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Electrochemical Behavior of Triethanolamine at a Carbon Paste Electrode

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Abstract: In this article, the electrochemical behavior of triethanolimine is described with a carbon paste electrode. A differential pulse voltammetric method was also developed for the determination of triethanolamine as an application to electroanalysis at a carbon paste electrode. The resultant voltammograms have revealed the irreversible electrochemical process that can be utilized to quantify the substances of interest, for triethanolamine, for which the detection limit (3σ) was estimated to be 2.8×10^{-5} mol L^{-1}.

Keywords: Carbon paste electrode; Differential pulse voltammetry; Cyclic voltammetry; Triethanolimine; DNA interactions

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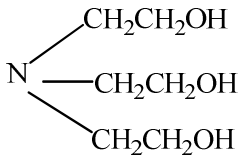
Introduction

Ethanolamines were commercially available in the early 1930s; they assumed steadily growing commercial importance as intermediates after 1945, because of the large-scale production of ethylene oxide. Since the mid-1970s, economical production of very pure, colourless ethanolamines has been possible. Ethanolamines are produced on an industrial scale exclusively by reaction of ethylene oxide [1] and excess ammonia. This reaction takes place slowly, but is accelerated by water. An anhydrous procedure uses a fixed-bed ion-exchange resin catalyst [2].

Triethanolamine (TEA, 2,2',2''-nitrilotriethanol; see scheme **1** overleaf) is used as a corrosion inhibitor in metal-cutting fluids, a curing agent for epoxy and rubber polymers, as a Cu–TEA complex to control freshwater algae on lakes and ponds and as a neutralizing agent in agricultural herbicides.

TEA is also extensively used in emulsifiers, thickeners and wetting agents in the formulation of consumer products such as cosmetics, detergents, shampoos and other personal products, its use can furher be as the constituent in adhesives, antistatic agents, cement and concrete work, coatings, in electroless and electroplating,in fuels, printing inks, lithography, metal-cleaning and lubricating, mining, paint and pigments, petroleum and coal production, as a pharmaceutical intermediate and an ointment-emulsifier, in polymers and polymer production, rubber processing, soldering flux, textile finishing, polyurethane production and use and wood pulping [3-5].



Scheme 1: *Triethanolamine.*

The general organic chemistry of alkanoamines is well established, but on the other hand the redox and autooxidation behavior of triethanolamine is not thoroughly investigated. This could be explained partly due to the use of TEA as an antioxidant or free radical trap in order to retard the autooxidation of a variety of compounds. Triethanolamine is known to be oxidized slowly by a variety of oxidizing agents, including alkaline hexacyanoferrate [6], microorganisms [7, 8], and many other reagents. Reported oxidation products and intermediates include formaldehyde, acetaldehyde, monoethanolamine, diethanolamine, hydroxyacetaldehyde, acetate, formate, and ammonia.

Triethanolamine is rapidly absorbed and excreted in urine (about 60 %) and faeces (about 20 %) mainly in the unchanged form. Biodegradation of triethanolamine to monoethanolamine or diethanolamine or to any other putative metabolite has not been shown in rodents, nor its incorporation into natural products [11]. It has been hypothesized that endogenous nitrosation of triethanolamine may produce a potent liver carcinogen, *N*-nitrosodiethanolamine [12], or that some other endogenous reactions convert triethanolamine to a putative carcinogen [13]. The formation of *N*-nitrosodiethanolamine in amounts that would cause liver cancer *in vivo* appears, however, unlikely since no treatment-related liver cancers have been observed in oral or dermal triethanolamine carcinogenicity studies in mice or rats [14]. The potential reported for triethanolamine to undergo nitrosative dealkylation and form *N*-nitrosodiethanolamine under physiological conditions (including gastric pH) is, in general, considered negligible in comparison with the nitrosation of secondary amines [15].

The broad utility of triethanolamine in a large number of industrial applications and consumer products may result in its release to the environment. Moreover, triethanolamine is in present as an ingredient in a large amount of cosmetic products which may be applied to or

come into contact with skin, eyes, hair, nails, mucous membrane and respiratory epithelium. Small amounts may be ingested from lipsticks. Therefore, there is a necessity of developing simple, fast and reliable techniques for the determination of TEA. TEA is, usually, determined by ion chromatography [16] in workplace air, gas chromatography–mass selective detection of silylated derivatives [17], isotachophoresis [18], capillary zone electrophoresis with indirect ultraviolet detection [19] and spectrophotometry [20] in metalworking and cutting fluids. TEA's determination in cosmetics and pharmaceuticals is done by ion-exclusion chromatography [21] and by reversed-phase high performance liquid chromatography [22]. Most of these detection methods are time consuming, laborious and sophisticated equipped techniques. Meanwhile, electroanalytical assays have gained the interest for many analytical applications where a high level of sensitivity is required, due to theirs simplicity, rapid response and relatively inexpensive instrumentation.

In this paper we report the electrochemical behavior using cyclic voltammetry (CV) at a carbon paste electrode (CPE) of TEA. Investigations of TEA's interaction mode with double stranded calf thymus DNA (dsDNA) using adsorptive stripping transfer voltammetry at a DNA modified carbon paste electrode have been also carried out. Moreover, we report the electroanalytical detection of TEA using differential pulse voltammetry (DPV) at a carbon paste electrode. To the best of our knowledge there are not any reports relative to the electrochemical oxidation and reduction or its electroanalytical detection of TEA although TEA participates in a variety of electrochemical applications [23].

Experimental

Chemicals, Reagents, Stock, and Standard Solutions

All reagents were of analytical grade unless stated otherwise and used as received. Dimethyl sulfoxide (DMSO) was used without any further purification. Borate buffer was purchased from Merck. Triethanolamine (TEA) was obtained from Sigma Chemical, Co. (St. Louis, MO, USA). Ethylene diamine tetra-acetic (EDTA, ACS reagent, 99.4-100.06%) was obtained from Sigma-Aldrich. Graphite powder was purchased from Fluka.

All aqueous solutions were prepared with doubly-distilled water. The stock solution of TEA was 0.7 mol L^{-1} in concentration and prepared after weighing a certain amount of the compound and dilution in DMSO. For the electrochemical behavior of TEA the buffer was

0.2 mol L^{-1} acetate buffer solution pH = 5.4 containing the appropriate mass concentration of TEA, unless stated otherwise.

Solutions used in the pH influence of the buffer solution on oxidation and reduction of triethanolamine were 0.1 mol L^{-1} HCl / KCl pH = 2.1 and 3.1, acetate buffer solution pH = 3.8, 4.0, 4.2, 4.4, 4.6, 4.8, 5.0, 5.2, 5.4 and 5.6, phosphate pH = 6.0 and 7.0, tris–HCl pH = 8.0, and borate buffer pH = 9.0 and 10.0 in 0.1 mol L^{-1} KCl.

Electrochemical Apparatus and Other Instrumentation

Voltammetric experiments were carried out using a μAutolab potensiostat/galvanostat (Eco Chimie, Utrecht, The Netherlands) controlled by a GPES 4.9.0005 Beta software. The pH of all solutions was measured by a Consort C830 pH meter.

Carbon Paste Electrode

Carbon Paste Electrode (CPE). The carbon paste was prepared in the usual way by hand-mixing graphite powder and mineral oil in a ratio of 75:25. The resulting paste was packed tightly into a Teflon sleeve of 3mm inner and 9 mm outer diameter. Electrical contact was devised with a stainless steel screw. The surface was polished to a smooth outlook before use.

Electroanalytical Measurements and Related Procedures

Studies were performed using cyclic voltammetry, differential pulse voltammetry and the so-called adsorptive transfer stripping voltammetry. A three electrode glass cell was used containing a platinum wire as counter and Ag / AgCl / 3 mol L^{-1} KCl as reference electrodes. A carbon paste electrode of 3mm inner and 9 mm outer diameter of the PTFE sleeve was utilized as a working electrode. Ultrapure nitrogen was used to deaerate the solutions of dissolved oxygen for 15 min before each experiment.

Cyclic voltammetry (CV). The respective measurements were carried out using 0.2 mol L^{-1} acetate buffer pH 5.4 unless stated otherwise. The scan rate was range of 10 – 200 m V s^{-1} unless indicated otherwise with a step potential of 5 m V s^{-1}. In most of experiments the scan started at 0.0 mV, reversed at 1200 mV and terminated at 0.000 mV. The electrochemical cells were cleaned with diluted nitric acid and rinsed with doubly-distilled water.

Differential pulse voltammetry (DPV). The electroanalytical detection (oxidation) of TEA in the differential pulse voltammetric mode consisted of the following two steps:

(i) *Conditioning of the CPE surface.* A freshly smoothed carbon paste surface was immersed into 0.2 mol L^{-1} acetate buffer pH 5.4 containing 0.02 mol L^{-1} NaCl and conditioned by applying a – 1500 mV potential for 8s.
(ii) *Signal Transduction*. After an equilibration time of 10 s voltammetric measurements were performed in the 0.2 mol L^{-1} acetate buffer pH 5.4 containing 0.02 mol L^{-1} NaCl with an initial potential of + 0.0 mV, an end potential of + 1200 mV, a modulation time of 0.07 s, an interval time of 0.6 s, a step potential of 3 mV s^{-1} and a modulation amplitude of 50 mV.

Processing and Evaluation of the Measurements. The raw data in the case of DPV were treated using the Savitzky and Golay filter (level 2) of the GPES software, followed by the GPES software moving the average baseline correction using a peak width of 0.03.

Results and Discussion

Cyclic Voltammetry

This technique is widely used for the initial characterization of electrochemically active systems. TEA gives an irreversible anodic peak at 903 mV, and an absence of cathodic peaks at a scan rate 10 mV^{-1}, Fig. 1.

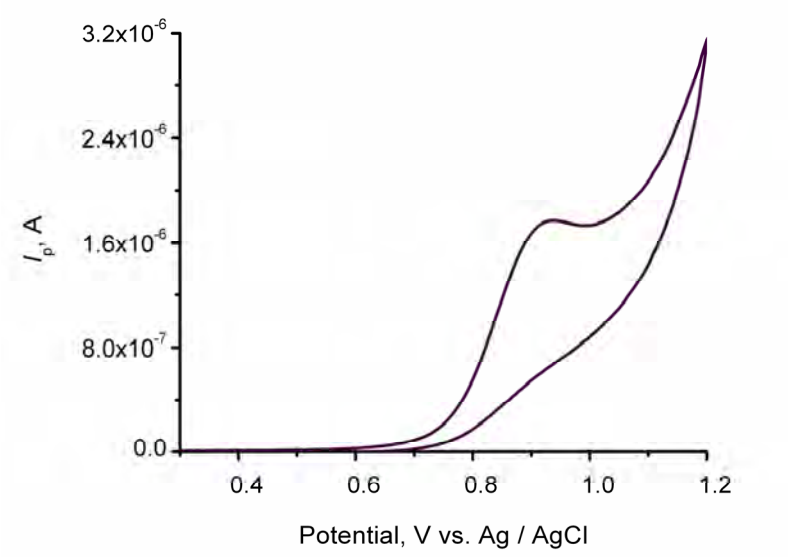


Fig. 1: *Cyclic voltammogramm of TEA.* Legend: CV of 195 mg L^{-1} TEA obtained in 0.2 mol L^{-1} acetate buffer pH 5.0 (voltammetric conditions: scan rate = 10 mV s^{-1}, first vertex potential = start potential = 0 V, second vertex potential = +1200 mV, step potential = 5 mV and number of scans = 3, other conditions as mentioned in the experimental section).

Effect of pH of the Respective Buffer on Cyclic Voltammetric Responses

The pH value seems to play an important role in the electrochemical behavior of triethanolamine. Hence, we tested the influence of the buffer pH on the redox behavior of manganese complex to further clarify the oxidation-reduction mechanism of the compound, Fig. 2.

It was found that for pH values lower than 4.8 there was an absence of peaks in the cyclic voltammograms of TEA. In addition, an anodic peak appeared at about for pH from 4.8 to 7.0, which was shifted toward less positive values with increasing pH (Fig. 2a) within this pH range. This peak could be attributed to the oxidation of one of the CH_2OH group of TEA. At pH higher than 8 two anodic peaks became obvious, while peak potential shifted to more positive values with the increase of pH from 8 to 10. The second anodic peak might be ascribed to the oxidation of one or two of the rest CH_2OH group existing in TEA's molecule.

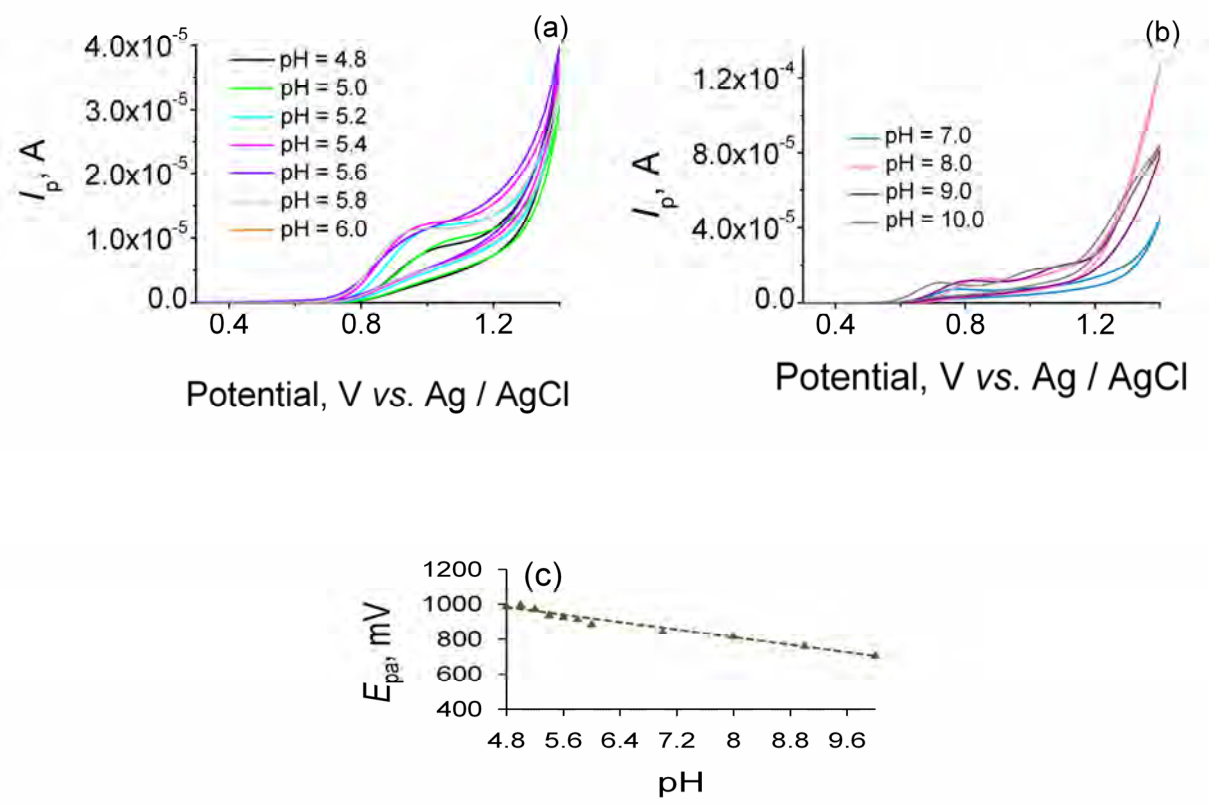


Fig. 2: *pH effect on cyclic voltammetry*. Legend: CVs of 195 mg L^{-1} of TEA at CPE in buffers with various pH values: (a) pH range from 4.8–6.0 and (b) pH range from 7.0–10.0 (start potential = first vertex potential = 0 mV, second vertex potential = 1200 mV, step potential = 5mV, scan rate = 25 mV and number of scans = 3) (c) dependence of anodic peak potential of TEA (other conditions are mentioned in the experimental part).

Furthermore, for TEA studied in the pH range between 4.8 and 10 the E_p *versus* pH plots (Fig. 2c) are linear with a slope of (–53.5 ± 3.131) mV per unit pH. The slope suggests the participation of protons in the electro-oxidation reaction. The slope obtained in this experiment for anodic peak is extremely close to the value of 59.2 mV per unit pH predicted from Nernst equation one proton oxidation and one electron oxidation or it suggests that equal number of protons and electrons participate in the electro-oxidation process.

Therefore, since TEA has three oxidizable groups of CH_2OH [10], it is possible that one, two or even three of them oxidized in a one-proton and one-electron, two-proton and two-electron, or even three-proton and three-electron process, respectively. In relation with the second oxidation peak which starts to appear at pH range between 8 and 10 the results showed that the variation of peak current with pH was nonlinear and thus we could not deduce any safe conclusion about the electrons and protons that take place in the electrochemical reaction.

From the data obtained (see Fig. 2a and 2b) the electrochemical oxidation signal of TEA was significantly enhanced when acetate buffer with pH 5.4. Thus, acetate buffer pH 5.4 was used for subsequent CV and DPV experiments.

Scan Rate in the CV Mode and Its Effect on the Electrochemical Process of TEA

As it was mentioned in the introduction section, tertiary aliphatic amines follow EC mechanism [9], where a relatively stable radical cation deprotonates and leads to a radical in the second step. It is this radical that binds to the surface of the electrode. Meanwhile, in the case of alcohol amines it can be assumed that the CH_2OH group is oxidized first and only after that the NH_2 group. As a result of the CH_2OH group oxidation the respective amino acid may be formed, which is then oxidized to different final products depending on the order of the carbon atom to which the amino group in the substrate molecule is attached [10].

For TEA with the amine group linked to the first ordered carbon atom, the final product could probably be oxalic acid (dicarboxylic acid) [10] and finally formaldehyde [6]. To examine whether the anodic peak correspond to a reversible reaction, CVs were recorded at different scan rates, between 1 and 200 mVs^{-1} at CPE for 195 mg $L^{-1}$of TEA (see the respective voltammograms in Fig. 3). It was found that the dependence of anodic peak current with scan rate was not linear (Fig. 4a), which suggests that the anodic process of TEA involves a complex mechanism. The results also show that the peak current increases linearly with the square root of scan rate up to 10 mV s^{-1} and above that value the behavior of the

system changes (Fig. 4b). In addition, the log ($I_{p,a}$) *versus* log(scan rate) plot is also linear up to 10 mV s^{-1} (Fig. 4c) with a slope of d log($I_{p,a}$)/d log(scan rate) ≈ 0.4. For higher scan rates the logarithm of peak current decreases with the increase of the logarithm of scan rate and after that remains almost unchanged. The magnitude of this parameter means that the mechanism of alcohol amine oxidation on CPE is not pure from the kinetic point of view and may indicate a mixed, i.e., diffusion–adsorption rate control, with TEA oxidation as for a pure diffusion process the slope should be equal to 0.5, while for a purely adsorption process equal to 1.

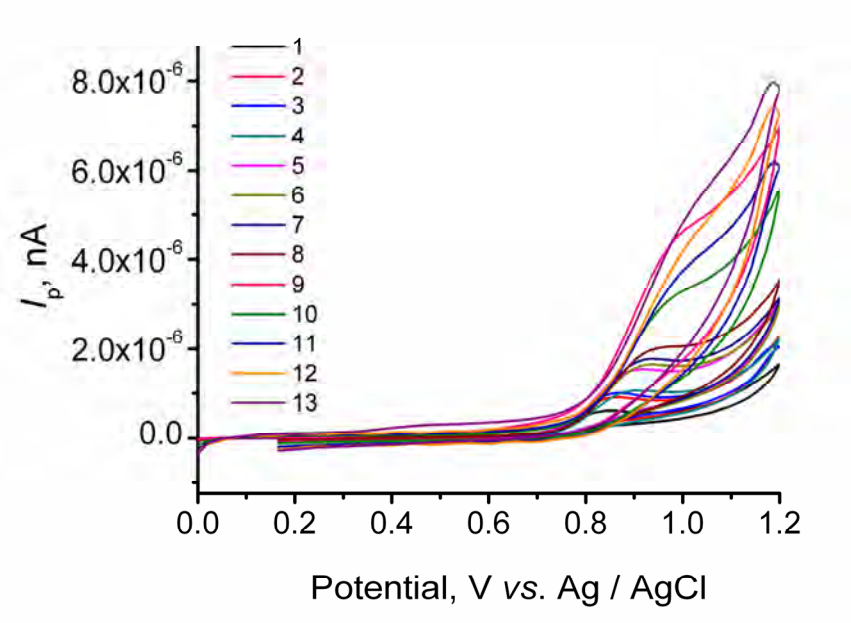


Fig. 3: *Cyclic voltammograms of TEA obtained at different scan rates.* Legend: Series of CVs of 195 mg L^{-1} TEA at: (1) 1, (2) 2, (3) 3, (4), 4, (5) 6, (6), 8, (7) 10, (8) 20, (9) 50, (10) 70, (11) 100, (12) 125 and (13) 200 mV s^{-1} (voltammetric conditions: first vertex potential = start potential = 0.0 V, second vertex potential = +1.2 V, step potential = 5 mV, number of scans = 3 and voltammograms were recorded in 0.2 mol L^{-1} acetate buffer pH 5.4-other conditions as mentioned in the experimental section).

On the other hand, the oxidation peak potential of TEA shifts positively with increasing the scan rate and it is directly proportional to the logarithm of scan rate with a slope of (0.073 ± 0.003) *i.e.* the electron transfer coefficient is *an* = 0.4, confirming the irreversibility of the electrochemical process (Fig. 4d). This value of electron transfer coefficient is lower than 0.5, which is compatible with the assumption of an adsorption step in the oxidation mechanism of TEA. As follows from the kinetic theory of electrode reaction, in the case of a single rate determining step, with no contribution of adsorption, and the electron transfer coefficient of only 0.120 V per decade should be found [10].

Differential Pulse Voltammetric Studies with TEA

Adsorptive stripping voltammetry serves a fast, simple, sensitive and low cost method to determine compounds in various samples. A differential pulse voltammetric (DPV) method was developed for the determination of TEA as an application to electroanalysis. Fig. 5 shows the voltammograms obtained by varying concentration of TEA, where one peak at anodic scan is in present at about 1250 mV.

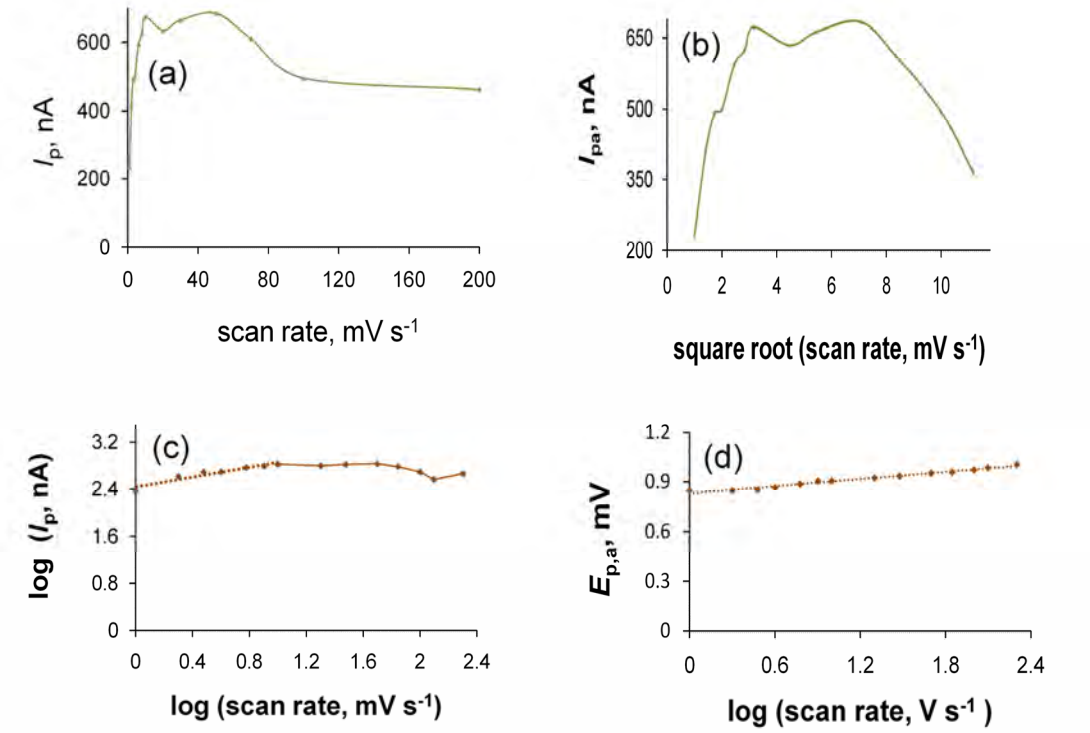


Fig.4: *Effect of scan rate on cyclic voltammetry*. Legend: (a) Anodic peak current (I_{pa}) as a function scan rate (b) anodic peak current (I_{pa}) as a function of the square root of scan rate (c) Plot of the logarith of anodic peak current against logarithm of scan rate in the range (d) Logarithm of peak current *versus* the logarithm of scan rate (voltammetric conditions: first vertex potential = start potential = 0.0 V, second vertex potential = +1.2 V, step potential = 5 mV number of scans = 3 and voltammograms were recorded in 0.2 mol L^{-1} acetate buffer pH 5.4-other conditions as mentioned in the experimental section).

The peak potential of oxidation peak shifted at less positive potentials with increasing the amount concentration of TEA as it can be seen from Fig. 5, which is typical of reaction involving adsorbed molecules. The obtained results are in accordance with those of CV. The different potential peak observed in CV (Fig.1; at 903 mV) and DPV (Fig. 5; at 1250 mV) could be explained by stabilization of the intermediate radical cation [9, 10] on CPE's surface in the later case, where the electron transfer occurred in higher potential.

The electrode was preconditioned at -1500 mV during 8 s without stirring and calibration curve were plotted, inset of Fig. 5. It was found that peak current of anodic peak increased with the continuous addition of TEA, and the analytical features of this compound are given in Table I. The limits of detection and quantization (c_L and c_Q) were calculated to be 3 xs_b/a and 10 xs_b/a respectively, where s_b and a are the standard deviation of the intercept and the slope of the calibration plot respectively [24].

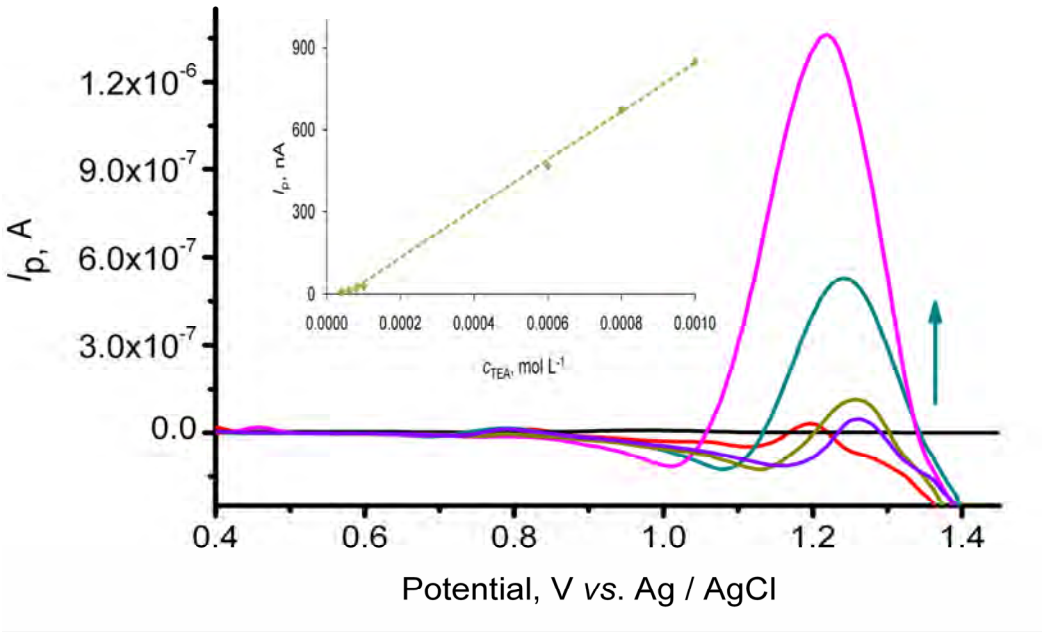


Fig 5: *Calibration plot of TEA*. Legend: DPVs of anodic scan at different mass concentrations. Inset of Fig 8: related calibration graph of TEA at amount concentration range 0-1 x10^{-3} mol L^{-1} (1) of anodic peak at 1250 mV (conditions as described in the experimental section).

Table I: *Determination of TEA with a DPV method*. Analytical characteristics of TEA.

Parameter, option	Anodic peak
Oxidation potential (mV)	1250
Linear range (mol L^{-1})	9.4 x10^{-5}–1.0 x10^{-3}
r	0.9990
s_r. (%) *(n=6)*	6–6.5[a]
c_L (mol L^{-1})	2.8 x10^{-5}
c_Q (mol L^{-1})	9.4 x10^{-5}

Legend: [a] Relative standard deviation at three levels of (1) amount concentration: 2.0 × 10^{-4}, 8.0 × 10^{-4} and 1.0 × 10^{-3} mol L^{-1}.

Conclusions

In this article, the electrochemical behavior of TEA was studied in terms of cyclic and differential pulse voltammetry on a carbon paste electrode. The CV results gave evidence that the electro-oxidation of TEA was an irreversible procedure and followed a mixed diffusion adsorption controlled mechanism in acetate buffer pH 5.6.

The results were also indicative that equal number of protons and electrons participated in the oxidation process. TEA and its oxidation product adsorbed at the electrode surface probably through an EC mechanism [10]. Differential pulse voltammetry results were in accordance with those obtained by CV. In addition, the present study describes an effective assay for the determination of TEA. This newly described method for the determination of TEA has for the first time involved the electrochemical principles. The respective procedure combines a carbon paste electrode and the subsequent voltammetric detection; the last named representing a simple, inexpensive but sufficiently sensitive and selective measurement.

Because the most important features of the method have already been discussed above; in the end, it can be stated that the proposed method represents an interesting and principally different alternative to the hitherto prevailing measurements based on ion chromatography, gas chromatography and related techniques and would therefore be convenient for occasional routine determinations. Nevertheless, some improvements are still possible and the respective investigations of continual interest.

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References

1. IARC; in *IARC monographson the evaluation of carcinogenetic risks on humans* vol ***60***, pp. 73–159. Lyon, IARCPress, 1994.
2. H. Hammer, W. Kornig, T. Weber, H. Kieczka; in *Ullmann's Encyclopedia of Chemical Technology* (W. Gerhartz, Y. S. Yamamoto, L. Kaudy, J. F.Rounsaville, G. Schulz, Eds), 5th rev. Vol. A10, pp. 1. VCH Publishers, New York, 1987.
3. K.H. Beyer, W.F. Bergfeld, W.O. Berndt, R.K. Boutwell, W.W. Carlton, D.K. Hoffmann, A.L. Schroeder: *J. Am. Coll. Toxicol*. ***2*** (1983) 183.

4. A. Santa María, J.M. Pozuelo, A. López, F. Sanz: *Ecotoxicol. Environ. Saf*. ***34*** (1996) 56.
5. R.J. West, S.J. Gonsior: *Environ. Toxicol. Chem*., ***15***, (1996) 472.
6. K.S. Shulka, P.C. Mathur, O.P. Bansal: *J. Inorg. Nucl. Chem.* ***35*** (1973) 1301.
7. G.R. Williams, A.G. Callely: *J. Gen Microbiol.* ***128*** (1982) 1203.
8. G. Speranza, C.F. Morelli, P. Cairoli, B. Muller, B. Schink: *Biochem. Biophys. Res. Comm.* ***349*** (2006) 480.
9. A. Adenier, M.M. Chehimi, I. Gallardo, J. Pinson, N. Vila: *Langmuir* ***20*** (2004) 8243.
10. T. Łuczak: *J Appl Electrochem* ***37*** (2007) 653.
11. IARC; in *IARC monographson the evaluation of carcinogenetic risks on humans* vol. ***77***, pp 431-401. Lyon, IARCPress, 2000.
12. W. Lijinsky, R.M. Kovatch: *Carcinogenesis* ***6*** (1985) 1679.
13. H. Hoshino, H. Tanooka: *Cancer Res.* ***38*** (1978) 3918.
14. Y. Konishi, A. Denda, K. Uchida, Y. Emi, H. Ura, Y. Yokose, K. Shiraiwa, M. Tsutsumi: *Fundam. Appl. Toxicol.* ***18*** (1992) 25.
15. J.B. Knaak, H.-W. Leung, W.T. Stott, J. Busch, J. Bilsky: *Rev. Environ. Contam. Toxicol.*, ***149*** (1997) 1.
16. P.M. Eller; in *NIOSH Manual of Analytical Methods* (DHHS (NIOSH) Publ. No. 94-113), 4th Ed., Cincinnati, OH, United States National Institute for Occupational Safety and Health [Method 3509], 1994.
17. E.M. Kenyon, S.K. Hammond, J. Shatkin, S.R. Woskie, M.F. Hallock, T.J. Smith: *Appl. Occup. Environ. Hyg.* ***8*** (1993) 655.
18. J. Sollenberg: *Proc. Cont. Quality* ***10*** (1997) 313.
19. B.A. Schubert, E. Hohaus, H.S. Dengel, W. Riepe, W. Maurer: *Gefahrstoffe—Reinhaltung der Luft* ***56*** (1996) 393.
20. L.A. Fernando: *J. Soc. Tribol. Lubric. Engin.* ***51*** (1995) 701.
21. M. Fukui, H. Konishi, K. Ohta, K. Tanaka: *Bunseki Kagaku* ***41*** (1992) T27.
22. W. Maurer, E. Hohaus, B. Schubert: *Parfüm. Kosmet.* ***77*** (1996) 262.
23. S. Karastogianni, C. Dendrinou-Samara, E. Ioannou, C. P. Raptopoulou, D. Hadjipavlou-Litina, S. Girousi: *J. Inorg. Biochem.* ***118*** (2013) 48.
24. C. Kokkinos, I. Raptis, A. Economou, T. Speliotis: *Electroanalysis* ***22*** (2010), 2359.