

Electrochemical studies of Tl(I) complexes with Ornithine monohydrogen chloride in aqueous media

RAJENDRA PRASADYADAV and O.D. GUPTA*

Department of Chemistry, University of Rajasthan, Jaipur - 302 004 (India).

(Received: October 12, 2010; Accepted: November 15, 2010)

ABSTRACT

The polarographic determination of stability constants of metal complexes of Thallium(I) with Ornithine monohydrogen chloride under varying temperatures 300K and 313K in aqueous media have shown the formation of 1:1, 1:2 and 1:3 complexes. The values of overall stability constants of complexes have been calculated by DeFord and Hume's method which is further verified by Mihailov's method. The reduction process was found to be reversible and diffusion controlled. The change in thermodynamic parameters ΔG° , ΔH° and ΔS° accompanying complexation have been also evaluated.

Key words:Thallium(I), Ornithine monohydrogen chloride, polarography, Mihailov's method, DeFord-Hume's method.

INTRODUCTION

The studies of complexation of metal with various ligands polarographically in aqueous media have been carried out from a long time. The number of electrochemical studies of metal ligand complexes are found to be very useful in various field such as analytical, biochemical and pharmaceutical¹⁻³. Kupppusanry Selveraj⁴, Jaganathan Malike and a behaviour of Co(II) in aceto-nitrile-water mixture at DME. Vijay Kumar and coworkers⁵ have evaluated stability constant of Cd(II) and Pb(II) with macrocyclic in ethanol-water mixture. Golube⁶⁻⁸ studied the influence of solvents on the thiocyanato complexes of number of metal ions. Rajendra Kumar Lohiya and coworkers⁹ evaluated the electrochemical studies at DME of copper-2-amino-lepedine complexes in aqueous 1,4-dioxan, DMF, acetonitrile and formamide mixture.

Electrochemical methods are most suitable to investigate the redox properties of new

drugs, which give insight into it. Electroanalytical technique are also used in clinical chemistry and laboratory medicine¹⁰.

Polarographic behaviour of divalent metal ion with acetate¹¹, isovalerate¹², 1,3-diaminopropane¹³ and oxalate¹⁴ has been studied and determined stability constants in aqueous medium.

Thallium, both in its +1 and +3 oxidation states forms complexes with different amino acids. Tl(I) complexes with different amino acids have been studied by some workers¹⁵⁻¹⁹ using different techniques.

The present study deals with polarographic study of complexes of Tl(I) with Ornithine monohydrogen chloride in aqueous medium at 300K and 313K temperatures. The overall formation constant of complexes have also been calculated using mathematical method of Mihailov.

EXPERIMENTAL

A CL-362 polarographic analyser was used to record polarograms using saturated calomel electrode as the reference electrode and dropping mercury electrode was used as microelectrode. All the chemicals which were used are of reagent grade purity. The stock solution of Thallium(I) was prepared from thallium chloride. Ornithine monohydrogen chloride was used as complexing agents and all solution were prepared in double distilled water.

The supporting electrolyte used was KNO_3 and requisite amount was added to maintain ionic strength constant ($m = 1.0\text{M}$). A solution of 0.002% triton X-100 was used as maxima suppressor. The temperature was kept constant using Haake-type ultra thermostat. Before polarographic measurements, purified N_2 gas was passed for 10 to 15 minutes, after presaturation with conductivity to be used in the study.

The capillary has the following characteristics, $m = 2.38 \text{ mg/s}$ and $t = 4.54 \text{ sec}$.

RESULTS AND DISCUSSION

Current-voltage curves were obtained. The concentration of Ornithine monohydrogen chloride was varied from 0.001M to 0.007M. Reduction of Tl(I) complex with ligand give well defined wave. The diffusion current was found to decrease with the increase of ligand concentration as a result of the complex formation and the value of half-wave potential for metal ions and their complexes shifted to more negative value on increasing the concentration of ligand.

The complex ion formed is of much larger size as compared to the aqueous metal ion hence there is the low value of i_d with the increase of ligand concentration. Direct proportionally of diffusion current to the square root of effective height of mercury column indicates the reduction to be diffusion controlled and reversible.

A plot of $E_{1/2}$ versus current resulted a curve indicating the formation of successive complexes. The method of DeFord and Hume's was applied to determine the value of stability constants of

Table 1.

System	Temperature	Methods	Stability Constant		
			$\log\beta_1$	$\log\beta_2$	$\log\beta_3$
Tl(I)-Ornithine monohydrogen chloride	300K	DeFord and Hume	3.17	4.30	5.00
		Mihailov	3.22	4.22	5.04
	313K	DeFord and Hume	3.09	4.15	4.85
		Mihailov	3.12	4.09	4.89

Thermodynamic functions (ΔG° , ΔH° , ΔS°) are recorded below

Metal	Complex species	$\Delta G^\circ (-)$ (Kcal mol ⁻¹)	$\Delta H^\circ (-)$ (Kcal mol ⁻¹)	$\Delta S^\circ (+)$ (Cal K ⁻¹ mol ⁻¹)
Tl(I)-Ornithine monohydrogen chloride	MX_1	4.43	2.61	5.80
	MX_2	5.93	5.11	2.61
	MX_3	6.93	5.12	5.80

M = Tl(I), X = Ornithine monohydrogen chloride

successive complexes. Mihailov's mathematical approach was applied to evaluate stability constants from $F_0(X)$ functions values and the following relation was used.

$$\beta_n = \frac{A.a^n}{n!}$$

where n is the number of complex formed which can be known from DeFord and Hume's method.

The stability constants obtained by two methods have been recorded in Table-1, which are in good agreement.

Thermodynamic parameters have been also calculated for which the complexation studies were carried out at two different temperatures.

This shows that the variation of temperature has no effect on the nature of reduction while the value of stability constants decrease with the increase in temperature because metal ligand bond is weaker at higher temperature and causing easy reduction and increased degree of reversibility i.e. lower temperature favours the formation of stable complexes.

ACKNOWLEDGMENTS

The authors are thankful to the Head, Department of Chemistry, University of Rajasthan, Jaipur for providing the facilities to carry out this research.

REFERENCES

1. R.N. Patal, H.C. Panday, and K.B. Panday, *Bull. Electrochem*, **12**: 612 (1966).
2. F. Khan, and P.L. Sahu, *Ultra Scientist Phys. Sci.*, **12**(1): 106 (2000).
3. B.K. Singh, C.L. Jain, and R.S. Sindhu, *Trans. SAEST*, **30**: 04 (1995).
4. S. Kuppusanry, J. Malike and A. Selveraj, *Oriental Journal of Chemistry*, **20**(1) : (2003).
5. V. Kumar, S. Ijeri and A.K. Shrivastava, *J. Chem. Eng. Data*, **47**(2): 346-350 (2002).
6. A.M. Golube and V.A. Kalibchuk, *Russ. J. Inorg. Chem.*, **11**: 320 (1960).
7. A.M. Golube and L.I. Pomanenko, *ibid*, **5**: 1085 (1960).
8. A.M. Golube and V.V. Skopenka, *ibid*, **6**: 140 (1961).
9. R.K. Lohiya, P.L. Pratihari, R.V. Singh and S.K. Mukherjee, *Oriental Journal of Chemistry*, **17**(3): (2001).
10. M.I. Walsh, M.K.S.E. Din, M.E. Metawally and M.R. Shabana, *J. Chin. Chem. Soc.* **52**(5) : 927-935 (2005).
11. N. Tanaka and K. Kato, *Bull. Chem. Soc., Japan*, **3** : 1412 (1960).
12. K.D. Gupta, K.K. Chaudhary and J.N. Gaur, *India J. Chemistry*, **16A**: 73C (1978).
13. K.D. Gupta, O.D. Gupta and J.N. Gaur, *Trans. SAEST*, **14**: 121 (1979).
14. L. Meites, *J. Am. Chem. Soc.* **72**: 184 (1990).
15. Yakovlev, Y.B., Kulba, Y.F., Ushakova, V.G. and Tezisy, D. Chugaevskoe Soveshch. *Khim, Kompleksh. Soedin*, **1**: 66 (1975).
16. Almagra, V., Pena, M.J. and Sancho, *J. An. Quim.*, **1**: 66 (1975).
17. Kulba, Y.F., Ushakova, V.G. and Yakovlev, Y.B. *Zh. Meorg. Khim.* **19**: 1785 (1974).
18. Tewari, R.C. and Srivastava, M.N. Vigyan Parishad Anushandhan, *Patrika* **16**: 66 (1973).
19. Melgaard, K.G., Univers. Microfilms, Dissert. Abstract **22**: 3847 (1962).