

SUMMARY

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- 1-In the first chapter a literature survey of the previous studies on azo compounds and their complexes with different metal ions is given. This survey includes spectrophotometric, conductometric and potentiometric studies on azo compounds and their chelates. It includes also the use of some azo compounds as analytical reagents for detection and determination of some transition metal ions spectrophotometrically.
- 2-The experimental part (Chapter II) includes the preparation of the azo compounds under investigation. It comprises also information about the instruments used for spectrophotometric, potentiometric, conductometric, ir, ^1H -nmr, magnetism as well as thermal analysis measurements.
- 3-Chapter III includes the results and discussion and consisting of four parts.
 - (A)The first part includes the studies of the electronic absorption spectra of the free ligands in the uv and visible regions using ethanol as solvent. The bands exhibited in the uv spectra of the compounds are assigned according to the nature of the band and spectral behaviour in different organic solvent. The band A is due to ($^1\text{L}_a \leftarrow ^1\text{A}$) and B is due to ($^1\text{L}_b \leftarrow ^1\text{A}$) transition of phenyl ring, respectively. On the other hand, the band C at 350 - 450 nm ranges represents a charge transfer transition through the molecule. The position of the CT band in different organic solvents of protic and aprotic nature is discussed in terms of different

empirical solvent polarity parameters and macroscopic solvent polarity parameters.

The electronic absorption spectra of the free ligands are studied in ethanolic buffer solution of different pH values and their ionization constants are evaluated. Also the ir and ^1H -nmr spectra of the compounds under investigation are studied and the different functional groups are assigned like $\nu_{\text{C=O}}$, $\nu_{\text{N=N}}$, ν_{CH} and ν_{OH} . On the other hand, the ^1H -nmr spectra for different types of hydrogen protons expected for the compounds under study (I-VI) can be enumerated, determined and correlated to the molecular structure of the compounds.

(B) This part is concerned with the studies in solutions of complexes formed between azo compounds and some transition metal ions (Cu^{2+} , Ag^+ , and Au^{3+}). The studies include spectrophotometric, conductometric and potentiometric techniques. The stoichiometry and stability constants of metal complexes are also evaluated from spectrophotometric methods namely the molar ratio and continuous variation methods. The optimum conditions for the complex formation are investigated. Universal buffer of 40% (v/v) ethanol was found to be the best medium for spectrophotometric studies. Optimum pH values, suitable wavelength as well as sequence of addition were also studied. From conductometric measurements the stoichiometry of different complexes is obtained. Potentiometric titrations of azo compounds with Cu^{2+} , Ag^+ and Au^{3+}

ions are performed in a medium of perchloric acid and sodium perchlorate. The proton-ligands stability constants $\log K^H$ are determined as well as the formation constants of complexes ($\log K_M$). The results obtained indicate that a satisfactory agreement is observed between stability constant values evaluated using spectrophotometric and potentiometric methods.

(C) Part C of chapter III includes studies of the solid chelates which contain elemental analysis molar conductivity measurements, TGA, DTA, ir, magnetic measurements, and electronic absorption spectra. The molar conductance of complexes in DMF shows that these chelates are electrolytes in nature. The chemical formula of solid chelates were determined using the data obtained from thermal methods of analysis (TGA and DTA) as well as dehydration and elemental analysis. The ir spectra of metal chelates are studied and compared with those of the free ligands indicating that the coordinate and covalent bonds occurs through the oxygen atoms of carbonyl groups and the metal ions. The ir spectra of the metal chelates exhibit a very broad band around 3300 cm^{-1} which is due to the water molecule coordinated to the central metal ions. The magnetic susceptibilities of some representative solid Cu^{2+} -chelates are measured using the *GOUY* method, from which the magnetic moments (μ_{eff}) and the number of unpaired d-electron in the Cu^{2+} -ion are determined. The stereochemistry of these chelates were then detected

using *Paulling's* theory. The absorption spectra of some selected solid chelates are studied in both DMF and nujol mull. The variation of the position of the CT band in the two media indicates the variation of the environment of the central metal ion in DMF solution than in the solid state. The CT band due to $L \longrightarrow M$ or $M \longrightarrow L$ transition appears at longer or shorter wavelength to CT band of the free ligand confirming the interaction between the metal ions and the ligands.

(D)The part D include the analytical microdetermination of the metal ions(Cu^{2+} , Ag^+ and Au^{3+}) with azo compounds under investigation using the spectrophotometric techniques (*Beer's* and *Ringbom* methods). It includes also the effect of ligands concentration, the effect of foreign ions on the absorbance and also the use of such compound in the micro-determination of metal ions under consideration.