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Voltammetric distinction between dopamine and ascorbic acid using bare platinum disc electrode catalysed by bisethylenediaminecopper(II)

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Bare platinum disc electrode in presence of bisethylenediaminecopper(II), $[Cu(en)_2]^{2+}$ where en = $H_2NCH_2CH_2NH_2$, in the electrolytic medium excellently distinguishes between dopamine (DA) and ascorbic acid (AA) in their aqueous mixture by cyclic voltammetry and square wave voltammetry. Both DA and AA independently changes the irreversible cyclic voltammogram of $[Cu(en)_2]^{2+}$ into a quasi reversible ones with redox potential value +0.045 V and +0.150 V respectively. The redox currents are linear function of DA and AA concentration. Interaction of $[Cu(en)_2]^{2+}$ with DA and AA mixture resulted quasi reversible cyclic voltammogram with a pair of redox couples with potential +0.220 V and +0.530 V due to DA and AA respectively.

Keywords: Ascorbic acid, Dopamine, Cyclic voltammetry, Copper, Ethylenediamine

Dopamine (DA) is an important neurotransmitter which plays vital role in the functioning of central nervous, renal, cardiovascular and hormonal systems of mammals[1,2]. Low level of DA in brain is the main reason behind Parkinson's disease which causes tremor during rest, inability for movement, muscle rigidity and lack of facial expression[3-5]. Hence, a rapid but simple method for DA detection is of great importance. A good number of methods based on different techniques have been reported for DA detection such as – spectrometry[6-9], chromatography[10,11], chemiluminescence[12,13], electro chemiluminescence[14,15] etc.

Electrochemical methods, compared to other methods, for detection of DA are rapid, more sensitive, low cost, involves miniaturized instrumentation and proficient in in-situ applications. Although DA is electroactive it cannot be detected directly in biological fluids because of the co-existence of ascorbic acid (AA) which interferes electrochemical detection of DA by virtue of its similar redox potential with DA. Further, DA fouls the electrode surface by the formation of electroinactive film after a few electrochemical scans. Modified electrodes based on different modifying agents and methods have been developed to overcome this problem of co-existence of similar redox potential of DA and AA in their mixture[16-20].

Copper(II) complex modified electrodes as DA sensor is emerging as a new area of research on DA sensor. A dimeric Cu(II) complex containing bidentate 2-(2-hydroxyethyl)pyridine) ligand has been used to modify glassy carbon paste electrode to act as voltammetric sensor for DA[21]. Gold electrode surface modified using binuclear copper complex and chitosan film could eliminate the interference from ascorbic acid and uric acid in the determination of DA[22]. Glassy carbon (GC) electrode modified with tris (2,2′-bipyridil) copper (II) chloride complex has been reported as amperometric sensor for DA[23]. GC electrode modified with nafion membrane doped with $[Cu(bipy)_2]Cl_2 \cdot 6H_2O$ complex is another report in this line[24]. Bipyridine bridged copper(II) complex modified GC electrode as voltammetric DA sensor is reported by Wang ***et al.***[25]. Binuclear complex of copper^{2+}, $[LCu^{2+}(CH_3COO)_2Cu^{2+}L](CH_3COO)_2$ where L is N,N bis(phthalimide)ethylenediamine, was encapsulated in ZSM-5 zeolite to modify GC electrode surface for voltammetric DA detection[26].

The report on bare electrode for the detection of DA in presence of AA is rare. Indium-tinoxide (ITO) electrode has been reported based on its ability to selectively adsorb DA[27]. The copper(II) complexes mentioned above are effective towards DA detection only when employed as electrode modifying agent. There is no report that copper(II) complex in solution can differentiate the redox potential of DA and AA at bare electrode. In this paper we report that detection of DA in presence of AA is possible at bare platinum electrode when bisethylenediaminecopper(II) ($[Cu(en)_2]^{2+}$) complex is present in electrolytic medium.

Experimental Section

Reagents and general condition

Ethylenediamine and $CuSO_4$ were purchased from LobaChemie, dopamine hydrochloride was purchased

from SIGMA. The electronic spectra were recorded on a UV-1800 Shimadzu spectrophotometer. The FTIR spectra were recorded using KBr pallet (4000-400) cm^{-1} on a Perkin-Elmer spectrum RXI FTIR system.

CHI 600B Electrochemical analyzer (USA) with a three electrode cell assembly was used for electrochemical studies. Electrochemical experiments were carried out under a blanket of Nitrogen gas after passing the gas through the solution for 10 min. The working electrode is platinum disc, reference electrode is Ag/AgCl (3 M NaCl) and $NaNO_3$ (0.1 M) is the supporting electrolyte. In the Square Wave Voltammetry (SWV) experiments, the square wave amplitude is 25 mV, the frequency is 15 Hz and the potential height for base stair case wave front is 4 mV. The working electrode is cleaned as reported [27].

Synthesis and characterization of $[Cu(II)(en)_2]^{2+}$

$[Cu(en)_2]^{2+}$ has been synthesised as per reported procedure[28]. The complex has been characterized by UV/Visible spectrum and FT-IR spectrum. The synthesised complex showed UV/Visible absorption peak at $_{max}$ = 540 nm which is close to the reported value of 546 nm[28]. Further we observed another peak at $_{max}$ 230 nm which is of ethylenediamine origin. In FT-IR spectrum peaks were observed at 3400 cm^{-1} and 1620 cm^{-1} due to $–NH_2$ which confirms the formation of the bisethylenediaminecopper(II) complex[28].

Results and Discussion

Cyclic voltammogram of 10^{-4} M $[Cu(en)_2]^{2+}$ in aqueous phosphate buffer (PBS) (***p***H 7.0) showed an irreversible voltammetric response with a reduction peak at -0.200 V. This peak potential value was confirmed by square wave voltammetry. When cyclic voltammogram was recorded at different scan rates increase in reduction current of the irreversible peak was observed. The current versus $(Scan\ Rate)^{1/2}$ plot was linear till 1.000 Vs^{-1} scan rate.

Effect of AA on cyclic voltammetry and square wave voltammetry of $[Cu(en)_2]^{2+}$ in aqueous PBS

Cyclic voltammogram of 10^{-4} M $[Cu(en)_2]^{2+}$ was recorded at different added concentration of AA in PBS at ***p***H 7.0 (Fig. 1). The irreversible cyclic voltammogram due to $[Cu(en)_2]^{2+}$ gradually transformed towards reversibility and at 1:1 concentration ratio of $[Cu(en)_2]^{2+}$:[AA] quasi reversible cyclic voltammogram was obtained. Inset of Fig.1 shows the quasi reversible cyclic voltammogram due to 1:1 mixture of $[Cu(en)_2]^{2+}$ and AA. The oxidation and reduction peaks were observed at +0.345 V and +0.045 V respectively. The redox potential value calculated was +0.150 V with the separation in peak potential as 0.300 V. Thus, the interaction between $[Cu(en)_2]^{2+}$ and AA has resulted a quasi reversible cyclic voltammogram. The exact reason for the conversion of the irreversible cyclic voltammogram in quasi reversible one is not known to us.

The interaction between AA and $[Cu(en)_2]^{2+}$ was also investigated by square wave voltammety. Figure 2 shows the square wave voltammogram of $[Cu(en)_2]^{2+}$ at different added concentration of AA. The initial peak at -0.200 V was found to decrease with AA concentration and a new peak appeared at +0.170 V.

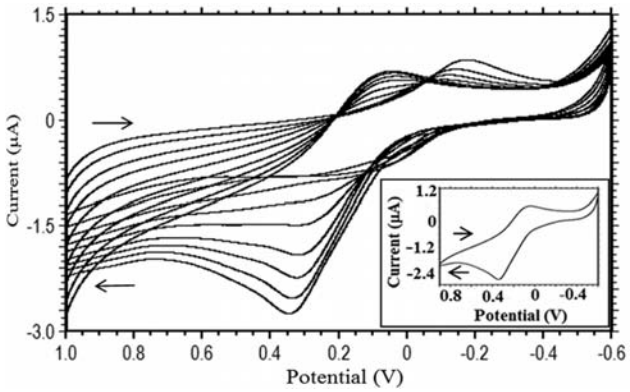

Fig. 1 — Cyclic voltammogram of 10^{-4} M $[Cu(en)_2]^{2+}$ at different added concentration of AA in PBS at pH 7.0. Inset: quasi reversible cyclic voltammogram when $[Cu(en)_2]^{2+}$:[AA] is 1:1. (WE: Pt disc, RE: Ag-AgCl, 0.1 M $NaNO_3$).

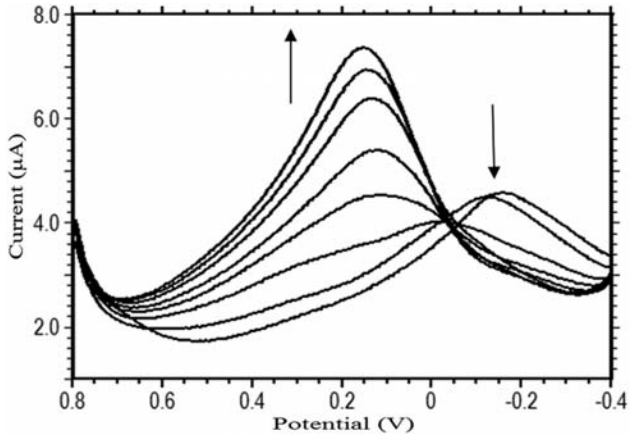

Fig. 2 — Square wave voltammogram of $[Cu(en)_2]^{2+}$ at different added concentration of AA. (WE: Pt disc, RE: Ag-AgCl, 0.1 M $NaNO_3$).

Effect of DA on cyclic voltammetry and square wave voltammetry of $[Cu(en)_2]^{2+}$ in aqueous PBS

Cyclic voltammogram of $[Cu(en)_2]^{2+}$ (10^{-4} M) in aqueous PBS was recorded at different added concentration of DA. The irreversible peak of $[Cu(en)_2]^{2+}$ disappeared and quasi reversible cyclic voltammograms appeared. The quasi reversible cyclic voltammograms at 1:1 concentration ratio of $[Cu(en)_2]^{2+}$ and DA has been shown in Fig. 3. The oxidation peak was observed at +0.220 V and reduction peak at -0.130 V with redox potential +0.045 V with separation in peak potential 350 mV. The exact reason for the conversion of the irreversible cyclic voltammogram in quasi reversible one is not known to us. Figure 4 shows the square wave voltammogram of $[Cu(en)_2]^{2+}$ alone and in presence of one equivalent of DA. The square wave voltammograms clearly shows the effect of DA on the redox potential of $[Cu(en)_2]^{2+}$.

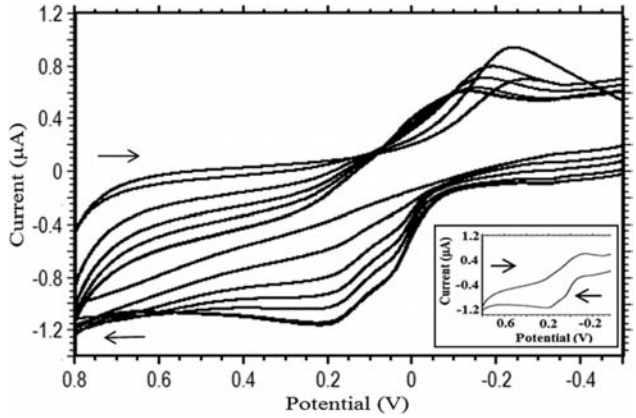

Fig. 3 — Cyclic voltammogram of 10^{-4} M $[Cu(en)_2]^{2+}$ at different added concentration of DA in PBS at pH 7.0. Inset: Cyclic voltammogram of 10^{-4} M $[Cu(en)_2]^{2+}$ in presence of 10^{-4} M DA. (WE: Pt disc, RE: Ag-AgCl, 0.1 M $NaNO_3$).

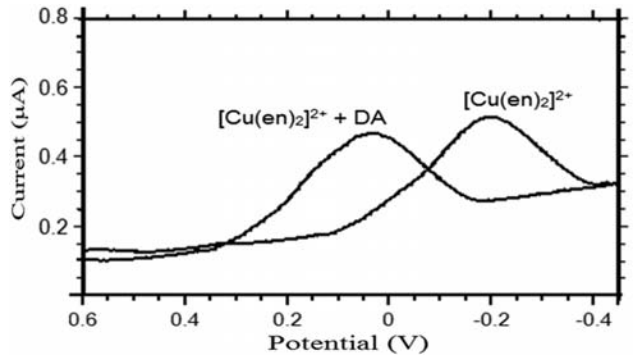

Fig. 4 — Square wave voltammogram of (A) 10^{-4} M $[Cu(en)_2]^{2+}$ alone and (B) 10^{-4} M $[Cu(en)_2]^{2+}$ in presence of equal amount of DA. (WE: Pt disc, RE: Ag-AgCl, 0.1 M $NaNO_3$).

Effect of DA and AA mixture on cyclic voltammogram and square wave voltammogram of $[Cu(en)_2]^{2+}$ in aqueous PBS

Cyclic voltammogram of 10^{-4} M $[Cu(en)_2]^{2+}$ was recorded in PBS (***p***H 7.0) when concentration of both DA and AA increased in the solution. Figure 5 shows the effect of DA and AA concentration on the cyclic voltammogram of $[Cu(en)_2]^{2+}$. The irreversible cyclic voltammogram of $[Cu(en)_2]^{2+}$ gradually converted into two quasi reversible cyclic voltammograms with redox potential values +0.220 V (ΔE=0.150 V) and +0.530 V (ΔE=0.160 V). Inset of Fig. 5 shows the quasi reversible cyclic voltammogram of $[Cu(en)_2]^{2+}$ when the individual concentrations of DA and AA became 10^{-4} M which is equal to that of $[Cu(en)_2]^{2+}$.

Square wave voltammograms were also recorded for aqueous solution of $[Cu(en)_2]^{2+}$ in PBS (***p***H 7.0) at different added concentration of AA and DA mixture. From Fig. 6 it is clear that $[Cu(en)_2]^{2+}$ could generate well separated square wave voltammograms

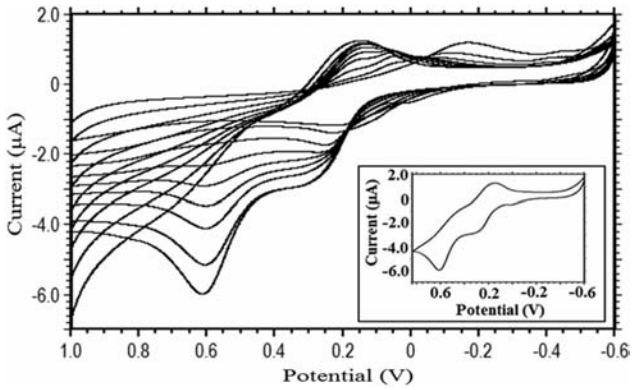

Fig. 5 — Cyclic voltammogram of 10^{-4} M $[Cu(en)_2]^{2+}$ when concentration of both DA and AA is increased in the electrolytic medium till their concentration becomes 10^{-4} M. Inset: Cyclic voltammogram of 10^{-4} M $[Cu(en)_2]^{2+}$ at DA and AA concentration 10^{-4} M. (WE: Pt disc, RE: Ag-AgCl, 0.1 M $NaNO_3$).

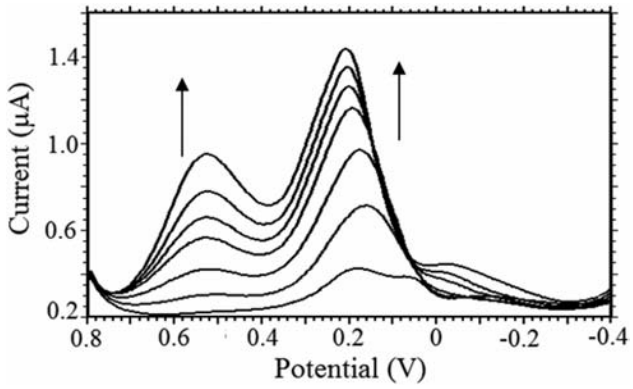

Fig. 6 — Square wave voltammogram of 10^{-4} M $[Cu(en)_2]^{2+}$ when concentration of both DA and AA is increased in the electrolytic medium till their concentration becomes 10^{-4} M. (WE: Pt disc, RE: Ag-AgCl, 0.1 M $NaNO_3$).

corresponding to AA and DA. The peak corresponding to AA was appeared at +0.520 V while that for DA was observed at +0.210 V, separation of the peaks being 0.310 V.

UV/Visible spectral studies of interaction between $[Cu(en)_2]^{2+}$ with DA, AA and their mixture

To understand the interaction between $[Cu(en)_2]^{2+}$ and DA and AA, UV/visible spectra were recorded for $[Cu(en)_2]^{2+}$ at different added concentration of DA, AA and their mixture in PBS (***p***H 7.0) (Fig. 7). Fig. 7a shows the effect of AA on the UV/Visible spectra of $[Cu(en)_2]^{2+}$. In case of the peak at $_{max}$ = 230 nm, AA could not shift the peak position but the absorbance found to increases by a little. Addition of DA to the aqueous solution of $[Cu(en)_2]^{2+}$ in PBS (***p***H 7.0) had a significant effect (Fig. 7b). A new peak was observed at 285 nm while the original peak of $[Cu(en)_2]^{2+}$ at $_{max}$ 230 nm gradually became shoulder and then vanished with increasing DA concentration. The addition of DA and AA mixture to aqueous solution of $[Cu(en)_2]^{2+}$ in PBS (pH 7.0) showed the peak corresponding to DA and the original peak of $[Cu(en)_2]^{2+}$ at $_{max}$ gradually became a shoulder and then vanished (Fig. 7c). Thus, the effect of DA and AA mixture on $[Cu(en)_2]^{2+}$ is similar to the effect of individual DA on $[Cu(en)_2]^{2+}$. This indicates a stronger interaction between DA and $[Cu(en)_2]^{2+}$ than between AA and $[Cu(en)_2]^{2+}$. In case of the UV/Visible peak at $_{max}$ = 540 nm DA could not shift the peak position but the absorbance enhanced by a little while AA shifted the peak to 670 nm with a decrease in absorbance.

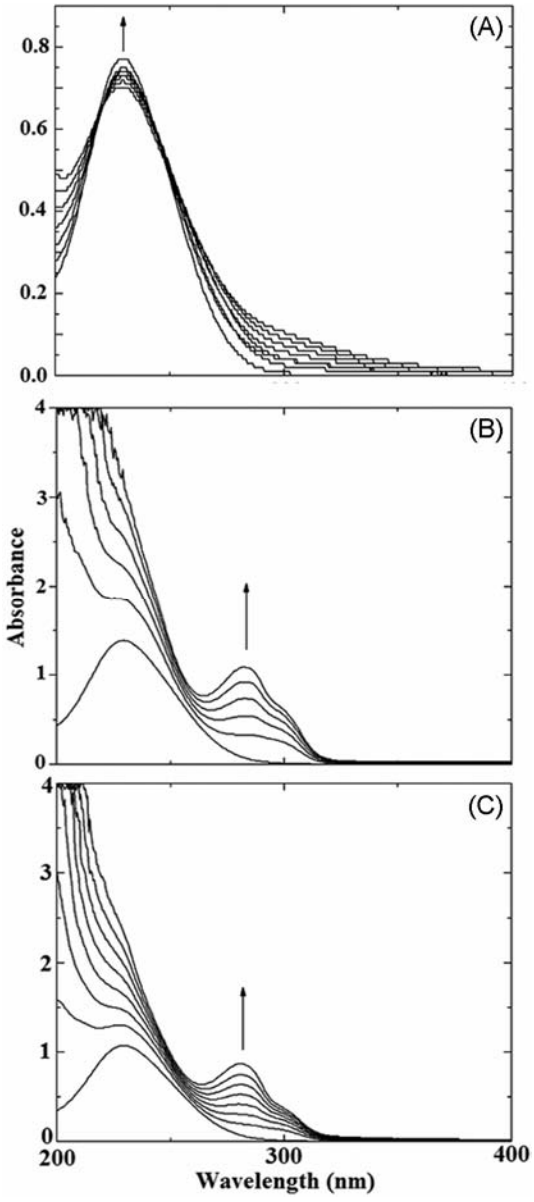

Fig. 7 — UV/Visible spectra of 10^{-4} M $[Cu(en)_2]^{2+}$ in PBS (pH =7.0) at different added concentration of AA (A), DA (B) and AA+DA (C).

Conclusion

It is concluded that DA and AA in their mixture can be distinguished by cyclic voltammetry and square wave voltammetry in aqueous medium using bare platinum disc electrode when bisethylenediaminecopper(II) complex is present in the solution. A +0.300 ± 0.010 V separation in redox potentials of DA and AA in their mixture was observed.

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