

# AN ELECTROCHEMICAL STUDY OF THE S-DERIVATIVES OF 2-AMINO CYCLOPENTENE- 1-DITHIOCARBOXYLIC ACID IN AQUEOUS ETHANOLIC MEDIA

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**ABSTRACT:** *A systematic study on the electrochemical behaviour of the S-derivatives of 2-amino cyclopentene-1-dithiocarboxylic acid (ACDA) has been carried out in aqueous ethanolic solutions by means of polarography, coulometry and voltammetry. All the compounds studied exhibited a well defined anodic wave corresponding to a diffusion controlled process. Controlled potential coulometry gave  $n=1$  per mole for the anodic waves of the S-methyl and N-methyl S-methyl derivatives of ACDA, while for the dimer of ACDA a two electron oxidation wave was obtained.*

**KEY WORDS:** *Electrochemical study, Dithiocarboxylic acid derivatives, Aqueous ethanolic media.*

## INTRODUCTION

The electroanalytical behaviour of 2-amino cyclopentene-1-dithiocarboxylic acid and some of its acid derivatives in aqueous solution and on mercury electrode has been recently studied [1]. It has been shown that the anodic waves obtained in the case of these compounds correspond to mercury compound formation as was proved for other sulfur compounds [2-8]. Due to the importance of these compounds such as

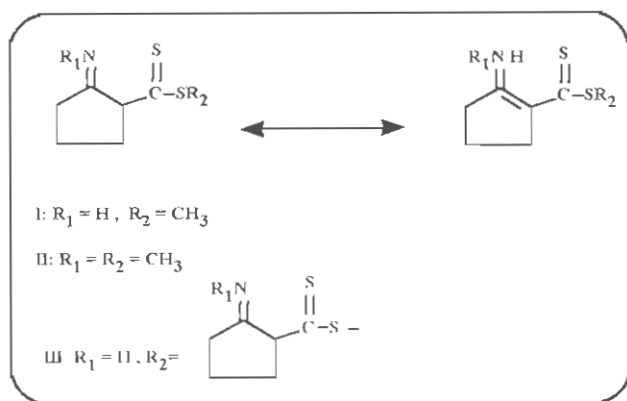
their antifungal activities [9,10] and the use of their metal complexes as models of sulfur metal proteins [11], the electrochemical behaviour of the S-derivatives of ACDA in which one of the sulfur atoms is blocked through alkylation or dimerization is verified in this paper. Since the compounds were not soluble in aqueous media but soluble in aqueous ethanolic solutions, they were studied in the latter media.

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## EXPERIMENTAL

### Apparatus

All electrochemical measurements were performed with a Princeton Applied Research Corp. (PAR) electrochemical system, model 170 polarographic analyzer. A Metrohm hanging mercury drop electrode was used for cyclic voltammetry. A three-electrode system was used in all works. The reference electrode was a SCE and the auxiliary electrode was a platinum wire. All the measurements were made at  $25 \pm 0.2$  °C.

### Reagents

The supporting electrolyte was 0.1 M  $KNO_3$  in 50% ethanol-water mixture. For studying the dimer, 0.1 M  $KNO_3$  was used in 75% ethanol-water mixture.

The ligands were prepared and purified according to *Bordas et al.* [10].

$10^{-2}$  M stock solution of each ligand was prepared in pure ethanol (*Merck*).

## RESULTS AND DISCUSSION

The polarograms of compounds I, II and III all showed a well defined wave with half wave potentials of +0.18, +0.17 and +0.17 V, respectively. Typical examples of polarograms are given for I, in Fig. 1. The heights of the anodic waves for all these compounds showed a linear dependence with concentration and the products of  $i(h_{corr}^{-1/2})$  was also constant, which showed the diffusion behaviour of the mass transfer process associated with these anodic waves.

With increasing concentration of each of the ligands, half wave potentials were remained essen-

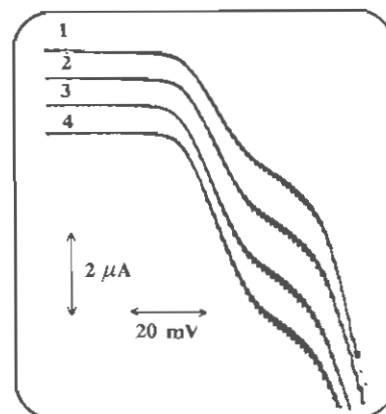


Fig. 1: polarogram of compound I at concentration 1) 5.00; 2) 8.89; 3) 12.00; 4)  $14.50 (\times 10^{-4} M)$ . Polarograms were recorded from  $-0.2$  V vs. SCE towards more positive potentials.

tially constant. This is an indication of a 1:1 (ligand: metal) mercury complex formation [12]. No change was observed in the half wave potential of the anodic waves of I, II and III in the apparent *pH* values of 1-9. This shows that the electrode process in this range does not involve  $H^+$ . The anodic wave due to the dimer (compound III) had a limiting current per unit concentration that was approximately twice that for the anodic waves of the alkyl derivatives (compounds I and II).

The electrocapillary curves for the above ligands did not show any decrease in the drop time of the DME in the potential range studied which is an indication of the fact that there is no adsorption of the product of the anodic reaction.

Controlled potential coulometry at a potential on the plateau of the anodic wave gave  $n=1$  per mole for both compounds I and II, while coulometry of compound III at a potential on the plateau of its anodic wave gave  $n=2$  per mole.

Plots of  $E$  against  $\log i_d - i/i$  were straight lines with correlation coefficients not less than 0.999 and slopes of 0.069, 0.085 and 0.100 for compounds I, II and III, respectively.

It is interesting at this point to compare the esters and dimer of ACDA (compounds I-III), with the acid derivatives in which both sulfur atoms are free for mercury compound formation. The main difference is that, whereas the acid derivatives exhibit at least two anodic waves, one of them being adsorption limited

and another diffusion limited [1], only one diffusion limited wave was observed in the case of compounds I-III. The presence of the adsorption prewave in the case of the acid derivatives was attributed [1] to a monomolecular layer of mercury compound on the mercury electrode and the second wave was assumed to be the result of further deposition of the insoluble mercury complex on the electrode surface. However, analogous adsorption prewave was not observed in the case of compounds I-III, presumably because the mercury complexes of these ligands are likely to be less ordered structurally, so that they are unable to form a compact layer as in the case of the acid derivatives and are only loosely bounded to the electrode. The occurrence of the anodic wave of the acid derivatives at  $\sim -0.4$  V, shows the expected fact that the formation constants of the complexes formed between mercury and the acid derivatives of ACDA are much larger than those of mercury complexes of I-III.

The attribution of the anodic waves of I-III to mercury compound formation was further verified as follows. Linear sweep voltammetry of the compounds I-III on Pt and glassy carbon electrodes showed no oxidation wave in the voltage range observed in the case of the use of mercury electrodes. The wave due to the oxidation of the ligand itself occurs at much more positive potentials (e.g.,  $\sim +0.9$  V for compound I). Moreover, when the products of electrolysis at the potential on the plateau of the anodic waves of compounds I-III were compared by their IR and UV spectra, with the mercury (II) complexes of the corresponding ligands which were prepared classically, they were found to be the same (Fig. 2). These findings together with coulometric data support the idea that the anodic wave observed in the above cases is due to mercury (I) compound formation. The mercury (I) complex then disproportionate to mercury (II) complex as is illustrated below:



In the case of the dimer (compound III), a solution of concentration "C" of the dimer behaves like a

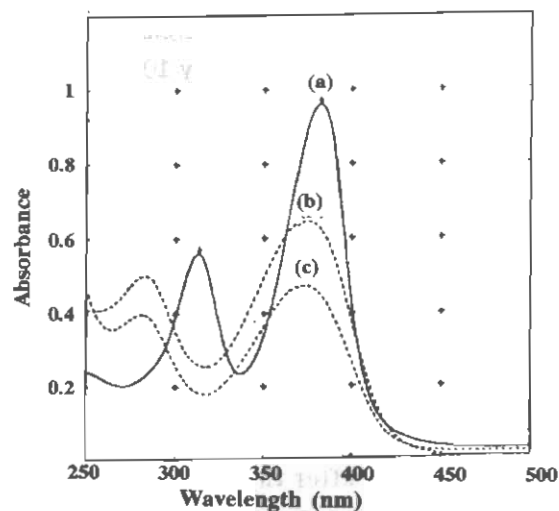


Fig. 2: Visible spectra of a) ligand II and b) synthetically prepared mercury(II) complex of ligand II and c) electrochemically prepared mercury(II) complex.

solution of I of a concentration "2C". The results of coulometric analysis also showed  $n=2$ . The fact that one two-electron step is observed in the case of the dimer (compound III), indicates that the scheme suggested for oxidation of mercury in the presence of compounds I and II is in principle followed and that the two groups behave like separate independent reaction centers and the mercury compound formation at the electrode surface can proceed at both groups practically simultaneously, rather than in a series of successive processes.

The cyclic voltammograms of the above compounds reflect the DC polarographic pattern, (Fig. 3). The diffusion behaviour of the anodic peak was confirmed for all three compounds. For example, for compound I,  $i_{p,a} \propto C$  up to at least  $6 \times 10^{-4}$  M ( $r=0.999$ ) at  $\nu=500$   $\text{mV s}^{-1}$  and  $i_{p,a} \propto \nu^{1/2}$  up to  $\nu=500$   $\text{mV s}^{-1}$  at concentration  $3.6 \times 10^{-4}$  M, ( $r=0.998$ ). Further analysis of the cyclic voltammograms show that an increase in scan rate, resulted in some changes in cyclic voltammetry parameters [13,14]. Full details are given elsewhere [15], but briefly taken compound I as an example, an increase in scan rate from 0.02 to 0.2  $\text{V s}^{-1}$  resulted in an increase of the peak-to-peak separation,  $E_{pp}$ , from 115 to 175 mV with the cathodic peak potential,  $E_{p,c}$ , shifting more than the anodic peak potential,  $E_{p,a}$  (10 mV),  $E_{p,c/2} - E_{p,c}$ , where  $E_{p,c/2}$  is the potential at half-

peak height, i.e., when  $i=i_p/2$ , increased by 27 mV, whereas  $E_{p,a/2} - E_{p,a}$ , increased only 10 mV. Similarly the values  $i_{p,c}/\nu^{1/2}$  was increased from 11.0 to 13.5 whilst  $i_{p,a}/\nu^{1/2}$  was approximately constant at  $13.3 \pm 0.1$  and  $i_{p,c}/i_{p,a}$  was increased from 0.85 to 1.0 by increasing the scan rate. Clearly, from the foregoing information, the asymmetry of the cyclic voltammograms for compound I, arises from the increasingly drawn out nature of the cathodic branch with increasing scan rate, whereas, the anodic wave remains essentially constant. The most likely reason for this is that the reduction process is affected by a coupled chemical reaction after the electron transfer step [13,14]. This is in agreement with the polarographic and coulometric results that the oxidation of mercury to mercury(I), in the presence of ligands (I-III), is followed by disproportionation of mercury (I) complex to mercury (II) complex.

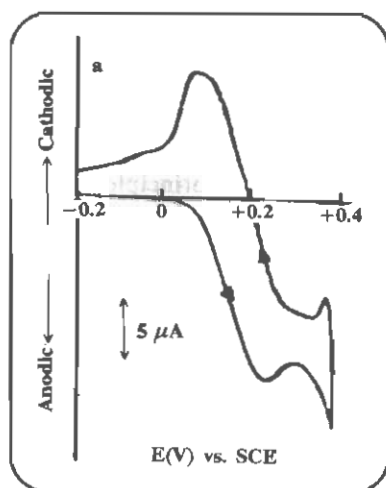


Fig. 3: Cyclic voltammogram of compound I.

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