

Spectrophotometric Studies of La (Iii), Ce (Iii), Pr (Iii),Nd (Iii),Sm (Iii) and Eu (Iii) Complexes With Substituted Dihydro Pyrimidin 2-(1H)-One



Science

KEYWORDS : Metal-ligand complexes, Substituted dihydropyrimidin-2(1H)-one, Stability constant and Job's method of continuous variation.

Yuvraj K.Meshram

G.S science Arts and Commerce College Khamgaon, Dist- Buldhana

Gaurav R.Nimbarte

G.S science Arts and Commerce College Khamgaon, Dist- Buldhana

Suresh B.Rewatkar

Mohsinbhai Zaweri Arts,Commerce and Science College,Desaiganj(Wadsa) Dist-Gadchiroli.

ABSTRACT

The formation of complexes of La (III), Ce (III), Pr (III),Nd (III),Sm (III) and Eu (III) complexes with 5-ethoxy carbonyl-4-(4-chloro phenyl)-6-methyl-3,4-dihydropyrimidine-2(1H)-One was studied spectrophotometrically at (302 ± 0.1) K and ionic strength $\mu = 0.1$ mol.dm. The stability constants have been investigated in a 70% THF-aqueous mixture by the Job's continuous variation method. The results obtained of stability constants are in good concordance the values obtained by the real stability constant by pH metric technique.

Introduction:

The basic principle of the spectrophotometric technique is the measurement of interaction between radiation energy and electrons of the substance. Spectrophotometric technique is an analytical method used for estimating concentration of metal ion in liquid solution. Spectrophotometry is one of the most powerful method for the investigation of solution equilibria. Spectrophotometric is differ than pH-metric because pH-metric methods are limited to the pH-range 2.0 to 11.0, whereas spectrophotometric method are not limited to any pH-range or non-aqueous solutions.

Substituted dihydropyrimidin-2(1H)-one have become more popular in the world of chemistry due to their activities such as antibacterial, antiviral, antihypertensive, anti-inflammatory, antitumor¹. substituted dihydropyrimidin-2(1H)-one have gained a lot of interest due to their importance as good ligands and its complexes have been widely used in diverse areas because of their unique structural features, chemical functionalities.² Keeping in view analytical applications of these heterocyclic drugs, Substituted dihydropyrimidin-2(1H)-one are selected as a ligand in the present study.

Several workers have investigated the metal-ligand stability constant of the several metal ions with organic compound viz.,substituted sulphonic acid^{3,4}.substituted isoxazoline^{5,6} aromatic ketones, alkyl-monamines⁷,substituted benzothiazoles⁸, substituted coumarines⁹, and substituted pyrazoline¹⁰. Swami¹¹ has studied the effect of substitution upon the stability of palladium chelates of substituted hydroxytriazene. Gharib and et al¹².have reported the complexation of methyl ion with glutonic acid using spectrophotometric technique. The metal- ligand stability constants in some peptides, diketones, pyrazoles and pyrazolines have been studied by many workers^{13,14}.

The extensive literature given above clearly indicates that metal complexes show that complex formation, stability constant physical parameter etc. Several complexes especially transition metal ions containing with heterocyclic ligands have been reported. However, it is noted that little work has been done on complexes based on Substituted dihydropyrimidin-2(1H)-one. Therefore the present work is undertaken to make a systematic study.

Experimental:

All chemicals used were of analytical grade. The 5-ethoxy carbonyl-4-(4-chloro phenyl)-6-methyl-3,4-dihydropyrimi-

dine-2(1H)-One were prepared by known literature method. The absorbance of the liquid solution and their metal complexes have been measured by UV-Visible spectrophotometer model 1700 (Shimadzu, Japan), accuracy(± 0.005) having spectral range 180 nm to 1100 nm. The equimolar solution of La (III), Ce (III), Pr (III),Nd (III),Sm (III) and Eu (III) with 5-ethoxy carbonyl-4-(4-chloro phenyl)-6-methyl-3,4-dihydropyrimidine-2(1H)-One were mixed indifferent ratio form 1: 5 to 5:1. The pH in the range 2.4 and ionic strength ($\mu=0.1$) maintained constant throughout by addition of sodium perchlorate (NaClO₄).

Table – 1

Job's Variation Method

System: La (III) – L (THF)

$\lambda_{max} = 420$ nm Temp = 29°C (±0.10°C) pH = 2.4

% Composition	Optical Density (O.D.)	
	Before Dilution (B.D)	After Dilution (A.D)
10	0.487	0.415
20	0.626	0.519
30	0.882	0.718
40	1.212	1.006
50	1.354	1.13
60	1.231	1.031
70	0.992	0.836
80	0.798	0.682
90	0.573	0.492

Table – 2

Job's Variation Method

System: Ce (III) – L (THF)

$\lambda_{max} = 400$ nm Temp = 29°C (±0.10°C) pH = 2.4

% Composition	Optical Density (O.D.)		Dilution
	Before Dilution (B.D)	After (A.D)	
10	0.521	0.463	
20	0.654	0.579	

30	0.872	0.763
40	1.149	0.992
50	1.324	1.128
60	1.193	1.003
70	0.964	0.855
80	0.702	0.626
90	0.538	0.487

Table – 3

Job’s Variation Method

System: Pr (III) – L (THF)

$\lambda_{max} = 370 \text{ nm}$ **Temp = 29°C (±0.10°C)** **pH = 2.4**

% Composition	Optical Density (O.D.)	
	Before Dilution (B.D)	After Dilution (A.D)
10	0.365	0.309
20	0.591	0.494
30	0.817	0.667
40	1.055	0.863
50	1.293	1.053
60	1.389	1.1248
70	1.108	0.887
80	0.818	0.612
90	0.532	0.441

Table – 4

Job’s Variation Method

System: Nd (III) – L (THF)

$\lambda_{max} = 410 \text{ nm}$ **Temp = 29°C (±0.10°C)** **pH = 2.4**

% Composition	Optical Density (O.D.)	
	Before Dilution (B.D)	After Dilution (A.D)
10	0.354	0.291
20	0.467	0.398
30	0.718	0.579
40	1.034	0.858
50	1.334	1.062
60	1.172	0.919
70	0.874	0.735
80	0.696	0.588
90	0.439	0.385

Table – 5

Job’s Variation Method

System: Sm (III) – L (THF)

$\lambda_{max} = 390 \text{ nm}$ **Temp = 29°C (±0.10°C)** **pH = 2.4**

% Composition	Optical Density (O.D.)	
	Before Dilution (B.D)	After Dilution (A.D)
10	0.436	0.342
20	0.592	0.475
30	0.884	0.697
40	1.094	0.904
50	1.247	1.119
60	1.138	0.964
70	0.943	0.783
80	0.751	0.617
90	0.548	0.455

Table – 6

Job’s Variation Method

System: Eu (III) – L (THF)

$\lambda_{max} = 400 \text{ nm}$ **Temp = 29°C (±0.10°C)** **pH = 2.4**

% Composition	Optical Density (O.D.)	
	Before Dilution (B.D)	After Dilution (A.D)
10	0.479	0.412
20	0.647	0.532
30	0.892	0.712
40	1.194	0.984
50	1.378	1.122
60	1.245	1.023
70	0.981	0.823
80	0.723	0.612
90	0.627	0.512

Fig. 1 - System: La (III) – Ligand (THF)

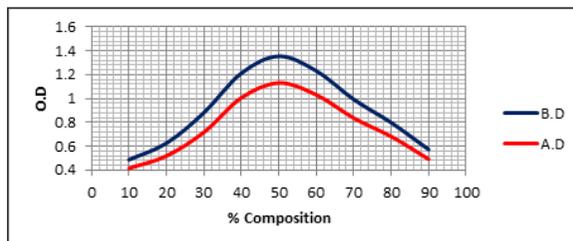


Fig. 2 - System: Ce (III) – Ligand (THF)

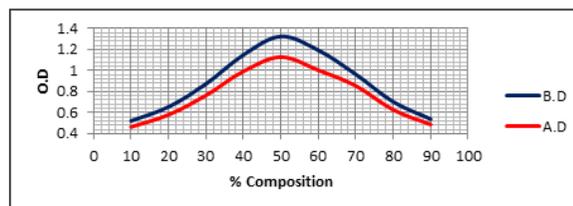


Fig. 3 - System: Pr (III) – Ligand (THF)

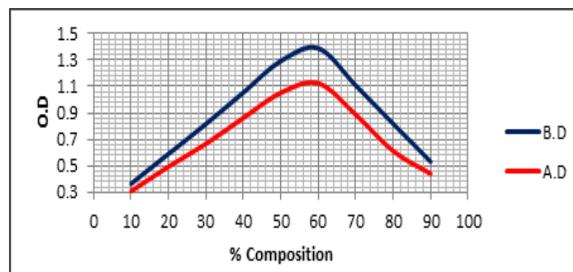


Fig. 4 - System: Nd (III) – Ligand (THF)

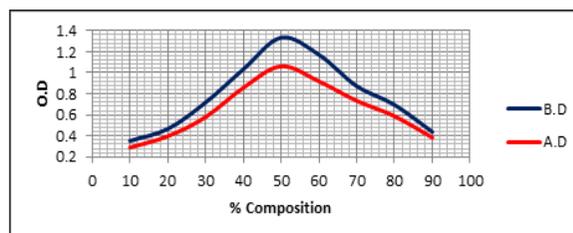


Fig. 5 - System: Sm (III) – Ligand (THF)

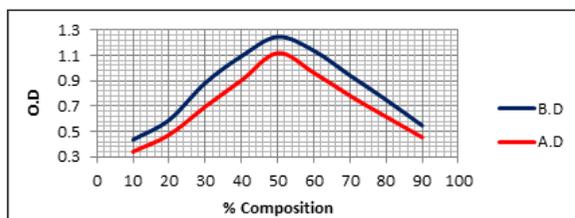
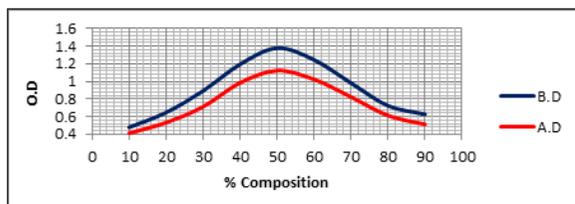


Fig. 6 - System: Eu (III) – Ligand (THF)



Result and Discussion:

Job's¹⁵ has described a procedure for determining the formula of an additive complex which is called method of continuous variations. The Spectrophotometric data obtained by Job's continuous variation method are presented in table No. 1 to 6. The Job's curve of this system are shown in fig 1 to 6.

It is observed that from all curves that there is a formation of 1:1 complex in the pH range 2.4. In addition to the wavelength of maximum (λ) some other wavelengths were selected as proposed by Vosburgh and Gould¹⁶. The conditional stability constant for all systems was calculated by using following expression :

$$K = \{ x / [(a_1 - x) (b_1 - x)] \}$$

$$K = \{ x / [(a_2 - x) (b_2 - x)] \}$$

Where a_1, a_2 = concentration of metal ions, and b_1, b_2 = concentration of ligand, x = Concentration of complex and K = conditional metal-ligand stability constant.

The values of conditional stability constants are found to be lesser than the real stability constant (Irving-Rossotti method). This is because the concentration of free acid at a particular pH was not taken into account as well as the weaker interaction between them.

System	Spectrophotometric (log K)	pH-metric (logK)
La (III)	4.30	4.67
Ce (III)	4.80	5.09
Pr (III)	5.38	6.04
Nd (III)	5.16	5.59
Sm (III)	5.60	6.43
Eu (III)	4.94	5.13

Conclusion:

It could be concluded that the agreement between the values obtained by the both techniques is fairly good. There is no appreciable change in the log K values.

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