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pH-Metric studies of substituted dihydropyrimidin-2(1H)-one with La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III) metal ions at 0.1M ionic strength

Science

KEYWORDS : Substituted dihydropyrimidin-2(1H)-one, Ionic strength, Proton ligand stability constant, Metal ligand stability constant

*** Yuvraj K.Meshram** G.S science Arts and Commerce College Khamgaon, Dist- Buldhana
* Corresponding author

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 interaction of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III) metal ions with 5-ethoxy carbonyl-4-(4-chloro phenyl)-6-methyl-3,4-dihydropyrimidine-2(1H)-One (ligand-1) and 5-ethoxy carbonyl-4-(4-fluro phenyl)-6-methyl-3,4-dihydropyrimidine-2(1H)-One (ligand-2) have been investigatedby pH-metric technique at 0.1 M ionic strength at 29 ± 0.1 ºC in 70 % THF-water mixture. The data obtained were used to estimate the values of proton-ligand stability constant (pK) and metal-ligand stability constant log K. It is observed that La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III) metal ions formed 1:1 and 1:2 complexes with all the ligands.

Introduction:
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.1 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, antitumor2. 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 acid33,44 .substituted isoxazoline55,66 aromatic ketones, alkyl-monomines7,substituted benzothiazoles8, substituted coumarines9, and substituted pyrazoline10

In view of analytical applications it is worthwile to know the effect of substitutes on proton- ligand stability constants. Therefore the present work is undertaken to make a systematic study for determining proton- ligand stability constants pH- metrically at 0.1M ionic strength in 70% THF-water mixture.

Experimental work: In the present investigation, chemicals such as sodium hydroxide, perchloric acid, sodium perchorate were used are of AR grade. Ligands L1, and L2 were prepared according to literature method. All ligands were crystalized and their purity were chekced by TLC before use. The solution of ligands were prepared in 70% THF-water as a solvent. The other solutions were prepared in double distilled water.

pH metric titration were carried out with Elico(L1-613) pH meter using combined glass and calomel electrode assembly having accuracy of ±0.01pH unit. The instrument was calibrated by using 0.05M potassium hydrogenphthalate solution (pH=4) and standard buffer tablet (pH=9). All titrations carried out at constant temperature to keep ionic strength μ=0.1M NaClO4,total volume (25ml) and concentration of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III) metal ions and ligand are kept constant at the beginning of each titration. Each titration was repeated at least twice.

The method of Irving and Rossotti11was applied to evaluate the value of n and pL.The overall 0.1M ionic strength of solution was calculated by expression μ=½ΣCiZi2. The contribution of other ions in addition to Na+ and ClO4- were also taken into consideration.

Fig : 1- Ligand 1.

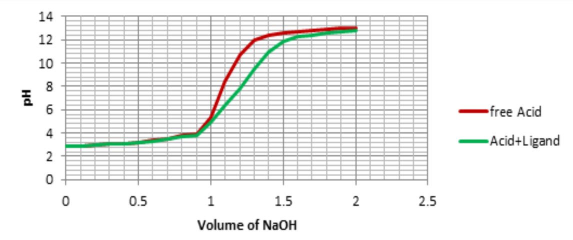


Fig :1.1- Formation curve between nA Vs pH of Ligand 1.

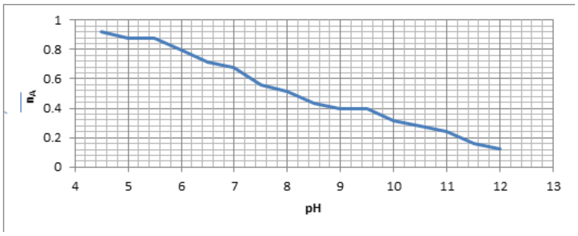


Fig : 2- Ligand 2.

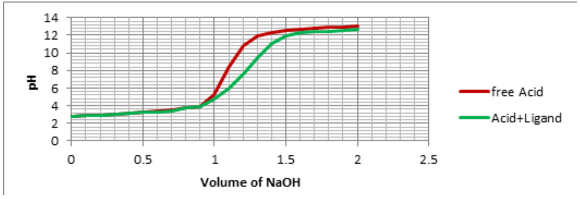
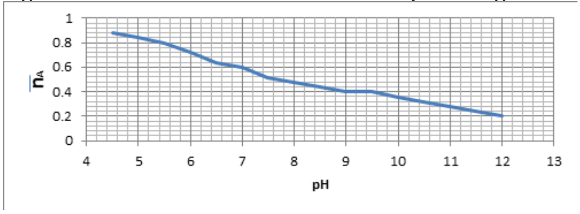


Fig :2.1- Formation curve between nA Vs pH of Ligand 2.



Results And Discussion:
Proton-ligand stability constant: Substituted drugs may be considered as a monobasic acids having only one replaceable H+ ion from –OH group dissociate completely above pH 9 and can there fore be represented as HL.

$$HL \longleftrightarrow H^{+} + L^{-}$$

The titration data is used to construct the curves between volume of NaOH vs. pH. Free acid, acid-ligand and acid-ligand-metal curve.

It is observed from titration curves for all the systems that ligand curves start deviating from free acid (HClO4) curves at about pH 3.57 and deviated continuously upto pH 12.5. The deviation shows that dissociation of –OH group in substituted drugs.

The value of nA at various pH values were calculated from the acid titration curves (A) and ligand titration curves (B) by using formula of Irving and Rossotti811. Proton – ligand stability constants were calculated from the plot nA vs.pH , the values of pK were determined.(half integral method). By noting the pH at which nA = 0.5. The accurate value of pK were estimated by pointwise calculation method (Table-1).

Table-1 Determination of proton ligand stability constant (pk) Of Substituted dihydropyrimidin-2(1H)-one at 0.1 m ionic strength.

SR No	System	Constant pK	
		Half integral	Point wise-calculation
L1	5-ethoxy carbonyl-4-(4-chloro phenyl)-6-methyl-3,4-dihydropyrimidine-2(1H)-0ne.	8.19	8.19
L2	5-ethoxy carbonyl-4-(4-fluro phenyl)-6-methyl-3,4-dihydropyrimidine-2(1H)-0ne.	7.74	7.64

From the Table:1, it could be seen that the dissociation constant of substituted hetrocyclic drugs in present investigation found to be below pH 12.5. This shows that the dissociation proton (H+) from phenolic –OH group of substituted drugs.

The pK value of Ligand 1, is found to be Grater then pK value of Ligand 2. i.e. L1 > L2.

The pK value for different ligand is different i.e. greater of smaller is due to the electron withdrawing group that reduce the pK value but increases the dissociation, while in case of electron releasing group that decreases the dissociation and increases the dissociation constant pK.

Metal-Ligand Stability Constants:
The metal ligand stability constants of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III) complexes with some substituted drugs were determined by employing Berrum-Calvin pH –titration technique as adopted by Irving and Rossotti11. It was observed that the metal-ligand curve is well separated from the ligand titration curves suggesting thereby that the liberation of proton is due to ring formation.

From the formation curves, the value of stability constant log K1 and log K2were determined which corresponds to the pL values at n = 0.5 and 1.5 respectively (Table-2).

Table-2 Determination of metal ligand stability constant (log k) of metal ion complexes with Substituted dihydropyrimidin-2(1H)-one at 0.1 m ionic strength.

SYSTEM	log K1 i.e. pL1	log K2 i.e. pL2
La (III) – L-1	4.67	5.99
Ce (III) – L-1	5.09	6.31
Pr (III) – L-1	6.04	7.01
Nd (III) – L-1	5.59	6.80
Sm (III) – L-1	6.43	7.54
Eu (III) – L-1	5.13	6.38
La (III) – L-2	4.62	6.13
Ce (III) – L-2	5.09	6.82
Pr (III) – L-2	4.81	6.13
Nd (III) – L-2	6.34	7.49
Sm (III) – L-2	5.72	6.81
Eu (III) – L-2	5.52	7.16

The relation of log K = a pK + b, was also studied. The order of stability of complex is as follows :

(I) log K1 for Ligand -1
Sm > Pr > Nd > Eu > Ce > La

(II) log K1 for Ligand -2
Nd >Sm > Eu > Ce > Pr > La

These values are also observed by Tambatkar et al12, Sonune et al13 and Y.K.Meshram et al7.

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