POTENTIOMETRIC STUDY OF Fe(II), Co(II), Ni(II) AND Cu(II) WITH β-DIKETONE COMPLEXES

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ABSTRACT:

Potentiometric study of β–diketone complexes of iron, cobalt, nickel and copper was carried out in aqueous media by titrating with standard NaOH solution. The complexes formation between Fe(II), Co(II), Ni(II) and Cu(II) metal ions and 1-(5-bromothiophen-2-yl)-3-(2,4-dihydroxyphenyl)propane-1,3-dione (L) have been studied at 0.1 M ionic Strength at room temperature. It is observed that iron, cobalt, nickel and copper metal ions formed 1:1 and 1:2 complexes with ligands (L). The obtained data were used to compare the values of pH and metal-ligand stability constants.

KEY WORDS: Potentiometric study, β–diketone, metal ions, pH and Stability Constants.

1. INTRODUCTION:

Various binary complexes of transition and inner transition metals had studied potentiometrically [1]. The complexes are also useful for comparative studies of metal ions, as starting materials in the preparation of organometallic compounds [4] and as catalyst for organic synthesis. Metal complexes of β-diketone have been extensively studied, because β-diketone has good synthetic flexibility, selectivity and sensitivity towards the central metal atom.

The β-diketone 1-(5-bromothiophen-2-yl)-3-(2,4-dihydroxyphenyl)propane-1,3-dione (L1) was prepared by using 2,4-dihydroxyacetophenone and 5-bromothiophene-2-carboxylic acid at RT & when this β-diketone reacts with metal ions like Fe(II), Co(II), Ni(II) and Cu(II) to form the (O,O') chelates of [M(β-dik)n] which soluble in organic solvents and used as analytical reagents [3-2]. The literature survey may gives data on the transition metal complexes but complexes of β-diketone have been less investigated as ligands.[5] so to synthesize some β-diketone derivatives as a ligand and their Fe(II), Co(II), Ni(II) and Cu(II) complexes.

In present paper reported that potentiometric study [6] of β-diketone (L1) derivatives of complexes of iron, cobalt, nickel and copper metal ions, as extensive literature search shows that no such work has been previously reported. As investigated these metal complexes comparing their stability constant [8-7]. β-diketones have gained a lot of interest due to their importance as good ligands [11-10]. β-diketone and its metal complexes have been widely used in diverse areas because of their unique structural features, chemical functionalities, and toughness for light and heat as electroluminescence materials [9].

2. MATERIALS AND METHOD:
2.1. EXPERIMENTAL

Micro analysis of ligand was performed at the Central Drug Research Institute. The H^1 NMR spectrum of ligand was recorded on EM-360 spectro-photometer at RSIC, Chandigarh (India). IR spectra of ligands were recorded in KBr pellet on FTIR-4100.

An equip-tronics digital pH meter model EQ-601 in conjunction with an Elico combined electrode consisting of reference and glass electrodes in a single entity of type CL - 51 was used for the pH measurements.

2.2. REAGENTS AND CHEMICALS
The glass distilled water was collected in a Stoppard bottle and always used fresh. Its pH was about 6.65 to 6.85. Metal nitrates obtained from Sigma Aldrich Chem. Co., U.S.A. All other chemicals like Potassium hydroxide, Sodium hydroxide Nitric acid, and Potassium nitrate were of A.R. grade, obtained either from E. Merck. The solutions of above reagents were prepared in CO_2 free glass distilled water by taking precautions to avoid errors in glass electrodes in a single entity of the type CL-51 was used for the emf measurements. All weighing were carried out on electronic balance model AB54.

2.3. SYNTHESIS AND CHARACTERIZATION OF Β−DIKETONE:
Synthesis of β-diketones: (1-(5-bromothiophen-2-yl)-3-(2,4-dihydroxyphenyl)propane-1,3-dione):[L]

To the mixture of 2,4-dihydroxyacetophenone (1.52 g, 0.01mol) and 5-bromothiophene-2-carboxylic acid (2.07g, 0.01mol), a dry pyridine (5mL) and $POCl_3$ (1ml) were added drop wise with constant stirring at RT. Then reaction mixture was stirred for about 5-6 hrs. And in this solution powdered KOH (1.12 g, 0.02mol) was added and the reaction mixture was stirred for about 1-2 hrs. After completion of the reaction (monitored by TLC), the reaction mixture was poured on ice cold water and acidified with conc. HCl. The yellowish solid obtained was filter and crystallized by ethanol for pure product. Yield: 83%; Mp: 272°C.

2.4. CHARACTERIZATION OF LIGANDS:

The structural features were elucidated with the help of elemental analysis. Synthesized ligand was stable to air and moisture ligand soluble in ethanol, methanol, but insoluble in water and ether. The obtained ligand (1-(5-bromothiophen-2-yl)-3-(2,4-dihydroxyphenyl)propane-1,3-dione) was scanned for IR, ^{1}H NMR, ^{13}C-NMR and UV/Visible spectroscopy. Following are the scanning results given below.

FT-IR (KBr) cm^{-1}: 3349(Ar-O-H), 1644(C=O), 1232 (C-O), 3083(=C-H), 3146(Ar-C-H), 1584(C=C), 687(C-S)

^{1}H-NMR (300MHz, CDCl$_3$-d6); δ =7.47 (d, 1H, Ar-H), 6.48 (d, 1H, Ar-H), 6.39 (s, 1H, Ar-H), 7.6(s,1H, H—═), 7.39 (d, 1H, Thioph-H), 7.26(d, 1H, Thioph-H), 5.0(s, 2H, -OH), 15.0(s, 1H, Enolic-OH).

^{13}C-NMR (300MHZ,CDCl$_3$); δ=189.7(s,C-1,C=O), 99.0(d,C-2,-CH=), 195.5(s,C-3), 115.3(s,C-1'), 163.2(s,C-2'), 104.1(d,C-3'), 165.7(s,C-4'), 109.0(d,C-5'), 132.7(d,C-6'), 138.1(s,C-2''), 128.6(d,C-3''), 131.5(s,C-4''), 116.8(d,C-5'')

Elemental analysis : C, 46.03; H, 3.71; Br, 24.50; O, 15.94; S, 9.83

UV/Vis (DMSO)nm: 360,410

2.5. Potentiometric titration of β-diketone [L] with metal ion M(II) [M= Fe, Co, Ni or Cu]:
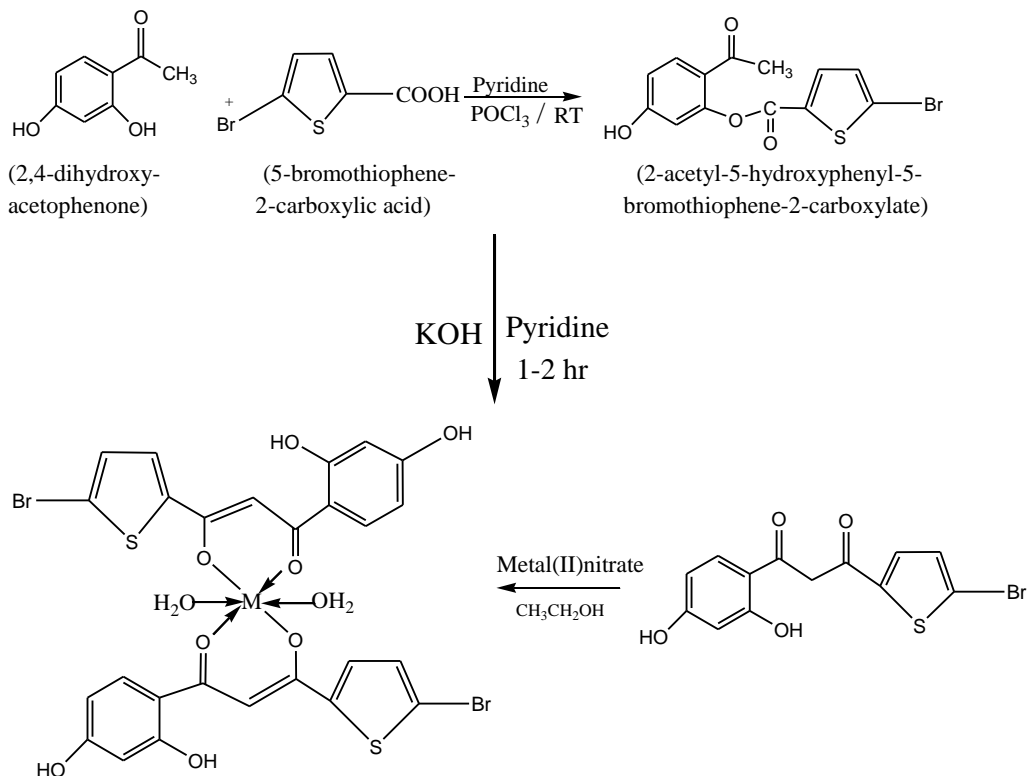
Potentiometric titrations were carried out in aqueous solution at RT and ionic strength 0.2N HClO$_4$ against 0.2N NaOH, using digital pH-meter in conjunction with a combined electrode consisting of glass and reference electrodes in a single entity with an accuracy of ± 0.01 pH at RT. The mixture of (0.01 M) of compound L and (0.01M) of M(II) nitrate was added in 20 ml anhydrous ethanol(total volume 50 ml). This solutions contains metal ions and the ligands in the ratio 1:2 (M^{2+}: 2L) have been titrated against carbonate-free 0.2N NaOH under constant stirring.

According to experimental procedure observed Potentiometric titrations of solutions -

  1. Free HClO$_4$ (A)

  2. Free HClO$_4$ + Ligand (A+L)

  3. Free HClO$_4$ + Ligand +Metal ion (A+L+ M)

Data obtained from each titration was plotted as Emf Vs volume of NaOH added and corresponding volume at successive pH for each set is determined and calculated.

These solutions were titrated against standard solution of sodium hydroxide. The concentrations of β-diketone L and M was 0.01M and 0.01M. The ionic strength of the solutions was maintained constant by adding of appropriate amount of 1M NaClO$_4$ solution. The titrations were carried out at room temperature. The readings on pH-meter recorded from each titration is plotted as pH Vs volume of NaOH added and in order to evaluate stability constants.

(2,4-dihydroxy-acetophenone) (5-bromothiophene-2-carboxylic acid) (2-acetyl-5-hydroxyphenyl-5-bromothiophene-2-carboxylate)

KOH | Pyridine 1-2 hr

Metal(II)nitrate
CH₃CH₂OH

L

Metal complexes of β-diketone [L]
M: Fe, Co, Ni or Cu

(1-(5-bromothiophen-2-yl)-3-(2,4-dihydroxyphenyl)propane-1,3-dione)

3. RESULT AND DISSCUTION:

Most of the β-diketones and their metal complexes were found to be either insoluble or sparingly soluble in water; a reaction medium consisting of anhydrous ethanol was used. Ethanol has the advantage of a cheapest very good organic solvent than other solvents at 25 ºC, thus preventing decomposition of the metal chelates and have only a small hygroscopic character. One of the most important factors relating to the coordination compound is their stability constants or formation constants. A reaction between a metal ion and a ligand may be represented as,

$$mM \; + \; nL \; \rightleftharpoons \; M_m L_n$$

The stability (or formation) constant Ks is given by

$$K_S = \frac{[M_m L_n]}{[M]^m [L]^n} \ldots\ldots(1)$$

the dissociation (or instability) constant, Ki of the chelate is given by

$$K_i = \frac{[M]^m [L]^n}{[M_m L_n]} \quad \ldots\ldots\ldots\ldots(2)$$

if 'a' represents the initial concentration of the metal, 'b' that of the ligand and 'X' the concentration of the chelate formed at equilibrium, then the stability constant Ks is given by,

$$K_S = \frac{X}{[a-mX]^m[b-nX]^n} \quad \ldots\ldots\ldots\ldots (3)$$

So, the determination of 'X' gives a calculation of the value of Ks, 'a' and 'b' being known. The stability constant is measure the stability of the complex in solution with reference to the dissociation into metal ions and free ligands. The method was introduced by G. Biederman and L. G. Sillen [12] and the fundamental idea of their method is to control activity coefficient by keeping the ionic strength constant, because in dilute solution activity coefficient of a given strong electrolyte is the same in all solutions of identical ionic strength. F. C. Rossotti and H. R. Rassotti [13] have modified the methods for determining stability constant. The values of the stoichiometric constants are reliable under a given set of experimental conditions and are useful for practical purposes.
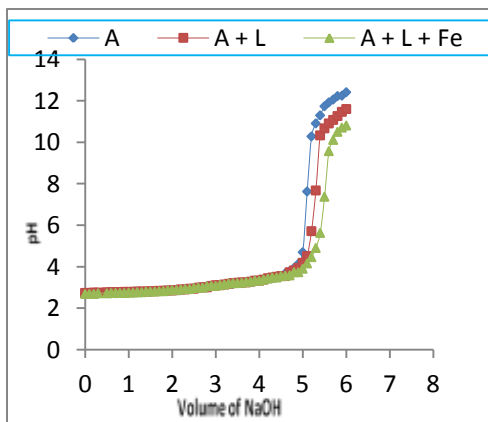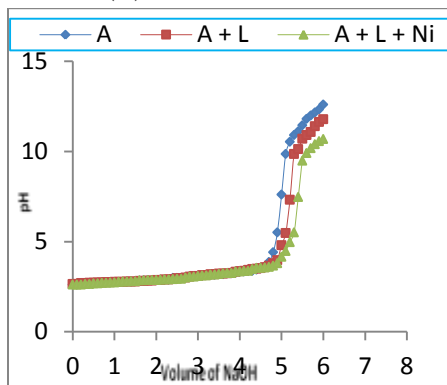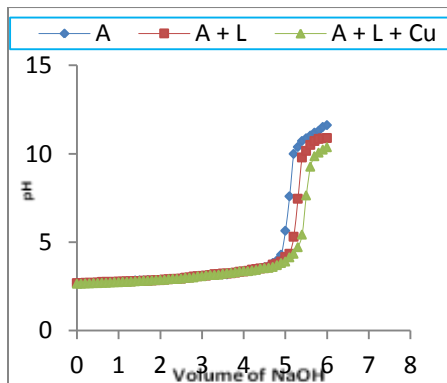
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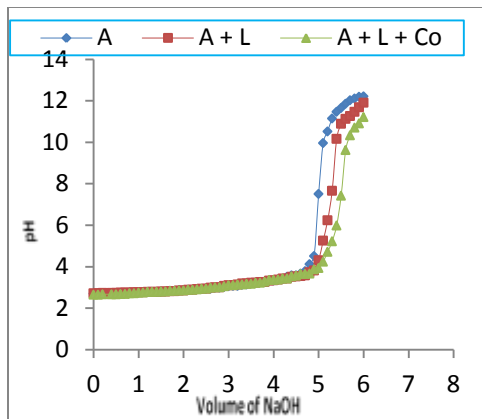
B

1)Pot. titration curve of L with Fe (II) metal ion **2)**Pot. titration curve of L with Co (II) metal ion

C

D

3)Pot. titration curve of L with Ni (II) metal ion **4)** Pot. titration curve of L with Cu (II) metal ion

Fig.1-4 is Potentiometric titration curves of β-diketone [L] with Fe, Co, Ni & Cu metal ions.

Table 1: Determination of stability constants

Complex compounds	Stability constants
1) Fe(II) complex Compound	2.978
2) Co(II) complex Compound	2.998
3) Ni (II) complex Compound	3.019
4) Cu(II) complex Compound	3.087

Metal-Ligand stability constant:-

It is observed that (Table 1) no large difference between in stability constant values of formation of complex between metal ion M(II) and ligand L. Then there is less difference between stability constant values indicates Copper (II) is comparatively more stable than other three Iron (II), Cobalt(II), Nickel (II) metal ions with Ligand (L) complexes.

4. CONCLUSION:

On the basis of above study the stability of metal complexes has been found in the following order Cu(II)>Ni(II)>Co(II)>Fe(II). The observed order of stability of complexes may be correlated with the increasing polarisability of metal ion due to their decrease in size and increase in ionic potential.

5. ACKNOWLEDGEMENT:

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