Polarographic Study of Some Nitrosonaphthols at d.m.e. in Aqueous Solutions & Water-Ethanol Mixtures of Varying pH

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The reduction of β-nitroso-α-naphthol or α-nitroso-β-naphthol and its halogen derivatives yields one wave involving four electrons. This wave corresponds to the reduction of the -N=O group to the amine stage. In the case of 3-carboxy-1-nitroso-2-naphthol the reduction consumes two electrons with the reduction proceeding to the hydroxylamine stage only. The E1/2's shift to less negative values on going from β-nitroso-α-naphthol to α-nitroso-β-naphthol and the halogen derivatives to the -COOH compound. The strength of the intramolecular H-bond as gathered from E1/2 shifts is in the order H > Cl > Br > COOH.

The polarographic behaviour of nitroso-compounds has been studied by several authors. Smith and Waller found that nitrosobenzene is reduced to N-phenylhydroxylamine through a single reduction step in solutions of pH 4-10. Kolthoff and Lingane reported a well-defined quantitative step for the reduction of α-nitroso-β-naphthol in acetate buffer of pH ≤ 6 and borate buffers of higher pH's. This compound gave a polarogram consisting of two waves in 0·1N KCl (ref. 3). Polarographic data for some nitrosonaphthols were reported by Cleghorn to determine whether significant differences are associated with the nitrosoxime equilibria.

The behaviour of some nitrosonaphthols at the d.m.e. has been studied with a view to having an insight into the effect of molecular structure on the polarographic behaviour of these compounds. The electrode reaction and effect of addition of ethanol to the medium are also discussed.

Materials and Methods

The compounds involved in the present study have the general formula:

![Chemical Structures]

where X = H (I), Cl (II), Br (III) or -COOH (IV).

The compounds were obtained from commercial sources (I and V, BDH) or prepared. These compounds were purified by recrystallization from petroleum ether. Their purity were checked by measurements of m.p., elemental analysis and paper chromatography. 10-4M stock solutions of the nitroso-naphthols under investigation were prepared by dissolving the appropriate amount of each reagent in the suitable volume of absolute ethanol purified by recommended procedures.

The modified universal buffer series of Britton (pH 2-12), used as supporting electrolyte, was prepared as given before. The pH of these solutions was checked using a radiometer pH-meter model 28, accurate to ± 0·05 unit.

The experimental technique and the electrolysis cell were as previously described. The polarograph was a Radiometer P04F type. The capillary characteristics were m = 1·97 mg/sec, t = 4·55 sec, at a height of 48·5 cm Hg. All the polarograms were recorded at 25°.

Results and Discussion

The reduction of the N=O group is investigated for five nitrosonaphthols, containing different substituents. The electrodeposition of nitrosonaphthol in universal buffer solutions of pH 2-11·5 yields a well-defined single wave, the height of which is not apparently influenced by changing the pH of the medium. The wave-height for the compounds deprived of the -COOH group corresponds to 4 electrons whereas for the 3-carboxy-1-nitroso-2-naphthol corresponds to 2 electrons only. In pure aqueous buffer solution of pH < 7·5, 3-bromo-1-nitroso-2-naphthol is insoluble, hence no satisfactory results could be obtained.

The E1/2 values of the reduction waves shift to more negative potentials on increasing the pH of the solution, indicating the contribution of H+ ions in the electrode process. However, E1/2 is not affected much with pH change indicating that the number of electrons involved in the electrode reaction is not influenced by the pH of the medium used.
Generally, the reduction of the nitroso-group involves the uptake of four electrons proceeding to amine stage through the intermediate formation of the hydroxylamine (Eqs. 1 and 2).

\[
R-\text{NO} + 2\text{H}^+ + 2e^- \rightarrow R-\text{NHOH} \quad \ldots(1)
\]

\[
R-\text{NHOH} + 2\text{H}^+ + 2e^- \rightarrow R-\text{NH}_2 + \text{H}_2\text{O} \quad \ldots(2)
\]

This is the common behaviour in acid solutions. In alkaline media, on the other hand, the reduction of the nitroso-compounds should correspond to two electrons. However, for the compounds under investigation, except for compound IV the reduction to the amine stage in alkaline media, in analogy to the case of o-nitrophenol, is favoured by the presence of the OH-group in o-position to the NO group. Thus in alkaline media, 1-nitroso-2-naphthol is reduced in two-electron step to the hydroxylamine (VI) which is converted into the intermediate (VII). VII is readily reduced by a two-electron step to the amine stage.

In the case of 3-carboxy-1-nitroso-2-naphthol the current is almost half of that for other compounds, indicating that the reduction process involves two electrons forming the hydrogen bonded hydroxylamine derivative (VIII).

The formation of hydrogen bond as in (VIII) leads to a decreased tendency towards the transformation to the keto-oxime structure, hence the reduction is only effected to the hydroxylamine stage.

**Nature of the waves** — (i) The effect of mercury pressure on the limiting current reveals that value of the exponent \( x \) in the relation \( i_i = K_i h^x \) varies between 0-4 and 0-7, indicating that the process of reduction is mainly diffusion-controlled with partial kinetic or adsorption contribution. These factors vary in magnitude according to the nature of depolarizer and \( \phi \) of solution. (ii) On analysis of the reduction waves, using the fundamental equation for polarographic waves, straight lines were obtained. From the slopes \( S \) of the log \( (i_i/\phi-i) \) vs \( E \) plots (Table I), values of the \( \alpha \)-parameter are calculated using the relation

\[
\alpha = \frac{0.0591 \cdot S}{n_a} \text{ at } 25^\circ
\]

where \( n_a \) is the number of electrons involved in the rate determining step.

The results given in Table I show that values of \( \alpha \) are in the range of 0·23-0·90, indicating that the process of reduction of nitrosonaphthols is irreversible to quasi-reversible. The degree of irreversibility depends on both the nature of depolarizer and medium used. Also the rate determining step involves most probably two electrons. Hence, the reduction to the hydroxylamine stage is the rate determining step in the electrode reaction.

**\( E_{1/2}-\phi \) curves** — The \( E_{1/2} \) values of the reduction waves shift to more negative potentials with increasing \( \phi \); the plot of \( E_{1/2} \) as a function of \( \phi \) is more or less linear. Substituting the values of \( 1X_{ij} \) (Table I) in the relation (3):

\[
(\Delta E_{1/2}/\Delta \phi) = \frac{0.0591}{\alpha n_a} Z_{H^+} \ldots(3)
\]

it becomes clear that the number of hydrogen ions \( (Z_{H^+}) \) and electrons \( (n_a) \) involved in the rate determining step for the reduction of the \(-\text{NO}\) group are almost \( \phi \) independent. The most probable values of the \( \alpha \)-parameter, given in Table I, indicate that \( n_a = 2 \) and \( Z_{H^+} = 2 \).

### Table 1 — Polarographic Data of Nitrosonaphthols in Solutions of Varying \( \phi \)

<table>
<thead>
<tr>
<th>Naphthol</th>
<th>( \phi )</th>
<th>( E_{1/2} ) (V)</th>
<th>( i_i ) (( \mu A ))</th>
<th>Slope ( (\mu A/V) )</th>
<th>( \alpha n_a )</th>
<th>( Z_{H^+} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( (\text{a}) )</td>
<td></td>
<td>( (\text{b}) )</td>
<td>( n_a = 4 )</td>
<td>( n_a = 2 )</td>
</tr>
<tr>
<td>1-Nitroso-2-</td>
<td>3.06</td>
<td>-0.055</td>
<td>5.5</td>
<td>25.4</td>
<td>1.50</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>6.85</td>
<td>-0.14</td>
<td>5.4</td>
<td>29.0</td>
<td>1.71</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>11.37</td>
<td>-0.424</td>
<td>4.95</td>
<td>21.0</td>
<td>1.24</td>
<td>0.31</td>
</tr>
<tr>
<td>2-Nitroso-1-</td>
<td>3.06</td>
<td>0.0</td>
<td>6.7</td>
<td>21.5</td>
<td>1.27</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>6.85</td>
<td>-0.22</td>
<td>7.0</td>
<td>21.5</td>
<td>0.077</td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td>11.38</td>
<td>-0.535</td>
<td>6.25</td>
<td>21.5</td>
<td>1.27</td>
<td>0.32</td>
</tr>
<tr>
<td>3-Chloro-1-nitroso-2-</td>
<td>2.8</td>
<td>+0.055</td>
<td>4.9</td>
<td>22.4</td>
<td>1.32</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>7.0</td>
<td>-0.155</td>
<td>5.85</td>
<td>30.3</td>
<td>0.06</td>
<td>1.79</td>
</tr>
<tr>
<td></td>
<td>11.0</td>
<td>-0.378</td>
<td>6.45</td>
<td>25.7</td>
<td>1.53</td>
<td>0.38</td>
</tr>
<tr>
<td>3-Carboxy-1-nitroso-2-</td>
<td>3.01</td>
<td>+0.12</td>
<td>3.25</td>
<td>8.0</td>
<td>0.47</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>6.85</td>
<td>-0.13</td>
<td>3.45</td>
<td>16.0</td>
<td>0.94</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>11.34</td>
<td>-0.49</td>
<td>3.25</td>
<td>10.3</td>
<td>0.61</td>
<td>—</td>
</tr>
</tbody>
</table>

(a) Slope of log \( i_i/\phi-i \) vs \( E \); (b) slope of \( E_{1/2}-\phi \) curves within the \( \phi \) range (5-11-5).
**Effect of substituents on \(E_{1/2}\):** The \(E_{1/2}\) values are found to be influenced by the nature of the substituents attached to the naphthalene ring in ortho-position to the OH group. It is found that the magnitude of shift in \(E_{1/2}\) to less negative values is more in (V) as compared with (I) due to stronger intramolecular H-bond in the latter\(^{11}\). The \(E_{1/2}\) also shifts to less negative potentials the magnitude being less in (II) as compared with (I). A similar behaviour is exhibited by compounds (III) and (IV). The shift to less negative values is in accordance with the acceptor character of the substituents.

The plot of \(E_{1/2}\) as a function of the \(\sigma\) (Hammett) constant is more or less linear with a negative slope. The behaviour of the carboxy derivative is unusual in that \(E_{1/2}\) values in acid media are in accordance with the \(E_{1/2}\)-\(\sigma\) plot. In alkaline solutions, however, shifts of \(E_{1/2}\) to more negative potentials are observed. This is due to the presence of the carboxyl group since the carboxylate ion behaves as an electron donor, causing the shift to more negative values.

**Effect of varying ethanol concentration on \(i_d\) and \(E_{1/2}\):** The study was carried out at \(pH\) 4-5 and 11.0. The effect of increasing ethanol content of the medium (4-35%, by weight) is restricted to 

(i) a decrease in \(i_d\) along the whole polarogram, and

(ii) a shift of \(E_{1/2}\) to more negative potentials (Figs. 1 and 2). The magnitude of the decrease in \(i_d\) denotes a medium effect without appreciable influence on the mode of reduction. The plot of \(i_d\) as a function of ethanol content of the medium is shown in Fig. 1. The change of current was explained by changes in the effective diffusion coefficient due to viscosity (\(\eta\)) changes and variation of the effective size of the depolarizer\(^{12}\). The plot of the current corrected for viscosity effect \((i_{d,\text{corr}})\) versus the weight % of ethanol (Fig. 3) reveals that the current decreases with increase in the ethanol content in the medium. The decrease of reduction current may be ascribed to decreased effective diffusion coefficient as a result of the increased volume of the diffusing species. The increase in the volume of the reducible species is most probably due to the higher tendency of these species to be solvated by the molecules of ethanol than with water. The change in current should, accordingly, be the resultant effect of increased viscosity and the molecular volume which in turn lowers the diffusion coefficient. This is gathered from the Stokes-Einstein equation\(^{12}\):

\[
D_0 = \frac{3.32 \times 10^{-8}}{\sqrt{\eta}} \quad \text{cm}^2 \text{sec}^{-1} \quad \text{(4)}
\]

Substituting for \(D_0\) in the Ilkovic equation\(^{14}\) we get

\[
i_d = 607 \text{ncm}^2 \text{pA} \left(\frac{3.32 \times 10^{-8}}{\sqrt{\eta}}\right)^{1/2} \quad \text{mA} \quad \text{mA}^{-1/2} \quad \text{sec}^{-1/2} \quad \text{(5)}
\]

Assuming that the diffusing particles are spherically symmetrical, one obtains the relation:

\[
i_d = 607 \text{ncm}^2 \text{pA} \left(\frac{3.32 \times 10^{-8}}{(4/3}\pi \eta N)^{1/2} \right) \quad \text{mA} \quad \text{mA}^{-1/2} \quad \text{sec}^{-1/2} \quad \text{(6)}
\]

where \(i_d\) is the reduction current (in mA), \(n\) the number of electrons consumed in the reduction process, \(c\) the concentration of the depolarizer in mM (\(n = 2\) and \(c = 0.5\) mM in this case), \(r\) the radius of the diffusing particle (in cm), \(m\) the rate of flow of mercury (mg sec\(^{-1}\)), \(t\) drop time (sec) and \(N\) is the Avogadro's number.

Eq. (6) can be given in the following form:

\[
r = K^2/c^3 \eta
\]

where \(K = (2.996\text{ncm}^2\text{pA}^{1/2}/\text{sec})\) \(10^{-4}\).

The data shown in Table 2 indicate that the change in the radius \((r)\) of the reducible species is
The observed shift in $E_{1/2}$ can be attributed to several factors, namely dielectric constant ($\varepsilon$), changes in the solvation of ions and adsorption of organic solvent at the electrode surface. The variation of $E_{1/2}$ with $\varepsilon$ is given by the Takahashi relation:

$$E_{1/2} = E_{1/2}(\varepsilon) - K \left( \frac{1}{\varepsilon} + \frac{1}{\varepsilon(\infty)} \right)$$

in which $E_{1/2}(\varepsilon)$ and $E_{1/2}(\infty)$ are the half-wave potentials in pure aqueous solutions and water-organic solvent mixtures respectively, and $K$ is a constant.

If the dielectric constant change is the dominant factor, the shift in $E_{1/2}$ would be a linear function of $1/\varepsilon_0$, which is not the case with the nitroso-compounds under investigation. The addition of organic solvents to water causes a destruction of the normal structure of water. The destruction of the associated molecules readily influences the hydration layer surrounding the ions leading to a shift of $E_{1/2}$ to less negative values. However, the shift of $E_{1/2}$ to more negative values, observed with the nitroso-compounds in the present work, can be ascribed to the adsorption of the organic solvent molecules at the electrode surface. The accumulation of solvent molecules near the electrode surface retards the adsorption of the reducible species and also blocks the active centres on the electrode surface. Thus the reduction process requires higher energy and hence the $E_{1/2}$ shifts to more negative potentials.

Values of some kinetic parameters ($K_0$, rate constant and $\Delta G^*$, energy of activation) of the electrode reaction were calculated at different pH's and/or at different solvent compositions using Koutecky's equation as simplified by Issa et al. The values of $K_0$ (3 $\times$ 10$^{-2}$ - 2 $\times$ 10$^{-2}$ cm/sec) and $\Delta G^*$ (38 - 40 kcal) indicate that the electrode reaction at different pH values is quasi-reversible. The degree of reversibility or irreversibility depends on the medium used and nature of the substituents.

### References

10. Stocesova, D., Collection, 14 (1949), 613.