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A Study on Metal Ligand Stability Constant with some Substituted Ketones and Chalcones

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ABSTRACT

The interaction of Ce (III), Dy (III) and Nd (III) metal ions with 2-hydroxy-3-nitro-5-methyl aceto phenone,2-hydroxy-4-methyl-5-chloro acetophenone,2'-hydroxy -3'-bromo-5'-methyl-4-methoxy chalcone,2'-hydroxy-3'-iodo-5'-methyl-4-methoxy chalcone have been studied at 0.1 M ionic strength in 70% THF-Water mixture. It is observed that Ce (III), Dy (III) and Nd(III) form 1:1 and 1:2 complexes with substituted ketones and chalcones. The data obtained used to compare the P^k (proton ligand stability constant) and log K (metal ligand stability constant) and to study the effect of substituent on the complex. Here the metal ligand stability constant have been studied P^H metrically by Calvin Bjerrum Titration.

Keywords: Stability constant, THF-water mixture, Substituted ketones and chalcones.

INTRODUCTION

Co-ordination complexes cover a wide range of applications in various fields of human interest such as biochemistry, analytical chemistry. Considerable research work has been done on the study of complexes in solutions. The development in the field was initiated by Jannik Bjerrum [**1**] dissertation published in 1941. The stability of complex in solution is governed by the nature of central atom and ligand. Metal-ligand stability constant of complexes of transition metal ions, lanthanides and nuclear metal ions with dihydroxy compounds, amino hydroxyl phenols, naphtha's, peptides have been reported by Number of workers [**2, 3**]. The efficiency of chalcones as an analytical reagent for spectophotometric estimation of number of metal cations has been reported. Narwade *et al* have been studied stability constant of transition metal ion with some substituted chalcones by pH metrically [**4**]. Mandkmare *et al* have investigated the formation constant of complexes of transition metal ions with some substituted 1,3,5 triazines at different ionic strength [**5**]. Sawalakhe *et al* studied the metal ligand stability constant of Fe(III), Cr(III) and Al (III) metal ions with some substituted pyrazolones [**6**]. Meshram, Mandakmare *et al* have investigated stability constant of Cu(III) chelates with some substituted caumarins at 0.1 M ionic strength pH metrically [**7**]. Raghuvanshe *et al* have investigated conditional stability constant of some substituted chalcones and isoxazolines [**8**].

In the present work, the systematic study of complexes of some substituted chalcones and ketones with Dy (III),Nd (III) and Ce(III) have been performed by pH metrically.

MATERIALS AND METHODS

The solution of substituted chalcones and ketones were prepared by dissolving requisite quantities in purified solvent such as THF subsequently diluted to the final volume. Rare earth nitrates Dy (III), Nd (III) and Ce(III) were used .The metal content in the solution was estimated gravimetrically .

Mearurement: All the pH measurement and titrations are carried out with P^H meter.L_1-L_{10} T (Elicomake) (accuracy 0.01) with a glass and calomel electrode assembly. The instrument could read pH in the range 0 to 14.00 in step of 0.005. This pH meter has built in internal electronic voltage stabilizer for -10% fluctuations in voltage supply with temperature compensator converting the range 0 to 100°C. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The pH meter was standardized before each titration with a buffer solution of pH 4.1, 7.0 and 9.15.

Procedure: The experimental procedure involved the following titrations

1. Free acid titration: a solution containing perchloric acid (0.01M) in 70% THF-Water mixture was titrated against standard sodium hydroxide (0.1M).

2. Free acid –ligand titration: A solution containing perchloric acid (0.01M) and ligand (0.002M) in 70% THF-Water mixture was titrated against standard sodium hydroxide.(0.1M)

3. Free acid-metal-ligand titration: A solution containing (0.01M) and ligand (0.002M) and metal salt (0.004M) in 70% THF-Water mixture was titrated against standard sodium hydroxide (0.1M). The graph is plotted between pH of the solution and volume of alkali (NaOH) added for the system.

RESULTS AND DISCUSSION

The ligand used in the present work is monoprotonic and represented as,

$$HL \rightarrow H^+ + L^-$$

The proton ligand formation number ($\bar{n}_A$) was investigated by using Irving and Rossotti expression

$$\bar{n}_A = \gamma - \frac{(V_2-V_1)(E^\circ+N)}{(V_0+V_1)(T^0_L)}$$

Where, V_0-Initial volume of solution, E^0-Concentration of the acid, T^0-Concentration of the ligand V_1-Volume of alkali required during acid titration, V_2-Volume of alkali required during ligand titration, γ- number of replaceable hydrogen ions, N –Normality of NaOH

.

The linear equation was solved for different values of n and p^L and average values was taken as a correct value of log K_1.

Similarly the metal ligand formation can be calculated by

$$\bar{n} = \frac{(V_3 - V_2)(N + E^0)}{(V_0 + V_2)(T_M^0)(\bar{n}_A)}$$

Where V_3–volume of alkali required to obtain the same pH as the ligand and acid titration. T_M^0 is the total concentration. The other terms have the same significance for ligand titration. The linear equation was solved for different values of n and p^L and average values was taken as a correct value of log K_2 .

The value of log K_1 and log K_2 for Ce (III), Nd (III) and Dy(III) metal ion complexes are shown in the following table 1.

Table 1. The value of log K_1 and log K_2 for Ce (III), Nd (III) and Dy(III) metal ion complexes

S.No.	System	LogK 1 P^L1	LogK 2 P^L2
1	2-hydroxy-3-nitro-5-methyl-acetophenone		
	a) Ce (III)	3.5	2.0
	b) Dy (III)	5.6	3.25
	c) Nd (III)	4.5	3.20
2	2-hydroxy-3-bromo-5-methyl-4-methoxy-chalcone		
	a) Ce (III)	4.5	3.4
	b) Dy (III)	7.5	4.25
	c) Nd (III)	4.0	2.9
3	2-hydroxy-4-methyl-5-chloro-acetophenone		
	a) Ce (III)	4.80	4.25
	b) Dy (III)	5.6	3.25
	c) Nd (III)	5.00	4.20
4	2-hydroxy-3-iodo-5-methyl-4-methoxy-chalcone		
	a) Ce (III)	4.10	2.25
	b) Dy (III)	4.10	3.3
	c) Nd (III)	4.25	3.6

APPLICATION

Stability constant of a complex is the measure of strength of interaction between reagents that comes together to form complexes.PH metric determination of stability constant provide information required to calculate the concentration of complex in solution.

CONCLUSION

It is observed from the table that the stability constants of Ce (III) , Dy (III) and Nd (III) are found to be greater for 2-hydroxy-4-methyl-5-chloro-acetophenone and 2-hydroxy-3-bromo-5-methyl-4-methoxy-chalcone than 2-hydroxy-3-iodo-5-methyl-4-methoxy-chalcone and 2-hydroxy-3-nitro-5-methyl-acetophenone. This may be due to the effect of nitro group as a electron withdrawing groups .This reduces the stability constants of complexes. It is also observed that first stability constant of metal ion complexes in most of the cases is found to be greater. This may be due to the stable nature of metal ion.

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