Thermodynamic studies of rare earth metal complexes with Rifampicin in mixed solvent system

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ABSTRACT

The determination of stability constant of Rifampicin complexes with rare earths metal ions in temperature range 303-318 K at constant ionic strength 0.1M.in 50% dioxane-water mixture by adopting pH metric technique been studied. The thermodynamic parameters ($\Delta G, \Delta H$ 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.

Key word: Thermodynamic parameters, Stability constant, ionic strength, pH-metric.
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INTRODUCTION

Rifampicin is anti-tuberculosis, protein transporter, anti-hyperglycemic, anti-epileptic, neuropsychiatry therapeutics an anti-bacterial [1].The complex of Rifampicin with cyclodextrin is used as anti-tubercular drug [2].Rifampicin is used combination with Imipenem or Salbactum in the treatment of Marine Pnuemonia [3].Rifamipicin inhibits of bile acid. Synthesis may be a protective mechanism against drug and bile acid induced chiertasis [4]**.**

Parihar et.al. has been studied the stability constant and thermodynamic parameters of Cadmium complexes sulfonamides and Cephapirin at 0.1M ionic strength [5]. The stability constant and thermodynamic parameters such as Gibb's free energy, Enthalpy change and Entropy change for complex formation of transition metal complexes derived from 3-methyl-1 phenyl and 1, 3-diphenyl-4-aryllazo-5-pyrazolines were determined by adopting potentiometric technique [6]. Vyas et. al. have been studied proton-ligand stability constant and metal-ligand stability constant of rare earths metal complexes of hydroxyl benzoic acid by pH-metric titration technique . They

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studied the stability constant at different temperatures and determined the thermodynamic parameters. The observed value of thermodynamic parameters favours the complex formation [7].Sharma [8] et. al. have been investigated the ΔG, ΔH and ΔS of complex formation of La(III) ,Ce(III), Pr(III) and Nd(III) with amino pyridines at different temperature and also different solvent systems. Jain [9] et. al. have been studied the chelates of O-(N-α-oxindolimino)benzoic acid and O-(N-α-oxindolimino) propanoic acid. They studied the stability constant and thermodynamic parameters of complexes of Lanthanum (III).Sarin [10] et. al. have been investigated thermodynamic stability constant and parameters of complexes in the presence of 0.1N NaCl in the temperature range 25- 45^{0}C by Irving Rossotti method.

After review of literature survey, the detail study of complex under identical set of experimental condition is still lacking. It was thought of interest to study the effect of temperature on thermodynamic parameters of complexes of Rifampicin with Ce(III),Dy(III), Gd(III),Yb(III) and Pr(III) in 50% dioxane-water mixture at constant ionic strength (0.1M) by pH metrically.

EXPERIMENTAL SECTION

Determination of stability constants:-
The pH measurements were carried out with equip-tronic EQ-610 pH meter (accuracy $\pm$ 0.01 units) using combine glass electrode at Temperature range from 303 K -318K. 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 drugs (5, 6, 9, 17, 19, 21-Hexahydroxy-23-methoxy-2, 4, 12, 16, 18, 20, 22-heptamethyl-8-[*N*-(4-methyl-1-piperazinyl) formimidoyl]-2,7-(epoxypentadeca [1, 11, 13]trienimino)-naphtho[2,1-*b*]furan-1,11(2*H*)-dione 21-acetate.) was prepared in solvent .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 [11].The overall ionic strength of solution was constant maintains by adding NaClO4. 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 jacketed titration cell connect to the constant temperature circulating bath.

The temperature of reaction cell is constant by circulating water from Thermostat (0.1^{0}C).
The experimental procedure involved pH metric titrations of solutions of –

1) Free HClO$_4$ (A)
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 added 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 freer 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 (1)

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-ΔG = 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.

$$\Delta H = 2.303 \, RT_1T_2 \, / \, (T_2-T_1) \, \log K \quad --------------------(2)$$
$$\Delta S = (\Delta G - \Delta H) \, / \, T \quad ------------------------------------(3)$$

RESULTS AND DISCUSSION

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

Temperature	pK	logK	Ce(III)	Dy(III)	Gd(III)	Yb(III)	Pr(III)
303K	6.1835	$logK_1$	7.65	7.50	7.35	7.50	7.90
		$logK_2$	4.90	4.75	4.80	4.60	4.75
308K	5.9779	$logK_1$	7.40	7.05	7.12	7.15	7.55
		$logK_2$	4.45	4.35	4.65	4.20	4.40
313K	5.8675	$logK_1$	6.95	6.75	6.85	6.75	7.10
		$logK_2$	4.15	4.15	4.20	4.00	4.10
318K	5.7327	$logK_1$	6.45	6.40	6.45	6.35	6.65
		$logK_2$	3.80	3.85	3.95	3.85	3.80

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

System	-ΔG (J/Mol.)				-ΔH (J/Mol.) $_{1}$	ΔS (J/Mol.) (313K)
	303K	308K	313K	318K		
Ce (III)	44382.12	43640.17	41651.74	39272.70	166127.0	397.69
Dy (III)	43511.88	41576.10	40453.12	38968.26	129210.0	542.06
Gd (III)	42641.64	41870.97	41052.43	39577.14	99675.5	449.61
Yb (III)	43801.96	42165.84	40453.12	38663.82	147669.0	601.03
Pr (III)	45832.51	44524.76	42550.69	40490.46	166127.0	666.70

The proton-ligand stability constants values decreases with increase in temperature for all systems. 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.

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The values of metal-ligand stability constant decreases with increase in temperature. This suggests that the complex formation is exothermic and favourable at lower temperature. The negative values of ΔH and ΔG of complex formation indicates the complex formation process is spontaneous [12].The all values of entropy change are positive indicating that the disorder of system increases more rapidly than the increase in the order taking place in complexation[13]. The values of ΔH and ΔS are very large and are mainly responsible for complex formation. The stabilities of these metal complexes were found as the following order Pr(III)>Ce(III)>Yb(III)> Gd(III)> Dy(III).

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