

Thermodynamic Data for the Interaction of CuCl_2 with Safranin (Saf) in KBr Solution at 19.1°C Using Glassy Carbon Electrode (CGE)

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Abstract

The reduction and oxidation mechanisms for copper chloride were studied in 0.1M KBr in absence and presence of safranin (Saf) at 19.1°C . The mechanism of oxidation and reduction was examined. The effect of scan rate for the redox reaction of CuCl_2 in absence and presence of safranin (Saf) was carried out to explain the type of reactions for this electrochemical process. Thermodynamic parameters such as stability constants and Gibbs free energies for the complex formation of the interaction of CuCl_2 with safranin (Saf) were evaluated and discussed.

Keywords: Cyclic Voltammetry Safranin; Stoichiometric complexes; Thermodynamic parameters; Effect of concentration; Effect of different scan rates

Introduction

Metal ion extraction as pollutants from aqueous solutions by using electrochemical technique is very interesting [1-6]. Several metal ions in aqueous solutions can be examined by the reductions at different cathodic materials [6, 7]. In our work, the estimation and electrochemical voltammetric analysis of copper ions in 0.1 M KBr was studied to explain and illustrate the characteristics for their discussion in environmental samples. The binding of copper with ligands is treated as remediation of Cu in vivo and vitro [7]. Copper in large quantities cause many problems, headaches, irritation in nose, mouth and eye. It also may cause kidney and liver damage [7]. The large amount of it may cause vomiting and diarrhea. Copper is the third most abundant metal in the human body [8].

Experimental

The chemicals used KBr, CuCl_2 and Safranin are of high purity and obtained from Sigma Aldrich Co. The volume of the experiment is 30 ml in three electrodes cell was used can jointed to potentiostat at of the type DY2100. Ag/AgCl using KCl_{sat} reference electrode was used. Carbon glassy electrode (CGE) was used as working electrode. Platinum wire was also used as auxiliary electrode. Flow of N_2 as was done for about 5 min to remove oxygen dissolved in the supporting electrolyte. The carbon glassy electrode (CGE) is prepared in our laboratory by joining pure carbon piece with copper wire and covered with heat shrink polymer to ensure the closing of the electrode tip and the surroundings of the electrode to prevent migration of solutions during experimental work. The carbon glassy electrode

(CGE) is polished with aluminum oxide powder on wool piece area of electrode is 0.502 cm².

Results and discussion

Cyclic voltammetry of CuCl₂ in absence of safranin (Saf)

The cyclic voltammograms (CV) for the redox behavior of CuCl₂ in 0.1 M KBr electrolyte medium at 19.1°C was studied in the range from the range of 1V to -1V in the reduction process, whereas the oxidation proceed in the range of -1V to 1V. Studying different scanning effect in the range between 1V to -1V permits the copper reduction process and ligand reduction. Change of Cu (II) to Cu (I) state (d⁸ low spin) involves reduction of metal ion radii [9]. Voltammograms shown between 1 and -1V illustrate reduction processes involving Cu (II) / Cu (I) and Cu (I) / Cu (0) processes appear in Fig(1) that indicate a relation between current in Ampere (Amp)and potential in volt(E/V).

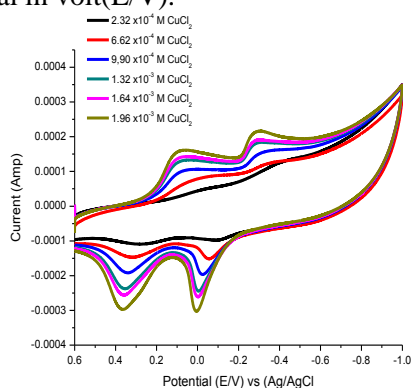


Fig. 1: Voltammograms of different concentration of CuCl₂ in 0.1MKBr solutions at 19.1°C

Scan rate was studied for 1 mM (CuCl₂) at 0.01, 0.02, 0.05 and 0.1 V/S. All redox voltammograms are increased by increasing the scan rate as shown in Fig.2.

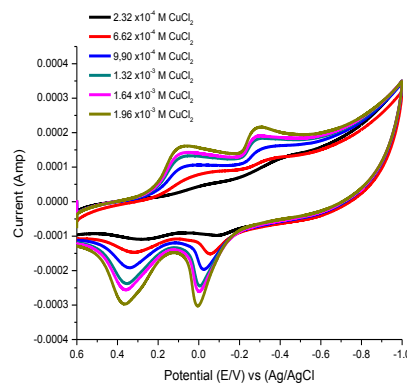


Fig. 2: Voltammograms of different scan rates of CuCl₂ in 0.1M KBr at 19.1°C.

Voltammograms of CuCl₂ in presence of safranin (Saf)

Cyclic voltammograms of CuCl₂ in presence of ligand Safranin (Saf) was carried out in the range the range of 1 to -1 V. The reduction of Cu(II) to Cu(I) is studied and the cyclic voltammograms given in Fig. 3 .

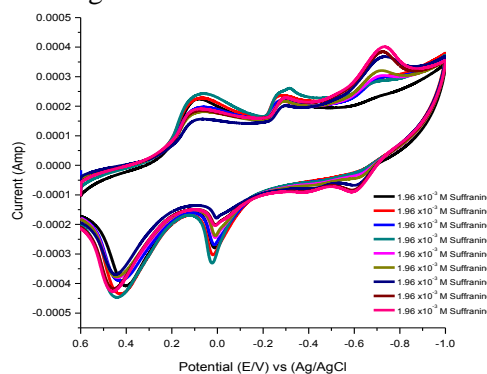


Fig. 3: Voltammograms of the interaction of different concentrations of safranin with 1mM CuCl₂ in 0.1M KBr supporting electrode.

Scanning voltammograms of the complex formed between CuCl₂ and safranin (Saf) in the range 1 to -1V show two cathodic peaks at ~ 0.1 and ~-0.3 V. In the reverse direction anodic two peaks are formed at ~0.425, and ~ 0.03 Volt (V).

Table 1: Effect of concentration for ligand safranin (Saf) at 0.1 scan rate at 19.1°C (Cu⁺¹ ↔ Cu⁰).

L x10 ⁻⁴	(-) Epc/2	Ana	Ksc x10 ⁻⁴	Γc X10 ⁻⁸	Qc x10 ⁻⁵	Γa x10 ⁻⁸	(-)Qa x10 ⁻⁴	Log βj	βj	(-)ΔG (KJ/mol)
0.326	0.2429	3.7207	6.57	2.4983	3.37	4.3241	1.31	0.4071	2.5533	2.2780
0.649	0.2338	1.6416	10.8	1.1113	6.97	5.1879	1.57	0.5112	3.2450	2.86062
0.971	0.2404	1.79588	8.29	2.2991	5.04	4.0423	1.22	0.5140	3.2658	2.8761
1.29	0.2407	1.0008	14.3	1.6620	8.66	5.7297	1.74	0.4681	2.9386	2.6196
1.61	0.2444	1.3577	9.04	2.8601	5.83	4.8463	1.47	0.4853	3.0572	2.7158
1.92	0.2515	1.76889	8.42	1.9231	4.80	3.4098	1.03	0.5459	3.5144	3.05448
3.77	0.2586	1.63718	7.63	1.5845	4.62	2.7346	8.28	0.6852	4.8442	3.8343
5.56	0.2558	1.6914	10.8	2.0336	6.16	3.6193	1.10	0.8773	7.5391	4.9092
7.27	0.2603	1.8174	10.6	1.8768	5.69	3.0849	9.35	1.1817	15.1935	6.6123

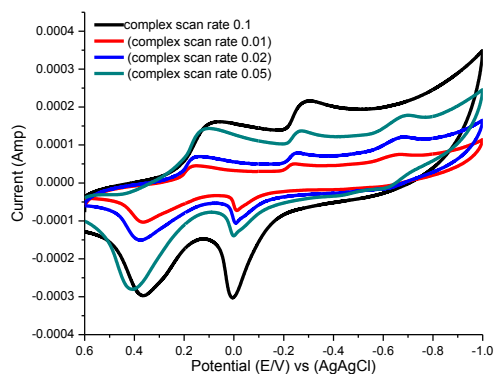


Fig. 4: Effect of different scan rates on 1:1 (Metal/Saf) stoichiometric complexes.

The ratio for cathodic current of the peaks and square root plan ($I_{pc} / v^{1/2}$) is constant. All data prove the quasireversibility of reactions involving one electron transferred by diffusion mechanism [10]. The new reduction wave was observed at $i(\sim -0.72)$ Indicating the reduction process for the complex formed from the interaction of CuCl₂ with safranin (Saf) consuming two electrons.

[Cu(II) Saf]+ 2e⁻ ⇌ [Cu(II)Saf] (1)
The oxidation process can be observed specially on the use of complexes which appear in the splitting of the oxidation peak at ~ -0.7 into two steps. Reaction of CuCl₂ with gradual addition of ligand safranin (Saf) was recorded until 1:3 (ML/Ligand) molar ratio was reached. All scan rates effect for CuCl₂ in absence and presence of Safranin (Saf) indicate that the electrochemical redox reactions here studied are diffusion controlled. This was supported from the straight lines relations obtained from the effect of scan rates. The potential reduction of Cu(II)/Cu(I) processes is studied. The electro chemical activity in range studied showed pattern at all CuCl₂ concentrations that may considered as sum of individual processes. Voltammetric response of complexes explains the reduction and oxidation of metal centered processes.

Analysis of voltammograms obtained

The equations used for the cyclic voltammogram (CV) analysis and further calculations are [11-14]:

$$IP = 0.443n^{3/2}F^{3/2} D^{1/2} AC v^{1/2} (RT)^{-1} \quad (2)$$

$$D^{1/2} = (\text{slope}, I_p \& v^{1/2}) * 0.4463 v^{-3/2} F^{3/2} AC (RT)^{-1/2} \quad (3)$$

$$\Delta E_p = E_{p,a} - E_{p,c} = 2.303 RT/nF \quad (4)$$

$$\Psi = \gamma^{\alpha} k_s (\pi a v Da)^{-1/2} \quad (5)$$

$$\gamma = (Da/Dc)^{1/2} \quad (6)$$

$$a = nF/RT \quad (7)$$

where Ψ , is the transefer parameter and taken to be one for better and easier calculation [13], α : is charge transfer coefficient, K_s : is standard rate constant for electron transfer, v : velocity of scan, D_a , diffusion coefficient of the reduced species, n , number of electron, F , Faraday constant, R , universal gas constant, T :is the absolute temperature for experiment done, A , is the area of electrode. From Fig.(3), the interaction of CuCl₂ 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 values for oxidization. Besides the specific peak appears for the complex formed at ~ -0.72 from the interaction of with CuCl₂ safranin (Saf.). The complex stability constant (B) for the interaction of CuCl₂ with safranin (Saf) in 0.1 M KBr form complex is calculated by the use of equation (8) [15-17].

$$(E_p)_M - (E_p)_C = 2.303 RT/nF \log B_C + 2.303 RT/nF \log (x) \quad (8)$$

Where $(E_p)_M$, is the peak potential in volts for the salt in 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.)

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

All data obtained applying equations (8) and (9) are given in Table (1), indicating the increase of thermodynamic parameters by increase in Safranin (Saf.) concentration due to its increase in complexation ability with CuCl₂.

Conclusions

Safranin (Saf) affect the redox properties and solution properties of CuCl₂ in 0.1 M KBr. By more adding Safranin (Saf) to CuCl₂ solutions increase in the electron transfer rate constants observed and also the cationic and anionic surface coverage at the electrode were increased. Quantity of electricity for both cationic and anionic parts of CuCl₂ solutions in 0.1M KBr are decrease on using analysis of the first couple redox waves. The opposite trend were observed for following the second redox waves according to more illustrating waves were observed here. The thermodynamic parameters are clear represented in the second redox waves indicating more increase in the stability constants and Gibbs free energies of interactions between CuCl₂ and Safranin (Saf).

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عنوان البحث: البيانات الديناميكية الحرارية لتفاعل CuCl₂ مع Safranin (Saf) في محلول KBr عند ١٩,١ درجة مئوية باستخدام قطب كربون زجاجي (CGE)

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يتضمن دراسة السلوك الفولتا ميترى لكلوريد النحاس باستخدام قطب الكربون الزجاجي في وجود محلول بروميد البوتاسيوم كمحلول الكتروليتي. أيضا دراسة السلوك الكهروكيميائي للأكسدة واختزال النحاس في كلوريد النحاس في غياب وجود السفرانيين كمادة مخليبية. كذلك تم دراسة تأثير التركيزات المختلفة من كلوريد النحاس والسفرانيين على الموجات حيث تم الحصول عليها. تم دراسة تأثير سرعة القياس على الموجات الخاصة بالأكسدة والاختزال لكلوريد النحاس في غياب وفي وجود السفرانيين.