PART - II

ANALYTICAL STUDIES WITH o-HYDROXY ACETOPHENONE GUANYLHYDRAZONE

CHAPTER-IV

SYNTHESIS AND CHARACTERISATION OF o-HYDROXY ACETOPHENONE GUANYLHYDRAZONE

4.1 INTRODUCTION

In the 1st Chapter of the 1st part of the dissertation, literature study of the topic have been discussed. In this 4th chapter of the 2nd part of the dissertation we have introduced another analytical reagent o-hydroxy acetophenone guanylhydrazone (HAG) to study the metal complexes.

HAG can be used for the determination of nickel and cobalt.

4.2. EXPERIMENTAL

4.2.1 Apparatus :

As reported in the 1st chapter.

4.2.2 Reagents :

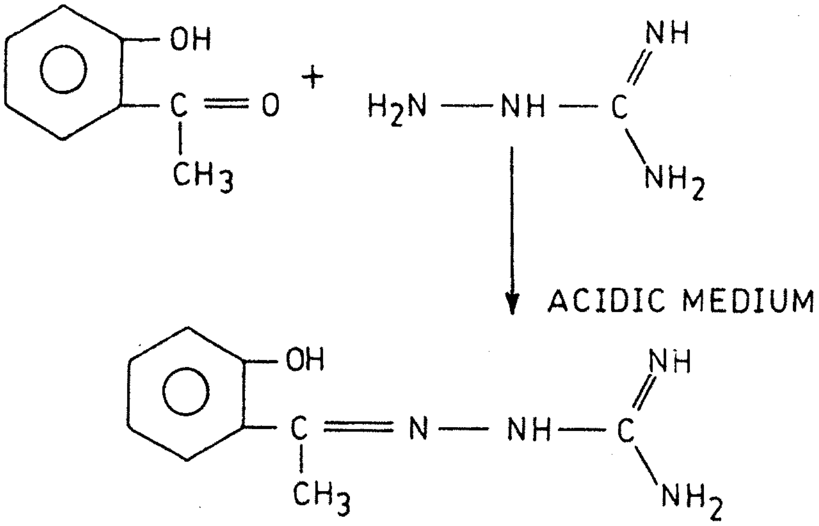
As reported in the 1st chapter.

4.2.3 Synthesis of HAG :

For the synthesis of o-hydroxy acetophenone guanylhydrazone (HAG), aminoguanidine bicarbonate was used to get the better yield.

2.0 g of aminoguanidine bicarbonate was dissolved in concentrated nitric acid (till evolution of carbon dioxide was completely stopped). 2.0 ml of o-hydroxy acetophenone was diluted with 10 ml ethanol and the two solutions were mixed together. The mixture was kept as such for about

24 hours. The white coloured product was formed which was filtered and crystallised from water to give shining white crystals of o-hydroxy acetophenone guanylhydrazone (~ 1.7 g) M.P. = 230 - 232°C. The compound is quite stable for months. The reaction is



4.2.4 Solubility :

The reagent is soluble in water, ethanol, methanol, but insoluble in chloroform and carbon tetrachloride.

The solution of the reagent in water was stable for months without any deterioration.

4.2.5 Characterisation of HAG :

HAG is stable in air. There is no action of light on the reagent. So, no special care is required to protect it from light.

The microelemental analysis of the chromatographically purified reagent confirmed the formula to be $C_9H_{12}N_4O$. Calculated percentage of elements are C = 56.24 %, H = 6.25 %, N = 29.17 % and O = 8.33 %. Experimentally found percentage of elements are C = 56.13 %, H = 6.30 %, N = 29.15 % and O = 8.42 %.

4.2.6 Ultraviolet spectra of the reagent (HAG) :

Fig. 4.1 shows the ultraviolet absorption spectra of the reagent (HAG) in water (1.0×10^{-4}M) at different pH values.

Absorption maxima and molar extinction coefficients of the reagent at different pH values are given in table 4.1.

Table 4.1 : Spectral characteristics of the reagent (HAG)

pH	Absorbances at λ		Molar extinction coefficients, ϵ l mole^{-1} cm^{-1} at λ	
	322 nm	355 nm	322 nm	355 nm
6.0	0.275	0.075	0.275×10^4	0.075×10^4
7.0	0.255	0.09	0.255×10^4	0.09×10^4
8.0	0.245	0.11	0.245×10^4	0.11×10^4
9.0	0.225	0.14	0.225×10^4	0.14×10^4
9.5	0.21	0.15	0.21×10^4	0.15×10^4
10.0	0.19	0.215	0.19×10^4	0.215×10^4
10.5	0.16	0.30	0.16×10^4	0.30×10^4
11.0	0.15	0.325	0.15×10^4	0.325×10^4
12.0	0.14	0.35	0.14×10^4	0.35×10^4

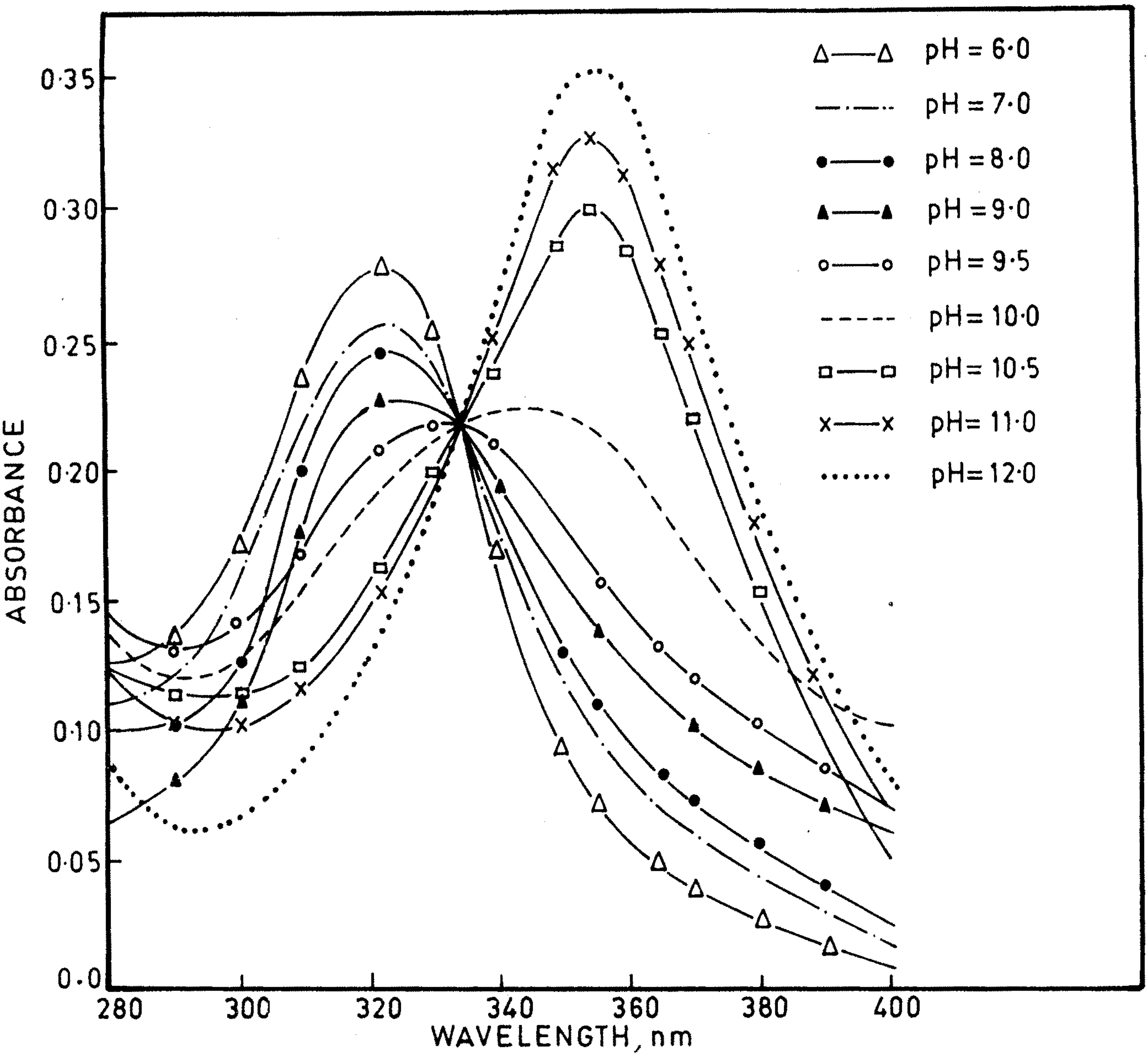


FIG. 4·1 - ULTRAVIOLET SPECTRA OF REAGENT (HAG).

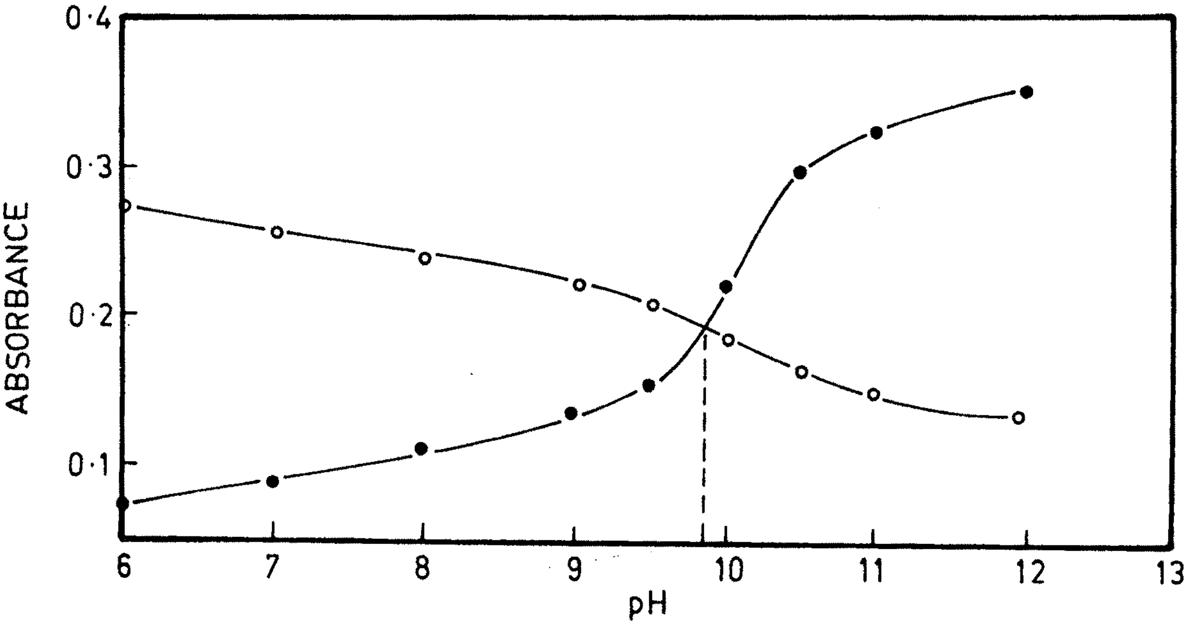


FIG. 4·2 - DETERMINATION OF pK.

○—○ 322 nm ●—● 355 nm

4.2.7 Infrared spectrum of the reagent (HAG) :

Infrared absorption spectrum in the range 4000 to 200 cm^{-1} was run on Perkin Elmer 221 IR spectrophotometer in Nujol mull. (Fig. 4.3). The characteristic absorption bands were observed as follows :

3400 cm^{-1}	→	NH stretch
3200 cm^{-1} (broad)	→	OH — N internally bonded
3200 - 3100 cm^{-1}(broad)	→	NH$_2$ stretching
2920 cm^{-1}	→	= N — Vibrations
1680 - 1600	→	NH$_2$ deformation
1650 - 1490 cm^{-1}	→	N$_2$C = N guanidine group, absorption due to NH deformation and CN stretching vibrations.
1490 cm^{-1}	→	Aromatic band phenyl ring
1460 cm^{-1}	→	Nujol Scissoring band H - C - H
1380 cm^{-1}	→	Nujol symmetric deformation of terminal methyl group
1170, 1045, 770 cm^{-1}	→	Ortho substitution pattern
760, 750, 730 cm^{-1}	→	4 adjacent H wag
719 cm^{-1}	→	Nujol band

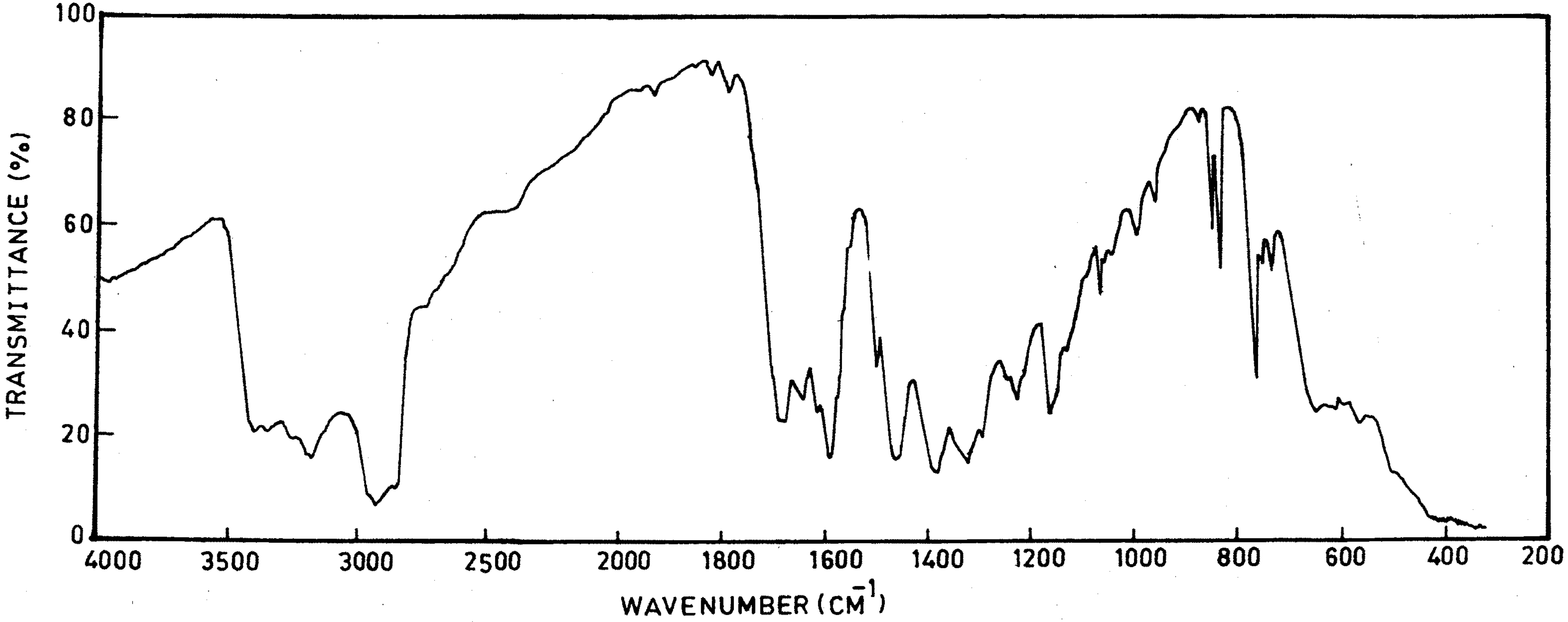


FIG.4·3 – INFRARED SPECTRUM OF REAGENT (HAG).

4.2.8 Determination of ionization constant of HAG :

The ionization constant of the reagent (HAG) was obtained both by spectrophotometric method and by pH - metric method.

a) By Spectrophotometric Method :

The ultraviolet absorption spectra of the reagent are shown in fig. 4.1. At pH 6.0, the reagent shows the absorption band with λ_{max} 322 nm, which lowers in intensity as pH increases. With increasing value of pH, the absorbance at longer wavelength increases, and at pH 12.0, highest intensity band with λ_{max} at 355 nm appears. All the spectral curves pass through the isosbestic point at 335 nm, thereby indicating a dynamic equilibrium between ligand and its deprotonated species, assuming that at pH 6.0, the molecular form of the ligand is exclusively present and the deprotonated species is absent and that at pH 12.0, the deprotonated species is present exclusively and the molecular form is absent. By using Henderson equation and from the half height[1] of the sigmoid curve (Fig. 4.2), the pk value for the deprotonation of the ligand is found to be 9.88.

b) By pH-metric Method :

5.0 ml of 0.01 M HAG was taken in a thermostated titration vessel at 30 ± 1°C containing 20.0 ml distilled water. The solution was titrated with 0.1 M NaOH. An ELICO Digital pH meter was used. The pH meter was calibrated with pH 4.01 and 9.18 by phthalate and borax buffers respectively. The ionization constants were calculated from the pH values. The pk was determined by using the formula :

$$pk = pH + \log \frac{[HA]}{[A^-]}$$

HA represents the reagent HAG. The log $[H^+]$ values were read from the pH meter.

The titration was repeated until two sets of values differing within ± 0.01 pH units were obtained. The results of study are summarised in table 4.2 which show that the pk is 9.88 for o-hydroxy acetophenone guanylhydrazone (HAG).

Table 4.2 : Determination of ionization constant of HAG at 30 ± 1°C.
[HAG] = 0.01 M; NaOH = 0.1 M.

NaOH ml	pH	Stoichiometric concentration		$\log \frac{[HA]}{[A^-]}$	pk
		HA	A^-		
0.5	8.89	0.018	0.002	0.954	9.844
1.0	9.40	0.016	0.004	0.602	10.002
1.5	9.66	0.014	0.006	0.367	10.027
2.0	9.81	0.012	0.008	0.176	9.986
2.5	9.93	0.010	0.010	0.000	9.930
3.0	10.02	0.008	0.012	- 0.176	9.844
3.5	10.07	0.006	0.014	- 0.367	9.703
4.0	10.10	0.004	0.016	- 0.602	9.498
4.5	10.13	0.002	0.018	- 0.954	9.176
				Mean pk =	9.88

4.2.9 Complex formation :

The reagent (HAG) forms complexes with Ni(II) and Co(II). A detailed account of the complex formation with these two metals is discussed in the following chapters.

4.3 REFERENCES

1. Stenstrom, W. and Goldsmith, N., J. Phys. Chem., 30, 1683 (1926).