CHAPTER 2

POLAROGRAPHIC DETERMINATION OF CURRENT CHARACTERISTICS OF AZO DYES
2.1. INTRODUCTION

Aromatic azo dyes, particularly solochrome mordant dyes are an important class of compounds which find an immense use in quantitative determination of metal ions through complexation (1-4). Recently Gupta, Kachru and Bhat (5) used solochrome fast navy 245 as an indicator for complexometric titrations of metal ions.

As early as in 1926, Conant and Pratt (6) reported the polarographic reduction behaviour of twenty seven azo dyes at dme. However, their results were not comparable with the studies carried out at latter stages, as they had used the dyes of doubtful purity. The polarographic studies of some purified dyes such as orange (II) (7), metanil yellow (7), methyl red (8), methyl orange (9) and several azo compounds (1) indicate that the impurities affect adversely the electrode mechanism. Keeping this in mind, the purification of dyes was given utmost attention as described in Chapter 1.

In this class of dyes, azo benzene is the basic unit and in general it undergoes two electron reduction at dme, however, they show peculiar behaviour in the presence of substituted groups (10).

The analysis of polarographic waves for six solochrome mordant dyes obtained in the presence of various buffers at different pH values reveals that these are reduced partly reversibly and yield cathodic diffusion controlled waves at dme. The kinetic parameters $k^0_{f,h}$ and $\alpha_n$ of these dyes have been evaluated to throw light on the behaviour of reduction.
2.2. EXPERIMENTAL

2.2.1. Apparatus:

A manual polarographic unit (Toshniwal, India) was used in conjunction with supersensitive multiflex spot galvanometer. Unless otherwise stated, all current measurements were made at damping 1, h = 42.5 cm (height of Hg-column) and at temperature of 25°C ± 0.1. The dme had following characteristics, \( m = 5.533 \text{ mg s}^{-1} \), \( t = 3.335 \left( \frac{m^{2/3} t^{1/6}}{3.82 \text{ mg}^{2/3} \text{s}^{-1/2}} \right) \) measured at zero volt vs. SCE in 1M azo-benzene at pH 4.8. All potentials reported were measured against SCE. Consequent on the installation of AC/DC recording polarograph (redelkis, Budapest) type OH-105 in 1979 in this laboratory it was thought worthwhile to repeat the work (with \( m^{2/3} t^{1/6} = 2.109 \text{ mg}^{2/3} \text{s}^{-1/2} \)) to serve as a check on the previous work. The results obtained were highly reproducible.

The Philips pH meter PR 9405 previously standardized by KH-Phthaleine (pH 4.0) and Boxen (pH = 9.15) with a wide range glass electrode was used for measuring pH values.

2.2.2. REAGENTS:

Trans-azobenzene AnalAr (BDH) and Triton X-100 (SDF'S) were used without any further purification. Pyridine AnalAr (BDH) with 99.7% purity and with minimum assay of non volatile substances (0.001%) was used.

BUFFERS:

The following standard buffer solutions (11) were prepared.

1. Britton-Robinson (B.R.) buffer (pH 1.8-11.8).
2. Thell-Schulz and Coch buffer (pH 4.0 - 5.0).
3. Kollhoff buffer (pH 4.0 - 4.8).
iv. 1N phosphate buffer of NaOOCCH₃ / CH₃COOH (pH 4.0-4.9)

v. N₂O₃ (KCl) buffer of NaOOCCH₃ / KCl (pH 3.9-4.9).

v. Clark-Lubs(C.L.) buffer of KH-phthalate / NaOOCCH₃ (pH 4.0-4.8)

vi. Pelitzech buffer (pH 7.2-8.8)

vii. Sorensen buffer (pH 7.2-8.8)

2.2.3 Preparation of solutions:

10mM solutions of the following compounds were prepared, 4-hydroxyazo benzene, SY 2GS, 1-(2-hydroxyphenylazo)-2-naphthol, SR FV5, SR 2RS, 1-(3-hydroxy naphthylazo)-2-naphthol, SR WDRA and 3DB B150 in 10% pure ethanol and SR ERS in 10% pyridine.

2.2.4 Procedure

1mM concentration of each dye was maintained by diluting the stock solutions with buffer. Ionic concentration was kept at 0.15 by adding requisite amount of KCl solution. The solutions were deaerated by bubbling pure hydrogen for five minutes before subjecting to current voltage measurements.

2.3 RESULTS AND DISCUSSION

All dyes except solochrome red ERS (SR ERS) were studied in Britton-Robinson buffer pH range (1.8-11.8). A few polarograms of differentazo compounds in various buffers at different pH values are shown in Fig. 2.1(a) and 2.1(b) as representative cases. The studies were extended in other buffer systems at several pH values in order to find the effect of buffer constituents
and pH values on \( E_\text{f} \) of these dyes. SR ERS could not be studied in 10% alcohol-water instead the studies were done in 10% pyridine, the polarographic measurements could therefore be possible above pH 7, and the well-defined waves were obtained in the pH between 7.2 to 9.0. It is seen that in all these dyes \( E_\text{f} \) shifts towards more negative potential with increasing pH, and no break at higher pH was noted, an observation in contrast to the results of Caster and Saylor (12). In general the well-defined waves were obtained in all buffers at various pH values.

Table 2.1 contains \( E_\text{f} \) - pH equations and the calculated Hammett substituent constants for various dyes at pH 5.4. The \( \sum S^\text{A} \) values obtained compare favourably with the results available in literature (1).

No appreciable effect of buffer constituents and their pH values on the limiting current and \( E_\text{f} \) was noted. Further, the plots of \( \log i \) vs. \( \log h \), \( \log i \) vs. \( \log C \), and the temperature coefficients show that current is diffusion controlled (Fig. 2.2, 2.3 and Table 2.2).

The dye Sy 285 and SRN 28S gave maxima at pH > 5.0 at higher concentrations, whereas at lower concentrations maxima was absent, for example, at concentrations of 0.5 mM no maxima appeared; the maxima was fairly acute in case of SY 285 (refer Fig. 2.1 a-d) while a mild maxima appeared for the SRN 28S (not shown in the figures). Maxima's were also eliminated even in 1 mM without any distortion to the original wave by the addition of 0.0002% Triton X-100. At higher concentrations dyes are known to undergo adsorption at dye which subsequently results in polarographic maxima (13). At lower concentrations the adsorption effects are minimised thereby maxima gets eliminated. The diffusion controlled
nature of the reduction of dyes is in confirmation to work of many authors (10,13,14).

The value of $n = 2$ in all the six dyes was obtained at low and moderate pH values by the method of DeVries and Kroon (15) as well as diffusion current constant $I$, indicating that the dye was reduced to stable hydrosso derivative by consuming two electrons.

The reduction of the dye can be represented by

$$\begin{align*}
R & \quad +2H^+ + 2e^- \\
\rightarrow & \\
R' &
\end{align*}$$

where $R$ and $R'$ are substituent groups.

The approximate relationship between $E^\|_b$ and pH is

$$E^\|_b = E^{0'} - 0.0591 \text{ pH} \quad \ldots \quad (2.2)$$

The factor $E^{0'}$ represents the redox potential of irreversible system and can be obtained from the intercept of $E^\|_b$ vs. pH (Table 2.1). The values of $E^{0'}$ determined independently by potential mediator method (Fig.1.3) by reduction in an inert medium with Cr$^{3+}$ (givens in chapter 1) agrees well with the polarographic results (16) in turn confirms 2-electron reduction mechanism.

The log plot analysis revealed that the reduction was not a reversible one but it was partly irreversibly controlled. The kinetic parameters
were calculated from the equation

\[ E_{d,e} + 0.2412 = \frac{0.05915}{\alpha n} \log \frac{1.349 k_{f,h}^{0}}{p^{0.5}} - \frac{0.0542}{\alpha n} \left[ \log \frac{1}{1 - 0.546 \log t} \right] \]

... 2.3.

A plot of \( E_{d,e} \) vs. \( \left[ \log \frac{1}{1 - 0.546 \log t} \right] \) gave a slope equal to

\[ 0.0542 \]

and an intercept of value \( E_{f}^{0} \), where

\[ E_{f}^{0} = -0.2412 + \frac{0.05915}{\alpha n} \log \frac{1.349 k_{f,h}^{0}}{p^{0.5}} \]

substituting \( \alpha n \) and \( E_{f}^{0} \), the \( k_{f,h}^{0} \) values for various dyes was obtained. The kinetic parameters are of the values of \( 1.0 \times 10^{-3} \) to \( 6.9 \times 10^{-4} \) in all dyes except in solochrome red ERS, as its studies were not possible under similar conditions. Table 2.3 provides further evidence that the reduction of dyes is partly irreversible. Malik and Gupta (10) concluded in a study on similarazo compounds a totally irreversible reduction wave. But this could not be confirmed by these observations. However, the present view has been very widely accepted in a later publication (16).

The partial reversible reduction behaviour may be mostly due to adsorption of these dyes on electrode surface, pH of the solution, the nature and type of the buffer, type of the electrode material, surfactants added and above all on the nature of substituted groups. This may also be due to unsymmetrical nature of dyes. Such reduction behaviour of these dyes at dme is justifiable in the light of explanations already advanced by various authors (10, 17, 18).


4. S.N. Latimer, ... Talanta, 15 (1968) 1.


<table>
<thead>
<tr>
<th>Compound</th>
<th>Substituent</th>
<th>$E_\frac{1}{2}$-pH equation</th>
<th>$-E_\frac{1}{2}$ at pH 5.4/V(SCE)</th>
<th>$\Delta E_{1/2}$</th>
<th>$\rho$</th>
<th>$\sum \delta^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Hydroxy azobenzene</td>
<td>none</td>
<td>$E_\frac{1}{2} = +0.065-0.077$</td>
<td>0.35</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Solochrome yellow 2GS</td>
<td>2(COOH),4'($SO_3H$)</td>
<td>$E_\frac{1}{2} = +0.06-0.062$</td>
<td>0.27</td>
<td>+0.08</td>
<td>0.14</td>
<td>+0.571</td>
</tr>
<tr>
<td>1-(2-Hydroxy phenylazo)-2-naphthol</td>
<td>none</td>
<td>$E_\frac{1}{2} = -0.033-0.064$</td>
<td>0.36</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Solochrome black FVS</td>
<td>5(OH),5'($SO_3H$)</td>
<td>$E_\frac{1}{2} = +0.03-0.057$</td>
<td>0.33</td>
<td>+0.055</td>
<td>0.16</td>
<td>+0.344</td>
</tr>
<tr>
<td>Solochrome fast navy 2 RS</td>
<td>6,9'($SO_3H$)2(Cl)</td>
<td>$E_\frac{1}{2} = +0.023-0.060$</td>
<td>0.32</td>
<td>+0.065</td>
<td>0.16</td>
<td>+0.406</td>
</tr>
<tr>
<td>Solochrome red EHS</td>
<td>4'($SO_3H$),3(phenyl),3(methyl)</td>
<td>$E_\frac{1}{2} = -0.133-0.053$</td>
<td>0.43</td>
<td>-0.045</td>
<td>0.16</td>
<td>-0.287</td>
</tr>
<tr>
<td>1-2-Hydroxy napthyl azo)-2-naphthol.</td>
<td>none</td>
<td>$E_\frac{1}{2}$</td>
<td>0.42</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Solochrome black WDR</td>
<td>3($SO_3H$),6(NO$H_2$)</td>
<td>$E_\frac{1}{2} = -0.03-0.06$</td>
<td>0.38</td>
<td>+0.04</td>
<td>0.18</td>
<td>+0.222</td>
</tr>
<tr>
<td>Solochrome dark blue B130</td>
<td>4($SO_3H$)</td>
<td>$E_\frac{1}{2} = +0.02-0.059$</td>
<td>0.31</td>
<td>+0.11</td>
<td>0.18</td>
<td>+0.618</td>
</tr>
</tbody>
</table>
### Table 3.2: Polargraphic current characteristics \( \sigma^{2/3} \xi^{1/4} = 3.62 \) eq \( 2/3 \) s \( -1/4 \), Temperature 25°

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \frac{V^6 \sigma}{cm^2 \text{s}^{-1}} )</th>
<th>( \Delta \xi )</th>
<th>( \Delta \log I/I_0 )</th>
<th>( \log I_0/\log h )</th>
<th>( \frac{d(\text{log I})}{dr} )</th>
<th>( I \text{(us)} ) buffer pH</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solochrome yellow 23°C</td>
<td>11.78</td>
<td>4.091</td>
<td>2</td>
<td>0.20 (pH 3.95)</td>
<td>3.0 (pH 4.4)</td>
<td>0.992</td>
<td>1.60</td>
</tr>
<tr>
<td>Solochrome black PVS</td>
<td>7.29</td>
<td>3.228</td>
<td>2</td>
<td>0.59 (pH 4.2)</td>
<td>1.32 (pH 4.2)</td>
<td>1.00</td>
<td>1.66</td>
</tr>
<tr>
<td>Solochrome dark blue 8150</td>
<td>7.02</td>
<td>3.214</td>
<td>2</td>
<td>0.52 (pH 4.4)</td>
<td>1.94 (pH 4.6)</td>
<td>1.02</td>
<td>1.69</td>
</tr>
<tr>
<td>Solochrome red BRS</td>
<td>6.94</td>
<td>3.179</td>
<td>2</td>
<td>0.25 (pH 8.0)</td>
<td>1.50 (pH 9.0)</td>
<td>0.999</td>
<td>1.56</td>
</tr>
<tr>
<td>Solochrome black WDF9</td>
<td>6.61</td>
<td>3.091</td>
<td>2</td>
<td>0.53 (pH 6.8)</td>
<td>1.66 (pH 6.8)</td>
<td>1.00</td>
<td>1.60</td>
</tr>
<tr>
<td>Solochrome fast navy 2RS</td>
<td>6.53</td>
<td>3.053</td>
<td>2</td>
<td>0.40 (pH 6.0)</td>
<td>2.72 (pH 6.8)</td>
<td>3.997</td>
<td>1.70</td>
</tr>
</tbody>
</table>

\[ 607n \sigma^{2/3} \left[ (1+34.7) \left( \frac{V^6 \sigma}{cm^2 \text{s}^{-1}} \right)^{1/3} \right] + 100 \left( \frac{V^6 \sigma}{cm^2 \text{s}^{-1}} \right)^{1/3} \]
Table 2.3  Kinetic parameters of azo dyes in B.A. Buffer pH 4.0, Temperature 25°C.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$E^0 / V$</th>
<th>$\alpha n$</th>
<th>$k^0_{f,h}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solochrome yellow 2GS</td>
<td>-0.202</td>
<td>0.164</td>
<td>$3.276 \times 10^{-3}$</td>
</tr>
<tr>
<td>(SY 2GS)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solochrome black WDMW</td>
<td>-0.307</td>
<td>0.375</td>
<td>$4.365 \times 10^{-4}$</td>
</tr>
<tr>
<td>(SB WDMW)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solochrome fast navy 2AS</td>
<td>-0.237</td>
<td>1.290</td>
<td>$2.938 \times 10^{-3}$</td>
</tr>
<tr>
<td>(SFN 2AS)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solochrome black PVS</td>
<td>-0.265</td>
<td>0.334</td>
<td>$1.467 \times 10^{-3}$</td>
</tr>
<tr>
<td>(SB PVS)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solochrome dark blue B150</td>
<td>-0.285</td>
<td>0.650</td>
<td>$6.064 \times 10^{-4}$</td>
</tr>
<tr>
<td>(SB B150)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Solochrome red E4S (Sr E4S) is not included.
FIG. 2.1 (a) Some typical polarograms of azo compounds at various concentrations, at different pH in various buffers and at different heights indicated against them (a) Azo benzene $\times 10^{-3}$ M in Britton-Robinson buffer pH 5.4, at 50 cm. (b) Azo benzene $1 \times 10^{-3}$ M in Britton-Robinson buffer pH 10.0 at 50 cm.
(c) SY 2GS $1 \times 10^{-3}$ M in Britton-Robinson buffer pH 4.5 at 45 cm.
(d) SY 2GS $1 \times 10^{-3}$ M in Britton-Robinson buffer pH 9.25 at 35 cm.
(e) 1-(2-hydroxy phenyl azo) 2-naphthol $1 \times 10^{-3}$ M in Clark-Lubs buffer pH 5.0 at 40 cm.
(f) 1-(2-hydroxy phenyl azo) 2-naphthol $1 \times 10^{-3}$ M Clark Lubs buffer pH 5.0 at 45 cm.
(g) 5B PVS 0.33 $1 \times 10^{-3}$ M in Walpole buffer pH 5.4 at 50 cm.
(h) 5B PVS 0.7 $1 \times 10^{-3}$ M in Walpole buffer pH 10.5 at 40 cm.
FIG. 2.2 log h vs log i PLOTS.
FIG. 2.3 THE PLOTS OF $\log I$ vs $\log C$ OF SOLOCRHOME YELLOW 2GS (SY 2GS).
FIG. 2.4 PLOT OF E\textsubscript{de} VS \[ (\log\left(\frac{i}{id-i}\right) - 0.546 \log t) \] FOR THE REDUCTION OF DYES IN B.R. BUFFER pH 4.0.