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Electrocatalytic oxidation of sulfite by acetylferrocene at glassy carbon electrode

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The electrochemical oxidation of sulfite catalyzed by acetylferrocene (AFc) at a glassy carbon electrode (GCE) in 0.2 M $NaClO_4$ aqueous solution has been studied by cyclic voltammetry. Although sulfite itself showed a sluggish electrochemical response at the GCE, the response could be enhanced greatly by using AFc as a mediator, which enables a sensitive determination of the substrate (sulfite). The reaction rate constant for catalytic oxidation was evaluated as $(7.02 \pm 0.05) \times 10^4$ M^{-1} s^{-1} by chronoamperometry. Experimental conditions that maximize the current efficiency of the electrocatalytic oxidation, such as the pH and both the catalyst (AFc) and substrate (sulfite) concentrations, were also investigated. The electrochemical kinetics of electrocatalytic oxidation of sulfite by AFc has been studied by cyclic voltammetry. In the presence of 5×10^{-4} M AFc, the oxidation current is proportional to the sulfite concentration and the calibration plot was linear over the concentration range 2×10^{-4}–2.4×10^{-3} M. This result can be applied in the determination of real samples. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: electrocatalytic oxidation; sulfite; acetylferrocene; glassy carbon electrode; electrochemical kinetics

INTRODUCTION

Sulfites are commonly used as a preservative in the food industry due to their addition to some products, such as vegetables, fruits and several beverages, to prevent oxidation, inhibit bacterial growth and assist in preserving vitamin C.[1] Despite these great advantages, the sulfite content in both 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. The existing methods allowing accurate measurement of sulfite are very important for the food and other industries in order to control the product and surrounding quality, therefore great attention has been drawn to the development of these methods for its determination during recent years.[2–15,18]

The previous methods for sulfite determination have included titration,[2] spectrophotometry,[3,4] chemiluminescence[5,6] and flow injection analysis (FIA).[7] Several electrochemical techniques and electrode materials have been explored in the research of their detection, determination and electrochemical oxidation. It has been demonstrated also that sulfite can be electrocatalyzed oxidatively with a glassy carbon electrode (GCE) that has been chemically modified with iron hexacyanoferrate film,[8] polymeric iron tetra(4-aminophenyl) porphyrin,[9] cobalt pentacyanonitrosylferrate film[10] or polymer films.[11] A metal aluminum electrode modified with nickel pentacyanonitrosylferrate film[12] and a platinum-based glassy carbon electrode (Pt-CME)[13] were also investigated in the catalytic electrochemical oxidation of sulfite. The reactions of sulfite with homogeneous mediators such as iron phenanthrolines[14] or water-soluble iron porphyrins[15] have been reported previously.

Ferrocene derivatives have found a number of applications in organic synthesis as well as in materials,[16] and recently the ferrocene/ferricenium cation system has found an interesting field of application as a mediator in biosensors.[17] Ferrocenemonocarboxylic acid, one of the ferrocene derivatives used as a homogeneous mediator to

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catalyze the electrochemical oxidation of sulfite, has been reported previously[18] but the reaction of sulfite with acetylferrocene (AFc) has not been reported in the literature.

As a continuation of our previous work[19,20] it was found that direct oxidation of sulfite at a GCE is sluggish, but AFc in 0.2 M $NaClO_4$ aqueous solution can catalyze the electrochemical oxidation of sulfite dramatically and can make the oxidation potential shift negatively by ~0.15 V and greatly enhance the oxidation peak current. Thus, AFc can be used as a homogeneous mediator for catalytic oxidation of sulfite. The influence of the experimental conditions on catalytic peak currents and potentials was also investigated by cyclic voltammetry. The reaction rate constant was evaluated by chronoamperometry and the electrocatalytic kinetic behavior of sulfite oxidation in the presence of AFc on GCE was also investigated in this work. This result can open a new avenue for the electrochemical determination of sulfite using AFc as a mediator.

EXPERIMENTAL

Chemicals

Acetylferrocene was synthesized and purified as described previously[21] and sodium sulfite (analytical grade, from Shanghai Chemical Reagent Company) was used without further purification. All solutions were prepared by using deoxygenated and doubly distilled water. All other chemicals were analytical grade and used as received.

Apparatus

The electrochemical measurements were recorded using a computer-controlled CHI660A Electrochemistry Workstation (CH Instrument, USA) with a conventional three-electrode configuration. A CHI102 GCE with a geometric area of ~0.15 cm^2 served as the working electrode, a CHI115 platinum wire provided the counter-electrode and a CHI150 saturated calomel reference electrode (SCE) completed the single cylindrical compartment cell assembly with a volume of 20 cm^3. The reference electrode was connected to the main body of the cell through a Luggin capillary whose end was centered on the working electrode and positioned closed to the electrode surface. All potentials measured and reported in this work were versus SCE.

Procedure

A GCE was polished with 0.3 μm α-Al_2O_3, rinsed with doubly distilled water and sonicated in 5 M H_2SO_4 for 3 min and rinsed with doubly distilled water again before every run. The electrolyte solution was 0.2 M $NaClO_4$ aqueous solution. All solutions were thoroughly flushed with high-purity nitrogen for 5 min, to remove oxygen from the solutions in the electrochemical cell. All experiments were carried out at room temperature.

RESULTS AND DISCUSSION

Cyclic voltammetric behavior of AFc in aqueous sodium perchlorate solution

The electrochemical redox reaction of AFc at a GCE in aqueous 0.2 M $NaClO_4$ solution is a quasi-reversible process with $\Delta E_p \sim 60$ mV and $I_{pa}/I_{pc} \sim 1$, as shown in Fig. 1c. The plot of peak current versus the square root of the scan rate ($v^{1/2}$) for the redox couple is a straight line, as expected for a diffusion-limited electrochemical process.

Stability of AFc

The stability of AFc in various media could be observed easily from cyclic voltammograms. The voltammetric behavior of AFc at scan rates of 20, 50 and 100 mV s^{-1} in different supporting electrolyte solutions, such as aqueous NaCl, NaAc, $NaNO_3$, Na_2SO_4, $NaClO_4$ and $Na_2HPO_4 + NaH_2PO_4$, has been investigated. From cyclic voltammograms in aqueous $NaNO_3$, Na_2SO_4 and $NaClO_4$ solutions, the peak potential difference ΔE_p and the I_{pa}/I_{pc} ratio were unaffected by the scan rate, which means that the cation AFc^+ is stable in these media. In aqueous NaCl and NaAc solutions, the peak potential difference ΔE_p was virtually unaffected (it stayed at 70–80 mV) but the cathodic current was obviously decreased and the I_{pa}/I_{pc} ratio increased with the increasing scan rate. However, in aqueous $Na_2HPO_4 + NaH_2PO_4$ solution there was an irreversible cyclic voltammogram in which the cathodic peak current almost disappeared. This possibly means that the cation AFc^+ has a stronger association capability with $HPO_4^{2-} + H_2PO_4^-$ than with Cl^-, Ac^-, NO_3^-, SO_4^{2-} and ClO_4^- in aqueous solution systems due to the 'ion-pair' effect.[22] Also, the influence of the concentration of the supporting electrolyte on the cyclic voltammetric behavior of AFc in the concentration range of 0.1–0.5 M was examined.

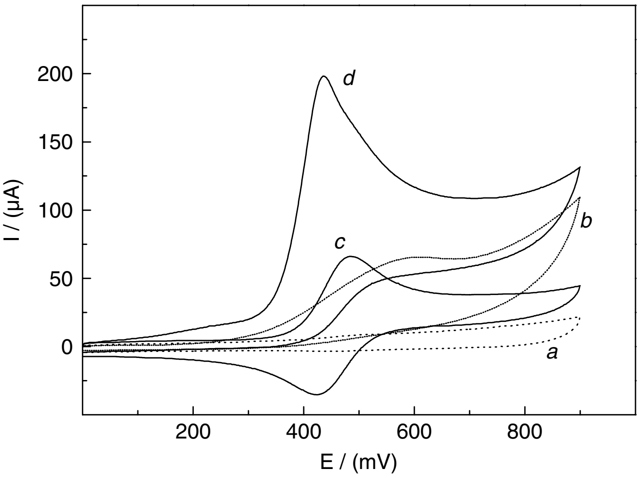

Figure 1. Cyclic voltammograms of: (a) 0.2 M $NaClO_4$; (b) 0.2 M $NaClO_4 + 2 \times 10^{-3}$ M sulfite; (c) 0.2 M $NaClO_4 + 5 \times 10^{-4}$ M AFc; (d) 0.2 M $NaClO_4 + 2 \times 10^{-3}$ M sulfite $+5 \times 10^{-4}$ M AFc. Scan rate = 50 mV s^{-1}.

The experimental results showed that in 0.2 M $NaClO_4$ aqueous solution AFc has a well-defined electrochemical quasi-reversible redox, reaction.

The effect of solution pH on the stability of AFc and its cation AFc^+ was investigated in 0.2 M $NaClO_4$ solution, whose acidity was adjusted with 0.5 M $HClO_4$ or 0.5 M NaOH. The experimental results show that AFc and its cation AFc^+ are more stable in acidic and neutral aqueous solutions than in basic solution. The peak potentials of AFc hardly changed at pH 2–9, which means that the voltammetric behavior of AFc does not involve a proton transfer process, just a single-electron transfer process under the experimental conditions (see curves in Fig. 2). The peak currents of the catalytical oxidation increased slightly at pH 2–4 but hardly changed at pH 4–8. However, it should be noted that the anodic peak current decreased in basic solutions of pH > 8, in which the ratio of anodic peak current to cathodic peak current deviated greatly from unity. This observation accounted for the decomposition of AFc,[21] therefore the redox couple of AFc at a GCE is a single-electron transfer process without proton participation and is assigned the following electrode reaction:

$$\mathrm{AFc} \rightleftharpoons \mathrm{AFc}^+ + \mathrm{e}$$

Electrochemical oxidation of sulfite in the absence and presence of AFc

Sulfite oxidation in the absence of a mediator occurred irreversibly with a peak potential of nearly +0.60 V, as shown in Fig. 1b. When AFc was added to the solution, a large irreversible oxidation peak wave emerged in cyclic voltammograms at about +0.45 V in Fig. 1d, that shifted negatively by ~0.15 V, and in the given level of AFc concentration the oxidation peak current increased with increasing sulfite concentration. This concentration range can be varied by varying the mediator concentration of AFc. This electrochemical behavior is typical for electrocatalytic oxidation by a mediator.

It can also be noted from the experimental results that with increasing scan rates the catalytic oxidation peak potential shifts positively, suggesting a kinetic limitation in the reaction between the mediator (AFc) and the substrate (sulfite). However, the catalytic peak current increase linearly with the square root of the scan rate ($\nu^{1/2}$) in the range 20–1000 mV s^{-1}, which suggests that at sufficient overpotential the reaction is mass transportation controlled.[23]

Effects of experimental conditions on catalytic peak currents and potentials

The catalytic oxidation peak current of sulfite depends on the concentration of AFc. The peak current increased with increasing AFc concentration at a constant sulfite concentration of 2×10^{-3} M (Fig. 3). If the AFc concentration is $>1.8 \times 10^{-4}$ M, the catalytic peak current increases weakly with increasing AFc concentration, departs from linearity and gradually reaches a plateau line. The anode oxidation peak potential shifted negatively when the concentration of AFc was increased.

The influence of solution pH on the catalytic peak currents and potentials was assessed by examining the electrode response in solutions buffered at pH 1–9 (Fig. 4). The variation curve of I_P vs. pH behavior shows that the catalytic oxidation peak current decreases steadily as the acidity of the solution is increased (pH 4–1) and also decreases as the acidity of the solution is decreased (pH 8–9). In the pH range 4–8 the variation of the catalytic peak current with pH is slight and almost a straight line. In the pH range 1–4 the peak potential of the catalytic oxidation decreases by ~57 mV with pH unit increase. Within the pH range 4–9 the peak potential hardly changed, which shows that this electrocatalytic oxidation process involves proton participation. From Fig. 4 it can be seen that the plot of E_P vs. pH gives a straight line with a slope of −0.057 V.

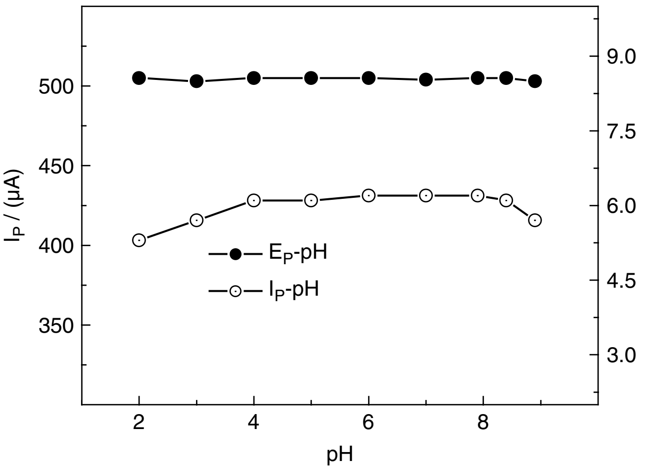

Figure 2. Dependence of I_P and E_P of 5×10^{-4} M AFc on pH in 0.2 M $NaClO_4$ aqueous solution. Scan rate = 50 mV s^{-1}.

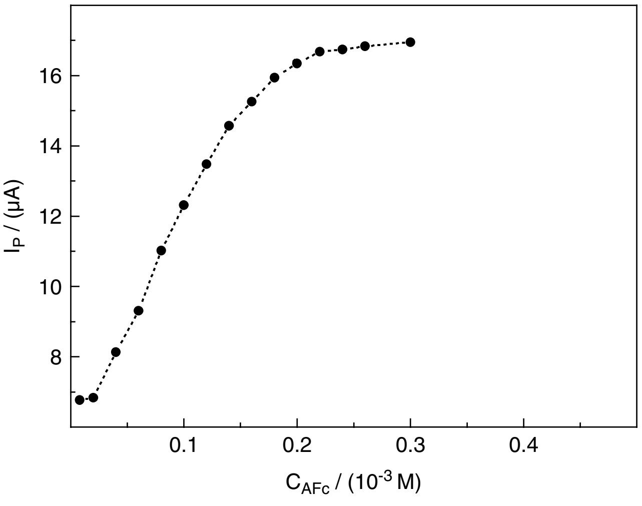

Figure 3. Plot of I_P vs. concentration of AFc in the presence of 2×10^{-3} M sulfite. Scan rate = 50 mV s^{-1}.

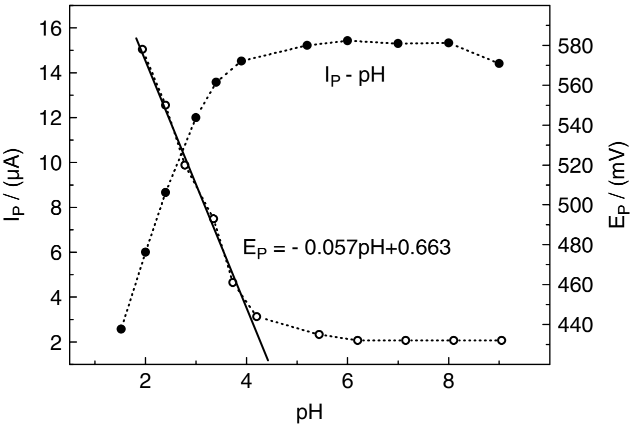

Figure 4. Dependence of I_P and E_P on pH in 0.2 M $NaClO_4$ solution. The concentrations of AFc and sulfite are 5×10^{-4} M and 2×10^{-3} M, respectively. Scan rate = 50 mV s^{-1}.

According to the Nernst equation of the electrocatalytic oxidation reaction of sulfite with AFc, we know that there are two protons involved and two electron transfers as well.

Chronoamperometric experiments

Because AFc can act as a homogeneous mediator for electro-oxidation of sulfite, it should follow a chronoamperometric equation as follows[24]

$$I_C/I_L = \lambda^{1/2}[\pi^{1/2}\, erf(\lambda^{1/2}) + \exp(-\lambda)/\lambda^{1/2}] \qquad (1)$$

where I_C is the catalytic current in the presence of sulfite, I_L is the diffusion-limited current in the absence of sulfite and $\lambda = kC^0t$ (k is the rate constant of the following chemical reaction, namely the rate constant of the electrocatalytic oxidation of sulfite by AFc, C^0 is the bulk initial concentration of sulfite) is the argument of the error function. In the cases where λ exceeds 1.5, the error function is almost equal to unity and the reaction zone is in the pure kinetic region, Eqn (1) can be reduced to

$$I_C/I_L = \pi^{1/2}\lambda^{1/2} = \pi^{1/2}(kC^0t)^{1/2} \qquad (2)$$

This equation can be used to calculate the rate constant of the catalytic process, k. Having measured the catalytic current, i.e. I_C, it is possible to carry out the electrode process in identical conditions but in the absence of sulfite, in order to determine I_L. Knowing that the value of I_C/I_L is proportional to $\lambda^{1/2}$, a plot of I_C/I_L vs. $\lambda^{1/2}$ can be given by combining Eqn (1) with Eqn (2) and used as a working curve for chronoamperometry. In this way, $\lambda^{1/2}$ can be determined from the working curve after measuring I_C and I_L, and then one can simply calculate the value of the rate constant k from the slope if C^0 (a given concentration of substrate) and t are known. The advantage of this method is that it is unnecessary to know the diffusion coefficient or the electrode area.

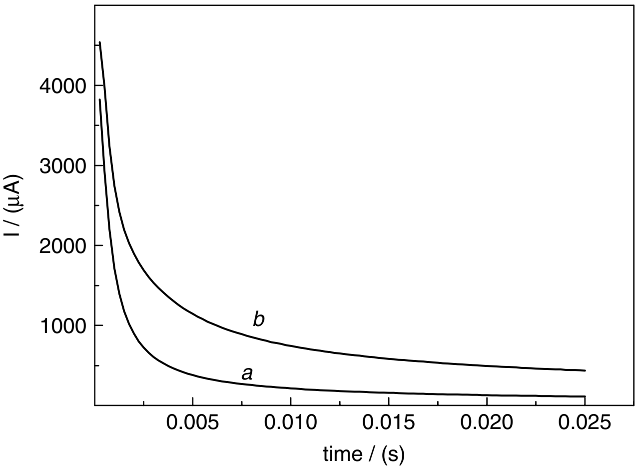

Figure 5. Chronoamperograms of 5×10^{-4} M AFc in the absence (a) and presence (b) of 2×10^{-3} M sulfite.

The chronoamperograms in the absence and presence of sulfite are shown in Fig. 5. The potential was stepped from 0 to 0.90 V. It is apparent that the current decayed slowly in the presence of sulfite due to the reaction of AFc and sulfite. Both I_C and I_L were measured at $t = 2.25$ ms, where $I_C/I_L > 2.2$, and the catalytic rate constant k was calculated to be $(7.02 \pm 0.05) \times 10^4$ M^{-1} s^{-1}.

Electrocatalytic kinetics of sulfite oxidation on GCE in the presence of AFc

For information on the rate-determining step, a Tafel plot was drawn using the data derived from the rising part of the current–voltage curve at a scan rate of 50 mV s^{-1}. A slope of 114.87 mV per decade is obtained, indicating a two-electron transfer to be rate limiting, assuming a transfer coefficient of $\alpha = 0.51$ (Fig. 6a). The other Tafel slope (Fig. 6b) has been obtained by another method. Figure 6 shows that the peak potential E_P is proportional to log ν. The E_P vs. log ν plot has a slope of $\partial E_P/\partial \log \nu = 58.72$ mV. The Tafel slope may be estimated according to the equation for a totally irreversible diffusion-controlled process[25]

$$E_P = (b \; \log \; \nu)/2 + \text{constant}$$

On the basis of the equation, the slope of E_P vs. $\log \nu$ is $b/2$, where b indicates the Tafel slope (Fig. 6b). Thus $b = 2 \times \partial E_P/\partial \log v = 117.44$ mV. This result is close to that obtained from polarization measurements. From the equation $b = 2.303\ RT/n\alpha F$ we can calculate $n\alpha = 1.02$, because $n = 2$ and so $\alpha = 0.51$. This indicates a two-electron transfer to be the rate-determined step, assuming a transfer coefficient of $\alpha = 0.51$.

The catalytic peak current I_P is proportional to the concentration of sulfite in the concentration range 2×10^{-4}–$2.4 \times$

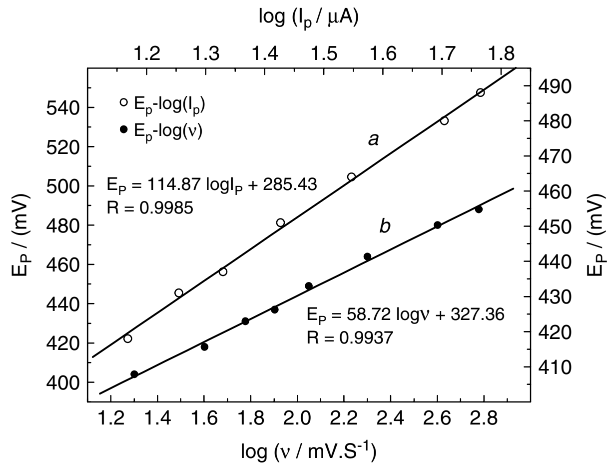

Figure 6. Tafel plot of AFc and sulfite: (a) E_P vs. $\log I_P$; (b) E_P vs. $\log v$. The concentrations of AFc and sulfite are 5×10^{-4} M and 2×10^{-3} M, respectively. Scan rate = 50 mV s^{-1}.

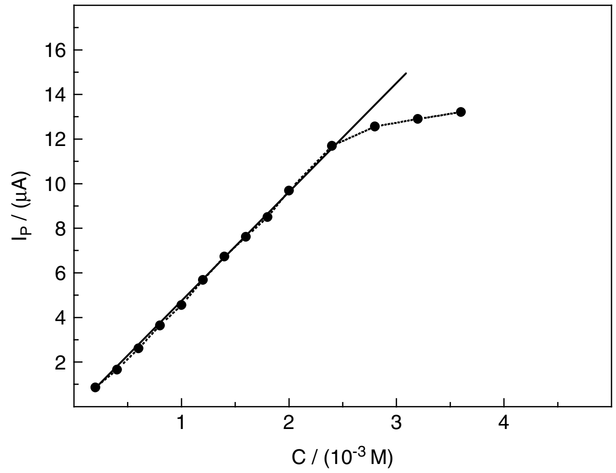

Figure 7. Plot of I_P vs. sulfite concentration in the presence of 6×10^{-5} M AFc. Scan rate = 50 mV s^{-1}.

10^{-3} M in 0.2 M $NaClO_4$ aqueous solution containing 6×10^{-5} M AFc, with correlation coefficient $R = 0.9997$, as shown in Fig. 7. The plot of $\log I_P$ vs. $\log C$ is a straight line (Fig. 8) with a slope that is virtually unity (0.997), indicating that the catalytic reaction obeys quasi-first-order kinetics with respect to sulfite at a constant AFc concentration in solution. This catalytic oxidation reaction of sulfite with AFc can be applied readily for the determination of sulfite in real boiler-water samples. Our experimental results showed that, within a concentration of 1000-fold, Ba^{2+}, Cd^{2+}, Pb^{2+}, Ca^{2+} and Mg^{2+} do not interfere with the electrochemical determination of sulfite in real boiler-water samples, the relative standard deviation is 0.3–1.7%, and the recovery is 97.7–104.8%. The electrochemical determination results were in agreement with those of the conventional method.[2]

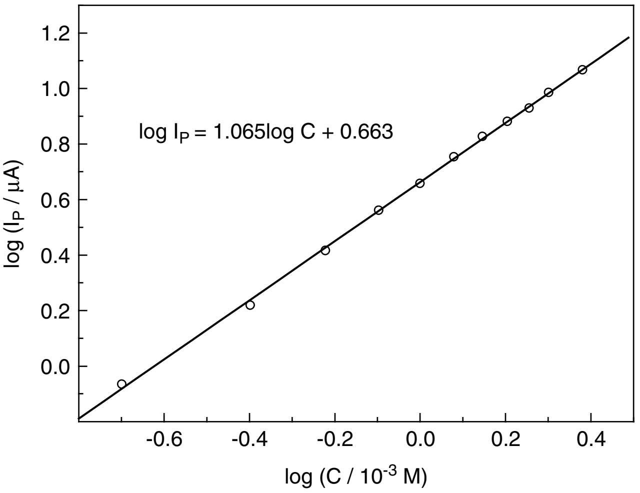

Figure 8. Effect of concentration on peak currents with respect to sulfite. Line is $\log(I_P)$ vs. $\log C$.

CONCLUSIONS

The electrochemical oxidation of sulfite catalyzed by AFc at a GCE in 0.2 M $NaClO_4$ aqueous solution has been studied by cyclic voltammetry. Although sulfite itself showed a sluggish electrochemical response, with an oxidation peak potential of 0.60 V at GCE, the response could be enhanced greatly by using AFc as a mediator. Thus, AFc can act as a homogeneous catalyst for the catalytic oxidation of sulfite. The catalytic rate constant of the reaction was evaluated as $(7.02 \pm 0.05) \times 10^4$ M^{-1} s^{-1} by chronoamperometry. Experimental conditions that maximize the current efficiency of the electrocatalytic oxidation, such as pH and the concentration of the catalyst (AFc) and the substrate (sulfite), were also investigated. Because AFc can work as a homogeneous catalyst for the oxidation of sulfite, it is possible to use AFc to modify the surface of the electrode for further research on the reactions. The linear relationship of I_P and the sulfite concentration range of 2×10^{-4}–2.4×10^{-3} M was used for determination of sulfite in boiler-water samples and the results are inagreement with those of the conventional method. This shows that the method is simple, precise, suitable for routine quality control and can be carried out directly without any separation or pretreatment due to the selective electrocatalytic oxidation of sulfite.

Acknowledgments

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