THE POLAROGRAPHIC AND VOLTAMMETRIC DETERMINATION OF 4-AMINOAZOBENZENE*

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The polarographic reduction of genotoxic 4-aminoazobenzene was studied, a mechanism was proposed and conditions were found for the analytical determination using Tast polarography in the range $1 . 10^{-4}$–$2 . 10^{-6}$ mol l^{-1} and differential pulse polarography in the range $1 . 10^{-4}$–$2 . 10^{-7}$ mol l^{-1}. The sensitivity can be further increased by using fast scan differential pulse voltammetry at a hanging mercury drop electrode combined with adsorptive accumulation of the test substance on the surface of the working electrode, permitting the determination to be carried out in the range $1 . 10^{-7}$ – $2 . 10^{-10}$ mol l^{-1}. The anodic oxidation of 4-aminoazobenzene was also studied at a glassy carbon solid electrode and conditions were found for its analytical utilization in the range $1 . 10^{-4}$–$2 . 10^{-6}$ mol l^{-1} using classical or differential pulse voltammetry at a rotating disk electrode.

The aminoderivatives of azobenzene are suspected of being chemical carcinogens[1,2] that, even in trace amounts, can have a detrimental effect on biological processes. Study of the action of these substances requires sensitive and selective methods for their determination[3].

The ready polarographic reduction of azocompounds, whose mechanism is discussed in monographs[4–6], permits the very sensitive determination of a number of genotoxic derivatives of azobenzene[7–10], whose selectivity can be increased by combination with TLC[8] or HPLC[11]. The sensitivity can be increased by using modern polarographic or voltammetric techniques, or by combination with adsorptive accumulation of the test substance on the surface of a hanging mercury drop.

The ready anodic oxidation of the amino group on an aromatic ring suggests the possibility of determining 4-aminoazobenzene by voltammetry at a solid electrode. The oxidation of some azobenzene derivatives has been studied orientatively to determine optimum conditions for their electrochemical detection in combination

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with HPLC[11] and a number of references to the electrochemical oxidation of aromatic amines can be found in the monographs[12,13]. These data suggested that – as for the oxidation of aniline – the reaction would first involve one-electron oxidation of 4-aminoazobenzene with formation of a radical cation which would then undergo further reactions. The determination limit attainable on the basis of anodic oxidation on solid electrodes is usually higher than that at mercury electrodes. However, strongly acid media can be used, where the reduction of the azo group begins to coincide with the dissolution of mercury. Further, it can be expected that anodic voltammetry will be useful for the determination of aromatic amines formed by reductive splitting of the test azo substance, which would be useful for analytical study of the efficiency of destruction of this genotoxic compound.

Consequently, this work deals with the determination of 4-aminoazobenzene by modern polarographic and voltammetric methods, both on the basis of its cathodic reduction and utilizing its anodic oxidation. Work was carried out in mixed methanol–water medium, ensuring sufficient solubility of the test substance.

EXPERIMENTAL

Reagents

Solutions of 4-aminoazobenzene in methanol were stored in the dark. Spectrophotometric study of their stability indicated that $1 . 10^{-3}$ to $1 . 10^{-5}$ mol l^{-1} solutions are stable for 60 days. More dilute solutions were prepared daily. The purity of the substance was checked by thin layer[14] and high performance liquid[11] chromatography and the concentrations of the stock solutions were checked titanometrically[15]. A 0·5% solution of Triton X-100 (alkylphenylpolyethyleneglycol, Serva, Heidelberg) and common Britton–Robinson buffer solutions were employed. The chemicals and solvents employed were of p.a. purity and water was doubly distilled in a quartz apparatus. All the solvents and solutions were stored in glass vessels as contact with polyethylene leads to contamination by traces of substances that are detrimental to adsorptive accumulation.

Apparatus

The polarographic and voltammetric measurements were carried out using a PA 4 polarographic analyzer with an XY 4105 recorder (Laboratorní přístroje, Prague), in a three-electrode arrangement with a platinum foil auxiliary electrode and silver chloride reference electrode, to which the potential values are related. Tast and differential pulse polarography were carried out using a dropping mercury working electrode with a reservoir height of $h = 36$ cm, flow rate of $m = 1{\cdot}62$ mg s^{-1} and drop time of $\tau = 2{\cdot}11$ s (measured at an applied potential of 0 V vs the silver chloride electrode in a medium of 0·1M-KCl). Where not stated otherwise, a polarization rate of 5 mV s^{-1}, mercury reservoir height of 36 cm, electronically controlled drop time of 1 s and pulse height in DPP of -100 mV were employed. Fast scan differential pulse voltammetry (FS DPV) and cyclic voltammetry were carried out using a static mercury drop electrode, SMDE 1 (Laboratorní přístroje, Prague), with a capillary diameter of 0·136 mm, connected as a hanging mercury drop electrode (HMDE). Where not stated otherwise, a polarization rate of 20 mV s^{-1} and maximum drop size given by opening the valve for 160 ms were employed.

The anodic oxidation was studied using a rotating disk electrode, RDE 1 (Laboratorní přístroje, Prague), in either the rotating or stationary mode. The electrode was fitted in a teflon cylinder with a diameter of 12 mm, with a glassy carbon electroactive part with a diameter of 3 mm. Where not stated otherwise, a rotation rate of 2 000 r.p.m. was employed. Prior to each measurement, the electrode was polished lightly with velvet and the curve for the base electrolyte was recorded. Nitrogen was purified as described in the previous communication[10]. A wash bottle containing a mixture of methanol and water in the same ratio as in the test solution was placed prior to the polarographic vessel. The coulometric and spectrophotometric measurements were carried out using the instruments described in the previous work[10]. For the pH measurements of the methanol–buffer (1 : 1) mixture, the pH-meter was calibrated using acetate, borate and phosphate buffers in 50% (v/v) methanol[16,17]. All measurements were carried out at laboratory temperature.

Procedure

The polarographed solution was prepared by adding the required amount of methanol to the solution of 4-aminoazobenzene and diluting to the mark with Britton–Robinson buffer. It was necessary to retain this order of solvent addition, to prevent precipitation of the azo compound from solution. The calibration curves were measured in triplicate and evaluated by linear regression. The determination limit in the concentration range $(2-10) \cdot 10^{-x}$ mol l^{-1} was found[18] as ten times the standard deviation for 10 determinations of the analyte with a concentration of $2 \cdot 10^{-x}$ mol l^{-1}. The peak height in the pulse techniques was measured from the line connecting the minima on both sides of the peak. Otherwise, the procedures were analogous to those described in the previous work[10].

RESULTS AND DISCUSSION

Tast Polarography and Differential Pulse Polarography of 4-Aminoazobenzene on a Dropping Mercury Electrode

The test substance yields a single peak or wave over the whole pH range studied. At pH < 5, the Tast polarograms contained maxima that could be suppressed by the addition of 50 μl of 0·5% Triton X-100 in methanol to 10 ml of polarographed solution. Table I documents the effect of the pH on the Tast and DP polarographic curves. The observed limiting currents are diffusion-controlled, reflected in their linear dependence on the square root of the height of the mercury reservoir.

The observed shift in the half-wave potential of the test substance to more positive values with decreasing pH in the range pH 2·5 to 8 can be described by the relationship $E_{1/2}$(mV) = 66·4 − 78·6 pH (correlation coefficient 0·9987) and, in the range pH 8 − 13·5, by the relationship $E_{1/2}$(mV) = −212·5 − 43·4 pH (correlation coefficient 0·9957). The variation of the peak potential with the pH at pH 2·5 − 8 is described by the relationship E_p(mV) = 78·9 − 75·8 pH (correlation coefficient 0·9977) and, at pH 8 − 13·5, by the relationship E_p(mV) = −165·0 − 45·5 pH (correlation coefficient 0·9754). The character of this dependence can be explained in terms of prior protonation of the azo group, leading to a decrease in the electron density in the region around the N=N bond, thus facilitating the reduction.

It follows from the dependence of the limiting current on the pH (Table I) that twice as many electrons are exchanged in the acidic region compared to the alkaline region. It was confirmed by constant potential coulometry at −750 mV vs SCE that 4 electrons are exchanged at pH 2·5 and 7·9, while only 2 electrons are exchanged at pH 13·4 and at −1 V vs SCE. The coulometric reduction was monitored in acidic and neutral media by Tast polarography and the wave of 4-aminoazobenzene decreased linearly with the charge passed; no new wave appeared. In contrast, an anodic wave appeared at pH 13·4 and formed an almost reversible pair with the cathodic wave; this anodic wave apparently corresponds to the oxidation of 4-aminohydrazobenzene (see Fig. 1). Spectrophotometric study of the coulometric reduction (see Fig. 2) confirms this conclusion as the absorption maximum in the region around 250 nm can apparently be assigned to the hydrazogroup. Logarithmic analysis indicated that this is an irreversible process, and that the degree of irreversibility depends on the pH. This was also confirmed by cyclic voltammetry at the HMDE (see Fig. 3). The presence of the anodic peak at pH 7·9 indicates that 4-aminohydrazobenzene is also a reaction intermediate in the four-electron reduction. It can be assumed in agreement with earlier works[19–22] that four-electron reduction to the corresponding amines occurs in acidic and neutral media. This apparently occurs through an ECE mechanism that includes disproportionation of the intermediary 4-aminohydrazobenzene to form aniline and quinone diimine which is immediately reduced further to *p*-phenylene diamine. (This mechanism is more probable than

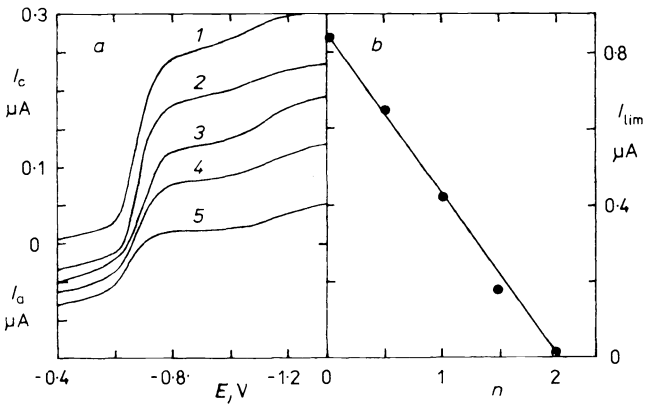

FIG. 1

Tast polarographic study of the coulometric reduction of 4-aminoazobenzene ($c = 1 . 10^{-4}$ mol . l^{-1}) at a constant potential of −1 V vs SCE in Britton–Robinson buffer–methanol medium (1 : 1) at pH 13·4. *a* Tast polarograms after passage of charge corresponding to $n = 0$ (*1*), 0·5 (*2*), 1·0 (*3*), 1·5 (*4*), and 2 (*5*); *b* dependence of the limiting current at −1 V on the charge passed recalculated to the number of electrons *n* corresponding to one molecule of 4-aminoazobenzene

that proposed by Leitinen[23], involving disproportionation of two molecules of 4-aminohydrazobenzene to form the initial 4-aminoazobenzene, aniline and *p*-phenylene diamine.)

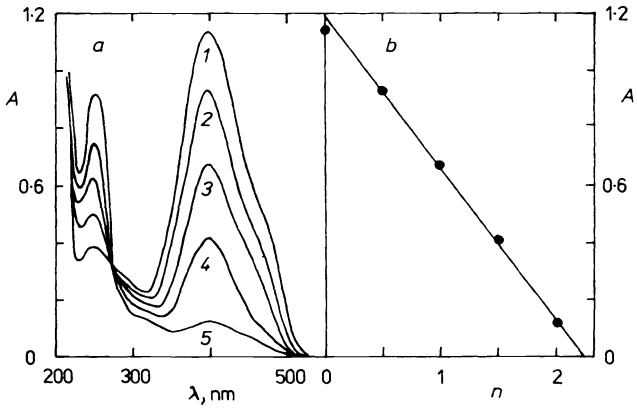

FIG. 2

Spectrophotometric study of the coulometric reduction of 4-aminoazobenzene ($c = 1 . 10^{-4}$ mol . $.l^{-1}$) at a constant potential of -1 V vs SCE in Britton–Robinson buffer–methanol medium (1 : 1 at pH 13·4. *a* Spectra of the solution after passage of charge corresponding to $n = 0$ (*1*), 0·5 (*2*), 1 (*3*), 1·5 (*4*) and 2·0 (*5*); *b* dependence of the absorbance at 400 nm on the charge passed recalculated to the number of electrons *n* corresponding to one molecule of 4-aminoazobenzene

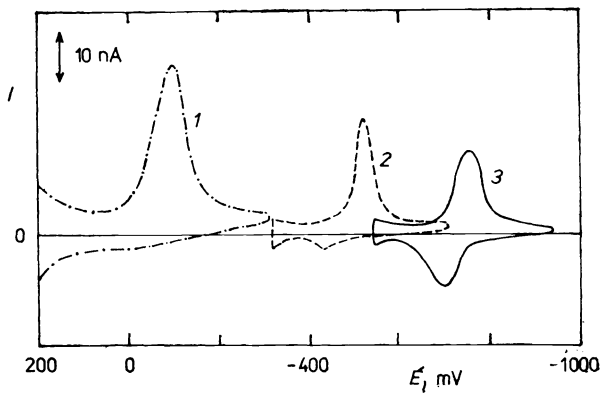

FIG. 3

Cyclic voltammogram of 4-aminoazobenzene ($c = 1 . 10^{-4}$ mol l^{-1}) at a hanging mercury drop electrode in Britton–Robinson buffer–methanol medium (1 : 1) at pH 2·5 (*1*), 7·9 (*2*) and 13·4 (*3*) at a polarization rate of 50 mV s^{-1}

TABLE I

The effect of the pH on the Tast and DP polarographic curves of 4-aminoazobenzene ($c = 1 . 10^{-4}$ mol l^{-1}) in Britton–Robinson buffer–methanol medium (1 : 1)

pH	$E_{1/2}$ mV	I_{lim} μA	Slope[a] mV	E_p mV	I_p μA
2·5	−125	2·15	64	−110	4·13
3·5	−212	2·10	62	−190	4·11
5·0	−323	1·95	56	−295	4·42
5·9	−383	1·97	51	−350	4·05
7·0	−485	1·37	35	−450	3·63
7·9	−556	1·12	42	−530	3·12
8·6	−589	1·05	39	−550	2·98
9·6	−621	1·07	41	−585	2·95
10·4	−659	1·02	41	−630	3·05
11·5	−721	1·00	51	−720	1·91
12·5	−763	1·00	49	−750	2·13
13·4	−782	1·02	49	−745	2·40

[a] Slope of the logarithmic analysis.

TABLE II

The parameters of the calibration curves and determination limits for 4-aminoazobenzene by cathodic voltammetry at a mercury electrode

Method	c mol l^{-1}	Slope μA mol^{-1} l	Intercept μA	Correlation coefficient	L_Q[a] mol l^{-1}
Tast[b]	$(2-10) . 10^{-5}$	$2·00 . 10^4$	$5 . 10^{-3}$	0·9983	—
	$(2-10) . 10^{-6}$	$1·96 . 10^4$	$2 . 10^{-2}$	0·9998	$9 . 10^{-7}$
DPP[b]	$(2-10) . 10^{-5}$	$2·07 . 10^4$	$2 . 10^{-1}$	0·9994	—
	$(2-10) . 10^{-6}$	$2·80 . 10^4$	$3 . 10^{-2}$	0·9998	—
	$(2-10) . 10^{-7}$	$2·39 . 10^4$	$7 . 10^{-3}$	0·9981	$1 . 10^{-7}$
FSDPV[c]	$(2-10) . 10^{-8}$	$1·13 . 10^6$	$-6 . 10^{-3}$	0·9990	—
	$(2-10) . 10^{-9}$	$1·02 . 10^6$	$3 . 10^{-3}$	0·9910	$2 . 10^{-9}$
FSDPV[d]	$(2-10) . 10^{-9}$	$5·35 . 10^6$	$3 . 10^{-4}$	0·9990	—
	$(2-10) . 10^{-10}$	$2·31 . 10^7$	$-4 . 10^{-4}$	0·9991	$2 . 10^{-10}$

[a] Determination limit; [b] Britton–Robinson buffer–methanol (1 : 1), pH 5·9; [c] ten-fold diluted Britton–Robinson buffer–methanol (1 : 1) with pH 7·49 and 300 s accumulation in unstirred solution; [d] 100-fold diluted Britton–Robinson buffer–methanol (95 : 5) with pH 7·19 and 300 s accumulation in stirred solution (recorded 10 s after termination of stirring).

The dependence of the peak height on the pH in differential pulse polarography (DPP) (see Table I) reflects both a change in the number of electrons exchanged and also a change in the reversibility of the studied process. The highest and best developed waves and peaks were obtained at pH 2·5, where the concentration dependences were measured. In Tast polarography at pH 2·5 it was necessary to add Triton X-100 to suppress the maxima formed; the calibration straight line for the concentration range $(2-10) \cdot 10^{-6}$ mol l^{-1} did not pass through the origin. It is thus preferable to employ a pH of 5·9, where a linear calibration curve was obtained for the range $1 \cdot 10^{-4}$ to $2 \cdot 10^{-6}$ mol l^{-1}, with the parameters listed in Table II. The potential of the DPP peak was shifted to more positive values with decreasing concentration, apparently connected with the irreversible character of the electrode process. The peaks of the test substance at pH 2·5 in the concentration range $(2-10) \cdot 10^{-7}$ mol l^{-1} coincide with the dissolution of mercury, complicating evaluation of the peak height. In addition, the dependence of the peak height on the concentration of 4-aminoazobenzene was no longer linear at concentrations above $8 \cdot 10^{-5}$ mol. l^{-1}. It would thus once again seem preferable to employ a medium with pH 5·9, in which a linear concentration dependence with the parameters listed in Table II is obtained in the concentration range $1 \cdot 10^{-4}$ to $2 \cdot 10^{-7}$ mol l^{-1}. It should be pointed out that, as the concentration decreases, the intercept on the ordinate increases, so that it is not longer possible to employ the method of standard additions at concentrations below $1 \cdot 10^{-5}$ mol l^{-1}.

Fast Scan Differential Pulse Voltammetry of 4-Aminoazobenzene at a Hanging Mercury Drop Electrode

Attempts to decrease the analysis time and to improve its sensitivity led to the use of fast scan differential pulse voltammetry (FS DPV). It was found that the dependence of the peak height for 4-aminoazobenzene on the concentration is non-linear (parabolic) in Britton–Robinson buffer–methanol (1 : 1) medium with pH 5·9 in the concentration range $2 \cdot 10^{-7}$ to $1 \cdot 10^{-4}$ mol l^{-1}; this makes analytical use complicated. This phenomenon is apparently a result of passivation of the working electrode, whose surface was not renewed during the measurement, by the products of the electrode reaction. This assumption was also confirmed by the fact that the peak height measured by DPP at a static mercury drop electrode with a constant surface area decreases with increasing drop time and its width simultaneously increases. These problems can be eliminated to a certain degree by employing higher methanol contents. The FS DPV calibration curves are linear in the range $1 \cdot 10^{-4}$ to $2 \cdot 10^{-7}$ mol l^{-1} in a Britton–Robinson buffer–methanol medium (1 : 9) at pH 6·0, although the lines for the concentration ranges $(2-10) \cdot 10^{-6}$ and $(2-10) \cdot 10^{-7}$ mol. l^{-1} do not pass through the origin, so that the method of standard additions cannot be employed.

The sensitivity of the FS DPV method can be further increased on the basis of the fact that the peak height depends on the time elapsed between formation of the drop and recording the voltammogram; this increase can be explained in terms of adsorptive accumulation of 4-aminoazobenzene on the surface of the hanging mercury drop electrode. It can be seen from the measured dependence of the potential and height of the peak on the pH after 60 s of accumulation in unstirred medium (see Fig. 4) that the optimum pH is about 8. The dependence of the peak height on the accumulation time indicates (see Fig. 5) that 300 s accumulation is sufficient to greatly increase the sensitivity. The dependence of the peak height on the concentra-

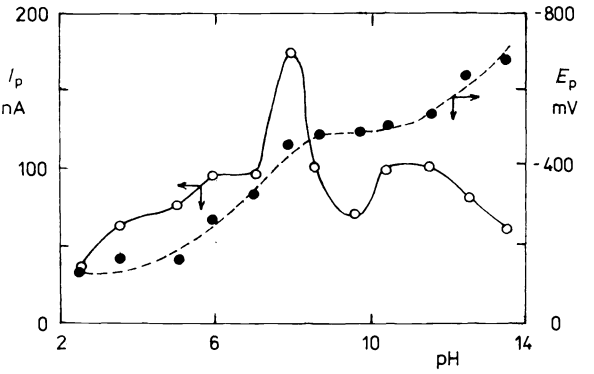

FIG. 4

The effect of the pH on the potential (E_p) and height (I_p) of the peak of 4-aminoazobenzene ($c = 1 . 10^{-6}$ mol l^{-1}) in FS DPV at the HMDE with 60 s accumulation in unstirred Britton–Robinson buffer–methanol medium (1 : 1)

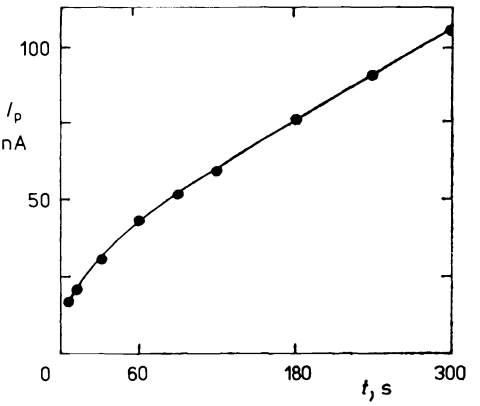

FIG. 5

Dependence of the height of the peak of 4-aminoazobenzene ($c = 1 . 10^{-7}$ mol l^{-1}) on the accumulation time in FS DPV at the HMDE in unstirred Britton–Robinson buffer–methanol medium (1 : 1) at pH 7·9

tion of 4-aminoazobenzene is parabolic in the concentration range $(2-10) \cdot 10^{-7}$ mol. l^{-1}, apparently connected with the maximum possible coverage of the working

TABLE III

The effect of the pH on the DC voltammetric curves of 4-aminoazobenzene ($c = 1 \cdot 10^{-4}$ mol. l^{-1}) in Britton–Robinson buffer–methanol mixture (1 : 1) at a rotating (RDE) and stationary (SDE) glassy carbon disk electrode

pH	RDE[a]		SDE[b]	
	$E_{1/2}$ mV	I_{lim} μA	E_p mV	I_p nA
2·46	915	5·9	900	500
3·46	885	7·2	875	425
4·95	880	6·2	870	475
5·92	865	5·3	860	475
6·95	810	5·9	810	475
7·89	755	2·6	750	325
8·63	690	3·8	680	500
9·57	685	2·0	675	125
10·36	675	2·9	670	100
11·46	640	1·8	—[c]	—[c]
12·49	610	2·0	—[c]	—[c]
13·39	—[c]	—[c]	—[c]	—[c]

[a] Rotation rate 2 000 r.p.m., [b] the DC voltammograms are peaks with a maximum of I_p at potential E_p; [c] the DC voltammograms are so deformed by electrode passivation that they cannot be evaluated.

TABLE IV

The parameters of the calibration curves and determination limits for 4-aminoazobenzene by anodic voltammetry at a rotating disk electrode (2 000 r.p.m.)

Method	c μmol l^{-1}	Slope μA mol^{-1} l	Intercept μA	Correlation coefficient	L_Q[a] μmol l^{-1}
DCV[b]	20—100	$5{\cdot}67 \cdot 10^4$	0·1	0·9997	—
	2—10	$1{\cdot}90 \cdot 10^5$	0·1	0·9992	1·4
DPV[c]	20—100	$5{\cdot}25 \cdot 10^4$	0·5	0·9991	—
	2—10	$1{\cdot}12 \cdot 10^5$	0·1	0·9992	1·2

[a] Determination limit; [b] 1M-CH_3COOH–CH_3OH (1 : 1); [c] Britton–Robinson buffer–methanol (1 : 1), pH 5·92.

electrode by the adsorbed substance. It is useful to suppress the effect of impurities in the base electrolyte by diluting the Britton–Robinson buffer ten-fold, shifting the pH of the mixed medium to a value of 7·49. Under these conditions, a linear concentration dependence with the parameters given in Table II can be obtained in the concentration range $1 . 10^{-7}$ to $2 . 10^{-9}$ mol l^{-1}. The adsorptive accumulation can be increased by stirring the solution and decreasing the methanol content, as the methanol is partly adsorbed on the HMDE and also increases the solubility of 4-aminoazobenzene. A decrease in the methanol content in the polarographed solution to 5% (v/v) yields a linear concentration dependence with the parameters listed in Table II for the concentration range $1 . 10^{-8} - 2 . 10^{-10}$ mol l^{-1}.

Anodic Oxidation of 4-Aminoazobenzene at a Glassy Carbon Disk Electrode

DC Voltammetry

Table III describes the effect of the pH on the classical voltammetric (DCV) curves of 4-aminoazobenzene at rotating and stationary electrodes in a Britton–Robinson buffer–methanol mixture (1 : 1). A single wave was obtained at a rotating electrode in acidic medium, with a half-wave potential that shifted to more positive values with decreasing pH, apparently as a result of protonation of the amino group, leading to

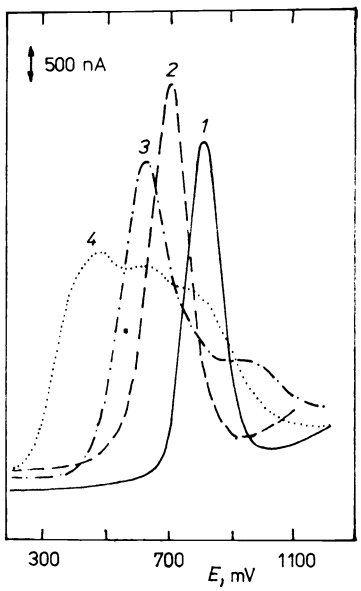

FIG. 6

DP voltammograms of 4-aminoazobenzene ($c = 1 . 10^{-4}$ mol l^{-1}) at a rotating disk electrode (2 000 r.p.m.) in Britton–Robinson buffer–methanol medium (1 : 1) at pH 2·46 (1), 5·92 (2), 8·63 (3) and 12·49 (4)

a decrease in the electron density at the site of most probable electron exchange. The wave is considerably deformed in neutral and alkaline media as a result of electrode passivation, so that the listed half-wave potential and current values are only orientative. This passivation was even more marked for the stationary electrode, where a useful voltammogram cannot be obtained in the alkaline region. Two waves were observed in a 1M-H_2SO_4–CH_3OH (1 : 1) medium with pH 1·23 and in mixtures of 1M-H_3PO_4 and 1M-$HClO_4$ with methanol.

A 1M-CH_3COOH–CH_3OH (1 : 1) medium is best for analytical purposes and yields a single well-developed, reproducible wave at the rotating electrode. The reproducibility of the results can be ensured by polishing the electrode with metallographic paper and velvet and triple recording of the curves of the base electrolyte in a potential range where electrode reduction and oxidation do not occur; this procedure should be repeated before each measurement. When this procedure is followed, the limiting current is controlled by convective diffusion and it is directly proportional to the concentration of 4-aminoazobenzene in the range $1 . 10^{-4}$ to $2 . 10^{-6}$ mol l^{-1} (see Table IV).

DP Voltammetry

The effect of the pH on the differential pulse voltammetric (DPV) curves of 4-aminoazobenzene at a rotating disk electrode is depicted in Fig. 6. The observed shift in the peak potential with decreasing pH to more positive values is once again connected with protonation of the amino group, while the variation of the peak height with the pH reflects the effect of protonation on the reversibility of the studied process, apparently also involving increasing passivation of the electrode in alkaline media.

Medium with pH 5·9 would appear most useful for analytical purposes as it yields the highest, most reproducible and most easily evaluated curves. Concentration dependences in this medium are linear in the range $1 . 10^{-4}$–$2 . 10^{-6}$ mol l^{-1} (see Table IV). The DPV recordings are easier to evaluate and have somewhat higher selectivity than the DCV recordings. The greater dependence on the state of the electrode surface is a disadvantage. The somewhat higher sensitivity of DPV is not reflected in a decrease in the determination limit.

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