SUMMARY

The polarographic study of complexes of metals in aqueous medium has been the subject matter of this thesis. The introduction deals mainly with the review of the polarographic work done by different authors (from 1969 onwards) on various metal ions with different ligand systems.

The first chapter deals with purity considerations of the substance (dyes) used in these investigations, because the impurities are known to affect adversely the electrode mechanism at the time. The process of recrystallization has been employed and purity has been assessed by spectrophotometry, paper chromatography, nitrogen, sulphur estimation as well as potentiometrically. The third recrystallized product ranged between 99.3% to 99.7% compared to commercial samples of approximately 80% purity.

The second chapter contains the polarography of the following azo compounds:

4-hydroxy azo benzene, solochrome yellow 235, 1-(2-hydroxy phenyl azo)-2-naphthol, solochrome black PVS, solochrome fast navy 245, 1-(2-hydroxy-naphthyl azo)-2-naphthol, solochrome black WESA, solochrome dark blue 8150 and solochrome red ERS. The current characteristics studied through the effect of the height of the mercury column, temperature, buffer constituent and pH indicate the electro reduction to be diffusion controlled. The $E_1 - pH$ relationships were determined in various buffers at different pH values. The log plot analysis revealed partly reversible character of the wave. The kinetic parameter $k^0_{T, H}$ was found to range between $1.4 \times 10^{-3}$ to $6.0 \times 10^{-4}$ while $\infty n$ gave values between 0.16 to 1.29.
The potentiometric, spectrophotometric and conductometric determination of dissociation constants of six dyes is the content of third chapter. This study has been undertaken to establish the favourable conditions for the complex formation. The first dissociation constant of these dyes range between 6.01 to 6.35, thereby establishing the condition that pH 4.2 is the most suitable for the study of complex formation (as dye molecule will be neutral at this pH value).

The $E_1$ -pH relationship studied potentiographically is connected with dissociation constant ($pK$) of these dyes. The Hammett substituent effect of the groups attached to the dye molecules have been correlated with $E_1$ and $pK$ values by the equation.

$$\Delta E_1 = (pK - N) \frac{C_{H_2}R}{m}$$

The difference in $\Delta E_1$ by two methods are minor and has been attributed to the structural modifications, due to the presence of polymsubstituents.

The fourth chapter contains the polarographic determination of 'stepwise', 'overall' stability constants and 'coordination number' of $Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Tl^+$ and $Zn^{2+}$ with solochrome yellow 2B5, solochrome black 8BFA, solochrome fast navy 2RS and solochrome dark blue 8150, in different buffer systems at constant ionic strength. The reduction has been found to be diffusion controlled and reversible in most cases. The shifts in $E_1$ to more negative potentials with increasing ligand concentration indicate complex formation. The 'overall' stability constant and 'coordination number' are determined by employing Lingane method. The use of
Deford and Hume method has been made in calculating the 'stepwise' stability constants of the complexes formed. The reduction of Co$^{2+}$ and Ni$^{2+}$ with all the four ligands was found to be irreversible. The reversible half wave potential ($E^R$) from the observed irreversible half wave potentials ($E^i$) were calculated by Gellings treatment of graphical extrapolation method. The 'stepwise' and 'overall' stability constants were then calculated by the above methods using $E^R$. The percentage distribution of metal ions and its various complexes have been plotted as a function of ligand concentration, the plots clearly reveal the consecutive reactions during the complex formation.

The log of 'overall' stability constants (log $K$) of the complexes with structurally similar ligand has shown a linear dependence on the dissociation constant ($pK$) of the ligands by the following equation

$$\log K = mpK + b$$

The factor 'b' has been found to range between 1.1 to 4.0 for different metal-ligand systems; this has been suggested quantitatively as a measure of $\Pi$ bond character of metal-ligand bond which has been found to be the highest for Fe$^{2+}$ and the lowest for Ti$^+$. Different slopes indicate the variation in the $\Pi$ - electron interaction which accounts for the position in which molecule is substituted in a coordination compound.
The fifth chapter deals with the study of complexometric EDTA 'titration' of metal ions e.g., Ca$^{2+}$, Mg$^{2+}$, admixture of Ca$^{2+}$ and Mg$^{2+}$, Co$^{2+}$, Cu$^{2+}$, Fe$^{2+}$, Ni$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ using solochrome fast navy 2AS as an indicator. The polarographically determined stability constants of this dye with metal ions have been made use in these titrations. The results have been found to be comparable with many metal ions, while with some metal ions like Pb$^{2+}$ and Cu$^{2+}$ it shows better results than its related dyes, Eriochrome black T and solochrome blue black B. In the case of Fe$^{2+}$ and Ni$^{2+}$ it can be used for direct titration. Another advantage is the ease of preparation of its solution and higher stability in aqueous medium compared to Eriochrome black T.
Polarographic Studies of Azo Dyes in Aqueous Medium

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DENKI KAGAKU Vol. 46, No. 2 p. 92 (1978) Reprints
Polarographic Studies of Azo Dyes in Aqueous Medium

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Polarographic reduction of six azo dyes reveals that these were reduced partly reversibly at the DME and the current characteristic was diffusion controlled. The formal standard electrode potential calculated from \( E_{1/2} \) -pH relationship agrees well with the values obtained independently from the potential mediator method.

1 Introduction
Aromatic azo dyes, particularly solochrome mordant dyes are an important class of compounds which find immense use in the quantitative determination of metal ions through complex formation\(^{11,12}\). Helleck\(^{3}\) studied the polarographic reduction behaviour of solochrome violet RS in LiCl-methanolic solution and established that this dye can be used very successfully for the estimation of Al (III). In all the azo dyes, azobenzene is the basic unit and at DME it shows a peculiar behaviour\(^{10}\), whereas the substituent groups in the aromatic ring bring about changes in the nature of reduction\(^{5}\).

The analyses of the polarographic waves for six dyes obtained in the presence of various buffers at different pH values reveal that these were reduced partly reversibly and yield diffusion controlled waves at the DME.

2 Experimental
2.1 Apparatus
A manual polarographic unit (Toshiwal, India) was used in conjunction with a supersensitive multiflex spot galvanometer. Unless otherwise stated, all current measurements were made at damping 1, \( h = 42.5 \text{cm} \) (height of the mercury column) and at temperature of 25 ±0.1°C. The DME had the following characteristics, \( m = 5.533 \text{mg s}^{-1} \), \( t = 3.38 \text{s} \) (\( m^{1/3} t^{1/4} = 3.82 \text{mg}^{1/3} \text{s}^{1/4} \)) measured at zero volt vs. SCE in 1 mM azobenzene, at pH 4.8. All potentials reported were measured against SCE.

2.2 Reagents
Dyes: The commercial dyes (I.C.I. India) were purified by repeated (three) recrystallizations from 50% spectroscopic alcohol and the product dried over BaO in vacuum desiccator for several days. The purity of the third recrystallised product was tested by spectrophotometry and paper chromatography and was estimated by elemental analysis. Purity, as determined by potentiometric reduction titration with CrSO\(_4\) was found to range between 99.31 to 99.78% for different dyes.
Azobenzene: A.R. trans-azobenzene (BDH) was used without further purification.
Buffers: The following standard buffer solutions\(^{10}\) were prepared

- (i) Britton-Robinson buffer (pH 1.8 to 10.8)
- (ii) Thiel Schulz and Coch buffer (pH 4.0-5.0)
- (iii) Kolthoff buffer (pH 4.0-4.8)
- (iv) Walpole buffer of NaOOCCH\(_3\)/CH\(_3\)COOH (pH 4.05-4.95); NaOOCCH\(_3\)/HCl (pH 3.95-4.95)
- (v) Clark Lubs buffer of K-Hph/NaOOCCH\(_3\) (pH 4.0 to 4.8); H\(_3\)BO\(_3\)/(KCl)/NaOH (pH 7.4 to 8.8)
- (vi) Palitzsch buffer (pH 7.2-8.8)
- (vii) Sorensen buffer (pH 7.2-8.8)

2.3 Procedure
1 mM concentration of each dye was maintained by diluting it with buffer solution. The solutions were deaerated by bubbling pure hydrogen for five minutes before subjecting to current-voltage measurements.

3 Results and Discussion
The shifts in \( E_{1/2} \) values towards more negative potential with the increase in pH values
have been observed. No break at higher pH was noted, an observation partly in contrast with the results of Caster and Saylor1.

Table 1 contains $E_{1/2}$ -pH equations for various dyes at pH 5.4. The $\Sigma$ values obtained compare favourably with the results reported in literature1.

No appreciable effect of the buffer constituents and their pH value on the limiting current and $E_{1/2}$ 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 (Table 2). Maxima's were encountered but were eliminated without any distortion to the original wave by 0.0002% Triton x-100. The value of $n=2$ was obtained at high, low and moderate pH values by Devries and Kroon's method as well as diffusion current constant I, indicating that the dye was reduced to stable hydroazo derivative by consuming two electrons.

The reduction of azo dye can be represented

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**Table 1**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Substituents</th>
<th>$E_{1/2}$-pH equation</th>
<th>$E_{1/2}$ at pH</th>
<th>$dE_{1/2}/V$</th>
<th>$\rho$</th>
<th>$\Sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Hydroxy azo benzene</td>
<td>none</td>
<td>$E_{1/2} = +0.85-0.077$ pH</td>
<td>0.350</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Solochrome yellow 2 GS</td>
<td>3 (COOH), 4'(SO$_3$H)</td>
<td>$E_{1/2} = +0.08-0.062$ pH</td>
<td>0.270</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>$E_{1/2} = -0.03-0.064$ pH</td>
<td>0.385</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Solochrome black PVS</td>
<td>5 (OH), 5'(SO$_3$H)</td>
<td>$E_{1/2} = +0.03-0.057$ pH</td>
<td>0.330</td>
<td>+0.066</td>
<td>0.16</td>
<td>+0.344</td>
</tr>
<tr>
<td>Solochrome fast navy 2 RS</td>
<td>6,3'(SO$_3$H), 5 (Cl)</td>
<td>$E_{1/2} = +0.025-0.060$ pH</td>
<td>0.320</td>
<td>+0.065</td>
<td>0.16</td>
<td>+0.406</td>
</tr>
<tr>
<td>Solochrome red ERS</td>
<td>4'(SO$_3$H), 3 Phenyl 5 methyl</td>
<td>$E_{1/2} = -0.135-0.053$ pH</td>
<td>0.430</td>
<td>-0.045</td>
<td>0.16</td>
<td>-0.267</td>
</tr>
<tr>
<td>1-(2-Hydroxy naphthylazo)-2-naphthol</td>
<td>none</td>
<td>-</td>
<td>0.420</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Solochrome black WDFA</td>
<td>3 (SO$_3$H), 6 (NO$_2$)</td>
<td>$E_{1/2} = -0.03-0.06$ pH</td>
<td>0.380</td>
<td>+0.04</td>
<td>0.18</td>
<td>+0.222</td>
</tr>
<tr>
<td>Solochrome dark blue B 150</td>
<td>4 (SO$_3$H)</td>
<td>$E_{1/2} = +0.02-0.059$ pH</td>
<td>0.31</td>
<td>+0.11</td>
<td>0.18</td>
<td>+0.618</td>
</tr>
</tbody>
</table>

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**Table 2** Polarographic current characteristics, temperature 25°C, $m^{1/2} t^{1/4} = 3.82$ mg$^{1/2}$ s$^{-1/2}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$10^6 D_i$ cm$^2$ s$^{-1}$</th>
<th>$n$</th>
<th>$i$ measured</th>
<th>$\log i/\log h$</th>
<th>$(1/dh) \ln (i_i/i_i')$</th>
<th>$\log i_i/\log c$</th>
<th>$i$ (ma) buffer pH</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solochrome yellow 2 GS</td>
<td>11.784.091</td>
<td>2</td>
<td>0.2 (pH 3.95)</td>
<td>3.0 (pH 4.4)</td>
<td>0.992</td>
<td>0.212 (B.R. pH 8.6)</td>
<td>well defined waves</td>
<td></td>
</tr>
<tr>
<td>Solochrome black PVS</td>
<td>7.293.228</td>
<td>2</td>
<td>0.30 (pH 4.2)</td>
<td>1.32 (pH 4.2)</td>
<td>1.00</td>
<td>0.30 (Walpole pH 3.95)</td>
<td>distorted in Britton Robinson</td>
<td></td>
</tr>
<tr>
<td>Solochrome dark blue B 150</td>
<td>7.023.214</td>
<td>2</td>
<td>0.52 (pH 4.4)</td>
<td>1.94 (pH 4.8)</td>
<td>1.02</td>
<td>0.190 (B.R. pH 3.0)</td>
<td>deformed in pH 6.0</td>
<td></td>
</tr>
<tr>
<td>Solochrome red ERS</td>
<td>6.943.179</td>
<td>2</td>
<td>0.25 (pH 8.0)</td>
<td>1.50 (pH 9.0)</td>
<td>0.999</td>
<td>0.180 (Sorensen pH 7.2)</td>
<td>ill defined in acid medium</td>
<td></td>
</tr>
<tr>
<td>Solochrome black WDFA</td>
<td>6.613.061</td>
<td>2</td>
<td>0.53 (pH 6.8)</td>
<td>1.65 (pH 6.8)</td>
<td>1.00</td>
<td>0.364 (Walpole pH 4.0)</td>
<td>well formed</td>
<td></td>
</tr>
<tr>
<td>Solochrome fast navy 2 RS</td>
<td>6.533.053</td>
<td>2</td>
<td>0.40 (pH 6.0)</td>
<td>2.72 (pH 6.8)</td>
<td>0.997</td>
<td>0.140 (B.R. pH 5.0)</td>
<td>deformed in other buffers</td>
<td></td>
</tr>
</tbody>
</table>

$* = 607 n D^{1/2} (1 + 34.7)(D^{1/2} i^{1/4}(m^{1/2}) + 100 (D^{1/2} i^{1/4}(m^{1/2})}$

(B.R. and C.L. stand for Britton-Robinson and Clark-Lubs, respectively)
by

\[
\begin{array}{c}
\text{R} \quad \text{N} = \text{N} \quad \text{R'} \\
\text{H} \quad 2\text{H}^+ + 2e^-
\end{array}
\]

where R and R' are the substituent groups.

The approximate relationship between \( E_{1/2} \) and pH is

\[ E_{1/2} = E^\circ - 0.0591\sigma \text{pH}. \]

The factor \( E^\circ \) is known as formal standard potential, and can be obtained from the intercept of \( E_{1/2} \) vs. pH (Table 1). The formal standard potential \( E^\circ \) (vs. SCE) as determined independently from potential mediator method (Fig. 1) by reduction in securely inert medium with CrSO\(_4\) agrees well with the polarographic results. This further confirms two electrons reduction mechanism.

Malik and Gupta\(^5\) established that the azo dyes are reduced irreversibly in Britton-Robinson buffer. The work in this respect was extended to other buffers also. The values of \( k, J \) were found to range between \( 10^{-3} - 10^{-4} \), which indicates that the reduction of dyes is partly reversible and not completely irreversible, contrary to the conclusions drawn by the above authors.

The diffusion controlled and partly reversible reduction behaviour of these dyes at the DME is chemically justifiable in the light of the explanation already advanced by various authors\(^5\),\(^6\),\(^7\),\(^8\),\(^9\).

**Acknowledgement**:
Authors are grateful to W.U. Malik, Vice-Chancellor Bundelkhand University, for the suggestions received from him during the preparation of this manuscript. Authors thankful to C.S.I.R. New Delhi for providing research fellowship to one of us (SAB) and to I.C.I. India for free gift of the dyes.

\(<E519>(\text{Received Sep. 6, 1977})\)

**References**: