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Estimation of thermodynamic parameters by stability constants of lanthanides (III) complexes with 5-bromo, ortho hydroxy acetophenone – N– (4'– nitrophenyl) imine at 25^{0}C

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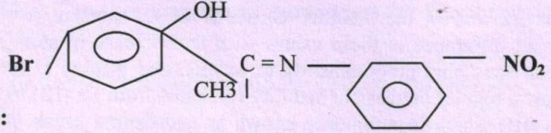
Abstract:
Estimation of thermodynamic parameters by stability constants of trivalent lanthanides complexes with 5-bromo, ortho hydroxy acetophenone – N – (4'– nitrophenyl) imine at 25^{0}C have been determined in 50 % (v/v) ethanol-water medium at 25^{0}C and $\mu = 0.1$ M ($NaClO_4$) ionic strength by Irving – Rossotti method. A knowledge of enthalpy and entropy for these complex formation of rare earths enable us to interpret the trends inn log K values of complexes in solution. The thermodynamic parameters for the formation of 1:1 and 1:2 complexes have been calculated.

Key words: *Thermodynamic parameters like enthalpy and entropy, lanthanides, Schiff bases.*

Introduction: Estimation of thermodynamic parameters by stability constants of metal complexes has not been revealed to the enough extent so far particularly on the trivalent lanthanide complexes of Schiff base derived from 5-bromo, ortho hydroxy acetophenone – N – (4'– nitrophenyl) imine. The aim of the present paer is to explain the coordination behavior of this Schiff base towards lanthanides (III) ions in 50 % (v/v) alcohol-water medium. The observed values of stability constants of these complexes have been explained on the basis of ionic size of the metals, basicity of ligand, gadolinium break and tetrad effect and also used in the determination of thermodynamic parameters. The changes in thermodynamic parameters are used to explain the stability of these complexes.



Experimental:
All the chemicals used for the synthesis of bidentate ligand and their complexes were AR grade. The Schiff base 5-bromo, ortho hydroxy acetophenone – N – (4'– nitrophenyl) imine was synthesized by reported method.[3] The solutions of lanthanide complexes were prepared in the double distilled water and standardized.[4] The initial ionic strength of all the solutions was maintained at 0.1 M by $NaClO_4$. An Elico LI – 120 P^{H} meter in conjunction with a combined electrode was used. The measurements were made at 25^0 C (±0.01°) and $\mu = 0.01$M $NaCLO_4$ in 50 % aqueous ethanol. The log K^H and log K values were computed by half – integral method, point wise calculations and also by the method of least squares. The average log K values were used to calculate ΔG from the Van't Hoff's isotherm. The ΔH and ΔS values were calculated from the Van't Hoff's isochore and the equation $\Delta G = \Delta H - T\Delta S$, respectively. The data are listed in Table – 2. The higher Pk values of 2-hydroxy-5-methyl acetophenone and 2-hydroxy-5-bromo acetophenone than that of their parent phenols are attributed to the predominant effect of intermolecular hydrogen bonding between phenolic OH group and $COCH_3$ group present in the acetophenone. The pK_1 value of synthesized Schiff base 5-bromo, ortho hydroxy acetophenone – N – (4'– nitro phenyl) imine which represents the de-protonation of NH group at azomethine nitrogen atom and phenolic OH group were determined at $n_A = 0.5$. The values were further checked from the plots of log $[(2-n_A)\sqrt{(n_A-1)}]$ vs B and log $n_A/(1-n_A)$ vs B (B = pH meter reading) and are given in Table -1. The pK_1 value of ligand is lower since it is having bromo substituent at *para* position to amino group. This can be attributed on the basis of domination nature of -M effect of bromide group.

Table – 1: Complex formation of lanthanides (III) with 5-bromo, ortho hydroxy acetophenone – N – (4'– nitro phenyl) imine

Temp →		25 °C
Ligand	pK_1	9.76

Results and Discussions:

Table – 2: Stability constants and thermodynamic parameters of lanthanides (III) complexes of bidentate Schiff base 5-bromo, ortho hydroxy acetophenone – N – (4'– methyl phenyl) imine at 25° C ± 0.02° C and 0.1 M $NaClO_4$.

Complexes	log K	-ΔG KJ Mol^{-1}	-ΔH KJ Mol^{-1}	ΔS KJ Mol^{-1}
La (III)	5.96	34.008	15.956	60.577
Ce (III)	6.04	34.465	11.967	75.495
Pr (III)	6.13	34.978	16.754	61.155
Nd (III)	6.34	36.177	13.762	75.216
Sm (III)	6.40	36.519	13.430	77.480
Eu (III)	6.48	36.975	16.754	67.856
Gd (III)	6.36	36.291	14.506	73.104
Tb (III)	6.45	36.804	16.986	66.505
Dy (III)	6.68	38.117	13.677	82.013
Ho (III)	6.54	37.318	14.183	77.632
Yb (III)	6.34	36.177	13.762	75.216

It is clear from the figure that the ligand 5-bromo, ortho hydroxy acetophenone – N – (4'– nitro phenyl) imine follows the following order of stability of their complexes.

Cu > Zn > Ni > Cd > Co > Mn

The screening of *4f* –electrons is showed in the stability constants of the present rare earth metal complexes, which exhibits very small difference in these values with the increase in atomic number. In these complexes the rare earth metal ions bind predominantly to oxygen and weakly to nitrogen of the Schiff bases.[2] These complexes show a regular increase of stability constants from La (III) to Eu (III) with a discontinuity of Gd (III) and Tb (III) which is commonly known as gadolinium break. After Tb (III), stability constant increases up to Dy (III) and then decreases for Ho (III) as shown in Table – 2. This shows occasional maxima and minima after gadolinium break. The change in free energy is directly related to log K values. The stability constants of trivalent La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho complexes with 5-bromo, ortho hydroxy acetophenone – N – (4'-- methyl phenyl) imine follows the order Dy > Ho > Eu > Tb > Sm > Gd > Yb = Nd > Pr > Ce > La. These stabilities are similar to the observations made by number of workers [7-10] and are accordance with Irving – Williams orer.[11] The thermodynamic parameters for lanthanide complexes with Schiff base were obtained from log K_1 and log K_2 at 25°C temperature. It seems that the log K_1 and log K_2 values decrease with increase in temperature, indicating that the high temperature does not favour the formation of stable complexes. The ΔH values are all negative, while ΔS are all positive. The resulting ΔG values are all negative. The more negative values of ΔG indicate that the 1:1 and 1:2 complex formation is thermodynamically favored. The negative values of ΔH also lead to the same inference. The entropy effect is found to be predominant over the enthalpy effect which is indicated by the high positive values of entropy.

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Stability Constants and Thermodynamic Parameters of Lanthanides (III) Complexes with 5-Bromo, Ortho Hydroxy Acetophenone – N – (4'– Methyl Phenyl) Imine at 250C

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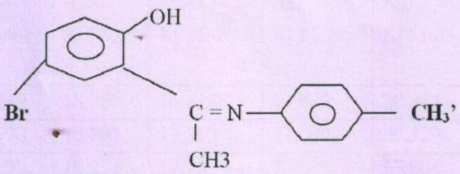
ABSTRACT

Stability constants of some trivalent lanthanides (La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Yb and Ho) complexes with Schiff base 5-bromo, Ortho hydroxy Acetophenone – N – (4'– methyl phenyl) imine (R_1), have been determined in 50 % (v/v) ethanol-water medium at 25°C and $\mu = 0.1$ M ($NaClO_4$) ionic strength by Irving – Rossotti method. The log K^H and log K values are used to discuss the effect of substituents and atomic size of the trivalent lanthanides. The thermodynamic parameters for the formation of 1:1 and 1:2 complexes have been calculated.

Keywords : Stability Constants, Thermodynamic Parameters, Lanthanides, Schiff Base.

I. INTRODUCTION

Literature survey has revealed that there not enough systematic study has been recorded so far on the trivalent lanthanide complexes of Schiff base derived from 5-bromo, ortho hydroxy acetophenone – N – (4'– methyl phenyl) imine. The objective of the present investigation is to ascertain the coordination behavior of this Schiff base towards lanthanides (III) ions in 50 % (v/v) alcohol-water medium. The observed values of stability constants of these complexes have been explained on the basis of ionic size of the metals, basicity of ligand, gadolinium break and tetrad effect. The changes in thermodynamic parameters are used to explain the stability of these complexes.



II. EXPERIMENTAL

All the chemicals used for the synthesis of bidentate ligand and their complexes were AR grade. The Schiff base 5-bromo, ortho hydroxy acetophenone – N – (4'– methyl phenyl) imine was synthesized by reported method.[3] The solutions of lanthanide complexes were prepared in the double distilled water and standardized.[4] The initial ionic strength of all the solutions was maintained at 0.1 M by $NaClO_4$. An Elico LI – 120 P^H meter in conjunction with a combined electrode was used. The measurements were made at 25° C (±0.01°) and μ = 0.01M $NaClO_4$ in 50 % aqueous ethanol. The log K^H and log K values were computed by half – integral method, point wise calculations and also by the method of least squares. The average log K values were used to calculate ΔG from the Van't Hoff's isotherm. The ΔH and ΔS values were calculated from the Van't Hoff's isochore and the equation ΔG = ΔH - TΔS, respectively. The data are listed in Table – 2.

The pK_1 and pK_2 values of synthesized Schiff base 5-bromo, ortho hydroxy acetophenone – N – (4'– methyl phenyl) imine which represent the de-protonation of NH group at azomethine nitrogen atom and phenolic OH group were determined at $\bar{n}_A$ = 1.5 and 0.5 respectively. The values were further checked from the plots of log $[(2-\bar{n}_A)\sqrt{(\bar{n}_A-1)}]$ vs B and log $\bar{n}_A/(1-\bar{n}_A)$ vs B (B = pH meter reading) and are given in Table -1. The pK_1 value of ligand is lower since it is having bromo substituent at *para* position to amino group. This can be attributed on the basis of domination nature of -M effect of bromide group.

Table – 1: Complex formation of lanthanides (III) with 5-bromo, ortho hydroxy acetophenone – N – (4'– methyl phenyl) imine

Temp →		
		25 °C
Ligand	pK_1	4.66
	pK_2	9.74

III. RESULTS AND DISCUSSIONS

Table – 2: Stability constants and thermodynamic parameters of lanthanides (III) complexes of bidentate Schiff base 5-bromo, ortho hydroxy acetophenone – N – (4'– methyl phenyl) imine at 25° C ± 0.02° C and 0.1 M $NaClO_4$.

Complexes	log K_1	log K_2	$-\Delta G_1$ KJ Mol^{-1}	$-\Delta G_2$ KJ Mol^{-1}	$-\Delta H_1$ KJ Mol^{-1}	$-\Delta H_2$ KJ Mol^{-1}	ΔS_1 KJ Mol^{-1}	ΔS_2 KJ Mol^{-1}
La (III)	5.99	4.46	34.179	25.449	18.731	16.412	51.839	30.324
Ce (III)	6.13	4.66	34.978	26.590	13.791	17.552	71.099	30.329
Pr (III)	6.33	5.14	36.119	29.329	15.231	12.765	70.095	55.584
Nd (III)	6.39	5.23	36.462	29.843	15.414	17.036	70.631	42.976
Sm (III)	6.45	5.32	36.804	30.356	16.455	13.677	68.286	55.971
Eu (III)	6.58	5.59	37.546	31.897	11.584	17.682	87.120	47.700
Gd (III)	6.17	5.26	35.206	30.014	14.913	19.973	68.099	33.694
Tb (III)	6.28	5.38	35.834	30.699	12.067	15.018	79.756	52.621
Dy (III)	6.62	5.87	37.774	33.495	15.956	12.644	73.214	69.967
Ho (III)	6.25	5.36	35.663	30.584	13.962	18.530	72.823	40.451

*Standard deviation for log K_1 and log K_2 are ± 0.019 and ± 0.035 respectively.

The shielding of the *4f* –electrons is exhibited in the stability constants of the present rare earth complexes, which shows very little difference in these values with the increase in atomic number. In these complexes the rare earth metal ions bind predominantly to oxygen and weakly to nitrogen of the Schiff bases.[2] These complexes show a regular increase of stability constants from La (III) to Eu (III) with a discontinuity of Gd (III) and Tb (III) which is commonly known as gadolinium break. After Tb (III), stability constant increases up to Dy (III) and then decreases for Ho (III) as shown in Table – 2. This shows occasional maxima and minima after gadolinium break. In all cases, Gd (III) and Eu (III) chelates have lower value of log K_1 in relation to those of Dy (III) to Ho (III) chelates.

The change in free energy is directly related to log K values. The stability constants of trivalent La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho complexes with 5-bromo, ortho hydroxy acetophenone – N – (4'–methyl phenyl) imine follows the order Dy > Eu > Sm > Nd > Pr > Tb > Ho > Gd > Ce ≥ La. These stabilities are similar to the observations made by number of workers. [7-10] and are accordance with Irving – Williams orer.[11] The thermodynamic parameters for lanthanide complexes with Schiff base were obtained from log K_1 and log K_2 at 25°C temperature. It seems that the log K_1 and log K_2 values decrease with increase in temperature, indicating that the high temperature does not favour the formation of stable complexes. The ΔH_1 and ΔH_2 values are all negative, while ΔS_1 and ΔS_2 are all positive. The resulting ΔG_1 and ΔG_2 values are all negative. The more negative values of ΔG_1 and ΔG_2 indicate that the 1:1 and 1:2 complex formation is thermodynamically favored. The negative values of ΔH_1 and ΔH_2 also lead to the same inference. The entropy effect is found to be predominant over the enthalpy effect which is indicated by the high positive values of entropy.

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