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Synthesis and spectrophotometric studies of Mn(II)-HMCNP complex and their use as an analytical reagent

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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 Mn(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 Mn(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

4-Hydroxy-8-methylcoumarin;
Spectrophotometric determination;
Mn(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 Mn(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]

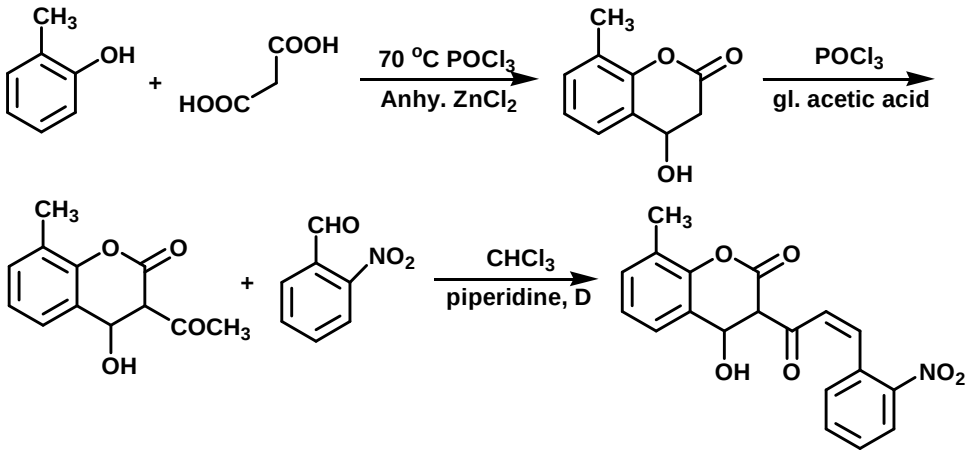
o-Cresol (10.8 g, 0.01mol) and malonic acid (10.4 g, 0.1mol) were added to a mixture of phosphorus oxychloride (40 ml) and anhydrous zinc chloride (30 g). The reaction mixture was heated on a waterbath at 70 °C for 18-20 hrs. The content was cooled and decomposed with ice-water giving solid, which was 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°C.

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°C.

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%.



Scheme 1

Preparation of standard solution of Mn(II)

Manganese sulphate 2.113 g was dissolved in little acid and double distilled water and diluted 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.

Reaction of HMCNP with Mn(II)

1.0 % solution of the reagent in dioxane was used in all detection and gravimetric determination. IR (KBr, cm^{-1}): 3058, 3030, 2950, 2853, 1716, 1605, 1441, 1385, 1341, 1261, 1200, 770.

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

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

Stability of chelate

Dark green Mn(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.

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

pH	Buffer	Observation
7.0	$NaOH + KH_2PO_4$	Green opalescene
7.5	$NaOH + KH_2PO_4$	Green colouration
8.0	$NH_3 + NH_4Cl$	Dark green precipitate
8.5	$NH_3 + NH_4Cl$	Dark green precipitate
9.0	$NH_3 + NH_4Cl$	Dark green precipitate
9.5	$NH_3 + NH_4Cl$	Dark green precipitate
10.0	$NH_3 + NH_4Cl$	Dark green precipitate
10.5	$NH_3 + NH_4Cl$	Dark green precipitate

Gravimetric determination of Mn(II) with HMCNP

A 1.0 % solution of the reagent in dioxane was used. Manganese sulphate solution (0.05 M, 10 ml) taken in a clean beaker was diluted to about 100 ml with distilled water. A small excess of reagent HMCNP was added to (1%, 14ml). Then the pH was adjusted to 8.50 to 9.0 using ammonia and ammonium chloride buffer. The dark green precipitates of manganese chelate formed were kept at room temperature for 24 hours. The precipitate was filtered through a previously weighed sintered glass funnel (G4) and washed with warm water, followed by the dioxane to remove excess of the reagent. The chelate was dried to constant weight at 80-85 °C in hot air oven, cooled and weighed.

The experiment was repeated at different pH of solution. The experiment was also repeated with different aliquots keeping the optimum pH to evaluate its applicability. The results are given in TABLE 2.

TABLE 2 : Gravimetric estimation of Mn(II) using HMCNP ligand (Cu: 0.02750 g)

pH	Mn (II) Complex In (g)	Mn (II) found In (g)	Error	
			In(g)	%
7.5	0.1495	0.02684	-0.00074	-2.68
7.5	0.1506	0.02695	-0.00063	-2.28
8.0	0.1512	0.02701	-0.00057	-2.06
8.0	0.1523	0.02712	-0.00046	-1.66
8.5	0.1536	0.02758	+0.00008	+0.29
8.5	0.1544	0.02766	+0.00016	+0.58
9.0	0.1551	0.02773	+0.00023	+0.83
9.0	0.1558	0.02780	+0.00930	+1.08

Spectrophotometric study of Mn(II) complex

The Mn(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 100 ml of dioxane and absorbance of this solution was measured at different wave length in the range of 340-600 nm.

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 520 nm and hence all the measurements were carried out at 520 nm. Absorption Spectra of Mn(II)-HMCNP complex is shown on Figure 1.

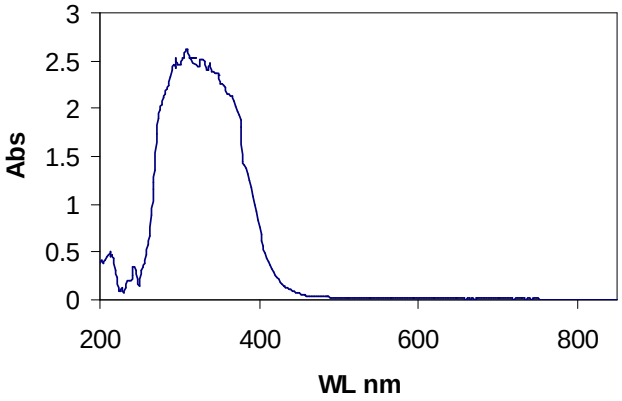

Figure 1 : Absorption spectra of Mn(II)-HMCNP complex

Verification of Beer's Law

To 8 ml of solution (0.01 M) of the reagent HMCNP, varying amounts of the metal ion solution (0.001 M) were added and the pH was adjusted to 9.0 using $NH_3 - NH_4Cl$ 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 520 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 15.4 ppm of Mn(II). The standard graph thus obtained may be used for the determination of Manganese in an unknown solution using HMCNP reagent. The results are tabulated in TABLE 3. The graph is shown on Figure 2.

TABLE 3 : Verification of Beer's law at 520 nm

Mn (II) solution taken in ppm.	Mn (II) on taken in ppm.	Absorbance
0.3	2.2	0.112
0.6	4.4	0.195
0.9	6.6	0.295
1.2	8.8	0.362
1.5	11.0	0.454
1.8	13.2	0.558
2.1	15.4	0.594

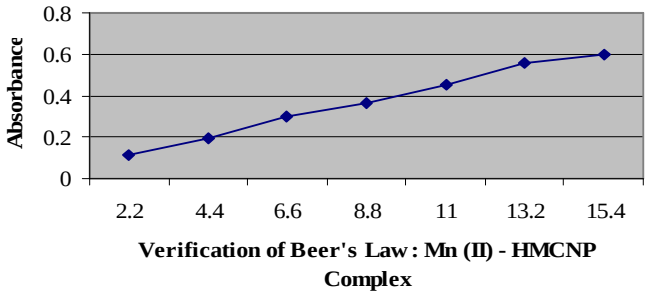

Figure 2 : Verification of Beer's law

Molar absorptivity calculated from Beer's law plot was found to be 9×10^2 lit $mol^{-1}cm^{-1}$ for Mn(II)-HMCNP reagent at 520 nm.

Composition of chelate

The composition of Mn(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 Mn(II)-HMCNP complex by Job's method of continuous variation

A 0.001 M solution of Mn(II) was prepared by suitable dilution of the standard solution. The solution of reagent (0.001 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 9.0. 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 520 nm. The results are tabulated in TABLE 4.

From the graph is shown on Figure 3, it has been found that maximum occurs at 0.33 ratio of metal ion concentration to the total metal and ligand concentration indicating the formation of 1:2 (M : L) complex.

TABLE 4 : Data obtained from Job's method of continuous verification

Metal ion solution ml.	Ligand solution ml.	Cm/Cm +CL	Absorbance
1.	11	0.08	0.703
2.	10	0.17	0.753
3.	9	0.25	0.762
4.	8	0.33	0.895
5.	7	0.42	0.79
6.	6	0.50	0.770
7.	5	0.58	0.764
8.	4	0.66	0.758
9.	3	0.75	0.699
10.	2	0.83	0.647
11.	1	0.91	0.632

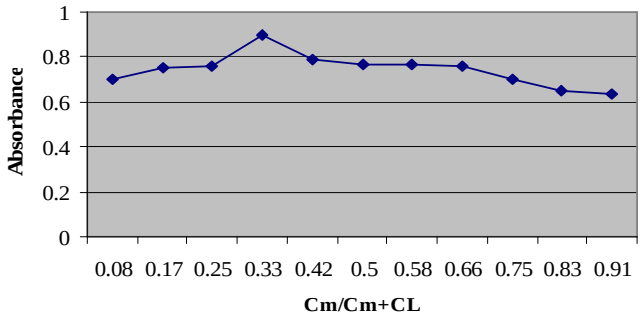

Figure 3 : Result of Job's method of continuous verification

Yoe and Jones mole ratio method

In this method, equimolar solutions of the Manganese (II) and the reagent (0.001 M) were used. A series of solutions were prepared, keeping the reagent solution (5.0 ml) constant while varying the amount (from 1 to 5.0 ml) of 0.001 M metal solution.

pH of the solutions were adjusted to 9.0. The resulting precipitate was extracted in chloroform and final volume of chloroform extract was adjusted to 25 ml. Absorbance were recorded at 520 nm and plotted against the ratio of concentration of metal ion to reagent. The results are tabulated in TABLE 5 and Graph shown on Figure 4.

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.

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TABLE 5 : Data obtained from Yoe and Jones mole ratio method

Metal ion solution ml.	Ligand solution ml.	Cm +CL	Absorbance
1.	6	0.17	0.575
2.	6	0.33	0.610
3.	6	0.50	0.622
4.	6	0.66	0.632
5.	6	0.83	0.632
6.	6	1.00	0.632
7.	6	1.16	0.632
8.	6	1.33	0.632

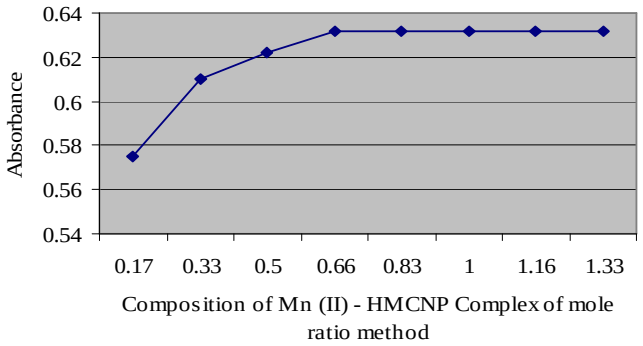

Figure 4 : Result of Yoe and Jones mole ratio method

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 Mn(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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