

**POLAROGRAPHY
OF N,N-DIMETHYL-4-AMINO-4'-HYDROXYAZOBENZENE
IN WATER-METHANOL MIXTURES***

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The polarographic reduction of N,N-dimethyl-4-amino-4'-hydroxyazobenzene in water-methanol medium was investigated. Evidence is presented for adsorption of the depolarizer on the electrode, and a reduction mechanism is proposed. Conditions are indicated for the determination of this compound in the concentration range 10^{-4} – 10^{-6} mol/l by d.c. polarography, 10^{-5} to $3 \cdot 10^{-7}$ mol/l by Tast polarography, and 10^{-5} – $3 \cdot 10^{-8}$ mol/l by differential pulse polarography.

During the past decade, there has been a considerable growth of interest in the polarographic behaviour of azo derivatives^{1–4}, which is partly related to the carcinogenic properties of many of them^{5–7}. Attention has been paid to the polarography of azobenzene and its monosubstituted derivatives in water-alcohol mixtures^{8–16}, in dimethylformamide^{17,18}, acetonitrile^{19–24}, and pyridine²⁵, and further to their voltammetric behaviour^{3,4,26}. Polarographic reduction of a number of disubstituted azobenzene derivatives has been investigated in the medium of acetonitrile^{27,28}.

N,N-dimethyl-4-amino-4'-hydroxyazobenzene is one of the metabolites of the familiar carcinogenic N,N-dimethyl-4-aminoazobenzene, and shows also carcinogenic properties^{6,7}. Besides analytical aspects, we were therefore interested also in the mechanism of its electroreduction, which may be made use of in the correlation between electrochemical and biological properties. To increase the sensitivity of the determination, we used Tast polarography and differential pulse polarography, which has been used with success in the determination of a number of azo derivatives in trace amounts in biological materials^{29–33}.

EXPERIMENTAL

Reagents

A solution of N,N-dimethyl-4-amino-4'-hydroxyazobenzene in *p.a.* methanol (0.01 mol/l) was prepared by dissolving 0.2413 g of the pure substance (Research Institute of Organic Synthe-

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ses, Pardubice - Rybitví) and making up to 100 ml. More dilute solutions were prepared by dilution of the stock solution with methanol. They were stored under exclusion of light. Britton–Robinson buffers³⁴ were prepared as usual in redistilled water.

Apparatus

A polarograph of the type PA 2 combined with an XY 4103 type pen recorder (Laboratorní přístroje, Prague) was used in the three-electrode mode. The dropping mercury electrode had a rate of flow of 3.80 mg/s at a height of mercury column 25 cm, the drop time was 3.27 s in the medium of equal volumes of methanol and Britton–Robinson buffer of pH 4.0 at a potential of 0 V. The reference electrode was saturated calomel and the auxiliary electrode was Pt wire. The all-glass polarographic vessel was tempered by means of a U 3 thermostat (Mechanik Prüfgeräte, Medingen). Dissolved oxygen was removed by bubbling with purified nitrogen saturated with methanol vapour.

Constant-potential coulometry was carried out with an automatic coulometric analyser OH 404 (Radelkis, Budapest) with automatic compensation of the residual current and electronic integration of the charge passed. An all-glass vessel of 200 ml holding capacity was used, the cathodic and anodic compartment being separated by fritted glass. A mercury pool at the bottom served as cathode, a platinum foil as anode, and a saturated calomel electrode as reference. The solution was magnetically stirred during the analysis and was constantly bubbled with nitrogen.

Spectrophotometric measurements were done with a Specord UV VIS apparatus (Zeiss, Jena) in 2 cm thick quartz cuvettes.

The solution pH was measured with a PHM 62 apparatus (Radiometer, Copenhagen) with a combined glass and saturated calomel electrode. Small volumes were dosed by means of a microburette (Aglá, Burroughs Wellcome, London).

Procedures

Prior to recording the polarographic curve, 10 ml of the solution (buffer, methanol, depolarizer, eventually gelatin) was bubbled with nitrogen for 10 min. The rate of change of the potential was 2 mV/s, temperature 20°C and height of mercury column 49 cm. In Tast and DP polarography, the drop time was maintained at 1 s.

In electrocapillary measurements, the drop time was measured with an electronic stop watch as an average from 10 drops in a mixture of equal volumes of methanol and Britton–Robinson buffer of pH 6.04 or 9.45. The concentration of N,N-dimethyl-4-amino-4'-hydroxyazobenzene was 10^{-6} – 10^{-3} mol/l, oxygen was repelled by nitrogen, and no gelatin was added. To increase the sensitivity of the measurement, the capillary had a smaller internal diameter than in the polarographic measurements. The rate of flow of mercury was 1.25 mg/s at a height of mercury column 25 cm, the drop time was 7.37 s in a mixture of equal volumes of methanol and Britton–Robinson buffer at 0 V. The surface tension was calculated from the drop time t according to $\Delta\sigma/\sigma = 0.973 \Delta t/t$, where σ and t refer to 0.1M-HNO₃ and the increments $\Delta\sigma$ and Δt refer to the change due to passing into the studied solution³⁵. The surface concentration Γ of the adsorbed substance was calculated from the slope of the dependence of the surface tension σ on the logarithm of the molar concentration³⁶

$$\Gamma = -(1/2 \cdot 303RT) (\partial c/\partial \log c)_{E,T,p}$$

at a given pH.

In coulometric determination of the number of exchanged electrons, 81, 45, or 9 ml of the Britton–Robinson buffer was mixed with 8, 44, or 80 ml of methanol, oxygen was repelled, and

the solution was preelectrolysed for 30 min at a potential by 200 mV more negative than the half-wave potential in the same medium. Afterwards, 1 ml of $5 \cdot 10^{-3}$ M N,N-dimethyl-4-amino-4'-hydroxyazobenzene in methanol solution was added, from which oxygen had been removed by nitrogen. The reduction was carried out at the mentioned constant potential and finished after 40 min, when the electrolytic current dropped to the residual current level found previously.

The acid-base properties of the tested compound were investigated by absorption spectrometry in the visible region. Solutions were prepared from 9 ml of Britton-Robinson buffer of pH 2–5, 0.7 ml of methanol, and 0.3 ml of a 10^{-3} mol/l solution of the studied substance in methanol. The resulting pH was also measured.

RESULTS AND DISCUSSION

D.C. POLAROGRAPHY

Influence of pH

In the absence of gelatin, a maximum appeared on the polarographic wave of the studied compound³⁷, which increased with the content of methanol, increasing additions of gelatin being necessary for its suppression. Increasing pH had an opposed effect. Therefore, 0.1 ml of 0.5% gelatin solution was added to 10 ml of the solution in the polarographic cell. The dependence of the polarographic parameters on pH is indicated in Table I, whence it follows that the dependence of $E_{1/2}$ on pH consists of two linear portions. Their parameters calculated by the linear regression method are given in Table II.

Character of the Current

The dependences of the limiting current on the square root of the height of the mercury column, temperature, and depolarizer concentration indicate that the wave height is limited by diffusion of the depolarizer, regardless of the value of pH and content of methanol. The linear dependence of the limiting current on the depolarizer concentration is of analytical importance; its parameters are given in Table III.

Adsorption Phenomena

In the medium of water with or without methanol, aromatic azo compounds are strongly adsorbed on the dropping mercury electrode^{36,38,39}. Therefore, we measured electrocapillary curves (Fig. 1) and calculated the dependence of the surface concentration of the depolarizer on the potential (Fig. 2). It follows from the form of the electrocapillary curves that the depolarizer is adsorbed on the electrode. The sharp increase of the value of Γ at potentials close to -0.6 V can, in analogy to methyl red³⁶, be attributed to reorientation of molecules enabling a larger number of molecules to occupy the same area.

Number of Exchanged Electrons

The slope of the logarithmic analysis (Table I) in the medium of 10 vol.% methanol at pH 7–12 corresponds to the transfer of 1.9 ± 0.1 electron. A somewhat higher

TABLE I

Influence of pH on the polarographic behaviour of $3 \cdot 10^{-5}$ mol/l N,N-dimethyl-4-amino-4'-hydroxyazobenzene at various concentrations of methanol

10 vol.% methanol					
pH	2.60	3.17	4.14	5.14	6.24
$E_{1/2}$, mV	-123	-174	-257	-332	-411
I_{lim} , nA	650	643	650	660	633
Slope ^a , mV	28	26	24	24	26
pH	7.25	8.19	9.12	10.14	11.13
$E_{1/2}$, mV	-490	-554	-607	-664	-728
I_{lim} , nA	653	690	675	605	608
Slope ^a	32	34	31	28	28
50 vol.% methanol					
pH	3.43	4.14	5.01	6.02	7.16
$E_{1/2}$, mV	-191	-250	-320	-396	-493
I_{lim} , nA	640	595	595	590	600
Slope ^a , mV	31	31	31	33	44
pH	8.24	9.00	9.64	10.58	11.78
$E_{1/2}$, mV	-561	-604	-636	-689	-772
I_{lim} , nA	560	560	535	475	445
Slope ^a , mV	45	45	44	41	44
90 vol.% methanol					
pH	4.84	5.47	6.24	7.19	8.30
$E_{1/2}$, mV	-338	-396	-452	-524	-610
I_{lim} , nA	805	820	840	870	795
Slope ^a , mV	59	57	55	56	62
pH	9.33	9.84	10.18	10.77	11.68
$E_{1/2}$, mV	-650	-673	-691	-732	-813
I_{lim} , nA	585	525	485	430	320
Slope ^a , mV	60	59	56	69	66

^a Slope of logarithmic analysis.

number, 2.3 ± 0.2 electron, at pH 2–6 may be due to inaccurate measurement caused by a maximum on the polarographic curve; the limiting current is practically independent of pH. In contrast, in the medium of 50 or 90 vol.% methanol, the limiting current decreases with pH, while the slope of the logarithmic analysis

TABLE II

Parameters of the dependence of $E_{1/2}$ on pH ($E_{1/2} = A \cdot \text{pH} + B$) for N,N-dimethyl-4-amino-4'-hydroxyazobenzene in water-methanol medium

Content of CH ₃ OH vol. %	pH range	A mV	B mV	Correl. coeff.
10	3–8	–78.1	73.8	–0.9994
10	8–12	–60.0	–60.3	–0.9995
50	3–8	–80.3	83.8	–0.9998
50	8–12	–62.9	–35.2	–0.9964
90	4–8	–78.2	36.8	–0.9989
90	8–12	–59.3	–100.4	–0.9787

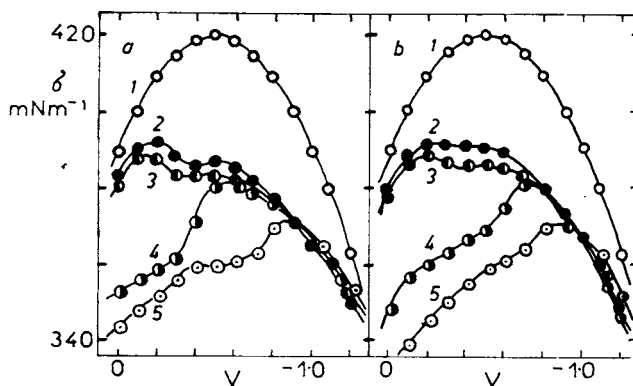


FIG. 1

Dependence of surface tension on potential for 0.1M-NaNO₃ 1 and solutions of N,N-dimethyl-4-amino-4'-hydroxyazobenzene of pH 6.04 (a) and 9.45 (b) containing 50 vol.% methanol at 25°C. Height of mercury head 25 cm, depolarizer concentration (mol/l): 2 0; 3 $1 \cdot 10^{-5}$; 4 $1 \cdot 10^{-4}$; 5 $1 \cdot 10^{-3}$

increases; both effects become more accentuated at higher methanol content (Table I) and can be interpreted in terms of increasing irreversibility.

From coulometry at constant potential, the number of transferred electrons was determined as 4 regardless of the pH value and methanol content (the values were found in the range 3.85–3.95 with standard deviation 0.11).

It was found by comparison that the wave height of *N,N*-dimethyl-4-amino-4'-hydroxyazobenzene in the medium of 10 vol.% methanol is in the whole pH region approximately twice as large as that of non-substituted azobenzene (Fig. 3),

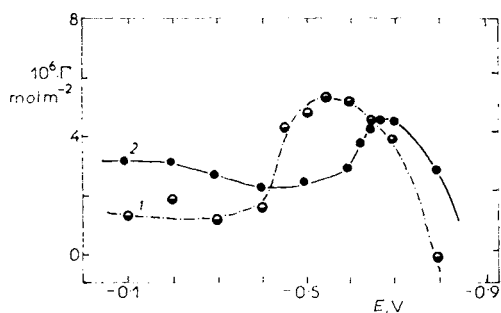


FIG. 2

Dependence of surface concentration Γ of adsorbed *N,N*-dimethyl-4-amino-4'-hydroxyazobenzene on potential at 25°C in presence of 50 vol.% methanol. Height of mercury head 25 cm; pH 6.04 1 and 9.45 2

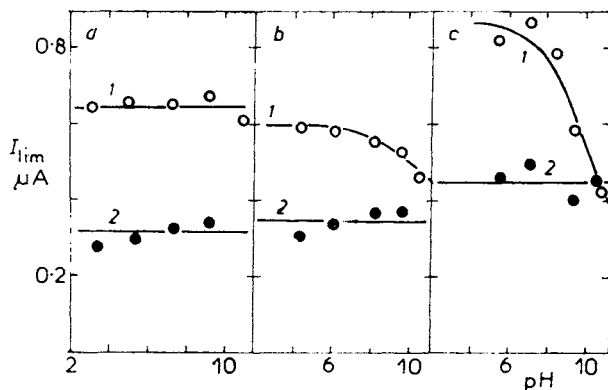


FIG. 3

Dependence of I_{lim} on pH for *N,N*-dimethyl-4-amino-4'-hydroxyazobenzene 1 and azobenzene 2 in the presence of 10 (a), 50 (b), and 90 vol.% (c) methanol. Depolarizer concentration $3 \cdot 10^{-5}$ mol/l, height of mercury head 25 cm

which is known^{8,13,40} to be reduced by two electrons in the whole pH region. This is in accord with the coulometric measurement mentioned above. In the medium of 50 or 90 vol.% methanol, the transfer of 4 electrons can be assumed only in the acidic region, while in the alkaline region the wave heights of both substances are roughly the same, *i.e.* correspond to 2 electrons.

Number of Exchanged Protons

The slope of the dependence of $E_{1/2}$ on pH suggests that at pH 8–12 the same number of protons and electrons is exchanged in the electrode process regardless of the content of methanol. A higher slope at lower pH values is probably related to protonation of the depolarizer in acidic medium (see below). To estimate the number of exchanged protons, use was made of the polarographic behaviour of the depolarizer in weakly buffered medium⁴¹, where the wave is splitted into two waves. The splitting occurs if the concentration of the proton donor is so low that its limiting diffusion current is lower than that of the depolarizer. The more positive wave corresponds to reduction in which the hydrogen ions are supplied by the present acid, whereas for the negative wave the hydrogen ions are supplied by water. The number of exchanged protons, p , can be calculated as⁴¹ $p = (c_{H^+}/c_{dep})(D_{H^+}/D_{dep})^{1/2}$, where c_{H^+} denotes the concentration of H^+ ions at which the more negative wave has just appeared. In our case, $c_{dep} = 5 \cdot 10^{-5}$ mol/l and the approximate values of the diffusion coefficients are^{16,41} $D_{H^+} = 9.3 \cdot 10^{-5}$ cm²/s and $D_{dep} = 3.5 \cdot 10^{-6}$ cm²/s. The polarographic curves are shown in Fig. 4; the more negative wave appears at pH 4.62 ($c_{H^+} = 2.4 \cdot 10^{-5}$ mol/l), hence calculated $p = 2.47$.

Spectrophotometric Study of Acid-Base Equilibrium

The higher slope of the $E_{1/2}$ -pH dependence in acidic medium and the colour changes of the depolarizer are evidence for the role of protonation preceding the electrode

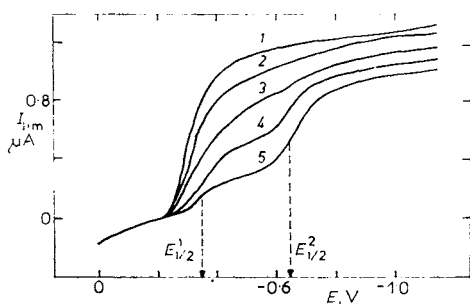


FIG. 4

Polarographic waves of N,N-dimethyl-4-amino-4'-hydroxyazobenzene in nonbuffered medium containing 50 vol.% methanol. Depolarizer concentration $5 \cdot 10^{-5}$ mol/l; pH: 1 4.35; 2 4.48; 3 4.62; 4 4.81; 5 5.36. $E_{1/2}^1$ and $E_{1/2}^2$ denote half-wave potentials

reaction proper. Therefore, we studied the acid–base equilibrium of *N,N*-dimethyl-4-amino-4'-hydroxyazobenzene in 10 vol.% methanol by spectrophotometry in the visible region. The spectra are shown in Fig. 5*a*, the absorbancy of the protonated (red) and nonprotonated (yellow) form as function of pH in Fig. 5*b*. The dissociation constant $K = [H^+][B]/[HB^+]$, where B denotes the studied dye and HB^+ its protonated form, was determined as $pK = 3.3$. Since the protonation of azobenzene does not cause a change in its colour⁴⁰, the observed colour changes may be explained⁴² on the basis of Eq. (A)

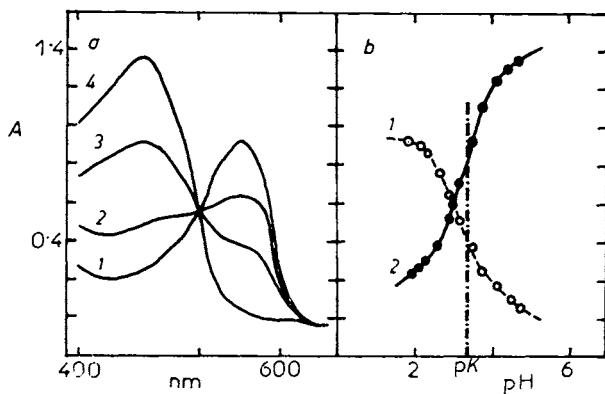
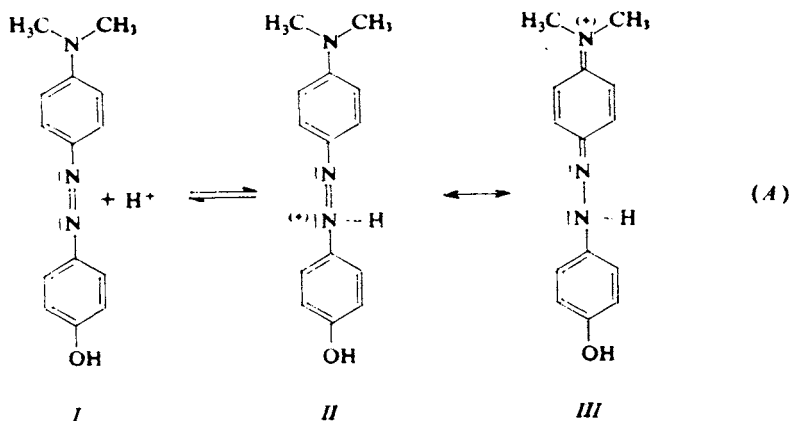


FIG. 5

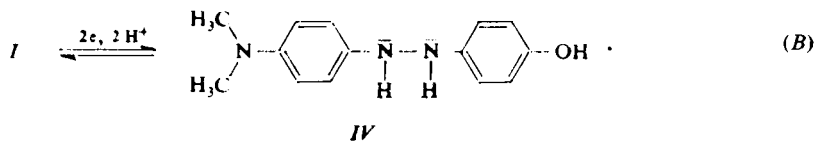
Acid–base behaviour of *N,N*-dimethyl-4-amino-4'-hydroxyazobenzene. *a* Visible absorption spectra of its $3 \cdot 10^{-5}$ mol/l solution in the presence of 10 vol.% methanol at pH: 1 1.89; 2 2.89; 3 3.47; 4 4.64. *b* Dependence of absorbancy of protonized (red) form 1 at 555 nm and nonprotonized (yellow) form 2 at 455 nm on pH

The intense red colour of the dye in acidic medium is apparently due to the presence of conjugated double bonds in the quinone-diummonium grouping of the form III.

Probable Reduction Mechanism

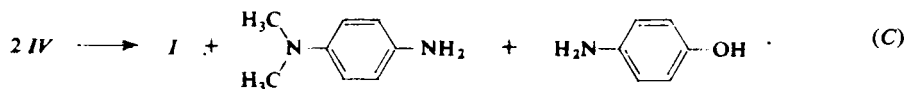
For the polarographic reduction of compounds of the type $R-C_6H_4-N=N-C_6H_4-OH$, where R stands for halogen, H, OH, CH_3 , NO_2 , $COOH$, or SO_3H , in water-alcohol mixtures a reaction mechanism was proposed¹⁶, based on two consecutive one-electron reductions proceeding on the azo group and followed by protonation. In acidic medium, the hydrazo group thus formed is further reduced by two electrons to the corresponding amines. This reaction is, however, slowed down with increasing pH until it stops at 6–7. The described mechanism elucidates the irreversible character of the observed waves as well as the dependence of $E_{1/2}$ and I_{lim} on pH (the value of I_{lim} drops roughly to one half on passing from the acidic to the alkaline medium). However, it cannot be fully valid for the case under study since the observed waves in the medium of 10 vol. % methanol are reversible and the limiting current is independent of pH.

To elucidate the experimental facts, we assume that the rate-determining step in the given medium involves a reversible two-electron reduction of the depolarizer to the corresponding hydrazo compound according to the equation



At pH 7–12, this assumption is in agreement with the slope of the logarithmic analysis and of the $E_{1/2}$ -pH dependence. A higher value of this slope at pH 2–7 is probably due to preceding protonation of the depolarizer in acidic medium (Eq. (A)) causing a decrease of the electron density at the azo group and thus enhancing its reduction.

The fact that a four-electron transfer is derived both from the wave height and coulometry at constant potential in the whole pH range can be elucidated by disproportionation of the formed hydrazo derivative according to



When the disproportionation proceeds rapidly enough, the regenerated azo compound can undergo reduction leading to the apparent value of $n = 4$ found from the wave height and coulometry. Since the single step involving transfer of electrons

is the reduction of the azo group, the slope of the logarithmic analysis corresponds to the transfer of two electrons. The mentioned disproportionation certainly proceeds very rapidly in acidic medium, since the dependence of the limiting current on the square root of the reservoir height and on the temperature brings no evidence for a kinetic process. The half-time of the disproportionation must be incomparably shorter than the drop time, since the limiting current in the medium of 10 vol.% methanol is practically independent of pH. Our deductions are confirmed by the results of the kinetic study of the analogous disproportionation of 4-aminohydrazobenzene-4'-sulphonic acid⁴³. The difference between the values of n found polarographically ($n = 2$) and coulometrically ($n = 4$) in the case of 4-aminoazobenzene, N,N-dimethyl-4-aminoazobenzene¹⁵ and some complicated azo dyes³⁸ was explained analogously. The fact that the mentioned disproportionation does not take place in the case of azobenzene⁹ and its 4-methyl, 4-methoxy, and 4-carboxy derivatives¹⁵, both polarography and coulometry leading to $n = 2$, may be attributed to the electron donor properties of the substituents^{15,16}.

In the medium of 50 or 90 vol.% methanol, the polarographic waves become less reversible and the limiting current decreases with increasing pH (Table I). The former effect may be related to adsorption of methanol on the mercury drop electrode causing hindrance of the electrode reaction, while the latter effect can be attributed to the rate of disproportionation decreasing with increasing pH and content of methanol. At a sufficiently high pH, the half-time of this reaction is apparently much longer than the drop time, so that the wave height of N,N-dimethyl-4-amino-4'-hydroxyazobenzene decreases to a value corresponding to $n = 2$. The coulometrically found value of $n = 4$, however, in the alkaline medium suggests that the mentioned half-time is still much shorter than the time of the coulometric measurements. The assumed drop in the disproportionation rate with increasing pH is also in accord with the mentioned study of the disproportionation of 4-aminohydrazobenzene-4'-sulphonic acid⁴³, according to which the reaction is of the first order with respect to hydrogen ions.

Use in Analysis

N,N-Dimethyl-4-amino-4'-hydroxyazobenzene can be determined by d.c. polarography in the concentration range $10^{-6} - 10^{-4}$ mol/l. The best medium is 50 vol.% methanol, since at lower methanol contents the solubility of the depolarizer is too low. The optimum pH value is 5 or 9, at which the curves have the most suitable form. The linear concentration dependence enables the use of the method of the calibration curve as well as the method of standard addition. At concentrations below 10^{-6} mol/l, the charging current interferes with the measured wave and makes the determination unreliable.

Tast Polarography

Preliminary experiments showed³⁷ that the most suitable medium for Tast polarography is a Britton–Robinson buffer of pH 4 or 9 containing 10 vol.% methanol and 1 drop of 0.5% gelatin per 10 ml. The parameters of the concentration dependence calculated by the linear regression method are given in Table III. The detection limit can be estimated as the concentration at which the wave height is equal to the 5-fold standard deviations of the noise, and is approximately equal to $3 \cdot 10^{-7}$ mol/l. Thus, the sensitivity of the determination by Tast polarography is sensibly increased in comparison with d.c. polarography.

TABLE III

Parameters of the dependence of I_{lim} or I_p on the concentration of N,N-dimethyl-4-amino-4'-hydroxyazobenzene ($I = A \cdot c + B$) in the medium of 50 vol.% (d.c. polarography) or 10 vol.% (Tast and DPP) methanol

Concn. range $\mu\text{mol/l}$	pH	A nA $\mu\text{mol/l}$	B nA	Correl. coeff.
D.c. polarography				
1–10	5.01	25.1	5.2	0.9996
1–10	9.61	23.2	2.3	0.9996
10–100	5.01	22.1	5.8	0.9993
10–100	9.61	19.8	–0.9	0.9999
TAST polarography				
1–10	4.14	25.3	0.3	0.9995
1–10	9.12	23.5	8.4	0.9989
0.4–1	4.14	23.9	–1.4	0.9966
0.4–1	9.12	33.6	1.4	0.9917
DPP				
1–10	4.14	92	22	0.9997
1–10	9.12	64	10	0.9994
0.1–1	4.14	101	0.5	0.9997
0.1–1	9.12	87	0.5	0.9992
0.03–0.1	4.14	112	0.4	0.9918
0.03–0.1	9.12	103	0.9	0.9949

DIFFERENTIAL PULSE POLAROGRAPHY

Stability of stock solutions. The higher sensitivity of this method makes it necessary to prepare more dilute stock solutions; their concentration was checked by DPP at 30 days intervals and the results are given in Table IV. It is seen that the solutions were quite stable except for the most dilute one (10^{-5} mol/l), which should be freshly prepared every two months.

Influence of pH. The dependences of the peak current, I_p , and peak potential, E_p , on pH in 10 vol.% methanol are given in Table V. It was found by linear regression that the coefficients of the equation $E_p = a \cdot \text{pH} + b$ are $a = -79.7$ mV and $b = 115.4$ mV at pH 2–6 (correlation coefficient -0.9986), and $a = -56.5$ mV, $b = -48.6$ mV at pH 7–12 (correlation coefficient -0.9373). The decrease of I_p with increasing pH can be attributed to decreasing reversibility of the system under study caused by inhibition of the electron transfer by adsorbed depolarizer molecules¹.

Concentration dependence. At low concentrations (below 10^{-6} mol/l) in the polarographic cell according to Novák, where the mercury flowing out from the capillary

TABLE IV

Stability of stock solutions of N,N-dimethyl-4-amino-4'-hydroxyazobenzene in absence of light (in per cent of original concentration)

c, mol/l	Time, days				
	—	0	30	60	120
10^{-2}	100.0	100.0	100.0	100.0	100.0
10^{-3}	100.0	100.0	100.0	100.0	99.7
10^{-4}	100.0	99.8	99.6	99.6	99.0
10^{-5}	100.0	99.6	99.6	99.6	95.3

TABLE V

Dependence of E_p and I_p on pH in Britton-Robinson buffer containing 10 vol.% methanol; $3 \cdot 10^{-5}$ M N,N-dimethyl-4-amino-4'-hydroxyazobenzene; pulse height 100 mV; drop time 1 s

pH	2.14	3.17	4.14	5.14	6.24	7.25	8.19	9.12	10.14	11.13	12.01
E_p , mV	-57	-134	-221	-284	-387	-465	-514	-557	-611	-680	-735
I_p , μ A	2.80	3.12	3.00	2.97	3.01	2.95	2.39	1.96	1.85	1.80	1.77

remains at the bottom, the peak current I_p decreased with the time. This effect is not due to instability of the depolarizer in the medium used (Table IV). Also, no evidence for adsorption of the azo compound on the glass walls of the polarographic cell was obtained. However, its adsorption on the relatively large surface of mercury in the cell did take place as shown by two experiments. First, we compared samples of solutions taken at 10 min intervals from two vessels, one containing mercury at the bottom of about 25 cm² surface area, the other without mercury. The peak height for samples from the first vessel decreased with the time, whereas for samples from the other it remained constant. Second, we used a modified polarographic cell in which the mercury at the bottom was allowed to flow out through an outlet tube and the holding capacity of which was higher by a factor of 6. No decrease of I_p with the time was observed in this case. Thus, we measured the dependence of I_p on the depolarizer concentration at pH 4.14 and 9.12 (10 vol.% methanol and 90 vol.% Britton–Robinson buffer solution). The data were treated by the linear regression method and the results are given in Table III. The detection limit can be estimated as the depolarizer concentration at which I_p is equal to the 5-fold standard deviation of the noise, and is equal to $3 \cdot 10^{-8}$ mol/l. Thus, the use of the DPP method brings an order of magnitude higher sensitivity than Tast polarography.

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