

The Characterization of Electrode Processes by the Chronoamperometric Technique in the Mo(VI) + Sulfuric Acid System

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Received: April 30, 1994; September 3, 1994

A caracterização de processo catalítico na presença de nitrato durante a redução eletroquímica do Mo(VI) em meio sulfúrico foi efetuada empregando-se técnica cronoamperométrica. Com base nos dados cronoamperométricos e utilizando-se equações apropriadas determinou-se a constante de velocidade da reação entre a espécie catalítica de molibdênio (Mo(IV)) e o substrato (nitrato), obtendo-se o valor de $2.3 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$. A técnica cronoamperométrica também foi utilizada nesse sistema para determinação da constante de dimerização da espécie Mo(V), gerada na superfície do eletrodo pela redução do Mo(VI). A análise dos dados obtidos com a técnica de duplo degrau de potencial permitiu a determinação da constante de velocidade da reação química posterior à redução do Mo(VI) (dimerização do Mo(V)), encontrando-se o valor de $2.4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$.

The chronoamperometric technique was used for the characterization of both a catalytic process and a dimerization coupled reaction in the electroreduction of Mo(VI) aquo-ion in sulfuric medium. The catalytic reaction was observed in the presence of nitrate, the second polarographic wave (Mo(V) \rightarrow Mo(IV)) becoming higher owing to the regeneration of the electroactive species (Mo(V)) at the electrode surface. The rate constant found for the reaction between nitrate and the Mo(IV) intermediate, using chronoamperometric data and an appropriate equation described in the literature, was $2.3 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$. The dimerization of the Mo(V) form generated after the reduction of Mo(VI) was investigated by the double potential step mode, and the rate constant obtained was $2.4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$.

Keywords: *chronoamperometry, molybdenum, catalytic electrode process, dimerization reaction*

Introduction

The application of the chronoamperometric technique in mechanistic studies involving coupled chemical reactions or reversibility analysis has been largely developed due to its simplicity and the good results that can be attained. The basis of the technique consists of disturbing the equilibrium at the double layer of the steady state by applying a potential step. Hence, the system relaxes to a new steady state and the transient response (*i.e.*, the current) can be analyzed, the information about the electrochemical processes occurring at the electrode interface being extractable. If the potential is abruptly changed to the initial value (double-step mode), the species generated at the electrode diffuses back to the surface to promote the charge transfer, the current then flowing to the opposite side.

Therefore, the comparison of cathodic and anodic currents can lead to information regarding any chemical reaction occurring after the first forward potential pulse. Data acquisition at a constant potential is an advantage of the technique since there are no non-Faradaic contributions for some time after the potential step, when the double layer is charged. The literature shows several examples of both one-step and double-step chronoamperometric studies regarding the characterization of electrode processes^{1,2} and the extraction of kinetic parameters³. Efforts have been made to determine these parameters from computational methods⁴, including corrections for the non-linearity of the diffusion pattern⁵.

The aim of this work is to confirm the presence of both a subsequent chemical step and a catalytic process in the Mo(VI) + sulfuric acid system using chronoamperometry.

The current and time data were analyzed according to the Cottrell equation⁶, the double-step method also being employed in the study of the dimerization of the Mo(V) species generated in the electroreduction of Mo(VI).

Experimental

All chemicals were reagent grade and used without further purification. The polarograms were recorded by using a Tacussel PRG 5 instrument and an EPL 3 recorder. The working electrode was a mechanically controlled dropping mercury electrode. The saturated NaCl calomel electrode reference was separated from the solution by a glass frit. The auxiliary electrode was a platinum wire. The chronoamperometric experiments were carried out with a Tacussel Polaroprocasseur attached to an EGM 2000T cell stand and an HP 7090A plotter to attain fast measurements. The chronoamperograms were obtained after the respective polarograms, from a potential where the faradaic current was not flowing at the desired potential. In previous experiments using Cd(II) and CrO₄²⁻, problems associated with non-linear diffusion were minimized when performed in an sufficiently short time, assuring that the thickness of the diffusion layer was thin in comparison to the curvature radius of the drop. Consequently, the chronoamperometric experiments were carried out with a relatively large pendant mercury drop (radius > 0.5 mm) for the acquisition data in the reversibility tests (Cottrell equation). The current in the chronoamperograms was corrected by subtracting the residual current, recorded in the same way, and just employing the supporting electrolyte. All solutions were deoxygenated with argon, and the temperature for all experiments was 25 °C.

Results and Discussion

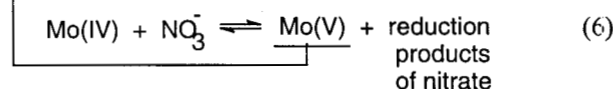
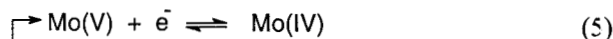
The initial experiments were carried out with well-known systems in order to test the experimental arrangement and the capability of the analysis of the selected data from chronoamperometric curves by the Cottrell equation. Hence, both the reversible Cd(II) in NaClO₄⁷ and the irreversible CrO₄²⁻ in NaOH⁸ systems were tested, the results being in agreement with the literature.

The polarographic behavior of the Mo(VI) species in 0.1 M H₂SO₄ follows the reaction scheme below, as previously reported⁹:



In the presence of oxidants like NO₃⁻¹⁰ or HN₃¹¹ a catalytic cycle takes place due to the regeneration of the depolarizer (Mo(V) species) at the double layer, the Mo(V)

form returning to the electrode to gain another electron. Figure 1 presents a polarogram of 4×10^{-4} M Mo(VI) in 0.1 M H₂SO₄, and the pattern established by Reactions 1-4 can be recognized. After the addition of nitrate the height of the second polarographic wave increases due to the catalytic effect, as the equations below show for nitrate as the substrate:



Chronoamperometry demonstrates this behavior by the attainment of a steady state current for a longer electrolysis time, as can be seen in Fig. 2. The I vs. $t^{1/2}$ plot shown in the inset of Fig. 2 is also useful for verifying the non-compliance of this system regarding the simple diffusion process, as a consequence of the replenishment of Mo(V) close to the electrode surface through Reaction 6.

Information regarding the rate of the chemical reaction between the catalyst and the substrate (*i.e.* the rate constant k) can be obtained by calculating the I_c/I_d ratio (I_c = catalytic current, I_d = diffusion current) for different times along the chronoamperometric curves. The adjustment of these experimental points, according to the equation shown below^{12,13}, allows the determination of the rate constant:

$$\frac{I_c}{I_d} = (\pi \cdot C_{\text{ox}} \cdot t \cdot k)^{1/2} \quad (7)$$

This equation only is valid for conditions where $k \cdot C_{\text{ox}} \cdot t > 1.5$ in which the catalytic effect predominates to a large extent over the diffusion. In Eq. 7, C_{ox} represents

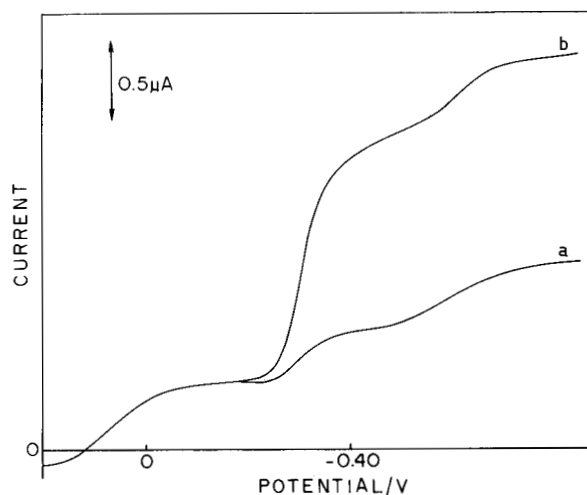


Figure 1. Fast polarograms for 4×10^{-4} M Mo(VI) solution before (a) and after (b) the addition of 10 mM nitrate (supporting electrolyte = 0.1 M H₂SO₄, drop time = 2.0 s).

the substrate concentration and t is the time after the application of the potential pulse.

Using a 4×10^{-4} M Mo(VI) solution (0.1 M sulfuric acid), the determination of the k value was performed, after the addition of 10 mM of nitrate, considering only the currents associated with the second polarographic wave. Thus, the discount of the faradaic current related to the first reduction process ($\text{Mo(VI)} \rightarrow \text{Mo(V)}$) was done by recording the chronoamperogram for a potential step from +0.20 V (the potential prior to the first wave) to the plateau of the first wave. The difference between this chronoamperogram and the one obtained after the potential step from +0.20 V to the plateau of the second wave provided the current which refers to the $\text{Mo(V)} \rightarrow \text{Mo(IV)}$ electroreduction, I_d . The same procedure was used after the addition of nitrate, when the I_c current values were obtained. Several I_c/I_d experimental data corresponding to time values selected in the chronoamperograms were adjusted according to Eq. 7 by means of a non-linear regression algorithm, and the k value was found to be $2.3 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$. Figure 3 shows the I_c/I_d data and the curve fitted after the adjustment, using t rather than $t^{1/2}$ as the independent variable. The value obtained in this work is similar to that reported by Kolthoff and Hodara¹⁰ in 0.05 M sulfuric acid ($2.5 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$). However, Edmonds¹⁴ found a higher rate constant value in nitric medium using differential pulse polarography ($1.26 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$). A possible explanation for the disagreement could be related to both the eventual complexation effect of sulfate on the catalytic molybdenum intermediate and the use of different methods to determine the rate constant.

The existence of a subsequent chemical reaction in the present system was preliminarily proven from po-

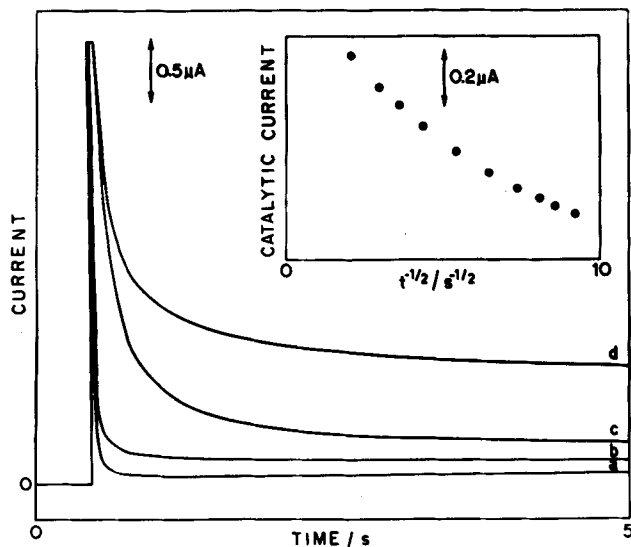


Figure 2. Chronoamperograms obtained after potential steps from +0.20 V to -0.10 V (a,b) and -0.45 V (c,d). Curves correspond to the following solutions: 0.1 M H_2SO_4 (a), a 4×10^{-4} M Mo(VI) (b, c) and b + 10 mM nitrate (d). The inset shows the dependence of the catalytic current (the difference between chronoamperograms d and c) on $t^{1/2}$.

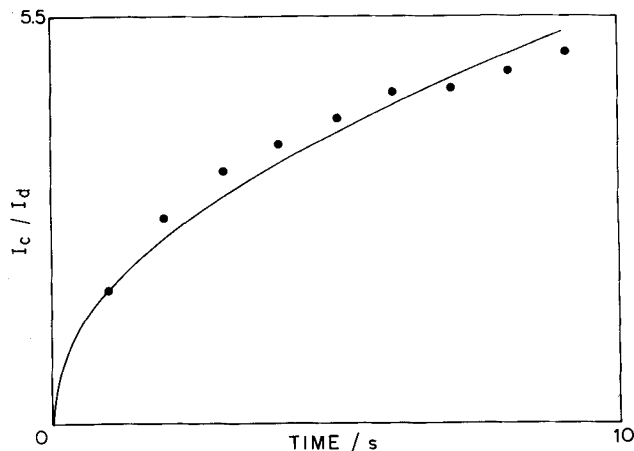


Figure 3. I_c/I_d experimental data obtained from chronoamperometric curves after the potential step from +0.20 V to -0.45 V (plateau of the second polarographic wave) when the catalytic (I_c) and diffusional (I_d) currents were recorded for the 4×10^{-4} M Mo(VI) + 0.1 M H_2SO_4 system before and after the addition of 10 mM of nitrate. These currents were corrected by subtracting the chronoamperometric current obtained after the potential step from +0.20 V to -0.10 V (the plateau of the first wave). The solid line corresponds to the adjustment of the experimental data relating to Eq. 7.

larographic studies where the time for the chemical reaction occurring at the electrode surface was varied. Since the chemical step is dependent on time (the larger the time the greater the extent to which the generated species can be transformed by the chemical reaction), a shift of the potential toward more positive values is expected. Differential pulse polarograms were recorded at several drop times in order to verify the presence of the dimerization reaction in this system, as suggested by Eq. 3. As the drop time was shorter, the peak potential for the first wave was shifted to more negative potentials, proving that there is a chemical reaction coupled to the electroreduction of the Mo(VI) form. The characterization of this chemical step was also proven by chronoamperometry, using the double potential step technique. In this case, the potential was made more negative by a pulse from +0.20 V to -0.10 V (the plateau of the first wave), when the Mo(V) is expected form and the dimerization takes place. After some delay in time, the potential returns to its initial value (+0.20 V) and the amount of Mo(V) that was not consumed by the chemical reaction can be reoxidized to Mo(VI), resulting in a minor anodic current rather than the cathodic one. The chronoamperometric curves obtained from this experiment are shown in Fig. 4. The evaluation of the dimerization rate constant was made by handling working curves from the literature¹⁵, where the experimental parameters τ (forward pulse time), t_r (time when the anodic current is sampled), I_c (measured at $t_r - \tau$), and I_a are related to rate constant k . The determination of k from this procedure resulted in the value of $2.4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, having the same order of magnitude as the rate

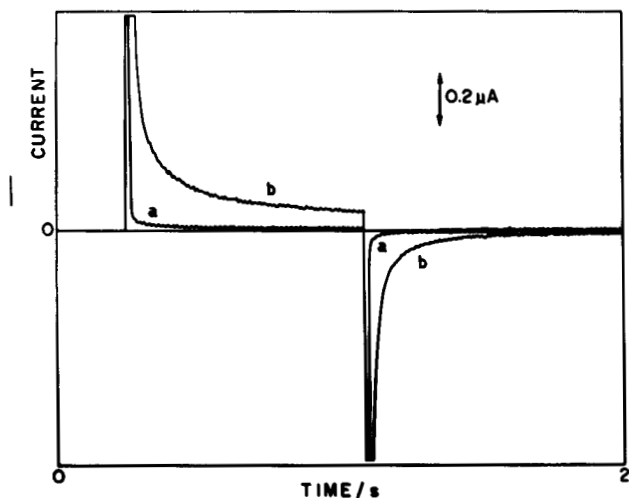


Figure 4. Chronoamperometric curves for a double-step potentiostatic experiment for the 4×10^{-4} M Mo(VI) + 0.1 M H₂SO₄ system (the potential step from +0.20 V to -0.10 V and the return to the initial potential).

constant reported by Paffett and Anson¹⁶ for trifluoromethanesulfonic acid using chronocoulometric data.

Acknowledgments

The authors acknowledge FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) for financial support.

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