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A Polarographic Study of Cd(II) and Pb(II)-Imidazole-Sulphosalicylate Mixed Ligand Complexes

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The stability constant of mixed ligand complexes of imidazole and sulphosalicylate with Cd(II) and Pb(II) were determined polarographically. The values of stability constants of these soluble mixed ligand complexes [Cd(Im) (SSA)], $[Cd(Im)\ (SSA)_2]^{2-}$, $[Cd(Im)_2\ (SSA)]$ and [Pb(SSA) (Im)] are found to be log β_{11} = 4.19, log β_{12} = 3.70, log β_{21} = 4.38 and log β_{11} = 4.08, respectively at pH = 7.4 and 25 ± 0.1 ºC.

Key Words: Pb(II), Cd(II), Polarography, Mixed ligand complexes, Stability constants.

INTRODUCTION

The excess of lead and cadmium in the human blood causes stone problem and cancer in gall bladder. Hence, it is imperative that the excess amount of cadmium and lead in human blood is excreted by means of complexes which make lead and cadmium soluble and excrete it through urine. Complexation[1-13] has been used to influence biological process that are metal dependent. Many drugs behaves as ligands coordinating to metals, which affect their homeostasis.

In present study, the polarographic study of soluble mixed ligands complexes of Cd(II) and Pb(II) with imidazole (Im) and sulphosalicylic acid (SSA) are reported.

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 Cd(II) and Pb(II) was maintained at 1×10^{-3} M. Polarograms[14] 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. In case of lead, Triton-X-100 (2×10^{-3} %) was also used as maximum suppressor. 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 = 2.129 mg/s, t = 3.5 s, $m^{2/3}\ t^{1/6}$ = 2.10 $mg^{2/3}\ s^{-1/2}$, h_{corr} = 40 cm.

RESULTS AND DISCUSSION

The reduction of Cd(II) and Pb(II) in imidazole and sulphosalicylic acid 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 linear plots of id *vs.* $h^{½}_{corr}$ passed through the origin. The stability constants of simple complexes of Cd(II) and Pb(II) with imidazole and sulphosalicylic acid were determined separately prior to the study of mixed ligand system. Identical conditions were maintained in both the simple and mixed systems.

Simple system: The simple systems of Cd(II) and Pb(II) with imidazole and sulphosalicylic acid were studied by the method of Deford and Hume[15]. The results are detailed below:

System	Complex species	Stability constants
Pb(II)-Imidazole	$[Pb(Im)]^{2+}$	$\log \beta_1 = 2.84$
	$[Pb(Im)_2]^{2+}$	$\log \beta_2 = 4.77$
	$[Pb(Im)_3]^{2+}$	$\log \beta_3 = 7.17$
Pb(II)-Sulphosalicylate	[Pb(SSA)]	$\log \beta_1 = 1.39$
	$[Pb(SSA)_2]^{2-}$	$\log \beta_2 = 3.04$
Cd(II)-Imidazole	$[Cd(Im)]^{2+}$	$\log \beta_1 = 2.60$
	$[Cd(Im)_2]^{2+}$	$\log \beta_2 = 4.00$
	$[Cd(Im)_3]^{2+}$	$\log \beta_3 = 6.04$
	$[Cd(Im)_4]^{2+}$	$\log \beta_4 = 6.71$
Cd(II)-Sulphosalicylate	[Cd(SSA)]	$\log \beta_1 = 0.60$
	$[Cd(SSA)]^{2-}$	$\log \beta_2 = 1.77$

Mixed system: Lead-sulphosalicylate-imidazole system was studied by varying the concentration of $[SSA]^{2-}$ from 0.025 to 0.20 M keeping [Im] constant at 0.04 M while cadmium-imidazole-sulphosalicylate system at the varying concentration of [Im] from 0.04 to 0.18 M and keeping $[SSA]^{2-}$ constant at 0.10 M. The systems were repeated at another concentration [Im] = 0.08 M in case of Pb(II) and $(SSA)^{2-}$ = 0.20 M in case of Cd(II). The $E_{½}$ values were more negative than those obtained in absence of imidazole in case Pb(II) and in the absence of SSA^{2-} in case of Cd(II), thereby showing the formation of mixed complexes. The method of Schaap and McMaster[16] was used to determine the values of stability constants of mixed complexes (Tables 1 and 2).

The stability constants of mixed complexes were calculated from these constants A, B, C and D. Three mixed complexes as noted below are formed in case of Cd(II)- Im-SSA system, while only one is formed in case of Pb-SSA-Im system.

TABLE-1
Cd(II)-IMIDAZOLE-SULPHOSALICYLATE SYSTEM [Cd] = 1×10^{-3} M, μ = 1.5 M ($NaNO_3$), pH = 7.4, Temp. = 25 ± 1 ºC, $(E_{½})_S$ = - 0.584 V

[Im]	$-E_{½}$	log I_m/I_c	F_{00} [X,Y]	F_{10} [X,Y] $\times 10^{-2}$	F_{20} [X,Y] $\times 10^{-3}$	F_{30} [X,Y] $\times 10^{-5}$
Series-I [SSA] = 0.1 M (Fixed)						
0.04 M	0.652	0.06105	229.5	49.8	74.6	–
0.06 M	0.664	0.06105	584.3	92.3	120.6	15.9
0.08 M	0.673	0.06105	1177.7	143.5	154.3	16.1
0.12 M	0.686	0.08635	3435.5	283.8	219.8	16.2
0.18 M	0.700	0.08635	13309.4	663.9	321.9	15.5
Series-II $[SSA]^{2-}$ = 0.2 M (Fixed)						
0.04 M	0.656	0.08203	328.9	62.2	63.05	–
0.06 M	0.668	0.08635	845.7	127.6	151.00	16.8
0.08 M	0.676	0.08635	1576.8	187.1	187.60	17.2
0.12 M	0.688	0.10863	4225.8	345.5	257.10	17.2
0.18 M	0.702	0.10863	12570.07	693.9	364.90	17.4

Series I: log A = 1.47, log B = 3.3, log C = 4.39, log D = 6.20
Series II: log A = 1.90, log B = 3.56, log C = 4.69, log D = 6.24

TABLE-2
Pb(II)-SULPHOSALICYLATE-IMIDAZOLE SYSTEM
[Pb] = 1×10^{-3}M, μ = 1.5 M ($NaNO_3$), pH = 7.4, Temp = 25 ± 1 ºC,
(Triton-X-100) = 2×10^{-3} %, $(E_{½})_S$ = -0.401 V (SCE)

$[SSA]^{-2}$ M	$-E_{½}$ V	log I_m/I_c	F_{00} [X,Y]	F_{10} [X,Y] $\times 10^{-1}$	F_{20} [X,Y] $\times 10^{-2}$
Series-I [Im] = 0.04 M (Fixed)					
0.025	0.429	0.66377	10.31	11.24	16.96
0.050	0.434	0.07442	15.50	16.01	18.0
0.100	0.443	0.09520	32.78	25.28	18.2
0.150	0.449	0.09948	57.10	33.06	18.7
0.200	0.456	0.09948	91.1	41.8	18.4
Series-II [Im] = 0.08 M (Fixed)					
0.025	0.434	0.070380	15.36	17.4	–
0.050	0.438	0.086770	21.78	21.5	23.1
0.100	0.447	0.099480	45.20	34.2	24.2
0.150	0.454	0.112577	80.35	46.1	24.1
0.200	0.460	0.112577	128.22	58.6	24.3

Series I: log A = 0.87, log B = 1.84, log C = 3.26
Series II: log A = 1.04, log B = 2.00, log C = 3.38

[Cd (Im) (SSA)]	$\log \beta_{11} = 4.19$
$[Cd (Im) (SSA)_2]^{2-}$	$\log \beta_{12} = 3.70$
$[Cd (Im)_2 (SSA)]$	$\log \beta_{21} = 4.38$
[Pb (SSA) (Im)]	$\log \beta_{11} = 4.08$

The mixing constants (K_M) for the reactions:

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

$$½[Cd(Im)_4]^{2+} + ½[Cd(SSA)_2]^{2-} \rightleftharpoons [Cd(Im)_2\ (SSA)] \quad (2)$$

are given by the following equations.

$$\log K_{M(1)} = \log \beta_{11} - ½\ (\log \beta_{20} + \log \beta_{02})$$

$$\log K_{M(2)} = \log \beta_{21} - ½\ (\log \beta_{40} + \log \beta_{02})$$

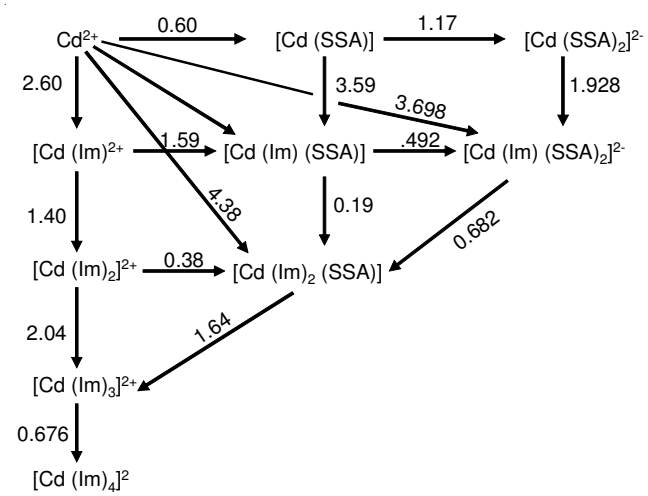
The values of $\log K_{M(1)}$ and $\log K_{M(2)}$ work out to be +2.31 and +0.137, respectively.

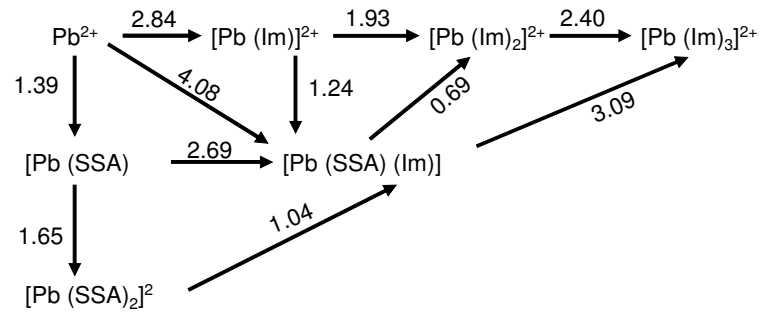
Similarly, the mixing constants K_M for the reaction

$$½[Pb(SSA)_2]^{2-} + ½[Pb(Im)_2]^{2+} \rightleftharpoons [Pb(SSA)\ (Im)]$$

works out to be 0 + 0.175. The positive log values show that the mixed complexes of Cd(II) and Pb(II) with imidazole and sulphosalicylate are more stable than their simple complexes.

The results of the present study are summarized below where the numerical values shows are logarithms of the equilibrium constants for the reaction indicated.





It can be concluded from the above examination that as cadmium and lead forms soluble and stable simple as well as mixed complexes with imidazole and sulphosalicylic acid therefore, they may be excreted through urine.

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