Potentiometric Determination of Stability Constants of Chelates of Indium And Gallium

Neeta Kanoongo[1], ShiellaTikku[2], Anita Kothari[3], VandanaMathur[4]
[1, 2, 3, 4] Dept of Chemistry
[1, 2, 3, 4] S.P.C .Government College, Ajmer(Rajasthan)305001

Abstract- *Potentiometric determination of the chelate of In(III), Ga(III) with three substituted pyridines viz., 2,3-dihydroxypyridine, 2-amino-3-hydro-oxypyridine and 3-hydroxypyridine-2-thiol have been carried out in 50% dioxane-water medium at ionic strength μ= 0.1 M ($NaClO_4$) and temperature 35 ±0.1°C. Although there are many methods available to study the stability of metal-ligand complexes, pH-metry is most frequently used. In extension of our study on solution equilibrium, we used Irving and Rossetti method for the calculation of stability constants, In all cases the order of stability (log K_1,) is In>Ga.*

Keywords- Potentiometric, stability, metal, stability constant.

I. INTRODUCTION

Potentiometric methods are widely used in many areas of solution chemistry. Much attention has been paid to the use of potentiometric methods in the study of binary and ternary complexes of transition metals with biological and pharmaceutical molecules [1-3]. The importance of the potentiometric method is the most accurate and widespread.

The potentiometric titration method is one of the techniques for determining stability constants because this method is based on a powerful and simple electro analytical method. In addition, potentiometric operation offers advantages such as low cost, fast response, easy instrumentation, low detection limit and dynamic range. At the same time, the potentiometric method requires constant ionic strength compensation to ensure that the activity coefficient remains constant for all species in the experimental operating environment [4-5]. Metal ions usually bind to ligands through selective and strong bonds. The strength and selectivity of the metal-ligand bond depend on the stability constant.

Technique in studies related to the ionic equilibrium of different complexes.2,3- Dihydroxypyridine (DHP), 2-amino -3- hydroxyl pyridine (AHP) and 3 –hydroxyl pyridine -2 - thiol (HPT) form a set of chelating agents containing a phenolic group in combination with three different donar groups.The chelates of some metal ions formed with these ligands have been studied spectrophotometrically, polaro graphically and potentiometrically [6-9]. However previously no work has been done on the chelates of Ga(III) and In (III) with these ligands. In view of this, it was considered worthwhile to carry out Potentiometric studies on the chelates of Ga(III) and In (III) metals with DHP, AHP and HPT.

II. MATERIAL AND METHODS

All the reagents were of analytical grade.DHP and AHP procured from Aldrich Chemical Company, U. 8. A. and HPT from Fluka AG, Switzerland were used as such and their solutions were prepared in distilled dioxane. Stock solutions of $Ga(NO_3)_3$ and $InCl_3$, were prepared and used after standardisation. All the potentiometric measurements were carried out on pH-meter model ELE international, using combined glass electrode (accurate total 0.01 pH units).A constant temperature (35 + 0,1°C) was maintained. The following solutions (Total volume 20 ml) were titrated against standard tetra methyl ammonium hydroxide (TMAH) (0. 1M) in an inert atmosphere of nitrogen and an ionic strength of μ = 0.1M ($NaClO_4$)

(i) 3ml $HClO_4$, (0.01 M) + 1 ml $NaClO_4$, (2.0 M) + 1.0 ml KNO_3, or KCI (0.01 M) + 5 ml water + 10 ml dioxane.

(ii) 3ml $HClO_4$, (0.01. M) + 1 mi $NaClO_4$, (2.0 M) + 1,0 ml KNO_3, or KCl (0.01 M) + 10 ml ligand (0.01 M) + 5 ml water.

(iii) 3 ml $HClO_4$, (0.01 M) + 1 mi $NaClO_4$, (2.0 M) + 1 ml metal nitrate or chloride (0.01M) ++ 10 m) ligand (0.01 M) + 5 ml water.

The Irving and Rossetti technique of proton-ligand and metal ligand was applied to find out the values of Proton-ligand and metal ligand stability constants. The approach of Irving-Rossetti to binary systems was applied for the mixed system. The results are summarized in Table 1.

$$M + L \leftrightarrow ML$$

$$ML + L \leftrightarrow ML2$$

III. RESULT AND DISCSSION

The plots of volume of alkali ($NaClO_4$) against pH-meter readings were used to evaluate the proton-ligand stability constants.

All pH measurements were performed at 25˚C ± 0.1˚C. The medium was aqueous acid and ionic strength 0.1 M NaClO4. From the titration curves of solutions (i) and (ii)n_A values at corrected pH values were calculated in all the systems and for each system a curve between n_A values and the corresponding pH values was plotted. The values of log $K_{1H}$and log K_{2H} (the first and second proton formation constants, respectively) are the pH values corresponding to n_A= 0.5 and 1.5, respectively. The values of log $K_{1H}$and log$K_{2H}$are tabulated in Table 1.

Table-1

METAL	CONSTANTS	LIGAND		
		DHP	AHP	HPT
H^+	$\log k_1^H$	9.84	9.93	9.02
	$\log k_2^H$	-	6.08	-
Ga (III)	$\log k_1$	9.96	7.80	7.56
In(III)	$\log k_1$	8.32	7.18	7.02

In case of DHP and HPT second proton-ligand constant could not be determined because DHP and HPT which are capable of existing in two resonant Keto -enol forms but exist almost entirely in the Keto forms. However, in case of AHP two proton ligand stability constants (log $K_{1H}$and log K_{2H})were determined since in this case NH, group would accept a proton from the acidic medium and thus two inflexions would be shown in presence of mineral acids, first corresponding to the dissociation of conjugate acid of AHP and other due to the neutralization of phenolic group. In all potentiometric studies on the Chelates of Ga(III) and In(III) cases log K_{1H}corresponds to the proton of the phenolic group on 3-position and log K_{2H}corresponds to the proton of conjugate acid of AHP. PL and n values calculated from the titration curves. The values of the stability constants given in table 1. It was not possible to evaluate the value of log k2 as hydrolysis of metal Chelates takes place at n>1. [10]

IV. CONCLUSION

In the present article, strength of metal donar bond for these metal complexes is therefore expected to follow the order O>N>S. The three ligands under study contain respectively phenolic (DHP), amino (AHP), thiol (HPT) groups ortho to a phenolic group. The stability of these metal Chelates should follow the order DHP>AHP>HPT. The same is found true for these ligands.

The order of stability constants for the metal Chelates irrespective of the ligand is Ga>In. Our results are in conformity with the earlier observation. The reported data in this study will make an important contribution to the literature.

V. ACKNOWLEDGMENT

We are thankful to The Principal, Head chemistry department, S.P.C.Govt. College Ajmer for providing research facilities.

REFERENCES

[1] Daniele, P., Zerbinati, O., Zelano, V. and Ostacoli, G. Thermodynamic andSpectroscopic Study of Copper(II)-glycyl-L-histidylglycine Complexes in Aqueous Solution. Journal of the Chemical Society , Dalton Transactions , 10, 2711-2715 , 1998.

[2] Amrallah, H., Abdalla, A. and El-Haty, Y. Mixed Ligand Complexes of Benzimidazoleand Pyrimidine Hydroxyazo Dyes with Some Transition Metals andGlycine, DL-Alanine or DL-Leucine. Talanta, 46, 491-500 , 1998.

[3] Inci, D. and Aydin, R. (2017) Potentiometric Studies on Complexation of Cu(II) Ionwith Methyl/Nitro-Substituted 1,10-Phenanthrolines and Selected Amino Acids.Journal of Solution Chemistry , 46, 124-138, 2017.

[4] ANSARI[1] FB, Farooqui M, Quadri SH. Complexation of some metal ions with metformin hydrochloride in acidic aqueous solutions. Oriental Journal of Chemistry.;26(2):667-70,2010.

[5] Hussain S, Qasem A, Mohsin M. Study of Stability constant of binary & ternarycomplexes of Cefpodoxime and glycine with some metal ions by potentiometric titration method. JUC; 12(3) : 64-70, 2016.

[6] V.Kushwsha,MKatyal and R P Singh, Talenta 21,863, 1974.

[7] Y.L Mehta, B.S.Garg and R P Singh Indian .J.Chem 140,1004,1976.

[8] H.L. kalrra, J.S.halik and V.gera, indianJ.Chem SOC 9, 1427,1982.

[9] R.S. sindhu, K.S pandaya and R.P singh, bonatshefta fur cherie 108, 361,1977.

[10] H M irving and H S rosotti , j chem soc 3397,1953.