



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

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Keywords:

Education
Human intelligence
Higher education
Teaching method
Problem solving
Problem formulating.

Received: 8 July 2020

Revised: 13 August 2020

Accepted: 25 August 2020

Published: 8 September 2020

Abstract

The body of literature on human intelligence includes studies that stimulate human thinking and shed light on which we are as living entities and how we survive in complex situations. However, these studies lack one vital aspect of intelligence. What is lacking is an acknowledgement of the interconnectedness and interdependence of the embodied mind, human sociocultural and sociohistorical evolution, and transpersonal dynamics of who we are and how we make sense of our day-to-day living and enactment. Therefore, the intention of this research report is to explore a holistic approach to human intelligence and its implications for education in general and in mathematics education as an exemplar.

Funding: This study received no specific financial support.

Competing Interests: The authors declare that they have no competing interests.

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 CuBr₂ 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].

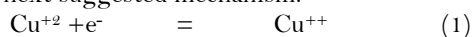
2. Experimental

The chemical CuBr₂, 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. N₂ 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 Al₂O₃ on wool piece. The electrode area is 0.502cm².

3. Results and Discussion

3.1. Cyclic Voltammetry of CuBr₂ in Absence of Oxalic Acid

The cyclic voltammetry for the redox behaviour of CuBr₂ in 0.1M KBr at 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. CuBr₂ shows also two oxidation peaks at -0.18V and 0.2V indicating the reverse of the reduction process as explained in next suggested mechanism:



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 CuBr₂ 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 CuBr₂ in Presence of Oxalic Acid as Complexing Agent

We used oxalic acid as ligand by different concentrations ranging from 9.523×10^{-4} to 0.0103 M. By increasing oxalic acid concentration shift in CuBr₂ 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 CuBr₂ 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 (v) 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.

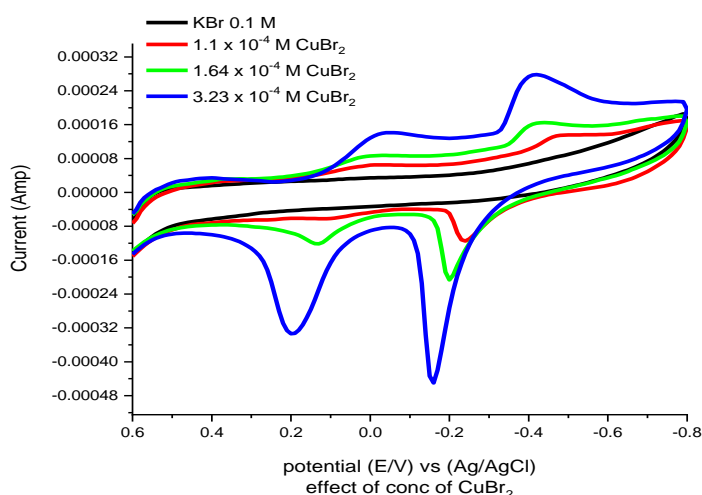


Figure-1. Cyclic voltammograms of different concentrations of CuBr₂ in 0.1M KBr.

Table-1. Cyclic voltammetry data for CuBr₂ 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 x10 ⁻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 x10 ⁻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

v	v ^{^(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/cm ²)	(+) Qc x10 ⁻⁴	Γa x10 ⁻⁸ (mol/cm ²)	(-) Qa x10 ⁻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

v	v ^{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/cm ²)	(+) Qc x10 ⁻⁵	Γa x10 ⁻⁸ (mol/cm ²)	(-)Qa 10 ⁻⁴
0.05	0.2236 06798	1.2	1.61	0.1850 63824	- 0.035491 563	220.555 3865	-2.07	6.75	3.06910 674	3.70	3.92454	0.0535 88131	0.5244 33472	1.12	0.896 419	6.79	-2.7512	-2.08
0.02	0.1414 21356	1.2	1.61	0.1862 40013	- 0.009595 429	195.835 4417	-1.68	3.32	5.07023 9441	6.10	2.37409	0.0633 00436	0.6408 64513	0.372	1.102 39	8.35	-5.58937	-4.23
0.01	0.1	1.2	1.61	0.2137 53827	0.000540 333	213.213 4943	-2.04	8.94	2.28272 2711	18.0	34.4686	0.0918 06432	0.5118 69941	1.26	5.940 37	45.0	-13.5602	-10.3

Table-5. Cyclic voltammetry data for Oxalic acid - CuBr₂ 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	- 0.4159 7888	0.7579 33405	1.17	7.645 29	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	- 0.2131 0133	1.1370 01723	1.26	6.274 66	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	- 0.2041 7525	0.8951 82833	1.30	5.699 66	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	- 0.2414 744	0.8824 98832	2.26	6.421 39	4.86	-3.06947	-2.32

Table-6. Cyclic voltammetry data for Oxalic acid - CuBr₂ 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-CuBr₂ complex

MI 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-CuBr₂ complex

MI 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

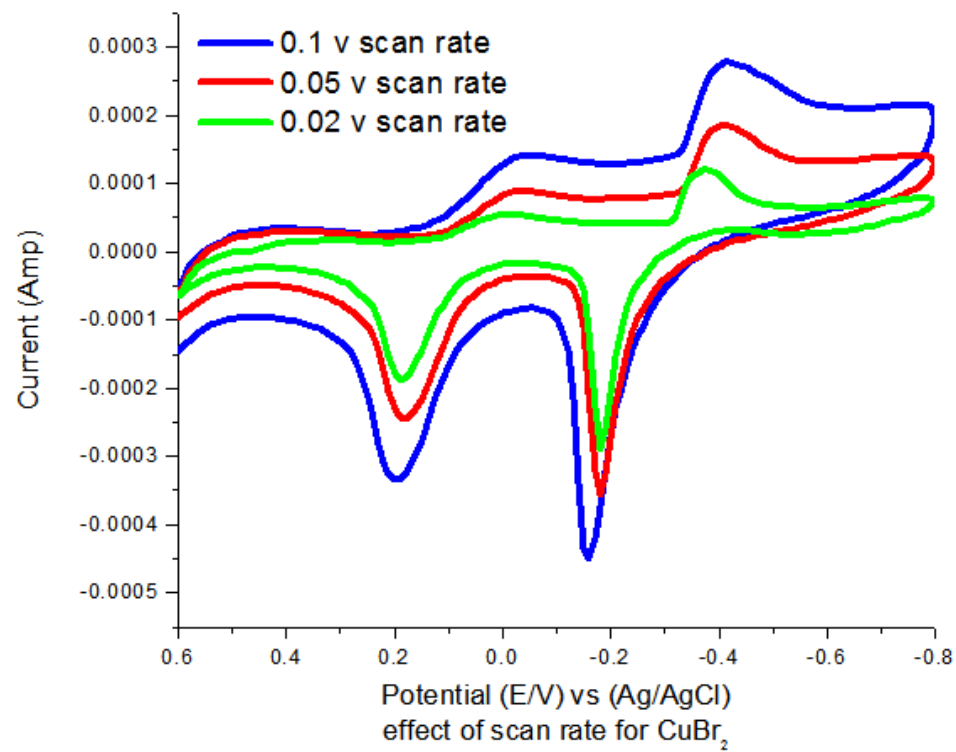


Figure-2. Effect of different scan rates on cyclic voltamogram of CuBr₂.

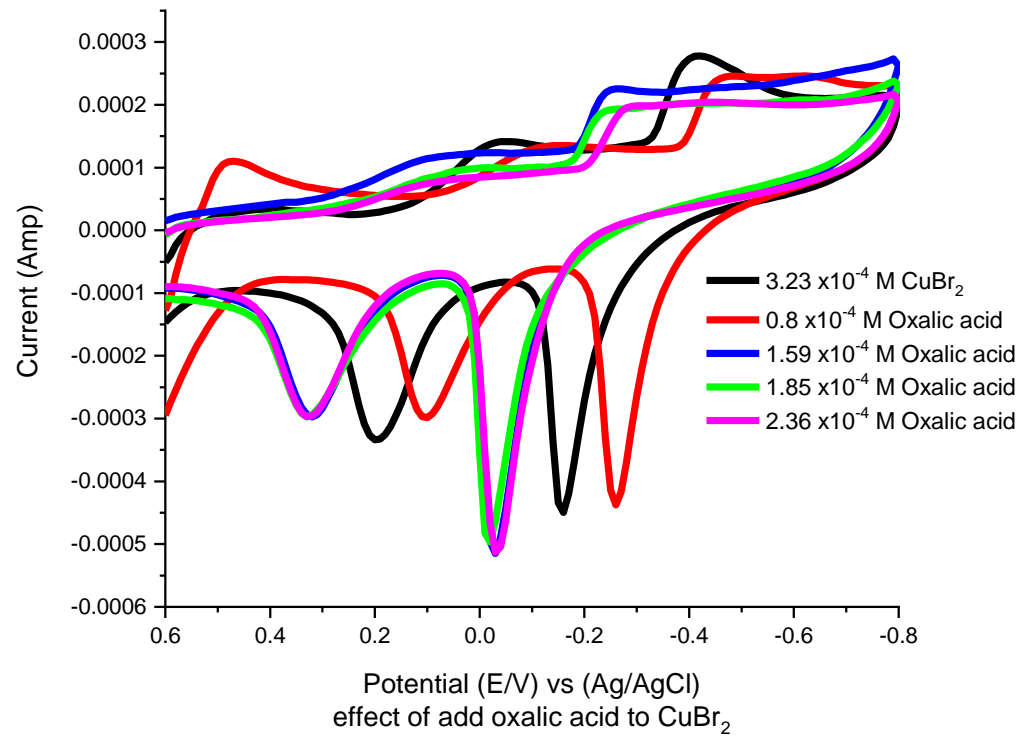


Figure-3. Effect of different concentrations of oxalic acid on the cyclic voltamogram of CuBr_2 .

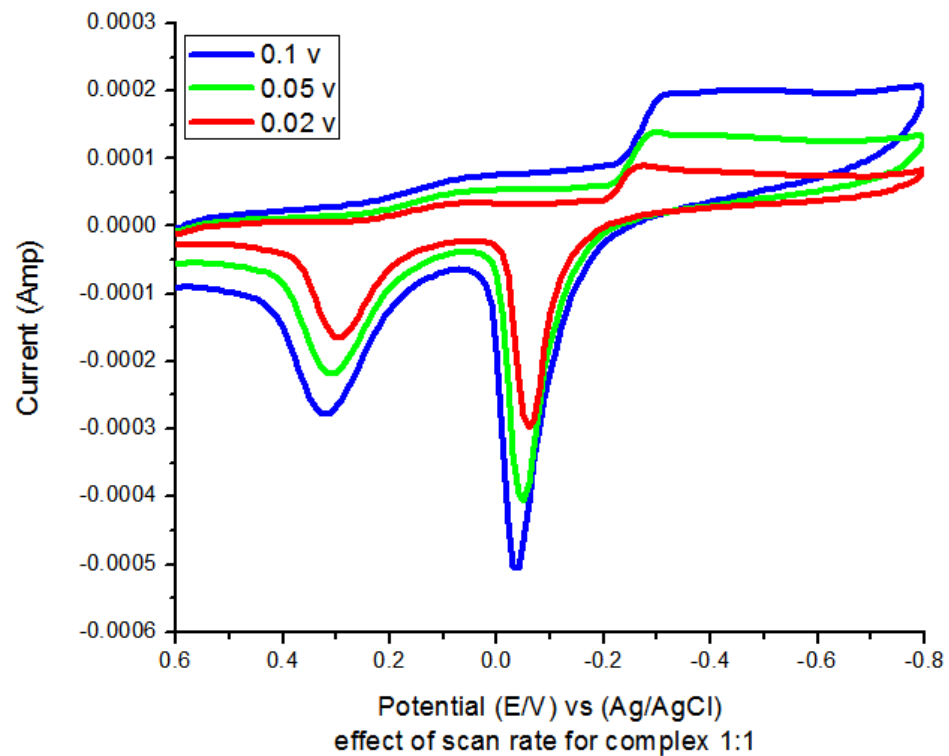


Figure-4. Effect of different scan rates on the cyclic voltammogram of oxalic acid + CuBr₂.

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

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

v	v ^(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/cm ²)	(+) 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.

v	v ^(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/cm ²)	(+) Qc x10 ⁻⁵	Γa x10 ⁻⁸ (mol/cm ²)	(-) 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-CuBr₂ at different scan rates of the first peak

MI 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-CuBr₂ at different scan rates of the second peak

MI 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 scan 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-CuBr₂ complex thermal properties

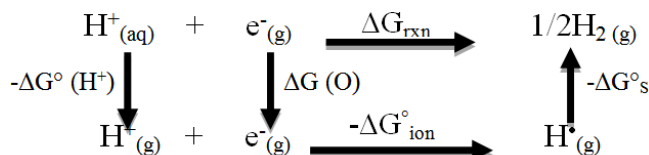
Thermal property	Oxalic acid	Oxalic acid-CuBr ₂ complex
Dipole moment	0	4.9107 Debye
Quadrupole moment (XX)	-32.2683	-71.654
Octapole moment (XXX)	0	0.204
Hexadecapole moment (XXXX)	-36.7838	-19.1175
Translational energy	0.889 k.cal/Mol.K	0.889 k.cal?Mol.K
Heat capacity at constant volume (Cv)	2.981 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-CuBr₂ 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-CuBr₂ has greater dipole moment than that of oxalic acid alone indicate its activity. The quadrupole 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 CuBr₂ + Oxalic acid:

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



When we study the cycle given above we can estimate the ESHE the standard hydrogen electrode potential under our conditions applying equation (3) and the $\Delta G^\circ_{\text{ion}}$ under the complex reaction between CuBr₂ and oxalic acid.

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

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

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

The corresponding $\Delta_f G^\circ(\text{H}^+)$ based on Fermi-Dirack statistics is 1095 kJ/mole [31, 32].

Applying the above cycle the solvation free energy for hydrogen ion $\Delta G^\circ_{\text{s}}(\text{H}^+)$ 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 CuBr₂ with oxalic acid in 0.1M KBr.This indicate that the scan rate has little effect of the solvation of hydrogen ion.The sum of $\Delta G^\circ_{\text{ion}} + \Delta G^\circ_{\text{atm}}$ for hydrogen ion was evaluated by applying equation (5) and know that $\Delta G^\circ_{\text{atm}}$ is concluded in all measurements ,therefore the values of $\Delta G^\circ_{\text{ion}} + \Delta G^\circ_{\text{atm}}$ 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 CuBr₂ and oxalic acid decrease the hydrogen ion activity.The free energy of hydrogen ion is decreased when the complex is formed between the reaction of CuBr₂ 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.

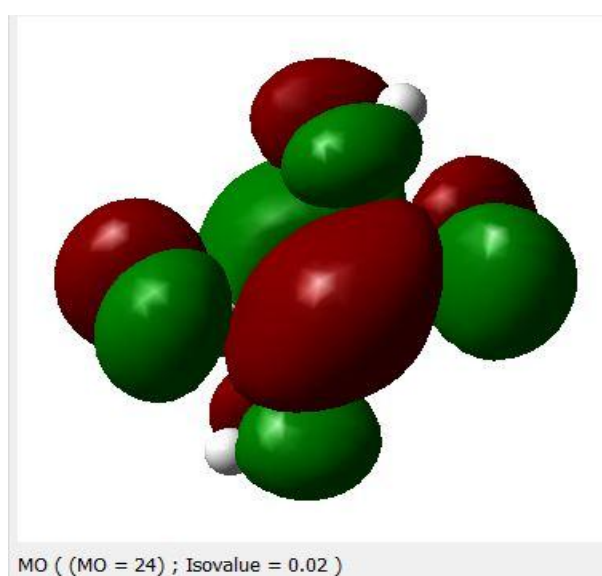
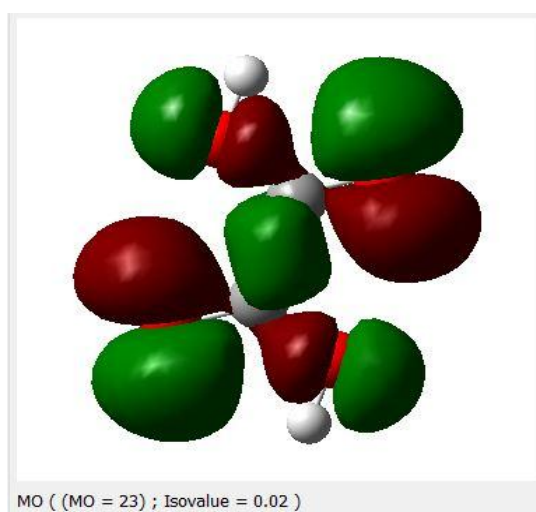
4. Conclusions

CuBr₂ 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 copper bromide and oxalic acid studied here.

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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 YYYY= -6.8845 YYYZ= 0.0000 ZZZX= 0.0000
 ZZZY= 0.0000 XXY= -102.5791 XXZZ= -43.7167 YYZZ= -58.0004
 XXYZ= 0.0000 YYXZ= 0.0000 ZZZY= -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) KCal/Mol	CV Cal/Mol-Kelvin	S 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 YYYYX= -18.5880 YYYZ= 0.0000 ZZZX= 0.0000

ZZZY= 0.0000 XYYX= -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) KCal/Mol	CV Cal/Mol-Kelvin	S 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