CHAPTER V

A.C. VOLTAMMETRY AT THE TUBULAR GRAPHITE ELECTRODE
A.C. VOLTAMMETRY AT THE TUBULAR GRAPHITE ELECTRODE

A.C. voltammetry has shown tremendous increase in interest over the last few years. The technique now stands high in importance amongst the various electrochemical methods of analysis. A fairly good amount of work has been done on reductive a.c. voltammetry at the dropping mercury electrode (12, 14, 26, 37, 49, 50, 55, 68, 71, 165). Bond (25) has given an excellent review of work on a.c. voltammetry in its modern form. Commendable work on higher harmonic a.c. polarography at DME has been carried out by Devay, Garai and coworkers (42, 43).

However, only a few applications of the method using solid micro-electrodes have been reported in literature so far (86, 87, 169, 203, 204). The most important paper appears to be the one reported by Walker, Adams and Juliard (204) in which a.c. voltammetry of a variety of aromatic amino compounds on platinum as well as carbon paste and graphite electrodes has been reported, using 60 cps sine wave at low a.c. voltages varying from 2 to 20 mV. This field, however, appears to have remained more or less unexplored so far.

Keeping in view the specific advantages which a.c. voltammetry happens to have over the conventional d.c. voltammetry, it has been thought of interest to study a.c. voltammetry of some specific organic compounds including some pharmaceutics and drugs at the tubular graphite electrode with a view to seeing if the data could be utilized for carrying out qualitative/quantitative estimations of these compounds.

Materials

The following compounds were selected for a.c. voltammetric studies: All the nine phenothiazine derivatives, described in the
last chapter; some sulpha drugs, namely, sulphanilamide, sulphapyridine, sulphadiazine, sulphaguanidine; some phenolic acids, namely, DOPA, caffeic acid, gallic acid, and some other miscellaneous organic compounds including o-anisidine, p-anisidine, o-dianisidine, o-phenetidine, p-phenetidine, pyrogallol, p-aminophenol, p-methoxyphenol, o- and p- phenylene diamines, ascorbic acid, p-acetylsalicylic acid, uric acid, etc.

All the compounds selected as above are those which did not cause filming of the electrode surface during d.c. voltammetry and thus gave highly reproducible voltammograms.

**General Conditions of Operation**

The various a.c. voltammetric measurements were carried out under the following conditions:

1. **Supporting Electrolyte** : $0.1 \text{M} \text{H}_2\text{SO}_4$
2. **Concentration of Key Material** : $10^{-4} \text{M}$
3. **Volumetric Flow Rate** : 10 ml./min.
4. **Electrode Length** : 1.2 cm.
5. **A.C. Frequency** : Around 1 cps.
6. **Superimposed A.C. Voltage** : 20 mV
7. **Polarograph** : Sargent, Model XXI in conjunction with a multifrequency plug-in Auxiliary Unit fabricated by Sharma et al. (179).

8. **Cell** : H-type cell with SCE as the reference electrode.
The solution under test, taken in the gravity feed, was allowed to flow through the electrode at a constant flow rate of 10 ml. per minute. A gradually increasing d.c. voltage was applied to the cell from the polarograph as usual. An a.c. voltage of 20 mV from the sine wave oscillator of the Auxiliary Unit, at a frequency around 1 cps, was then superimposed on the cell. The current from the cell at each applied potential comprised of both d.c. and a.c. The auxiliary unit converted these currents into voltages, blocked the d.c. voltage, amplified and then rectified the a.c. voltage to give d.c. voltage which was fed to the recorder through a potential divider. In this way, complete a.c. voltammogram was scanned for the anodic oxidation of the test material present in the solution.

RESULTS AND DISCUSSION

The a.c. voltammograms were obtained for the oxidation of all the above mentioned compounds selected for the present investigations. However, only a few voltammograms have been presented in Figs. 73-83 by way of illustration. As can be seen from Figs. 73-76, all the phenothiazine derivatives give two distinct peaks indicating that each phenothiazine derivative oxidises in two steps in 0.1M H₂SO₄ at the graphite surface. As can be recalled, similar results were obtained for the oxidation of phenothiazines through d.c. voltammetry as well. The peak potentials in all the four cases are seen to be quite close to the corresponding halfwave potentials.
A.C. Voltammograms for the Oxidation of Some N-Substituted Phenothiazines

Figure 73: Promethazine Hydrochloride

Figure 74: Promazine Hydrochloride

Figure 75: Diethazine Hydrochloride

Figure 76: Chlorpromazine Hydrochloride

PLATE-12

First Scan
Second Scan

A.C. Voltage vs SCE
A.C. Voltammetric studies on the oxidation of some biologically important compounds.
A.C. VOLTAMMOGRAMS FOR THE OXIDATION OF SOME TYPICAL ORGANIC COMPOUNDS

PLATE-14

CURRENT, μA (r.m.s.)

D.C. VOLTAGE VS SCE

FIG. 81 o-ANISIDINE

FIG. 82 p-ANISIDINE

FIG. 83 p-AMINOPHENOL
From subsequent Figs. 77-83, it is evident that all those substances which oxidise in one step during d.c. voltammetry, exhibit only one peak during a.c. voltammetry as well. This is exactly what was expected. Likewise, p-anisidine (Fig. 82) which oxidises in two steps during d.c. voltammetry, shows two distinct peaks in a.c. voltammetry also. The peak potentials are again fairly close to the corresponding halfwave potentials.

Oxidation of p-aminophenol reveals an interesting feature. The anodic oxidation of the compound through d.c. voltammetry has been reported (2) to be a 2-electron process involving simultaneous oxidation of both the amino and the phenolic groups. On the tubular graphite electrode also, only one wave corresponding to a 2-electron oxidation reaction was observed. Since the halfwave potential of aniline (0.913 V) is slightly lower than the halfwave potential of phenol (0.949 V), we should have expected two oxidation waves, one for the oxidation of the amino group at a lower potential and the other for the oxidation of the phenolic group at a slightly higher potential. However, we get only one wave. This is evidently because the difference between the two halfwave potentials is very small. Nevertheless, the a.c. voltammogram of the p-aminophenol (cf. Fig. 83) clearly shows the formation of two peaks (kinks) at close potentials. This indicates that in p-aminophenol, the oxidation of amino and phenolic groups takes place in steps and not simultaneously. Thus a.c. voltammetry gives better information about the oxidation mechanism of p-aminophenol than the conventional d.c. voltammetry.
As can be seen from Figs. 73-88, the charging currents in all cases are considerably high as compared to the faradaic currents.

Reproducibility of Voltammogram

Successive voltammograms taken on one and the same electrode exhibited poor reproducibility in all cases. The second scan almost invariably showed a hump at about the same potential of about 0.30V vs. SCE, in all cases. The height of this hump was seen to increase gradually with each subsequent scan. The appearance of this hump can, evidently, be attributed to the adsorption of the oxidation product at the electrode surface. With each successive scan, the base current also shifted upwards.

However, if successive voltammograms were recorded on fresh electrodes, the reproducibility was good. The successive waves were then found to be almost identical to one another. It is thus absolutely essential to record each a.c. voltammogram on a fresh electrode.

Current-Concentration Relations

In order to study the current-concentration relationship, a.c. voltammograms were recorded using different concentrations of chlorpromazine (a representative member of substances oxidising in two steps) as well as uric acid (a representative member of substances oxidising in one step), in the concentration range of $4 \times 10^{-5}$ to $6 \times 10^{-4}$M, keeping all other parameters constant. The peak currents obtained at different concentrations for both
the substances are given in table VII. The corresponding
$P/C$ values are given in appropriate columns. As can be seen,
the $P/C$ ratios vary considerably from one another in the entire
range of concentration. The variations for the second peak
currents in the case of chlorpromazine are even greater. The
wide variations in the values of $P/C$ ratios can be attributed
to comparatively high magnitudes of charging currents and their
poor reproducibility. Another factor responsible for these
variations is the non-availability of the identical electrode
surface when different electrodes are to be used for scanning
different voltammograms.

Because of wide variations in the values of $P/C$ ratios,
the a.c. voltammetric data could not be used for quantitative
work.

**Current-Flow Rate Relationship**

In order to study the current-flow rate relationship,
a.c. voltammograms for the oxidation of a number of substances
were obtained at different flow-rates in the laminar flow
regime; keeping all other parameters the same. A fresh or
a redrilled electrode, however, was used for each case. The
peak currents were found to be independent of flow rates in all
cases.

**Current-Frequency Relationship**

In order to study the relation between peak current and
frequency, a.c. voltammograms for the oxidation of $10^{-4}$M solutions
of sulphaguanidine were scanned at different frequencies in the
TABLE VII
CURRENT-CONCENTRATION RELATIONSHIP IN THE OXIDATION OF
CHLORPROMAZINE AND URIC ACID

Supporting Electrolyte: 0.1 M sulphuric acid
Electrode Length: 1.2 cm.
Volume Flow Rate: 10 ml. per minute

Oxidation of Chlorpromazine

<table>
<thead>
<tr>
<th>Concentration (C) (mole/litre)</th>
<th>First peak current ($I_{p1}$) ($\mu A$)</th>
<th>Ratio $I_{p1}/C$</th>
<th>Second peak current ($I_{p2}$) ($\mu A$)</th>
<th>Ratio $I_{p2}/C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4 \times 10^{-5}$</td>
<td>1.8</td>
<td>$450 \times 10^{2}$</td>
<td>1.0</td>
<td>$250 \times 10^{2}$</td>
</tr>
<tr>
<td>$6 \times 10^{-5}$</td>
<td>2.5</td>
<td>$416$</td>
<td>1.4</td>
<td>233</td>
</tr>
<tr>
<td>$8 \times 10^{-5}$</td>
<td>3.4</td>
<td>$425$</td>
<td>1.9</td>
<td>237</td>
</tr>
<tr>
<td>$1 \times 10^{-4}$</td>
<td>3.8</td>
<td>380</td>
<td>2.1</td>
<td>210</td>
</tr>
<tr>
<td>$2 \times 10^{-4}$</td>
<td>7.8</td>
<td>390</td>
<td>5.0</td>
<td>250</td>
</tr>
<tr>
<td>$4 \times 10^{-4}$</td>
<td>16.2</td>
<td>405</td>
<td>6.6</td>
<td>165</td>
</tr>
<tr>
<td>$6 \times 10^{-4}$</td>
<td>21.6</td>
<td>360</td>
<td>10.8</td>
<td>180</td>
</tr>
</tbody>
</table>

Oxidation of Uric Acid

<table>
<thead>
<tr>
<th>Concentration (C) (mole/litre)</th>
<th>Peak Current ($I_p$) ($\mu A$)</th>
<th>Ratio $I_p/C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4 \times 10^{-5}$</td>
<td>$1.2$</td>
<td>$300 \times 10^{2}$</td>
</tr>
<tr>
<td>$6 \times 10^{-5}$</td>
<td>$1.6$</td>
<td>266</td>
</tr>
<tr>
<td>$8 \times 10^{-5}$</td>
<td>$1.7$</td>
<td>212</td>
</tr>
<tr>
<td>$1 \times 10^{-4}$</td>
<td>$2.2$</td>
<td>220</td>
</tr>
<tr>
<td>$2 \times 10^{-4}$</td>
<td>$5.7$</td>
<td>285</td>
</tr>
<tr>
<td>$4 \times 10^{-4}$</td>
<td>$11.4$</td>
<td>310</td>
</tr>
<tr>
<td>$6 \times 10^{-4}$</td>
<td>$14.4$</td>
<td>240</td>
</tr>
</tbody>
</table>
range of 1-20 c.p.s. However, since the voltammograms at frequencies higher than 5 c.p.s. became more and more unsymmetrical, accompanied by greater and greater masking of the faradaic current, it was not possible to compute the peak currents from these voltammograms. Hence, it was not possible to establish any mathematical correlation between current and frequency in the present case.

**Current–Alternating Voltage Amplitude Relationship**

With a view to studying the variation of the peak current with the amplitude of the superimposed alternating voltage, a.c. voltammograms for the oxidation of sulphaguanidine were scanned by superimposing alternating voltages of different amplitudes varying from 5 to 30 mV. An excellent linear relationship was seen to exist between the two parameters.

**General Observations in Respect of A.C. Voltammetric Measurements**

Some of the general observations made during the study of the a.c. voltammetric behaviour of these compounds may be summed up as follows:

1. The number of a.c. peaks is the same as the number of d.c. oxidation steps (except in p-aminophenol).
2. The peak potentials deviate from the corresponding halfwave potentials by not more than 20 mV.
3. The second successive waves in all cases exhibit a hump at about the same potential when successive waves are scanned on one and the same electrode.
4. There is a general shift in the magnitude of base current for each successive scan on the same electrode.
The peak currents are independent of the volumetric flow rate of the electrolytic solution.

The linearity of current-concentration relation is poor and hence the a.c. voltammetry cannot be used for quantitative estimations of organic compounds.

Charging currents are generally very high in relation to faradaic currents.

In case of p-aminophenol, a.c. voltammetry has given a better insight into the mode of its oxidation than the conventional d.c. voltammetry.