

1/T (Fig. 2) gave straight lines obeying the relationship¹² $\log \nu \text{ (Hz)} = c_1 - c_2/T$. The slope of these straight lines decreased with the rise of

temperatures. This type of behaviour at low temperature may be correlated with the decrease in trap depth.

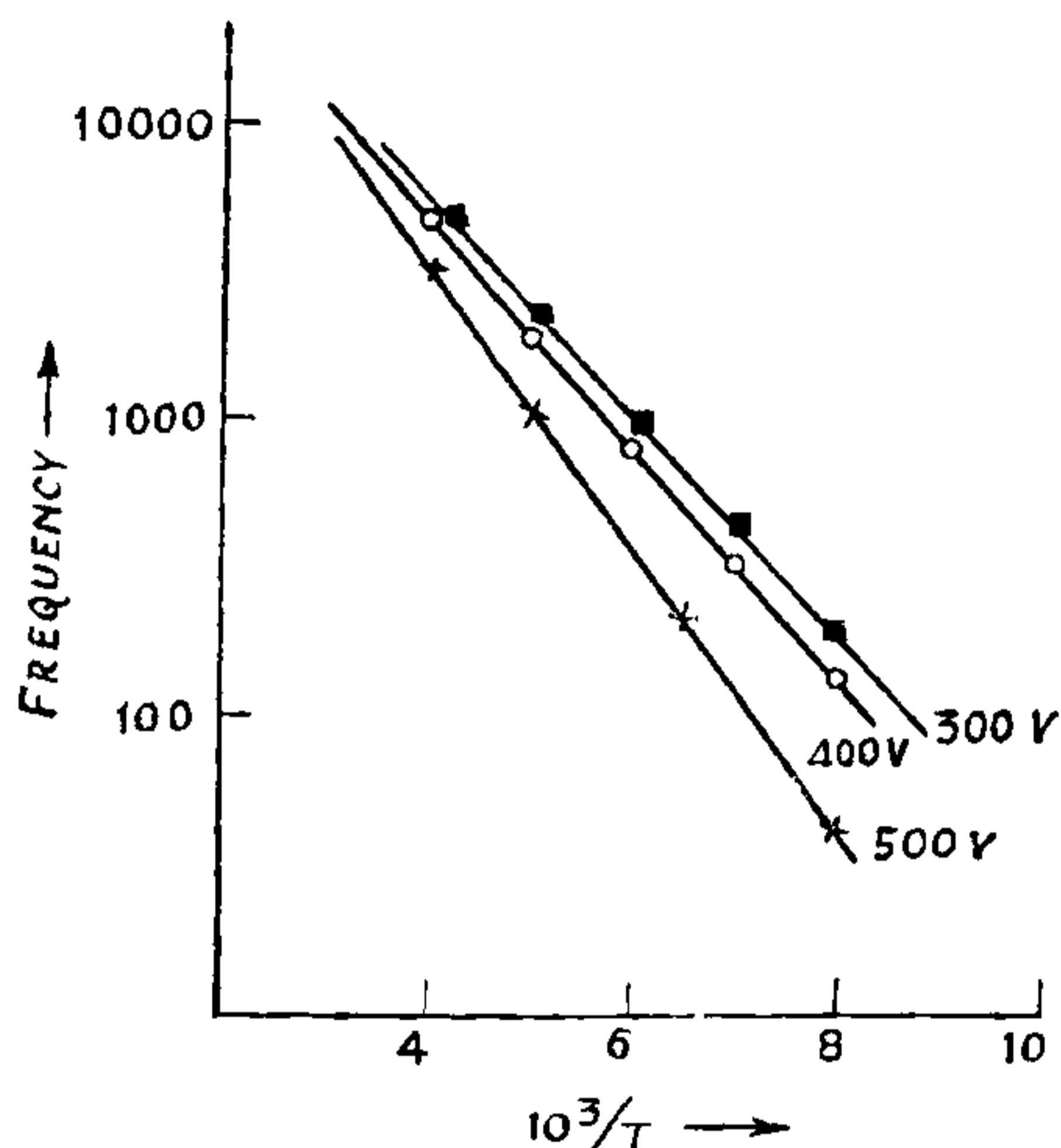


FIG. 2. Dependence of threshold frequencies of excitation with the temperature for/ZnO : Mn/. excitation voltages, which means, higher threshold frequencies are required at the lower voltages for excitation.

Voltage Dependence.—Increase in voltage enhances the brightness (Fig. 3) at different temperatures but no peak shift is observed. This peak is found around 20°C when the excitation field frequency is kept at 1.5 kc/s. At 600 volts, the brightness is enhanced considerably at low tem-

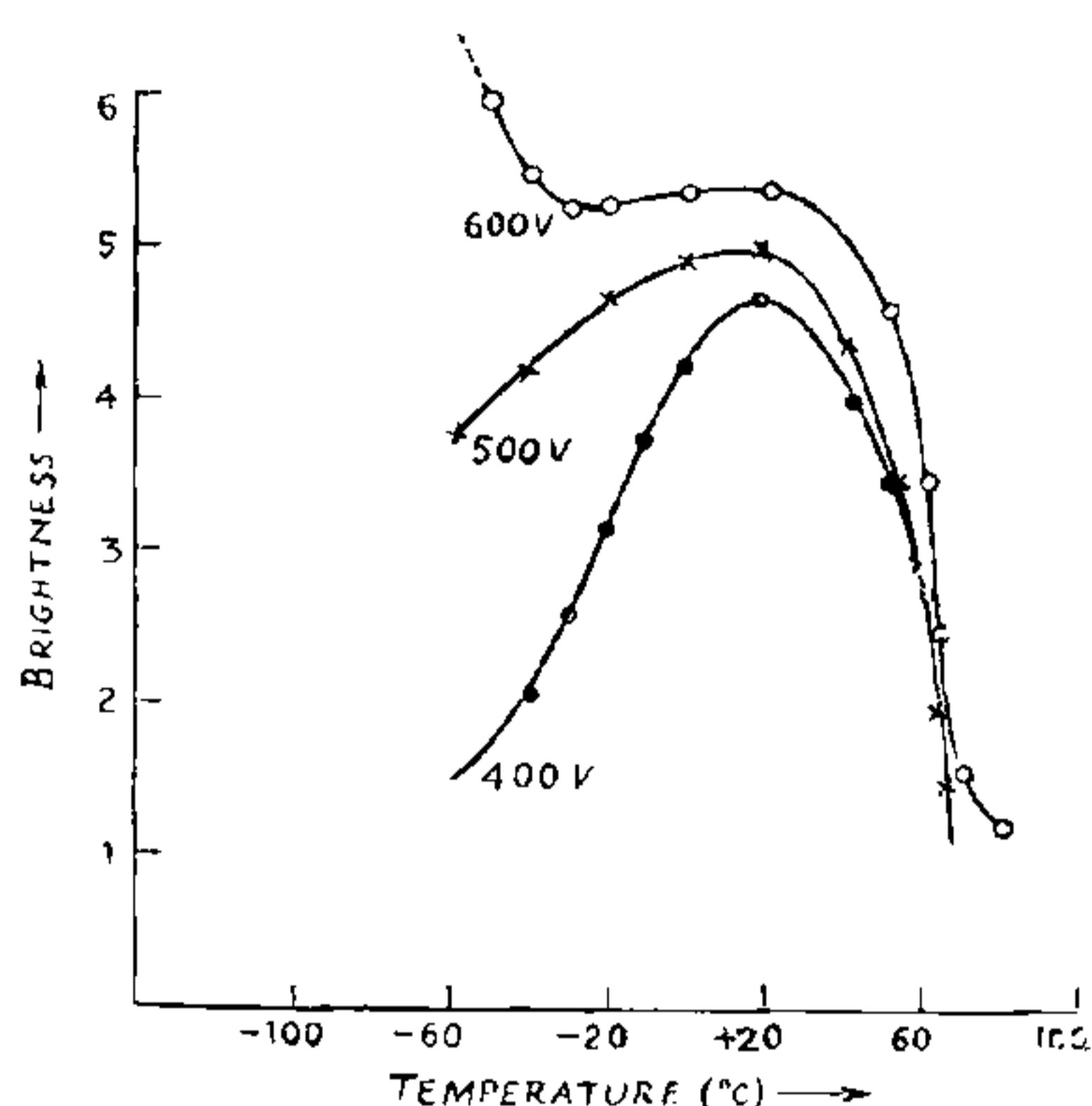


FIG. 3. Brightness vs Temperature curves for the electroluminophor/ZnO : Mn/ excited by different a.c. voltages with fixed frequencies (1500 c/s) of field.

1. Destriau, G., *Phil. Mag.*, 1947, 38, 700.
2. Gobrecht, H. *et al.*, *Z. Physik*, 1954, 136, 623.
3. Roberts, S., *J. Opt. Soc. Am.*, 1952, 42, 850.
4. Halsted, R. E., *Phys. Rev.*, 1954, 93, 349.
5. Neumark, G. F., *Ibid.*, 1956, 103, 41.
6. Mattler, J., *J. Physique Rad.*, 1956, 17, 42.
7. Thornton, W. A., *Phys. Rev.*, 1955, 102, 38.
8. Haake, C. H., *J. Opt. Soc. Am.*, 1957, 47, 881.
9. Osiko, V. V., *Opt. and Spect.*, 1959, 7, 459.
10. Nuvarejeva, V. V. *et al.*, *Ibid.*, 1964, 17, 42.
11. Georgobiani, A. N. *et al.*, *Ibid.*, 1963, 15 (1), 48.
12. *Proc. (Trudy) of the P. N. Lebedev, Phys. Inst.*, Vol. 50, Edited by D. V. Skobeltsyn.

2-HYDROXY-3,5-DICHLOROACETOPHENONE OXIME AS AN ANALYTICAL REAGENT : GRAVIMETRIC DETERMINATION OF COPPER, NICKEL AND COBALT

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ABSTRACT

2-Hydroxy-3,5-Dichloroacetophenone Oxime (HDCAO) has been found to be a good reagent for gravimetric estimation of copper, nickel and cobalt and for their separation from other ions. The composition of the complexes is 1 : 2 as determined by modified continuous variation method.

OXIMES have been used as analytical reagents for the gravimetric as well as spectrophotometric determination of a number of metal ions¹⁻³. In an earlier communication⁴, conductometric, potentiometric, micro-analysis and I.R. spectral

studies were reported for these metal complexes. The reagent has now been successfully employed for the gravimetric determination of copper, nickel and cobalt and their separation from a number of other ions.

EXPERIMENTAL

2-Hydroxy-3,5-Dichloroacetophenone Oxime (HDCAO) was prepared as described earlier¹. An ethanolic solution of the ligand was employed. Solutions of copper, nickel and cobalt salts were prepared from B.D.H. (A.R.) samples and standardized gravimetrically. Solutions of other ions were prepared from Reagent Grade samples. Systronic pH meter type 322 was used for pH measurement.

Determination of Copper.—The thiocyanate⁵ method suffers from the disadvantage of a low conversion factor and takes a long time (~ 6 hr) for complete precipitation. Salicylaldoxime and *o*-hydroxyacetophenone oxime complexes are somewhat soluble in ethanol. As a consequence, excess of reagent which gets precipitated is difficult to wash. But the complexes of HDCAO with copper, nickel and cobalt are insoluble in 60% ethanol and the excess of reagent that is precipitated can easily be washed. The pH ranges for complete precipitation and also separation of copper from nickel and cobalt are wider as compared to salicylaldoxime and *o*-hydroxy acetophenone oxime.

The pH of an aqueous solution (~ 100 ml) containing about 10 mg of copper was adjusted to known value using acetic acid and ammonia buffer. The solution was heated to 60–70° C and treated with an ethanolic solution of HDCAO (0.5%) dropwise (about twice the theoretical value) with constant stirring. The buff coloured precipitate was digested on a water bath for about 30 min. It was filtered while hot, through a sintered glass crucible (G-4) and washed with hot water. The precipitate was finally washed several times with 50% ethanol and was dried at 100–120° C to constant weight. It has been found that copper can be quantitatively determined in the pH range 3.0–10.0 although the precipitation starts at pH 2.0. The conversion factor (metal/metal complex) is 0.1267.

Study of Interference.—By suitable adjustment of pH, excess of the following cations (five to ten times) could be tolerated: Fe (II), Fe (III) Bi (III), Sb (III), As (III) (at pH 3.0); Ni (II), Co (II), Zn (II), Cd (II), Mo (VI), Hg (II), Mn (II), Mg (II), W (VI), UO₂ (II) (at pH 4.0). About 10–100 times of molar excess of several anions could be tolerated at pH 4.0 (PO₄⁻³, Cl⁻, Br⁻, I⁻, F⁻, B₄O₇⁼, SO₄⁼, S₂O₃⁼ and tartrate).

Determination of Copper in Alloys.—A known amount of the alloy (brass, aluminium-bronze, manganese-bronze) was dissolved in conc. HNO₃. The excess of acid was evaporated. The stannic oxide was removed by filtration. Copper was determined in the filtrate at pH 3.0, as described

earlier. The other ions did not interfere. It has been found that the percentage of copper obtained in different alloys using this method agrees with the reported values within experimental errors.

Determination of Nickel.—It has been found that HDCAO can precipitate (green) nickel quantitatively in about 100 ml solution containing 8 mg nickel ion in the pH range 5.0–9.0 using acetic acid and ammonia buffer for adjusting the pH. The experimental procedure for the precipitation of nickel was the same as described in the case of copper. The conversion factor is 0.1182.

Study of Interference.—Wherever possible, the interfering ions have been masked with suitable masking agents, e.g., Fe (III), Sb (III), Bi (III) by tartaric acid (1 gm). In some cases, the interference has been removed by changing the pH of the mixed solution, e.g., cations like Zn (II), Mn (II) (at pH 5.5); Cd (II), UO₂ (II), Mg (II), Mo (VI), W (VI), Hg (II) (at pH 6.0); Fe (III), Sb (III), Bi (III), As (III) (at pH 7.5) (from 5–10 times excess) and sufficiently large excess of anions like PO₄⁻³, Cl⁻, Br⁻, I⁻, F⁻, SO₄⁼, S₂O₃⁼, B₄O₇⁼ and tartrate (at pH 6.0).

Determination of nickel in alloys.—A known amount of the alloy (aluminium-bronze, high tensile brass and coin) was dissolved in conc. HNO₃ and the tin removed as SnO₂. The copper in the filtrate was first determined at pH 3.0 and the nickel was then estimated by raising the pH of the filtrate to 8.0.

Determination of Cobalt.—HDCAO has also been found to precipitate (orange) cobalt quantitatively. The pH of cobalt solution about 100 ml containing 9 mg of cobalt was adjusted to 8–9 using acetate-borax buffer. The experimental procedure for the precipitation of cobalt was the same as described in the case of copper. The precipitate was washed with hot water and finally with 25% alcohol. The conversion factor was 0.1186.

Study of Interference.—The cations Zn (II), Mn (II), Mg (II), Cd (II), As (III), Mo (VI), W (VI) (five to seven times) and excess of the anions Cl⁻, Br⁻, I⁻, SO₄⁼, S₂O₃⁼ and tartrate do not interfere in the determination of cobalt at pH 7.5.

From the solution, containing both copper and cobalt, the copper was precipitated as described earlier at pH 3.0 and from the filtrate cobalt was precipitated by the addition of more reagent and adjusting pH to 7.5.

Accuracy of the estimation.—Copper, nickel (5–50 mg) could be estimated with an accuracy of ± 0.3% while in the case of cobalt (10–50 mg) the percentage error was ± 0.4%. At lower concentrations of the metals (3–5 mg) the percentage error was about 5% higher.

The composition of the complexes as determined above and also by using modified continuous variation method⁶ is 1 : 2.

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1. Welcher, F., *Organic Analytical Reagent*, Vol. III, D. Van Nostrand Co., Inc., New York, 1947, 162, 239, 259.

2. Poddar, S. N., *Z. Analyt. Chem.*, 1957, 154, 254; 1957, 155, 327.
3. Katyal, M. and Singh, R. P., *Curr. Sci.*, 1962, 31, 373.
4. Gupta, S. P., Srivastava, S. K. and Lal, K., *Indian J. Chem.* (In press).
5. Erdy, L., *Gravimetric Analysis*, Part 2, Pergamon Press, London, 1965, p. 74.
6. Fenger, J., Siekieska, K. E. and Jensen, B. S., *J. Inorg. Nucl. Chem.*, 1971, 33, 4366.

ZIRCONIUM(IV) COMPLEXES WITH MULTIDENTATE SCHIFF BASES

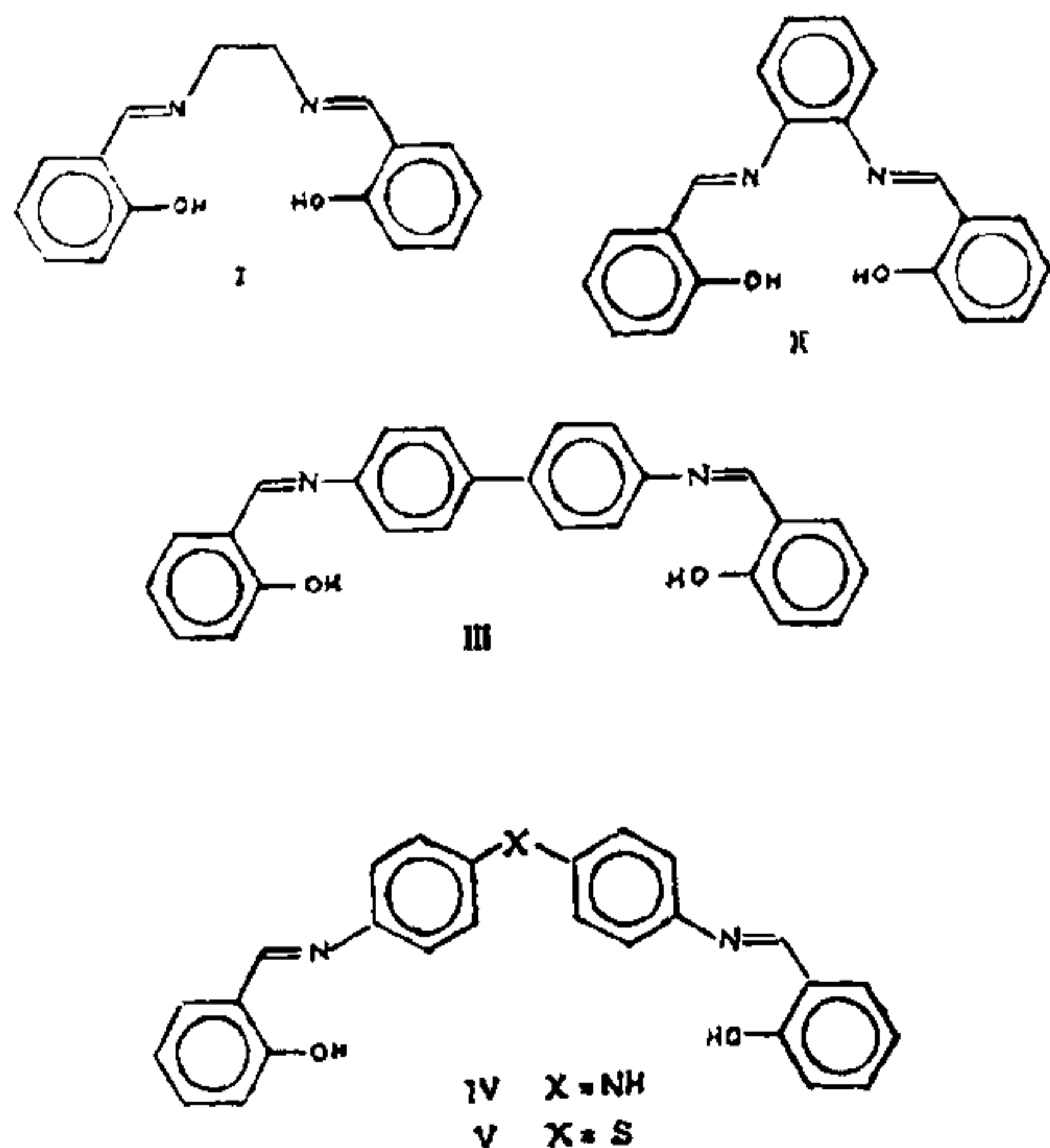
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INTRODUCTION

IN the previous papers we showed that zirconium exhibits coordination numbers five and eight when complexed with bidentate and tetradentate Schiff bases¹⁻³. Macarovici *et al.*⁴ have demonstrated that zirconium forms complexes of coordination number six with Schiff bases derived from benzidine. There is not much information on the zirconium (IV) complexes with multidentate Schiff bases⁴⁻⁵.

In this paper we report the synthesis and spectral study of a few zirconium (IV) complexes with multidentate Schiff bases shown below.



EXPERIMENTAL

Zirconyl chloride used for preparing the complexes was of Fluka make. *p, p'*-Diaminodiphenyl

sulphide was prepared by the known method⁶. Schiff bases were prepared by Biradar's method⁷.

Zirconyl chloride in methanol was treated with a slight excess of Schiff base in the same solvent. This mixture was refluxed for 2-3 hours on water bath. The complex separated out was filtered and washed free from the reagent with methanol, then with ether and dried in vacuum. The complexes were analysed for zirconium, nitrogen and chloride contents⁸.

RESULTS AND DISCUSSION

It is evident from the elemental analysis [Table I] that these bases form the complexes of 1 : 1 stoichiometry.

Infrared Spectra.—Infrared spectra of the Schiff bases and complexes in Nujol mulls have been taken with a Perkin Elmer 137 B spectrometer. The strong band in the region 1618-1613 cm^{-1} attributable to the C=N stretching is found in the region 1640-1626 cm^{-1} in these zirconium (IV) complexes. The shift towards higher frequency indicates coordination through the azomethine nitrogen.

The broad weak band in the region 2800-2700 cm^{-1} due to the intramolecular hydrogen bonded OH is not observed in the complexes and the band due to the phenolic C-O in the region 1280-1270 cm^{-1} is found around 1300 cm^{-1} . These observations show that the hydroxy groups of the base are involved in the bond formation. Analogous observations have been made by Kovacic^{9a} in copper (II) Schiff base complexes and Marvel *et al.*^{9b}.

It has been established that when a compound contains M=O, the infrared spectrum shows a narrow intense band in the region 1100-800 cm^{-1} whereas a broad intense band in the corresponding region indicates the presence of a polymeric M-O-M