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RESEARCH ARTICLE

DETERMINATION OF STABILITY CONSTANT OF METAL COMPLEXES OF Co(II), Ni(II) AND Cu(II) WITH SCHIFF BASES OF 3-BROMO-4-AMINO TOLUENE BY POTENTIOMETRIC TITRATION TECHNIQUE.

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Abstract

Schiff base namely 1-(2-bromo-4-methyl phenyl)-2-(4-chlorophenyl) azomethine *i.e.*BMPCA and 1-(2-bromo-4-methyl phenyl)-2-(4-nitrophenyl) azomethine *i.e.*BMPNA have been synthesized and characterized by Elemental analyses, IR and ^{1}H NMR. Stability constant of BMPCA and BMPNA and its Metal complexes with Cu (II), Co (II) and Ni (II) have been determined by using Calvin – Bjerrum pH -metric titration technique as adopted by Irving-Rossotti. The potentiometric studies were carried out at constant temperature 27˚±0.5˚C and at ionic strength of 0.1 M KNO_3 in 60:40 % (V/V) 1,4-dioxane – water system . In this work we have calculated proton- ligand stability constant (pK_1^H) and metal-ligand stability constant $(\log k_1)$ values by Pointwise calculation method and Half Integral method. The order of the stability constants of the formed complexes observed in BMPCA is Co>Cu>Ni and in BMPNA is Co>Ni>Cu.

Introduction:-

Schiff bases are important class of ligands in co-ordination chemistry [1,2]. They were first reported by a German chemist H. Schiff, a nobel prize winner of the year 1864 [3]. Studies on characteristics of co-ordination compounds of transition metals with Schiff bases are based on nature of metal as well as the type of ligands and their structures. Metal complexes containing organic molecule with hetero atom in the physiological system play vital role to the existence, growth, maintenance and formation of entire living being. Review of research work indicates that the pH-metric studies have shown considerable interest in the study of binary, ternary and quaternary systems [4,5,6,7]. In the present work stability constants of M(II) – Schiff base of Cu(II), Ni(II) and Co(II) have been calculated by using Calvin-Bjerrum [8] pH-metric titration technique as adopted by Irving-Rossotti [9]. Literature survey reveals that this technique has been reviewed by many authors to derive proton–ligand stability constant and metal-ligand stability constant for both the binary and ternary systems [10,11,12,13,14]. Stability constant determination is useful for the practical application of complexation between metal and ligand under specific conditions. A complete complex formation can be predicted on the basis of the pH of the solution. As the pH of the solution is very sensitive criteria since ligands or chelating agents are also either acids or bases and chelation or complex formation is accompanied by the removal of hydrogen or by the lowering in concentration of base. In pH titration technique glass electrode, quinhydrone electrode or H_2 - gas electrode can be used [13,15,16].

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Experimental:-

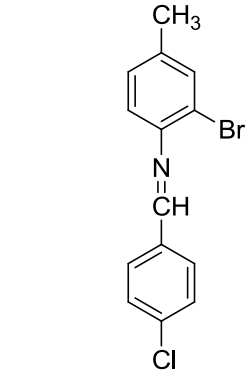
Materials:-

All chemicals used were of A.R. grade, purchased from Sigma-Aldrich and E. Merck and used as received without any further purification. The stock solutions of metal ions Cu(II), Co(II) and Ni(II) were prepared from their nitrate salts and standardized. Other chemicals used were KOH, HNO_3 and 1,4-Dioxane. All the solutions were prepared in doubly distilled water and solutions of ligands were prepared in 1,4-Dioxane. The pH measurements were recorded using combined electrode on Equiptronics pH meter with pH range 0-14.The temperature was maintained at 27˚±0.5˚C and 1.0 M KNO_3 solution was used to keep the ionic strength constant during the titration studies.

Synthesis of Schiff Bases:-

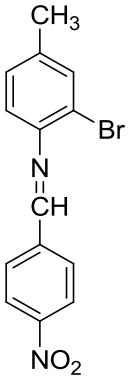
Methanolic solution of 3-bromo-4-amino toluene and p-chloro benzaldehyde in 1:1 molar ratio were mixed and refluxed with constant stirring at 50 - 60˚C for 2-3 hrs till solid separation . Schiff base was obtained by slow evaporation method . The product was washed with Sodium bisulphite solution to remove excess aldehyde and then washed with chilled methanol to remove other impurities. The product was dried by ether and recrystalized from hot methanol.

Synthesized Schiff base BMPCA was characterized by Elemental Analysis, ^{1}H NMR and IR spectra. The IR and ^{1}H NMR spectral studies provide the information regarding presence of azomethine group.



1-(2-bromo-4-methyl phenyl)-2-(4-chloro phenyl) azomethine

[BMPCA]



1-(2-bromo-4-methyl phenyl)-2-(4-nitro phenyl) azomethine

[BMPNA]

Fig. 1:– Structural formula of Schiff Base BMPCA and BMPNA

Another Schiff base BMPNA has been synthesized by the reaction between 3-bromo-4-amino toluene with p-nitro benzaldehyde in same manner as Schiff base BMPCA at optimal temperature.

Potentiometric Procedure:-

The pH-metric titrations were performed at 27˚±0.5˚C. During pH titration to maintain the homogeneneity a mixed solvent consisting 60:40 % V/V 1,4-dioxane-water system has been used. For the evaluation of proton-ligand stability constant (pK_1^H), three sets of solutions were prepared as given below:

Set-1 : HNO_3 (0.2M, 5 ml) + KNO_3 (1M, 9.0 ml) + D.D.W. (6.0 ml) + 30 ml 1,4-dioxane

Set-2 : HNO_3 (0.2M, 5 ml) + KNO_3 (1M, 8.9 ml) + Ligand solution (0.02M, 5ml) + D.D.W. (6.1 ml) + 25ml 1,4-dioxane

Set-3: HNO_3 (0.2M, 5 ml) + KNO_3 (1M, 8.8 ml) + Ligand solution (0.02M,5ml) + Metal nitrate Solution (0.02M,5ml) + D.D.W. (1.2ml) + 25 ml 1,4-dioxane

In this titration technique, the metal nitrate and ligand are taken in the molar ratio 1:1 for binary system and total volume of each set is 50 ml by adding distilled water and 1.0 M KNO_3 to maintain the ionic strength. These solutions were pH-metrically titrated by 0.2 M KOH solution.The change in the pH of solution with each addition of

alkali was recorded. The titration curves were obtained by plotting pH against volume of alkali added. In the respect of Set-1, Set-2 and Set-3 titration curves are named as acid curve, reagent curve and metal curve.

Result and Discussion:-

Characterization of ligands:-

The ligands BMPCA and BMPNA were characterized by Elemental analyses, IR spectra and ^{1}H NMR. Percentage of C, H, N were theoretically calculated and derived using CHN/S/O Analyzer, Perkin Elmer, series11, 2400. The data of % C, H and N are given in Table 1.

Table-1:-Characterization Data of Schiff Bases

Molecular Formula	Molecular Weight in gm mol^{-1}	M. P. (°C)	Yield (%)	Color	% of C, H,N Calculated (found)		
					%C	%H	%N
$C_{14}H_{11}NClBr$	308	218-220°C	75%	Light Brown	54.54 (53.19)	3.57 (3.46)	4.54 (4.60)
$C_{14}H_{11}O_2N_2Br$	319	112°C	82%	Bright Yellow	52.66 (52.90)	3.45 (3.51)	8.77 (7.70)

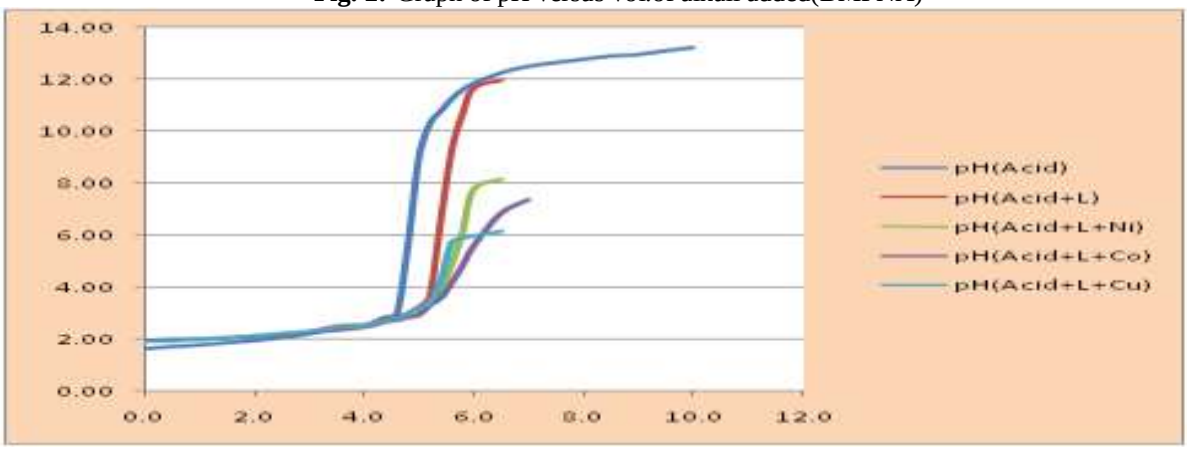
The IR spectra gives information about the nature of functional group present in the Schiff base. FTIR spectra of Schiff bases were recorded in the range 4000-400 cm^{-1} on a Perkin Elmer 16 FPC FT-IR using KBr Pellet technique. In the spectra of BMPCA and BMPNA the absorption band of azomethine group (ν HC=N) appears at 1602 and 1611Cm^{-1} respectively. The spectral band (ν C-Br) str. Of Bromo group is observed between 1080-1100 Cm^{-1}.

Vibrations of the aromatic hydrogens (ν C-H) str. are appeared around 3100 cm^{-1} region in the spectra. Other bands *i.e.* (ν C-Cl) and (ν C-NO_2) are appeared at 836 Cm^{-1} and 1349- 1521Cm^{-1} region respectively. The ^{1}H NMR were recorded on Bruker spectrophotometer (300 MHz) using TMS as an internal standard and $CDCl_3$ as solvent at ambient temperature. Proton of azomethine (-CH=N-) group appears at 8.058 δppm and 8.463 δppm respectively in BMPCA and BMPNA and the multiplets of aromatic (phenylic) hydrogen are observed in the range from 6.9 to 7.65 δppm. The alkylic hydrogen of methyl group (-CH_3) appears at 2.363 δppm in the ^{1}H NMR spectrum.

Potentiometric Studies:-

In this research work we have used Calvin-Bjerrum pH-metric titration technique as adopted by Irving - Rossotti. Evaluated values of stability constants show the behaviour of ligands and their interaction with metal ion in solution. The stability constants are depending on experimental conditions of solvent system *i.e.* 60:40 % V/V 1,4- dioxane-water system at 27˚± 0.5˚C. Metal nitrates of Cu (II), Co (II) and Ni (II) are used in the present investigation to minimize the interference of anion complexing. $\bar{n}$ values are in accordance with the formation of 1:1 type metal-ligand complex. The discussion of *log K* values are fully restricted in the studies of system at constant ionic strength (μ = 0.1M KNO_3). Irving-Rossotti explained that the formation curve of metal complex directly calculated from the pH- meter reading without any knowledge of Hygrogen ion concentration or activity. pH-metry data can be converted into stability constant using computational method as given by Irving and Rossotti. The formation curves were obtained by the pH values plotted against the volume of alkali as given in Fig.(2)for BMPNA .It is evident that the metal – titration curve is depressed below the reagent titration curve and a distinct color appears at particular pH value and it is the reason of complex formation in solution. The stability constants are calculated between pH range 2.5 to 4.5 where precipitation is not observed for any system and metal hydroxides can also not be precipitated.

Fig. 2:-Graph of pH versus vol.of alkali added(BMPNA)



Proton-Ligand Stability constant:-

The ligand act as a base and the basicity of ligand is one of the important factor which is helpful in deciding the stability of resulting complex. So, if other factors are same the stability is propotional to the proton-ligand stability constant *log* pK_1^H. The values of proton-ligand stability constant have been obtained by linear plot of pH against log ($\bar{n}_H/(1-\bar{n}_H)$)as fig.(3) of BMPNA where $\bar{n}_H$ values were calculated from the horizontal difference between acid curve and reagent curve. Derived values of proton-ligand stability constant are given in Table-2.

Fig. 3:- Graph of pH -> log($\bar{n}_H$ /(1-$\bar{n}_H$)) for BMPNA

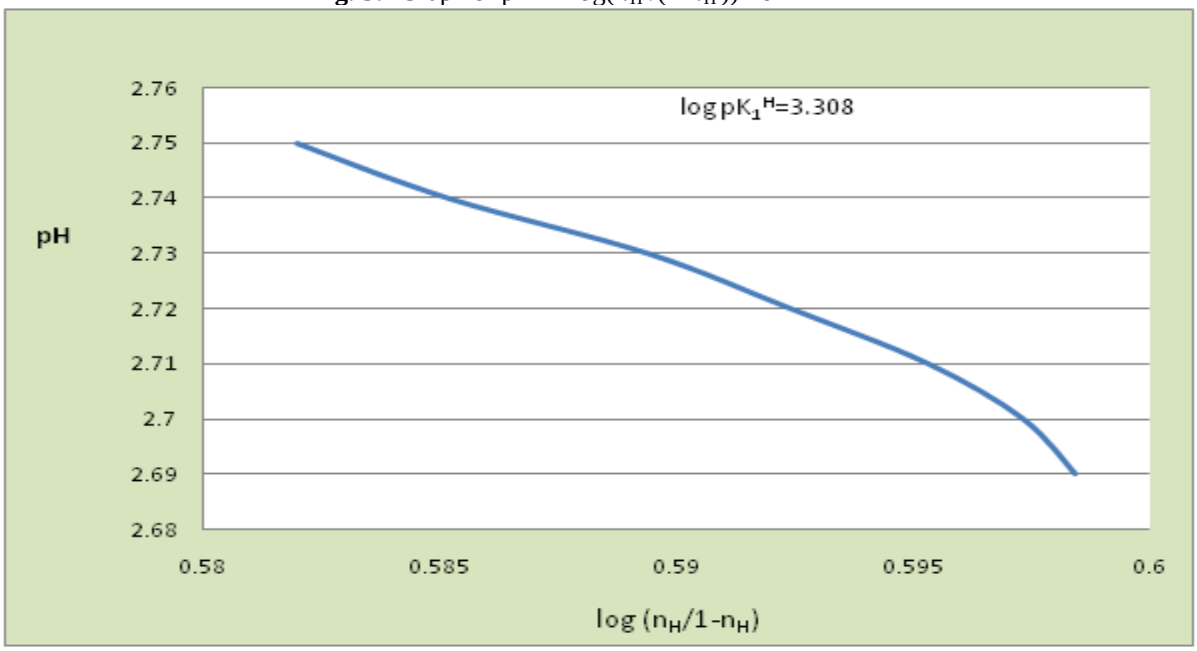


Table-2:-Proton-Ligand Stability Constant Of Schiff Bases

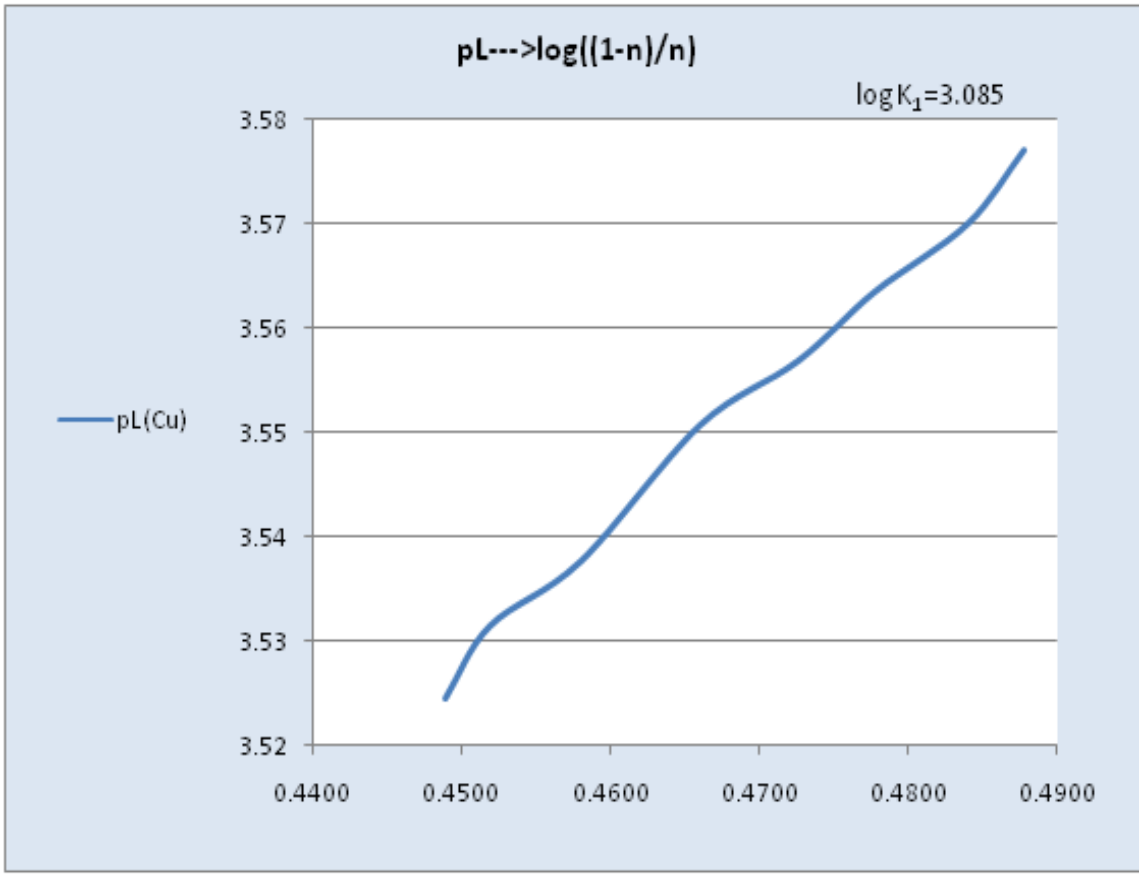
Sr. No.	Ligand	*Log* pK_1^H	pK_1^H
1.	BMPCA	5.24	1.7378×10^5
2.	BMPNA	3.308	2.032×10^3

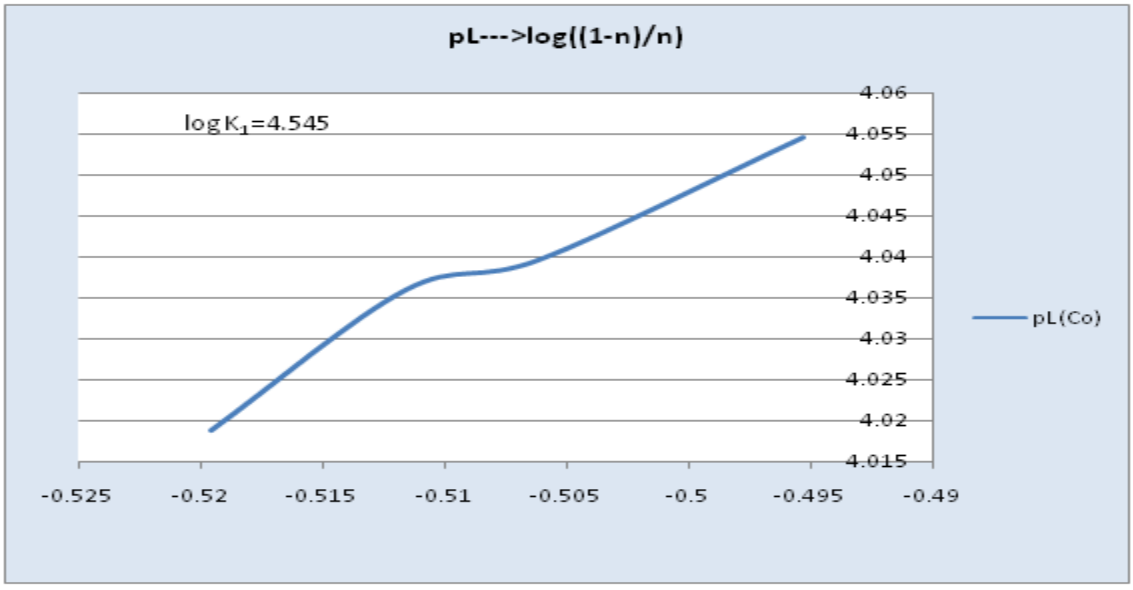
From the data of log pK_1^H, the order of proton-ligand stability constant is BMPCA > BMPNA .
The main influencing factors for proton – ligand stability constant are Inductive effect and Electrostatic effect.

Metal-Ligand Stability Constant:-

In this present study the pointwise calculation method is used to calculate the metal- ligand stability constant. The value of *log* K_1 is obtained by constructing a plot of $pL \rightarrow log\ ((1-\bar{n})/\bar{n})$ as given below in Fig.(4). where, $\bar{n}$ is average number of ligand bound per metal ion and *pL* is the free ligand exponent. Metal-ligand Stability Constant *log* K_1 derived for Co(II), Ni(II) and Cu(II) are given in Table - 3.

Fig.4:-Graph of $pL \rightarrow log\ ((1-\bar{n})/\bar{n})$ for BMPNA with metals





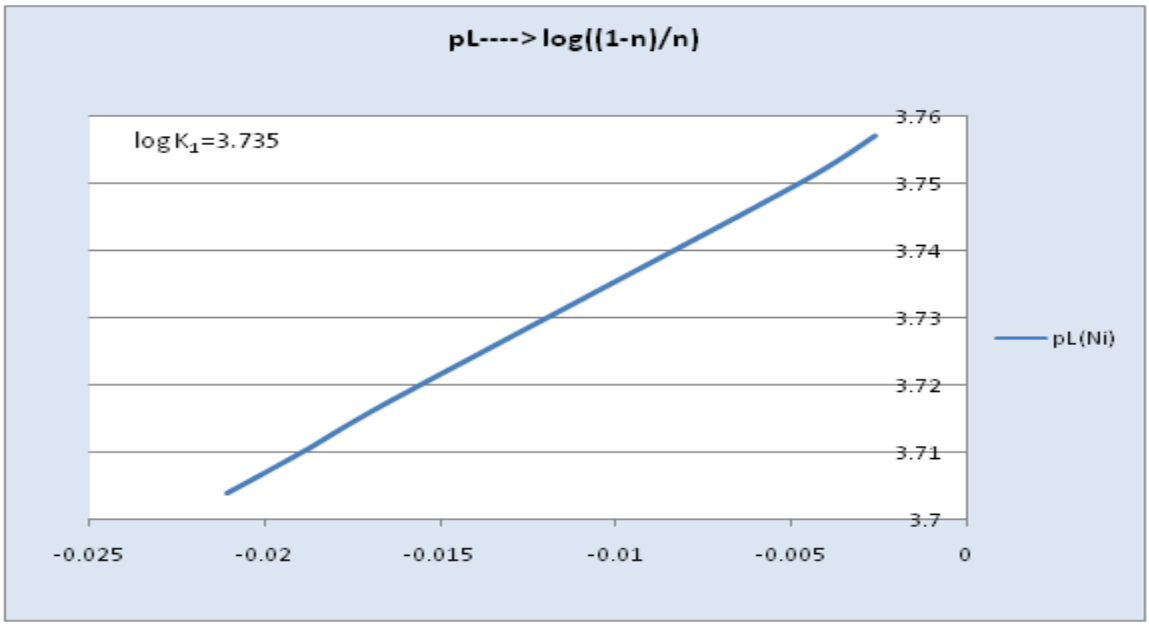


Table-3:- Stability Constant of Metal Complex

Sr. No.	Ligand	*Log K_1*		
		Co	Ni	Cu
1.	BMPCA	4.25	2.635	4.142
2.	BMPNA	4.545	3.735	3.085

As it can be seen from the results of *Log K_1* value of complex of Co (II) is quite high in both the ligands and on the other hand complexes of Cu (II) and Ni (II) have low values of stability constant. From the data of *Log K_1*, the order of metal – ligand stability constant in BMPCA is Co>Cu>Ni and in BMPNA is Co>Ni>Cu.

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