Voltammetric Study For Cuso₄ in Presence of Safranin (Saf) in Hcl Solutions using New Multicarbon Nanotubes Doped with Nano Tantalum Pentoxide Working Electrode

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Abstract

Redox reaction for $CuSO_4$ in the absence and presence of safranin (suffranine) was studied. We applied new electrode made from multicarbon nanotubes (MCNT) and nano (Ta_2O_5) in a mixture with 80% MCNT and 20% (Ta_2O_5) by weight. Two drops paraffin oil was added, drying till dryness in tip of copper electrode covered with heat shrink polymer to do good isolation. The electrode was purified and put in oven at 90°C till working in the morning. Scan rate effect was done for the redox reactions in absence and presence of safranin to explain the type of the used reactions in the study electrode chemically. The stablilty constants and Gibbs free energies of complexation resulting from the interaction of $CuSO_4$ with safranin in 0.1 M HCl at 27.5°C were evaluated and discussing their resulting data.

Keywords : Voltammetry , Thermodynamic Properties , Copper Sulphate , Multicarbon Nanotubes (MCNT) , Stability Constants and Gibbs Free Energies of Complexation.

1.Introduction

By cyclic voltammetry we can study the interaction of cationic salts with organic ligands[1].Active cationic salts like $CuSO_4$ can from complrexes through interaction with functional group in the organic ligands like azo, amino , amido or hydroxy group [2] The complex interaction can be observed by change in peak heights and shift in cathodic or anodic wave potentials [3] . Other techniques like absorption spectroscopy , emission spectroscopy , polarography , potentiometery and other electrochemical methods for studying the complexation interaction of the organic compound with metal ion [4]. Here we prepared in our laboratory,multicarbon nanotubes (MCNT) doped with nano tantalum pentoxide (Ta_2O_5) jointed with copper electrode we always study the voltammagrams at the steady state .i.e. at equilibrium.

2.Experimental

The chemical used safranin is provided from sigma Aldrich Co., $CuSO_4$ and hydrochloric acid are provided from Al-Gomheria pharmaceutical Co. Bidestilled water with conductivity 2.7 µs was used. DY2000 potentiostat was used for developing the cyclic voltammagrams at different scan rates. We bubbled pure N_2 for 10 minutes in each solution to insure the escaping of dissolved oxygen. Three different electrodes were used and applied for potentiostat Measurements**,** The first electrode is the reference Ag / Agcl electrode filled with saturated KCl. Platinum wire as auxiliary electrode and the prepared multi carbon nanotube (MCNT) doped with nano Ta_2O_5 deposited upper the Tip of copper electrode dried , washed and polished well.in Al_2O_3 powder put in woolen piece of cloth. TEM Images of electrode material and preparation of new electrode. The prepared electrode material of 80% multi carbon nanotube (MCNT) plus 20% nano tantalum pentoxide (Ta_2O_5) by weight was crashed in Murter and scanned by transmission electron microscope and obtained images are illustrated in Fig. 1.It is clear from the pictures given in Fig.1. , the nano layers for multi carbon nanotube (MCNT) with also the traces of Ta_2O_5 on them two drops of paraffin oil was added to this mater doped material and then pasted to copper electrode and dried in low heat oven for 24 hour at 70°C , polishing after words in woolen piece of cloth wet with little Al_2O_3.

TEM Images for Multicarbon Nanotubes Dopped with Nano Ta_2O_5 :

The multicarbon nanotubes were supplied from Egyptian Petroleum Institute (EPRI) with diameter ranging form 10-40 nm and lengh ranged from 10 to 100 micro meter and the number of walls nearly 40-50 walls. Nano Tantalum pentoxide (Ta_2O_5) appears as black balls in images ranging from 15-35 nm.
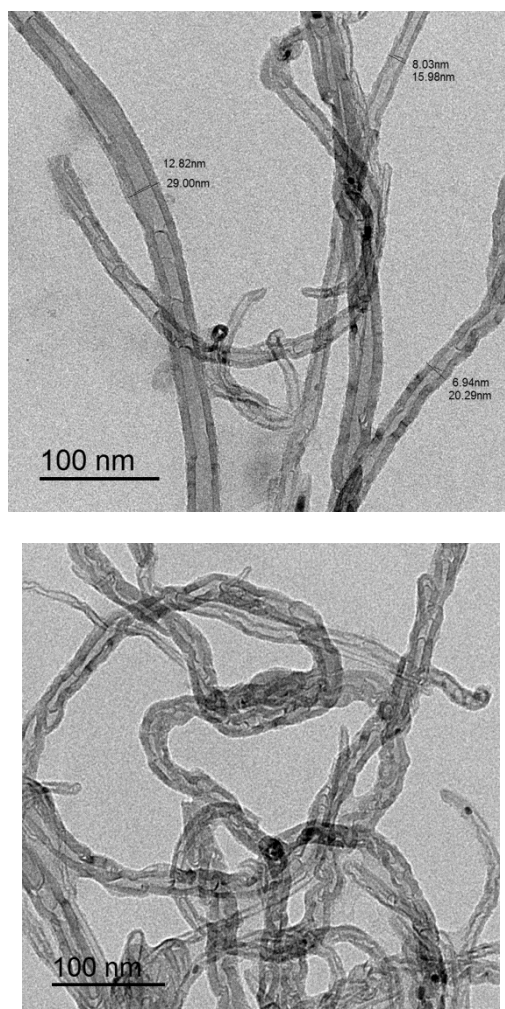

Fig (1) : Multicarbon nantubes doped with nano Ta_2O_5

3. Results and Discussion:

Cyclic voltammetry of $CuSO_4$ in the absence of safranin (Saf)

The cyclic voltammograms (CV) for the redox behavior of $CuSO_4$ in 0.1 M HCl electrolyte medium at 27.5°C was studied in the range from 1V (Volt) to – 1V. the reduction process took place , whereas the oxidation proceed in the range of -1V to 1V. Voltommograms shown between 1V and – 1V illustrate reduction processes involving Cu (II) / Cu (I) that indicate a relation between current in Ampere (Amp)and potential in volt(E/V). Both oxidation and reduction waves are slightly affected by the scan rates at 27.5° C Fig.2. Also Table 1 includes the detailed experimental and calculated results[1-15].
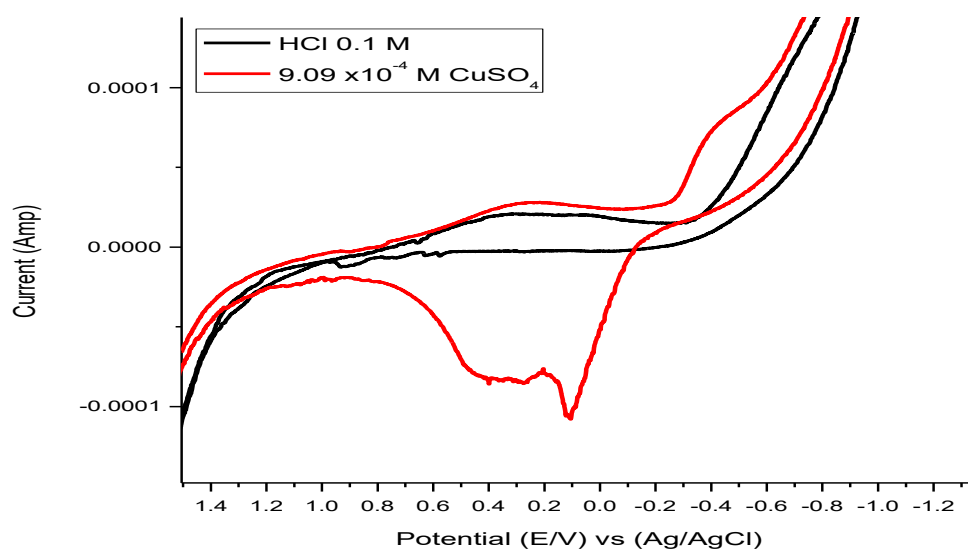
**Fig.2. :Voltammograms of CuSO₄ in 0.1 HCl solutions at 27.5°C**

The effect of scan rate specially the kinetic parameters, like electron transfer rate constant (k_s), cathodic surface coverage (Γ_c), anodic surface coverage (Γ_a), cathodic quantity of electricity (Qc), anodic quantity of electricity (Qa) and α_{na} are clearly represented in Table 2. All the data in Table 2. indicate increase in all the kinetic parameters mentioned above by the decrease in scan rate . Fig .2. Which explains the relation between current in ampere (Amp) and potential in volt(E/V). Four different scan rates indicate the diffusion control reaction mechanism for the redox reactions
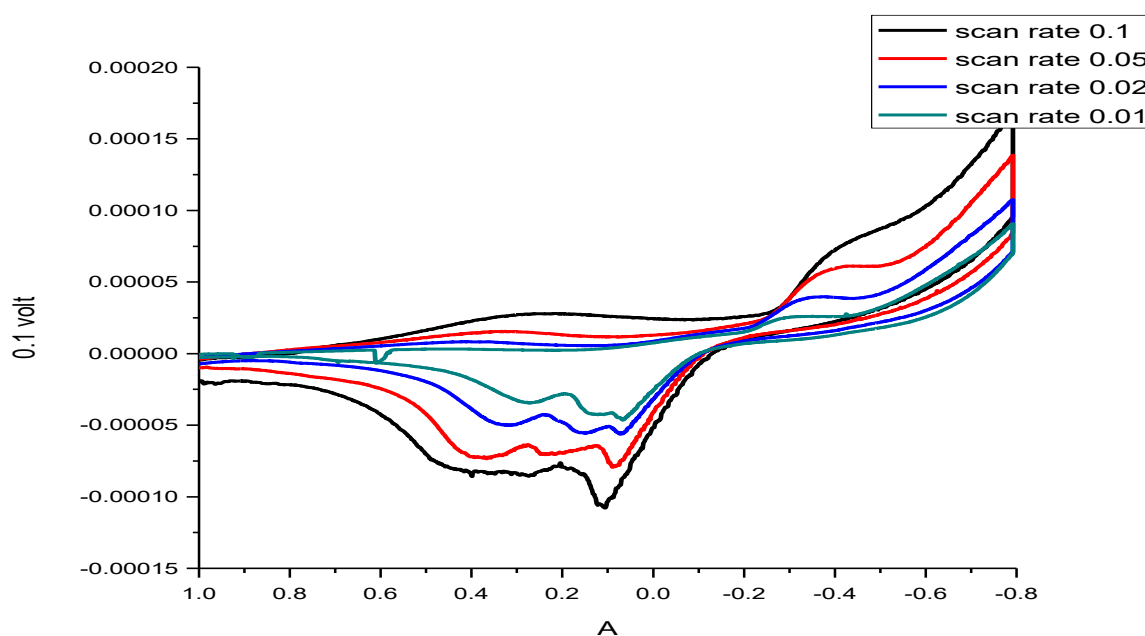
**Fig.3 : Voltammograms of different concentration on scan rate of CuSO₄ in HCl solutions at 27.5°C**

Electrochemical behavior redox processes for CuSO₄ of the multicarbon Nanotubes doped with Nano Tantalum pentoxide and Voltammograms of CuSO₄ in the presence of Safranin (Saf).

Electro chemical behavior of CuSO₄ in presence of safranin (Saf) in 0.1 M HCl.The effect of safranin concentration using 8.33×10^{-4}, 1.54×10^{-3}, 2.14×10^{-3} were added to 9.09×10^{-4} CuSO₄ and the voltammogram were recorded and represented and the voltammogram is show in Fig.3 complex is obtained from the interaction of CuSO₄ plus safranin ,Saf (suffranine) from the decrease in all wave height and shift in all peak potentials [15-20].
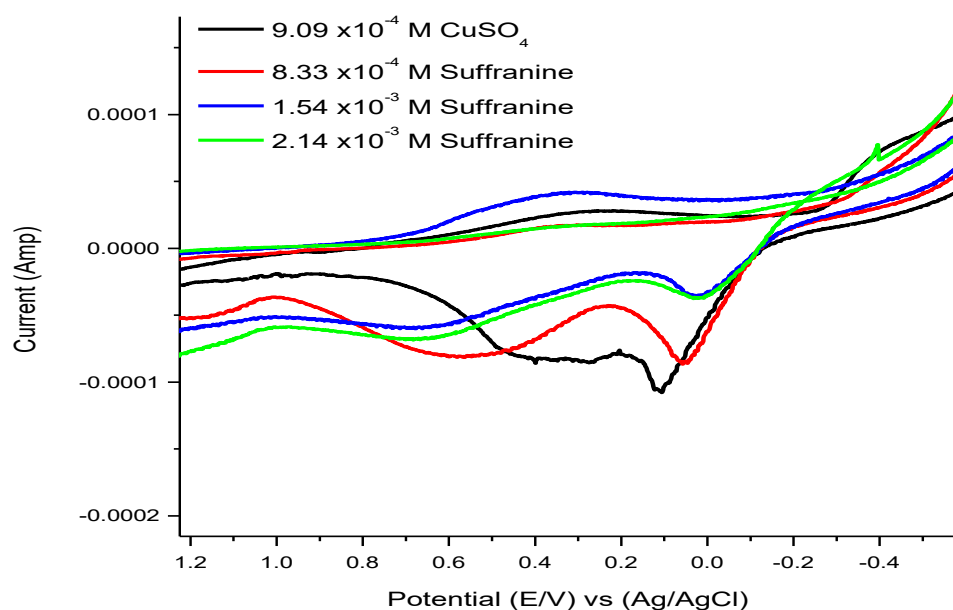
Fig. 4: Voltammograms of the interaction of different concentrations of Safranin,suffranine (Saf) with 1 mM CuSO4 in 0.1M HCl supporting electrode.

Scanning voltammograms of the complex formed between CuSO₄ and Safranin (Saf) in the range 1 to – 1V show cathodic peak using the range of +2v to -2V and with the blank voltammogram in the absence of CuSO4. We noticed one cathodic peak at ν 0.5 V and two oxidation peaks at 0.5 and 0.7 V as shown in Fig. 4.
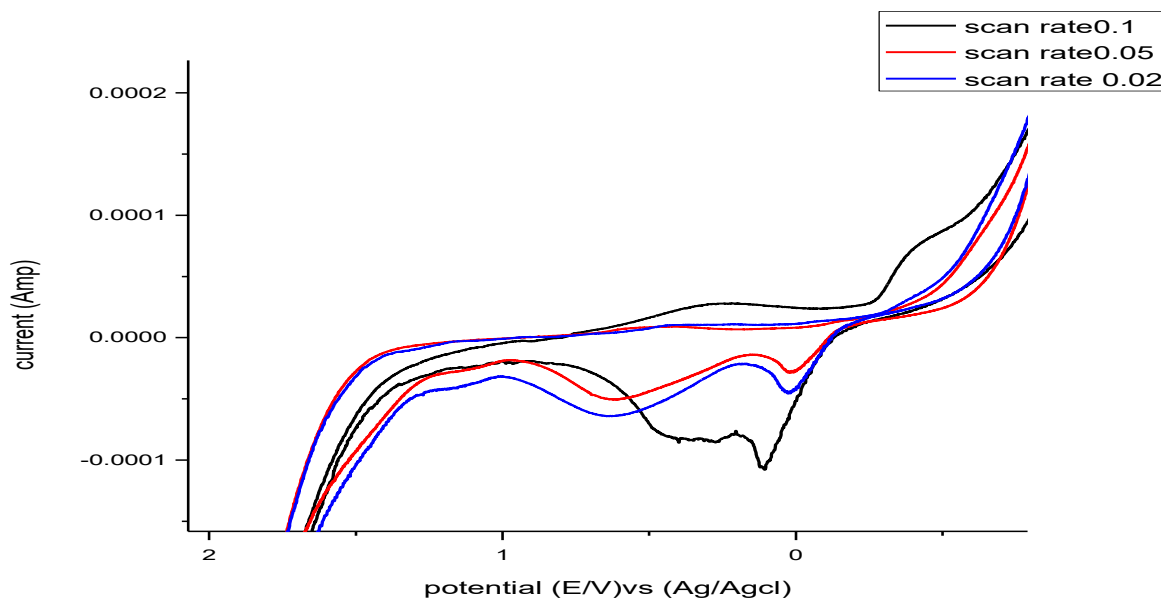
Fig.5 : Effect of different scan rates on 1:1 (Metal/Saf) stoichiometric complexes.

Electrochemical behavior of CuSO$_4$ in case of absence and presence of safranin,suffranine (Saf)

Electrochemical behavior of CuSO$_4$ in case of the absence of safranin, the cyclic voltammetry of 9.09×10^{-4} M CuSO$_4$ was studied in 0.1MHCl as supporting electrolyte and in using the range of +2V to -2V and with the blank voltammogram in the absence of CuSO$_4$. We noticed one cathodic peak at ~ 0.5 V and two oxidation peaks at 0.5 and 0.7 V.
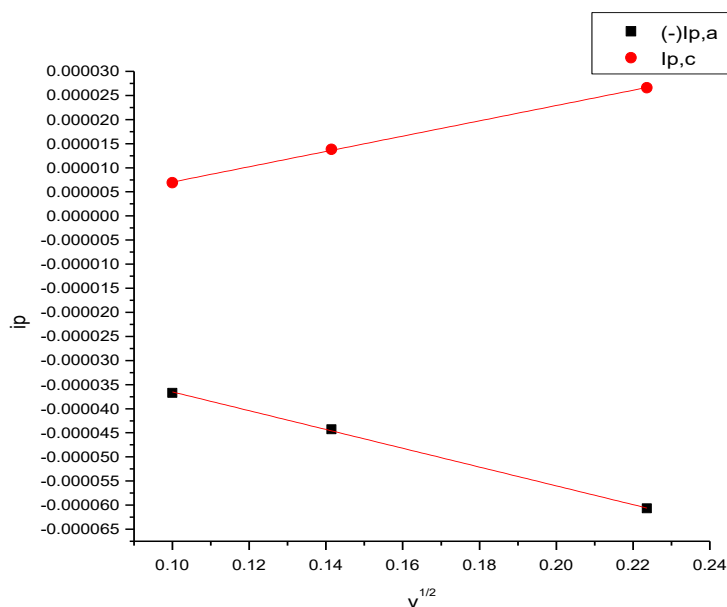
Fig. 6: The relation between ip and v1/2 for the wave in absence of (Saf).

The reduction of copper from the Cuppric divalent state to zero point state is responsible for the reduction at v0.5 V Consuming two electrons. The oxidation peaks appear at ~ 0.5 and ~0.7 at 27°C, involving one electron for every step, explaining the oxidation of zero valent copper to monovalent one and the monovalent copper to divalent copper with suggested mechanism [20-31] .

$$Cu \rightleftarrows \quad Cu^+ + e\ \text{-}...............................(1)$$

$$Cu^+ + e\text{-} \rightleftarrows Cu^{+2}...............................(2)$$
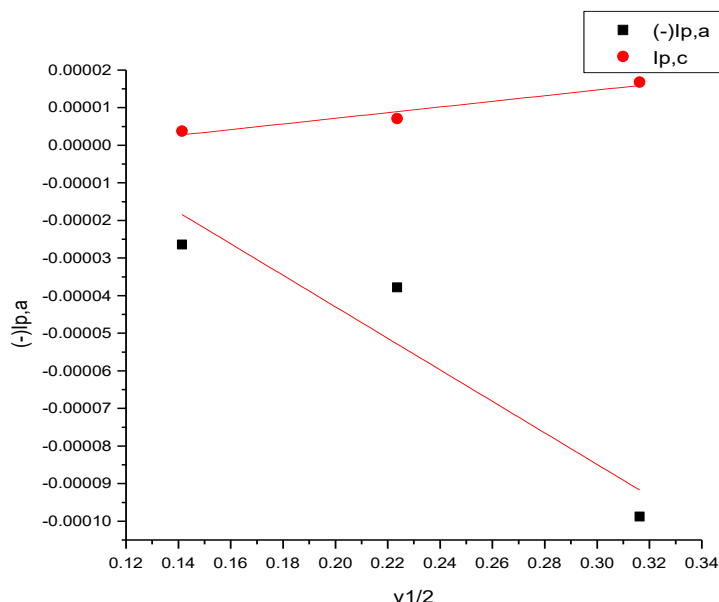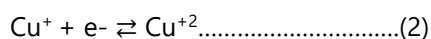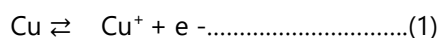
Fig . 7 : The relation between ip and v1/2 for the wave in presence of (Saf).

From the peak potentials for the cyclic voltammetry curves the complex stabilization constants are obtained and represented in Table 5.The stability constants were transformed to the Gibbs free energies of complexation and also the obtained data are also given in Table 5 .It is clear from that Table 4, that the thermodynamic parameters Bi and ΔG are increased with increase in safranin (Saf) concentrations indicating more complexation.

Analysis of Voltammograms Obtained

The redox processes for $CuSO_4$ at the multicarbon nanotubes (MCNT) doped with tantalum pentoxide deoposited on the copper wire electrode were studied at equilibrium conditions. The obtained cyclic waves were analyzed by by Eq.1. [1,6].

$$i_P = (2.69 \times 10^{-5})\ n^{3/2}\ A\ D^{1/2}\ v^{1/2}\ C................... (3)$$

Where i_P is the current in ampere unit ,A is the surface area of the electrode,D is the diffusion coefficient in cm^3/sec, v IS the scan rate in v/s and C is the ionic salt concentration (copper sulfate concentration). The voltamonograms were recorded by the use of working electrode multicarbon nanotubes (MCNT) doped with Ta_2O_5 from starting potential of +2 V to final – 2 V. The measured cyclic Voltammetry depend on the ions moment and electron transfer reaction.

$$k_f = k^o\ exp\frac{-\alpha nf}{RT}\ -\alpha\ nF\ (E\text{-}E^°)........................(4)$$

Where: k_f is forward rate constant, k^o is the electron transfer rate constant which indicate the introduction of the compound in ionic form with electrode surface used. E is the potential for reduction and α is the transfer coefficient we take α $\cong$ **0.5** because it depend on the shape and surface free energies for reactants and products.

when scan rate is measured, the already reduced species at the working electrode is oxidized back to return to the original starting conditions The electron transfer rate constant for reverse reactions (oxidation) is controlled by applying voltage [7-15].

$$k_r = k^o \exp\frac{(1-\alpha)nf}{RT} (E-E^{`}) \dots\dots\dots\dots (5)$$

If the reaction proceeds reversibility, the separation in peak potentials., ΔE_P will close to 58/n in mv (at 25° C) .This relation can be used for evaluation of the electron. In reversible reaction, the reduction is fast for obtaining the oxidized and reduced ions or species in equilibrium. The equilibrium between the two forms of ions is determined using the Nernst equation.

$$E = E^o - \frac{RT}{nF} \ln\left(\frac{[R]}{[o]}\right) \dots\dots\dots\dots\dots (6)$$

Where [O] and [R] are the oxidized and reduced forms. When the reaction is the fast reversible reaction may happen ΔE will show decrease in trend and the reaction depend on the stress that is applied to the system. The reaction is reversible if h^o is greater than 0.3 $v^{1/2}$ [q], where the scan used is v . Electron transfer reaction with scan rate greater that 10m/sec will be reversible. With increasing scan rate quasi-reversible reactions. There are widely separated ($k^o \leq 2 \times 10^{-5} v^{1/2}$ am/s). some examples of irreversible reactions involve bond breaking further fruit full relation is dependent on peak height with square root of the scan rate $v^{1/2}$. For quasireversible system, the peak current not exactly proportional to $v^{1/2}$ except when peaks are widely separated.

Some other words used the half wave potential value for peak current explaining reversibility mechanism which is:

$$E_{p/2} = E_{1/2} \pm \frac{28}{n} mv \dots\dots\dots\dots (7)$$

The sign is positive for the reduction processes. Theoretically when the scan rate is increased, slow electron transfer make a shift in peak potentials, this indicate no symmetry about $E\frac{1}{2}$ For oxidation and reduction reactions. The analysis for redox recation is based on the relative heights of the anodic and cathodic peaks.

The interaction of $CuSO_4$ with safranin (Saf.) forming complexes from the cathodic and anodic decrease in current and potential shift to more negative values for reduction and less position value for oxidization. The complex stability constant (B) for the interaction of $CuSO_4$ with safranin (Saf) in 0.1 M HCl form complex is calculated by the use of equation (8) [15-17.]

$(E_p)_M-(E_p)_C =$ 2.303 RT/nF logBc+2.303RT/nF log (x) .... (8)

Where $(Ep)_M$, is the peak potential in volts for the salt in the absence of ligand Safranin (Saf.), $(E_p)_C$, is the peak potential of the complex, (C) , is the concentration of the salt used in presence of ligand Safranin (Saf.) [18-40].

$\Delta G = \quad -2.303RT \log B_C$ ....(9)

All data obtained applying equations (8) and (9) are given in Table 5, indicating the increase of thermodynamic parameters by increase in Safranin (Saf.) concentration due to its increase in complexation ability with $CuSO_4$.

Table 1: Analysis of the wave of CuSO4 at different concentrations of the depolizer at 27.5°C for reaction, $(Cu^{+2} \leftrightarrow Cu^{+1})$.

M x10^-4	E_{Pa} Volt	E_{pc} Volt	ΔE_P volt	(+)ipa x10^-5	ipc x10^-5	i_{pa}/i_{pc}	E^0	Da x10^-11	Dc x10^-11	$E_{pc/2}$	αna	Ks x10^-1	Γc x10^-9	Qc x10^-5	Γa x10^-9	(-)Qa x10^-5
9.09	0.0849	0.4398	0.5248	8.09	5.36	1.51	0.1774	5.74	25.3	0.3349	0.4587	36.5	2.94	2.78	4.43	4.19

Table 2 : Effect of different scan rates on $CuSO_4$ at 27.5°C for reaction, $(Cu^{+2} \leftrightarrow Cu^{+1})$

υ	Epa Volt	(-)Epc Volt	ΔEp volt	(-)ipa x10^-5	ipc x10^-5	ipa/ipc	(-)E^0	Da x10^-11	Dc x10^-12	(-)Epc/2	αna	Ks x10^-2	Γc x10^-9	Qc x10^-5	Γa x10^-9	(-)Qa x10^-4
0.1	0.0868	0.5012	0.5880	9.41	0.71	13.23	0.2072	7.77	0.44	0.3529	0.3245	13.8	0.39	0.37	5.15	0.487
0.05	0.0682	0.4027	0.4709	6.07	2.66	2.28	0.1673	6.46	12.4	0.3275	0.6391	7.56	2.91	2.76	6.64	0.629

| **0.02** | 0.0593 | 0.3408 | 0.4001 | 4.43 | 1.38 | 3.22 | 0.1408 | 8.61 | 8.30 | 0.2860 | 0.8767 | 1.17 | 3.76 | 3.56 | 12.11 | 1.15 |
| **0.01** | 0.0567 | 0.2965 | 0.3532 | 3.67 | 0.69 | 5.31 | 0.1199 | 11.9 | 4.20 | 0.2532 | 1.1116 | 0.27 | 3.78 | 3.58 | 20.10 | 1.90 |

Table 3: Analysis of the wave of Cuso4 at different concentrations of the depolizer at 27.5°C for reaction, ($Cu^{+2} \leftrightarrow Cu^{+1}$).

L $\times 10^{-4}$	E_{Pa} Volt	E_{pc} Volt	ΔE_P volt	(+)ip_a $\times 10^{-5}$	ipc $\times 10^{-5}$	i_{pa}/i_{pc}	E^0	D_a $\times 10^{-11}$	D_c $\times 10^{-13}$	$E_{pc/2}$	αna	K_s $\times 10^{-3}$	Γc $\times 10^{-9}$	Q_c $\times 10^{-5}$	Γa $\times 10^{-9}$	(-)Q_a $\times 10^{-5}$
8.33	0.0330	0.3819	0.3489	8.18	0.73	11.15	0.2075	6.99	5.62	0.4532	0.6755	2.22	0.41	0.38	4.48	4.24
7.69	0.0001	0.4159	0.4160	3.42	2.00	1.71	0.2079	1.44	48.9	0.5406	0.3859	18.0	1.09	1.04	1.87	1.77
7.14	0.0137	0.3759	0.3896	3.16	0.66	4.79	0.1811	1.42	6.18	0.4917	0.4156	4.00	0.36	0.34	1.73	1.64

Table 4 : Analysis of the wave of Cuso4 at different concentrations of the depolizer at27.5°C for reaction, ($Cu^{+2} \leftrightarrow Cu^{+1}$).

υ	Ep_a Volt	Ep_c Volt	ΔEp volt	(-)ipa $\times 10^{-5}$	ipc $\times 10^{-5}$	ip_a/ip_c	E^0	D_a $\times 10^{-11}$	D_c $\times 10^{-11}$	$Epc/2$	αna	K_s $\times 10^{-10}$	Γc $\times 10^{-10}$	Q_c $\times 10^{-6}$	Γa $\times 10^{-9}$	(-)Q a $\times 10^{-5}$
0.1	0.0879	0.2859	0.198	9.88	1.68	5.8645	0.1869	10.20	2.46	0.4596	0.2770	8.50	9.22	8.73	5.41	5.12
0.05	0.0013	0.4229	0.4216	3.78	0.71	5.3299	0.2121	2.98	1.05	0.5321	0.4405	6.02	7.75	7.34	4.13	3.91
0.02	0.0008	0.5408	0.5416	2.64	0.38	6.9882	0.2700	3.63	0.74	0.6206	0.6027	0.37	10.32	9.77	7.21	6.83

Table 5: Effect of concentration for Ligand safranin (Saf) at 0.1 scan rate at27.5°C for reaction, $(Cu^{+2} \leftrightarrow Cu^{+1})$.

M x10^{-4}	L x10^{-3}	(-)EPa Volt	Epc volt	ΔEp Volt	Log βj	Bj	(-)ΔG (KJ/mol)	
8.33	0.83	17.74	0.2075	0.3849	9.5307	0.339	54.8641	
7.69	1.54	17.74	0.2079	0.3853	12.085	1.215	69.5659	
7.14	2.14	17.74	0.1811	0.3586	14.017	1.040	80.689	

4. Conclusions

Safranin (Saf) affect the redox properties and solution properties of CuSO4 in 0.1 M HCl. On adding Safranin (Saf) to CuSO$_4$, an increase in the electron transfer rate constants observed and the cationic and anionic surface coverage at the electrode were increased. Quantity used for electricity in both cationic and anionic parts of CuSO4 in hydrochloric acid 0.1 M solutions are decreased by analysis of the redox waves. The thermodynamic parameters are represented in the the text and tables indicating more increase in the stability constants (B) and Gibbs free energies (ΔG) of interactions between CuSO$_4$ and Safranin (Saf).

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