

DYNAMIC BEHAVIOR OF ZINC ANODE IN NITRIC ACID – POTASSIUM DICHROMATE MEDIA. INFLUENCE OF THE ELECTROLYTE COMPOSITION

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Zinc anode of an electrochemical cell may present potential or current oscillations.^{1,2} When electrolyte composition changes, dynamic behavior changes too, so that the system passes from steady state, through simple oscillations (period 1 or 2), to chaos. This experimental work describes the influence of nitric acid and potassium dichromate concentration on the system behavior. A qualitative model, which explains oscillations, is given.

INTRODUCTION

Many chemical systems present interesting dynamic behaviors, from simple or complex oscillations of one of the parameters (color, concentration, current, potential) to quasiperiodicity and chaos. Oscillations were observed in both homogeneous or nonhomogeneous chemical systems and electrochemical systems. Latter these are more studied because the response (potential or current) can be easily measured and noise is very low.

The electrochemical systems, which are frequently studied, are those that imply anodic dissolution of metals, in various media (acids, bases, salts). Anodic dissolution of iron in sulfuric acid or nitric acid is the most studied and for this system was proposed a series of mathematical models that describe its dynamic behavior.³⁻⁶

Appearance of the oscillations is related to a precipitation-dissolution process of a chemical species (salt, oxide or hydroxide) at the electrode surface. For the anodic dissolution of iron, current oscillations were associated with mechanical oscillations of the electrolyte level⁷ or with passive and active zones appearance at the electrode surface, depending upon working electrode-counter electrode distance.⁸

This work describes a new electrochemical system that shows interesting dynamic behavior,

which uses a zinc anode immersed in nitric acid – potassium dichromate solution. This system presents potential or current oscillations, according to which of these parameters are measured. Potential oscillations depending upon nitrate ions concentration were presented in a previous work.¹ In this study we discuss the influence of nitric acid and potassium dichromate concentration on the shape of oscillations and we give a qualitative explanation of this behavior.

RESULTS

System behavior was investigated for 0.06M – 1.7M nitric acid concentration and 0.03M – 0.37M potassium dichromate concentration, respectively. No oscillations were observed either for concentration of nitric acid lower than 0.24M or for concentration of potassium dichromate lower than 0.04M.

Each recording represents about 90 seconds and was enlarged for a better view of the shape of the oscillations.

Depending upon the electrolyte composition, the system presents different dynamic behaviors, from steady state to chaos, as shown in Fig. 1. When the ratio nitric acid/potassium dichromate concentration increases, the complexity of the oscillations increases too.

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	Conc. HNO_3 /Conc. $\text{K}_2\text{Cr}_2\text{O}_7$ (mol/L)	Shape of oscillations
a)	0.286/0.27	
b)	0.333/0.25	
c)	0,375/0.236	
d)	0.412/0.22	
e)	0.444/0.21	
f)	0.474/0.20	
g)	0.50/0.189	
h)	0.625/0.142	

Fig. 1 – Oscillations obtained according to the composition of the system. One can observe an increasing of the oscillations complexity as the ratio nitric acid/potassium dichromate concentration increases.

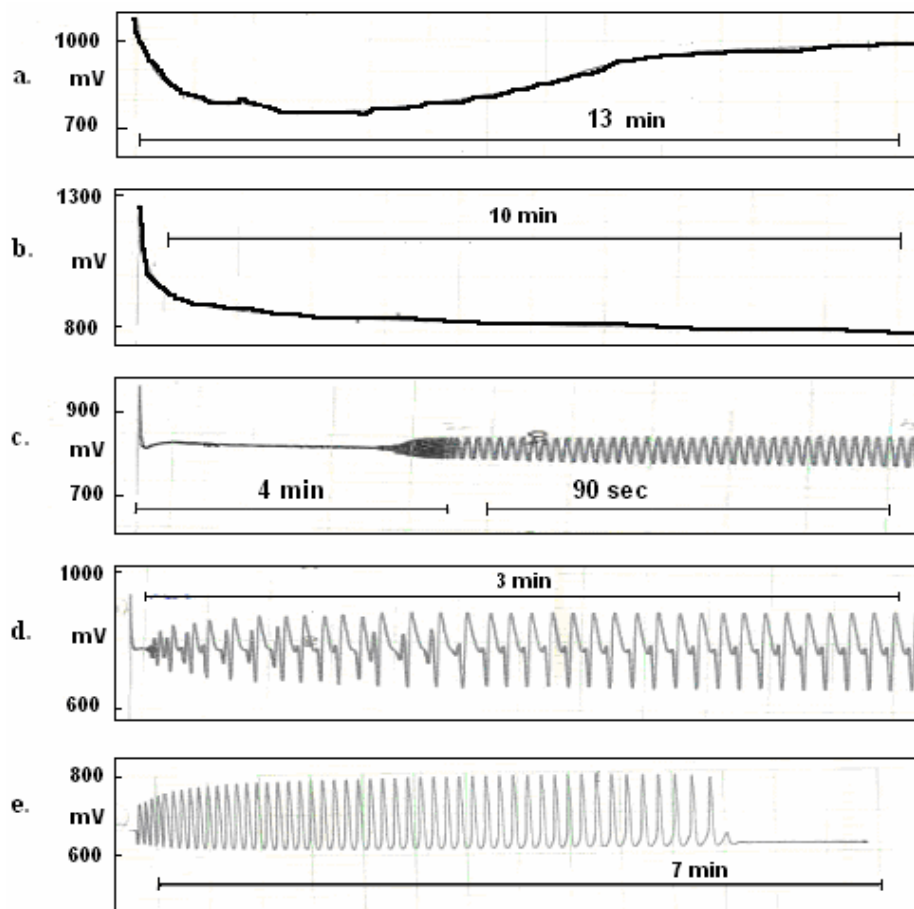


Fig. 2 – System behavior for nitric acid/potassium dichromate concentration ratio equal to 2. Nitric acid concentration is: a = 0.1 mol/L ; b = 0.2 mol/L ; c = 0.3 mol/L ; d = 0.4 mol/L ; e = 0.5 mol/L, and potassium dichromate concentration is: a = 0.05 mol/L ; b = 0.1 mol/L ; c = 0.15 mol/L ; d = 0.2 mol/L ; e = 0.25 mol/L.

Fig. 1a shows a stable steady state due to a passivation layer made by zinc oxide. The electrode surface is grayish, and becomes yellow by warming (typical for zinc oxide). Fig. 1b – 1h present some dynamic behaviors, from simple oscillations to chaos.

In order to elucidate if the molar ratio nitric acid/potassium dichromate is responsible for the shape of oscillations, we have studied the behavior of the system for the same molar ratio (2 in this case) nitric acid/potassium dichromate, as Fig. 2 shows.

We concluded that not molar ratio is responsible for the shape of oscillations. For the

same molar ratio, different behaviors were observed, from steady state to period-two and complex oscillations. The nitric acid concentration influences the shape of oscillations and the dichromate concentration influences the amplitude and duration of them. For higher concentrations of potassium dichromate, the oscillations duration decreases. The electrode surface is covered with a brownish layer of zinc polychromates ($\text{ZnCr}_3\text{O}_{10}$, which has a low solubility), and under that is a thin layer of zinc oxide.

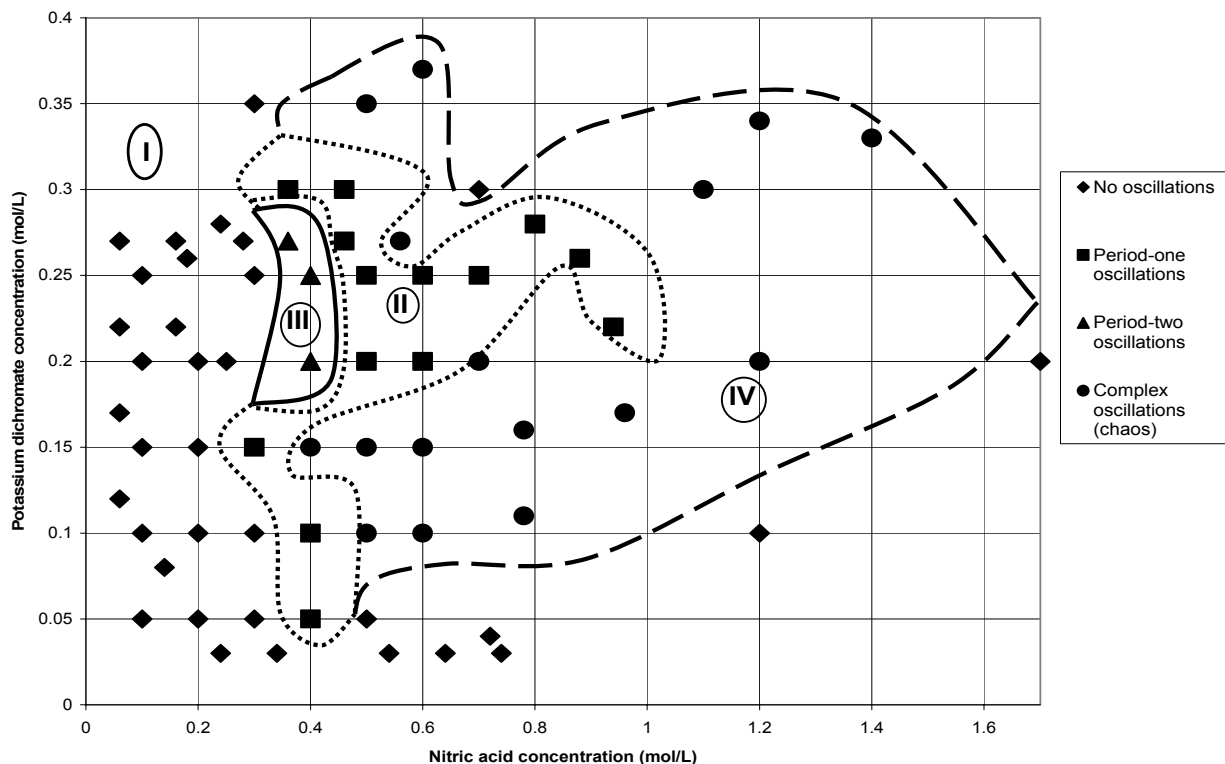


Fig. 3 – System behavior in coordinates: potassium dichromate concentration-nitric acid concentration. One can observe four domains: I – no oscillations occur; II – period-one oscillations; III – period-two oscillations; IV – chaos.

Fig. 3 presents a map of the system behavior, made up using various system compositions and different areas were found and shown here. We found the following domains: I – a domain with no oscillation (outside of the lines), where the system presents stable steady states; II – a second domain (inside the dotted line), with period-one oscillations. Simple oscillations occur, with period one, but with different amplitudes; III – a third domain (inside the solid line), with period-two oscillations. The system presents simple oscillations with period two. This is a very small domain, comparative to the others; IV – the fourth domain (between the dotted line and the long dashed line) is a large area with very complex oscillations (chaos).

DISCUSSION

The dynamic behavior of the system is strongly influenced by hydrogen ions concentration near the electrode surface. Over a critical threshold, the system leaves the steady state and, after an induction period, passes into a dynamic regime characterized by potential oscillations. Potential drop at the passivation layer surface depends upon its thickness. The passivation film is not uniform and, because of that, zones where it is destroyed by H^+ ions appear, allowing the contact of the electrode surface with solution and anode dissolution. The oscillations complexity depends

upon passivation layer thickness. At greater concentrations of hydrogen ions, the rate of the formation-dissolution increases and process occurs alternatively on small regions of the electrode surface, leading to the coupled oscillating systems and total potential is the result of these coupled oscillators potential variation.⁹

The oxide layer initially formed forbids the access of the H^+ ions to the electrode surface. As the concentration of the nitric acid increases, the hydrogen ions concentration near the electrode surface increases too and the oxide film dissolves. The electrode becomes active, its dissolution starts and zinc ions accumulate blocking the hydrogen ions access to the electrode. These ions migrate away to the bulk, pH increases and zinc hydroxide precipitates, so that the electrode passivates and zinc ions production stops. At this moment, hydrogen ions migrate back from the bulk to the electrode surface, pH decreases and the passivation layer dissolves. Zinc anode becomes active again and cycle repeats itself until the electrolyte is exhausted (hydrogen ions concentration decreases under a critical threshold). Arguments for this mechanism were taken-out by Cui and coworkers.¹⁰

As Fig. 1 shows, it seems the concentration ratio of the components influences the oscillations shape. However, from the experimental results, one can observe that not the nitric acid/potassium dichromate concentration ratio is responsible for the dynamic of the system. In Fig. 2 we present different dynamic behaviors of the system at the acid/dichromate concentration ratio = 2. The time series 2c shows a long induction period and simple sinusoidal period-one oscillations. Fig. 2d presents a time series with simple period-two oscillations, and in 2e time series one can observe simple period-one oscillations, but of relaxation type. System executes transitions between passive-active states, and after five minutes, oscillations cease and system remains in a passive state. This behavior (presented in Fig. 2e) is influenced by dichromates ions. When the concentration of these ions passes over a critical threshold, zinc polychromates deposition starts. The thickness of this layer of polychromates, whose deposition rate is greater than the dissolution rate, grows, blocking the access of H^+ ions to the electrode surface, oscillations cease and system remains in a passive state.

EXPERIMENTAL

Experiments were carried out using an electrochemical cell with two electrodes, at room temperature. The working

electrode was a zinc rod, Merck, 99.9% purity, with eight mm diameter, embedded in an insoluble muff, so that only the end of the rod was exposed to the solution. Active surface of the electrode was around 50 mm². Reference electrode was a platinum wire, one mm diameter.

The electrolyte was prepared from analytical grade reagents and purified Millipore water (>18 M Ω *cm resistivity). We used a potassium dichromate solution 0.4M, prepared from potassium dichromate Riedel-deHaën 99.8 % purity and nitric acid solutions with different concentrations (1M; 2M; 4M and 8M) prepared from nitric acid Fluka 65 % purity. The total volume of the solution, for each determination, was 100 mL, by mixing potassium dichromate and nitric acid solutions described above and water. The working electrode was polished with 600 and 1000 grade emery paper, washed with water and wiped prior to each experiment. The potential oscillations were recorded using a Speedomax XL recorder, 4 M Ω internal resistances. A magnetic stirrer stirred system.

CONCLUSIONS

According to the experimental results, potential oscillations in Zn/HNO₃-potassium dichromate system occur within a certain concentrations range. Oscillations are strongly influenced by nitric acid and potassium dichromate concentration. Dichromate ions seems to influence the amplitude and duration of the oscillations. A high concentration of dichromate leads to a thicker layer of polychromates deposition and potential drop is higher due to an increasing of electrical resistivity near the electrode surface. At the same time, the oscillations duration decreases dramatically due to a thick layer of zinc polychromates, as we have described above, in "DISCUSSION" section. Oscillations may be explained by precipitation-dissolution mechanism and it is possible to exist a chemical reactions mechanism with participation of the potassium dichromate that can lead the system to self-organization. Further investigations are necessary to elucidate the real mechanism of the oscillations and for finding a mathematical model, which may describe system behavior.

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