

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

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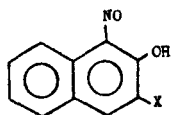
The reduction of β -nitroso- α -naphthol or α -nitroso- β -naphthol and its halogen derivatives yields one wave involving four electrons. This wave corresponds to the reduction of the $-N=O$ group to the amine stage. In the case of 3-carboxy-1-nitroso-2-naphthol the reduction consumes two electrons with the reduction proceeding to the hydroxylamine stage only. The $E_{1/2}$'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 $E_{1/2}$ shifts is in the order $H > Cl > Br > COOH$.

THE polarographic behaviour of nitroso-compounds has been studied by several authors¹⁻⁴. Smith and Waller¹ found that nitrosobenzene is reduced to N-phenylhydroxylamine through a single reduction step in solutions of pH 4-10. Kolthoff and Lingane² 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 Cleghorn⁴ to determine whether significant differences are associated with the nitroso-oxime equilibria.

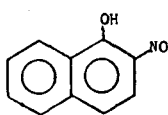
The behaviour of some nitrosonaphthols at the d.m.e. has been studied with a view to having an insight into the effect of molecular structure on the polarographic behaviour of these compounds. The electrode reaction and effect of addition of ethanol to the medium are also discussed.

Materials and Methods

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



(I-IV)



(V)

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

The compounds were obtained from commercial sources (I and V, BDH) or prepared⁵. These compounds were purified by recrystallization from petroleum ether⁵. Their purity were checked by

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measurements of m.p., elemental analysis and paper chromatography. 10⁻²M 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 procedures⁶.

The modified universal buffer series of Britton⁷ (pH 2-12), used as supporting electrolyte, was prepared as given before⁸. 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 described⁸. The polarograph was a Radiometer PO4F 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°.

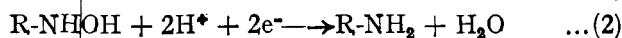
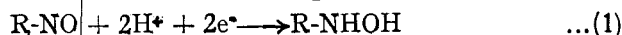
Results and Discussion

The reduction of the $N=O$ group is investigated for five nitrosonaphthols, containing different substituents. The electroreduction 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 $E_{1/2}$ 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, i_p 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.

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4 11 70

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).



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 electrons⁹. 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*-nitrophenol¹⁰, 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 trans-

formation 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 α in the relation ($i_l = Kh_{\text{eff}}^\alpha$) 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 pH 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 ($i/i_a - i$) vs E plots (Table 1), values of the α -parameter are calculated using the relation

$$\alpha = \frac{0.0591.S}{n_a} \text{ at } 25^\circ$$

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

The results given in Table 1 show that values of α 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}-pH curves — The $E_{1/2}$ values of the reduction waves shift to more negative potentials with increasing pH; the plot of $E_{1/2}$ as a function of pH is more or less linear. Substituting the values of αn_a (Table 1) in the relation (3):

$$(\Delta E_{1/2}/\Delta \text{pH}) = \frac{0.0591}{\alpha n_a} Z_{\text{H}^+} \quad \dots(3)$$

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 pH independent. The most probable values of the α -parameter, given in Table 1, indicate that $n_a = 2$ and $Z_{\text{H}^+} = 2$.

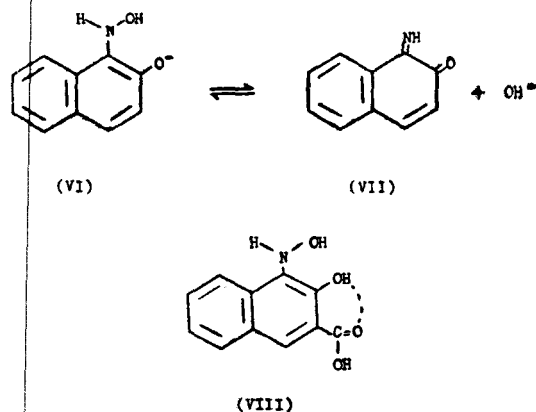


TABLE 1 — POLAROGRAPHIC DATA OF NITROSONAPHTHOLS IN SOLUTIONS OF VARYING pH

Naphthol	pH	$E_{1/2}$ (V)	i_a (μA)	Slope		αn_a	α		Z_{H^+}
				(a)	(b)		$n_a = 4$	$n_a = 2$	
				(V ⁻¹)	(V)				
1-Nitroso-2-	3.06	+0.055	5.5	25.4		1.50	0.38	0.75	2.0
	6.85	-0.14	5.4	29.0	0.077	1.71	0.43	0.85	
	11.37	-0.424	4.95	21.0		1.24	0.31	0.62	
2-Nitroso-1-	3.06	0.0	6.7	21.5		1.27	0.32	0.64	1.7 (≈ 2)
	6.85	-0.22	7.0	21.5	0.077	1.27	0.32	0.64	
	11.38	-0.535	6.25	21.5		1.27	0.32	0.64	
3-Chloro-1-nitroso-2-	2.8	+0.055	4.9	22.4		1.32	0.33	0.66	1.8 (≈ 2)
	7.0	-0.155	5.85	30.3	0.06	1.79	0.45	0.90	
	11.0	-0.378	6.45	25.7		1.53	0.38	0.76	
3-Carboxy-1-nitroso-2-	3.01	+0.12	3.25	8.0		0.47	—	0.23	2.0
	6.85	-0.13	3.45	16.0	0.14	0.94	—	0.47	
	11.34	-0.49	3.25	10.3		0.61	—	0.31	

(a) Slope of log $i/i_a - i$ vs E ; (b) slope of $E_{1/2}$ -pH curves within the pH 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 latter¹¹. 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 σ (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 $E_{1/2}$ - σ 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 (η) changes and variation of the effective size of the depolarizer¹². The plot of the current corrected for viscosity effect ($i_d\eta^{1/2}$) 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 equation¹³.

$$D_0 = \frac{3.32 \times 10^{-5}}{V^{1/3}\eta} \quad \dots(4)$$

Substituting for D_0 in the Ilkovic equation¹⁴ we get

$$i_d = 607 ncm^{2/3}t^{1/6} \left(\frac{3.32 \times 10^{-5}}{V^{1/3}\eta} \right)^{1/2} \quad \dots(5)$$

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

$$i_d = 607 ncm^{2/3}t^{1/6} \left(\frac{3.32 \times 10^{-5}}{(4/3\pi r^3 N)^{1/3}\eta} \right)^{1/2} \quad \dots(6)$$

where i_d is the reduction current (in μA), n the number of electrons consumed in the reduction

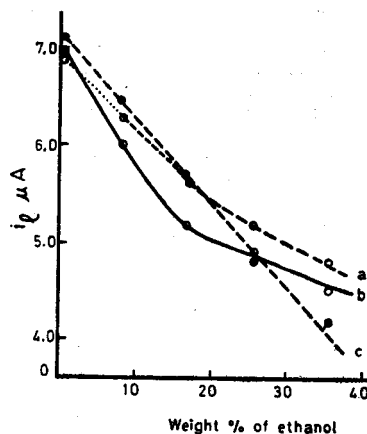


Fig. 1— Plots of i_d versus ethanol content (%) [(a) and (b) 1-Nitroso-2-naphthol at pH 4.55 and 11.0 respectively; (c) 2-nitroso-1-naphthol at pH 11.0]

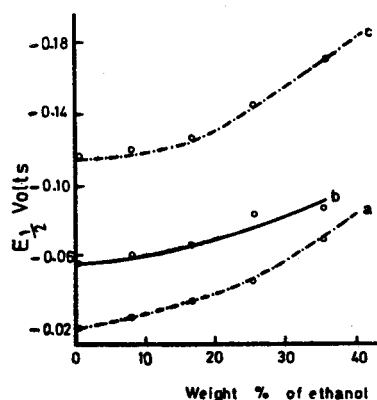


Fig. 2— Plots of $E_{1/2}$ versus ethanol content (%) at pH 4.55 [(a) 1-Nitroso-3-chloro-2-naphthol; (b) 1-nitroso-2-naphthol; (c) 2-nitroso-1-naphthol]

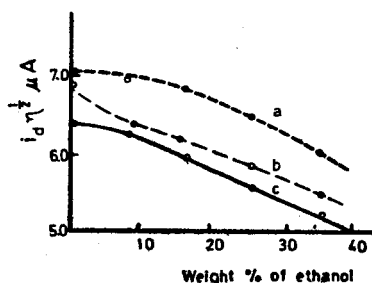


Fig. 3— Plots of the current corrected for viscosity effect ($i_d\eta^{1/2}$) versus ethanol content (%) [(a) 1-Nitroso-3-chloro-2-naphthol at pH 4.55; (b) 2-nitroso-1-naphthol at pH 11.0; (c) 1-nitroso-3-bromo-2-naphthol at pH 11.0]

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:

$$r = K^2 / i_d^2 \eta$$

where $K = (2.996 ncm^{2/3}t^{1/6}) 10^{-4}$.

The data shown in Table 2 indicate that the change in the radius (r) of the reducible species is

TABLE 2 — RADIUS (r) OF α -NITROSO- β -NAPHTHOL SPECIES AND ITS DERIVATIVES IN BUFFER SOLUTIONS OF DIFFERENT pH AND IN A MEDIUM CONTAINING DIFFERENT CONCENTRATIONS OF ETHANOL AT 25°C

Compound	pH	wt % (ethanol)	$i_{d,r_{1/2}}$ (μA)	$r \times 10^8$ (cm)
(I)	4.55	0.0	6.94	3.05
		8.07	6.65	3.32
		16.5	5.53	3.45
		25.3	6.24	3.77
	11.0	34.5	5.96	4.14
		0.0	7.0	3.10
		8.07	6.43	3.65
		16.6	5.94	4.18
(II)	4.55	25.3	5.88	4.24
		34.5	5.71	4.51
		0.0	6.8	3.18
		16.5	6.64	3.33
	11.0	34.5	5.93	4.16
		0.0	7.0	3.01
		16.5	6.41	3.57
		34.5	5.71	4.51
(III)	11.0	0.0	6.2	3.82
		16.5	5.84	4.31
		34.5	5.21	4.52

a function of the ethanol concentration in the medium.

The observed shift in $E_{1/2}$ can be attributed to several factors, namely dielectric constant (ϵ), changes in the solvation of ions and adsorption of organic solvent at the electrode surface¹². The variation of $E_{1/2}$ with ϵ is given by the Takahashi relation¹⁵:

$$E_{1/2(s)} = E_{1/2(w)} - K \left(\frac{1}{\epsilon(w)} + \frac{1}{\epsilon(s)} \right)$$

in which $E_{1/2(w)}$ and $E_{1/2(s)}$ 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 $E_{1/2(s)}$ would be a linear function of $1/\epsilon(s)$ 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 ΔG^* , energy of activation) of the electrode reaction were calculated at different pH 's and/or at different solvent compositions using Koutecky's equation¹⁶ as simplified by Issa *et al.*¹⁷ The values of K_0 (3×10^{-3} – 2×10^{-2} cm/sec) and ΔG^* (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.

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