Available online at www.sciencedirect.com
SCIENCE DIRECT®
Talanta 67 (2005) 579–584
Talanta
www.elsevier.com/locate/talanta

Electrocatalytic activity of Ce(III)–EDTA complex toward the oxidation of nitrite ion

Abdolkarim Abbaspour*, Masoud Ayatollahi Mehrgardi

Department of Chemistry, Shiraz University, Shiraz 71454, Iran

Received 21 December 2004; accepted 8 March 2005
Available online 1 August 2005

Abstract

The electrochemical behavior of Ce(III) ion in the presence of EDTA and their application for electrocatalytic oxidation of nitrite ion is described in this manuscript. The electrochemical properties of Ce(III)–EDTA complex as well as the two-electron oxidation of nitrite ion were investigated using cyclic voltammetry and hydrodynamic voltammetry methods. Kinetic parameters such as transfer coefficient, homogeneous rate constant for electrocatalytic oxidation of nitrite ion at the experimental conditions, were obtained. Also the possible mechanism for oxidation of nitrite ion using Ce(III)–EDTA complex is proposed. The detection limit of 4.8×10^{-6} M and dynamic linear range 1.0×10^{-5} to 1.0×10^{-2} M were obtained for determination of nitrite ion using electrocatalytic oxidation of this ion by Ce(III)–EDTA complex.

Keywords: Nitrite ion; Electrocatalytic oxidation; Ce(III)–EDTA complex

---

1. Introduction

Sodium and potassium nitrite find extensive use as preservatives (E249, E250) and in the fixation of color in the food products. The presence of nitrite in most food groups can arise through the bacterial reduction of nitrate-based fertilizer residues [1–4]. Also nitrite is an important source of nitrogen in green plants and its complete reduction is achieved in nature by nitrite reductase enzymes, which contain complex proteins having an iron–sulfur unit and an iron isobacteriochlorin [5]. Industrially, it is used to inhibit corrosion in industrial water. The effects of nitrite can occur by several mechanisms. It combined with blood pigments to produce metha-hemoglobin in which oxygen is no longer available to the tissues. Also it may combine in the stomach with amines and amides to produce highly carcinogenic *N*-nitrosamine compounds [6–8]. There has been considerable research into nitrite detection in a range of matrices with a significant variety of strategies available covering spectroscopic [9–13], chromatographic [8,14–18] and electrochemical techniques [19–23], especially electrocatalytic determination [24–30].

Ce(IV) had been found to be very effective in oxidizing coal slurries [31,32] and organic alcohols [33] and also for electrocatalytic oxidation of aniline as major pollutant in wastewater from dye industries [34].

In this report, the electrocatalytic activity of Ce(III)–EDTA complex toward the oxidation of nitrite ion was demonstrated. The kinetic parameters such as transfer coefficient and homogeneous rate constant for this system were obtained.

2. Experimental

Voltammetric experiments were performed using a Metrohm electroanalyzer (model 757 VA Computrace) connected to a 633 MHz Pentium II computer. The system was operated and measurements recorded using VA Computrace version 2 (Metrohm) that run under Windows XP. The three electrodes system consists of a platinum disk electrode as working electrode, Ag|AgClI3 M KCl as a reference

---

[*] Corresponding author. Tel.: +98 9117184524; fax: +98 7112280926.

0039-9140/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2005.03.036

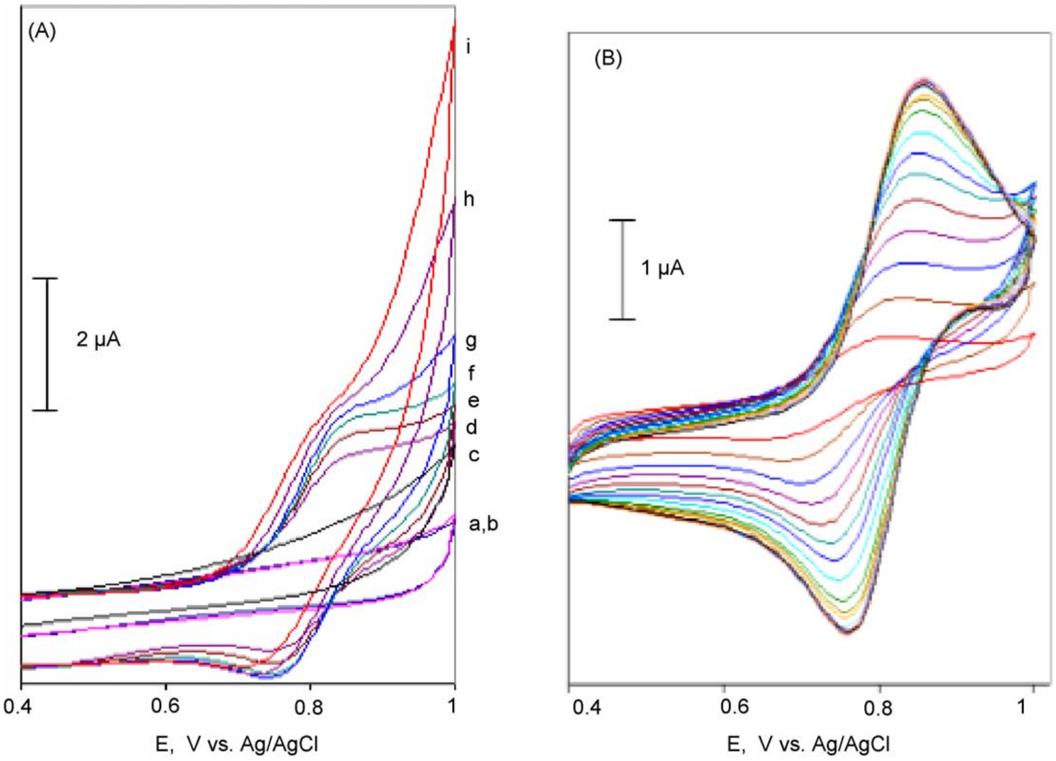

Fig. 1. (A) Cyclic voltammograms of 1 mM Ce(III) nitrate at different concentrations of EDTA: (a) blank; (b) 0.0 mM EDTA; (c) 1 mM EDTA in the absence of cerium; (d) 0.4 mM EDTA; (e) 0.6 mM EDTA; (f) 0.8 mM EDTA; (g) 1.0 mM EDTA; (h) 1.2 mM EDTA; (i) 2.0 mM EDTA (from the bottom to the top). (B) Cyclic voltammograms of 1 mM EDTA at different concentrations of Ce(III) nitrate ions: 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.4, 1.6, 1.8, 2, 3, and 4 mM Ce(III) ions (from the bottom to the top), supporting electrolyte of all experiments was 0.2 M KCl; scan rate: 50 mV s^{-1}.

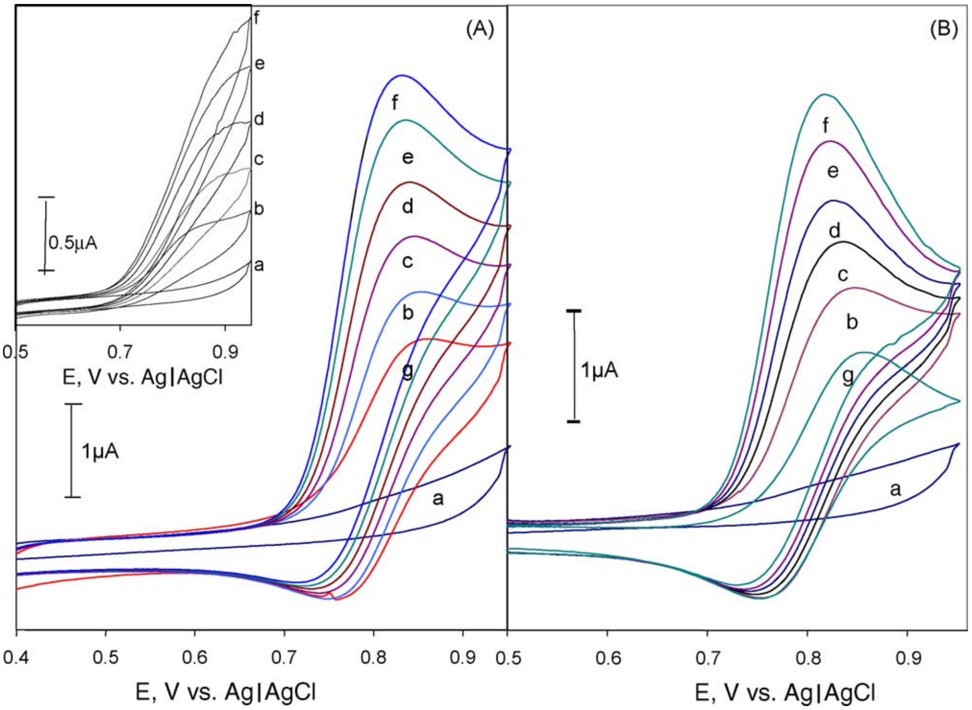

Fig. 2. (A) The electrocatalytic oxidation: (a) blank; (b) 0.1 mM; (c) 0.2 mM; (d) 0.3 mM; (e) 0.4 mM; (f) 0.5 mM; and (g) 0.0 mM of nitrite ion in the presence of 1 mM of Ce^{3+} and EDTA and also in the absent of the complex (inset) (B) As (A) except that the inset voltammograms are subtracted (supporting electrolyte of all experiments was 0.2 M KCl; scan rate: 50 mV s^{-1}).

electrode and a platinum wire as an auxiliary electrode. The working, auxiliary and reference electrodes used were all from Metrohm. Prior each experiment, the working electrode was first polished with alumina slurry using a polishing cloth and then rinsed with distilled water. The area of this electrode was $0.046 \pm 0.004\,\mathrm{cm}^2$ which calculated from chronocoulometric experiments.

Sodium nitrite, cerium(III) nitrate, dipotassium salt of ethylene diamine tetraacetic acid and potassium chloride were obtained from Merck or Fluka and selected AR grade or better and were used without further purifications. Doubly distilled deionized water was used throughout the work. The supporting electrolyte of all experiments was 0.2 M KCl.

3. Results and discussion

3.1. Electrochemical properties of cerium-EDTA complex

Cerium and EDTA gave no oxidation peak over potential range of 0–1 V versus Ag|AgCl. By addition of a complexing agent such as EDTA to 1 mM cerium(III) nitrate solution, reversible redox peaks appear around 0.85 V versus Ag|AgCl as shown in Fig. 1A. The peak currents enhance by increasing the concentration of EDTA, but as illustrate in Fig. 1A, at concentrations higher than equimolar (1 mM), the reversibility of redox peak is decreased and hence the equimolar concentration was selected as optimized concentration for further studies. Also in independent series of experiments, the concentration of EDTA solution was held constant at 1 mM level but the concentration of solution with respect to cerium(III) ion was increased at each experiment. As shown in Fig. 1B, the peak currents enhance by increasing the concentration of cerium(III) ions but reach to approximately constant values at equimolar level concentration of cerium(III) ions with EDTA. The latter demonstrates that the complex formation between cerium and EDTA occur at mole ratio 1:1.

3.2. Electrocatalytic oxidation of nitrite in the presence of Ce–EDTA complex

The electrocatalytic oxidation of nitrite in the presence of cerium–EDTA complex is shown in Fig. 2. Fig. 2A shows the cyclic voltammograms of 0.1–0.5 mM of nitrite ion in the presence of 1mM cerium(III) ion and 1 mM EDTA, whereas the insert in Fig. 2A shows the cyclic voltammograms of nitrite at the same concentrations of Fig. 2A but in the absence of Ce–EDTA complex. The anodic peak current of Ce–EDTA complex increased due to the presence of nitrite ion, whereas cathodic peak current of this complex decreased accordingly. It should be mentioned that the peak potential is not affected considerably in the presence of Ce–EDTA complex. Therefore, an enhancement of peak current is achieved in this system, which clearly demonstrates the occurrence of an electrocatalytic process. Since the current measurement with Ce–EDTA complex may be perturbated by the current from the possible direct oxidation of nitrite, in Fig. 2B we subtract the currents of the oxidation of nitrite in the absence of Ce–EDTA complex (insert voltammograms) from the currents in the presence of the Ce–EDTA complex. As shown in Fig. 2B, the current related to direct oxidation of nitrite is not significant within the potential of the electrocatalytic oxidation. The electrocatalytically effect can be shown more distinctly at higher concentrations of nitrite ion (1–3 mM) in the presence of 1 mM Ce(III)–EDTA complex as illustrated in Fig. 3. As seen, there is an increase in anodic peak current with the increasing of nitrite concentration.

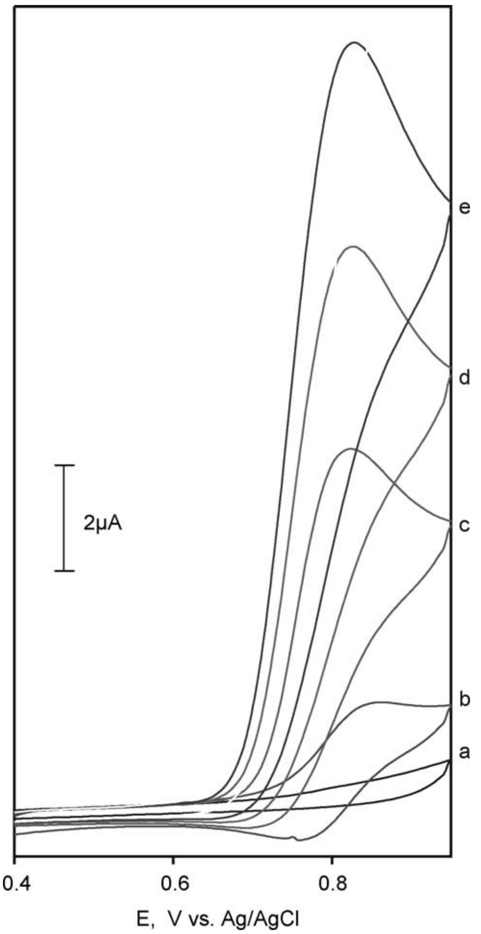

Fig. 3. Electrocatalytic oxidation of: (a) blank (in the absence of Ce–EDTA complex); (b) 0 mM; (c) 1 mM; (d) 2 mM and; (e) 3 mM of nitrite ion in the presence of 1 mM of Ce^{3+} and EDTA (supporting electrolyte of all experiments was 0.2 M KCl; scan rate: $50\,\mathrm{mV\,s}^{-1}$).

The pH effect studies show that the peak current of the system is pH independent over the range of 3.00–11.00 (results not shown). This independency demonstrates that nitrite ions are not oxidized directly on the surface of electrode and increase of peak current of the system in the presence of nitrite ions is only due to chemical oxidation of nitrite ions by electrogenerated Ce(IV) ions that serves regeneration of

Ce(III) ions at the surface of electrode. This is another evidence for the electrocatalytic mechanism.

The cyclic voltammograms of 1 mM nitrite ion in the presence of 1 mM Ce(III) and 1 mM EDTA at various scan rates (not shown) gives a linear correlation between anodic peak current and square root of scan rate, suggesting that kinetics of the overall process are controlled by mass transport of nitrite ion from the bulk solution to the electrode surface. It must be mentioned that the catalytic oxidation peak potential (E_p) shifts slightly to more positive potentials with increasing the scan rates. From the slope of the linear plot of E_p versus $\log(I_p)$, a Tafel plot slope of 50.38 mV decade^{-1} were obtained that demonstrate the possibility of a two-electron mechanisms with transfer coefficient, α, equal to 0.59. Also the Tafel slope b can be obtained from the linear relationship between E_p versus $\log(\nu)$ by using the following equation [35]:

$$E_p = \frac{b}{2}\log(\nu) + \text{constant}$$

The slope of this plot is equal to 24.50 mV decade^{-1} and therefore b value is 49.0 (mV decade^{-1}). By using this value, α can be calculated as 0.60 that is the same value (0.59) obtained from the linear plot of E_p versus $\log(I_p)$.

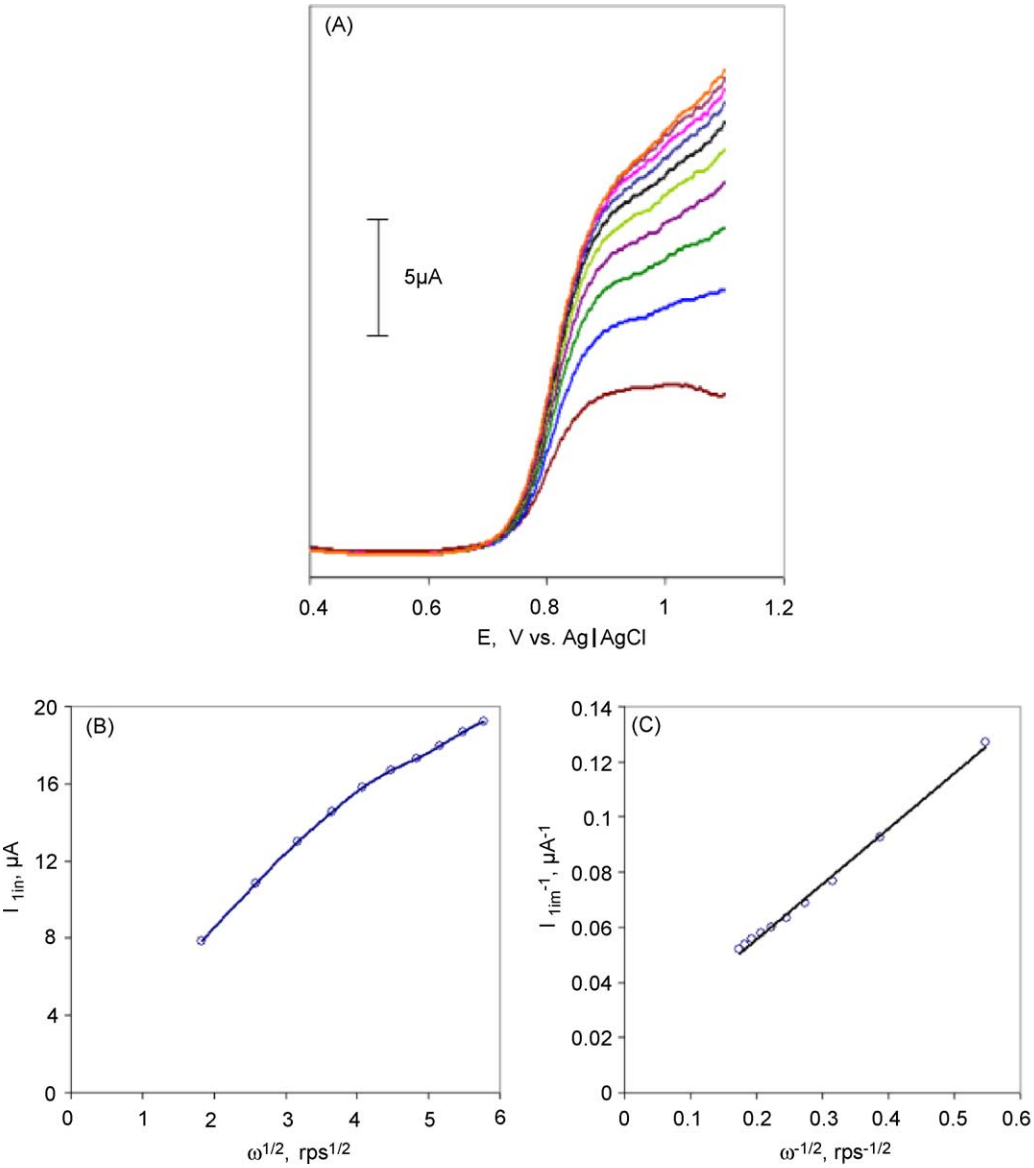

Fig. 4. (A) hydrodynamic voltammograms of 1 mM Ce–EDTA complex at the presence of 0.1 mM nitrite ion at various rotation speeds (from the bottom to the top): 200, 400, 600, 800, 1000, 1200, 1400, 1600, 1800, and 2000 rpm. For each voltammogram, the potential scan rate was 20 mV s^{-1}; (B) Levich plot and (C) Koutecky–Levich plot (1/limiting current (μA^{-1}) = 0.20 $\omega^{-1/2}$ + 0.016) of the hydrodynamic voltammograms (supporting electrolyte of all experiments was 0.2 M KCl).

3.3. Hydrodynamic voltammetric studies at rotating disk electrode

For evaluating the rate constant (k) of the catalytic reaction between nitrite ion and Ce(IV), the RDE voltammetric studies were performed. The hydrodynamic voltammograms of 0.1 mM nitrite in the presence of 1 mM Ce(III) and 1mM EDTA were recorded at different rotation rates over range of 200–2000 rpm (Fig. 4A).

Using these voltammograms, the limiting currents at different rotating rates versus square root of rotating rate were plotted as shown in Fig. 4B (Levich plot). It could be expected from Levich equation that this plot should be linear, but as can be seen from Fig. 4B, linearity is not observed and limiting current also tends to level off at higher rotation rates. This non-linearity suggests a kinetic limitation in the coupled chemical reaction. Because the electron transfer between Ce–EDTA complex is very fast (reversible voltammograms as shown in Fig. 1 demonstrate this point) hence, the rate-determining step is chemical oxidation of nitrite ion. So, the following mechanism could be expected for the system:

$$2\mathrm{Ce}^{3+}_{\mathrm{complex}} \rightleftarrows 2\mathrm{Ce}^{4+}_{\mathrm{complex}} + 2\mathrm{e}$$

$$2\mathrm{Ce}^{4+}_{\mathrm{complex}} + \mathrm{NO_2}^{-} + 2\mathrm{H_2O} \rightarrow 2\mathrm{Ce}^{3+}_{\mathrm{complex}} + \mathrm{NO_3}^{-} + 2\mathrm{H}^{+}$$

Under the conditions that the Ce–EDTA complex is present in large excess, i.e. its concentration is essentially unchanged during the voltammetric experiments, therefore the couple chemical reaction can be considered as pseudo first-order reaction.

There is a linear correlation between inverse of limiting current and inverse of square root of rotating speed (Koutecky–Levich equation) that illustrated in Fig. 4C. Its equation can be formulated as follows:

$$\frac{1}{I_{\mathrm{lim}}} = \frac{1}{I_{\mathrm{k}}} + \frac{1}{I_{\mathrm{Levich}}}$$

where I_{lim} is the limiting current and I_{k} represent the plateau current limited by the kinetic step and I_{Levich} is limiting current that is expected from Levich equation.

The reaction thickness layer ($\delta_{\mathrm{reaction}}$) for EC′ process with a pseudo first-order couple chemical reaction is given by:

$$\delta_{\mathrm{reaction}} = \frac{D}{k}$$

where k is a pseudo-first order rate constant of homogeneous catalytic reaction. In the couple chemical reaction:

$$\text{rate of couple chemical reaction} = k[\mathrm{NO_2}^{-}]$$

The rate of couple chemical reaction determines the kinetically limited current by the following equation:

$$k[\mathrm{NO_2}^{-}] = \frac{I_{\mathrm{k}}}{nFA\delta_{\mathrm{reaction}}}$$

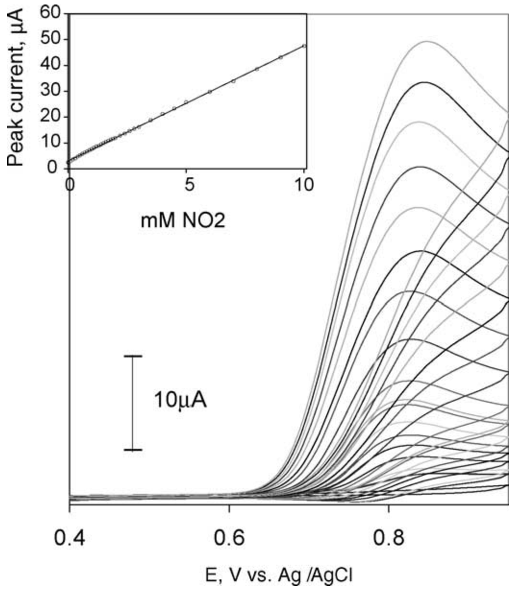

Fig. 5. Cyclic voltammograms of various concentrations of nitrite ion in the presence of 1 mM Ce^{3+} and 1 mM EDTA. The calibration curve that was obtained from these voltammograms is shown in inset (peak current (μA) = 4.47× mM of nitrite ion + 3.00). Supporting electrolyte of all experiments was 0.2 M KCl; scan rate: 50 mV s^{-1}.

Therefore,

$$I_{\mathrm{k}} = nFAD^{1/2}k^{1/2}[\mathrm{NO_2}^{-}]$$

The rate constant, k, calculated from the intercept of Koutecky–Levich plot is equal 1.86 s^{-1}.

Fig. 5 displays the cyclic voltammograms of various concentrations of nitrite ion ranging from 1.0×10^{-5} to 1.0×10^{-2} M in the presence of 1 mM Ce^{3+} and 1 mM EDTA. The calibration curve that was obtained from these voltammograms is shown in the inset of this figure. The detection limit of 4.8×10^{-6} M for nitrite ion was estimated at these conditions based on $3s_{\mathrm{b}}$ ($n = 12$).

Acknowledgement

We gratefully acknowledge the support of this work by the Shiraz University Research Council.

References

[1] J. Davis, R.G. Compton, Anal. Chim. Acta 404 (2000) 241.
[2] J.B. Fox, CRC Crit. Rev. Anal. Chem. 15 (1985) 283.
[3] C.D. Usher, G.M. Telling, J. Sci. Food Agric. 26 (1975) 1793.
[4] J.K. Foreman, K.J. Goodhead, J. Sci. Food Agric. 26 (1975) 1771.
[5] T. Brittain, R. Blackmore, C. Greenwood, A.J. Thomson, Eur. J. Biochem. 209 (1992) 793.
[6] S.S. Mirvish, Cancer Lett. 93 (1995) 17.
[7] S.D. Gangoli, P.A. van den Brandt, V.J. Feron, C. Jonzowski, J.H. Koeman, G.J.A. Peijers, B. Spiegelhalder, B. Walker, J.S. Wishnok, Eur. J. Pharm., Environ. Toxicol. Pharmacol. 292 (1994) 1.
[8] I.A. Wolf, A.E. Wasserman, Science 177 (1972) 15.

[9] G.M. Greenway, S.J. Haswell, P.H. Petsul, Anal. Chim. Acta 387 (1999) 1.
[10] A.A. Ensafi, A. Kazemzadeh, Anal. Chim. Acta 382 (1999) 15.
[11] R. Kadowaki, S. Nakano, T. Kawashima, Talanta 48 (1999) 103.
[12] Z. ZhiQi, G. LouJun, Z. HanYing, L. QianGuang, Anal. Chim. Acta 370 (1998) 59.
[13] T. Hamano, Y. Mitsuhashi, N. Aoki, M. Semma, Y. Ito, Y. Oji, Analyst 123 (1998) 1127.
[14] I. ElMenyawi, S. Looareesuwan, S. Knapp, F. Thalhammer, B. Stoiser, H. Burgmann, J. Chromatogr. B 706 (1998) 347.
[15] D.C. Siu, A. Henshall, J. Chromatogr. A 804 (1998) 157.
[16] V. DiMatteo, E. Esposito, J. Chromatogr. A 789 (1997) 213.
[17] K. Kohler, M. Nowak, A. Seubert, Fresenius J. Anal. Chem. 358 (1997) 551.
[18] Z.M. Liu, W.D. Xi, S.J. Dong, E.K. Wang, Anal. Chim. Acta 345 (1997) 147.
[19] X.H. Chen, C.M. Ruan, J.L. Kong, J.Q. Deng, Anal. Chim. Acta 382 (1999) 189.
[20] S.M. DaSilva, L.H. Mazo, Electroanalysis 10 (1998) 1200.
[21] I.G. Torro, J.V.G. Mateo, J.M. Calatayud, Anal. Chim. Acta 366 (1998) 241.
[22] V. Mori, M. Bertotti, Talanta 47 (1998) 651.
[23] P. Liu, J. Lu, J. Yan, J. Electroanal. Chem. 469 (1999) 96.
[24] A.C. Caro, F. Bedioui, J.H. Zagal, Electrochim. Acta 47 (2002) 1489.
[25] H. Winnischofer, S.S. Lima, K. Araki, H.E. Toma, Anal. Chim. Acta 480 (2003) 97.
[26] B. Keita, F. Girard, L. Nadjo, R. Contant, R. Belghiche, M. Abbessi, J. Electroanal. Chem. 508 (2001) 70.
[27] A.P. Doherty, M.A. Stanley, D. Leech, J.G. Vos, Anal. Chim. Acta 319 (1996) 111.
[28] J.E. Toth, F.C. Anson, J. Am. Chem. Soc. 111 (1989) 2444.
[29] S.M. Chen, J. Electroanal. Chem. 457 (1998) 23.
[30] D. Mimica, J.H. Zagal, F. Bedioui, J. Electroanal. Chem. 497 (2001) 106.
[31] P.M. Hooge, D.E. Stilwell, S.-M. Park, J. Electrochem. Soc. 129 (1982) 1719.
[32] P.M. Hooge, S.-M. Park, J. Electrochem. Soc. 130 (1983) 1029.
[33] J.C. Farmer, F.T. Wang, P.R. Lewis, L.J. Summer, J. Electrochem. Soc. 139 (1992) 3025.
[34] Y.H. Chung, S.M. Park, J. Appl. Electrochem. 30 (2000) 685.
[35] J.A. Harrison, Z.A. Khan, J. Electroanal. Chem. 28 (1970) 153.