



Original Research Article

Interaction parameters for CuCl_2 plus orange G (OG) at 19.1 °C using carbon glassy electrode (CGE) in KCl aqueous solutions

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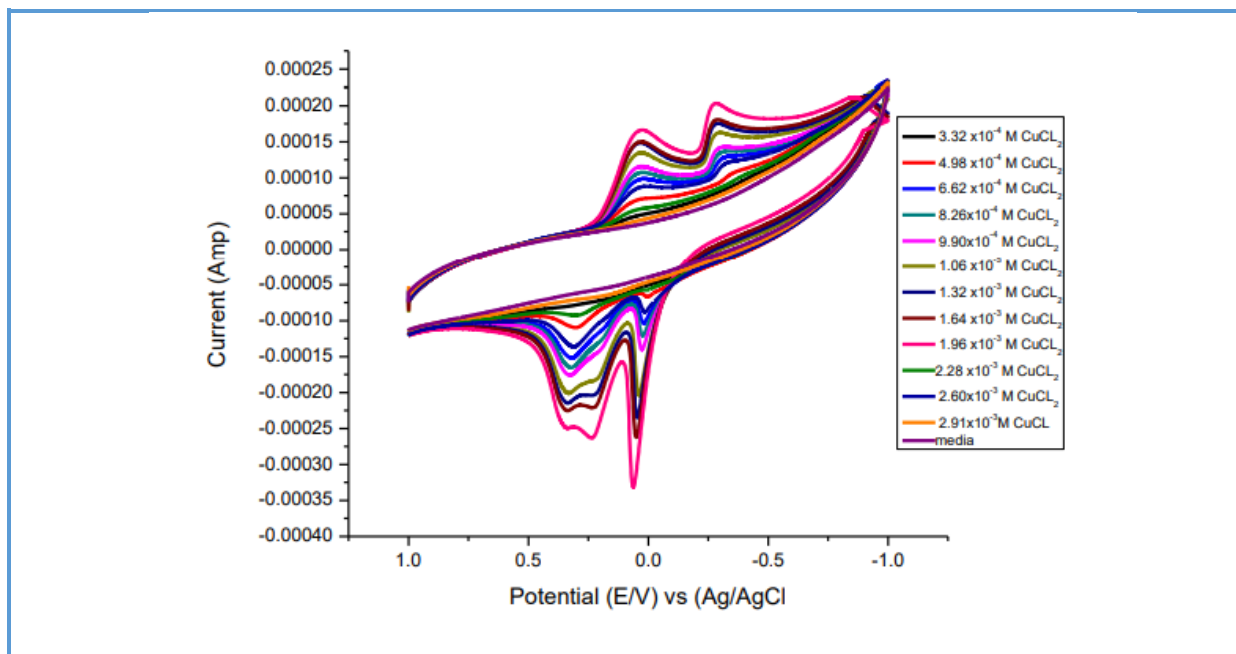
KEYWORDS

Solvation Parameters
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orange G (OG)
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ABSTRACT

The redox mechanisms were examined for copper chloride in the absence and presence of Orange G (OG) as organic ligand at 19.1 °C using carbon glassy electrode (CGE). The supporting electrolyte was 0.1 M KCl whose effect of scan rate was also studied for the redox reactions for CuCl_2 alone and in the presence of the ligand, orange G (OG). Stability constants for the complex formed from the interaction of CuCl_2 + Orange G (OG) were evaluated with the different thermochemical data. Effect of different scan rates was done for cupric chloride in the absence and presence of the ligand Orange G (OG). The different scans are 0.1, 0.05, 0.02 and 0.01 V/Sec. The stability constants and Gibbs free energies of complexation were also estimated for the interaction of CuCl_2 with Orange G (OG) in 0.1M KCl supporting electrolyte.

Graphical Abstract



Introduction

Extraction of metal ions as pollutants from environmental aim [1-6]. Several metal ions aqueous solutions using electrochemical in solutions can be recorded and examined methods is very interesting for by the reduction of the different cathode materials [6,7].

In this work, estimation and electrochemical voltammetric analysis of copper ions in 0.1 M KCl was studied to explain the characteristics for evaluating it in the environmental samples. Bending copper with ligands is a treatment for remediation of Cu in vivo and vitro [7]. Long exposure to copper causes many problems, irritation in eyes, nose, mouth, causes headaches, dizziness, vomiting and diarrhea. High uptake copper causes kidney and liver damages [7].

Copper is vital dietary, small amount of metal is needed for well-being [8]. Copper [9] is most third abundant metal in the body [8-10].

In this work, estimation and electrochemical voltammetric analysis of copper ions in 0.1M

KCl was studied for explaining the characteristics for evaluating it in the environmental samples.

Experimental

The used chemicals, CuCl_2 , KCl, are of high purity from Sigma Aldrich Co. Orange G (OG) is of the type Ranken (Ranbaxy). The volume of the experimental solution is 30 mL. Three electrodes cell was used to connect to potential DY 2000 Potentiostat, Ag /AgCl, KCl sat., reference electrode, carbon glassy electrode (CGE) was used as working electrode, platinum wire was also used as auxiliary electrode. N_2 flow was done to ensure oxygen removal. The carbon glassy electrode (CGE) is prepared in our laboratory from pure carbon piece, polished with aluminum oxide on wool piece. Area of electrode is 0.502 cm^2 .

Results and Discussion

Electrochemical behavior of CuCl_2 in absence of Orange G (OG)

Studying the electrochemical behavior for CuCl_2 in 0.1M KCl supporting at 19.1°C was done in the range from +1V to -1V. In the range -1 to +1V oxidation took place, but scanning in the range of +1 and -1 permits and allows the copper reduction processes and ligand

reduction. The change of Cu (II) to the Cu (I) state involves the reduction of metal ion radius [11]. Cyclic voltammogram between 1 and -1 V (Volt) show redox processes explaining C(II) / Cu(I) and Cu(I)/Cu(0) processes appearing in Figure 1.

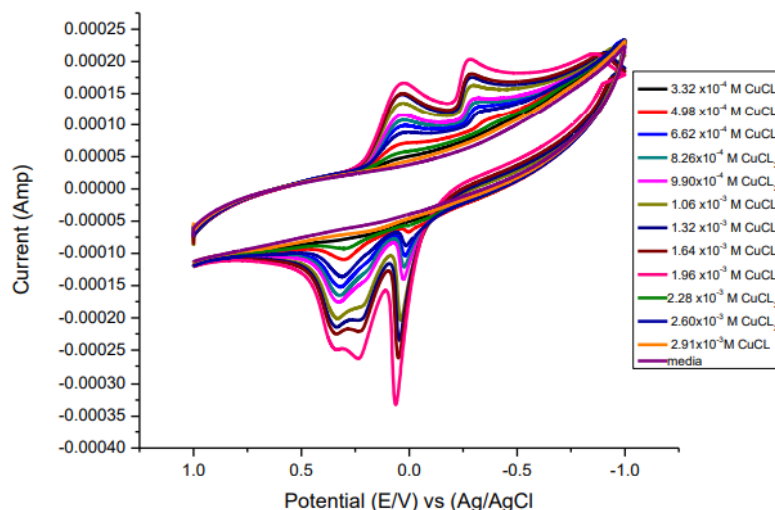


Figure 1. Cyclic voltammograms of different concentration of CuCl_2 in 0.1M KCl solutions at 19.1°C .

Scan rate was also studied for 6.62×10^{-4} M redox waves were appeared to increase with of CuCl_2 , at 0.01, 0.02, 0.05 and 0.1V/S, which are

100, 10, 20, 50 mV/Second. All redox waves were appeared to increase with increasing scan rates as shown in Figure 2.

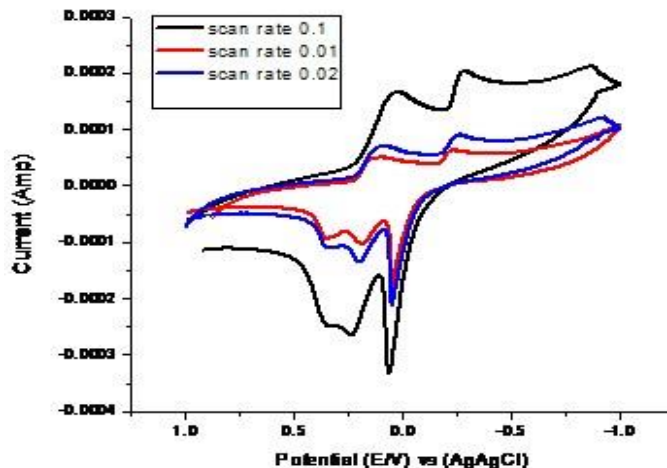


Figure 2. Different scan rates of 6.62×10^{-4} M CuCl_2 in 0.1M KCl at 19.1°C .

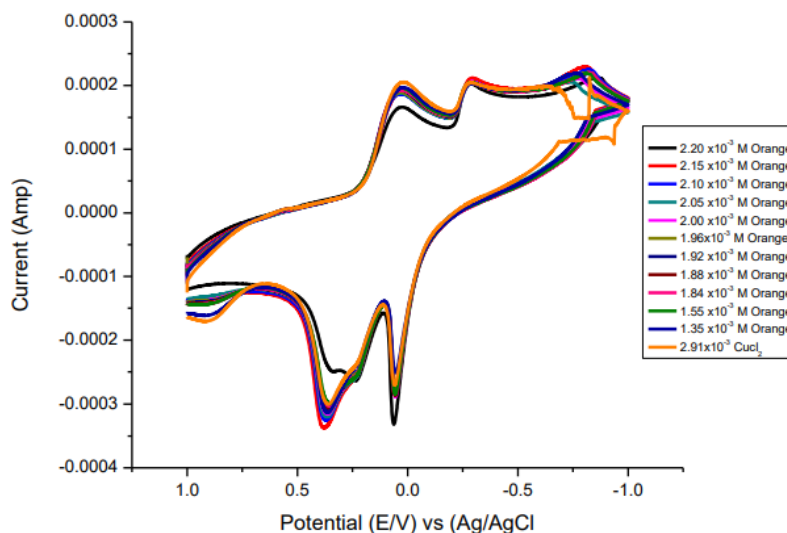


Figure 3. Voltammograms of the interaction of different concentrations of Orange G (OG) with 1 mM CuCl_2 in 0.1M KCl supporting electrolyte.

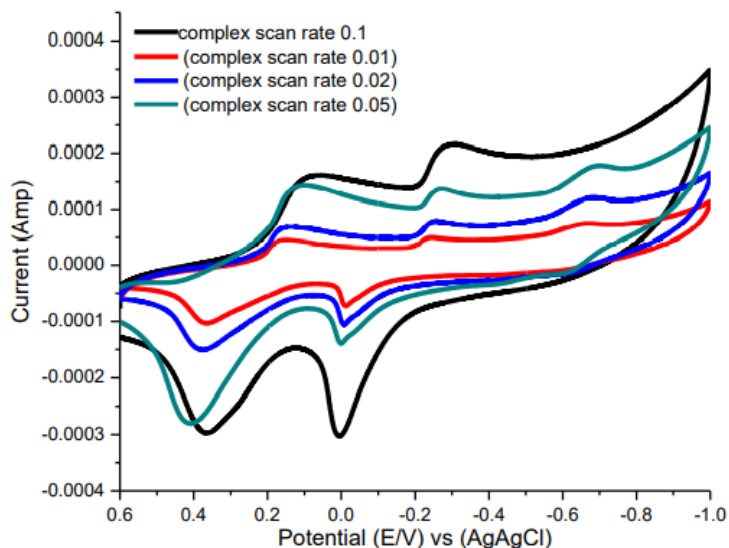


Figure 4. Effect of different scan rates for 1:1 (Metal/OG) stoichiometries complexes.

Diffusion reactions are supported from the relation of an ip against $v^{1/2}$.

Cyclic Voltammetry of CuCl_2 in presence of ligand Orange G

The electrochemical behavior of the complex, formed from the interaction of CuCl_2 with Orange G, was studied cyclic voltammetrically in the range of 1 to -1V. The potential reduction of Cu(II)/Cu(I) processes are studied. The electrochemical activity in the

range studied showed pattern at all CuCl₂ concentrations that may consider as the sum of individual processes [11-14].

[Cu (III) OG]+e- \rightleftharpoons [Cu(I)OG] (1)
Diffusion controlled reaction are appearing and proved from the relation between ip and $v^{1/2}$

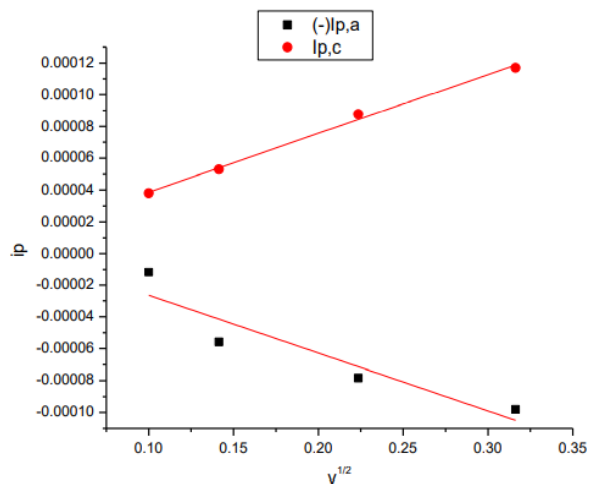


Figure 5. The relation between ip and $v^{1/2}$ for first redox couple waves in absence of (OG).

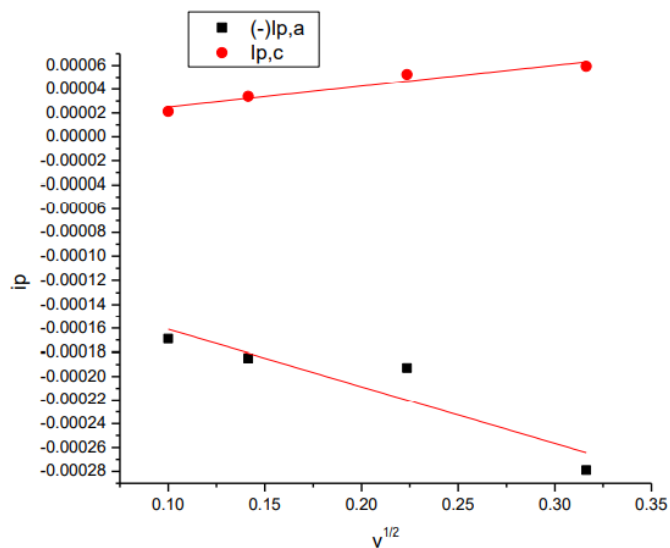


Figure 6. The relation between ip and $v^{1/2}$ for second redox couple waves in the absence of (OG)

Voltammetric response of complexes explains the reduction and oxidation of metal centered processes.

Cyclic Voltammetry scanning of the complex formed from the interaction of CuCl₂ with

orange G (OG) between +1 and -1V (Volts) show two cathodic peaks and two anodic peaks.

The ratio between cathodic current of the peak and square root of scan ($IPC/v^{1/2}$) is approximately constant.

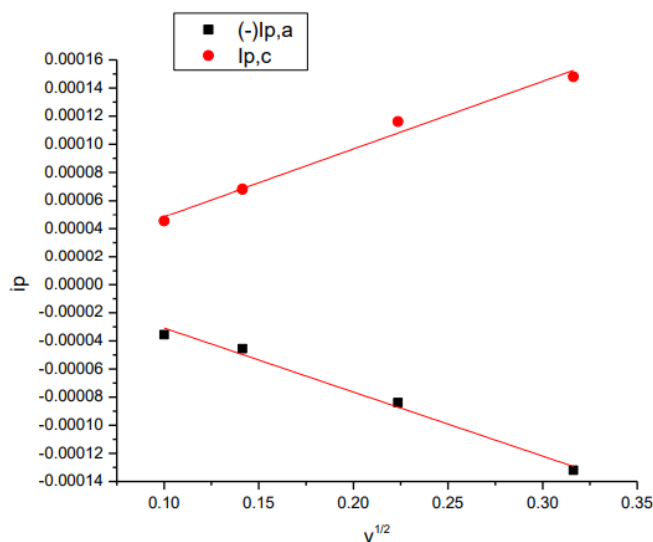


Figure 7. The relation between i_p and $v^{1/2}$ for first redox couple waves in presence of (OG).

Reaction of CuCl_2 with gradual addition of ligand orange G (OG) was recorded until 1:3 (M/Ligand) molar ratio was reached. Change in color and in electrochemical behavior was clear from the first addition. The changes increase when the ligand additions increase. Wave Cu (III)/Cu(I) complexes appears at higher concentrations of orange G (OG).

The relations between i_p and $v^{1/2}$ for CuCl_2 solutions in the absence and presence of Orange G (OG) for the first copper ion couple of redox reactions and second couple of redox reaction gave straight lines proving the reversibility of the system studied, (Figures 5-8).

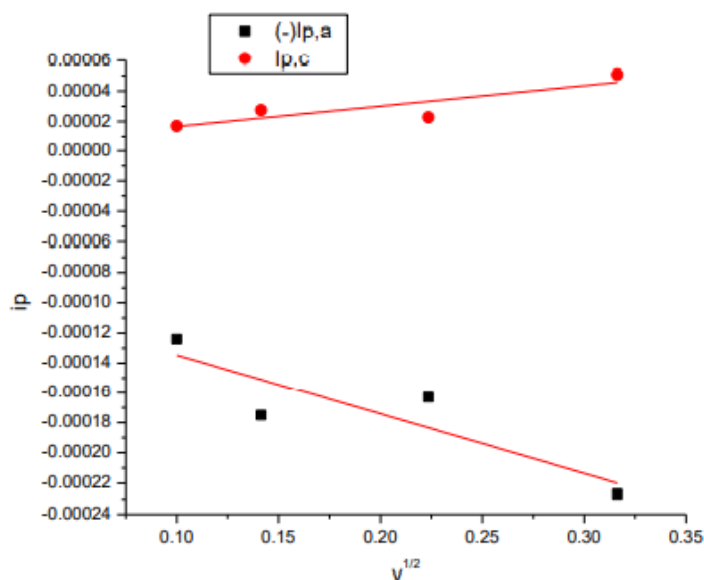


Figure 8. The relation between i_p and $v^{1/2}$ for first redox couple waves in presence of (OG).

The equations used for the cyclic calculations are explained in references [11-14].

Table 1. Analysis data for the different cyclic voltammograms of copper chloride ions in absence of orange G (OG) in 0.1M KCl.

M x10 ⁻⁴	EPa (V)	Epc (V)	ΔEP	ipa X10 ⁻⁵ (A)	ipc X10 ⁻⁵ (A)	ipa/ipc	(-)Eo (V)	Da X10 ⁻¹⁰ cm ² .s ⁻¹	Dc x10 ⁻¹⁰ cm ² .s ⁻¹	(-)Epc/2 (V)	αna	Ks Cx10 ⁻⁴ cm.s ⁻¹	Γ Cx10 ⁸ (mol.cm ⁻²)	(+) Qcx10 ⁻⁵ (C)	Γ ax10 ⁻⁸ (mol.cm ⁻²)	(-) Q ax10 ⁻⁵ (C)
6.62	0.0033	0.37	0.370	0.26	0.717	0.364	0.188	0.0215	0.16	0.34	1.84	9.41	0.2385	0.7.2	0.0869	0.264
99.0	0.0102	0.31	0.321	3.12	2.53	1.234	0.150	1.3703	0.90	0.27	1.43	12.0	0.8412	2.55	1.0383	3.15
13.2	0.0113	0.30	0.311	0.11	2.15	0.530	0.144	0.1031	0.36	0.27	1.93	8.05	0.7135	2.16	378.65	11.5
16.4	0.0173	0.20	0.313	5.90	2.35	2.51	0.13	1.7848	0.28	0.26	1.66	6.67	0.780	2.37	1.9620	5.94
19.6	0.0311	0.28	0.312	11.2	3.32	3.38	0.12	4.5219	0.39	0.25	1.83	8.24	1.102	3.34	3.7353	11.3
22.8	0.0406	0.27	0.319	15.7	4.15	3.78	0.11	6.5594	0.45	0.25	1.72	9.17	1.381	4.19	5.2315	15.8
26.0	0.0426	0.01	0.042	19.9	5.35	3.72	0.02	8.1153	0.58	0.24	0.19	0.22	1.778	5.39	6.6287	20.1
29.1	0.0541	0.27	0.326	21.6	4.75	4.54	0.10	7.5679	0.36	0.24	1.67	8.67	1.579	4.79	7.1781	21.7
8.26	0.0063	0.32	0.326	1.99	1.25	1.58	0.15	0.7965	0.31	0.29	2.15	9.16	0.415	1.26	0.6607	2.00
6.62	0.0033	0.37	0.370	0.26	0.71	0.36	0.18	0.0215	0.16	0.34	1.84	9.41	0.238	0.7.2	0.0869	0.264
99.0	0.0102	0.31	0.321	3.12	2.53	1.23	0.15	1.3703	0.90	0.27	1.43	12.0	0.841	2.55	1.0383	3.15

Table 2. Effect of concentration for ligand Orange G (OG) at 0.1 scan rate for 1mM CuCl₂ at 19.1^oC (Cu⁺¹ ↔ Cu⁰).

Lx10 ⁻³	Dc cm ² .s ⁻¹ x 10 ⁻¹⁰	(-)Epc/2 (V) Volt (V)	αnac	Ks (cm.s ⁻¹) X10 ⁻³ cm .s ⁻¹	Γ c x10 ⁻⁸ Mol.cm ⁻²	(+) Qc X10 ⁻⁵ (C)	Γ a x10 ⁻⁸ Mol.cm ⁻²	(-) Q a X10 ⁻⁴ (C)Coulomb	Log βj	βj	(-)ΔG (KJ/mol)
0.244	1.18	0.2392	1.2417	1.36	2.1373	6.48	5.8547	1.77	1.0712	11.7830	5.9945
0.477	1.02	0.2419	1.2539	1.20	1.9387	5.87	6.4259	1.95	1.2497	17.7714	6.9931
0.699	0.896	0.2424	1.3540	1.13	1.7792	5.39	5.8861	1.78	1.5033	31.8675	8.4123
0.911	1.17	0.2397	1.2380	1.35	1.9905	6.03	6.0955	1.85	1.8139	65.1610	10.1506
1.11	1.09	0.2374	1.3675	1.26	1.8766	5.69	6.0421	1.83	2.0829	121.0331	11.6554
1.31	1.06	0.2399	1.4124	1.29	1.8062	5.47	5.9930	1.82	2.3104	204.3756	12.9285
1.49	0.982	0.2404	1.2753	1.22	1.7039	5.16	6.9036	2.09	2.4972	314.2204	13.9739
1.67	1.16	0.2374	1.4246	1.30	1.8151	5.50	7.6951	2.33	2.7790	601.2465	15.5508
1.84	1.02	0.2378	1.4748	1.23	1.6685	5.06	7.0411	2.13	3.0133	1031.1666	16.8618
3.11	0.63	0.2463	1.5380	1.21	1.2939	3.92	6.3887	1.94	4.9354	86180.2459	27.6173
4.04	19.1	0.2408	0.5526	0.150	5.2626	15.9	4.6934	1.42	14.7890	6.15201x10 ¹⁴	82.7556

The cyclic voltammetry analysis data given in Table 1 like the electron rate constant at the working electrode in analysis of CuCl₂ alone and other analysis are done in presence of Organe G (OG) . Most of the data given in Table 2 are greater than that given in Table 1 indicating ligand effect of the cyclic voltammograms.All data in Table 1 and Table 2 are calculated using equations explained previously in other work [11].

The complex stability constant which measure the strength and power of interaction

between CuCl₂ and Orange G (OG) is very important. The complexation stability constant(B) for the interaction of CuCl₂ with Orange G (OG) forming complex in 0.1M KCl is calculated by applying equation (2) [15-17]. ks the electron transfer rate constant,The surface coverage for the electrode in the anodic part Γ C of measurements and surface coverage of working electrode during the anodic measurements Γ a,quantity of electricity at the working electrode in anodic and cathodic cyclic voltammograms measurements indicate good

complexation between CuCl_2 and Orange G (OG)[14-16].

$$(E_p)_m - (E_p)_c = 2.303 \frac{RT}{nF} \log \beta_c + 2.303 \frac{RT}{nF} \log (2) (C_x)$$

Where $(E_p)_m$ is peak potential for the metal salt in absence of orange G (OG) and $(E_p)_c$ is the peak potential of the complex, R gas constant & C_x is the concentration, solution of metal salt in presence of orange G (OG). The thermochemical Gibbs free energy of interaction, salvation of CuCl_2 + orange G (OG) were calculated [17, 18] using equation (3). Thermochemical parameters for complex interactions between CuCl_2 with Orange G (OG) prove the stability of the complex formed (Table 1).

All data given in proving the reversible diffusion process of the system under consideration.

$$\Delta G = -2.303RT \log \beta_c \quad (3)$$

Conclusion

Reversible diffusion interaction between CuCl_2 and Orange (G) was concluded. The stability constants and Gibbs free energies of complex interactions are increased with increase in ligand orange G (OG) concentrations indicating more interactions forming complex in the solutions. The electron transfer rate constant k_s , surface coverage anodic (Γ_a) and cathodic (Γ_c) are mainly decreased by increase in orange G (OG) concentration, indicating more complexation. Also, the anodic and cathodic quantity of electricity around the working electrode during measurement is increased with increase orange G concentration due to the complex formed.

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Disclosure Statement

No potential conflict of interest was reported by the authors.

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