Electrochemical Investigation of 4′-Haloderivatives of N,N-Dimethyl-4-Aminoazobenzene

Mustafa UÇAR, Ali Osman SOLAK[*]
Ankara University, Faculty of Science, Department of Chemistry, Tandoğan, Ankara-TURKEY
e-mail: A.Osman.Solak@science.ankara.edu.tr
M. Levent AKSU
Gazi University, Faculty of Education, Department of Chemistry, Beşevler, Ankara-TURKEY
Mehmet TOY
Ondokuz Mayıs University, Faculty of Education, Department of Chemistry, Amasya-TURKEY

In this study, the electrochemical behaviour of 4′-halogene-N,N-dimethyl-4-aminoazobenzene derivatives were investigated using various polarographic and voltammetric methods. The peak potentials of these derivatives were observed to shift towards negative values with increase in pH. The standard rate constants were determined with (Laviron technique) or without (Nicholson and Klingler-Kochi techniques) taking the adsorption phenomena into account. The diffusion coefficients were calculated from the cyclic voltammetric data using the method developed by Garrido. The amount of adsorbed substances (surface excess values) and transfer coefficients for the electron transfer were also determined. These compounds can be quantitatively determined between 1×10^{-5} M to 2×10^{-7} M with DPP.

Key Words: Azo compounds, polarography, cyclic voltammetry, rate constant, adsorption.

Introduction

The electrochemical behaviour of azo compounds has attracted great interest in recent years due to their carcinogenic potency and their use in textile and pharmaceutical industries as dyes and colouring agents[1−3]. They are also the starting materials in the synthesis of many organic compounds[4−5]. Therefore, the electrochemical investigation of these compounds can shed light on their various usages. Kolthoff and Lingane[6] were the first to examine the polarographic reduction of azobenzene and its derivatives.

The electrochemical behaviour of azo compounds in acidic and basic media was investigated by the use of constant potential coulometry, differential pulse polarography, ac polarography, sampled current polarography, cyclic voltammetry, and linear sweep voltammetry[7−13].

Although the electrochemical behaviour of these compounds in both aqueous and non-aqueous media has been widely studied, there is no systematic study concerning the effect of adsorption upon the electro-

[*]To whom any correspondence should be addressed

chemistry and kinetics of these compounds in the literature. Adsorption plays an important role in their behaviour. The only mention of this effect appeared in studies by Florence[14], and Pezzatini and Guidelli[15].

This paper mainly concerns the electrochemical behaviour and mechanism of various 4′-halogen-N,N-dimethyl-4-aminoazobenzene derivatives in the presence of adsorption using the methods developed by Laviron[16] and Garrido[17]. The data without taking adsorption phenomena into account using Nicholson[18] and Klingler-Kochi[19] methods are also given. Also, the surface excess concentration, transfer coefficients, standard heterogeneous rate constants (k_s) and the number of electrons transferred of 4′-halogene-N,N-dimethyl-4-aminoazobenzene derivatives (I, II, III) were determined using chronocoulometry and constant potential electrolysis.

The general structure of the 4′-halogene-N,N-dimethyl-4-aminoazobenzene derivates investigated is

$$X \longrightarrow \text{\Large\bigcirc} \longrightarrow N=N \longrightarrow \text{\Large\bigcirc} \longrightarrow N(CH_3)_2$$

4′-halogene-N,N-dimethyl-4-aminoazobenzene

where X= Cl (I), Br (II), I (III).

Experimental

Apparatus

The polarographic measurements were carried out with a BAS 100B Electrochemical Analyser equipped with a BAS 100B Cell Stand, a PAR 303A static mercury drop electrode (SMDE) and a PAR Model 305 stirrer. All solutions were deaerated for 10 min with pure nitrogen, deoxygenated with vanadium chloride solution, concentrated HCl and amalgamated zinc, and blanketed thereafter. The pH values of the solutions were recorded by an ORION 720A pH-meter. The buffer solutions used were Britton-Robinson type with pH values of 2-12. The polarographic and voltammetric experiments were carried out with SMDE in a three-electrode cell equipped with Pt wire auxiliary and Ag/AgCl reference electrodes. Cyclic voltammetric, and chronoamperometric experiments were performed with a hanging mercury drop electrode (HMDE) having a surface area of $0.0145\,\text{cm}^2$. The constant potential electrolysis was carried out using a mercury pool electrode with a surface area of $19.6\,\text{cm}^2$. The number of electrons was calculated from the amount of charge passed ($Q = nFN$) after 68.15 minutes of electrolysis. All the measurements were taken at laboratory temperature ($25 \pm 1°C$) and no maximum suppressor was used.

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 ELGASTAT water purification system.

The aromatic azo compounds used were synthesized according to the literature[20] and their purities were checked with mp determination, and UV, IR and NMR spectroscopy.

Results and Discussion

Voltammetric results

4′-halogene-N,N-dimethyl-4-aminoazobenzene derivatives were found to give two reduction waves in both acidic and basic media. However, the second peaks are too ill defined to be of use for quantitative and qualitative purposes. The cyclic voltammograms of 4′-Cl-N,N-dimethyl-4-aminoazobenzene obtained in both acidic and basic media are given in Figures 1a and 1b as an example. The first cathodic peak is due to the reduction of -N=N- group to -NH-NH- in basic, and the breakage of the -NH-NH- bond in acidic media. The second cathodic peak is most probably due to the catalytic hydrogen wave, as mentioned in the literature[21−24]. The first reduction peak of 4′-Cl-N,N-dimethyl-4-aminoazobenzene was observed at -419 mV in acidic ($\approx$pH 5) and -633 mV in basic media ($\approx$pH 9). There appears an anodic peak corresponding to the first reduction peak of 4′-halogene-N,N-dimethyl-4-aminoazobenzene derivatives above a pH value of 7. The reduction peak potentials shift to negative values as the medium becomes more basic.
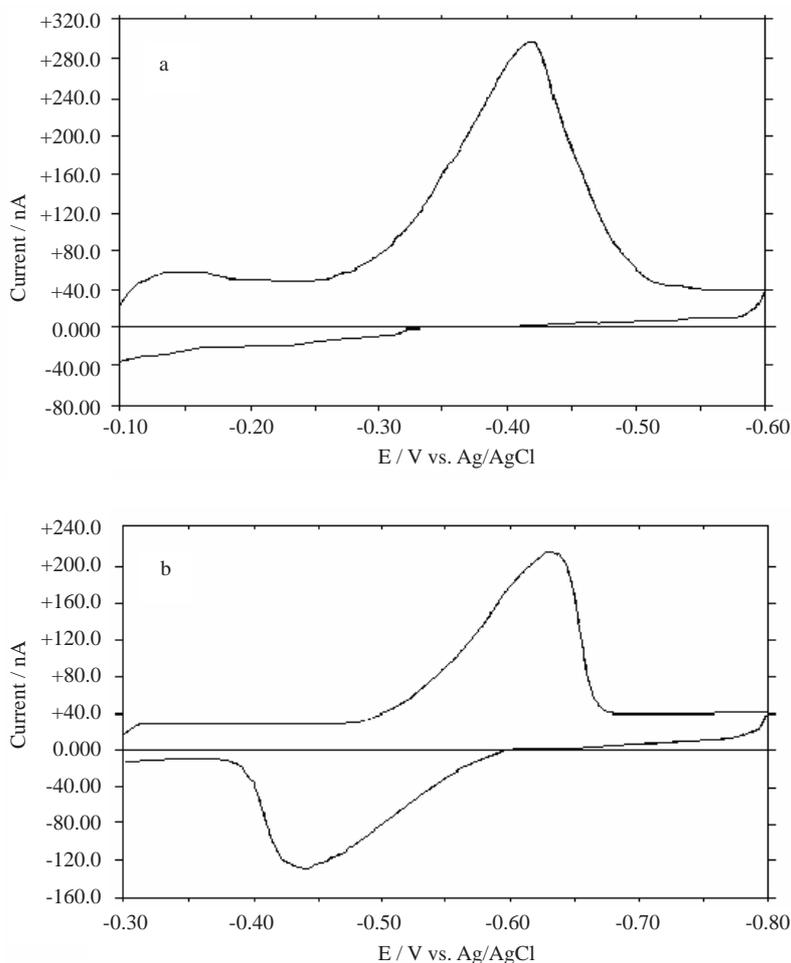

Figure 1. The cyclic voltammogram of 1.67×10^{-5} M 4′-Cl-N,N-dimethyl-4-aminoazobenzene in (a) acidic (pH 5.23), (b) basic media (pH 9.01) *[The medium: 1:5 v/v (EtOH:BR), Scan Rate = 100 mV/s, with HMDE and Ag/AgCl reference electrode)].*

The $E_{1/2}$-pH graphs of sampled current polarographic experiments for all derivatives were found to be linear (Figure 2). The observed shift in $E_{1/2}$ with decreasing pH to more positive values can be explained by the preliminary protonation of the azo group, leading to a decrease in the electron density in the region of the bond between two nitrogen atoms, thus easing the reduction. This dependence indicates that there is a proton transfer in electrode reactions.
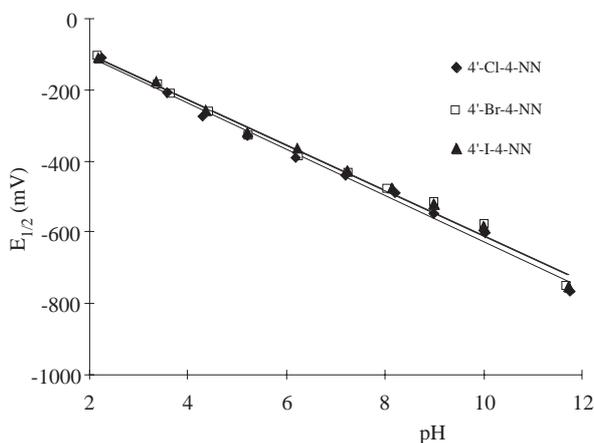

Figure 2. The change in half wave potentials ($E_{1/2}$) of 1.67×10^{-5} M 4'-halogene-N,N-dimethyl-4-aminoazobenzene derivatives with pH *[The medium: 1:5 v/v (EtOH:BR), Scan Rate = 10 mV/s, Drop time: 1 s with SMDE and Ag/AgCl reference electrode)].*

The limiting currents of N,N-dimethyl-4-aminoazobenzene derivatives with pH give an S-shaped curve (Figure 3). It can also be seen from Figure 3 that the limiting current observed in acidic medium is roughly twice as large as that in basic medium, which can be explained by a change in the number of exchanged electrons on transition from acidic to alkaline solution. This is in complete accordance with the literature[25-26].
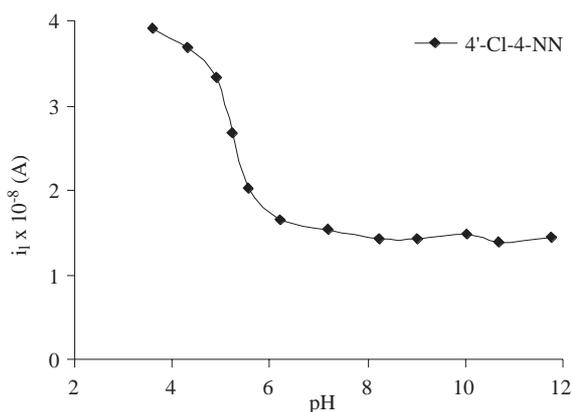

Figure 3. The change in limiting current of 1.67×10^{-5} M 4'-chloride-N,N-dimethyl-4-aminoazobenzene with pH *[The medium: 1:5 v/v (EtOH:BR), Scan Rate=10 mV/s, Drop time=1 s with SMDE and Ag/AgCl reference electrode].*

The effect of 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 (1×10^{-5} M),

which may be attributed to the adsorption phenomenon. The linear increase in current with concentration at lower concentration range creates the possibility of quantitative determination of these compounds using differential pulse polarography.

Table 1. The change in the peak potentials and the peak currents belonging to the first reduction waves of 4′-iodine-N,N-dimethyl-4-aminoazobenzene derivatives with concentration in acidic medium (pH 5.08) *[The medium: 1:5 v/v (EtOH:BR), and Ag/AgCl reference electrode)].*

	DPP	
C (mol/L)	E_p (mV)	i_p A
1.67×10^{-7}	-340	6.00×10^{-9}
5.00×10^{-7}	-340	1.16×10^{-8}
1.67×10^{-6}	-340	1.43×10^{-8}
5.06×10^{-6}	-350	4.54×10^{-8}
1.67×10^{-5}	-340	1.52×10^{-7}

(R) for C (mol/L) – peak current (A) regression coefficient 0.9987 for DPP.

The dependence of the peak heights and peak potentials on concentration of the depolarizer is linear between 1.67×10^{-7} to 1×10^{-5} M. These results are given in Table 1.

The Nicholson-Shain criteria[27] (i.e. the plot of current function against the logarithm of the scan rate) revealed that the reduction of the –N=N- bond is quasi-reversible for all the derivatives investigated and the degree of reversibility changed from one derivative to another. The half wave potentials are observed to change with the drop time, which indicates that the system is not reversible. The graph of potential against log $(i_d$-i)/i is supposed to be linear in a reversible case with a slope of 59/n mV. The slope of this linear graph is more than 59/n mV, indicating irreversibility, which may arise from slow electron transfer, adsorption or chemical complications. Cathodic peak current increased with an increase in $v^{1/2}$ and the i_p^a / i_p^c ratio tended to be unity[28].

Effect of adsorption

4′-halogene-N,N-dimethyl-4-aminoazobenzene derivatives are large molecule compounds. That is why one has to determine whether adsorption phenomenon is present and affects the electrode reaction. The most useful electroanalytical technique to investigate the adsorption phenomena is cyclic voltammetry and there are a few ways of determining adsorption using this technique[28,29].

The logi_p versus log$v$ plots are given for each compound in Figure 4. The slopes of these graphs are greater than 0.5 and approximately 0.8 for all these derivatives. These results indicate that the adsorption phenomenon has an effect[28−30]. Also the linear shape of i_p^c/C versus C graph at low concentrations (Figure 5) and the decrease of current function $(i_p^c/Cv^{1/2})$ with the increasing scan rate are further indications of adsorption[31].
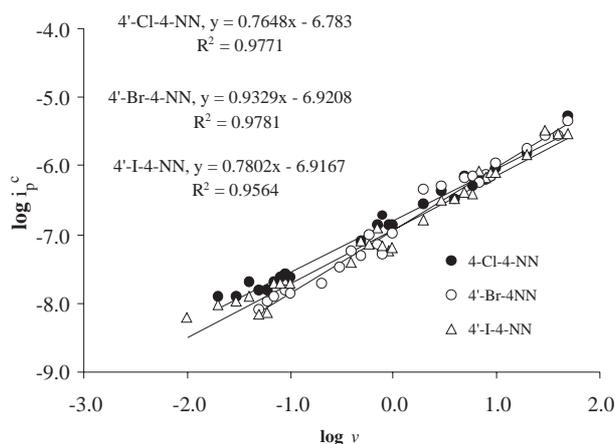
Figure 4. $\log i_p$-$\log v$ graphs of 1.67×10^{-7} M 4′-halogene-4-N,N-dimethylaminoazobenzene derivatives in basic medium *[The medium: 1:5 v/v (EtOH:BR), with HMDE and Ag/AgCl reference electrode].*
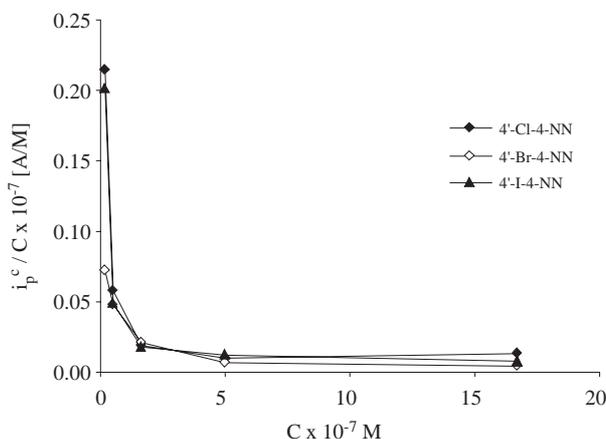

Figure 5. The change in i_p^c/C ratio of 1.67×10^{-7} M 4′-halogene-N,N-dimethyl-4-aminobenzene derivatives with concentration in basic medium *[The medium: 1:5 v/v (EtOH:BR), Scan Rate =100 mV/s, with HMDE and Ag/AgCl reference electrode)].*

The surface excess Γ values were determined by the use of Q-$t^{1/2}$ graphs. The extrapolation of the Q-$t^{1/2}$ graph of the supporting electrolyte and the solution containing N,N-dimethyl-4-aminoazobenzene derivatives to $t^{1/2} = 0$ point gives us 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 $Q_{ads} = nFA\Gamma$ [32].

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

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.[33] determined the maximum adsorption of azobenzene in water + ethanol to be 2.5×10^{-10} mol.cm^{-2}. However, they carried out their study in the presence of surface-active reagents.

Table 2. Diffusion coefficients, the amount of reactant adsorbed on the mercury surface (Γ, mol.cm^{-2}), standard rate constants (k$_s$) values in 1:5 v/v (EtOH:BR buffer), C $= 1.67 \times 10^{-5}$ M 4′-halogene-N,N-dimethyl-4-aminoazobenzene derivatives in basic media (pH 9.32).

Compound	(a) Cottrell Diffusion coefficient (D) (cm^2 s^{-1}) D $\pm$ ts/N$^{1/2}$	(b) Garrido Diffusion coefficient (D) (cm^{2}s^{-1}) D $\pm$ ts/N$^{1/2}$	(c) Klingler-Kochi k$_s$ (cms^{-1}) k$_s\pm$ ts/N$^{1/2}$	(d) Nicholson k$_s$ (cms^{-1}) k$_s\pm$ ts/N$^{1/2}$	(e)* Laviron k$_s$ (s^{-1}) k$_s\pm$ ts/N$^{1/2}$	(f) Γ (mol.cm^{-2}) $\Gamma\pm$ ts/N$^{1/2}$
4′-Cl-4-N,N	$2.10\times10^{-5}\pm$ 1.30×10^{-6}	$6.58\times10^{-6}\pm$ 1.78×10^{-7}	$0.93\times10^{-4}\pm$ 0.67×10^{-5}	$69.02\times10^{-4}\pm$ 38.47×10^{-5}	$2.47\times10^{-1}\pm$ 2.23×10^{-2}	$2.40\times10^{-11}\pm$ 1.08×10^{-12}
4′-Br-4-N,N	$5.72\times10^{-4}\pm$ 2.80×10^{-5}	6.63×10^{-6} $\pm$ 2.08×10^{-7}	$1.89\times10^{-4}\pm$ 1.25×10^{-5}	$79.13\times10^{-4}\pm$ 56.86×10^{-5}	$3.01\times10^{-1}\pm$ 1.64×10^{-2}	$5.97\times10^{-11}\pm$ 3.08×10^{-12}
4′-I-4-N,N	$1.58\times10^{-5}\pm$ 1.21×10^{-6}	8.22×10^{-6} $\pm$ 1.63×10^{-7}	$1.84\times10^{-4}\pm$ 0.72×10^{-5}	$81.61\times10^{-4}\pm$ 35.83×10^{-5}	$3.76\times10^{-1}\pm$ 2.76×10^{-2}	$1.32\times10^{-11}\pm$ 1.03×10^{-12}

The medium: 1:5 v/v (EtOH:BR), and Ag/AgCl reference electrode.

a: 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: Calculated from Eq (3), considering adsorption (t$_p$ = 15 s),

c: Calculated from Eq (4-5), ignoring adsorption (mean α value for the cathodic peak is 0.40),

d: Calculated from Eq (6), ignoring adsorption,

e*: C $= 1.67 \times 10^{-7}$M, Calculated from Eq (7), considering adsorption (for confidence interval of 95 %, mean α value for the cathodic peak is 0.40),

f: Q$_{dl}$ $= 3.3 \times 10^{-9}$ C (Eq 1), (Pulse amplitude 250 ms , E$_1$ = -400 mV and E$_2$ = -900 mV).

Determination of standard rate constants

The standard rate constants of 4′-halogene-N,N-dimethyl-4-aminobenzene derivatives were calculated by three different methods. Two of these methods, namely the Klingler-Kochi and Nicholson, assume diffusion controlled current. Another method, by Laviron, assumes adsorption at the 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 the Cottrell equation

$$i = \frac{nFACD^{1/2}}{\pi^{1/2}t^{1/2}} \tag{2}$$

This equation is very useful in the determination of diffusion coefficients. However, it is only applicable for those cases where 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 the Cottrell equation. In the case of adsorption the following equation derived by Garrido et al. at 25°C is applicable[17].

$$i_p = 1.06 \times 10^6 n^2 ACvD^{1/2}t_p^{1/2} \tag{3}$$

where a Langmuir type of adsorption was assumed with a non-compact monolayer film of adsorbed molecules upon the mercury surface. Here t$_p$ is the adsorption time from the beginning of the life of the drop until 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 lower and more reasonable than those obtained for the uncomplicated case using the Cottrell equation (Table 2). Hence, in all the equations for the calculation of standard rate constants, diffusion coefficients found by Garrido methods were used (Table 2).

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

Klingler-Kochi method for the determination of rate constants

Klingler and Kochi[19] derived the following equation of the standard rate constant for heterogeneous electron transfer (k_s):

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

where

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

As the scan rate is increased, the peak width becomes larger and the transfer coefficient, α, becomes smaller. The mean α values determined for the cathodic peaks were found to be 0.3–0.4 for all the different methods employed. The mean value of the 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[19]. The diffusion coefficients used in equation (4) are the values determined by the Garrido method. The number of electrons was taken as two in basic and four in acidic media as determined by constant potential electrolysis. The number of electrons for the first wave were determined by taking the suitable limiting current values. The k_s values determined for all N,N-dimethyl-4-aminobenzene derivatives in basic media are given in Table 2.

Nicholson method

The k_s value of the electron transfer reaction was also determined by the use of the technique developed by Nicholson[18], using:

$$\psi = \frac{\left(\frac{D_O}{D_R} \right)^{\frac{nFv}{2RT}} k_s}{\sqrt{\pi \frac{nFv}{RT} D_O}} \tag{6}$$

where ψ values were determined from the working graph given by Nicholson and D_O/D_R was taken as unity. The change of $\Delta E_p \times n$ versus k_s value was found to reach a limiting value at high scan rates in basic media (pH 9.32) (Figure 6).

This method requires a continuous equilibrium condition upon the electrode surface and is not suitable for very high or 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 standard rate constants determined by the use of these methods were found to be in good accordance with each other in certain ranges of the scan rate (Table 2).
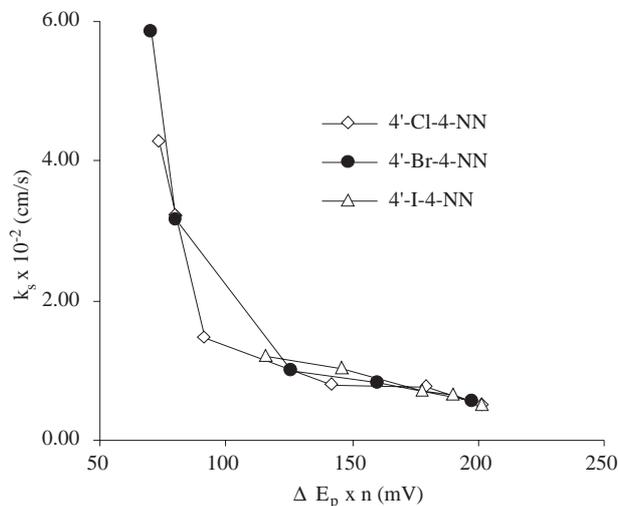

Figure 6. The plot of k_s values of 1.67×10^{-5} M 4′-halogene-4-N,N-dimethylaminoazobenzene derivatives obtained by Nicholson method against $\Delta E_p \times$ n in basic medium (pH 9.32).

Laviron method

Since the adsorption phenomenon was found to have an effect, the rate constants were determined by the use of the method developed by Laviron, which takes the effect of adsorption into account [16]. The k_s values were calculated using

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

The α values were determined from the slope of $E_{p,c}$ vs $\log v$ plot for the cases $\Delta E_p > 200/n$ mV. The number of electrons (n) transferred was taken as two for the basic and four for the acidic media as mentioned above. The k_s values, determined by these three different methods, are tabulated in Table 2. The standard rate constants determined by the Klingler-Kochi and Nicholson methods were found to be different from those determined by the Laviron method, which indicates the presence of adsorption (Table 2). The halogen atoms are easily deformed and can act as electron bridges in some electrode reactions, resulting in a change in the values of the charge transfer coefficients.

All these methods were used in the conditions they respectively apply. In other words, the standard rate constants for the Nicholson and Klingler-Kochi methods were determined at high concentrations where adsorption had no effect, while the rate constants determined by the use of the Laviron method are those obtained in the conditions where the adsorption phenomenon was operative (i.e. at low concentrations).

Mechanism of the electrode reaction

The number of electrons transferred in the polarographic wave was determined by constant potential coulometry. Bulk electrolysis was continued until the current dropped to about 1% of its original value.

The results indicate that the number of electrons transferred is about 4 for acidic (pH 5.2, $E_{p,c}$= -700 mV) and 2 for basic (pH 9.0, $E_{p,c}$= -900 mV) media respectively, which is in good compliance with other studies[25,26,29]. The effects of adsorption were minimized by the use of high concentrations and low scan rates. The reduction of the N,N-dimethyl-4 aminoazobenzene derivatives was found to be quasi-reversible due to the facts that ΔE_p is larger than 59/n (mV), which increased with the scan rate, and the shift of the cathodic peak potential $E_{p,c}$ towards negative values with increasing scan rate. The case $2 \times 10^{-5}v^{1/2} < k_s < 0.3v^{1/2}$ corresponds to a quasi-reversible situation. The k_s values obtained in this study fall into this range.

The ill-defined second peak is most probably due to a catalytic hydrogen wave. This conclusion is based upon the fact that the peak current decreases and $E_{1/2}$ value shifts to negative potential with increasing pH, while the peak currents become stabilized after a certain pH value and the suppression of the peak after the addition of surface active compounds such as Triton X-100. These are the most important features of the catalytic hydrogen waves. The absence of anodic peak even at very high scan rates (50000 mV/s) further verifies this conclusion.

Accordingly, the electrode reaction mechanism of N,N-dimethyl-4-aminoazobenzene derivatives in acidic and basic media is given as follows:
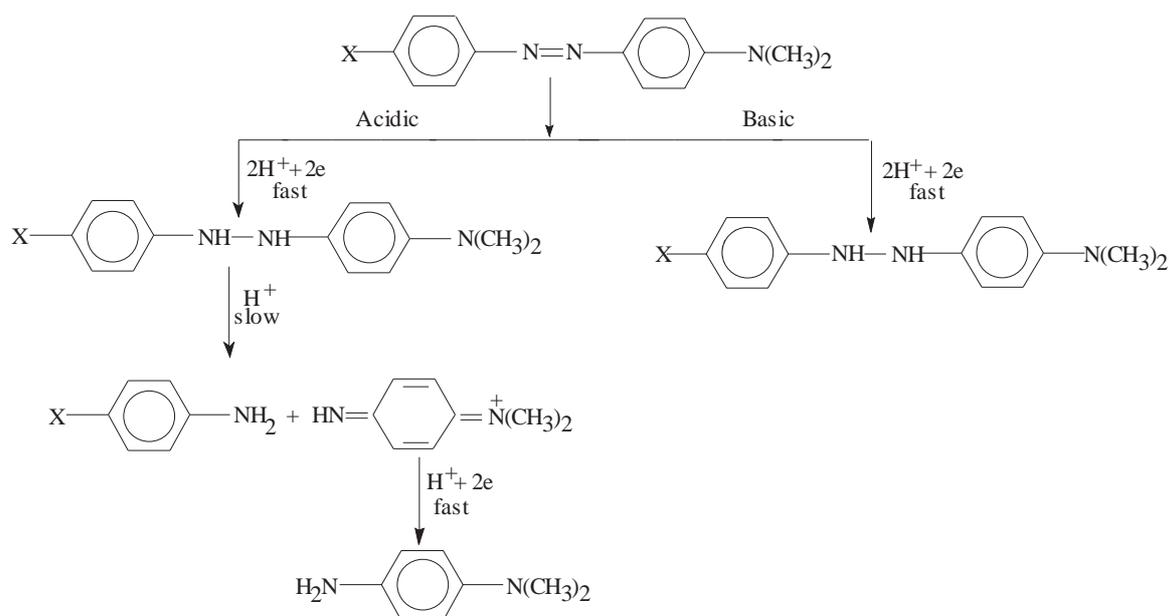
There was no anodic peak observed for the reduction of N,N-dimethyl-4-aminoazobenzene derivatives in acidic media, which verifies this mechanism. Since all the steps in this mechanism take place at the same potential there occurs a single reduction peak corresponding to the transfer of four electrons. This reaction stops at the first step in basic media with two-electron transfer[25,26,29]. The TLC analysis of the bulk electrolysis products gave similar results to the literature[25,26,34]. The polarographic reduction products of azo compounds have also been analysed by HPLC[35].

Acknowledgements

References

1. J. Miller, E. C. Miller and G. C. Finger, **Cancer Res**. **17**, 387 (1975).

2. H. Egan. (Ed): **"Environmental Carcinogens"**. IARC Scientific Pub, Vol, 4. No. 40, Lyon, 1981.

3. C. Carruthers, **Anal. Chim. Acta.**, **86**, 273 (1976).

4. T. M. Florence, **J. Electroanal. Chem.**, **50**, 113 (1974), ibid. **52**, 115 (1974).

5. F. G. Thomas and K. G. Boto, **"The Electrohemistry of Azoxy, Azo and Hydrazo Compounds**. in **The Chemistry of Hydrazo, Azo and Azoxy Groups."** (Ed: S. Patai). Part 1. Chapter 12, John Wiley & Sons. London. p. 443, 1975.

6. I. M. Kolthoff and J. J. Lingane, **"Polarography"** New York, Interscience, 1952.

7. J. P. Stradins and V. T. Glezer, **"Azo, Azoxy and Diazo Compounds**. in. **Encyclopedia of Electro-chemistry of the Elements: Organic Section"** Vol:**XIII**. (Eds: A.J. Bard and H. Lund). Chapter 4, Marcel Dekker, New York p.163, 1984.

8. W. M. Schwarz and I. Shain, **J. Phys. Chem.**, **69**, 30 (1965).

9. J. Barek, A. Berka and J. Zima, Collect. Czech. Chem. Commun., **50**, 1819 (1985).

10. P. N. Gupta and A. Raina, **J. Ind. Chem.**, **62**, 363 (1985).

11. G. Klopman and N. Doddapaneni, **J. Phys. Chem.**, **78**, 1825 (1974).

12. N. Menek, **Analytical Letters.**, **31**, 275 (1998).

13. N. Menek, S. Topçu and M. Uçar, **Analytical Letters.**, **34 (10)**, 1733 (2001).

14. T. M. Florence, **Aust. J. Chem.**, **18**, 609 (1965), ibid. 18, 619 (1965).

15. G. Pezzatini and R. Guidelli, **J. Chem. Soc. Faraday. Trans I**., **69**, 794 (1973).

16. E. Laviron, **J. Electroanal. Chem.**, **101** 19 (1979).

17. J. A. Garrido, R. M. Rodriguez, R. M. Bastida and E. Brillas, **J. Electroanal. Chem.**, **324**, 19 (1992).

18. R. S. Nicholson, **Anal. Chem. 37**, 1351 (1965).

19. R. J. Klingler and J. K. Kochi, **J. Phys. Chem.**, **85**, 1731 (1981).

20. S. Yamamoto, N. Nishimura, and S. Hasegawa, **Bulletin of the Chemical Society of Japan.**, **44**, 2018 (1971).

21. H. A. Laitinen and T. J. Kneip, **J. Amer. Chem. Soc.**, **78**, 736 (1956).

22. I. M. Issa, R. M. Issa, Y. M. Temerk and M. R. Mahmoud, **Electrochim. Acta.**, 18, 139 (1973).

23. L. Holleck, S. Vavricka and M. Heyrovsky, **Electrochimica Acta.**, **15**, 45 (1970).

24. L. Holleck, D. Jannakoudakis. and A.Videnau, **Electrochim Acta.**, **121**, 523 (1967).

25. J. Barek, H. Halodova-Blahova and J. Zima, **Collect. Czech. Chem. Commun.**, **54** 1549 (1989).

26. J. Barek, J. Kubickova, V. Mejstrik, O. Petira and J. Zima, **Collect. Czech. Chem. Commun.**, **55**, 2904 (1990), ibid. **55**, 2636 (1990).

27. R. S. Nicholson and I. Shain, **Anal. Chem.**, **36**, 706 (1964).

28. A. J. Bard and L. R. Faulkner, **"Electrochemical Methods: Fundamentals and Applications"**, John Wiley and Sons, New York 1980.

29. M. Uçar, PhD. Thesis, Ankara University, Ankara (1998).

30. D. K. Gosser. **"Cyclic Voltammetry"**. VCH Publishers, Inc., New York 1994.

31. R. H. Wopschall and I. Shain, **Anal. Chem.**, **39**, 1514 (1967); ibid. **39**, 1527 (1967); ibid. **39**, 1535 (1967).

32. F.C. Anson, **Anal. Chem.**, **38**, 54 (1966).

33. M.L. Foresti, F. Pergola and R. Guidelli., **J. Chem. Soc. Faraday Trans. I**, **75**, 155 (1979).

34. J. Barek, T. J. Pastor, S. Votavova and J. Zima, **Collect. Czech. Chem. Com.**, **52**, 2149 (1987).

35. A. Burcinova, K. Stulik, V. Pacakova, **J. Chromatography**. **389**, 397 (1987).