www.ijbar.org
ISSN 2249-3352 (P) 2278-0505 (E)
Cosmos Impact Factor-5.86

Determination of stability constant (K) and ΔG^0, ΔH^0 and ΔS^0 of La(III), Nd(III), Dy(III), and Er(III) of rare earths metal complexes prepared from Schiff's base derivative of amino acid in mixed solvent system

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ABSTRACT:- In the present study determination of stability constant (K) and determination of thermodynamic parameters ΔG^0, ΔH^0 and ΔS^0 of metal complexes of derivative of amino acid L-Tryptophan -3-(1H-Indol-3-yl)-2 [(4-methoxy-bezylidene)-amino]-propionic acid(4-methoxy - benzylidene) - hydrazide (IMBAPAMBH) as a ligand and La(III), Nd(III), Dy(III), and Er(III) of rare earths metal ions are performed. $RT\ln K = -\Delta G^0$ is the link between thermodynamic data and the equilibrium constant (stability constant) K[1]. When $\Delta rG^{\ 0} > {}^{0}K <$ 1, This stability constant (K) of complexes with Free energy (G) useful to calculate two thermodynamic dissociation parameters such as $\Delta H°$, $\Delta S°$. At the temperatures 298k, 303K, 308K,313K[2] at constant ionic strength 0.1 M 0f KNO_3 in 50% dioxane-water mixture[3] by adopting pH metric technique has been studied. The Determination of stability constant K of the complexes formed with rare earths metal ions La(III), Nd(III), Dy(III), and Er(III) chlorides and sulphate. The formations of metal complexes were found to be spontaneous and exothermic nature[4].

Key word:- Amino acid derivative – Schiff's base, pH-metric study, Stability constant of metal complexes (K), ionic strength (u), Thermodynamic parameters (ΔG^0, ΔH^0, and ΔS^0).

Introduction- pH-metric titration (e.g., Irving and Rossotti method): This method involves titrating a metal ion solution with a ligand in a buffer solution while monitoring the pH. The resulting titration curve allows for the determination of the formation constants (stability constants)[5]. To determine a complex's stability constant (K) and its related change in thermodynamic parameters (Gibbs free energy, enthalpy, and entropy), you first measure the stability constant at various temperatures. Then, use the Van't Hoff equation to find the enthalpy change (ΔH). With K and ΔH, you can calculate the standard free energy change ($\Delta G°$) using $\Delta G° = -RT\ln K$, and the standard entropy change ($\Delta S°$) using the Gibbs-Helmholtz equation: $\Delta G° = \Delta H° - T\Delta S°$.[6] Research papers in chemistry often determine the stability constant of a metal complex and its associated thermodynamic parameters (free energy (ΔG), enthalpy (ΔH), and entropy (ΔS)) by measuring the stability constant at different temperatures using methods such as pH-metric titration or spectrophotometry. The stability constant, which reflects the affinity of a metal ion for a ligand, is then used to calculate $\Delta G°$ (e.g., using $\Delta G° = -2.303\ R\ T\ \log K$), and the Van't Hoff equation can be applied to the stability constants obtained at varying temperatures to find ΔH and ΔS, enabling discussion of the complex's spontaneity and stability.

The different method are used for determination of thermodynamic parameters such Gibbs free energy change ($\Delta G°$), entropy change ($\Delta S°$) and enthalpy change ($\Delta H°$). These parameters state the physiochemical properties of a chemical system. Previously, many techniques have been applied to find the solubility products of various systems. These techniques include spectral studies; viscosity, refractive index and some electro-analytical method like conduct metric, potentiometric, polarography and voltammetry etc. Most of the researchers aimed to infer data of very precise solubility product of these systems that are extremely less soluble or nearly insoluble in aqueous systems[7]. Method of very precise evaluation of K_{sp} values of various types of reagents having structural dissimilarities is reported. Clark also suggested a method to evaluate solubility product constant for various compounds along with a practical aspect pertaining to the problems associated with the determination of such compounds. Methods for Determination

Spectrophotometry: This technique involves measuring the absorbance of the solution at different wavelengths, which can be used to determine the concentration of metal complexes and their stability constants.

Polarography: Used in some studies to determine stability constants for complexes involving sulfonamides and other ligands, as seen in studies on cadmium complexes.

Calculating Thermodynamic Parameters

Stability Constant (K) Measurement: The stability constant (K) is determined experimentally at a fixed temperature, often by one of the methods above.

Free Energy (ΔG): The standard free energy change (ΔG°) is calculated directly from the stability constant using the equation: $\Delta G^\circ = -2.303\ R\ T \log K$ Where: R is the ideal gas constant and T is the temperature in Kelvin. Enthalpy (ΔH) and Entropy (ΔS).The stability constants are measured at several different temperatures (e.g., at intervals of 10°C).The Van't Hoff equation is then used to determine ΔH.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. By performing the pH- metric titrations namely A, A+L, A+L+M, log K values were determine by adopting usual procedure (Irving - Rossotti and Ramamoorthy – Santappa)[8.]

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

$$n = \frac{\text{Total concentration of ligand bound to metal}}{\text{Total concentration of metal ion}} \qquad \text{------------ } 1$$

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:

$$n = \frac{(V_3 - V_2)(N + \varepsilon^0)}{(V_0 + V_2)nA\ T^0M} \qquad \text{---------------- } 2$$

Where 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 by using the expression:

$PL = -\log L$ --------------------3

EXPERIMENTAL:-

2.1 Determination of stability constants:- The pH measurement were out with equip-tronic EQ-610 pH meter (accuracy ± 0.01 units) using combine glass electrode at temperature range from 303K – 318K[8]. Pure rare earth nitrates (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 L-Tryptophan -3-(1H-Indol-3-yl)-2 [(4-methoxy-bezylidene)-amino]-propionic acid (4-methoxy - benzylidene) - hydrazide (IMBAPAMBH)[1] and all metal complexes with La(III), Nd(III), Dy(III), and Er(III) chlorides and sulphate ions was prepared in solvents. The pH metric reading in 50% 1,4 dioxane-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[9]. 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°C). 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 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.

$\Delta G = 2.303\, RT \log K$ ------------------------------------- (1)

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.

$\Delta H = 2.303\, RT_1T_2 / (T_2-T_1) \log K$ ------------------------ (2)

$\Delta S = (\Delta G - \Delta H) / T$ --- (3)

Table -1 Thermodynamic stability constant K of IMBAPAMBH complexes with rare earths metal ions at 0.1 M ionic strength KNO_3 in 50% dioxane-water mixture.

Temparature	La(III)	Nd(III)	Dy(III)	Er(III)
298k	2.769	2.075	3.784	4.125
303K,	3.521	2.134	3.869	4.258

308K,	3.738	2.386	4.125	4.379
313K,	3.948	2.417	4.289	4.483

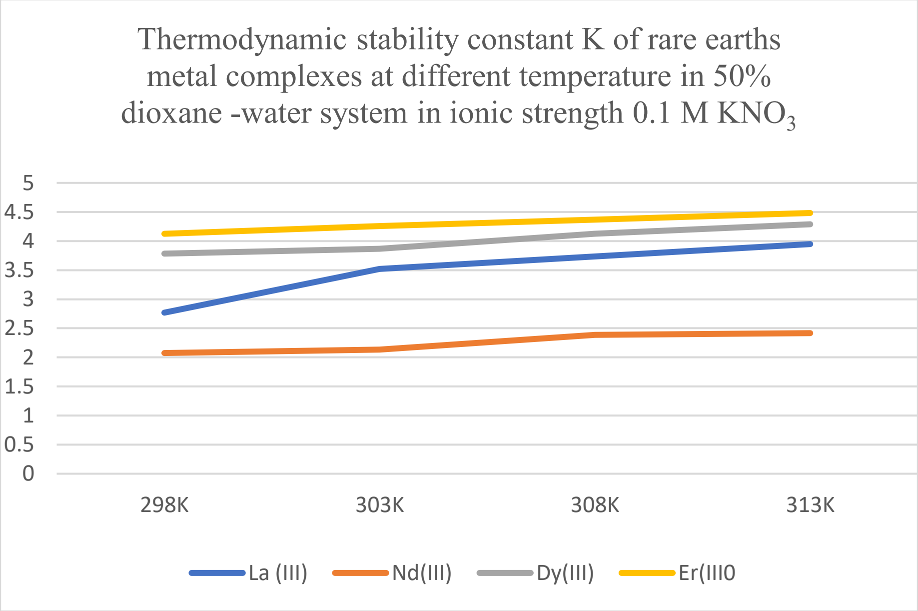

Table-2- Thermodynamic parameters of IMBAPAMBH complexes with rare earths metal ions at 0.1M ionic strength in 50% dioxane-water mixture.

System	**-ΔG (J/Mol.)**				**-ΔH (J/Mol.) (308K)**	**ΔS (J/Mol.) (313K)**
Temperature	**298K**	**303K**	**308K**	**313K**		
La(III)	62.385	59.468	57.986	55.748	1.438 x10^{-1}	1.3776x10^{-1}
Nd(III)	60.583	58.781	57.0156	56.045	6.378 x10^{-1}	1.770x10^{-1}
Dy(III)	65.745	64.698	64.245	63.799	7.694 x10^{-1}	2.034x10^{-1}
Er(III)	75.638	74.369	72.896	71.584	6.891 x10^{-1}	2.2651x10^{-1}

RESULT AND DISCUSSION:- The proton-ligand stability constants values increase with increase in temperature for all systems. This suggested that liberation of protons becomes easier at higher temperature[10]. The liberation of proton is easier due to the presence of –OH group at meta and para position. The values of metal-ligand stability constant values 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[11]. The all values of entropy change ΔS are positive indicating that the disorder of system increases more rapidly than the increase in the order taking place in complexation. The values of ΔH and ΔS are lesser and are mainly responsible for complex formation. The stabilities of these metal complexes were found as the following order Er(III)>Dy(III)>La(III)>Nd(III).

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