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Interaction of $CuBr_2$ with Succinic acid in KCl Solution (Cyclic Voltammetry) Using Glassy Carbon Working Electrode (GWE)

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Abstract The electrochemical behavior was studied for $CuBr_2$ in the absence and presence of Succinic acid (SuA) separately in 0.1M KCl solution. The Glassy carbon electrode was prepared in our laboratory, which used as working electrode for measuring the voltammograms of $CuBr_2$ in 0.1M KCl at 18.7°C. Stability constant and Gibbs free energy of interaction for $CuBr_2$ + Succinic acid was done and their values were discussed.

Keywords Copper Bromide, voltammetric study, electrochemical parameters, solvation parameters, stability constants and gibbs free energy of complexation

Introduction

Interaction between salts with organic active compounds, metal ions oxides can be followed by cyclic voltammetry [1-5]. The interaction between ligand and metal occurs as the ligand has a specific group withdraw the metal from solution and combine with it forming the complex compound. The complex formation can be evaluated by cyclic voltammogram like appear a new complex wave, a shift in cathodic and anodic potentials [2-5]. The glassy carbon electrode was prepared in our laboratory, polishing with Al_2O_3 put in woolen piece of cloth. We get rid of dissolved O_2 by passing purified N_2 gas.

Experimental

$CuBr_2$, KCl from Merck and new prepared ligand in our laboratory. All chemicals were used without any treatment. For cyclic voltammetry parameters DY 2000 potentiostate was used at different scan rates (0.1, 0.05, 0.02, 0.01 V/Second). The voltammogram cell was prepared by immersing three electrodes in exact 30 ml of 0.1M KCl, the first electrode (Ag/AgCl), is the standard reference electrode filled with saturated KCl, the auxiliary electrode is platinum wire, glassy carbon electrode is the working electrode. Distilled water of conductivity 6 μs was used in the practical work. The voltammograms for $CuBr_2$ in the absence and presence of succinic acid were obtained. The system was applied in window range with 0.8 V to -0.75 V potential and (0.1 v/s) scan rate at (291.85K).

Results and Discussion

At 18.7°C and in a supporting electrolyte (30ml of 0.1M KCl), the cyclic voltammograms of $CuBr_2$ (0.05 M) with different concentrations by using glassy carbon electrode and potential window from 0.8 to -0.75 V were experimentally measured with analysis data labeled in Table (1-a) and represented in (Fig.1). We observed two reduction wave approximately at 0.08, -0.3V and two oxidation peak at 0.2, 0.01V respectively for $CuBr_2$. A blank

solution of 0.1M KCl shows no specific wave. (Cu^{2+} / Cu) system is reversible by transferring two electrons.

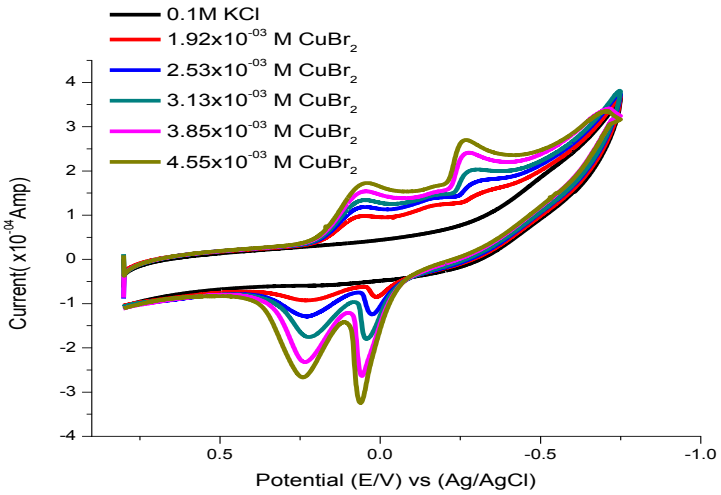

Figure 1: Cyclic Voltammogram of increasing of concentration of $CuBr_2$ at scan rate 0.1 v/sec, 291.85K.

Mechanism of redox reaction of $CuBr_2$ in absence of Succinic acid, Kinetic and Solvation parameters

The cyclic voltammogram for $CuBr_2$ shows two reduction peaks at 0.08 and -0.03 which return to the reduction of Cu^{++} to Cu^{+} and by increasing the potential, the monovalent reduced to zero valent (Cu^{+} to Cu^{0}) [6]. When the potential reversed to the opposite direction, the two oxidation peaks appear at 0.2 and 0.01 V, which mean that the (Cu^{++} to Cu^{0}) is a reversible system, so Cu^{0} oxides again and give Cu^{+} and the second peak due to oxidize of Cu^{+} to Cu^{++}.

$$Cu^{++}_{(aq)} \Leftrightarrow Cu^{+}_{(aq)}$$

$$Cu^{+}_{(aq)} \Leftrightarrow Cu^{0}_{(aq)}$$

We can get kinetic parameters like i_p (peak current) by applying in eq (1):

$$i_p = 2.69 \times 10^5 n^{3/2} A C D^{1/2} v1^{/2} \quad (1)$$

n, number of electrons transfer, A, surface area, C, concentration, D, diffusion coefficient, v, scan rate.

And the different between anodic- cathodic peak [7-9] from eq. (2):

$$\Delta E = E_{pa} - E_{pc} \quad (2)$$

Solvation parameters also determined through some equations, for example:

The heterogeneous transfer coefficient K_s, given by eq (3), [10-17]

$$k_s = 2.18 (D_c n_a \alpha F v/RT)^{1/2} \exp (\alpha^2 \Delta E nF /RT) \quad (3)$$

α, coefficient of the charge transfer and n_a, number of electron transfer. α also be calculated at different temperatures ex. (291.85K), [8,9] by eq (4):

$$\alpha n_a = 1.857 RT / (Ep_c - Ep_c /2) F \quad (4)$$

The surface coverage Γ easily get which help to know the amount of charge, consume Q [7,8,10-15] that's from eq.(5,6):

$$\Gamma = i_p 4RT /n^2 F^2 A v \quad (5)$$

$$Q = \Gamma A n F \quad (6)$$

Effect of scan rate in absence of Succinic acid:

In the absence of Succinic acid, different scan rates (0.1, 0.05, 0.02, 0.01) have been used in the cyclic voltammograms of $CuBr_2$, by decreasing scan rate, the diffusion process decrease. The effect of scan rate on the final addition of $CuBr_2$ listed in Fig. 2 ,and Table (1-b) with cyclic voltammetry data .

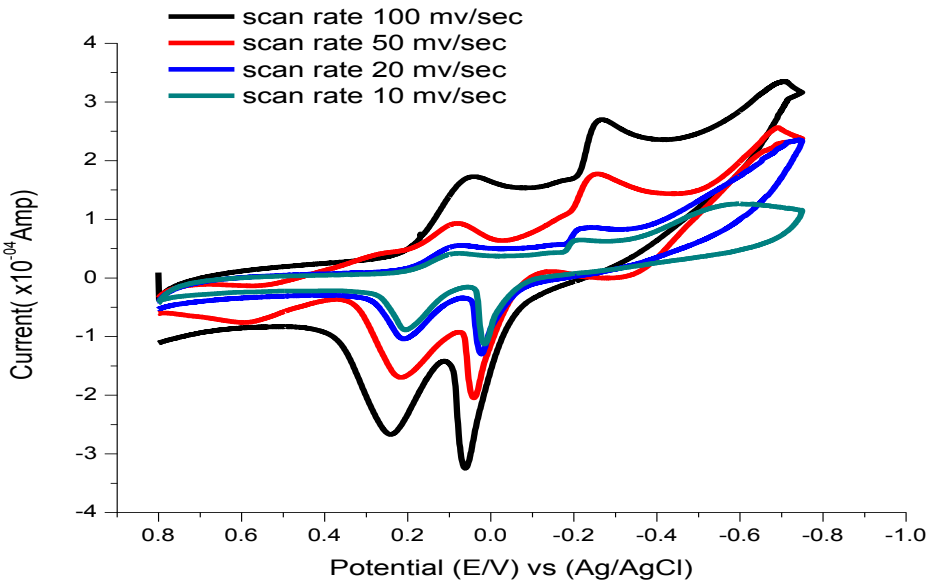

Figure 2: Cyclic Voltammogram of effect of different scan rates on $CuBr_2$ at 291.85K

Table (1-a): Solvation and Kinetic parameters (D, k_s, Γ and Q) of $CuBr_2$ in the absence of (Succinic acid) at 291.85K, scan rate 0.1 V/Sec

First wave

[M] x10^{-3} mol/lit	**Ep$_a$ (volt)**	**Ep$_c$ (volt)**	**ΔEp (volt)**	**Ip$_a$/Ip$_c$**	**E° (volt)**	**Da x10^{-11}**	**Dc x10^{-11}**	**Ep$_{c/2}$ x10^{-01} (volt)**	**αn$_a$**	**k$_s$ x10^{-05}**	**Γ$_c$**	**(+) Q$_c$ x10^{-09}**	**Γ$_a$ x 10^{-05}**	**(-) Q$_a$ x10^{-09}**
1.92	0.2175	0.0822	0.1353	0.2786	0.1499	0.1514	1.95	1.33	0.9124	7.04	8.538	4.235	5.14	1.181
2.53	0.2269	0.0708	0.1561	0.5691	0.1488	0.6637	2.05	1.30	0.7442	8.28	6.857	5.715	6.93	3.252
3.13	0.2132	0.0710	0.1422	0.7105	0.1421	1.114	2.21	1.31	0.7721	7.38	5.271	7.320	8.88	5.200
3.85	0.2279	0.06687	0.1610	0.8401	0.1474	1.361	1.93	1.32	0.7188	8.02	5.636	8.420	10.2	7.074
4.55	0.2339	0.0585	0.1753	0.8337	0.1462	1.450	2.09	1.29	0.6616	9.23	6.260	10.353	12.6	8.631

Table (1-b): Solvation and Kinetic parameters (D, k_s, Γ and Q) of effect of scan on final addition of $CuBr_2$ in absence of (Succinic acid) at 291.85K

v^(1/2)	**Ep$_a$ (volt)**	**Ep$_c$ (volt)**	**ΔEp (volt)**	**Ip$_a$/Ip$_c$**	**E° (volt)**	**Da x10^{-10}**	**Dc x10^{-10}**	**Ep$_{c/2}$ x10^{-01} (volt)**	**αn$_a$**	**k$_s$ x10^{-4}**	**Γ$_c$**	**(+) Q$_c$ x10^{-8}**	**Γ$_a$ x10^{-4}**	**(-) Q$_a$ x10^{-8}**
0.3162	0.2339	0.0585	0.1753	0.8337	0.1462	1.09	**1**.561	1.29	0.6616	2.52	6.260	1.035	1.26	0.863
0.2236	0.2152	0.0961	0.1191	1.7838	0.1557	0.736	0.231	0.135	1.193	0.528	3.284	0.564	0.683	1.005
0.1414	0.2072	0.0886	0.1186	1.4054	0.148	1.66	0.842	0.1459	0.8154	0.524	3.0441	1.700	2.06	2.389
0.1	0.2049	0.0956	0.1094	2.4493	0.150	3.48	0.581	0.1390	1.075	0.322	2.416	2.00	2.42	4.889

The plot represents the relation between i_p (peak current) versus $v^{1/2}$ (square root of different used scan rates 0.1, 0.05, 0.02, 0.01 V/Sec) at 291.85K shown in Fig.5.

Mechanism of redox reaction of $CuBr_2$ in presence of Succinic acid:

By starting add Succinic acid ($1.47x10^{-03}$ M) to $CuBr_2$ ($4.55 x10^{-03}$ M), the complex formation can be detected, as the shift in peak potential for anodic and cathodic peak from (0.08 to 0.03 anodic and 0.2 to 0.3 for cathodic one) and also the decrease in peak current, by increasing the concentration of Succinic acid from (4.17 to $7.69x10^{-3}$ M)

the formation of complex by(1:1 and 1:2 molar ratio) complex metal to ligand respectively , see Fig. 3, with cyclic data in Table (2-a).

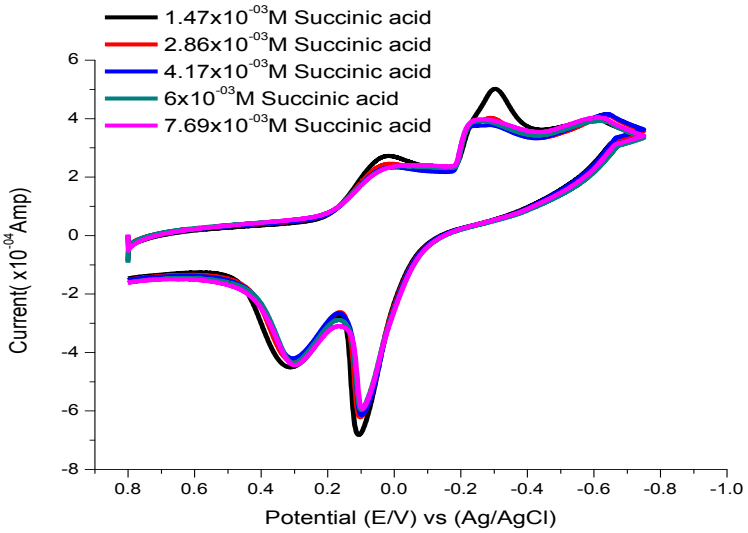

Figure 3: Cyclic Voltammogram of different concentration of Succinic acid at scan rate 0.1 V/Sec, 291.85K.

Effect of scan rate in presence of Succinic acid:

In the presence of Succinic acid, different scan rates (0.1, 0.05, 0.02, 0.01) have been used in the cyclic voltammograms of $CuBr_2$, by decreasing scan rate, the diffusion process decrease. The effect of scan rate on 1:1 molar ratio of complex ($CuBr_2$+ Succinic acid) listed in Fig. 4 and voltammetry data in Table (2-b).

The plot represents the relation between i_p (peak current) versus $v^{1/2}$ (square root of different used scan rates 0.1, 0.05, 0.02, 0.01 V/Sec) at 291.85K shown in Fig. 6.

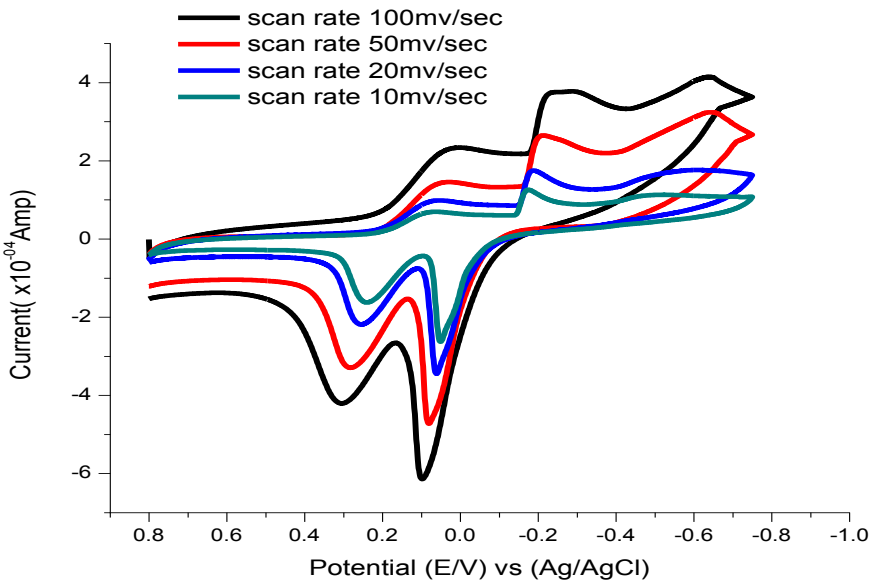

Figure 4: Cyclic Voltammogram of effect of different scan rates on Succinic acid at 291.85K

Table (2-a): Solvation and Kinetic parameters (D, k_s, Γ and Q) of $CuBr_2$ in the presence of Succinic acid at 291.85K, scan rate 0.1 V/Sec.

First wave

[M] x10^{-3} mol/lit	Ep_a (volt)	Ep_c (volt)	ΔEp (volt)	Ip_a/Ip_c	E° (volt)	Da x10^{-10}	Dc x10^{-10}	$Ep_{c/2}$ (volt)	αn_a	k_s x10^{-4}	Γ_c x10^{-8}	(+) Q_c x10^{-4}	Γ_a x10^{-8}	(-) Q_a x10^{-4}
1.47	0.3034	0.0380	0.2654	0.801	0.171	1.380	2.15	0.1119	0.6316	7.09	5.793	1.75	4.639	1.41
2.86	0.2985	0.0370	0.2614	0.731	0.168	1.217	2.28	0.1202	0.5614	6.62	5.794	1.76	4.232	1.28
4.17	0.3025	0.0369	0.2656	0.977	0.170	1.830	1.92	0.1187	0.2331	4.08	5.168	1.57	5.046	1.53
6	0.2990	0.0385	0.2611	1.073	0.169	1.755	1.53	0.0750	1.2797	8.14	4.423	1.34	4.745	1.44
7.69	0.2966	0.0238	0.2728	0.986	0.160	1.556	1.60	0.1043	0.5799	6.31	4.357	1.32	4.295	1.30

Table (2-b): Solvation and Kinetic parameters (D, k_s, Γ and Q) of effect of scan of addition of Succinic acid at 291.85K

v^(1/2)	Ep_a (volt)	Ep_c (volt)	ΔEp (volt)	Ip_a/Ip_c	E° (volt)	Da x10^{-10}	Dc x10^{-10}	$Ep_{c/2}$ x10^{-1} (volt)	αn_a	k_s x10^{-4}	Γ_c x10^{-7}	(+) Q_c x10^{-4}	Γ_a x10^{-7}	(-) Q_a x10^{-4}
0.3162	0.3025	0.0369	0.2656	0.9765	0.1697	1.730	1.81	0.1187	0.0003	0.130	0.5167	1.57	0.504	1.53
0.1	0.2385	0.0796	0.1588	2.2202	0.1590	10.478	2.125	0.1448	0.7162	0.822	1.769	5.36	3.927	11.9
0.1414	0.2535	0.0762	0.1773	1.873	0.1649	7.504	2.138	0.1413	0.7173	1.40	1.254	3.80	2.350	7.12
0.2236	0.2767	0.0533	0.2234	1.364	0.1650	4.407	2.37	0.1359	0.5652	3.28	0.835	2.53	1.139	3.45

Comparison between effect of scan rates for $CuBr_2$ in absence and presence of succinic acid

On comparing the relation between Ip anodic and cathodic peak potentials against square root of the scan rates for $CuBr_2$ in the absence and presence of succinic acid as ligand we found more ordered curves obtained in presence of succinic acid as seen in Figs.5 &6 indicating more ordered reaction in presence of succinic acid. Also, no detectable deviation in the slopes of lines given in Figs.5 and d indicating that the mechanism is diffusion one in absence and presence of succinic acid.

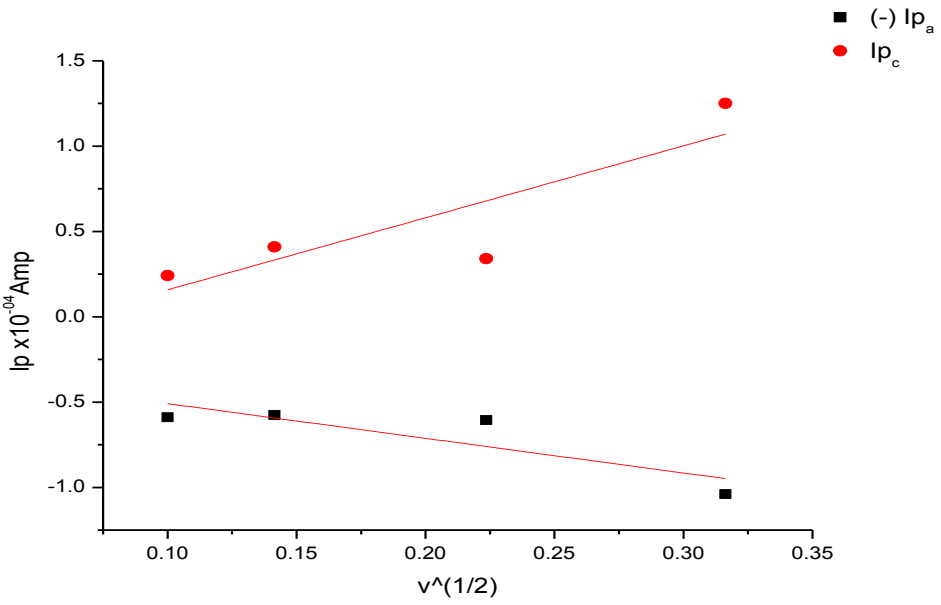

Figure 5: v^1/2 vs. Ip for effect of different scan rates on $CuBr_2$ at 291.85K

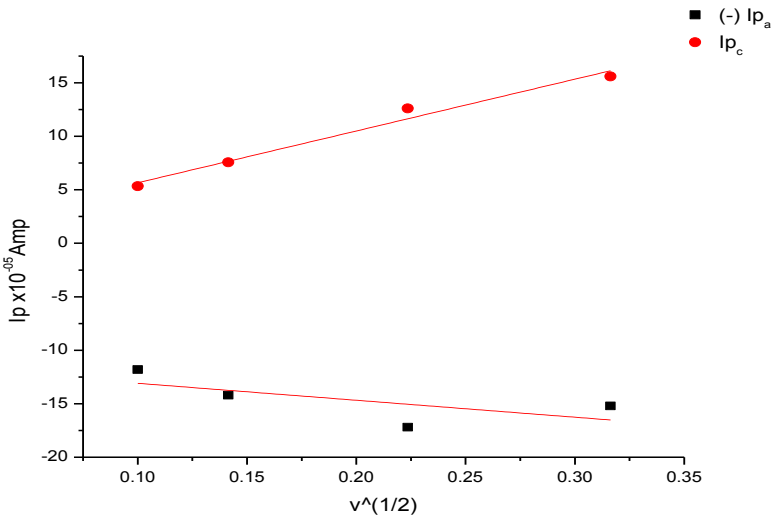

Figure 6: v^1/2 vs. Ip for effect of different scan rates on Succinic acid at 291.85K

Thermodynamic parameters of $CuBr_2$ in presence of succinic acid and effect of scan rate on it

By adding succinic acid to $CuBr_2$, the formation of the complex started taking place, and by increasing the concentration of succinic acid, we need a tool to make sure the stability of complex formation, like stability constant (β_{MX}) that give information about complex stability [16-33] by applying eq. (7):

$$\Delta E^\circ = E^\circ_C - E^\circ_M = 2.303\ (RT/nF)\ (\log \beta_{MX} + j \log C_X) \quad (7)$$

E°_C, the peak potential for ($CuBr_2$ + succinic acid) complex after each addition of Succinic acid, E°_M, the peak potential of the final addition of $CuBr_2$, β_{MX}, stability constant, T, temperature (291.85K).

There are other useful of stability constant, that we can calculate the Gibbs free energy by using eq (8) [11-30]:

$$\Delta G = -2.303\ RT \log (\beta_{MX}) \quad (8)$$

All terms in the given equations are explained in previous papers [20-33].

The parameters of stability constants and Gibbs free energies of different concentrations of succinic acid on the final addition of $CuBr_2$ by molar ratio (1:1) complex represented in Table (2-c).

The effect of scan rate of cyclic voltammetry data of thermodynamic parameters of molar ratio (1:1) complex also has been reported in Table (2-d).

Table 2-c: Cyclic voltammetric data in presence Succinic acid by molar ratio (1:1) at 291.85K for first couple redox waves

[M] x10^{-3}	[L] x10^{-4}	(E°)M (volt)	(E°) C (volt)	ΔE (volt)	Log [L]	ΔG (KJ/mol)	Log β_{MX}
4.41	1.47	-0.0982	0.1707	-0.2689	-2.8325	20.6682	-3.6986
4.29	2.86	-0.0982	0.1677	-0.2660	-2.5441	16.1844	-2.8962
4.17	4.17	-0.0982	0.1697	-0.2679	-2.3802	12.5479	-2.2455
4.00	6.00	-0.0982	1.0726	-1.1709	-2.2218	94.3471	-16.8836
3.85	7.69	-0.0982	0.9856	-1.0839	-2.1139	80.9495	-14.4861

Table 2-d: Cyclic voltammetric data of effect of scan on complex by molar ratio (1:1) at 291.85K for second couple redox waves.

υ	[M] x10^{-3}	[L] x10^{-3}	(E°)M (volt)	(E°) C (volt)	ΔE (volt)	Log [L]	ΔG (KJ/mol)	Log β_{MX}
0.1	4.17	4.17	0.1462	0.1697	-0.0235	-2.38	-11.0369	1.9751
0.01	4.17	4.17	0.1502	0.1590	-0.0088	-2.38	-12.4513	2.2282
0.02	4.17	4.17	0.1479	0.1649	-0.0170	-2.38	-11.6658	2.0876
0.05	4.17	4.17	0.1557	0.1650	-0.0093	-2.38	-12.4025	2.2195

Conclusion

The cyclic voltammetry of $CuBr_2$ was done in the absence and presence of succinic acid as ligand in 0.1M KCl. Mechansims for the redox reaction was studied and explained. Succinic acid form complexes with $CuBr_2$ which little affected by the increase in succinic acid concentration as detected for the evaluated free energy of complexation values using the first and second couple of redox copper waves.

Conflict of Interest

The authors declare that no any conflict given regarding the publication of this paper.

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