# New complexanes. XXXVI. Polarographic study of the mercury(II) chelates of alkanedithio-bis(2-aminopropane) acids

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This paper deals with the study of the mercury(II) complexes of five structurally related complexanes of the type of alkanedithio-bis(2-aminopropane) acids. The working method is based on investigation of the polarographic functional relationship  $E_{1/2} = f(pH)$ . The values of stability constants of the investigated complexes have been determined, the region of existence of normal complexes has been characterized and it has been evidenced that the interaction of all acids studied with mercury(II) ions results in formation of chelates in the ratio 1:1, *i.e.* of the type HgL. The investigated new ligands form with Hg(II) relatively very stable chelates the stability of which almost attains the stability of the EDTA complexes.

Методом исследования полярографической функциональной зависимости  $E_{1/2} = f(pH)$  изучены комплексы ртути(II) с пятью структурно близкими комплексонами типа алкандитио-бис(2-аминопропановых) кислот. Были определены константы устойчивости изучаемых комплексов, охарактеризована область существования нормальных комплексов и было доказано, что все изучаемые кислоты образуют при взаимодействии с ионами ртути(II) хелаты в отношении 1:1, типа HgL. Исследованные новые лиганды образуют с Hg(II) относительно очень прочные хелаты, устойчивость которых достигает почти устойчивости комплексов EDTA.

In continuing our foregoing publications [1, 2], we have been concerned in this paper with polarographic study of the mercury(II) complexes formed from five complexanes — MDCy, EDCy, PDCy, BDCy, and HPDCy — of the type of alkanedithio-bis(2-aminopropane) acids or S,S'-alkylenedicysteines

Abbreviations:

- MDCy S,S'-methylenedicysteine.
- EDCy S,S'-ethylenedicysteine.
- PDCy S,S'-propylenedicysteine.
- BDCy S,S'-butylenedicysteine.
- HPDCy S,S'-2-hydroxypropylenedicysteine.

$$\begin{array}{c} H_2N - HC - CH_2 - S - Y - S - CH_2 - CH - NH_2 \\ | \\ COOH \\ HOOC \\ \end{array}$$

by using the method based on investigation of the relationship  $E_{1/2} = f_1(pH)$  or  $E_{1/2} = f_2(\log A)$ .

The fundamental theoretical relationship valid for the polarographic functional relationship  $E_{1/2} = f(pH)$  adapted for the real case of the investigated dicarboxylic acids has the following form

$$E_{1/2} = \frac{RT}{nF} \ln \left( 1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_2 K_1} \right) + E_0 + \frac{RT}{nF} \ln \sqrt{\frac{D_{\kappa}}{D_{\Lambda}}} - \frac{RT}{nF} \ln K_{ML}$$
(1)

where

$$\log A = \log \left( 1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_2 K_1} \right)$$
(2)

Thus the calculation of stability constants of the complexes has been based on the subsequent equation

$$\log K_{\rm HgL} = \log A + \log \sqrt{\frac{D_{\rm K}}{D_{\rm A}}} + \frac{E_0 + E_{1/2}}{0.029}$$
(3)

#### Experimental

The method of preparation of solutions, instrumental technique, and the kind of experimental performance of individual measurements are described in paper [2].

The diffusion character of current and perfect polarographic reversibility of the investigated system are basic conditions for the suitability of the method involving investigation of the relationship  $E_{1/2} = f(pH)$  for the determination of stability constants and have been, therefore thoroughly verified.

In evidencing the diffusion character of current, all chelate-forming agents studied exhibited: (i) a linear relationship  $\bar{I}_d = f_1(\sqrt{h_{H_a}})$  or  $\bar{I}_d = f_2(c)$ , (ii) independence of  $\bar{I}_d$  from pH and kind of the buffer solution used, and (iii) the experimental values of temperature coefficients of the diffusion current were in the range  $\omega = 1.45 \div 1.55\%$ , which was in good agreement, within the range of experimental errors, with the data published in literature [3].

The reversibility of the investigated systems was confirmed for MDCy, EDCy, PDCy, and BDCy by (i) identity of  $E_{1/2}$  corresponding to cathodic and anodic wave at equal pH, (ii) simple waves continuously passing from cathodic to anodic side, obtained by means of the Kalousek commutator [4], and (iii) logarithmic analysis of the anodic polarographic curves in which the values of slope of these linear functional relationships corresponded to two-electron exchange in all cases.

The investigation of the HPDCy complex revealed that the difference between  $E_{1/2}$  values of the anodic and cathodic wave was as far as 52 mV, *i.e.* the system did not fulfil the requirements of polarographic reversibility. As the stability constant should be loaded with a great error in this case, it was not evaluated.

The values of  $E_{1/2}$  used for calculation of the stability constants as well as verification of reversibility of the investigated systems were discontinuously measured for all systems (*i.e.* point after point) by the method of three electrodes in current-less state [5]. Electrode system: separated saturated calomel electrode—mercury electrode—auxiliary SCE.

The relationship  $E_{1/2} = f(pH)$  was determined for all investigated complexanes in eight systems with approximately uniformly graduated pH in the pH range  $5.5 \div 8.5$ . The well-developed anodic waves were measured in the medium of the Britton—Robinson buffer solution.

## **Results and discussion**

The experimental data of the functions  $E_{1/2} = f_1(pH)$  and  $E_{1/2} = f_2(\log A)$  obtained from anodic waves are given in Tables 1 and 2. The values of log K were evaluated from eqn (3). The dissociation constants of the investigated acids and  $E_0$  were taken from our preceding publications [1, 2]. The term  $\log \sqrt{\frac{D_K}{D_A}}$  was negligible.

The graphic representation of the function  $E_{1/2} = f_2(\log A)$  (Fig. 1) has given evidence that the interaction of all investigated complexanes with the mercury(II) ions yields chelates of the type HgL (ratio 1:1) in the investigated pH range  $(5.5 \div 8.5)$  and no hydrogen- or hydroxocomplexes arise.

MDCy _					EDCy				
No.	pН	<i>E</i> <sub>1/2</sub> mV	log A	$\log K_{HgL}$	No.	pН	<i>E</i> <sub>1/2</sub> mV	log A	$\log K_{HgL}$
1	5.54	236	6.38	19.01	1	6.28	169	4.83	19.73
2	6.04	205	5.37	18.88	2	6.84	135	3.73	19.70
3	6.46	180	4.54	19.01	3	7.32	105	2.80	19.90
4	6.93	151	3.61	19.08	4	7.70	90	2.10	19.72
5	7.29	132	2.91	18.92	5	7.97	76	1.62	19.72
6	7.56	117	2.40	19.05	6	8.24	67	1.20	19.61
7	7.80	98	2.01	19.18	7	8.31	56	1.11	19.90
8	8.02	85	1.59	19.21	8	8.51	50	0.77	19.77

Table 1

Experimental values of the function  $E_{1/2} = f_1(pH)$  and  $E_{1/2} = f_2(\log A)$  evaluated from anodic waves for the mercury(II) complexes of MDCy and EDCy

 $I = 0.10 (KNO_3); T = 293 K$ 

#### Table 2

Experimental values of the functions  $E_{1/2} = f_1(pH)$  and  $E_{1/2} = f_2(\log A)$  evaluated from anodic waves for the mercury(II) complexes of PDCy and BDCy I = 0.10 (KNO<sub>3</sub>); T = 293 K

		PDC	су.		BDCy				
No.	pН	<i>E</i> <sub>1/2</sub> mV	log A	log K <sub>HgL</sub>	No.	pН	<i>E</i> <sub>1/2</sub> mV	log A	log K <sub>hgl.</sub>
1	5.58	207	6.38	19.98	1	6.05	180	5.55	20.07
2	6.24	172	5.06	19.89	2	6.30	163	5.06	20.16
3	6.66	145	4.22	19.97	3	6.62	141	4.43	20.29
4	6.90	127	3.74	20.09	4	7.01	120	3.66	20.24
5	7.24	106	3.08	20.14	5	7.36	102	2.97	20.18
6	7.36	99	2.85	20.16	6	7.72	85	2.29	20.08
7	7.83	75	1.98	20.12	7	8.09	59	1.63	20.32
8	8.20	56	1.30	20.14	8	8.32	53	1.26	20.16



Fig. 1. The function  $E_{1/2} = f_2(\log A)$  for the mercury(II) complex of PDCy (anodic waves; I = 0.10, T = 293 K).

Table 3 contains the resulting stability constants of the mercury(II) complexes of all investigated complexanes. These are mean values because eight systems were measured for all agents, which enabled us not only to check the results of measurements several times but also ensured the optimum precision of the determined logarithms of stability constants.

Resultant logarithms of stability constants of the mercury(II) complexes of alkanedithio-bis(2-aminopropane) acids $I = 0.10 \text{ (KNO}_3); T = 293 \text{ K}$										
Complexane	MDCy	EDCy	PDCy	BDCy	HPDCy					
$\log K_{HgL}$	19.04	19.76	20.06	20.19						

Table 3

It results from the chelate-forming characteristics of the investigated complexanes which contain sulfur atoms in the skeleton of the molecule and represent four-donor chelate-forming ligands of the type of dicarboxylic acids that they form with Hg(II) relatively very stable complexes HgL the stability of which is quite comparable to that of the complexes of such analytically important agents as the complexanes of the diamine type or EDTA (log  $K_{Hg-EDTA} = 21.8$ ). An increase in number of the methylene groups in the carbon chain linking the S atoms in the investigated homologous series of ligands brings about a gradual increase in stability of the Hg complexes by one decimal order while the greatest change occurs between the chelates of MDCy and EDCy and a stabilization of log K at the limiting value (log  $K_{HgL} = 20.1$ ) starts to appear from the complexane PDCy. More general conclusions concerning the chelate-forming properties of the above series of complexanes will be published after their investigation by structural methods.

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