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Research Article

Preparation of Beta-Diketone Complex under Potentiometric Study with Fe (II) and Co (II) Transition Metal Ions

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Abstract— Potentiometric study of β–diketone complexes of iron, cobalt was carried out in aqueous media by titrating with standard NaOH solution. The complexes formation between Fe(II) and Co(II) metal ions and 1-(5-methoxythiophen-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.

Keywords— Potentiometric Study, B–Diketone, Metal ions, pH and Stability Constant

1. Introduction

Potentiometric study of various binary complexes of transition metal ions [1]. The transition metal complexes usedfor preparation of organ metallic compounds [4] and as a catalyst in organic synthesis reaction. β-diketone containingMetal complexes can be studied, because β-diketone has good synthetic flexibility, sensitivity towards the central metal atom of metal complexes and selectivity. Theβ-diketone1-(2,4-dihydroxyphenyl)-3-(5-methoxythiophen-2-yl)-propane 1,3 dione(L) was prepared by using 2,4-dihydroxyacetophenoneand 5-methoxythiophene-2-carb-oxalic acid at Room Temperature& when this β-diketone reacts with metal ions like Fe(II) and Co(II) to form Metal complexes[3] .In the transition metal complexes use of β-diketonevery less.[5] so to synthesize some β-diketone derivativesas a ligand and prepare their Fe(II) and Co(II) complexes.

In this paper metal complexes of β-diketones (L) derivatives of Iron and Cobalt metal ions[6] stability constant compare with other metal complexes [7-8]. β-diketone and their metal complexes used in various areas because of their unique structuralfeatures,chemical functionalities, and toughness to light and heat as electroluminescence materials [9].β-diketones importance as good ligands [10-11].

2. Materials And Method:

2.1 Experimental

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 [12].All weighing were carried out on electronic balance model AB54.

Preparation of Standard Solutions of Metal Ions:-
(a) Preparation of Standard Solution ofFe(II) :
Ion solution are prepared as a stock solution by taking 2.780 g of $FeSO_4.7H_20$ in the pure water and it is acidify by HCl in 1 L. and this solution can be standardized volumetrically using a solution 0.1 M. KMnO4.
Procedure:
Pipette 25 ml of Fe (II) ion solution and few drops of H_3PO_4 and this will be done titration with a KMnO4 when it reach to a pink colour and the strength of Fe(II) ion solution can be calculated
1.0 M, $KMnO_4$ = 5.57 mg. Fe(II)

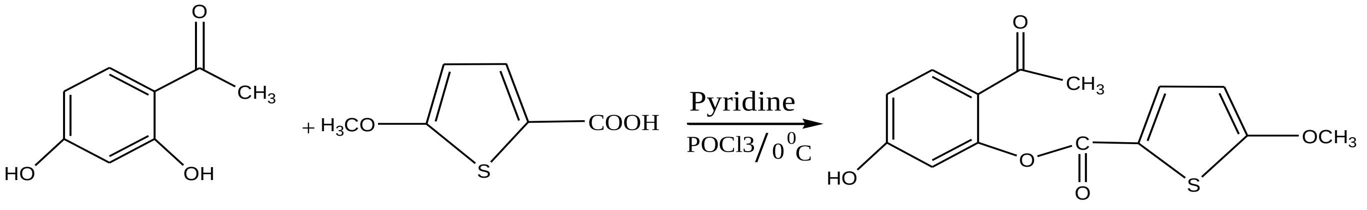
(b) Preparation of Standard Solution (Co(II) :
Cobalt (II) ion (0.01 Molar) containing 3.207 gm of cobalt sulphate $7H_20$ in pure water and add HCl and standardized 0.1 molar EDTA 1-B solution.
Procedure:
Pipette out 25 ml Co solution and add 250 ml pure water and Xylanol orange as a indicator 2-3 drops and add dil. H_2SO_4 solution just colour red to yellow and warm the given solution

in 38 degreeCelsius and titration takes place EDTA 1-B solution the colour change red to orange.
0.1 M, EDTA 1-B = 6.41 mg Co(II)

2.2. Synthesis And Characterization Of B–Diketone:

[A] Synthesis of 2-acetyl-5-hydroxyphenyl 5-methoxythiophene-2-carboxylate :

To the mixture of 2,4-dihydroxyacetophenone (1.52 g, 0.01mol) and 5-methoxythiophene-2-carboxylic acid (1.58g, 0.01mol), a dry pyridine (5mL) and $POCl_3$ (1ml) were added drop wise with constant stirring at 0 ^oC. Then reaction mixture was stirred for about 4-5hrs. After completion of the reaction (monitored by TLC), the reaction mixture was poured into 100ml 1M HCl containing 50g of crushed ice and solid obtained was filtered and washed with 10ml ice-cold methanol and then with 10ml of water. It was recrystallized from ethanol, filtered, and dried.Yield:82%; mp: 177°C

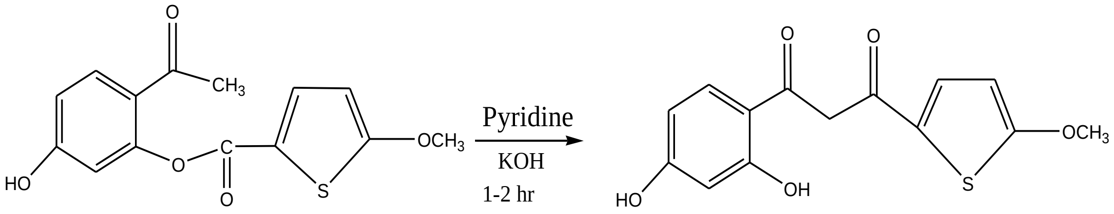


(2,4-dihydroxy-acetophenone) (5-methoxythiophene-2-carboxylic acid) (2-acetyl-5-hydroxyphenyl-5-methoxythiophene-2-carboxylate)

Synthesis of 2-acetyl-5-hydroxyphenyl 5-methoxythiophene-2-carboxylate

[B]Synthesis of 1-(5-methoxythiophen-2-yl)-3-(2,4-dihydroxyphenyl)propane-1,3dione:(L3)

2-acetyl-5-hydroxyphenyl 5-methoxythiophene-2-carboxylate (2.92 g, 0.01mol) was dissolved in dry pyridine (10 ml). To this 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 yellow solid obtained was filtered off and crystallized from absolute ethanol to obtain pureproduct.Yield:83%;Mp:276°C.



(2-acetyl-5-hydroxyphenyl-5-methoxythiophene-2-carboxylate) (1-(5-methoxythiophen-2-yl)-3-(2,4-dihydroxyphenyl)propane-1,3-dione)

Synthesis of β-diketone ligand [L3]

2.3 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[13]. The obtained ligand (1-(5-methoxythiophen-2-yl)-3-(2,4-dihydroxyphenyl)propane-1,3dione) was scanned for IR, 1H NMR, 13 C-NMR andUV/Visible spectroscopy. Following arethe scanning results given below.

FT-IR(KBr)cm^{-1}: 3358(Ar-O-H),1631 (C=O),1233 (C-O), 3085(=C-H), 3147(Ar-C-H), 1589(C=C), 681(C-S)

^{1}H-NMR (300MHz, CDCI$_3$-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–═), 7.23 (d, 1H, Thioph-H), 6.37(d, 1H, Thioph-H), 5.0(s, 2H, -OH), 15.0(s, 1H, Enolic-OH), 3.73(s,3H,-OCH$_3$) .

^{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'), 122.3(s,C-2''), 125.2(d,C-3''), 105.1(s,C-4''), 172.0(d,C-5''), 56.6(q,C-1''')

UV/Vis (DMSO)nm: 360,410

Elemental analysis : C, 54.98; H, 4.07; O, 28.00; S, 12.95

2.4. Potentiometric titration of β-diketone [L] with metal ion M(II)

[M= Fe or Co]:

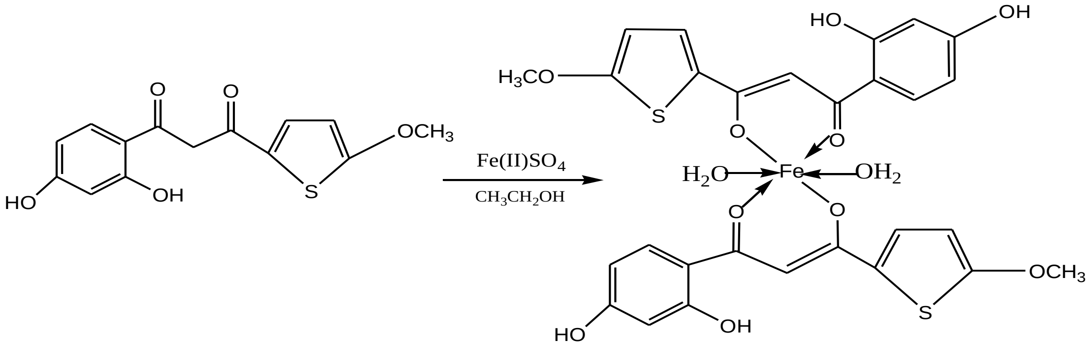
1.1 The titration of metal-ion Fe (II) with L3 B-diketone:

The solutions of potassium nitrate, oxalic acid, sodium hydroxide and metal-ion are always prepared from distilled water and the pH and conductivity of that water is 6.7 and 1.61 x 10^{-6} mhos and this sodium hydroxide solution is standardized using oxalic acid and following are the chemicals is used for titration. Borosil quality glass used for further experiment and the digital potentiometer is connected with aelico combined electrode which consist a glass electrode and reference electrode in a single unit and this is used for measurement of Emf of solution careful handle a electrodes used in the experiment.

The ferrous sulphate and the ligand mixture i.e. 2.78 gm of metal-ion solution and 5.88 gm ligand compound is pour in unhydrous ethanol of 20 ml and this reaction mixture of metal-ion and ligand of ratio 1:2 is titrated with a carbon free sodium hydroxide under a constant stirring and the experimental producer of binary metal complexes. The further titrations are carried out as below.

1. Free (0.02M) HNO_3 [A]
2. Free (0.02M) HNO_3 + (0.02M) Ligand [A+L3]
3. Free (0.02M) HNO_3 + (0.02M) Ligand + (0.01M) Metal ion [A+L3+Fe (II)]

The above solutions are titrated with a sodium hydroxide solution and the ligands and metal-ion concentration is 0.02 molar and 0.01 molar respectively. Ionic strength of above solutions are keep constant 0.02 molar which is added and maintain using potassium nitrate solution and this will be carried out in room temperature. The recorded readings on potentiometer which can be of each titration plotted volume of sodium hydroxide against Emf and this will be determine and calculate the dissociate constant and stability constant.



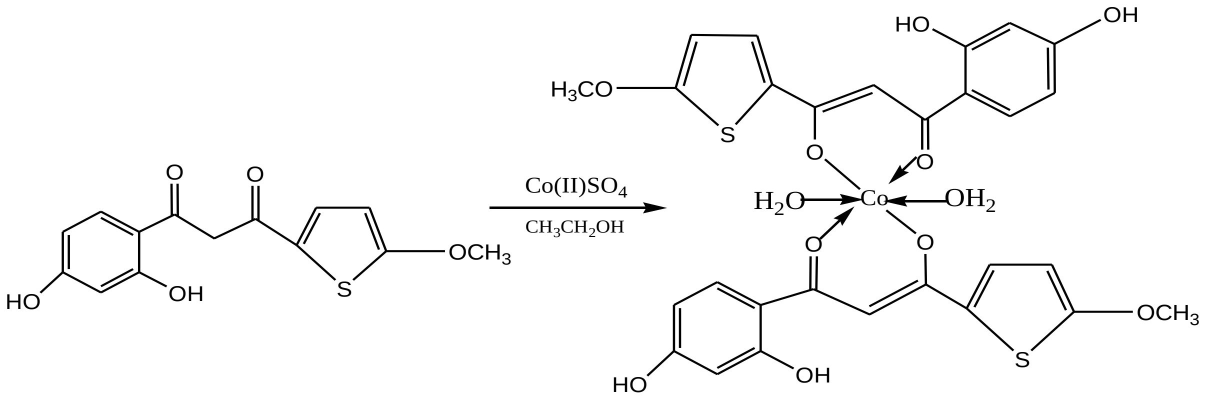
A B

A = 1-(5-methoxythiophen-2-yl)-3-(2,4- dihydroxyphenyl)propane-1,3-dione:(L3)
B = Fe (II) metal complex of β-diketone
Synthesis of Fe (II) metal complexes

1.2 The titration of metal-ion Co (II) with L3 B-diketone:

The mixture of ligand L3 is 5.68 gm and the metal-ion copper sulphate of 2.18 gm is added in water free ethanol of 20 ml and this solutions of metal-ions and ligands of ratio 1:2 and this titrates against a strong base like a 0.01 molar sodium hydroxide solution with a constant stirring condition and the followings are the titrations experimental procedure for binary metal-complexes.

1. Free (0.02M) HNO_3 [A]
2. Free (0.02M) HNO_3 + (0.02M) Ligand [A+L3]
3. Free (0.02M) HNO_3 + (0.02M) Ligand + (0.01M) Metal ion [A+L3+ Co (II)]



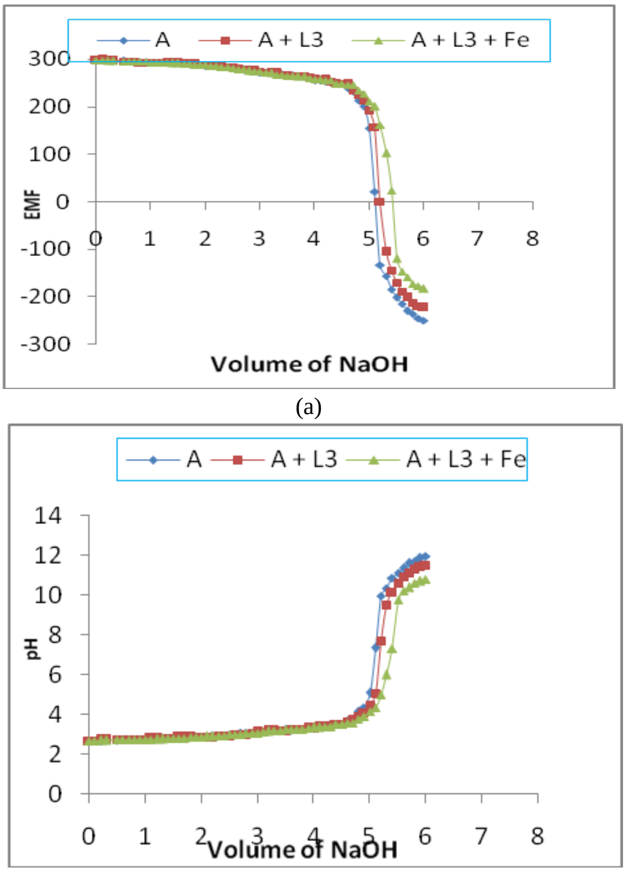
A B

A = 1-(5-methoxythiophen-2-yl)-3-(2,4- dihydroxyphenyl)propane-1,3-dione:(L3)
B = Co (II) metal complex of β-diketone
Synthesis of Co(II) metal complexes

3. Results and Discussion

Table 1: Determination of pH of Fe (II) ligand [L3] complex

Vol. NaOH (cm^{3})	Emf A	Emf A+ L3	Emf A+ L3+ Fe	pH A	pH A+ L3	pH A+ L3+ Fe
0	298	299	297	2.67	2.65	2.69
0.5	296	295	295	2.70	2.72	2.72
1	293	293	293	2.75	2.75	2.75
1.5	291	291	291	2.79	2.79	2.79
2	286	288	287	2.87	2.84	2.85
2.5	280	283	280	2.97	2.92	2.97
3	272	273	274	3.11	3.09	3.07
3.5	266	267	265	3.2	3.19	3.23
4	255	259	258	3.40	3.33	3.35
4.5	248	248	248	3.51	3.51	3.51
5	155	192	210	5.09	4.46	4.16
5.5	-202	-171	-120	11.13	10.60	9.74
6	-250	-223	-183	11.94	11.48	10.81



(a)

(b)

Graph 1.1 Potentiometric titration curve of (L3) with transition metal Fe (II) NaOHVs pH b) NaOHVsEMF

A) Potentiometric titration of 1(5-methoxythiophen-2-yl)3-(2,4-dihydroxyphen yl)-propane 1,3 dione [L3] with metal ion [Fe(II)]:

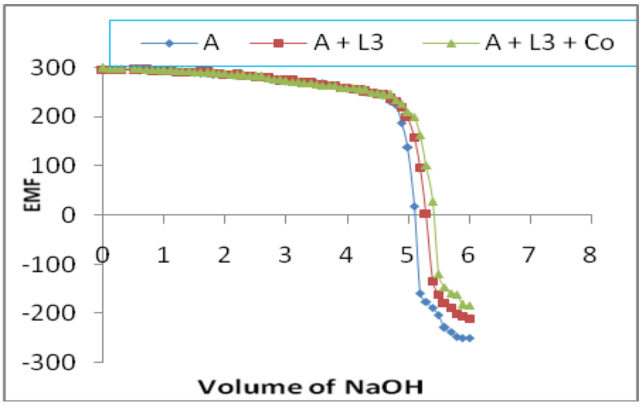
From above table 1.1 we can conclude that when the volume of 0.01M NaOH added in 0.02 M Nitric acid(A), the emf value decreases regularly with increase in value of pH reading at 5.1 ml NaOH solution added and it suddenly decreases and goes to minus value with continuous increase in pH value. In second case volume of 0.01M NaOH added in 0.02 M Nitric acid(A) the emf value decreases again regularly with increase in pH value at 5.2 ml NaOH solution added and it suddenly decreases and goes to again minus value with continuous increase in pH value. In the third case volume of 0.01M NaOH added in 0.02 M Nitric acid (A) + Metal ion Fe(II) , the emf value decreases again slowly with increase in pH value at 5.4 ml NaOH solution added and it again suddenly decreases the emf readings and goes to minus value with continuous increase in pH value.

According to the results obtained from figure 1.1 i.e. graphical representation of emf vs. volume of NaOH added, have two protonation constants. The one of the value Potentiometric titration curves of Fe(II)system, protonsat pH 7.32 And from figure 1.1 we also conclude that thetitration curves of the Fe(II) complex is lower from that of the free β-diketone ligand (L3) curve, indicating formation of Fe (II) complex with β-diketone ligand(L3), by displacement of protons.

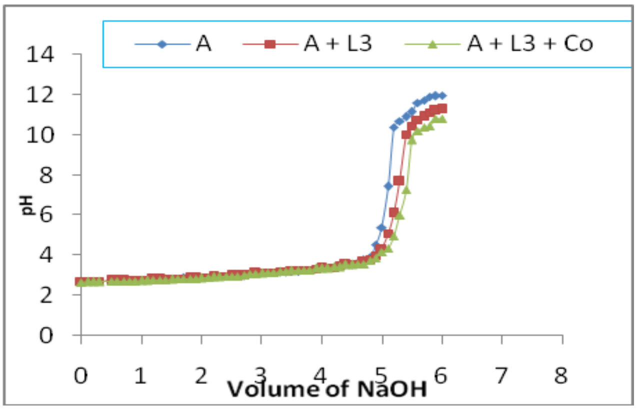
According to the graphical representation of fig. 1.1 we evaluated concentration of H^{+} ions in the solutionfrom pH value and stability constant value of Fe(II)complex separately, it is seen that the values for proton ion 0.864 and stability constant value is 2.957.

Table 2: Determination of pH of Co (II) ligand [L3] Complex

Vol. NaOH (cm^{3})	Emf A	Emf A+ L3	Emf A+ L3 +Co	pH A	pH A+ L3	pH A+ L3+ Co
0	296	295	299	2.70	2.72	2.65
0.5	295	294	297	2.72	2.74	2.69
1	293	293	294	2.75	2.75	2.74
1.5	289	290	291	2.82	2.80	2.79
2	286	286	287	2.87	2.87	2.85
2.5	280	280	282	2.97	2.97	2.94
3	272	272	273	3.11	3.11	3.09
3.5	268	265	266	3.18	3.23	3.22
4	257	258	258	3.36	3.35	3.35
4.5	248	247	248	3.51	3.53	3.51
5	138	199	210	5.38	4.34	4.16
5.5	-203	-161	-120	11.15	10.43	9.74
6	-250	-210	-183	11.94	11.26	10.81



(a)



(b)

Graph1.2 Potentiometric titration curve of (L3) with transition metal Co (II)
NaOHVs pH b) NaOHVsEMF

B) Potentiometric titration of 1(5-methoxythiophen-2-yl)3(2,4-dihydroxypheny- l)-propane 1,3 dione [L3} with metal ion [Co(II)] :

According to the results obtained from figure 1.2 i.e. graphical representation of emf vs. volume of NaOH added, have two protonation constants. The one of the value potentiometric titration curves of the Co (II)system, protonsat pH 7.25 And from figure 1.2 we also conclude that the, titration curves of the Co(II) complex is lower with β-diketone ligand(L3), by displacement of protons.

According to the graphical representation of fig. 1.2 we evaluated concentration of H$^+$ ions in the solutionfrom pH value and stability constant value of Co(II)complex separately, it is seen that the values for H$^+$ 0.860 and stability constant value is 2.929

Complex Compounds	Stability Constants
1)Fe(II)complex Compound	2.957
2)Co(II)complex Compound	2.929

4. Conclusion

In the investigation it is observed that the metal complexes of Co (II)-L3 and Fe (II)-L3 of β-diketone with transition metals obtained in pH rang 7.25 to 7.32. In that Co (II)-L3 complex formed in lower pH i.e. 7.25. And Fe (II)-L3 complex formed in higher pH i.e. 7.32 as compare to other metal complexes. The stability constant of metal-ion complexes are Fe (II)-L3=2.957 and Co (II)-L3=2.929,

The order of stability is Fe>Co. 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.

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