Electrocatalytic Determination of Sulfite using 1-[4-(Ferrocenylethynyl)phenyl]-1-ethanone Modified Carbon Paste Electrode

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The electrochemical behaviour of sulfite studied at the surface of 1-[4-(ferrocenylethynyl)phenyl]-1-ethanone modified carbon paste electrode (4-FEPEMCPE) in aqueous media using cyclic voltammetry and double step potential chronoamperometry. It has been found that under optimum condition (pH 8) in cyclic voltammetry, the oxidation of sulfite occurred at a potential about 280 mV less positive than that unmodified carbon paste electrode. The kinetic parameters such as electron transfer coefficient, α and catalytic reaction rate constant, K'_h were also determined using electrochemical approaches. The electrocatalytic oxidation peak current of sulfite shows a linear calibration curve were obtained in the range 3.0×10^{-4} M–1.2×10^{-2} M and 4.0×10^{-6} M–1.0×10^{-4} M of sulfite concentration with cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods, respectively. The detection limit (2δ) was determined as 1.4×10^{-5} M and 1.8×10^{-7} M by CV and DPV methods.

Key Words: 1-[4-(Ferrocenylethynyl)phenyl]-1-ethanone, Sulfite, Electrocatalysis, Chronoamperometry, Differential pulse voltammetry, Cyclic voltammetry.

INTRODUCTION

Sulfite is commonly used as a preservative, antioxidant and antibacterial agents in the food, pharmaceutical and brewing industries, respectively. Despite these advantages, the sulfite content in foods and beverages should be strictly limited due to its potential toxicity and products containing more than the established threshold level must be adequately labeled[1]. In particular, sulfiting agents have received widespread attention as a result of their allergic effect on those individuals who are hypersensitive[2]. This compound can be present in spent photofinishing solutions and their recovery or conversion to alternate forms is desired to minimize unwanted environmental contamination. In large quantities, sulfite and its oxidation products are pollutants. Therefore, more attention has been drawn to the development of methods for determination of sulfite during the last years.

In the literatures, several methods using titration[3], spectrophotometry[4,5], spectrofluorometry[6], flow injection analysis[7], enzymatic techniques[8], phosphorimetry[9] and chemiluminescence methods[10-12] have been reported for the measurement of sulfite. However, the majority of these methods require extensive sample pre-treatment and reagent preparation. In this sense, the development of electrochemical sensors for sulfite determination based on electrochemical properties have several advantages such as rapid response, high selectivity and sensitivity, low cost and no need of sample preparation. Investigation of electrochemical behaviour of sulfite showed a slow kinetic electron transfer in aqueous media at the surface of common metal electrodes[13]. Hence, acceleration of its electrochemical reaction by electrode modification is necessary. In the recent years some chemically modified electrodes with various mediators such as conductive polymers[14,15], iron(III) complexes of 1,10-phenanthrolines[16] metals penta-cyanonitrosylferrate[17,18], iron hexacyanoferrate[19] and copper hydroxide[20] immobilized at the surface of electrode have been designed. Such electrode modification s have the objective of increasing the stability of the electrode response, decreasing the stability of the electrode response, decreasing the overpotential associated with the electrode process and/or increasing the oxidative current of the sulfite. The incorporation of electrocatalysts into the electrode matrix can help to improve the instability of the attached or adsorbed modifiers on the electrode arising in the utilization of chemically modified electrodes[21,22]. Therefore, carbon paste electrodes spiked with catalyst may be suitable for this purpose. Because, the ease and fast low residual current, porous surface, control the amount of modifier and low cost are some advantages of chemically modified carbon paste electrodes[23].

On the other hand the ferrocene group of mediators has been successfully applied to the quantitation of several compounds and has been particularly important in the development of sensors[24]. We have previously reported the construction of some ferrocene derivatives modified carbon paste electrodes for electrocatalytic determination of some biological compounds[25-27].

In this paper, we describe the use of 1-[4-(ferrocenylethynyl) phenyl]-1-ethanone as a meditor for the electrooxidation of sulfite in aqueous media. In addition, the suitability of the 1-[4-(ferrocenyl-ethynyl) phenyl]-1-ethanone modified carbon paste electrode in the electrocatalysis and determination of sulfite are discussed by cyclic voltammetry, double potential step chronoamperometry and differential pulse voltammetry.

EXPERIMENTAL

The solvent used for the electrochemical studies was twice distilled water. Buffer solutions were prepared from orthophosphoric acid and its salts in the pH ranges 3-9. High viscosity paraffin (density = 0.88 g cm^{-3}) from Fluka was used as the pasting liquid for the carbon paste electrode. Graphite powder (particle diameter = 0.1 mm) from Merck was used as the working electrode (WE) substrate. The 1-[4-(ferrocenylethynyl)phenyl]-1-ethanone was prepared by a reported procedure[28]. Sodium sulfite was from Merck and was used as received. All other reagents were of analytical grade.

Working electrode: A 1 % (w/w) 1-[4-(ferrocenylethynyl)phenyl]-1-ethanone spiked carbon powder was made by dissolving the given quantity of 1-[4-(ferrocenyl-ethynyl)phenyl]-1-ethanone in diethyl ether and hand mixing with 99 times its weight of graphite powder with a mortar and pestle. The solvent was evaporated by stirring a 1:1 (w/w) mixture of 1 % 1-[4-(ferrocenyl-ethynyl)phenyl]-1-ethanone spiked carbon powder and paraffin oil was blended by hand-mixing and the resulting paste was inserted in the bottom of a glass tube (with internal radius 3 mm). The electrical connection was implemented by a copper wire lead fitted into a glass tube. A carbon paste electrode without 1-[4-(ferrocenylethynyl) phenyl]-1-ethanone was used as a blank to determine background current.

The electrochemical experiments were carried out using a Potentiostat/ Galvanostat (BHP 2061-C Electrochemical Analysis System, Behpajooh, Iran) coupled whit a Pentium II personal computer connected to a HP laser jet 6L printer and experiments were performed in three compartment cell. A platinum wire was used as the auxiliary electrode. The 1-[4-(ferrocenyl-ethynyl) phenyl]-1-ethanone modified carbon paste electrode (4-FEPEMCPE) was used as the working electrode. The pH-meter (Ion Analyzer 250, Corning) was used to read a pH of the buffered solution.

RESULTS AND DISCUSSION

Electrochemical behaviour of 4-FEPEMCPE

We have recently constructed 4-FEPEMCPE by incorporation of 1-[4-(ferrocenylethynyl)phenyl]-1-ethanone into carbon paste matrix and studied its electrochemical properties in buffered aqueous solution by cyclic voltammetry and double step potential chronoamperometry. Its cyclic voltammograms exhibits an anodic (E_{pa} = 0.63 V) and corresponding cathodic peaks with E_{pc} = 0.42 V *vs.* Ag|AgCl|KCl$_{sat}$ (Fig. l) related to Fc/Fc$^+$ redox couple with quasi-reversible behaviour[27]. The obtained result also shows that the redox process of Fc/Fc$^+$ in 1-[4-(ferrocenylethynyl) phenyl]-1-ethanone is independent on the pH of aqueous solution.
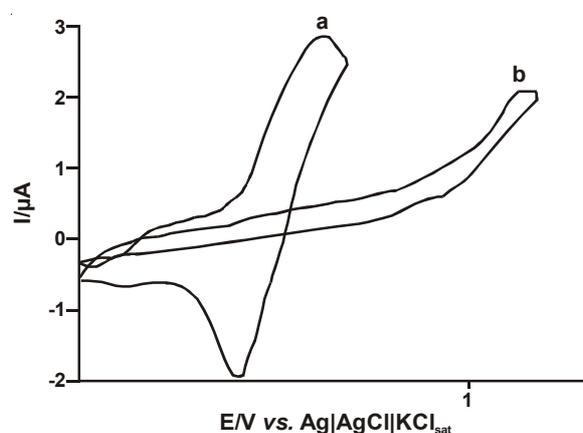
Fig. 1.   (a) Cyclic voltammogram of 4FEPEMCPE in 0.1 M phosphate buffer
solution (pH 7) (b) as (a) at the surface of bare carbon paste electrode
(scan rate 10 mV s^{-1})

Double step potential chronoamperometry was employed for investi-
gation the electrochemical processes of 4-FEPEMCPE. Fig. 2a shows the
current-time curve of the 4-FEPEMCPE obtaining by setting the working
electrode potential at 0.7 V (at the first potential step) and 0.35 V (at the
second potential step) *vs.* Ag|AgCl|KCl$_{sat}$ in a buffered aqueous solution
(pH 7). The results show symmetrical chronoamperograms with an equal
charge consumed for the oxidation and reduction of the redox couple in
the CPE. The plot of net electrolysis current *vs.* $t^{-1/2}$ shows a straight line
(Fig. 2b), which extrapolates close to the origin. Therefore, this type of
near-Cottrellian behaviour is not due to a linear semi-infinite diffusion
process but may be caused by finite diffusion in a thin film, where the
near-Cottrell equation behaviour can be approximated over a short time
period[29,30].

Consequently, we can assume diffusion controlled behaviour for charge
transfer at 4-FEPEMCPE and use the potential-step chronoamperometric
experiments to estimate the diffusion coefficient of 1-[4-(ferrocenyl-
ethynyl)pheny]-1-ethanone into the paraffin oil used for paste preparation.
The slope of the linear region of the I-t$^{-1/2}$ plot in the short time region
produces the apparent diffusion coefficient (D$_{app}$) of the spiked 1-[4-
(ferrocenylethynyl) phenyl]-1-ethanone into 4-FEPEMCPE by using the
Cottrell equation[31]:

$$I = n \, F \, A_g \, D_{app}^{1/2} \, c \, \pi^{-1/2} \, t^{-1/2} \tag{1}$$

where c is the known concentration, D$_{app}$ is the apparent diffusion coeffi-
cient of spiked 1-[4-(ferrocenylethynyl)phenyl]-1-ethanone in paraffin oil
and A$_g$ is the geometric area of this electrode. The diameter (d) of the

4-FEPEMCPE was measured and then the geometric area of the 4-FEPEMCPE was calculated according to $[\pi(d/2)^2]$. Therefore, we calculated the apparent diffusion coefficient for 1-[4-(ferrocenylethynyl)phenyl]-1-ethanone (Fig. 2b) in carbon paste matrix. It was found 1.1×10^{-10} cm^2 s^{-1}. While, in the equation n = 1, F = 96485 C mol^{-1}, A_g = 0.0907 cm^2 and corresponding c value was selected. This method has been used for estimation of D_{app} for 1,4-naphthoquinone and some its derivatives[30].
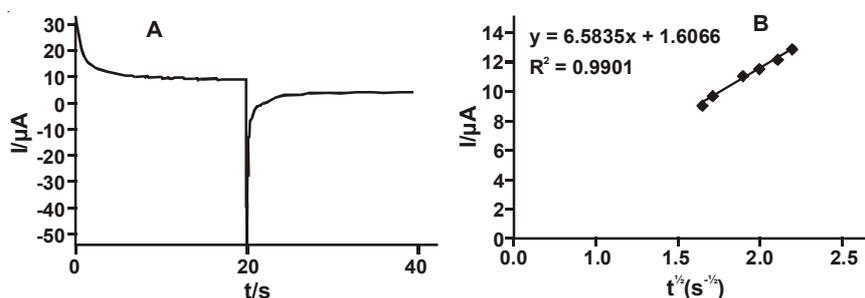
Fig. 2. (A) Double step potential chronoamperogram obtained at the 4-FEPEMCPE in absence of sulfite in 0.1 M phosphate buffer solution (pH 7). First and second potential step were 0.700 and 0.30 V *vs.* Ag|AgCl|KCl$_{sat}$ (B) Cottrell plot for curve (A)

Electrooxidation of sulfite at the surface of 4FEPEMCPE

It is well known that the electrochemical behaviour of sulfite is dependent on pH value of the aqueous solution, whereas the electrochemical properties of Fc/Fc$^+$ redox couple are independent pH. Therefore, we studied the electrochemical behaviour of sulfite in 0.1 M phosphate buffered solution with various pH (3 < pH < 9) at the surface of 4FEPEMCPE by cyclic voltammetry. The result shows that the catalytic current increases as pH increasing. This is probably due to a reaction mechanism involving proton transfer (equation):

$$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^- \qquad (2)$$
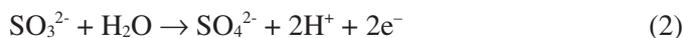
Therefore, pH has effect on the kinetic of the catalytic reaction. Fig. 3 shows the variation of I_{pa} *vs.* the variation of pH. As can be seen, that maximum electrocatalytic current was obtained at pH 8. Therefore, pH 8 was chosen as the optimum pH for electrocatalysis of sulfite oxidation at the surface of 4-FEPEMCPE. Hence, all electrochemical experiments were done at this pH.

The cyclic voltammograms obtained for an unmodified carbon paste electrode and for 4-FEPEMCPE in a phosphate buffer solution (0.1 M, pH 8) in the presence (1.0 mM) and absence of sulfite are illustrated in Fig. 4. At an unmodified CPE, the sulfite oxidation occurs irreversibly with a
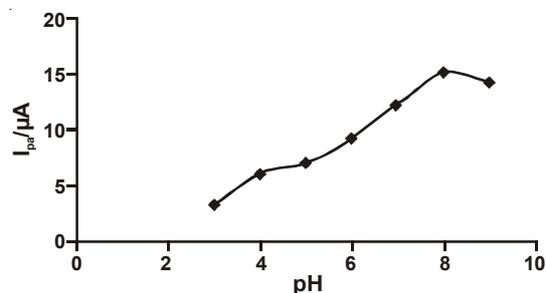
Fig. 3. Current-pH curve for electrooxidation of 1 mM sulfite in 0.1 M phosphate
buffer solution with various pH values: a) 3.00, b) 4.00, c) 5.00, d) 6.00, e)
7.00, f) 8.00 and h) 9.00 at the surface of 4FEPEMCPE (scan rate 10 mV s^{-1})

peak potential of nearly 0.910 V *vs.* Ag|AgCl|KCl$_{sat}$ (Fig. 4b), in the
absence of sulfite no peaks appears (Fig. 4a). In 1 mM of sulfite solution,
the anodic peak that is observed for 4-FEPEMCPE in the absence of sulfite
increases appreciably, while the corresponding cathodic wave disappears
on the reverse scan (Fig. 4c and d). This behaviour is typical that expected
for electrocatalysis at chemically modified electrodes. The sulfite oxida-
tion occurs at 0.630 V *vs.* Ag|AgCl|KCl$_{sat}$ at 4-FEPEMCPE surface; there-
fore, it is shifted about 0.280 V toward less positive potential.
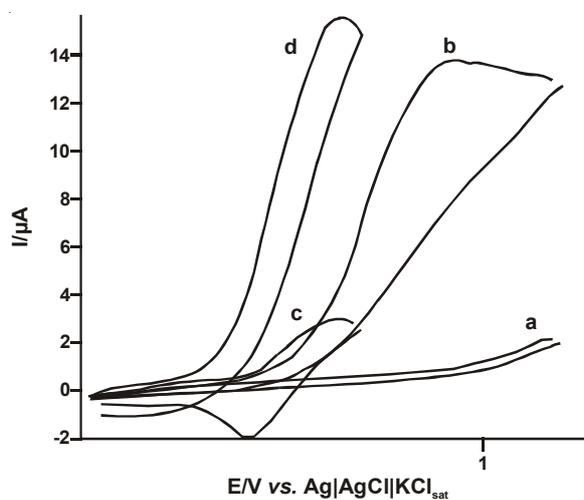
Fig. 4.   Cyclic voltammograms of a) CPE in 0.1 M phosphate buffer solution (pH 8)
b) as a) in the presence of 1 mM sulfite c) as a) and d) as b) at the surface of
4-FEPEMCPE (scan rate 10mV s^{-1})

The above results show the oxidation of sulfite is facilitated and cata-
lyzed by the presence of 1-[4-(ferrocenylethynyl)phenyl]-1-ethanone spiked
in to carbon paste electrode. The presence of 1-[4-(ferrocenylethynyl)
pheny]-1-ethanone as a mediator on the surface electrode provides an

alternative reaction site to carbon paste for electron transfer process of sulfite. Therefore, current due to the oxidation of sulfite is increased when a 4-FEPEMCPE was used.

In order to get the information on the rate determining step, Tafel slope (b) determinates using the following equation for a totally irreversible diffusion controlled process[32]:

$$E_P = b/2 \log \nu + \text{constant} \tag{3}$$

Based on eqn. 3, the slope of E_p vs. $\log \nu$ is b/2, where b indicates the tafel slope. The slope of E_p vs. $\log \nu$ plot was found to be 0.0737 V in this work (Fig. 5), thus, $b = 2 \times 0.0737 = 0.1474$ V. This slope value indicated an electron transfer process, which is the rate limiting step by assumption of a transfer coefficient (α) equal to 0.41. Also, the values of αn_α (where α is the transfer coefficient and n_α is the number of electrons involved in the rate determining step) were calculated for the oxidation of sulfite at pH 8 at both modified and unmodified CPEs according to the following equation[29]:

$$\alpha n_\alpha = 0.048/(E_P-E_{P/2}) \tag{4}$$

Here, $E_{P/2}$ is the potential corresponding to $I_{P/2}$. The values for αn_α, were found to be 0.4 and 0.19 for the oxidation of sulfite at the surface of 4-FEPEMCPE and CPE, respectively. These values clearly show that not only the overpotential for sulfite oxidation is reduced at the surface of 4-FEPEMCPE, but also the rate of the electron transfer process is appreciately enhanced. This phenomenon is thus confirmed by the larger I_a values recorded during cyclic voltammetry at 4-FEPEMCPE.

Chronoamperometric studies

Double step potential chronoamperometry was also employed to investigate the electrochemical behaviour of aqueous buffered solution (pH 8) containing of various concentration of sulfite at 4-FEPEMCPE by setting the working electrode potential at 0.7 V (at the first potential step) and 0.35 V (at the second potential step) vs. Ag|AgCl|KCl$_{sat}$. The results show that, there is not any net cathodic current corresponding to the reduction of 1-[4-(ferrocenyl-ethynyl) pheny1]-1-ethanone ion in the presence of sulfite, when the potential is stepped from 0.7 to 0.35 V vs. Ag|AgCl|KCl$_{sat}$. However, in the presence of sulfite the charge value associated with forward chronoamperometry is significantly greater than that observed for backward chronoamperometry. The linearity of electrocatalytic current vs. $v^{1/2}$ indicates that the current must be controlled by diffusion of sulfite from bulk solution toward surface of electrode. Therefore the slope of this linear plot can be used to estimate the diffusion coefficient (D) of sulfite. The mean value of the D found to be 3.56×10^{-6} cm^2 s^{-1}. Therefore, the results show that mediator at the surface of 4-FEPEMCPE can catalyze the oxidation of sulfite.

The rate constant for the chemical reaction between sulfite and redox sites in 4-FEPEMCPE, K'_h can be evaluated by chronoamperometry according to the reported method[33]:

$$I_C/I_L = \gamma^{1/2} [\pi^{1/2} \text{ erf } (\gamma^{1/2}) + \exp (-\gamma)/\gamma^{1/2}] \tag{5}$$

where I_C is the catalytic current of 4-FEPEMCPE in the presence of sulfite and I_L is the limited current in the absence of sulfite and $\gamma = k_h C_b t$ (C_b is the bulk concentration of sulfite, mol cm^{-3}) is the argument of error function. In the cases where γ exceeds 2, the error function is almost equal to 1 and the above equation can be reduced to:

$$I_C/I_L = \pi^{1/2} \gamma^{1/2} = \pi^{1/2} (k_h C_b t)^{1/2} \tag{6}$$

where k_h and t are the catalytic rate constant (cm^3 mol^{-1} s^{-1}) and time elapsed (s) respectively. The above eqn. 6 can be used to calculate the rate constant of catalytic process, k_h. Having measured the catalytic current, *i.e.* I_C, it is possible to carry out the electrode process in identical condition, but in the absence of sulfite, in order to determine I_L. From the slope of I_C/I_L *vs.* $t^{1/2}$ plot the value of k_h can be simply calculated for a given concentration of substrate. The calculated value of k_h is 1.05×10^4 cm^3 mol^{-1} s^{-1} using the slope of I_C/I_L- $t^{1/2}$ plot (Fig. 6). This value of k_h explains as well as the sharp feature of the catalytic peak observed for catalytic oxidation of sulfite at the surface of 4-FEPEMCPE. On the other hand, the surface coverage (Γ) of a modified electrode prepared at optimum condition was obtained from the equation $\Gamma = Q/nFA$, where Q is the charge obtained by integration the anodic peak under the background correction, A is the geometric area of electrode and other symbols have their usual meanings. The calculated value of Γ was 7.2×10^{-8} mol cm^{-2} at pH 8. Using this value of coverage, the heterogeneous rate constant of catalytic reaction was calculated as $K'_h = 2.1 \times 10^{-1}$ cm s^{-1}.
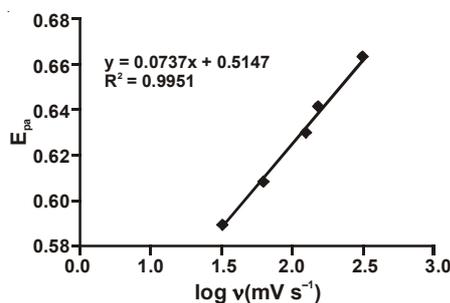
Fig. 5. The peak potential, E_p dependence on log (ν) for the oxidation of sulfite at the surface of 4-FEPEMCPE
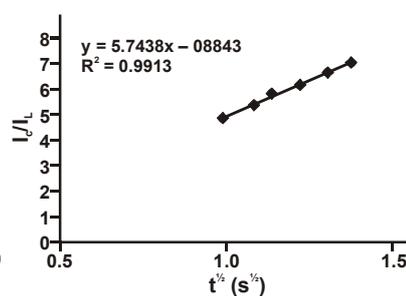
Fig. 6. Dependence of I_c/I_L on the $t^{1/2}$ driven from the chronoamperogram data

Electrocatalytic determination of sulfite: The electrocatalytic peak current of sulfite oxidation at the surface of the 4-FEPEMCPE can be used for determination of sulfite in solution. Therefore, cyclic voltammetry and differential pulse voltammetry experiments were performed using 4-FEPEMCPE in phosphate buffer solution containing various concentration of sulfite. The results show that the electrocatalytic peak current of sulfite oxidation at the surface of 4-FEPEMCPE was linearly dependent on the sulfite concentration and the range of this linearity depended on the amount of mediator in the electrode matrix. The mediated oxidation peak currents of sulfite at the surface of 4-FEPEMCPE were proportional to the concentration of the sulfite within the ranges 3×10^{-4}–1.2×10^{-2} M (with the correlation coefficient of 0.995) and 4×10^{-6}–1×10^{-4} M (with the correlation coefficient of 0.9964) in the cyclic voltammetry and differential pulse voltammetry, respectively (Figs. 7a and b). The detection limits (2σ) were 1.4×10^{-5} and 1.8×10^{-7} M for CV and DPV, respectively.
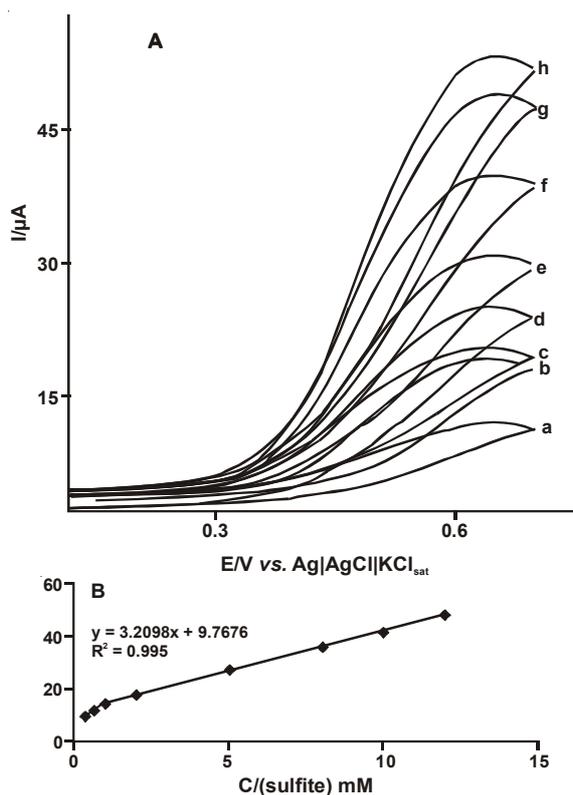
Fig. 7. (A) Cyclic voltammograms of sulfite at various concentration: a) 0.3; b) 0.5; c) 1; d) 2; e) 5; f) 8; g) 10 and h) 12 mM at the surface of 4-FEPEMCPE in 0.1 M buffer solution (pH 8.00) at a scan rate of 10 mV s^{-1} (B) Plot of electrocatalytic peak current [from CV of (A)] *vs.* the sulfite concentrations

Determination of sulfite in real samples: In order to demonstrate the catalytic oxidation of sulfite in a real sample, we examined this ability in determining sulfite in weak liquor from the wood and paper industry. Fig. 8 shows the cyclic voltammograms recorded for the diluted weak liquor in the phosphate buffer 0.1 M and $LiClO_4$ 0.1 M (curve a). As can be seen in this Figure, adding sulfite to the solution caused an increase in the oxidation peak height (curves b and c). Thus the peak was attributed to sulfite oxidation. This peak appeared about 980 mV which is 70 mV more than the 910 mV related to standard solutions of sulfite due to matrix effect. The determination of sulfite in a sample was carried out by the standard addition method for presentation of any matrix effect. By this method sulfite concentration in the weak liquor from the wood and paper factory of Mazandaran province in Iran was about 0.1 M. The relative standard deviation obtained from the line equation ($R^2 = 0.9986$) for the real sample was 4.3 %. The accuracy was examined by comparison of data obtained from this method with a recognized common method[34] for determination of sulfite (oxidation-reduction titration in acid solution of KIO_3/ KI in the presence of starch as indicator). The results from the statistical calculation indicate good agreement between the mean values (t-test) and precision (f-test) for the two methods.

Interference study: A class of wood extractive materials is phenolic compounds which seem electroactive and exist in wood[35]. Thus the interference effect of some phenolic compounds such as gallic acid, ellagic acid and chrysin in the determination of sulfite in a weak liquor solution has been investigated. The cyclic voltammogram for the weak liquor (Fig. 9 curve b) shows that in the range of the sweep potential only the sulfite oxidation peak is observed, while after addition of gallic acid from its standard solution to the same weak liquor a new oxidation peak (Fig. 9, curve c) appears at 0.250 V that is related to gallic acid oxidation. Other phenolic compounds show similar effects.

Thus, trace phenolic compounds do not interfere with this electrocatalytic method for sulfite determination in weak liquor solution.

Conclusions

This work shows the ability of 1-[4-(ferrocenyl-ethynyl) phenyl]-1-ethanone as a modifier in carbon paste electrode for electrocatalysis of sulfite oxidation. The results demonstrated that the electrooxidation of sulfite at the surface 4FEPEMCPE occurs at potential about 280 mV less positive that bare carbon paste electrode. The kinetic parameter of the electrocatalytic process, the diffusion coefficients of sulfite in an aqueous solution and 1-[4-(ferrocenyl-ethynyl) phenyl]-1-ethanone in carbon paste matrix were determined. Finally, the electrocatalytic oxidation currents of
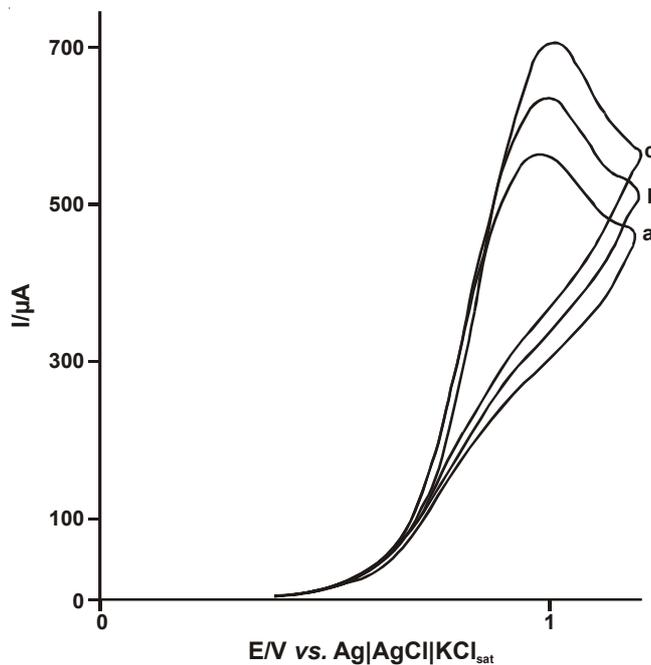
Fig. 8.   Cyclic voltammograms of a) solution of 5 order dilution of weak liquor from wood and paper factory in the presence of 0.1 M LiClO$_4$ + 0.1 M phosphate buffer at pH 8.00 b), c) as a) after addition sodium sulfite 2 and 4 mM, respectivity (ν = 10 mV s^{-1})
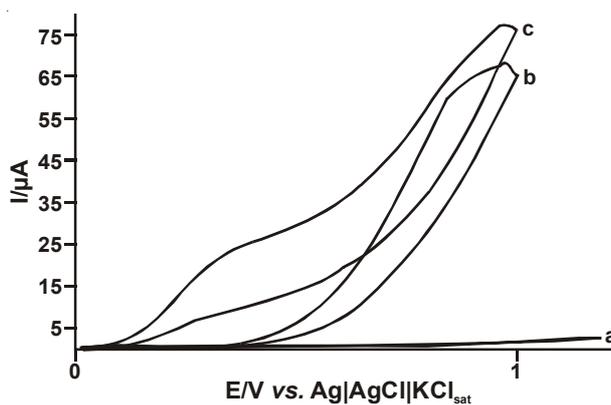
Fig. 9.   Cyclic voltammograms of a) 0.1 M phosphate buffer + 0.1 M LiClO$_4$; b) as a) + 0.5 mL of weak liquor solution; c) as b) + 1mm of gallic acid; pH 8.00 (ν = 10 mV s^{-1})

sulfite at the surface of 4-FEPEMCPE were linear to concentration of sulfite. In addition, results show some phenolic compounds such as gallic acid, ellagic acid and chrysin have not any interference effect in the determination of sulfite in a weak liquor solution.

REFERENCES

1. R. Walker, *Food. Add. Contam.*, **2**, 5 (1985).
2. L.G. Decnopweever and J.C. Kraak, *Anal. Chim. Acta*, **337**, 125 (1997).
3. G. Monnier and S. Williams, *Analyst*, **95**, 119 (1972).
4. M.A. Segundo, A.O.S.S. Rangel, A. Cladera and V. Cerda, *Analyst*, **125**, 1501 (2000).
5. I.V. Polyayeva, N.L. Yegorova, L.P. Experiandova and A.B. Blank, *Anal. Chim. Acta*, **357**, 239 (1997).
6. X.F. Yang, X.Q. Gue and Y.B. Zhao, *Anal. Chim. Acta*, **456**, 121 (2002).
7. X. Su, W. Wei, L. Nie and S. Yao, *Analyst*, **123**, 221 (1998).
8. M. Situmorang, D.B. Hibbert, J.J. Gooding and D. Barnett, *Analyst*, **124**, 1775 (1999).
9. D. Papkovsky, M.A. Uskova, G.V. Ponomarev, T. Korpela, S. Kulmala and G.G. GuIlbault, *Anal. Chim. Acta*, **374**, 1 (1998).
10. R.L. Bonifaio and N. Coichev, *Anal. Chim. Acta*, **517**, 125 (2004).
11. F.W. Wu, Z.K. He, H. Meng, L.J. Yoang and X.Y. Li, *Fresenius' J. Anal. Chem.*, **362**, 566 (1998).
12. D.A. Paulls and A. Thownshend, *Analyst*, **120**, 467 (1995).
13. S.M. Chen, *Inorg. Chim. Acta*, **429**, 143 (1996).
14. S. Marcos, N. Alcubierre, J. Galban and J.R. Castillo, *Anal. Chim. Acta*, **502**, 5027 (2004).
15. R. Carballo, V.C. Dall, Orto, A.L. Balbo and I. Rezzano, *Sens. Actua, B*, **88**, 155 (2003).
16. S.M. Chen, *J. Electroanal. Chem.*, **401**, 147 (1996).
17. M.H. Pournaghi-Azar, M. Hydarpour and H. Dastangoo, *Anal. Chim. Acta*, **479**, 133 (2003).
18. M.H. Pournaghi-Azar and R.E. Sabzi, *Electroanalysis*, **16**, 860 (2004).
19. T. Garcia, E. Casero, E. Lorenzo and F. Pariente, *Sens. Actuators, B*, **106**, 803 (2005).
20. I.G. Casella, M. Contursi and E. Desimnoni, *Analyst*, **127**, 647 (2002).
21. T. Kuwana, C. Ueda and D.C.S. Tae, *Anal. Chem.*, **54**, 850 (1982).
22. M.C. Pham and J.E. Dubois, *J. Electroanal. Chem.*, **199**, 153 (1986).
23. G. Dryhrst and D.L. McAallister, in eds.: P.T. Kissinger and W.R. Heinman, Laboratory Techniques in Electroanalytical Chemistry, Marcel Dekker, New York (1984).
24. S.A. Wring and J.P. Hart, *Analyst*, **117**, 1215 (1992).
25. J.B. Raoof, R. Ojani and A. Kiani, *J. Electroanal. Chem.*, **515**, 45 (2001).
26 J.B. Raoof, R. Ojani and M. Kolbadinezhad, *Electroanalysis*, **17**, 2043 (2005).
27. J.B. Raoof, R. Ojani, R. Hosseinzadeh and V. Ghasemi, *Anal. Sci.*, **19**, 1251 (2003).
28. R. Hosseinzadeh, Ph.D. Thesis, Justus-Liebig-Universitate, Giessen, Germany (1999).
29. E.S. Takeuchi and R.W. Murray, *J. Electroanal. Chem.*, **188**, 49 (1985).
30. S.M. Golabi and J.B. Raoof, *J. Electroanal. Chem.*, **416**, 75 (1996).
31. R. Greef, R. Paet, L.M. Peter, D. Pletcher and J. Robinson, Instrumental Methods in Electrochemistry, Ellis Horwood, Chichester (1990).
32. M.H. Pournaghi-Azar and H. Razmi-Nerbin, *J. Electroanal. Chem.*, **488**, 17 (2000).
33. Z. Galus, Fundamentals of Electrochemical Analysis, Ellis Horwood, New York (1976).
34. J. Berglund, P. Werndrap and L.I. Elding, *J. Chem. Soc., Dalton Trans.*, 1435 (1994).
35. E. Sjostron, Wood Chemistry, Fundamentals and Application, Academic Press (1981).