

Electrochemical Solvation Parameters for The Interaction of CuBr_2 With Carbazine 720 (LC) in NaClO_4 Using Glassy Carbon working electrode (cyclic voltammetry)

Esam A. Gomaa ^{a*}, Moustafa A. Diab ^b, Adel Z. El Sounbati ^b, Hamed M. Abou El-Nader ^a, Asmaa M. Helmy ^b

^aChemistry Department, Faculty of Science, Mansoura University, 35516-Mansoura, Egypt

^bChemistry Department, Faculty of Science, Damietta University, Damietta, Egypt.

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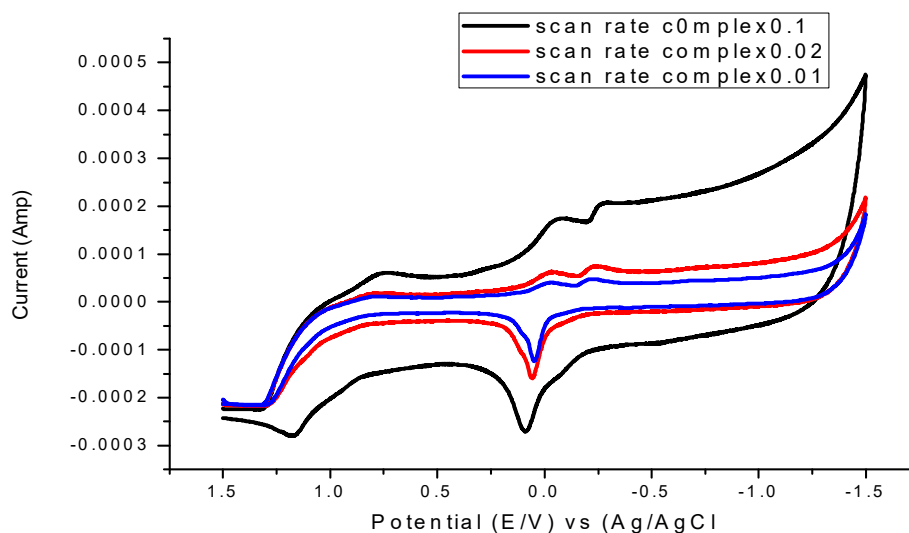
kinetic parameters

ABSTRACT

The redox mechanisms were examined for Copper bromide in the absence and presence of (LC) using cyclic voltammetry. The mechanisms of reduction and oxidation were examined while using new glassy carbon electrode prepared in laboratory from pure carbon piece jointed with copper wire and isolated by heat shrink polymer to avoid contact with solutions. In order to explain the type of the used reaction in electrochemical study, the complexation stability constants and Gibbs free energies of complex formation obtained from the interaction of CuBr_2 with (LC) were obtained from the experimental part and their values were discussed. The prepared glassy carbon electrode was polished with Al_2O_3 and put in a woolen clear piece, washed and used for cyclic voltammetry measurements.

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GRAPHICAL ABSTRACT



1. Introduction

Cyclic voltammetry, the interaction of different salts with organic active chelating compounds can be explained ¹ for different salts by the interaction of metal ion with active chelating group in the organic compound like amino, hydrazo, azo hydroxyl or carboxylic groups.² Complexation in cyclic voltammetry can be explained by the change in peaks heights, and shift in both anodic and cathodic potentials. Half wave potential shift can also be used for measuring the complex formation parameters.³ We can use further techniques for complex behavior in solutions like conductivity, potentiometry and cyclic voltammetry.

The complex ability can be studied by the peaks height decrease and the anode or cathodic potentials shift.³ We can also use other techniques like, absorption, emission spectroscopy polarography and other electrochemical methods for study the complexation interaction of the organic compound with metal ions.⁴⁻⁷

2. Result and discussion

2.1. Electro Chemical behavior redox processes for CuBr_2 at glassy carbon electrode (GCE)

* Corresponding Author:

E-mail address: eahgomaa65@yahoo.com (E. A. Gomaa)

Was studied the equilibrium conditions at room temperature at 19.1 °C and pressure 1 atm. The obtained cyclic voltammograms were explained by eq.(1).⁸⁻¹²

$$I_p = (2.69 \times 10^{-5}) n^{3/2} A D^{1/2} \nu^{1/2} C \dots \dots \dots (1)$$

Where I_p is the current in ampere unit, A is the surface area of silver working electrode, D is the diffusion coefficient in cm^2/sec , ν the scan rate in V/s and C is the concentration of the depolizers. The voltammogram were developed by the the using of glassy carbon electrode. The measured cyclic Voltammetric results depend on Cu^{2+} ion movement and the transfer of electrons.¹²⁻¹⁵

$$k_f = k^0 \exp\left(\frac{-\alpha n f}{RT}\right) (E - E^0) \dots \dots \dots (2)$$

k_f is rate constant in forward direction, k^0 is the standard electron transfer rate constant for interaction, E is reduction potential and α is the transfer coefficient.⁶⁻¹⁷ When reversing the scan in our program the reduced species at the glassy carbon electrode is oxidized back to come back to the starting conditions. The electron transfer constant for the reverse reaction, k_r is the (oxidation) is controlled by equation (3).

$$k_r = k^0 \exp\left(\frac{(1-\alpha) n f}{RT}\right) (E - E^0) \dots \dots \dots (3)$$

If the reaction is reversible, the peak, separation in potentials will be near to $58/n$. This relation can be used for the evaluation of number of electrons in the redox reactions. For any reversible reactions, the reduction process is partly for obtaining the reduced and oxidized species in equilibrium.⁷⁻²⁰ The equilibrium between the two forms of ions is determined by applying Nernst equation:

$$E = E^0 - \frac{RT}{nF} \ln \left(\frac{[R]}{[O]} \right) \dots \dots \dots (4)$$

Where $[R]$ and $[O]$ represent the reduced and oxidized forms concentration, the reaction is a fast and reversible one which can occur. The reaction is reversible if the k^0 is greater than $0.3 \nu^{1/2}$ since ν is the scan rate. The reactions where cyclic voltammetry are shifts apart from each other with increasing scan rates are quasi-reversible reactions. Some reactions go through bond breaking, indicating irreversible reaction. For quasi reversible reactions, peak currents not exact proportional²⁰⁻³⁰ to $\nu^{1/2}$.

$$E_{p/2} = E_{1/2} \pm \frac{28}{n} \text{mv} \dots \dots \dots (5)$$

The sign is positive for reduction process.

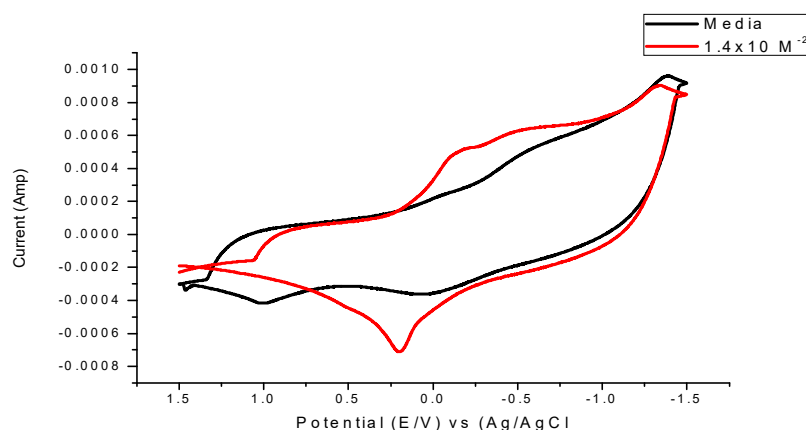


Fig. 1 Blank cyclic voltammetry for the medium and that for 14×10^{-2} M CuBr_2 in 0.1M NaClO_4 solutions at 19.1°C.

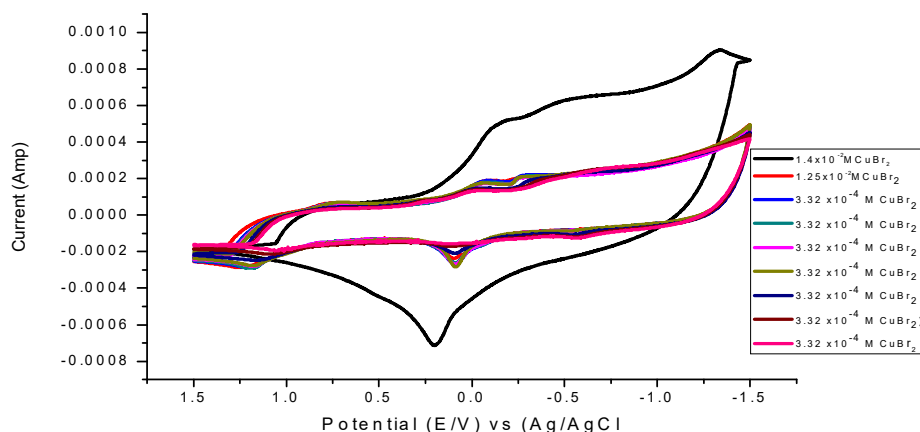


Fig. 2 Cyclic voltammograms of different concentration of CuBr_2 in 0.1M NaClO_4 solutions at 19.1°C.

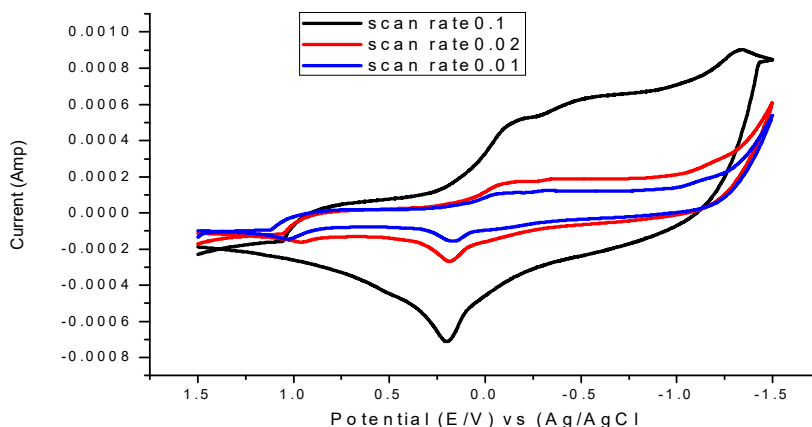


Fig. 3 Effect of different scan rates on metal (CuBr_2).

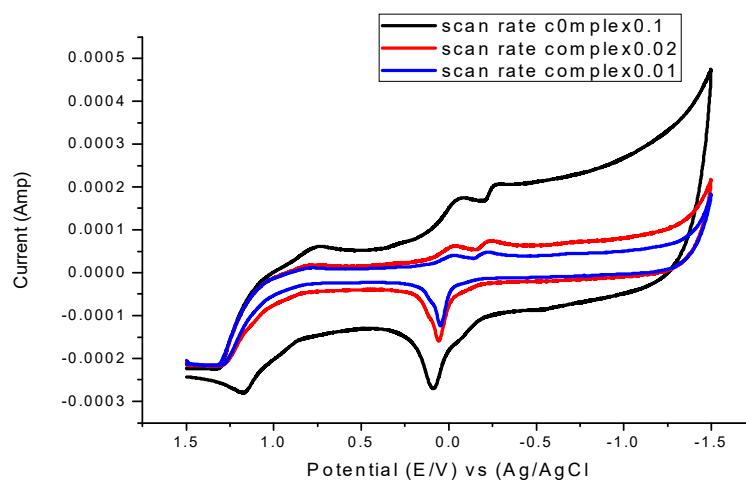
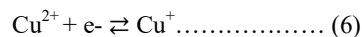


Fig. 4 Effect of different scan rates on 1:3 (Metal/LC) stoichiometric complexes.

The cyclic voltammograms were firstly recorded for the blank solution of the supporting electrolyte and $1 \times 10^{-2} \text{M}$ CuBr_2 as given in Figure 1 giving two reduction waves and one oxidation peak for copper ions as shown in Fig. 1. Fig. 2 represents the effect of different concentration of CuBr_2 the redox behavior. Also, in Fig. 3, the effect of scan rate on the redox behavior of CuBr_2 has been illustrated. The interaction of CuBr_2 with LC was studied and scan rate was studied at 1:3 M/LC molar ratio and explained in Fig. 4. From all curves given in Figures 1-4 different solution redox, kinetic parameters were evaluated and given in the following Tables (Supplementary information). All the kinetic parameters³⁰⁻⁴¹ for CuBr_2 calculated from cyclic voltammetry, like potential difference ΔE_p , current ratio anodic to Cathodic i_{pa}/i_{pc} , anodic diffusion coefficient, cathodic diffusion coefficient, D_a, D_c , cathodic surface coverage Γ_c , anodic surface coverage Γ_a and quantity of electricity are increased with decrease of scan rate indicating the reversibility of the waves (Table 3).

2.2. Electro Chemical behavior of CuBr_2 in absence of (LC)

The cyclic voltammetry for CuBr_2 with different concentrations using 0.01M NaClO_4 supporting electrolyte was done. We used NaClO_4 as supporting electrolyte because of its considered as a less complexing agent. We observed two reduction and oxidation waves in Fig. 1. The blank 0.01 M NaClO_4 is presented (supporting electrolyte). The reduction of cupric ions to monovalent and finally to zero valence is responsible for reduction consuming one electron for each process⁴²⁻⁵⁰:



The scan rate relation between i_p and $v^{1/2}$ were presented for CuBr_2 alone in Fig. 5 with straight line relations for the anodic and cathodic peaks. Anodic peak gave good indication and is well developed and can be better followed for CuBr_2 salt. This wave indicates reversible process. The scan rate for CuBr_2 plus LC show better developed waves than for metal salt alone in NaClO_4 electrolyte and from the anodic and cathodic lines in Fig. 6 we conclude the slope which is near to 0.5 indicating reversibility of the cyclic voltammograms in presence of ligand LC.

The oxidation peaks explaining the reverse reduction direction. The oxidation peaks involving one electron for each explain the opposite trend for equations (6) and (7). The effect of scan rates and the electrochemical kinetic parameters like solution electron transfer rate constant k_s , cathodic surface

coverage (T_c), anodic surface coverage (T_a), cathodic quantity electricity Q_c , anodic quantity electricity Q_a , and αn_a , are shown in further Table indicating the increase all the above kinetics parameters by decrease in scan rates.

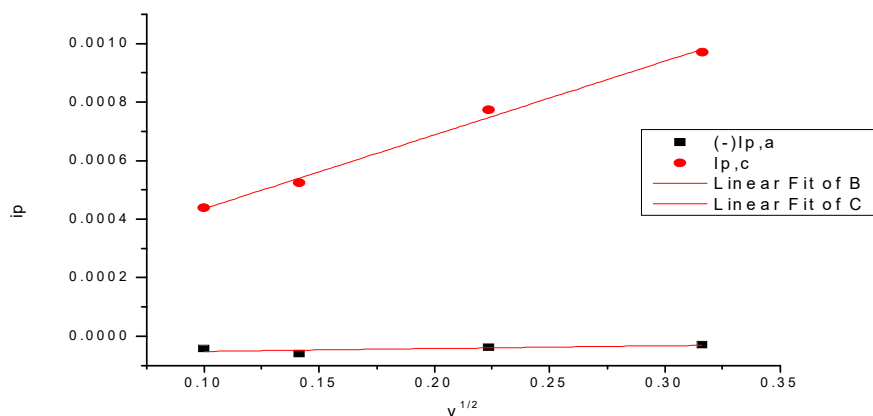
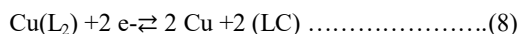


Fig. 5 The relation between i_p and $v^{1/2}$ for first redox couple waves in absence of (LC).

2.3. Electro chemical behavior of CuBr_2 in presences of (LC)

In 0.01M NaClO_4 at silver working electrode (SWE) the effect of different concentration of (LC) on CuBr_2 cyclic voltammogram are done and explained in Fig.(2). Complexation between CuBr_2 and (LC) was formed explain the interaction between Cu^{2+} and the drug is suggested as³⁵⁻⁵⁰:



The complexation stability constants and Gibbs free energy of complex reaction is great on using small concentrations of ligand LC till full complexation ability and afterwards decrease in the thermodynamics of complexation due to the interaction by association between the LC compounds.

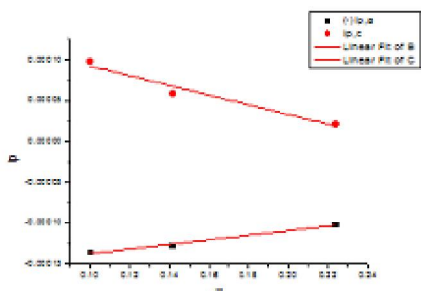


Fig 6. The relation between i_p and $v^{1/2}$ for first redox couple waves in presence of (LC).

4. Conclusions

From the peak potentials and current height, the stability constants and the Gibbs free energies were evaluated and presented in Table 1, it is clear from Table 3 that increase in (LC) concentration on CuBr_2 is followed by stronger complexation results. The thermodynamic parameters are

great at the beginning of adding Ligand LC to CuBr_2 in the supporting electrode and, then, decrease due to more association of ligand molecules.

4. Experimental

Sodium perchlorate was prepared in our laboratory by adding NaOH to freshly prepared perchloric acid provided from Al-Gomhoria Co., specific concentration and titration with NaOH till the appearance of neutral solution, carbazine 720 (CL) from Oxford Co. was used. DY2000 potentiostat was applied for measuring the cyclic voltammograms at different scan rates. Three different electrodes were used for developing the voltammograms discussed. The first electrode is Ag/AgCl standard reference electrode filled with saturated KCl in the outer connection jacket. Pt wire auxiliary electrode was used with Glassy carbon electrode prepared in the laboratory from pure carbon piece jointed with copper wire, isolated with heat shrink polymer and polished with Al_2O_3 put in a woolen clear piece. Ionized water with the conductivity of $2.7 \mu\text{S}$ ($\text{micro Ohm}^{-1} \cdot \text{cm}^2$, micro semiens) was used. 10 minutes nitrogen was passed for each measurement to insure the removal of O_2 in measuring media.

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