Artigo

ADSORPTION OF A COPPER (II) COMPLEX ON CALCIUM PHOSPHATE INTERCALATED WITH 4-AMINOBENZOIC ACID – SYNTHESIS AND ELECTROCHEMICAL INVESTIGATION

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In this study, the adsorption isotherm of copper (II) on a calcium phosphate host intercalated with 4-aminobenzoic acid in an ethanol solution was investigated. This gave a maximum adsorption capacity of 1.74 mmol g^{-1}. The material was incorporated into a carbon-paste electrode, and its electrochemical properties were investigated. However, for a dopamine solution, the anodic peak current increased owing to the electrocatalytic oxidation. The electrode presented the same response for at least 150 successive measurements, showing good repeatability. The modified electrode is very stable and reproducible. The electrode sensor was successfully applied for dopamine determination in pharmaceutical preparations.

Keywords: calcium phosphate; intercalation; carbon-paste electrode.

INTRODUCTION

The usability of chemically modified electrodes has been extensively investigated because of not only the advantages offered by these devices[1,2] but also their ability to improve selectivity and sensitivity. Selectivity and sensitivity are the key properties for detecting electroactive species dispersed in various media.[3] From the viewpoint of applicability, most of the immobilized active centers are able to mediate the electron transfer processes and are useful for fabricating electrochemical sensors.[4-7]

The effectiveness of such chemical modification involves covalent bonding within a given matrix, thus enabling adsorption, intercalation, electrodeposition, or mixing for conducting particles with a specific reagent for preparing electrodes from carbon paste.[8-11]

Owing to the significance of monitoring biochemical and biomedical applications, the development of new methods of analysis employing electrochemical sensors based on carbon paste,[12-14] carbon fiber,[15,16] glassy carbon,[17,18] thick-film carbon,[19,20] and polymer-coated electrodes[21,22] has been attracting research attention.

A large number of inorganic compounds are suitable as hosts for such an investigation, particularly a class of crystalline layered phosphate compounds presents high ion exchange capacity and conductivity.[23] Owing to these characteristics, a crystalline layered phosphate compound can be used as a matrix for immobilization of electroactive species.[24]

This investigation focuses on the electrochemical behavior of copper (II) as it is adsorbed on 4-aminobenzoic acid intercalated calcium phosphate. This newly synthesized compound was first used to prepare a carbon-paste electrode. The resulting material was used to test dopamine oxidation. This active molecule was chosen because it is one of the most significant catecholamines and plays a very important role in the functioning of the central nervous system, as well as the cardiovascular, renal, and hormonal systems. Its concentration in extracellular fluid is less than that of ascorbic acid (AA). A deficiency of dopamine in the central nervous system can cause serious abnormalities such as schizophrenia and Parkinson's disease.

Consequently, the analysis of these compounds in real-world biological samples and the identification of neurotransmission changes are important. Neurotransmission changes may correlate to the behavioral state of an animal and are obvious targets of enormous importance in the scheme of neurochemical studies. Therefore, the quick determination of dopamine *in vitro* and in living creatures has attracted considerable attention.[25-28] This paper proposes an electrochemical procedure employing an innovative, stable inorganic support.

EXPERIMENTAL

Synthesis of calcium phosphate

Calcium phosphate (CaP) was synthesized by slowly adding a dilute solution of calcium chloride dehydrated to a 1.50 mol dm^{-3} dibasic ammonium phosphate solution. The mixture was heated to 360 K. The resulting suspension was stirred for 1 h as the solid began to settle. The precipitate was filtered and dried at 320 K. Finally, the resulting compound was heated at 440 K for 48 h to eliminate ammonia.

Intercalation procedure

About 50 mg of CaP was immersed in 20.0 cm^3 of 1.0×10^{-3} mol dm^{-3} aqueous 4-aminobenzoic acid (PABA), and the suspension was shaken in an orbital mechanical stirrer for 1 h. This stir time was determined for a constant concentration of PABA after varying the solid/solution ratios and contact time up to 12 h in order to obtain the best intercalation condition for this guest molecule. The resulting solid was filtered, washed with doubly distilled water, and dried at 323 K.

Characterization

Calcium and phosphorus[29,30] elemental analyses were performed by atomic absorption spectroscopy using a Perkin Elmer atomic absorption spectrometer, model 5100, and other spectrophotometric methods using a Shimadzu spectrophotometer, model MultiSpec-1501.

The amount of PABA intercalated into calcium phosphate

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was determined by nitrogen elemental analysis on a Perkin-Elmer Analyzer 2400 series H CHNS/O apparatus.

X-ray diffraction patterns were obtained with nickel-filtered CuKα (0.154 nm) radiation in the range 2–65° at a speed of 0.033° s⁻¹ and a step of 0.050° on a Shimadzu XD3-A diffractometer (30/20 kV/mA).

Infrared spectra of the samples were collected on a Perkin-Elmer FTIR spectrophotometer, model 1600, using pressed KBr pellets in the 4000-400 cm⁻¹ range at a resolution of 4 cm⁻¹.

Copper (II) concentration in the supernatant was measured by atomic absorption spectroscopy using a Perkin-Elmer atomic spectrometer, model 5100.

The UV-Vis spectra of the CaP/PABA with adsorbed copper (II) were obtained in Nujol on a Beckman DU 640 spectrophotometer.

Adsorption isotherms

Using a batchwise method, the adsorption isotherm of $CuCl_2$ in the ethanol solution was obtained. For each isotherm, a series of samples containing 100 mg of CaP intercalated with PABA was shaken for 3 h (as previously established)[31] in an orbital bath with various concentrations of the metal halide at a constant temperature of 298 ± 1 K. The concentration of copper in the solution at equilibrium with the solid phase was determined by atomic adsorption spectrometry. The amount of copper adsorbed n_f was determined by applying the equation: $n_f = (n_i - n_s)/m$, where m is the mass of the adsorbent, and n_i and n_s are the initial and equilibrium amounts of the number of moles of copper cations in the solution phase, respectively.

Electrochemical measurements

The modified carbon-paste electrode was prepared by mixing 30 mg of the intercalated/adsorbed copper (II) calcium phosphate, 30 mg of graphite (Fluka), and a drop of mineral oil (2.0×10^{-2} cm³). The paste was deposited into a cavity on the surface of a platinum disk, which was fused at the end of a glass tube with an inner diameter of 3 mm. This proportion produced a good response in a preliminary test after a detailed study of the paste composition. This electrode is referred to as CaP/PABA/Cu(II) hereafter.

Electrochemical measurements were performed using the CaP/PABA/Cu(II) electrode as the working electrode, a saturated calomel (SCE) as the reference electrode, and a platinum wire as the auxiliary electrode. The electrochemical properties of copper (II) adsorbed on calcium phosphate intercalated with 4-aminobenzoic acid were studied by means of cyclic voltammetry (CV) using a PAR 273A (EG&G) potentiostat/galvanostat. The experiments were conducted in a 0.10 mol dm⁻³ of phosphate buffer electrolyte solution under a pure argon atmosphere. The pH was adjusted by adding HCl or NaOH to the solution. Different supporting electrolytes were also tested. The response of the electrode used for dopamine determination was evaluated by an amperometric technique in a 0.010 mol dm⁻³ standard aqueous solution. Fixed volumes (50 μdm³) of the standard dopamine solution were added successively to an electrochemical cell containing a 0.10 mol dm⁻³ phosphate buffer electrolyte solution, in order to obtain a total volume of 1.0 cm³. The calibration plot obtained from this experiment was used to determine the dopamine concentration in commercial samples (Revivan) and a standard reference material (dopamine hydrochloride injection (DHI)). The commercial and reference samples were made by dissolving 2.0 cm³ of Revivan and DHI in doubly distilled, degassed water and diluted to 10.0 cm³ (solution A and solution B), respectively. The chronoamperometric response was obtained by adding solution A or B to a cell filled with a 10.0 cm³ phosphate buffer electrolyte solution in increments of

200μL. All chronoamperometric measurements were performed at pH 7.2 under a pure argon atmosphere.

RESULTS AND DISCUSSION

Characterizations

Elemental analysis of the synthesized compound indicated that the compositions of calcium and phosphorous were 26.3 and 17.2%, respectively. The values are very close to the expected compositions of 26.5 and 17.1% (respectively) for the proposed formula $Ca(H_2PO_4)_2$. On the basis of these values, the corresponding molar amounts of these elements were calculated to obtain a phosphorus to calcium ratio of 2:1. The quantity of PABA intercalated into CaP was determined through nitrogen content analysis. A composition of 4.2% of nitrogen atoms within the guest molecule corresponds to 3.0 mmol g⁻¹.

The layered structural feature of the crystalline calcium phosphate shows an interlayer distance that is dependent on the size of the cation or the molecule intercalated into the host. An X-ray powder diffractogram is a good tool for observing the change in the interlayer distance in order to examine the uptake process.

The powder X-ray diffraction patterns of the synthetic compound and the form intercalated with 4-aminobenzoic acid are shown in Figure 1. Sharp peaks signify the crystallinity of the resulting solids. The intense peak at 2θ = 12.8° corresponds to an interlayer distance of 712 pm for the original lamellar compound,[32,33] as shown in Figure 1a. As expected, the interlayer distance increases when this inorganic support is suspended in the aqueous solution containing dissolved 4-aminobenzoic acid molecules. The result is a sharp peak at 2θ = 5.6° that corresponds to an interlayer distance of 1578 pm, which is nearly double the value of the original lamellar compound, as shown in Figure 1b.
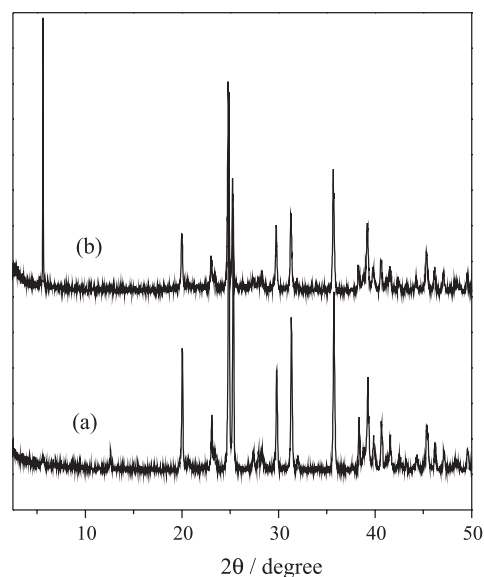

Figure 1. *X-ray diffraction patterns of calcium phosphate (a) and (b) its 4-aminobenzoic acid form*

The OH groups of the phosphate in the lamellar calcium phosphate exhibit stretching at 3400 cm⁻¹ and weak deformation at 1630 cm⁻¹ bands in the infrared spectrum. The intense characteristic stretching bands for phosphate groups are located at 1033 and 1010 cm⁻¹.[32] However, after intercalation with 4-aminobenzoic acid, the bands attributed to OH vibrations remain in the spectrum and decrease in intensity. This mainly occurs to the deformation band, as observed for

other systems.[7,34] There is no clear evidence of NH vibration bands at 3580 and 3077 cm^{-1}

Adsorption of copper

Adsorption isotherms for Cu^{2+} cations in an ethanol solution were investigated in relation to the intercalated crystalline lamellar compound. Initially, our investigation demonstrated that the original matrix without PABA does not adsorb this cation. The adsorption isotherm of the CaP/PABA system is shown in Figure 2. The amount of copper cations on the host surface was found to be 1.68 mmol per gram of the solid. The electronic absorption spectrum of the copper (II) complexed within the intercalated compound is shown in Figure 3. The observed spectrum is similar to that observed for square planar copper (II) complexes on chemically modified silica gels containing pendant chains with amine groups,[35] as well as on chemically modified cellulose acetate membranes.[36] The Gaussian components of the absorption bands show a peak maxima at 550 and 640 nm, which correspond to a complex with D_{4h} local crystal field symmetry and can be assigned to the $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{2g}$ d-d transitions,[37-40] respectively.
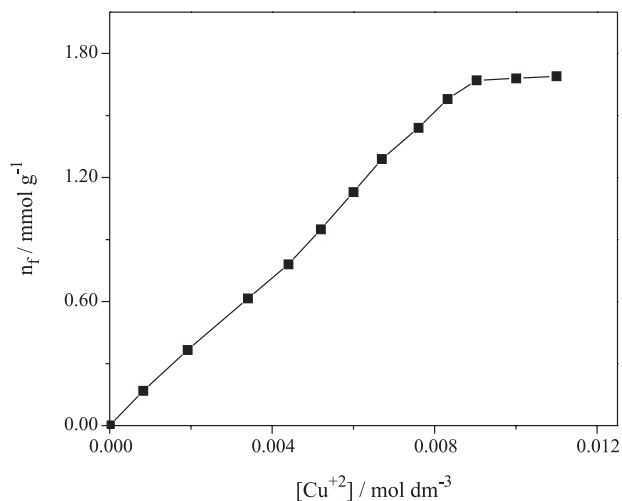

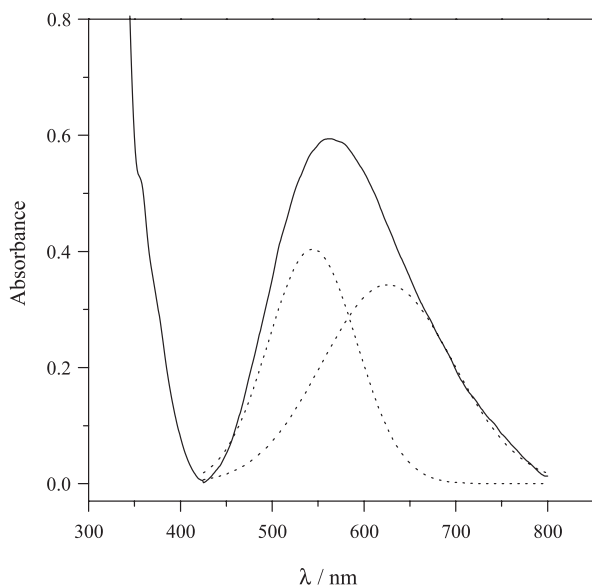**Figure 2.** *Isotherm of copper complexation on 4-aminobenzoic acid in CaP compound*

Figure 3. *Electronic transition spectrum of CaP/PABA/Cu(II)*

Electrochemical studies

Cyclic voltammetry (CV) was performed using a carbon-paste electrode modified with the material. No current peaks are observed for an electrode modified with only calcium phosphate intercalated with 4-aminobenzoic acid. However, CV curves for carbon-paste electrodes prepared with CaP/PABA with complexed copper (II) were obtained. In this case, a current peak is observed with a midpoint potential at $E_m = 0.16$ V, where $E_m = (E_{pa} + E_{pc})/2$, and E_{pa} and E_{pc} are the observed anodic and cathodic peak potentials, respectively. This low midpoint and an anodic peak potential near zero are very important for sensor/biosensor development. In comparison with earlier results, this wave can be attributed to the process of transfer of an electron in the coupling,[41-43] as shown in equation 1:

$$[Cu^{II}(CaP/PABA)_4] + s^+ + e^- \rightleftharpoons [sCu^I(CaP/PABA)_4], \qquad (1)$$

where the supporting electrolyte in the redox process, namely s$^+$, must diffuse into or move out of the surface of the structured complex.

Cycling the potential several times helped in verifying the stability of the electrode. The peak current intensities do not decrease, indicating that the complexed Cu(II) strongly adheres to the 4-aminobenzoic acid intercalated calcium phosphate and is not released to the solution phase under the operating conditions.

Cyclic voltammograms obtained at different scan rates indicate that the value of ΔE_p ($\Delta E_p = E_{pa} - E_{pc}$) increases at higher rates. This result suggests that the electron transfer on the electrode surface is not sufficiently fast. This is a consequence of the high resistance of the matrix. The correlation of the peak currents, I_{pa} and I_{pc}, against $v^{1/2}$ (v is the scan rate) is linear, as shown in Figure 4. This is similar to a diffusion controlled process. Because the electroactive species strongly adheres to the matrix, the mechanism may be explained by the transport of an ion from the supporting electrolyte on the electrode surface for charge compensation.[44] The supporting electrolytes studied here (phosphate buffer and KCl) did not have any significant influence on E_m, whose values varied between 0.16 and 0.17 V. These results indicate that the supporting electrolytes are not interacting with the matrix surface and produce no significant change in the midpoint potential. It was also observed that the ion could compensate the charge irrespective of the hydrated radius. A similar behavior was observed in osmium-complex-modified electrodes.[45]
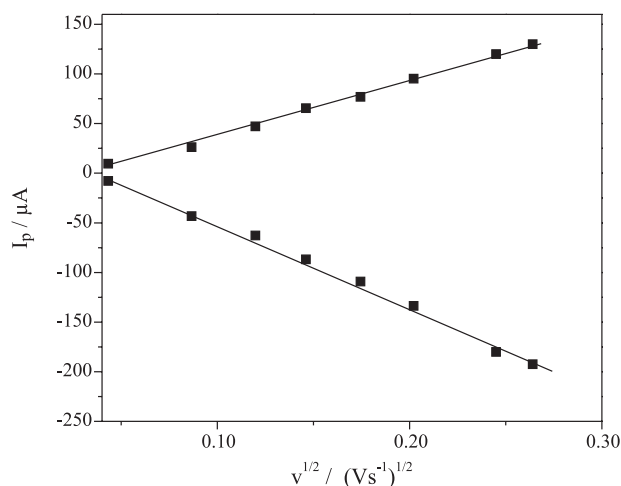

Figure 4. *Anodic (I_{pa}) and cathodic (I_{pc}) current peaks against square root of the scan rate $v^{1/2}$ for a CaP/PABA/Cu(II) electrode in 0.10 mol dm^{-3} phosphate buffer at pH 7.2*

Electrocatalytic oxidation

Dopamine (DA) oxidation on the surface of the CaP/PABA/Cu(II) electrode is shown in Figure 5. The CV curves in the presence of 2.5×10^{-5} mol dm^{-3} dopamine solution at pH 7.2 show a considerable increase in the anodic peak current. The cathodic peak can be associated with the stronger interaction between the copper complex present in the electrode surface and the matrix surface.[46] Alternatively, the cathodic peak can be associated with the products of the dopamine oxidation. This was verified by using a glassy carbon electrode in the presence of the dopamine solution. A similar behavior was observed in other systems.[47] Dopamine electrochemical oxidation has been investigated mostly on carbon-paste electrodes,[48-50] and the complete effect corresponds to a two-electron process, followed by a two-proton process, as represented in equation 2. The reaction indicates the oxidation of DA into DA *o*-quinone (DAQ).[51]
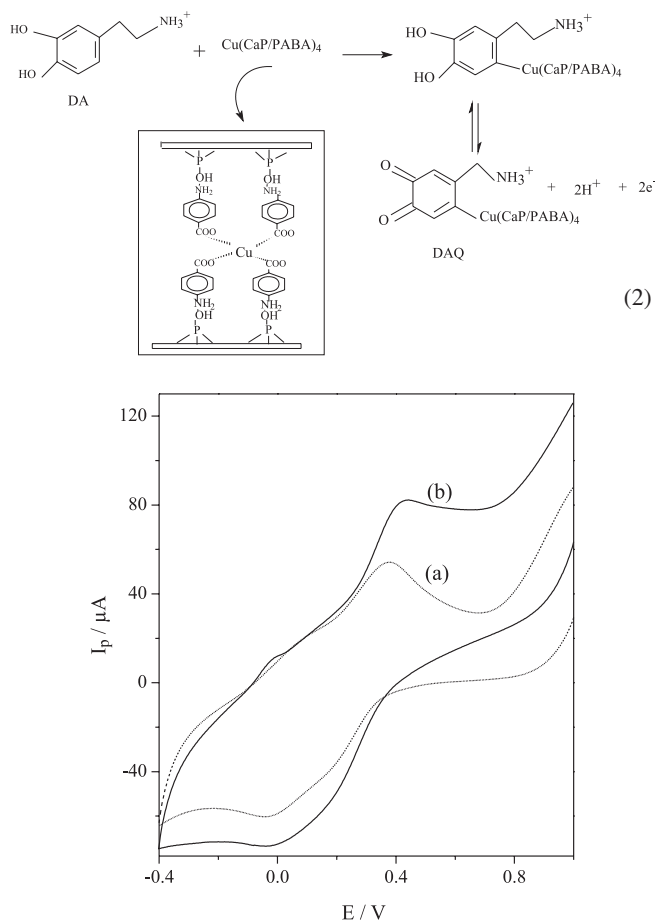

$$(2)$$

Figure 5. *Cyclic voltammogram curves for the CaP/PABA/Cu(II) electrode in the (a) absence and (b) presence of dopamine (0.10 mol dm^{-3} phosphate buffer) at pH 7.2. Scan rate of 20 mVs^{-1}*

Chronoamperometry

To assess the possibility of using the electrode, which is fabricated from adsorbed copper in 4-aminobenzoic acid intercalated calcium phosphate, as a sensor for DA, chronoamperometric experiments were conducted. First, amperometric studies were conducted in order to determine the best potential to be applied. The potential was chosen by measuring the intensities of catalytic currents at 298 K for a solution containing 1.0×10^{-3} mol dm^{-3} DA at pH 7.2. The plot of the current peak intensities against the different potentials (figure not shown) showed that the catalytic currents remain constant at 0.38 V.

The effect of solution pH on the response of DA was investigated (data not shown). Normally, the solution pH influences the oxidation of dopamine.[52] In the present case, the CaP/PABA/Cu(II) electrode was immersed in a 0.10 mol dm^{-3} phosphate buffer solution with [DA] $= 1.0 \times 10^{-3}$ mol dm^{-3}. The pH was varied between 3.0 and 8.0. The current practically remained constant throughout the interval. While at a pH level lower than 4.5, a considerable decrease in the response was detected. Therefore, the difference in the pH dependence of DA means that DA oxidation uses different proton and electron-transfer mechanisms. According to the Nernst equation, the slope of -55.7 mV/pH unit reveals that the proportion of the electrons and protons involved in the reactions is 1:1. Since DA oxidation is a two-electron process, the number of protons involved is also expected to be two.

Figure 6 shows the amperometric curve obtained by successively adding 50 μdm^3 of a 0.010 mol dm^{-3} DA solution with the phosphate buffer at pH 7.2 into an electrochemical cell fixed at $E_{pa} = 0.38$V. The response time is low at about 1.5 s for the current to achieve the maximum value, as shown in the Figure 6 inset.
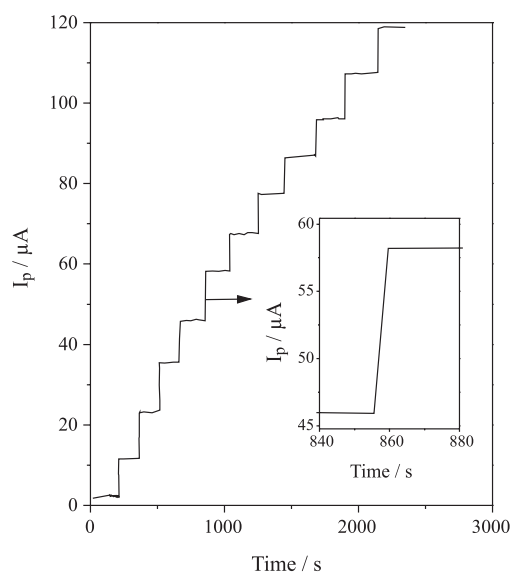

Figure 6. *Chronoamperogram obtained with CaP/PABA/Cu(II) electrode in 0.10 mol dm^{-3} phosphate buffer solution at pH 7.2 and an applied potential of 0.38 V. Successive additions of 50 μdm^3 of a 0.010 mol dm^{-3} DA solution. The inset figure represents the peak current against time*

The plot of the current peak against dopamine concentration is shown in Figure 7. A linear correlation with the concentration of the acid between 1.1×10^{-6} to 7.4×10^{-4} mol dm^{-3} is observed with a detection limit of 1.1×10^{-6} mol dm^{-3}. The proposed electrode presents a higher detection limit for DA, which makes the sensor very attractive for determination of dopamine in drugs in comparison with other modified electrodes.[47,53,54]

The performance of electrode over a period of six months with measurements of the oxidation peak currents for a 0.010 mol dm^{-3} DA solution in a 0.10 mol dm^{-3} phosphate buffer solution (pH 7.2) was observed on each consecutive day. This serves as an indicator of the stability of the modified electrode toward dopamine. The electrode was used daily. The experimental results indicated that the current responses showed a relative standard deviation of 3.77%, suggesting that the modified electrode possesses good stability.

The reproducibility of the electrode was investigated. Repetitive measurements were performed in 0.010 mol dm^{-3} DA. The results of 150 successive measurements show a relative standard deviation of 1.07%. Thus, the modified electrode is very stable and good reproducibility is observed.
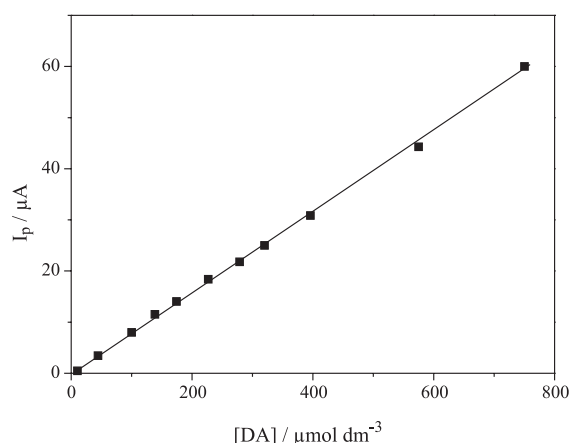
Figure 7. *Plot of anodic peak current (I_{pa}) against dopamine concentration in a 0.10 mol dm^{-3} phosphate buffer solution at pH 7.2. Scan rate is 20 mVs^{-1}*

Interference study

The major sources of interference in dopamine determination are a few commonly coexisting species in biological fluids; this could lead to either new voltammetric peaks or an overlap with the existing ones, thereby influencing their voltammetric response. The effects of citric acid, tartaric acid, glucose, uric acid, ascorbic acid (AA), and sodium chloride (NaCl) on the voltammetric peak response of 1.0×10^{-3} mol dm^{-3} of dopamine was examined. It was observed that 300-fold concentrations of NaCl, tartaric acid, and glucose, a 100-fold concentration of citric acid, and 10-fold concentrations of uric acid and AA have no significant influence on the voltammetric peak response of 1.0×10^{-6} mol dm^{-3} DA. The peak current signal change was below 5% in all cases.

Determination of dopamine in real samples

The result obtained from CV for a commercial sample and DHI with the CaP/PABA/Cu(II) electrode is 5.01 ± 0.16 and 5.04 ± 0.18 mg cm^{-3}, respectively. These results are in good agreement with the label value of 5.0 mg cm^{-3}, with a confidence interval of 95% for n = 10. This indicates the feasibility of using the electrode for DA determination in real samples.

CONCLUSIONS

The elemental analysis data obtained in this study enabled the determination of the molecular formula for the crystalline lamellar $Ca(H_2PO_4)_2$ compound. The expansion of the basal distance was detected by X-ray diffraction patterns, whose lamellar structure was maintained after intercalation. The availability of the basic centers in the intercalated compound allows this material to adsorb cations from an ethanol solution at the solid/liquid interface. This is shown by the isotherms of Cu(II) cations.

The results obtained from the electrode containing CaP/PABA/Cu(II) are very promising considering the fact that other chemical species that may have been present did not interfere with the determination. The advantages of using the proposed CaP/PABA/Cu(II) electrode have been established by our analytical procedures, and its development is simple. The electrode did not show significant changes in response after six months of use, thus showing good chemical stability. These characteristics make this material very attractive for use as a sensor for dopamine determination. The electrode showed a reasonable detection limit with the chronoamperometric technique, with the detection limit of dopamine reaching 1.1×10^{-6} mol dm^{-3}.

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