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Studies on Thermodynamic Stability of Constant of Clobetasol Propionate with Ce(III) Complex

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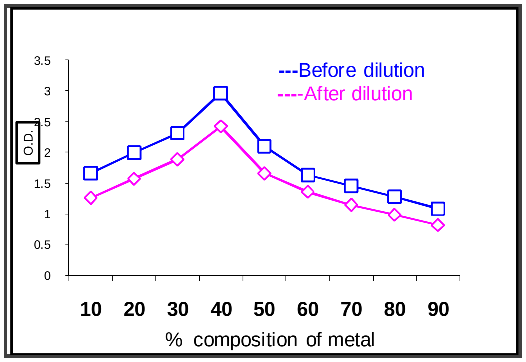
ABSTRACT

The thermodynamic stability constant of the complexes were also calculated. The formation of complexes has been studied by Job's method. The results obtained of stability constant were good agreement. The metal-ligand and proton–ligand stability constant of Ce(III) with Clobetasol propionate was determined at various ionic strength by pH metric titration .$NaClO_4$ *was used to maintain ionic strength of solution. The results obtained were, extrapolated to the zero ionic strength using an equation with one individual parameter. The thermodynamic stability constant of the complexes were also calculated.*

Graphical Abstract



Ligand +Ce(III).

Keywords: Stability constant, Ionic strength.

INTRODUCTION

Clobetasol propionate is used for the treatment of various skin disorders including eczema, herpes labialis [1]. The effect of ionic strength of medium on stability constant of Cu(II) complex of 2-amino-5- Chloro benzene sulphonic acid is at 301K [2]. The stability constant of Co(III) with 1-Amidino-0-methylurea is as primary ligand at different ionic strength [3]. The influence of ionic strength of medium on complex is equilibria [4]. Association and dissociation constant of Pr(III) complexes with 3-(2-hydroxy-3-Iodo-5-methyl phenyl)1,5 diphenyl pyrazoline at different ionic strength [5]. Stability constant of vanadium with glycine at various ionic strengths was determined by Potentiometric titration technique [6]. The stability constant of Mo(IV) with iminodiacetic acid at different ionic strengths using sodium per chlorate was investigated [7]. Effect of ionic strength and solvent effect was determined using thermodynamic parameters [8]. They have also studied the mechanism of protonation and complex formation of binary complexes of La(III), Ce(III), Pr(III) and Nd(III) with aminopyridines. The apparent metal-ligand stability constants and confirmation of complexes studied [9] .The composition of complexes was confirmed by Job's method as modified by Vasburgh and Gold [10]. Omar H. Al-Obaidi have been studied the stability constant of metal complex with flavone by spectrophotometry [11].

In this work, we have determined the pK, metal-ligand stability constant at different ionic strength. We have studied at the 70% ethanol-water mixture. We have thought of interest to study the effect of ionic strength on thermodynamic parameters of complexes of ligand with Ce(III), metals in 70% ethanol-water mixture by pH metrically and Spectrophotometrically.

MATERIALS AND METHODS

The pH measurements were carried out with equip-tronic EQ-610 pH meter (accuracy ± 0.01 units) using combine glass electrode at 208 K. Pure rare earth nitrates (99.9% Pure) was used. All metal nitrates available from Sigma Aldrich Chem. Co., U.S.A. Metal nitrate was prepared in triply distilled water and concentration was estimated by standard method. The solution of drugs was prepared in 70% ethanol. The pH metric readings in 70% ethanol–water mixture were converted to $[H^+]$ value by applying the correction proposed by Van Uitert Haas. The overall ionic strength of solution was constant maintains by adding NaClO4. All the solutions were titrated with standard carbonate free NaOH (0.2 N) solution at different ionic strength. The titration was carried out at ionic strength by adding $NaClO_4$ (0.02-0.08 M)

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 versus volume of NaOH added and corresponding volume at successive pH for each set is determined and calculated.

The metal-ligand stability constant of lanthanide metals complexes with ligand was investigated spectrophotometrically. The absorbances measured were carried out with Shimadzu UV-1800 ENG 240V, Japan spectrophotometer. The solutions of metal nitrates and ligand were prepared in 70% ethanol–water mixture. $NaClO_4$ was used for maintaining the constant ionic strength. The different composition of metal ion ($1x10^{-4}$M) and ligand ion ($1x10^{-4}$M) were prepared in ten series. For determination of $\lambda_{max,}$ 50% metal ion solution at which maximum absorbance observed. The absorption of all composition was measured at constant wave length (λ_{max}) and at constant pH.

RESULTS AND DISCUSSION

In the present investigation the dependence of proton-ligand stability constant and metal-ligand stability constant on ionic strength of medium was examined by taking fix concentration of metal nitrates and ligand solution during pH metric titration. The system has been studied at 0.02, 0.04, 0.06, 0.08M ionic strength by varying the concentration of sodium per chlorate. The total ionic strength of medium is calculated by equation.

$$\mu = \Sigma\ 1/2\ \mathbf{C_i Z_i}^2$$

$C_{i\,,}$ Z_i are the concentration and valences of i^{th} ion respectively.

The values of proton-ligand and metal-ligand constant of Ce(III) complexes at different ionic strength 0.02,0.04,0.06 and 0.08M determined. These values were determined by using Irving-Rossotties method.

From table 1, it was seen that the values of proton–ligand stability constant (pK) decreases with increasing ionic strength of medium. The metal-ligand stability constant (logK) also decrease with increasing ionic strength.

For determination of stability constant at zero ionic strength the Bronsted equation is used.

$$\log K = \log K^\circ + A\,\Sigma\,\Delta\,Z^2\sqrt{\mu}$$

$$\pi K = \pi K^\circ - A\,\Delta\,Z^2\,\sqrt{\mu}$$

Where, K° is the formation constant at zero ionic strength. pK° is proton-ligand stability constant at zero ionic strength . 'A' is the Debye-Huckel constant. The pK° and logK° values were calculated by plotting the graph of pK, $\log K_1$, $\log K_2$ versus $\sqrt{\mu}$.

Table 1. Proton–ligand (pK) and metal-ligand stability constant (Log K) values for Ce(III) with ligand at various ionic strength(μ)

μ	$\sqrt{\mu}$	$\sqrt{\mu}/1+\sqrt{\mu}$	$[\sqrt{\mu}/1+\sqrt{\mu}]-0.3\sqrt{\mu}$	pK	$\mathrm{Log}K_2$	$\mathrm{Log}K_1$
Silymarin + Yb(III)						
0.02	0.1414	0.1239	0.0815	7.7184	7.05	4.45
0.04	0.2000	0.1667	0.1067	7.5057	6.60	4.15
0.06	0.2450	0.1968	0.1233	6.9692	6.45	3.85
0.08	0.2828	0.2205	0.1356	5.7830	5.80	3.75

From table 2, it was seen that the good agreement among thermodynamic constant obtained from different plots. The plots pK, $\log K_1$, $\log K_2$ versus $\sqrt{\mu}$ gives straight line over the entire range of ionic strength for both systems. It shows that the Bronsted relationship is valid for dissociation equilibrium.

The conditional stability constant of metals complex was determined for system by using equation.

$$K = x/(a_1-x)\,(b_1-x) = x\,/\,(a_2-x)\,(b_2-x)$$

K= Conditional stability constant, x = Concentration of complex, a_1 and b_1 were concentration of metal ion and ligand before dilution. A_2 and b_2 were concentration of metal ion and ligand after dilution.

The values of 'x' were calculated from graph optical density Vs % composition of metal ions in solution (Fig. 1-4).

Table 2. Thermodynamic stability constant (pK°and Log K°) values for Ce(III) with mixed ligands

Plots	Ligand + Ce(III)		
	pK°	$\mathrm{Log}\ K_1^\circ$	$\mathrm{Log}\ K_2^\circ$
P^K Vs $\sqrt{\mu}$	9.805	--	--
$\mathrm{Log}K_2$ Vs $\sqrt{\mu}$	--	8.248	--
$\mathrm{Log}K_1$ Vs $\sqrt{\mu}$	--	--	5.169

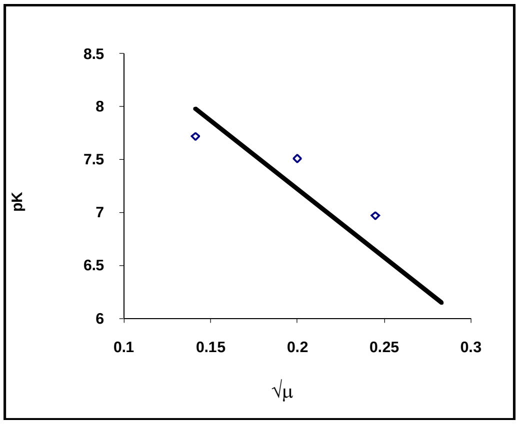


Figure 1. Plot of pK vs √μ.

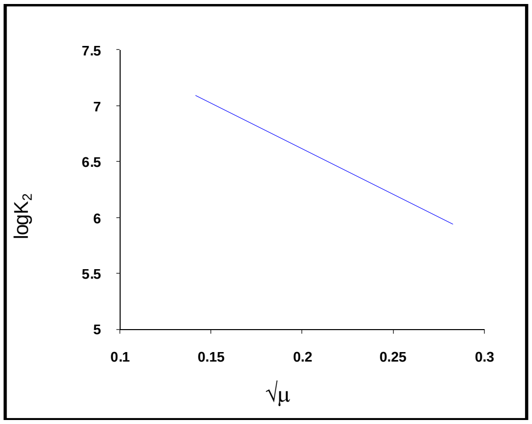


Figure 2. Plot of logk_2 vs √μ.

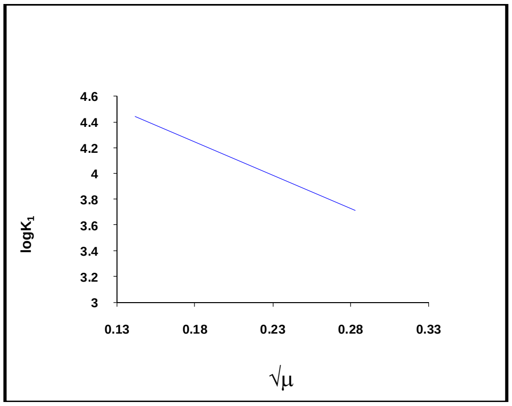


Figure 3. Plot of log $k_1$vs Om.

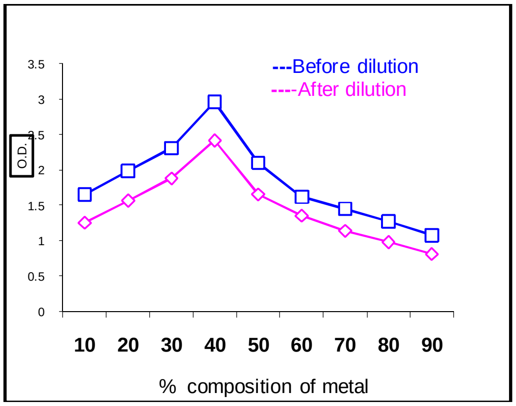


Figure 4. Ligand +Ce(III).

From table 3, it was seen that the good agreement among thermodynamic constant obtained from pH metry and spectrophotometrically.

Table 3. Metal-ligand stability constants (Log K) values obtained by pH-metry and Spectrophotometry technique (Ionic strength = 0.08m)

System	pH metry	Spectrophotometry
Ce (III)+ ligand	4.45	4.6143

APPLICATION

Stability constant is well known tool for solution chemist, biochemist, and chemist in general to help determine the properties of metal-ligand reactions in water and biological system. In the detection and determination of inorganic ions, various organic and inorganic chelating agents are useful. Sometimes chelating agents form inner complexes with metal ions, which are sparingly soluble.

CONCLUSION

The calculated values of stability constant at different ionic strength are high. From data the conclusion is, the complexes of ligand with Ce(III) metal ion was quite stable at over all range of ionic strength. The values of thermodynamic parameters are nearly same from all plots was good agreement of results. The values of conditional metal-ligand stability constant shows good agreement with the values determined by pH metrically.

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