CHAPTER 1

GENERAL INTRODUCTION

1.1 Introduction

In 1946, Schwarzenbach (1) noted that the ascertained end point in EDTA titration might be observed by the use of metal-sensitive indicators. As the consequence, the use of Eriochrome Black T (2) which was an o-hydroxyazo dye as metal indicator was introduced in 1946. These discoveries led to a search among organic compounds and several more metallochromic reagents were soon found.

Many substances have been proposed as complexometric titrations indicators and as metallochromes for spectrophotometric determination of metal-ions. Close, Belcher and West (3) described the investigation of a number of commercially available dyestuffs of the hydroxyazo type and showed that several of them could be used with advantages as complexometric indicators. Only one of the dyestuffs examined showed any specificity in its colour reaction with copper ion, this was Fast Sulphon - Black F (Fig.1.1). Cabrera (4) examined the potentialities of this reagent for the determination of trace amounts of copper. It was found that the reagent may be regarded to be comparatively more selective than other orthohydroxy-

azo dyes, which was probably due to the positioning of the hydroxyl groups at the ortho and peri positions with respect to the azo bond as against the usual o,o'-position.

O,o'-dihydroxyazo compounds are excellent metallochromic reagents, but are entirely unspecific in their reactions. Close and West (5) studied several closely related trishydroxybisazo dyestuffs such as Acid Alizarin Black SN (AABSN) and Acid Alizarin Black SE (Fig. 1.2) as metallochromic indicators for calcium in dilute solution. The former was found to be more satisfactory. AABSN was also used as a spectrophotometric reagent for the determination of copper (6) at pH 11.2 using glycine-ammonia as a buffer solution. The molar absorptivity of the copper-AABSN complex was 2.8×10^4 and cobalt, thorium, iron and bismuth were reported to interfere. Thorium, vanadium(V), vanadium(IV) and uranium were also determined spectrophotometrically using AABSN as a reagent (7). The molar absorptivities were 2.8×10^4, 1.85×10^4, 2.2×10^4 and 1.7×10^4 respectively.

In the studies of hydroxyazo metallochromic indicators, Close and West (8) devised a reagent cyclo-tris-7-(1-azo-8-hydroxynaphthalene-3,6-disulphonic acid) now known as Calcichrome (Fig.1.3) and recommended it as a highly selective chromogenic reagent for calcium. At pH 12 this reagent reacted only with calcium ions (ionic radius 0.99 A^o), whereas strontium (1.12 A^o) and barium (1.34 A^o) were too big to fit into this cage.

In the search for hydroxyazo dyes as spectrophotometric reagents for copper, Hosain and West (6) synthesised 2,6-bis(1,8-dihydroxy-3,6-disulpho-2-naphthylazo)-phenol-4-sulphonic acid (HR 7, Fig.1.4) and used it as a reagent for the determination of copper spectrophotometrically at pH 2-4. The molar absorptivity of the complex was 3.9×10^4 at 630 nm. This reagent was also used for the spectrophotometric determinations, at pH 4, of thorium, vanadium(V), vanadium(IV) and uranium (8). The molar absorptivities were reported to be of 5×10^4 (625 nm), 3.5×10^4(620 nm), 4.1×10^4(640 nm) and 2.5×10^4(625 nm) respectively.

1.2 Reason for Undertaking this Work

From the above information, it can be seen that Fast Sulphon Black F is a comparatively more selective o,o-dihydroxyazo dye. The occurence of selectivity for calcium ion in the case of Calcichrome dye shows the evidence that specificity for cations is possible among azo dyes though in rare cases.

It is hoped that specificity of azo dyes may be obtained by the syntheses of new dye molecules. Sensitivity of reaction may be increased by increasing the size of the dye molecule with extensively conjugated bond system in order to increase the light-capture cross section of the complex molecule. To achieve this, syntheses of bis-hydroxy-bis-azodyes are preferable to hydroxy-mono-azodyes.

The present work described the attempts to synthesis

bishydroxyazo dyes and investigation of their metallochromic properties as spectrophotometric reagents.

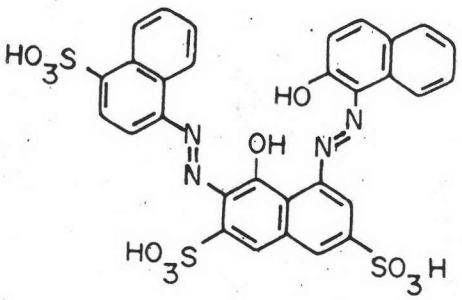
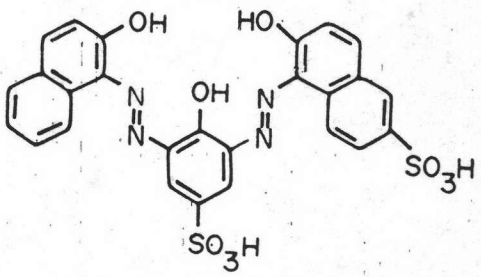


Fig 1.1 : Fast Sulphon Black F



Acid Alizarin Black SN (AABSN)

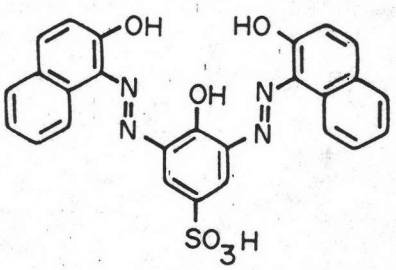


Fig 1.2 : Acid Alizarin Black SE

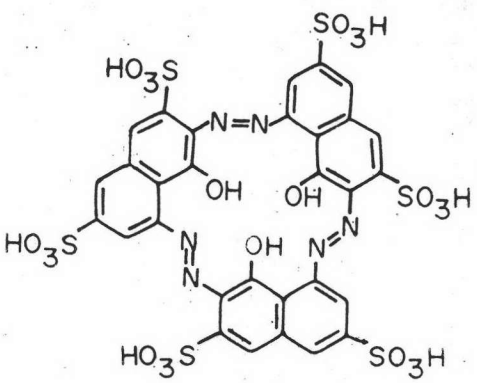


Fig 1.3 : Calcichrome

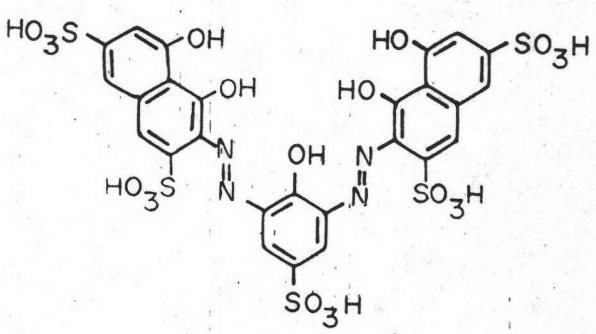


Fig 1.4 : HR 7