Spectrophotometric Investigation of Cu (II) and Fe (III) Schiff Base Complexes based on 2-hydroxybenzilidene-4-Methoxybenzene

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Abstract

Metal complexes of 2-hydroxybenzilidene-4-methoxybenzene with Fe (III) and Cu (II) ions in neutral 96% ethanolic solution have been prepared and studied. Ligand to metal ratio for the complexes has been investigated using mole ratio method. The unstable 2:1 complexes absorb light in the region 200-600nm. Formation constants have also been determined.

The spectrophotometric investigation of the metal complexes indicated that it is possible to detect 4×10^{-6} M of Cu (II) and 2.5×10^{-6} M of Fe (III) ions with linear calibration curves up to 4×10^{-5} for both ions. No interferences with most transition metal ions were detected under our experimental conditions.

الخلاصـــة

تم تحضير عدد من قواعد شف المشتقة من السلسلديهايد وحضرت معقدات النحاس (II) والحديد (III) مع المركب 2-هيدروكسي بنزليدين -4-ميثوكسي بنزين في محلول الايثانول المتعادل 96% وتمت دراسة نسبة العضيد إلى الفلز للمعقدات باستخدام طريقة النسبة المولية .

لقد أعطت المعقدات المتكونة بنسبة 1:2 امتصاصاً في المنطقة 200-600 نانومتر كما تم حساب ثوابت التكوين للمعقدات المتكونة بطريقة نصف القيمة ، وأثبتت الطريقة الطيفية إمكانية تقدير النحاس بحد كشف 4×10^{-6} مولاري والحديد بحد كشف 2.5×10^{-6} مولاري ، كما تمتاز الطريقة بعدم تدخل أيونات الحديد (II) في تقدير أيونات الحديد (III) .

Introduction

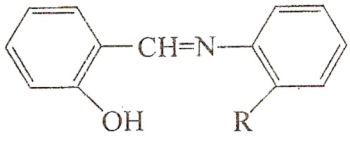
Several metal complexes of diferent schiff bases derived from salicylaldehyde have been prepared and studied extensively during the past few years by many workers (Al-Allaf et. al , 1996) (Mustafa et. al , 2001) (Keypour et. al , 2002) (Tai et. al , 2003). Some schiff bases of salicylaldehyde with aliphatic, aromatic and heterocyclic amines form stable 3:1 complexes with Lanthanides ions (Titinchi , 1997).

On the other hand complexes of both Fe (II) and Fe (III) ions with 2,2′-dipyridyl ketone schiff bases in ethanolic solutions have been reported previously (Saeed et. al , 1985).

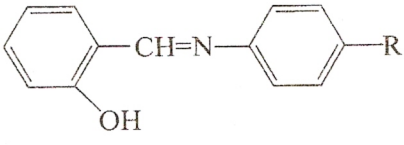
In this work the investigation of unstable complexes between schiff bases derived from salicylaldehyde and Fe (III) and Cu (II) metal ions is reported.

Experimental:

Two series of salicylaldehyde schiff bases with ortho and para substituted aromatic amines (scheme 1) were prepared by treatment of salicylaldehyde with diferent substituted anilines in boiling ethanol for 2-3 hours, the yellow solid products were recrystalized twice from ethanol.



O-Series



P-Series

Where R = H , Br , NO_2 , CH_3 , OCH_3

Scheme 1

The produced schiff bases were characterized by their IR spectra recorded as KBr discs using pye Unicam SP3-300 spectrophotomter. Fig.(1) shows the infrared spectrum of 2-hydroxy benzilidene-4-methoxybenzene as an example :

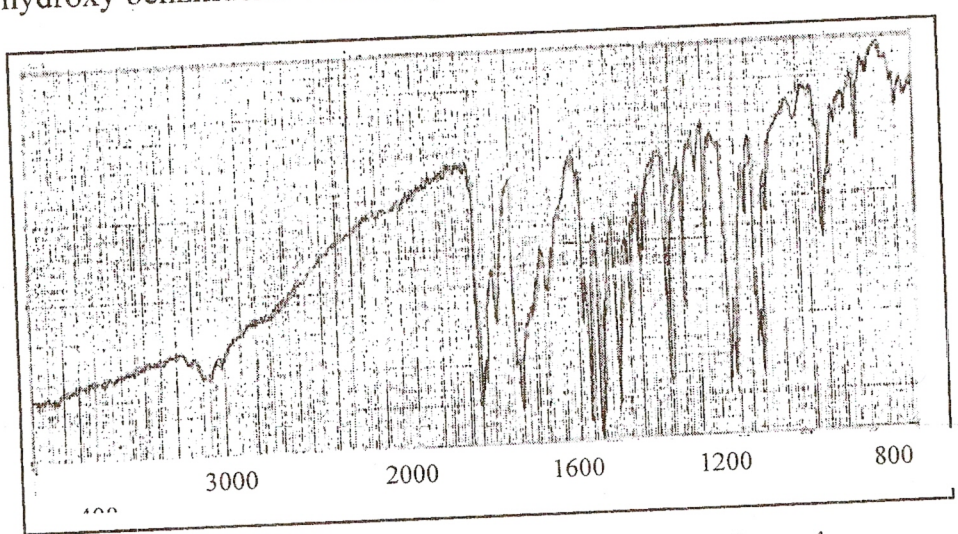


Fig.(1): IR spectrum of 2-hydroxy benzilidene-4-methoxybenzene (ligand V_p).

All the compounds gave satisfactory elemental analysis, table (1) shows the CHN of some of the prepared compounds.

All metal salts were as nitrates due to their good solubilities in 96% ethanolic solution. The UV-Visible spectra of schiff bases and their metal complexes were measured using Philips PU8620 specctrophotometer with a quartz cell of 1.0cm pathlength.

Table (1): Melting point , elemental analysis and yeild of some of the prepared compounds.

Compound	Melting point °C	Value	Elemental Analysis			Yeild %
			C	H	N	
p-Br	78-80	calc.	56.54	3.65	5.07	84
		found	56.69	4.38	5.58	
p-NO_2	148-150	calc.	64.43	4.16	11.56	75
		found	63.76	4.76	11.50	
p-CH_3	54-56	calc.	79.59	6.20	6.63	89
		found	79.25	5.43	6.91	
p-OCH_3	80-82	calc.	73.99	5.77	6.16	86
		found	75.60	5.39	7.09	

Results and Discussion

Metal Complexes

Spot test (Saeed et. al , 1985) was used for the formation of metal complexes of the prepared compounds with divalent Pb, Cu, Zn, Mn, Co, Ni, Fe, and Cd; trivalent Cr, Fe, In, and Ga. Only Fe (III) ions gave colored complexes with all the prepared schiff bases, this could be attributed to the fact that all the

prepared schiff bases are of phenolic nature. Phenolic compound usually gives colored complexes with Fe (III) ions (Silverstein and Webster , 1998) .

The only other ion which gave a colored complex was Cu (II) with only one compound namely 2-hydroxy benzilidene-4-methoxybenzene, thus this ligand was used for the spectrophotometric investigation of both Fe (III) and Cu (II) ions. Figs. (2,3 & 4) shows the absorption spectra of the used ligand (V_p), its complexes with Fe (III) and Cu (II) ions respectively in 96% ethanolic solution.

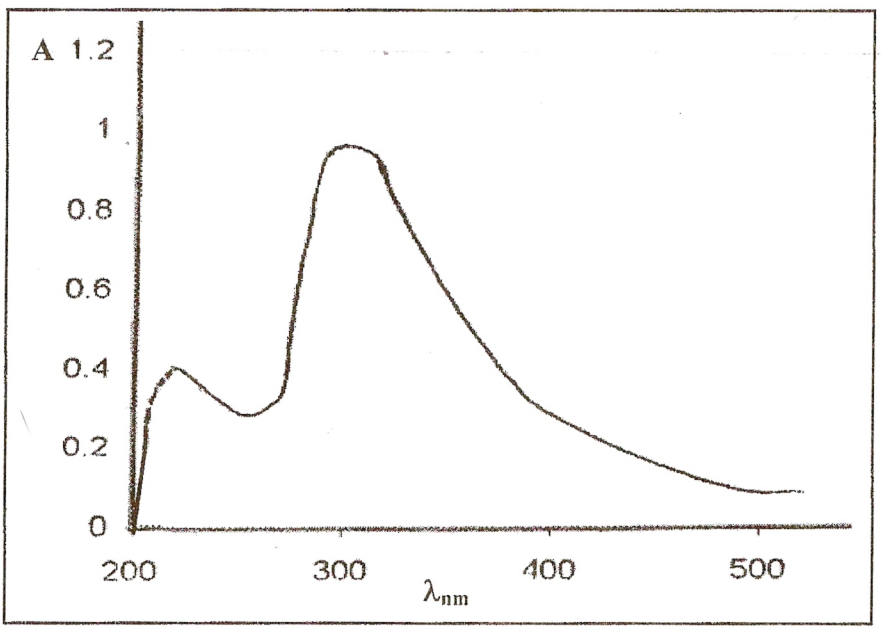


Fig. (2): Absorption Spectra of Ligand V_p

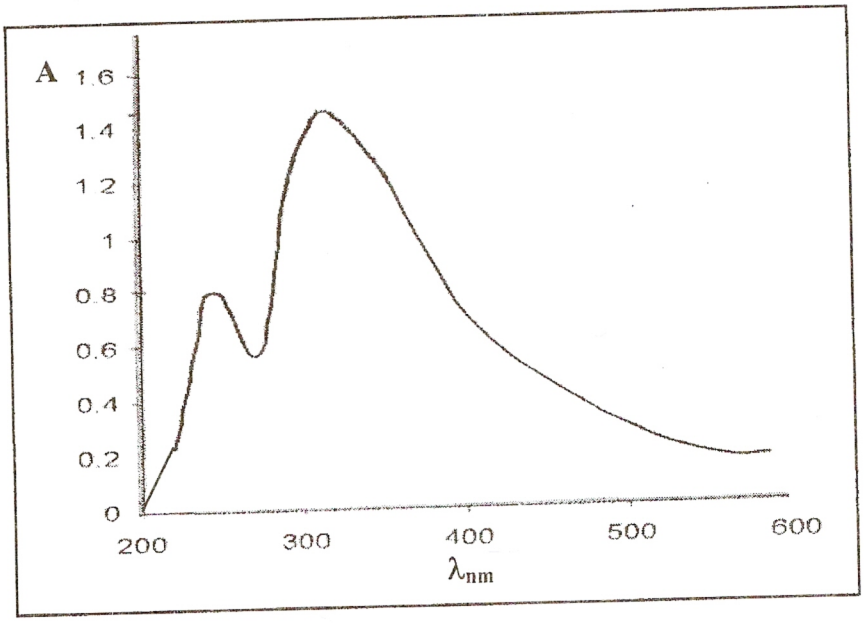


Fig.(3): Absorption Spectra of Cu(II) complexes

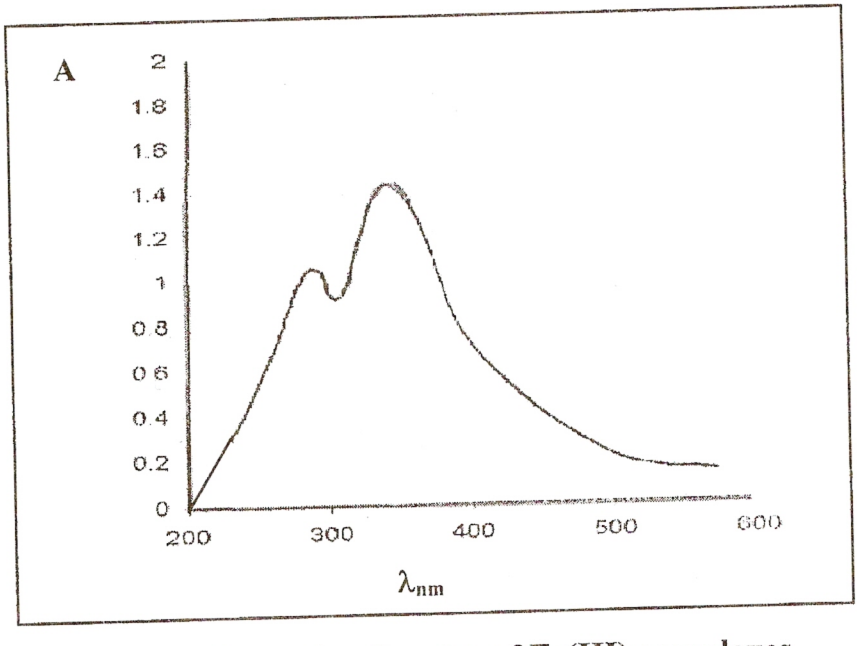


Fig.(4): Absorption Spectra of Fe(III) complexes

Molar Ratio Method of the Complexes

A plot of the concentration ratio of Schiff base (Vp) to Fe (III) or Cu (II) against the optical density of the formed complexes – Figs. (5&6) show a plateau above the concentration ratio 2, Schiff base concentration was varied and that of the metal ion was kept constant (Basset et. al , 1978), Figs. (5&6) indicates that the concentration of 2-hydroxy benzilidene-4-methoxybenzene with both Fe (III) and Cu (II) is of the ratio 2:1 in our study conditions.

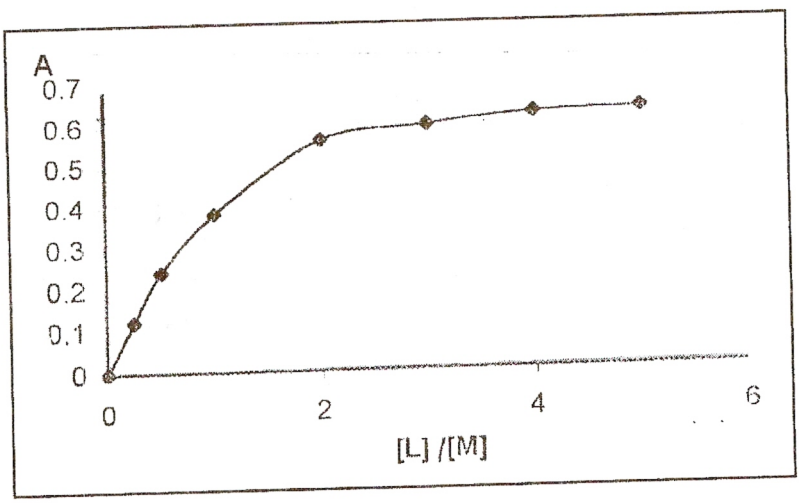


Fig.(5): Mole ratio method for Fe(III) complex at (λ_{max} = 340nm)

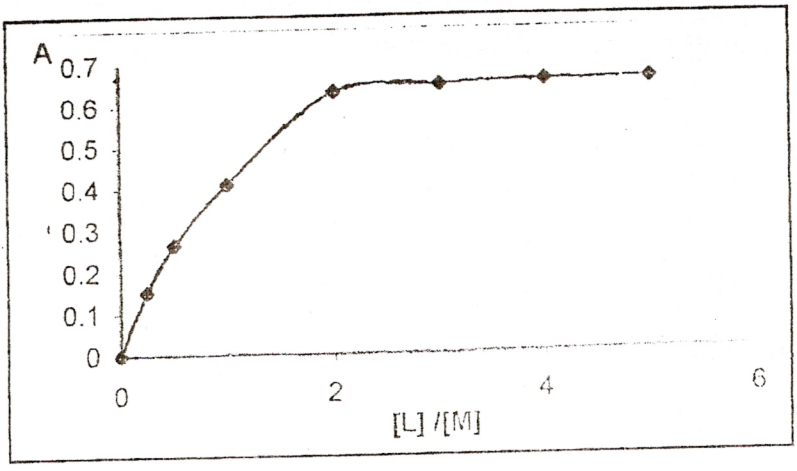


Fig.(6): Mole ratio method for Cu (II) complex at (λ_{max} = 305nm)

Calibration Curves

Calibration curves for both Fe (III) and Cu (II) ions were linear in the range ($0\text{-}4\times10^{-5}$) molar, a slight positive deviation takes place in concentrations higher than 4×10^{-5} M. detection limits (Pietrzyk and Frank , 1979) were 2.5×10^{-6} M and 4×10^{-6} M for Fe (III) and Cu (II) ions respectively.

Formation constants

The initial and final formation constants of the complexes are calculated the formation curve was obtained by plotting the formation constant values (n) vs the negative logarithm of free ligand concentration (Beck , 1970) , Figs. (7&8).

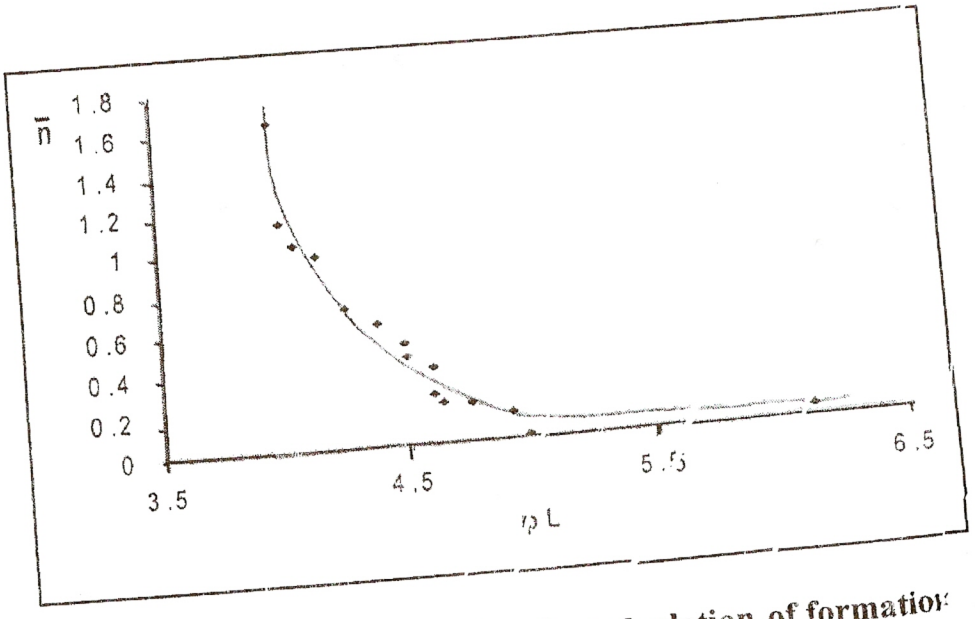


Fig. (7): Half value method for the calculation of formation constants of Cu (II) complex

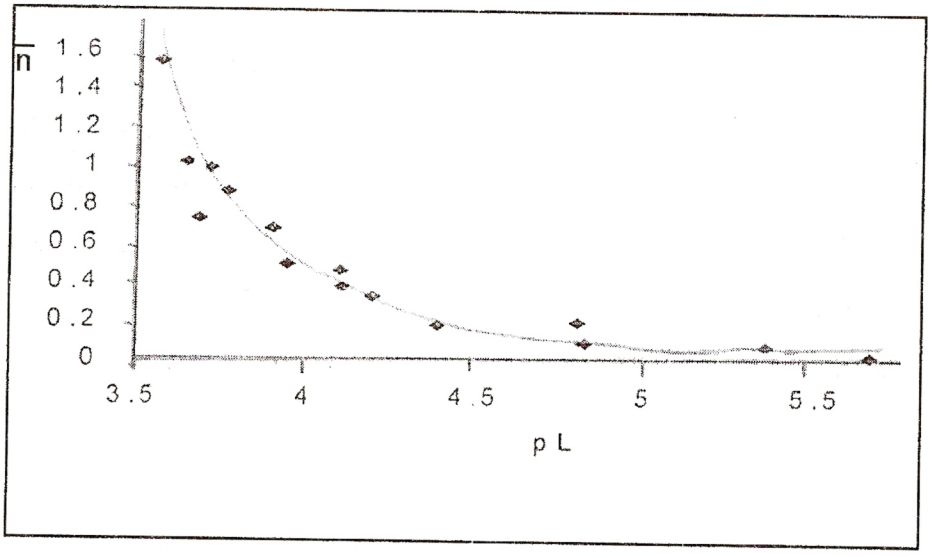


Fig. (8): Half value method for the calculation of formation constants of Fe (III) complex

From the above figures we find that (pL) value for Fe (III) complex at n=0.5 equal to $\log K_1$ of 3.94 and at n=1.5 equal to $\log K_2$ of 3.55 while (pL) value of Cu (II) complex at n=0.5 equal to $\log K_1$ of 4.5 and at n=1.5 equal to $\log K_2$ of 3.9.

Conclusion

Ligand V_P (2-hydroxy benzliidene-4-methoxybenzene) was the only compound among the prepared schiff bases that gave complex with Cu (II) ion as a colored solution, this may be attributed to the presence of – OCH_3 group in the para position of the aniline moiety of the molecule, this strongly electron

donating group tend to increase the electronagativity of the azomethine nitrogen making it a strong electron donor (Al-Azzawy , 1989) thus enhances the complexation with metal ions as the formation of metal complexes with schiff bases was interpeted in term of increasing the electron density of nitrogen atom in the azomethine groups (Saeed and Ritha , 1991).

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