Study on Redox Behaviour of Dopamine and its Complexes with Cu (II) and Mg (II) ions

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ABSTRACT: The complexations of dopamine with Cu (II) and Mg (II) ions and their redox behaviour have been studied in aqueous solution using electrochemical methods such as, cyclic voltammetry (CV) and chrono coulometry (CC). The redox behaviour of Cu (II) and Mg (II) ions in absence and in presence of dopamine has been investigated. Dopamine hydrochloride (DPH) shows a two-electron transfer quasi-reversible charge transfer reaction on platinum electrode and similar redox behaviour was observed in case of Mg (II). A two-step redox process is observed for Cu (II) in aqueous solution. The values of charge transfer rate constants for the ligand DPH and for pure metals Cu (II) and Mg (II) are higher than those of Cu (II)–DPH and Mg (II)-DPH system indicating considerable complexation. CC data was analyzed to evaluate the extent of adsorption of the reactants or products on the surface.

Key words: Complexation, Adsorption, Redox behaviour, Charge transfer

INTRODUCTION

The Complexation of organic compounds with selected metal ions has a wide variety of applications in medicinal chemistry, surface chemistry, and analytical chemistry. Complexation of medicinal substances with metal ions influence the bioavailability of drugs in the body and the biological action affects the stability of medicinal compounds since a large number of metals are taken into the body system either with drugs or in the form of diet.[1] The complex formation has been suggested as one of the important mechanisms for certain drug action.[2] The metal chelating phenomena are used to reduce the toxic effect of drugs in human physiology.[3] The study of redox behaviour of biologically and biochemically important compounds are gaining importance because such redox phenomena are close to natural processes occurring in human and other living organisms. Dopamine is a naturally occurring catecholamine (3,4-dihydroxy phenyl ethylamine). It is a central neurotransmitter and possesses important intrinsic pharmacological properties. Many aspects of pharmacology of dopamine have been reviewed by Goldberg.[4] Dopamine is significantly important from clinical viewpoints.[5-14]

Copper is found in enzymes and is able to carry oxygen as hemoglobin does. Cupric ion is the best catalyst in oxidation-reduction process. The cupro-proteins use molecular oxygen as an electron acceptor and most of them contain an even number of copper ions. In human body, liver stores copper and eating of liver and shellfish provide our source of copper. Magnesium ions are found to be complexed with nucleic acids inside cells and are necessary for nerve impulse transmissions, muscle contraction and the metabolism of carbohydrates[1]. Magnesium in excess results in acute and chronic renal disease and contributes to central nervous features associated

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with uraemia[1]. In the present study the redox behaviour of DPH at Pt electrode and its complexation with Cu (II) and Mg (II) have been investigated in aqueous medium by using electrochemical methods.

MATERIALS AND METHODS

Materials. Biochemical grade DPH (Fluka, Switzerland), analar grade KCl, $CuCl_2.2H_2O$, $MgSO_4.7H_2O$ (E. Merck), ammonium metavanadate, concentrated HCl, amalgamated zinc (BDH, UK) were used without further purification. Deionized and double distilled water, polishing cloths, alumina powder (0.3 μ), micropipette 1-100 μl with tips (Gilson, France) were used in the present experiment.

Purification of Commercial Nitrogen. The commercial nitrogen was purified by passing through a solution that was prepared by boiling 2 g of ammonium metavanadate with 25 ml of concentrated HCl acid and diluting with water to 250 ml. This solution was transferred to a gas-washing tower and 10-15 g of amalgamated zinc was added to it. The amalgamated zinc was prepared by placing about 10 g of granular zinc in a beaker, covering it with deionized water and adding 2 drops of concentrated HCl acid. Rejuvenation was accomplished by adding some amalgamated zinc or a few drops of concentrated HCl acid.

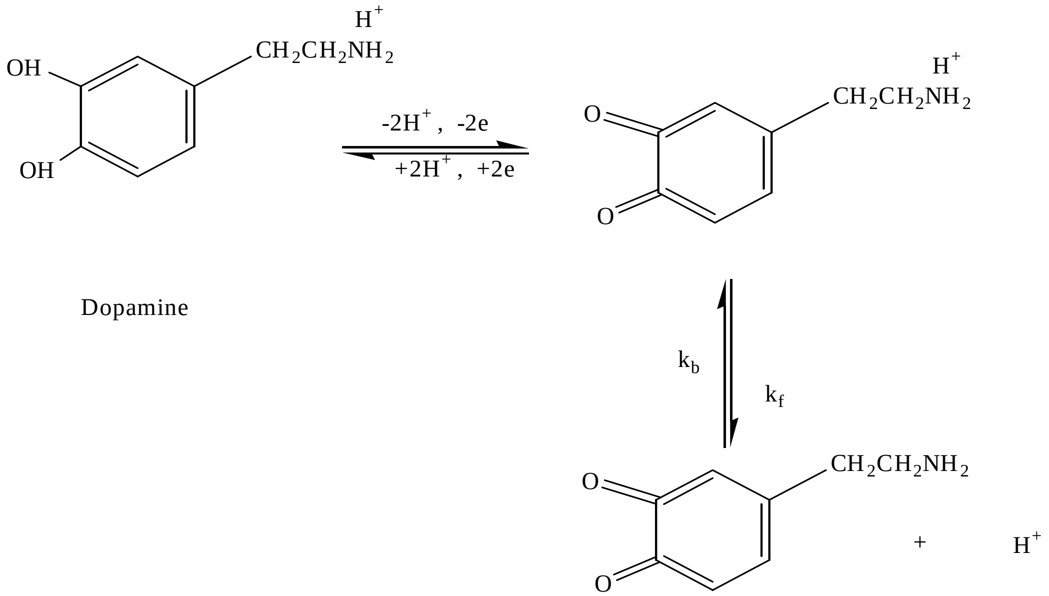
The Electrochemical Methods. Cyclic voltammetry (CV): A single wall three electrodes micro cell with a Pt bead working electrode, a saturated Ag/AgCl reference electrode and a Pt wire counter electrode (Bioanalytical system, USA) was used for electrochemical measurements. The cell and the working electrode were cleaned properly with distilled water and deionized water. The cell was then filled with 10 mL of 0.1 M KCl and the electrodes were immersed in it. The solution was then de-oxygenated for 20-30 minutes by purging nitrogen. After purging the nitrogen tube was kept above the solution during the experiments. The solution was then allowed to become quiet for 5 minutes before running the experiment.

Cyclic voltammetry was carried out by scanning the potential from an initial value (where no electron-transfer takes place) to a vertex potential where the rate of electron transfer was very high. This was the forward scan; this scan was then reversed at the same scan rate until the potential reaches to a final value (usually same as the initial potential). The potential window was chosen so that the electrochemical reactions of the compounds take place on the electrode surface under diffusion-controlled manner. Initially a blank CV was performed in KCl solution and this gave the background current of the supporting electrolyte, KCl solution. Then the CV of metals, ligand and metal-ligand solutions were taken separately in KCl solution under different conditions.

Chronocoulometry (CC). Immediately after performing the CV measurements each solution is subjected to appropriate potential pulse to observe the charge-potential response. In chronocoulometry the integral of the current-time response is measured as a function of charge-time curve. The potential step applied consisted of a pulse height between a maximum of 700 mV to minimum –400 mV and the delay between pulses is 250 ms. Three steps CC is employed in this experiment. The first step is used to ensure no current flows while the system is at the initial potential. In the second step, reduction takes place and oxidation occurs in the third step. The CC of KCl solution, Dopamine solution, Cu (II)-Dopamine, Mg (II)-Dopamine solutions have been carried out in order to investigate the electrode kinetics and adsorption phenomena.

RESULTS AND DISCUSSION

Figure 1 shows CVs for (i) 1 mM, (ii) 2 mM and (iii) 3 mM Dopamine solutions in 0.1 M KCl solution on Pt electrode at a scan rate of 0.1 V s^{-1}. The potential was stepped from an initial potential of –300 mV to a positive direction and reversed back to the initial value after reaching to +900 mV. An anodic peak was observed at + 550 mV and a cathodic peak was observed at ca. +260 mV. The intensity of both the peak increases with increasing concentrations. The anodic peak is due to the transfer of two electrons from the DPH to form dehydrogenated molecule and the cathodic peak is due to the formation of the original molecule by taking two electrons. From the analysis of CV it is reasonable to consider that DPH shows a two-electron charge transfer quasi-reversible reaction. The proposed mechanism can be represented by the following scheme:



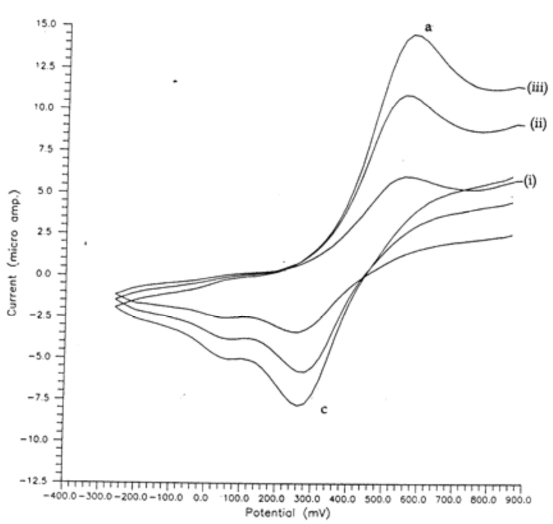


Figure 1. Cyclic voltammogram of (i) 1.0 mM, (ii) 2.0 mM and (iii) 3.0 mM DPH in 0.1 M KCl

Fig. 2. represents CVs on Pt button electrode for (i) 1.0 mM and (ii) 2.0 mM Cu (II) ion in 0.1 M KCl solution, recorded at a scan rate of 100 mV s^{-1}. The potential was stepped from +800 mV where no deposition of copper takes place towards negative potentials and reversed back to the original value after – 600 mV. Two cathodic peaks were observed at +80 mV and at –240 mV respectively for 1.0 mM Cu (II) ion indicating two-step reduction of Cu (II) ion to Cu (I) and Cu (0) states. In the reverse scan, two anodic peaks were observed at –80 mV and +160 mV respectively. These peaks are related to the desorption of metallic copper. The intensities of the peaks increased with increasing concentrations.

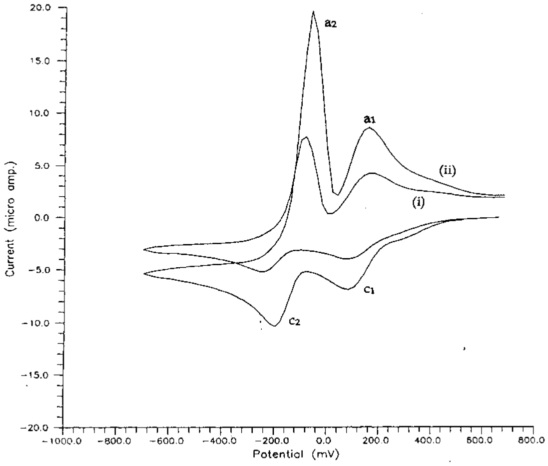


Figure 2. Cyclic voltammogram of (i) 1.0 mM and (ii) 2.0 mM Cu (II) ion in 0.1 M KCl on Pt button electrode at 100 mV s^{-1} scan rate.

CVs for (i) 2.0 mM Cu (II)-DPH and (ii) 3.0 mM Cu (II)-DPH in 0.1 M KCl solution at a scan rate of 100 mV s^{-1} are shown in Fig 3. It was observed that the voltammograms are almost similar to those of pure Cu (II) ion system except a third anodic peak at about 600 mV. The appearance of this third anodic peak is related to the oxidation of -OH group present in the side chain of pure DPH. The covalent attachment of DPH with Cu (II) forming a complex is evident by the peak separation. The potential value of the first anodic peak is shifted towards positive value and the second cathodic peak is shifted towards more negative value giving a large peak separation, which is the characteristic of complexation[15].

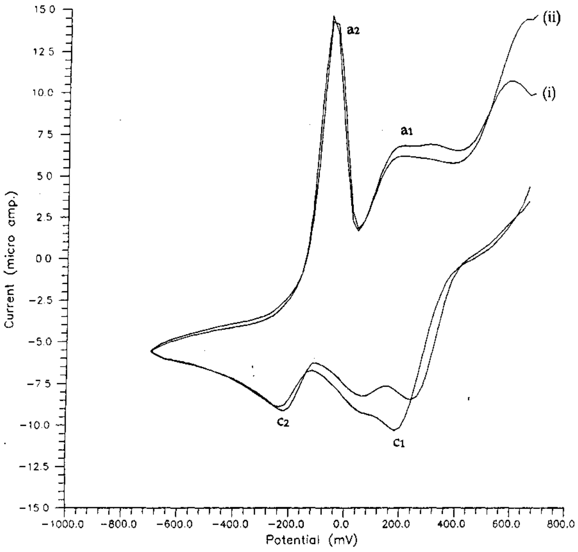


Figure 3. CV for Cu (II) - DPH system on Pt button electrode at 100 mV s^{-1} at different concentrations (i) 2.0 mM and (ii) 3.0 mM

Figure 4. Cyclic voltammogram of (i) 1.0 mM and (ii) 3.0 mM Mg(II) ion solution in 0.1 M KCl solution on Pt button electrode at 100 mV s^{-1}.

Figure 5. CV for Mg(II) -DPH system on Pt button electrode at 100 mV s^{-1} at different concentrations (i) 1.0 mM and (ii) 3.0 mM.

CVs for 1.0 mM and 2.0 mM Mg (II) ion on Pt button electrode are presented in Fig. 4. Analysis of CV data indicates that Mg (II) ion undergoes a two-electron transfer reduction process. From the analysis of CV data (Fig. 5) for Mg (II)-DPH system it is evident that a remarkable complexation takes place here since the peak separation is quite large[15-16].

Chronocoulometric kinetic plot for 3 mM Cu (II)–DPH system is shown in Fig. 6 and that of 3 mM Mg(II) –DPH system is presented in Fig. 7. It can be concluded that in case of Cu (II) DPH system neither the reactant nor the product is adsorbed on the electrode surface considering the criteria of adsorption as summarized by Case and Anson[16]. However in case of Mg (II) –DPH system small amount of reactant is found to be adsorbed on the electrode surface based on the above adsorption kinetics. It is evident from CC data that a small amount of the reactant adsorbed on the electrode surface in case of Mg (II)-dopamine system. However, for Cu (II)-dopamine system neither reactant nor the product is adsorbed on the electrode surface.

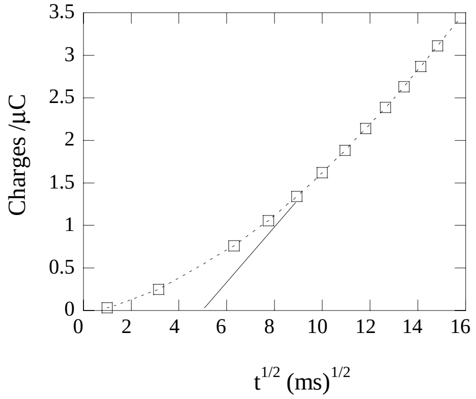


Figure 6. Chronocoulometric kinetic plot for 3 mM Cu(II)-DPH system

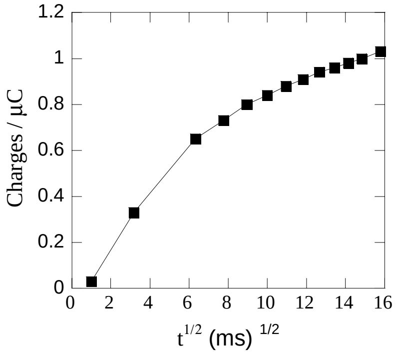


Figure 7. Chronocoulometric kinetic plot for 3 mM Mg(II)-DPH system

Table 1 shows the charge transfer rate constants (k_f) values for DPH, Cu (II)-DPH and Mg (II)-DPH systems calculated from the analysis of (i) CV and (ii) CC data. The k_f values for the free ligand DPH is found to be 4.68×10^{-4} cm s^{-1} which decreases to 3.7×10^{-4} for Cu (II)-DPH system and the value is 0.57×10^{-4} for Mg (II)-DPH system. From the analysis of CV data it is evident that Cu (II) and Mg (II) ions form complexes with the ligand DPH and complexation of DPH follow the order Mg (II) > Cu (II). The k_f value calculated from CC data follow a similar trend for Cu(II)-DPH system where neither the reactant nor the product is adsorbed on the electrode surface. However, the k_f values follow a reverse trend for Mg (II)-DPH system that may be due to adsorption of reactant or product on the electrode surface. The study can help to analyze the dopamine and other neurotransmitters by measuring the charges of complexes of biomolecules after reactions with metal ions. Further study can be performed for modifying the electrode with necessary precursor for electrochemical sensing of biological molecules.

Table 1. Charge transfer rate constant (k_f) for DPH , Cu(II)-DPH and Mg(II)-DPH system calculated from the analysis of (i) CV and (ii) CC data.

(i)

System	αNa	D (cm^2s^{-1}) × 10^7	k_f (cm s^{-1}) × 10^4
DPH	0.598	4.040	4.68
Cu(II)-DPH	0.595	5.143	3.715
Mg(II)-DPH	0.597	1.620	0.575

(ii)

System	Slope	Intercept	k_f (cm s^{-1}) × 10^3
DPH	0.064	0.831	5.18
Cu(II)-DPH	0.595	5.170	3.80
Mg(II)-DPH	0.069	0.853	5.50

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