THE EFFECT OF SUBSTITUTED AMMONIUM COMPOUNDS ON POLAROGRAPHIC MAXIMA

By
WILLIAM JORDAN BARRETT

A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA
June, 1950
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Part</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LIST OF TABLES</td>
<td>ii</td>
</tr>
<tr>
<td></td>
<td>LIST OF FIGURES</td>
<td>iii</td>
</tr>
<tr>
<td>Part I</td>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>Part II</td>
<td>EXPERIMENTAL</td>
<td>11</td>
</tr>
<tr>
<td>Part III</td>
<td>DESCRIPTION AND DISCUSSION OF POLAROGRAMS</td>
<td>17</td>
</tr>
<tr>
<td>Part IV</td>
<td>SUMMARY</td>
<td>52</td>
</tr>
<tr>
<td>Part V</td>
<td>BIBLIOGRAPHY</td>
<td>54</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td></td>
<td>56</td>
</tr>
<tr>
<td>BIOGRAPHICAL NOTE</td>
<td></td>
<td>57</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Analyses of Substituted Ammonium Compounds</td>
<td>16</td>
</tr>
<tr>
<td>II</td>
<td>Molar Concentrations Necessary to Suppress Maxima Completely</td>
<td>20</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>1.</td>
<td>Effect of Concentration of n-Heptyl Ammonium Bromide on Height of Nickel Maximum</td>
<td>22</td>
</tr>
<tr>
<td>2.</td>
<td>Height of Nickel Maximum as a Function of Number of Carbon Atoms in the Alkyl Group of the tri-n-Alkyl Ammonium Bromides</td>
<td>27</td>
</tr>
<tr>
<td>3.</td>
<td>Nickel Waves with Increasing Concentrations of n-Butyl Ammonium Bromide</td>
<td>34</td>
</tr>
<tr>
<td>4.</td>
<td>Nickel Waves with Increasing Concentrations of di-n-Butyl Ammonium Bromide</td>
<td>34</td>
</tr>
<tr>
<td>5.</td>
<td>Nickel Waves with Increasing Concentrations of tri-n-Butyl Ammonium Bromide</td>
<td>35</td>
</tr>
<tr>
<td>6.</td>
<td>Nickel Waves with Increasing Concentrations of tetra-n-Butyl Ammonium Iodide</td>
<td>35</td>
</tr>
<tr>
<td>7.</td>
<td>Manganese Waves with Increasing Concentrations of n-Amyl Ammonium Bromide</td>
<td>36</td>
</tr>
<tr>
<td>8.</td>
<td>Manganese Waves with Increasing Concentrations of di-n-Amyl Ammonium Bromide</td>
<td>36</td>
</tr>
<tr>
<td>9.</td>
<td>Manganese Waves with Increasing Concentrations of tri-n-Amyl Ammonium Bromide</td>
<td>37</td>
</tr>
<tr>
<td>10.</td>
<td>Nickel, Manganese, and Barium Waves with $10^{-4}$ M tri-n-Butyl Ammonium Bromide</td>
<td>37</td>
</tr>
<tr>
<td>11.</td>
<td>Nickel Waves with $10^{-3}$ M Monoalkyl Ammonium Bromides</td>
<td>38</td>
</tr>
<tr>
<td>12.</td>
<td>Nickel Waves with $5 \times 10^{-4}$ M Monoalkyl Ammonium Bromides</td>
<td>38</td>
</tr>
<tr>
<td>13.</td>
<td>Nickel Waves with $10^{-5}$ M Monoalkyl Ammonium Bromides</td>
<td>39</td>
</tr>
<tr>
<td>14.</td>
<td>Manganese Waves with $10^{-3}$ M Monoalkyl Ammonium Bromides</td>
<td>39</td>
</tr>
<tr>
<td>15.</td>
<td>Barium Waves with $10^{-3}$ M Monoalkyl Ammonium Bromides</td>
<td>40</td>
</tr>
<tr>
<td>16.</td>
<td>Nickel Waves with $10^{-4}$ M di-n-Alkyl Ammonium Bromides</td>
<td>40</td>
</tr>
<tr>
<td>17.</td>
<td>Nickel Waves with $10^{-5}$ M di-n-Alkyl Ammonium Bromides</td>
<td>41</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>18.</td>
<td>Nickel Waves with $10^{-6} \text{ M} \text{ di-}n\text{-Alkyl Ammonium Bromides}$</td>
<td>41</td>
</tr>
<tr>
<td>19.</td>
<td>Manganese Waves with $5 \times 10^{-4} \text{ M} \text{ di-}n\text{-Alkyl Ammonium Bromides}$</td>
<td>42</td>
</tr>
<tr>
<td>20.</td>
<td>Manganese Waves with $10^{-4} \text{ M} \text{ di-}n\text{-Alkyl Ammonium Bromides}$</td>
<td>42</td>
</tr>
<tr>
<td>21.</td>
<td>Nickel Waves with $10^{-5} \text{ M} \text{ tri-}n\text{-Alkyl Ammonium Bromides}$</td>
<td>43</td>
</tr>
<tr>
<td>22.</td>
<td>Nickel Waves with $10^{-6} \text{ M} \text{ tri-}n\text{-Alkyl Ammonium Bromides}$</td>
<td>43</td>
</tr>
<tr>
<td>23.</td>
<td>Nickel Waves with $10^{-7} \text{ M} \text{ tri-}n\text{-Alkyl Ammonium Bromides}$</td>
<td>44</td>
</tr>
<tr>
<td>24.</td>
<td>Manganese Waves with $10^{-4} \text{ M} \text{ tri-}n\text{-Alkyl Ammonium Bromides}$</td>
<td>44</td>
</tr>
<tr>
<td>25.</td>
<td>Nickel Waves with $10^{-6} \text{ M} \text{ tetra-}n\text{-Alkyl Ammonium Halides}$</td>
<td>45</td>
</tr>
<tr>
<td>26.</td>
<td>Manganese Waves with $10^{-4} \text{ M} \text{ tetra-}n\text{-Alkyl Ammonium Halides}$</td>
<td>45</td>
</tr>
<tr>
<td>27.</td>
<td>Nickel Waves with $10^{-5} \text{ M} \text{ Ethyl Ammonium Bromides}$</td>
<td>46</td>
</tr>
<tr>
<td>28.</td>
<td>Nickel Waves with $10^{-6} \text{ M} \text{ n-Butyl Ammonium Halides}$</td>
<td>46</td>
</tr>
<tr>
<td>29.</td>
<td>Nickel Waves with $10^{-6} \text{ M} \text{ n-Amyl Ammonium Bromides}$</td>
<td>47</td>
</tr>
<tr>
<td>30.</td>
<td>Nickel Waves with Three Concentrations of the n-Hezyl Ammonium Bromides</td>
<td>51</td>
</tr>
<tr>
<td>31.</td>
<td>Manganese Waves with $10^{-4} \text{ M} \text{ n-Butyl Ammonium Halides}$</td>
<td>47</td>
</tr>
<tr>
<td>32.</td>
<td>Nickel Waves with $10^{-5} \text{ M} \text{ Benzyl Ammonium Bromides}$</td>
<td>48</td>
</tr>
<tr>
<td>33.</td>
<td>Nickel Waves with $10^{-6} \text{ M} \text{ Benzyl Ammonium Bromides}$</td>
<td>48</td>
</tr>
<tr>
<td>34.</td>
<td>Manganese Waves with $5 \times 10^{-4} \text{ M} \text{ Benzyl Ammonium Bromides}$</td>
<td>49</td>
</tr>
<tr>
<td>35.</td>
<td>Nickel Waves with Increasing Concentrations of Hexadecyl Trimethyl Ammonium Bromide</td>
<td>50</td>
</tr>
<tr>
<td>36.</td>
<td>Manganese Waves with Increasing Concentrations of Hexadecyl Trimethyl Ammonium Bromide</td>
<td>50</td>
</tr>
</tbody>
</table>
Part I

INTRODUCTION

Polarographic maxima are significant for both practical and theoretical reasons. In quantitative analysis the appearance of a maximum in the current-voltage curve makes it difficult in some cases and impossible in others to measure accurately the limiting diffusion current. Fortunately, in practical work most maxima are effectively eliminated by the addition of small quantities of gelatin or other surface-active substances. From the theoretical point of view polarographic maxima are of interest as a phenomenon closely related to the concept of the electrical double layer. Many experimental studies have been made of the processes taking place at the surface of the dropping mercury electrode. The invention and development of the polarographic method evolved from efforts to establish a single electrode of absolute potential. This early work was based upon the fact that at the maximum of the electrocapillary curve of mercury the surface of the mercury is uncharged; while on either side of the maximum a residual charge is carried by the mercury drop, resulting in a lowered interfacial tension between mercury and solution.

Heyrovsky, the inventor of the polarograph, made the first attempt to explain maxima on a theoretical basis. The reducible substance, ion or dipole molecule, is adsorbed on the mercury surface.
When the applied voltage reaches a sufficiently high value, the reduction process begins and the current increases as ions are discharged. As long as the rate of adsorption exceeds the rate of reduction the current will continue to increase. The current reaches a peak value when the rates of the two processes become equal. As expressed by Heyrovsky, the condition for the maximal current is that voltage at which the rate of electrodeposition in equivalents per unit area is equal to the amount adsorbed in unit time per unit area. A further small increase in voltage establishes a condition of complete concentration polarization, and the current decreases suddenly to a value determined by the rate of diffusion of the reducible substance.

If a non-reducible substance is present which is more strongly adsorbed than that undergoing reduction, then the adsorption of the reducible species is correspondingly weakened. The rate of adsorption of the reducible substance will not exceed its rate of reduction, and no maximum will appear.

The force at the electrode which causes adsorption is an electrokinetic potential which is analogous to the Freundlich adsorption potential and which changes sign at the electrocapillary zero. Heyrovsky distinguishes this potential from the Nernst thermodynamic potential and states that no conclusions concerning the "absolute zero" can be drawn from studies with the dropping mercury electrode. These ideas were supported by the work of Rasch, Varasova, Heyrovsky and Dillinger, Rayman, Hamamoto, and Heyrovsky and Vascautzanu.
Ilkovic developed a mathematical interpretation of the forces involved in the occurrence of maxima. However, his idea of the nature of the potential drop extending from the mercury surface into the solution differed from that of Heyrovsky, who believed it to be due to electrokinetic forces. Ilkovic supposed that this potential difference was equal to the IR drop across the interfacial film; I being the charging, or non-faradic current, and R the resistance of the film. His work was supported by current-time curves of the oxygen reduction taken for the life of a single drop at a fixed applied voltage. These curves agreed well with those calculated from theoretical considerations for intensity of current versus time. The whole polarographic wave, extending over a range of voltage, was obtained by plotting the mean current observed during the life of a single drop at a fixed voltage against the voltage. These were identical with the normal experimental current-voltage curves.

Thus, the Heyrovsky-Ilkovic theory is based on the concept of relative adsorbabilities of the various ions and polar molecules present in the solution.

Kolfhoff and Lingane point out a serious defect in the Heyrovsky-Ilkovic theory. As mentioned previously, the mercury drop is positively charged on one side of the capillary maximum and negatively charged on the other. Therefore, on the positive side only negatively charged particles should be adsorbed by electrical attraction, and on the negative side only positively charged particles
should be adsorbed. But the positive thallous ion and the positive nickel ion, for example, both exhibit maxima although they are reduced on opposite sides of the electrocapillary maximum. To further demonstrate the inadequacy of the adsorption theory, it has been found that in some cases a positive ion will suppress a maximum on the positive side of the electrocapillary curve.\textsuperscript{9,23} Also, the opinion has been expressed that the number of ions or reducible particles adsorbed in the surface layer is too small to account for the large currents observed at the maximum.\textsuperscript{2}

A second theory, one which appears to be more in favor at present, was proposed by Antweiler and von Stackelberg.\textsuperscript{1,2,25} This was based on microscopic observations of streaming effects and differences in interfacial tension on the surface of the mercury drop. Photographs were made of the drop in various solutions and over a range of applied voltages. Streaming of the electrolyte in the diffusion layer was observed in that part of the current-voltage curve just preceding the maximum. Either when the current reached its limiting value or when the maximum was suppressed, the streaming disappeared and a normal diffusion layer was observed. Two different types of streaming were noted — a downward streaming of the electrolyte on the positive side of the electrocapillary maximum and a sideward streaming on the negative side.

These effects were explained as follows: The glass of the electrode acts as an obstruction in the path of ions migrating or
diffusing to the mercury drop. Thus, the rate of adsorption of ions at the top of the drop will be less than at the bottom where no obstruction exists. A difference in current density will result, and a tangential potential gradient will be established from top to bottom. This causes a gradient in the interfacial tension along the mercury surface and an electro-osmotic stirring action occurs. The stirring, or streaming, disrupts the diffusion layer which is responsible for concentration polarization, and more ions are carried to the electrode to be reduced than would be carried by the normal diffusion process. The current increases to values higher than the limiting diffusion current.

The result of disturbing the diffusion layer was illustrated in a graphic manner by Eyring, Marker, and Ting-Chang Kwoh.\(^5\) It is shown that the current, \(I\), is inversely proportional to the thickness of the diffusion layer; that is,

\[
I = \frac{k}{\delta}
\]

If the thickness of the diffusion layer is reduced by stirring from \(\delta\) to \(\delta'\), then \(I\) is increased to \(\delta/\delta'\) times its original value.

Previous experimental work which is closely related to that described in this dissertation began in 1929, when Rasch studied the suppressive effect of a series of organic acids on the oxygen maximum.\(^22\)
He found that the normal aliphatic acids become better suppressors as the length of the carbon chain increases. The acids used were formic, propionic, butyric, valeric, palmitic, and stearic. Concentrations of palmitic and stearic acids of the order of $10^{-5}$ M completely eliminated the oxygen maximum in 0.01 M potassium hydroxide saturated with air.

Capitanio and Pittoni made similar studies with buffered solutions of lauric acid and sulfonaphthyl stearic acid (Twitchell's Reagent). They found that the specific suppressive effects on oxygen were of the same order of magnitude for both the undissociated molecules and their anions, indicating that molecule and anion were equally adsorbed and that the length of the carbon chain was an important factor.

Semerano showed that the extent of the lowering of the oxygen maximum is a function of the concentration of the suppressing substance (tropolein 000, basic fuchsin, adrenaline) in the solution.

Rayman studied the effect of various organic dyes; including fuchsin, methylene blue, alizarin, phenolphthalein, and others; on the oxygen maximum. Those which eliminated the maximum in the lowest concentrations, he concluded, were most strongly adsorbed.

Hamamoto made a similar study of alkaloids (morphine hydrochloride, atropine sulfate, quinine hydrochloride, etc.). Each alkaloid was characterized by an adsorption coefficient based on its effectiveness in suppressing the oxygen maximum. The relationship
between the extent to which the maximum was suppressed and the concentration of the alkaloid was represented by an equation of the type of the Freundlich adsorption isotherm:

\[ H - H' = \alpha C^{1/n} \]

\( H \) is the height of the oxygen maximum in a solution of potassium chloride saturated with air and \( H' \) is the height in a solution to which an alkaloid has been added in the concentration \( C \). \( \alpha \) and \( n \) are constants for a particular system. A plot of \( \log (H - H') \) against \( \log C \) gave a straight line. Heyrovsky, in a note attached to Hamamoto's paper, attempted to show that the specific adsorption coefficient of Hamamoto could be directly related to the adsorption coefficient of the Langmuir equation.

A study of the effect of several surface-active compounds (sodium butylnaphthalene sulfonate, sodium oleate, sodium lauryl sulfonate, etc.) on the oxygen maximum was made by Thiesse and Belon. They found that the logarithm of the extent to which the maximum was suppressed was directly proportional to the concentration of suppressor, or:

\[ \log \left( 1 - \frac{H_0 - H}{H_0} \right) = -KC \]

\( H_0 \) is the height of the oxygen maximum with no suppressor added, \( H \) is the height at concentration \( C \), and \( K \) is designated the adsorption constant of the compound added. Furthermore, \( K \) was related to the
temperature by an equation of the Arrhenius type, \( K = B e^{-\frac{Q}{RT}} \), where \( Q \) is the activation energy of adsorption, \( B \) is a constant called the specific limiting volume toward which \( K \) tends as \( T \), the temperature, increases; and \( R \) is the gas constant. A plot of \( \log K \) against \( \frac{1}{T} \) gave a straight line from which \( Q \) and \( B \) could be evaluated. Unfortunately, the only numerical data given are the final values of \( Q \) and \( B \) for each compound. This is, however, an interesting approach to the problem of polarographic maxima.

Numerous studies of the surface properties of charged mercury drops have been made by Frumkin and co-workers in Russia. These are summarized in a paper by Frumkin, "New Electrocapillary Phenomena." In general, their work supports the theory that maxima are directly related to stirring effects.

A recent paper by Khlopin emphasizes the fact that actually much remains to be learned about the complex processes going on at the surface of the dropping mercury electrode. Motion pictures of the mercury drops during electrolysis were made at magnifications of ten to twenty times. Finely divided talc, carbon, and other inert substances were used to make motions in the solution visible. Five different reactions were studied. These were the reductions of cupric, cadmium, cobaltous, and arsenic ions, and of cysteine. All normally show maxima except cadmium, the reduction of which occurs at the electrocapillary zero. It was stated that no simple relationship could be found between the appearance of maxima and flow phenomena.
around the cathode. Maxima were observed without any motion in the
diffusion layer, and motions were observed without the formation of
maxima. Gelatin reduces the height of maxima but has very little
effect on motion. The drop time affects both height and motion of
electrolyte. It was concluded that the height of a polarographic
maximum is determined by factors other than motions around the cathode.

All of the observations and interpretations of maxima which
have been given leave several of their characteristics unexplained.
Most of these are probably related to the relative adsorbability of
the various ionic and molecular species on the liquid mercury surface
under its continually changing conditions of electric charge. For
example, the relation between the height of a maximum of a particular
ion and its concentration has not been settled. Furthermore, two
different ions which are reduced at about the same potential do not
give maxima of the same height under identical conditions of ionic
concentration.

It has been shown by Van Rysselberghe and Gropp\(^7\) that the
well-known Ilkovic equation is not applicable to the waves of certain
quaternary ammonium ions without an empirical correction factor which
presumably is dependent upon their adsorbability. The experimental
work to be described in this dissertation is an attempt to relate
the structure of ammonium ions substituted with various hydrocarbon
radicals to their adsorbability. To carry out this objective the
effects of mono-, di-, tri-, and tetra-m-alkyl (including benzyl)
ammonium bromides on the maxima of nickel, manganese, and barium have been studied.
Part II

EXPERIMENTAL

A Sargent-Heyrovsky Model XII photographically recording polarograph was used in this work. The electrolysis vessel was the simple Erlenmeyer type. Tank nitrogen was used without special purification for removing dissolved oxygen from solutions.

The mercury used was purified by passage in a fine stream through columns of dilute nitric acid and dilute sulfuric acid and by a final distillation under reduced pressure. A large mercury pool was used as the anode.

Since it is well known that the height of a maximum is affected by the rate at which the mercury drops fall, the drop time was regulated to 2.0 to 2.2 seconds. No differences were observed with different capillaries as long as the drop time was kept within these limits. All current measurements were made at a galvanometer sensitivity of 0.49 microamperes per millimeter.

The potassium bromide, lithium chloride, nickel chloride, manganous chloride, and barium bromide used were reagent grade chemicals. Solutions were prepared by dilution in "Normax" grade volumetric flasks.

Potassium bromide was chosen as supporting electrolyte for the nickel and manganese reductions in order that most of the anions present would be of one kind. For the reduction of barium it was
necessary to use lithium chloride as the supporting electrolyte since the reduction potentials of barium and potassium are too close together for a good separation of the waves.

Some of the substituted ammonium salts have not been mentioned in the literature. Therefore, their preparation will be described briefly. They are most easily prepared, purified, and stored as the bromides.

The mono- and di-\(n\)-alkyl ammonium bromides from ethyl through \(n\)-amyl and dimethyl through di-\(n\)-amyl were already available from another research project. Di-\(n\)-heptyl amine could not be procured, and its omission constitutes a gap in the di-\(n\)-alkyl series.

\(n\)-Hexyl and \(n\)-heptyl ammonium bromides were prepared by adding a small excess of 48 per cent hydrobromic acid to 10 g. of the amine. Since these salts are difficult to crystallize in the presence of water, they were dried by azeotropic distillation with benzene. The \(n\)-hexyl salt was recrystallized from an acetone-benzene mixture, and the \(n\)-heptyl salt from acetone alone.

\(n\)-Octyl ammonium bromide was prepared by adding a small excess of 48 per cent hydrobromic acid to the amine and recrystallizing the product from acetone. Removal of water was not necessary.

Di-\(n\)-hexyl and di-\(n\)-octyl ammonium bromides were prepared also by adding hydrobromic acid to the amines. The di-\(n\)-hexyl salt was recrystallized from an ethanol-diethyl ether mixture, and the di-\(n\)-octyl salt from a 50 per cent ethanol-water mixture.
Trimethyl ammonium bromide was prepared by saturating 48 per cent aqueous hydrobromic acid with gaseous trimethyl amine, evaporating to dryness, and washing with cold acetone.

The tri-n-alkyl series from ethyl to n-butyl was prepared by direct addition of 48 per cent hydrobromic acid to the amines, evaporating to dryness, and washing with cold acetone.

Tri-n-amyl and tri-n-hexyl ammonium bromides were prepared by saturating the amines with dry gaseous hydrogen bromide and recrystallizing the salts from carbon tetrachloride. Since the amount of tri-n-hexyl ammonium bromide obtained in this manner was too small for analysis, a solution was prepared by adding an equivalent amount of hydrobromic acid to a 50 per cent ethanol-water solution of the amine. No difference was observed between the compounds obtained from these two preparations in their effect on the maxima of nickel and manganese.

Benzyl and dibenzyl ammonium bromides were prepared by adding hydrobromic acid to solutions of the amines in acetone. They were recrystallized from ethanol-water or acetone-water mixtures.

Tribenzyl ammonium bromide was prepared in the same manner, but the salt is relatively insoluble in acetone and was not further purified.

Tetramethyl and tetraethyl ammonium bromides were Eastman White Label chemicals. The tetraethyl salt was recrystallized from ethanol-water mixtures. Tetra-n-butyl ammonium iodide was also an Eastman
White Label chemical. A solution of tetra-n-propyl ammonium bromide was prepared by neutralizing a dilute solution of tetra-n-propyl ammonium hydroxide to pH 7.0 with a standard solution of hydrobromic acid.

Hexadecyl trimethyl ammonium bromide was used as obtained from Fine Organics, Inc. The manufacturer states that this product consists of 90 per cent hexadecyl, 6 per cent octadecyl, and 4 per cent octadecenyl ammonium bromide.

Analyses of most of the compounds are given in Table I. Bromide determinations were made by the Volhard method. In the cases of di-n-octyl and tri-n-amyl ammonium bromides, which are difficultly soluble in water, the titrations were carried out in 50 per cent ethanol-water solution with silver nitrate standardized under the same conditions against potassium bromide. Tribenzyl ammonium bromide, because of its low solubility, was not analyzed.

A standardized procedure was used in the preparation of solutions for electrolysis. A 0.1 M solution of potassium bromide was used as the supporting electrolyte for the nickel and manganese reductions and 0.1 M lithium chloride for the barium reduction. The concentration of the reducible ion was $2.0 \times 10^{-3}$ M in all cases.

To 10.00 ml. of 0.1 M potassium bromide or lithium chloride in the electrolysis cell, 0.20 ml. of 0.100 M solution of the metallic ion was added. Oxygen was removed from this solution by bubbling tank nitrogen through it at the rate of 2-4 bubbles per second for 10 minutes.
Three consecutive polarograms of the metallic ion alone were run. A solution of the substituted ammonium salt was then added in appropriate increments. The solution was mixed in the cell by bubbling nitrogen through it for about one minute. Three polarograms were recorded after each addition. All polarograms were taken with at least two different sets of solutions and found to be reproducible.

Tri-n-hexyl, di-n-octyl, and tri-benzyl ammonium bromides were dissolved in a 50 per cent ethanol-water mixture for addition to the electrolysis cell. These salts are rather insoluble in water, and addition of saturated aqueous solutions would have resulted in excessive dilution. It was demonstrated that the small quantity of ethanol introduced (up to 1 per cent) had no effect on the maxima. This was done by comparing polarograms of nickel solutions to which di-n-octyl ammonium bromide dissolved in water had been added with polarograms of nickel solutions to which di-n-octyl ammonium bromide dissolved in 50 per cent ethanol-water solution had been added.

Since the heights of these acute maxima are not perfectly reproducible, an average value was obtained from the three polarograms. This average value was used in preparing the figures. The reason for this irregularity appears to be that the maximal current observed depends upon the exact stage in the life of the drop at which the applied voltage reaches the particular value corresponding to the maximum.

The effect of decreasing the metallic ion concentration by adding small volumes of reagent to the cell solution was shown to be negligible as far as the characteristics of the maxima were concerned. In
extreme cases, as with 0.001 M solutions of amine salts where dilution sometimes amounted to 10 per cent, the expected decrease in the diffusion current was observed; but the difference in height of the maxima was still within the average deviation of a series of measurements on a given solution.

### TABLE I

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bromine, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated</td>
</tr>
<tr>
<td>n-Hexyl ammonium bromide</td>
<td>43.88</td>
</tr>
<tr>
<td>n-Heptyl ammonium bromide</td>
<td>40.75</td>
</tr>
<tr>
<td>n-Octyl ammonium bromide</td>
<td>38.03</td>
</tr>
<tr>
<td>Di-n-hexyl ammonium bromide</td>
<td>30.01</td>
</tr>
<tr>
<td>Di-n-octyl ammonium bromide</td>
<td>24.79</td>
</tr>
<tr>
<td>Trimethyl ammonium bromide</td>
<td>57.79</td>
</tr>
<tr>
<td>Triethyl ammonium bromide</td>
<td>44.44</td>
</tr>
<tr>
<td>Tri-n-propyl ammonium bromide</td>
<td>36.10</td>
</tr>
<tr>
<td>Tri-n-butyl ammonium bromide</td>
<td>30.39</td>
</tr>
<tr>
<td>Tri-n-amyl ammonium bromide</td>
<td>25.92</td>
</tr>
<tr>
<td>Benzyl ammonium bromide</td>
<td>42.49</td>
</tr>
<tr>
<td>Dibenzyl ammonium bromide</td>
<td>28.73</td>
</tr>
</tbody>
</table>
Part III

DESCRIPTION AND DISCUSSION OF POLAROGRAMS

The data obtained in this work are presented largely in the form of polarographic waves rather than in tabular form because of the previously mentioned fact that the height of the acute maximum is not exactly reproducible with the recording polarograph and because the results in general are shown much more graphically by polarographic waves than by tables of numerical data. The figures (3-36) are tracings of the original waves. In most cases an average is taken for the peak of the maximum from two or more different recordings. In each case, the first curve is that of the metallic ion with no maximum suppressor added. Approximately 1100 polarographic waves were made in the course of this research.

The waves are arranged in several groups according to:

(1) Increasing concentration of the added amine salt,
(2) Increasing molecular weight of the amine salt in a homologous series,
(3) Increasing number of alkyl groups of one kind in the ammonium ion,
(4) Increasing reduction potential of the metallic ion.

Nickel, manganese, and barium were chosen for this work for several reasons. Their reductions occur on the negative side of the electrocapillary maximum. The work of Heyrovsky and his students on maxima was done with oxygen, which is reduced on the positive slope
of the electrocapillary curve and which is an uncharged molecule. Nickel, manganese, and barium give maxima of similar characteristics, and their reduction potentials cover a considerable range of voltage. Nickel is reduced at about \(-1.0\) volts (measured against the saturated calomel electrode), manganese at about \(-1.5\) volts, and barium at about \(-1.9\). Under equal conditions of ionic concentration, their maxima are distinguished by increasing sharpness as the reduction potential increases. All form maxima of about the same height, and their diffusion coefficients are not greatly different. All of the substituted ammonium compounds are reduced at potentials more negative than barium and therefore do not interfere with the reduction of any of the three metallic ions.

None of the three metallic ions exhibits a maximum in \(0.1 \text{ M}\) potassium bromide when the concentration of the ion is as low as \(4 \times 10^{-4}\) molar. When the concentration is \(8 \times 10^{-4} \text{ M}\), a small maximum is formed; and as the concentration is increased, the maximum grows. A concentration of reducible ion of \(2 \times 10^{-3} \text{ M}\) is near the upper limit feasible for polarographic analysis, and it is to be expected that at this concentration the maximum would be most difficult to suppress. For this reason \(2.0 \times 10^{-3} \text{ M}\) solutions of nickel, manganese, and barium were used to obtain the polarograms.

Gelatin,\(^{26}\) methyl cellulose,\(^{26}\) and horse serum albumin,\(^{16}\) when used as maximum suppressors, will cause a reduction in the limiting diffusion current of as much as 25 per cent if their concentrations
exceed certain limits. Presumably, this is due largely to an increase in the viscosity of the solution and a consequent decrease in the diffusion coefficient of the reducible substance. This lowering of the diffusion current was not noticed with any of the amine salts, most of which are completely ionic and do not affect the viscosity appreciably in very dilute solutions. It should be noted that some multivalent metallic ions like calcium and lanthanum can eliminate maxima without affecting the diffusion current.\textsuperscript{30}

Table II shows the approximate minimum concentrations of the various substituted ammonium ions necessary to suppress completely the nickel and manganese maxima. Some of these values were obtained by interpolation. For the nickel maximum, the lowest effective concentration found was $2 \times 10^{-6} \text{M}$ for di-$n$-hexyl, di-$n$-octyl, tri-$n$-butyl, tri-$n$-amyl, tetra-$n$-butyl, and dibenzyl ammonium bromides. For manganese, the lowest value was $10^{-7} \text{M}$ for tri-$n$-amyl, tetra-$n$-butyl, and hexadecyl trimethyl ammonium bromides. For purposes of comparison, it may be mentioned that Zlotowski and Kolthoff\textsuperscript{30} found that $5 \times 10^{-5} \text{M}$ lanthanum would eliminate the maximum in the wave of $10^{-3} \text{M}$ calcium; and Kolthoff and Lingane,\textsuperscript{18} p. 119, show that the lead maximum is eliminated by the sodium salt of methyl red in a concentration of about $10^{-5}$ molar. Gelatin is usually used in a concentration of 0.01 per cent. A $2 \times 10^{-6} \text{M}$ di-$n$-hexyl ammonium bromide solution is approximately $5 \times 10^{-5}$ per cent di-$n$-hexyl ammonium bromide. Gelatin, of course, cannot be compared with the amine salts on a molar basis.
TABLE II
MOLAR CONCENTRATIONS NECESSARY TO SUPPRESS MAXIMA COMPLETELY

<table>
<thead>
<tr>
<th>Compound</th>
<th>Nickel</th>
<th>Manganese</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl ammonium bromide</td>
<td>...a</td>
<td>...a</td>
</tr>
<tr>
<td>Ethyl ammonium bromide</td>
<td>...a</td>
<td>...a</td>
</tr>
<tr>
<td>n-Propyl ammonium bromide</td>
<td>...a</td>
<td>...a</td>
</tr>
<tr>
<td>n-Butyl ammonium bromide</td>
<td>...a</td>
<td>...a</td>
</tr>
<tr>
<td>n-Amyl ammonium bromide</td>
<td>0.001</td>
<td>...a</td>
</tr>
<tr>
<td>n-Hexyl ammonium bromide</td>
<td>0.0002</td>
<td>...a</td>
</tr>
<tr>
<td>n-Heptyl ammonium bromide</td>
<td>0.00005</td>
<td>...a</td>
</tr>
<tr>
<td>n-Octyl ammonium bromide</td>
<td>0.00002</td>
<td>...a</td>
</tr>
<tr>
<td>Dimethyl ammonium bromide</td>
<td>...a</td>
<td>...a</td>
</tr>
<tr>
<td>Diethyl ammonium bromide</td>
<td>...a</td>
<td>...a</td>
</tr>
<tr>
<td>Di-n-propyl ammonium bromide</td>
<td>0.0003</td>
<td>...a</td>
</tr>
<tr>
<td>Di-n-butyl ammonium bromide</td>
<td>0.00002</td>
<td>...a</td>
</tr>
<tr>
<td>Di-n-amyl ammonium bromide</td>
<td>0.000004</td>
<td>0.001</td>
</tr>
<tr>
<td>Di-n-hexyl ammonium bromide</td>
<td>0.000002</td>
<td>0.0005</td>
</tr>
<tr>
<td>Di-n-octyl ammonium bromide</td>
<td>0.000002</td>
<td></td>
</tr>
<tr>
<td>Trimethyl ammonium bromide</td>
<td>...a</td>
<td>...a</td>
</tr>
<tr>
<td>Triethyl ammonium bromide</td>
<td>0.0002</td>
<td>...a</td>
</tr>
<tr>
<td>Tri-n-propyl ammonium bromide</td>
<td>0.000006</td>
<td>0.001</td>
</tr>
<tr>
<td>Tri-n-butyl ammonium bromide</td>
<td>0.000002</td>
<td>0.0004</td>
</tr>
<tr>
<td>Tri-n-amyl ammonium bromide</td>
<td>0.000002</td>
<td>0.0001</td>
</tr>
<tr>
<td>Tri-n-hexyl ammonium bromide</td>
<td>0.000004</td>
<td>...</td>
</tr>
<tr>
<td>Tetramethyl ammonium bromide</td>
<td>...a</td>
<td>...a</td>
</tr>
<tr>
<td>Tetraethyl ammonium bromide</td>
<td>0.00002</td>
<td>0.0005</td>
</tr>
<tr>
<td>Tetra-n-propyl ammonium bromide</td>
<td>0.000004</td>
<td>0.001</td>
</tr>
<tr>
<td>Tetra-n-butyl ammonium iodide</td>
<td>0.000002</td>
<td>0.0001</td>
</tr>
<tr>
<td>Benzyl ammonium bromide</td>
<td>0.0002</td>
<td>...a</td>
</tr>
<tr>
<td>Dibenzyl ammonium bromide</td>
<td>0.000002</td>
<td>0.0005</td>
</tr>
<tr>
<td>Tribenzyl ammonium bromide</td>
<td>...c</td>
<td>...d</td>
</tr>
<tr>
<td>Hexadecyl trimethyl ammonium bromide</td>
<td>0.00001</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

aGreater than 0.001
bGreater than 0.0001
cGreater than 0.00001
dNot sufficiently soluble
Figures 3 through 9, 35, and 36 were selected to show the
effect of increasing concentration of substituted ammonium ion on
the nickel and manganese maxima. These are typical of the polaro-
grams obtained for most of the amine salts. They show that increasing
concentration of the amine salt progressively reduces the maximum
until a normal S-shaped wave is obtained.

For a more detailed analysis of the effect of increasing
concentration, the relationship between the height, $H$, of the nickel
maximum and the concentration, $C$, of n-heptyl ammonium bromide is
shown in the graph in Figure 1. The n-heptyl compound was chosen for
this analysis because the low concentrations required do not necessi-
tate the addition of appreciably large quantities of solution to the
cell. At low concentrations of the n-heptyl ammonium ion, the curve
is very nearly straight; and at higher concentrations, it approaches
the value of the limiting diffusion current. The height, $H$, is measured
in millimeters from the base line of the wave to the top of the acute
maximum. The considerable scattering of points results from the fact
that maxima are not perfectly reproducible when recorded photographically.

In order to test the applicability of the Freundlich adsorp-
tion equation as used by Hamamoto [page 7] for the oxygen maximum, log
$H$ is plotted against log $C$ on the same graph. It is clear that this
relationship does not hold in the case of nickel with n-heptyl ammon-
ium bromide.

Figure 10 shows the effect of a single amine salt, tri-n-butyl
ammonium bromide, on the maxima of nickel, manganese, and barium.
Figure 1. A. Effect of concentration of n-heptyl ammonium bromide on height of nickel maximum
   B. Log height plotted against log concentration
As the reduction potential of the metallic ion increases, the effectiveness of the suppressor decreases. It would appear reasonable to expect that the strength of adsorption of a univalent ammonium ion would be dependent upon the negative potential of the dropping mercury electrode. In other words, the tri-n-butyl ammonium ion should be adsorbed more strongly at -1.9 volts than at -1.5 volts, and more strongly at -1.5 volts than at -1.0 volts: The strength of adsorption should be directly proportional to the charge of the cathode for a given ion. The same consideration should apply to a divalent positive ion or to a group of three such ions. Barium should be more strongly adsorbed at its reduction potential, -1.9 volts, than is manganese at its reduction potential, -1.5 volts; and manganese should be more strongly adsorbed at -1.5 volts than nickel at -1.0 volts. However, the polarographic data indicate that tri-n-butyl ammonium ions are not able to displace barium ions in the adsorption layer as easily as they displace manganese ions and are not able to displace manganese ions as easily as nickel ions. Adsorption of tri-n-butyl ammonium ions does not appear to increase with increasing voltage at as great a rate as does adsorption of the divalent ions. This fact may be related to the polarizability of the ions.

None of the amine salts studied were able to eliminate the barium maximum at concentrations of $10^{-3}$ M, although barium gives a normal S-shaped wave in solutions in which tetraethyl ammonium iodide is the supporting electrolyte, and probably would do so in a similar
solution of any other ion which is as effective as tetraethyl ammonium iodide at low concentrations.

Figures 11 to 15 illustrate the effect of lengthening the carbon chain on the suppression of maxima. These sets of polarograms were made by adding the hydrobromides of the primary amines to solutions of nickel, manganese, and barium. Because of the progressively lower concentrations required, three groups of curves had to be assembled for nickel in order to cover the entire range of methyl to octyl.

Increasing the length of the chain reduces the maximum peak at a given concentration of suppressor. This is true for all of the metallic ions, although the manganese maximum is not entirely eliminated by $10^{-3}$ M n-octyl ammonium bromide [Figure 14], the longest chain in this group. The barium maximum is affected only slightly [Figure 15].

It is generally accepted that the substituted ammonium ion is a tetrahedron with the nitrogen atom in the center and with its four covalent bonds directed toward the apices. In the monosubstituted ion, the size of the alkyl radical so far exceeds the size of the hydrogen atom that the ion approaches the configuration of a chain, thus:

\[
\begin{array}{cccc}
H & H & H \\
\ldots & C & C & N & H \\
H & H & H \\
\end{array}
\]

The single net positive charge may be considered to reside in the
equilateral triangle formed by the three hydrogen atoms attached to the nitrogen. This end of the ion is positively charged. It has been shown in previous work that alkyl groups become increasingly electron-positive as the chain length increases. The longer the carbon chain, the greater is its push on the bonding pair of electrons toward the nitrogen atom. Thus, as the alkyl group lengthens, the hydrocarbon end becomes more positive, and the nitrogen atom becomes less positive. The tendency for the ion to lie flat on the mercury surface probably becomes greater as the hydrocarbon group increases in length. The mercury surface is therefore completely covered by lower concentrations as the number of carbon atoms increases. In addition to this increase in adsorbability, the larger area covered by the longer chain lowers the concentration necessary to form a complete layer.

The effect of greater chain length in the di-n-alkyl series is seen in Figures 16 to 20. In all except Figure 18, the suppression of the maximum is similar to that shown by salts of the primary amines: The longer the hydrocarbon radical, the lower the peak at a given concentration. But Figure 18 indicates that the nickel maximum with \(10^{-6} \text{ M} \ \text{di-n-octyl ammonium bromide}\) is slightly greater than with \(10^{-6} \text{ M} \ \text{di-n-hexyl ammonium bromide}\). Apparently the rate of increase in ability to suppress the maximum becomes smaller as the size of the ion increases and finally reaches a point at which the trend is reversed. This is also suggested by the curves for manganese with \(10^{-4} \text{ M} \ \text{di-n-hexyl and} \ 10^{-4} \text{ M} \ \text{di-n-octyl ammonium bromides}\) [Figure 20], although
the point of maximum effectiveness has not quite been reached in this case. Some possible explanations will be mentioned later in the discussion of the tri-n-alkyl series where this phenomenon is much more pronounced.

Increasing the chain length in the tri-n-alkyl series gives the results shown in Figures 21 to 24. It is observed in Figures 22 and 23 that tri-n-butyl and tri-n-amyl ammonium ions are almost equally effective on nickel, that both are better suppressors than tri-n-propyl, and that both are better than tri-n-hexyl. The tendency shown by the di-n-alkyl series to reach a maximum effectiveness is repeated here. Figure 2 plots the height of the nickel maximum against the number of carbon atoms in the alkyl radical for $10^{-6}$ M and $10^{-7}$ M concentrations of the tri-n-alkyl ammonium ions. This could not be confirmed with manganese because of its higher reduction potential and because tri-n-hexyl ammonium bromide is soluble only to the extent of about $10^{-5}$ moles per liter.

The explanations which are presented must include the possibility of some change in distribution of electric charge in the substituted ammonium ion, such as was postulated for the monoalkyl series from ethyl to octyl, and which could be correlated with adsorbability. In connection with this the effects of steric or space relationships of the hydrocarbon groups within the ion must also be considered. For example, the tri-n-alkyl ammonium ion could not possibly be considered to be linear, although it might be nearly planar. The difficulties and complexities involved in trying to
Figure 2. Height of nickel maximum plotted against number of carbon atoms in the alkyl group of the tri-n-alkyl ammonium bromides at two concentrations of the amine salts.
construct as detailed a picture as the adsorption of a di- or tri-
substituted ammonium ion on the mercury surface make this approach
seem to have little possibility of success.

A much better clue is found in the work of Ralston and
Hoerr\(^2\) on the conductivities of a series of amine salts ranging
from n-octyl ammonium chloride to n-octadecyl ammonium chloride.
The conductivity measurements show that the tendency of these electro-
lytes to form colloidal micelles increases with increasing molecular
weight. Octyl ammonium chloride does not form a colloidal solution
at any concentration up to about 1.0 M at 60°C. It acts entirely
as a uni-univalent electrolyte in accordance with the Onsager Theory.
Sharp decreases in equivalent conductivity at 60°C. occur with larger
cations, indicating a transition to micellar aggregates at the
following concentrations:

<table>
<thead>
<tr>
<th>Number of Carbon Atoms</th>
<th>Concentration (Moles/liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.04</td>
</tr>
<tr>
<td>12</td>
<td>0.013</td>
</tr>
<tr>
<td>14</td>
<td>0.004</td>
</tr>
<tr>
<td>16</td>
<td>0.0008</td>
</tr>
<tr>
<td>18</td>
<td>0.0003</td>
</tr>
</tbody>
</table>

From Figure 2, we find that the reversal of the trend toward
increasing effectiveness as a maximum suppressor occurs at tri-n-
hexyl, which has 18 carbon atoms. The concentration of the tri-n-
hexyl ammonium ion, \(10^{-5}\) M, is, however, considerably less than the
critical concentration for micelle formation shown [page 28] for the straight chain of 18 carbon atoms. The difference in temperature and the conditions of the polarographic experiments hardly permit a direct comparison of critical concentrations.

However, it seems very likely that a transition from simple ions to colloidal aggregates may well account for the observation that a maximum effectiveness is approached as the size of the hydrocarbon portion of the ion is increased. Further evidence in support of this will be presented.

Increasing length of the carbon chain in the tetra-n-alkyl series produces the results illustrated for nickel in Figure 25, and for manganese in Figure 26. As with the other series, the longer the chain, the lower the nickel maximum at a given concentration of quaternary ion. Reduction of the maximum proceeds in the order: tetramethyl, tetraethyl, tetra-n-propyl, and tetra-n-butyl. No limit of effectiveness is reached with the fourth member of the series. The manganese maxima, however, do not follow the expected pattern. No explanation for the fact that tetra-n-propyl is out of place in the series can be offered at present.

In order to determine the effect of a quaternary ammonium ion with a very long chain, hexadecyl trimethyl ammonium bromide was added to solutions of nickel and manganese with the results illustrated in Figures 35 and 36. It was expected that a highly surface-active compound of this type would be an especially good maximum suppressor,
but the polarograms show that it is less effective with nickel than some others; and with manganese it is no better than several other salts [Table II, page 20]. It is possible that further investigation of compounds of this type might lead to the discovery of a suppressor as universally useful as gelatin and without its effect on the diffusion current and its susceptibility to decomposition.

It should be noted here that the tetraalkyl bases are very strong and that the primary, secondary, and tertiary amines are weak bases with ionization constants of $10^{-3}$ or less. The question of hydrolysis of the substituted ammonium ion does not enter into consideration. Calculations will show that hydrolysis does not exceed one per cent in any case. The hydrogen ion concentration in all solutions is too small to be detected polarographically at the galvanometer sensitivity used and differs only very slightly from that of so-called "equilibrium" water.

The question of relative basic strength of the amines naturally arises. The ionization constants of the primary amines are practically identical from methyl amine [$K = 5.0 \times 10^{-4}$] to octadecyl amine [$K = 4.0 \times 10^{-4}$]. The ionization constants of the corresponding secondary amines are about twice as great, and those of the tertiary amines are nearly the same as primary amines. No relationship appears to exist between these ionization constants and the effect of the cation on polarographic maxima. In contrast to the amines, it has been found that the acid strength of the normal aliphatic
acids decreases with increasing chain length up to about 9 or 10 carbons, where it levels off and remains practically constant up to about 17 or 18 carbons.8

In Figures 27 to 31, curves have been assembled for the series from the monoalkyl ammonium ion to the tetraalkyl ammonium ion. These curves show how increasing the number of alkyl groups of one kind on the nitrogen atom affects the nickel and manganese maxima. Figure 27 shows that a concentration of $10^{-5}$ M ethyl and diethyl ammonium ions have little effect on the nickel maximum; that triethyl ammonium ion reduces the height about 10 per cent; and that the tetraethyl ammonium almost produces the normal S-shaped wave.

Similar results are obtained with $10^{-6}$ M n-butyl substituted ammonium ions [Figure 28]. But in the case of the n-amyl substituted ammonium ions it was found that the maxima of nickel with $10^{-6}$ M di-n-amyl and $10^{-5}$ M tri-n-amyl ammonium ions are very nearly the same height, both being lower than that of the maxima with mono-n-amyl [Figure 29]. Furthermore, with the n-hexyl substituted ammonium ions, the di-n-hexyl is more effective than either the mono- or the tri-n-hexyl [Figure 30].

Here, again, the effectiveness as a maximum suppressor increases with increasing size of the ion, then levels off, and finally decreases. Again, the most probable explanation for the decrease seems to be that of increasing tendency to form colloidal solutions. The generally accepted structure of the micelle in water is that of a globular shaped agglomeration of ions with the hydrocarbon portion pointing
inward toward the center and with the hydrophilic ends forming the outer surface. Such a particle seems to be less strongly adsorbed on the mercury drop than the single cation. The polarographic behavior of cationic colloidal electrolytes is a subject which warrants further investigation.

The benzyl substituted ammonium ions produce the polarograms shown in Figures 32 to 34.

Tribenzyl ammonium bromide is too insoluble to affect the manganese maximum appreciably. A saturated solution is less than $5 \times 10^{-4}$ molar. This was estimated from the formation of a precipitate which failed to redissolve when a solution of the tribenzyl salt was added to the electrolysis cell.

The effectiveness on the nickel maximum of increasing number of benzyl groups is in the order: benzyl, tribenzyl, dibenzyl. The formation of a colloid is improbable since there is no long hydrocarbon chain.

The dibenzyl ammonium ion is more strongly adsorbed than the benzyl ammonium ion, but the tribenzyl ammonium ion is less strongly adsorbed than the dibenzyl. The preponderance of phenyl groups, which are known to be more negative than paraffinic groups, although not necessarily reducing the electropositivity of the tribenzyl ammonium ion with respect to the dibenzyl ammonium ion, does lower the adsorbability. It appears that the benzyl ammonium ion is adsorbed with the phenyl group away from the negative mercury surface and with the nitrogen and three hydrogen atoms adjacent to it. The dibenzyl ammonium ion
is attached in the same manner and is attracted to the mercury surface by a stronger force. But in the tribenzyl ammonium ion, the point of attachment of the ion is practically blocked off by the three surrounding benzene rings, and the forces of adsorption are reduced.
Figure 3
Nickel waves with increasing concentrations of n-butyl ammonium bromide

Figure 4
Nickel waves with increasing concentrations of di-n-butyl ammonium bromide
Nickel waves with increasing concentrations of tri-n-butyl ammonium bromide

Figure 5

Nickel waves with increasing concentrations of tetra-n-butyl ammonium iodide

Figure 6
Manganese waves with increasing concentrations of n-amyl ammonium bromide

Figure 7

Manganese waves with increasing concentrations of di-n-amyl ammonium bromide

Figure 8
Manganese waves with increasing concentrations of tri-n-amy1 ammonium bromide

Nickel, manganese and barium waves with $10^{-4}$ M tri-n-butyl ammonium bromide
Figure 11
Nickel waves with
$10^{-3} \text{M}$ mono-alkyl ammonium bromides

Figure 12
Nickel waves with
$5 \times 10^{-4} \text{M}$ mono-alkyl ammonium bromides
Figure 13
Nickel waves with
$10^{-5}$ M mono-alkyl ammonium bromides

Figure 14
Manganese waves with
$10^{-3}$ M mono-alkyl ammonium bromides
Figure 15
Barium waves with
$10^{-3} \text{ M mono-alkyl ammonium bromides}$

Figure 16
Nickel waves with
$10^{-4} \text{ M di-n-alkyl ammonium bromides}$
Nickel waves with $10^{-5}$ M di-n-alkyl ammonium bromides

Figure 17

Nickel waves with $10^{-6}$ M di-n-alkyl ammonium bromides

Figure 18
Figure 19
Manganese waves with
$5 \times 10^{-4} \text{ M di-n-alkyl ammonium bromides}$

Figure 20
Manganese waves with
$10^{-4} \text{ M di-n-alkyl ammonium bromides}$
Figure 21
Nickel waves with
$10^{-5}$ M tri-n-alkyl ammonium bromides

Figure 22
Nickel waves with
$10^{-6}$ M tri-n-alkyl ammonium bromides
Figure 23
Nickel waves with $10^{-7} \text{M}$ tri-n-alkyl ammonium bromides

Figure 24
Manganese waves with $10^{-4} \text{M}$ tri-n-alkyl ammonium bromides
Figure 25
Nickel waves with
$10^{-6} \text{ M}$ tetra-n-alkyl ammonium halides

Figure 26
Manganese waves with
$10^{-4} \text{ M}$ tetra-n-alkyl ammonium halides
Figure 27
Nickel waves with
$10^{-5} \text{M}$ ethyl ammonium bromides

Figure 28
Nickel waves with
$10^{-6} \text{M}$ n-butyl ammonium halides
Figure 29
Nickel waves with
$10^{-6} \text{ M } n$-amyl ammonium bromides

Figure 31
Manganese waves with
$10^{-4} \text{ M } n$-butyl ammonium halides
Figure 32
Nickel waves with
$10^{-5} \text{M} \text{ benzyl ammonium bromides}$

Figure 33
Nickel waves with
$10^{-6} \text{M} \text{ benzyl ammonium bromides}$
Figure 34
Manganese waves with
$5 \times 10^{-4} \text{ M benzyl ammonium bromides}$
Figure 35
Nickel waves with increasing concentrations of hexadecyl trimethyl ammonium bromide

Figure 36
Manganese waves with increasing concentrations of hexadecyl trimethyl ammonium bromide
Figure 30
Nickel waves with three concentrations of the n-hexyl ammonium bromides
Part IV

SUMMARY

An effort has been made to contribute to the problem that Kolthoff and Ligane,\textsuperscript{18} page 124, have called one of the most difficult problems in polarography, the interpretation of maxima.

The effects of several substituted ammonium halides on the maxima of nickel, manganese, and barium have been studied. These ammonium salts included the hydrobromides of the primary amines from methyl amine to n-octyl amine; of the secondary amines from dimethyl amine to di-n-octyl amine, excepting di-n-heptyl; and of the tertiary amines from trimethyl to tri-n-hexyl. In addition, the effects of the halides of the tetra-n-alkyl bases from tetramethyl to tetra-n-butyl; the benzyl, dibenzyl, and tribenzyl ammonium bromides; and hexadecyl trimethyl ammonium bromide have been studied.

It has been found that the height of the maximum of the metallic ion is inversely proportional to the concentration of the substituted ammonium ion, to the length of the carbon chain in the alkyl group, and to the number of alkyl groups of one kind attached to the nitrogen atom.

It has been found also that when the substituted ammonium ion reaches a sufficiently large size for the formation of micelles, the effect on the maxima decreases. It has been observed that the
degree of difficulty of suppressing a maximum is in direct relation to the electropositivity of the reducible substance. The results have been interpreted in terms of the relative adsorbabilities of the cations on the mercury drop.
BIBLIOGRAPHY

27. Thiesse and Belon, Compt. rend., 223, 794 (1946).
ACKNOWLEDGMENTS

The author is happy to acknowledge the very valuable instruction and assistance and the inspiring direction of Dr. Armin H. Gropp. Special thanks are due to Mr. Eugene Childers for the preparation of several of the compounds and to Dr. C. B. Pollard for procuring some of the amines.

Without the encouragement and help of the author's wife this work could not have been completed.
William Jordan Barrett was born at Harrison, Georgia, November 7, 1916. He was awarded the degrees of Bachelor of Arts and Master of Arts by Mercer University in 1936 and 1937, respectively. He served as Teaching Fellow in Chemistry at New York University from 1937 to 1940. In 1940 he was employed by the Halliburton Oil Well Cementing Company, Duncan, Oklahoma, as a research assistant; and in 1941 he went to the United States Naval Base in Key West, Florida, to establish an Analytical and Testing Laboratory. During his employment by the United States Navy Mr. Barrett received the Meritorious Civilian Service Award. He came to the University of Florida as an Interim Instructor in 1947.
COMMITTEE REPORT

This dissertation was prepared under the direction of the Co-Chairmen of the Candidate's Supervisory Committee and has been approved by all members of the Committee. It was submitted to the Graduate Council and was approved as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Date: June 5, 1950

______________________
Dean

______________________
A. H. Losap
Co-Chairman

______________________
A. P. Black
Co-Chairman

______________________
R. A. Edwards

______________________
N. J. Jackson

______________________
Paul Farrell

______________________
J. T. Hawkins