STUDY OF (Cd II–8–HYDROXY QUINOLINE – MALATE/TARTRATE) SYSTEM AS A TOOL IN REMOVAL OF EXCESS CADMIUM FROM HUMAN BLOOD: A POLAROGRAPHIC APPROACH

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ABSTRACT

The excess of heavy metals such as Cadmium, Chromium, Lead etc. are highly injurious to health. With the assumption the heaviness and toxicity are interrelated, heavy metals also include metalloides, such as arsenic; that are able to induce toxity. 8-Hydroxy Quinoline is used as complexing reagent with almost every metal to form un charged chelates . We have been studied mixed ligand complexes of 8-Hydroxy quinoline (8-HQ), malate (mal^{2-}) and tartrate (tart^{2-}) with Cd (II) which make Cd soluble and excrete it through urine. The stability constants of these soluble complexes [Cd(8-HQ) (mal)], [Cd(8-HQ) (mal)$_2$]$^{2-}$, [Cd(8-HQ) $_2$ (mal)] and complexes [Cd(8-HQ) (tart)], [Cd(8-HQ)(tartl)$_2$]$^{2-}$, [Cd(8-HQ) $_2$ (tartl)] are log β_{11} = 6.677, log β_{12} = 7.243, log β_{21} =10.841 and log β_{11} = 5.949, log β_{12} = 6.883, log β_{21} =9.799   respectively at pH 7.4 and 25±0.1^{0}C. The value of stability constant is determined by polarographic method.

 Keyword: Polarography, Mixed Ligand Complexes, Stability Constants, Equilibrium Constant Disproportion.

I. INTRODUCTION

The excess of some metals such as Cadmium, Chromium, Lead etc. are highly injurious to health. . With the assumption the heaviness and toxicity are interrelated, heavy metals also include metalloides , such as arsenic; that are able to induce toxicity[1]. The main route of exposure to Cadmium is via inhalation of cigarette smoke and ingestion of food[2,3]. Several studies have demonstrated that reactive oxygen species (ROS) production and oxidative stress play a key role in the toxicity and carcinogenicity of heavy metals such as cadmium and lead[4-6]. Hence it is imperative that the excess amount of Cadium in the human blood excreted by means of complexes which make Cadmium soluble and excreted it through urine.

The present study is aimed at presenting complexes which make excess cadmium soluble. Hence it is highly useful for the health of children as well as for adults. It will have tremendous medicinal value in future. From the survey of literature[7-22] it appears that polarographic studies of mixed complexes of Cd(II) with 8-HQ and malate and tartrate are still lacking. Hence the present work has been under taken. The communication deals with the studies of mixed ligand complexes of Cd(II) with 8-HQ, malate and tartrate.

II. EXPERIMENTAL

All reagents were analytical grade and their solutions were prepared in conductivity water. The ionic strength was maintained constant at $\mu=1.5$ M using $NaNO_3$ as supporting electrolyte. The concentration of Cd(II) was maintained at 1×10^{-3}M. $NaNO_3$ was used as supporting electrolyte and also to maintain a constant ionic strength ($\mu = 1.5$ M). Triton X–100 (2×10^{-3} %) was used as a maximum suppressor. All the measurements were made at $25\pm0.1°$C and pH 7.4. A saturated calomel electrode (S.C.E.) was used as reference electrode[23]. The d.m.e. had the following characteristics (in 0.1 M $NaNO_3$, open circuit): m=2.219 mg/sec., t=3.5 sec, $m^{2/3} t^{1/6} = 2.10$ $mg^{2/3}$ $sec^{-1/2}$, $h_{corr} = 40$ cm.

The simple system of Cd(II) with 8-HQ, malate and tartrate were studied at different concentrations from 0.10 M to 0.60 M separately prior to the study of mixed system. In case of mixed systems 8-HQ concentration was varied from 1×10^{-4} M to 6×10^{-4} M and that of malate and tartrate was kept constant at 0.10 M. The system was repeated at another concentration of malate and tartrate (0.20 M)

III. RESULTS & DISCUSSION

The reduction of Cd(II) in β-picoline, malate, and tartrate were found to be reversible and diffusion controlled. The same was true for the mixed system. The slopes of linear plots of log i/id-i vs $E_{d.m.e.}$ were in the range 30-32 mv and the plots of id vs $h^{1/2}_{corr}$ were linear and passed through the origin with the addition of increasing amounts of 8-HQ it is seen that $E_{1/2}$ of Cd (II) is shifted, in each case, to more negative values there was showing the formation of complexes. The plots of $E_{1/2}$ Vs log [8-HQ] 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[24]. The results are detailed below:
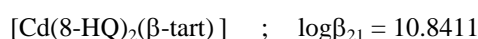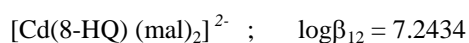
Table: Composition and Stability constants

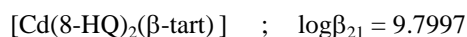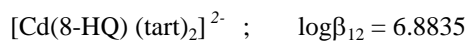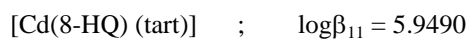| System	Complex species	Stability constants
Cd(II) – β-8-HQ	$[Cd (β-8-HQ)]^{2+}$	log β_1 = 4.6919
	$[Cd (β-8-HQ)_2]^{2+}$	log β_2 = 8.5788
	$[Cd (β-8-HQ)_3]^{2+}$	log β_3 = 12.7427
Cd(II) – mal^{2-}	$[Cd (mal)]$	log β_1 = 1.7923
	$[Cd (mal)_2]^{2-}$	log β_2 = 2.8027
	$[Cd (mal)_3]^{4-}$	log β_3 = 3.3673
Cd(II)– $tart^{2-}$	$[Cd (tart)]$	log β_1 = 1.5947
	$[Cd (tart)_2]^{2-}$	log β_2 = 2.0280
	$[Cd (tart)_3]^{4-}$	log β_3 = 2.8102

The method of Schaap and McMaster[25] was used to determine the values of the stability constants of mixed complexes. The results are detailed below:
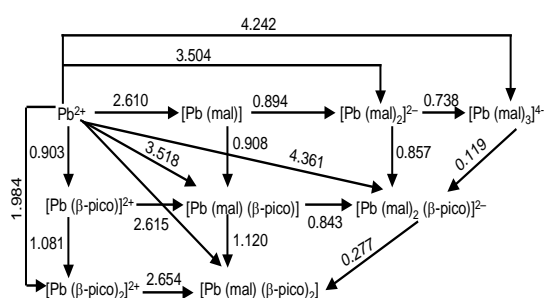
Cd(II)- 8-HQ– Malate system

[Cd(8-HQ) (mal)] ; $\log\beta_{11} = 6.6772$

$[Cd(8\text{-}HQ)(mal)_2]^{2-}$; $\log\beta_{12} = 7.2434$

$[Cd(8\text{-}HQ)_2(\beta\text{-}tart)]$; $\log\beta_{21} = 10.8411$

Cd(II) – 8-HQ – Tartrate system

$[Cd(8\text{-}HQ)(tart)]$; $\log\beta_{11} = 5.9490$

$[Cd(8\text{-}HQ)(tart)_2]^{2-}$; $\log\beta_{12} = 6.8835$

$[Cd(8\text{-}HQ)_2(\beta\text{-}tart)]$; $\log\beta_{21} = 9.7997$

The overall results of the present study are summarized in the following diagrams (Scheme I & II), where the numerical values shown are the logarithms of the equilibrium constants for the reactions indicated:
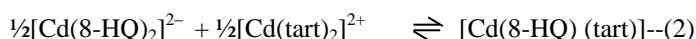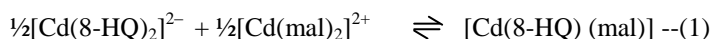

Scheme I: Cd (II)-8-HQ-Malate system
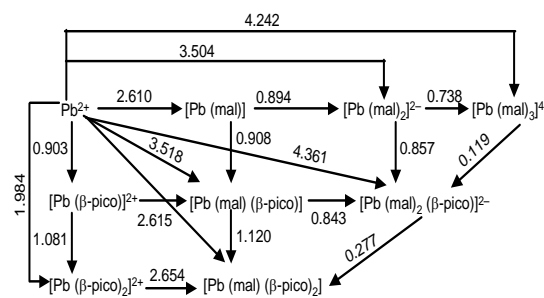
Scheme II: Cd (II)-8-HQ-Tartrate system
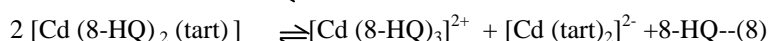
The mixing constant (K_M) for the reactions :

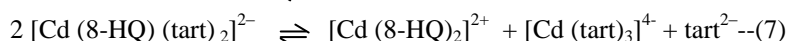$\frac{1}{2}[Cd(8\text{-}HQ)_2]^{2-} + \frac{1}{2}[Cd(mal)_2]^{2+} \rightleftharpoons [Cd(8\text{-}HQ)(mal)]$ --(1)

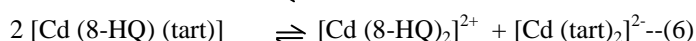$\frac{1}{2}[Cd(8\text{-}HQ)_2]^{2-} + \frac{1}{2}[Cd(tart)_2]^{2+} \rightleftharpoons [Cd(8\text{-}HQ)(tart)]$ --(2)
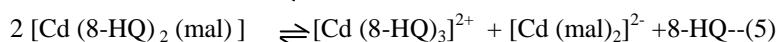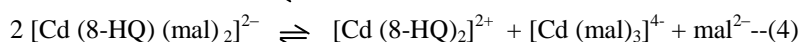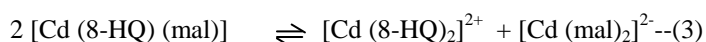
is given by the relation

$\log K_M = \log \beta_{11} - \frac{1}{2} (\log \beta_{20} + \log \beta_{02})$

These works out to be +0.986 and +0.645 for the reactions 1 and 2 respectively. The positive values shows that the mixed complexes are more stable than simple complexes.

The equilibrium constant (log values) for the following disproportionation reactions:

$2[Cd(8\text{-}HQ)(mal)] \rightleftharpoons [Cd(8\text{-}HQ)_2]^{2+} + [Cd(mal)_2]^{2-}$--(3)

$2[Cd(8\text{-}HQ)(mal)_2]^{2-} \rightleftharpoons [Cd(8\text{-}HQ)_2]^{2+} + [Cd(mal)_3]^{4-} + mal^{2-}$--(4)

$2[Cd(8\text{-}HQ)_2(mal)] \rightleftharpoons [Cd(8\text{-}HQ)_3]^{2+} + [Cd(mal)_2]^{2-} + 8\text{-}HQ$--(5)

$2[Cd(8\text{-}HQ)(tart)] \rightleftharpoons [Cd(8\text{-}HQ)_2]^{2+} + [Cd(tart)_2]^{2-}$--(6)

$2[Cd(8\text{-}HQ)(tart)_2]^{2-} \rightleftharpoons [Cd(8\text{-}HQ)_2]^{2+} + [Cd(tart)_3]^{4-} + tart^{2-}$--(7)

$2[Cd(8\text{-}HQ)_2(tart)] \rightleftharpoons [Cd(8\text{-}HQ)_3]^{2+} + [Cd(tart)_2]^{2-} + 8\text{-}HQ$--(8)

works out to be -1.972,-2.547, -6.136, -1.291, -2.378 and -4.828 for the disproportion reactions 3, 4,5,6,7 and 8 respectively. The negative log values for the equilibrium constants show that the formation of mixed complexes is favored over simple ones.

IV. CONCLUSION

The value of the stability constant show that the soluble the mixed ligand complexes of Cd (II) with 8-HQ, malate and tartrate are stable. So 8-HQ, malate and tartrate can form the soluble complexes with the Cadmium present in the human blood and they can excrete it through urine.

V. ACKNOWLDGEMENT

REFERENCES

[1] Duffus JH. Heavy metals-a meaningless term? Pure Appl Chem. 2002;74(5):793–807.

[2] . International Agency for Research on Cancer (IARC) Monographs – Cadmium.Lyon, France: 1993.

[3] . Paschal DC, Burt V, Caudill SP, Gunter EW, Pirkle JL, Sampson EJ, et al. Exposure of the U.S. population aged 6 years and older to cadmium: 1988–1994. Arch Environ Contam Toxicol. 2000;38:377–383. [PubMed]

[4] Tchounwou PB, Ishaque A, Schneider J. Cytotoxicity and transcriptional activation of stress genes in human liver carcinoma cells (HepG$_2$) exposed to cadmium chloride. Mol Cell Biochem. 2001;222:21–28. [PubMed]

[5] 5 Yedjou GC, Tchounwou PB. N-acetyl-cysteine affords protection against lead-induced cytotoxicity and oxidative stress in human liver carcinoma (HepG$_2$) cells. Intl J Environ Res Public Health. 2008;4(2):132–137. [PMC free article] [PubMed]

[6] Tchounwou PB, Yedjou CG, Foxx D, Ishaque A, Shen E. Lead-induced cytotoxicity and transcriptional activation of stress genes in human liver carcinoma cells (HepG$_2$) Mol Cell Biochem. 2004;255:161–170. [PubMed]

[7] Kim, K., Park, Y.K., Suh, J.D. and Lee, C.H., Chem. Abstr. 80, 103, 1730 (1974).

[8] Khurana, S.C. and Gupta, C.M., J. Inorg-Nucl. Chem. 35, 209 (1973).

[9] Nema, K. and Khan, F., J. Indian Chem. Soc., 64, 629 (1987).

[10] Khan, F., J. Indian Chem. Soc., 65, 464 (1988).

[11] Khan, F. and Nema, K., J. Indian Chem. Sco., 66, 17 (1989).

[12] Chaturvedi, D.N. and Gupta, C.M., J. Inorg. Nucl. Chem. 36, 2155 (1974).

[13] Khurana, S.C. and Gupta, C.M., Aust. J. Chem. 40, 2089 (1978).

[14] Chandel, C.P.S., Gupta, C.M. and Sachan, N.P., Chemica Scripta 20, 229 (1982).

[15] Sachan, N.P., Chandel C.P.S. and Gupta, C.M., Chemica Scripta 20, 11 (1982).

[16] Gupta, Nishi, Chandel, C.P.S., Gupta, P.C. and Gupta, C.M., Bull Chem. Soc. (Japan) 56, 3138 (1983).

[17] Gupta, C.M., Kumari, R. and Chandel, C.P.S., Indian J. Chem. 25A, 677 (1986).

[18] Khan, Firoj and Khan, Farid, J. Indian Chem. Soc. 74, 171 (1997).

[19] Jain, Alok and Khan, Farid, J. Indian Chem. Soc., 75, 31 (1998).

[20] Singh, S.K. and Chandel, C.P.S., Oriental J. Chem. 17(2), 239 (2001).

[21] Khan, Farid and Sahu, P.L., J. Indian Chem. Soc. 79(3), 176 (2002).

[22] Sharma, G. and Chandel, C.P.S., Asian. J. Chem. Soc. 14(11), 23 (2002).

[23] Meites, L., 'Polarographic Techniques' Inter Science Publ., New York, p.219 (1965).

[24] Deford, D.D. and Hume D.N., J. Am. Chem. Soc. 73, 5321 (1951).

[25] Schaap, W.B. and Mc Master, D.L., J. Am. Chem. Soc., 83, 4699 (1961).