 [H] e^{\frac{-\beta \eta F}{RT}} \qquad (7)$$

The magnitudes of k_3 and k_4 appear to be such that for $\eta > 0.03$ volts the second term can be neglected in comparison to the first, and under this circumstance one can write:

$$i = k_3 \left[H^+\right] e^{\frac{\alpha \eta F}{RT}} \qquad (8)$$

Since one has assumed the activity of hydrogen ions in the double layer constant,

$$\eta = a + b \text{ Log } i \qquad (9)$$

where:

$$b = \frac{2.3\ RT}{\alpha F}$$

As $\alpha = 0.5$, this gives the experimentally determined value of b.

Gurney (21, 22) developed essentially the same theory from a quantum mechanical background.

Frumkin (23,24,25) has enlarged upon the Erdy-Gruz Volmer theory by considering the structure of the double layer. Frumkin uses the Stern theory of double layer; that is he considers a Gouy diffused layer in addition to a Helmholtz non-diffused layer.

Frumkin also considers the activity of the hydrogen ions in the double layer in relation to the bulk ionic activity. In this way, he is able to predict the effect of foreign electrolytes on the overvoltage, as well as the pH dependence of overvoltage.

Eyring (26) proposed that the rate determining step is the transfer of a proton from a solvent molecule in solution to a solvent molecule attached to the cathode surface. It is generally agreed that this process involves the discharge of hydrogen ions; therefore the theory is grouped with the slow discharge theory. This theory is an advance over the original theory in that it gives us a suggestion as to the cause of the energy of activation.

In a recent article Van Rysselberghe (27) gives a very excellent discussion of the slow discharge theory. He makes use of chemical and electrochemical potentials to develop the theory. In this article he gives a more detailed discussion of the transfer coefficient of Erdy-Gurz and Volmer. He also proceeds to calculate the free energy of the discharge process and shows that the mechanism is entirely plausible.

2. Catalytic combination theory

From the historical point of view this is the oldest theory of overvoltage. It assumes reaction path (b) is the cause of overvoltage. After Tafel (8) discovered his empirical equation, he immediately attempted a theoretical explanation.

He assumed reaction 1-(b) was fast and reaction 2-(b) was slow and essentially irreversible. The rate of formation of hydrogen atoms can be written:

$$\frac{d\,[H]}{dt} = k_1 i - k_2 [H]^{\alpha} \tag{1}$$

where k_1 and k_2 are the rate constants for the respective reactions and α is the kinetic order of reaction 2-(b).

If one now assumes a steady state; i.e. $\frac{dH}{dt} = 0$, then:

$$[H] = \left(\frac{k_1}{k_2} i\right)^{\frac{1}{\alpha}} = k_3\, i^{\frac{1}{\alpha}} \tag{2}$$

The Nernst Equation requires:

$$E = E^{o} + \frac{RT}{F} \text{ Log } \frac{[H]}{[H^{+}]} = \frac{RT}{F} \text{ Log } \frac{[H]}{[H^{+}]} \qquad (3)$$

Substituting equation (2) into (3) gives

$$E = \frac{RT}{F} \text{ Log } \frac{k_3 i}{[H^{+}]}^{\frac{1}{\alpha}} \qquad (4)$$

At equilibrium equation (3) can be written

$$E_R = \frac{RT}{F} \text{ Log } \frac{[H]}{[H^{+}]}^{eq} \qquad (5)$$

where E_R refers to the reversible potential.

According to our definition of overvoltage:

$$\eta = E - E_R \qquad (6)$$

therefore one can say:

$$\eta = \frac{RT}{F} \text{ Log } \frac{k_3}{[H^{+}]} i \frac{1}{\alpha} - \frac{RT}{F} \text{ Log } \frac{[H]}{[H^{+}]}^{eq}$$

or

$$\eta = \frac{RT}{F} \text{ Log } \frac{k_3}{[H]_{eq}} + \frac{RT}{\alpha F} \text{ Log } i = a + b \text{ Log } i \qquad (7)$$

Since the experimentally determined value of b is 0.118, α must equal 0.5.

This theory was modified somewhat by Glasstone (28) by taking into account the reverse of reaction 2-(b). His modification eliminated one of the disadvantages of the theory by not allowing to decrease indefinitely as i is reduced to zero.

The slow discharge theory was given its last major revision by Hickling and Salt (29) in 1942. Their treatment was essentially the same as that given above except that the concentration of atomic hydrogen as calculated from equation (2) was related to the pressure of atomic hydrogen in equilibrium with the electrode by the Freundlich isotherm:

$$[H] = k\,P^{\frac{1}{n}}$$

It is then assumed that $[H]$ in equation (3) should be replaced by $([H]/k)^n$ in light of this relation.

In order to obtain the correct value for the Tafel constant b, it was necessary to assume a value of 4 for the empirical constant n in the Freundlich equation. This is a very reasonable value in view of the data available for adsorption of gases.

This latest revision eliminates one of the main difficulties of the slow discharge theory in that it allows the reaction to be second order in atomic hydrogen in place of half order as required by the original Tafel treatment.

3. Slow discharge - electrochemical theory

According to this theory reaction path (c) is responsible for the overvoltage phenomena. Although the possibility of such a mechanism has been noticed by several authors (24,29), it was not until the work of Bockris (17) that it was thoroughly investigated.

The rate determining step is the same as in the slow discharge theory, and so the Tafel equation can be derived in an analogous manner. There are, however, some differences in the two theories.

To release one molecule of hydrogen gas, reaction path (a) requires two acts of the rate determining step while for reaction path (c) only one act is required. This is an important difference implying different rate constants in the two cases.

At sufficiently high currents the slow discharge step must become fast compared to the other reactions. If these experimental conditions are realizable, then the rate determining step becomes either:

$$MH + MH \longrightarrow H_2$$

or

$$MH + H_3O^+ + e \longrightarrow H_2 + H_2O$$

Under these conditions, reaction path (a) degenerates to reaction path (b) and reaction path (c) into (d). It should, therefore, be possible to distinguish between them.

Bockris has pointed out in several papers (17,18,30,31) that with the data ordinarily available it is impossible to distinguish between the two theories.

4. Electrochemical theory

This theory was originally developed by Horiuti (32,33) in Japan and Frumkin (24) in Russia around 1937. It assumes reaction path (d).

The following reactions are considered:

$$H_3O^+ + e \longrightarrow MH \qquad (i)$$

$$MH \longrightarrow H_3O^+ + e \qquad (ii)$$

$$MH + H_3O^+ + e \longrightarrow H_2 + H_2O \qquad (iii)$$

If the electrode is negatively charged, the following rate equations can be written:

$$R_1 = k_1 \left(1 - \frac{[H]}{n}\right) [H^+] e^{\frac{EF}{2RT}} \qquad (1)$$

$$R_2 = k_2 \frac{[H]}{n} e^{-\frac{EF}{2RT}} \qquad (2)$$

$$R_3 = k_3 \frac{[H]}{n} [H^+] e^{\frac{EF}{2RT}} \qquad (3)$$

where n is the number of adsorption centers on the surface; $[H]$ is the concentration of atomic hydrogen on the surface; and $[H^+]$ is the activity of the hydrogen ions in the double layer.

This treatment is similar to the slow discharge theory; in fact the value of the constant α in the Erdy-Grus and Volmer theory is assumed to apply in this case. It is for this reason that in the preceding rate equations the exponential terms are raised to the $\frac{EF}{2RT}$ power.

At a steady state one can write:

$$k_1 \left(1 - \frac{[H^+]}{n}\right) [H^+] e^{\frac{EF}{2RT}} - k_2 \frac{[H]}{n} e^{\frac{EF}{-2RT}} - k_3 \frac{[H]}{n} [H^+] e^{\frac{EF}{2RT}} = 0 \qquad (4)$$

or

$$\frac{[H]}{n} = \frac{k_1 [H^+]}{k_1 [H^+] + k_2 e^{-\frac{EF}{RT}} + k_3 [H^+]} \qquad (5)$$

For strong polarization:

$$(k_1 + k_3) \; [H^+] >> k_2 \; e^{-\frac{EF}{RT}} \qquad (6)$$

therefore:

$$\frac{[H]}{n} = \frac{k_1}{k_1 + k_3} \qquad (7)$$

As one has assumed reaction (iii) is rate determining:

$$i = 2F \; k_3 \; \frac{[H]}{n} [H^+] \; e^{\frac{EF}{2RT}} \qquad (8)$$

Now substituting equation (7) into equation (8) gives us:

$$i = \frac{2F \; k_1 \; k_3}{k_1 + k_3} \; [H^+] \; e^{\frac{EF}{2RT}} \qquad (9)$$

According to our definition of overvoltage:

$$E = \eta + E_R \qquad (10)$$

Combining equations (9) and (10) gives us

$$i = \frac{2F \; k_1 \; k_3}{k_1 + k_3} [H^+] \; e^{\frac{E_R F}{2RT}} \; e^{\frac{\eta F}{2RT}} \qquad (11)$$

or

$$\eta = a + b \text{ Log } i$$

Bockris (17,30,31) developed this theory according to the absolute rate theory of Glasstone, Laidler and Eyring (34). This method differs from the above treatment in that it does not introduce the Erdy-Gruz Volmer constant α. A term for the electrochemical free energy of activation is introduced, and this must be evaluated from experimental data. It is not, therefore, certain whether the derivation is an improvement over the one given or not.

Salzburg and Schuldiner (35) have criticized the development of the theory by Bockris; however, it is felt that much of the criticism is unjust. Bockris (36) in his reply to the above authors has carefully answered most of the questions raised and is convinced that in some instances this mechanism is responsible for the overvoltage curves.

C. General Discussion of the Theories

All of the theories presented in the preceeding sections indicate that the true picture of the hydrogen overvoltage phenomena is still unclear. Certain experimental evidence can be advanced to support each of the theories; however, each theory has its own drawbacks.

The slow discharge theories (a) and (c) give a qualitative explanation of foreign salt and pH effects on overvoltage. They also explain the fact that the initial growth of hydrogen overvoltage is directly proportional to the quantity of electricity passed. It is claimed that the slow discharge theories lead to the correct "b" constant in the Tafel equation; however, as was indicated, this derivation involves an adjustable constant, and this is given a value that will give the correct value for the constant "b".

The slow discharge theories fail to explain the marked dependence of hydrogen overvoltage on the cathode material; that is they fail to give even a qualitative explanation of the Tafel constant "a". The second drawback to the slow discharge theory arises from the fact that the discharge of most other ions proceeds without marked overvoltage. It is unclear why the discharge of protons should be exceptional in discharge mechanism.

The catalytic combination theory, on the other hand, suggests a relation between the cathode material and the Tafel "a" constant. The theory also tends to do away with the idea that hydrogen overvoltage is a special electrochemical process. Hickling and Salt (29) assert that their revision of the theory eliminates the chief difficulty of the original theory by giving the correct value of the Tafel "b" constant. It should be pointed out that as with the slow discharge theory an adjustable constant is introduced into the calculations, and it is given an appropriate value to obtain the desired result.

The catalytic theory has its main difficulty in explaining certain "solution effects" of hydrogen overvoltage; such as the effect of foreign salts and pH. It must also be pointed out that the pressure of atomic hydrogen needed to account for an overvoltage of 1 volt is only 10^{-17} atmospheres. This suggests that a physical meaning can not be attached to the term atomic hydrogen pressure, but we are referring to the activity of the hydrogen atoms.

The electrochemical theory is really an attempt to combine the slow discharge and catalytic combination theories. It does not explain the observed pH effects, and the relation between electrode material and the Tafel "a" constant is rather vague. Like all of the other theories, this one is rather qualitative, and so it can not be unequivocally tested by experiment.

Several experimental quantities might give some insight as to the true mechanism of overvoltage. The so-called stoichiometry number, which is defined as the number of acts of the rate determining step required to release one molecule of hydrogen, would be of great value in illustrating the mechanism. For path (a) the stoichiometry number is 2 while for paths (b), (c) and (d) the stoichiometry number is 1. Bockris and Potter (37) have indicated that this quantity in principle can be determined experimentally.

The stoichiometry number arises by considering an unspecified rate determining step from the theory of absolute reaction rates (34). Essentially this theory was followed in the development of the slow discharge mechanism of overvoltage; however, the theory was modified to the particular slow discharge mechanism by considering that only one electron is involved in the rate determining step. To release one molecule of hydrogen requires the over-all reaction to involve two electrons; therefore, the passage of one unit of reactants in the rate determining step to obtain one molecule of hydrogen involves $\frac{2}{\lambda}$ electron charges where λ is the stoichiometry number. Equation (5) of the slow discharge section now becomes

$$\frac{i_o}{F} = k_1 \left[H^+\right] e^{\frac{2\alpha E_R F}{\lambda RT}} = k_2 \left[H\right] e^{-\frac{2\beta E_R F}{\lambda RT}} \tag{1}$$

where i_o is the current flowing at the equilibrium potential. Equation (6) becomes

$$\frac{i}{F} = k_1 \left[H^+\right] e^{\frac{2\alpha(E_R + \eta)F}{\lambda RT}} - k_2 \left[H\right] e^{-\frac{2\beta(E_R + \eta)F}{\lambda RT}} \tag{2}$$

If one combines these two equations and apply the restriction $\alpha + \beta = 1$ one finds

$$i = i_o \left[e^{\frac{2\alpha\eta F}{\lambda RT}} - e^{-\frac{2(1-\alpha)\eta F}{\lambda RT}} \right] \tag{3}$$

At small overvoltages one can take the first two terms of the exponential expansion and the equation becomes

$$i = i_o \left[1 + \frac{2\alpha\eta F}{\lambda RT} - 1 + \frac{2\eta F}{\lambda RT} - \frac{2\alpha\eta F}{\lambda RT} \right] \tag{4}$$

or

$$i = \frac{2 i_o \eta F}{\lambda RT} \tag{4}$$

If one differentiates this equation one has

$$\lambda = \frac{2 i_o F}{RT} \left(\frac{d\eta}{di} \right)_{i \rightarrow 0} \tag{5}$$

It is easily seen that the application of equation (5) requires measurements at very low current densities where overvoltage values are very difficult to obtain. An extrapolation is also required to obtain the i_o value. As the article points out, the errors are difficult to assess, and one is probably biased toward high values. If a cleaner experimental method could be devised to obtain the information, this would be of great value in our discussion of the reaction mechanism.

The extent to which atomic hydrogen covers the surface of the cathode would be of value; however, an unambiguous method of its determination is not at present available. Reaction paths (b) and (d) would require a larger surface coverage of atomic hydrogen than paths (a) or (c).

The effect of pH on overvoltage is important. The qualitative nature of all the overvoltage theories makes the expected pH variation obscure, and so observed effects are difficult to interpret in light of the mechanism.

At sufficiently high current densities the surface must become saturated with atomic hydrogen. If the slow discharge mechanism is rate determining, then a change in mechanism would be expected at sufficiently high current densities. As has been mentioned earlier, this permits a distinction between reaction paths (a) and (c). If no break occurs it would indicate that the slow discharge mechanism is not responsible for overvoltage. It must be born in mind that accurate overvoltage values at high current densities are very hard to make owing to the presence of concentration and resistance polarisation. To completely eliminate these at high current densities is impossible, and so certain corrections are introduced into the results that render them less accurate.

The prerequisite for any theory of overvoltage is that the Tafel equation must be derived from it. The correct value of the Tafel "b" constant is also required for an overvoltage theory to be accepted. Each of the four theories presented satisfy these requirements, but are derived from different points of view. These theories are very intriguing and the whole overvoltage phenomenon is mechanistically curious. It is not, however, the primary aim of this research to attempt to explain the mechanism of hydrogen overvoltage.

The method employed to obtain adsorption isotherms from steady state current-overvoltage measurements requires only that the Tafel equation be valid. As all of the theories of overvoltage satisfy this, the results should be correct regardless of the true overvoltage mechanism. In the same light, results obtained from double layer capacitance should be independent of the mechanism.

III. OBJECTIVES

The introduction section indicated that adsorption results on metal surfaces are very scarce and that a rapid method of obtaining such results was not available. In view of this, the primary aim of this research was to develop a suitable method for obtaining adsorption isotherms on small metal surfaces.

A quantitative measure of adsorption of organic compounds on silver and copper has not previously been reported. The homologous series of acids were chosen in an effort to determine the effect of chain length on the adsorption process. By comparing the adsorption isotherms of normal acid, alcohol, and aldehyde, the effect of the functional group on the adsorption process could be determined.

IV. MATERIALS

A. Adsorbents

1. Silver

The silver cathodes were obtained from Eastern Smelting and Refining Corporation and were listed as 99.94 per cent pure. They were approximately 4 cm^2 in geometric area.

The silver cathodes, prior to inclusion in the apparatus, were heated to 700° C in air, cooled in nitrogen, and immediately placed in the apparatus. Cathodes prepared by vacuum sputtering and by outgassing in vacuo at 700° C, in both cases breaking bulbs containing them under the solution to avoid all contact with air, gave the same results within experimental error as those prepared by the simpler technique.

2. Copper

The copper electrodes were obtained from A. D. Mackey Incorporated and were listed as 99.97 per cent pure. The geometric area was approximately the same as that of the silver electrodes.

The copper cathodes were cleaned with 1:1 nitric acid to free dissolution and washed thoroughly with water before placing in the apparatus.

B. Hydrogen

Hydrogen was purified by passage over copper turnings at 600° C, followed by passage through charcoal at 77° K. This purification treatment has been studied by Winslow (38) and has been found to reduce the oxygen content to less than 0.0001 per cent.

C. Organic Compounds

All the organic compounds used were the central fractions obtained from distillation of Eastman's best grade chemicals (except for n-caproic acid and n-heptaldehyde which were Eastman's practical grade) through a 30-plate Oldershaw column at 10-1 reflux ratio. The boiling points of the fractions used include:

	Boiling point	Pressure
Acetic acid	117.0 - 117.5°C	739 mm. Hg.
n-caproic acid	202 - 204° C	745 mm. Hg.
n-Heptylic acid	221 - 222° C	734 mm. Hg.
n-Octanoic acid	151 - 153° C	70 mm. Hg.
Heptanol-1	176 - 177° C	760 mm. Hg.
n-Heptaldehyde	150 - 151° C	740 mm. Hg.

The heptaldehyde was distilled immediately before use to minimize air oxidation.

V. EXPERIMENTAL METHOD

A. General Overvoltage Apparatus

In order to obtain reliable results, it was necessary to include in the apparatus design all the precautions necessary for reliable overvoltage measurements. These precautions are extensive and have been well summarized by Bockris and co-workers (39,40,41).

The apparatus designed and used in this research is illustrated in Figure 1. The procedure used in this research was as follows:

Perchloric acid was placed in the still compartment D, and it was sealed off. The auxiliary cathode E and the cathode K, both of the metal under investigation and suitably prepared, along with the reference electrode M (silver-silver chloride) were placed in the apparatus. The U-tube U_1 was frozen, and the standard tapered joints T_1, T_2, T_3 were sealed with mercury. The apparatus was then evacuated through stopcock S_1.

After the evacuation was completed, the apparatus was filled with hydrogen which entered the system through stopcocks S_3 and S_5. (These stopcocks were isolated from the apparatus by means of charcoal, liquid nitrogen traps N_1 and N_2.)

When the apparatus was filled with hydrogen, the U-tube U_1 was unfrozen and distilled water was allowed to flow through the reducing ion exchange column A designed to remove dissolved oxygen (42) and thence into the water still compartment B. When sufficient water had entered the still compartment, the U-tube was refrozen.

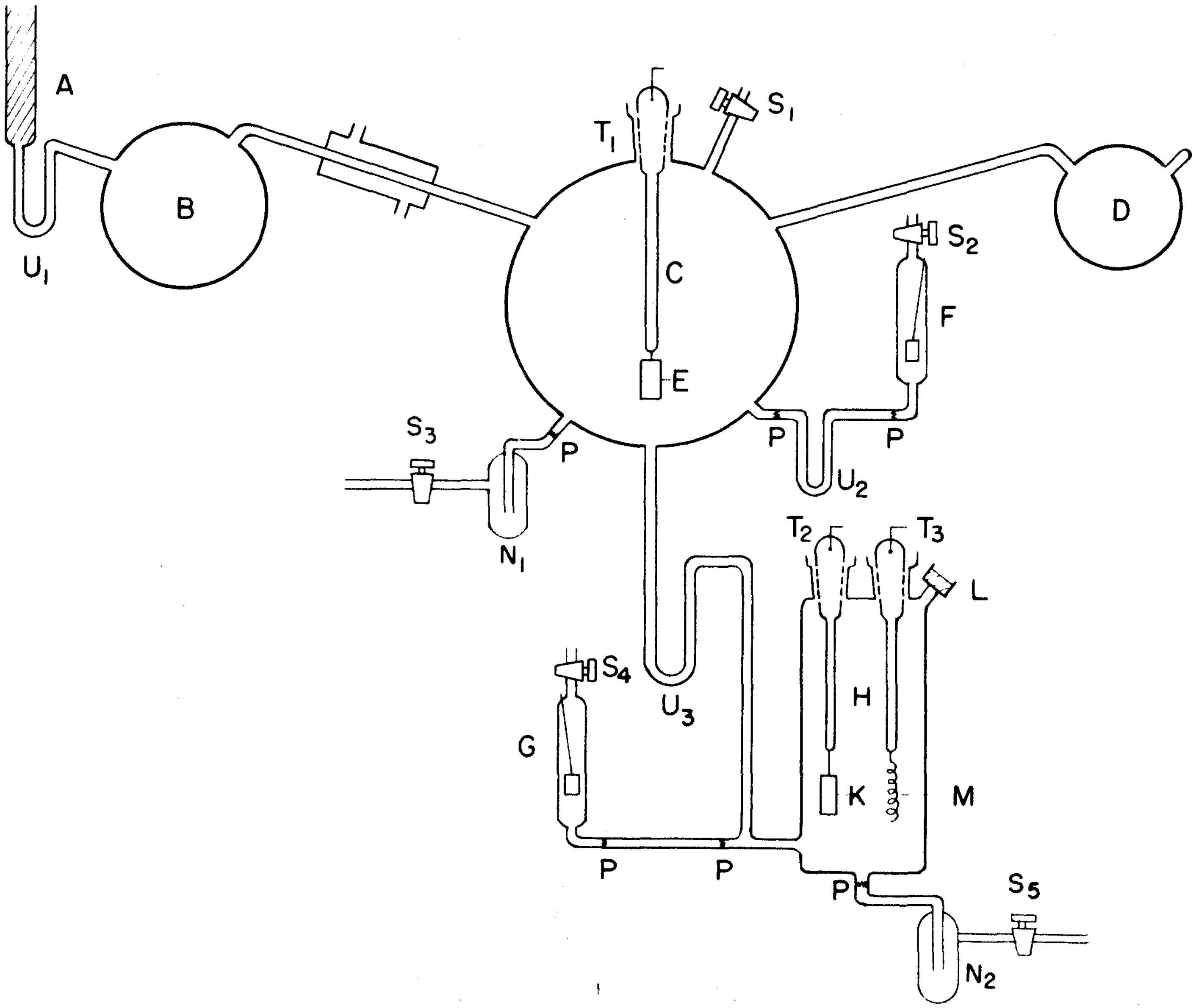


Figure 1. Hydrogen Overvoltage Apparatus

The system was re-evacuated, and the water and perchloric acid were distilled into the pre-electrolysis chamber C. The U-tube U_3 was frozen during this period to keep the water in the chamber. Hydrogen was now bubbled through the solution through stopcock S_3, and the pressure in the apparatus restored to atmospheric.

The auxiliary anode compartment F was now evacuated through stopcock S_2. The solution in the pre-electrolysis chamber C flowed through the porous plugs P and into the auxiliary anode chamber. After the chamber was filled, U-tube U_2 was frozen at about -10° C. The solution was now pre-electrolyzed for at least 12 hours at 10^{-3} amperes. The electrolysis was carried out between the auxiliary cathode E and an auxiliary platinum anode in F. The elaborate precautions for the separation of the anode and cathode compartments were necessary in order to insure that none of the oxygen released at the anode mixed with the cathode solution.

Following the pre-electrolysis, the U-tube U_3 was unfrozen. Due to gravity, the solution entered the reaction chamber H. After the solution entered the reaction chamber H, the anode compartment G was evacuated through stopcock S_4, and it was filled with the solution in the same manner as F. The anode compartment was separated from the reaction cell by means of two porous plugs P.

A concentrated potassium chloride solution was now added to the reaction chamber by means of a hypodermic syringe piercing the small rubber diaphram L which was covered with mercury.

During all the measurements, a reasonable efficient stirring was obtained and concentration polarization thereby reduced by bubbling hydrogen from stopcock S_5 through a porous plug into the solution in the neighborhood of the electrode surface. Excess hydrogen was released from the apparatus by means of a mercury bubbler.

All the measurements were made with reference to the silver-silver chloride electrode M. The solutions were approximately 0.1 N in perchloric acid and 0.001 N in potassium chloride.

B. Current Source

Current was supplied from a 250 volt source with suitable resistances in series, so that variations in current due to opposing polarization as well as the resistance of the solution were negligible. The opposing polarization would have to be larger than 2.5 volts to reduce the current even 1 per cent.

C. Steady State Method

The current source was connected to the cathode K and the platinum anode in G and the specified current applied. The potential of the cathode K was measured with reference to the silver-silver chloride electrode M by means of a Leeds and Northrup No. 7552 potentiometer. The potential was measured periodically until it changed less than 2 millivolts in 30 minutes (about three to four hours). This appears to be common practice in overvoltage measurements (39,43); it is admittedly unsatisfactory, and results from the fact that the overvoltage actually increases steadily, although in a small amount, over a period of days, and it is uncertain whether this increase is attributable to the basic electrode process.

Without switching the current off, a measured quantity of adsorbate was added to the reaction chamber by means of a hypodermic syringe piercing the rubber diaphram L. The potential was again followed until constant in the same sense (about one hour). The process was repeated at all the desired concentrations. The polarizing currents employed were 5×10^{-5} and 5×10^{-4} amperes.

D. Double Layer Capacitance Method

In measurements of double layer capacitance, a 30 minute electrolysis at the current subsequently used for measurement was carried out for the purpose of reducing any oxides on the surface of the cathode K. The potential was then allowed to decay to zero within experimental error. (This required from 30 minutes to one hour.)

The potential was followed as a function of time by connecting electrodes K and M to the Y input of a Dumont 304-H oscillograph. The current of either 5×10^{-5} or 5×10^{-4} amperes and the oscillographic sweep were triggered with a simultaneous Western Electric 275 E mercury relay switch, and a photo of the sweep taken. The initial portions of the potential-time sweeps are quite linear, and little difficulty was encountered in computing their slope.

The oscillographic sweep is calibrated with reference to time by means of time markers introduced to the oscillograph from a time generator by means of the Z input. Each picture was calibrated for potential by measuring a known potential applied to the Y input immediately after the above sweep was made.

A measured amount of adsorbate was added and after one hour the process was repeated. Although physical adsorption is rapid (44), approximately one hour was required for the cathode to return to its equilibrium potential. For this reason, about one hour was required between each capacity measurement. The process was repeated at all the desired concentrations.

VI. METHOD OF CALCULATION

A. Steady State Method

Inference of adsorption from solution from steady state current-overvoltage measurements depends on the assumption that the adsorbed material acts only as an inert blanket on the electrode surface; so that if A denotes the original electrode surface area and θ the fractional coverage by adsorbed material, then an area $A(1 - \theta)$ remains to contribute to the steady state rate of hydrogen evolution. The steady state dependence of overvoltage on current is given by the Tafel (8) equation

$$\eta = a + b \operatorname{Log} j \qquad (1)$$

in which η is the overvoltage; j the current density; and a and b, constants.

A given overvoltage implies a fixed current density; assuming that the accessible area is $A(1 - \theta)$ there results

$$\theta = 1 - \frac{i}{i_{\theta = 0}} \qquad (\eta \text{ fixed}) \qquad (2)$$

the currents being measured at the same overvoltage. Measurements at several overvoltages then permit a check for self consistency.

If the overvoltages are measured at constant current, one obtains

$$\theta = 1 - e^{\frac{\Delta\eta}{b}} \qquad (i \text{ fixed}) \qquad (3)$$

$\Delta\eta$ represents the difference in overvoltage due to introduction of adsorbate. Measurement at several currents then permits a check for self consistency.

Ch'iao and Mann (11) used equation (2) to determine their adsorption isotherms. In order to apply this equation, several current-overvoltage curves must be determined and an equal potential line drawn on the resulting graph. Because several curves must be determined experimentally, the method is time consuming, and the experimental conditions can not be kept at the optimum.

All of the steady state current-overvoltage results were obtained by means of equation (3). The constant b was taken as 0.051 = (0.118/2.303). The change in overvoltage caused by addition of the adsorbate could easily be measured with a potentiometer, and so the results could be rapidly obtained without plotting the experimental results.

B. Double Layer Capacitance

Inference of adsorption from double layer capacitance measurements depends upon the same basic assumption as that for steady state current-overvoltage measurements; namely that the adsorbed material acts only as an inert blanket on the electrode surface.

The double layer capacitance is measured by the initial rate of increase of potential with current, thus

$$C = \frac{dQ}{dE} = \frac{i}{\frac{dE}{dt}} \qquad (4)$$

since this capacity is assumed proportional to the area of surface free from adsorbate there follows immediately

$$\theta = 1 - \frac{C}{C_{\theta = 0}} \tag{5}$$

Apparent fractional surface coverages were obtained from double layer capacitance measurements by means of equation (5).

VII. EXPERIMENTAL RESULTS

A. Overvoltage Values

The object of this research was not so much to determine the overvoltage itself but the potential changes on the addition of organic compounds. It is, however, felt that the observed overvoltage values may be an indication of the cleanness of the experimental method.

The overvoltage values for silver and copper as measured in this research are compared in Table 1 with values obtained by other workers in this field. Most authors assume that the geometric surface area of the electrode is equal to the true one when calculating current density. This assumption was also made in computing the overvoltage values in this work. As the geometric area is different from the true surface area by an amount dependent on the particular electrode used, the true current densities are in error, and consequently the overvoltage values reflect the somewhat erroneous current densities used. For this reason the results presented in Table 1 show considerable variation depending on the particular worker. As the workers cited in Table 1 are experts in the field, it is felt that the major portion of the variation is due to incorrect current density values. The observed overvoltage values are believed to be in reasonable agreement with those of other workers.

B. Adsorption on Silver

The experimental results for the adsorption of the various organic compounds on silver as determined from steady state current-overvoltage

Table 1. Reported Overvoltage Values

Electrode	Current density	η*	Literature reference	
Silver	1×10^{-5}	.169	Kortum and Bockris	(45)
		.220	Bockris and Conway	(46)
		.245	Wetterholm	(12)
		.250	Hickling and Salt	(43)
		.250	This Research	
Silver	1×10^{-5}	.260	Kortum and Bockris	(45)
		.304	Bockris and Conway	(46)
		.329	Wetterholm	(12)
		.330	Hickling and Salt	(43)
		.338	This Research	
Silver	1×10^{-4}	.299	Kortum and Bockris	(45)
		.340	Bockris and Conway	(46)
		.364	Wetterholm	(12)
		.366	This Research	
		.370	Hickling and Salt	(43)
Copper	1×10^{-5}	.205	Bockris and Pentland	(18)
		.285	Wetterholm	(12)
		.328	This Research	
		.354	Kortum and Bockris	(45)
		.360	Hickling and Salt	(43)
Copper	1×10^{-5}	.287	Bockris and Pentland	(18)
		.350	Wetterholm	(12)
		.411	This Research	
		.436	Kortum and Bockris	(45)
		.440	Hickling and Salt	(43)
Copper	1×10^{-4}	.322	Bockris and Pentland	(18)
		.378	Wetterholm	(12)
		.446	This Research	
		.472	Kortum and Bockris	(45)
		.480	Hickling and Salt	(43)

*Overvoltage in volts.

measurements are presented in Tables 2 through 7. The change in the reversible potential was zero except in the case of acetic acid.

Corresponding results from double layer capacitance measurements are presented in Tables 8 through 13.

The results as obtained by both methods are presented in Figures 2 through 6. Points on the graphs are the observed points. With the exception of the n-heptaldehyde, it is felt that the points obtained by the two methods agree within experimental error; and therefore only one curve is drawn through them. With the n-heptaldehyde system, it is felt the deviation between the two methods was sufficient to warrant the drawing of two curves.

C. Adsorption on Copper

Experimental results obtained for the adsorption of various organic compounds on copper as determined from steady state current-overvoltage measurements are presented in Tables 14 through 17.

Double layer capacitance results are compiled in Tables 18 through 21.

The results as obtained by both methods are presented in Figures 7 through 10. Points on the graph are experimental points. Adsorption of all the organic compounds on copper gave slightly different results by the two methods. In light of this, two curves were drawn to indicate the adsorption isotherms as determined by the two methods.

Table 2. Adsorption of Acetic Acid on Silver

Current (ampers)	a*	ΔE (volts)	ΔE rev. (volts)	% surface covered
5×10^{-5}	.05	.0174	.0170	-1%
5×10^{-5}	.09	.0300	.0324	-4%
5×10^{-5}	.11	.0340	.0345	-1%

*Activity data are from F. A. Miller, Ph. D. Thesis, Iowa State College (1953)

Table 3. Adsorption of n-Caproic Acid on Silver

Current	C/Co	ΔE	% surface covered
5×10^{-5}	.06	.0027	5
5×10^{-5}	.13	.0041	8
5×10^{-5}	.26	.0076	14
5×10^{-5}	.45	.0113	21
5×10^{-5}	.61	.0133	24
5×10^{-5}	.74	.0147	26
5×10^{-4}	.05	.0050	10
5×10^{-4}	.16	.0070	13
5×10^{-4}	.29	.0090	17
5×10^{-4}	.42	.0100	20
5×10^{-4}	.55	.0111	22
5×10^{-4}	.68	.0117	23
5×10^{-4}	.82	.0121	23
5×10^{-4}	.95	.0122	23
5×10^{-5}	.05	.0039	7
5×10^{-5}	.11	.0053	10
5×10^{-5}	.22	.0076	14
5×10^{-5}	.33	.0106	19
5×10^{-5}	.44	.0133	23
5×10^{-5}	.56	.0149	25

Table 4. Adsorption of n-Heptylic Acid on Silver

Current	C/C_o	ΔE	% surface covered
5×10^{-5}	.03	.0029	6
5×10^{-5}	.07	.0050	10
5×10^{-5}	.16	.0080	15
5×10^{-5}	.32	.0144	25
5×10^{-5}	.43	.0184	31
5×10^{-4}	.05	.0044	9
5×10^{-4}	.15	.0078	15
5×10^{-4}	.25	.0105	19
5×10^{-4}	.35	.0144	26
5×10^{-4}	.45	.0159	28
5×10^{-4}	.55	.0189	32
5×10^{-4}	.65	.0191	32
5×10^{-4}	.75	.0201	33
5×10^{-4}	.85	.0205	34
5×10^{-4}	.95	.0216	35
5×10^{-5}	.1	.0074	14
5×10^{-5}	.2	.0120	21
5×10^{-5}	.3	.0150	26
5×10^{-5}	.4	.0175	30
5×10^{-5}	.5	.0188	32
5×10^{-5}	.6	.0190	32
5×10^{-5}	.7	.0205	34
5×10^{-5}	.8	.0213	35

Table 5. Adsorption of n-Octanoic Acid on Silver

Current	C/C_o	ΔE	% surface covered
5×10^{-5}	.047	.0040	8
5×10^{-5}	.097	.0076	15
5×10^{-5}	.190	.0119	22
5×10^{-5}	.290	.0194	33
5×10^{-5}	.380	.0222	36
5×10^{-5}	.480	.0235	38
5×10^{-5}	.670	.0290	44
5×10^{-5}	.860	.0322	47
5×10^{-4}	.10	.005	11
5×10^{-4}	.15	.0096	17
5×10^{-4}	.25	.0153	26
5×10^{-4}	.40	.0242	39
5×10^{-4}	.60	.0303	47
5×10^{-4}	.80	.0305	47
5×10^{-5}	.05	.0045	9
5×10^{-5}	.19	.0149	26
5×10^{-5}	.34	.0222	36
5×10^{-5}	.48	.0257	40
5×10^{-5}	.67	.0290	45
5×10^{-5}	.86	.0291	45

Table 6. Adsorption of Heptanol-1 on Silver

Current	C/C_0	ΔE	% surface covered
5×10^{-4}	.06	.0064	12
5×10^{-4}	.12	.0128	23
5×10^{-4}	.24	.0203	34
5×10^{-4}	.37	.0253	40
5×10^{-4}	.52	.0273	43
5×10^{-4}	.67	.0293	45
5×10^{-4}	.82	.0310	47
5×10^{-5}	.07	.0070	14
5×10^{-5}	.14	.0119	25
5×10^{-5}	.27	.0179	30
5×10^{-5}	.43	.0209	35
5×10^{-5}	.60	.0257	40
5×10^{-5}	.77	.0304	46
5×10^{-5}	.94	.0349	50

Table 7. Adsorption of n-Heptaldehyde on Silver

Current	C/C_o	ΔE	% surface covered
5×10^{-5}	.045	.0146	25
5×10^{-5}	.09	.0249	40
5×10^{-5}	.135	.0287	44
5×10^{-5}	.18	.0362	52
5×10^{-5}	.27	.0442	59
5×10^{-5}	.39	.0534	64
5×10^{-5}	.61	.0590	70
5×10^{-5}	.84	.0606	71

Table 8. Adsorption of Acetic Acid on Silver

	Current 5 x 10^{-5}		Current 5 x 10^{-4}	
A*	Capacity x 10^{-4} (Farads)	% surface covered	Capacity x 10^{-4} (Farads)	% surface covered
0.000	1.359		1.136	
0.000	1.361		1.141	
.047	1.361	0	1.092	5
.084	1.573	-15	1.125	1
.110	1.564	-15	1.316	-15
0.000	1.162		.9710	
0.000	1.140		.9754	
.047	1.008	13	.9290	5
.084	1.290	-11	.9910	- 2
.110	1.374	-18	1.015	- 4

*Activity data are from F. A. Miller, Ph. D. Thesis, Iowa State College (1953).

Table 9. Adsorption of n-Caproic Acid on Silver

	Current 5 x 10^{-5}		Current 5 x 10^{-4}	
$\frac{C}{C_o}$	Capacity x 10^{-4}	% surface covered	Capacity x 10^{-4}	% surface covered
0.00	4.090		3.068	
0.00	3.982		3.046	
.04	3.712	8.0	2.947	3.6
.10	3.584	11.2	2.874	6.0
.21	3.329	17.5		
.31	3.287	18.5	2.510	17.9
.52	2.979	26.2	2.482	18.8
.73	2.892	28.4	2.441	20.2
.93	2.888	28.5	2.414	21.0
0.00	3.933		3.070	
0.00	3.960		2.999	
.04	3.623	8.2	2.799	7.8
.10	3.423	13.2	2.643	12.9
.21	3.361	14.9		
.31	3.188	19.2	2.556	15.8
.52	3.131	20.7	2.436	20.0
.73	3.094	21.4	2.387	21.3
.93	3.117	21.1	2.400	20.9
0.00	4.237		2.802	
0.00	4.254		2.833	
.04	3.885	8.5	2.731	3.1
.10	3.626	14.6	2.651	6.0
.21			2.611	10.0
.31	3.437	19.1	2.427	13.9
.52	3.399	20.0	2.312	18.0
.73	3.406	19.8	2.250	20.2
.93	3.283	22.7	2.250	20.2

Table 10. Adsorption of n-Heptylic Acid on Silver

$\frac{C}{C_o}$	Current	Capacity x 10^{-4}	% surface covered
0.00	5×10^{-5}	4.140	
.07	5×10^{-5}	3.710	10.4
.13	5×10^{-5}	3.600	13.0
.27	5×10^{-5}	3.140	24.2
.40	5×10^{-5}	2.870	30.7
.66	5×10^{-5}	2.790	32.6
.93	5×10^{-5}	2.870	30.7
0.00	5×10^{-5}	3.200	
0.00	5×10^{-5}	3.200	
.05	5×10^{-5}	3.090	3.4
.05	5×10^{-5}	2.780	13.1
.11	5×10^{-5}	2.690	15.9
.21	5×10^{-5}	2.520	21.2
.32	5×10^{-5}	2.480	22.5
.43	5×10^{-5}	2.320	27.5
.64	5×10^{-5}	2.300	28.1
.85	5×10^{-5}	2.310	27.8
1.00	5×10^{-5}	2.290	28.4
0.00	5×10^{-4}	2.420	
0.00	5×10^{-4}	2.420	
.02	5×10^{-4}	2.350	3.0
.04	5×10^{-4}	2.220	8.3
.06	5×10^{-4}	2.220	8.3
.09	5×10^{-4}	2.110	12.8
.14	5×10^{-4}	2.110	12.8
.19	5×10^{-4}	2.080	14.0
.28	5×10^{-4}	1.810	25.2
.46	5×10^{-4}	1.680	30.6
.65	5×10^{-4}	1.660	31.6
.84	5×10^{-4}	1.660	31.6
0.00	5×10^{-5}	2.230	
0.00	5×10^{-5}	2.290	
0.00	5×10^{-5}	2.230	
.02	5×10^{-5}	2.170	3.6
.05	5×10^{-5}	1.970	12.4
.09	5×10^{-5}	1.900	15.6
.19	5×10^{-5}	1.830	18.7
.28	5×10^{-5}	1.810	19.6
.47	5×10^{-5}	1.670	25.8

Table 10. (continued)

$\frac{C}{C_o}$	Current	Capacity x 10^{-4}	% surface covered
.56	5×10^{-5}	1.620	28.0
.74	5×10^{-5}	1.590	29.5
.93	5×10^{-5}	1.590	29.5
.93	5×10^{-5}	1.590	29.5
.93	5×10^{-5}	1.590	29.5

Table 11. Adsorption of n-Octanoic Acid on Silver

$\frac{C}{C_o}$	Current	Capacity x 10^{-4}	% surface covered
0.00	5×10^{-4}	6.620	
0.00	5×10^{-4}	6.680	
0.00	5×10^{-4}	6.680	
.04	5×10^{-4}	6.840	- 2.7
.07	5×10^{-4}	6.150	7.7
.11	5×10^{-4}	5.530	17.0
.18	5×10^{-4}	5.140	22.8
.29	5×10^{-4}	4.750	28.7
.43	5×10^{-4}	4.620	30.6
.57	5×10^{-4}	4.200	37.0
0.00	5×10^{-5}	2.690	
0.00	5×10^{-5}	2.670	
0.00	5×10^{-5}	2.740	
.05	5×10^{-5}	2.930	- 8.5
.10	5×10^{-5}	2.600	3.7
.15	5×10^{-5}	2.160	20.0
.20	5×10^{-5}	2.015	25.4
.25	5×10^{-5}	1.910	29.3
.30	5×10^{-5}	1.830	32.2
.40	5×10^{-5}	1.720	36.3
.50	5×10^{-5}	1.570	41.9
.60	5×10^{-5}	1.820	32.6
.70	5×10^{-5}	1.600	40.8
.80	5×10^{-5}	1.490	44.8
.90	5×10^{-5}	1.310	51.5
1.00	5×10^{-5}	1.210	54.2
0.00	5×10^{-5}	2.520	
.10	5×10^{-5}	2.250	10.7
.14	5×10^{-5}	2.020	19.9
.19	5×10^{-5}	1.940	23.0
.24	5×10^{-5}	1.780	29.4
.29	5×10^{-5}	1.790	29.0
.38	5×10^{-5}	1.700	32.5
.48	5×10^{-5}	1.600	36.5
.57	5×10^{-5}	1.550	38.5
.67	5×10^{-5}	1.460	42.1
.76	5×10^{-5}	1.440	42.9
.86	5×10^{-5}	1.370	45.6
.95	5×10^{-5}	1.440	42.9
1.00	5×10^{-5}	1.370	45.6
0.00	5×10^{-4}	2.750	
0.00	5×10^{-4}	2.750	

Table 11. (continued)

$\frac{C}{C_o}$	Current	Capacity x 10^{-4}	% surface covered
.10	5×10^{-4}	2.560	6.9
.20	5×10^{-4}	2.010	26.9
.30	5×10^{-4}	1.840	33.1
.40	5×10^{-4}	1.780	35.3
.60	5×10^{-4}	1.640	40.4
.70	5×10^{-4}	1.540	43.0
.80	5×10^{-4}	1.520	43.7
.90	5×10^{-4}	1.450	46.3
1.00	5×10^{-4}	1.350	50.0

Table 12. Adsorption of Heptanol-1 on Silver

	Current 5 x 10^{-5}		Current 5 x 10^{-4}	
$\frac{C}{C_o}$	Capacity x 10^{-4}	% surface covered	Capacity x 10^{-4}	% surface covered
0.00	5.615		4.323	
0.00	5.740		4.195	
.06	4.696	16.3	3.611	15.3
.12	4.305	24.2	3.160	25.8
.21	3.690	35.1	2.889	32.2
.30	3.381	40.5	2.645	37.9
.47	3.332	41.3	2.584	39.3
.67	3.332	41.3	2.584	39.3
.87	2.916	48.7	2.267	46.8
0.00	5.271		4.021	
0.00	5.271		3.966	
.06	4.920	6.7	3.272	18.1
.12	3.974	24.6	2.890	27.6
.21	3.638	31.0	2.690	34.7
.30	3.589	32.0	2.445	38.8
.47	3.333	36.8	2.445	38.8
.67	3.333	36.8	2.439	38.9
.87	3.010	42.9	2.416	40.0
0.00	4.612		3.355	
0.00	4.696		3.306	
.06	4.132	11.2	2.733	18.0
.12	3.270	29.8	2.575	22.7
.21	3.228	30.7	2.225	33.2
.30	3.110	33.2	2.033	39.0
.47	2.916	37.4	2.104	36.9
.67	2.916	37.4	2.071	37.8
.87	2.777	40.4	1.950	41.5

Table 13. Adsorption of n-Heptaldehyde on Silver

	Current 5 x 10^{-5}		Current 5 x 10^{-4}	
$\frac{C}{C_o}$	Capacity x 10^{-4}	% surface covered	Capacity x 10^{-4}	% surface covered
0.00	2.836		2.269	
0.00	2.836		2.302	
.05	1.663	41.4	1.505	34.2
.10	1.377	51.5	1.231	46.1
.14	1.176	58.6	1.039	54.5
.20	1.071	61.2	.9076	60.3
.30	1.026	63.8	.9372	59.0
.40	1.052	63.0	.4087	60.3
.58	1.016	64.2	.8519	62.7
.75	1.016	64.2	.8455	63.0
.93	.971	65.8	.8455	63.0
0.00	2.143		1.906	
0.00	2.192		1.863	
.05	1.303	40.0	1.151	38.9
.10	.9098	58.0	.9271	50.8
.14	.7777	64.0	.7698	59.1
.20	.7534	65.2	.6789	64.0
.30	.7091	67.3	.6632	64.8
.40	.7097	67.3	.6441	65.8
.58	.7097	67.3	.6491	65.6
.75	.7097	67.3	.6367	66.2
.93	.7097	67.3	.6367	66.2
0.00	2.243		2.174	
0.00	2.296		2.116	
.05	1.377	39.4	1.204	43.9
.10	1.176	48.2	.9172	57.2
.14	.7778	65.7	.8948	59.0
.20	.8173	64.0	.7185	66.5
.30	.7653	66.3	.6953	67.6
.40	.7577	66.6	.6815	68.2
.58	.7577	66.6	.6649	69.1
.75	.7642	66.4	.6970	67.5
.93	.7577	66.6	.6970	67.5

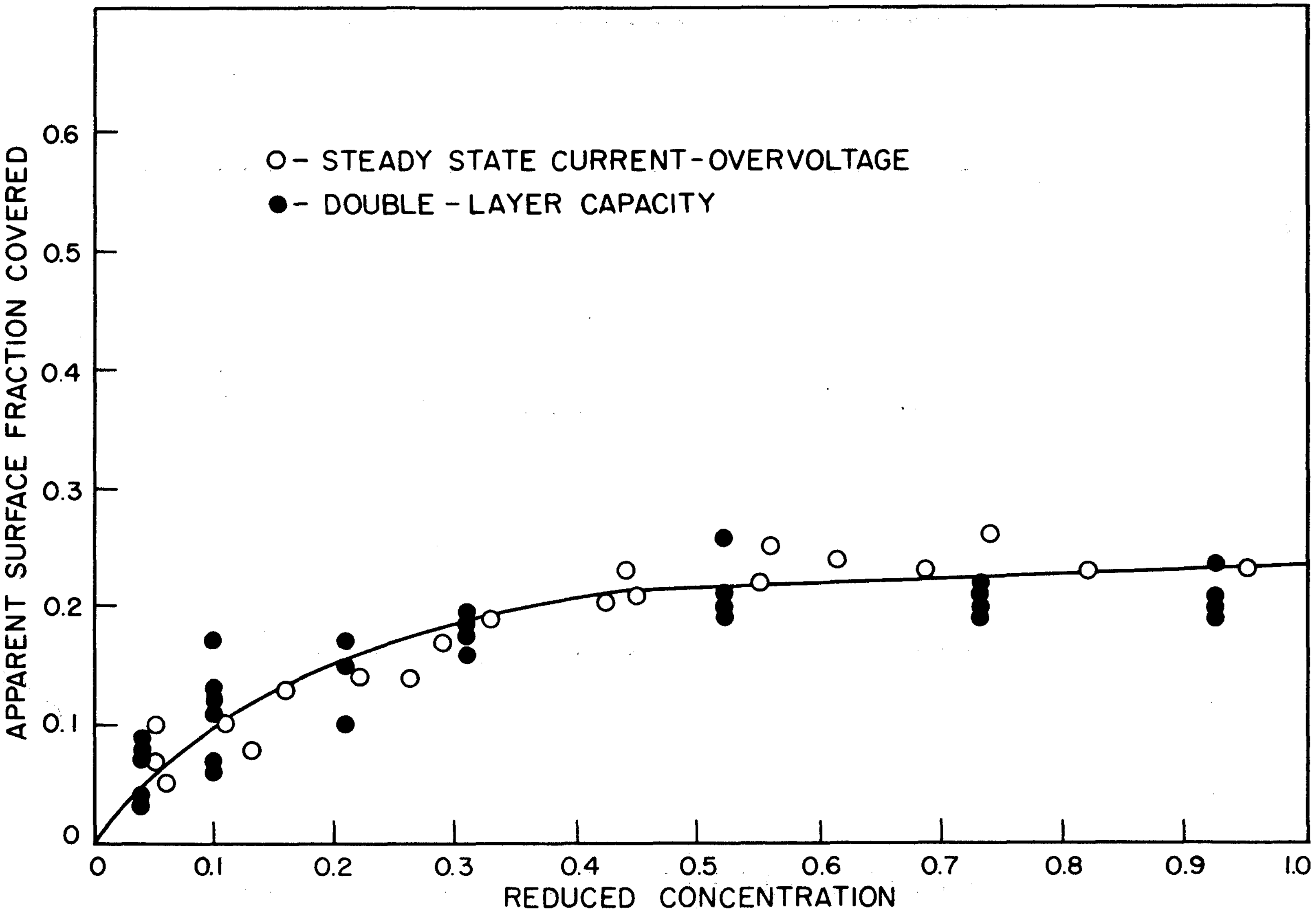


Figure 2. Adsorption of n-Caproic Acid on Silver

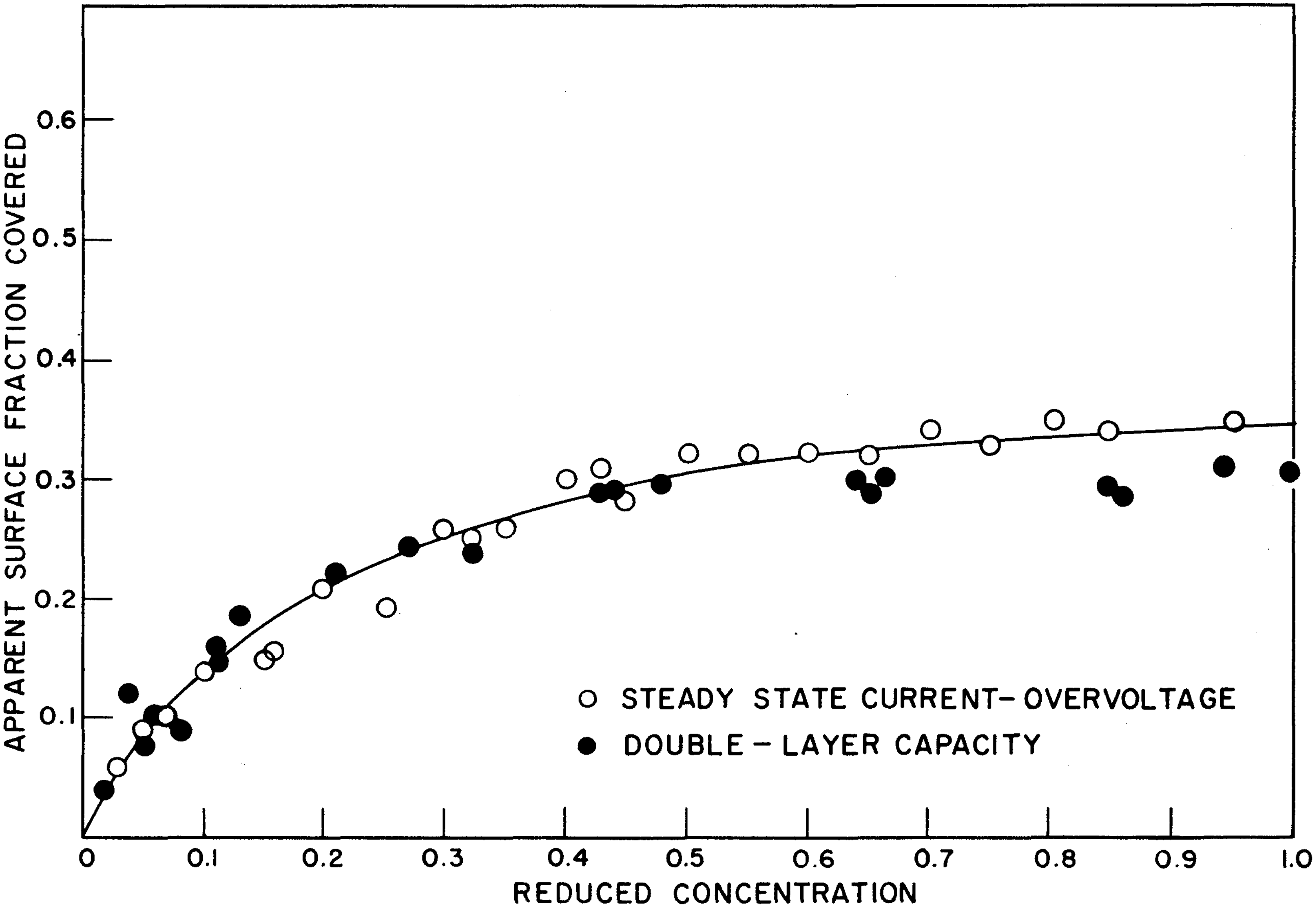


Figure 3. Adsorption of n-Heptylic Acid on Silver

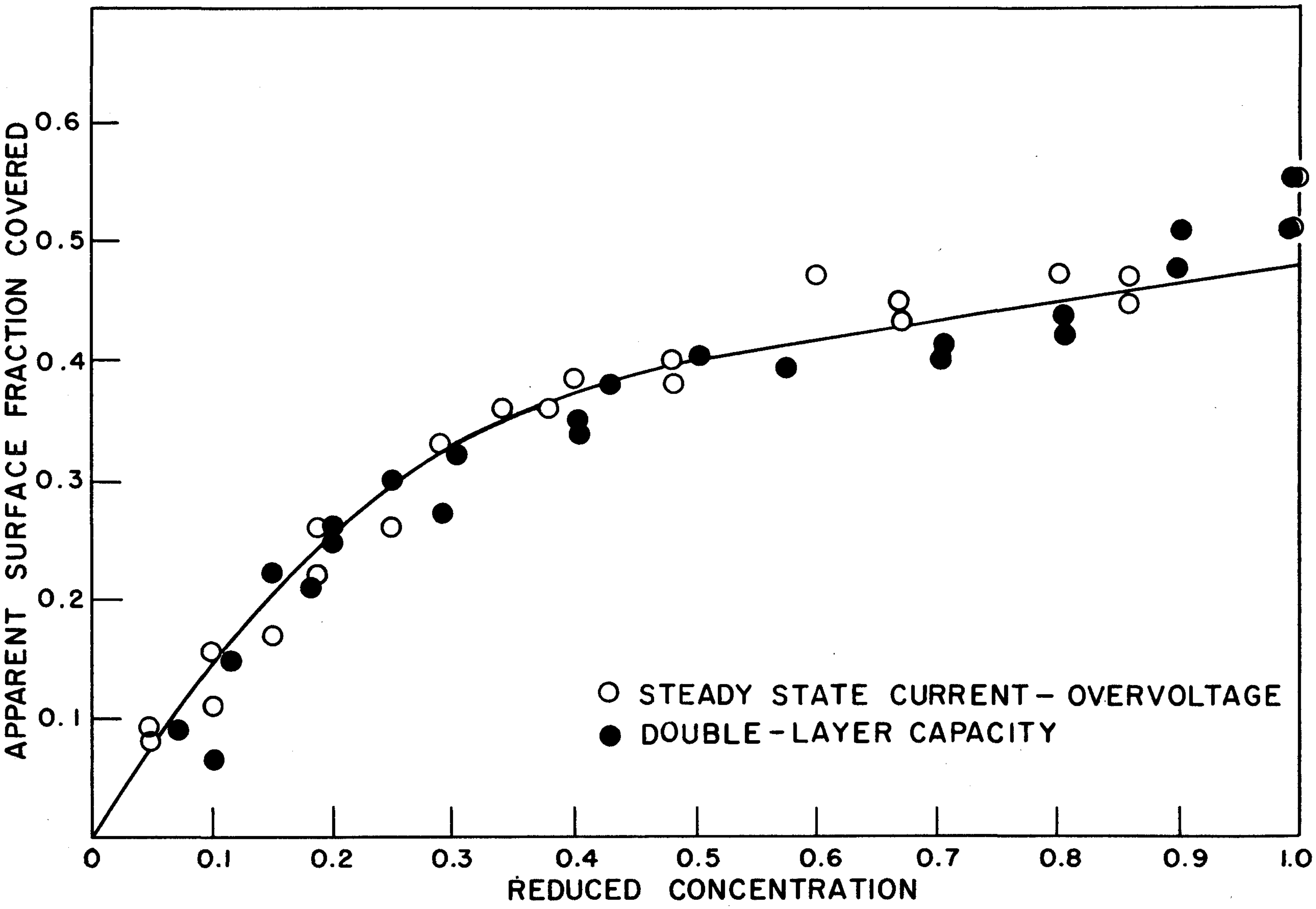


Figure 4. Adsorption of n-Octanoic Acid on Silver

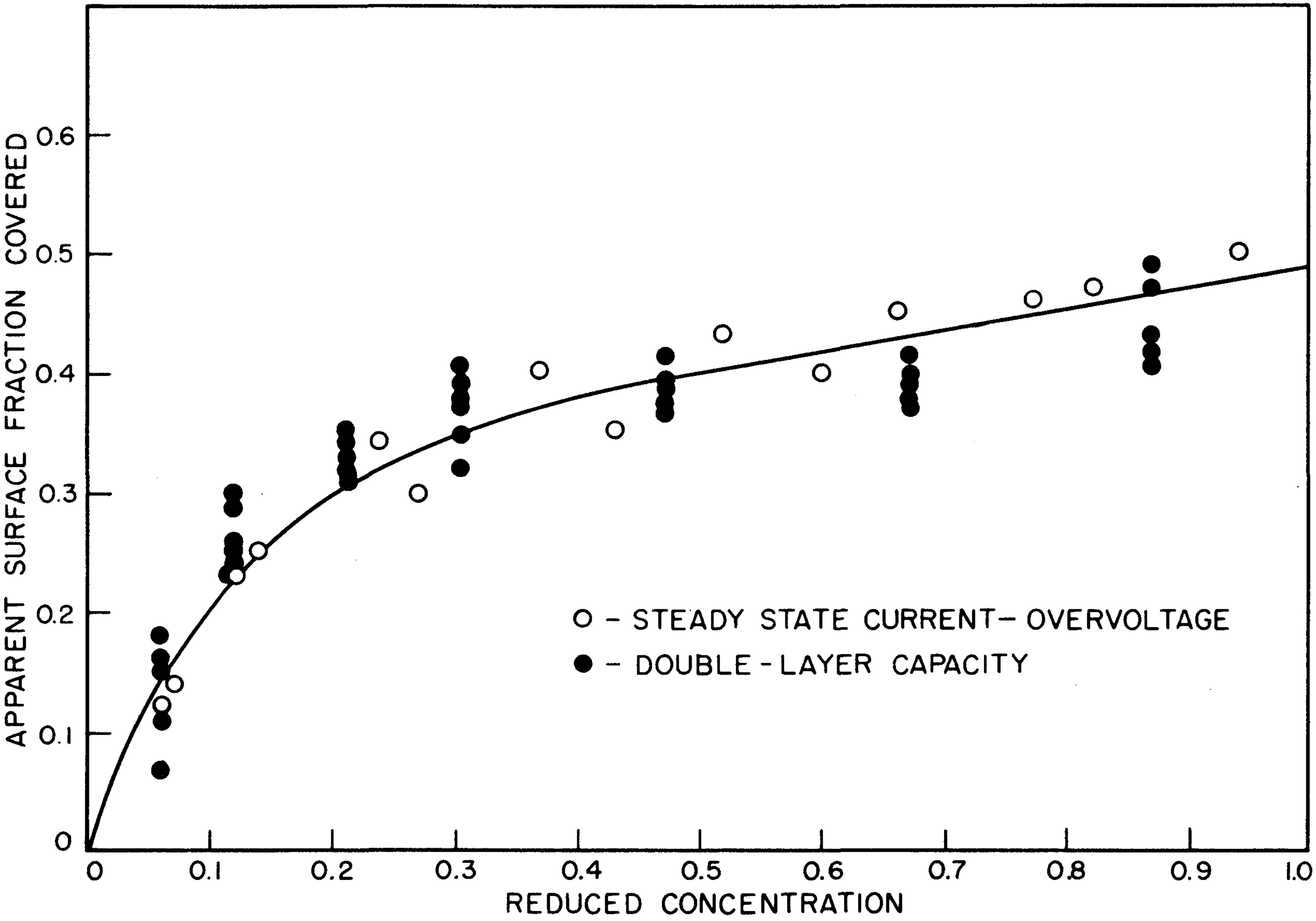


Figure 5. Adsorption of Heptanol-1 on Silver

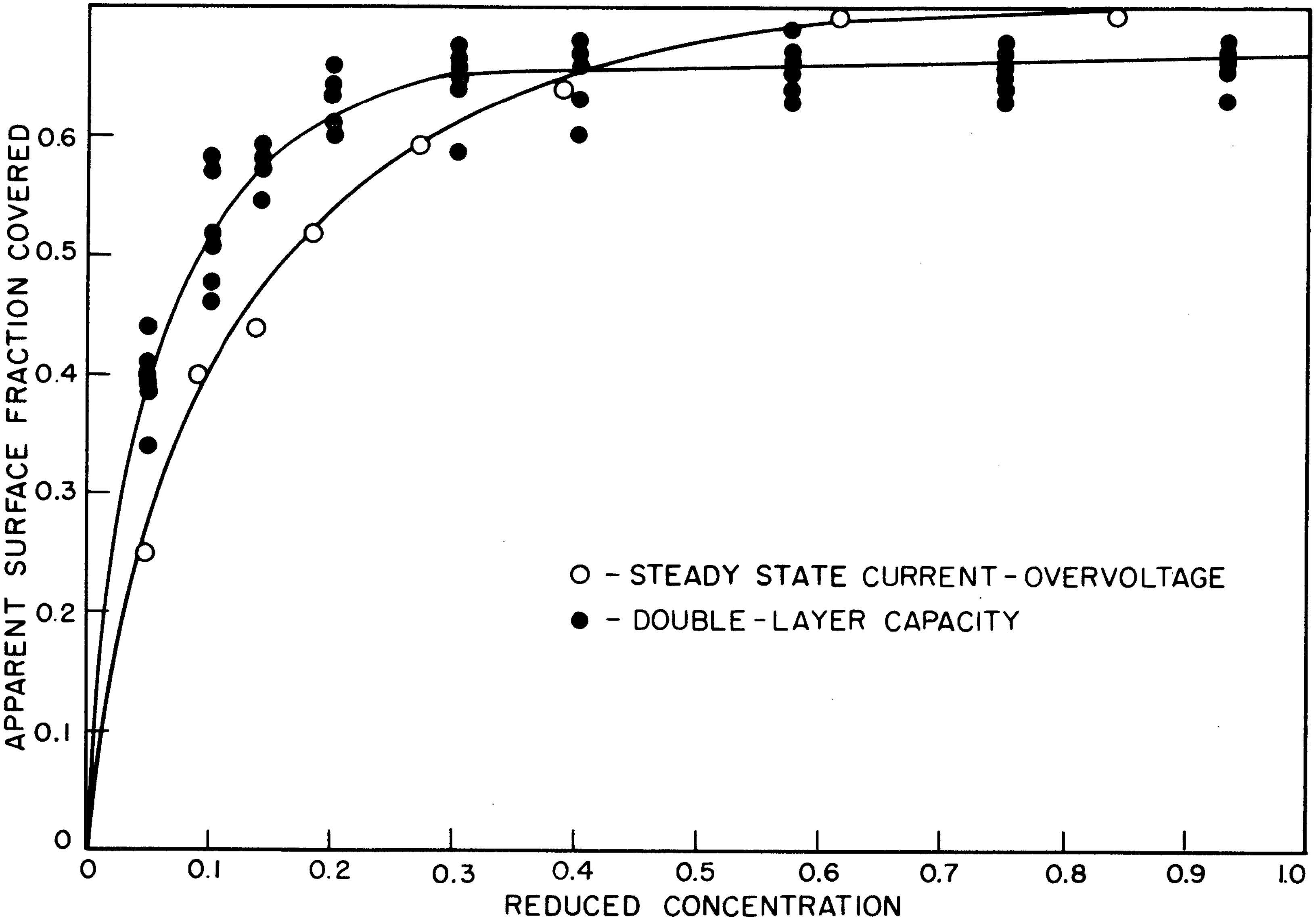


Figure 6. Adsorption of n-Heptaldehyde on Silver

Table 14. Adsorption of n-Heptylic Acid on Copper

Current (ampers)	C/C_o	ΔE (volts)	% surface covered
5×10^{-4}	.04	.0015	3
5×10^{-4}	.10	.0027	5
5×10^{-4}	.22	.0044	9
5×10^{-4}	.34	.0066	13
5×10^{-4}	.46	.0072	14
5×10^{-4}	.71	.0100	19
5×10^{-4}	.95	.0126	23
5×10^{-5}	.06	.0027	5
5×10^{-5}	.11	.0029	6
5×10^{-5}	.22	.0041	8
5×10^{-5}	.34	.0058	12
5×10^{-5}	.45	.0061	12
5×10^{-5}	.68	.0076	15
5×10^{-5}	.90	.0099	19
5×10^{-5}	.06	.0025	5
5×10^{-5}	.12	.0048	9
5×10^{-5}	.17	.0051	10
5×10^{-5}	.23	.0066	13
5×10^{-5}	.35	.0079	15
5×10^{-5}	.58	.0090	17
5×10^{-5}	.81	.0115	21

Table 15. Adsorption of n-Octanoic Acid on Copper

Current	C/C_o	ΔE	% surface covered
5×10^{-4}	.05	.0020	4
5×10^{-4}	.15	.0102	19
5×10^{-4}	.25	.0108	20
5×10^{-4}	.41	.0147	25
5×10^{-4}	.56	.0175	30
5×10^{-4}	.71	.0213	35
5×10^{-4}	.86	.0221	35
5×10^{-5}	.10	.0041	8
5×10^{-5}	.15	.0074	14
5×10^{-5}	.20	.0099	19
5×10^{-5}	.25	.0111	20
5×10^{-5}	.44	.0125	23
5×10^{-5}	.64	.0142	26
5×10^{-5}	.84	.0167	30
5×10^{-5}	.05	.0033	7
5×10^{-5}	.10	.0053	11
5×10^{-5}	.20	.0084	16
5×10^{-5}	.35	.0107	19
5×10^{-5}	.49	.0128	23
5×10^{-5}	.69	.0165	31
5×10^{-5}	.89	.0203	34

Table 16. Adsorption of Heptanol-1 on Copper

Current	C/C_o	ΔE	% surface covered
5×10^{-5}	.06	.0039	8
5×10^{-5}	.12	.0085	16
5×10^{-5}	.25	.0104	19
5×10^{-5}	.40	.0139	25
5×10^{-5}	.55	.0169	29
5×10^{-5}	.72	.0183	32
5×10^{-5}	.91	.0240	39
5×10^{-4}	.07	.0065	12
5×10^{-4}	.14	.0090	17
5×10^{-4}	.22	.0114	21
5×10^{-4}	.36	.0147	26
5×10^{-4}	.50	.0164	29
5×10^{-4}	.65	.0199	33
5×10^{-4}	.80	.0218	36
5×10^{-4}	.07	.0082	15
5×10^{-4}	.14	.0108	20
5×10^{-4}	.22	.0136	24
5×10^{-4}	.36	.0171	29
5×10^{-4}	.50	.0184	31
5×10^{-4}	.65	.0214	35

Table 17. Adsorption of n-Heptaldehyde on Copper

Current	C/C_0	ΔE	% surface covered
5×10^{-5}	.03	.0026	5
5×10^{-5}	.07	.0072	14
5×10^{-5}	.12	.0153	26
5×10^{-5}	.17	.0190	32
5×10^{-5}	.25	.0309	47
5×10^{-5}	.35	.0400	55
5×10^{-5}	.45	.0444	59
5×10^{-5}	.66	.0459	61
5×10^{-5}	.86	.0465	61
5×10^{-4}	.05	.0042	8
5×10^{-4}	.11	.0136	24
5×10^{-4}	.16	.0201	33
5×10^{-4}	.21	.0266	42
5×10^{-4}	.32	.0369	53
5×10^{-4}	.43	.0442	59
5×10^{-4}	.53	.0477	62
5×10^{-4}	.75	.0479	62
5×10^{-4}	.96	.0483	63

Table 18. Adsorption of n-Heptylic Acid on Copper

	Current 5 x 10^{-5}		Current 5 x 10^{-4}	
$\frac{C}{C_o}$	Capacity x 10^{-4} (Farads)	% surface covered	Capacity x 10^{-4} (Farads)	% surface covered
0.00	4.193		3.413	
0.00	4.193		3.354	
.05	3.857	8.0	3.153	6.8
.10	3.709	11.6	3.018	10.8
.16	3.444	17.9	2.674	21.0
.31	3.215	23.4	2.577	23.8
.45	3.215	23.4	2.577	23.8
.54	3.215	23.4	---	—
.64	3.111	25.9	2.457	27.4
.84	3.215	23.4	2.457	27.4
0.00	4.384		3.762	
0.00	4.592		3.912	
.05	4.384	2.4	3.706	3.5
.10	4.018	10.5	3.521	8.3
.16	3.857	14.1	3.107	19.0
.31	3.709	17.4	3.018	21.4
.45	3.572	20.5	2.934	23.6
.54	3.215	28.4	2.780	27.5
.64	3.215	28.4	2.780	27.5
.84	3.215	28.4	2.780	27.5
0.00	4.384		3.544	
0.00	4.384		3.581	
.05	4.018	8.4	3.301	7.4
.10	4.018	8.4	3.201	10.2
.16	3.709	15.4	2.894	18.8
.31	3.325	24.2	2.641	25.9
.45	3.325	24.2	2.708	24.0
.54	3.215	26.7	2.641	25.9
.64	3.215	26.7	2.608	26.8
.84	3.215	26.7	2.608	26.8

Table 19. Adsorption of n-Octanoic Acid on Copper

$\frac{C}{C_o}$	Current 5×10^{-5}		Current 5×10^{-4}	
	Capacity $\times 10^{-4}$	% surface covered	Capacity $\times 10^{-4}$	% surface covered
0.00	4.342		3.134	
0.00	4.383		3.276	
.06	3.757	13.9	2.755	14.1
.13	3.682	15.6	2.656	17.1
.26	3.255	25.4	2.450	23.6
.39	3.158	27.6	2.227	30.5
.51	2.839	34.9	2.194	31.5
.71	2.851	34.7	—	—
.90	2.851	34.7	2.066	35.5
0.00	4.911		3.446	
0.00	5.009		3.398	
.06	4.368	11.9	3.057	10.7
.13	4.065	18.0	2.811	17.9
.26	3.369	32.0	2.539	25.8
.39	3.485	29.7	2.452	28.4
.51	3.325	33.0	2.302	32.7
.71	3.187	35.7	2.196	35.8
.90	3.187	35.7	2.200	35.8

Table 20. Adsorption of Heptanol-1 on Copper

	Current 5×10^{-5}		Current 5×10^{-4}	
$\frac{C}{C_o}$	Capacity x 10^{-4}	% surface covered	Capacity x 10^{-4}	% surface covered
0.00	4.337		3.890	
0.00	4.337		3.825	
.05	3.325	23.3	3.326	13.8
.10	3.325	23.3	3.102	19.6
.20	3.025	30.3	2.732	29.2
.40	2.771	36.1	2.495	35.3
.55	2.494	42.5	2.427	37.1
.72	2.558	41.4	2.427	37.1
.90	2.494	42.5	2.326	39.7
0.00	3.695		3.375	
0.00	3.695		3.362	
.05	3.117	15.7	2.799	16.4
.10	2.850	22.9	2.608	20.0
.20	2.494	32.5	2.318	30.8
.40	2.267	38.7	2.086	37.8
.55	2.267	38.7	2.042	39.0
.72	2.169	41.3	2.042	39.0
.90	2.169	41.3	1.994	40.5
0.00	3.837		3.586	
0.00	3.837		3.478	
.05	3.117	18.8	3.101	12.3
.10	2.934	23.6	2.732	22.7
.20	2.771	27.8	2.522	28.6
.40	2.625	31.6	2.295	35.0
.55	2.558	33.4	2.236	36.7
.72	2.375	38.1	2.236	36.7
.90	2.375	38.1	2.204	37.6

Table 21. Adsorption of n-Heptaldehyde on Copper

$\frac{C}{C_o}$	Current 5×10^{-5}		Current 5×10^{-4}	
	Capacity x 10^{-4}	% surface covered	Capacity x 10^{-4}	% surface covered
0.00	4.508		3.090	
0.00	4.508		3.141	
.05	3.945	12.5	2.813	9.7
.10	3.264	27.6	2.298	26.3
.20	2.491	44.8	2.142	31.2
.35	2.152	52.3	1.682	46.0
.50	1.932	57.2	1.523	51.1
.70	1.932	57.2	1.449	53.5
.90	1.932	57.2	1.449	53.5
0.00	3.787		3.094	
0.00	3.945		3.046	
.05	3.381	12.6	2.267	26.2
.10	2.559	33.9	1.990	35.2
.20	2.367	38.8	1.625	47.1
.35	1.721	55.5	1.466	52.3
.50	1.753	54.7	1.250	59.3
.70	1.479	61.8	1.189	61.3
.90	1.413	63.5	1.196	61.1
0.00	4.508		3.247	
0.00	4.508		3.305	
.05	3.381	25.0	2.377	27.5
.10	2.958	34.4	2.166	34.0
.20	2.630	41.7	2.031	38.1
.35	1.970	56.3	1.598	51.2
.50	1.856	58.9	1.535	53.2
.70	1.893	58.1	1.477	55.0
.90	1.821	59.7	1.434	56.3

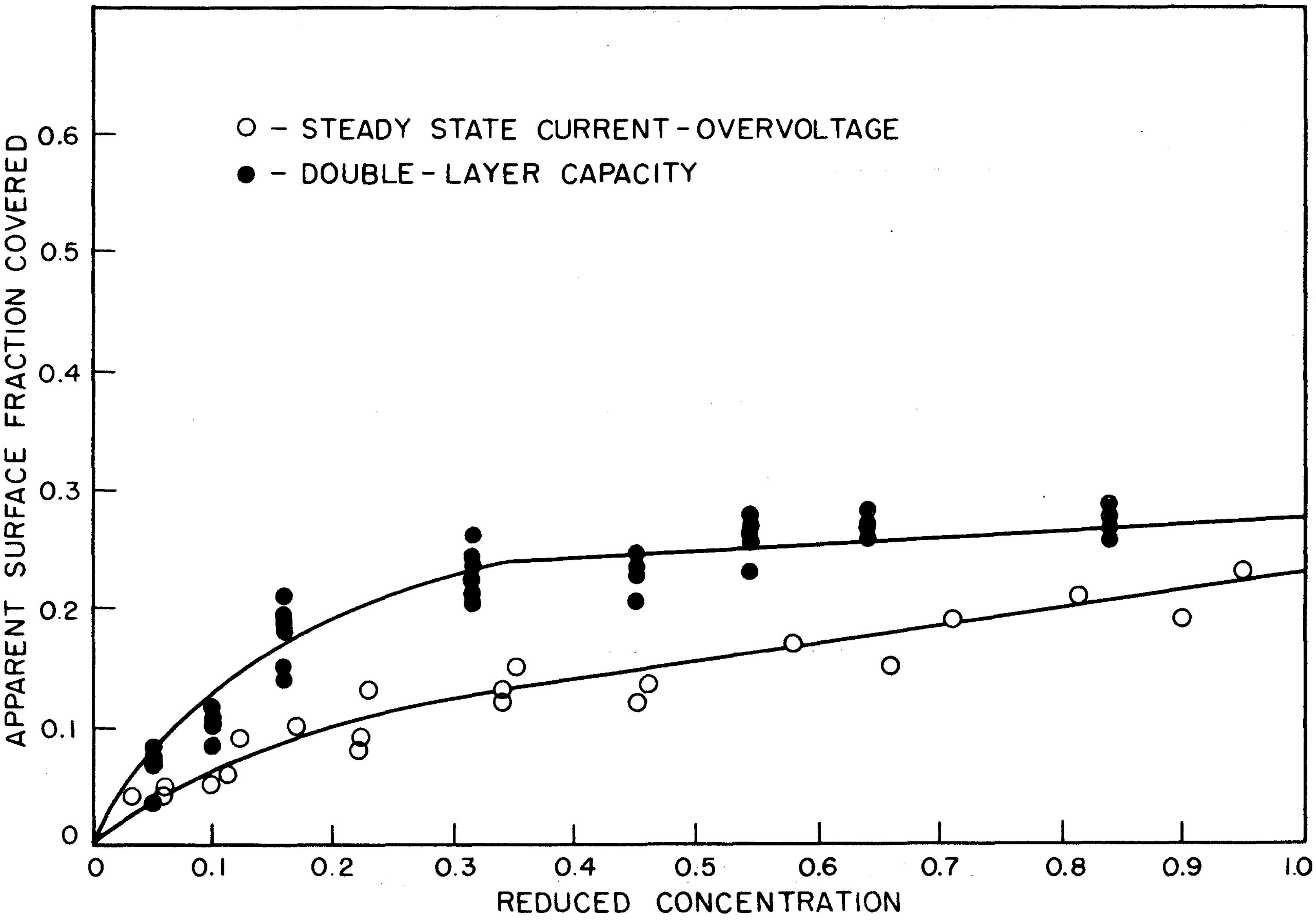


Figure 7. Adsorption of n-Heptylic Acid on Copper

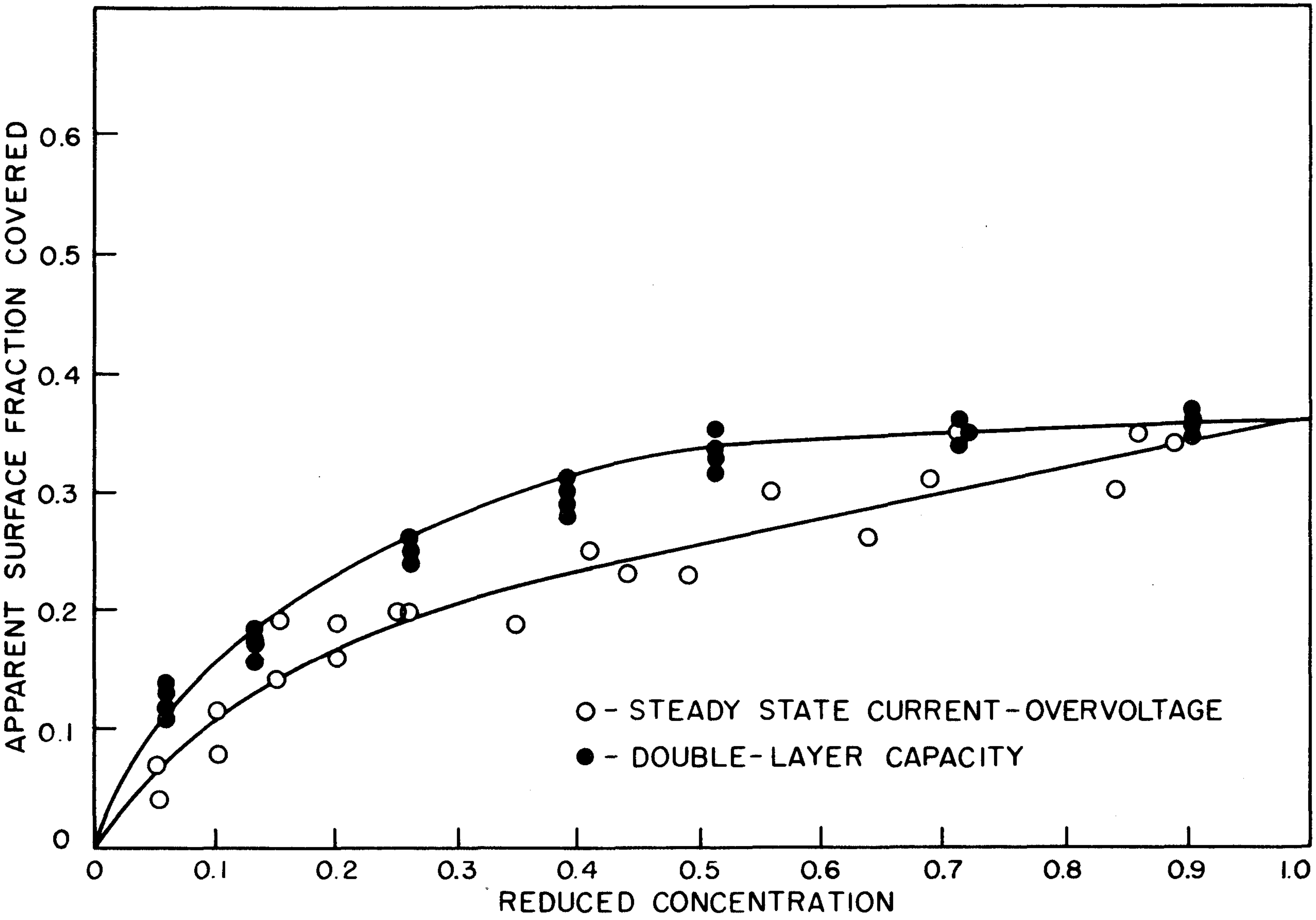


Figure 8. Adsorption of n-Octanoic Acid on Copper

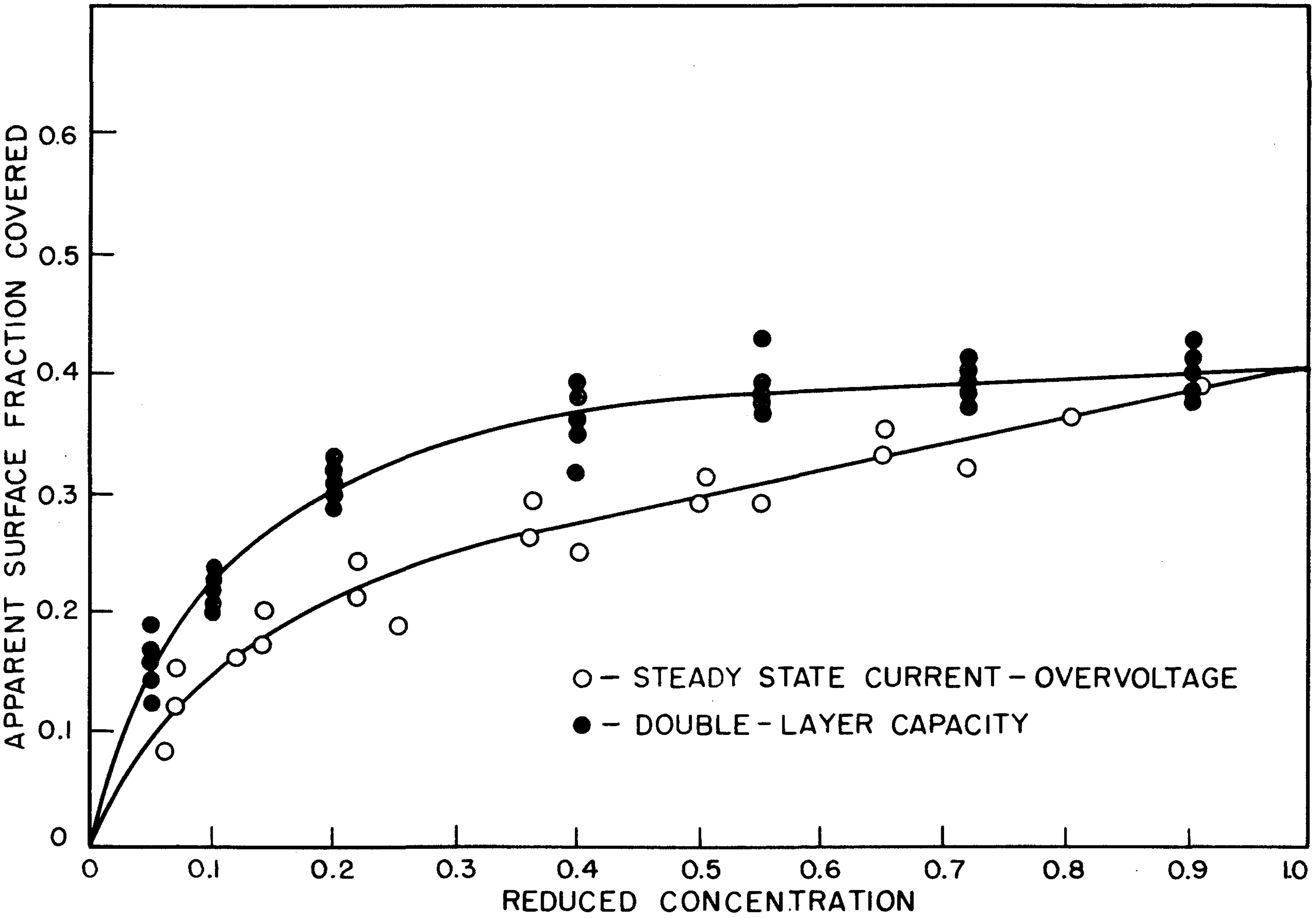


Figure 9. Adsorption of Heptanol-1 on Copper

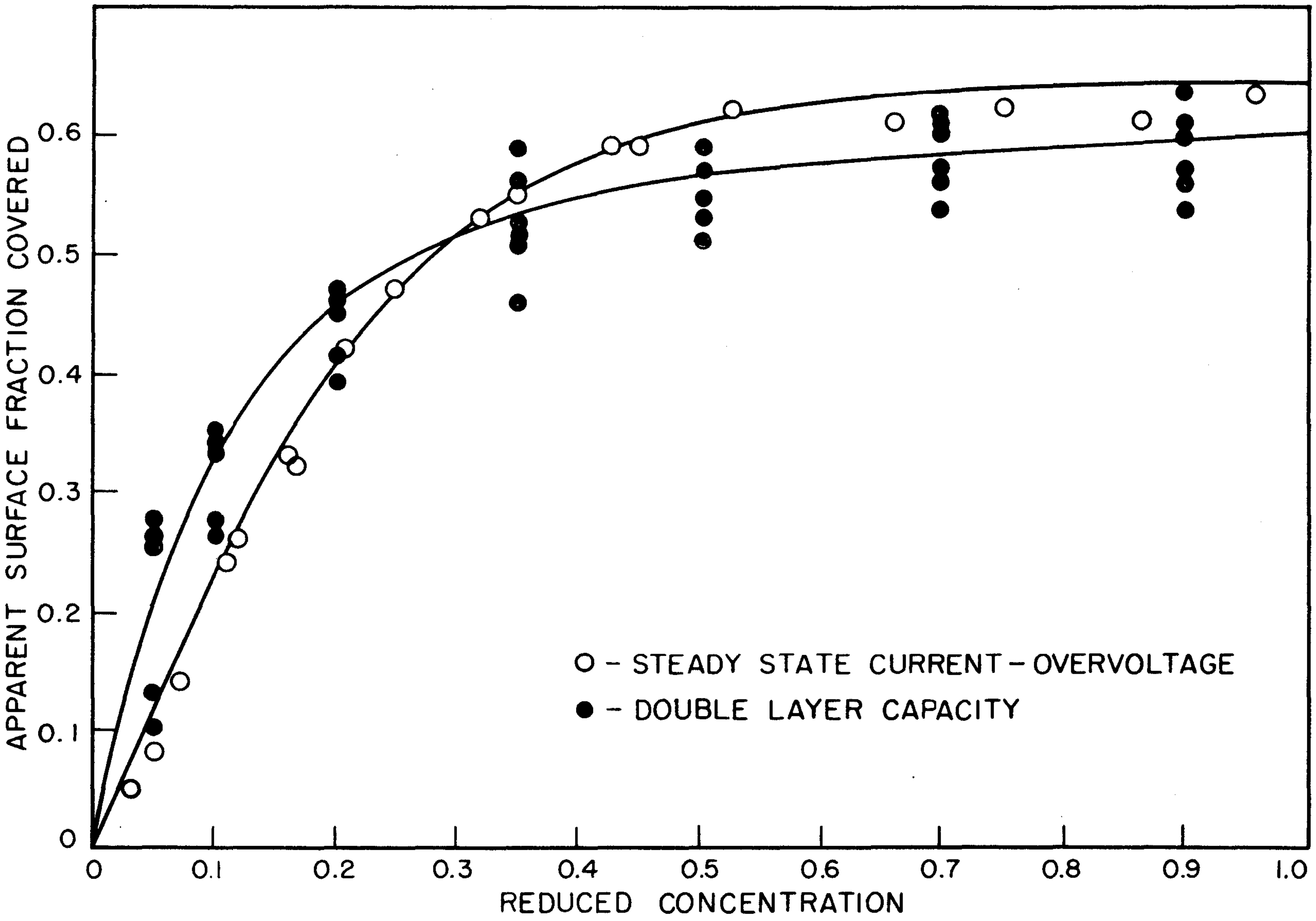


Figure 10. Adsorption of n-Heptaldehyde on Copper

D. Solubilities

The solubilities used in this research are given in Table 22. All the values were determined experimentally except the value for heptanol-1 which was determined previously at this laboratory.

The solubility of the various organic acids was determined interferometrically (44). The solubility of n-heptaldehyde was estimated by preparing solutions from 0.220 to 0.240 weight per cent in increments of 0.0025 weight per cent and visually inspecting the solutions to note the concentration at which two phases appeared.

Table 22. Solubility in 0.1 N Perchloric Acid at 25° C

Solute	Molarity	Weight %
Caproic acid	.0872	1.012[a]
Heptylic acid	.0201	0.261[b]
Octanoic acid	.0051	0.0734[c]
Heptanol-1	.0148	0.1726[d]
n-Heptaldehyde	.0202	0.230 [e]

[a] Values for pure water include: 1.018 by R. P. Craig, Ph. D. Thesis, Iowa State College (1952); 1.018 R. S. Hansen, Ph. D. Thesis, University of Michigan (1948).

[b] Values for pure water include: 0.281 by R. P. Craig, Ph. D. Thesis, Iowa State College (1952); 0.291 W. D. Harkins and Y. C. Cheng, J. Am. Chem. Soc. 43, 35 (1921).

[c] D. N. Eggenberger, F. K. Broome, A. W. Ralston, H. J. Harwood, J. Organic Chem. 14, 1108 (1949) obtained 0.076 for pure water.

[d] Value used was that determined for pure water by R. P. Craig, Ph. D. Thesis, Iowa State College (1952).

[e] W. D. Harkins and Y. C. Cheng, J. Am. Chem. Soc. 43, 35 (1921) obtained 0.235 for pure water.

VIII. DISCUSSION

A. Evaluation of Experimental Data

1. Other types of overvoltage

Every effort was made in this research to eliminate concentration polarization (overvoltage caused by the solution surrounding the cathode being at a lower concentration than bulk concentration) and resistance overvoltage (a potential caused by the resistance of the solution between the cathode and reference electrode). For the current densities employed, it has been reported (31,39,41) that both of these effects are negligible.

Resistance overvoltage should rise instantaneously with time and should, therefore, be detected as a vertical line at the beginning of the oscillographic sweep. This was not observed except for the few test runs made at 5×10^{-3} amperes. Even if resistance polarization was present, it is difficult to see how it could affect the double layer capacitance measurements. The slope of the curve after the instantaneous rise is the portion of the curve we are interested in and should be unaffected.

The results obtained by steady state current-overvoltage measurements should likewise be independent of resistance polarization. The method of calculation requires measurement of the change in overvoltage caused by addition of the adsorbate. It is difficult to conceive that the addition of a small amount of adsorbate would appreciably alter the resistance of the solution. As the resistance of the solution is approximately the same before and after addition of adsorbate, the resistance polarization must be approximately the same. The change in overvoltage is computed by subtracting the two potentials; and so if the resistance polarization is the same in each case, it will not affect the potential difference.

A similar line of reasoning can be employed to show that even if concentration overvoltage is not completely eliminated it will not affect the steady state results. This, of course, requires the assumption that the concentration polarization is the same before and after addition of adsorbate. This may not be a strictly valid assumption as the surface tension of the solution is greatly altered by addition of adsorbate; and consequently the size of the bubbles of hydrogen gas stirring the solution is altered.

Concentration polarization would be less likely to be a factor in the double layer capacitance measurements as the current is only applied for a fraction of a second, and the solution in the neighborhood of the electrode is only slightly disturbed from the equilibrium condition. If concentration polarization were present it would cause the initial build up curves to be non linear. As all the curves were reasonably linear it is concluded that the effect is not present.

2. Highly soluble adsorbates

No apparent adsorption of acetic acid, within the limits of experimental error, was observed up to concentrations of 2.5 molar (activity 0.11). This is in conflict with observations of Wetterholm (12). As Table 2 indicates, an increase in cell potential was observed but was compensated for within limits of experimental error by a corresponding increase in reversible potential. It would appear from Wetterholm's discussion that he did not correct for this effect.

This correction will be important whenever the adsorbate concentration is sufficient to alter the dielectric properties of the solution. The change in reversible potential was found to be negligible in the systems involving slightly soluble adsorbates.

In addition to the change in reversible potential, Bockris (47) found that the actual overvoltages on copper and lead were lowered by acetic acid. The lowering in the case of copper was (estimated from a figure given by Bockris) about 7 millivolts per per cent increase in acetic acid concentration. This reflects a lowering of the Tafel "a" constant, contrary to assumptions used in deriving equations (2) and (3).

The double layer capacitance measurements for acetic acid are irreproducable as seen in Table 8. When the acetic acid activity is 0.11, it is felt that the capacity of the double layer is somewhat greater than for pure water. This conclusion receives some support from the work of Bowden and Crew (48), who found the double layer capacitance on mercury was about 2½ times larger in pure formic acid than in pure water.

The double layer capacitance results tend to support the conclusion that no adsorption of acetic acid takes place, and that the observed effects are due to alteration of the dielectric property of the solution.

3. Reference electrode

The potential of the silver-silver chloride electrode depends on the concentration of chloride in solution. In order to insure that the concentration of chloride ion remains essentially constant, a small amount of potassium chloride was added to the solution. The solution was usually about 0.001 N in potassium chloride; however, no special care was taken to obtain exactly this normality. The potential of the reference electrode is immaterial as the interest is in the potential difference caused by addition of adsorbate.

The silver-silver chloride electrodes were prepared by the thermal-electric method (49). In testing the reliability of the method, it was found that none of the electrodes deviated more than 0.1 millivolt from the average potential of the group of 6 electrodes prepared.

It is not likely that the addition of slightly soluble adsorbates affects the activity of the chloride ions. If the adsorbate covers part of the surface of the reference electrode it should not affect the potential, as the potential of reversible electrodes is independent of surface area. These conclusions were verified in that the reversible hydrogen potential (with reference to a silver-silver chloride electrode) was unaffected by addition of slightly soluble adsorbates.

4. Experimental errors, steady state current-overvoltage

The most perplexing problem connected with steady state current-overvoltage measurements is that a steady state never actually exists. As was mentioned previously, the procedure followed consisted of following the potential until it increased less than 2 millivolts in a half hour; then adding the adsorbate and following the potential until it was constant in the same sense. This is admittedly an unsatisfactory procedure because of the difficulty of separating the potential rise caused by addition of adsorbate and the potential rise associated with the so-called steady state condition. Despite the difficulties listed a better method of procedure is hard to devise.

It is felt that in the measurement of the potential difference caused by addition of the adsorbate an uncertainty of 5 millivolts exists. This uncertainty will be reflected as a maximum error of 10 per cent in the apparent surface coverage. An uncertainty of 5 millivolts, of course, will reflect itself as a much smaller relative error at high solution activity.

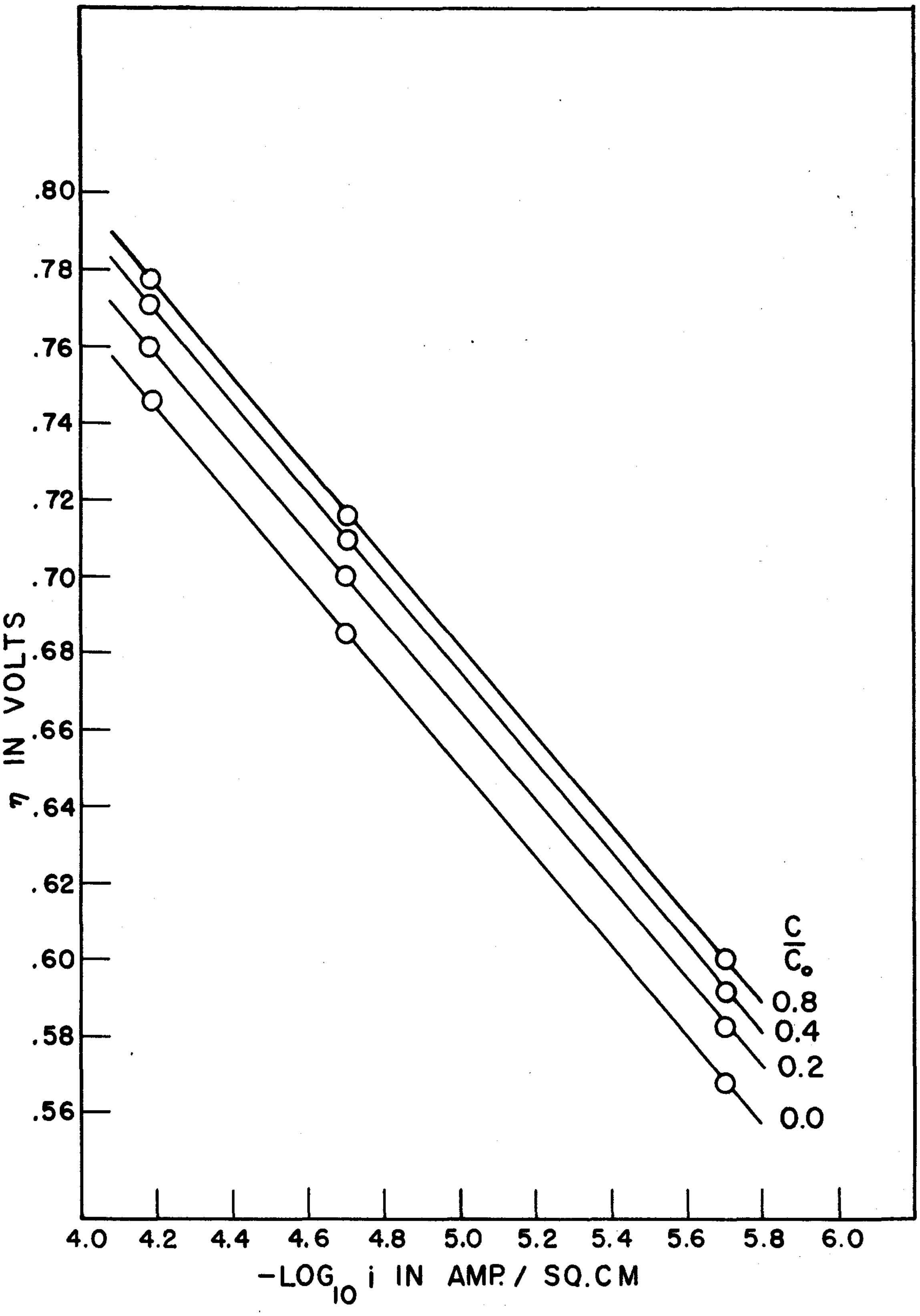
The steady state method should be independent of the current employed. Steady state current-overvoltage measurements at three different current to geometric area ratios are shown in Figure 11. The fact that the lines are parallel demonstrates that for the system illustrated the data are self-consistent.

5. Experimental errors, double layer capacitance

On all but the very latest oscillographs, measurements are complicated by the slight curvature of the screen. Because the screen is non-planar, straight lines will appear slightly curved on a photograph of the sweep. Unless the measurements are made in the center of the screen, some inaccuracy is introduced into the results.

Every effort was made to make the measurements in the center of the screen; however, it is felt that an uncertainty of 1 millimeter exists in

Figure 11. Steady State Current-overvoltage Values at Various Current Densities for the System Silver-octanoic Acid


.80
.78
.76
.74
.72
.70
.68
.66
.64
.62
.60
.58
.56
η IN VOLTS
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
$-\text{LOG}_{10}$ i IN AMP. / SQ.CM
$\frac{C}{C_o}$
0.8
0.4
0.2
0.0

each measurement made on the photograph. The greatest part of this uncertainty is due to the curvature of the oscillographic screen.

An estimation of the relative error introduced to the apparent surface coverage was made by the approximation of differentials technique (50), assuming that each measurement of the photograph had an uncertainty of 1 millimeter. It was found that an error of 8 per cent was introduced into the apparent surface coverage. A large part of this error could be eliminated with an oscillograph containing a planar screen.

As with the steady state method, the double layer capacitance results should be independent of the current used. Although the results indicate a slight variation of capacitance with the two currents employed, the adsorption results appear to be independent of the current employed provided C_θ and $C_{\theta=0}$ are measured at the same current. The dependence of capacity of the double layer on current density has been noted by other workers (18,37,48); however, the physical significance of this has not been determined. It is not surprising that the dependence of capacitance on current density does not affect the adsorption results, since a change in current density by a factor of ten alters the capacity by only 15 per cent. Changes in current density caused by addition of adsorbates are small, and so the effect on capacity is correspondingly small. It is not believed that this effect causes any major error in the results.

B. Comparison of the Results Obtained by Steady State Current-overvoltage and Double Layer Capacitance Measurements

Figures 2 through 6 indicate that for silver, with the exception of n-heptaldehyde, adsorption results obtained by the two methods agree within limits of reproducibility. The results for copper, as seen in Figures 7 through 10, show that although the limiting coverage is the same for the two methods, the shapes of the adsorption isotherms appear to differ significantly.

This difference on copper may be most simply explained by assuming that although the steady state potential at the time of measurement has become constant in the same sense that it was before addition of the adsorbate, the potential rise caused by the addition of adsorbate has not been completed. This would say that any adsorption point obtained by the steady state current-overvoltage method would be somewhat low; however, if one waited a longer period of time, the adsorption point would appear to be increased because of the increase in potential associated with the steady state. It is for this reason that the steady state adsorption isotherms show a gradual rise even when the corresponding portions of the adsorption isotherms obtained from double layer capacitance have leveled off.

The chief difficulty with this explanation is that it is hard to account for the difference in behavior of copper and silver electrodes. It might be pointed out, however, that copper has a higher hydrogen overvoltage than silver, and the rate of attainment of steady state conditions after addition of adsorbate may be related to this.

Physical adsorption is usually rapid (44), and the reason the steady state potentials require approximately one hour to return to the original condition is not clear. It should be pointed out that if hydrogen overvoltage is dependent on the amount of atomic hydrogen on the surface of the cathode, it may require some time for this equilibrium to be re-established after being disturbed by addition of the adsorbate. The rate of attainment of steady state conditions after addition of the adsorbate may be used as evidence to support the hypothesis that hydrogen overvoltage is dependent on the extent of surface coverage by atomic hydrogen.

C. Use of Reduced Concentrations

The abscissas in Figures 2 through 10 are reduced concentrations. This was made necessary as activity data for slightly soluble organic compounds were not available. To be strictly valid, this approximation requires Henry's law to hold and water to be completely insoluble in the organic compound. For the substances employed, reduced concentrations are a very close approximation to absolute activity.

For easier comparison of the adsorption of different members of a homologous series of organic acids, the data of Tables 3, 4, 5, 14, and 15, have been plotted with all members of the series on a single graph for a particular metal. These plots are shown in Figures 12 and 13. In Figures 14 and 15 are collected the data of Tables 4, 6, 7, 14, 16, and 17, showing the adsorption of various C_7 compounds on silver and copper. As in the other figures, the abscissas are reduced concentrations.

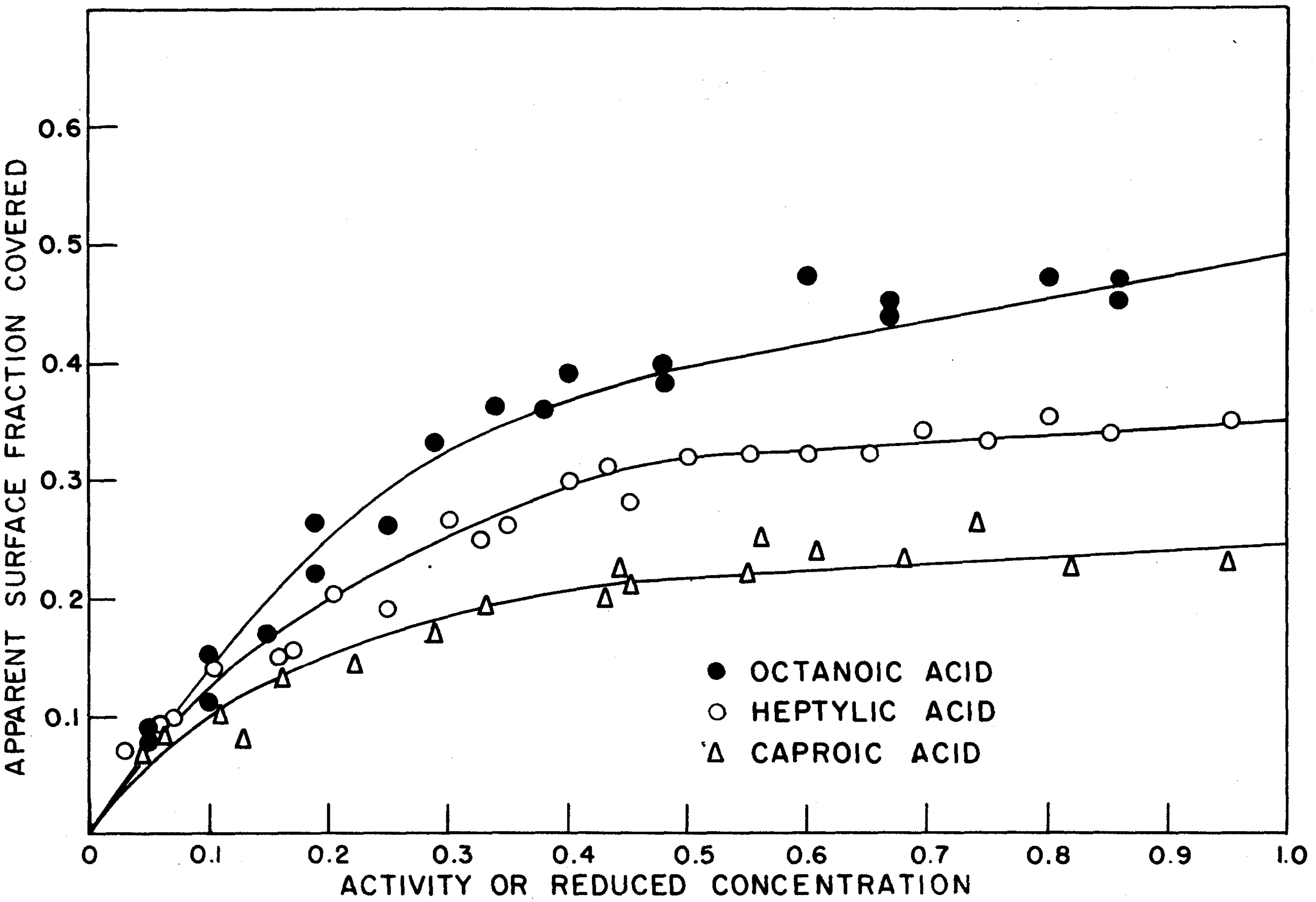


Figure 12. Adsorption of Normal Aliphatic Acids on Silver

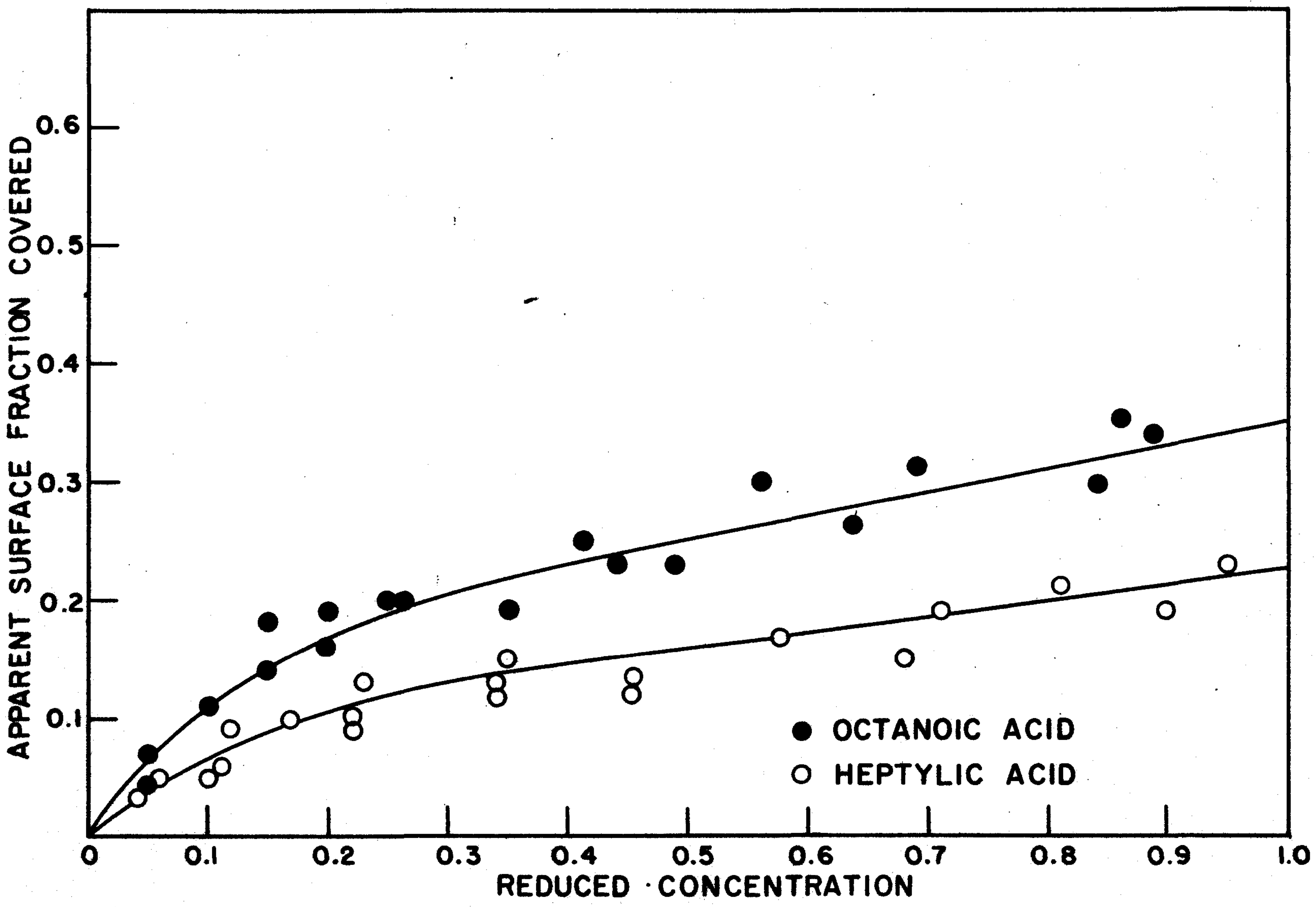


Figure 13. Adsorption of Normal Aliphatic Acids on Copper

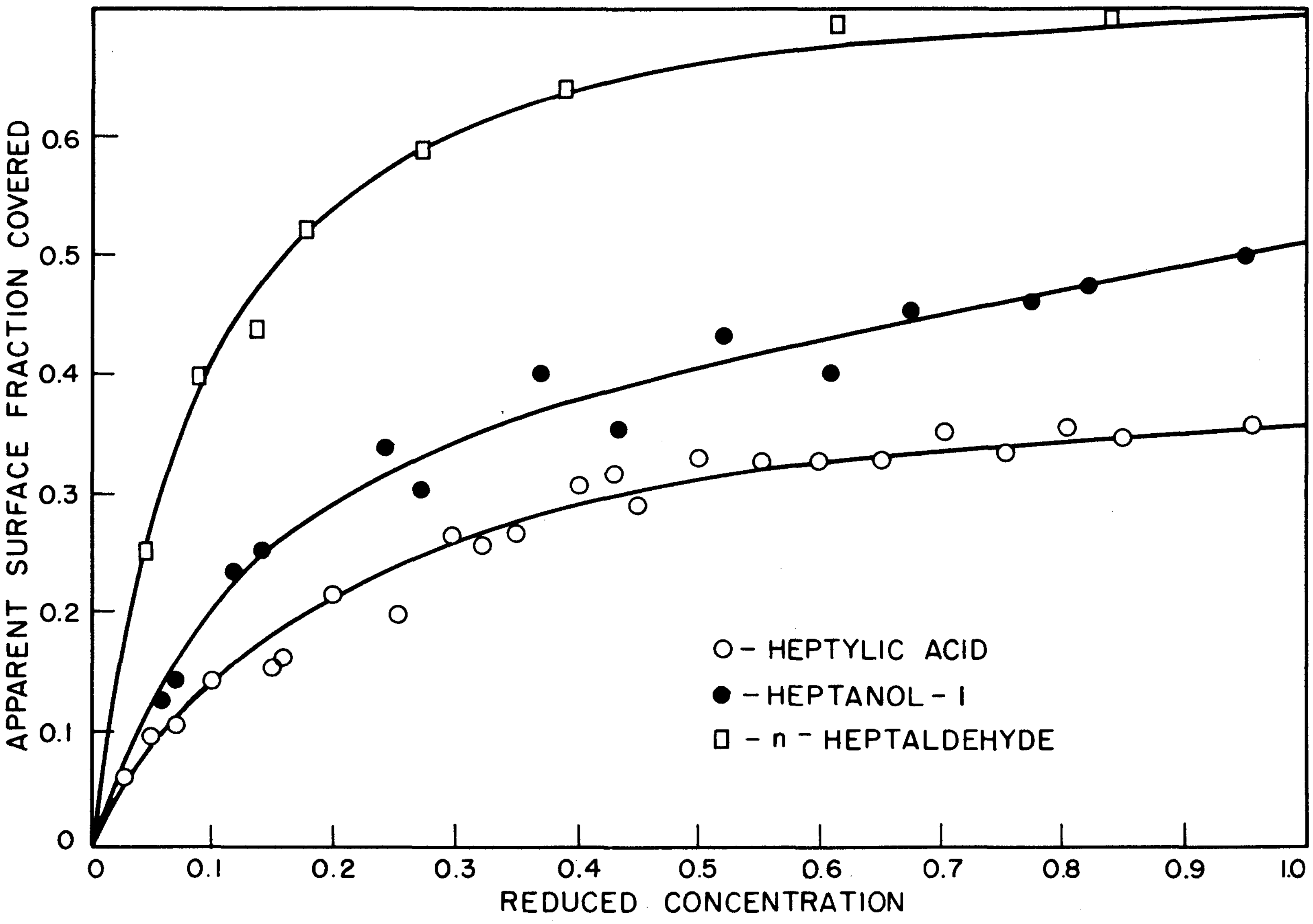


Figure 14. Adsorption of Normal C_7 Compounds on Silver

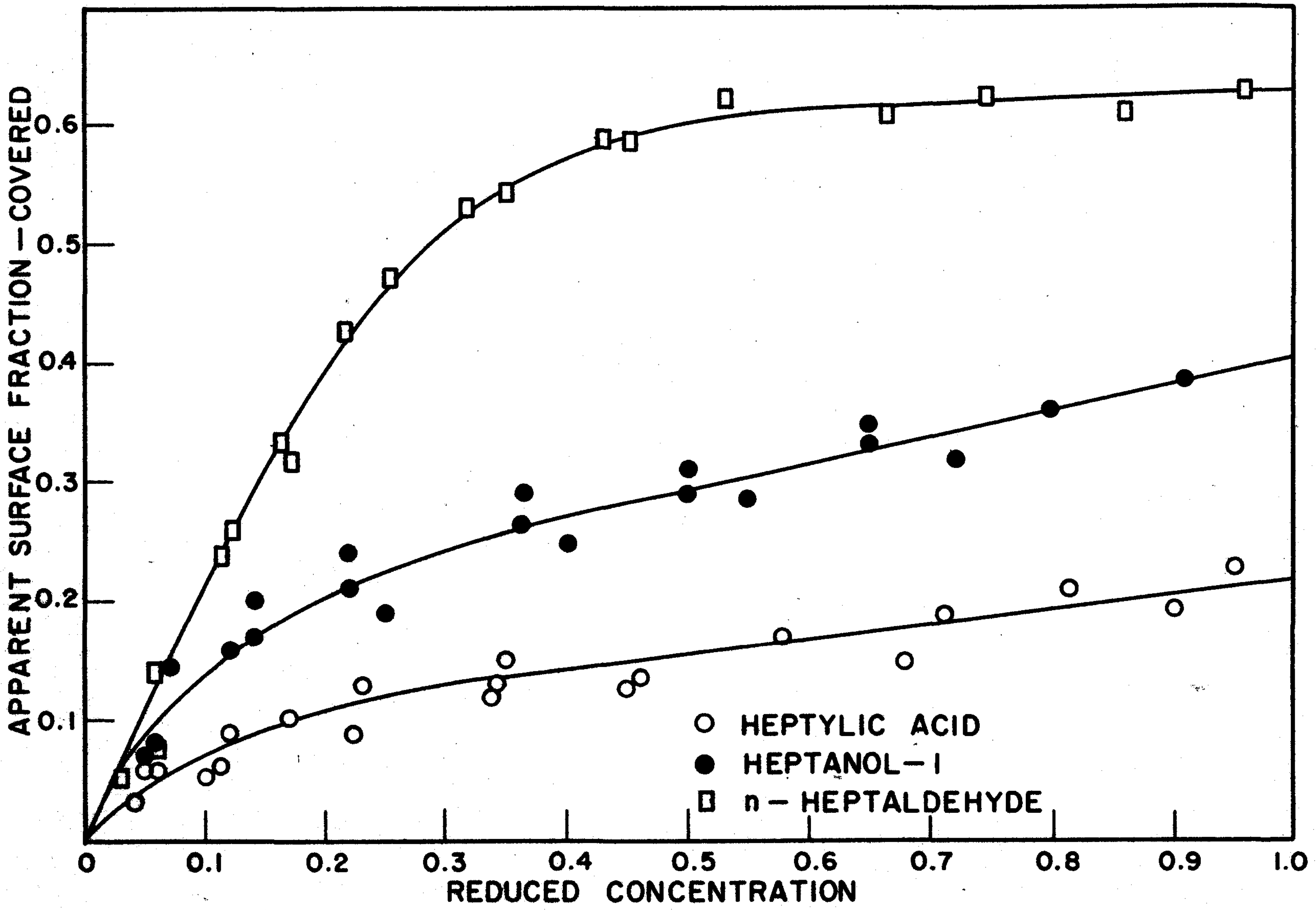


Figure 15. Adsorption of Normal C_7 Compounds on Copper

D. Reservations Regarding the Results

1. General discussion of the results

The results presented in Figures 12 through 15 are in general reasonable. Figures 12 and 13 indicate that in none of the aliphatic acid-water systems was an apparent coverage greater than 50 per cent observed. A similar result can be computed from the work of Bockris and Conway (51). As the activity approaches unity, it is generally believed that close to a monolayer coverage (i.e. $\theta \simeq 100\%$) of the surface will occur; however, this was not observed.

An unambiguous interpretation of these results as well as the results presented in Figures 14 and 15 is not possible at this time. Three possible explanations of the results are:

(1) The results are incorrect because of hydrogen discharge through the adsorbed layer.

(2) The results are correct, and there is an actual increase in the energy of adsorption with chain length.

(3) The results are correct, with the adsorbed monolayer containing an amount of water proportional to the saturation concentration of water in the organic adsorbate.

Each of these possibilities will now be discussed in some detail.

2. Interpretation of the results if the adsorbed layer is not completely inert

The low surface coverage at unit activity leads us to suspect the validity of some of the assumptions used to determine the adsorption isotherms from hydrogen overvoltage measurements. The two methods employed gave approximately the same results. This suggests that the assumption that is error is one held in common by the two methods. Both methods assume that the adsorbed layer acts as an inert blanket, and it is believed that this is the assumption that may not be strictly valid. Any current carried by reduction of, or hydrogen discharge through, the adsorbed layer would lead to an apparent surface coverage less than the actual coverage.

Figures 14 and 15 indicate a marked progression in apparent adsorption of the form, n-heptaldehyde > heptanol-1 > n-heptylic acid. This again suggests that the adsorbed layer may not be acting as an inert blanket.

The addition of a strong acid to pure solutions of organic acids, alcohols, and aldehydes is believed to give rise to the ions $RCOOH_2^+$, ROH_2^+, and RCH_2O^+ (52,53). A small number of these are very likely present in the adsorbed layer. It is reasonable to believe that the ease of hydrogen removal from these ions would be in the order, acid > alcohol > aldehyde. Direct evidence to support this assumption is lacking; however, indirect evidence, at least for the acid, is available from polarographic data.

Polarographic work indicates that aliphatic acids give a reduction wave at the dropping mercury electrode due to the discharge of hydrogen from the acid molecule (54). An attempt was made to repeat and extend this work to solid microelectrodes; however, the results were not reproducible.

Reduction of aliphatic aldehydes is possible at a dropping mercury electrode (54). This is probably not extensive at the high acidities employed. This work was repeated and it was found that a pH of 10 or above was required to obtain an aldehyde reduction wave on a dropping mercury electrode. Work on solid microelectrodes gave irreproducible results.

The above discussion appears to offer a reasonable explanation for the low apparent surface coverage of the adsorbed molecules and for the observed behavior of aldehydes, alcohols, and acids. The observed effect of chain length on the adsorption of aliphatic acids is very difficult to explain. The results would seem to indicate that the longer the chain length the more difficult the reduction of the $RCOOH_2^+$ ions.

It seems reasonable that a certain number of hydrogen ions would have sufficient energy to penetrate the alkyl part of the adsorbed layer. If we represent the number of hydrogen ions penetrating the alkyl part of the adsorbed layer as

$$\frac{d\left[H^+\right]}{dt} = \frac{k}{d}$$

where k is a constant, and d is the thickness of the adsorbed layer, then

$$\Theta_{apparent} = \Theta_{actual}\left(1 - \frac{k'}{d}\right)$$

where the Θ's refer to the fraction of the surface covered. Assuming that the adsorbed layer consists entirely of adsorbed acid molecules (i.e. $\Theta_{actual} = 1$) and that the limiting values of $\Theta_{apparent}$ corresponds to the complete coverage, the following values for the constant k' were obtained for the aliphatic acids.

Acid	$\Theta_{apparent}$ (limiting)	Number of Carbon Atoms	k'
n-caproic	0.22	6	4.7
n-heptylic	0.35	7	4.6
n-octanoic	0.48	8	4.2

It is not necessary to assume the adsorbed layer consists entirely of acid molecules to evaluate the constant k'. One needs only to assume that the surface fraction covered is the same for all acids in the homologous series.

It is thus possible to formulate a reasonable explanation for the observed effect of chain length assuming that the adsorbed layer is not completely inert.

3. Interpretation of the results with reference to the energy of adsorption

Figures 12 and 13 indicate that with increasing chain length a somewhat larger number of acid molecules will be adsorbed at a given activity. The fact that there is a greater surface coverage by C_8 molecules than by C_6 molecules indicates that the C_8 molecules are in a more ordered state (i.e. they have a lower entropy) than the C_6 molecules at the same solution activity; consequently the energy of adsorption must be correspondingly greater.

Figures 14 and 15 indicate that variation of the function group causes a large alteration in adsorption properties of aliphatic compounds of the same chain length. The order, aldehyde > alcohol > acid suggests that this is the order of the heats of adsorption of these compounds on metal surfaces.

The indicated effect of functional group and chain length are in agreement with the work reported by Zisman (55) on the adsorption of long chain acids and alcohols by platinum from organic solvents. Zisman observed the effect of temperature on the formation of oleophobic films adsorbed from organic solvents. He found that for a given concentration of polar solute C a critical temperature T existed above which oleophobic films no longer formed. A plot of Log C against $\frac{1}{T}$ resulted in a straight line. The heat of adsorption was estimated from the slope of this line. A plot of the heat of adsorption for a homologous series of compounds against the number of carbon atoms was essentially linear, indicating that the results could be represented by the formula

$$U = U_o + Nu$$

where U is the heat of adsorption and N the number of carbon atoms in the compound. U_o is the energy of adsorption associated with the functional group and u the energy of adsorption associated with each methylene group.

An application of this formula to the particular compounds employed in this research gave the following values for the heats of adsorption:

n-caproic acid	7480 calories/mole
n-heptylic acid	7680 calories/mole
n-octanoic acid	7890 calories/mole
heptanol-1	7920 calories/mole

These values seem very reasonable and the effect of chain length and functional group are in conformity with the results of this research.

An interesting fact regarding the heats of adsorption obtained by Zisman is that the heats of adsorption of n-octanoic acid and heptanol-1 are approximately the same. One would, therefore, expect the adsorption isotherms to be similar. This is again in conformity with the results of this research.

The part of the adsorption energy associated with the polar group (i.e., U_o) may be due to the interaction of the dipole and the metal surface. A simple treatment for this interaction energy consists in calculating the forces involved between a dipole and its mirror image, The following formula results:

$$U_o = \frac{\mu^2 N_o}{4r^3}$$

where μ, r, and N_o are the dipole moment, the distance of the dipole from the surface, and Avagadro's number, respectively. The dipole moments are in the order, aldehyde > alcohol > acid; therefore, if the dipoles are the same distance from the surface the adsorption energies would be in the observed order. Assuming reasonable values for the distance from the surface, calculated adsorption energies were of reasonable magnitude only in the case of the aldehyde; calculated adsorption energies for alcohols and acids were too low.

The lateral interaction of the methylene groups is probably the reason for the observed effect of chain length on the energy of adsorption. This lateral interaction may be estimated by the following formula:

$$U = \frac{3}{4} \quad \frac{E\alpha^2}{r^6}$$

where E, α, and r are the ionization energy, polarizability, and distance of closest approach, respectively. The polarizability is related to the molar refractivity [R] by:

$$[R] = N_o \frac{4}{3} \pi \alpha$$

where N_o is Avogodro's number. Combining these equations gives:

$$U = \frac{0.0427\ [R]^2 E}{N_o{}^2 r^6}$$

The interatomic distance r can be estimated from the work of Langmuir (56). He found the cross-sectional area of monomolecular organic adsorbed films to be 20.5°A. It is also known that the molar refractivity shows a constant increase of 7.6 for each methylene group added. Substituting these values into the equation, a lateral interaction energy of 280 calories/mole is obtained for each methylene group. This is in reasonable agreement with the value of 212 calories/mole found by Zisman for organic acid molecules.

In the discussion of the energies of adsorption, it has been assumed that the adsorbed molecules are oriented perpendicular to the surface with polar end adjacent to the metal surface. Craig (44) investigated the adsorption of normal aliphatic acids and alcohols on various carbon based adsorbents. He found that at a given solution acitivity the amount adsorbed was independent of chain length. He also observed that variation of the functional group on an aliphatic chain has only a secondary effect on the amount of adsorption at carbon surfaces from aqueous solutions of the organic substance at a given activity. He concluded from his work that the interaction between the organic adsorbate and a carbon surface involves primarily the alkyl rather than the functional group. The results on metal surfaces as seen in Figures 12 through 15 differ from those found by Craig on carbon surfaces, and it is, therefore, reasonable to assume that the orientation on metal surfaces is different from that on carbon surfaces.

4. Interpretation of the results with reference to the structure of the monolayer

One might consider that an adsorbed monolayer has the same composition as a saturated solution of water in the organic adsorbate. If one considers the adsorbed layer to have a thickness t, then the adsorbed volume is t/cm^2 of surface. This adsorbed volume will contain ct moles of water where c is the saturation concentration of water in the organic adsorbate. If one considers all the water in the adsorbed layer to be on the surface, then the area occupied by the water will be ct times the area occupied per water molecule. Assuming water has a cross sectional area of 10 $\mathring{A}^2$, the fraction of the surface covered by water in a monolayer is

$$f = 0.006\ ct$$

where c is expressed in moles/liter and t in angstroms.

The thickness of the adsorbed layer can be estimated by multiplying the number of carbon atoms in the compound by 1.3. Craig (44) determined the solubility of water in n-caproic acid and n-heptylic acid. Substituting the appropriate values into the equation gives:

n-caproic acid $f = 0.006(3.0)(7.8) = 0.14$
n-heptylic acid $f = 0.006(1.3)(8.1) = 0.07.$

If one calls the fraction of the surface covered by acid saturated with water Θ_{real}, then

$$\Theta_{apparent} = \Theta_{real}\ (1-f).$$

If one computes Θ_{real} for the two acids, he finds the isotherms are much nearer coincidence. It is felt that Craig's solubility data are somewhat low, and so the calculated surface fraction of water in a monolayer of acid may be somewhat low.

This explanation makes plausible the observed effect of chain length without recourse to adsorption energies. The explanation seems reasonable, and in certain respects it is preferable to the adsorption energy treatment.

5. Suggested extensions of the work

Further experimentation in the field of polarography would be of great value to our discussion of the possiblity of hydrogen discharge through the adsorbed layer. Study of the reduction of organic acids and aldehydes at solid microelectrodes is especially needed. Investigation of the effect of pH on the half wave potential of these compounds is also needed.

Extension of the methods developed for obtaining adsorption isotherms to non-aqueous systems would be of interest. There is nothing in the theory of the two methods that hinders their application to non-aqueous systems. Certain experimental difficulties are present in non-aqueous solvents that are lacking in water, but they could be eliminated by modification of the apparatus.

The effect of highly charged salts on the adsorption results would be of interest. If the adsorption process is dependent in some manner on the dipole moment of the adsorbed molecules, then the adsorption of a highly charged ion on the surface of the electrode would greatly alter the amount of adsorption of the organic compounds.

IX. SUMMARY

1. An apparatus has been developed for obtaining adsorption data on small metal surfaces. In principle two independent methods of procedure are set forth for obtaining such data; however, both methods are dependent upon the hydrogen overvoltage phenomena. The first method depends upon steady state current-overvoltage relationships; while in the second method the double layer capacity of the metal-solution interface is measured.

2. The two methods have been employed to obtain adsorption isotherms for the following systems; silver - n-caproic, silver - n-heptylic acid, silver - n-octanoic acid, silver - heptanol-1, silver - n-heptaldehyde, copper - n-heptylic acid, copper - n-octanoic acid, copper - heptanol-1, copper - n-heptaldehyde. The results by the two methods agree within limits of reproducibility for most of the silver systems investigated. Results by the two methods on copper give slightly different curves; however, the same limiting surface coverage is obtained by both methods.

3. All of the results appear to be reasonable in order of magnitude; however, two points cause some concern. First, in no fatty acid-water system was an apparent coverage greater than 50 per cent observed. Secondly, the marked progression, n-heptaldehyde > heptanol-1 > n-heptylic acid, is in contrast to results for the adsorption of these compounds by carbon. Three possible interpretations of these facts are presented.

4. The application of the methods to highly soluble adsorbates is complicated by the alteration of the dielectric properties of the solution. In this case, care must be taken to correct for change in reversible cell

potential. With slightly soluble adsorbates the dielectric properties of the solution are not appreciably altered and the methods can be more simply applied.

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