Full Paper

Kinetics of Cupferron Electroreduction on the Dropping Mercury Electrode

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Abstract- Cupferron electroreduction was studied polarographically in buffer media with pH 4.3-7.5 and 8-10. Irreversible reduction with slow transfer of the first electron was found, with α=0.45 in alkaline and α=0.33 in acidic solutions. In acidic media $E_{1/2}$ of cupferron wave depends on pH linearly with a slope 0.125 V. This implies reversible protonation step preceding the electron transfer. The wave shape at the lowest pH studied clearly indicates adsorption influence on kinetics of the process, i.e. protonated cupferron reduces from adsorbed state. Mairanovskii model of surface waves was successfully applied, with α values corrected to 0.38. There is no prior protonation in alkaline solutions, but some kinetics features (such as unusually high slope of $E_{1/2}$, $\log t_1$ dependence) also imply some influence of adsorption. Analysis of published data revealed that contribution of slow tautomeric equilibrium proposed in earlier works is very doubtful. Double protonation of cupferron anion at low pH should be considered instead.

Keywords- Cupferron, Polarography, Electroreduction, Dropping mercury electrode, Adsorption

1. INTRODUCTION

Cupferron is an ammonium salt of N-nitroso-N-phenylhydroxylamine (NPHA). In the last decades of the 20th century this reagent became popular in determination of trace amounts of metal ions by different voltammetric methods, including adsorptive stripping voltammetry,

catalytic polarography, and other sensitive techniques. For example, cupferron may be used in analysis of rare earth elements [1], vanadium [2-4], uranium [5-8], thorium [9], molybdenum [10,11], lead [12], titanium [13], zirconium [14,15], aluminum [16], cadmium [17]. Some attention was paid to simultaneous determination of Mo and Cu [18]. Metal-cupferron systems can be useful in biochemical analysis, due to inhibitory effect by protein [19,20] or DNA [21].

The analytical signal in these methods originates from very complex cathode process, the mechanism of the reactions is often marked by catalysis [1,10,13,22]. Catalytic reaction is poorly understood; usually cupferron is regarded as oxidizing substrate of catalytic reduction. It is known that cupferron and its structural analogs may be reduced on cathode [23-29]. This process has been studied quite extensively, but its nature is not understood completely. It is known that there are several pH regions where cupferron waves have different properties. Quite misleading, these waves are traditionally called as the first, the second, and the third cupferron wave [24], but usually only a single wave is observed on polarogram. Processes attributed to these waves are often controversial. As the mechanism of electrochemical reduction of free cupferron is not quite certain, it is difficult to elucidate the mechanism of analytically important cathode reactions of cupferron metal complexes.

The present work was aimed to study the kinetics of the electroreduction of cupferron in weakly acidic, neutral, and alkaline solutions.

2. EXPERIMENTAL

Cupferron is unstable when stored, and requires purification. Reagent was dissolved in water in the presence of activated charcoal. After filtration, the solution was cooled with ice and acidified by HCl to pH~2 to precipitate NPHA. Diethyl ether was added to a solution with the precipitate until NPHA was dissolved. Two layers formed were separated and the aqueous layer was extracted with ether. The combined ethereal solutions were dried over sodium sulfate, and then a mixture of ethanol and concentrated aqueous ammonia (1:1) was added until noticeable ammoniacal odor. Cupferron precipitate was filtered and washed with ether and then recrystallized from ethanol. The sodium salt of NPHA (which will be referred after as NaNPHA) was obtained in similar way. In this case, NaOH solution in ethanol was added to the NPHA solution in ether.

Sodium sulfate (reagent grade) and lithium sulfate (pure) were used as supporting electrolytes; the latter reagent was purified by recrystallization. Acetate, urotropine, phosphate, and borate buffers were used to maintain constant pH. Urotropine was purified by recrystallization from water and chloroform. Sodium hydro- and dihydrophosphate, and sodium acetate (reagent grade) were used without purification. Borate buffer was made by boric acid (reagent grade) and lithium metaborate $LiBO_2 \cdot 8H_2O$, synthesized according to [30]. All solutions were prepared immediately before experiment; usually they contained 0.1

M of supporting electrolyte, 4×10^{-2} M buffer components (total concentration) with pH range 4.3-10.0, and 2×10^{-3} M cupferron. More acidic solutions are difficult to investigate because of cupferron decomposition. In borate buffer NaNPHA was used instead of cupferron. The dissociation constant of NPHA is $K_a=5.3\times10^{-5}$ [31], so in all these solutions cupferron was in the anionic form (at least predominantly).

Double-distilled water was used for solutions, reagents purification, etc. Polarograph PU-1 was used in tast mode with recording time t_1 ranged from 0.7 to 4.4 seconds, mercury flow rate was 0.949×10^{-3}, 1.039×10^{-3}, and 2.244×10^{-3} $g\cdot s^{-1}$. The cell was a standard cell of the PU-1 kit. Calomel reference electrode was filled by saturated NaCl; all potentials given hereinafter were measured relative to this electrode.

Cupferron is not stable in aqueous solutions as it is sensitive to aerial oxidation. To prevent this, cupferron (or NaNPHA) 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 30-40 minutes to remove dissolved oxygen. After this, argon passed through the solution for 20-30 minutes. During polarogram recording argon was passed over the solution. No surfactant was added for polarographic maxima suppression. The solution temperature was set 25.0 ± 0.2 °C with aerial thermostat.

3. RESULT AND DISCUSSION

3.1. Alkaline solutions

The experimental data can be divided into two groups depending on the pH of the solution tested. The simplest kinetics results were obtained in alkaline solutions (pH 8-10). Under these conditions cupferron reduces at high negative potentials, so even the presence of sodium salts in high concentration makes difficult to investigate this process due to superposition of the sodium ion reduction current. For this reason, tetraalkylammonium salt [24] or lithium salt [23] can be selected as the supporting electrolyte. We used the latter option, as it simplifies purification of electrolytes and preparation of buffer components.

In alkaline solutions cupferron reduces with consumption of four electrons to form benzene and dinitrogen according to the equation [24]:

$$C_6H_5N_2O_2^- + 3H_2O + 4e^- \rightarrow C_6H_6 + N_2 + 5OH^- \qquad (1)$$
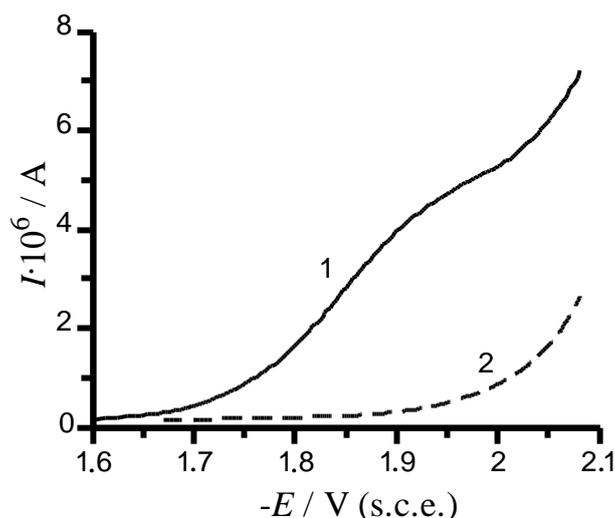
Fig. 1. Polarograms recorded in solutions with NaNPHA concentration: (1) 2×10^{-3} M, (2) 0 M. Other conditions: 0.25 M Li_2SO_4, 10^{-2} M $LiBO_2 \cdot 8H_2O$, 2×10^{-2} M H_3BO_3, pH 8.47, t_1=1.1 s

A typical cupferron reduction wave in borate buffer and Li_2SO_4 is shown in Fig. 1. Half-wave potential $E_{1/2}$ is independent on pH (at pH 8-10), which is consistent with [23,24], and its value was -1.81 ÷ -1.87 V (depending on t_1). Published value -1.85 V was found from the classical polarogram [23,24], and it is within this interval. Traditional semi-log plot analysis gives a slope b=~130 mV, indicating the irreversibility of the electrochemical process. This value is consistent with slow transfer of the first electron, α=0.45. There is no available data published on the values of b or α in this pH range.

The dependence of the half-wave potential of NaNPHA on t_1 was studied (Fig. 2). We found that the shift of $E_{1/2}$ in a positive direction with increasing t_1 was much more pronounced than it should be expected from the values b obtained; the slope of the linear dependence $E_{1/2}$, logt_1 gives b=215 mV which is close to 3/2 of the value calculated from the semi-log plot.

The dependence of the limiting current (I_d) on t_1 has an exponent 0.3. The deviation from the theoretical value for the diffusion current (1/6, Ilkovič equation) can be accounted to so-called transfer of concentration polarization. Unfortunately, the discrepancy between experiment and theory is usually less pronounced, typical experimental exponent is approximately 1/5-1/4 [32,33], and our result falls out of this range. We suppose that some adsorption phenomena could influence our results, as well as they can influence slop of $E_{1/2}$, logt_1 plot. First of all, we should consider adsorption of the reaction product, benzene. It is known that adsorption of reaction product can influence the shape of I, t curves in polarography [34]. Unfortunately, the paper mentioned considers reversible reactions only, but probably it may be partially applied to such irreversible process as cupferron reduction.
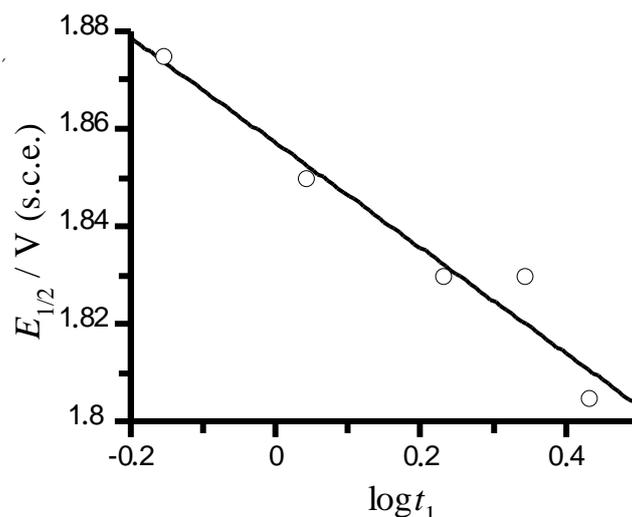
Fig. 2. Dependence of the half-wave potential of NaNPHA on t_1

It is possible that the abnormally high slope of $E_{1/2}$, $\log t_1$ plot is due to adsorption of depolarizer. It has been shown theoretically that at low surface coverage (in the region of the Henry isotherm) the dependence of $E_{1/2}$ on t_1 may be unusually high [35]. Probably this theory can be applied to our data. It should be noted that the adsorption of anionic species at high negative charges of the electrode surface is unlikely, but perhaps in a very small extent it does happen, possibly as ionic pair (or complex) with supporting electrolyte cation.

The data we obtained in alkaline solutions are consistent with the direct reduction of predominant NPHA anions without prior protonation, as was stated earlier in [23]. But some unusual fitures such as very high slope of $E_{1/2}$, $\log t_1$ or $\log I_d$, $\log t_1$ plot implies very complex mechanism of reduction, with adsorption as a possible stage that can influence the overall kinetics.

3.2. Mild acidic and neutral solutions

Solutions with lower pH 4.3-7.5 give well-defined polarographic wave of cupferron, but these polarograms have abnormal features (maxima) at lower pH values. Typical polarographic wave has a slop of semi-log plot equal to 178±10 mV. This value is much higher than that found for alkaline solutions. Obviously this is consistent with slow transfer of the first electron with $\alpha=0.33$. There are no kinetics parameters in literature for this pH range. But these data are in good agreement with the published values for the kinetics of cupferron reduction in strong acidic media: $b=182$ mV at pH 1.0 [23], and $\alpha=0.30-0.35$ [27], $\alpha=0.34-0.35$ [28] at pH 1-4.

At the lowest pH (less than 5.5), we obtained the waves that often have form of wide asymmetrical maximum (Fig. 3), that may be characteristic for surface waves [35]. The limiting currents observed in this pH range were lower than in neutral solutions, and the slope

of the semi-log plot was slightly higher. Such a behavior was more evident for solutions of urotropine buffer.
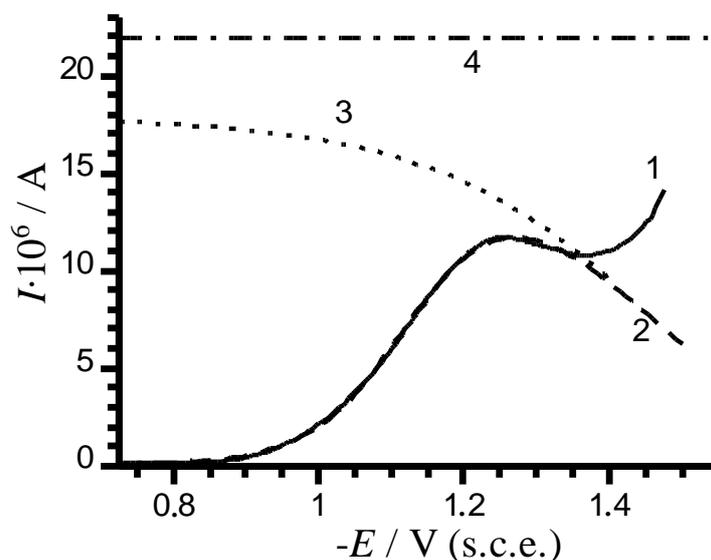
Fig. 3. (1) Polarogram recorded in 2×10^{-3} M cupferron, 0.1 M Na_2SO_4, and urotropine buffer (pH 4.65) at t_1=1.1 **(2)** Curve calculated according to eq. 6 with fitted parameters (I_d=18.4×10^{-6} A, $E_{1/2}$ = -1.132 V, b=0.154 V, A=3.31, B=3.74 V^{-2}) **(3)** Calculated dependence I_{lim}, E **(4)** I_d calculated from Ilkovič equation

In weak acidic and neutral solutions, half-wave potential of cupferron depends linearly on pH. This relationship is presented in Fig. 4. For this pH range, a dependence of the type

$$E_{1/2} = E_{1/2}^0 - k \cdot pH \qquad (2)$$

Has been described earlier for cupferron waves with the parameter values: $E_{1/2}^0$=-0.58 V, k=0.128 [23]; $E_{1/2}^0$=-0.52 V, k=0.120 V [24]. Our experiment gives the values $E_{1/2}^0$=-0,625 V, k=0.125 V for t_1=1.1 s. Thus, we found that the slope of the dependence of half-wave potential on the pH is in good agreement with previously published data, and the parameter $E_{1/2}^0$ is also close to the value given by Kolthoff and Liberti [23].

The slope of $E_{1/2}$, pH dependence for cupferron close to -120 mV was considered in [23,24] as an evidence for $E_{1/2}$ changes with the second power in hydrogen ion concentration. This interpretation implies the feasibility of the Nernst equation that is questionable for such an irreversible cathodic process. More likely this dependence indicates reversible protonation preceding slow electron transfer, i.e. this cathodic wave is a quasi - diffusion kinetic wave in the terms of Mairanovskii [35].
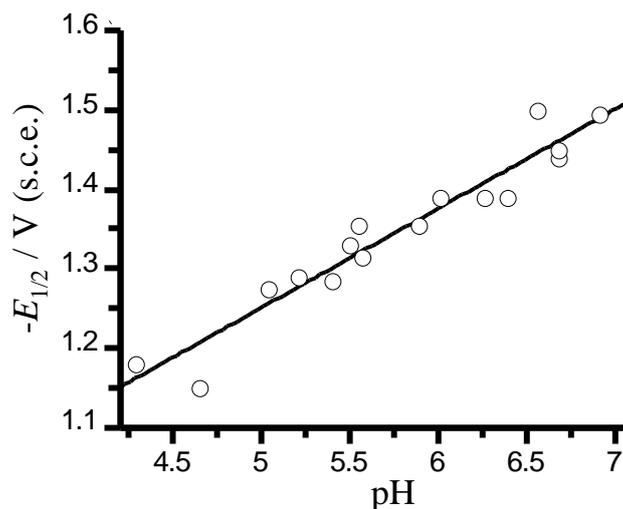
Fig. 4. PH dependence of cupferron half-wave potential

In this pH range cupferron exists predominantly as an anion in solution, and the total cathodic process corresponds to the equation [23,24]

$$C_6H_5N_2O_2^- + 8H^+ + 6e^- \rightarrow C_6H_5NHNH_3^+ + 2H_2O \qquad (3)$$

The dependency (2) indicates that there is no direct reduction of NPHA anion prevailing in the solution, but prior protonation takes place:

$$C_6H_5N_2O_2^- + H^+ \leftrightarrow C_6H_5N_2O_2H_{ads} \qquad (4)$$

$$C_6H_5N_2O_2H_{ads} + e^- \rightarrow C_6H_5N_2O_2H^- \qquad (5)$$

Index "ads" indicates that NPHA resulted from the reaction (4) adsorbs on the electrode. A shape of waves which is characteristic of the adsorption polarographic waves (Fig. 3) implies this. Equation (5) describes a slow electron transfer (rate limiting step) only, further reduction gives phenylhydrazine.

If equations (4) and (5) are valid for the process, the slope of dependence (2) should be equal to the *b* coefficient [35]. However, the experimental value of the slope of (2) is substantially lower than the value of *b* for this pH range. One of explanation could be the process autoinhibition by adsorbed product, benzene. Its effect may be comparable with adsorption of some foreign organic substance, for instance, butanol [37]. Alternatively, this effect can be attributed to the properties of cathodic wave with adsorbed depolarizer, i.e. a quasi - surface diffusion wave [35]. In this case such a difference in slope can be predicted theoretically. Unusually low transfer coefficient can also be related to the nature of the cathodic surface waves [35].

Quantitative treatment of polarograms obtained at low pH was made in accordance with surface polarographic wave model developed by Mairanovskii. We tried to demonstrate applicability of this model to cupferron. In this case the chemical stage of protonation is

rapid, so only the dependence of the limiting current on desorption of the depolarizer was taken into account [35] :

$$\ln\left(\frac{I_{\lim}}{I_d - I_{\lim}}\right) = A - B \cdot (E - E_m)^2 \tag{6}$$

where $I_{\lim}$ - limiting current, in this case $I_{\lim} < I_d$ due to desorption of the depolarizer as the electrode potential deviates from the potential of maximum adsorption E_m, which can be approximated by the potential of zero charge E_z at the calculations. Parameter A depends on the maximal adsorption (Γ_∞) of depolarizer, limiting diffusion current I_d, the concentration of hydrogen ions that is constant during the experiment, and some other constants. Parameter B characterizes the dependence of the depolarizer adsorption constant on potential in Frumkin equation [35].

According to equation (6), the shape of adsorption wave is influenced by large number of parameters; experimental determination of some of them is very tedious. We tried to find their values by curve fitting (non-linear least squares method), but fitting was unsuccessful until E_m was set to a constant value $E_m = E_z = $ -0.47 V (the value for 0.1 M Na$_2$SO$_4$ [39]). Then a good fitting with the experimental polarograms was observed (Fig. 3). Corrected values of b fell within the range of 150 - 160 mV (α=0.38). It is difficult to discuss the accuracy of these values. It should be noted that the calculated I_d were lower (by 15-20%) then the diffusion currents calculated from Ilkovič equation (see Fig. 3); cupferron diffusion coefficient $8.81 \cdot 10^{-6}$ cm$^2 \cdot$s^{-1} was used [25]. At least, our results are semi-quantitatively consistent with the theory, developed by Mairanovskii.

Our data indicate that cupferron reduction process is irreversible; one (the first) electron is transferred in the slow electrochemical step. This is consistent with the conclusions made in [27,28]. In mild acidic solutions cupferron reduction proceeds through prior protonation, whereas in alkaline media no preceding chemical step is observed.

It is known that at pH~7- 9 two waves of cupferron are observed simultaneously, with a kinetic limiting current of NPHA wave [23]. Unfortunately, in our experiments this transition region between acidic and alkaline solutions was very narrow (less than 1 pH unit), and we encountered great difficulties in investigating such a solutions. No reproducible data were obtained, presumably due to low capacity of borate buffer at pH~7.5.

The region of low pH~0-4 (which was left out in present work) is also of interest, as it corresponds to "the first cupferron wave" [24]. This wave differs in $E_{1/2}$ values from the wave in mild acidic media [24,25,27,28]. It has been supposed that two different waves of NPHA in acidic solutions are formed by different NPHA tautomers [24].

It is known that tautomeric equilibrium with a proton transfer can really influence the electrochemical reduction. 3-Thianaphthenone solution is a well studied example where electrochemical investigation was fully supported by spectroscopic and kinetic data [40,41]. But one should suppose that in strong acidic media proton transfer being very fast and could not influence the kinetics of cupferron reduction. More possible reason for observed change in wave parameters is protonation of NPHA in strong acidic media, producing cationic $HNPHA^+$. NPHA protonation constant is not known as it is very instable in strong acidic solution, but analogous substance with cyclohexyl radical instead of phenyl, N-nitroso-N-cyclohexylhydroxylamine, has a protonation constant pK=0.42 [42]. NPHA may have reasonably close value of protonation pK, so "the first cupferron wave" most probably is due to the reduction of protonated cationic form. It is interesting that at pH ~ 4 kinetic limitations due to slow protonation were observed [27,28], this situation is similar to pH 7–9 region. This favors $HNPHA^+$ reduction, but the influence of tautomeric equilibrium should be ruled out.

CONCLUSION

Cupferron electroreduction was studied polarographically in buffer media with pH 4.3-7.5 and 8-10. Irreversible reduction with slow transfer of the first electron was found in acidic solutions. $E_{1/2}$ of cupferron wave depends on pH linearly with a slope 0.125 V in acidic pH. This implies reversible protonation step preceding the electron transfer. Mairanovskii model of surface waves was also successfully applied, with α values corrected to 0.38. There is no prior protonation in alkaline solutions, but some kinetics features (such as unusually high slope of $E_{1/2}$, $\log t_1$ dependence) also imply some influence of adsorption. Analysis of published data revealed that contribution of slow tautomeric equilibrium proposed in earlier works is very doubtful. Double protonation of cupferron anion at low pH should be considered instead.

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