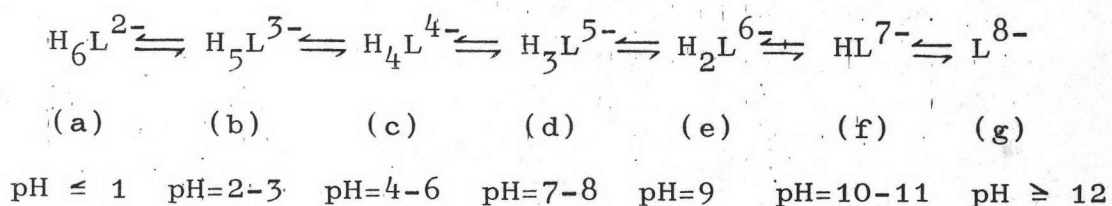




## CHAPTER IV

## CONCLUSION AND SUGGESTION FOR FUTURE WORK

In the present investigation, the 1,3-bis(1,8-dihydroxy-3,6-disulfo-2-naphthylazo)benzene (m-X dye) has been synthesised and studied the possibility to use it as a metallochromic reagent. m-X Dye is a bis-azo compound which is composed of two chromotropic acid groupings and one benzene ring as a nucleus. Depending on the acidity, it is proposed that the dye may exist as seven species in aqueous solution. Those species may be shown in the following equilibria and also in Fig 4.1.



In strongly acidic media, two protons are protonated at -N azo positions. The deprotonization appears in weakly acidic and neutral conditions. m-X Dye same as general bis-azo compounds in moderately acid solution (pH 1 up to 8) exists only in the azo form. In alkaline media (pH > 8), ionization destroys the symmetry of the molecule, an azo and quinone-hydrazone forms coexist and cause bathochromic effect. It is violet in colour as a result of the conjugation of both parts of the molecule and of the planar structure.

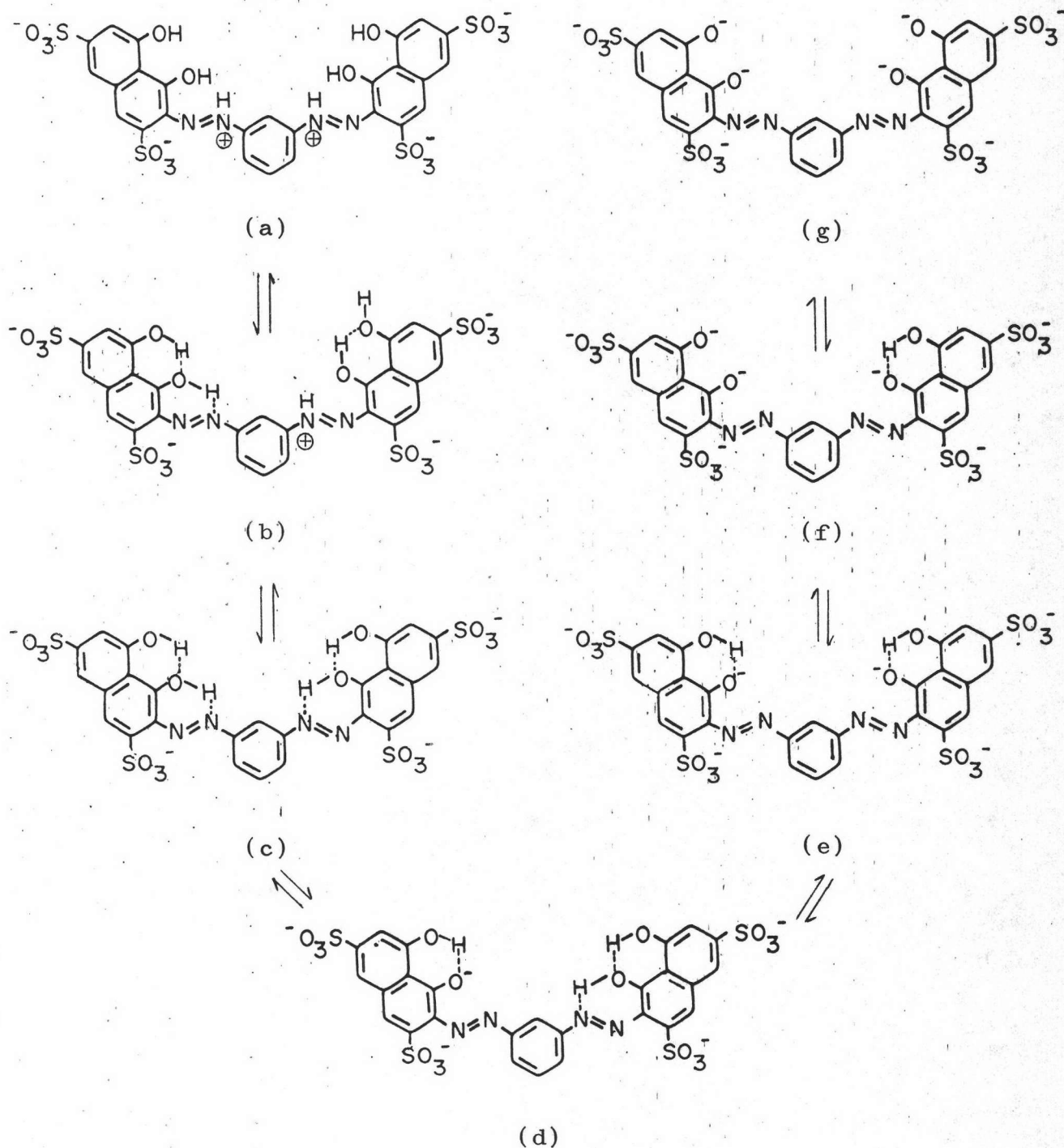
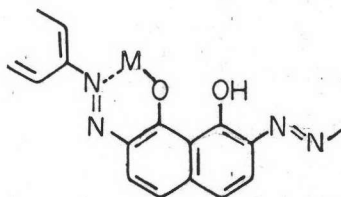
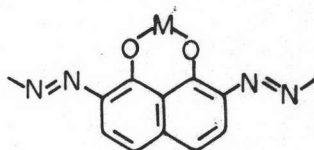


Fig 4.1 : Proposed structural formula of m-X dye species in aqueous solutions at various pH

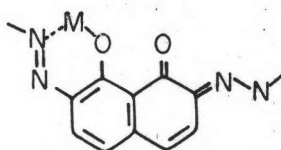
Metal complex formation of bis-azo dye can be described in three types(32,33). In the first, at pH 6-7 it is believed that the chelate formed in the positions shown below.



In the second type of reaction, occurring in alkaline solutions (pH 10-12, where the ionization of OH groups in the naphthylene ring occurs), the product is probably formed as follows

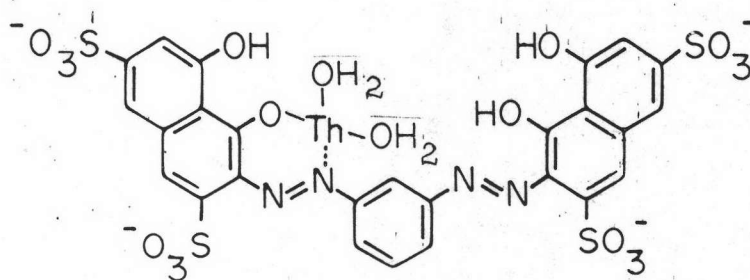


and the  $\epsilon$  max of the complex is generally not greater than  $4 \times 10^4$ . The third type of reaction occurs in solutions of rather low pH (2.5-3 and a little higher); the chelate formed has exceptionally high  $\epsilon$  values, up to  $1.8 \times 10^5$ . The following structure is suggested for these chelates :



For thorium - mX dye complex, the evidence for the structure of the complex was obtained from spectral studies, the method of continuous variation, the mole ratio method and the slope ratio method. It was found that thorium reacts with m-X dye at pH 4.0 to form a 1 : 1 metal-ligand complex. The following possible

structure may be assigned :



The complex is formed by thorium bonding to -O of one phenolic groups in chromotropic acid and to an azo -N. Although the second diazo component is not directly involved in metal chelation, it affects the reactivity of the functional groups and the absorption spectrum with the increase in radiant absorption of the metal chelate.

In the case of p-X dye, it is rather reasonable to assume that the complex formation with thorium(IV) is in the similar manner as the one of m-X dye since the conditions for chelate formation (colour development and pH) are the same. Unfortunately, the sensitivity of the thorium - pX dye system is considerably lower than the one of m-X dye, this is probably due to the presence of second azo grouping in the benzene nucleus thus makes this p-X dye less active toward various metal ions.

It is seen from this research work that 1,3-bis-(1,8-dihydroxy-3,6-disulfo-2-naphthylazo)benzene can be used as a spectrophotometric reagent for thorium. The developed method gives the molar absorptivity value at 610 nm. of  $1.3 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  of which is conventionally accepted as a sensitive method (34). Furthermore, in term

of specificity, through the control of pH of the solution the method may also be regarded as one of the reasonable selective methods. (see p.p.60-63)

It may be relevant to give suggestion for further study that if a series of bishydroxyazo compounds are synthesised by fixing the central nuclei of a system as being the benzene rings but varying the phenolic compounds which are used for coupling to azo groups (in place of chromotropic acids), some interesting reagents with significant metallochromic properties may be obtained.