

## THE POLAROGRAPHIC AND VOLTAMMETRIC DETERMINATION OF THE 3'-HALOGEN DERIVATIVES OF N,N-DIMETHYL-4-AMINOAZOBENZENE\*

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The polarographic reduction of the 3'-halogen derivatives of N,N-dimethyl-4-aminoazobenzene was studied in mixed water-methanol medium and optimum conditions were found for the determination of these genotoxic substances by fast polarography in the concentration range  $1 \cdot 10^{-4}$  to  $2 \cdot 10^{-6}$  mol l<sup>-1</sup>, differential pulse polarography at a dropping mercury electrode in the range  $1 \cdot 10^{-4}$  to  $2 \cdot 10^{-7}$  mol l<sup>-1</sup> and fast scan differential pulse voltammetry at a hanging mercury drop electrode in the range  $1 \cdot 10^{-6}$  to  $2 \cdot 10^{-8}$  mol l<sup>-1</sup>. The increase in the sensitivity resulting from adsorptive accumulation of the studied substances on the surface of a hanging mercury drop can be utilized in the determination using the latter method in the concentration range  $1 \cdot 10^{-8}$  to  $2 \cdot 10^{-9}$  mol l<sup>-1</sup>.

The 3'-halogen derivatives of N,N-dimethyl-4-aminoazobenzene are suspected of chemical carcinogenicity<sup>1-4</sup>. Toxicological studies of these substances can only be carried out on the basis of a sufficiently sensitive and selective method for their determination. The ready polarographic reducibility of azo groups, whose mechanism is discussed, e.g., in monographs<sup>5-7</sup>, permits the determination of very small amounts of azobenzene derivatives using modern polarographic or voltammetric methods. These methods have already been found useful, e.g., for the determination of trace amounts of N,N-dimethyl-4-aminoazobenzene<sup>8</sup> and its 4'-amino<sup>9</sup>, 4'-hydroxy<sup>10</sup> and 4'-halogen<sup>11</sup> derivatives. Of the 3'-substituted derivatives of N,N-dimethyl-4-aminoazobenzene, only the 3'-methyl derivative has so far been subjected to a polarographic and voltammetric study<sup>12</sup>.

Consequently, this work describes a detailed study of the polarographic and voltammetric behaviour of N,N-dimethyl-4-amino-3'-fluoroazobenzene (*I*), N,N-dimethyl-4-amino-3'-chloroazobenzene (*II*), N,N-dimethyl-4-amino-3'-bromoazobenzene (*III*) and N,N-dimethyl-4-amino-3'-iodoazobenzene (*IV*). To ensure solubility

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of these substances, work was carried out in mixed Britton–Robinson buffer–methanol (1 : 9) medium.

## EXPERIMENTAL

### Reagents

The studied 3'-halogen derivatives of N,N-dimethyl-4-aminoazobenzene were prepared by coupling of the diazonium salts of the corresponding halogen amines with N,N-dimethylaniline, purification by column chromatography on silica gel and recrystallization from a mixture of benzene and ethanol. The purity of the substances prepared was checked by TLC and HPLC. The structures were confirmed by mass spectrometry and NMR spectroscopy and the contents of the elements were found by elemental analysis and titanometrically.

The stock solutions of the studied substances in methanol ( $c = 1 \cdot 10^{-3} \text{ mol l}^{-1}$ ) were prepared by dissolving a precisely weighed amount of the substance in freshly redistilled solvent. It was confirmed by spectrophotometry in the visible region that these solutions are stable for at least 2 months. Solutions with lower concentrations were prepared by diluting the stock solutions. Solutions with concentrations of  $1 \cdot 10^{-4}$  and  $1 \cdot 10^{-5} \text{ mol l}^{-1}$  were prepared fresh each week and more dilute solutions were prepared daily. All the solutions were stored in the dark.

All the chemicals used were of p.a. purity (Lachema, Brno); water was doubly redistilled in a quartz apparatus. Methanol was stored only in glass vessels as contact with polyethylene leads to extraction of substances that are detrimental to the determination of low concentrations of the test substances.

### Apparatus

The PA 4 polarographic analyzer with the XY-4106 xy recorder (both from Laboratorní přístroje, Prague) were employed. DC, tast and DP polarography were carried out using a classical dropping mercury electrode with the following parameters: at a mercury reservoir height of  $h = 36 \text{ cm}$  the flow rate was  $m = 2.94 \text{ mg s}^{-1}$  and drop time was  $\tau = 3.51 \text{ s}$  (measured in  $0.1\text{M-KCl}$  at an applied voltage of  $0 \text{ V}$  vs a saturated silver chloride electrode). Where not stated otherwise, a polarization rate of  $5 \text{ mV s}^{-1}$ , electronically controlled drop time of  $1 \text{ s}$ , mercury reservoir height of  $36 \text{ cm}$  and differential pulse polarography (DPP) modulation pulse amplitude of  $-100 \text{ mV}$  were employed. Fast scan differential pulse voltammetry (FS DPV) and linear scan voltammetry (LSV) were carried out using an SMDE 1 static mercury drop electrode (Laboratorní přístroje, Prague) connected as a hanging mercury drop electrode (HMDE). Where not stated otherwise, a polarization rate of  $20 \text{ mV s}^{-1}$  and maximum drop size attained by opening the valve for  $160 \text{ ms}$  were used. All the techniques employed a three-electrode arrangement with a platinum auxiliary electrode and saturated silver chloride reference electrode, to which all the potential values are related. Prior to entering the polarographic vessel, nitrogen was passed through a pre-bubbler containing a methanol–water mixture (9 : 1). The pH value of the methanol–buffer (9 : 1) solutions was measured using a glass electrode calibrated using oxalate and succinate buffers in 90% (v/v) methanol<sup>13</sup>. The coulometric and spectrophotometric measurements were carried out using the instruments described in earlier publications<sup>11,12</sup>.

### Procedures

The calibration curves were measured in triplicate and evaluated by the least squares linear regression method. The determination limit in the concentration range  $(2-10) \cdot 10^{-x} \text{ mol l}^{-1}$

was calculated as ten times the standard deviation for 10 determinations of  $2 \cdot 10^{-x} \text{ mol l}^{-1}$  of the analyte<sup>14</sup>. The coulometric determination of the number of electrons exchanged was carried out analogously to the procedure in previous works<sup>11,12</sup>.

## RESULTS AND DISCUSSION

### *Tast Polarography at the Dropping Mercury Electrode*

The effect of the pH on the tast polarographic curves of the studied substances is given in Table I and Fig. 1. At certain pH values, a maximum appeared on the tast polarograms and complicated analytical use; it can be suppressed by the addition of Triton X 100.

Similar to the previous communication<sup>11</sup>, the observed linear dependence of  $E_{1/2}$  on the pH can once again be explained in terms of prior protonation of the azo group. It follows from the observed dependence of  $I_{lim}$  on the pH that a greater number of electrons are exchanged in acidic than in alkaline medium. It was found by constant potential coulometry at a large-surface mercury electrode that all the studied substances exchange four electrons in Britton–Robinson buffer–methanol (1 : 9) medium at pH 6.1. The results of logarithmic analysis indicate that the process is irreversible.

It was found<sup>15</sup> by cyclic voltammetry of the studied substances ( $c = 1 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1}$ ) at a polarization rate of  $5-100 \text{ mV s}^{-1}$  in Britton–Robinson buffer–methanol (1 : 9) medium that the process is completely irreversible at pH 1.8 and 6.1 (no anodic peak was found). At higher pH values, an anodic peak appears (see Fig. 2); however, the ratio of the heights of the anodic and cathodic peaks at pH 11.7 is between 0.2 and 0.5 and the difference between the potentials of the anodic and cathodic peaks is 250–450 mV, so that the system cannot be described as quasireversible. The fact that the value of the expression  $I_p^k/v^{1/2}$  (where  $I_p^k$  is the height of the cathodic peak and  $v$  is the polarization rate) is not constant indicates that a complex electrode process is involved rather than a simple charge transfer process. The  $I_p^k$  value could also be increased as a result of accumulation of the test substances on the surface of the working electrode (see below).

The substituents do not greatly affect the half-wave potential of the studied substances because of the similar Hammett  $\sigma$  constant values for halogen in the *meta*-position<sup>16</sup>.

It can be concluded on the basis of the observed facts and the already described polarographic behaviour of a number of other derivatives of azobenzene<sup>5-7,9</sup> that the test substances undergo a four-electron reduction in acid medium to form N,N-dimethyl-*p*-phenylenediamine and 3-halogen aniline, while a two-electron reduction occurs in alkaline medium to form N,N-dimethyl-4-amino-3'-halogen hydrazobenzene. (It can be assumed that the particular hydrazo compound is also formed

TABLE I

The effect of the pH on the fast polarographic curves of the test substances I–IV ( $c = 2 \cdot 10^{-4}$  mol  $\cdot$  l $^{-1}$ ) in Britton–Robinson buffer–methanol medium (1 : 9)

pH	I			II			III			IV		
	$E_{1/2}$ mV	$I_{lim}$ $\mu$ A	slope <sup>a</sup> mV	$E_{1/2}$ mV	$I_{lim}$ $\mu$ A	slope <sup>a</sup> mV	$E_{1/2}$ mV	$I_{lim}$ $\mu$ A	slope <sup>a</sup> mV	$E_{1/2}$ mV	$I_{lim}$ $\mu$ A	slope <sup>a</sup> mV
1.7 <sup>b</sup>	-120	2.14	70	-120	2.15	73	-115	2.65	— <sup>c</sup>	-140	2.06	130
4.2	-410	2.00	73	-420	1.93	— <sup>c</sup>	-365	2.33	— <sup>c</sup>	-370	1.83	127
5.4	-455	1.80	57	-480	1.69	47	-430	2.13	55	-460	1.40	48
6.1	-500	1.63	50	-490	1.53	51	-490	2.07	64	-485	1.29	47
7.0	-540	1.54	55	-530	1.40	50	-525	1.97	60	-530	1.20	52
8.3	-645	1.46	62	-620	1.38	48	-620	1.83	72	-635	1.20	59
9.1	-700	1.43	64	-675	1.33	45	-720	1.74	68	-680	1.25	75
9.6	-725	1.40	73	-735	1.38	— <sup>c</sup>	-745	1.80	— <sup>c</sup>	-705	1.23	70
9.8	-760	1.46	80	-740	1.45	— <sup>c</sup>	-790	1.83	— <sup>c</sup>	-730	1.23	73
10.4	-830	1.43	82	-810	1.45	— <sup>c</sup>	-820	1.75	— <sup>c</sup>	-775	1.15	83
10.9	-850	1.43	93	-820	1.45	63	-815	1.70	63	-780	1.20	81
11.7	-835	1.46	95	-815	1.45	62	-830	1.73	95	-800	1.25	76

<sup>a</sup> Slope of the logarithmic analysis; <sup>b</sup> attained using a 0.1M-HClO<sub>4</sub>-CH<sub>3</sub>OH (1 : 9) mixture; <sup>c</sup> logarithmic analysis was not carried out because of the presence of maxima on the curves.

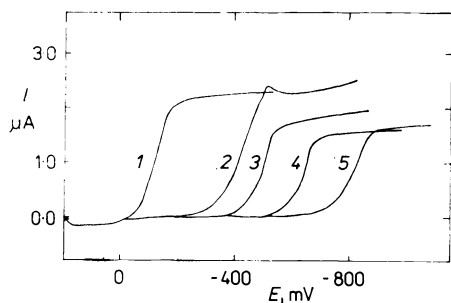


FIG 1

Fast polarograms of II ( $c = 2 \cdot 10^{-4}$  mol  $\cdot$  l $^{-1}$ ) in a mixture of 0.1M-HClO<sub>4</sub>-CH<sub>3</sub>OH (1 : 9) at pH 1.7 (1) and Britton–Robinson buffer–methanol (1 : 9) at pH 4.2 (2), 6.1 (3), 8.3 (4), and 10.9 (5)

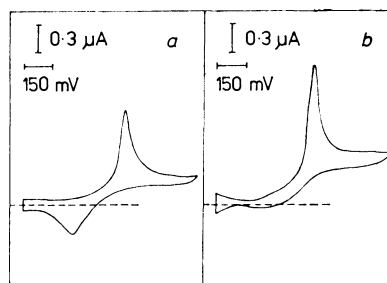


FIG. 2

Cyclic voltammograms of II ( $c = 1 \cdot 10^{-4}$  mol l $^{-1}$ ) in Britton–Robinson buffer–methanol medium (1 : 9) at pH 11.7 (a) and 6.1 (b) at a polarization rate of 100 mV s $^{-1}$ . Initial potential -200 mV (a) and 0 mV (b). The dashed line corresponds to zero current

in acid medium<sup>9</sup>, but undergoes acid-catalyzed disproportionation leading to the formation of quinone diimine, which is immediately reduced to the corresponding amine.)

The best-developed, reproducible and most readily evaluated polarograms were obtained at pH 6.1. It was shown<sup>15</sup> that the wave height in DC polarography in this medium is directly proportional to the square root of the mercury reservoir height and the dependences of the limiting current in fast polarography on the mercury flow rate and drop time also correspond to the Ilkovich equation. It follows that the limiting current is diffusion-controlled, which is also confirmed by the linearity of the concentration dependence in the range  $1 \cdot 10^{-4}$  to  $2 \cdot 10^{-6}$  mol l<sup>-1</sup> (see Table II). The observed shift in  $E_{1/2}$  with decreasing depolarizer concentration to more positive values<sup>15</sup> is apparently connected with the irreversibility of the polarographic reduction of the test substances.

#### *Differential Pulse Polarography at the Dropping Mercury Electrode*

The effect of the pH on the position ( $E_p$ ) and height ( $I_p$ ) of the DPP peaks is given in Table III. The dependence of  $E_p$  on the pH has the same character as the dependence of  $E_{1/2}$  on the pH and can be explained in the same way. The dependence of  $I_p$  on the pH is apparently affected by the effect of the pH on the number of electrons exchanged and on the reversibility of the given processes. Similarly as for fast polarography, a pH of 6.1 was selected for DPP measurements as it yielded the best developed and most readily evaluated curves. The stability of the solutions of the studied substances is sufficient in this medium and the peak height does not change within 30 minutes after preparation of voltammetric solutions with concentrations of the test substances from  $1 \cdot 10^{-4}$  to  $1 \cdot 10^{-6}$  mol l<sup>-1</sup> within experimental error.

Concentration dependences are linear in this medium in the range from  $1 \cdot 10^{-4}$  to  $2 \cdot 10^{-7}$  mol l<sup>-1</sup> (see Table IV); curvature occurs only for substances I and II in the range  $(2-5) \cdot 10^{-5}$  mol l<sup>-1</sup>, possibly connected with the effect of the products of the electrochemical reduction on the reversibility of the reaction. The peak height was measured from the baseline for the base electrolyte; this was essential especially at low concentrations because of the peaks of impurities that could not be completely removed either by buffer dilution or by a decrease in the methanol content.

#### *Fast Scan Differential Pulse Voltammetry at a Hanging Mercury Drop Electrode*

Table V gives the effect of the pH on the FSDP voltammetric curves. It can be seen that the dependences have the same character as for fast or DPP. However, the optimum peak height is obtained at pH 5.3 (see Fig. 3), and should be measured from the baseline for the base electrolyte. Under these conditions, the dependences

TABLE II

Parameters of the calibration straight lines and determination limits of the test substances for the fast polarographic method in Britton–Robinson buffer–methanol (1 : 9) medium at pH 6.1

Compound	$c$ $\text{mol l}^{-1}$	Slope $\mu\text{A mol}^{-1} \text{l}$	Intercept $\mu\text{A}$	$r^a$	$L_Q^b$ $\text{mol l}^{-1}$
<i>I</i>	$(2-10) \cdot 10^{-5}$	$7.90 \cdot 10^3$	$1.70 \cdot 10^{-2}$	0.9935	$1.5 \cdot 10^{-6}$
	$(2-10) \cdot 10^{-6}$	$7.98 \cdot 10^3$	$5.49 \cdot 10^{-3}$	0.9998	
<i>II</i>	$(2-10) \cdot 10^{-5}$	$6.58 \cdot 10^3$	$4.05 \cdot 10^{-2}$	0.9973	$2.1 \cdot 10^{-6}$
	$(2-10) \cdot 10^{-6}$	$7.30 \cdot 10^3$	$3.20 \cdot 10^{-3}$	0.9980	
<i>III</i>	$(2-10) \cdot 10^{-5}$	$8.88 \cdot 10^3$	$5.50 \cdot 10^{-3}$	0.9986	$1.7 \cdot 10^{-6}$
	$(2-10) \cdot 10^{-6}$	$9.75 \cdot 10^3$	$2.70 \cdot 10^{-3}$	0.9999	
<i>IV</i>	$(2-10) \cdot 10^{-5}$	$5.23 \cdot 10^3$	$2.75 \cdot 10^{-2}$	0.9974	$2.2 \cdot 10^{-6}$
	$(2-10) \cdot 10^{-6}$	$6.85 \cdot 10^3$	$5.00 \cdot 10^{-4}$	0.9973	

<sup>a</sup> Correlation coefficient; <sup>b</sup> determination limit.

TABLE III

The effect of the pH on the DP polarographic curves of the test substances *I–IV* ( $c = 2 \cdot 10^{-4} \text{ mol l}^{-1}$ ) in mixed Britton–Robinson buffer–methanol (1 : 9) medium

pH	<i>I</i>		<i>II</i>		<i>III</i>		<i>IV</i>	
	$E_p$ mV	$I_p$ $\mu\text{A}$	$E_p$ mV	$I_p$ $\mu\text{A}$	$E_p$ mV	$I_p$ $\mu\text{A}$	$E_p$ mV	$I_p$ $\mu\text{A}$
1.7 <sup>a</sup>	–85	3.17	–80	3.10	–85	3.60	–105	2.73
4.2	–415	1.71	–430	1.70	–390	2.56	–390	1.63
5.4	–435	2.54	–465	2.50	–425	2.96	–450	2.43
6.1	–465	2.77	–480	2.70	–455	3.50	–465	2.34
7.0	–520	2.66	–510	2.65	–515	3.48	–520	2.23
8.3	–640	1.94	–615	2.23	–620	2.44	–630	2.00
9.1	–695	1.46	–675	2.10	–730	2.08	–680	1.88
9.6	–750	1.35	–740	1.68	–755	2.29	–715	1.78
9.8	–765	1.43	–750	1.65	–795	2.35	–735	1.75
10.4	–825	1.63	–795	1.88	–820	2.61	–790	1.63
10.9	–830	1.88	–800	2.13	–815	2.79	–785	1.68
11.7	–815	1.97	–795	2.25	–820	2.83	–795	1.85

<sup>a</sup> Attained using a mixture of 0.1M-HClO<sub>4</sub> and CH<sub>3</sub>OH (1 : 9).

of the peak heights on the concentration are linear in the range from  $1 \cdot 10^{-6}$  to  $2 \cdot 10^{-8} \text{ mol l}^{-1}$  (see Table VI), while a deviation from linearity occurs in the range  $1 \cdot 10^{-5} - 1 \cdot 10^{-6} \text{ mol l}^{-1}$ , apparently as a result of electrode passivation, as the electrode surface is not renewed during the measurement.

TABLE IV

Parameters of the calibration straight lines and determination limits for the test substances using the DPP method in Britton-Robinson buffer-methanol medium (1 : 9) with pH 6.1

Compound	$c$ $\text{mol l}^{-1}$	Slope $\mu\text{A mol}^{-1} \text{ l}$	Intercept $\mu\text{A}$	$r^a$	$L_Q^b$ $\text{mol l}^{-1}$
I	$(2-10) \cdot 10^{-5}$	— <sup>c</sup>	— <sup>c</sup>	— <sup>c</sup>	
	$(2-10) \cdot 10^{-6}$	$2.30 \cdot 10^4$	$4.90 \cdot 10^{-3}$	0.9949	
	$(2-10) \cdot 10^{-7}$	$2.31 \cdot 10^4$	$9.65 \cdot 10^{-4}$	0.9999	$1.6 \cdot 10^{-7}$
II	$(2-10) \cdot 10^{-5}$	— <sup>c</sup>	— <sup>c</sup>	— <sup>c</sup>	
	$(2-10) \cdot 10^{-6}$	$2.28 \cdot 10^4$	$-5.96 \cdot 10^{-8}$	0.9970	
	$(2-10) \cdot 10^{-7}$	$1.85 \cdot 10^4$	$1.60 \cdot 10^{-3}$	0.9978	$2.2 \cdot 10^{-7}$
III	$(2-10) \cdot 10^{-5}$	$2.19 \cdot 10^4$	$4.50 \cdot 10^{-2}$	0.9971	
	$(2-10) \cdot 10^{-6}$	$2.55 \cdot 10^4$	$2.00 \cdot 10^{-3}$	0.9999	
	$(2-10) \cdot 10^{-7}$	$2.51 \cdot 10^4$	$1.10 \cdot 10^{-3}$	0.9998	$1.5 \cdot 10^{-7}$
IV	$(2-10) \cdot 10^{-5}$	$1.52 \cdot 10^4$	$1.22 \cdot 10^{-1}$	0.9947	
	$(2-10) \cdot 10^{-6}$	$1.92 \cdot 10^4$	$2.10 \cdot 10^{-3}$	0.9994	
	$(2-10) \cdot 10^{-7}$	$1.66 \cdot 10^4$	$2.69 \cdot 10^{-4}$	0.9939	$2.9 \cdot 10^{-7}$

<sup>a</sup> Correlation coefficient; <sup>b</sup> determination limit; <sup>c</sup> data not evaluated because of nonlinearity of the calibration curves.

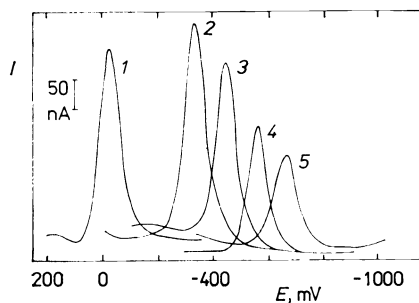


FIG. 3  
FS DP voltammograms of II ( $c = 1 \cdot 10^{-5} \text{ mol l}^{-1}$ ) in a mixture of  $0.1\text{M} \cdot \text{HClO}_4\text{-CH}_3\text{OH}$  (1 : 9) at pH 1.7 (1) and Britton-Robinson buffer-methanol (1 : 9) at pH 5.3 (2), 7.0 (3), 9.1 (4), and 11.7 (5)

TABLE V

The effect of the pH on the FSDP voltammetric curves of the test substances *I–IV* ( $c = 1 \cdot 10^{-5} \text{ mol l}^{-1}$ ) in mixed Britton–Robinson buffer–methanol (1 : 9) medium

pH	<i>I</i>		<i>II</i>		<i>III</i>		<i>IV</i>	
	$E_p$ mV	$I_p$ nA	$E_p$ mV	$I_p$ nA	$E_p$ mV	$I_p$ nA	$E_p$ mV	$I_p$ nA
1.8 <sup>a</sup>	–60	167.5	–25	357.5	5	285.0	–35	300.0
4.0	–245	185.0	–260	252.5	–200	267.5	–250	312.5
5.3	–320	325.0	–330	400.0	–280	267.5	–335	590.0
6.0	–365	332.5	–370	437.5	–320	269.0	–385	635.0
7.0	–430	247.5	–435	325.0	–375	207.5	–435	465.0
8.3	–515	185.0	–525	245.0	–450	152.5	–515	430.0
9.1	–575	175.0	–550	235.0	–510	145.0	–560	405.0
9.5	–570	167.5	–570	262.5	–610	120.0	–590	435.0
9.8	–580	165.0	–585	250.0	–575	115.0	–605	375.0
10.5	–620	175.0	–625	202.5	–595	117.5	–630	360.0
11.0	–640	132.5	–655	167.5	–650	80.0	–650	360.0
11.7	–680	150.0	–685	240.0	–685	62.5	–695	410.0

<sup>a</sup> Attained using a mixture of 0.1M-HClO<sub>4</sub> and CH<sub>3</sub>OH (1 : 9).

TABLE VI

Parameters of the calibration straight lines and determination limits for the test substances for the FS DPV method in Britton–Robinson buffer–methanol (1 : 9) medium with pH 5.3

Compound	$c$ mol l <sup>-1</sup>	Slope $\mu\text{A mol}^{-1} \text{ l}$	Intercept $\mu\text{A}$	$r^a$	$L_Q^b$ mol l <sup>-1</sup>
<i>I</i>	$(2-10) \cdot 10^{-7}$	$7.20 \cdot 10^4$	$3.00 \cdot 10^{-3}$	0.9993	—
	$(2-10) \cdot 10^{-8}$	$8.25 \cdot 10^4$	$-8.50 \cdot 10^{-4}$	0.9936	$2.8 \cdot 10^{-8}$
<i>II</i>	$(2-10) \cdot 10^{-7}$	$1.03 \cdot 10^5$	$7.60 \cdot 10^{-3}$	0.9989	—
	$(2-10) \cdot 10^{-8}$	$9.25 \cdot 10^4$	$-1.50 \cdot 10^{-4}$	0.9931	$2.9 \cdot 10^{-8}$
<i>III</i>	$(2-10) \cdot 10^{-7}$	$1.23 \cdot 10^5$	$1.75 \cdot 10^{-2}$	0.9961	—
	$(2-10) \cdot 10^{-8}$	$1.19 \cdot 10^5$	$7.50 \cdot 10^{-5}$	0.9965	$2.5 \cdot 10^{-8}$
<i>IV</i>	$(2-10) \cdot 10^{-7}$	$1.30 \cdot 10^5$	$1.02 \cdot 10^{-2}$	0.9980	—
	$(2-10) \cdot 10^{-8}$	$9.88 \cdot 10^4$	$3.45 \cdot 10^{-4}$	0.9908	$3.3 \cdot 10^{-8}$

<sup>a</sup> Correlation coefficient; <sup>b</sup> determination limit.



The sensitivity of FS DPV was further increased by using adsorptive accumulation of the test substances on the surface of the hanging mercury drop. The following dependence of the peak height ( $I_p$ ) on the time elapsed between drop formation and recording of the voltammogram ( $t$ ) was found:

$t$ , s:	15	30	60	120	300
$I_p$ , nA:	12	27	51	97	201

This dependence was measured in ten-fold diluted Britton–Robinson buffer–methanol medium (1 : 9) at pH 2.8, which was found to be optimum, especially from the point of view of the effect of the peaks of impurities in the buffer on the baseline for the base electrolyte. Accumulation was carried out at a potential of +100 mV in stirred solution and the recording was made 10 s after termination of stirring. A linear concentration dependence can be obtained under these conditions in the range  $(2-10) \cdot 10^{-9} \text{ mol l}^{-1}$  (see Table VII).

#### *Linear Scan Voltammetry at a Hanging Mercury Drop Electrode*

It was found<sup>15</sup> that the pH has the same effect on the LS voltammetric curves as for the other techniques. The largest and best developed peaks were obtained in medium with pH 4.0, where a linear concentration dependence can be obtained in the range  $(2-10) \cdot 10^{-7} \text{ mol l}^{-1}$ . In contrast to FS DPV, reliable results in the range  $(2-10) \cdot 10^{-8} \text{ mol l}^{-1}$  cannot be obtained using LSV. Partial regeneration of the electrode in FS DPV between pulses could be important here.

TABLE VII

Parameters of the calibration curves for determination of the test substances in the range  $(2-10) \cdot 10^{-9} \text{ mol l}^{-1}$  by the FS DPV method with accumulation in ten-fold diluted Britton–Robinson buffer–methanol medium (1 : 9) at pH 2.8

Compound	Slope $\mu\text{A mol}^{-1} \text{ l}$	Intercept $\mu\text{A}$	$r^a$	$L_Q^b$
<i>I</i>	$1.41 \cdot 10^6$	$-3.75 \cdot 10^{-4}$	0.9983	$1.9 \cdot 10^{-9}$
<i>II</i>	$1.34 \cdot 10^6$	$1.75 \cdot 10^{-4}$	0.9957	$2.8 \cdot 10^{-9}$
<i>III</i>	$1.40 \cdot 10^6$	$3.85 \cdot 10^{-3}$	0.9980	$2.1 \cdot 10^{-9}$
<i>IV</i>	$9.63 \cdot 10^5$	$-7.75 \cdot 10^{-4}$	0.9991	$1.7 \cdot 10^{-9}$

<sup>a</sup> Correlation coefficient; <sup>b</sup> determination limit.

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