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Study of [Pb(II) and Cd(II)-Malonate-triazole] System as a Tool in The Removal of Excess Lead and Cadmium from Human Blood : A Polarographic Approach

R.K. PALIWAL
Department of Chemistry, Narain Postgraduate College, Shikohabad-205 135, India

This paper is mainly focusing on this aspect that the simple and mixed complexes of Pb and Cd with malonate (mal) and triazole (Tr) are soluble and stable and hence may be excreted through urine. The stability constants of soluble mixed ligand complexes [Pb(mal) (Tr)] (Cd(mal) Tr], [Pb(mal) $(Tr)_2$], [Cd(mal) $(Tr)_2$], $[Pb(mal)_2(Tr)]^{2-}$, $[Cd(mal)_2 Tr]^{2-}$ are log β_{11} = 3.01, 1.698, log β_{12} = 3.79, 3.176, log β_{21} = 4.97] 3.146, respectively at the pH of human blood *i.e.* at 7.4. The values of stability constant is determined polarographically.

Key Words: Polarography, Mixed ligand complexes, Stability constants.

INTRODUCTION

The excess of lead and cadmium which is due to the mixing of dangerous chemicals and industrial effluents in river water is highly dangerous to those who dwell in the belt of these rivers. When this polluted water is used by the people, these toxic elements become a part of food chain.

The present study is aimed at presenting complexes which makes excess lead and cadmium soluble. From the survey of literature[1-17] it appears that polarographic studies of mixed complexes of Pb(II) and Cd(II) with malonic acid and triazole from this point of view needs attention. Hence the present work has been undertaken, at the pH of the human blood.

EXPERIMENTAL

All reagents were analytical grade and their solutions were prepared in conductivity water. The ionic strength was maintained at μ = 1.5 M using $NaNO_3$ as supporting electrolyte. The concentration of Pb(II) and Cd(II) was maintained at 1×10^{-3} M. $NaNO_3$ was used as supporting electrolyte and also to maintain a constant ionic strength (μ = 1.5 M). Triton-X-100 (2×10^{-3} %) was used as a maximum suppressor. Polarograms were obtained by means of a manual polarograph (Toshniwal CL 02) in conjunction with Toshniwal polyflex galvanometer (PL 50). All the measurements were made at 25 ± 0.1 ºC and pH 7.4. A saturated calomel electrode (SCE) was used as reference electrode. The d.m.e. had the following characteristics (in 0.1 M $NaNO_3$, open circuit): m = 2.219 mg/s., t = 3.5 s, $m^{2/3} t^{1/6}$ = 2.10 $mg^{2/3} s^{1/2}$, h_{corr} = 40 cm.

The simple system of Pb(II) and Cd(II) with triazole (from 0.04 to 0.20 M) and malonate (from 0.025 to 0.30 M) were studied separately prior to the study of mixed system. In case of mixed systems malonate concentration was varied from 0.025 to 0.30 M and that of [Tr] was kept constant at 0.04 M. The system was repeated at another concentration of [Tr] at (0.08 M).

RESULTS AND DISCUSSION

The reduction of Pb(II) and Cd(II) in triazole and malonate was found to be reversible and diffusion controlled. The same was true for the mixed system. The slops of linear plots of log i/id-i *vs.* $E_{d.m.e.}$ were in the range 30-33 mv and the plots of id *vs.* $h^{½}_{corr}$ were linear and passed through the origin with the addition of increasing amounts of malonate it is seen that $E_{1/2}$ of Pb(II) is shifted, in each case, to more negative values thereby showing the formation of complexes. The plots of $E_{1/2}$ *vs.* log [mal] log [Tr] are smooth curves thereby indicating the formation of successive complexes. The composition and stability constants of the simple complexes have been determined by DeFord and Hume's method[18]. The results are detailed below:

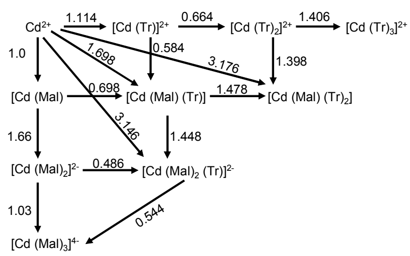
System	Complex Species	Stability constants
Pb(II)- Tr	$[Pb(Tr)]^{2+}$	log β_1 = 1.080
	$[Pb(Tr)_2]^{2+}$	log β_2 = 2.480
Pb(II)- Mal	[Pb(Mal)]	log β_1 = 2.690
	$[Pb(Mal)_2]^{2-}$	log β_2 = 3.500
	$[Pb(Mal)_3]^{4-}$	log β_3 = 4.290
Cd(II)- Tr	$[Cd(Tr)]^{2+}$	log β_1 = 1.113
	$[Cd(Tr)_2]^{2+}$	log β_2 = 1.778
Cd(II)- Mal	[Cd(Mal)]	log β_1 = 1.000
	$[Cd(Mal)_2]^{2-}$	log β_2 = 2.660
	$[Cd(Mal)_3]^{4-}$	log β_3 = 3.690

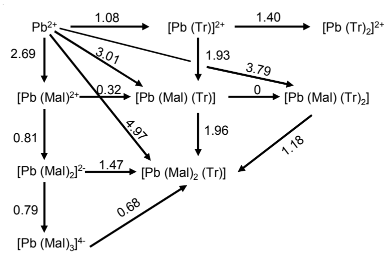
The method of Schaap and McMaster[19] was used to determine the values of the stability constants of mixed complexes. Three mixed complexes are formed in each system. The results are detailed below:

Pb(II)-Malonate-triazole system: [Pb(Mal)(Tr)] log β_{11} = 3.01; $[Pb(Mal)(Tr)_2]$ log β_{12} = 3.79; $[Pb(Mal)_1(Tr)]^{2-}$ log β_{21} = 4.97.

Cd(II)-Malonate-triazole system: [Cd(Mal)(Tr)] log β_{11} = 1.698; $[Cd(Mal)(Tr)_2]$ log β_{12} = 3.176; $[Cd(Mal)_2(Tr)]^{2-}$ log β_{21} = 3.146.

The overall results of the present study are summerised in the following diagrams (**Schemes I** and **II**), where the numerical values shown are the logarithms of the equilibrium constants for the reactions indicated:





Scheme-I: Cd(II)-Malonate-triazole system **Scheme-II:** Pb(II)-Malonate-triazole system

The mixing constant K_M for the following reactions

$$½[Cd(Tr)_2]^{2+} + ½[Cd(Mal)_2]^{2-} \rightleftharpoons [Cd(Mal)(Tr)] \quad (1)$$

$$½[Pb(Tr)_2]^{2+} + ½[Tr(Mal)_2]^{2-} \rightleftharpoons [Pb(Mal)(Tr)] \quad (2)$$

is given by relation

$$\log K_M = \log \beta_{11} - ½(\log \beta_{20} + \log \beta_{02})$$

This works out to be -0.52 and +0.02 respectively for the reaction (1) and (2). This shows that while [Cd)Mal)(Tr)] is less stable than parent binary complexes $[Cd(Mal)_2]^{2-}$ and $[Cd(Tr)_2]^{2+}$ on the other hand [Pb(Mal)(Tr)] is more stable than its binary complexes $[Pb(Tr)_2]$ and $[Pb(Mal)_2]^{2-}$.

The equilibrium constants (log values) for the following disproportionation reactions.

$$2[Cd(Mal)(Tr)] \rightleftharpoons [Cd(Mal)_2]^{2-} + [Cd(Tr)_2]^{2+} \quad (1)$$

$$2[Cd(Mal)(Tr)_2] \rightleftharpoons [Cd(Mal)_2]^{2-} + [Cd(Tr)_3]^{2+} + Tr \quad (2)$$

$$2[Cd(Mal)_2(Tr)]^{2-} \rightleftharpoons [Cd(Mal)_3]^{2-} + [Cd(Tr)_2]^{2+} + Mal^{2-} \quad (3)$$

works out to be + 1.04, -0.508, -0.824, respectively. The +ve log value of equilibrium constant for reaction (1) indicates that the mixed complex [Cd(Mal)(Tr)] is less stable than their simple binary complexes, while the -ve log values for reaction (ii) and (iii) indicates that the formation of ternary complexes $[Cd(Mal)(Tr)_2]$ and $[Cd(Mal)_2(Tr)]^{2-}$ is favoured over the simple ones.

However in case of disproportionation reactions of [Pb(Mal)(Tr)] and $[Pb(Mal)_2(Tr)]^{2-}$ the equilibrium constants (log value) works out to be -0.04 and -3.17 which shows that ternary complexes are more stable than their simple complexes $[Pb(Mal)_2]^{2-}$, $[Pb(Tr)_2]^{2+}$, $[Pb(Mal)_3]^{4-}$.

Thus it can be concluded that Pb(II) and Cd(II) can be excreted as soluble simple as well as mixed complexes through urine as they are sufficiently stable.

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