spectrohotometric and analytical studies of some chlates of ace naphthenone monop henyl hydrazone derivatives with transition metaliows

gamal owes el sayed

1 - In the first chapter, a literature survey of the previous studies on hydrazones and their complexes with different metal ions is given. This survey includes polarographic, spectrophotometric, poten-tiometric and conductometric studies on hydrazorie compounds and their chelates. It includes also the use of some hydrazones as analytical reagents for detection and determination of various metla ions.2 - The experimental part (chapter II) includes the preparation of the compounds under investigation. It comprises also informations about the equipments used for polarographic, spectrophotometric, poten-tiometric, conductometric, ir, nmr as well as thermal analysis.3 - Chapter III which includes the results and disscu-sion consists of four parts, the first of them is part (A) which contains the polarographic andspectrophotometric studies of the free ligands.(a) The polarographic behaviour of the compounds under concideration is studied in ethanolic buffer solutions over the pH range 2-12. The results show that the reduction process of these compounds is mainly controlled by diffusion for ligand I and IIand by diffusion with some adsorption contribution for ligand III. The results of analysis of the polarographic waves denote that the rate-determin-ing step of the electrode process involves one electron in acidic solutions and two in alkaline ones. The polarograms obtained for different concentrations of the ligands indicate the validity cf Ilkovic equation and the possible application of the polarographic method for the determination of these compounds.(b) The electronic absorption spectra of the ligands are studied in ethanolic buffer solutions and their ionization constants are evaluated.The electronic absorption spectra of the free ligands in pure ethanol -exhibit three different bands. These bands result from local excitation of Tr electrons of the phenyl ring and charge transfer transitions through the whole molecule. The posi-tion of the CT band in different organic solvents of protic and aprotic nature is discussed in terms of different imperical solvent polarity parameters and macroscopic solvent polarity parameters.4 - Part (B) of chapter III includes studies on the metal chelation of the hydrazone compounds under investigation and Co2+, Ni2+, Cu2+, La3+, Gd3+ andPt 4+ .ions in solution. The studies include conduc-tometric, potentiometric, polarographic and spectrophotometric techniques. from coriductometric measurements the stoichiometry of different chelates is obtained. Potentiometric titration of hydrazone compounds with Co2+, Ni2+, Cu2+, La3+and Gd3+ions are performed in a medium

of perchloric acid and sodium perchlorate. The proton-ligand stability constants pKH are determined as well as the forma-tion constants of the chelates. from the data of the polarographic study of the complexes of Co2+, Ni2+ and Cu2+ with ligands I, II and III in buffered solutions containing 30% (v/v) ethanol, the values of the stability constants are given. The stoichio-metry and stability of metal chelates are also evaluated from spectrophotometric methods namely the molar ratio, straight line and continuous variation methods. The results obtained indicate the satisfactory agreement is observed for stabi-lity constant values obtained using the three different methods.5 - Part (C) of chapter III contains the studies of the solid complexes which include elemental analysis, molar conductivity measurements, TGA, DTA, ir, 1Hnmr, electronic absorption spectra andmagnetic measurements. The molar conductance of complexes in DMF shows that some complexes are covalently bonded and the others are ionic in nature. The chemical formula of the solid chelates is determined using the data obtained from TGA, dehydration and chemical analysis. The ir-spectra of the metal chelates are studied and compared with those of free ligands which indicate that coordination and covalent bonds occur through carbonyl-oxygen, the nitrogen atom attatched to the phenyl ring and the oxygen atom of the carbo-xylic group (ligand I) and that of the methoxy group (ligand II).The 1H-nmr spectra of La3+ complexes with the ligands under investigation are studied in deute-rated DNS° and compared with those of the free ligands. The main signals due to the protons of the phenyl ring, CH, NH, COOH or CH3 groups are detected. It is found that the signals of protons of the NH group completely disappeared indicating that complex formation takes place through proton elemination from the imino group. The disapperance of the signal due to the proton of the carboxylic group of compound I indicates that this ligand acts as dibasic bidentate one.The electronic spectra of the solid chelates are studied in nujol mull and DMF. The spectral data shows that V(cm-1) of the CT band of metal chelates suffers red or blue shift compared to those of the free ligands, the fact which confirms that this series of ligands interact with the metal ion forming solid chelates. On the other hand, the electronic spectra of Co2+, Ni2+ and Cu2+ complexes in the solid state show some weak bands corresponding to the d-d transition within the complex from which, and by the aid of the data obtained from magnetic measurements, the geometry of the complex is defined.6 - Part (D) of chapter III includes the polarographic micro determination of Co2+, Ni2+ and Cu2+ ions using the hydrazone compounds under consideration. It includes also the use of such compounds in the spectrophotometric determination of Co2+, N.2+, Cu2+, La3 , Gd3+ and Pt4+ ions.