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Investigation of Electrochemistry Behavior of Hydroxylamine at Glassy Carbon Electrode by Indigocarmine

*Mohammad Mazloum-Ardakani**, *Zahra Taleat*

Department of Chemistry, Faculty of Science, Yazd University, Yazd, 89195-741, Iran
*E-mail: mazloum@yazduni.ac.ir

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The electrocatalytic oxidation of hydroxylamine on glassy carbon electrode (GCE) in neutral media has been characterized using cyclic voltammetry, chronoamperometry and differential pulse voltammetry (DPV). GCE as an electrochemical sensor exhibited strongly catalytic activity toward the oxidation of hydroxylamine in solution of modifier of indigocarmine. The electron transfer coefficient (α) and charge transfer rate constant (k) for the oxidation of hydroxylamine as the kinetic parameters were determined by cyclic voltammetry. The diffusion coefficient of hydroxylamine was estimated by chronoamperometry. Hydroxylamine can be determined in the range of $5.0 \times 10^{-7} - 1.8 \times 10^{-5}$ M with the detection limit of 1.6×10^{-7} M (k=3). The application of the GCE in measurement of hydroxylamine in real sample is considered in this paper.

Keywords: Hydroxylamine, Glassy carbon electrode, Electrocatalysis, Indigocarmine

1. INTRODUCTION

Hydroxylamine reactivity in an electrochemical environmental is important as a kind of reducing agents, which is widely used in industrial synthesis and pharmacy. In industry, hydroxylamine, a key intermediate in ε-caprolactam production and a compound with various applications in technology, is obtained by the liquid-phase catalytic hydrogenation of nitric oxide or nitrate at carbon-supported platinum or palladium catalysis [1]. Hydroxylamine is recognized as a mutagenic substance, moderately toxic and harmful to human, animals and plants [2]. It has also been identified as an intermediate in synthesis of pharmaceutical and drug substances. Therefore quantitative determination of hydroxylamine is very important in biochemistry and industrial processes. Many methods have been developed for the determination of hydroxylamine because of its toxicity, biological function and broad industrial utilization [3-8]. The most of these methods are complicated because they need derivatization or combination with various detection methods. Also, some these methods had high detection limit, thus development of more sensitive method is necessary.

Application of redox species as the electron mediator to modify electrodes is an interesting field in analytical chemistry. One of the most important effects of mediator is lowering the overpotential required for electrochemical reaction and enhancement of sensitivity (current) and selectivity of the method. Homogenous catalysis of electrochemical reductions (or oxidation) involves essentially two types of process. In chemical catalysis the key step is the formation of an adduct between the reduced (or oxidized) form of the catalyst and the substrate. The catalyst is then regenerated either by spontaneous decomposition of the adduct or after a further electron transfer. In redox catalysis the catalyst couple is involved in an outer-sphere electron transfer reaction with the substrate, playing then simply the role of an electron carrier between the electrode and the substrate [9]. In an outer-sphere electrode reaction, the reactant and product do not interact strongly with the electrode surface, and they are generally at a distance of at least a solvent layer from the electrode. Although one of the more complex electrochemical techniques, cyclic voltammetry is very frequently used because it offers a wealth of experimental information and insights into both the kinetic and thermodynamic details of many chemical systems. Because of significant advances in the theoretical understanding of the technique, today, even complex chemical systems such as electrodes modified with film or particulate deposits may be studied quantitatively by cyclic voltammetry. However, it was soon realized that the time dependence of signals can provide useful kinetic data [10].

The IUPAC name of Indigo carmine is 3,3'-dioxo-2,2'-bis-indolyden-5,5'-disulfonic acid disodium salt (IND). The primary use of Indigo carmine is as a pH indicator. It is blue at pH 11.4 and yellow at 13.0. Indigo carmine is also a redox indicator, turning yellow upon reduction. It is also used as a dye in the manufacturing of capsules. Indigo carmine is used as a diagnostic dye. No reports linking its use with congenital defects have been located. Intra-amniotic infection has been conducted without apparent effect on the fetus [11-13]. Because of its known toxicities after IV administration, however, the dye should not be considered totally safe [14].

Previously we reported that alizarine red S and quinizarine as mediators can catalyze oxidation of hydrazine and sulfite, two important in the chemical industry [15, 16]. Present study was designed to investigate the electro-catalytic oxidation of hydroxylamine with indigo carmine as a homogeneous mediator on the glassy carbon electrode and some parameters influencing the performances of this electrode in the determination of hydroxylamine are discussed.

2. EXPERIMENTAL PART

2.1. Chemicals and solutions

Indigo carmine (3,3'-dioxo-2,2'-bis-indolyden-5,5'-disulfonic acid disodium salt, $C_{16}H_8N_2Na_2O_8S_2$) (IND) and hydroxylamine were obtained from Merck and used without further treatment. All the solutions were prepared from the chemicals of analytical grade, by using double distilled water, and used without any further purification. Hydroxylamine and IND solutions were freshly prepared, prior to every experiment and all the experimental procedures were carried out at an ambient temperature. Phosphate buffer (pH 7.0) was used for the optimum measurements. Phosphoric acid and sodium hydroxide were used for decreasing and increasing the pH of the buffer.

2.2. Apparatus

The electrochemical experiments were performed using a µAUTOLAB, potentiostat/galvanostat (Eco Chemie Utrecht, Netherlands) connected to a 125 mL three-electrode cell (incorporated with ACE glass), equipped with GPES 4.9 software. A personal computer for data acquisition and potential control was used for electrochemical measurements.

The cell configuration contained a glassy carbon disk electrode with a diameter of 2.0 mm as a working electrode, a Pt wire (directly immersed in the solution) as an auxiliary electrode and a silver/silver chloride electrode (KCl, Saturated) as the reference electrode. All the potentials were recorded with respect to the reference electrode. A Metrohm 691 pH/ion meter was also used for pH measurements.

2.3. Preparation of the electrode

The glassy carbon electrode surface was polished mechanically with 0.05 µm alumina powders, using a polishing cloth until the electrode surfaces had a mirror-finish and then rinsed thoroughly with double distilled water, successively.

3. RESULTS AND DISCUSSION

This work demonstrates that the IND acts as an intermediate of electron transfer during hydroxylamine oxidation at the surface of glassy carbon electrode.

3.1. Electrochemical properties of indigocarmine at glassy carbon electrode

The indigocarmine is soluble in aqueous media; therefore we used GCE and studied its electrochemical properties in a buffer aqueous solution (pH 7.0) and IND by cyclic voltammetry. Cyclic voltammograms of IND in the buffer solution (pH 7.0) exhibited an anodic and corresponding cathodic peak, whereas cyclic voltamograms of GCE in supporting electrolyte showed no anodic and cathodic peaks. Experimental results show (Fig. 1) that well-defined and reproducible anodic and cathodic peaks related to the IND redox system (with E_{pa}= 0.34 V, E_{pc}= 0.3 V vs. Ag/AgCl reference electrode) can be used as mediators for the electrocatalysis of hydroxylamine with slow electron transfer. The E mechanism in cyclic voltammetry numerically, ΔE_p is ~ 60/n mV at 298 K. Figure 1 shows that the peak separation potential, ΔE_p= (E_{pa}-E_{pc}= 0.04 V). As shown it was greater than the

59/n mV expected for a reversible system. Therefore suggests that an ING redox couple at GCE shows quasi-reversible behavior in an aqueous media.

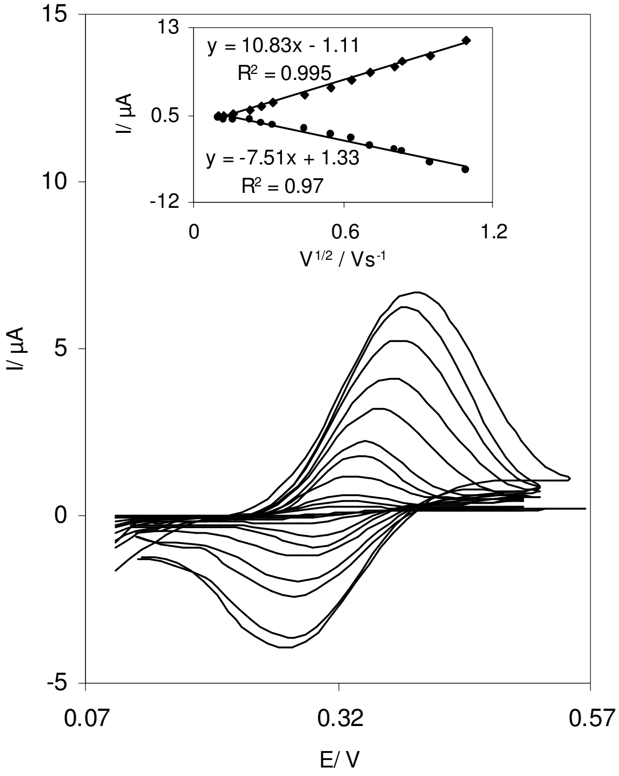

Figure 1. Cyclic voltammograms of a IND-GCE in 0.1M phosphate buffer solution of pH 7.0 at various scan rate (1) 10, (2) 25, (3) 50, (4) 75, (5) 100 (6) 200 (7) 300 (8) 400 (9)500 and (10)650 mVs^{-1}. Inset shows variations of Ip vs. the square root of scan rate.

The formal potential of the couple, is often calculated as $E^{0\prime}= (E_{pa}+E_{pc})/2= 0.32$ V, which is valid for a Nernstian system.

Fig. 1 shows the cyclic voltammograms of an IND at GCE for various scan rates (10- 650 mV s^{-1}). Inset of Fig. 1 show anodic and cathodic peak currents (I_p) values were linearity dependent on $\upsilon^{1/2}$ (at different scan rates, in the range 10-650 mV s^{-1}). A theoretical expression for the peak current for a reversible cyclic voltammogram was derived as a function of the scan rate to give the Randles-Sevcik expression [17]. According to this relationship, the dependence of the peak current, I_p, on scan rate, $\upsilon^{1/2}$, follows a characteristic square root law which provides a telltale sign of the presence of a diffusion-controlled process [9].

If values of $n\Delta E_p> 200$ larger than 200 mV can be obtained experimentally, α can be easily determined [18]. A graph of $E_p = f(\log\upsilon)$ yields two straight lines with slopes equal to $-2.3RT/\alpha nF$ for the cathodic, and $2.3\ RT/(1-\alpha)nF$ for the anodic peak. α can be determined from the slope of the straight lines. Using this plot the value of α was 0.61 for GCE in the presence of 0.1 M phosphate buffer and 0.1 M IND.

3.2. Effect of solution pH

The redox reactions of organic compounds are influenced by the acid-base properties of the solvents. For the reversible processes, the number of hydrogen ions participating in the reduction can be determined from the pH-dependence of the standard potential or the voltammetric half-wave potential [19]. The electrochemical behavior of IND at GCE was characterized on the pH value of the aqueous solution. Therefore, we studied the electrochemical behavior of IND in buffered solutions with different pH values (2.0<pH<11.0) at the surface of GCE by cyclic voltammetry (Fig. 2). In all cases, the ionic strength was adjusted to 0.1 M. As seen from Fig. 2, (A) the best choice for the ability to give the best shape and highest current was pH 7.0. Also, can be seen in Fig. 2 (B), the half-wave potential, $E_{1/2}$ of IND was pH-dependent. One linear segment was found with slope values of -54 mV/pH. The total number of protons that also participates in the redox process of IND may vary in accordance with the pH range. Depending on the number of protons taking part in the redox process with two electron transfer, the $E_{1/2}$ will shift by -59.2 mV/pH ($2H^+$), -29.6 mV/pH ($1H^+$) and 0.0 mV/pH (without H^+) [20]. So there are two protons transferred in the redox reaction in the pH range of 2.0–11.0. Thus the thermodynamic driving force for the catalysis will vary with pH, making the peak currents and the shapes of the cyclic voltammetry change at different pH values. The results obtained show that the pH 7.0 is optimum for electrochemical behavior of IND by GCE.

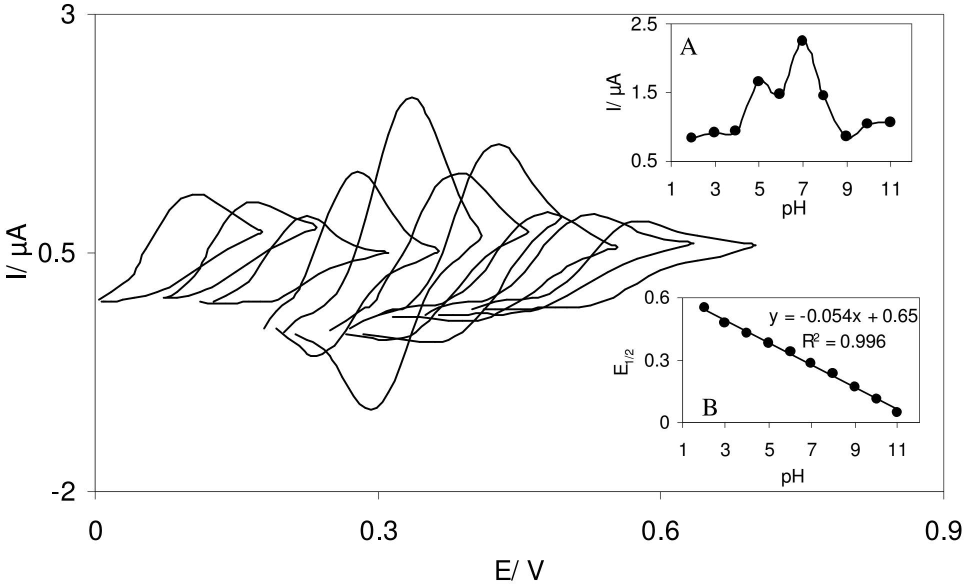

Figure 2. Cyclic voltammograms (at 100 mV s^{-1}) of an IND-GCE in 0.1M phosphate buffer solution of pH 2.0 to 11.0 (respectively right to left). (A) Plot of Ip vs. pH. (B) Plot of $E_{1/2}$ vs. pH.

3.3. Electrocatalysis of hydroxylamine oxidation

In order to evaluate the electrocatalytic oxidation of the IND at GCE toward of hydroxylamine, CVs were obtained in comparison GCE in hydroxylamine (without modifier) with GCE in solution of

IND and hydroxylamine (with modifier) as shown in Fig. 3. For the electro-oxidation of hydroxylamine at glassy carbon electrode, without IND requires a large over-potential and it shows small anodic current from the oxidation of hydroxylamine, during the present experiment but no cathodic peak was found (Fig. 3 b). Fig. 3 (curve d) shows the catalytic oxidation of hydroxylamine in the presence of IND. A Large anodic peak current and decrease in over-potential in the cyclic voltammograms can be seen with addition of hydroxylamine to the cell. It is noting that, the increment of catalytic current and the decrease in the over-potential are two important factors in evaluating the catalytic effect. The cyclic voltammetric behavior of IND, at glassy carbon electrode, in a supporting electrolyte is also shown in Fig. 3 (curve c).

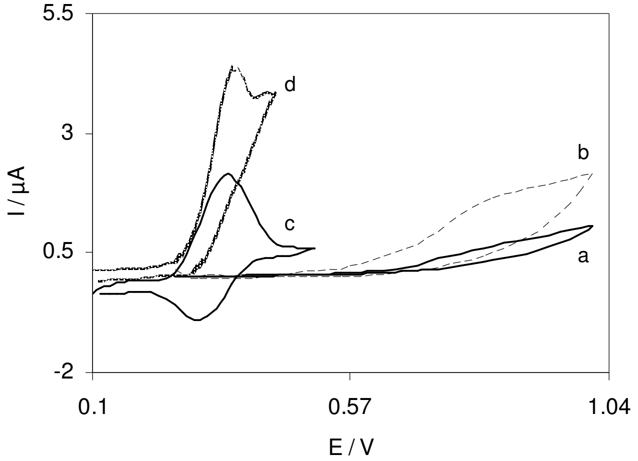

Figure 3. Cyclic voltammograms of bare glassy carbon electrode in 0.1M phosphate buffer solution of pH 7.0 (a) in absence of, (b) in 0.5 mM hydroxylamine and IND-GCE(c) as (a) and (d) as (b).

The reaction scheme for the determination of hydroxylamine is given the following sequence:

$$\text{IND}_{(aq)red} \rightarrow \text{IND}_{(aq)ox}$$
$$\text{IND}_{(aq)ox} + \text{Hydroxylamine}_{(aq)} \rightarrow \text{IND}_{(aq)red} + \text{Hydroxylamine}_{o(aq)ox}$$

The above reaction shows that during the first step, IND can be oxidized at the surface of glassy carbon electrode and second step in the presence of hydroxylamine, the oxidized IND can be oxidize the hydroxylamine and converts to its initial form, while the IND itself can be oxidized further, so the peak current of IND increases in the presence of hydroxylamine.

In the aqueous solution, hydroxylamine is oxidized mainly through a two-electron process with the final product of N_2O:

$$2NH_2OH + 4\ OH^- \rightarrow N_2O + 5H_2O + 4e^-$$

3.4. Effects of pH and IND concentration

The influence of variables such as pH and IND concentration on the response of IND-GCE was studied.

The results showed that the pH affects the electrochemical behavior of IND and hydroxylamine activities. Fig. 4 states that the pH value of buffer medium has an important effect on the efficiency of the electrocatalytic oxidation of hydroxylamine. We found that at the pH 7.0, the best results were obtained, so this medium was chosen for the subsequent experiments.

The influence of IND concentration on the peak currents was studied for the range of 10.0 to 500 µmol L^{-1} IND concentration, in the solutions containing 0.5 mM of hydroxylamine at pH 7.0. The results showed that by increasing the IND concentration up to 100 µmol L^{-1}, the peak current increased, whereas higher concentration of IND caused a slight decrease in the magnitude of peak current, probably due to the formation of IND aggregates.

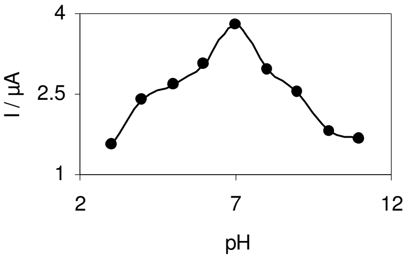

Figure 4. Effect of the pH of 0.1 M buffer (salts of phosphate) on the peak current in the presence of 0.5 mM hydroxylamine at scan rate 100 mVs^{-1}.

3.5. Chronoamperometry methods

In potential step methods, the potential of the working electrode is changed instantaneously between potentials E_1 and E_2, and the current-time curve is recorded. Chronoamperometry has no unique analytical utility, but it is useful for the evaluation of diffusion coefficients, rates of electrode processes, adsorbtion parameters, and rates of coupled chemical reactions. Measurements should be made over as long a time period as possible to ensure reliable results. During the first 100-300 µs much of the current is due to charging the double response. At longer times natural convection disturbs the current response. Therefore, the responses over the range from 1 ms to 10 s commonly are recorded [21].

The chronoamperograms, for a series of hydroxylamine solutions with various concentrations, are shown in Fig. 5. It can be seen that an increase in anodic currents obtained for a potential step of 550 mV vs. Ag/AgCl reference electrode with an increase in the concentration of hydroxylamine. In the presence of hydroxylamine at long experimental times (t > 4s), the IND oxidation is completed and the rate of electro-catalyzed oxidation of hydroxylamine exceeds that of hydroxylamine diffusion from the diffusion layer to the IND (formerly diffused to the electrode surface), and under conditions, the process is diffusion controlled. In chronoamperometric studies, the diffusion coefficient of hydroxylamine can be determined. The Cottrell equation describes relationship between diffusion coefficient and bulk concentration [20, 22]:

$$I = nFAD^{1/2} C_b / \pi^{1/2} t^{1/2} \qquad (1)$$

Where, D and C_b are diffusion coefficient ($cm^2\ s^{-1}$) and the bulk concentration (mol/cm^3), respectively. The level of Cottrell current, measured for 6 s, increased with the increase of hydroxylamine concentration. Inset A of Fig. 5 shows the plot of I vs. $t^{-1/2}$, under the diffusion control. Then slopes of the resulting straight line from the inset A of Fig. 4 were plotted vs. the hydroxylamine concentration. From slope of this line, we can calculate a diffusion coefficient of $4.8 \times 10^{-6}\ cm^2\ s^{-1}$ for hydroxylamine.

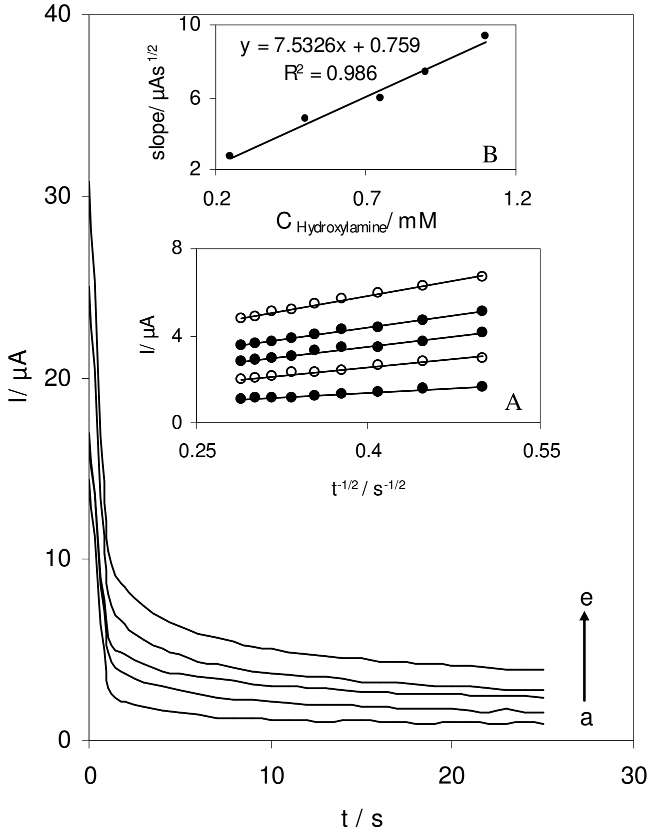

Figure 5. Chronoamperograms for the following concentrations of hydroxylamine: 0.25, 0.50, 0.75, 1.00 and 1.15 mM of hydroxylamine (from a to e). Insets: (A) Plots of I vs. $t^{-1/2}$ from the data of chronoamperograms for different concentration of hydroxylamine. (B) Plot of the slope of straight lines against the hydroxylamine concentration.

Chronoamperometric method can be used to evaluate the catalytic rate constant. At intermediate time interval (> 0.1 s in present experiment), the catalytic current ($I_{cat.}$) is dominated by the rate of electrocatalytic oxidation of hydroxylamine. On the basis of the equation presented follow it possible to calculate the rate constants of catalytic processes. After measurement of the catalytic current, the electrode process is carried out the same conditions but in the absence of catalyst. The catalytic reaction then does not take place and it possible to determine the limiting current value I_L [20, 22]. So, the rate constant for the chemical reaction between hydroxylamine and oxidized form of IND is determined according to the equation, described in the literature [20, 22]:

$$I_{cat.} / I_L = \gamma^{1/2}[\text{л}^{1/2}\, \mathrm{erf}\, (\gamma^{1/2}) + \exp\, (-\gamma)/ \gamma^{1/2}] \qquad (2)$$

Where $I_{cat.}$ and I_L are the currents of IND in the presence and absence of hydroxylamine, respectively. $\gamma = kC_0t$ (C_0 is the bulk concentration of hydroxylamine in mol L^{-1}), k is the catalytic rate constant (M^{-1} s^{-1}) and t is time elapsed (s) and erf ($\gamma^{1/2}$) is the argument of error function. It follows from Eq. (2) that for catalytic process the low limit of the ratio $I_{cat.}$ / I_L is 1. During the treatments, it is assumed that hydroxylamine is present in the large excess rather than IND, in addition where γ exceed 2, the error function is almost equal to 1. The second term in brackets in Eq. (2) then becomes negligible compared with $\pi^{1/2}$. Thus for γ ½ > 2 Eq. (2) can be reduced to:

$$I_{cat.} / I_L = \gamma^{\,1/2}\, \text{л}^{\,1/2} = \text{л}^{1/2}\, (kC_0t)^{1/2} \qquad (3)$$

The slope of $I_{cat.}/I_L$ vs. $t^{1/2}$ for 1.0 mmol L^{-1} hydroxylamine was determined and k was calculated to be $2.38\times10^{+3}$ (M^{-1} s^{-1}).

3.6. Effect of scan rate and Tafel plot

The cyclic voltammetry technique used for investigation of the effect of scan rate on the electro-catalytic oxidation of hydroxylamine at the GCE. As can be observed in Fig.6, cyclic voltammograms at low scan rate have peak-to-peak separations close to the value theoretically expected for a reversible process of ΔE_p= 57 mV at 298 K and the peak current increases with the square root of the scan rate. Under these conditions, the process is diffusion controlled and termed electrochemically “reversible” or “Nernstian” within the time scales applicable to the experiment under consideration. Hence, as with all reversible systems operating under thermodynamic rather than kinetic control, no information concerning the rate of electron transfer at the electrode surface or the mechanism of the process can be obtained from data obtained at slow scan rate. The increase of I_p with υ may be interpreted as follows. Recall that Ip shows the flux of material reacting at the electrode surface and that near E_p this is controlled by the rate of diffusion of hydroxylamine [23, 24]. Fig. 6 A shows a plot of peak height (Ip) against square root of scan rate ($\nu^{1/2}$), in range of 10-170 mVs^{-1}, which was found to be linear, which is expected for a diffusion-controlled electrode process. . Also, a plot of the sweep rate of normalized current ($I_p/\nu^{1/2}$) vs. sweep rate (Fig. 6B) exhibits the characteristic shape, typical for an EC_{cat} process [20].

Also Fig. 7 shows a Tafel plot that was drawn from data of the rising part of the current–voltage curve recorded at a scan rate of 100 mVs^{-1}. A slope 0.0899 V $decade^{-1}$ is calculated indicating a one electron transfer to be rate limiting assuming a transfer coefficient of $\alpha = 0.34$.

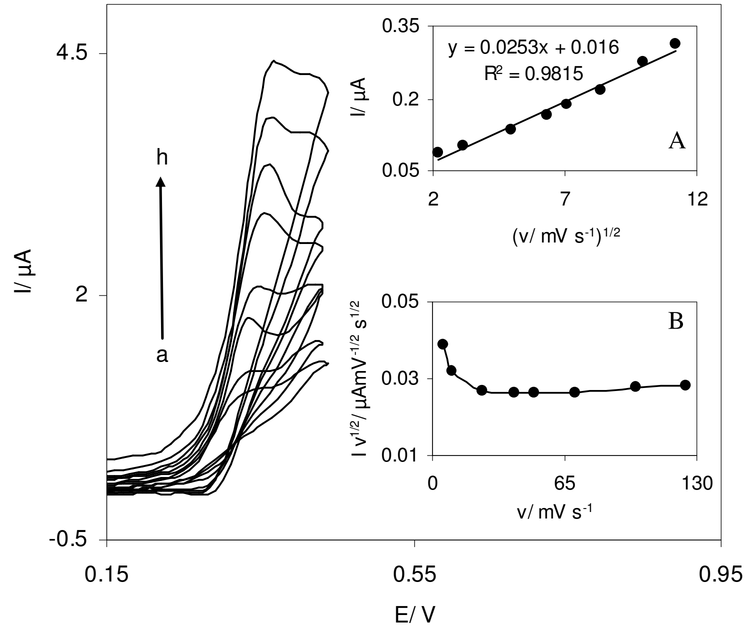

Figure 6. Cyclic voltammograms of an IND-GCE in 0.1 M phosphate buffer (pH 7.0) containing 1.0 mM hydroxylamine at different scan rates. The curves of a to h correspond to 10, 25, 50, 70, 90, 125, 150 and 170 mVs^{-1} scan rates, respectively. Insets: (A) Variation of the electrocatalytic currents versus the square root of scan rate (B). Variation of the scan rate normalized current $(Ip/v^{1/2})$ with scan rate.

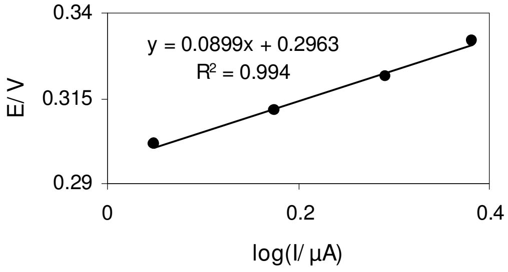

Figure 7. Tafel plot derived from the current potential curve recorded at scan rate of 100 mV s^{-1}.

3.7. Effects of chemical interferences

Determination of hydroxylamine in presence of other compounds is important problem. Therefore influence of different compounds, as potential interference on the determination of hydroxylamine, was investigated under the optimum conditions with 1.0×10^{-3} M of hydroxylamine concentration. The tolerance limit was defined as the maximum concentration of the potential interfering substance causing an error, less than 3%, during the determination of hydroxylamine concentration at 1.0×10^{-3} M. The results show that the peak current of hydroxylamine is not affected by several cations and anions such as Na^+, K^+, Co^{2+}, NADH, NO_3^-, NO_2^-, SO_4^{2-}, SCN^-, Cl^-, CO_3^{2-}.

3.8. Differential pulse voltammetry investigations

Sensitivities in differential pulse voltammetry (DPV) are better than other techniques of voltammetry. The importance of DPV in chemical analysis is based on its superior elimination of the capacitive/back ground current. The electrocatalytic peak height of hydroxylamine at the surface of GCE varied linearly with concentration of hydroxylamine by DPV method. Calibration curve is shown in insets A and B of Fig. 8. In inset of A Fig. 8 show two segments with two range of concentration of hydroxylamine (0.5-3.2; and 3.2-18.0 μM). For low concentrations [Fig. 8, (B)], a linear correlation is observed in the range 0.5- 3.2 μM; with a correlation coefficient better that 0.9821. The detection limit (3σ) was 1.6×10^{-7} M.

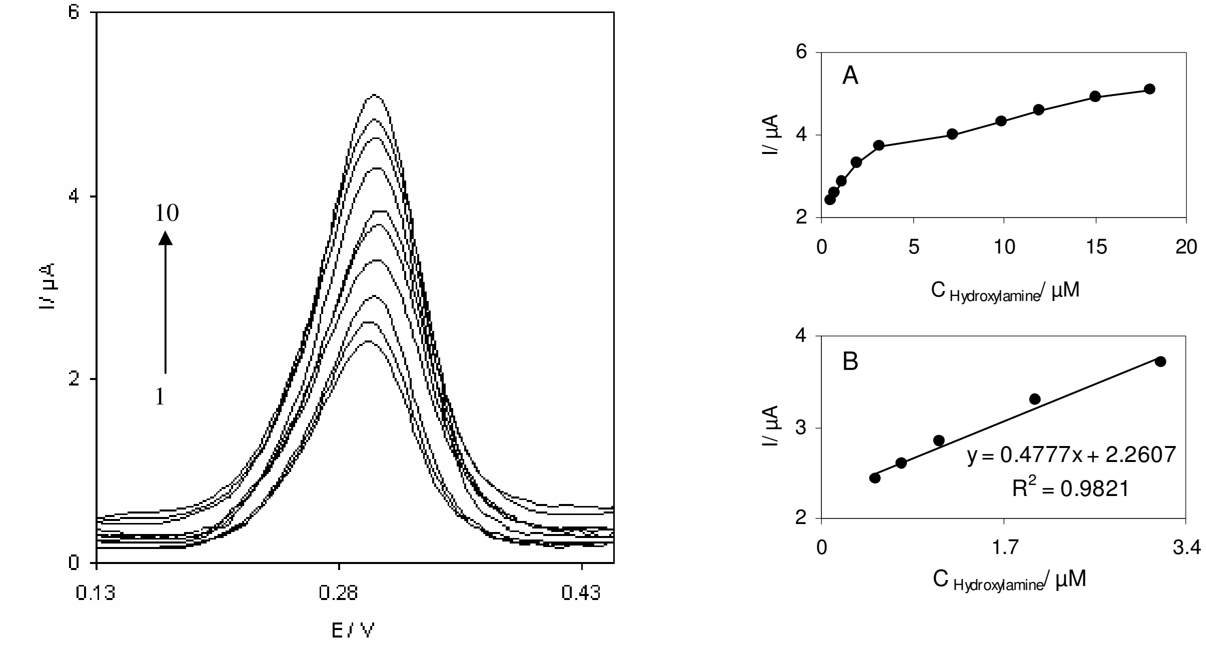

Figure 8. Differential pulse voltammograms of IND-GCE in 0.1 M phosphate buffer solution (pH 7.0) containing different concentrations of hydroxylamine. The numbers of 1–10 correspond to 0.5, 0.8, 1.1, 2.0, 3.2, 7.2, 9.9, 12.0, 15.0 and 18.0 μM hydroxylamine. Insets show the plots of the electrocatalytic peak current as a function of hydroxylamine concentration in the range of (A) 0.5–18.0 μM and (B) 0.5–3.2 μM.

3.9. Determination of hydroxylamine in real sample

This method was found to work well under the laboratory conditions. To assess the applicability of this method in real samples, an attempt was made to determine hydroxylamine in several water samples, using the spike method. The hydroxylamine recovery was determined in drinking-water. The data, given in Table 1, shows the satisfactory results.

Table1. Recovery of hydroxylamine from water sample.

Sample	Hydroxylamine added (μM)	Hydroxylamine found (μM)[a]	Recovery(%)
Drinking Water	–	<Detection limit	
Drinking Water	7	6.89	98.4
Drinking Water	10	10.32	103.2
Drinking Water	13	12.3	94.6
Drinking Water	15	15.6	104

[a] Average of five determinations

4. CONCLUSIONS

Indigocarmine allows low-potential detection of hydroxylamine and shows an excellent electrocatalytic behavior toward hydroxylamine oxidation in the aqueous phosphate buffer (pH 7.0) solution, with an over-potential of about 600 mV less than that on a bare glassy carbon electrode. This technique offers a number of advantages over other conventionally modified glassy carbon electrodes, especially in its simplicity because it does not need to be prepare as for the modified electrodes. On the basis of Tafel plot and considering that the charge-transfer step of the rate-limiting reaction is a one-electron process, the transfer coefficient (α) was obtained to be 0.34. The other kinetic parameters such as, catalytic reaction rate constant (k) and diffusion coefficient were also determined by using the chronoamperometry.

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