STUDIES ON BISAZOCOMPOUNDS
II. Polarographic Behaviour of 4, 4'-Bisazobenzene-di [B-1 Amino naphthalene 4-sodium sulphonate]

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(Received June 1978; accepted July 1978)

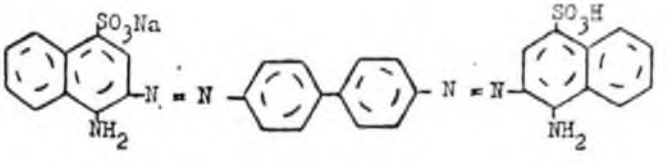
The polarographic behaviour of 4, 4' -bisazobenzene-di [B-1 Aminonaphthalene 4-sodium sulphonate] is studied in aqueous buffered solutions and aqueous-alcohol mixtures of different pH's containing 40% either ethyl, methyl or isopropyl alcohol. The reduction of the two azo linkages is discussed. Medium effect on $E_{\frac{1}{2}}$ and i_l of the reduction wave is investigated. The values of the kinetic parameters of the electrode reaction are determined.

Although the polarographic behaviour of monoazo-compounds were the subject of many investigations in the past, it seems that few studies has been carried out describing the reduction of bisazocompounds[1–4].

In continuation to our work on the polarographic behaviour of bisazocompounds[4] the present communication reports on the reduction of 4, 4' –Bisazobenzene-di [B–1, Aminonaphthalene 4-sodium sulphonate] (Congo Red) in aqueous buffered and aqueous-alcohol mixtures of different pH's at the dropping mercury electrode. No work on this bisazo compound from the present stand point has been published. The influence of the substituents attached to the terminal rings of the molecule is considered.

Experimental

A–Solution of bisazocompound: The bisazo-compound used was a BDH grade and has the structure given in Reaction(1) 4, 4' –Bisazobenzene-di [B–1, aminonaphthalene 4-sodium sulphonate] 5×10^{-4} M solution of the depolarizer was prepared by adding the appropriate volume of stock solution to the calculated volume of buffer solutions or aqueous-alcohol mixture of different pH's.



B–Buffer solutions and organic solvents: Universal buffer solutions were prepared according to Britton[5]. The pH values were checked using W 6 PYE model 290 pH–meter. Alcohols (methanol, ethanol, isopropyl) were purified by the recommended methods[6].

C–Working procedure and apparatus: The experimental technique and electrolysis cell were as previously described[7]. The characteristics of the capillary are m = 1.5 mg sec^{-1} and t = 4.5 sec/drop (open circuit) at 45 cm. Hg. The average current-voltage curves were recorded using an ink recording Polarograph of LP 60 type.

Results and Discussion

The polarograms of 5×10^{-4} M of dye in an aqueous buffered solutions and aqueous-alcohol mixtures of different pH's containing 40% of either ethyl, methyl or isopropyl alcohol consist of single reduction wave (viz. Fig. 1). The height of

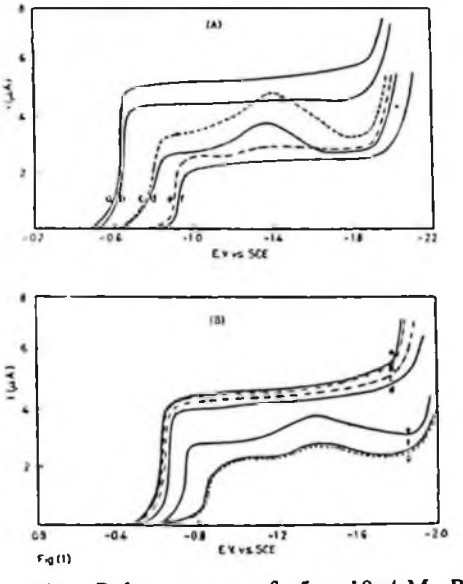


Fig. 1: (A) Polarograms of 5×10^{-4} M Bisazo-compound in universal buffer solution containing 40% ethanol: (a) pH 6.0, (b) pH 7.2, (c) pH 8.8, (d) pH 9.2, (e) pH 10.2, (f) pH 11.2.

(B) Polarograms of 5×10^{-4} M Bisazcom-pound in universal buffer solution containing 40% isopropyl alcohol: (a) pH 5.1, (b) pH 6.0, (c) pH 7.2, (d) pH 7.9, (e) pH 8.89, (f) pH 10.5, (g) pH 11.2

the wave decreases tremendously with increasing pH till it attains in alkaline solutions almost half its height in moderate acid media, whereas at intermediate pH the wave lies between the two values. From this behaviour it can be concluded that the electrons involved in the electrode reaction in weakly acid media are double those in alkaline ones. The effect of mercury pressure on the limiting current reveals that the value of the exponent X in the relation ($i_l = KH^x$) varies between 0.45 and 0.55 at the plateau of the i_l/pH curves. In other media studied, the value of X is either lower than 0.45 or higher than 0.55 indicating that the process of reduction is influenced in addition to diffusion by both adsorption and kinetic components which vary in magnitude according to the conditions.

The fundamental equation for testing thermodynamic reversibility of the wave is :

$$\Delta E_{dme}/\Delta \log\ [i/(i_d - i)] = \frac{0.059}{n} \text{ at } 25°C.$$

The slopes of E_{dme} vs log $[i(i_d - i)]$ plots indicate that the electroreduction of bisazocompound is irreversible (Table I) since the overall electrode reduction involves the uptake of 4 and 8 electrons in alkaline and acid solutions respectively. The slopes of Ca 0.05 obtained in several instances indicate that the electrode comprises a one-electron rate determining step.

TABLE—1 Kinetic parameters obtained for 4, 4' -Bisazobenzene-di [B-1, aminonaphthalene 4-sodium] sulphate at different buffer solutions.

Medium	pH	$\frac{0.059}{\alpha n_a}$	αn_a	n	K° cm/sec	$KD^{-\frac{1}{2}}$ K = K°	ΔG^* K. cal/ mole	K_f cm sec	$K_f D^{-\frac{1}{2}}$	ΔG_f^* K. Cal/ mole $K_f = K°$
Buffer solution	8.26	0.075	0.79	5.9	5.8×10^{-25}	4.5×10^{-22}	169.5	1.1×10^{-4}	0.8×10^{-1}	52.2
40% iso-propanol	8.89 11.25	0.044 0.05	1.34 1.18	5.85 4.04	1.5×10^{-24} 3.1×10^{-26}	1.8×10^{-21} 3.9×10^{-23}	167.0 176.8	9.7×10^{-5} 7.0×10^{-5}	1.2×10^{-2} 8.0×10^{-2}	52.5 53.3
40% Ethanol	8.81 11.24	0.066 0.073	0.89 0.8	6.0 3.92	1.0×10^{-15} 1.7×10^{-17}	1.0×10^{-12} 1.8×10^{-13}	116.0 120.4	1.8×10^{-4} 1.3×10^{-4}	1.9×10^{-1} 1.6×10^{-1}	50.9 51.4
40% Methanol	8.45 10.80	0.047 0.035	1.25 1.68	6.5 4.1	1.9×10^{-22} 6.3×10^{-32}	1.9×10^{-19} 6.3×10^{-29}	154.8 210.0	2.1×10^{-4} 1.7×10^{-4}	2.1×10^{-1} 1.7×10^{-1}	50.6 50.8

Medium effect on $E_{\frac{1}{2}}$ and i_l : The observed shift in $E_{\frac{1}{2}}$ of the reduction waves to more negative potentials with increasing pH, indicate that H^+ ions are consumed in the electrode process. With respect to the effect of solvent on $E_{\frac{1}{2}}$, it is found that the solvent increases the shift in $E_{\frac{1}{2}}$ to more negative potentials. The shift becomes more apparent with rise of the molecular weight of alcohol. The observed shift of $E_{\frac{1}{2}}$ in presence of organic solvent can be attributed to the decrease in the dielectric constant ϵ, as a result the electrode reaction needs higher energy which in turn leads the reduction potentials to more negative value.

From the plots in Fig. 2 it is apparent the total reduction current decreases with increasing pH, tending to attain a more or less constant value at higher pH's. This constant value of the current equals almost half the value in acid medium. It is also evident that the total current decreases more in the presence of alcohols than in aqueous medium due to an increase in the pH of the solution and to increase viscosity η of the medium. This phenomenon is more pronounced in the case of isopropyl alcohol than in the case of the other two alcohols on account of the higher viscosity of its solution and variation of the effective size of depolarizer.

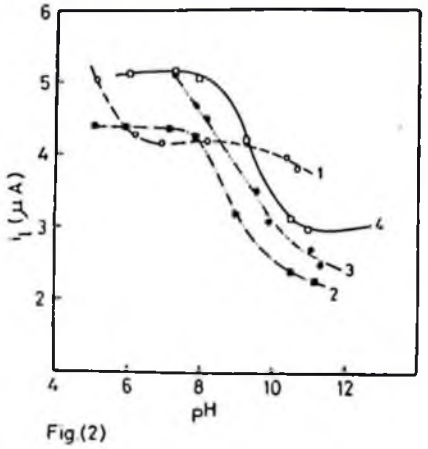


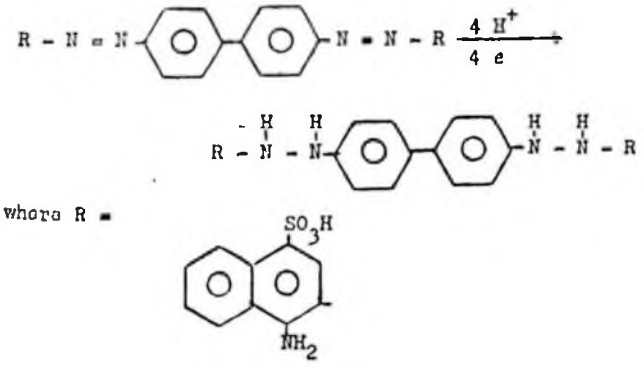
Fig (2)

Fig. 2 : i_l – pH

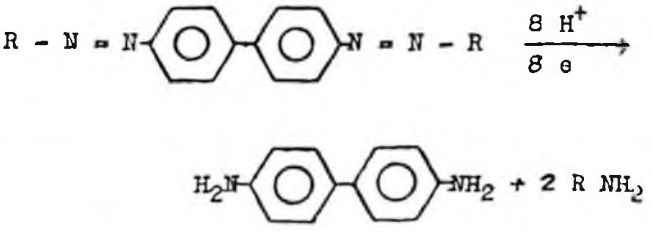
(1) aqueous solutions. (2) 40% isopropanal.
(3) 40% ethanol (4) 40% methanol.

The electrode reaction and mechanism of the reduction :

In order to elucidate mechanism for the electrode reduction process, the number of electrons involved along the reduction wave at the various pH's has been calculated, This can be done by the aid of the Ilkovic equation provided that D°, the diffusion coefficient of the compound is determined. Using the value of D° for bisazobenzene as given by Saber et al[2] as equal to 2.1×10^{-6} cm²/sec, the number of electrons calculated at the same pH amount to 4.9. Since the reduction of the two azo linkages in alkaline media consumes only 4 electrons, the value of D° has been calculated on the basis that n equals 4 and is found to be 1.59×10^{-6} cm²/sec. The values of n consumed at the various pH's are then obtained by applying the Ilkovic equation as given in Table 1. These values indicate that reduction leads to the formation of bishydrazo-derivatives in alkaline medium. The reduction step takes place for both azo groups simultaneously via the uptake of 4-electrons to yield bishydrazo derivatives, as given in Reaction–(2).



In acid solution the protonation of the amino group will diminish the electron donating character of the NH_2 group. The electron accepting character of the sulphonate group on the other hand will decrease the electron density on the azo groups rendering them more susceptible to reduction. In alkaline solution the reduction process becomes more difficult due to electron-donating character of the NH_2 group. Consequently all 8 electrons are taken up in one step in acid medium causing simultaneous splitting up of the azo centers yielding the corresponding amines, as given in Reaction(3)



At intermediate pH's (pH 7, 8) the number of electrons lies between 4 and 8 so that both mechanisms are involved in the reduction process to varying extents depending upon the number of H^+ in the rate determining step as well as the change of the transfer coefficient.

The mechanism of the reaction is not changed in presence of alcohol despite the shift in $E_{\frac{1}{2}}$ and decrease in the reduction current. In order to prove that the mechanism is not affected by the nature of the alcohol, the values of the diffusion coefficient are calculated in presence of alcohols with respect to those in aqueous medium by using this relation :

$$\frac{\eta_{aq}^{\frac{1}{2}}}{\eta_{alc}^{\frac{1}{2}}} = \frac{D_{alc}^{\frac{1}{2}}}{D_{aq}^{\frac{1}{2}}}$$

Taking the viscosity of H_2O as equal to unity, η for 40% either ethyl, methyl and isopropyl alcohol is equal to 2, 1.85, 3.24 respectively and the value D° in aqueous solution is equal 1.69×10^{-6} cm²/sec, the D° values in the organic solvent-water mixtures are evaluated. These $D°_{alc.}$ values are used for calculating the number of electrons in each case. The approximate constancy of n in all cases proves that the mechanism of the reduction remains unchanged in the presence of alcohols.

Kinetic parameters of the Electrode Reaction : The different kinetic parameters for the electrode reaction have been calculated using the equations due Koutecky[8] and Delahay[9]. In addition to the usual parameters (K°, $\triangle G^\circ KD^{-\frac{1}{2}}$) the values of the formal constants corresponding to the reversible half wave potential $E^r_{\frac{1}{2}}$ are also evaluated (Table 1). The values of $E^r_{\frac{1}{2}}$ have been evaluated by the method of Gelling[10]. These parameters (Table 1) indicate that the process of reduction takes place irreversibly. The values of K_f do not correspond to K_s since $E^r_{\frac{1}{2}}$ does not coincide with E° of the reversible system. The irreversibility is brought about on the one hand by the adsorption of the depolarizer or its reduction product on the electrode surface. This is evident from the shift on $E_{\frac{1}{2}}$ with rise of concentration of the depolarizer to more negative potentials and from the decrease of surface tension of the solution in its presence (electrocapillary curves). It is also evident that the rate constants K° and K_f decrease with increase of pH while $\triangle G^*$ and $\triangle_f^*$ increase in the same direction. This is in favour of the fact that process of reduction becomes more difficult as the pH of the solution increases. In presence of the organic solvents the values of K° and K_f are lower than in the aqueous medium. This difference is brought about by the shift of $E_{\frac{1}{2}}$ to more negative potentials in the solvent containing solution. The shift of $E_{\frac{1}{2}}$ is caused on the one hand by the increase of pH value and by adsorption of the alcohols on the electrode surface on the other. The adsorbability of the alcohol apparently increases with increase of its chain length.

Analytical Applications: The plots of i_d vs C are straight lines passing through the origin (Fig. 3). The value of i_d/C is constant confirming the applicability of the Ilkovic equation except in the case of

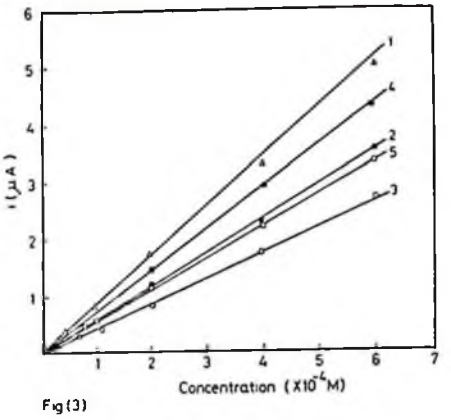


Fig. 3 : Effect of consentrations of Bisazcompound at different pH's :
(1) pH 8.2.
(2) 8.89 (40% isopropanol).
(3) pH 11 25 (40% isopropanol)
(4) pH 8.8 (40% ethanol).
(5) pH 11.2 (40% ethanol).

aqueous medium at higher pH's. The constancy of i_d/C values indicate that the polarographic method can be applied for the determination of the bisazocompound under study within concentration range 1×10^{-4} M to 6×10^{-4} M.

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