THE POLAROGRAPHIC AND VOLTAMMETRIC DETERMINATION OF N,N-DIMETHYL-4-AMINO-3'-METHYLAZOBENZENE*

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The polarographic reduction of N,N-dimethyl-4-amino-3'-methylazobenzene has been studied, a mechanism has been proposed and conditions have been found for the determination of this depolarizer using TAST polarography and differential pulse polarography at a classical dropping mercury electrode and using fast scan differential pulse voltammetry and linear scan voltammetry at a hanging mercury drop electrode. The detection limit at this electrode is about 10^{-8} mol 1^{-1}; a further decrease can be attained using adsorption accumulation of the determined azo-substance on the surface of the working electrode. In conclusion, the practical usefulness of these methods combined with extraction or thin-layer chromatography was verified.

The 3'-substituted derivatives of N,N-dimethyl-4-aminoazobenzene have been suspected of chemical carcinogenity[1,2]. In this connection, their chemical oxidation has been studied in detail[3,4], while far less attention has been paid to their reduction reactions. Thus, this work was carried out to study the polarographic behaviour of N,N-dimethyl-4-amino-3'-methylazobenzene to determine the reduction mechanism and find conditions for the sensitive determination of this substance, especially using fast scan differential pulse voltammetry (FSDPV) and linear scan voltammetry (LSV). These methods have already been found useful for the determination of low concentrations of N,N-dimethyl-4-aminoazobenzene[5] and its 4'-substituted derivatives[6,7]. The low solubility of the studied depolarizer in water made it necessary to employ a 1 : 9 mixture of Britton–Robinson buffer and methanol.

EXPERIMENTAL

Reagents

The stock solution of N,N-dimethyl-4-amino-3'-methylazobenzene ($1 . 10^{-3}$ mol 1^{-1}) was prepared by dissolving the pure substance (Research Institute for Organic Synthesis, Pardubice-

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-Rybitví) in redistilled methanol. More dilute solutions were prepared by precise dilution of the stock solution with methanol. The purity of the test substance and its content in solution were controlled using paper chromatography[8] and titanometrically[9]. The Britton–Robinson buffer solutions were prepared in the usual manner[10]. The actual value of the pH of the solutions in the 9 : 1 methanol–buffer mixture was determined using a combined glass and calomel electrode, calibrated using oxalate and succinate buffers in 90% (v/v) methanol[11]. Water was doubly distilled in a quartz apparatus. The remaining chemicals employed were of *p.a.* purity.

Apparatus

The PA 3 polarographic analyzer with XY 4105 recorder was employed (Laboratorní přístroje, Prague). A potential scan rate of 5 mV s^{-1} was employed for DC, TAST, and DP polarography at a DME and, where not stated otherwise, a drop time of 1 s, mercury reservoir height of 25 cm and DPP modulation amplitude of -100 mV were employed. A classical dropping mercury electrode with the following parameters was employed: At $h = 25$ cm, $m = 3.95$ mg s^{-1}, and $t = 3.13$ s in 0.1 mol l^{-1} KCl with an applied voltage of 0 V.

The working electrode for FSDPV and LSV was a SMDE 1 static mercury electrode (Laboratorní přístroje, Prague) employed as a hanging mercury drop electrode (HMDE). Where not stated otherwise, measurements were carried out at a potential scan rate of 20 mV s^{-1}, maximal drop size attained by opening the valve for 160 ms and FSDPV modulation amplitude of -100 mV. All measurements were carried out in a three-electrode arrangement with a saturated calomel reference electrode and a platinum foil auxiliary electrode with a surface area of about 1 cm^2. Oxygen was removed from the analyzed solutions by passage of nitrogen for 10 min. The nitrogen purification line contained an alkaline solution of sodium anthraquinone-2-sulphonate and solutions of chromium (II) ions in dilute hydrochloric acid over zinc amalgam. A wash bottle containing 90% (v/v) methanol was placed prior to entrance into the polarographic vessel.

Coulometric measurements were carried out using an OH 404 coulometric analyzer (Radelkis, Budapest) in a 200 ml vessel. The mercury pool was used as the cathode and the anode and cathode spaces were separated by a glass frit. A saturated calomel reference electrode and platinum foil auxiliary electrode with a surface area of about 5 cm^2 were employed. The solution was stirred during the determination using a magnetic stirrer and nitrogen was passed over the surface of the solution.

Spectrophotometric measurements were carried out on a PU 8800 instrument (Pye Unicam, Great Britain) using 0.5 cm quartz cuvettes.

Thin-layer chromatography was carried out using commercial Silufol UV 366 plates (Kavalier, Votice, Czechoslovakia).

All measurements were carried out at laboratory temperature.

Procedures

Polarographed solutions were prepared by measuring the appropriate amount of the depolarizer solution in methanol, adding 8 ml of methanol and 1 ml of Britton–Robinson buffer with the appropriate pH and diluting with methanol to 10 ml. Calibration curves were measured in triplicate and evaluated by the linear regression method. The Skogerboe and Grant[12] detection limit was found as the ts/a value, where s is the standard deviation of the experimental points from the calibration straight line calculated by the linear regression method, a is the slope of this straight line, and t is the Student coefficient at the 99% confidence level, dependent on the number of points used in construction of the calibration curve.

Constant potential coulometry was carried out by measuring 80·0 ml methanol and 10·0 ml of buffer with the appropriate pH into the coulometric vessel and bubbling with nitrogen. Pre--electrolysis at a selected constant potential was also commenced. After about 20 min the residual current value decreased to less than 0·2 mA and no longer changed. The parameters for the circuit for automatic compensation of the residual current were adjusted and 10·0 ml of a 1 . . 10^{-3} mol l^{-1} solution of the studied depolarizer were added. Completion of electrolysis was indicated by a decrease in the current to the residual value. The time required for the electrolysis was about 45 to 60 min, and the charge passed was determined by digital integration of the current passed.

The drop time in measurement of the electrocapillary curves was found using an electronic stopwatch as the average for 10 drops. The surface tension σ was found from the drop time t using the relationship $\Delta\sigma/\sigma = 0.973\ \Delta t/t$, where σ and t are the values for an aqueous solution of 0·1 mol l^{-1} $NaNO_3$ and $\Delta\sigma$ and Δt are the changes in the given quantity for transfer to the studied solution[13].

The substance was separated using thin-layer chromatography in the ascending arrangement in atmosphere saturated with the vapours of the elution mixture (chloroform–methanol, 95 : 5). An amount of 5—125 µl of 1 . 10^{-3} or 1 . 10^{-4} mol l^{-1} of a solution of the studied substance was applied to the thin layer in a band using a mircopipette. The elution distance from the start was 15 cm. No detection was necessary because of the yellow colour of the test azodye.

After development and drying the chromatogram was cut so that the spot lay in a rectangle with dimensions of about 1·5 × 5·0 cm. The spot was developed with methanol in a descending manner directly into the polarographic vessel in a medium of saturated methanol vapour. The solvent was evaporated by warm air and 9·00 ml methanol and 1·00 ml Britton–Robinson buffer with pH 2·02 were added and the solution was polarographed in the usual manner.

The extraction-polarographic determination of N,N-dimethyl-4-amino-3′-methylazobenzene was carried out by extracting 10·00 ml of an aqueous solution containing 2·5—10 nmol of the studied substance, with pH adjusted to a value of 7·0, six times with 10 ml of diethyl ether. The combined extracts were evaporated on a rotary vacuum evaporator to dryness, the residue was dissolved in 9·00 ml methanol and 1·00 ml Britton–Robinson buffer with pH 2·02 and analyzed using FSDPV or LSV at an HMDE.

RESULTS AND DISCUSSION

First the stability of the stock solution of 10^{-4} mol l^{-1} N,N-dimethyl-4-amino-3′--methylazobenzene in methanol was checked spectrophotometrically. The absorbance of this solution was measured in a 0·5 cm-cuvette at a wavelength of 407 nm, where this substance exhibits an absorbance maximum. It was found that no observable decrease in the concentration of the studied substance occurred over 5 months. A solution with a concentration of 10^{-5} mol l^{-1} was prepared fresh every 14 days and more dilute solutions were prepared daily and stored in the dark.

The stability of 10^{-5}, 10^{-6}, and 10^{-7} mol l^{-1} solutions of N,N-dimethyl-4--amino-3′-methylazobenzene in the polarographic medium (*i.e.* in a 1 : 9 mixture of Britton–Robinson buffer and methanol with pH 4·53 and 9·55) was studied using TAST polarography (10^{-5} and 10^{-6} mol l^{-1} solutions) and DPP at a DMF (10^{-7} mol . l^{-1}). No observable change in concentration of the depolarizer in the polarographed solution was found after two hours even for the most dilute solutions.

TAST *Polarography at a Dropping Mercury Electrode*

The effect of the pH on the polarographic behaviour of N,N-dimethyl-4-amino-3'-
-methylazobenzene in a 1 : 9 mixture of Britton–Robinson buffer and methanol
is reflected in the results in Table I. The value $\Delta E_{1/2}/\Delta pH = 56\cdot3$ mV was found
by linear regression. The observed shift in $E_{1/2}$ with decreasing pH to more positive
values can be attributed primarily to protonation of the azo group, resulting in a de-
crease in the electron density in the region of the double bond between the two
nitrogen atoms and thus facilitating reduction. It follows from the observed depen-
dence of I_{lim} on the pH that twice as many electrons are exchanged in acid medium
as in alkaline medium. The best developed waves were obtained in a medium with
pH 4·53 and 9·55. All the subsequent dependences were measured in these media.

The dependence of the wave height on the depolarizer concentration is linear
in the range $1 . 10^{-4} - 2 . 10^{-6}$ mol l^{-1}; its parameters and the calculated detection
limit are listed in Table II. The dependence of the half-wave potential on the de-
polarizer concentration is apparently connected with the irreversible character of
the electrode process:

c, mol l^{-1}	$10 . 10^{-5}$	$4 . 10^{-5}$	$1 . 10^{-5}$
$E_{1/2}$ at pH 4·53, mV	−325	−285	−260
$E_{1/2}$ at pH 9·55, mV	−693	−660	−630

The determined linear dependence of I_{lim} on the depolarizer concentration confirms
the diffusion character of the limiting current in both acid and alkaline media. This
fact was further confirmed by measuring the dependence of the limiting current
measured by DC polarography on the square root of the reservoir height. At pH
4·53 and 9·55 a linear dependence passing through the origin was found. At pH 7·58,
this dependence has a smaller slope and does not pass through the origin, reflecting
kinetic complications in the studied process. The temperature coefficient found
at this pH is 2·0%, so that participation of kinetic currents is small.

Study of Reversibility

It followed from the logarithmic analysis of the TAST polarographic curves that
this is not a reversible process. This fact was further confirmed by DPP with positive
and negative pulse polarity[14] and by cyclic voltammetry (CVA)[15]. An orientative
study of the reversibility using DPP was carried out using a pulse height of 50 mV
to investigate the effect of the pH on the peak potential difference $E_{p,c} - E_{p,a}$ and
peak current ratio $I_{p,a}/I_{p,c}$ for the cathodic (subscript c) and anodic (subscript a)
pulse polarity. The following values were found:

TABLE I

The effect of the pH on the TAST and DP polarograms of $1 \cdot 10^{-4}$ mol l^{-1} N,N-dimethyl-4--amino-3'-methylazobenzene in a 1 : 9 mixture of Britton–Robinson buffer and methanol

pH	$E_{1/2}$ mV	I_{lim} μA	Slope of log. analysis mV	E_p mV	I_p μA
4·53	−325	1·79	74	−345	2·525
5·63	−437	1·75	85	−435	2·805
6·40	−478	1·68	62	−470	3·000
6·98	−520	1·55	51	−494	3·010
7·58	−559	1·38	45	−525	3·015
8·62	−625	0·90	41	−605	2·725
9·55	−673	0·91	39	−640	2·625
9·98	−693	0·88	33	−660	2·625
10·16	−703	0·88	38	−675	2·425
10·55	−712	0·89	44	−700	2·025
10·98	−735	0·98	53	−735	1·525
11·59	−790	1·05	89	−785	1·375

TABLE II

The calibration curve parameters and calculated detection limits for various methods of determining N,N-dimethyl-4-amino-3'-methylazobenzene

Method	pH	Concentration μmol l^{-1}	Slope μA mol^{-1} l	Intercept μA	Correl. coef.	DL[a] μmol l^{-1}
TAST at DME	4·53	1—10	$1·73 \cdot 10^4$	$1·00 \cdot 10^{-3}$	0·9988	2·7
TAST at DME	9·55	1—10	$9·50 \cdot 10^3$	$2·00 \cdot 10^{-3}$	0·9954	1·8
DPP at DME	4·53	0·01—0·1	$1·37 \cdot 10^5$	$2·45 \cdot 10^{-3}$	0·9985	0·03
DPP at DME	9·55	0·01—0·1	$6·94 \cdot 10^4$	$8·90 \cdot 10^{-4}$	0·9835	0·02
FSDPV at HMDE[b]	4·53	0·01—0·1	$3·20 \cdot 10^4$	$3·00 \cdot 10^{-5}$	0·9970	0·013
FSDPV at HMDE[b]	9·55	0·01—0·1	$1·82 \cdot 10^4$	$1·85 \cdot 10^{-4}$	0·9959	0·015
FSDPV at HMDE[c]	4·53	0·01—0·1	$1·65 \cdot 10^6$	$6·30 \cdot 10^{-3}$	0·9986	0·009
FSDPV at HMDE[c]	9·55	0·01—0·1	$1·00 \cdot 10^6$	$2·20 \cdot 10^{-3}$	0·9982	0·010
LSV at HMDE[b]	4·59	0·1—1	$4·50 \cdot 10^4$	$4·00 \cdot 10^{-4}$	0·9924	0·1
LSV at HMDE[d]	4·59	0·01—0·1	$2·01 \cdot 10^6$	$2·00 \cdot 10^{-4}$	0·9998	0·003

[a] Detection limit; [b] without accumulation (recorded immediately after drop formation); [c] with 60 s accumulation in stirred solution (recorded 10 s after stopping stirring); [d] with 120 s accumulation in unstirred solution.

pH	4·53	7·58	9·55
$\lvert I_{p,a}/I_{p,c}\rvert$	0·90	0·73	0·64
$E_{p,c} - E_{p,a}$, mV	50	50	50

According to the diagnostic criteria derived by Birke[14] for simple charge transfer, these values correspond to an irreversible process.

The effect of pH on CVA at the HMDE was also studied. The measured voltammograms exhibited an anodic peak (see Fig. 1). However, the large difference between the potentials of the cathodic and anodic peaks prevents designation of the system as quasireversible, although it can be seen that the system approaches quasireversible behaviour with increasing pH (see Table III).

TABLE III

The effect of the pH on the position (E_p) and height (I_p) of the cathodic (subscript c) and anodic (subscript a) peak of $1 . 10^{-4}$ mol l^{-1} N,N-dimethyl-4-amino-3'-methylazobenzene in cyclic voltammetry at the HMDE in 90% (v/v) methanol[a]

pH	$E_{p,c}$ mV	$E_{p,a}$ mV	$I_{p,c}$ μA	$I_{p,a}$ μA	$I_{p,a}/I_{p,c}$	$E_{p,a} - E_{p,c}$ mV
9·03[b]	−595	−115	0·105	0·021	0·20	480
9·55[b]	−610	−200	0·112	0·028	0·25	410
10·20[b]	−735	−300	0·105	0·027	0·26	435
11·10[b]	−780	−345	0·090	0·022	0·24	435
11·65[b]	−780	−345	0·090	0·027	0·30	435
12·46[c]	−810	−390	0·083	0·032	0·39	400
13·28[c]	−875	−665	0·082	0·041	0·49	210

[a] Polarization rate 100 mV s^{-1}; [b] using Britton–Robinson buffer; [c] using 0·1 or 1 mol l^{-1} sodium hydroxide.
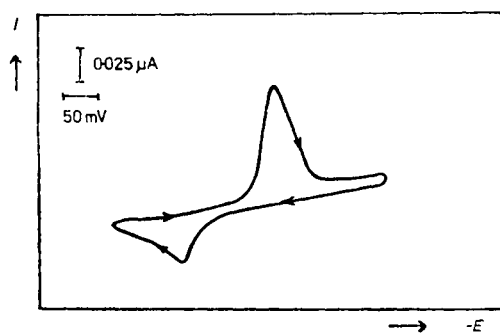

FIG. 1

The cyclic voltammogram of $1 . 10^{-4}$ mol . l^{-1} N,N-dimethyl-4-amino-3'-methylazobenzene in a mixture of 1 mol l^{-1} NaOH––methanol, 1 : 9, pH 13·28. Initial potential −600 mV, polarization rate 50 mV s^{-1}

The effect of the polarization rate on the position and height of the cathodic and anodic peaks was studied in $1 \, mol \, l^{-1}$ NaOH–methanol medium, $1 : 9$, with pH 13·28 (see Table IV). It was found that the peak height increases with the square root of the polarization rate faster than would correspond to a linear dependence. This fact is apparently connected with complication of the studied process by adsorption of the depolarizer on the surface of the mercury drop (see below). The large value of the difference $E_{p,a} - E_{p,c}$ and its independence on the polarization rate confirm that the process is irreversible.

Determination of the Number of Electrons Exchanged

Coulometry at constant potential using a mercury pool cathode confirmed that a total of four electrons are exchanged in acid (pH 4·53, $E = -750 \, mV$) and alkaline (pH $= 9·55$, $E = -1\,400 \, mV$) media.
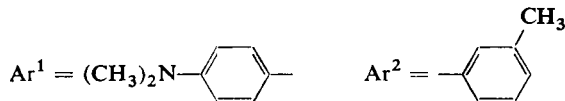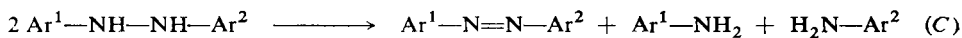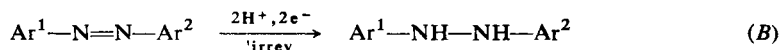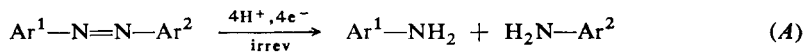
Proposed Reaction Mechanism

The observed dependence of I_{lim} on the pH can be explained by a direct exchange of four electrons in acid medium with splitting of the azogroup to form two amines according to Eq. (A), while in alkaline medium only two electrons are exchanged, with reduction to the corresponding hydrazocompound according to Eq. (B). The difference between the number of exchanged electrons determined from the wave height and from potentiostatic coulometry can be explained by irreversible disproportionation of the hydrazocompound formed (Eq. (C)). If disproportionation occurs during the droptime, the regenerated azocompound can undergo further reduction, resulting in an overall value of $n = 4$. In the alkaline region, the rate of disproportionation is so slow that the wave height decreases to a value corresponding to ex-

TABLE IV

The effect of the polarization rate (v) on the position (E_p) and height (I_p) of the cathodic (subscript c) and anodic (subscript a) peak of $1 . 10^{-4} \, mol \, l^{-1}$ N,N-dimethyl-4-amino-3'-methylazobenzene in cyclic voltammetry at the HMDE in a mixture of $1 \, mol \, l^{-1}$ NaOH–methanol, $1 : 9$, pH 13·28

$v^{1/2}$ $mV^{1/2} \, s^{-1/2}$	$I_{p,a}$ μA	$I_{p,c}$ μA	$I_{p,a}/I_{p,c}$	$I_{p,a}/v^{1/2}$	$I_{p,c}/v^{1/2}$	$E_{p,a}$ mV	$E_{p,c}$ mV	$E_{p,a} - E_{p,c}$ mV
14·14	0·062	0·132	0·47	0·0044	0·0093	−670	−870	210
10·00	0·041	0·082	0·49	0·0041	0·0082	−665	−875	210
7·07	0·030	0·050	0·60	0·0042	0·0070	−660	−875	215
4·47	0·019	0·028	0·68	0·0042	0·0062	−660	−870	210
3·16	0·014	0·018	0·77	0·0044	0·0057	−665	−875	210

change of two electrons. Under these conditions the disproportionation half time is less than the time of the coulometric experiment (about 60 minutes), which thus yields a value of $n = 4$ for alkaline medium.

$$Ar^1—N{=}N—Ar^2 \xrightarrow[\text{irrev}]{4H^+, 4e^-} Ar^1—NH_2 + H_2N—Ar^2 \qquad (A)$$

$$Ar^1—N{=}N—Ar^2 \xrightarrow[\text{irrev}]{2H^+, 2e^-} Ar^1—NH—NH—Ar^2 \qquad (B)$$

$$2\,Ar^1—NH—NH—Ar^2 \longrightarrow Ar^1—N{=}N—Ar^2 + Ar^1—NH_2 + H_2N—Ar^2 \quad (C)$$

$$Ar^1 = (CH_3)_2N—\!\!\left\langle\!\!\bigcirc\!\!\right\rangle\!\!— \qquad Ar^2 = —\!\!\left\langle\!\!\bigcirc\!\!\right\rangle\!\!^{CH_3}$$

These concepts are in agreement with earlier findings on the polarographic behaviour of a number of other azobenzene derivatives[5,6,16].

Differential Pulse Polarography at a Dropping Mercury Electrode

The effect of the pH on the position and height of the peak is given in Table I. It can be seen that the dependence of E_p on the pH has the same character as the dependence of $E_{1/2}$ on the pH. A value of $\Delta E_p/\Delta pH = 55{\cdot}2$ mV was found by linear regression method. The dependence of the peak height on the pH is apparently a combination of the effect of the pH on the number of exchanged electrons and on the reversibility of the studied process. Similarly to TAST polarography, the best developed peaks were obtained in media with pH 4·53 and 9·55 and these media were employed for measurement of the other dependences.

In agreement with theory, it was found that the peak height and thus the sensitivity of the determination increase with increasing pulse height; however, the resolution decreases as a result of peak broadening. It was also found, in agreement with theory, that the peak height increases with increasing electronically controlled drop time and with the height of the mercury reservoir.

The dependence of the peak height on the concentration is linear in the concentration range $1 \cdot 10^{-4} - 2 \cdot 10^{-8}$ mol l^{-1} and its parameters are given in Table II together with the calculated detection limit.

Fast Scan Differential Pulse Voltammetry at a Hanging Mercury Drop Electrode

It has been found that the peak height depends on the time between drop formation and recording[17]. This fact can be explained by adsorptive accumulation of the studied depolarizer at the surface of the hanging mercury drop. This phenomenon was confirmed by measuring the electrocapillary curves which exhibited a decrease

in the surface tension resulting from addition of the depolarizer to the solution of base electrolyte. It was found that the increase in the peak height at the HMDE as a result of adsorptive accumulation is practically independent of the pH, methanol content and accumulation potential and can be increased by stirring. The fact that the peak height approaches a limiting value with increasing accumulation time is apparently associated with attainment of sorption equilibrium. Thus, the calibration curves are nonlinear at higher concentrations (above 10^{-6} mol l^{-1}). A Britton––Robinson buffer – methanol 1 : 9 medium with pH 4·53 or 9·55, accumulation potential of 0 or 300 mV, respectively, and accumulation time of 60 s in stirred solution were selected as optimal.

In determination without accumulation, *i.e.* recording immediately after drop formation, the calibration curves are linear in the range $10^{-5}-2 . 10^{-8}$ mol l^{-1}. For 60 s accumulation with stirring and recording 10 s after stopping stirring, the calibration curves are linear in the range $10^{-6}-5 . 10^{-9}$ mol l^{-1}. The parameters of the calibration straight lines and calculated detection limit are given in Table II.

Linear Scan Voltammetry at a Hanging Mercury Drop Electrode

Voltammograms were measured in dependence on the pH immediately after drop formation and after 60 s accumulation in unstirred solution. The largest and best--developed peaks were obtained in both cases in Britton–Robinson buffer –methanol 1 : 9 medium with pH 4·59. The peak growth as a result of adsorptive accumulation is also greatest in this medium. With increasing pH and decreasing methanol content, the heights of the peaks recorded immediately and after adsorptive accumulation both decrease. The growth of the peak height as a result of adsorptive accumulation can be increased by stirring. However, after 60 s accumulation in stirred solution, the calibration curves are steeper but nonlinear at concentrations greater than $2 . 10^{-7}$ mol l^{-1}. In contrast, after 120 s accumulation in unstirred solution at a potential of 0 V the calibration curves are linear in the concentration range $10^{-5}-2 . 10^{-8}$ mol l^{-1}. Their parameters and the calculated detection limits are given in Table II. A further increase in the accumulation time by two-fold results in only a slight increase in the peak height (about 3−5%). In contrast, concentrations below $2 . 10^{-7}$ mol l^{-1} cannot be determined without accumulation.

Determination of N,N-*Dimethyl-4-amino-3'-methylazobenzene*
After Separation by Thin-Layer Chromatography

Solutions prepared after separation of the studied depolarizer on a thin layer were analyzed by FSDPV and LSV at an HMDE without accumulation. The peak height obtained was compared with that for a solution prepared directly by measuring the appropriate volume of 10^{-3} or 10^{-4} mol l^{-1} of an N,N-dimethyl-4-amino-3'--methylazobenzene solution and mixing with the base electrolyte.

It can be seen from Table V that very good results can be obtained primarily at low concentrations. At higher concentrations, the results are apparently affected by incomplete elution of the substance from the thin layer, so that the yield decreases considerably. LSV is not useful for this analysis as a result of the effect of surface-active substances extracted from the thin layer on the rate of the electrode reaction and thus also on the peak height.

An R_F value of 0·95 was found under the given conditions.

TABLE V

The determination of N,N-dimethyl-4-amino-3′-methylazobenzene by the FSDPV and LSV methods after prior separation by thin-layer chromatography

Taken μg	c^a mol l^{-1}	Found, % theory	
		FSDPV	LSV
1·195	5·00 . 10^{-8}	99·7	—^{b}
5·975	2·50 . 10^{-7}	99·4	—^{b}
11·950	5·00 . 10^{-7}	99·3	—^{b}
17·925	7·50 . 10^{-7}	98·7	—^{b}
23·900	1·00 . 10^{-6}	95·8	—^{b}
59·750	2·50 . 10^{-6}	94·7	91·4
119·500	5·00 . 10^{-6}	92·8	88·9
179·250	7·50 . 10^{-6}	88·2	85·2
239·000	1·00 . 10^{-5}	84·7	80·1
298·750	1·25 . 10^{-5}	80·6	75·6

^{a} Concentration of analyte in the measured solution; ^{b} voltammograms cannot be evaluated.

TABLE VI

The determination of N,N-dimethyl-4-amino-3′-methylazobenzene after extraction with diethyl ether

Taken μg	c^a μmol l^{-1}	Found, % theory	
		FSDPV	LSV
5·975	0·25	97·6	96·5
11·950	0·50	97·1	95·5
17·925	0·75	99·0	96·9
23·900	1·00	98·9	96·7

^{a} Concentration of analyte in the extracted solution.

The Determination of N,N,-*Dimethyl-4-amino-3'-methylazobenzene*
After Extraction

Under the given conditions, a value of 1·34 was found for the distribution ratio for the studied substance between water and diethyl ether. Thus, six-fold extraction was employed for quantitative separation. Solutions prepared after extraction were analyzed by FSDPV at the HMDE without accumulation and by LSV at the HMDE with 120 s accumulation in unstirred solution. The peak height was compared with the values obtained using solutions prepared by addition of the appropriate volume of 10^{-5} mol l^{-1} depolarizer directly to a mixture of 9·00 ml methanol and 1·00 ml Britton–Robinson buffer with pH 2·02. It follows from the results in Table VI that the FSDPV determination is sufficiently accurate. The somewhat lower results obtained for LSV are apparently connected with the effect of surface-active substances on the peak height, which could be partly eliminated by the method of standard additions.

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