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SPECTROCOLORIMETRIC STUDY OF THE COMPLEXATION REACTION BETWEEN MOLYBDENUM(VI) AND RESACETOPHENONE OXIME

RESACETOPHENONE OXIME (2, 4-dihydroxy acetophenone oxime) forms chelates with many metal ions. This reagent is widely employed in these laboratories for the estimation of many metal ions¹⁻⁷ as well as anions such as fluoride⁸⁻⁹. The present paper describes the results on the composition and the stability constant of the complex between molybdenum(VI) and the oxime in hydrochloric acid medium. The yellow complex is formed from buffer solutions of pH 1 to 4 and also in unbuffered dilute acid solutions. The spectra in the visible range (400-700 nm) of the complex showed maximum absorbance at 400 nm. The absorbance of the complex is found to be higher in HCl medium as compared with other acid media (Table II). Even though it is not easy to assign specific reasons for the higher extinction in HCl medium, the (polymeric \rightleftharpoons monomeric) equilibrium of the molybdate species seems to play a significant role¹⁰. Hence the detailed studies are carried out at 400 nm and in 4×10^{-3} M HCl medium. This method is simple and rapid. Further the colour is formed rapidly and is stable for several days. The present method offers advantages over several methods reported in the literature since these methods generally involve extraction.

Resacetophenone oxime was prepared by the standard procedure¹¹⁻¹² and its solution was prepared in 50% aqueous ethanol. All the other chemicals used were of BDH Analytical Grade.

Experimental

Effect of pH.—A mixture of 2 ml of Mo(VI) (2×10^{-2} M), 1 ml of the oxime (0.1 M) and 5 ml of the buffer solution (pH 1-10) were taken in 25 ml measur-

ing flasks and in each case, the volume was made up to the mark with distilled water. The absorbance of the reaction mixture was measured at 400 nm. and the results (Fig. 1) show that the yellow colour increased with pH and remained constant in the range 2-4.

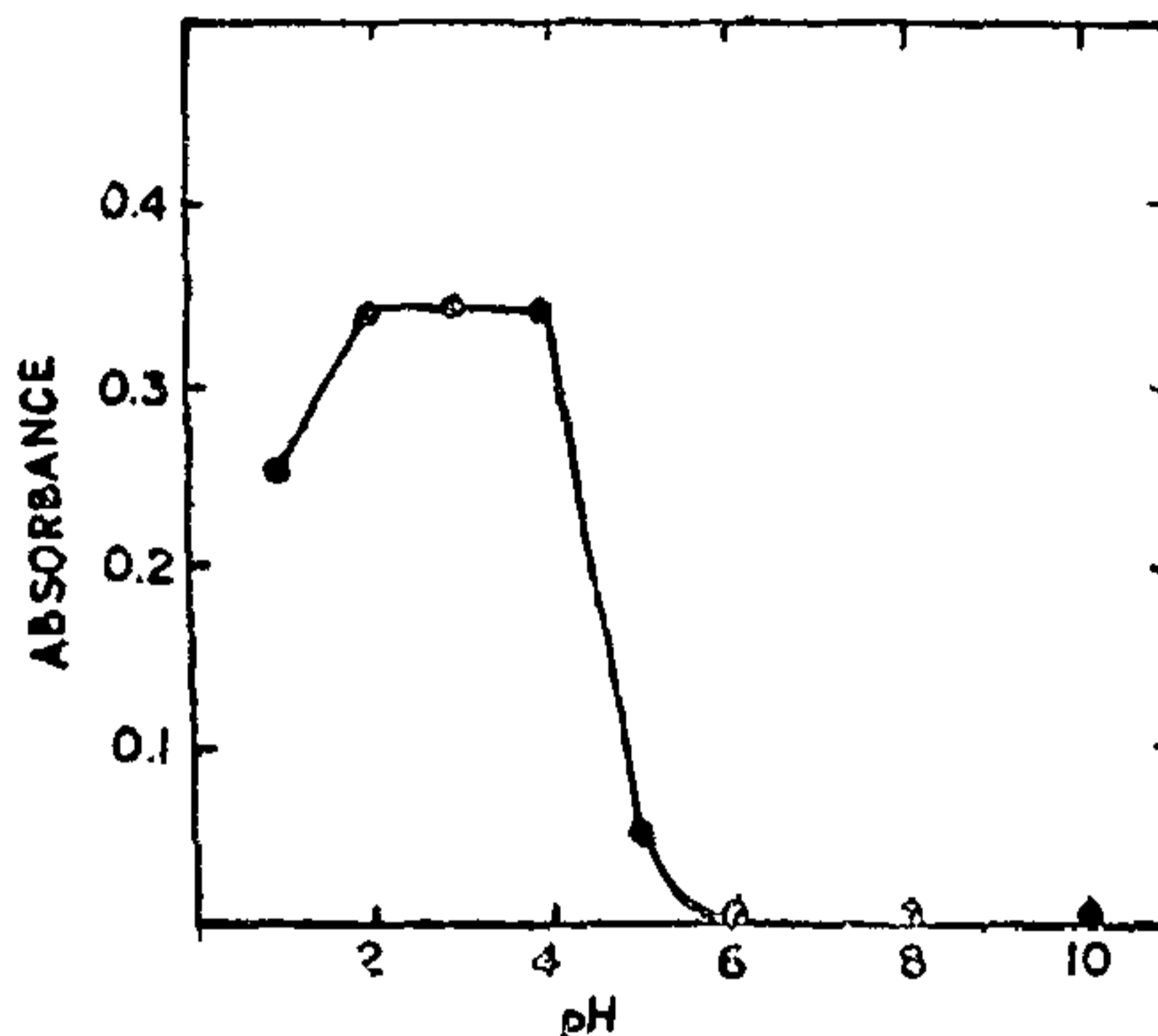


FIG. 1. Plot of pH vs. absorbance.

Effect of the oxime.—Different amounts of the oxime were added to a constant amount of the metal ion in 4×10^{-3} M HCl and the absorbance of the resulting solutions was measured at 400 nm. and the data (Table I) indicated the metal ; ligand ratio as 1 : 2.5 for quantitative results.

TABLE I
Effect of ligand concentration on absorbance
[Mo (VI)] = 1.6×10^{-3} M
[HCl] = 4×10^{-3} M

Metal : Ligand	Absorbance
1 : 1	0.23
1 : 2.5	0.39
1 : 5	0.40
1 : 10	0.42
1 : 20	0.44
1 : 30	0.45

Applicability of Beer's Law.—Linear plot is obtained between the absorbance and the amount of the metal ion upto 230 ppm of the metal.

Composition and Stability Constant of the Complex.—Job's continuous variation method¹³, molar ratio method¹⁴, slope ratio method¹⁵, and the limiting logarithmic method¹⁶, indicated the composition of the complex as 1 : 1. The stability constant of the complex,

TABLE II
Effect of various acids on the absorbance
[Mo(VI)] = 1.6×10^{-3} M
[Acid] = 4×10^{-3} M
[Oxime] = 4×10^{-3} M

Acid	Absorbance
HCl	0.39
H ₂ SO ₄	0.29
HClO ₄	0.31
HNO ₃	0.18
H ₃ PO ₄	Very little
CH ₃ COOH	0.27
CH ₃ · CH ₂ · COOH	0.24

calculated using the data obtained in Job's method is 1×10^4 .

Effect of Diverse Ions.—It was found that K⁺, Na⁺, Cl⁻, NO₃⁻, SO₄⁼, I⁻ did not interfere and oxalate, tartrate, citrate, phosphate; borate, acetate, EDTA, Fe³⁺ and Al³⁺ interfered. W⁶⁺, V⁵⁺ and V⁴⁺ interfere when their respective concentrations exceed 184, 1.5 and 15 ppm. Cr³⁺ and fluoride interfere if the amount exceeds 1.5 and 150 ppm respectively. Fe³⁺ (<18 ppm) is successfully masked by the addition of fluoride (>150 ppm). Higher amounts of Fe³⁺ can effectively be masked by potassium iodide and the iodine liberated is removed by adding the just sufficient amount of sodium thiosulphate solution. A 40 fold excess of Zn²⁺, Mn²⁺, Cd²⁺, and Ni²⁺ do not interfere.

The present method can therefore be employed for the analysis of molybdenum in high speed and alloy steels.

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A SPECIFIC SPOT TEST FOR PALLADIUM USING DIPHENYLDISULPHIDE 2:2'-DICARBOXYLIC ACID

DURING the course of our studies on the reactions of thio-salicylic acid with metal ions, it was observed that the oxidised product of this compound, *viz.*, diphenyldisulphide 2:2'-dicarboxylic acid yielded a color reaction with palladium but not with other metal ions. Since the reagent is easy to prepare and the reaction is found to be highly specific for palladium, its potentialities as a spot test reagent for palladium were investigated.

Experimental—Reagents:

Palladium chloride solution: Palladium chloride solution (1 ml \approx 0.5 mg) was prepared using Johnson & Matthey sample. The strength of the solution was ascertained gravimetrically using dimethylglyoxime¹. More dilute solutions were prepared from this stock solution.

Diphenyldisulphide 2:2'-dicarboxylic acid solution:

(a) This reagent could be prepared starting from *o*-amino benzoic acid and sodium disulphide². A 0.1% (W/V) solution in absolute alcohol was used.
(b) The reagent could be more conveniently prepared starting from thio-salicylic acid as follows:

Thio-salicylic acid solution, in alcohol (5 ml of 1%) was taken in a centrifuge tube and treated with hydrogen peroxide. A white precipitate separated out. It was then centrifuged, the precipitate washed thrice with alcohol (5 ml each time) and again shaken up with alcohol to obtain the saturated solution of the reagent. The solubility of the reagent in absolute alcohol was about 150 mg per 100 ml of alcohol.

Procedure: A drop (0.04 ml) of the palladium chloride solution which is not more than 0.05 M with respect to hydrochloric acid (but of any concentration with respect to other mineral acids) is placed on a spot plate and treated with a drop of the reagent solution.