CHAPTER - VIII

SUMMARY AND DISCUSSION
An analysis of the literature survey reveals that contradictory views are put forward in the electrochemical studies of thiols, in general, and TU, in particular. It is, therefore, desirable to re-investigate the behaviour of TU at HMDE as well as at a solid electrode, such as, a gold-disc electrode using different complementary techniques (under diverse experimental conditions) in order to elucidate the electrode reaction mechanism(s) during anodic and cathodic depolarization.

8.1.1 PROPERTIES OF TU:

Thiourea has been described as a weak base\textsuperscript{59} and over pH range 3.0-7.5, it exists predominantly in the molecular form\textsuperscript{26}. In aqueous solutions, it exists in thioketo, iso- and zwitterionic forms (eqn.4.1). It exhibits amphoteric character analogous to that of glycine (eqns. 4.2 and 4.3), and exists in zwitterionic form even in strongly alkaline media\textsuperscript{61}. An aqueous solution of TU is susceptible to air oxidation on long exposure. It has been established that TU is moderately toxic and allergenic; and its presence in urine is a non-specific indicator of cancer. The solution chemistry of TU is not well understood. Besides the species mentioned above, other species, such as

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{H}_2\text{N} \\
\text{C} & \quad \text{C} \\
\text{SH} & \quad \text{S}^- \\
\text{NH}_2 & \quad \text{HN} \\
\text{(+cationic or protonated)} & \quad \text{(anionic)}
\end{align*}
\]
do exist in solution as a function of pH. While literature is silent on the formation of an aquo-species, a species such as

\[
\begin{align*}
\text{HO} & \quad \text{C} \quad \text{SH} \\
& \quad \text{NH}_2
\end{align*}
\]

may probably exist in aqueous solution. The chemical oxidation of TU is a complicated process giving different oxidation products depending upon the acidity and oxidizing agents used; and the electro-oxidation of TU using a solid electrode may throw light on its chemical oxidation. TU reacts with heavy metal ions and these reactions are important in the study of binding of heavy metals in biological systems. However, the formation of salts such as \(\text{Hg}_2(\text{RS})_2\) and \(\text{RSHgCl}\) is not established.

6.1.2 LITERATURE REVIEW:

Kappel interpreted the anodic wave of TU at the DME to be due to the oxidation of TU itself. However, according to the literature review upto 1958, it was believed that the anodic wave of TU at the DME was due to the formation of insoluble \(\text{Hg(ous)}\) i.e. \(\text{Hg}^{2+}\) and \(\text{Hg(ic)}\) compounds; and the different waves obtained were interpreted in terms of partial surface\(^\text{\textsuperscript{\chi}}\) coverage thereby leading to electrode surface inactivation. With particular reference to TU, three such
waves were reported, wave $i_a$ due to HgRS, $i_1$ also due to Hg(RS) and $i_A$ probably due to Hg(RS)$_2$. Edsberg$^{20}$, however, described the wave $i_1$ to be due to an insoluble compound formed by the oxidation of Hg to Hg$^{+2}$ with TU. Later on, it was pointed out by Kies$^{25}$ and others that the wave $i_1$ was, in fact, due to the formation of a soluble species such as $[\text{Hg(TU)}]^{+2}$. The existence of a protonated species (eqn.4.7) of TU, as proposed by Fedoronko et al$^{23}$, was ruled out by Nyman and Parry$^{26}$.

8.1.3 CHOICE OF SUPPORTING ELECTROLYTE:

In strongly acidic solutions ($>1.0\text{M}$), and particularly in HNO$_3$, TU is rapidly oxidised to the disulphide on standing, thus obscuring the main anodic wave due to the soluble cationic species $[\text{Hg(RS)}]^{+2}$. However, the studies show that any of the mineral acids (HCl, H$_2$SO$_4$, HNO$_3$) may be used if it is sufficiently dilute (0.1N). However, HNO$_3$ is disadvantageous as it contains nitrous acid (photodecomposition) to give different oxidation products (eqns. 4.8 and 4.9).

8.2 EFFECT OF pH AND CONCENTRATION OF TU ON THE MAIN ANODIC WAVE:

Half-wave potential, $E_1$, of the main anodic wave due to $[\text{Hg(TU)}]^{+2}$ was independent of pH in acidic solutions, thus indicating that $\text{H}^+$ ions do not participate in the anodic process. However, $E_1$ is a linear function of
pH in alkaline media. The anodic waves are well defined over the entire pH region, except the transition pH region (5.0 – 8.0). The anodic process in acidic medium is replaced by the one in alkaline medium whereby electrode surface is progressively covered by the insoluble electrode product formed; and this affects the $E_1^2$ – pH dependence over the transition pH region. A study of the anodic waves observed for a few sulfhydryl compounds shows that TU is peculiar in its behaviour (Fig. 1.1) and Fig. (4.3). Thus, the polarography of TU can be studied even in an unbuffered acidic media.

According to the data of Nyman and Parry\textsuperscript{26}, $i_d \propto \ln$ concentration of TU, the increase in the slope (logarithmic analysis) is entirely due to the irreversibility, as higher complexes are formed beyond 10 mM TU. However, Edsberg\textsuperscript{20} showed current-concentration linearity to be valid only upto $1.8 \times 10^{-3}$ M. Thus, an element of uncertainty, as to whether the irreversibility is due to a slow charge transfer step or the formation of successive higher complexes, still exists. This aspect was, therefore, reinvestigated at pH 1.3 and ~6.0; and the results were in perfect agreement with those of Edsberg\textsuperscript{20} thus indicating that successive higher complex species were formed even below 10 mM TU, and that the irreversibility was due to the formation of successive higher complexes. At low concentration ($<1.8$ mM) of TU, however, the anodic wave is reversible.
8.3 CYCLIC VOLTAMMETRY IN ACID AND NEUTRAL SOLUTION:

The cyclic voltammogram of TU was studied at pH = 1, in 0.1N each of HClO₄, H₂SO₄, HNO₃ and in 0.5M KNO₃ (Fig. 4.2). A plot of $i_p / \sqrt{V}$ vs $\sqrt{V}$ (Fig. 4.5) shows that the electrode reaction is diffusion-controlled in these supporting electrolytes, at least up to 1.8 mM TU (Fig. 4.4). The ratio $i_c / i_p$ was 1.1 ± 0.02 and $(E_p - E_{1/2})_a$ was ~45 mV indicating that the electrode reaction (eqn. 4.5) corresponding to the anodic peak was of the second order and reversible. The reversibility was further confirmed by the $\Delta E_p$ value at low ligand concentrations (< 2.0 mM). Any deviation from the $\Delta E_p$ value for a reversible process reflects a backlash error of polarographic gears particularly at a higher scan rate, formation of successive higher complexes, reactant adsorption and activation energy associated with the cathodic processes. Although the wave is reversible, $E_p$ changes with ligand concentrations, as eqn. (4.6) is applicable to the polarographic wave.

8.3.1 CYCLIC VOLTAMMETRY AT pH = 4.0:

Only the anodic wave due to the formation of $[\text{Hg(TU)}_2]^{+2}$ in acidic solution was studied by Nyman and Parry. Cyclic voltammetric study at pH = 4.0, showed that an additional anodic peak was obtained at $\approx +0.45$V. The anodic product formed corresponding to this wave was
shown to be insoluble and characterised by adsorption on the electrode surface and hence amenable to CSV studies (cf. Chapter V, Sec. 5.3). The $E_\frac{1}{2}$-pH and $E_\frac{1}{2}$ vs log $[TU]$ dependence studies (eqn. 4.6) show that the wave is due to the formation of Hg(HS)$_2$. This wave has been shown to be catalysed by reactant adsorption at concentrations as low as $4 \times 10^{-6}$ M, where the main anodic wave does not appear. A working curve over the concentration range $4 \times 10^{-6}$ to $6.5 \times 10^{-5}$ M could, therefore, be established by the LSV technique. This aspect has not been reported in the literature, although it has been described as being due to the formation of an insoluble divalent mercury salt and is independent of concentration.

A cyclic voltammogram obtained by reversing the potential at $\sim +0.45$ V shows two anodic waves excluding the prewave usually obtained in H$_2$SO$_4$ at higher acidities (pH = 1) and three cathodic waves, the first cathodic wave at more anodic potential being due to reduction of Hg(HS)$_2$ formed during the anodic process (eqn. 4.11), second due to the reduction of $[\text{Hg(TU)}_2]^{+2}$ and the third due to the reduction of HgS formed by preceding chemical reactions (eqns. (4.12) and (4.13)).

8.3.2 CYCLIC VOLTAMMETRY IN PHOSPHATE BUFFER (pH = 6.2):

The cyclic voltammetric behaviour of TU in phosphate buffer was studied to see whether a method could be developed...
to determine TU at ng/ml by CSV. A cyclic voltammogram (Fig. 4.12) shows two anodic and three cathodic peaks of which only two are well defined. The anodic peak at +0.16V is due to the formation of $[\text{Hg(TU)}_2]^{+2}$ and the other at +0.24V is due to the formation of an insoluble salt. The origin of this peak and the cathodic peak at +0.12V was investigated by CV and CSV. It is shown that both TU and $\text{PO}_4^{-3}$ contribute to the anodic current-forming process (eqn. 4.14). The current, however, is governed by the concentration of the lesser species. The origin of the cathodic peak at -0.53V is explained on the basis of eqn. (4.15).

8.3.3 CHRONOPOTENTIOMETRY AND CHRONOAMPEROMETRY OF THE MAIN ANODIC WAVE IN ACIDIC MEDIUM:

Diagnostic criteria were applied to test the reversibility, diffusion controlled nature, the absence or otherwise of any kinetic or catalytic process, order of the electrode reaction and nature of the oxidation product (soluble or insoluble) by using chrono-techniques.

8.4.1 CYCLIC VOLTAMETRY IN ALKALINE SOLUTION:

Smyth and Osteryoung studied TU and its derivatives in alkaline media including 1.0M NaOH, using DPP and LSVCSV techniques; and they determined TU even at ng/ml. They, however, could not envisage the transformation of the anodic product to HgS. The CSV peak current due to the reduction of HgS was, however, shown to decrease exponentially with
increase in OH$^-$ ion concentration. An explanation for the exponential decrease, and mechanistic interpretation for the stabilization of the cathodic current is proposed in eqns. (4.16), (4.17). Similar decrease in current was observed in the CSV behaviour of TU. The authors, thus, seem to have chosen an unfavourable experimental condition.

According to the authors the main anodic wave was due to the formation of Hg$^{II}$O$_2$(TU)$_2$. The system was reinvestigated in detail for its pH vs log [TU] dependence. If, however, the hydroxy complex species, according to eqn. (4.18) is not probable, an alternate electrode reaction pathway is proposed (eqn. 4.19). The anodic product Hg(RS)$_2$, amenable to CSV, is insoluble; besides the anodic peak current is governed by limiting concentration of TU, thus leading to inactivation of electrode surface. A postwave, obtained at a more anodic potential, probably indicates beginning of a complicated process leading to multilayer (bulk) plating. Although Hg(RS)$_2$ is insoluble in acidic solution, it undergoes hydrolysis in alkaline media and in presence of TU gives HgS in eqns. (4.20) and (4.21) which is cathodically reduced (eqn. 4.23). Eqn. (4.22) read with eqns. (4.19), (4.20) and (4.21) explains that the redox couple of the anodic process (eqn. 4.19) and cathodic process (eqn. 4.23) are different, and this accounts for usually large $\Delta E_p$ value in the CV of TU in alkaline media.
8.4.2 CHRONO-TECHNIQUES IN ALKALINE MEDIA:

The large value of $\Delta E_{\pi/4}$ (i.e. $E_{\pi/4}(a) - E_{\pi/4}(c)$) apparently indicates total irreversibility. However, the cathodic chronopotentiogram is invariably well defined; and, therefore, the irreversibility, by itself, cannot account for such a large value for $\Delta E_{\pi/4}$. This observation is in agreement with the large $\Delta E_p$ values obtained in CV and could be explained on the basis of the two couples $\text{Hg/Hg(S)}_2$ and $\text{Hg/HgS}$.

8.5 SAMPLED-CURRENT VOLTA METRY:

This technique, described in Chapter III, Sec.3.6.5, avoids the disadvantages associated with the use of DME. The S-shape curve obtained by plotting sampled current vs. applied step-up potential was examined for logarithmic analysis. It was observed that two electrons were involved in the anodic process as indicated by the value of the slope (30 mV) at lower concentration ($< 1.8$ mM) of TU. The results showed that the electrode reaction obeys the Nernst equation and is reversible, especially at lower concentration where only the single species $[\text{Hg(TU)}_2]^{+2}$ exists. The increase in slope, however, is ascribed to the formation of successive higher complexes even at relatively higher concentrations. Equation (4.26) applies to the anodic process, especially at low concentration, indicating that the process is reversible and is of the second order. These results comply with the
reaction proposed by Kies \(^{25}\); and are in agreement, by and large, with the observation of Nyman and Parry \(^{26}\).

8.6 CYCLIC VOLTAMMETRY IN MIXED SOLVENTS:

The cyclic voltammetric study was carried in mixed solvents in order to understand the relative merits and demerits of different solvent-electrolyte systems. It is useful in situations where it may not be possible to work in pure aqueous solutions. A situation may arise where the sample containing TU may also contain a non-aqueous component in significant proportions.

The voltammetric behaviour was studied in mixed aquo solvents i.e., 25, 50 and 75\% each of acetonitrile, methanol, ethanol, allyl alcohol, propanol, iso-propanol and formamide. From Table 4.2, it is apparent that \( \Delta E_p \) increases with decrease in dielectric constant. The anomalous behaviour of formamide in this respect may be ascribed to adsorption of the decomposition products. The solution chemistry of TU in water is not well understood; and this applies to other solvents as well. The increase in the \( \Delta E_p \) value can be ascribed to the decrease in conductance and consequent IR drop even after compensation. Ionization of the inert electrolyte (such as \( \text{KNO}_3 \)) decreases with decrease in dielectric constant and the solubility is not due to complete ionization. The solution, therefore,
contains ion-pairs in large proportion and free K⁺ and NO₃⁻ ions. The overvoltage due to the residual IR drop would thus account for the increase in ΔEᵱ value. It has been observed that the anodic wave due to soluble complex \([\text{Hg(TU)}_{2}]^{+2}\) is nearly reversible at low TU and solvent concentration.

Both \(i_{p_a}\) and \(i_{p_c}\) decrease with decrease in dielectric constant. Except in the case of acetonitrile, \(i_{p_a}\) and \(i_{p_c}\) values are nearly equal, thereby indicating that the redox process is apparently reversible. But the ΔEᵱ value is much larger than 29 mV. The \(i_{p_c}\) value should, therefore, be significantly lower than that observed experimentally. The 'increase' in the \(i_{p_c}\) value may be due to adsorption of the anodic product. Aqueous media containing large proportions of acetonitrile seem to favour such product adsorption as indicated by large \(i_{p_c}\) value at 75% solvent concentration.

8.7 VOLTMETRIC BEHAVIOUR OF ALLYL THIOUREA

It has been pointed out that the voltammetric behaviour of the derivatives of TU is not similar to that of TU. As BITU behaves entirely differently being directly oxidised at the HMDE, a study of the voltammetric behaviour of allyl thiourea (ATU) was desirable. The study was carried out over the entire pH range using different electroanalytical techniques. Characteristics such as the reversi-
bility, diffusion control, reaction order, stoichiometry and kinetic complications, if any, together with the possible electrode reaction pathways were studied. Two anodic waves were observed in acidic solutions of which the first was due to the formation of $[\text{Hg(ATU)}_2]^{+2}$ while the second could be ascribed to the insoluble Hg(HS)$_2$. $E_1$ - pH dependence, logarithmic analysis, diffusion control and CSV behaviour was studied for both anodic waves and it was found to be similar to that observed in the case of TU. In acidic solutions, $i_{\text{pa}}$ due to the formation of $[\text{Hg(ATU)}_2]^{+2}$ was proportional to ATU upto 2.0mM while at pH = 6.0, the relationship holds good only upto 1.2 mM.

Two anodic waves were also observed in alkaline solutions depending on the concentration of ATU. These waves correspond to the formation of the same insoluble anodic product viz., Hg(HS)$_2$ and not HgS according to the reaction,

$$\text{Hg} + \text{H}_2\text{C}_3\text{NH} \xrightarrow{\text{C}} \text{SH} + 2 \text{OH}^-$$

$$\xrightarrow{\text{HN}} \text{HgS} + \text{C}_2\text{H}_5\text{NH}_2\text{CN} + 2\text{H}_2\text{O} + 2e^- \quad \text{...(8.1)}$$

Though this reaction accounts for pH dependence, it is inadequate to explain the value of the slope in logarithmic analysis; besides the product HgS cannot be justifiably referred to as an element of the original couple. HgS is,
however, formed by the transformation of the anodic product, Hg(HS)_2 as explained in Sec. (4.1.5.1). Therefore, the pathway referred to \( \text{eqn.}(8.1) \) above is basically untenable.

The characteristics referred to above were studied for the main anodic wave and irreversibility was explained on the basis of the transformation of the anodic product to HgS as in the case of TU. As the CSV peaks of TU and ATU overlap, it was not possible to determine TU in presence of ATU even if present at trace level. In alkaline solution (0.1M NaOH), \( i_\text{P} \) is proportional to \([\text{ATU}]\) over the range \( 5 \times 10^{-6} M - 3 \times 10^{-5} M \). At higher concentrations, the slope changes, because of the formation of higher complexes. By using CSV, however, it may be possible to go down by at least two orders of magnitude.

The main anodic wave in acidic and that in alkaline medium were studied by chrono-techniques to obtain additional evidence regarding their characteristics. The study clearly brings out that the voltammetric behaviour of ATU is, by and large, similar to that of TU in acidic, neutral and alkaline media.

8.8 CATHODIC STRIPPING VOLTAMMETRY:

The CSV technique is gaining ground as an analytical tool during the last two decades. The principles underlying
this technique have been briefly discussed in Chapter III and the parametric considerations are described under Sec.5.6. The development of HgDE and solid electrodes, e.g., Pt, Au, VC etc. on which Hg could be plated in situ made it possible to estimate depolarizers, e.g. halides, sulphides and organic compounds, e.g., mercaptans which form insoluble compounds with the electrolytically generated Hg\(^{+2}\) (or Hg\(^+\)). These compounds are accumulated on the electrode surface and are reduced at appropriate potentials during the cathodic sweep. While the peak potential is a function of the concentration of the depolarizer, the height depends strictly on the surface activity of the deposit. Solubility product is a critical factor determining the lowest limit and the calibration curve is necessarily empirical in nature.

In spite of these limitations, it is usually possible to estimate substances present in solutions at concentrations as low as a few tenths of a \(\mu\text{g/ml}\). This technique is definitely superior to ASV in that its detection limit is lower by at least an order of magnitude and is due to the fact that the surface activity of the deposit is always greater than the activity of the metal in the amalgam.

8.9 CATHODIC STRIPPING VOLTMETRY OF TU AT pH=4.0

In the CV studies of TU in the acidic solutions [cf. Sec.4.1.4.5(9)] it was shown that the second anodic wave\(^{21}\) was due to the formation of an insoluble mercuric salt of
the type Hg(RS)$_2$. The height of this wave increased with
the deposition time and was proportional to the concent-
tration of TU (over the range $6 \times 10^{-8} - 10^{-6}$M) for a
2-minute accumulation period. This anodic wave was observed
at a more positive potential ($E_{pa} \approx +0.45$V). That an
insoluble anodic product (corresponding to the second wave)
was formed at more anodic potentials was proved by carrying
out two parallel chemical experiments (cf. Sec. 5.3). This
insoluble product, Hg(RS)$_2$, is quite stable in acidic
solutions; but it undergoes hydrolysis in neutral and
alkaline media.

The CSV studies further revealed that the second CSV
peak obtained at $\approx -0.38$V was due to the reduction of HgS,
the origin of which was explained on the basis of previous
chemical reactions (cf. eqns. (4.12) and (4.13)). The CSV
peak current due to this wave was found to be proportional
to the concentration of TU over the range $4 \times 10^{-9} - 4 \times 10^{-8}$M,
beyond which the current attained a limiting value probably
because the HgO formed prevented further oxidation of
mercury.

8.10 CATHODIC STRIPPING VOLTAmetry OF TU IN NEUTRAL
SOLUTIONS :

Berge, H., and Jeroschanski$^{27}$ identified the CSV
peak of TU in phosphate buffer (pH = 6.82) to be due to
the reduction of HgS. However, the authors$^{27}$ did not throw
any light on the mechanism as to how HgS was formed. Our study indicated that the second anodic peak in phosphate buffer (pH = 6.2) was a function of the concentration of both TU and PO$_4^{-3}$ ions (Fig. 4.13) and Fig. 4.14). A mechanistic interpretation based on this observation is proposed to describe the anodic current-forming process. In a phosphate buffered medium, the contribution due to the PO$_4^{-3}$ ion to form the anodic product would evidently be governed by the concentration of the lesser ion (species), i.e. TU (zwitterion). The structure, based on the zwitterionic species of TU, of the anodic product is given (cf. Sec. 4.1.4.6). The fact, that what is reduced cathodically is HgS, indicates that the anodic product undergoes transformation to give HgS; and this transformation is rapid as is evidenced by the CSV calibration curve (Fig. 5.4).

In phosphate buffer (pH = 6.2), it was possible to establish a calibration curve over the range 0.76 - 7.6 ng/ml TU using the scan rate, $V = 100$ mV/S for 2-minute deposition; and 0.15 ng/ml of TU could be determined for a deposition time of 5 minutes (Fig. 5.4). This is an improvement over the range reported by the authors.$^{27}$

The cyclic voltammogram of TU in phosphate buffer (pH = 6.2) (Fig. 4.12) shows that the system is irreversible as indicated by a large $\Delta E_p$ value (> 800 mV). However, it is surprising that the cathodic peak is
invariably sharp corresponding to a reversible reduction. Thus, the large $\Delta E_p$ values cannot be explained on the basis of irreversibility alone. However, the mechanistic interpretation based on the transformation of the anodic product, does account for such a large $\Delta E_p$ value.

The second anodic peak obtained in a weakly acidic (pH = 6.2) medium may be used to determine TU at trace level by CSV. As the supporting electrolyte contains impurities also at trace level, the effect of these impurities on the CSV behaviour of TU is studied (Table 5.2). It was possible to eliminate the interference due to Cu$^{+2}$ ion by adding an appropriate quantity of EDTA.

8.11 CATHODIC STRIPPING VOLTAMMETRY IN AN ALKALINE MEDIUM:

According to Smyth and Osteryoung, in 1.0M NaOH, Hg$^{II}$(OH)$_2$(TU)$_2$ is the predominant species, formed anodically at very low concentrations of TU. Their observation that the anodic wave is reversible has been confirmed. However, a cyclic voltammogram of TU gave a large $\Delta E_p$ value (> 300 mV) indicating irreversibility. But the cathodic peak was sharp and therefore, indicative of a reversible (cathodic) process. These observations are explained on the basis of an alternative scheme proposed, involving the transformation of the anodic product, Hg(RS)$_2$ instead of Hg$^{II}$(OH)$_2$(TU)$_2$ to give HgS. That the cathodic peak was due to the reduction of HgS
was confirmed by comparing a cyclic voltammogram of TU with that of $S^{2-}$ ion in an alkaline medium (0.1M NaOH). This was further confirmed by carrying out a parallel chemical experiment conducted under conditions approximately analogous to those available under LSV for getting the oxidation product (cf. Sec. 5.5). It was observed that the cathodic peak obtained in the presence of TU in cyclic voltammetry decreases with increase in OH$^-$ ion concentration; and a composite supporting electrolyte as suggested by Tommo Miwa et al. is necessary to get reproducible peaks.

Attention has been focussed on the experimental parameters, e.g., accumulation potential, pre-electrolysis time, voltage scan rate, rate of stirring, geometry of the electrolysis cell, concentration of TU and the solution resistance in order to get reproducible CSV peaks. It has been shown in CSV the calibration curve is empirical in nature as the anodic peak potential shows a negative shift with decrease in TU concentration. The importance of the pre-electrolysis time is stressed in view of the fact that a reproducible CSV peak would not be obtained if the electrode surface is covered by more than a monolayer deposit; and the effect of supporting electrolyte to minimize the solution resistance in stripping voltammetry is discussed, as both the peak potential and peak height are critically dependent on the solution resistance (Table 5.3).
8.12 NEED OF A TRULY INERT ELECTRODE:

In the voltammetric behaviour of thiourea (TU) at the HMDE (cf. Chapter IV), it has been shown that at a mercury working electrode TU is not oxidised; but the oxidation waves correspond to the oxidation of mercury in the presence of TU as a ligand. Mercury, thus, behaves as an attackable electrode; and the need of a truly inert electrode to study the redox behaviour of thiols (including TU and its derivatives), thus, becomes imperative. While Pt and g.c. electrodes have been employed, for this purpose, the feasibility of gold electrode to study the oxidation of TU is not fully explored. Chapter VI deals with the voltammetric behaviour of TU/formamidine disulphide system, in particular, and further oxidation products, if any, in acetonitrile and aqueous media using a gold-disc electrode.

8.13 POTENTIOMETRIC BEHAVIOUR:

Although sulfhydryl compounds usually undergo irreversible oxidation probably due to the poisoning of the Pt electrode surface, an apparent exception to this generalization is the reversible oxidation of TU to formamidine disulphide. The fact that the formal potential depends on the initial (absolute) concentration of TU and not on the ratio of the concentration of the oxidised to that of the reduced form, shows that the system is not
reversible in the Nerstian sense. Thus, the system does not behave as a strictly reversible redox couple as it could be separated in two successive univalent steps.

This, in fact, did provide a clue for its study by the voltammetric technique. On examining the voltammograms it was found, as expected, that the system behaved irreversibly.

8.14 VOLTMETRIC BEHAVIOUR IN ACETONITRILE

In acetonitrile, TU undergoes a straightforward oxidation to give the corresponding disulphide ion which is reduced back to TU. The oxidation process involves a slow 1-e⁻ charge transfer step to give a radical which undergoes fast dimerization to give formamidine disulphide. Higher oxidation products are conspicuous by their absence even at more positive potentials.

8.15 VOLTMETRIC BEHAVIOUR IN AQUEOUS SOLUTIONS (pH < 4):

In aqueous acidic (pH < 4) and neutral (pH = 6.0) solutions, the oxidation of TU seems to be more complicated. In addition to the oxidation and reduction peaks observed in acetonitrile, a new, rather broad peak of an irreversible nature appears at $\sim +1.0$V at pH = 1.0 Fig.(6.1) in agreement with the observations of Jitka Kirchnerova and W.C.Purdy63. Surprisingly, Reddy and Krishnan91 however, did not report such a peak. The two anodic peaks and the
cathodic peak at +0.16V are observed over pH region 0.0-4.0 Fig.(6.1), beyond which cathodic peak disappears. Two anodic peaks, however, persist in weakly acidic solutions (pH 4.0-6.8) [Fig (6.2)] and even in alkaline media.

8.16 IDENTIFICATION OF THE FIRST ANODIC PEAK:

In order to identify the first anodic peak obtained at ∼+0.6V, TU was oxidised in 3.0N HNO₃, and the crystallised salt (dithiodiformamidinium dinitrate) was dissolved in 0.1N HNO₃. The cyclic voltammogram (first cycle) run on this solution did not show any anodic wave at ∼+0.6V. However, a cathodic peak at +0.16V corresponding to the reduction of the oxidised species (the dimer) did appear. The cyclic voltammogram (second cycle) however, showed two anodic and one cathodic peak as expected Fig.(6.5).

8.17 ELUCIDATION OF THE ELECTRODE REACTION MECHANISM (FIRST ANODIC PEAK):

It has been observed that both the height and the peak potential of the first anodic peak is virtually independent of pH at least upto pH 4.0 [Table (6.1)]. This observation together with the presence of the cathodic peak and the value of n (apparent), as also the effect of scan rate on peak potentials resulting in large ΔEₚₐ (> 400 mV) (Table 6.2) can be explained on the basis of a slow charge transfer step as:
Reddy and Krishnan\textsuperscript{91}, however, interpreted the first anodic peak in terms of a neutral species with the liberation of a proton even in strongly acidic solutions\textsuperscript{94}. This interpretation is erroneous as the shift in $E_{pa}$ values, reported by the authors\textsuperscript{94}, per pH unit, is not significant. According to Jitka Kirchnerova and W.C. Purdy\textsuperscript{63}, the oxidation processes in weakly acidic (pH 4.0–6.0) and alkaline media are different from those at pH < 4.0 at a Pt or g.c. electrode. Their findings are, by and large, confirmed in the present investigations at a gold-disc electrode. However, the observed merging of the waves at pH > 7.0 at the g.c. electrode\textsuperscript{63} has been shown to be a function of TMA concentration and scan rate. The oxidation process in neutral (pH 4.0–6.8) and alkaline solution, being different from that in acidic media (pH < 4.0), are explained on the basis of the different electrode reaction mechanisms [vide eqns. (6.6), (6.7), (6.8) & (6.9)].

S.13 \textbf{ORIGIN OF THE SECOND ANODIC WAVE:}

In aqueous solutions, the free radical (II) probably undergoes hydration – because in acetonitrile, the second
anodic wave is conspicuous by its absence - to give a relatively stable aquo-complex which, in acidic solution pH (< 4.0), is oxidised to give di protonated sulfenic acid (IV) corresponding to the second anodic wave as:

$$\begin{align*}
\text{NH}_2 & \quad \text{S} + \text{H}_2\text{O} \\
\text{NH}_2 & \quad \text{OH} \\
\text{(II)} & \quad \text{(IV)}
\end{align*}$$

Electrolysis, at a constant potential, at +0.7V and +1.2V at pH 3.5 gives an apparent 'n' value equal to one (corresponding to first anodic peak) and two at respective potentials. This shows that the second anodic wave upto pH 4.0 involves the transfer of only one electron.

At lower acidities (pH, 4.0-7.0), this oxidation peak possibly involves deprotonation with transfer of two more electrons as indicated by eqns. (6.6) and (6.7). Thus, the increase (due to coalescence) in the height of the second anodic wave, with increase in pH upto 7.0, could be accounted for. Moreover, constant potential electrolysis data using g.c. and gold electrode lends support to the above observations in terms of the apparent number of electrons, 'n', involved in weakly acidic (n = 4.0) and strongly acidic (n = 2) solutions.
8.19 BEHAVIOUR IN ALKALINE MEDIA:

In a moderately alkaline medium ($\rho\text{OH} = 2.6$) the oxidation of TU proceeds in three steps [Fig.(6.7)], if TU concentration is relatively high; and the merging of the waves to give a single peak is seen to be a function of the ligand concentration and scan rate. These steps are possibly associated with the tautomeric changes in the TU molecule\(^{63}\). The zwitterionic tautomer is progressively neutralized in alkaline solutions giving the anion which is probably oxidised in two steps to give formamidine sulfinic acid [vide eqn. (6.8)]. The third step, presumably due to the oxidation of (VI) to formamidine sulfonic acid (VII), may be represented as:

$$\begin{align*}
\text{NH}_2\text{C} - \text{S}^-\text{O}^- & \quad -2e^- \quad \text{H}_2\text{O} \quad \text{NH}_2\text{C} - \text{S}^-\text{O}^- + 2\text{H}^+ \quad (6.9)
\end{align*}$$

A total transfer of 6 electrons, however, could not be accounted for by a constant potential electrolysis experiment because surface oxidation of the electrode is enhanced in alkaline media resulting in large background currents and rendering the electrode surface passive\(^{91}\).

8.20 EFFECT OF ADSORPTION ON VOLTAAMMETRIC REVERSIBILITY:

(FIRST ANODIC WAVE):

The oxidation of TU is accomplished by adsorption at
a Pt or g.c. electrode. It is intriguing to note that despite adsorption, the irreversibility of the first anodic wave was attributed to a slow charge transfer step. However, in the present study, it has been shown that adsorption is conspicuous by its absence. In this respect, the gold electrode is superior to Pt and g.c. Thus, in the absence of any adsorption, it was possible to trace the irreversibility to a slow charge transfer step alone.

8.21 Effect of pH on the Nature of Anodic Waves:

The pH of the solution plays a great role in as much as it affects the nature of the anodic waves. The height and peak potential of both the anodic waves are independent of pH (< 4.0), in accordance with eqns. (6.2) and (6.5). However, at lower acidities (pH 4 - 6.8), both the anodic waves are affected by pH [vide eqns. (6.3), (6.6) and (6.7)]. The disappearance of the cathodic peak at pH > 4.0 definitely indicates that the nature of the oxidation process changes in weakly acidic solutions.

In an alkaline medium, the oxidation process is probably associated with tautomeric changes in the TU molecule. If the pH of the solution is relatively high (i.e. alkaline), the zwitterionic species undergoes deprotonation to give the anion which is probably the electroactive species undergoing oxidation giving the corresponding
sulfonic acid \([\text{eqn.}(6.8)\) and \((6.9)]\).

Reddy and Krishnan\textsuperscript{91} erroneously interpreted that the same oxidation process is operative over the entire pH region. This follows from the appearance of the multiple waves at more anodic potentials at a g.c.\textsuperscript{63} or gold electrode and constant potential (+1.2V) electrolysis data.

Jitka Kirchnerova and W.C. Purdy\textsuperscript{63} considered different sites for the oxidation of the active species to the total neglect of zwitterionic form in aqueous acidic media. Besides, the authors\textsuperscript{63} studied the coloumetric behaviour in 2.0N HNO\textsubscript{3}. This is definitely an unfavourable medium; as TU will be, at least partly, oxidised to give the dimeric salt. Dilute HNO\textsubscript{3} (0.1N) would have been preferable.

8.22 CONCLUSIONS:

The study in aqueous media, thus, indicates that in weakly acidic solution (pH \(4.0 - 6.8\)) TU undergoes stepwise oxidation to give compound VI (formamidine sulfinic acid) and this involves a total transfer of 4 electrons. It has been shown that in acidic solutions (pH \(< 4\)) both the first and second anodic peaks correspond to a slow 1-e\textsuperscript{-} transfer in each case; and in weakly acidic solutions further oxidation involving 2 more electrons probably proceeds in two steps of very nearly identical potentials.
In acidic and neutral solutions, the oxidation proceeds via a slow electron transfer reaction producing an unstable radical (II). The latter is oxidised at higher potentials to give diprotonated sulfenic acid (IV) or formamidine sulfenic acid (VI) depending on the acidity involving the hydration and proton transfer equilibria. Alternatively, at lower potentials radical (II) undergoes fast dimerization to give compound (III). Compound (VI) is prone to further oxidation to give the corresponding sulfonic acid involving a transfer of two electrons. However, this could not be observed at a gold anode probably because the anodic cut-off potential in weakly acidic solution is +1.0V, vs SCE. A higher potential cannot be used because it introduces interference due to surface oxidation of gold. In a moderately alkaline medium (pH ≈ 11.4) the oxidation proceeds in three steps at a relatively high concentration of TU (4.0 mM) and is a function of scan rate. These steps are probably associated with tautomeric changes in the TU molecule; and the corresponding oxidation processes are given by eqns. (6.8) and (6.9) respectively. A total transfer of 6 electrons, however, could not be accounted for by an electrolysis experiment at a constant potential because oxidation of the electrode surface is enhanced in alkaline media, resulting in large background currents and rendering the electrode passive.
8.23 **POTENTIOMETRIC TITRATIONS OF TU**

A brief review of the various methods i.e. volumetric, electrometric (amperometric and coulometric), complexometric and methods based on precipitation and desulphurisation etc. is given in Chapter VII.

Besides, the potentiometric determination of TU at lower concentration in aqueous and aquo-non-aquo media using Ag/SCE, Ag⁺/Au⁻ and Au⁺/Au⁻ is also discussed. The results obtained with Ag/SCE system in acidic solution were explained on the basis of eqn. (7.2).

It has been shown that using the bimetallic (dissimilar) system, Ag⁺/Au⁻, it is possible to titrate TU with AgNO₃ in aqueous and DMSO media at 10⁻⁴M. The potential drift at lower concentration could be overcome by using the Ag(Hg)⁺/Au⁻ or Ag⁺/Au(Hg)⁻; and the lower limit of 10⁻⁵M TU could be reached in acetonitrile. The results were explained on the basis of eqn. (7.4).

8.24 **DEP TITRATION OF TU**

The DEP technique with the Au⁺/Au⁻ system was used to study the titration of TU with AgNO₃ at concentrations <10⁻⁵M in aqueous solutions; and it was found that there was good agreement between the observed and expected end points. While at relatively higher concentrations of TU the peak was sharp, the same was not true at lower
concentration, probably because the electrode process takes longer time to attain equilibrium (time effect).

DEP titrations of TU with AgNO₃ were carried out in acetonitrile using the same Au⁺/Au⁻ system (as used in aqueous medium) to see whether the peak height increases. Under similar condition, the peak height in acetonitrile was invariably less than that in aqueous medium. While the decrease in peak height may be ascribed to preferential adsorption of acetonitrile on the electrode surfaces (thus affecting the reversibility), the limiting concentration of TU in acetonitrile that can be titrated is 10⁻⁶ M.

Urea being one of the reaction products eqn.(7.4), it was expected that it might not interfere with titration even if present in large excess. It was found, however, that the peak heights were considerably smaller (indicating significant adsorption) than those obtained in the absence of urea; but observed end points were within experimental error. In spite of these limitations, it is surprising that TU at 10 ppm level in urea could be estimated by this method.

THE HIGHLIGHTS OF THE WORK

(1) The electro-chemical oxidation of TU cannot be studied at a Hg electrode, because Hg behaves as an attackable electrode in the anodic voltametry of thiols, in general, and TU and its derivatives, such as PTU, ANTU...
and ATU etc., in particular, except BITU.

(2) The anodic dissolution of Hg in the presence of TU has been indicated to proceed via two paths, as:

\[ \text{Hg} \rightleftharpoons \text{Hg}^{+2} + 2e^- \quad \text{(1)} \]
\[ 2\text{Hg} \rightleftharpoons 2\text{Hg}^{+2} + 2e^- \quad \text{(2)} \]

in order to maintain the ratio \( \frac{\text{Hg}^{+2}}{\text{Hg}^{+2}} = 120 \). This observation is based on the Kies reaction and the multistage dissolution of Hg in the presence of a depolarizer, which follows from:

\[ \text{Hg} + \text{Hg}^{+2} \rightleftharpoons 2\text{Hg}^{+2} \quad \text{(3)} \]

In the literature, however, only the reaction (1) referred to above, is reported in this context.

(3) While three anodic waves (including the prewave \( i_a \) obtained only in \( 0.1\text{NH}_2\text{SO}_4 \)) corresponding to the formation of \( \text{HgRS, } 2\text{Hg(TU)}^{+2} \) and \( \text{Hg(RS)}_2 \) are observed in acidic solution; only two anodic waves, each corresponding to the same species \( \text{Hg(RS)}_2 \) are obtained in alkaline medium. The second wave in alkaline medium probably indicates the beginning of a complicated process leading to multilayer plating. The mechanisms of these processes are indicated, and the transformation of \( \text{Hg(RS)}_2 \) to \( \text{HgS} \) by hydrolysis in alkaline solutions is proposed to explain the large \( \Delta E_p \) value in C.V. studies. The chronopotentiometric behaviour, in this connection, is also studied, and the results of a
parallel chemical experiment to support the transformation theory were taken into consideration. The role of pH, ligand concentration, applied potential etc. is also discussed. The wave due to Hg(RS)₂ in acid solution is studied by LSV and CSV; and the limits of determination are reported for the first time. This wave is catalysed by reactant adsorption.

The formation of HgS by preceding chemical reactions in acid solutions is studied by CSV; and the CSV determination of TU at ng/ml in phosphate buffer is studied with special reference to the anodic product formed and the cathodic product reduced. These aspects are not reported in the literature. Stabilisation of the cathodic stripping current in alkaline medium is explained in terms of the reactions proposed and it is shown that an alkaline medium is unfavourable for the CSV determination of TU.

The anodic wave due to \( \text{Hg(TU)}_2 \)^\(+2\) has been reinvestigated; it is reversible and diffusion controlled only at low concentrations of TU, (i.e., 0.1mM- 2.0 mM). At higher concentrations, however, it is neither diffusion controlled nor reversible because of the formation of successive higher complexes.

(4) Unlike BITU, the voltammetric behaviour of ATU at the HWE is almost similar to that of TU, and, therefore, the observations made above do apply to the voltammetry of ATU also.
(5) In aquo-nonaqueous media, the anodic waves of TU are irreversible and diffusion controlled. The irreversibility is ascribed to, besides adsorption and double layer effects, ion-pair formation, thus resulting in decrease in conductivity with a large IR drop even after compensation.

(6) Mercury being attackable, as seen above, the electro-chemical oxidation of TU was studied at a Au - disc electrode. The anodic waves are irreversible and accomplished by adsorption except for the first wave in acid solution. While in acetonitrile, the oxidation is straight forward leading to the corresponding disulphide; in aqueous medium it appears to be complicated by hydration, proton transfer and hydroxyl ion equilibria. The zwitterionic tautomer plays an important role in the oxidation processes both in acidic and alkaline media. The first anodic wave is independent of pH upto pH=4, thus giving rise to a cationic free radical which is oxidised at higher potentials involving the transfer of one more electron. Further oxidation is a complicated process which is necessarily a function of pH. Coulometric evidence and/or product identification is taken into consideration to interprete the various waves.

(7) The potentiometric titration of TU with AgNO₃ is studied with different bimetallic (both similar and dissimilar) electrode systems in aqueous and acetonitrile media.
It is possible to titrate TU at $10^{-4}$M and $10^{-5}$M by using $\text{Au}^-/\text{Ag}^+$ and $\text{Au(Hg)}^-/\text{Ag}^+$ systems respectively. At still lower concentrations, the $\text{Au}^-/\text{Ag}^+$ system in conjunction with the DEP technique is advantageous. The determination of TU at 10 ppm level in the presence of a large excess of urea could be carried out with good accuracy. Theoretical aspects regarding the nature of the peaks at the end point are considered and the appropriate chemical reactions under the experimental conditions are indicated.