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**CHELATING TENDENCIES OF O-HYDROXY PHENYL
AZO-ACETYL ACETONE WITH TRANSITION METAL
IONS**

Annotation: The binary complexes of Mn (II), Fe (III), Ni (II) with O-Hydroxy phenyl azo-acetyl acetone (O-HPAA) in 1:1 molar ratio have been prepared and investigated using spectrophotometric and pH-titration methods in 50% (v/v) ethanol medium, ionic strength 0.1 M NaClO₄ and at 25 °C. The ionization constants of the ligand and relative stability of each complex were determined potentiometrically. A comparison of stability constants of the transition and non-transition metal ion complexes has been done. The possibilities of forming complexes were inferred from the electronic absorption measurements at different pH-values. The absorption spectra provide that the reagent (O-HPAA) is more sensitive and selective for manganese than other metals.

Keywords: non-transition, pH-titration, pH-values.

Аннотация: Бинарные комплексы Mn (II), Fe (III), Ni (II) с О-гидроксифенилазоацетилацетоном (О-НРАА) в молярном соотношении 1:1 были приготовлены и исследованы с использованием спектрофотометрического и pH-титрования. Проведено сравнение констант устойчивости комплексов ионов переходных и непереходных металлов. Возможности формирования комплексов были выведены из электронных

измерений поглощения при различных значениях pH. Спектры поглощения показывают, что реагент (О-НРАА) более чувствителен и селективен в отношении марганца, чем другие металлы.

Ключевые слова: Бинарные комплексы, непереходный, pH-титрование, значения pH.

1. Introduction:

Azo dyes are one of the most important class of coloring materials of fibers . The provide many useful pigments and analytical colorimetric reagents[1,c.113 /2,c.128] . Photometric methods are therefore particularly attractive and available for the determination of metal ions [3,c.171 /4,c.172].

o-NHAA is a well known azo compound which is used as pH indicator and it is used for the identification of many transition and non- transition cations [5,c.195 / 6,c.1197] . Although this type of ligand is capable of formation strong (N=N)→M bond , but with Hg(ii) through C=O only [7,c.71] .

In the present work the stability and the composition of complexes investigated potentiometrically and spectrophotometrically [8,c.3122] . It is well improved to combine the spectrophotometric and potentiometric methods to get maximum information on the equilibria in solution [9,c.182/ 10,c.2904].

Experimental

1-Chemicals and solutions:

All materials employed in the present investigation were of analytical pure grade . o-aminopheol, acetylacetone ,HCl , NaNO₂, MnSO₄.H₂O ,Fe(NO₃)₃.9H₂O , NiCl₂.6H₂O were sigma products.. stock solution (5mM) of the liquid was prepared by dissolving the accurately weighted amount of the reagent in appropriate volume of pure ethanol . stock solution of metal ion was prepared in the deionized water and diluted as necessary to prepare standard working solution (2,5 x 10⁻³ M) .

2-Apparatus:

A perkin Elmer 3B double –beam UV-visible spectrophotometer controlled by a mat sub a 386/33 DX computer was used for the absorbance measurements . A corning 215 pH meter with a combined electrode was used for record the pH values . The pH- values in the partially aqueous solutions were recorded by Douheret . Infrared spectra for liquid was performed by a Shimadzu IR 470 computerized spectrophotometer . ^1H NMR spectra for ligand was recorded on Varian AMEM 390 ^1H NMR spectrophotometer (90MHz₂) . The ligand under investigation was prepared as recommended in literature and the structure of the ligand has been confirmed by the elemental microanalysis . The analytical data calculated for $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_3$, 60%C, 5,45%H , 12,72%N,found 60%C , 5,4% H, 12,75% N . The IR spectra shows a weak band at 3000-3500 cm^{-1} which can assigned to hydrozo group . But the strongly broad band at 3450 cm^{-1} is given for VOH . The band position of conjugated C=O band at 1685 cm^{-1} . ^1H NMR spectrum in CDCl_3 showed signals as Fig.1 .

$\delta=7-8$ (4H,Ar-H) , $\delta=5,5-6,9$ (1H,CH) and $\delta=0,1-0,5$ (6H,CH₃) .

3-Potentiometric procedure :

The Irving Rossetti and its modification methods was employed for the determination of the formation constants of the different binary complexes under investigation . To determine a chelae stability constants , three titrations were carried out :

- Perchloric acid plus ligand (conc., $\text{TC}_L^0=0,25\text{mM}$) was titrated against N^0M NaOH.

- Perchloric acid plus ligand and metal (conc . = $\text{TC}_m^0=1/2\text{TC}_L$) was titrated against NaOH .

- Perchloric acid at concentration of $\text{E}^0=0,02\text{M}$ was titrated against N^0M NaOH ($\text{N}^0= 0,035\text{M}$) .

pH titration were carried out at 25⁰C and $\text{I}=0,1\text{M}$ (NaClO_4). The initial volume of titration solution in eath case was V^0 .values V^1 , V^{11} , V^{111} of alkali were

consumed in titration a,b,c, respectively to give identical values of pH . A ligand – proton formation curve was obtained by plotting the degree of formation (n_H) of the ligand-proton association against pH , using the relationship derived by Irving and Rossetti .

$$\bar{n}_H = Y + \frac{(V^I - V^{II})(N^0 + E^0)}{(V^0 + V^I)T_{CL}} \dots \dots \dots (1)$$

Where Y is the total number of dissociation protons per ligand molecule added at the beginning of the titration .

A complex-ligand formation curve was then obtained by plotting the degree of formation of complex n against the negative logarithm of the concentration of non protonated ligand (pL) using the following equations .

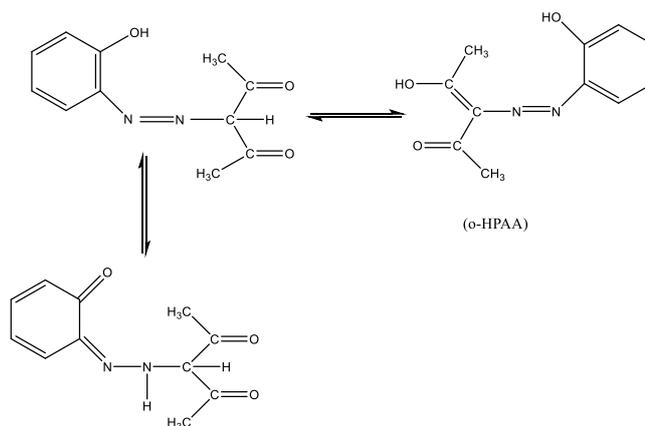
$$\bar{n} = \frac{(V^{III} - V^{II})(N^0 + E^0) + T_{CL}(Y - \bar{n}_H)}{(V^0 + V^I)\bar{n}_H T_{CM}^0} \dots \dots \dots (2)$$

$$PL = \log \frac{\sum_{n=0}^{n=1} \beta_n^H [H^+]^n}{T_{CL} - \bar{n} T_{CM}^0} \cdot \frac{V^0 + V^{III}}{V^0} \dots \dots \dots (3)$$

Results and Discussion

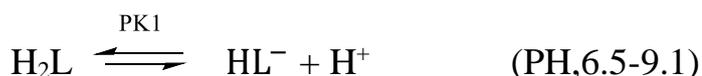
Representative plots for the titration curves of (o-HPAA) in the absence and in the presence of metal ions are shown in Fig(2)

The structure of the ligand (o-HPAA) is :



0-HPAA is considered as H_2L ligand and the following species are involved in the dissociation behavior H_2L , HL^- , L^{2-} . The hydrozo structure established by different techniques

So the equilibrium are given as following :



$$K_{\text{H}_2\text{L}}^{\text{H}} = \frac{[\text{HL}^-][\text{H}^+]}{[\text{H}_2\text{L}]}$$



$$K_{\text{HL}^-}^{\text{H}} = \frac{[\text{L}^{2-}][\text{H}^+]}{[\text{HL}^-]}$$

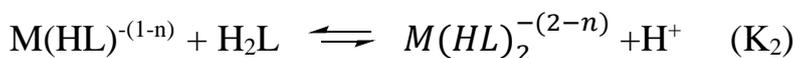
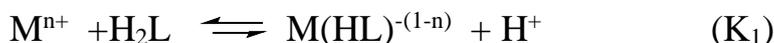
pK_1 (8,32) and pK_2 (9,78) values are the dissociation for the ionization of the phenolic OH groupe and enolic acetyl acetone respectively . The difference of the values of pK_1 and pK_2 of (o-HPAA) than those of the parent acetyl acetone substance , is due to the presence of azide group , which affects the ionization of both the phenolic and enolic acetyl acetone groups . The acid-base equilibria of (o-HPAA) under our experimental conditions as in the pH range investigated (3,5-11,5) , phenolic proton is dissociated in addition to enolic proton . The monoanionic species of (o-HPAA) (HL) undergoes ionization on increasing the pH .

The values of the dissociation constants as depicted from the titration curves (fhg.2) , were recorded in table 1.

The metal – ligand stability constants of Mn , Fe ,Ni and se with (o-HPAA) binary complexes were studied in water –ethanol (v/v) medium at 25⁰C and in 0,1M NaClO₄. The titration were carried out with the solutions containing metal and the ratio 0:1 , 1:1, 1:2 with 0,035 M NaOH . Initial lowering of pH of the solution containing metal-ligand in 1:1 ratio indicate complex formation . From the pH titration curves the metal ligand titration curves are well separated from the ligand titration curve at lower buffer regions . Thus the replacement of hydrogen ion , decrease in pH is due to complication . However further titration with NaOH shows two inflections corresponding to the consumption of 1 and 2 moles of alkali .

The absence of polynuclear species ,etc. was confirmed by repeating the experiment of the reactants , where the results obtained were identical .

The corresponding equilibria may represent by :



Where M=Mn²⁺ , Ni²⁺ and L= (o-HPAA)

The released two protons consume one mole of alkali and second mole of alkali is required for deprotonation of two phenolic group of the ligand molecules for each one molecule of metal ions mentioned above .

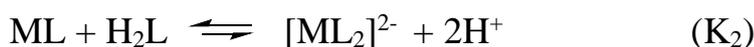
The potentiometric titration curves for binary systems containing Mn²⁺ , Ni²⁺ with (o-HPAA) in 1:1 molar ratio (fig.2)exhibits two inflections at m=1 ,and m=2 (m= number of moles of alkali added per mole of metal ion) corresponding to the stepwise formation of ML and ML₂ .

Complex species Results investigated are shown in (table 1) , the potentiometric titration curvesfor binary systems containing Fe³⁺ with (o-HPAA) in 1:1 molar ratio exhibite an inflection at m=4 indicating deprotonation of two phenolic and two enolic groups of two ligand molecules . The results pointed the formation of Fe³⁺ - L binary complexes equilibria and can be represented by the following schemes :

Fe³⁺ -L binary system :



For SeO²⁺ -L binary complex:



The order of stability constants can be represented as :



- SPETROPHOTOMETRIC STUDY

Absorption spectra and optimum Ph

The visible spectra of o-HPAA at different pH's exhibit an isosbestic points indicating the existence of an equilibrium between two different forms. The intensity and position of the absorption bands are depended on the pH of medium. In solutions of $\text{pH} \leq 6,2$, $\lambda_{\text{max}}=390 \text{ nm}$, but at higher pH's λ_{max} shifted to longer wavelength, ($\lambda_{\text{max}}=445\text{nm}$). These absorption band are attributed to $n \rightarrow \pi$ transition of the hydrazone and azo form. The spectra of 1:1 Mn(II)-o-HPAA complex, with reagent blank as reference are characterized by an absorption band at 475 nm in the pH range 6,0- 9,8. The absorption maxima at pH 7,8. the formation of binary complex is accompanied by a bath chronic shift. In alkaline media, at $\text{pH} > 9,8$, the band is shifted to longer wavelength, this behavior refers to probable formation of another type of complex. The absorbance of a solution containing 1:1Fe(II) –o-HPAA complex as a function of pH were measured at 468nm, the maximum absorbance of the binary complex was obtained in the pH range 5-5,6 define the obtained pH for maximum colour development. The absorption spectra of 1:1 Ni(II)-o-HPAA complex was characterized by absorption band at $\lambda_{\text{max}}= 448 \text{ nm}$. The absorption maximum of binary Ni(II) complex was obtained at pH 8,2.

The absorbance n-pH curves,(fig.4), shows the various range of formation and existence of the equilibria in solution. The curves obtained at the selected wavelengths indicate the existence of basic complication equilibria within the pH range 3,0- 11,5.

The study provides that the reagent (o-HPAA) is more sensitive for manganese than the other metals under investigation

Table (1) : Logarithms of the stability constants of (M-O-HPAA) binary complexes determined by potentiometric pH titrations in 50% (v/v) Ethanol at 25 °C and 1- 0,1 M (NaClO₄)

Cation	Log K ₁	Log K ₂	Log β
Mn	7.64	7.13	14.77
Fe	9.29	8.75	18.04
Ni	6.94	6.18	13.12
Cu	8.14	7.50	15.19
Ir	7.87	7.21	15.08
Hg	7.58	6.73	14.31
In	8.36	7.76	16.12
SeO	7.95	7.39	15.34

Table (2) : The optimal pH ranges , absorption maxima and molar absorptivities of some metal -O-HPAA complexes in 50% (v/v) Ethanol .

Metal ion	Optimal PH range	Molar Absorbivity L mol ⁻¹ cm ⁻¹	λ _{max} (nm)	μg cm ⁻² Sensitivity
Mn	6 – 9.8	4000	475	1.56
Fe	2.4 – 6	800	468	0.039
Ni	4.5 – 9	4320	448	1.35
Cu	2 – 9.2	5580	458	1.87
Ir	2.8 – 4.9	1430	420	0.0015
Hg	2.9 – 6.4	1440	400	0.026
In	5.5–10.5	480	500	0.058
SeO	4.1–10.4	920	510	0.0179

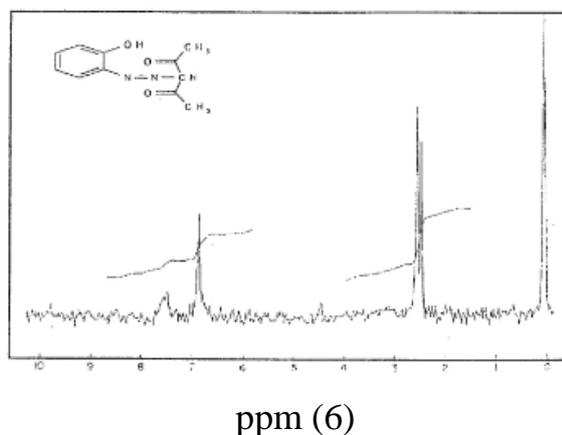


Fig.(1): HNMR Spectrum of ligand (O- HPAA)

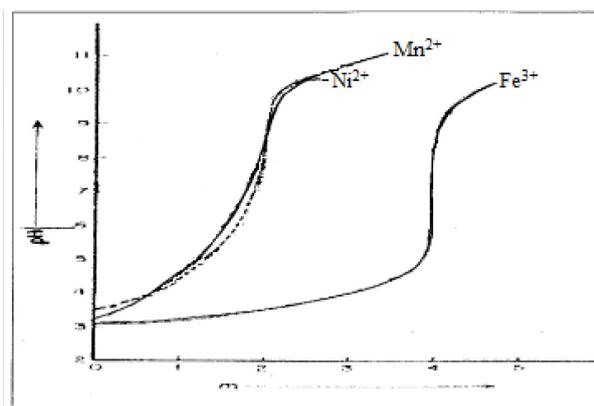


Fig . (2): Potentiometric titration curves of 1) o-HPAA and its binary complex systems of 2) Mn^{2+} , 3) Fe^{3+} , Ni^{2+} in 50% ethanol , $I=0,1$ M $NaClO_4$, at $25^{\circ}C$ and , m = number of moles of alkali added per mole of ligand .

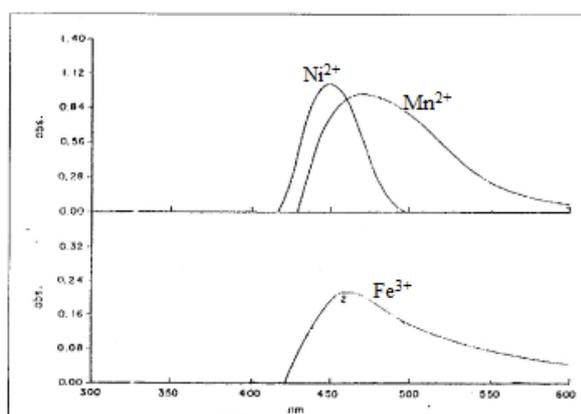


Fig . (3) : Electronic absorption maxima of M -o-HPAA (1:1) binary complex in 50% eth. Water , $0,1$ M $NaClO_4$, at $25^{\circ}C$, and the optimum pH where $M=$ 1)Mn(11) , 2) Fe (111) , 3) Ni (11) .

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