PART I

GENERAL INTRODUCTION
CHAPTER 1

POLAROGRAPHIC REDUCTION OF AZO COMPOUNDS
The earlier investigations on the electrochemistry of azo group \((-\text{N}=-\text{N}-)\) were mostly concerned with the electrolytic preparation of aromatic azo and hydrazo compounds. With the advent of polarography and the related techniques, the emphasis shifted from preparative studies to the investigation of the electrode reactions. These studies became essential because of

1. the importance of the azo compounds in dye stuff industry,
2. the carcinogenic properties of the azo compounds, and
3. the usefulness of the azo compounds in the indirect determination of non-electroactive metals.

Eventhough much work was done on the electrochemical reduction of azo group, many questions remained unanswered. This is because most of the studies were carried out in aqueous solutions and the major problem encountered when water is present is the adsorption of many of these compounds at the electrode-solution interface. Such an adsorption will result in the appearance of pre-waves and these will complicate the interpretation of the results. However, techniques such as cyclic voltammetry have enabled to establish detailed redox mechanisms.
The use of protolytic solvents such as water and aqueous alcohols results in electrode reactions involving an even number of electrons and protons. Che-Man Chang has reviewed extensively the literature relating to the electrochemistry of aromatic azo-hydrazone redox systems in aqueous media.

\[ N=N-\text{d} + 2e^- + 2H^+ \rightarrow NH-NH-\text{d} \]

Aromatic azo compounds in general exhibit 2-electron reduction at the dropping mercury electrode. Strong electron donating groups such as -OH, -NH2 make the reduction proceed via a 4-electron step to the amines. Even though the overall reaction (Equation 1) is quite straightforward, the electro-reduction reactions are shown to be complex. The half-wave potentials are found to be dependent on

(a) concentration of the azo compound,
(b) solvent composition,
(c) presence of surfactants and
(d) the pH of the solution.
If reaction represented by equation (1) is reversible, the half-wave potential is expected to change by -0.059 V for every unit increase in the pH of the solution. It was however reported that in many cases the $E_{1/2} - \text{pH}$ plot was non-linear or consisted of two linear portions and the slope was different from -0.059 V. These observations are traced to the irreversibility of the reduction process or to the influence of surface adsorption. The reversibility of the reaction represented in equation (1) is found to depend on the type and concentration of the buffer used. Adsorption of the azo compound or the hydrasyl compound at the dropping mercury electrode in aqueous solutions is reported to be one of the major factors affecting the reversibility of the electrode process. It was reported\textsuperscript{5} that the rate of electrode reaction in 30 per cent methanol in the pH range 1 to 7 is determined by the adsorption kinetics of the species involved. Holleck and his co-workers\textsuperscript{12,13} observed that surfactants that are most strongly adsorbed at the mercury solution interface than the azo compound inhibit the electrode reactions. The reduction of the azo compounds is more reversible at the extremes of the pH range\textsuperscript{5,6,8}.

The factors such as, buffer capacity, nature and
concentration of the buffer components and the solvent composition which affect the supply of the protons at the electrode surface influence the mechanism of the reduction and introduce unusual features in the polarograms. In most cases multi-step waves were observed due to the depletion of the protons at the electrode surface during the course of the reduction. Delahay and his co-workers made use of this observations to study the kinetics of the dissociation of mono chloro acetic acid by using the first reduction wave of azobenzene. It was also reported that the nature of the final products of the reduction of azo compounds is influenced by the pH of the solutions. In alkaline solutions the reduction product is hydrazo benzene and this is reoxidised to azobenzene. In acid solutions hydrazo-benzene rearranges to form benzidine and diphenyline. The rate of this rearrangement depends on pH and this is faster at low pH's. Since these reduction products are not susceptible for reoxidation, the polarographic reduction of azo compounds in acid solutions becomes irreversible.

Electroactive or strong electron donating groups are found to influence the reduction of the azo compounds to a great extent as mentioned earlier. The latter made the reduction a four electron process instead of the usual two-electron process. The products of these reductions are the amines resulting from the splitting of the azo bond. A typical reaction is shown below (cf. Chart 1 a).
Since (2) and (4) are fast and (3) occurs at the same potential as (1), only a single four-electron polarographic wave is observed.

Chart 1 a.

† Taken from The Chemistry of the Hydrazo, azo and azoxy groups - Part I by S. Patai (John Wiley and Sons).
Based on the factors mentioned earlier the mechanism of the reduction of azobenzene at mercury electrode can be represented as

Mechanism:

\[
\begin{align*}
\text{(ads.)} \quad \text{+ H}^+ & \quad \implies \quad \text{NH} = \text{N} \quad \text{Y} \\
\text{Hg electrode} & \\
\text{(ads.)} & \quad \implies \quad \text{NH} \text{N} \quad \text{Y} \\
\text{(ads.)} + 2 \text{e}^- & \quad \implies \quad \text{NH} \text{NH} \quad \text{Y} \\
\text{(ads.)} + \text{H}^+ & \quad \implies \quad \text{NH} \text{N} \quad \text{Y} \\
\text{Hg electrode} & \\
\text{(ads.)} & \quad \implies \quad \text{NH} \text{NH} \quad \text{Y} \\
\text{(ads.)} + 2 \text{e}^- + 2 \text{H}^+ & \quad \implies \quad \text{NH} \text{NH} \quad \text{Y} \\
\text{Hg electrode} & \\
\text{(ads.)} & \quad \implies \quad \text{NH} \text{NH} \quad \text{Y} \\
\end{align*}
\]

Chart 1b. *desorbed and/or further products.*
The relative positions of the nitro (-NO$_2$) and azo groups (-N=N-) in nitro substituted azobenzene plays an important role in the reduction process. The mechanism of the reaction and the nature of the final products are dependent on the position of the two groups. For example, 4-nitro compound takes twelve (12 electrons) compared to 9 electrons by 2-nitro derivatives for complete reduction. The products are also different. The position of the substituent, and the electro-reactivity of the substituent play a significant role in the polarography of the azo compounds.

Thus the overall reduction scheme of the azo compounds in protolitic media is very complex. It is therefore difficult to predict the reaction mechanism. Hence recording of polarograms of a particular compound in different aqueous organic solvents, in different pHs and in buffers of different components and in presence of different surfactants is very essential to understand the electrolytic reduction mechanism.