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Studies in Co-Ordination Complexes of Dy-(Iii) with Some Simple Hetero Cyclic Drugs by Ph-Metric and Spectro Photometric Technique in 70 % Ethanol-Water Medium.

KEYWORDS

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ABSTRACT *The interaction between Dy(III) and Lincomycin (ligand 1) and Pyridoxin (ligand 2) have been studied by pH-metric and spectrophotometric technique at 0.1 M ionic strength and (27+0.1 C) in 70 % ethanol-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 showed that Dy(III) ions forms 1:1 and 1:2 complex with simple substituted heterocyclic drugs like Lincomycin and Pyridoxin. The result obtained from pH-metric technique are confirmed with the help of spectrophotometric technique.

Introduction :

Simple heterocyclic drugs like Lincomycin and Pyridoxines are good complexing or chelating agents due to presence of electron donating nitrogen. They formed coloured complexes with metal ions in solid state [1]. Narwade et al [2] studied the formation constant and solubility constant of Th(IV) complexes with some substituted Pyrozoline. Meshram and et al [3] also studied the formation constant of Sm(III) complexes with some substituted Pyrazolines by pH-metric and Spectrophotometric technique in 70 % Dioxane-water media.

Mandakmare et al [4] have studied the stability constant of UO2(II) complexes with some substituted coumarins at 0.1 M ionic strength pH metrically and spectrophotometrically. M.R. Gadpayale [5] has studied the formation constant of Lanthanide ions with some substituted isoxazoline. Gudadhe et al [6] have determined the stability constant of Cu(II) with substituted isoxazoline in 70 % dioxane-water mixture. Sonune K. N. [7] have studied acidity and stability constants of Pr(III), complexes with some substituted heterocyclic drugs in 70 % dioxane-water mixture Spectrophotometrically. The stability constant of Pd(II), Cu(II), Ni(II), Zn(II) and Mn(II) complexes of various hydroxyl triazines using Bjerrum-Calvin pH titration technique and the stability sequence and linear correlationship pKa, log K_1, log K_2 have been reported by Purohit and co-researcher [8]. Sawalakhe et al [9] have studied the interaction of metal with 1,3 diketone, Pyrazoline and Pyrazoline Spectrophotometrically.

G. D. Tambatkar [10] have studied conditioned stability constant of some heterocyclic drugs. The study of the stability constant of Dy(III) complexes with simple heterocyclic drugs was still lacking. It was therefore thought of interest to study the chelating properties of some simple heteocyclic drugs under suitable conditions pH metrically and Spectrophotometrically.

Material And Methods :

pH meter ElicoL1-12T was used for measuring pH of solution. Dysprosium was used in the form of nitrate and sodium perchlorate used were of A. R. grade.

The simple heterocyclic drugs (ligands) were prepared in laboratory by standard and known method given in literature. Simple heterocyclic drugs are insoluble in water and hence 70% ethanol-water (v/v) was used as a solvent.

CALVIN-BJERRUM TITRATION TECHNIQUE :

The titration were carried out in an inert atmosphere of nitrogen. The ionic strength of solution was maintained constant by adding an appropriate amount of 1M NaCLO4 solution. The pH were recorded by pH meter. These values were converted to [H+] values by applying corrections proposed by Van-Vitert and Haas [11]. It could be seen from table No. 1 that agreement between pK values from both the methods is found to be good pK values of ligand no. 1 is greater than pK value of ligand no. 2 and 3 . This may be due to the fact of the presence of electron withdrawing groups.

Table 1

System	Log K_1	Log K_2
Dy(III) Lincomycin	7.70	5.55
Dy(III)- Pyridoxine	7.24	4.40
Dy(III)-Quinine	7.48	4.74

Metal-Ligand Stability Constant :

Metal-ligand stability constant of Dy(III) complexes with above ligand no. 1, ligand no. 2 and ligand no. 3 were determined by employing Bjerrum. Elvin pH titration technique as dopted by Irving and Rossotti.

The formation of chelates between Dy(III) and simple heterocyclic drugs was indicated by

1) The significant departure, starting at about pH 4.0-4.5, of the metal titration curves from ligand titration curves and
2) The change in colour from light yellow to brown as pH was raised from 4.8 to 6.8.

While calculating n (metal-ligand formation number) and pL (metal-ligand stability constants) the concentration were corrected for changes in volume produced by the addition of alkali during titration. The log K values were directly read from the formation curves (n vs pL) using half interpreted method. The most accurate values were calculated

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by pointwise calculations method. The log K1 and K2 (first and second stability constants) values obtained from both the methods are preented in table 2.

Table 2
Determination of Proton-ligand stability constants (pK) of some simple heterocyclic drugs at 0.1 M Ionic strength.

System	Half Integrd	Piontwise calculations
Ligand 1 (Lincomycin)	10.05	10.06±0.05
Ligand 2 (Pyridoxine)	10.31	10.38
Ligand 3 (Quinine)	9.87	9.88

The present work deals with the study of titration between Lanthanide ion Dy(III) and simple heterocyclic drugs like Lincomycin, Pyridoxine, and Quinine at 0.1 M ionic strength at 27 ± 0.01°C

Result And Discussion :
Simple heterocyclic drugs may be considered as monobasic acids having only one replacable H+ ion from phenolic –OH group and therefore is represented as HL.

The titration data were used to construct the curves between volume of NaOH Vs pH. They are called acid, ligand and metal titration curves. It is observed from titration curves for all systems that ligand curves start deviation from the free acid (HClO4) curves at absolute pH 5.25 for ligand no. 1 and at pH 5.75 for ligand no. 2 and at pH 5.15 for ligand no. 3. The deviation increases continuously upto 11.20 to 11.50. It indicate that –OH group start to dissociate at about 6.5 and complete its dissociation at about pH 11.5.

The average numbe of protons associated with ligand (nA) was determined from acid and ligand titration curves employing the equation of Irving and Rossotti. The proton ligand formation curves were then obtained by plotting the values of nA Vs pH from these groups, the value of log K, pK were determined (Half integral method) by noting the pH at which nA = 0.5. The accurate pK values were estimated by pointwise calculation method which are presented in table no. 1.

It is observed from table 2 that there is not as much as appreciable difference between log K_1 and log K_2 values. It shows that there is no formation of stepwise complexes but there may be formation of simultaneously formation of complexes. The values of (log K_1-log K_2) and (log K_1 / log K_2) are presented in table 3.

Table 3
Metal ligand Stability constant at 0.1 M ionic strength

System	Log K_1-log K_2	Log K_1/logK_2
Dy(III)-ligand no. 1	2.19	1.38
Dy(III)-ligand no.2	2.84	1.64
Dy(III)-ligand no.3	2.73	1.57

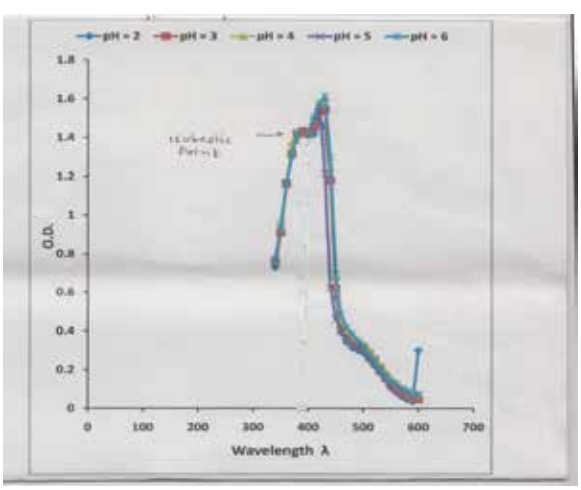
Smaller the difference between the log K_1 and log K_2 may be due to trans structure. The table 3 also shows that the ratio log K_1/log K_2 is positive in all the cases. It implies that there is little or no steric hindrance to the addition of secondary.

Spectrophotometric Technique :
The formation of 1:1 and 1:2 complexes from pH-metric is confirmed by spectrophotometric technique at 0.1 M ionic strength. Vareille's method of isobestic point was used to study the solubility constant of Dy(III) complexes with ligand no.1, 2 and 3. Various solutions of metal ions and ligand were prepared in the ratio 1:20; pH range of 2 to 6, the spectra were recorded by UV and visible spectrophotometer no. 108, systronic company (accuracy = ± 0.005 Abs).

The curves between wavelength and 0.01 % transmission (fig 1 to 3) were found to intersect at one point only (isobestic point) corresponding to wavelength 350 nm, 345 nm and 370 nm for ligand 1, 2 and 3 respectively indicating the presence of two complex species (1:1 and 1:2 complexes).

Graphs : One graph is shown for the system Dy(III)-L_3 i.e. Dy(III)-quinine system as below.

Fig : 1
Isobestic Point Method
System:Dy(III)-L3 (Quinine)



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