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Electrochemical behaviour of some transition metal complexes of thiosemicarbazones

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ABSTRACT

Objective: By this research work we tried to monitor UV-VIS spectral and structural changes accompanying electron transfer, the electrochemical properties of metal complexes particularly with sulphur donor atoms have been studied

Materials & Methods: The polarograph measurements were made on the degassed (all solution) was deoxygenated by passing nitrogen into DMF (dimethyl formamide) solution (10-3 M) for 10 minutes prior to the recording of polarograms. Solution (10-2 M) containing TEAFB (Tetraethyl ammonium fluroborate) was used as the supporting electrolyte. The three-electrode system consisting of drooping mercury (working), platinum wire (counter) and K/KCI (reference electrodes).

Results: The complex formation of thiosemicarbazones in the presence of Fe(II)ions was observed for both Fe(II)and Fe(III). The processes studied may help in understanding some of the features of the binding mechanism between copper ion and nucleic acid. The study will also contribute to a better understanding on the binding of Zn(II)and Fe(II)ions in biological systems.

Conclusion: By this research work we described the polarographic and spectroscopic behaviuor of thiosemicarbazones with of Fe(II)and Zn(II). Polarographic and electronic spectroscopy measurements have proved the complex for mation of thiosemicarbazones with metal ions.

Keywords: electrochemical properties; DMF; TEAFB; working electrodes; reference electrodes.

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1. INTRODUCTION

Thiosemicarbazone ligands, derived from the combination of a thiosemicarbazide and an aldehyde or ketone, a useful ligand type for obtaining coordination spheres with mixed N/S donors. Thiosemicarbazones and its metal complexes is clinically the most used sulfo drug in medicine as an antibacterial compounds. The transition metal complexes containing thiosemicarbazones derivatives have been extensively reported in the literature due to being more effective and desirable drugs than sulfonamides. Trace metals are important in many biological systems. In particular the interaction of divalent ions with nucleic acids plays an essential role in promoting and maintaining their functionalities. Among the metal ions, Fe(II)is the most effective available divalent ion for binding to organic molecules. These effects encourage us to study the interaction of pyrimidine contained sulfonamides especially with Fe(II)and Zn(II)ions considering that they are important in many biological systems. ^{4}N and ^{3}NH provide potential binding sites for metal ions, and any information on their coordinating properties is important to understand the role of the metal ions in biological systems. Biological activities of metal complexes differ from those of either ligands or the metal ions and increased and/or decreased biological activities have been reported for several transition metal complexes, like Fe(II)and Zn(II). The activity of these compounds is strongly dependent upon the nature of the heteroatom ring and the position of attachment of thiosemicarbazone to the ring as well as the form of the thiosemicarbazone moiety. These have been studied extensively due to their flexibility, selectivity and sensitivity towards the central metal atom, structural and similarities with natural biological substances and the presence of imine group (-N=CH-) which imparts the biological activity.

2. EXPERIMENTAL

All the chemicals were of analytical reagent grade and were commercially available and used as received. Thiosemicarbazide and ethanol were used for the preparation of the ligands (L). Metal ion solutions (1 × 10–3 M) were prepared from metal salts in ultra-pure triply distilled and deionized water. Owing to the insolubility of thiosemicarbazones (L) in aqueous solution, ethanol should be added to the solution (1 × 10–3 M) and was prepared fresh everyday by dissolving an accurate weight of the ligands in 10% (v/v) ethanol water mixture and protected from light and air. Solutions with lower concentrations were prepared by dilution with deionized triply distilled water. TEAFB (Tetraethyl ammonium fluroborate) act as supporting electrolyte, Different pH values were obtained by adding varying amounts of sodium hydroxide solution (0.5 M) into the sample solution, to obtain a pH range of 2–11. The polarographic measurements were recorded with a systronic polarograph Model 1634 coupled with Epson dot-matrix printer. Static mercury dropping electrode unit equipped with a platinum auxiliary electrode and a saturated KCl reference electrode. A digital pH meter (systronic MK VI) was used for monitoring the pH. Electronic spectra were recorded on a Unicam V2-100 UV-Vis spectrophotometer in the range of 200–900 nm with 1 cm cell length. Before each polarographic measurement, the supporting electrolyte solution was purged with nitrogen for 10 min. A known volume of a standard solution of the ligand was added to the polarographic cell, which was closed, deaerated, and blanketed with oxygen free nitrogen and the polarograph is recorded with supporting electrolyte. The addition of metal(II) complex solution to the cell with supporting electrolyte, and analyses the sample with polarograph and polarograms are recorded. All results were obtained at room temperature (approx. 25°C) with a nitrogen atmosphere maintained above the solution surface. The potential scans were recorded. Each measurement was carried out on a fresh mercury drop (working electrode). Electronic spectra of in aqueous solutions were recorded to follow the changes in absorbance at the wavelength of the maximum absorption.

3. RESULTS AND DISCUSSION

Electrochemical Behaviuor

Free ligands (L)

The polarograms of thiosemicarbazones in 0.04 M B–R buffer (pH 7) showed three reduction peaks at 0.01, –1.32 and –1.55 V, respectively (Fig.I). It has been observed that the peak potentials of thiosemicarbazones shift slightly towards more negative potentials if its concentration increases. In the polarograms, the peak at 0.01 V is, to our knowledge, not reported in the literature. Although this unexpected abrupt peak at 0.01 V could not be explained by the reduction of functional group in thiosemicarbazones, it could be attributed to the reduction of a mercury–thiosemicarbazones complex which had formed at the electrode surface. This is also supported by the solid state study of Hg(II) complex with thiosemicarbazones, where it is reported that Hg(II)–thiosemicarbazones complex is coordinated through the sulfonamide nitrogen, sulfonyl oxygen atom and pyrimidinyl nitrogen atom. The anodic peak of Hg(II)-thiosemicarbazones complex can be clearly seen in Fig. 1. The anodic peak at –0.04 V is attributed to the formation of Hg(II)-thiosemicarbazones complex adsorbed on the mercury electrode surface. This complex is formed by the oxidation of mercury in the presence of sulfamethazine. It is well known that at the determination of some sulfonamides, their adsorptive properties on the Hg electrode were analytically used.

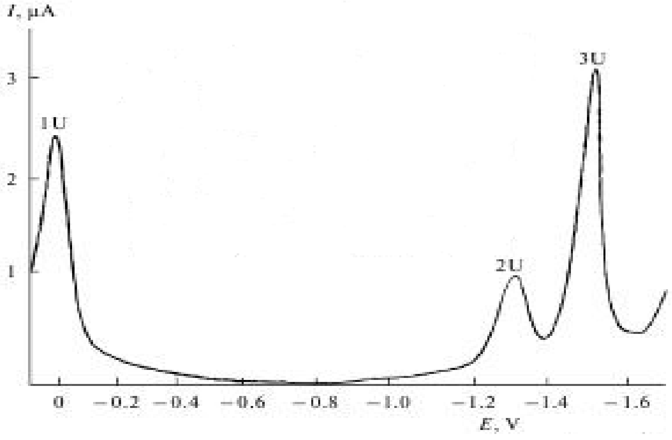

Fig.1- Polarograms of ligands

Finally, it can be said that thiosemicarbazones has an adsorption property on mercury electrode. In the case of thiosemicarbazones the peak may be attributed to the reduction of Hg(II) bound in the adsorbed Hg(II)-thiosemicarbazones complex which could be formed by the interaction between the positively charged mercury surface and the heterocyclic nitrogen atom of the pyrimidine moiety. It has been reported that compounds possessing azomethine group are polarographically reducible. The peak at –1.32 V is attributed to irreversible reduction of the azomethine group of the substituted pyrimidine ring of thiosemicarbazones. The reduction of the azomethine group involves two electrons and two protons. In the reduction process, a proton is bonded to the heterocyclic nitrogen at substituted pyrimidine, the other one is involved in reduction of one double bond of the pyrimidine ring. The peak at –1.55 V can be attributed to the reduction of the –SO2NH– group in the thiosemicarbazones. It has been reported that several arylsulfone compounds show polarographic reduction peaks at potentials ranging from –1.4 to –2.1 V. In general, the pH of the electrolysis medium is one of the variables that commonly and strongly influence the shape of the polarograms, and therefore it was important to investigate the effect of pH on the electrochemical behaviuor of the drug. The concentration of thiosemicarbazones (1 × 10–4 M) was maintained constant, and analyze is done at variable pH from 2 to 12 (Fig. 2). The investigation of pH of B–R buffer (pH 2–12) showed that thiosemicarbazones exhibits two reduction peaks most probably originating from reduction of the azomethine group of the substituted pyrimidine ring and from the reduction of the –SO2NH– group in the thiosemicarbazones at pH values lower than 5.5, whereas it has three cathodic peaks over pH 6. In alkaline medium (pH ≥ 10), no reduction peaks were seen, except for the peak at 0.01 V. The peak potentials and the peak currents of the cathodic peak at 0.01 V are strongly influenced by the pH of the solution. Due to the weak interaction of the adsorbed neutral thiosemicarbazones molecule with mercury, no peaks are seen at pH < 6. This phenomenon can easily be explained by the fact that the formation of deionized thiosemicarbazones which are stronger complexing agents than uncharged thiosemicarbazones occurs at pH ≥ 7. As the pH (2–9) increased, the peak potentials at –1.32 and –1.55 V were observed to shift towards more negative values indicating the existence of a protonation reaction coupled with the thiosemicarbazones reduction process. The current of the peak at 0.01 V was observed to increase with increasing pH in the pH range of 6 and 7.5, while it becomes pH independent at pH > 7.5. The currents of the peaks at –1.32 V and –1.55 V depend on the hydrogen ion concentration of the supporting electrolyte.

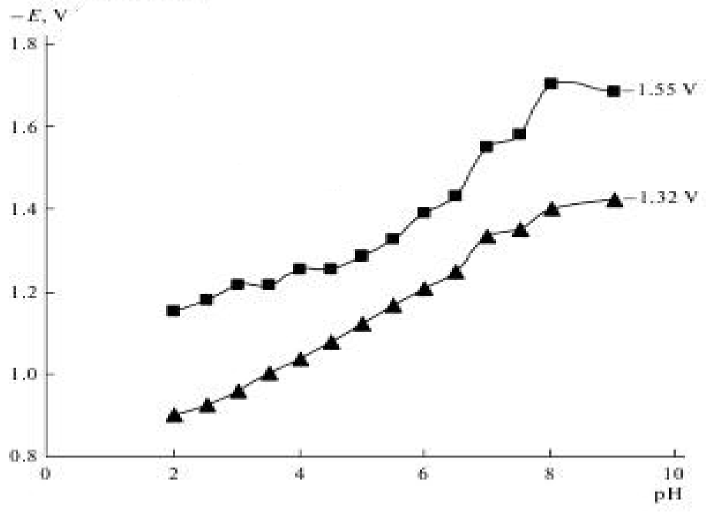

Fig.2- Analyze at variable pH

Ligands in the Presence of Fe(II)

The polarograms of 5 × 10–6 M Fe(II)ions in B–R buffer (pH 8) in the absence of thiosemicarbazones has a peak at a potential of –0.106 V. This peak was attributed to the reduction of Fe(II)ions to Fe(III). The addition of 5 × 10–6 M Fe(II)to the electrolyte containing 1 × 10–4 M thiosemicarbazones ions, over the potential range from 0.10 to –1.8 V, strongly modified the polarograms and two quasi- reversible peaks at –0.18 V and –0.35 V occurred (Fig. 2). With increasing the Fe(II)concentration (5 × 10–6 – 5 × 10–5 M), the potential of the peak at – 0.35 V is shifted towards slightly negative potentials and fixed at –0.38 V. The shape of this peak is well defined at –0.38 V. As can be seen in Fig. 8, thiosemicarbazones forms the complexes of both Fe(III) and Fe(II)ions. The behaviuor of the redox couple Fe(II)/Fe(III) in electrochemical reactions depends strongly on the presence of ligands. Indeed the redox mechanism Fe(II) may include the appearance of Fe(III) species if preferential stabilization of copper in this oxidation state takes place due to complex formation. However, the stabilization of Fe(III) species may also be due to d–π interactions between the copper, the d-orbitals and the aromatic π system. Similar behaviuor has already been observed for copper in the presence of some pyrimidine bases [34]. We propose that the first composed peak at –0.18 V corresponds to two processes: the reduction of Fe(II)L to Fe(III)L and the reduction of Fe(III)L to copper metal. The second peak at –0.38 V is attributed to the reduction of Fe(II)L2 complex to the copper metal. The currents of the cathodic peaks at –0.18 and –0.38 V showed a linear increase up to the Fe(II)concentration of 2.5 × 10–5 M; however, above this concentration, a plateau region was observed. Data obtained under these conditions show that the predominance of the copper complex increases with increasing Fe(II)concentrations. Adsorbed mercury complex in the presence of Fe(II)is transformed into an adsorbed copper complex. As a result of the formation of the copper complex, the peak current of free thiosemicarbazones (0.01 V) decrease with increasing Fe(II)concentration.

Ligands in the Presence of Zn(II)

The polarograms of Zn(II)in the absence of thiosemicarbazones is characterized by a cathodic peak at –1.08 V at 0.04 M B_R buffer (pH 6). The peak was inferred from irreversible reduction of the hydrated Zn(II)ions (Fig. 3). In the presence of thiosemicarbazones, the similar results to that with Co(II) ions have been observed with Zn(II)ions. It was noticed from the experimental steps that the thiosemicarbazones peak currents decreases (about 68 percent for the peak at –1.55 V) with addition of Zn(II)solution (5 × 10–5 – 8 × 10–4 M) to the cell containing 1 × 10–4 M thiosemicarbazones and that of the Zn(II)simultaneously increased, The potential and current of the peak at –0.77 V are dependent on the nickel concentration. The current of the peak at –0.77 V increases linearly with increasing Zn(II)concentration and then reaches plateau region, the peak potential shifting in a positive direction. Also, shifting peak potentials are indicative of the formation of labile complexes. By this we can concluded that the effect of Zn(II)concentration on the catalytic current is much smaller than that of Fe(II)concentration in the presence of thiosemicarbazones with fixed concentration[16]. According to the effect of metal ion . concentration, the similar results were also obtained in the Zn(II)-thiosemicarbazones complex system. This case indicates the electrochemical reduction of metal ions catalysed by adsorbed ligands. These experimental results also verify a decrease in the free thiosemicarbazones concentration and decreasing the surface excess of the adsorbed Hg-thiosemicarbazones complex. Because, it was observed that the peak currents of thiosemicarbazones and Hg–thiosemicarbazones complex decreased by increasing Fe(II)or Zn(II)concentration. The irreversible peak at more positive potential (–0.77 V) than that of the hydrated Zn(II)ions (–1.09 V) originates from the catalytic reduction of complexed Zn(II)with thiosemicarbazones. Thiosemicarbazones has catalytic activity on the reduction of Zn(II). It may be concluded that the polarographic process is the reduction of Zn(II)catalyzed by the formation of a complex between Zn(II)and thiosemicarbazones adsorbed on the electrode surfaced. The reduction of nickel ion is preceded by the elimination of an aqua molecule from the coordination sphere. Because this step requires high activation energy, the electrode reaction occurs only with the application of a very large overvoltage. However, in the presence of certain ligands present at the trace levels, the overvoltage is decreased. In this case, the reduction of the complexed nickel ions (represented as NiL2) occurs more readily at a more positive potential than that of Zn(II)hydrate (–1.09 V).

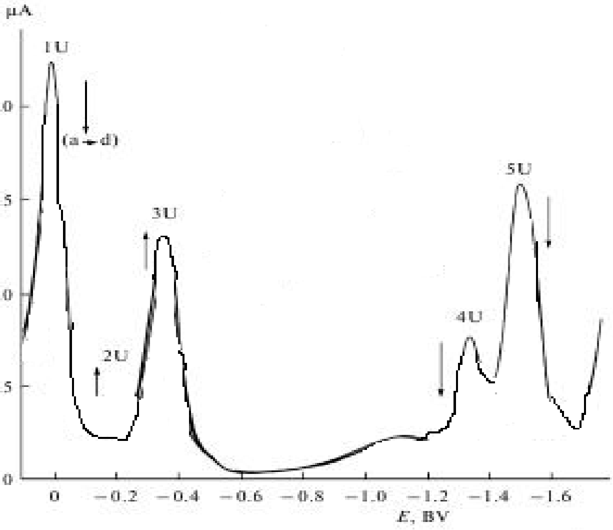

Fig.3- Polarograms of complex of Fe(II)

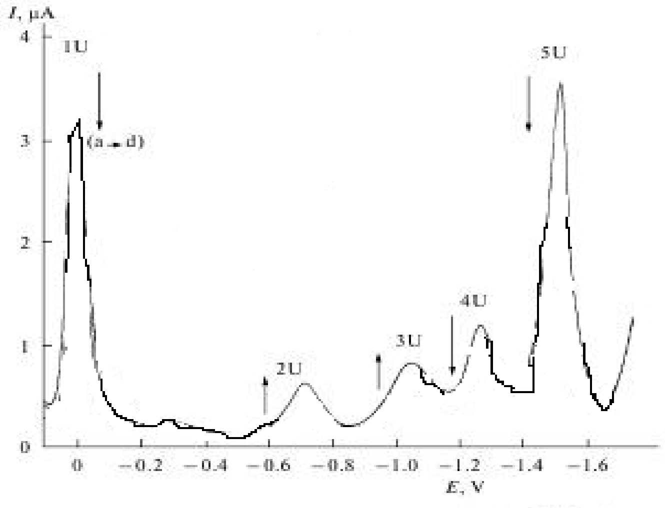

Fig.4- Polarograms of complex of Zn(II)

This electrode process involves two main steps:

(1) Formation of a reducible complex by reaction of the ligand catalyst with Zn(II)ion; and

(2) Reduction of nickel ion in this complex, resulting in the release of the ligand molecule, which can enter step (1) again. Such behaviour was also observed in some other Zn(II)complexes.

The catalytic reduction of Zn(II)is very dependent on the structure of the catalyst, providing it contains suitable binding sites required for the formation of a chelate complex with Zn(II). Thiosemicarbazones itself reacts as a complexing agent in aqueous solutions. The complexation takes place mainly via the sulfonamide nitrogen atom, pyrimidine nitrogen atoms and the oxygen of the sulfoxide group. The appearance of the complex at a more positive potential than that of Zn(II)hydrate clearly indicates the role of sulfonamide nitrogen atom and/or pyrimidine nitrogen atoms in facilitating complex reduction at the mercury electrode.

UV-Vis spectroscopy measurements

The interactions of copper and nickel with thiosemicarbazone (L) in solution were also studied by UV-Vis spectroscopy. We have determined the M (II): L molar ratio and stability constant of metal complexes in solution by Job’s method. The positions of the absorption band and stability constants of ligands and its complexes were given in table (1).

Table 1- Electronic absorption spectra of L and its Fe(II)and Zn(II)complexes

As can be seen in table, UV absorption bands (Band I) of the complexes can be assigned to the metal ligand charge transfer bands while their absorptions (Band II) in the visible region are attributed to the d –d transitions. From electronic spectra data of the complexes, their stoichiometries of 1: 2 (metal–ligand) in aqueous medium are determined. In the binary complexes, thiosemicarbazones binds to metal ions with sulfonamide nitrogen atom and pyrimidine nitrogen atoms. The results are consistent with the voltammetric studies. The stabilities of the complexes are in agreement with Irwing-Williams series (Fe < Zn) .

Compounds	**λmax, nm**		**Logβ**	**M(II) : L ratio**
	Band-1	**Band-1**		
Thiosemicarbazone (L)	286, 292,310	-	-	-
Fe(II)–L complex	297, 316	742	10.81	1:2
Zn(II)–L complex	299, 317	388, 659, 745	7.99	1:2

5. CONCLUSION

By this research work we described the polarographic and spectroscopic behaviuor of thiosemicarbazones with of Fe(II)and Zn(II). Polarographic and electronic spectroscopy measurements have proved the complex formation of thiosemicarbazones with metal ions. The complex formation of thiosemicarbazones in the presence of Fe(II)ions was observed for both Fe(II)and Fe(III). The processes studied may help in understanding some of the features of the binding mechanism between copper ion and nucleic acid. The study will also contribute to a better understanding on the binding of Zn(II)and Fe(II)ions in biological systems.

6. ACKNOWLEDGMENT

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