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Electrochemical Study of Complexes of Cu(II) and Ni(II) with thiosemicarbazone

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ABSTRACT

The synthesis of Cu(II) and Ni(II) complexes with thiosemicarbazone(L) ligand and their characterization have been reported in our previous research paper, J. Chem. Pharm. Res., 2011, 3(5):682-688. 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. 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).

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

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 [1]. The transition metal complexes containing thiosemicarbazones derivatives have been extensively reported in the literature due to being more effective and desirable drugs than sulfonamides [2, 3]. 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 [4, 5]. Among the metal ions, Cu(II) is the most effective available divalent ion for binding to organic molecules. On the other hand Cu(II) can readily undergo one electron redox reactions in the biological redox range producing a πdonor cation Cu(I), which is one of the most effective available monovalent ion for binding to organic molecules [6]. These effects encourage us to study the interaction of pyrimidine contained sulfonamides especially withCu(II) and Ni(II) ions considering that they are important in many biological systems. ^{4}Nand ^{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 Cu(II) and Ni(II)[7-9].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 [10].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.

EXPERIMENTAL SECTION

All the chemicals were of analytical reagent gradeand were commercially available and used as received.Thiosemicarbazide and ethanol were used for the preparation of the ligands (L) [11].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 systronicpolarograph 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.

RESULTS AND DISCUSSION

Electrochemical Behaviuor

Free ligands (L)

The polarograms of thiosemicarbazones in 0.04 MB–R buffer (pH 7) showed three reduction peaks at0.01, –1.32 and –1.55 V, respectively (Fig.I). It hasbeen observed that the peak potentials of thiosemicarbazones shiftslightly towards more negative potentials if its concentration increases.In the polarograms, the peak at 0.01 V is, to ourknowledge, not reported in the literature.Althoughthis unexpected abrupt peak at 0.01 V could not beexplained by the reduction of functional group inthiosemicarbazones, 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 statestudy of Hg(II) complex with thiosemicarbazones [12], where it isreported that Hg(II)–thiosemicarbazones complex is coordinatedthrough the sulfonamide nitrogen, sulfonyl oxygenatom and pyrimidinyl nitrogen atom [12]. The anodicpeak ofHg(II)-thiosemicarbazones complex can be clearly seen inFig. 1. The anodic peak at –0.04 V is attributed to theformation of Hg(II)-thiosemicarbazones complex adsorbed on the mercury electrode surface. This complex is formed by theoxidation of mercury in the presence of sulfamethazine. It is well known that at the determination of somesulfonamides, their adsorptive properties on theHgelectrode were analytically used [13]. Finally,it can be said that thiosemicarbazones has an adsorption property onmercury electrode. In the caseof thiosemicarbazones the peak may be attributed to thereduction of Hg(II) bound in the adsorbed Hg(II)-thiosemicarbazones complex which could be formed by the interaction between the positively charged mercury surfaceand the heterocyclic nitrogen atom of the pyrimidine moiety. It has been reported that compounds possessingazomethine 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 groupinvolves two electrons and two protons. In the reduction process, a proton is bonded to the heterocyclicnitrogen at substituted pyrimidine, the other one isinvolved in reduction of one double bond of the pyrimidine ring. The peak at –1.55 V can be attributed tothe reduction of the –SO2NH– group in the thiosemicarbazones[14]. It has been reported that several arylsulfone compounds show polarographic reduction peaks at potentials ranging from –1.4 to –2.1 V [15]. In general, the pH of the electrolysis medium is oneof the variables that commonly and strongly influencethe shape of the polarograms, and therefore it wasimportant to investigate the effect of pH on the electrochemical behaviuor of the drug. The concentrationof thiosemicarbazones (1 × 10–4 M) was maintained constant, and analyze is done at variable pH from 2 to 12 (Fig. 2). The investigation ofpH of B–R buffer (pH 2–12) showed that thiosemicarbazones exhibits two reduction peaks most probably originatingfrom reduction of the azomethine group of the substituted pyrimidine ring and from the reduction of the –SO2NH– group in the thiosemicarbazones at pH values lowerthan 5.5, whereas it has three cathodic peaks overpH 6. In alkaline medium (pH ≥ 10), no reductionpeaks were seen, except for the peak at 0.01 V. Thepeak potentials and the peak currents of the cathodicpeak at 0.01 V are strongly influenced by the pH of thesolution. Due to the weak interaction of the adsorbedneutral thiosemicarbazones molecule with mercury, no peaks areseen at pH < 6. This phenomenon can easily beexplained by the fact that the formation of deionizedthiosemicarbazones which are stronger complexing agents thanuncharged thiosemicarbazones occurs at pH ≥ 7. As the pH (2–9)increased, the peak potentials at –1.32 and –1.55 Vwere observed to shift towards more negative valuesindicating

the existence of a protonation reaction coupled with the thiosemicarbazones reduction process [16].The current of the peak at 0.01 V was observed toincrease with increasing pH in the pH range of 6 and 7.5, while it becomes pHindependent at pH > 7.5.The currents of the peaks at –1.32 V and –1.55 Vdepend on the hydrogen ion concentration of the supporting electrolyte.

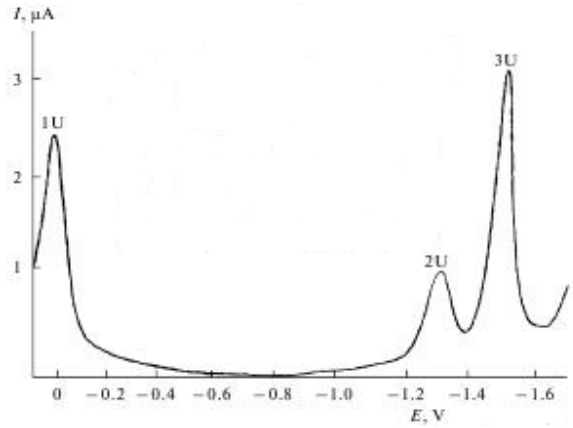

Fig.1- Polarograms of ligands

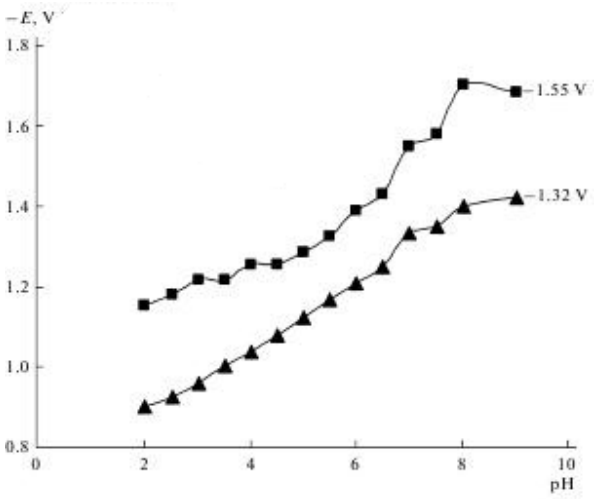

Fig.2- Analyze at variable pH

Ligands in the Presence of Cu(II)

The polarograms of 5×10^{-6} MCu(II) ions in B–R buffer (pH 8) in the absence ofthiosemicarbazones has a peak at a potential of –0.106 V. This peakwas attributed to the reduction of Cu(II) ions toCu(0). The addition of 5×10^{-6} M Cu(II) to the electrolyte containing 1×10^{-4} M thiosemicarbazones ions, over thepotential 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 Cu(II) concentration($5 \times 10^{-6} – 5 \times 10^{-5}$ M), the potential of the peak at –0.35 V is shifted towards slightly negative potentialsand fixed at –0.38 V. The shape of this peak is welldefined at –0.38 V. As can be seen in Fig. 8, thiosemicarbazonesforms the complexes of both Cu(I) and Cu(II) ions.The behaviuor of the redox couple Cu(II)/Cu(0) inelectrochemical reactions depends strongly on thepresence of ligands. Indeed the redox mechanismCu(II) Cu(0)

may include the appearance ofCu(I) species if preferential stabilization of copper in thisoxidation state takes place due to complex formation. However, the stabilization of Cu(I) species mayalso be due to d–π interactions between the copper, thed-orbitals and the aromatic πsystem. Similar behaviuor has already been observed for copper in the presence of some pyrimidine bases [34]. We propose thatthe first composed peak at –0.18 V corresponds to twoprocesses: the reduction of Cu(II)L to Cu(I)L and thereduction of Cu(I)L to copper metal. Thesecond peak at –0.38 V is attributed to the reductionof $Cu(II)L_2$ complex to the copper metal. The currents of the cathodic peaks at–0.18 and –0.38 V showed a linear increase up to theCu(II) concentration of 2.5 × 10–5 M; however, abovethis concentration, a plateau region was observed. Data obtained under these conditions show that thepredominance of the copper complex increases withincreasing Cu(II) concentrations. Adsorbed mercurycomplex in the presence of Cu(II) is transformed intoan adsorbed copper complex. As a result of the formation of the copper complex, the peak current of freethiosemicarbazones (0.01 V) decrease with increasing Cu(II) concentration.

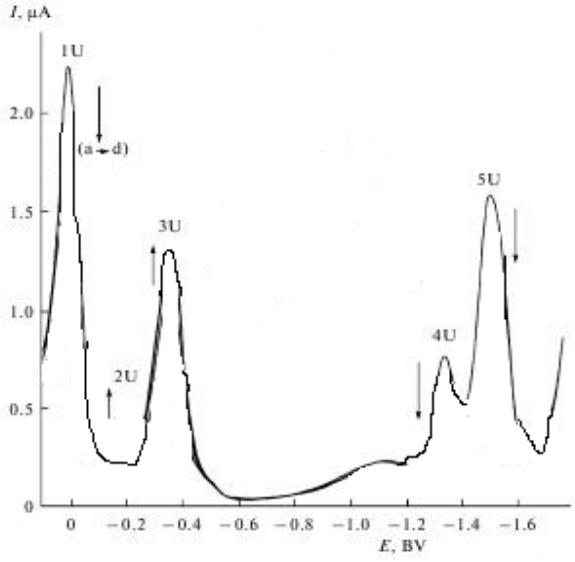

Fig.3- Polarograms of complex of Cu(II)

Ligands in the Presence of Ni(II)

The polarograms of Ni(II) in theabsence of thiosemicarbazones is characterized by a cathodic peak at–1.08 V at 0.04 M B_R buffer (pH 6). The peak wasinferred from irreversible reduction of the hydratedNi(II) ions (Fig. 3). In the presence of thiosemicarbazones, the similarresults to that with Co(II) ions have been observedwith Ni(II) ions. It was noticed from the experimentalsteps that the thiosemicarbazones peak currents decreases (about68 percent for the peak at –1.55 V) with addition of Ni(II) solution (5×10^{-5}–8×10^{-4} M) to the cellcontaining 1×10^{-4} M thiosemicarbazones and that of the Ni(II)simultaneously increased, The potentialand current of the peak at –0.77 V are dependent on thenickel concentration. The current of the peak at –0.77 Vincreases linearly with increasing Ni(II) concentration and then reaches plateau region, the peakpotential shifting in a positive direction. Also, shiftingpeak potentials are indicative of the formation of labilecomplexes. By this we can concluded that the effect of Ni(II) concentration on the catalytic current is much smaller thanthat of Cu(II) concentration in the presence of thiosemicarbazoneswith fixed concentration[16]. According to the effect ofmetal ion concentration, the similar results were alsoobtained in the Ni(II)-thiosemicarbazones complex

system[17]. This case indicates the electrochemical reduction of metal ions catalysed by adsorbed ligands. Theseexperimental results also verify a decrease in the freethiosemicarbazones concentration and decreasing the surface excess of the adsorbed Hg-thiosemicarbazones complex. Because, it wasobserved that the peak currents of thiosemicarbazones and Hg–thiosemicarbazonescomplex decreased by increasing Cu(II) or Ni(II)concentration.The irreversible peak at more positive potential(–0.77 V) than that of the hydrated Ni(II) ions (–1.09 V)originates from the catalytic reduction of complexedNi(II) with thiosemicarbazones. Thiosemicarbazones has catalytic activityon the reduction of Ni(II). It may be concluded thatthe polarographic process is the reduction of Ni(II)catalyzed by the formation of a complex betweenNi(II) and thiosemicarbazones adsorbed on the electrode surface[18]. The reduction of nickel ion is preceded by theelimination of an aqua molecule from the coordination sphere. Because this step requires high activation energy, the electrode reaction occurs only with theapplication of a very large overvoltage [19]. However,in the presence of certain ligands present at the tracelevels, the overvoltage is decreased. In this case, thereduction of the complexed nickel ions (represented as NiL_2) occurs more readily at a more positive potentialthan that of Ni(II) hydrate (–1.09 V).

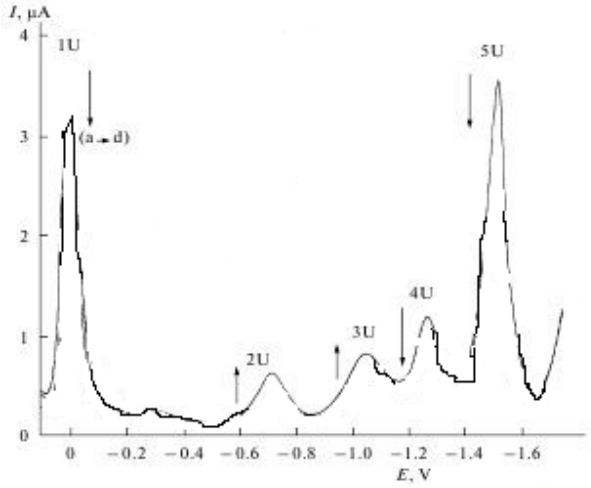

Fig.4-Polarograms of complex of Ni(II)

This electrode process involves two main steps:

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

(2) Reductionof nickel ion in this complex, resulting in the release ofthe ligand molecule, which can enter step (1) again.Such behaviour was also observed in some other Ni(II)complexes [20, 21].

The catalytic reduction of Ni(II) is very dependenton the structure of the catalyst, providing it containssuitable binding sites required for the formation of achelate complex with Ni(II). Thiosemicarbazones itselfreacts as a complexing agent in aqueous solutions. Thecomplexation takes place mainly via the sulfonamidenitrogen atom, pyrimidine nitrogen atoms and the oxygen of the sulfoxide group. The appearance of the complex at a more positive potential than that of Ni(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 spectroscopyMeasurements

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 ligandsand its complexeswere given in table (I). 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 [21-22]. The results are consistent with the voltammetric studies. The stabilities of the complexes are in agreement with Irwing-Williams series (Ni < Cu) [22].

Table 1-Electronic absorption spectra of L and its Cu(II) and Ni(II) complexes

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

CONCLUSION

By this research work we describedthe polarographic and spectroscopic behaviuor ofthiosemicarbazones with of Cu(II)and Ni(II).Polarographic and electronic spectroscopy measurements have proved the complex formation of thiosemicarbazoneswith metal ions. The complex formation of thiosemicarbazonesin the presence of Cu(II) ions was observed for both Cu(II) and Cu(I). 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 Ni(II) and Cu(II) ions in biological systems.

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