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Electrocatalytic Determination of Ascorbic Acid Using Glassy Carbon Modified with Nickel(II) Macrocycle Containing Dianionic Tetraazaannulene Ligand

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A symmetric Ni(II) tetraaza macrocycle modified glassy electrode shows electrocatalytic activity for the oxidation of L-ascorbic acid at pH 7. It was shown the peak potential shifted to the negative by 250 mV compared with that for the bare electrode in the cyclic voltammograms. The calibration curve was linear up to 5 mM with a detection limit of 2.5×10^{-4} mM and RSD% better than 2.8%. Excipients used as additives in pharmaceutical formulations and foods did not interfere in the proposed procedure. This new modified electrode was applied to commercial pharmaceutical tablets, injections and foods. The obtained results were identical to those obtained by the classical 2,6-dichlorophenolindophenol method.

Key Words: Ni(II) tetraaza macrocycle, Sensor, Electrocatalytic oxidation, L-Ascorbic acid.

Introduction

L-Ascorbic acid (AsA) is known for its reductive properties and for its use on a wide scale as an antioxidant agent in foods and drinks; it is also important for therapeutic purposes and biological metabolism. Therefore, recent advances in the food and pharmaceutical industries and the need for nutritional assessments necessitate the development of a selective, simple and accurate method to determine AsA.

Catalytic procedures are appreciated by analytical chemists for their sensitivity and simplicity in realization. Catalytic indicator reactions can be applied to the determination of a large number of compounds including the catalyst, inhibitors, activators, and compounds, which convert the catalyst into an active state (oxidizer, ligands), and catalytically inactive metal ions through the use of the competitive complexation principle. Due to its selectivity and sensitivity, an electrochemical method to determine AsA has been of considerable interest. A variety of examples of the electrochemical determination of AsA have been proposed. These include the glassy carbon electrode (GCE) and carbon paste electrode with complexes and organic compounds such as 1,5,8,12,Tetraaza-2,4,9,11-tetramethylcyclotetradecinatonickel(II)[1,2], cobalt hexacyanoferrate[3], *meso*-tetrakis(*o*-nitrophenyl)tetrabenzoporphyrin with Fe(III), Ni(II), Mn(III) and

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Co(II)[4], ferricyanide-doped Tosflex [5], ruthenium(III) diphenyldithiocarbamate[6], ferrocene[7], ferrocene with β-cyclodextrin[8], ferrocenecarboxylic acid, ferroceneacetic acid, ferrocenemetanol[9,10], ferrocene in lipid film[11], pentachloroiridite[12], benzoquinone[13], norepinephrine[14], pyrocatechol sulfonephthalein[15], poly(glutamic acid)[16], cellulose acetate film bearing 2,6-dichlorophenolindophenol[17] and aniline[18]. In addition, some chemically modified electrodes with various active mediators immobilized at the metal electrode surface, such as an aluminum electrode with pentacyanonitrosylferrate films[19], a gold electrode with electrodeposition of platinum[20], 3,4-dihydroxybenzoic acid and aniline[21], have been used for the mediated oxidation of AsA.

Nickel is frequently used in catalytic processes and occurs in industrial effluents. The electrochemical behaviors of a broad family of macrocyclic complexes of nickel have been studied by Busch and et al.[22]. Electrochemical studies have been carried out on an extensive series of macrocyclic complexes of nickel(II), which vary in the nature and degree of ligand unsaturation, charge type, and ring size[22]. The oxidation of complexes containing neutral and dianion ligand systems produces stable 6-coordinate and square planar nickel(III) species, respectively. The 1-electron reduction products of the parent nickel(II) macro-cycles exist as either d^9 nickel(I) complexes or as metal stabilized anion radicals, depending upon the nature of the ligand unsaturation. The overall redox behavior of the family of macrocycles is discussed in terms of their chemical reactivity patterns, stereochemistry, and charge type[22].

In this study, we prepared a symmetric 6,8,15,17-tetramethyl-5,9,13,14-(dibenzo)-tetraazacyclotetradecinatonickel(II) complex, and applied it for the modification of glassy carbon in the determination of ascorbic acid.

Experimental

Reagents and materials

6,8,15,17-tetramethyl-5,9,13,14-(dibenzo)-tetraazacyclotetradecinatonickel(II) (Figure 1a) was prepared as described by Jäger[23]. The solvents used for the electrochemical studies were acetonitrile (Merck, HPLC grade) and twice distilled water. Tetrabutylammonium perchlorate (TBAP) and lithium perchlorate (LP) from Fluka were used as the supporting electrolyte in nonaqueous and aqueous solutions. The ascorbic acid and tetrabutylammonium chloride (TBAC) were also from Fluka and were used as received. Buffer solutions were prepared from orthophosphoric acid and its salts in the pH range 3–9. All other reagents were of analytical grade. High purity (99.999%) nitrogen was used for deaerating the solution.

Instrumentation

The electrochemical experiments were carried out with a Metrohm Multipurpose instrument model 693VA processor, equipped with a 694-VA stand and a thermal printer. A Metrohm drive shaft for a rotating disk electrode was used. A single compartment cell with a 3 electrode configuration was used. The working electrodes were Pt and glassy carbon (GC) disk (2.00 mm diameter). A platinum wire was used as the counter electrode. All potentials are quoted vs. Ag/AgCl (sat'd), 0.1 KCl reference electrode in aqueous solutions and vs. Ag/AgCl (sat'd), 0.1 TBAC as a reference electrode in nonaqueous solutions.

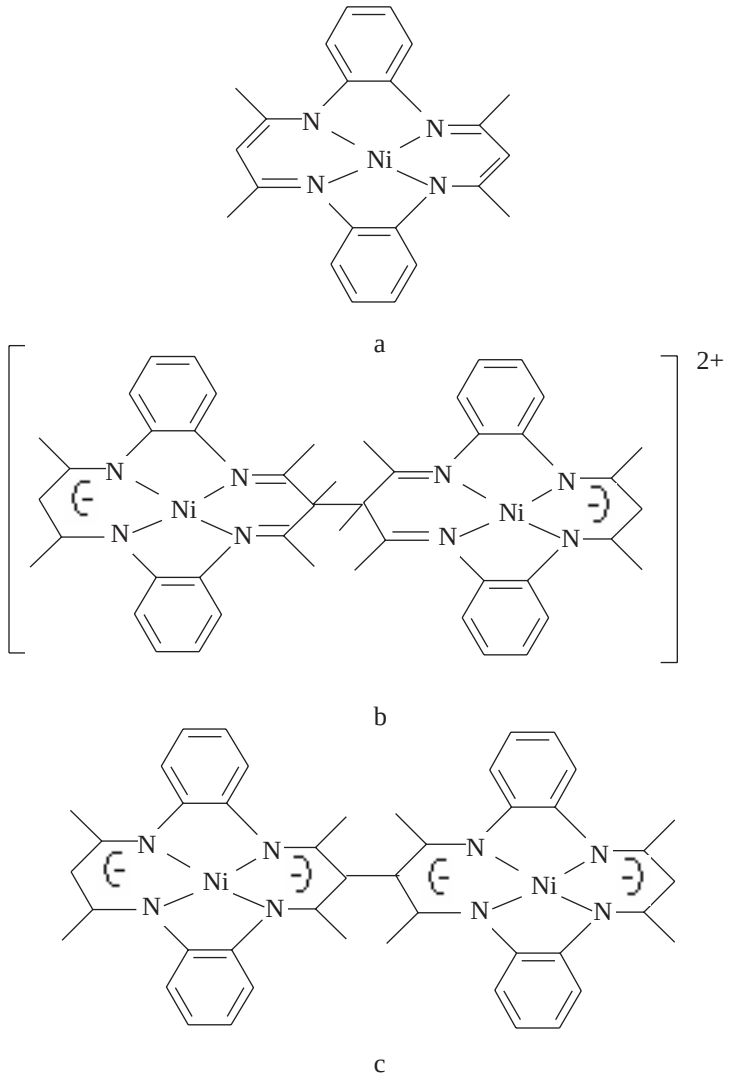

Figure 1. The structure of the a) symmetric Ni(II) macrocyclic complex, b) dimeric Ni(II) macrocyclic complex c) hindered biphenyl Ni(II) macrocyclic complex dimer.

Electrode modification

The GC electrode pretreatment and modification were as follows. Prior to use, the working electrode was polished mechanically with 0.05 μm alumina powder to obtain a mirror like surface and then washed with distilled water and dried. Electropolymerization of Ni(II)-macrocyclic complex was carried out by potential cycling of the clean GCE between -2.0 and +1.0 V at 0.1 V s^{-1} in freshly prepared acetonitrile solutions containing 5.0×10^{-4} M Ni(II)-macrocyclic complex and 1.0×10^{-3} M TBAP under a nitrogen atmosphere. After 10 potential cycles, the electrode was removed from the solution, rinsed with water and dried in air. A green polymer film was then visible on the electrode surface.

Procedure

Standard ascorbic acid or sample solution (5 mL) was pipetted into 25 mL balloons, and 5 mL of buffer solution of pH 7 was added, followed by dilution with re-distilled water to the mark.

Vitamin C tablets

Ten tablets of vitamin C drug were accurately weighed, ground, powdered and dissolved in doubly distilled water. The content of the flask was shaken for 5 min and then it was filtered. Titration with 2,6-dichlorophenolindophenol (DCPIP) was employed to validate the response of the method in the materials[24]. The samples were diluted to within the working range of the method and assayed.

Results and Discussion

Electrochemistry of nickel(II)-macrocyclic complex in acetonitrile solution

The oxidation cyclic voltammogram of Ni(II)-macrocyclic complex in acetonitrile solution on the surface of a Pt disk electrode is shown in Figure 2a. This complex exhibits 2 well-defined reversible voltammetric responses corresponding to the $Ni(L)^0/Ni(L)^+$ and $Ni(L)^+/Ni(L)^{2+}$ couples, as was reported earlier for some dianionic tetraazaannulene complexes[22].

McElroy[25] has shown with a number of physical techniques that the first oxidation of Ni(L) (16π) process yields the π cation radical complex $Ni(L^{\cdot})^+(15\pi)$. This complex actually exists in a dimer-monomer equilibrium containing a Ni-Ni bond. The compound also exhibits a second oxidation, which presumably leads to the formation of the aromatic structure $Ni(L)^{2+}$ (14π). Electrochemical oxidation of Ni(L) results in the formation of a dimeric compound of 2 macrocyclic units joined via a carbon-carbon single bond bridge (Figure 1b). The dimer is sensitive to bases and can be readily deprotonated to give a hindered biphenyl type macrocyclic dimer (Figure 1c)[25].

In Figure 2b, the cyclic voltammograms of Ni(II)-macrocyclic complex in selected ranges at various scan rates are shown. The plots of peak currents versus $(\text{scan rate})^{1/2}$ for both anodic and cathodic peaks (Figure 2c) are linear for sweep rates of 25-1800 mV s^{-1}(not shown). For both couples, the ratios of anodic and cathodic peak currents are unity and the separation between the cathodic and anodic peak potentials for the first and second couples are about 66 and 59 mV at a low scan rate (25 mV s^{-1}), as is expected for reversible diffusion controlled processes. The values of the cathodic and anodic peak potential shift slightly toward the negative and positive directions, respectively, with increasing scan rates. These results indicate that the electron transfer rate is not fast and the electrode process is quasi-reversible at high scan rates.

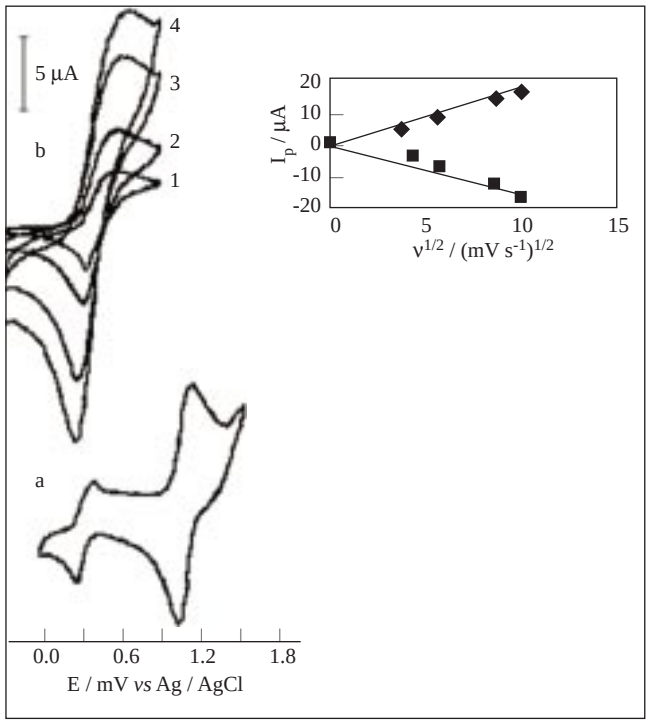

Figure 2. a) Cyclic voltammogram for 1 mM Ni(II) macrocyclic complex on Pt disk electrode (3 mm diameter) in an acetonitrile solution containing 0.1 M TBAP at scan rate 50 mV s^{-1}, b) Cyclic voltammograms for 1 mM Ni(II) macrocyclic complex in first wave potential range in an acetonitrile solution containing 0.1 M TBAP at scan rates 1) 25, 2) 40, 3) 80 and 4) 100 mV s^{-1}. c) The plots of the cathodic and anodic peak currents versus scan rate.

Electrocatalytic effect on oxidation of L-ascorbic acid

The electrocatalysis of ascorbic acid at a Ni(II) macrocyclic complex modified electrode and bare electrode was observed in buffer solution with pH 7.0 as shown in Figure 3. The cyclic voltammogram of the oxidation peak potential of L-ascorbic acid at the modified GCE shifted 250 mV in the negative direction compared with the bare GCE, and the peak current at the modified GCE also increased. The results indicate that the electrocatalytic activity of the modified electrode can be applied to the determination of L-ascorbic acid.

Optimization of the solution pH

The electrochemical behavior of ascorbic acid is dependent on the pH value of the aqueous solution. Therefore we studied the electrochemical behavior of ascorbic acid in buffered solutions with different pH values from 3 to 10.5 at the surface of macrocyclic Ni(II) by cyclic voltammetry. Cyclic voltammograms obtained with the macrocyclic Ni(II) for solutions containing ascorbic acid in strongly acidic media (e.g., pH 2) showed that ascorbic acid did not couple catalytically with the macrocyclic Ni(II). Therefore, optimization of the solution pH was necessary in order to obtain the catalytic couple. Variation in the electrolyte pH will result in variations in the formal potential of ascorbic acid. Therefore, the thermodynamic driving force for the catalysis will vary with pH, making the peak currents and the shapes of the cyclic voltammograms at different pH values. The anodic peak currents increased with an increase in pH up to 7.0, and then gradually decreased up to pH 10.5. Owing to its efficiency of oxidation, pH 7.0 was chosen as optimal.

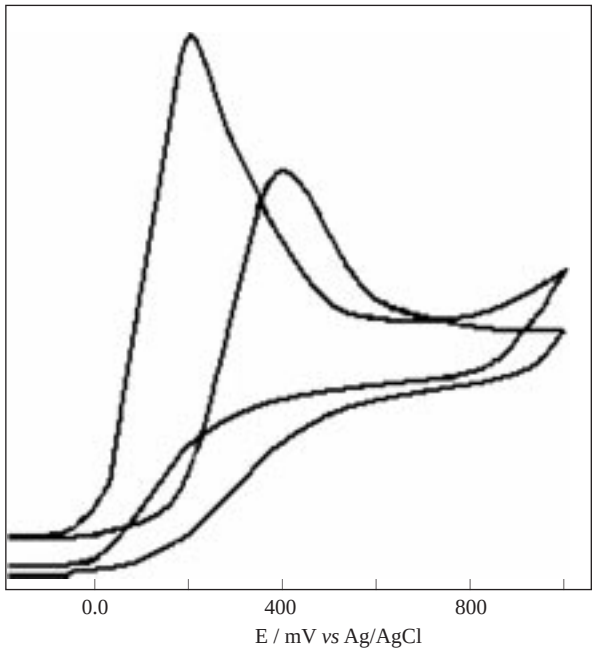

Figure 3. Cyclic voltammograms of 3 mM ascorbic acid at a bare glassy carbon electrode (a) and a modified glassy carbon electrode (b) in pH 7.0, scan rate 100 mV s^1.

Effect of the thickness of the modified electrode

The effect of polymer thickness on peak current was investigated by recording cyclic voltammograms of 2.0 mM L-ascorbic acid while increasing the number of scan cycles (Figure 5). Upon increasing the number of scan cycles, the peak potential rapidly shifted to a lower potential up to about 8 cycles, and then remained constant. The maximum peak current was obtained when the number of cycles was 8. The results indicate that the thickness and morphology of the polymer films formed on GCEs are essential for sensitivity in the determination of L-ascorbic acid using polymer-modified electrodes.

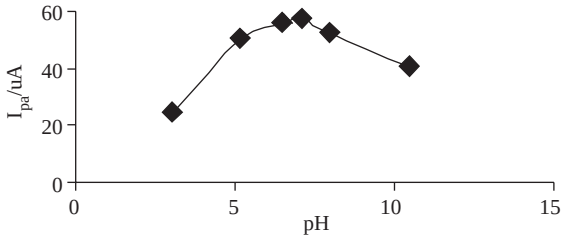

Figure 4. Influence of pH on the anodic current of cyclic voltammograms for 2 mM L-ascorbic acid.

Electrocatalytic determination of ascorbic acid

The electrocatalytic peak current of ascorbic acid at the surface of macrocyclic Ni(II) was linearly dependent on the ascorbic acid concentration and the range of this linearity depends on the amount of mediator in the electrode. The mediated oxidation peak current of L-ascorbic acid at the surface modified GCE is linear up to 5 mM and is described by the equation $I_{(\mu A)} = 8.89 + 24.1C_{AsA}$, r = 0.9986, n = 10, where $I_{(\mu A)}$is

the oxidation peak current, C_{AsA} is the analyte concentration (mM), r is the correlation coefficient and n represents the number of determinations. The detection limit (3σ) was 2.5×10^{-4} mM (Figure 6).

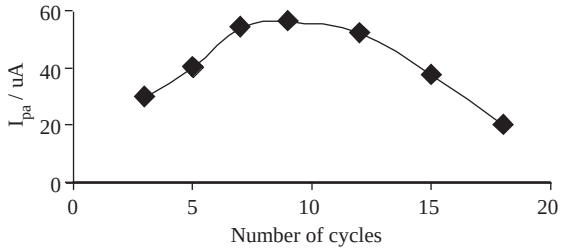

Figure 5. Dependence of the thickness of Ni(II)-macrocyclic complex polymer on the current response of oxidation of 2 mM L-ascorbic acid.

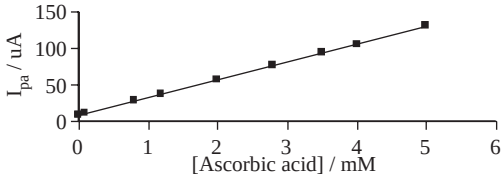

Figure 6. Plot of electrocatalytic peak currents from cyclic voltammograms vs. the ascorbic acid concentration: 1) 0.0009, 2) 0.009, 3) 0.1, 4) 0.8, 5) 1.2, 6) 2, 7) 2.8, 8) 3.5, 9) 4, 10) 5 mM.

This value is comparable with the values obtained by other research groups (Tzouwara-Karayanni et al.[26] (0.01 mM), Raoof et al.[10], 1.08×10^{-2} mM and Bae et al. (8.8×10^{-4}mM and 4.7×10^{-4} mM)[1,2]). Thus the catalytic oxidation of ascorbic acid can readily be applied for the determination of ascorbic acid.

Recovery tests

Recovery tests using the proposed method were performed using 3 different samples, and the test for each sample was carried out in triplicate. As shown in Table 1, the recoveries of ascorbic acid added to tomato juice, orange juice and grapefruit juice were all close to 100%. The results of the recovery tests are very good.

Table 1. Results of recovery test.

Sample	[AsA] added*	[AsA] found*	Recovery
Tomato juice	0.0	14.9 ± 1.02	——
	20.0	34.8 ± 2.1	99.5
Lime	0.0	0.0	——
	20.0	20.1 ± 2.9	100.5
Orange juice	0.0	310.1 ± 2.1	——
	20.0	329.9 ± 1.8	99.0
Grapefruit juice	0.0	12.2 ± 0.4	——
	20.0	31.9 ± 1.2	98.5

*mg/100 g

Interference study

A study of interference for AsA determination was performed with samples containing 0.5 mM ascorbic acid. When the permitted relative deviation from ΔI pa is less than ± 5%, no interference is observed from organic compounds such as citric acid, malic acid, lactic acid, tartaric acid, fumaric acid, sorbic acid, glucose, fructose and saccharose (Table 2).

Table 2. Tolerance towards foreign compounds.

Additive type	Tolerance[a]
Glucose, Sucrose, Fructose, Lactose, Mannitol, Saccharose, Malic acid, Sorbic acid, Tartaric acid, Fumaric acid, Calcium chloride, Sodium chloride, Citric acid	250[b]
Maleic acid, Benzoic acid, Salicylic acid, Salicylicamide, Lactic acid	120[b]

[a]Maximum weight ratio of foreign compound to L-ascorbic acid 0.5 mM giving an error of $< 5\%$.
[b]Maximum amount tested.

Application to real samples

The proposed method was applied to the determination of AsA in vitamin C tablets, vitamin C injections, cordials and fresh fruit juices from different locations in Iran. Table 3 lists the results obtained on application of the proposed method. These results are compared with those obtained with 2,6-dichorophenolindophenol, and indicate that the proposed method could be readily implemented on a very good and stable system.

Table 3. Determination of ascorbic acid in vitamin C tablets, vitamin C injection and Fresh fruit juice.

Sample	Proposed method	Standard method (DCPIP)
Vitamin C tablet (500 mg)	495.0 ± 4.8[a]	498.1 ± 4.7[a]
Vitamin C injection (192 mg/mL)	191.1 ± 3.2[b]	191.5 ± 1.5[b]
Orange cordial	74.3 ± 4.7[c]	74 ± 3.5
	64.5 ± 5.1[d]	65.4 ± 2.5
Grapefruit cordial	52.2 ± 4.3[c]	53.1 ± 3.6
	47.0 ± 3.7[d]	46.7 ± 4.0
Lemon cordial	45.5 ± 3.2[c]	46.7 ± 3.1
	54.7 ± 2.6[d]	55.1 ± 2.7
Fresh orange juices	553.1 ± 3.2[c]	554.1 ± 2.4
	490.3 ± 3.3[d]	491.7 ± 3.1
Fresh grapefruit juices	323.1 ± 2.2[c]	322.3 ±3.6
	292.5 ± 3.0[d]	294.2 ± 4.1
Fresh tomato juices	76.9 ±4.3[c]	78.0 ± 3.4
	59. ± 3.7[d]	58.1 ± 2.7

[a]mg/tablet

[b]mg/mL

[c]From Tonekabon city in Mazaderan province in Iran

[d]From Iranshahr city in Sistan and Baluchestan province in Iran

Conclusions

From the results mentioned above, we can conclude that as a new mediator the 6,8,15,17-tetramethyl-5,9,13,14-(dibenzo)-tetraazacyclotetradecinatonickel(II) polymer modified glassy carbon electrode can effectively catalyze the oxidation of L-ascorbic acid because in the reduced anodic overpotential of about 250 mV and the distinct increase in anodic peak current. It can also be concluded that this system may be used to develop a biosensor for the determination of L-ascorbic acid. Thus, it is concluded that this sensor is more applicable for the analysis of L-ascorbic acid in commercial pharmaceutical tablets, injections and foods.

Acknowledgments

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