CHAPTER 1

ELECTROCHEMICAL REDUCTION OF THE AZO GROUP AT THE DROPPING MERCURY ELECTODE

— A BRIEF REVIEW
1.1 Electrochemical reduction of the azo group at the dropping mercury electrode: a brief review

Organic compounds containing the characteristic group \(-\text{N}=\text{N}-\) are called azo compounds. This characteristic group may be linked to two aliphatic groups (R) or two aromatic groups or to aromatic group and an heterocyclic group as shown below.

\[
\text{R-N=N-R}
\]

\[
\text{N=N -- CH -- C -- R,}
\]

The azo group may be an exocyclic one, as in the above examples or it may be a part of the cyclic structure.

**Electroreduction of azo compounds**

Azo group undergoes electroreduction at the dropping mercury electrode (DME) irrespective of the nature of the moieties linked to it.

Azo compounds undergo electroreduction\(^1\)\(^-\)\(^3\) involving two or four electrons as below.

\[
\text{-N=N-} + 2\text{e}^-, 2\text{H}^+ \rightarrow \text{-NH-NH-} \quad (1)
\]

or

\[
\text{-N=N-} + 4\text{e}^-, 4\text{H}^+ \rightarrow \text{-NH}_2 + \text{H}_2\text{N-} \quad (2)
\]
The earlier electrochemical investigations mostly relate to the electrolytic preparations. But the emphasis has slowly shifted from the preparative studies to the investigatory studies on the electrode reaction mechanism in the recent times.

Azo compounds studies are both interesting and useful since these are extensively used in the dye stuff industry, in chemical analysis and above all they are of chemical carcinogenic nature.

Many questions relating to the electrochemical studies remained unanswered because these studies were mostly in solvent systems containing water.

Electrochemical studies in predominantly aqueous solution are susceptible to interference by adsorption of the depolarizer at the electrode-system interface. The adsorption problems can however be minimized to a large extent by adding sufficient volume of an organic co-solvent to water. Electrochemical reductions in aprotic media involve single electron step with the formation of radical ions while such studies in aqueous solutions involve even number of electrons. Aromatic\textsuperscript{1,2} and heterocyclic\textsuperscript{4-9} azo compounds in general exhibit two-electron reduction at the dropping mercury electrode.
Strong electron donating substituents such as -OH, -NH$_2$ present in the aromatic system$^7$ or the basicity of the heterocyclic moiety cause four electron reduction to the amines.$^1$

Electrochemistry of the azo group in protolytic solvents

Che-Man chang$^{12}$ has reviewed extensively the electrochemistry of the aromatic azo-hydrazone redox systems in aqueous solutions. Aromatic azo compounds generally undergo two electron reduction at the dropping mercury electrode.

\[
\begin{align*}
\text{X} & \begin{array}{c} N=\text{N} \\ \text{Y}
\end{array} & \begin{array}{c} \text{Y} \\ \text{X}
\end{array} 
\rightarrow 2\text{e}^- + 2\text{H}^+ \\
\text{X} & \begin{array}{c} \text{N} \cdot \text{N} \\ \text{Y}
\end{array} & \begin{array}{c} \text{Y} \\ \text{X}
\end{array}
\end{align*}
\]

Equation 5

The polarographic studies made on different azo compounds reveal that the polarographic behaviour is complex in nature.$^{13-17}$ The behaviour depends critically on

a) the pH of the solution$^{18}$

b) the solvent composition$^{19}$

c) the concentration of the compound$^{14,20}$ and

d) the presence of surfactant$^{15}$

The $E_{1/2}$ - pH relation of the reversible polarographic wave of the process represented in the equation (5) is given by the equation$^{21}$

\[
E_{1/2} = \text{constant} - \frac{0.059}{n} \text{pH}
\]

Equation 6
where $p$ and $n$ denote the number of protons and the number of electrons respectively involved in the reduction process.

If $p = n = 2$, the half-wave potential is expected to change by -0.059 V for every unit increase in the pH of the solution. Literature survey shows that for many azo compounds, the slope of $E_{1/2}$-pH plot differs considerably from this value of -0.059 V. $E_{1/2}$-pH plots in many instances are even nonlinear or consist of two linear portions. The reduction of the azo group is diffusion-controlled and the limiting current is proportional to the concentration of the compound at lower concentration. A deviation has been noticed in the linearity at higher concentrations of the substrate.

**Factors affecting the reversibility of the reduction**

The reversibility of the electrode reaction is very much influenced by

a) the pH of the solution and

b) the adsorpbivity of the depolarizer.

a) **Effect of pH**

The reduction of the azo compounds is highly reversible at the extremes of the pH range 1.0 - 6.0. However, acids with slow dissociation rate in the buffer systems caused multistep irreversible polarographic waves. Thus, factors which affect the supply of protons at the electrode surface are found to cause unusual features in the polarograms. Delahay and coworkers observed similar phenomenon in presence of acetic acid. Azobenzene-4-sulphonic and Azobenzene-4',4'-disulphonic acids in buffer solutions containing ammonia or ethanolamine at the vicinity of the pH 9.0 however exhibited
reversible waves. It is also observed that in many cases the pH of the solution decides the nature of the final product in the reduction. Hydrazobenzene obtained in the two-electron reduction of azobenzene, slowly rearranges to benzidine and diphenyl amine at the extremes of the pH range.

$$\begin{array}{c}
\text{X} \quad \text{NH-NH} \quad \text{Y} \\
\text{H}_2\text{N} \quad \text{NH}_2 \\
\text{X} \quad \text{H}_2\text{N} \\
\end{array} \xrightarrow{\text{H}^+}$$

Slow rearrangement causes reversible reduction while rapid rearrangement causes irreversible reduction. In strongly acidic aqueous or alcoholic solutions, the end products of the reduction are benzidine 70% and diphenylamine 30%.

b) Effect of adsorption on the electroreduction of the azo group

The major disturbances encountered in the electrochemistry of azo-hydrazo systems are due to the adsorption of the azo compound or the hydrazo compound on the dropping mercury electrode. This is predominant in the solvents containing higher water content.

The rate of the electrode reaction in 30% methanol in the pH range 1.0 - 7.0 is very much determined by the adsorption kinetics of the azo-hydrazo species involved. Most strongly adsorbed surfactants were found to inhibit the electrode reaction altogether.
(B) Effect of the structure of the moiety on the electrochemical reduction of the azo group

The moieties linked to the azo group may behave\textsuperscript{29} as $+R$ as well as $-R$ groups depending on the electronic requirements of the reaction. The electronic effects or phenylazo groups are examined in two ways. In the first instance $-N=N-C_6H_4$ functions as the single system which transfers the effects of the variable phenyl group to the reaction site in the side chain. The efficiency of this transfer process is referred to as transmission coefficient $\pi$. This is expressed as the ratio of the Hammett's reaction constants ($p$) for the phenyl azo series and the phenyl series.

Phenyl azo substituent behaves in most of its electrophilic substitution reactions as an electron withdrawing group with a $\sigma_p$ value of +0.34. Further p-phenyl azo group activates the aromatic system towards nucleophilic substitutions.

The results of polarographic reductions of the aromatic azo compounds reported in the literature are presented below in brief. These are presented under two heads namely two-electron reductions and four-electron reductions for convenience.

**Two-electron reductions of aromatic azo compounds**

Che-Man Chang\textsuperscript{12} comprehensively reviewed the different reports made on the electrochemistry of aromatic azo-hydrazo redox system in aqueous solutions. Some typical examples are presented in the Table 1.1.

These reports show that azo group linked between two phenyl rings, undergoes in general two-electron reduction to hydrazo stage. The substituted azobenzenes as well as the parent compound show similar behaviour and a good correlation has been observed between...
the polarographic half-wave potential \( (E_1^e) \) and the Hammett substituents constant \( (\sigma) \) for meta and para substituents.

\[
E_1^e (X) = E_1^e (H) + 0.136 \sigma_p (H) \tag{8}
\]

Where

\[
E_1^e (X) = \text{half-wave potential of the substituted azobenzene}
\]

\[
E_1^e (H) = \text{half-wave potential of the azobenzene}
\]

\[
\sigma_p (X) = \text{Hammett substituent (para) constant}
\]

The relationship was found\textsuperscript{10,30} valid for eight mono substituted azobenzenes in 20% ethanol at pH 0. But no linear relation was observed between the Hammett substituent constant (ortho) \( \sigma_o \textsuperscript{31} \) and \( E_1^e \) values probably due to steric factors.

The mechanism proposed for the two-electron reduction of the azo compounds at the dropping mercury electrode is presented in Chart 1.1.
TABLE 1.1

Some typical examples for two-electron reduction of azobenzenes

<table>
<thead>
<tr>
<th>Name of the compound</th>
<th>Solvent</th>
<th>pH range</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azobenzene</td>
<td>25-100%</td>
<td>0-12.4</td>
<td>19</td>
</tr>
<tr>
<td>Azobenzene-4-sulphonic acid</td>
<td>H2O</td>
<td>1.0-12.0</td>
<td>16</td>
</tr>
<tr>
<td>4-Methyl azobenzene</td>
<td>20% EtOH</td>
<td>1.0-12.0</td>
<td>10</td>
</tr>
<tr>
<td>Azobenzene-4-carboxylic acid</td>
<td>20% EtOH</td>
<td>1.5-13.0</td>
<td>10</td>
</tr>
<tr>
<td>4-(Phenylazo)anisole</td>
<td>20% EtOH</td>
<td>1.5-13.0</td>
<td>10</td>
</tr>
<tr>
<td>4-(Phenylazo)acetophenone</td>
<td>20% EtOH</td>
<td>1.5-13.0</td>
<td>10</td>
</tr>
<tr>
<td>Azobenzene-4,4'-disulphonic acid</td>
<td>H2O</td>
<td>1.0-12.0</td>
<td>16</td>
</tr>
<tr>
<td>4-N,N'-Dimethylaminoazobenzene-4'-sulphonic acid</td>
<td>10% EtOH</td>
<td>3.5-9.8</td>
<td>23</td>
</tr>
<tr>
<td>4-N,N'-Dimethylaminoazobenzene-4'-sulphonic acid</td>
<td>H2O</td>
<td>3.5-6.0</td>
<td>10</td>
</tr>
<tr>
<td>4,4'-Diaminoazobenzene</td>
<td>10% EtOH</td>
<td>3.5-9.8</td>
<td>23</td>
</tr>
<tr>
<td>2-(4'-N,N-Dimethyl aminophenylazo)benzoic acid</td>
<td>20% EtOH</td>
<td>9.0-13.0</td>
<td>10</td>
</tr>
<tr>
<td>4-(4'-Phenylazosulphonicacid)-1-naphthol</td>
<td>H2O</td>
<td>1.0-13.0</td>
<td>10</td>
</tr>
</tbody>
</table>
Chart 1.1*

*Taken from "The Chemistry of the Hydrazo, azo and azoxy groups" – Part I, by S. Patai (Johny Wiley and Sons).
Four electron reduction of substituted azobenzene dyes

Aromatic azo compounds generally undergo two-electron reduction at the dropping mercury electrode,\textsuperscript{12} but compounds containing strongly electron donating groups such as –OH, -NH\textsubscript{2} etc. show four-electron reduction to the amine.\textsuperscript{10} Methyl orange,\textsuperscript{10} methyl red\textsuperscript{10} and 4-hydroxy,\textsuperscript{3,32} 4.-amino\textsuperscript{10}, 4-N,N-dimethylamino\textsuperscript{10,22,23}, 4-hydroxy-4'-sulponic acid\textsuperscript{10}, 2,4-dihydroxy-4'-sulphonic acid\textsuperscript{10} and 2,2',4-trihydroxy-4'-sulphonic acid derivatives\textsuperscript{10} gave four-electron polarographic reduction waves. The end product is always the amine.

Typical examples of four-electron reductions are presented in the Table 1.2

A typical reaction scheme is shown in Chart 1.2
TABLE 1.2

Some typical examples for four-electron reduction of azobenzene dyes

<table>
<thead>
<tr>
<th>Name of the compound</th>
<th>Solvent</th>
<th>pH range</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-N,N-Dimethylamino azobenzene</td>
<td>20% EtOH</td>
<td>1.6-6.0</td>
<td>10</td>
</tr>
<tr>
<td>4-(phenylazo)aniline</td>
<td>20% EtOH</td>
<td>1.5-5.0</td>
<td>10</td>
</tr>
<tr>
<td>4-(N,N-Dimethylamino phenylazo)-4-sulphonic acid</td>
<td>H₂O</td>
<td>8.0-13.0</td>
<td>10</td>
</tr>
<tr>
<td>4-(4’-Phenylazo sulphonic acid)-resorcinol</td>
<td>H₂O</td>
<td>3.0-13.0</td>
<td>10</td>
</tr>
<tr>
<td>4-(4’-phenylazo sulphonic acid-1-naphthol</td>
<td>H₂O</td>
<td>1.5-6.0</td>
<td>10</td>
</tr>
<tr>
<td>2-(4’-phenylazo sulphonic acid-2-naphthol</td>
<td>H₂O</td>
<td>3.0-13.0</td>
<td>10</td>
</tr>
<tr>
<td>2(2’-Hydroxy naphthylazo)benzene-4-sulphonic acid</td>
<td>H₂O</td>
<td>3.0-13.0</td>
<td>10</td>
</tr>
<tr>
<td>2(2’-Hydroxy naphthylazo)phenyl-4-sulphonic acid</td>
<td>H₂O</td>
<td>3.0-13.0</td>
<td>10</td>
</tr>
<tr>
<td>2-(4’-Bromo-2’-pyridylazo)-5-(N,N-dimethyl)aminophenol</td>
<td>50% EtOH</td>
<td>11.2-13.5</td>
<td>33</td>
</tr>
<tr>
<td>2-(3’-Hydroxy pyridylazo)-1-naphthalene</td>
<td>50% EtOH</td>
<td>11.2-13.5</td>
<td>33</td>
</tr>
<tr>
<td>Benzeneazo-1-naphthol</td>
<td>50% EtOH</td>
<td>3.7-9.5</td>
<td>10</td>
</tr>
<tr>
<td>1-(Benzeneazo-4-sulphonic acid)-2,4-dihydroxy naphthalene</td>
<td>50% EtOH</td>
<td>3.7-9.5</td>
<td>10</td>
</tr>
<tr>
<td>2-(2’,4’-Dihydroxy naphthylazo)-1-phenol-5-sulphonic acid</td>
<td>50% EtOH</td>
<td>3.7-9.5</td>
<td>10</td>
</tr>
<tr>
<td>2-(2’,4’-Dihydroxy naphthylazo)-1-phenol-4-sulphonic acid</td>
<td>50% EtOH</td>
<td>3.7-9.5</td>
<td>10</td>
</tr>
<tr>
<td>1-(4’-Hydroxy naphthylazo)-1-phenol-4-sulphonic acid</td>
<td>50% EtOH</td>
<td>9.5</td>
<td>13</td>
</tr>
<tr>
<td>Phenylazo phenol</td>
<td>50% EtOH</td>
<td>3.0-12.0</td>
<td>13</td>
</tr>
<tr>
<td>4-Nitro azobenzene</td>
<td>50% EtOH</td>
<td>3.0-12.0</td>
<td>33</td>
</tr>
<tr>
<td>2-(3’-pyridyl azo)phenol</td>
<td>40% EtOH</td>
<td>3.0-12.0</td>
<td>34</td>
</tr>
<tr>
<td>1-(phenylazo)-3-pyridine</td>
<td>40% EtOH</td>
<td>3.0-12.0</td>
<td>33</td>
</tr>
<tr>
<td>1-(2’-Hydroxy quinonylazo)-4-pyridine</td>
<td>40% EtOH</td>
<td>3.0-12.0</td>
<td>35</td>
</tr>
</tbody>
</table>
\[
\text{C}_6\text{H}_5\text{N} = \text{N} + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{C}_6\text{H}_5\text{NNH}^+ - \text{N(CH}_3\text{)}_2 \quad (1)
\]

\[
\text{C}_6\text{H}_5\text{NNH}^+ - \text{N(CH}_3\text{)}_2 + \text{H}^+ \rightarrow \text{HN}^+ \text{N(CH}_3\text{)}_2 + \text{C}_6\text{H}_5\text{NH}_2 \quad (2)
\]

\[
\text{HN}^+ \text{N(CH}_3\text{)}_2 + 2\text{e}^- + \text{H}^+ \rightarrow \text{H}_2\text{N}^+ \text{N(CH}_3\text{)}_2 \quad (3)
\]

\[
\text{HN}^+ \text{N(CH}_3\text{)}_2 + \text{C}_6\text{H}_5\text{NNH}^+ \rightarrow \text{HN}^+ \text{N(CH}_3\text{)}_2 + \text{H}^+ \quad (4)
\]

**overall**

\[
\text{C}_6\text{H}_5\text{N} = \text{N} + 4\text{e}^- + 4\text{H}^+ \rightarrow \text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{N}^+ \text{N(CH}_3\text{)}_2 \quad (5)
\]

**Chart 1.2**

* Taken from "The Chemistry of the Hydrazo, azo and azoxy goups"-Part I, by S. Patai (John Wiley and Sons).
Reduction of heterocyclic azo compounds

Malik et al.\textsuperscript{36} after studying the polarographic reduction of 3,5-dimethyl-1-thiocarbonyl-4-phenylazo pyrazole and its derivatives, reported that ortho substituted pyrazoles are reduced more easily than the corresponding p-substituted compounds. Goyal and Rajeev Jain\textsuperscript{37} reported that arylazo pyrimidinyl pyrazoles exhibit a single two electron wave corresponding to the reduction of azo group. Rajeev Jain et al.\textsuperscript{9} observed a single two electron transfer in the reduction of benzyl sulphonyl arylazo pyrazoles. Some typical examples of two-electron reductions are presented in Table 1.3.

The following mechanism has been proposed for the two-electron reductions of the heterocyclic azo compounds at the dropping mercury electrode.
where $R' = -C\equiv C\equiv CR_1$

$R_1 - C\equiv C\equiv C\equiv C\equiv C\equiv CR_1$

$N\equiv S$

$NH_2$
### TABLE 1.3

Some typical examples for two-electron reduction of heterocyclic azo compounds

<table>
<thead>
<tr>
<th>Name of the compound</th>
<th>Solvent</th>
<th>pH range</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-(phenylazo)pyridine-4-(2’-Pyridylazo)phenyl</td>
<td>50% EtOH</td>
<td>1.0-13.0</td>
<td>33</td>
</tr>
<tr>
<td>4-(2’-Pyridylazo)resorcinol</td>
<td>50% EtOH</td>
<td>1.0-13.0</td>
<td>33</td>
</tr>
<tr>
<td>4-(2’-Pyridylazo)-5-resorcinol</td>
<td>50% EtOH</td>
<td>1.0-13.0</td>
<td>33</td>
</tr>
<tr>
<td>2-(2’-Pyridylazo)-5-aminophenol</td>
<td>50% EtOH</td>
<td>1.0-8.0</td>
<td>33</td>
</tr>
<tr>
<td>4-(2’-Pyridylazo)-5-(N,N-dimethyl)aminophenol</td>
<td>50% EtOH</td>
<td>1.0-8.0</td>
<td>33</td>
</tr>
<tr>
<td>2-[4’-(4’-Bromo-2’-pyridylazo)-5-(N,N-diethyl)aminophenol]</td>
<td>50% EtOH</td>
<td>1.0-8.0</td>
<td>33</td>
</tr>
<tr>
<td>4-(3’-Pyridylazo)phenol</td>
<td>50% EtOH</td>
<td>1.0-8.0</td>
<td>33</td>
</tr>
<tr>
<td>4-(3’-Pyridylazo)resorcinol</td>
<td>50% EtOH</td>
<td>1.0-8.0</td>
<td>33</td>
</tr>
<tr>
<td>1-(2’-Pyridylazo)-2-naphthol</td>
<td>50% EtOH</td>
<td>1.0-8.0</td>
<td>33</td>
</tr>
<tr>
<td>4-(2’-Pyridylazo)-1-naphthol</td>
<td>50% EtOH</td>
<td>1.0-8.0</td>
<td>33</td>
</tr>
<tr>
<td>4-(2’-Pyridylazo)-1-naphthyl amine</td>
<td>50% EtOH</td>
<td>1.0-8.0</td>
<td>33</td>
</tr>
<tr>
<td>1-(3’-Pyridylazo)-2-naphthol</td>
<td>50% EtOH</td>
<td>1.0-8.0</td>
<td>33</td>
</tr>
<tr>
<td>1-(4’-Pyridylazo)-2-naphthol</td>
<td>50% EtOH</td>
<td>1.0-8.0</td>
<td>33</td>
</tr>
<tr>
<td>2-(2’-Quinolylazo)-4-(N,N-diethyl)aminophenol</td>
<td>50% EtOH</td>
<td>1.0-8.0</td>
<td>33</td>
</tr>
<tr>
<td>N’-Benzyl sulphonyl-3,5-diphenyl-4-(substituted phenylazo)-pyrazoles</td>
<td>20% EtOH</td>
<td>2.0-11.0</td>
<td>9</td>
</tr>
<tr>
<td>3,5-Dimethyl-4-(substituted phenylazo)-isoxazoles</td>
<td>50% DMF</td>
<td>2.0-10.0</td>
<td>38</td>
</tr>
<tr>
<td>Solechrome red ERS</td>
<td>H₂O</td>
<td>1.8-8.0</td>
<td>5</td>
</tr>
<tr>
<td>N’-Benzoyl-3,5-dimethyl-4-(substituted phenylazo)pyrazoles</td>
<td>40% DMF</td>
<td>2.0-10.0</td>
<td>39</td>
</tr>
<tr>
<td>Name of the compound</td>
<td>Solvent</td>
<td>pH range</td>
<td>Reference</td>
</tr>
<tr>
<td>-------------------------------------------------------------------------------------</td>
<td>------------------</td>
<td>----------</td>
<td>-----------</td>
</tr>
<tr>
<td>N'-Benzoyl-3,5-diphenyl-4-(substituted phenylazo)pyrazoles</td>
<td>40% DMF</td>
<td>2.0-10.0</td>
<td>40</td>
</tr>
<tr>
<td>N'-Benzoyl-3-methyl-5-phenyl-4-(substituted phenylazo)pyrazoles</td>
<td>40% DMF</td>
<td>2.0-10.0</td>
<td>41</td>
</tr>
<tr>
<td>2-Amino-4,6-dimethyl-5-(substituted phenylazo)pyrimidines</td>
<td>20% EtOH</td>
<td>2.0-10.0</td>
<td>42</td>
</tr>
<tr>
<td>4-[8'-Hydroxy quinolyl]azo]benzene sulphonamide drugs</td>
<td>20% EtOH</td>
<td>3.3-11.2</td>
<td>43</td>
</tr>
<tr>
<td>N'-Phenylthiocarbamoyl-3,5-dimethyl-4-(substituted phenylazo)pyrazoles</td>
<td>20% EtOH</td>
<td>2.0-12.0</td>
<td>44</td>
</tr>
<tr>
<td>N'-(4',6'-Dimethyl pyrimidinyl)-3,5-diphenyl-(substituted phenylazo)pyrazoles</td>
<td>DMF</td>
<td>2.0-10.0</td>
<td>37</td>
</tr>
<tr>
<td>1-Thiocarbamoyl-3,5-diphenyl-4-(substituted phenylazo)pyrazoles and</td>
<td>40% DMF</td>
<td>2.0-10.0</td>
<td>4</td>
</tr>
<tr>
<td>1-Thiocarbamoyl-3,5-dimethyl-4-(substituted phenylazo)pyrazoles</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N'-Carbomoyl-3,5-dimethyl-4-(substituted benzeneazo)pyrazoles and</td>
<td>90% DMF+ 10% EtOH</td>
<td>2.0-10.0</td>
<td>6</td>
</tr>
<tr>
<td>1-phenyl-3,5-dimethyl-4-(substituted phenylazo)pyrazoles</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Amino-4-methyl-5-(substituted phenylazo)thiazoles</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Bannerjee et al. reported that 3,5-dimethyl-4-(4'-sulphonamido benzeneazo)pyrazoles exhibit a four-electron irreversible double wave in acidic solutions and a two-electron single wave in alkaline medium. They further proposed that the reduction in acidic medium does not involve the hydrazo-pyrazole as the intermediate. Fahmy, Abdel Aziz and Badran observed a well defined single polarographic wave for 5-arylazo-1-phenyl-2-thiohydantion in a wide range of pH conditions in the entire pH range. A similar wave was reported for other compounds containing the hydrazone linkage. The wave is different from the one observed with the compounds containing the hydrazone linkage. Darwish et al. reported that 5-arylazo-1-phenyl-4-thiohydantion derivatives exhibit two waves. The reductive splitting of the azo linkage by a four-electron irreversible process is ascribed to the first wave. The second wave is ascribed to the reduction of –CO-NH-CO-group in the resulting molecule. 5-Arylazo-8-hydroxy quinoline exhibits two waves as reported by Issa et al. The first wave was attributed to the four-electron reduction of the azo group to the amine. Elnagdi et al. reported that coupling products of 4-hydroxycoumarins with aryl diazonium salt exist in the azo form from their polarographic studies.

These compounds give a single pH dependent irreversible four electron wave in the pH range 2.0-11.0. Florence et al. observed that several differences occur between the electrode reactions of heterocyclic azo compounds, and their benzene or naphthalene counterparts. The hydrazo derivatives of heterocyclic dyes are more stable towards disproportionation. Issa et al. reported that azo-azomethine compound in universal buffer solutions of pH 2.0-12.0, exhibit two waves of almost equal heights due to the reduction of the –N=N- and >C=N- centres respectively. The reduction corresponds to 8-electrons per molecule, 4-electrons for each –N=N- and >C=N- centre. Mary suguna et al. reported that 2,4-dihydroxy-5-(4’-substitutied benzeneazo)acetophenone in the pH range 8.1-10.1,
containing 40% V/V dimethylformamide exhibit two waves in acidic solutions and one wave in alkaline solution. The first wave is ascribed to the four-electron reduction of the azo group to amine stage. Goyal\textsuperscript{11} noticed that p-(8-hydroxy quinolyl azo)benzene sulphonamide undergoes four electron reduction in a single well-defined wave in the pH range 3.0-11.8. p-Nitrophenyl diazoaryl sulphide, exhibits two waves\textsuperscript{58} in 40% ethanol-aqueous buffers (pH range 1.0-12.0). The first wave corresponds to the 4-electron reduction of the \(-N=N-\) group to form p-nitroaniline and the second wave to the 6-electron reduction of the nitroaniline to the diamine.

The mechanism for the four-electron reduction of the azo group to the amine via hydrazo stage can be represented as

\[
\text{Reduction of azo (-N=N-) group in the azomethine form (>C=N-NH-) [Four electron reduction]}
\]

Azo compounds exhibit cis, trans isomerism.\textsuperscript{59-60} Aromatic\textsuperscript{59-60} and heterocyclic\textsuperscript{61} azo compounds also exhibit azo-hydrazone tautomerism. Generally the phenyl hydrazones exist in the following structural forms and the hydrazone form is
predominant in non-polar solvents or in pure liquids\cite{62,63} while ene hydrazone form (R-\(\text{CH}=\text{CR}_i\)-NHC\(_6\text{H}_5\)) is predominant in polar solvents. The polarographic studies and the IR studies\cite{64} carried out on the phenyl hydrazones in aqueous methanol solutions\cite{53} showed the presence of all the three tautomeric forms. The hydrazo-azo tautomerism is strongly influenced by the nature of the solvent and is shifted towards the hydrazone form in polar solvents.

![Diagram 1](image1)

In non-polar solvent

![Diagram 2](image2)

In polar solvent

Ortho and para hydroxy-azo benzenes exhibit predominantly this tautomerism and the compounds exist largely in the hydrazone form in solutions and even in the solid state. The hydroxy-azo anthracenes exist in the hydrazone form,\cite{60} both in solution and the solid state. The azo group acts as a proton acceptor via hydrogen bond formation if hydroxyl group\cite{65} (-OH) or amino group (-NH\(_2\))\cite{66} is present in the molecule in ortho or para positions. Generally hydroxyl-azo aromatic compounds exist as intra-molecularly hydrogen bonded...
hydrazones in aqueous solutions and in methanol. An equilibrium exists between the azo and the hydrazone form.

![Diagram](image)

The hydrazone tautomer (7) is present predominantly in polar solvents. Huckel molecular orbital calculations support the above concept. The stability of the azo form or the hydrazone form depends on the following factors,

a) the presence or absence of intra molecular hydrogen bond

b) the electron withdrawing substituents and

c) the large ring system bearing the oxygen atom.

The increase in OH...N bond strength shifts the equilibrium towards the hydrazone form. The decrease in the electron density on the proton accepting nitrogen atom increases the stability of the hydrazone form.

The azo-hydrazone tautomerism is also present in the number of aromatic azo heterocycles and the nature of the substituents present in the heterocyclic system plays a significant role on the azo-hydrazone tautomerism.
Hydrazone-azo tautomerism is also observed in benzene-azo heterocycles as in benzeneazo pyrazolin-5-one.\textsuperscript{61,73,76} Further the azo-hydrazone tautomerism exists both in the solid state and in aqueous solution. However in the case of pyrazoles, the tautomerism depends on nature of the substituent present in the heterocyclic moiety.

1. Pyrazoles (structure A) with $R_2$ and $R_3$ as alkyl or phenyl groups do not exhibit azo-hydrazone tautomerisms.

2. On the other hand if $R_2$ or $R_3$ is $-\text{OH}$ or $=\text{O}$ group, they exhibits tautomerism.

Thus the nature of the substituent present in the heterocyclic moiety plays a significant role in the azo-hydrazone tautomerism. Polarography is generally employed as a tool to investigate this tautomerism since the reduction paths at the dropping mercury electrode differ for the two forms.

A brief account of the polarographic studies of the azo-heterocycles in the hydrazone form and undergoing 4-electron reduction cleavage to the amine is presented below.

5,5-Dimethylecyclohexane-2-benzothiozolyl hydrazone-1,3-diones in Britton-Robinson buffers in the pH range 2.0-12.0 undergo 4-electron reduction in a single wave.\textsuperscript{69} The following mechanism is suggested for the reduction process.
The reduction pattern of 2,3,4-pentane trione-3-phenyl hydrazone and some para substituted derivatives in the buffer solutions of pH 0.8-9.5, depends on the conversion of the hydrazone form to the azo form.\textsuperscript{70}

![Chemical structure](image)

1-Ethyl mercapto-3-(4H) isoquinolones in alcoholic media, undergo four electron reduction.\textsuperscript{71} The structure (B) is stable since it contains the conjugated double bond and this is further stabilized through hydrogen bonding between –OH group and the N attached to the aryl group.
2-Naphthylhydrazone-5,5-dimethyl cyclohexane-1,3-dione in buffered (pH 3.5-11.0) methanol-water mixture containing 60-80% V/V methanol exhibits a well-defined 4-electron reduction in the entire pH range. The compound in the hydrazone form (A) undergoes reduction to the primary amine, consuming four-electrons.
It was reported by Ravindranath et al. that 1-phenyl-3-amino-4-arylazo-pyrazolin-5-ones undergo reduction at mercury cathode in Britton-Robinson buffers (pH range 3.0-10.0) containing 40% V/V dimethylformamide according to the following mechanism.

\[ \text{R} \]

\[ \begin{array}{c}
\text{N} = \text{N} \quad \text{C} \quad \text{C} \quad \text{N} \\
\text{HO} \quad \text{C} \quad \text{N} \\
\text{N} \\
\text{R} 
\end{array} \]

\[ \begin{array}{c}
\text{N} = \text{N} \quad \text{C} \quad \text{C} \quad \text{NH}_2 \\
\text{HO} \quad \text{C} \quad \text{N} \\
\text{N} \\
\text{R} 
\end{array} \]

\[ \xrightarrow{\text{H}^+} \]

\[ \begin{array}{c}
\text{NH} \quad \text{N} = \text{C} \quad \text{C} \quad \text{NH}_2 \\
\text{HO} \quad \text{C} \quad \text{N} \\
\text{N} \\
\text{R} 
\end{array} \]

\[ \xrightarrow{2e^- , 2H^+} \]

\[ \begin{array}{c}
\text{HN} \quad \text{N} = \text{C} \quad \text{C} \quad \text{NH}_2 \\
\text{HO} \quad \text{C} \quad \text{N} \\
\text{N} \\
\text{R} 
\end{array} \]

\[ \xleftarrow{2e^- , 2H^+} \]

\[ \begin{array}{c}
\text{NH} \quad \text{N} = \text{C} \quad \text{C} \quad \text{NH}_2 \\
\text{HO} \quad \text{C} \quad \text{N} \\
\text{N} \\
\text{R} \quad \text{R} 
\end{array} \]
Ravindranath et al.\textsuperscript{74} also studied the electrochemical reduction of N'-(2-pyridine carbonyl)-3-methyl-4-(4'-substituted benzeneazo)-2-pyrazolin-5-ones in the pH range 2.10 - 10.10 at mercury cathode in 40% V/V dimethylformamide and reported the following mechanism of reduction.

\[ 4 \text{ e}^-, 4 \text{ H}^+ \rightarrow \text{aromatic rings} \]

\[ \text{NH}_2 + \text{aromatic rings} \]
Ravindranath et al.\textsuperscript{75} also reported the electrochemical reduction of 1-anilinomalonyl-3-methyl-4-(substituted benzeneazo)-5-pyrazolones and suggested a mechanism involving a four electron reductive cleavage of azomethine to an aromatic amine and heterocyclic amine. They also reported\textsuperscript{76,77} a similar four electron reductive cleavage of azomethine in N’-(2-hydroxybenzoyl)-3-methyl-4-(4’-substituted arylhydrazono)-2-pyrazolin-5-ones and 1-benzenesulfonfyl-3-benzenesulfanamido-4-(4’-substituted arylhydrazono)-2-pyrazolin-5-ones.

The following mechanism for the polarographic reduction of 3-phenyl-2,3-diketopropionitrile-2-phenylhydrazine was however reported by Sammour et al.\textsuperscript{78}
5-Arylazo-1-phenyl-2-thiohydantion in 40% V/V ethanolic aqueous buffers resembles the compounds containing the hydrazone linkage and deviates from those containing the azo group in the electrochemical behaviour.\textsuperscript{47}

\[
\begin{align*}
\text{N} &= \text{N} \quad \text{H}_2\text{C}_6 \\
\text{N} \quad \text{CH} \quad \text{C} &= \text{O} \\
\text{N} \quad \text{NH} \quad \text{C} \quad \text{S} \\
\text{S}
\end{align*}
\]

\[
\begin{align*}
\text{N} &= \text{N} \quad \text{H}_2\text{C}_6 \\
\text{N} \quad \text{NH} \quad \text{C} \quad \text{S} \\
\text{S}
\end{align*}
\]

Malik and Goyal\textsuperscript{79} reported that hydrazone tautomer plays a significant role in the four-electron reduction of 1-phenyl-2-substituted phenyl hydrazono-1,2,3-butan-triones in dimethylformamide.

\[
\begin{align*}
\text{R} \quad \text{N} &= \text{N} \quad \text{CH} \quad \text{C} = \text{O} \\
\text{R} \quad \text{C} = \text{R}_1 \\
\text{O} \quad \text{C} = \text{R}_2 \\
\text{R} \quad \text{NH}_2 \\
\text{R} \quad \text{NH}_2
\end{align*}
\]

\[
\begin{align*}
\text{R} \quad \text{N} &= \text{N} \quad \text{CH} \quad \text{C} = \text{O} \\
\text{R} \quad \text{C} = \text{R}_1 \\
\text{O} \quad \text{C} = \text{R}_2 \\
\text{R} \quad \text{NH}_2 \\
\text{R} \quad \text{NH}_2
\end{align*}
\]

\[
\begin{align*}
4\text{H}^+, 4\text{e}^- \\
E_{1/2}
\end{align*}
\]

\[
\begin{align*}
\text{R}_1 &= \text{CH}_3; \text{ R}_2 = \text{-C}_6\text{H}_5
\end{align*}
\]
The hydrazone tautomer is prominent and involves 4-electrons reduction in the polarographic reduction of 4-aryl hydrazono-N'-hippuryl-3-methyl-2-pyrazolin-5-ones in Britton-Robinson buffer in the pH range 2.0-12.0.\textsuperscript{80}

The polarographic studies\textsuperscript{55} reveal that 3-arylazo-4-hydroxycoumarine exists in the hydrazone form. Therefore the following mechanism is suggested for the polarographic reduction.
Guanyl pyrazolin-5-ones in Britton-Robinson buffers of pH range 2.0-10.0 undergo 4-electron, diffusion-controlled, irreversible reduction in the hydrazone form.61
The mechanism for the polarographic reduction of the aryl hydrazone of α-cyano ketones has been proposed as

\[
\text{H}_5\text{C}_6 - \text{N} = \text{N} - \text{CH} \quad \text{R} \quad \overset{\text{C} = \text{N}}{\leftrightarrow} \quad \text{H}_5\text{C}_6 - \text{NH}-\text{N} = \text{N} - \text{C} = \text{N} \quad \text{R} \quad 4 \text{H}^+, 4 \varepsilon^-
\]

\[
\text{R} = \text{-C}_6\text{H}_5\text{CO}, \text{-CH}_3\text{CO}, \text{-CH}_3\text{C=NH}
\]

It is thus evident that the nature of the reduction of azo group is very much influenced by the structural features of the moiety to which the group is linked.
1.2 Importance of pyrazolones and pyrazoles

The present investigation deals with the studies on the electrochemical behavior of pyrazolin-5-ones and pyrazoles. A survey of the literature\textsuperscript{82-97} shows that pyrazolin-5-ones, pyrazoles and related heterocycles possess different types of physiological activity. It was reported that 3,5-dimethyl-pyrazole(1), 5-methyl-3-pyrazole carboxylic acid(2) and 3,5-dimethyl-4-hydroxy-pyrazole(3) possess unusual potency as inhibitors of free fatty acid release and as hypoglycemic agents in infant rats.

Further it is seen from the literature\textsuperscript{2} that 2-benzoyl-3,5-dimethyl-pyrazole(4) is more active than 3,5-dimethyl-pyrazole(1). Similarly phenyl butazone(5), oxyphenabutazone(6), antipyrine(7), aminopyrine(8) and 4-(N-nicotinoylamino)-1-phenyl-2,3-dimethyl-5-pyrazole(9) were reported to possess antirhumatic\textsuperscript{98-100} antipyretic and analgesic activity.
Some typical examples of these types of compounds together with their activity are presented in Table 1.2.1.
**TABLE 1.2.1**

Pyrazolones and pyrazoles and their activities

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compound</th>
<th>Activity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3-(p-bromophenyl)-2-pyrazolin-5-one</td>
<td>Antituberculous</td>
<td>101</td>
</tr>
<tr>
<td>2</td>
<td>1-thiocarbamoyl-3-(4'-pyridyl)-2-pyrazolin-5-one</td>
<td>Antituberculous</td>
<td>101</td>
</tr>
<tr>
<td>3</td>
<td>1-thiocarbamyl-3-(p-substituted phenyl)-2-pyrazolin-5-one</td>
<td>Antituberculous</td>
<td>101</td>
</tr>
<tr>
<td>4</td>
<td>1-phenyl-3,5-dimethyl-4-(4'-bromo-2'-methylbenzeneazo)pyrazole and</td>
<td>M. tuberculosis</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>N'-phenyl-3-methyl-5-phenyl-4-(2'-methyl-4'-bromo benzeneazo)pyrazole</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>N'-phenyl-3-methyl-5-phenyl-4-(2'-bromo-4'-methyl benzeneazo)pyrazole</td>
<td>T. metagrophytes</td>
<td>103</td>
</tr>
<tr>
<td>6</td>
<td>3,5-Diaryl-4-(substituted sulphanamido benzeneazo)pyrazoles</td>
<td>E. Coli and S. aureus</td>
<td>104</td>
</tr>
<tr>
<td>7</td>
<td>3-methyl-5-(p-alkyl phenyl)-4-(N-substituted p-sulphanamyl benzeneazo)pyrazoles</td>
<td>E.Coli and S. aureus</td>
<td>105</td>
</tr>
<tr>
<td>8</td>
<td>3,5-Dimethyl-4-(substituted sulphanamido benzeneazo p-sulphla phenyl and sulphonaphthylazo)pyrazole</td>
<td>Antibacterial</td>
<td>106</td>
</tr>
<tr>
<td>9</td>
<td>3-Methyl-5-(4'-chloro-3'-methylphenyl)-4-(N-substituted p-sulphamyl benzeneazo)pyrazole</td>
<td>S. aureus</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td>Molecular Structure</td>
<td>Antibacterial Activity</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>-------------------------------------------------------------------------------------</td>
<td>---------------------------------------------</td>
<td>---</td>
</tr>
<tr>
<td>10</td>
<td>3,5-Diaryl-4-(N-substituted p-sulphanamyl benzeneazo)pyrazoles</td>
<td>E. Coli and S. aureus</td>
<td>108</td>
</tr>
<tr>
<td>11</td>
<td>1-Anilinomalonyl-3-methyl-4-(substituted phenylazo)-5-pyrazolones</td>
<td>S. typhi, E. coli, C. albicans, C. neoformelus, T. mentographynetes, M. canis and A. mgei</td>
<td>109</td>
</tr>
<tr>
<td>12</td>
<td>4-Methyl-5-(substituted phenyl)-5-aryazo/p-sulphonamyl benzeneazo)-pyrimidin-5-ol</td>
<td>Antibacterial</td>
<td>110</td>
</tr>
<tr>
<td>13</td>
<td>1-phenyl-3,5-diphenyl-4-sulphonamoylazopyrazoles</td>
<td>B. pumlus, P. mongiferae, V. cholera, S. aureus, S. pyrogenus</td>
<td>111</td>
</tr>
<tr>
<td>14</td>
<td>1-Thiocarbamoyl-3-methyl-4-(substituted aryl hydrazono)-2-pyrazoline-5-one</td>
<td>S. aureus, E. coli, S. typhe</td>
<td>112</td>
</tr>
<tr>
<td>15</td>
<td>1-Nicotinoyl-3-methyl-5-phenyl-4-(4'-sulphonamoyl)-azopyrazole</td>
<td>S. aureus, S. pyrogenus, B. pumlus, P. mongiferae, V. cholerae</td>
<td>113</td>
</tr>
</tbody>
</table>
Besides their use in medicine, benzeneazo-pyrazolin-5-ones were also used in dye industry.\textsuperscript{114} They are also used as indicators\textsuperscript{115-117} in complexometric titrations.

The brief account presented above indicates the importance of the compounds in medicine, industry and in chemical analysis. Therefore the synthesis and electrochemical studies on a new series of pyrazolones and pyrazoles were taken up for obtaining more fundamental information.
1.3 Objectives of the present investigations

The survey of the literature on the electrochemical behaviour of aromatic azo compounds and aromatic azo heterocycles revealed the following.

1. Azobenzene, substituted azobenzenes and phenylazo naphthols undergo reduction at the dropping mercury electrode involving 2-electron reduction to the hydrazo stage.

2. Phenylazo heterocycles such as phenylazo pyridines, phenylazo pyrazoles, phenylazo thiazoles and phenylazo pyrimidines also undergo 2-electron reduction to the hydrazo stage.

3. Substituted azobenzenes with electron donating groups such as -OH, -NH₂ exhibit -N=N- splitting involving 4-electron reduction.

4. Aromatic azo heterocycles undergo 4-electron reduction to the amine stage via hydrazo intermediate both in acidic and basic solutions and

5. Aromatic azo heterocycles undergo 4-electron reduction in the azomethine form to the amine stage through -N-N=C< splitting.

Keeping in view the importance as mentioned above, the synthesis, characterization, biological activity as well as polarographic and cyclic voltametric behaviour of

a. N′-(p-toluenesulphonyl)-3-methyl-4-(substituted arylhydrazono)-2-pyrazolin-5-ones

and

b. N′-(2-hydroxybenzoyl)-3,5-dimethyl-4-(substituted arylazo)pyrazoles

are taken up to investigate the effect of the following on the reduction process.
i) the nature of the substituent present in the ring,

ii) the nature of the heterocyclic ring present at one end of the azo group,

iii) the pH of the solution,

iv) organic co-solvent and

v) the effect of temperature.

The proposed study is expected to throw light on structure activity relationship and helps to correlate this relationship to the polarographic characteristics of these compounds.

The compounds investigated are shown in the Chart 1.3.1 and the results are incorporated in the relevant chapters.
N'-(p-toluenesulphonyl)-3-methyl-4-(substituted arylhydrazono)-2-pyrazolin-5-ones

R = -H, 4'-CH₃, 4'-OCH₃, 4'-Br, 4'-SO₂NH₂, 4'-NO₂, 2'-CH₃, 2'-OCH₃, 2'-Cl, 2'-NO₂

N'--(2-hydroxybenzoyl)-3,5-dimethyl-4-(substituted arylazo)pyrazoles

R = -H, 4'-CH₃, 4'-OCH₃, 4'-Cl, 4'-SO₂NH₂, 4'-NO₂, 2'-CH₃, 2'-Cl

Chart 1.3.1
References


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<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Authors</td>
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<td>---</td>
<td>----------------------------------</td>
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