IJARSCT
International Journal of Advanced Research in Science, Communication and Technology
International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal
ISSN: 2581-9429
Volume 6, Issue 22, April 2026
Impact Factor: 8.2

Determination of Thermodynamic Parameters of Transition Metal Complexes Prepared from Histidine Derivative in Ethanol-Water System

M. H. Salunke
Bhausaheb Nene College, Pen, Raigad-402107 M.S. (India)
drmadhusalunke1968@gmail.com

Abstract: *The Determination of stability constant of the complexes formed by derivative of histidine, 2-[(4-Hydroxy-3-methoxy-benzylidine)-amino]-3-(1H-indol-3-yl)-proponic acid (HMBAIA)[8]. Its complexes are formed with transition metal ions chlorides and nitrates Zr (II), Nb (III), Mo (III), Pb (II) at the temperatures 298k, 303K, 308K, 313K [6] at constant ionic strength 0.1 M 0f KNO3 in 50% ethanol-water mixture [4] by adopting pH metric technique has been studied by Calvin -Bejrrum method method. The thermodynamic parameters ΔG, ΔH and ΔS were calculated from values of stability constant at different temperatures. The formations of metal complexes were found to be spontaneous and exothermic nature [14]*

Keywords: Potentiometry, amino acid- histidine derivative, Stability constant of metal complexes, ionic strength, thermodynamic parameters.

I. INTRODUCTION

The potentiometric method has been used extensively in many areas of solution chemistry. The attention has been paid to the use of potentiometric methods in the study of transition metals with molecules of biological and pharmaceutical interest [3]. The importance of potentiometric methods as the most accurate and widely applicable technique in studies related to the ionic equilibrium of different complexes [11]. It should be noted that the presence of metal ions in biological fluids could have a significant effect on the therapeutic action of such organic compounds [5].

The potentiometric technique is very good to obtained the data, which is utilities for the evaluation of metal –ligand stability constants in aqueous media using Calvin -Bejrrum method and offers a simpler and generally applicable treatment of n and pL directly from the pH metric titration[12] By performing the pH- metric titrations namely A, A+L, A+L+M, log K values were determine by adopting usual procedure (Calvin -Bejrrum and Ramamoorthy – Santappa)

The metal - ligand formation number $\bar{n}$ are evaluated by using equation:

$$n = \frac{\text{Total concentration of ligand bound to metal}}{\text{Total concentration of metal ion}}$$

The existence of the complex species was inferred from the metal curve (A + R + M) which lies below the ligand curve (A + R).The metal –ligand formation number $\bar{n}$ was determined by using the expression [1].

V_3 = volume of alkali from (A + R + M) curve required to obtain the same pH as noted for (A) and (A + R) curve . T^0M = Initial concentration of metal solution. The free ligand concentration PL has been calculated. K1 and K2 are evaluated for pK1 and pK2, V0 = Initial Volume of the solution. $T^0 M$ and $T^0 L$ are the stiochiometric concentration of the metal and ligand , respectively[13]

DOI: 10.48175/IJARSCT-37026

IJARSCT
International Journal of Advanced Research in Science, Communication and Technology
International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal
ISSN: 2581-9429
Volume 6, Issue 22, April 2026
Impact Factor: 8.2

The log K1 and log K2 where determine by using the half – integral method (ή Vs PL) where ή at 0.50 was taken as log K1 and ή at 1.50 as log K2.

Factors affecting the stabilities of complexes:

The factor affecting the stability of complexes are temperature, concentration of metal ions, ionic strength, chelate formation and effects of substituents etc. but for this study temperature and ionic strength are taken into account [7]. In order to understand the dependence of temperature, ionic strength on the stability constants of the complex species the potentiometric titration is carried out and presented in the experimental part. The prominent factors which affect the stabilities are summarized as below:

The large number of complex compounds may be studied in the category of co-ordination compounds and are difficult as formation and stability of these complexes is greatly influenced by a variety of factors [9]

1.The charge and size on the metal ion – The charge and size of central metal ion is very important to forms a stable complex,

2. The nature of the ligand- The type of ligands such as monodentate, bidentate and polydentate ligands hold the central metal ion and forms a stable complex.

3.Presence of the chelating ring – Some time groups of ligands are attached to the central metal ion and formation of big structured complex taking place.

4. Temperature -

The effect of temperature on the stability of the complex is described by Van't Hoff's relation as-

$$\frac{d \ln K}{dT} = \frac{\Delta H^{\ominus}}{RT^2} \text{ ----------1}$$

$$\Delta G^0 = - 2.303 \text{ RT logK } \text{ ----------2}$$

The enthalpy ΔH and entropy ΔS can also be evaluated by the expression as:

$$\Delta H^0 = 2.303 \text{ R} T_1 T_2 \left\{ \frac{(\log K_2 - \log K_1)}{T_2 - T_1} \right\} \text{ -------3}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \text{ -------4}$$

Where $\log K_1$ and $\log K_2$ are the respective stability constants of the complex species at temperature T_1 and T_2 respectively.

5. Effect of varying Ionic strength: As the ionic strength changes the activity coefficients of the species involved which affect the stabilities depending upon the charge associated with the species[10], the stability decreases or increases with ionic strength can be maintained by using various supporting electrolytes.

6.Steric effect – Steric hindrance also play an important role for the stability of metal complexes because the size of metal ion and size of ligand should be get with less steric repulsion.

II EXPERIMENTAL

2.1 Determination of stability constants: -

All the potentiometric measurements were carried out on pH-meter model ELE international, using combined glass electrode (accurate total ± 0.01 pH units). Before and after each titration, the electrode was calibrated using standard buffer pH ≈ 4.01, pH ≈ 7.00 and pH ≈ 9.00.The experiment carried out at temperature range from 303K – 318K. Pure

IJARSCT
International Journal of Advanced Research in Science, Communication and Technology
International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal
ISSN: 2581-9429 Volume 6, Issue 22, April 2026 Impact Factor: 8.2

transition metal ions nitrates and chlorides (99.9% Pure) were used. All metal nitrates available from Sigma Aldrich Chem. Co., U.S.A. Metal nitrate was prepared in triply distill water and concentration was estimated by standard method.

The solution of 2-[(4-Hydroxy-3-methoxy-benzylidine)-amino]-3-(1H-indol-3-yl)-proponic acid (HMBAIA) and All metal complexeswas prepared in solvents. The pH metric reading in 50% ethanol-water mixture were converted to [H+] value by applying the correction proposed by Van Uitert Haas. The 1,4 dioxane was purified by the method described by Vogel [15]. The overall ionic strength of solution was constant maintains by adding KNO_3. All the solutions were titrated with standard carbonate free NaOH (0.2N) solution at constant ionic strength (0.1M). The titration was carried out in double wall glass jacked titration cell connect to the constant temperature circulating bath. The temperature of reaction cell is constant by circulating water from Thermostat (0.1^oC).

The experimental procedure involved pH metric titrations of solutions of –

1. Free $HClO_4$
2. Free $HClO_4$ + Ligand (A+L)
3. Free $HClO_4$ + Ligand + Metal ion (A+L+M)

Data obtained from each titration is plotted as pH Vs volume of NaOH and corresponding volume at successive pH for each set is determined and calculated.

2.2 Determination of the Thermodynamic parameters: -

The thermodynamic parameters such as Gibb's free energy, entropy change and enthalpy change for formation of complexes were determined. The free energy of formation of complexes is related to its stability constant by the relation.

$\Delta G = 2.303\ RT \log K$

R – Universal gas constant, T- temperature in K, log K – stability constant.

The enthalpy change and Entropy change for complex formation were calculated by using Gibb's-Helmoltz equations and other standard relations.

$\Delta H = 2.303\ RT_1T_2 / (T_2-T_1) \log K$

$\Delta S = (\Delta G - \Delta H) / T$

Table -1 Thermodynamic stability constant K of HMBAIA complexes with transition metal ions at 0.1 M ionic strength KNO_3 in 50% ethanol-water mixture.

Temparature	Zr(II),	Nb(III),	Mo(III),	Pb(II)
298k	3.492	3.015	2.351	1.523
303K,	3.531	3.107	2.368	1.559
308K,	3.542	3.128	2.381	1.591
313K,	3.556	3.157	2.397	2.057

Table-2- Thermodynamic parameters of HMBAIA complexes with transition metal ions at 0.1M ionic strength in 50% ethanol-water mixture.

System	-ΔG (J/Mol.)				-ΔH (J/Mol.) (308K)	ΔS (J/Mol.) (313K)
Temperature	298K	303K	308K	313K		
Zr(III)	87.647	74.693	62.478	18.753	2.450×10^{-1}	0..005
Nb(III)	61.589	56.596	53.367	16.679	7.896×10^{-2}	0.028
Mo(III)	58.019	52.458	48.796	13.682	6.478×10^{-2}	0.023
Pb(III)	95.436	91.489	84.745	81.856	4.869×10^{-2}	0.022

IJARSCT
International Journal of Advanced Research in Science, Communication and Technology
International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal
ISSN: 2581-9429
Volume 6, Issue 22, April 2026
Impact Factor: 8.2

III. RESULT AND DISCUSSION

In all complexes the proton-ligand stability constants values increase with increase in temperature for all increasing order experimental temperature. This suggested that liberation of protons becomes easier at higher temperature. The liberation of proton is easier due to the presence of –OH group at metal and para-position (negative inductive effect [10].

The values of metal-ligand stability constant values also increase with increase in temperature. This suggests that the complex formation is exothermic and favorable at higher temperature. The negative values of ΔH and ΔG of complex formation indicates the complex formation process is spontaneous [2]. The all values of entropy change ΔS are positive indicating that the disorder of system taking place in complexation[13]. The values of ΔS are very small in indicates the complexes less entropy even at higher temperature. The values of ΔH are very large and are mainly responsible for complex formation. The stabilities of these metal complexes were found as the following order Pb(II)>Zr(II)>Nb(III)>Mo(III).

REFERENCES

1. Alok Vyas and R.P. Mathur, J Rare Earths, 2009 27(3), 457-460
2. Daniele, P., Zerbinati, O., Zelano, V. and Ostacoli, G. (1998) Thermodynamic Study of Copper(II)-glycyl-L-histidylglycine Complexes in Aqueous Solution. Journal of the Chemical Society, Dalton Transactions, 10, 2711-2715.
3. E.H. EL –Mossalamy, Port. Eletrochimica Acta 2009, 27(2), 143-152.
4. E.Maria, Pachon Ibancz Felipe Fernanide, J of Antimicrobial Chemtheropy, 2006, Vol.58(3) 689-692
5. Kirschner, S., Wei, Y., Francis, D. and Bergam, J. (1966) Anticancer and Potential Antiviral Activity of Complex Inorganic Compounds. Journal of Medicinal Chemistry, 9, 369-372.
6. Kuchekar, Eastern Pharmacist, 1998, Vol.41 (492), 133-134.
7. Lata Jain, Suresh Jangid, Hanwant Singh and R.K. Mehta, J Ind. Inst. Sci 1992, 72, 495-499
8. M. Niemi, J.T. Buckmam, M.F. Fromm, ADIS International 2003, Vol.42, No.9:819-850
9. R. Sarin and K.N. Munshi, J Inorg Nuc Chem, 1972 Vol.34 (2) 581-590
10. Ramandeep Kaur and B.S. Sekhon, J. Ind Chem Soc. 2006 83, 645
11. Rossotti, F. and Rossotti, H. (1961) The Determination of Stability Constants and Other Equilibrium Constants in Solution. 4th Edition, McGraw-Hill Book Company Inc., New York.
12. Samir A. Abdel-Latif, Saber E. Mansour and Abdulrahman A. Fatouh, Natural Sci.,2010, 793-802
13. Sangeeta Sharma, M.C. Shah, Dipika Dalwadi, Falguni Thakkar and J.J. Vora. Res J.Chem. Env 2008 12(4) 29-34
14. Tiangang Li, John Y.L. Chiang Am. J. of Physical gastrointesinal Physiology, 2004, Vol.288, 74-84
15. Vogel's G.H. Jarffery S. Bassetl, R.C. Denney "Text Book of Quantitative Chemical Analysis" Vth edition, ELBS Longman, 1997,53.