



INTERNATIONAL JOURNAL OF ADVANCE RESEARCH, IDEAS AND INNOVATIONS IN TECHNOLOGY

ISSN: 2454-132X

Impact factor: 4.295

(Volume2, Issue6)

Available online at: www.ijariit.com

Physicochemical Studies on Schiff Bases Derived From Substituted Coumarins with Substituted Diamines in Aqueous- Alcohol Medium

Uma Desai, Suresh*

Department of Chemistry,

Ballari institute of Technology & Management, Ballari – 583 104, Karnataka

Abstract:-Schiff bases derived from substituted coumarins with substituted Diamines were synthesized by cyclo-condensation. Proton-ligand ionization constants and metal-ligand stability constants at constant ionic strength in aqueous-alcohol medium (50/50% V/V) were evaluated using Irving-Rossotti method. The ligands exhibit pKa values around 11.5 due to the phenolic – OH group. The metal ligand stability constants with Cu (II), Co (II), Ni (II), Zn (II), Cd (II) and Hg (II) were also determined. The effects of substitutions on the stability constants were studied.

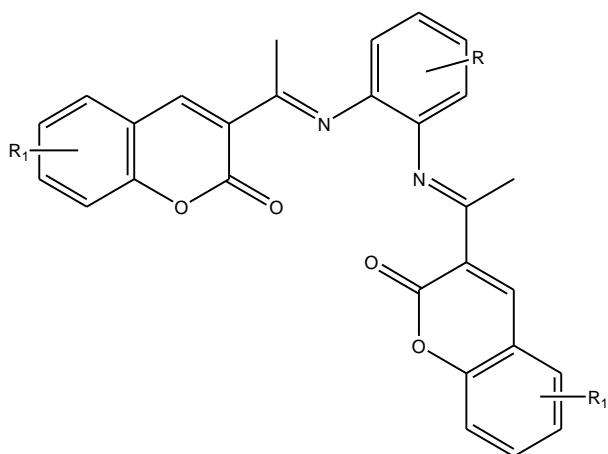
Key words: Metal-coumarin & substituted coumarin Schiff base complexes, stability constants.

I. INTRODUCTION

Condensed heterocycles namely benzodiazepines, benzimidazole, benzothiazoles and β - amino carbonyl compounds are biologically important molecules and are extensively used clinically. Benzodiazepines are pharmacologically important compounds because of their anti-convulsant, sedative, hypnotic, anti-anxiety, anti-microbial and other properties. The synthesis of coumarin derivatives has attracted considerable attention in organic and medicinal chemistry. Coumarin derivatives are used in food additives, fragrances, pharmaceuticals and agrochemicals. Schiff bases are prepared by cyclo - condensation of coumarins and substituted coumarins with Diamines. Cyclo- condensation reaction was carried out in ethanol medium for 4 to 5 hours.

II. EXPERIMENTAL

Chemicals used for synthesis are B.D.H. or Merck. The ligands OPD, OPD1, OPD2, EC, EC1, and EC2 are synthesized by refluxing equimolar ethanolic solutions of coumarins, substituted coumarins with Diamines for 4-5 hrs. The solids that separated during reflux were filtered, washed with ethanol and recrystallised with ethanol.



General structure of the compounds

Table 1

S.No.	R	R1
1	H	H
2	H	CH ₃
3	H	Cl
4	CH ₃	H
5	CH ₃	CH ₃
6	CH ₃	Cl
7	Cl	H
8	Cl	CH ₃
9	Cl	Cl

Carbon dioxide free double distilled water used for the preparation of solutions. Anal R grade sodium chloride, metal (II) chlorides, Perchloric acid, Sodium perchlorate were used for the preparation of standard solutions.

An Elico LI 127 pH meter with combined glass electrode was used for pH measurements. The changes in the pH can be measured with an accuracy of 0.01 pH units. The titration was carried out in 50:50 percent ethanols: water mixture. Sodium perchlorate was added to maintain constant ionic strength. Proton-ligand and metal-ligand stability constants are determined by Irving-Rosotti method.

Following titrations were performed as per Irving-Rosotti method.

1. Perchloric acid (5ml of 0.01 M) + Sodium perchlorate (5ml of 1.0 M) were pipetted in a beaker and titrated with standard sodium hydroxide (0.1 N)
2. Perchloric acid (5ml of 0.01 M) + Sodium perchlorate (5ml of 1.0 M) + Ligand (5ml of 0.01M) were pipetted in a beaker and titrated with standard sodium hydroxide (0.1 N)
3. Perchloric acid (5ml of 0.01 M) + Sodium perchlorate (5ml of 1.0 M) + Ligand (5ml of 0.01M), metal(II)chloride (5ml of 0.01 M) were pipetted in a beaker and titrated with standard sodium hydroxide(0.1 N).

III. RESULTS AND DISCUSSION

Figure 1,2,3,4. Indicates the plots of pH against volume of NaOH added for the Ligands and Various metal ions. The titration curves show that a drift towards right as more and more alkali is added indicating that a displacement of proton is preference to metal ions. This indicates the formation of metal complexes with this ligand.

Fig. 1 Titration curve of pH v/s vol of NaOH for compound 1

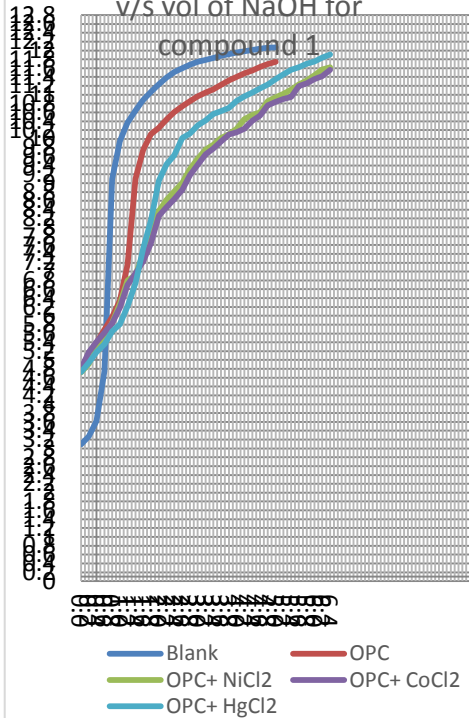


Fig. 2 Titration curve of pH v/s vol of NaOH for compound 3

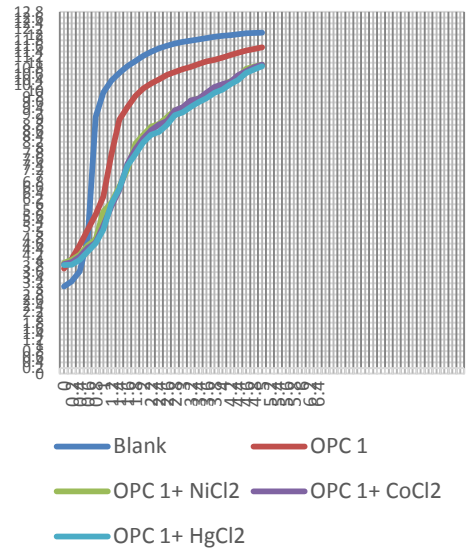


Fig.3 Titration curve of pH v/s vol of NaOH for compound 2

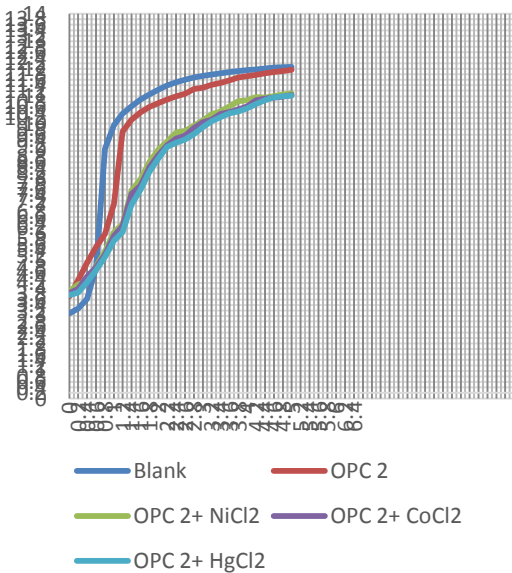
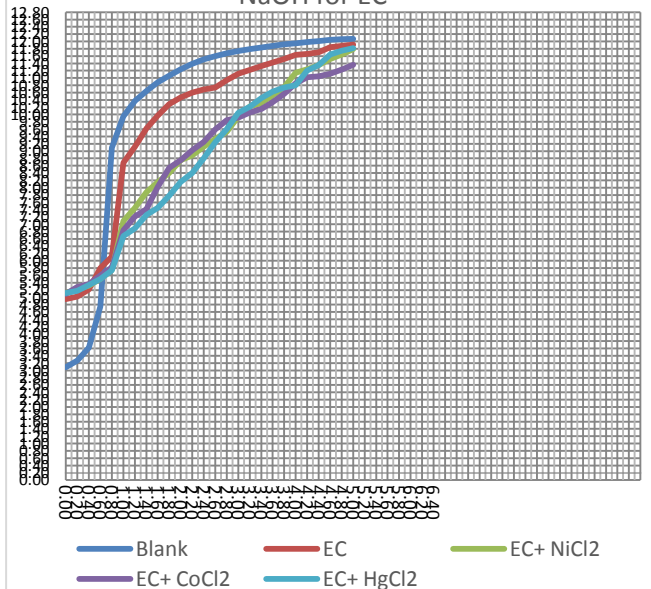
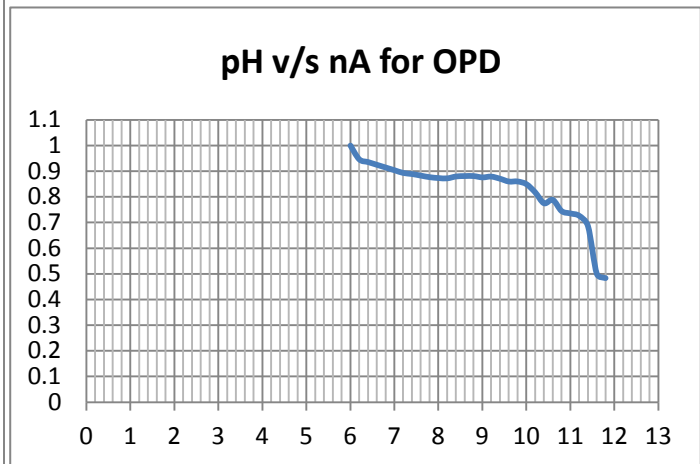
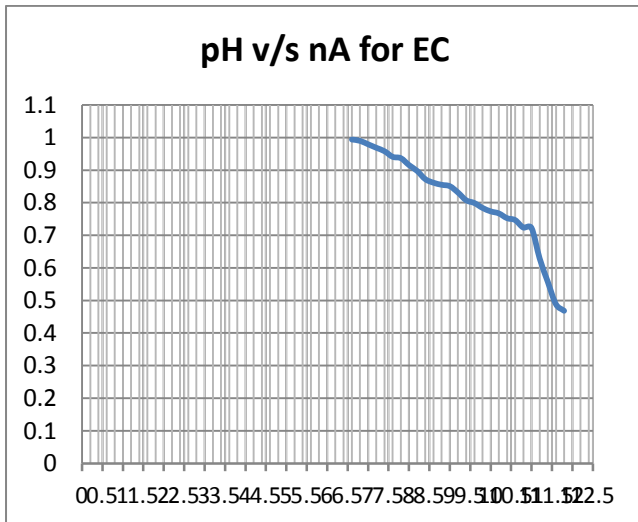


Fig 4: Titration curve of pH v/s Vol. of NaOH for EC

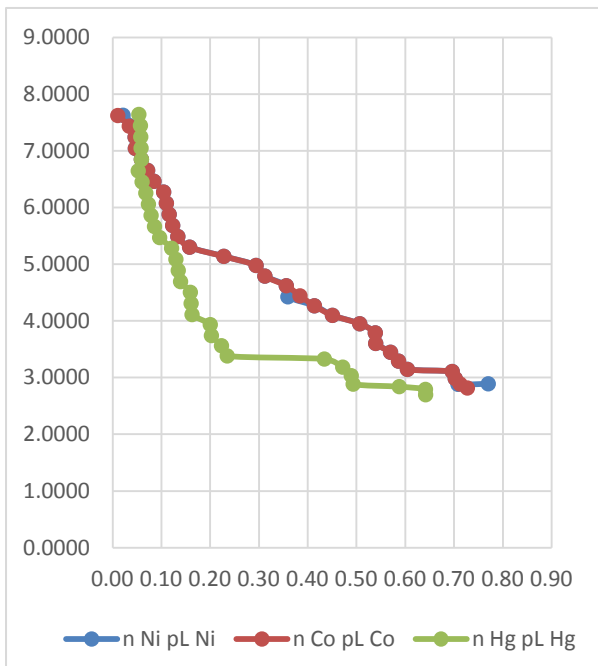


pKa values are evaluated by plotting nA against pH as shown below in graphs

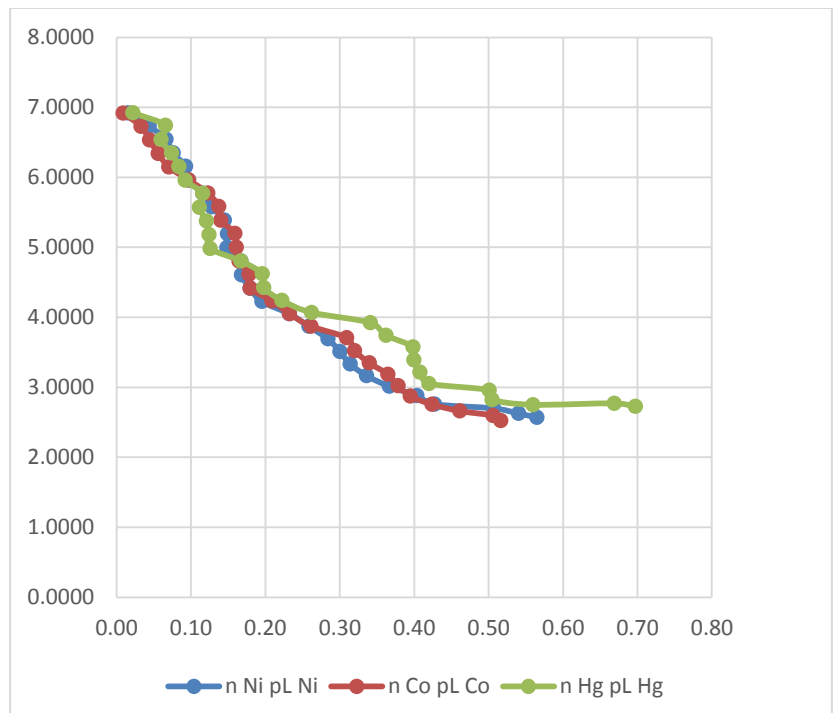


Metal ligand stability constants were evaluated by plotting \bar{n} (metal ligand formation number) against pL (free ligand exponent) as shown in the following figures.

\bar{n} v/s pL graph for OPD



\bar{n} v/s pL graph for EC



IONISATION AND STABILITY CONSTANTS OF COUMARINE SCHIFF BASES WITH NICKEL (II), COBALT (II) AND MERCURY (II) IN 50% V/V ETHANOL-WATER.

Sl. No.	Compound	pKa	Log K		
			NICKEL(II)	COBALT(II)	MERCURY(II)
1	OPD	11.55	4.05	3.90	2.90
2	OPD1	11.6	2.90	2.70	2.70
3	OPD2	11.6	3.70	3.90	3.00
4	EC	11.5	2.90	2.70	2.90
5	EC1	11.6	2.60	2.70	3.20
6	EC2	11.6	2.90	2.80	3.20

ACKNOWLEDGEMENT

The authors are thankful to BITM, Ballari,, CPDO, Bengaluru for providing lab facilities, The authors are thankful to Poornaprajna Institute of Scientific Research, Bengalru for getting the spectral data.

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