

S U M M A R Y

SUMMARY

1- In the first chapter, an introduction on the literature survey of previous studies on the physical properties of mono-azo and bis-azo compounds and its chelates with transition metals is given.

2- The second chapter includes the experimental part of the work such as preparation of the azo-compounds under investigation, the stock solutions together with their standardization. It compares also information about the equipments used for the ir-, uv.-vis, ^1H nmr or esr spectroscopy, potentiometric and conductometric titrations, TGA measurements as well as the methods used for the studies and applications of azo dyestuff on nylon 6.

3- Chapter III includes the studies of electronic structure of ligands using the electronic spectra in organic solvents or mixed - aqueous buffers, ir and ^1H nmr spectra.

a- The electronic absorption spectra of the ligands in ethanol exhibit three different bands. These bands result from either local excitation due to π -electrons of phenyl ring or charge transfer transitions through the whole molecule. The change in the colour of the ligands or the position of the CT band in different organic solvents of protic and aprotic nature can be discussed in terms of different empirical solvent polarity parameters which are termed microscopic character e.g polarity (π), acidity (α), basicity (β) of solvent molecules as well as E_T or Z-values of them. Also, the so-called macroscopic solvent polarity parameters which characterise the bulk properties

of the solvent medium such as dielectric constant or refractive index were employed. These parameter are plotted against λ_{\max} or $\Delta \nu$ (cm^{-1}) and it was found that no main factor predominates and can affect directly the change of band position. But the contribution of these factors as well as the solute - solvent interaction through H-bond formation play important role in changing the position of the bands.

b- In aqueous buffer solutions of various pH values containing 30 % (V/V) ethanol or dioxane, the CT bands of the ligands exhibit a shift in λ_{\max} and variation in molar extinction coefficient indicating that the aqueous medium may ionise these ligands and consequently changes their formula and subsequently the colour. The pK_a values were determined by applying four different methods. The pK_a values are affected on replacing the methyl groups by the phenyl one in the β -diketone part of the azo molecules.

c- The ir-spectra show that the ligands exhibit an intramolecular H-bond and the shift in band position of each of ν_{OH} or $\nu_{\text{C=O}}$ or that of N=N gives a qualitative indication for the strength of H-bond. Also, keto-enol tautomerism is liable to exist with these compounds in the solid state.

d- The ^1H nmr spectra of the free ligands are studied in CDCl_3 or DMSO-d_6 before and after deuteration. The main signals due to the protons of phenyl ring, CH_3 , CH , OH , COOH groups and the enolic OH in the molecules give satisfactory structural informations.

4- In chapter IV, the chelation of mono-azo dyes with Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} ions are studied in solution and in solid state.

a- conductometric titrations of mono-azo dyes with metal ions in ethanol solution are measured to determine the stoichiometry of the chelates.

ligands, at constant time (30 min.) and constant temperature (100°C), show that 8% of Fe^{3+} ion improves the fastness properties of dyed nylon by I_b , also 4% of Fe^{3+} ion is a good percent for fastness properties for dyed nylon by I_c , II_a , IV_a and IV_b . The 6% of Fe^{3+} ion is suitable for dyed nylon by III_a to the fastness properties. The studies show that 4% of Ni^{2+} ion is suitable treatment percent with dyed nylon by I_b and I_c , whereas 6% of Ni^{2+} is a fair good to improve the fastness of dyed nylon by II_a and III_a . At the same time the results show that 2 and 8% of Mn^{2+} are suitable percent for good fastness of nylon treated by IV_a and IV_b respectively.

2- The time of treatment of dyed nylon by metal ions (5%) has great effect at 100°C. 30 min. is suitable time for treatment of dyed nylon by I_b and III_b by Ni^{2+} ion, also Ni^{2+} ion improve the fastness properties at 120 min. for dyed nylon by II_b . 30 min. is a suitable time for treatment of dyed nylon by I_c , II_b , III_b and IV_b with Fe^{3+} ion, also the latter improves the fastness properties at 60 and 240 min. for dyed nylon by IV_a .

3- The treatment of dyed nylon (by the ligands under investigation) with the metal ions (5%) at 30 min. is performed at different temperatures. The latter has a great effect on the fastness properties of dyed nylon. The results show that at 80°C Ni^{2+} ion improve the fastness properties of dyed nylon by I_b and III_c whereas at 40°C it improves that of II_c . Also Fe^{3+} ion improves the fastness properties of dyed nylon by II_c , III_c and IV_a at 60°C, I_c at 40°C and IV_b at 80°C.

4- The treatment of dyed nylon with 10% metal ions at 30 min. and 100°C shows that Fe^{3+} ion is better than other metal ions for dyed nylon by I_a . Co^{2+} ion gives better fastness properties than other metal ions in coupling with II_{a-c} and III_a on nylon. Cu^{2+} ion is also a better one than other metal ions when coupled with III_b or III_c on nylon 6.