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Voltammetric Solvation Study for the Interaction of CuBr2 with Oxalic Acid in KBr Solution at 180C Using Glassy Carbon Electrode

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Abstract

The electrochemical behaviour for CuBr2 was studied in 0.1M KBr in absence and presence of different oxalic acid concentrations as ligand. The mechanism for the reduction and oxidation for CuBr2 in absence and presence of oxalic acid ligand were examined. The scan rates were done for the redox reaction of CuBr2 in absence and presence of oxalic acid for explanation of the type for the electrochemical reaction under consideration. Stability constants and complexation Gibbs free energies for the interaction of CuBr2 with oxalic acid were evaluated from the experimental part and their values were discussed.

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1. Introduction

The heavy metal ions known as pollutants and their interaction by electrochemical methods are interesting [1-6]. Some metal ions can be examined by the reduction at different cathodic materials [6, 7]. In this work, the estimation and evaluation of electrochemical voltammetry energies of $CuBr_2$ in 0.1 M KBr were studied to explain the redox mechanism. The binding of any copper salt with ligands is treated as remediation of copper ions in vitro and vivo [7]. Copper in big quantity cause headache, nose irritation, mouth and eye irritation. It can damage the kidney and liver [7]. Copper is the biggest third abundant metal ions in human body [8]. Excess of copper may cause vomiting and diarrhea [7, 8].

2. Experimental

The chemical $CuBr_2$, KBr are of highly pure from sigma Aldrich Company. Oxalic acid from Adwic company was also used. All chemicals not pre-treated to prevent any harmful effect on them. Conductivity deionized water was used with its conductance value of 2.7 µs. N_2 flow was done for 10 minutes to remove the dissolved oxygen for each run made. (G C E) glassy carbon electrode was prepared in our laboratory by joining pure carbon piece with copper wire and covered with heat shrink polymer to isolate it for different ions migration. The glassy carbon electrode (G C E) is polished well before each run with Al_2O_3on wool piece. The electrode area is 0.502cm^2.

3. Results and Discussion

3.1. Cyclic Voltammetry of $CuBr_2$ in Absence of Oxalic Acid

The cyclic voltammetry for the redox behaviour of $CuBr_2$in 0.1M KBr of 18°C was studied in range of from 0.6 to -0.8V. The reduction process proceeds in the range 0.6 to -0.8 V and the oxidation in the range -0.8 to 0.6V. Studying the effect of scan rate was done and presented in Figure 1 change of Cu(II) to Cu(O) by the two reduction steps at 0 V and -0.42 V are clear in Figures 1 & 2 .One electron mechanism was suggested for each reduction step. $CuBr_2$shows also two oxidation peaks at -.18V and 0.2V indicating the reverse of the reduction process as explained in next suggested mechanism:

$$Cu^{+2} + e^- \quad = \quad Cu^{++} \qquad (1)$$

$$Cu^{+} + e^- \quad = \quad Cu(O) \qquad (2)$$

The electrochemical kinetic parameters like electron transfer rate constant k_s , cathodic surface coverage (Γ_c) , anodic surface coverage (Γ_a) , cathodic quantity of electricity (Q_c) , anodic quantity of electricity (Q_a), diffusion coefficients for anode and cathode and αn_a are presented in Table 1 & 2 [8-20]. The data given in Table (1& 2) indicates the increase in all kinetic parameters by more adding $CuBr_2$ in solution favouring more diffusion controlled reductions.

From scan rate effect the different kinetic parameters mentioned before was done and listed in Table 3& 4 explaining also with Figure 2 that the reactions under or redox system is quasi reversible and diffusion controlled reaction.

3.2. Electrochemical Behaviour of $Cubr_2$in Presence of Oxalic Acid as Complexing Agent

We used oxalic acid as ligand by different concentrations ranging from 9.523x10^{-4} to 0.0103 M.

By increasing oxalic acid concentration shift in $CuBr_2$ waves specially reduction waves to more negative potentials. Also positive potential shift in oxidation peaks are observed indicating complex behaviour observed and complexation interaction between oxalic acid and copper bromide.

New reduction wave was observed at approximately 0.45V which is suggested as complex of oxalate wave. This wave or peak happens at more positive potentials indicating the ease of its formation.

The stability constant and Gibbs free energies of complexation were calculated and their values represented in Table 5 & 6. These data are obtained from $CuBr_2$ wave analysis for the first reduction wave with the first oxidation peak. Also the second reduction peak with the second oxidation peak.

The obtained thermodynamic parameters evaluated are representing in Table 7 & 8.

The scan rate wave studied and from Figure 4 supported the quasi reversible and diffusion control of redox reaction under consideration.

On drawing the relation between $\frac{ipa}{ipc}$versus scan rate (υ) for complex 1:1 (molar ratio) we can support the diffusion controlled system of redox reactions.

For more calculations, the stability complexation constant (B_c) and the Gibbs energies of complexation (G_c) were evaluated following the redox peak and the data are given in Table 9 & 10.

From the data given in Table 9 &10 we conclude complexation reaction between the salt and oxalic acid.

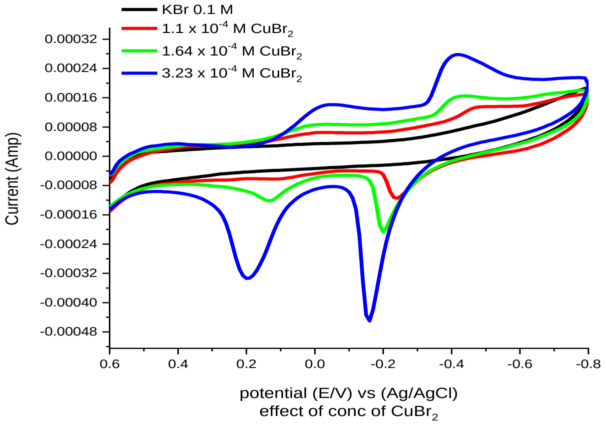

Figure-1. Cyclic voltammograms of different concentrations of CuBr2 in 0.1M KBr.

Table-1. Cyclic voltammetry data for $CuBr_2$ obtained from analysis of the first couple waves in 0.1 M.

ml of Metal	[M] x10-4	Ep,a (volt)	Ep,c (volt)	ΔEp (volt)	-ipa x10^{-4} (Amp)	ipc x10^{-5} (Amp)	-ipa/ ipc	Da x10^{-8}	Dc x10^{-10}	Epc/2	αna	ks x10^{-6}	Γc x10^{-9} (mol/cm^2)	(+) Qc x10^{-5}	Γa x10^{-8} (mol/cm^2)	(-)Qa 10^{-5}
0.4	1.1	-0.23717	2.2874E-05	-0.23719	0.779	1.89	4.122946874	0.564065	3.32	0.067903901	0.688209575	0.589	1.25577	0.951	-0.517745	-3.92
0.6	1.64	-0.19974	-0.001436	-0.1983	1.49	3.83	3.887611437	0.922958	6.11	0.075147348	0.610006663	1.63	2.54139	1.92	-0.987994	-7.48
1.2	3.23	-0.15533	-0.0403252	-0.11501	4.26	11.6	3.680567157	1.95657	14.4	0.059939264	0.465931343	11.5	7.69068	5.82	-2.83061	-21.4

Table-2. Electrochemical parameters of CuBr2 in KBr media by analysis of the second couple of peaks at 291.15 K.

ml of Metal	[M] x10-4	Ep,a (volt)	Ep,c (volt)	ΔEp (volt)	ipa x10^{-5} (Amp)	ipc x10^{-5} (Amp)	-ipa/ ipc	Da x10^{-9}	Dc x10^{-10}	Epc/2	αna	ks x10^{1}	Γc x10^{-9} (mol/cm^2)	(+) Qc x10^{-5}	Γa x10^{-8} (mol/cm^2)	(-)Qa 10^{-5}
0.4	1.1	0.109405	-0.4759611	0.585366	-1.51	2.52	0.60007111	0.211938	5.89	-0.44102695	1.337269069	1.38	1.67245	1.27	-0.100359	-0.760
0.6	1.64	0.136362	-0.4214486	0.557811	-6.54	4.14	1.580514509	1.78683	7.15	-0.38207449	1.186473391	0.827	2.75047	2.08	-0.434716	-3.29
1.2	3.23	0.195592	-0.4159459	0.611537	-22.0	13.8	1.594762346	5.19458	20.4	-0.35701114	0.792679151	3.32	9.14557	6.93	-1.4585	-11.0

Table-3. Scan rate kinetic parameters of CuBr2 for the first peak at 291.15 K

υ	ν^(1/2)	ml added from M	M x10^{-3}	-Ep,a (volt)	-Ep,c (volt)	ΔEp (volt)	-ipa x10^{-4} (Amp)	ipc x10^{-5} (Amp)	-ipa/ ipc	Da x10^{-10}	Dc x10^{-11}	-Epc/2	αna	ks x10^{-3}	Γc x10^{-8} (mol/cm2)	(+) Qc x10^{-4}	Γa x10^{-8} (mol/cm2)	(-)Qa 10^{-4}
0.05	0.223606798	1.2	1.61	0.178058059	0.40550807	227.450011	3.22	9.95	3.232645273	8.92	8.53893	0.35847049	0.993171247	2.60	1.32226	1.00	-4.27441	-3.24
0.02	0.141421356	1.2	1.61	0.181402084	0.373575153	192.173069	3.01	7.64	3.934172239	19.5	12.5849	0.33292042	1.149100587	1.07	2.53812	1.92	-9.98539	-7.56
0.01	0.1	1.2	1.61	0.145184582	0.367994078	222.809496	4.17	11.6	3.585229172	75.0	58.3782	0.31935987	0.960566209	2.73	7.73084	5.86	-27.7168	-21.0

Table-4. Scan rate kinetic parameters of CuBr2 for the second peak at 291.15 K

υ	ν^(1/2)	ml added from M	M x10^{-3}	Ep,a (volt)	Ep,c (volt)	ΔEp (volt)	ipa x10^{-4} (Amp)	ipc x10^{-5} (Amp)	-ipa/ ipc	Da x10^{-10}	Dc x10^{-11}	Epc/2	αna	ks x10^{-3}	Γc x10^{-8} (mol /cm2)	(+) Qc x10^{-5}	Γa x10^{-8} (mol/cm2)	(-)Qa 10^{-4}
0.05	0.223606798	1.2	1.61	0.185063824	-0.035491563	220.5553865	-2.07	6.75	3.06910674	3.70	3.92454	0.053588131	0.524433472	1.12	0.896419	6.79	-2.7512	-2.08
0.02	0.141421356	1.2	1.61	0.186240013	-0.009595429	195.8354417	-1.68	3.32	5.070239441	6.10	2.37409	0.063300436	0.640864513	0.372	1.10239	8.35	-5.58937	-4.23
0.01	0.1	1.2	1.61	0.213753827	0.000540333	213.2134943	-2.04	8.94	2.282722711	18.0	34.4686	0.091806432	0.511869941	1.26	5.94037	45.0	-13.5602	-10.3

Table-5. Cyclic voltammetry data for Oxalic acid - CuBr$_2$ complex obtained from analysis of the first couple waves in 0.1 M.

ml of Ligand	[L] x10-4	Ep,a (volt)	Ep,c (volt)	ΔEp (volt)	ipa x10^{-4} (Amp)	ipc x10^{-5} (Amp)	-ipa/ ipc	Da x10^{-8}	Dc x10^{-10}	Epc/2	αna	ks x10^{-2}	Γc x10^{-9} (mol/cm^2)	(+) Qc x10^{-5}	Γa x10^{-8} (mol/cm^2)	(-)Qa 10^{-4}
0.3	0.8	-0.25584	-0.4776154	0.221779	-3.68	11.5	3.195726603	1.45769	14.3	-0.41597888	0.757933405	1.17	7.64529	5.79	-2.44323	-1.85
0.6	1.59	-0.02906	-0.2541887	0.225124	-4.62	9.45	4.885856274	2.29509	9.61	-0.21310133	1.137001723	1.26	6.27466	4.75	-3.06571	-2.32
0.7	1.85	-0.01884	-0.2563617	0.237522	-4.49	8.58	5.231597488	2.17122	7.93	-0.20417525	0.895182833	1.30	5.69966	4.32	-2.98183	-2.26
0.9	2.36	-0.03474	-0.2944109	0.259675	-4.62	9.67	4.780077086	2.30072	10.1	-0.2414744	0.882498832	2.26	6.42139	4.86	-3.06947	-2.32

Table-6. Cyclic voltammetry data for Oxalic acid - $CuBr_2$ complex obtained from analysis of the second couple waves in 0.1 M.

ml of Ligand	[L] x10-4	Ep,a (volt)	Ep,c (volt)	ΔEp (volt)	ipa $x10^{-4}$ (Amp)	ipc $x10^{-5}$ (Amp)	-ipa/ ipc	Da $x10^{-9}$	Dc $x10^{-10}$	Epc/2	αna	ks $x10^{-3}$	Γc $x10^{-9}$ (mol/cm^2)	(+) Qc $x10^{-5}$	Γa $x10^{-8}$ (mol/cm^2)	(-)Qa 10^{-4}
0.3	0.8	0.102352322	-0.129539981	0.231892303	-2.33	7.81	2.988446399	5.87157	6.57	-0.01480769	0.407177199	7.14	5.18875	3.93	-1.55063	-1.17
0.6	1.59	0.32043734	0.059015852	0.261421488	-2.25	5.17	4.351156285	5.44593	2.88	0.167428463	0.430912718	8.74	3.43212	2.60	-1.49337	-1.13
0.7	1.85	0.332309219	0.021059568	0.311249652	-1.96	2.92	6.723904263	4.14532	0.917	0.102439928	0.574049718	15.3	1.93771	1.47	-1.3029	-0.987
0.9	2.36	0.326947691	0.040538909	0.286408782	-1.93	3.56	5.403273208	3.99763	1.37	0.152364759	0.417760053	9.75	2.36797	1.79	-1.27948	-0.969

Table-7. thermodynamic parameters obtained from the first peak of oxalic acid-$CuBr_2$ complex

Ml of ligand	[L] $X10^{-4}$	(Ep,a)M	(Ep,a)C	ΔE mv	j	Log βj	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (KJ/mol)
0.3	8.00E-05	-0.155331539	-0.25583682	0.100505281	0.25	4.493734173	-25.12001045	25.34085784	0.172840789
0.6	1.59E-04	-0.155331539	-0.029064641	0.126266898	0.5	6.258484448	-34.9849788	18.19531226	0.182155475
0.7	1.85E-04	-0.155331539	-0.018839231	0.136492308	0.583333333	6.889700905	-38.51348391	16.52830513	0.18853156
0.9	2.36E-04	-0.155331539	-0.034736254	0.120595285	0.75	6.883038331	-38.47624007	16.54430404	0.188458791

Table-8. thermodynamic parameters obtained from the first peak of oxalic acid-$CuBr_2$ complex

Ml of ligand	[L] $X10^{-4}$	(Ep,a)M	(Ep,a)C	ΔE mv	j	Log βj	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (KJ/mol)
0.3	8.00E-05	0.1955915	0.102352322	0.093239178	0.25	-2.194448637	12.26698567	-51.89234185	-0.219761355
0.6	1.59E-04	0.1955915	0.32043734	0.12484584	0.5	6.20942863	-34.71075638	18.33905913	0.181708565
0.7	1.85E-04	0.1955915	0.332309219	0.136717719	0.583333333	6.897482237	-38.55698162	16.50965887	0.188616683
0.9	2.36E-04	0.1955915	0.326947691	0.131356191	0.75	7.254511691	-40.55277916	15.69713906	0.192669698

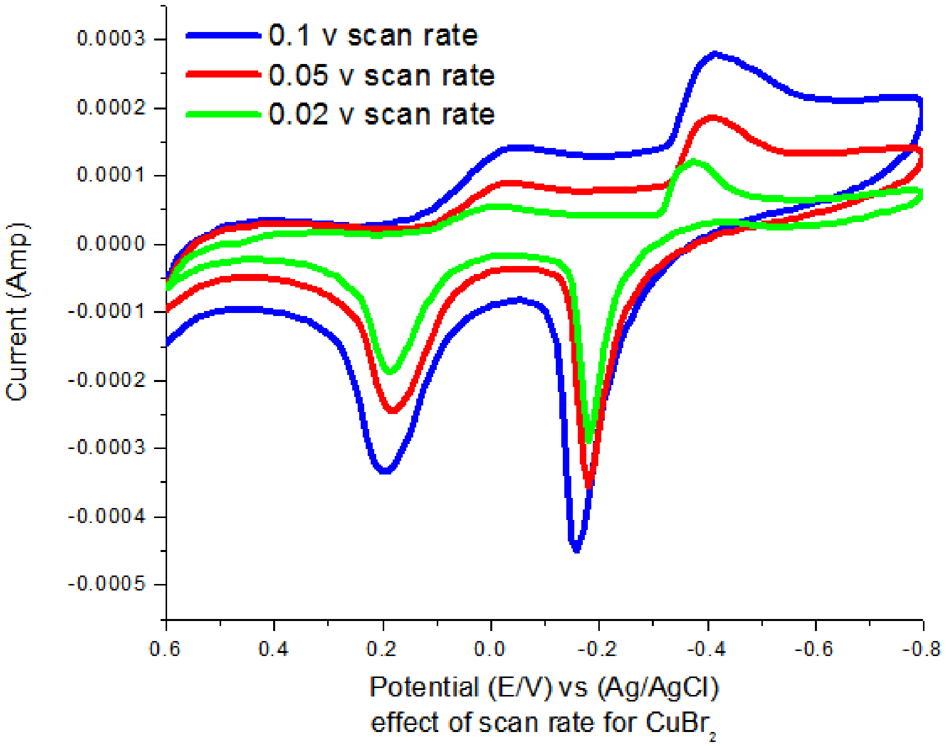

Figure-2. Effect of different scan rates on cyclic voltamogram of $CuBr_2$.

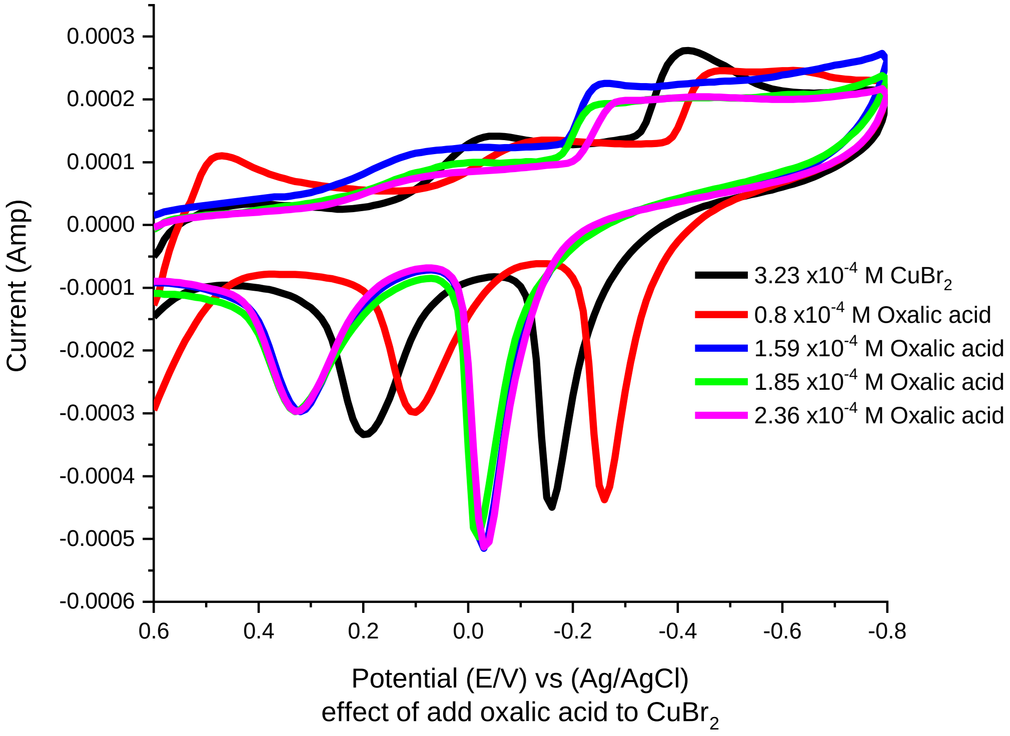

Figure-3. Effect of different concentrations of oxalic acid on the cyclic voltamogram of CuBr$_2$.

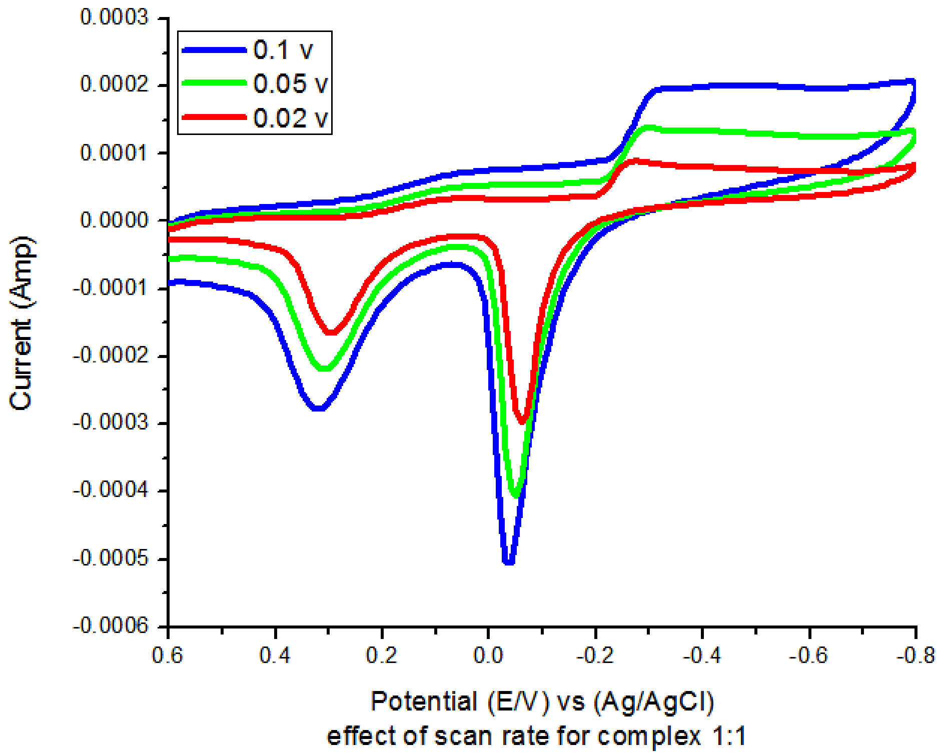

Figure-4. Effect of different scan rates on the cyclic voltamogram of oxalic acid + $CuBr_2$.

Effect of different scan rates as seen in Figure 3 indicate the diffusion controlled reaction which decreases by the decrease in san rate vales.

Table-9. Cyclic voltammetry data of Scan Rates Oxalic acid and CuBr2 complex for first couple of waves at 291.15 K.

υ	ν^(1/2)	ml added from M	M $x10^{-4}$	Ep,a (volt)	Ep,c (volt)	ΔEp (volt)	ipa $x10^{-4}$ (Amp)	ipc $x10^{-5}$ (Amp)	-ipa/ ipc	Da $x10^{-8}$	Dc $x10^{-8}$	Epc/2	αna	ks $x10^{-2}$	Γc $x10^{-8}$ (mol/ cm2)	(+) Qc $x10^{-4}$	Γa $x10^{-8}$ (mol/cm 2)	(-)Qa 10^{-4}
0.05	0.223606798	1.2	3.23	-0.048797293	-0.295931265	247.1339724	-3.91	8.00	4.885503275	3.29114	1.18933	-0.25016663	1.183799434	1.57	1.0627	0.805	-5.19182	-3.93
0.02	0.141421356	1.2	3.23	-0.064033542	-0.267851036	203.8174936	-2.98	4.74	6.301518508	4.79888	0.120851	-0.233770273	1.370754902	0.455	1.57305	1.19	-9.91257	-7.51
0.01	0.1	1.2	3.23	-0.033185921	-0.306026067	272.8401463	-4.97	10.5	4.728996576	26.5975	1.18933	-0.266562986	0.511869941	3.69	6.97884	5.29	-33.0029	-25.0

Table-10. Cyclic voltammetry data of Scan Rates Oxalic acid and CuBr2 complex for second couple of waves at 291.15K.

υ	ν^(1/2)	ml added from M	M $x10^{-4}$	Ep,a (volt)	Ep,c (volt)	ΔEp (volt)	ipa $x10^{-4}$ (Amp)	ipc $x10^{-5}$ (Amp)	-ipa/ ipc	Da $x10^{-19}$	Dc $x10^{-10}$	Epc/2	αna	ks $x10^{-3}$	Γc $x10^{-9}$ (mol/cm2)	(+) Qc $x10^{-5}$	Γa $x10^{-8}$ (mol/cm2)	(-)Qa 10^{-4}
0.05	0.223606798	1.2	3.23	0.308701313	0.065304612	243.396701	-1.50	3.15	4.750104674	4.82573	2.13873	0.159342368	0.496783153	4.00	4.18528	3.17	-1.98805	-1.51
0.02	0.141421356	1.2	3.23	0.294298648	0.074634865	219.6637832	-1.13	2.42	4.656409523	6.84191	3.15555	0.168540324	0.497483036	1.92	8.03811	6.09	-3.74287	-2.83
0.01	0.1	1.2	3.23	0.327533031	0.040381735	287.1512965	-1.98	3.54	5.585784971	42.1681	13.515	0.146945123	0.43839046	10.1	23.5255	17.8	-13.1409	-9.95

Table-11. Thermodynamic parameters for Oxalic acid-$CuBr_2$ at different scan rates of the first peak

Ml of ligand	[L] $X10^{-4}$	(Ep,a)M	(Ep,a)C	ΔE mv	j	Log βj	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (KJ/mol)
0.9	2.36E-04	-0.155331539	-0.034736254	0.120595285	0.75	6.883038331	-38.47624007	76.1531196	0.392633532
0.9	2.36E-04	-0.145184582	-0.033185921	0.111998661	0.75	6.586277368	-36.81734388	81.04029714	0.403691183
0.9	2.36E-04	-0.181402084	-0.064033542	0.117368542	0.75	6.771649075	-37.85357323	75.98973334	0.389941108
0.9	2.36E-04	-0.178058059	-0.048797293	0.129260766	0.75	7.182176292	-40.14842369	61.76636997	0.34908304

Table-12. Thermodynamic parameters for Oxalic acid-$CuBr_2$ at different scan rates of the second peak

Ml of ligand	[L] $X10^{-4}$	(Ep,a)M	(Ep,a)C	ΔE mv	j	Log βj	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (KJ/mol)
0.9	2.36E-04	0.1955915	0.326947691	0.131356191	0.75	7.254511691	-40.55277916	61.15049185	0.348358524
0.9	2.36E-04	0.213753827	0.327533031	0.113779204	0.75	6.647742842	-37.16093638	66.73196731	0.35585855
0.9	2.36E-04	0.186240013	0.294298648	0.108058635	0.75	6.450265137	-36.05703441	68.77499585	0.359075288
0.9	2.36E-04	0.185063824	0.308701313	0.123637489	0.75	6.988057154	-39.06329614	63.48215938	0.351243211

On comparing the different thermodynamic parameters .mainly the stability constants and Gibbs free energies of complex interaction [9-32] for the reaction of oxalic acid plus copper bromide by analysis of the two couples of peaks at different san rates, we noticed almost equal values were obtained by analysis of the first and second couples of peaks as the data represented in Tables 11 & 12.

3.3. Quantum Chemical Calculations

The different quantum chemical calculation were done using Gaussian 09 program and set DFT B3LYP/6-311G method of calculation [29]. From the many obtained data we obtained the HOMO and LUMO energy levels for oxalic acid. The difference between the two mentioned energy levels gave the gap energy which is good and indicate its reactivity Appendix 1.

Table-13. Comparison between oxalic acid alone and oxalic acid-$CuBr_2$ complex thermal properties

Thermal property	**Oxalic acid**	**Oxalic acid-$CuBr_2$ complex**
Dipole moment	0	4.9107 Debye
Quadrupole moment (XX)	-32.2683	-71.654
Octapole moment (XXX)	0	0.204
Hexadecapole moment (XXXX)	-36.7838	-19.1175
Translational energy	0.889 k.cal/Mol-K	0.889 k.cal?Mol-K
Heat capacity at constant volume (Cv)	2.981 cal/Mol.K	2.981 cal/Mol.K
Translational entropy	39.404 cal/Mol.K	42.314 cal/Mol.K

3.4. Comparison between Oxalic Acid and Oxalic Acid –Cubr$_2$ Complex in Thermal Properties.

The different thermal properties were evaluated from the theoretical calculation of the frequencies for both oxalic acid alone and oxalic acid-CuBr2 complex quantum mechanically in water .The main data is summarized in Table 13 and the whole data are given in Appendixes 2 and 3. It was observed that the complex oxalic acid-$CuBr_2$ has greater dipole moment than that of oxalic acid alone indicate its activity. The quadrupole moment. Octapole moment, heat capacity at constant volume and translational entropy are greater for the complex oxalic acid –copper bromide ,the we can use as active agent in biological application. All the complex parameter facilitate its uses .Other parameters are given in Appendixes 2 and 3.

Absolute solvation free energy of hydrogen ion under complexing conditions of $CuBr_2$ + Oxalic acid:

Estimation of real solvation free energy of the proton and the value of E_{SHE} which determined by the cycle [30].:

$$\begin{tikzcd} H^+_{(aq)} \arrow[d, "-\Delta G^\circ (H^+)"'] & + & e^-_{(g)} \arrow[d, "\Delta G (O)"] \arrow[r, "\Delta G_{rxn}"] & 1/2H_{2\,(g)} \\ H^+_{(g)} & + & e^-_{(g)} \arrow[r, "-\Delta G^\circ_{ion}"] & H^\bullet_{(g)} \arrow[u, "-\Delta G^\circ_S"'] \end{tikzcd}$$

When we stdy the cycle given above we can estimate the ESHE the standard hydrogen electrode potential under our conditions applying equation (3)and the ΔG°_{ion} under the complex reaction between $CuBr_2$ and oxalic acid.

$$E_{SHE} = -\Delta G/F \tag{3}$$

$$-\Delta G_{rxn} = \Delta G^\circ_{ion} + \Delta G^\circ_{atm} + \Delta G^\circ_S (H^+) = \Delta_f G^\circ (H^+) + \Delta G^\circ_S (H^+) \tag{4}$$

$$\Delta G^\circ_{ion} + \Delta G^\circ_{atm} = \Delta_f G^\circ (H^+) \tag{5}$$

The coresponding $\Delta_f G^\circ (H^+)$ based on Fermi-Dirack statistics is 1095 k.J/mole [31, 32].

Applying the above cycle the solvation free energy for hydrogen ion $\Delta G^\circ_S (H^+)$ can be calculated applying equation (4) for our results and gave values ranging from -1131kJ/Mol at scan rate 0.05 V/Sec to -1135 kJ/Mol at scan rate 0.01 V/Sec for interaction of $CuBr_2$ with oxalic acid in 0.1M KBr.This indicate that the san rate has little effect of the solvation of hydrogen ion.The sum of $\Delta G^\circ_{ion} + \Delta G^\circ_{atm}$ for hydrogen ion was evaluated by applying equation (5) and know that ΔG°_{atm} is concluded in all mmeasurents ,therefore the values of $\Delta G^\circ_{ion} + \Delta G^\circ_{atm}$ indication about the ionic solvation free energy of hydrogen ion with values are ranging from 1056 KJ/Mol at 0.1M scan rate to 1135 KJ/Mol at scan rate 0.01 V/Sec.This indicate the complex formed from the interaction of $CuBr_2$ and oxalic acid decrease the hydroen ion activity.The free energy of hydrogen ion is decreased when the complex is formed between the reaction of $CuBr_2$ and oxalic acid indicating the hydrogen ion is less movable than in medium without complex interaction..

It was also observed that many theoretical data for the complex studies are greater than that of oxalic acid alone. As example all the partition function data are greater for the complex than the used ligand specially the electronic and rotational partition functions which gave corresponding ally greater energy values.

4. Conclusions

$CuBr_2$ peaks are explained in absence and presence of oxalic acid as a ligand. Different solvation parameters were evaluated by analysis of the two couples of peaks for copper ions. The thermodynamic complexation properties were evaluated and found insure the complexation interaction between cupper bromide and oxalic acid studied here.

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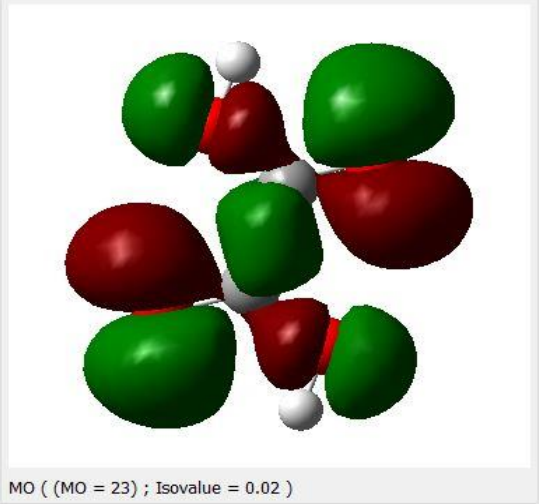
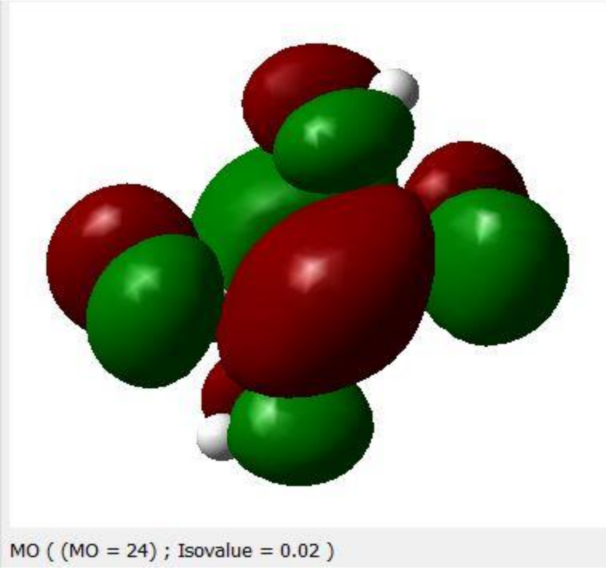


HOMO, (N=23)(-0.30111ev)



LUMO, (N=24)(-0.09138ev).

Appendix-1. HOMO & LUMO levels for oxalic acid.

Appendix-2. Physical properties of oxalic acid alone.

```
Dipole moment (field-independent basis, Debye):
   X=              0.0000    Y=              0.0000    Z=              0.0000  Tot=              0.0000
 Quadrupole moment (field-independent basis, Debye-Ang):
  XX=            -45.9262   YY=            -19.1403   ZZ=            -32.2683
  XY=              1.3844   XZ=              0.0000   YZ=              0.0000
 Traceless Quadrupole moment (field-independent basis, Debye-Ang):
  XX=            -13.4813   YY=             13.3046   ZZ=              0.1766
  XY=              1.3844   XZ=              0.0000   YZ=              0.0000
 Octapole moment (field-independent basis, Debye-Ang**2):
 XXX=              0.0000  YYY=              0.0000  ZZZ=              0.0000  XYY=              0.0000
 XXY=              0.0000  XXZ=              0.0000  XZZ=              0.0000  YZZ=              0.0000
 YYZ=              0.0000  XYZ=              0.0000
 Hexadecapole moment (field-independent basis, Debye-Ang**3):
 XXXX=           -268.2226 YYYY=           -167.5877 ZZZZ=            -27.9062 XXXY=            -36.7838
 XXXZ=              0.0000 YYYX=             -6.8845 YYYZ=              0.0000 ZZZX=              0.0000
 ZZZY=              0.0000 XXYY=           -102.5791 XXZZ=            -43.7167 YYZZ=            -58.0004
 XXYZ=              0.0000 YYXZ=              0.0000 ZZXY=             -6.9493
 N-N= 2.311045083462D+02 E-N=-1.350788684135D+03  KE= 3.749716196477D+02
 Symmetry AG   KE= 1.811837398941D+02
 Symmetry BG   KE= 8.499432461333D+00
 Symmetry AU   KE= 8.032598844166D+00
 Symmetry BU   KE= 1.772558484481D+02
 Exact polarizability:  60.502  -2.061  50.158   0.000   0.000  27.232
Zero-point correction=                           0.048716 (Hartree/Particle)
 Thermal correction to Energy=                    0.054282
 Thermal correction to Enthalpy=                  0.055226
 Thermal correction to Gibbs Free Energy=         0.019237
 Sum of electronic and zero-point Energies=           -378.311469
 Sum of electronic and thermal Energies=              -378.305903
 Sum of electronic and thermal Enthalpies=            -378.304959
 Sum of electronic and thermal Free Energies=         -378.340948

                     E (Thermal)             CV                S
                      KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                   34.062             18.538             75.744
 Electronic               0.000              0.000              0.000
 Translational            0.889              2.981             39.404
 Rotational               0.889              2.981             24.923
 Vibrational             32.285             12.576             11.417
 Vibration     1          0.594              1.984              5.803
 Vibration     2          0.675              1.727              1.590
 Vibration     3          0.789              1.410              0.866
 Vibration     4          0.794              1.399              0.850
 Vibration     5          0.885              1.184              0.587
 Vibration     6          0.977              0.995              0.421
                       Q            Log10(Q)             Ln(Q)
 Total Bot       0.141765D-08         -8.848430        -20.374263
 Total V=0       0.362433D+14         13.559228         31.221276
 Vib (Bot)       0.676668D-21        -21.169625        -48.744862
 Vib (Bot)    1  0.681126D+01          0.833228          1.918578
 Vib (Bot)    2  0.712891D+00         -0.146977         -0.338426
 Vib (Bot)    3  0.407968D+00         -0.389373         -0.896565
 Vib (Bot)    4  0.401807D+00         -0.395983         -0.911784
 Vib (Bot)    5  0.301784D+00         -0.520303         -1.198043
 Vib (Bot)    6  0.237511D+00         -0.624316         -1.437541
 Vib (V=0)       0.172995D+02          1.238033          2.850677
 Vib (V=0)    1  0.732959D+01          0.865080          1.991920
 Vib (V=0)    2  0.137075D+01          0.136960          0.315362
 Vib (V=0)    3  0.114532D+01          0.058927          0.135684
 Vib (V=0)    4  0.114144D+01          0.057454          0.132293
 Vib (V=0)    5  0.108402D+01          0.035035          0.080672
 Vib (V=0)    6  0.105354D+01          0.022653          0.052160
```

```
 Electronic     0.100000D+01          0.000000         0.000000
```

Appendix-3. Cu oxalate theoretical data.

```
Dipole moment (field-independent basis, Debye):
   X=             0.0663    Y=             4.9102    Z=             0.0000  Tot=             4.9107
 Quadrupole moment (field-independent basis, Debye-Ang):
   XX=           -91.9474   YY=          -114.3172   ZZ=           -71.6546
   XY=            -0.2874   XZ=             0.0000   YZ=             0.0000
 Traceless Quadrupole moment (field-independent basis, Debye-Ang):
   XX=             0.6923   YY=           -21.6775   ZZ=            20.9852
   XY=            -0.2874   XZ=             0.0000   YZ=             0.0000
 Octapole moment (field-independent basis, Debye-Ang**2):
  XXX=              0.8198  YYY=             55.7168  ZZZ=              0.0000  XYY=              0.2044
  XXY=             20.5202  XXZ=              0.0000  XZZ=              0.0291  YZZ=              1.9610
  YYZ=              0.0000  XYZ=              0.0000
 Hexadecapole moment (field-independent basis, Debye-Ang**3):
 XXXX=           -705.9591 YYYY=          -3600.9243 ZZZZ=            -59.2390 XXXY=            -19.1175
 XXXZ=              0.0000 YYYX=            -18.5880 YYYZ=              0.0000 ZZZX=              0.0000
 ZZZY=              0.0000 XXYY=           -724.5780 XXZZ=           -118.5522 YYZZ=           -458.3488
Zero-point correction=                           0.051032 (Hartree/Particle)
 Thermal correction to Energy=                    0.063515
 Thermal correction to Enthalpy=                  0.064459
 Thermal correction to Gibbs Free Energy=         0.009653
 Sum of electronic and zero-point Energies=           -2394.538381
 Sum of electronic and thermal Energies=              -2394.525898
 Sum of electronic and thermal Enthalpies=            -2394.524954
 Sum of electronic and thermal Free Energies=         -2394.579760

                     E (Thermal)             CV                S
                      KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                  39.856             42.355            115.348
 Electronic              0.000              0.000              1.377
 Translational           0.889              2.981             42.314
 Rotational              0.889              2.981             31.566
 Vibrational            38.079             36.393             40.090
 Vibration     1         0.594              1.983              5.556
 Vibration     2         0.594              1.981              5.210
 Vibration     3         0.602              1.957              3.672
 Vibration     4         0.604              1.949              3.463
 Vibration     5         0.606              1.942              3.281
 Vibration     6         0.628              1.870              2.358
 Vibration     7         0.643              1.825              2.039
 Vibration     8         0.658              1.778              1.796
 Vibration     9         0.662              1.766              1.744
 Vibration    10         0.691              1.677              1.428
 Vibration    11         0.704              1.641              1.324
 Vibration    12         0.725              1.581              1.180
 Vibration    13         0.739              1.542              1.097
 Vibration    14         0.788              1.414              0.872
 Vibration    15         0.791              1.406              0.861
 Vibration    16         0.806              1.367              0.804
 Vibration    17         0.825              1.321              0.744
 Vibration    18         0.945              1.058              0.471
 Vibration    19         0.954              1.039              0.455
                       Q            Log10(Q)             Ln(Q)
 Total Bot       0.362864D-04         -4.440256        -10.224068
 Total V=0       0.107895D+20         19.032999         43.825101
 Vib (Bot)       0.707643D-19        -19.150186        -44.094933
 Vib (Bot)    1  0.601198D+01          0.779018          1.793755
 Vib (Bot)    2  0.504664D+01          0.703002          1.618722
 Vib (Bot)    3  0.229876D+01          0.361493          0.832369
 Vib (Bot)    4  0.206136D+01          0.314153          0.723365
 Vib (Bot)    5  0.187405D+01          0.272781          0.628101
```

```
Vib (Bot)       6  0.113443D+01        0.054777        0.126128
Vib (Bot)        7  0.943237D+00       -0.025379       -0.058437
Vib (Bot)        8  0.813282D+00       -0.089759       -0.206678
Vib (Bot)       9  0.787101D+00       -0.103969       -0.239399
Vib (Bot)       10  0.638740D+00       -0.194676       -0.448258
Vib (Bot)       11  0.593359D+00       -0.226682       -0.521956
Vib (Bot)       12  0.532801D+00       -0.273435        -0.629607
Vib (Bot)       13  0.498781D+00       -0.302090        -0.695587
Vib (Bot)        14  0.410447D+00        -0.386743        -0.890508
Vib (Bot)        15  0.405957D+00        -0.391520        -0.901509
Vib (Bot)         16  0.384208D+00        -0.415433        -0.956571
Vib (Bot)         17  0.361154D+00        -0.442307        -1.018450
Vib (Bot)        18  0.257202D+00        -0.589726        -1.357894
Vib (Bot)        19  0.251126D+00        -0.600108        -1.381800
Vib (V=0)          0.210412D+05           4.323070         9.954236
Vib (V=0)          1  0.653274D+01         0.815095         1.876826
Vib (V=0)           2  0.557134D+01         0.745960          1.717636
Vib (V=0)           3  0.285251D+01         0.455227          1.048198
Vib (V=0)           4  0.262113D+01         0.418489          0.963606
Vib (V=0)           5  0.243960D+01         0.387319          0.891835
Vib (V=0)           6  0.173973D+01         0.240481          0.553729
Vib (V=0)            7  0.156757D+01         0.195226          0.449524
Vib (V=0)             8  0.145469D+01         0.162770          0.374791
Vib (V=0)             9  0.143248D+01         0.156090          0.359411
Vib (V=0)            10  0.131117D+01         0.117657          0.270916
Vib (V=0)             11  0.127593D+01         0.105829          0.243679
Vib (V=0)             12  0.123067D+01         0.090141          0.207558
Vib (V=0)             13  0.120625D+01         0.081436          0.187513
Vib (V=0)             14  0.114689D+01         0.059522          0.137054
Vib (V=0)             15  0.114405D+01         0.058445          0.134575
Vib (V=0)              16  0.113057D+01         0.053297          0.122720
Vib (V=0)               17  0.111679D+01         0.047972          0.110460
Vib (V=0)              18  0.106227D+01         0.026237          0.060413
Vib (V=0)              19  0.105952D+01         0.025110          0.057817
Electronic             0.200000D+01            0.301030          0.693147
Translational       0.145127D+09          8.161749         18.793122
Rotational         0.176665D+07          6.247150         14.384595
```