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Metal-ligand stability constants of Th(III), Sm(III), Nd(III) and Pr(III) metal ion complexes with 2-mercapto-4-substituted phenyl-6-substituted phenyl pyrimidines at 0.1 M ionic strength pH metrically

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ABSTRACT

The interaction between Th(III), Sm(III), Nd(III) and Pr(III) Metal Ions And 2-Mercapto-4-(4'-Aminophenyl)-6-(2'-Hydroxy-5'-Bromophenyl)Pyrimidine[M4AHBP](L_1) and 2-Mercapto-4-(2'-Chlorophenyl)-6-(2'-Hydroxy-5'-Bromophenyl)Pyrimidine[M2CHBP](L_2) have been studied at 0.1 M Ionic Strength in 70 % Dioxane-water mixture by Bjerrum method as adopted by Calvin and Wilson. It is observed that Th(III), Sm(III), Nd(III) and Pr(III) Metal ions form 1:1 and 1:2 complexes with ligands (L_1 & L_2). The data obtained were used to estimate and compare the values of proton-ligand stability constant (pK) and metal-ligand stability constants (log k). From estimated data (pK and log k), the effects of substituents were studied.

Key words: 2-Mercapto-4-Substituted Phenyl-6-Substituted Phenyl Pyrimidines, Dioxane-water mixture, Stability Constants.

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INTRODUCTION

The literature survey reveals that work has been done on heterocyclic compounds for their antibacterial activities on gram positive and gram negative bacteria also their antifungal activity on different fungi's. Pyrimidine derivatives have found to posses various biological and antibacterial and antifungal properties. Pyrimidine derivatives are known to shows antitumor, anti-inflammatory, anti malarial , anti diabetic, insecticidal and antimicrobial activities .

In a view of analytical applications of pyrimidines, it is interest to know the physiochemical properties such as stability of the complexes with lanthanide metal ions. The lanthanide compounds have remarkable importance in everyday life [1,2]. More explicitly in the previous

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decades their use in various organic technical processes led to a rapid growth especially in the field of complexes. In recent years the luminescence properties of rare earth metal complexes with different □-diketones have been widely studied due to their use in fabrication of polymer light emitting diodes to enable low cost, full color, flat panel display.

Considerable research work has been done in the past, on the study of complexes[3, 4]. The studies in metal-ligand complexes in solution of a number of metal ions with carboxylic acids, oximes, phenols etc. would be interesting which throw light on the mode of storage and transport of metal ions in biological kingdom. With the view to understand the bi-inorganic chemistry of metal ions, Banerjee et al[5] have synthesised a number of mixed-ligand alkaline earth metal complexes. Bjerrum's[6] dissertation has taken the initiative to develop the field. Metal complexation not only bring the reacting molecules together to give activated complex[7] but also polarised electrons from the ligands towards the metal. The relation between stability and basicity of the ligands is indicated by the formation constant and free energy change value. Bulkier group increases the basicity of ligands as well as stability. The stability of complexes is determined by the nature of central metal atom and ligands. The stability of complexes is influenced by the most important characteristics like degree of oxidation, radius and electronic structure. Irving and Williams[8] had studied the order of stability of metal complexes of transition metal ions by comparing the ionic radius and second ionisation potential of metal ions, as it is valid for most nitrogen and oxygen donor ligands. Narwade et al[9] have investigated metal-ligand stability constants of some lanthanides with some substituted sulphonic acids. Many workers[10-14] have reported their results on metal-ligand stability constants. Bodkhe et al[15] have reported the metal-ligand stability constants of some □-diketones. Tekade et al[16] investigated stability constants of some substituted pyrazolines, isoxalline and diketone. Shekhon[17] potentiometrically determined proton-ligand stability constants in various aqueous organic mixtures. Prasad[18] studied the stability of same metal complexes of β-diketones. Deosarkar[19] have studied stability constants of Al(III), Cr(III) and Fe(III) metal ion complexes with substituted sulphonic acid. Pund[20] have investigated interaction between La(III) and Nd(III) metal ions and 1-(4-hydroxy-6-methylpyrimidine)-3-substituted thiacarbamide of 0.1 M ionic strength pH metrically. Recently Speciation of binary complexes of Ca(II), Mg(II) and Zn(II) with L-glutamic acid in DMSO-water Mixtures has been studied [21].

The present paper describe the interactions between Th(III), Sm(III), Nd(III) and Pr(III) Metal Ions And 2-Mercapto-4-(4'-Aminophenyl)-6-(2'-Hydroxy-5'-Bromophenyl)Pyrimidine [M4AHBP] (L$_1$) and 2-Mercapto-4-(2'-Chlorophenyl)-6-(2'-Hydroxy-5'-Bromophenyl) Pyrimidine[M2CHBP](L$_2$) have been studied at 0.1 M Ionic Strength in 70 % Dioxane-water mixture at (30 ± 0.1) by Bjerrum pH metric method as adopted by Calvin and Wilson.

MATERIALS AND METHODS

The ligands [M4AHBP] L$_1$ & [M2CHBP] L$_2$ were synthesized in the laboratory by known literature method. The purity of these compounds exceeds 99.5% and structures were confirmed by NMR, IR and melting points. The stock solutions of the ligand was prepared by dissolving required amount of ligand in a minimum volume of dioxane subsequently diluted to final

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volume. Metal ion solution was prepared by dissolving metal nitrate (Sigma - Aldrich) and standardized by EDTA titration method as discussed in literature . Carbonate free sodium hydroxide solution was prepared by dissolving the Analar pellets in deionised water and solution was standardized [22]. The stock solution of percholric acid was prepared and used after standardization [23].

Measurements

All measurements were carried out at (30 $\square$ 0.1) ^{0}C. Systronic microprocessor based pH meter with magnetic stirrer and combined glass and calomel electrode assembly used for pH measurements. The sensitivity of pH meter is 0.01 units. The instrument could read pH in the range 0.00 to 14.00 in the steps of 0.005. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. It was calibrated before each titration with an aqueous standard buffer solution of pH 7.00 and 9.20 at (30 $\square$ 0.1) ^{0}C prepared from a 'Qualigens' buffer tablets. The hydrogen ion concentration was measured with combined glass electrode.

Procedure

The experimental procedure involved the titrations of

i.   Free acid $HClO_4$ (0.01 mol.dm^{-3})

ii. Free acid $HClO_4$ (0.01 mol.dm^{-3}) and ligand (20 x 10^{-4} mol.dm^{-3})

iii. Free acid $HClO_4$ (0.01 mole dm^{-3}) and ligand (20 x 10^{-4} mol.dm^{-3}) and metal ion (4 x 10^{-4} mol.dm^{-3}) against standard carbonate free sodium hydroxide (0.142 mol.dm^{-3}) solution using Calvin-Bjerrum and Calvin-Wilson pH titration techniques. The ionic strength of all the solutions were maintained constant by adding appropriate amount of $NaClO_4$ solution. All titrations were carried out in 70 percentages of Dioxane-water mixtures and reading were recorded for each 0.1 ml addition. The curves of pH against volume of NaOH solution were plotted [24-26] (fig 1,2). The Proton-Ligand constants were calculated from pH values obtained from the titration curves using the Irvin-Rossotti method and MATLAB computer program (Table 1) .

RESULTS AND DISCUSSION

The extent of deviation may be the dissociation of -OH group. 2-mercapto-4-substitued phenyl-6-substituted phenyl pyrimidine may be considered as a monobasic acid having one replaceable H^+ ion from phenolic -OH group and can be represented as

$$HL \ \rightleftharpoons \ H^+ + L^-$$
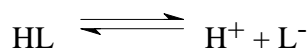
The titration data were used to construct the curves [acid curve (A), acid + ligand curve (A+L) and acid + ligand + metal ion curve (A+L+M)] between volume of NaOH against pH.

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The proton-ligand formation number n_A were calculated by Irving and Rossotti expression (Table1)

$$n_A = \frac{(E_0+N)\,(V_2-V_1)}{(V_0+V_1)\,T_L^0} \qquad .....(1)$$

where ☐ denotes the number of dissociable protons, N is the concentration of sodium hydroxide (0.1333 mol.dm^{-3}), (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, where V_2 and V_1 are the volume of alkali added to reach the same pH reading to get accurate values of (V_2-V_1): the titration curves were drawn on an enlarged scale: E^0 and T_L^0 are the resultant concentration of perchloric acid and concentration of Ligand, respectively. V_0 is the initial volume of reaction mixture (50 cm^3). Proton-Ligand stability constant pk values of Ligand were calculated by algebraic method point wise calculation and also, estimated from formation curves (fig 3, 4) n_A Vs pH (Half integral method) by noting pH at which n_A = 0.5 [Bjerrum 1957] (Table 2).

Metal-Ligand stability constants (log k) were determined by the half integral method by plotting n Vs pL. The experimental n values determined using expression

$$n = \frac{(E_0+N)\,(V_3-V_2)}{(V_0+V_2)\,T_m^0} \qquad .....(1)$$

Where N, E_0, V_o and V_2 have same significance as in equation (1), V_3 is the volume of NaOH added in the metal ion titration to attain the given pH reading and T^0_M (4 x 10^{-4} mol dm^{-3}) is the concentration of metal ion in reaction mixture. The stability constants for various binary complexes have been calculated (Table 3).

CONCLUSION

From the titration curve, it is observed that the departure between (Acid + Ligand) curve & (Acid +Ligand +Metal) Curve for all system of ligand-1 started from pH=2.5 to 3.0 and of ligand to started from pH=3.25 to 3.50, this indicate the commencement of complex formation. Also change in color from yellow to brown in pH range from 3.0 to 9.0 during the titration showed the complex formation between Metal & Ligand.

Proton-Ligand stability constant (pK):-
It is observed from titration curve in (fig. 1, 2) that the ligand curves starts deviating from free acid (HClO$_4$) curves at pH > 2.5. The extent of deviation s may be the dissociation of –OH group completely. The results reveal that (Table 2) , the pK Value of ligand- 2 is greater than pK Value of Ligand- 1.

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Table 1 : Proton-Ligand formation number (n_A) at (30± 0.1) ^{0}C and at ionic strength µ= 0.1 mol.dm^{-3} NaClO$_4$ in 70% Dioxane-Water mixure.

[M4AHBP]L$_1$

pH	V_1	V_2	V_2-V_1	n_A
3.0	1.72	1.75	0.03	0.9584
3.5	1.75	1.82	0.07	0.9031
4.0	1.78	1.86	0.08	0.8894
4.5	1.79	1.89	0.10	0.8617
5.0	1.80	1.92	0.12	0.8341
5.5	1.80	1.93	0.13	0.8202
6.0	1.80	1.95	0.15	0.7926
6.5	1.80	1.97	0.17	0.7649
7.0	1.80	1.98	0.18	0.7511
7.5	1.80	2.00	0.20	0.7234
8.0	1.80	2.02	0.22	0.6957
8.5	1.80	2.04	0.24	0.6681
9.0	1.80	2.06	0.26	0.6404
9.5	1.80	2.08	0.28	0.6128
10.0	1.80	2.11	0.31	0.5713
10.5	1.80	2.15	0.35	0.5159
11.0	1.80	2.20	0.40	0.4468
11.5	1.82	2.30	0.50	0.3087
12.0	1.82	2.46	0.64	0.1151

[M2CHBP]L$_2$

pH	V_1	V_2	V_2-V_1	n_A
3.0	1.72	1.74	0.02	0.9723
3.5	1.75	1.80	0.05	0.9308
4.0	1.78	1.84	0.06	0.9169
4.5	1.79	1.85	0.06	0.9169
5.0	1.80	1.87	0.07	0.9031
5.5	1.80	1.89	0.09	0.8963
6.0	1.80	1.90	0.10	0.8616
6.5	1.80	1.92	0.12	0.8340
7.0	1.80	1.93	0.13	0.8202
7.5	1.80	1.94	0.14	0.8064
8.0	1.80	1.95	0.15	0.7926
8.5	1.80	1.97	0.17	0.7649
9.0	1.80	1.98	0.18	0.7520
9.5	1.80	2.00	0.20	0.7234
10.0	1.80	2.02	0.22	0.6957
10.5	1.80	2.06	0.26	0.6404
11.0	1.80	2.10	0.30	0.5851
11.5	1.82	2.15	0.33	0.5437
12.0	1.82	2.25	0.40	0.4473

Metal-Ligand stability constant(Log K) :-

It is observed that (Table 3) sufficiently large difference between log K_1& log K_2. Values indicates the stepwise formation of complex between metal ion and ligand except Nd (III) &

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Pr(III) for ligand-1. It showed that less difference between log K_1 & log K_2 values indicates Nd(III) – Ligand-1 & Pr(III)- Ligand-1 complexes are occurring simultaneously.

The values of log K_1 & log K_2 for Th(III)-Ligand1 & Ligand 2 complexes are higher than Sm(III), Nd(III) & Pr(III)-Ligand-1 & Ligand 2 complexes, indicate that Th(III) forms more stable complex with ligand 1 & 2 than Sm(III) , Nd(III) & Pr(III) metal ions.

The higher value of ratio(Log K_1/ Log K_2) for Th(III) & Sm(III)- Ligand- 2 complex indicates the more stable stepwise complex formation as compare to Nd(III) & Pr(III) – Ligand 2 complexes.

Table 2:   Proton-Ligand Stability constants (pK).

Sr. No	System	pK	
		Half Integral method	**Point wise calculation method**
1	[M4AHBP] L_1	10.5276	10.4762
2	[M2CHBP] L_2	11.5761	11.6227

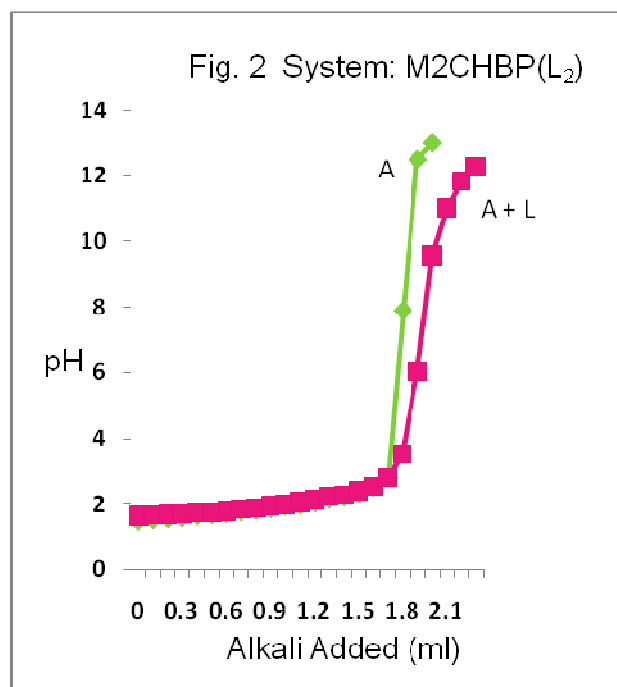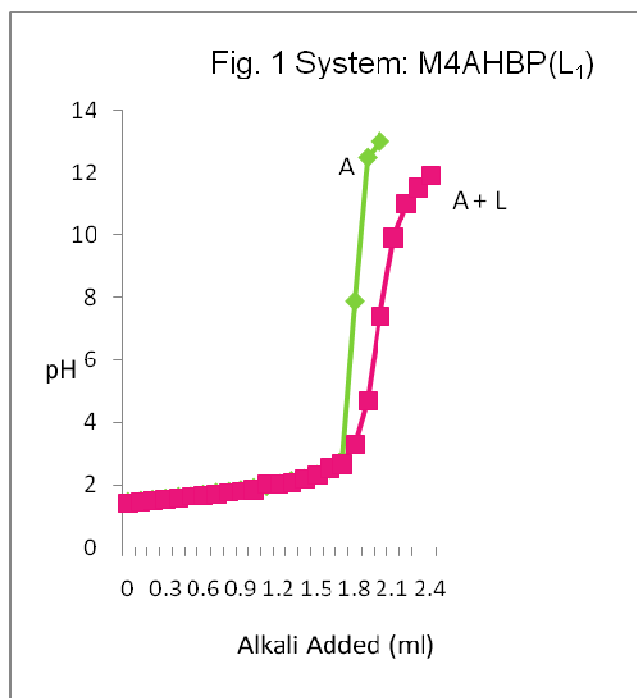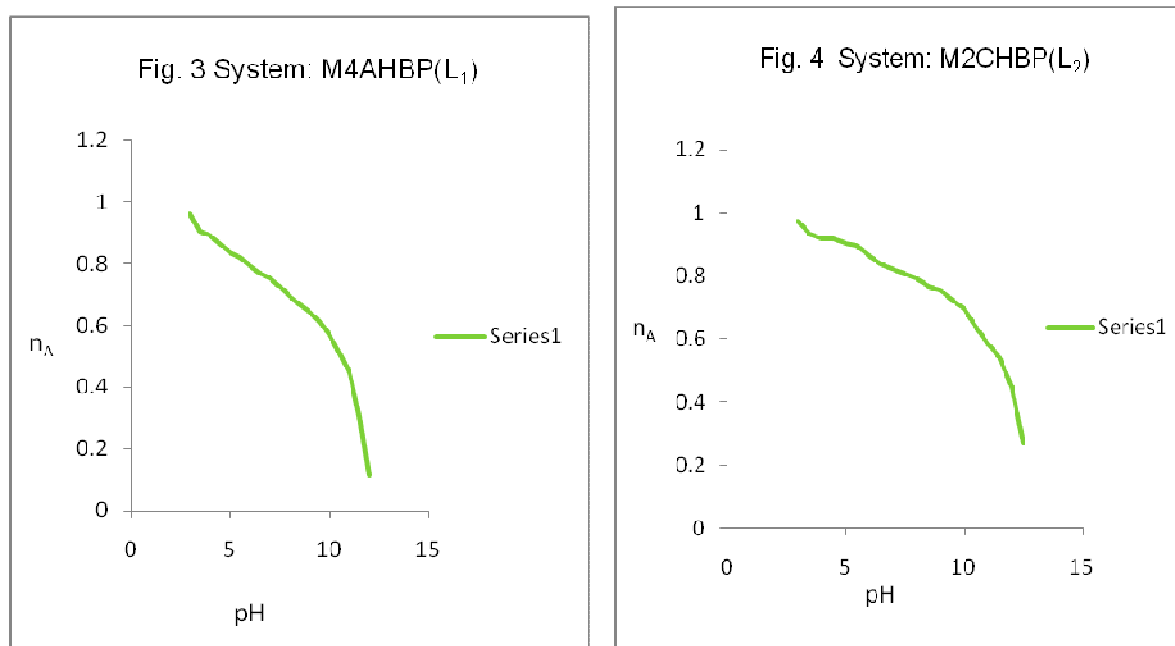**Fig 1 &2 : pH against volume of NaOH at µ= 0.1M at (30 ± 0.1) ^{0}C**

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Fig 3 &4 : Formation Curves of n_A against pH at µ= 0.1M at (30 ± 0.1) ^{0}C

Table 3: Metal-Ligand Stability constants (Log K).

System	Log K_1	Log K_2	Log K_1-Log K_2	Log K_1/Log K_2
Th(III)- L_1	10.2446	5.7958	4.4488	1.7675
Sm(III)- L_1	8.3646	4.3538	4.0108	1.9212
Nd(III)- L_1	8.2446	4.8538	3.3908	1.6985
Pr(III)- L_1	8.7447	5.2246	3.5201	1.6737
Th(III)- L_2	9.7447	4.7668	4.9779	2.0442
Sm(III)- L_2	8.9427	4.2638	4.6789	2.0973
Nd(III)- L_2	9.2446	4.7938	4.4508	1.9284
Pr(III)- L_2	8.8142	4.3538	4.4604	1.9761

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