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The electrochemical behaviour of 2′-halogenated derivatives of 4-methoxyazobenzene at a mercury electrode

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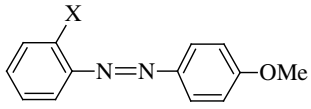
ABSTRACT

The electrochemical behaviour of 2′-halogenated-4-methoxyazobenzene derivatives were investigated using both polarographic and voltammetric methods. The number of electrons transferred, standard rate constant and diffusion coefficient were evaluated. The standard rate constant was determined using either a Laviron technique or Nicholson and Klingler–Kochi technique. Diffusion coefficients were calculated from cyclic voltammetric data using the method developed by Garrido. The adsorption and transfer coefficients of electron transfer were determined using chronocoulometry and constant-potential coulometry, respectively. The number of electrons transferred was found to be 4 (pH < 4) and 2 (pH > 4) for all derivatives studied. The compounds could be determined quantitatively at between 5×10^{-5} M and 5×10^{-7} M using sampled current polarography, differential pulse polarography and cyclic voltammetry.

1. Introduction

Azo dyes comprise >35% of global dye production [1]. Some azo dyes and their precursors pose an environmental threat as they are toxic and selected examples display potential carcinogenic properties [2–4]. Early studies on the polarography of azo dyes were reviewed by Zollinger [5]. The electrochemistry of both azo and hydrazo compounds in aqueous media has been extensively studied [6–12]. Westmoreland et al. [13] employed aqueous surfactant solution as reaction medium and reported that the electrochemical behaviour observed approached reversibility as surfactant concentration was lowered. Although the electrochemical behavior of azo and hydrazo compounds has been widely investigated, the adsorption phenomena which plays an important role in their electrochemistry has not been appropriately accounted for, as discussed by Florence [11], Pezzatini and Guidelli [14] and Uçar et al. [15–17]. Hydrazo compounds are known to be strongly adsorbed at a mercury electrode, resulting in increased effective surface concentration of the reactant which leads to higher disproportion rates [11].

In view of the importance of azo derivatives, it was decided to investigate the electrochemical behaviour of various 2′-halogenated-4-methoxyazobenzene derivatives (**I-III**) using the methods developed by Laviron [18] and Garrido [19] which are based upon adsorption phenomenon. These results were then compared with those obtained using Nicholson [20] and Klingler–Kochi [21] methods which disregard adsorption behaviour. In addition, the surface excess concentration, transfer coefficient, standard heterogeneous rate constant and the number of electrons transferred were determined. It is hoped that the data presented here will shed light on the electrochemical reaction mechanism of azobenzenes.



X: Cl (**I**), Br (**II**), I (**III**)

2. Experimental

2.1. Apparatus

Polarographic measurements were carried out using a BAS100B Electrochemical Analyzer equipped with cell stand, PAR 303A static

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mercury drop electrode (SMDE) and PAR Model 305 stirrer. All solutions were deaerated for 10 min by purging with nitrogen, prior to the electrochemical experiment and were blanketed thereafter. The pH values of the solutions were recorded using an Orion 720A pH-meter. The buffer solutions used were the Britton-Robinson (BR) buffer (comprising a mixture of a 0.04 M aq H_3BO_3, 0.04 M aq H_3PO_4 and 0.04 M aq CH_3COOH that is titrated to the desired pH using 0.2 M aq NaOH) of pH values between 2 and 12. Polarographic and voltammetric experiments were carried out using the SMDE in a three-electrode cell equipped with a Pt wire auxiliary and Ag/AgCl reference electrodes. Cyclic voltammetric (CV) and chronoamperometric (CA) experiments were performed using a hanging mercury drop electrode (HMDE) with a surface area of 0.0145 cm^2. Constant-potential electrolysis was carried out using a mercury pool electrode with a surface area of 19.6 cm^2. The number of electrons was calculated from the amount of charge passed ($Q = nFN$) after 68.15 min of electrolysis, this being the time for the current to drop by 1% of its initial value. All measurements were made at laboratory temperature (25 ± 1 °C) and no maximum suppressor was used.

2.2. Reagents

Acetic acid (BDH, Analar), phosphoric acid (Merck), boric acid (Riedel) ammonium metavanadate (Merck), and sodium hydroxide (Merck) were used without further purification. The water used in the preparation of the solutions was distilled and deionized by an ELGASTAT water purification system.

The azo compounds used were synthesized according to the method reported in the literature [22] and their purities were checked using melting point determination, as well as UV, IR and NMR spectroscopy.

3. Results and discussion

3.1. Characterization of the electrode reaction

The cyclic voltammogram for compound **I** was recorded on the HMDE in acidic conditions (pH 3.3) from 0 to −1000 mV and was shown in Fig. 1. There were two peaks observed in cathodic scan. The first peak has a corresponding oxidation peak in the reverse cycle while the second peak does not show such behavior (Fig. 1). Compound **I** in acidic media gave two cathodic peaks at −105 mV and −680 mV and an anodic peak at −62 mV in the reverse scan accompanying the first reduction peak.

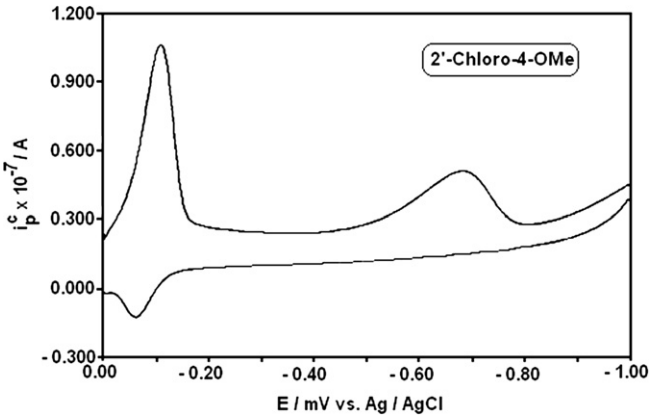


Fig. 1. Cyclic voltammogram of 1.67×10^{-5} M 2′-chloro-4-methoxyazobenzene in pH 3.31. [The medium: 1:5 v/v (EtOH:BR buffer), scan rate = 100 mV s^{-1}, with HMDE and $Ag/AgCl/KCl_{satd.}$ reference electrode].

The cyclic voltammograms of the compounds **I**–**III** on HMDE to the first reduction peaks in both acidic and basic media are shown in Fig. 2 and Fig. 3, respectively.

The first cathodic peak observed in basic media was attributed to the reduction of the −N═N− group to −NH−NH−. It was thought that the hydrazines afford the corresponding anilines upon further reduction process in acidic media. The peak potential ($E_{p,c}$) shifts towards negative values with increasing scan rate and as the medium becomes more basic. The second cathodic peak was thought to be due to the catalytic hydrogen reduction [23–26].

The first cathodic peak is quasi-reversible; since the difference between the anodic and the cathodic peak potentials was greater than 0.059/2 mV (approximately 0.234 V) and increased with the increase in scan rate (from 0.01 to 50 V/s).

The $E_{1/2}$-pH graphs of sampled current polarographic (SCP) experiments for compounds **I**–**III** were found to be linear (Fig. 4). Furthermore, Fig. 4 shows that the first reduction limiting currents for compounds **I**–**III** change in linear manner with increasing pH. This dependence of the half wave potentials on pH is indicative of a proton transfer in the electrode reaction [27]. The fact that the half wave potentials shift to negative values with the pH of the medium implies that the reduction is easier in the media where the proton concentration is high and more difficult in the media where the proton concentration is low [28,29]. The $E_{1/2}$-pH relationships for the first peak of the azo compounds investigated were as follows:

For chlorine derivative (**I**); $E_{1/2} = -58.55$ (±3.65) pH-58.93 (±28.70) $R^2 = 0.987$
For bromine derivative (**II**); $E_{1/2} = -67.81$ (±1.42) pH-137.18 (±11.12) $R^2 = 0.999$
For iodine derivative (**III**); $E_{1/2} = -65.15$ (±1.56) pH-81.12 (±12.05) $R^2 = 0.998$

This dependence may be explained in terms of preprotonation of the azo groups. The change of the potential of the first peak with pH is linear.

In all of the 2′-halogenated-4-methoxyazobenzene derivatives the number of electrons transferred in the first cathodic peak was found to be 4 above pH 4 and 2 below pH 4. In all these derivatives the first peak was observed to give a corresponding anodic peak in the reverse scan at all pH values studied.

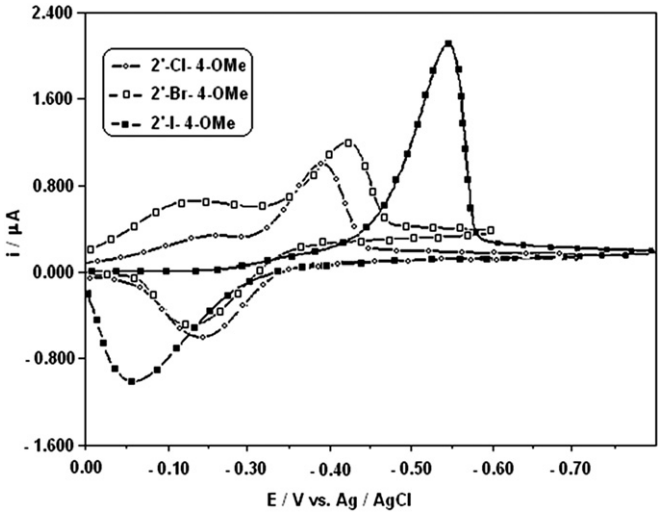


Fig. 2. Cyclic voltammograms of 1.67×10^{-5} M 2′-halogenated-4-methoxyazobenzene in pH 5.58. [The medium: 1:5 v/v (EtOH:BR buffer), scan rate = 100 mV s^{-1}, with HMDE and $Ag/AgCl/KCl_{satd.}$ reference electrode].

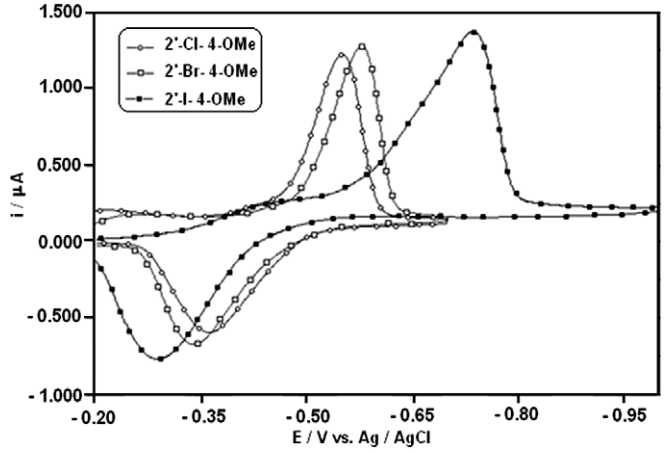


Fig. 3. Cyclic voltammograms of 1.67×10^{-5} M 2′-halogenated-4-methoxyazobenzene in pH 9.69. [The medium: 1:5 v/v (EtOH:BR buffer), scan rate = 100 mV s^{-1}, with HMDE and Ag/AgCl/$KCl_{satd.}$ reference electrode].

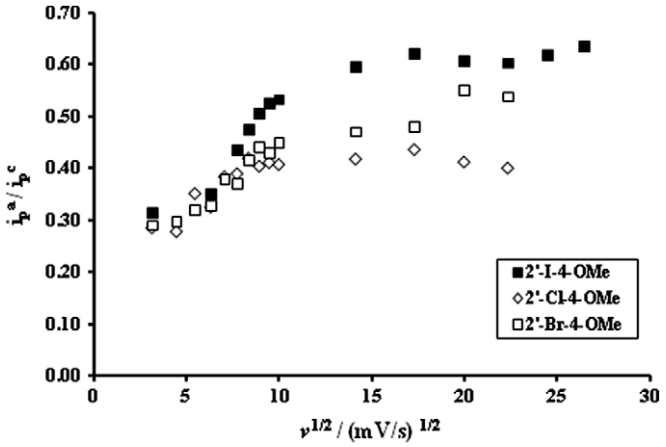


Fig. 5. Variation of the i_p^a/i_p^c ratio with $\nu^{1/2}$ for 1.67×10^{-5} M 2′-halogenated-4-methoxyazobenzene derivatives (pH 5.58).

The best criterion to check whether the irreversibility of the electrode reaction is due to slow electron transfer, adsorption or a chemical reaction, is the change of the i_p^a/i_p^c ratio with the scan rate. If the electrode reaction is preceded with a chemical reaction the cathodic peak current is much higher than its anodic counterpart and i_p^a/i_p^c ratio is lower than unity. As can be seen from Fig. 5 cathodic peak current increased with an increase in $\nu^{1/2}$ at low scan rates. However the i_p^a/i_p^c ratio approached unity as the scan rate is increased. These results show that the system behaves in a quasi-reversible manner [27] (Fig. 6).

The change of E against log $[(i_d - i)/i]$ according to Heyrovsky–Ilkovic equation, and the change of $E_{1/2}$ with the dropping time showed that the reduction of the –N=N– bonds are quasi-reversible for all of the derivatives investigated and the degree of reversibility changes from one derivative to another. The irreversible character of the first peak was also apparent from the relation of $E_p = E_{1/2} - \Delta E/2$ in SCP and differential pulse polarography (DPP).

The first peak currents for the studied compounds **I**–**III** were observed to increase up to a certain concentration. The effect of the concentration is shown in Table 1. The current increases with concentration in a linear fashion at lower concentration values. It becomes almost constant at higher concentrations (5×10^{-5} M), which may be attributed to an adsorption phenomenon. The linear increase in the current with concentration in the lower concentration range creates the possibility of a quantitative determination of these compounds using SCP, DPP and CV.

The limiting currents for compounds **I**–**III** with pH give an approximately constant change above pH 4. The limiting current observed in acidic medium is roughly as large as that observed in the basic medium (Fig. 6) which can be explained by the fact that the number of electrons exchanged is equal between pH 4–12. This is in complete accordance with literature [1,27,28].

The second cathodic peak observed in the voltammograms for **I**–**III** is completely irreversible and has the characteristics of a catalytic hydrogen wave such as the decrease in the half wave potential with the increasing pH (Fig. 7). This second peak was suppressed with the addition of surface-active reagents such as Triton X-100. The fact that there was no anodic peak at extreme scan rates in CV (above 50 V/s) is also indicative of the catalytic hydrogen wave. Çakır et al. [23], Holleck et al. [24], Issa et al. [25] and Uçar [26] have also claimed that this second reduction peak was due to catalytic hydrogenation.

3.2. Effect of adsorption

Since methoxyazobenzenes are large molecules it is necessary to check whether an adsorption phenomenon is present or not. The most suitable technique to investigate the effect of adsorption upon

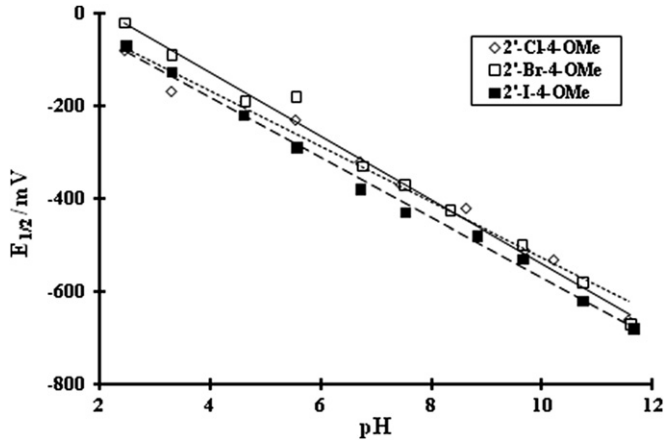


Fig. 4. The change of $E_{1/2}$ of 1.67×10^{-5} M 2′-halogenated-4-methoxyazobenzene derivatives with pH [The medium:1:5 (EtOH:BR buffer) with SMDE against Ag/AgCl/$KCl_{satd.}$ reference electrode, scan rate = 10 mV s^{-1}, drop time = 1 s].

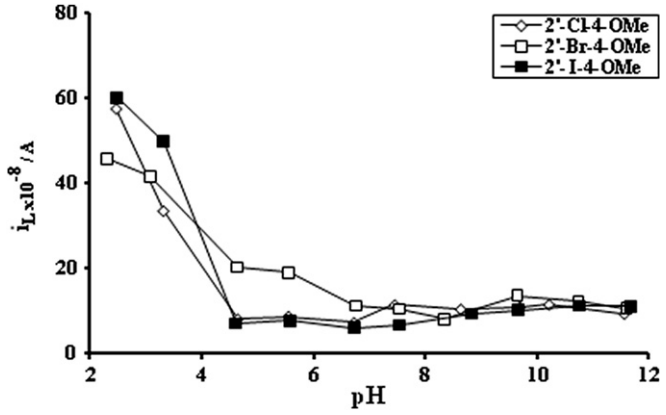


Fig. 6. Change in the limiting current of 1.67×10^{-5} M 2′-halogenated-4-methoxyazobenzene with the pH [The medium: 1:5 v/v (EtOH:BR buffer), scan rate = 10 mV s^{-1}, drop time = 1 s, with SMDE and Ag/AgCl/$KCl_{satd.}$ reference electrode].

Table 1
Change of the peak currents belonging to the first reduction peaks of 2′-halogenated-4-methoxyazobenzene derivatives with the concentration in a basic medium (pH 9.69) [The medium: 1:5 v/v (EtOH:BR buffer) vs.Ag/AgCl/$KCl_{satd.}$ reference electrode].

$C \times 10^{-7}$ (mol L^{-1})	SCP			DPP			CV		
	2′-Cl–4-OMe ($i_L \times 10^{-8}$/A)	2′-Br–4-OMe ($i_L \times 10^{-8}$/A)	2′-I–4-OMe ($i_L \times 10^{-8}$/A)	2′-Cl–4-OMe ($i_p \times 10^{-8}$/A)	2′-Br–4-OMe ($i_p \times 10^{-8}$/A)	2′-I–4-OMe ($i_p \times 10^{-8}$/A)	2′-Cl–4-OMe ($i_p^c \times 10^{-8}/A$)	2′-Br–4-OMe ($i_p^c \times 10^{-8}/A$)	2′-I–4-OMe ($i_p^c \times 10^{-8}/A$)
500.0	10.80	15.50	10.10	11.30	20.10	18.50	106.0	111.0	99.8
167.0	7.90	10.10	5.76	8.17	15.00	9.17	69.7	83.4	50.8
50.0	3.60	4.76	4.36	4.28	4.02	5.03	26.4	48.4	21.7
16.7	2.47	3.39	2.59	2.41	1.95	3.09	24.3	14.2	18.0
5.0	3.74	2.87	3.09	0.50	1.69	2.95	22.5	14.5	10.8

the electrode reaction is cyclic voltammetry. There are many approaches to determine the adsorption by the use of cyclic voltammetry [29].

The $\log i_p^c - \log \nu$ graph of 2′-iodo-4-methoxyazobenzene is shown in Fig. 8. The slope of this graph was found as 0.8. This result indicates that compound **III** is adsorbed on the mercury surface [26,29]. Similar results were obtained for the other derivatives **I**–**III** and also the graph of i_p^c/C *versus* C (Fig. 9) which show a sharp decrease at the beginning and stabilize later on further verify the presence of adsorption [26,29]. The decrease in i_p^c/C with the increase in concentration is another indication of adsorption. The change of i_p^c against $\nu^{1/2}$ provides further evidence for this quasi-reversible behavior (Fig. 10).

It is known from the previous studies that the azobenzene-hydrazobenzene system is adsorbed upon the mercury surface near the potential of the electrocapillary maximum based upon the pH of the medium [11,15–17]. In our studies it was observed that methoxyazobenzenes and derivatives were adsorbed on the mercury surface in 1:5 EtOH–BR buffered media at various pH values.

The presence of adsorption was further verified by the fact that the difference of anodic and cathodic peak potentials was less than $59/n$ mV at low scan rates. There were also maxima and splitting on the SCP due to the adsorption of the compounds. The experiments were repeated by the addition of Triton X-100 in order to suppress the maxima and a significant change in peak potentials was noted. After the addition of the suppressor the compounds were reduced at more positive potential, which led to the conclusion that the suppressing agent had changed the reduction mechanism as indicated by Westmoreland et al. [13]. The experiments were then carried without the addition of any suppression agent.

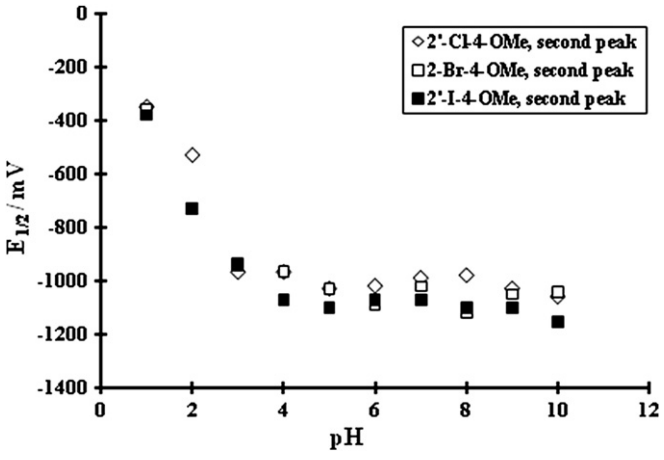


Fig. 7. The change of half peak potentials for the second cathodic peak of 1.67×10^{-5} M 2′-halogenated-4-methoxyazobenzene derivatives with pH [The medium: 1:5 (EtOH:BR buffer), with SMDE against Ag/AgCl/$KCl_{satd.}$ reference electrode, scan rate = 10 mV s^{-1}, drop time =1 s].

3.3. Surface concentration measurements

The surface concentrations of the adsorbed molecules of methoxyazobenzene derivatives were studied by chronocoulometry. The surface excess Γ values were determined using $Q - t^{1/2}$ graphs. The extrapolation of the $Q - t^{1/2}$ graph of the supporting electrolyte and a solution containing 2′-halogenated-4-methoxyoazobenzene derivatives to the $t^{1/2} = 0$ point gave the Q_{dl} and $Q_{t=0}$ values, respectively. The Q_{ads} values are calculated from $Q_{ads} = Q_{t=0} - Q_{dl}$. The surface excess values are then obtained from Equation (1) [30]:

$$Q = 2nFAC(Dt/\pi)^{1/2} + Q_{dl} + nFA\Gamma \quad (1)$$

Here, Q_{dl} is the charge due to the double layer, Γ is the amount of adsorbed reactant and the other symbols have their usual meanings. The amount of reactant adsorbed on the mercury surface (Γ, mol cm^{-2}) is given in Table 2. Foresti et al. [31] determined the maximum adsorption of azobenzene in water + ethanol to be 2.5×10^{-10} mol cm^{-2}. This value was determined between 1.3×10^{-11} and 6.0×10^{-12} mol cm^{-2} for 2′-haloganeted-*N*,*N*-dimethyl-4-aminoazobenzene and 7.3×10^{-11}–5.9×10^{-12} mol cm^{-2} for 4′-haloganeted-*N*,*N*-dimethyl-4-aminoazobenzene in our previous studies [16,17]. However, Foresti et al. [31] carried out their study in the presence of surface-active reagents. The effect of adsorption was minimized using high concentrations and low scan rates.

3.4. Determination of standard rate constants

The heterogeneous standard rate constants for the 2′-halogenated-4-methoxyazobenzene derivatives were calculated by three different methods. Two of these namely Klingler–Kochi [21] and Nicholson methods [20], assume diffusion-controlled current, and the other known as Laviron method [18] assumes adsorption at the

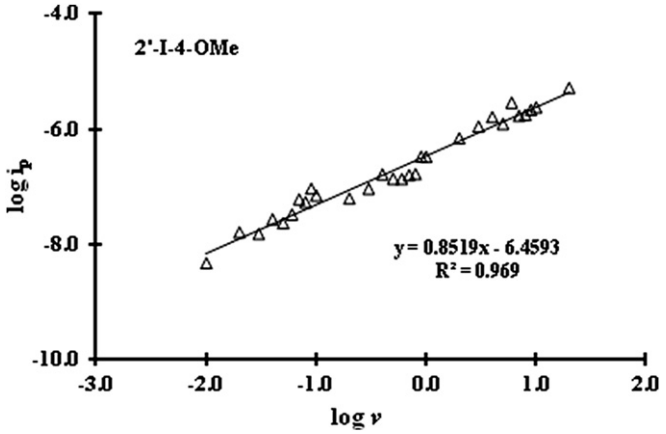


Fig. 8. Variation of the $\log i_p^c$ against $\log\nu$ for 1.67×10^{-5} M 2′-iodo-4-methoxyazobenzene derivative (pH 5.58).

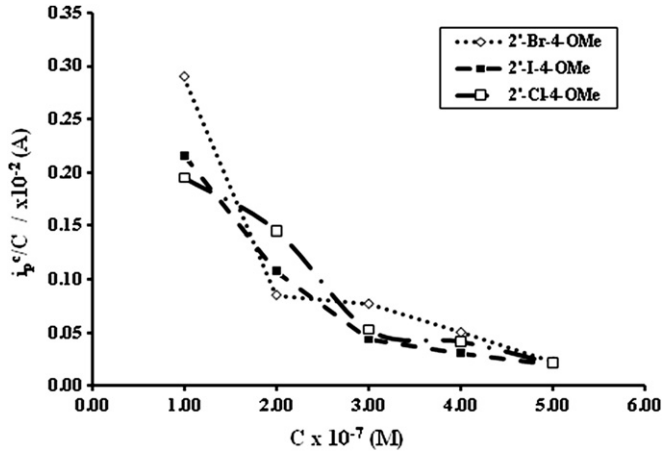


Fig. 9. Change of the i_p^c/C ratio of 2′-halogenated-4-methoxyazobenzene derivatives with the concentration in a basic medium (pH 9.69). [The medium: 1:5 v/v (EtOH:BR buffer), scan rate =100 mV s^{-1}, with HMDE and Ag/AgCl/KCl$_{satd.}$ reference electrode].

electrode surface. In the former methods calculation of diffusion coefficients is necessary. If the potential applied to the electrode falls into the diffusion-controlled region the current is given by Cottrell equation (Equation (2)):

$$i = \frac{n\mathrm{FACD}^{1/2}}{\pi^{1/2}t^{1/2}} \tag{2}$$

This equation is very useful in the determination of diffusion coefficients. However, it is only applicable for those cases where the electrode reactions are diffusion-controlled and do not have any adsorption or chemical complications. Therefore all the diffusion coefficients were elucidated under the diffusion-controlled conditions by the use of Cottrell equation. In the case of adsorption the Equation (3) derived by Garrido et al. at 25 °C is applicable [19]:

$$i_\mathrm{p} = 1.06 \times 10^6 n^2 ACvD^{1/2}t_\mathrm{p}^{1/2} \tag{3}$$

where a Langmuir type of adsorption was assumed with a non-compact monolayer film of adsorbed molecules upon mercury surface. Here, t_p is the adsorption time between the start of the mercury drop till E_p is reached. Other symbols have their usual meanings.

The values in basic media, where adsorption has a significant effect, were found to be higher and more reasonable than those obtained for the uncomplicated case using the Cottrell equation. Hence the diffusion coefficients found from the Garrido method

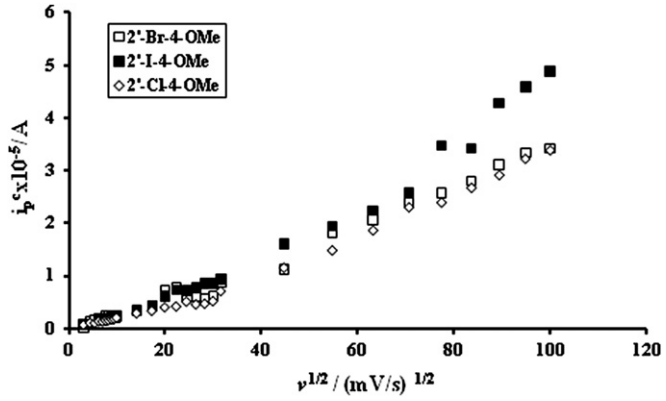


Fig. 10. Variation of the cathodic peak currents with $v^{1/2}$ for 1.67 × 10^{-5} M 2′-halogenated-4-methoxyazobenzene derivatives (pH 5.58).

Table 2
Diffusion coefficients, surface coverage (Γ, mol cm^{-2}), standard rate constants (k_s) values in 1:5 v/v EtOH:BR buffer, 2′-halogenated-4-methoxyazobenzene derivatives in different pH values.

Comp.	Cottrell[a]		Garrido[b]		Laviron[c]		Klingler–Kochi[d]		Nicholson[e]		$\Gamma \pm t_s/N^{1/2}$/mol cm^2 s^{-1}[f]
	Diffusion coefficient (D)/cm^2 s^{-1} $D \pm t_s/N^{1/2}$		Diffusion coefficient (D)/cm^{2}s^{-1} $D \pm t_s/N^{1/2}$		$k_s \pm t_s/N^{1/2}$/cm^2 s^{-1}		$k_s \pm t_s/N^{1/2}$/cm^2 s^{-1}		$k_s \pm t_s/N^{1/2}$/cm^2 s^{-1}		
	pH < 4	pH > 4	pH < 4	pH > 4	pH < 4	pH > 4	pH < 4		pH > 4		
2′-Cl–4-OMe	2.08 × 10^{-6} ±	1.90 × 10^{-6} ±	1.32 × 10^{-6} ±	2.92 × 10^{-6} ±	0.47 ± 0.03	1.10 ± 0.26	2.70 × 10^{-3} ±		3.40 × 10^{-3} ±		5.97 × 10^{-12} ±
	1.14 × 10^{-7}	1.09 × 10^{-7}	5.17 × 10^{-7}	7.56 × 10^{-7}			0.12 × 10^{-3}		0.05 × 10^{-3}		1.23 × 10^{-12}
2′-Br–4-OMe	3.55 × 10^{-6} ±	4.96 × 10^{-6} ±	6.34 × 10^{-6} ±	9.68 × 10^{-5} ±	0.34 ± 0.03	0.53 ± 0.3	7.20 × 10^{-3} ±		14.10 × 10^{-3} ±		6.70 × 10^{-12} ±
	1.49 × 10^{-7}	1.76 × 10^{-7}	7.44 × 10^{-7}	5.85 × 10^{-5}			0.15 × 10^{-3}		1.05 × 10^{-3}		2.01 × 10^{-12}
2′-I–4- OMe	3.90 × 10^{-6} ±	4.56 × 10^{-5} ±	6.51 × 10^{-6} ±	2.09 × 10^{-5} ±	0.20 ± 0.01	0.42 ± 0.28	5.10 × 10^{-3} ±		11.60 × 10^{-3} ±		7.30 × 10^{-11} ±
	1.56 × 10^{-7}	5.34 × 10^{-7}	1.03 × 10^{-6}	1.21 × 10^{-6}			0.09 × 10^{-3}		0.62 × 10^{-3}		1.60 × 10^{-11}

The medium: 1:5 v/v (EtOH:BR buffer),with HMDE vs. Ag/AgCl/KCl$_{satd.}$ reference electrode.
[a] $C = 1.67 \times 10^{-5}$ M, Calculated from Cottrell slope (Eq. (2)), the data was determined by the use of $i - t^{-1/2}$ plots in the diffusion region (Pulse amplitude 250 ms, $E_1 = -400$ mV and $E_2 = -900$ mV).
[b] $C = 1.67 \times 10^{-5}$ M, Calculated from Equation (3), considering adsorption ($t_\mathrm{p} = 15$ s).
[c] $C = 5 \times 10^{-7}$ M, Calculated from Equation (7), considering adsorption for confidence interval of 95%, mean α value for the cathodic peak is 0.410 (pH 3.31) and 0.256 (pH 9.69). $v = 5000-20{,}000$ mV s^{-1}.
[d] $C = 5 \times 10^{-5}$ M, Calculated from Equation (4), ignoring adsorption for confidence interval of 95%, mean $\alpha_{\mathrm{average}}$ value for the cathodic peak is 0.330 (pH 9.69), $v = 5000-20{,}000$ mV s^{-1}.
[e] 5×10^{-5} M, Calculated from Equation (6), ignoring adsorption, $v = 40-200$ mV s^{-1}.
[f] $Q_{dl} = 3.3 \times 10^{-9}$ C (Eq. (1)), Pulse amplitude, 250 ms; $E_1 = -400$ mV and $E_2 = -900$ mV.

were used in all the equations for the calculation of the standard rate constants, (Table 2).

In acidic media, it was observed that the difference between the values of diffusion coefficients determined by Cottrell and Garrido methods was not significant. This shows that adsorption is less effective in acidic media.

3.4.1. Klingler–Kochi method

Klingler and Kochi [21] derived the Equations (4) and (5) for the standard rate constant for heterogeneous electron transfer (k_s):

$$k_s = 2.18\left(\frac{D\alpha nF\nu}{RT}\right)^{1/2}\exp\left[-\frac{\alpha^2 nF}{RT}\left(E_p^a - E_p^c\right)\right] \quad (4)$$

where,

$$\alpha = 1,857\left[\frac{RT}{nF\left(E_p - E_{p/2}\right)}\right] \quad (5)$$

As the scan rate is increased, the peak width becomes larger and the transfer coefficient, α, becomes smaller. The mean α values for the cathodic peaks were found to be 0.3–0.4 for all the different methods employed. The mean value of transfer coefficient was calculated by averaging the values obtained for those cases where the difference between anodic and cathodic peak currents was more than 300 mV. The k_s values under these circumstances are independent of the scan rate [21]. The diffusion coefficients used in Equation (4) are the values determined by Garrido method. The number of electrons transferred is 4 when the pH of the solution is less than 4. On the other hand 2 electrons are transferred when the pH is above 4. The number of electrons transferred for the first reduction peak was determined by taking the suitable limiting current values. The k_s values determined for all 2′-halogenated-4-methoxyazobenzene derivatives in basic media are given in Table 2.

3.4.2. Nicholson method

The k_s value of the electron transfer reaction was also determined by the use of the technique developed by Nicholson [20], using:

$$\Psi = \frac{\left(\frac{D_O}{D_R}\right)^{\frac{nF\nu}{2RT}}k_s}{\sqrt{\pi\frac{nF\nu}{RT}D_O}} \quad (6)$$

where ψ values were determined from the working graph given by Nicholson by taking D_O/D_R as unity. This method requires a continuous equilibrium condition on the electrode surface and is not suitable for very high and very low scan rates. It is applicable for the peak separation of 60–220 mV. On the other hand the Klingler–Kochi method is applicable at high scan rates. The k_s values determined by the use of these methods were found to be in good agreement with each other at certain scan rates indicated in Table 2.

3.4.3. Laviron method

Since an adsorption phenomenon was found to be operating, the rate constants were determined by the use of the method developed by Laviron, which takes the effect of adsorption into account [18]. The k_s values were calculated using Equation (7):

$$\log k_s = \alpha\log(1-\alpha) + (1-\alpha)\log\alpha - \log\left(\frac{RT}{nF\nu}\right) - \alpha(1-\alpha)\frac{nF\Delta E_p}{2.3RT} \quad (7)$$

The α values were determined from the slope of $E_{p,c}$ *versus* logν plot for the cases $\Delta E_p > 200/n$ mV. The number of electrons (n) transferred was taken as 4 for pH < 4 and 2 for pH > 4. The standard rate constants determined by Klingler–Kochi and Nicholson methods were found to be different to those determined by Laviron method, which proves the presence of adsorption (Table 2). All of these methods were used in the conditions which they respectively apply. In other words the standard rate constants for Nicholson and Klingler–Kochi methods were determined at high concentrations where adsorption was not effective, while the rate constants determined by the use of Laviron method are those obtained in the conditions where adsorption phenomenon was operative (i.e. at low concentrations).

The standard rate constants determined by Klingler–Kochi and Nicholson methods were found to be different than those determined by Laviron method, which shows the presence of adsorption. The Laviron values were found to be approximately 1000 times larger than Klinger–Kochi and Nicholson values. This indicates that the adsorption phenomenon is operative in the reduction of these compounds.

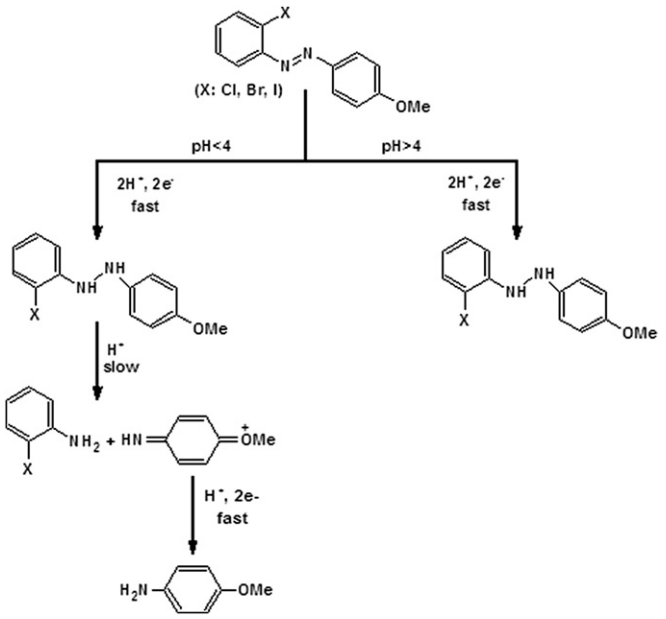
3.5. Electrode reaction mechanism

To propose an electrode reaction mechanism for compounds **I**–**III**, our experimental results and the data reported in literature was taken into consideration. The number of electrons transferred in the first reduction peaks for compounds **I**–**III** was found to be different for pH values above and below 4, as reported in literature [7, 11, 15–17, 25, 26].

Holleck et al. [24] reported that 2′-halogenated-4-methoxyoazobenzene derivatives gave a two electron transfer reaction for the first peak and indicated that the second peak corresponds to catalytic hydrogen wave, which disappeared upon the addition of a surface-active compound.

Accordingly, the electrode reaction mechanism of 2′-halogenated-4-methoxyazobenzene derivatives in media which above and below pH 4 are given as follows in Scheme 1.

Since the entire step in this mechanism takes place at the same potential, there occurs a single reduction peak corresponding to the transfer of four electrons. This reaction stops at the first step when pH > 4 only with two electron transfer [6,9,15–17]. A TLC analysis of



Scheme 1. Electrode reaction mechanism for 2′-halogenated-4-methoxyazobenzene derivatives on mercury electrode in aqueous media.

the bulk electrolysis products gave one and three products for pH > 4 and pH < 4, respectively. The polarographic reduction products of azo compounds have also been analyzed by TLC [6] and HPLC [32].

4. Conclusions

The reduction of the 2′-halogenated-4-methoxyazobenzene derivatives was found to be quasi-reversible since 2×10^{-5} $v^{1/2} < k_s < 0.3\ v^{1/2}$.

The electrochemical reduction of 2′-halogenated-4-methoxyazobenzene derivatives was found to take place by four and two electron transfers in pH < 4 and, pH > 4 media. The mechanistic criteria also show that the reaction follows ECE in pH < 4 and EC in pH > 4 media, respectively.

The irreversible second peak was attributed to the catalytic hydrogen wave. The half wave potential decreases (pH < 4) and stabilizes as the medium becomes more basic. The heterogeneous rate constants were found to be higher at higher pH values. The amount of 2′-halogenated-4-methoxyazobenzene derivatives adsorbed upon the electrode was found to follow the order of the molecular size of the substituents attached as I > Br > Cl.

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