

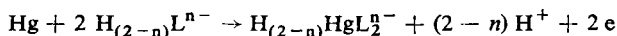
## ANODIC OXIDATION OF MERCURY IN THE PRESENCE OF THIOETHER ACIDS: METHANE-1,1-BIS-MERCAPTOACETIC ACID

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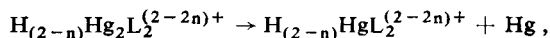
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The anodic oxidation of mercury in the presence of methane-1,1-bis-mercaptoacetic acid (MBMA) has been studied by  $DC_r$ , DP,  $AC_1$ , and  $AC_2$  polarography, cyclic voltammetry, and coulometry. The electrode process is controlled by the adsorption of the product formed according to:



with  $n = 0$  at  $pH < pK_1$ ,  $n = 1$  at  $pK_1 < pH < pK_2$ , and  $n = 2$  at  $pH > pK_2$ . No adsorption of MBMA is observed. The behaviour of MBMA at a hanging mercury drop electrode (HMDE) by cathodic stripping voltammetry (CSV) has been also studied. At MBMA concentrations above  $1 \cdot 10^{-6} \text{ mol l}^{-1}$ , the stripping voltammograms showed two well defined peaks, at c.  $-0.140 \text{ V}$  and at c.  $-0.300 \text{ V}$ . The anodic process occurring during the pre-electrolysis in CSV is described by the formation of a Hg(I) compound:  $2 Hg + 2 H_{(2-n)}L^{n-} \rightarrow H_{(2-n)}Hg_2L_2^{(2-2n)+} + 2 e$  followed by its disproportionation:



where  $n$  has the above-mentioned values.

Methane-1,1-bis-mercaptoacetic acid (MBMA),  $H_2C(S-CH_2-COOH)_2$ , is a sulphur containing diprotic acid ( $pK_1 = 3.16$  and  $pK_2 = 3.96$  at  $18^\circ\text{C}$  and  $\mu 0.1 \text{ mol l}^{-1}$ ) (ref.<sup>1</sup>), which forms 1:1 and 1:2 chelates with some divalent metals<sup>1-4</sup> and with  $Ag(I)$  ion<sup>5</sup>. No previous general voltammetric study on the anodic behaviour of MBMA is known. Parkinson and Anson<sup>6</sup> showed that MBMA has a little tendency towards adsorption on Hg, from quantitative data obtained in an adsorption study of carboxylic ligands containing thioether groups. At potentials more positive than  $-100 \text{ mV}$ , large increases in charge density at HMDE were produced by the presence of thioether carboxylate anions, probably due to the participation of the sulphur atom in the adsorption at the most positive potentials.

Saxena *et al.*<sup>7</sup> showed that MBMA is reduced at DME to  $HSCH_2COOH$ , in a reversible and diffusion-controlled process at pH above 11.

A systematic study of the anodic oxidation of mercury in the presence of MBMA is made in the present work using, as in previous voltammetric studies on other thioether compounds<sup>8</sup>, polarographic techniques: direct current—rapid ( $DC_r$ ), differential pulse (DP) and alternating current (first and second harmonic —  $AC_1P$ ,

AC<sub>2</sub>P), cyclic voltammetry, and coulometry. The application of cathodic stripping voltammetry (CSV) to the determination of MBMA is also studied.

## EXPERIMENTAL

### Chemicals and Instrumentation

Methane-1,1-bis-mercaptoacetic acid (Fluka *puriss.*) was purified by twice crystallization. Acetic acid, sodium acetate (Carlo Erba, A.R. grade) and sodium perchlorate (Merck A.R. grade) were used. The rest of the chemicals and reagents, and the instrumentation employed were described previously<sup>8</sup>.

### Procedure

Aqueous solutions of MBMA were prepared daily in air-free ultrapure filtered water (Culligan Purification Water System).

The experiments were performed at  $25^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$  and  $0.01 \text{ mol l}^{-1}$  total ionic strength in  $\text{KNO}_3$  plus acetate buffer, or in  $\text{NaClO}_4$ . Both buffered (acetate buffer) and unbuffered perchlorate media were studied. Polarographic techniques (including DC<sub>r</sub>, DP, and AC) as well as voltammetric and coulometric techniques were employed following the procedure described former<sup>8</sup>. CSV procedure was also described previously<sup>9</sup>.

## RESULTS

### *Electrocapillary Curves*

The electrocapillary curves obtained in the presence of MBMA agree with the adsorption results obtained by Parkinson and Anson<sup>6</sup>. The cathodic part of the plots coincides with that of supporting electrolyte alone, showing the very small tendency of thioether group towards adsorption<sup>6</sup>. The shift of the electrocapillary maximum towards more cathodic potentials and the decrease of the drop time above  $+0.2 \text{ V}$  show that the compound electrochemically formed is adsorbed on the electrode.

### *Polarography*

Like other ligands, MBMA reacts with  $\text{Hg(II)}$  ions formed by oxidation of mercury from DME. Attempts were made to find a supporting electrolyte of low pH with good buffering properties in which a well-defined polarographic wave and peak due to MBMA would be formed. Polarograms obtained in acetate buffered nitrate medium by DC<sub>r</sub>P, DPP, and AC<sub>1</sub>P are shown in Fig. 1. Waves and peaks obtained in unbuffered perchlorate medium are somewhat better developed, except AC<sub>1</sub> peaks which are poorly developed in all cases. Worse developed waves and peaks were observed in other usual complexing buffers.

An anodic wave or peak is observed in the pH range 2–9. At MBMA concentrations below  $1 \cdot 10^{-4} \text{ mol l}^{-1}$ , the anodic DC<sub>r</sub> waves are practically undistinguishable

from those of the supporting electrolyte, while the DP and AC anodic signals are not yet well defined.

The relationship between  $E_{1/2}$  or  $E_p$  and pH is shown in Fig. 2. Slope values of c. 60 and 30 mV/pH are observed at  $\text{pH} < \text{p}K_1$  and  $\text{p}K_1 < \text{pH} < \text{p}K_2$ , respectively. Plots of  $E_{1/2}$  or  $E_p$  vs  $\log [\text{MBMA}]$  are linear, with slope values of 30 mV.

The  $\text{DC}_r$  anodic limiting current,  $I_d$ , and the DP and AC anodic peak current,  $I_p$ , are independent of pH, in the range studied (2–9). By  $\text{DC}_r\text{P}$  and  $\text{DPP}$ , the values of  $I_d$  and  $I_p$ , respectively, are independent of MBMA concentration, at least in the range  $1 \cdot 10^{-4}$ – $2 \cdot 10^{-3} \text{ mol l}^{-1}$ , as that is expected in a full-covered electrode adsorption process. By  $\text{AC}_1\text{P}$  and  $\text{AC}_2\text{P}$ , at phase angle of  $0^\circ$ , plots of  $I_p$  vs  $[\text{MBMA}]$  were found to be linear, at least in the same range, but with slope values very low in comparison with those obtained previously for other thioether acids<sup>8</sup>:  $I_p = 2.4 \cdot 10^{-3} + 0.21 [\text{MBMA}]$ ,  $r^2 = 0.9950$ , and  $I_p = 6.4 \cdot 10^{-2} + 0.22 [\text{MBMA}]$ ,  $r^2 = 0.9937$ , at pH 2.55 by  $\text{AC}_1\text{P}$  and  $\text{AC}_2\text{P}$ , respectively ( $I_p$  and  $[\text{MBMA}]$  are given in mA and  $\text{mol l}^{-1}$ , respectively).

In the  $\text{DC}_r\text{P}$  study the following facts were observed: the plots of  $-E$  vs  $\log (I_d - I)^2/I$  are straight lines with slope values of c. 29 mV; the approximate de-

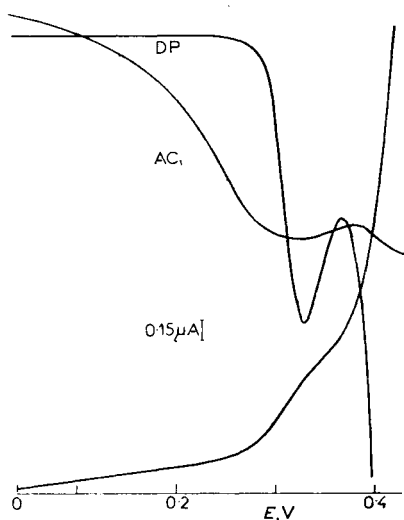


FIG. 1

Morphology of the anodic waves and peaks of a  $4.0142 \cdot 10^{-4} \text{ mol l}^{-1}$  MBMA solution in buffered  $0.01 \text{ mol l}^{-1} \text{ KNO}_3$  at pH 3.5;  $t = 1 \text{ s}$ ; DP:  $\Delta E = -40 \text{ mV}$ ;  $\text{AC}_1$ :  $\Delta E = 10 \text{ mV}$

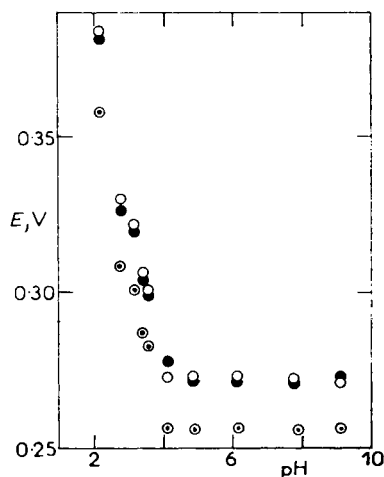


FIG. 2

Relationship between  $E_{1/2}$  or  $E_p$  and pH for a  $6.2997 \cdot 10^{-4} \text{ mol l}^{-1}$  MBMA solution by three polarographic techniques. DPP:  $\Delta E = 40 \text{ mV}$  ( $\circ$ );  $\text{AC}_1\text{P}$ :  $\Delta E = 5 \text{ mV}$  ( $\circ$ );  $\text{AC}_2\text{P}$ :  $\Delta E = 10 \text{ mV}$  ( $\bullet$ )

pendence of  $I_d$  on  $h$  ( $\log I_d = -7.35 + 0.78 \log h$ ,  $r^2 = 0.9971$ , for a  $2.8672 \cdot 10^{-3} \text{ mol l}^{-1}$  MBMA solution at pH 3.5 in the  $h$  range 40–80 cm) shows adsorption control as the main feature of the electrode process; the dependence  $I_d$  vs  $t$  cannot be satisfactorily studied, because at  $t > 3$  s the anodic wave is overlapped by the anodic current due to the supporting electrolyte. However, in the range 0.4–2 s,  $I_d$  decreases when  $t$  increases.

In the DPP experiments, the following results were obtained: the relationship between the values of the DPP peak potentials,  $E_p$ , and the pulse magnitude ( $\Delta E$ ) follows the expected equation for a reversible process<sup>10</sup>:  $E_p = E_{1/2} - \Delta E/2$ , where  $\Delta E$  is taken with its sign, ( $E_p = 0.307 - 0.55 \Delta E$ ,  $r^2 = 0.9944$ , for a  $4.0142 \cdot 10^{-4} \text{ mol l}^{-1}$  MBMA solution at pH 3.5 in the  $\Delta E$  range from  $-10$  mV to  $-90$  mV); the plots\*  $I_p$  vs  $(1 - \sigma)/(1 + \sigma)$  are linear in the  $\Delta E$  range below 60 mV ( $I_p = -0.023 + 3.35(1 - \sigma)/(1 + \sigma)$ ,  $r^2 = 0.9999$  for a  $4.0142 \cdot 10^{-4} \text{ mol l}^{-1}$  MBMA solution at pH 3.5, where  $I_p$  values are given in  $\mu\text{A}$ ), and the graphical extrapolation of the plot shows that the intercept in  $I_p$  axis is practically equal to zero. At  $\Delta E$  above 60 mV, the  $I_p$  values are higher than those predicted from the straight line; the half-peak widths ( $W_{1/2}$ ) are independent of pH and concentration; at pulse magnitudes below 50 mV, the  $W_{1/2}$  values are in agreement with the theoretical reversible values<sup>10</sup>, while at  $\Delta E$  above 50 mV are always lower than these; linear plots of  $E$  vs  $\log [(I_p/I)^2 \pm ((I_p - I)/I)^{1/2}]$  are obtained when the DPP peaks are well developed.

In the AC<sub>1</sub> experiments the following facts were also observed: the peaks are broader ( $W_{1/2}$  c. 60 mV) than those corresponding to a fully reversible process ( $90/n$  mV (ref.<sup>11</sup>)), as Fig. 1 also shows; the  $E_p$  values are independent of the sinusoidal amplitude ( $\Delta E$ ), while linear plots  $I_p$  vs  $\Delta E$  are obtained in the  $\Delta E$  range 5–30 mV ( $I_p = 3.16 \cdot 10^{-7} + 2.38 \cdot 10^{-7} \Delta E$ ,  $r^2 = 0.9968$ , for a  $4.0142 \cdot 10^{-4} \text{ mol l}^{-1}$  MBMA solution at pH 6 ( $I_p$  in A and  $\Delta E$  in mV)).

### Cyclic Voltammetry

Cyclic voltammograms, at the HMDE, run between  $-0.2$  V and  $0.4$  V for a  $2.0071 \cdot 10^{-4} \text{ mol l}^{-1}$  MBMA solution at pH 3.8 are shown in Fig. 3. At the three above-mentioned media only an anodic peak is observed which appears at c.  $0.290$  V in buffered and unbuffered perchlorate media, or at c.  $0.305$  V in buffered nitrate medium. In all cases  $I_p$  remains independent of concentration, at least in the concentration range  $1 \cdot 10^{-4}$ – $2 \cdot 10^{-3} \text{ mol l}^{-1}$ . The linear relationship between  $I_p$  and the scan rate,  $v$ , ( $I_p = 1.04 \cdot 10^{-7} + 5.18 \cdot 10^{-9} v$ ,  $r^2 = 0.9990$ , in the scan rate range  $10$ – $600 \text{ mV s}^{-1}$  for a  $4.0142 \cdot 10^{-4} \text{ mol l}^{-1}$  MBMA solution at pH 3.75) confirms the adsorption control. The differences between the peak potentials obtained in the anodic scan and its cathodic reversal,  $\Delta E_p = E_p^a - E_p^c$ , increase when

\*  $\sigma = \exp(\Delta E/2) (nF/RT)$ .

the scan rate increases; for a  $4.014 \cdot 10^{-4} \text{ mol l}^{-1}$  MBMA at pH 3.8 (nitrate buffered medium) the following data have been obtained:

$v, \text{ mV s}^{-1}$	10	50	100	200	300	400	500	600
$\Delta E_p, \text{ mV}$	7	11.5	13.5	23	25	32	39	55

For a reversible two-electron process, the difference should be 29 mV, independently of the scan rate. Those results show that the anodic reaction of MBMA is not fully reversible. When the anodic scan is stopped at the maximum of the voltammetric peak, the anodic current falls immediately to the ground current, as is to be expected for an adsorption controlled process. Several anodic scans applied successively to the same mercury drop reproduce the same waveform.

### Coulometry

The coulometric study was done at constant potential values within the diffusion plateau region of the polarogram previously recorded for the same solution, usually in the range from 0.280 V to 0.360 V depending on MBMA concentration.

At pH below 6 the results showed that there is a one-electron transfer *per* MBMA molecule, as it is to be expected from the formation of a 1 : 2 Hg(II) complex, as it is discussed later. On the contrary, at pH > 6 the coulometric study shows a two-electron transfer *per* MBMA molecule, probably due to the coulometric formation

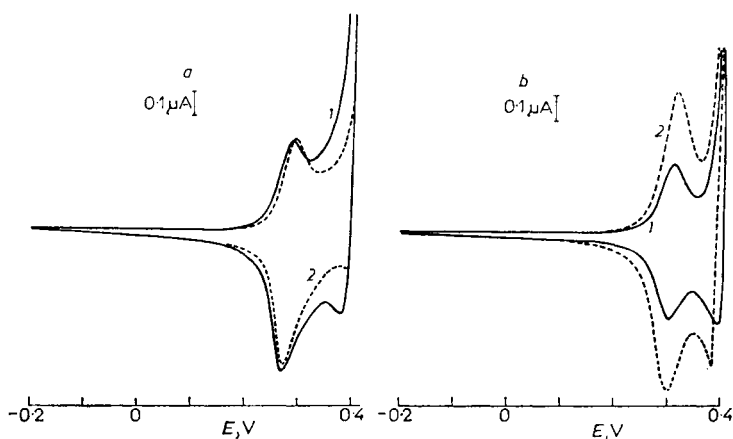


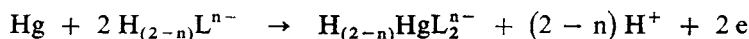
FIG. 3

Cyclic voltammograms of a  $2.0071 \cdot 10^{-4} \text{ mol l}^{-1}$  MBMA solution. *a* 1 perchlorate buffered medium, 2 perchlorate unbuffered medium,  $v = 50 \text{ mV s}^{-1}$ ; *b* nitrate buffered medium, 1  $50 \text{ mV s}^{-1}$ , 2  $100 \text{ mV s}^{-1}$

of mercuric basic salts, according to:  $\text{Hg} + \text{L}^{2-} + 2 \text{H}_2\text{O} \rightarrow \text{Hg}(\text{OH})_2\text{L}^{2-} + 2 \text{e}^- + 2 \text{H}^+$ . The difference between the polarographic and the coulometric behaviours at  $\text{pH} > 6$  can be explained on the basis of the very different electrode surfaces and time scales for both types of experiments; the formation of mercuric basic salts predominating at  $\text{pH}$  above 5 (ref.<sup>12</sup>) on the longer time scale.

#### Overall Electrode Processes

On the basis of the above described results, and assuming that one electron transfer *per* MBMA molecule is occurring by polarography, cyclic voltammetry and coulometry at  $\text{pH} < 6$ , the anodic process will be given by:



with  $n = 0$  at  $\text{pH} < \text{p}K_1$ ,  $n = 1$  at  $\text{p}K_1 < \text{pH} < \text{p}K_2$  and  $n = 2$  at  $\text{pH} > \text{p}K_2$ . Under the experimental conditions studied, the electrode process is controlled by the adsorption of the product formed. No adsorption of ligand is observed, in agreement with the results of Parkinson and Anson<sup>6</sup>. The usual reversibility polarographic criteria show a reversible anodic two-electron process, although the more restrictive cyclic voltammetric criteria show that the process is not fully reversible. The potential at which this reaction occurs depends on the stability of the Hg(II)-MBMA complex in the solution investigated. If this complex is more stable than those of mercury with other components in the supporting electrolyte, the anodic wave and peak will be connected with this complex formation. Because the anodic process was found polarographically reversible, the value of the stability constant of the  $\text{HgL}_2$  chelate was determined from the dependence of  $E_{1/2}$  upon the  $\text{pH}$  (ref.<sup>13</sup>). The average values obtained were found to be:  $\log \beta_2 = 10.25$  (0.36) (by DPP) and 10.20 (0.35) (by AC<sub>1</sub>P). The results obtained have constant values in the  $\text{pH}$  range up to 5. At  $\text{pH}$  above 5 the  $\log \beta_2$  values increase with increase in  $\text{pH}$ , like the results obtained by other authors in the study of relatively small stability chelates<sup>14</sup>; for relatively high stability complexes (Hg-EDTA) the increase was observed only at  $\text{pH}$  above 8 (ref.<sup>15</sup>). This increase may be explained by the predominating formation of Hg(II)-hydroxocomplexes at  $\text{pH}$  above 3 (ref.<sup>12</sup>).

In the coulometric studies at  $\text{pH} > 6$  it seems likely that a Hg(II) basic salt is formed.

#### Electrode Adsorption

The increase in charge density observed at HMDE<sup>7</sup> when potentials are more positive than  $-0.1 \text{ V}$  (ref.<sup>6</sup>) is probably due to the adsorption of the  $\text{H}_{(2-n)}\text{HgL}_2^{n-}$  complex. It seems likely that the sulphur atom of the thioether may participate in the adsorption<sup>6</sup>.

From polarographic adsorption currents, measured by DC, polarography, the approximate saturation values of the surface concentration,  $\Gamma_m$ , and the molecular surface area of the product,  $a$ , were determined<sup>16</sup> in the different media studied polarographically. In Table I the resulting mean values are given. The higher  $\Gamma_m$  and lower  $a$  values obtained in unbuffered medium strongly suggest that, in some way, acetate anion participates in the adsorption process.

### *Cathodic Stripping Voltammetry*

At concentrations below  $1 \cdot 10^{-6} \text{ mol l}^{-1}$  MBMA, the stripping voltammograms (obtained after a pre-electrolysis at 0.1 V during 3 min, on a  $2.20 \text{ mm}^2$  surface electrode) showed a poorly defined peak at c.  $-0.300 \text{ V}$ . The  $I_p$  values of the peak, at this concentration level, are poorly reproducible. At concentrations above  $1 \cdot 10^{-6} \text{ mol l}^{-1}$  MBMA, the stripping voltammograms showed two well defined peaks: one at c.  $-0.140 \text{ V}$  and a second sharper one at c.  $-0.300 \text{ V}$ , independently of MBMA concentration. For the stripping step, the best results were obtained with the differential pulse mode (DP-CSV), as Fig. 4 shows in comparison with the direct current mode (DC-CSV). Poorly defined and poorly reproducible peaks were obtained with the fundamental harmonic alternating current mode (AC<sub>1</sub>-CSV).

Further studies with the DP mode were made in unbuffered perchlorate medium, within the pH 3–4.

The stripping peak heights,  $I_p$ , of both peaks increase in the  $E_{pe}$  range up to 0.2 V, and decrease above 0.2 V. Maximum peak height was obtained when the pre-electrolysis potential was 0.2 V, by both scanning modes, DC and DP. At  $E_{pe}$  values above 0.3 V, mercury drop darkens and anomalous results are obtained. An  $E_{pe}$  value of 0.2 V was adopted as optimum for further experiments. This sort of variation in signal height with  $E_{pe}$  was observed by other authors. According to Bewick and co-workers<sup>17</sup>, at small overpotentials the rate of formation of a crystal in the surface film on the electrode is governed by the slow incorporation of Hg(I) ions into the

TABLE I

Saturation values of the surface concentration,  $\Gamma_m$ , and area of a molecule,  $a$ , of the product determined from DC, polarographic adsorption currents

Medium	$\Gamma_m, \text{ mol cm}^{-2}$	$a, \text{ nm}^2$
Nitrate, buffered	$2.1 \cdot 10^{-10}$	0.78
Perchlorate, buffered	$2.6 \cdot 10^{-10}$	0.63
Perchlorate, unbuffered	$3.0 \cdot 10^{-10}$	0.55

crystal lattice; at more positive potentials, these ions are formed so quickly that they cannot be incorporated and are desorbed, forming the Hg(I) compound in solution instead of on the electrode surface.

A linear relationship between  $I_p$  and pre-electrolysis time,  $t_{pe}$ , is observed at  $t_{pe}$  below 7 min for both peaks. At  $t_{pe}$  above 7 min, the  $I_p$  values are lower than those predicted from the straight line. A pre-electrolysis time of 3 min was adopted for convenience.

The variation of peak heights of both peaks *vs* the square root of the scan rate,  $v^{1/2}$ , in the range  $3-20 \text{ mV s}^{-1}$ , was studied for a  $5.893 \cdot 10^{-5} \text{ mol l}^{-1}$  MBMA solution, at pH 3.9, after a 3-min pre-electrolysis at 0.2 V. The following relationships were obtained:  $I_p = 4.73 \cdot 10^{-8} + 6.08 \cdot 10^{-9}v^{1/2}$ ,  $r^2 = 0.9874$  (for the peak at  $-0.140 \text{ V}$ ) and  $I_p = 2.36 \cdot 10^{-8} + 1.5 \cdot 10^{-8}v^{1/2}$ ,  $r^2 = 0.9925$  (for the peak at  $-0.300 \text{ V}$ ). According to Perchard and co-workers<sup>18</sup>, these facts show that the electrode process is controlled by diffusion of the product formed from the electrode surface layer to the bulk of solution.

A linear dependence was also obtained between peak height and electrode area:  $I_p = 6.6 \cdot 10^{-11} + 3.14 \cdot 10^{-8}A$ ,  $r^2 = 0.9993$  (for the peak at  $-0.140 \text{ V}$ ) and  $I_p = 2.89 \cdot 10^{-9} + 3.43 \cdot 10^{-8}A$ ,  $r^2 = 0.9976$  (for the peak at  $-0.300 \text{ V}$ ), obtained at above-mentioned conditions in the area range  $0.87-2.20 \text{ mm}^2$ . These relationships show that there was no diffusion of the species deposited on the electrode surface to the interior<sup>18</sup>.

When the following instrumental parameters are used for DP-CSV of MBMA:  $E_{pe} = 0.2 \text{ V}$ ,  $t_{pe} = 3 \text{ min}$ ,  $v = 10 \text{ mV s}^{-1}$ ,  $A = 2.20 \text{ mm}^2$  and pulse magnitude,  $\Delta E = -40 \text{ mV}$ , linear dependences between both peak heights and MBMA concentration are obtained, at least within the range from  $1 \cdot 10^{-5}$  to  $8 \cdot 10^{-4} \text{ mol l}^{-1}$ .

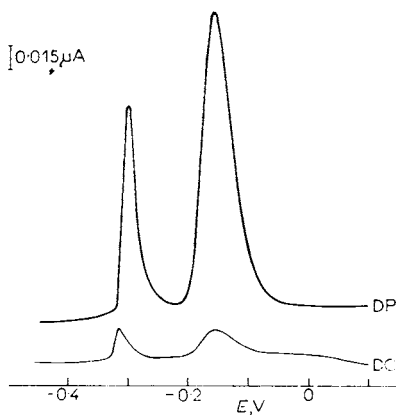


FIG. 4

Morphology of stripping voltammograms by two stripping modes, for a  $1.1787 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1}$  MBMA solution at pH 4;  $E_{pe} = 0.1 \text{ V}$ ;  $t_{pe} = 3 \text{ min}$ ;  $A = 2.20 \text{ mm}^2$ ;  $v = 10 \text{ mV} \cdot \text{s}^{-1}$ ; in DP stripping mode,  $\Delta E = -40 \text{ mV}$



The calibration functions are the following:  $I_p = 2.08 \cdot 10^{-8} + 7.49 \cdot 10^{-4} [\text{MBMA}]$ ,  $r^2 = 0.9930$  (for the peak at  $-0.140$  V) and  $I_p = -3.47 \cdot 10^{-9} + 1.67 \cdot 10^{-3} [\text{MBMA}]$ ,  $r^2 = 0.9992$  (for the peak at  $-0.300$  V). As a consequence the peak at  $-0.300$  V obtained by DP-CSV can be used preferably for MBMA determination in solution within the mentioned concentration range and with a limit of detection of  $6 \cdot 10^{-6} \text{ mol l}^{-1}$ .

The presence of two CSV peaks for MBMA shows that the CSV process is more complex than the polarographic one. The results obtained have a similitude with those obtained by Miller and Teva<sup>19</sup> in the CSV study of cysteine. These authors attributed the double peak observed to the presence of both a Hg(I) and a Hg(II) compound in the film, with the more positive peak being due to the Hg(I) compound. Stankovich and Bard<sup>20</sup> suggested that the double peak observed in the voltammetric study of cysteine could be due to the breaking of adsorbed layers associated with disproportionation processes.

According to these former studies, it seems likely to describe the anodic process occurring during the pre-electrolysis in CSV by the formation of a Hg(I) compound:



followed by its disproportionation:



where  $n = 0$  at  $\text{pH} < \text{p}K_1$ ,  $n = 1$  at  $\text{p}K_1 < \text{pH} < \text{p}K_2$  and  $n = 2$  at  $\text{pH} > \text{p}K_2$ , being the more positive peak (at c.  $-0.140$  V) due to the Hg(I) compound, and the less positive peak (at c.  $-0.300$  V) due to the Hg(II) one. This last process could explain the sharp form of the less positive peak, on the basis of the breaking of the adsorbed layer associated to the disproportionation process, as it was previously suggested<sup>20</sup>.

#### REFERENCES

1. Aplincourt M., Hugel R.: *J. Inorg. Nucl. Chem.* **35**, 345 (1974).
2. Ostacoli G., Campi E., Cibrario N., Saini G.: *Gazz. Chim. Ital.* **91**, 349 (1961).
3. Tiwari S. K., Jain S., Kumar A., Tiwari K. C.: *J. Indian Chem. Soc.* **57**, 571 (1980).
4. Saxena R. S., Parikh R. D., Gupta K. C.: *Monatsh. Chem.* **115**, 141 (1984).
5. Napoli A.: *Ann. Chim.* **71**, 361 (1981).
6. Parkinson B. A., Anson F. C.: *Anal. Chem.* **50**, 1886 (1978).
7. Saxena R. S., Parikh R. D., Gupta K. C.: *Acta Chim. Hung.* **115**, 213 (1984).
8. Casassas E., Esteban M.: *Electrochim. Acta* **31**, 327 (1986).
9. Casassas E., Ariño C., Esteban M.: *Anal. Chim. Acta* **176**, 113 (1985).
10. Parry E. P., Osteryoung R. A.: *Anal. Chem.* **37**, 1634 (1965).
11. Bond A. M.: *Anal. Chem.* **44**, 315 (1972).

12. Kotrlý S., Suchá L.: *Handbook of Chemical Equilibria in Analytical Chemistry*, p. 285. Ellis Horwood Ltd., Chichester 1985.
13. Esteban M., Casassas E., Fernández L.: *Talanta* **33**, 843 (1986).
14. Suznjevic D., Doležal J., Kopanica M.: *J. Electroanal. Chem. Interfacial Electrochem.* **20**, 279 (1969).
15. Matyska B., Doležal J., Roubalová D.: *This Journal* **21**, 107 (1956).
16. Meites L.: *Polarographic Techniques*, p. 188. Wiley, New York 1965.
17. Bewick A., Fleishmann M., Thirsk H. R.: *Trans. Faraday Soc.* **58**, 2200 (1962).
18. Perchard J. P., Buvet M., Molina R.: *J. Electroanal. Chem. Interfacial Electrochem.* **14**, 761 (1967).
19. Miller I. R., Teva J.: *J. Electroanal. Chem. Interfacial Electrochem.* **36**, 157 (1972).
20. Stankovich M. T., Bard A. J.: *J. Electroanal. Chem. Interfacial Electrochem.* **75**, 487 (1977).