



Catalytic polarographic wave in the vanadium–cupferron system



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ABSTRACT

Surface catalytic polarographic wave in vanadium(V)–cupferron system has been studied in the buffer media with pH 5 ÷ 7.5. The catalytic wave is observed at $-0.6 \div -0.7$ V (SCE), and it could be enhanced by addition of quaternary ammonium salts. This fact implies that catalytically active vanadium species are anionic. As the height of this wave is proportional to vanadium concentration, it may be useful as an analytical signal. Adsorbed anionic vanadium(II) complex with cupferron is supposed to be a catalyst in this process. A peak shaped wave at more negative potentials is assumed to be a result of catalytic action of vanadium(II) hydroxide. Some kinetic parameters of the catalytic wave in vanadium–cupferron system are presented.

The mechanism of catalytic reaction has been considered, and the rate constant of the surface chemical reaction between adsorbed vanadium(II) and cupferron has been evaluated: $k = (3 \pm 1) \cdot 10^6 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. pH dependence of k has not been observed; it implies that no prior protonation is encountered. The catalytic reduction of cupferron and its direct electrochemical reduction differ in some important aspects such as number of electrons transferred or presence of prior protonation reaction.

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1. Introduction

Cupferron is ammonium salt of N-nitroso-N-phenylhydroxylamine (NPHA). Since the last decades of the 20th century, cupferron became a popular reagent for electroanalytical determination of trace amounts of metal ions. It may be useful in analysis of rare earth elements [1,2], vanadium(V) [3–6], uranium(VI) [7,8], molybdenum(VI) [9], aluminum [10,11], cadmium [12], and gallium [13]. Simultaneous determination of Bi and U [14], Bi and Cd [15], Cd and Zn [16], Cd and U [17], Pb and V [18], Cr, U, and Fe(III) (V and Bi have been also tried) [19] is possible. Some additional relevant references are listed in Ref. [20].

A protocol for vanadium electroanalytical determination was developed by Wang et al. [4], but it met a serious criticism [21,22]. It was stated that in the presence of cupferron vanadium peak potential E_p is -0.7 V [21], but not -0.1 V as declared in Refs. [4,5]. Also it was mentioned that this process is analytically useless due to poor sensitivity [21]. Unfortunately, there is an evident discrepancy in the published values of the potential of this process. Later Wang et al. reported $E_p \approx -1.1$ V for vanadium–cupferron system [19]. $E_p = -0.72$ V was found by Abbasi et al. [18]; $E_p = -0.83$ V was reported by Du and Song [3]; up to three waves were found by Kheifets et al. with a catalytic one at -1.01 V [6]. The aim of this work was to check the potential range of cathodic process in vanadium–cupferron system, and elucidate

its mechanism, with a special attention to the catalytic reaction reported by Kheifets et al. [6]. Electrochemical process in metal–cupferron systems is often regarded as catalytic, but a few thorough studies of mechanism of catalysis have been made [1,8].

2. Materials and methods

Acetate and phosphate buffers were used to maintain pH (5–7.5); some preliminary experiments were made with pH up to 9 (borate buffer). Ammonium metavanadate was used as a vanadium(V) source. PU-1 polarograph (ZIP, Gomel, Belarus) was used in the fast mode with measuring times t_1 $0.7 \div 4.4$ s; mercury flow rate m was $1.039 \cdot 10^{-3} \text{ g} \cdot \text{s}^{-1}$. All the potentials were measured versus saturated calomel reference electrode. The solution temperature was set 25.0 ± 0.2 °C with aerial thermostat. Vanadium concentration was in $2 \cdot 10^{-6}$ – $1.2 \cdot 10^{-5}$ M range; further increase of concentration promoted distortions due to polarographic maxima. The solutions under study typically contained $2 \cdot 10^{-3}$ M cupferron, $4 \cdot 10^{-2}$ M buffer (total concentration), and 0.1 M sodium sulfate as a supporting electrolyte.

Cupferron is not stable in aqueous solutions as it is sensitive to aerial oxidation. To prevent this, cupferron was not added into solution initially. Weighted amount of cupferron was added directly into the solution of supporting electrolyte after the cell was poured by high purity argon for 10–15 min to remove dissolved oxygen. After this, argon passed through the solution for 10–15 min.

Other details (such as cupferron purification) were reported in Ref. [20].

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3. Results

3.1. Preliminary results

Polarographic reduction of vanadium(V) in the presence of cupferron starts at ~ 0 V (Fig. 1). The first wave with a halfwave potential $E_{1/2} \approx -0.1$ V is surely the reduction of vanadium(V) complex into vanadium(IV) oxidation state:



This equation needs some comments. We suppose that the solution initially contains a complex of vanadium(V) with cupferron $\text{V}^{\text{V}}\text{O}(\text{cupf})_2\text{OH}$, where cupf^- stands for cupferron anion [23]. According to Kojima and Miwa, this complex has an acidic OH-group, and it can react with basic substances. Presumably at $\text{pH} > 5.5$ the complex exists in solution as a soluble anionic form, $\text{V}^{\text{V}}\text{O}_2(\text{cupf})_2^-$. This preposition can explain a free diffusion of vanadium(V) to the mercury electrode at the conditions of the experiment. After reduction to vanadium(IV), the complex loses solubility, and it adsorbs on the electrode.

The second wave at more negative potentials (in the $-0.2 \div -0.6$ V region) is supposed to be the wave of reduction of vanadium(IV) to vanadium(III) complex. This wave is strongly distorted, possibly due to adsorption effects, and it is poorly resolved from the adjacent waves. As the concentration of vanadium is close to the detection limit for classical polarography, we have been unable to record the first two waves with sufficient accuracy due to large influence of background current. No further discussion of these waves is possible.

At more negative potentials ($-0.7 \div -1.0$ V) the third wave appears (Fig. 2). The currents of this wave are much larger than the currents of the first two waves. The third wave has a peak shape, a feature common for a surface catalytic wave (for instance, for catalytic hydrogen waves). We believe that $\text{V}(\text{III})/\text{V}(\text{II})$ system catalyzes the process of cupferron reduction; at least no catalytic wave has been observed in our experiments when vanadium reduces to $\text{V}(\text{IV})$ or $\text{V}(\text{III})$ state.

The catalytic wave is a composite one; a prewave is observed at large t_1 values (Fig. 2). This effect is evident for solutions with $\text{pH} < 8$ only. Experiments made with higher pH (borate buffer) revealed that the total mechanism of the process has been changed (Fig. 3). The appearance of the first wave was drastically altered, possibly due to partial hydrolysis of the initial complex. The third wave at these pH values is much lower than the wave at $\text{pH} < 8$, and no prewave is observed (Fig. 3). Further attempts have been aimed at better resolution of catalytic waves; the solution pH has been restricted by 7.5 value.

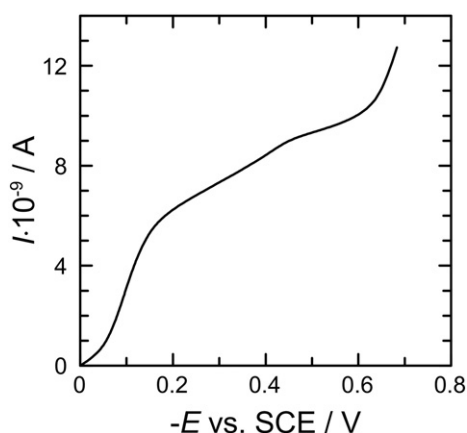


Fig. 1. Initial part of polarogram recorded at $t_1 = 1.7$ s in the solution of $2 \cdot 10^{-6}$ M $\text{V}(\text{V})$, $2 \cdot 10^{-3}$ M cupferron, phosphate buffer ($\text{pH} 7.19$), 0.1 M Na_2SO_4 .

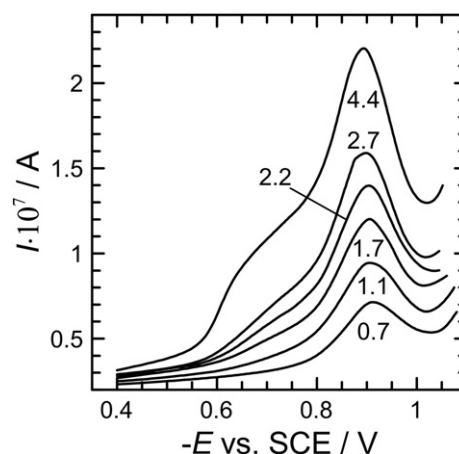


Fig. 2. Polarograms recorded in the solution of $6 \cdot 10^{-6}$ M $\text{V}(\text{V})$, $2 \cdot 10^{-3}$ M cupferron, acetate buffer ($\text{pH} 5.57$), 0.1 M Na_2SO_4 . The number at any curve represents the value of t_1 (s).

3.2. Effect of additives

Quaternary ammonium salt or gelatine addition was tried in order to dismiss reducing particles from the electrode surface, and make the prewave more resolved from the peak shaped wave. Good resolution and enhancement of catalytic waves have been achieved, but in spite of our expectations, this effect is due to advanced but not to decreased adsorption. At least more surface active $\text{N}(\text{Bu})_4\text{Br}$ have more pronounced effect than $\text{N}(\text{Me})_4\text{Br}$. Since then $2 \cdot 10^{-3}$ M $\text{N}(\text{Bu})_4\text{Br}$ was always added into solution.

Fig. 4 represents a typical polarogram of vanadium–cupferron– $\text{N}(\text{Bu})_4\text{Br}$ system in phosphate buffer. It can be seen that a well defined wave (hereafter referred as the third wave) appears in the presence of $\text{N}(\text{Bu})_4\text{Br}$, with a halfwave potential $E_{1/2} \approx -0.6 \div -0.7$ V. Additional peak shaped wave at $-1.0 \div -1.1$ V (the fourth wave) is surely due to the process causing the catalytic wave reported by Kheifets et al. [6], or the peak reported by Wang et al. [19].

The limiting current of the third wave ($I_{\text{lim}}^{(3)}$) is $1.05 \cdot 10^{-6}$ A in the solution of 10^{-5} M vanadium and $2 \cdot 10^{-3}$ M cupferron ($\text{pH} 5.57$, $t_1 = 2.2$ s); the diffusion current estimated by Ilkovič equation for $\text{V}(\text{III})$ to $\text{V}(\text{II})$ reduction is $\sim 2 \cdot 10^{-8}$ A. This means that the third wave is a catalytic wave with ~ 50 -fold current enhancement, with cupferron as an evident oxidant in the catalytic cycle.

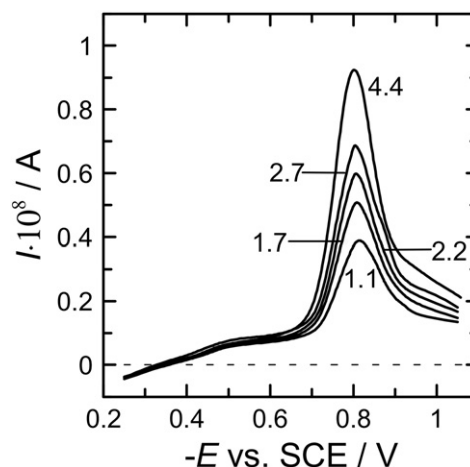


Fig. 3. Polarograms recorded in the solution of $2 \cdot 10^{-6}$ M $\text{V}(\text{V})$, $2 \cdot 10^{-3}$ M cupferron, borate buffer ($\text{pH} 8.81$), 0.1 M Na_2SO_4 . The number at any curve represents the value of t_1 (s).

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