

## Studies on Gallic Acid Complex with Magnesium and Estimation of Gallic Acid

M. PRASAD, J. K. SRIVASTAVA,  
(Miss) VEENA GUPTA and V. DUBEY

Department of Physical Chemistry,  
National Sugar Institute, Kanpur-208 017

Manuscript received 10 July 1981, revised 30 December 1981,  
accepted 10 December 1982

**POLYPHENOLS** are of considerable importance due to their complexing behaviour with metals.

They have an important role in sugar industry as they are present in sugar cane and because of the greater tendency to form complexes with metals ion in the juice and of the container vessel, create problem in clarification. The formation of deep red colour with iron<sup>1</sup> is well established and studied in detail. Banerjee and Halder<sup>2</sup> studied the iron complexes with phenols in detail. Because of chelation, catechol<sup>3</sup> forms stable complexes with metal ions. The complexes of gallic acid with molybdenum have been studied by Athavale *et al*<sup>4</sup> who found 1:1 molar ratio complex at pH 4.2. The authors have applied this complex for the determination of molybdenum. Gallic acid also complexes with titanium<sup>5</sup> and the complex has been used for estimation of titanium<sup>6</sup>.

In the present work, gallic acid is found to complex with magnesium ion at pH 8. The complex is studied spectrophotometrically. The evidences for the formation of complex have been reported. The feasibility of utilising the colour formation for the quantitative estimation of gallic acid (polyphenols) in solution has also been examined.

### Experimental

**Apparatus and reagent:** A digital pH meter, Toshniwal CL-46, was used for pH measurements. Spectrophotometric measurements were made on Beckmann, Model DU, uv spectrophotometer equipped with 1 cm path cell. Magnesium chloride (BDH, AR) solutions of different molarity as required were prepared in double distilled water. Gallic acid (E. Merck, AR) was used as such and dissolved in double distilled water as required. Buffer tablets and sodium phthalate and sodium hydroxide buffer were used for adjusting the pH.

### Results and Discussion

**Absorption spectra:** The absorption spectra of gallic acid  $1 \times 10^{-5}$  M solution and magnesium chloride  $1.0 \times 10^{-3}$  M solution were taken. The spectrum of the complex was also taken after mixing both the reactants and maintaining the pH of the solution at 8 with the help of buffer. Time taken for the formation of the complex was approximately 10 min. The absorption maxima of gallic acid was found at 265 nm and of the complex at

610 nm as shown in Figs. 1 and 2. The absorption curve of magnesium ion did not show any maxima (Fig. 1).

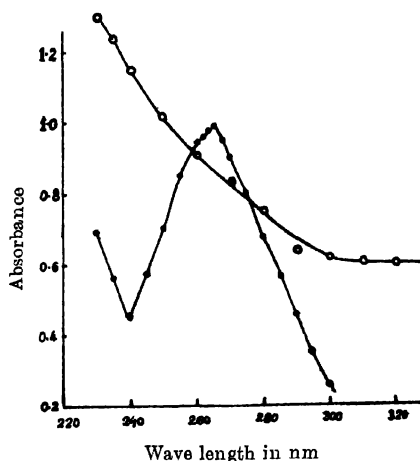


Fig. 1. Absorption maxima for Mg<sup>2+</sup> and gallic acid.

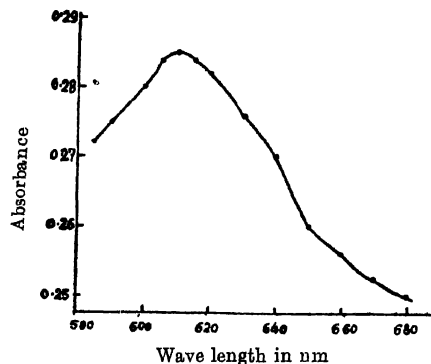


Fig. 2. Absorption maxima of the complex.

The absorbance value for the complex was obtained after allowing for the absorption due to the two reactants. The sharp shift of absorption maxima of gallic acid from 265 nm to 610 nm of the mixture strongly favours the formation of complex and the single absorption peak of the complex confirms the formation of only one complex.

Absorption measurements were also carried out to find out the stoichiometry of the complex. For this purpose Job's method was applied. Magnesium chloride  $1 \times 10^{-3}$  M and gallic acid  $1 \times 10^{-5}$  M solutions were taken and mixed in different molar ratios keeping the final molarity constant. Absorbance measurements showed that metal ligand ratio was 2:3 indicating the formation of  $M_2L_3$  type of complex.

**Effect of pH:** Preliminary experiments showed that the formation of the  $Mg^{2+}-C_7H_6O_5$  complex is strongly sensitive to hydrogen ion concentration and the complex formed only in alkaline medium. The complex showed maximum absorption at pH 8. The absorbance of the complex at pH 8 is reasonably constant for 2 hr, which is satisfactory for analytical purpose.

**Determination of polyphenols (gallic acid) :** For estimation of polyphenols a standard curve is first drawn as described below. Gallic acid solution is prepared. 20 ml of magnesium chloride solution (1%) was taken in each of ten 50 ml measuring flasks and 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 and 5.0 ml of gallic acid solution (0.1%) were added to the successive flasks. The pH of the mixture in each flask was maintained at 8 using buffer solution. Finally, the volume was made upto 50 ml. This was done to keep the concentration of gallic acid in the flasks between 10 to 100 ppm. The reaction mixture was allowed to stand for 10 min and absorbance of the solutions was measured at 610 nm. Unknown concentration of gallic acid can be estimated from the Beer's plot so obtained.

**Acknowledgement**

The authors thank Dr. N. A. Ramaiah, Director, National Sugar Institute, Kanpur for his interest in the work.

**References**

1. J. C. BAILAR, JR., "The Chemistry of Coordination Compounds", Reinhold Publishing Corporation, New York, 1956, p. 25.
2. S. BANERJEE and B. C. HALDER, *Nature*, 1950, **165**, 1012.
3. R. F. WEINLAND and KARL BINDER, *Ber.*, 1912, **45**, 148, 1113.
4. M. S. VERDE and V. T. ATHAVALE, *Proc. Ind. Acad. Sci.*, 1956, **44H**, 228.
5. C. H. VENKATESHWARLU, M. SANKAR DAS and V. T. ATHAVALE, *Proc. Ind. Acad. Sci.*, 1956, **44**, 241.
6. C. H. VENKATESHWARLU, M. SANKAR DAS and V. T. ATHAVALE, *Proc. Ind. Acad. Sci.*, 1954, **40A**, 260.

**Pyrolysis of Pd(II), Cu(II), Ni(II), Co(II) and Ti(IV) Chelates of 4,5-Dimethyl-2-hydroxyacetophenone Oxime**

(Mrs.) M. MITTAL, KEEMTI LAL and S. P. GUPTA

Department of Chemistry, D. N. College, Meerut-250 002

Manuscript received 26 October 1981, revised 4 August 1982, accepted 10 December 1982

IN continuation of our studies on 4,5-dimethyl-2-hydroxyacetophenone and its oxime<sup>1,2</sup>, the present work reports the thermal behaviour of Pd(II), Cu(II), Ni(II), Co(II) and Ti(IV) chelates of 4,5-dimethyl-2-hydroxyacetophenone oxime (DMHAO). A possible correlation of the thermal stability with the structure of the chelates is reported.

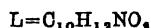
**Experimental**

Metal chelates of DMHAO were synthesized as reported earlier<sup>3</sup>. The elemental analyses of the complexes is reported in Table 1 which show the composition of the complexes as 1 : 2 (metal :

ligand) except Ti(IV) which is 1 : 1. Thermogravimetry of the chelates was carried out in the Department of Chemistry, Guru Nanak Dev University, Amritsar. The initial weights (mg) of the samples were 224.4, 153.0, 177.6, 173.0 and 215.0 of Pd(II), Cu(II), Ni(II), Co(II) and Ti(IV) chelates, respectively.

TABLE 1—ANALYTICAL DATA AND COLOUR OF THE METAL COMPLEXES

Compound	Colour	Analysis % ; Found (Calcd.)			
		C	H	N	Metal
PdL <sub>2</sub>	Yellow	51.66 (51.86)	5.16 (5.18)	6.00 (6.05)	23.03 (23.06)
CuL <sub>2</sub>	Buff	57.40 (57.20)	5.73 (5.72)	6.71 (6.67)	15.10 (15.14)
NiL <sub>2</sub>	Green	57.80 (57.87)	5.73 (5.78)	6.72 (6.75)	14.20 (14.15)
CoL <sub>2</sub>	Pink	57.90 (57.83)	5.77 (5.78)	6.72 (6.75)	14.16 (14.20)
TiO(OH)L	Yellow	46.30 (46.34)	5.01 (5.02)	5.35 (5.40)	18.33 (18.50)



**Results and Discussion**

According to Nikolaev *et al*<sup>4</sup> water eliminating below 150° can be considered as the crystal water and water eliminating above 150° may be due to water coordinated to the metal ions. In the present studies it is observed that all the chelates decompose after 200° which suggests the unhydrated nature of the chelates. The initial decomposition temperatures from the thermogram curves are taken as measure of thermal stability of the chelates. The decomposition temperatures of the chelates are reported in Table 2.

TABLE 2—PYROLYSIS DATA OF METAL CHELATES OF DMHAO

Chelate	Dec. Temp. °C	Initial weight mg	Residue, mg		Error mg	
			Exp. value	Theoretical value Metal Oxide		
Pd	280	224.4	48.5	51.48	59.26	1.98
Cu	240	153.0	30.0	23.16	29.00	1.00
Ni	280	177.6	32.0	25.13	31.98	0.02
Co	200	173.0	31.0	24.56	31.23	0.23
TiO	200	215.0	60.0	39.77	66.35	6.35

The thermogram of the Pd(II)-DMHAO chelate shows that the weight of the chelate remains constant upto 260° and above that a continuous loss of weight is observed upto 540° indicating the decomposition of the chelate. The weight of the product remains constant (79.0 mg) from 540-620°. This weight is much higher than the theoretical value of palladium oxide. This may be due to the presence of carbon with palladium oxide because further loss in weight of the product was observed at 640 to 720°. The weight becomes constant (48.5 mg) from 720° to 800°. This value is very close to the weight of palladium indicating that metallic palladium remains in the product.