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Spectrophotometric and synthesis study of complexation of Cu (II) with 1-(4'-hydroxy-8'-methyl coumarin-3'-yl)-3-o-nitropheny l-2-propene-2-one

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ABSTRACT

In the present investigation, 4-Hydroxy-8-methylcoumarin derivatives and metal complexes were synthesized and studies for chelate formulation with a metal ion Cu (II) using spectrophotometric method. 4-Hydroxy-8-methylcoumarin chalcones [1-(4'-hydroxy-8'-methyl coumarin-3'-yl)-3-o-nitrophenyl-2-propene-2-one] with Cu (II) complex was determined by mole ratio and job's method of continuous variation. The complexes of metal formed with coumarin derivative were compared with standard reagents.

KEYWORDS

1-(4'-Hydroxy-8'-methyl coumarin-3'-yl)-3-o-nitrophenyl-2-propene-2-one (HMCNP);
Cu (II) complex, Beer's law;
Mole ratio method;
Job's method of continuous variation.

INTRODUCTION

The theory of metal based mixed valence complexes (MBMV) is well documented[1,2]. The synthesis of hydroxy coumarins[3] remains of great interest due to the wide application as chelating agents to metal ion. Hydroxy coumarin derivatives forms complex with V, Ti (IV), Zr (IV), Ca, Pr, Na, Sm, Gd, etc,[4-8].

The physico chemical studies of the coumarins with chelating groups at appropriate positions and their metal-complexes reveal that the ligands could be potential analytical reagents[9-13].

The present communication deals with synthesis of HMCNP [1-(4'-hydroxy-8'-methyl coumarin-3'-yl)-3-o-nitrophenyl-2- propene-2-one], HMCNP complex with metal ion, this may be used as an analytical reagent. It belongs to chalcone series[14]. Chalcones are the compounds which are obtained by the condensation of aromatic ketone with an aldehyde; this is reacting with Cu (II). The ligand is found to form complexes with above metal ion in different pH ranges. The absorbtion spectra of the complex were recorded and the effects of pH on the absorbtion values were studied. The composition of complex was determined by Yoe and Jones mole ratio and job's method of continuous variation[15-16]. This has also been supported from thermo gravimetric analysis[17].

The structure of the synthesized compounds and complexes were assigned on the basis of ^{1}H NMR, IR spectra data and spectrophotometric study.

EXPERIMENTAL

All chemicals used throughout this work were of analytical grade. The absorbance measurements were done on a Shimadzu-UV-160-A Spectrophotometer. The pH of the solutions were measured on EQUIP TRONICS 614 pH meter and solutions of required pH were obtained using sodium-acetate-acetic acid, sodium acetate-HCl, NH_3-NH_4Cl or Borax-HCl buffer

of suitable concentration. The stoichiometric ratios of metal to reagent in the complexes were determined by Job's method of continuous variation, Yoe and Jones mole ratio method and gravimetric method. The entire practical were done at room temperature.

Preparation of 4-hydroxy-8-methyl coumarin[18-28]

O-Cresol (10.8 g, 0.01mol) and malonic acid (10.4 g, 0.1mol) were added to a mixture of phosphorus oxychloride (40 ml) and anhydrous zinc chloride (30 g). The reaction mixture was heated on a waterbath at 70^0C for 18-20 hrs. The content was cooled and decomposed with ice-water giving solid, which was filtered and washed with water. It was then treated with sodium carbonate solution and filtered. The filtrate was acidified with dilute hydrochloric acid. The precipitate was washed with water and crystallized from methanol. Yield 75%, M.P. 225^0C.

Synthesis of 3-Acetyl-4-hydroxy-8-methyl coumarin[29-34]

4-Hydroxy-8-methyl coumarin (1.56 g, 0.01mol) was dissolved in mixture of acetic acid (5 ml) and phosphorus oxychloride (4 ml) and refluxed it on waterbath for half an hour. The reaction mixture was poured into ice-cold water, the product was isolated and crystallized from ethanol. Yield 85%, M.P. 110^0C.

Synthesis of 1-(4'-Hydroxy-8'-methyl coumarin-3'-yl)-3-o-nitrophenyl-2- propene-2-one (HMCNP)

A mixture of 3-acetoacetyl-4-Hydroxy coumarin (1.98g, 0.01mol), o- nitrobenzaldehyde (1.06g, 0.01mol) and piperidine (1 ml) as a catalyst in chloroform (50 ml) was refluxed for 6 hrs on a water bath. The excess chloroform was distilled off and the residue was washed with methanol and crystallized from dioxane. Yield 68%, M.P.120°C. ^{1}H-NMR ($CDCl_3$), δppm: 2.46(s, 3H, Ar-CH_3), 7.11-8.45 (m, 7H, Ar-H); IR (KBr, cm^{-1}): 3402, 3112, 2950, 2850, 2337, 1724, 1604, 1442, 1384, 1261, 1195, 771; Analytical Calculated for $C_{19}H_{13}O_6N$: C, 64.95; H, 3.70; N, 3.99 ; Found : C, 64.91; H, 3.69; N, 3.95%.

Preparation of standard solution of Cu (II)

Stock solution of Cu (II) (0.05 M) was prepared by dissolving 3.121 g of $CuSO_4.5H_20$ in distilled water and little acid and diluting it to 250 ml. This solution was standardized volumetrically using EDTA. Experimental solutions of required concentration were prepared by appropriate dilution of the above stock solution.

TABLE 1: Reaction with Cu (II) at deferent pH values

pH	Buffer	Observation
2.0	HCl + CH_3COOH	Coloration
2.5	HCl + CH_3COONa	Buff Precipitate
3.0	HCl + CH_3COONa	Buff Precipitate
4.0	CH_3COOH + CH_3COONa	Buff Precipitate
5.0	CH_3COOH + CH_3COONa	Buff Precipitate
6.0	CH_3COOH + CH_3COONa	Buff Precipitate
7.0	NaOH+KH_2PO_4	Buff Precipitate
8.0	NH_3+NH_4Cl	Buff Precipitate
9.0	NH_3+NH_4Cl	Buff Precipitate
10.0	NH_3+NH_4Cl	Buff Precipitate

Reaction of HMCNP with Cu (II)

1.0 % solution of the reagent in dioxane was used in all detection and gravimetric determination. IR (KBr, cm^{-1}): 3061, 3030, 2950, 2850, 1716, 1604, 1442, 1385, 1342, 1261, 1199, 771.

Reaction of HMCNP with Cu (II) at different pH values

5 ml HMCNP solution was added to 2 ml of standard 0.05 M Cu (II) solution at different pH. The results are tabulated in TABLE 1.

Stability of chelate

The buff colour Cu (II) chelate is insoluble in water and ethanol, while it is soluble in chloroform, dioxane, DMF, ethyl acetate. The solution of the chelate was stable and could be kept for long time without any decomposition.

Spectrophotometric study of Cu (II) complex

The Cu (II) - HMCNP chelate has been found to be soluble in chloroform, benzene, carbon tetrachloride, DMF, ethyl acetate. This enabled to verify the Beer's law and its application for spectrophotometric determination.

Absorption spectra

To record the absorption spectra, 5 mg of chelate was dissolved in 25 ml of dioxane and absorbance of this solution was measured at different wave length in the range of 350-600 nm.

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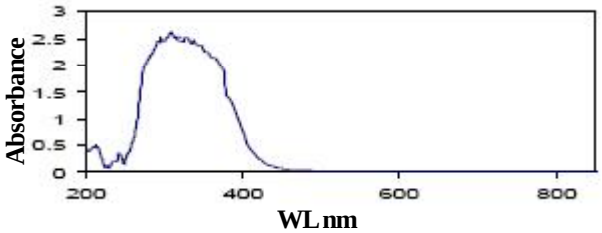


Figure 1: Absorption spectra of Zn (II)-HMCPP complex

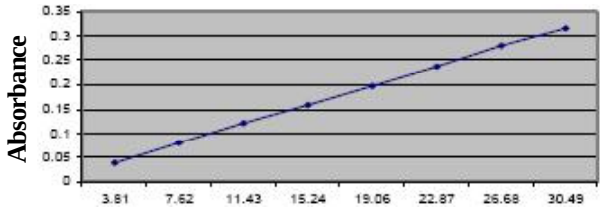


Figure 2: Verification of Beer's law

TABLE 2: Verification of Beer's law at 410 nm

Cu (II) solution taken in ppm.	Cu (II) on taken in ppm.	Absorbance
0.3	3.81	0.040
0.6	7.62	0.080
0.9	11.43	0.121
1.2	15.24	0.159
1.5	19.06	0.198
1.8	22.87	0.237
2.1	26.68	0.281
2.4	30.49	0.317

TABLE 3: Data obtained from Job's method of continuous verification

Metal ion solution ml.	Ligand solution ml.	Cm/Cm +CL	Absorbance
1.	11	0.08	0.212
2.	10	0.17	0.224
3.	9	0.25	0.236
4.	8	0.33	0.251
5.	7	0.42	0.28
6.	6	0.50	0.275
7.	5	0.58	0.254
8.	4	0.66	0.240
9.	3	0.75	0.222
10.	2	0.83	0.210
11.	1	0.91	0.207

The absorbance was plotted against wave length to get absorption spectra. It was observed that the absorbance of the coloured solution of chelate increases continuously towards the shorter wave length. A shoulder is observed at 410 nm and hence all the measurements were carried out at 410 nm. Absorption Spectra of Cu (II)-HMCNP complex is shown on figure 1.

Verification of Beer's law

To 5 ml of solution (0.01 M) of the reagent HMCNP, varying amounts of the metal ion solution (0.005 M) were added and the pH was adjusted to 5.0 using $CH_3COONa + CH_3COOH$ buffer. The insoluble complex precipitated was extracted in chloroform using three 5 ml portions of chloroform and final volume of the chloroform extract was adjusted to 25 ml. The absorbances of these solutions were measured at 410 nm against chloroform as the blank. Absorbance values were plotted against the metal concentration expressed in ppm. A straight line passing through the origin, indicating the obeyance of Beer's law as was obtained upto 30.49 ppm of Cu (II). The standard graph thus obtained may be used for the determination of copper in an unknown solution using HMCNP reagent. The results are tabulated in TABLE 2 the graph is shown on figure 2.

Molar absorptivity calculated from Beer's law plot was found to be 10×10^2 lit $mol^{-1}cm^{-1}$ for Cu (II)-HMCNP reagent at 410 nm.

Composition of chelate

The composition of Cu (II) chelate with the reagent HMCNP has been determined on the basis of Job's method of continuous variation and Yoe and Jones mole ratio method.

Composition of Cu (II)-HMCNP complex by Job's method of continuous variation

A 0.005 M solution of Cu (II) was prepared by suitable dilution of the standard solution. The solution of reagent (0.005 M) was prepared in dioxane. The solution of metal salt and the reagent were mixed in varying proportions as under:

Metal ion solution : 0, 1, 2, 3, - - - - 11, 12 ml
Reagent solution : 12, 11, 10, 9, - - - - 1, 0 ml

pH of the solution was adjusted to 5.0. The precipitated complex was extracted with three 5 ml portions of chloroform and final volume of chloroform extract was adjusted to 25 ml. The absorbance of chloroform extracts were measured at 410 nm. The results are tabulated in TABLE 3.

From the graph is shown on figure 3, it has been found that maximum occurs at 0.8 ratio of metal ion concentration to the total metal and ligand concentra-

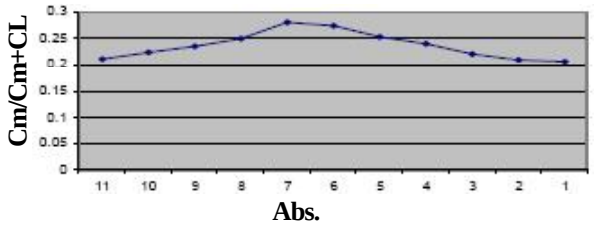


Figure 3: Result of Job's method of continuous verification

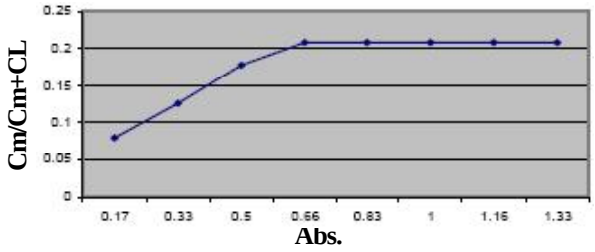
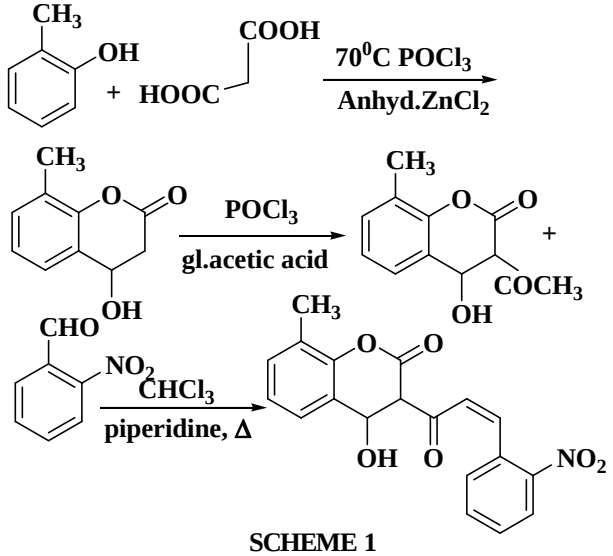


Figure 4: Result of Yoe and Jones mole ratio method

TABLE 4: Data obtained from Yoe and Jones mole ratio method

Metal ion solution ml.	Ligand solution ml.	Cm +CL	Abs.
1.	6	0.17	0.080
2.	6	0.33	0.126
3.	6	0.50	0.178
4.	6	0.66	0.208
5.	6	0.83	0.208
6.	6	1.00	0.208
7.	6	1.16	0.208
8.	6	1.33	0.208



SCHEME 1

tion indicating the formation of 1:2 (M : L) complex.

Yoe and Jones mole ratio method

In this method, equimolar solutions of the copper (II) and the reagent (0.005 M) were used. A series of solutions were prepared, keeping the reagent solution (6.0 ml) constant while varying the amount (from 1 to 7.0 ml) of 0.005 M metal solution.

pH of the solutions were adjusted to 5.0. The resulting precipitate was extracted in chloroform and final volume of chloroform extract was adjusted to 25 ml. Absorbance were recorded at 410 nm and plotted against the ratio of concentration of metal ion to reagent. The results are tabulated in TABLE 4 and Graph shown on figure 3.

It is evident from the graph that absorbance gradually increases upto molar composition of metal to the reagent and after that it becomes constant indicating 1:2 stoichiometry of the complex.

RESULT AND DISCUSSION

In the current paper, 4-Hydroxy-8-methylcoumarin was synthesized by the condensation of o-cresol with malonic acid. 4-Hydroxy-8-methylcoumarin was acetylated and subjected to fries migration to give 3-acetoacetyl-4-hydroxy-8-methylcoumarin. The acetyl coumarin was condensed with o-nitro benzaldehyde to yielded compound 1-(4'-hydroxy-8'-methyl coumarin-3'-yl)-3-o-nitrophenyl-2- propene-2-one.

In the present study the reagent HMCNP form complexes with Cu (II) in the various range of pH.

The composition of complexes determined by mole ratio and job's method of continuous variation, was found to be 1:2 (M: L), this has also supported by gravimetric analysis. The synthesized reagents are quite stable at room temperature for long time without showing any sign of decomposition. The reagents are well suited as gravimetric reagents.

CONCLUSION

From the finding, we are concluded that, coumarin derivatives as an analytical reagent has found extensively used in analytical determination of various metal ions.

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REFERENCES

[1] N.S.Hush; Prog.Inorg.Chem., **8**, 391 **(1967)**.
[2] T.J.Meyer; Acc.Chem.Res., **11**, 94 **(1978)**; C.Creutz; Prog.Inorg.Chem., **30**, 1 **(1980)**.
[3] R.Anschtz; Chem.Ber., **36**, 465 **(1903)**.
[4] H.B.Singh; Ph.D.Thesis, Delhi University, **(1966)**.
[5] M.Katyal and H.B.Singh; Talanta, **15**, 1054 **(1968)**.
[6] G.S.Manku; Ph.D.Thesis, Delhi University, **(1970)**.
[7] A.K.Kalara; Ph.D.Thesis, Delhi University, **(1972)**.
[8] N.Kohli; Ph.D.Thesis, Delhi University **(1974)**.
[9] K.Jagnadha, K.L.Omprakash; J.Indian Chemical Soc., **L12**, **(1985)**.
[10] A.K.Kalra, R.P.Singh; J.I.C.S., **1**, 49 **(1972)**.
[11] H.B.Singh; J.Inst.Chemists (India), 54 July **(1982)**.
[12] G.P.Pokhariyal; J.Indian.Chem.Soc., 74 **(1997)**.
[13] K.B.Gudasi, T.R.Goudar; J.I.C.S., 74 Oct. **(1997)**.
[14] K.H.Popat, K.S.Nimavat, S.L.Vasoya, H.S.Joshi; Indian journal of chemistry, **42B**, 1497-1501 **(2003)**.
[15] R.S.Bakry, O.A.Razak, A.F.Walily, S.F.Belal; J.Pharma Biomed Anaal., **17(1)**, 95-101 **(1998)**.
[16] A.K.Malik, K.N.Kaul, B.S.Lark, W.Faubel, A.L.J.Rao; Turk J.Chem., **25**, 99-105 **(2001)**.
[17] S.R.Mwelase, J.Bariyanga, Journal of Molecular Structure, **60(2-3)**, 235-244, May **(2002)**.
[18] **(a)** R.Anschutz; Ann., **367**,169 **(1909)**.
(b) I.M.Helborn, D.W.Hill; J.Chem.Soc., 1704 **(1927)**.
(c) K.C.Ghosh; J.Ind.Chem., **24**, 321 **(1947)**.
[19] H.Kneyuki; Bull.Chem.Soc., Japan, **35**, 579 **(1962)**.
[20] A.Sonn; Ber., **50**, 129 **(1917)**.
[21] K.G.Baner and F.Scholder; Arch.Pharma., **53**, 259 **(1929)**.
[22] K.Howsch; Ber., **48**, 1122 **(1915)**.
[23] **(a)** S.Iguchi; J.Pharma.Soc.Japan, **72**, 122 **(1952)**.
(b) S.Iguchi; N.Utshugi; J.Pharma.Soc.Japan, **73**, 1290 **(1953)**.
[24] J.F.Garden.N.F.Hafes, R.H.Thomson; J.Chem. Soc., 3315 **(1956)**.
[25] E.Ziegler, H.Junkek; Montch, **86**, 29 **(1955)**; C.A., **50**, 256 **(1956)**.
[26] K.Ziegler, H.Junkek; Montch, **87**, 212 **(1956)**; C.A., **51**, 7365 **(1957)**.
[27] V.R.Shah, J.L.Bose, R.C.Shah; J.Org.Chem., **25**, 677 **(1960)**.
[28] F.Dallaeker, P.Kratzer, M.Lip; Ann., **643**, 97-109 **(1961)**.
[29] V.N.Dholakia, M.G.Parekh, K.N.Trivedi; Aust.J. Chem., **21**, 2345-7 **(1968)**.
[30] H.R.Eisenhaur, K.P.Link; J.Am.Chem.Soc., **75**, 2044 **(1953)**.
[31] R.Anschtz; Ber., **36**, 465 **(1903)**.
[32] H.Pauly, K.Lockmann; ibdi., **48**, 28 **(1915)**.
[33] A.Sonn; ibdi., **50**, 1292 **(1917)**.
[34] M.A.Stahmenn, I.Wolff, K.P.Link; J.Am.Chem. Soc., **65**, 2285 **(1943)**.