

THE INFLUENCE OF 2,3-DIHYDROXYBENZALDEHYDE THIOSEMICARBAZONE ON CATALYTIC CURRENTS IN THE SYSTEM MOLYBDENUM(VI) – POTASSIUM CHLORATE IN ACID SULFATE SOLUTIONS

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Abstract: The polarographic catalytic current in acid solutions of Mo(VI), 2,3-dihydroxybenzaldehyde thiosemicarbazone (TSC 2,3-DHBA) and chlorate ions has been investigated. The scheme of reactions, taking place in the solutions and on the electrode, has been proposed. The increase of the catalytic current is explained by the formation of an active intermediate complex [Mo(V)-TSC 2,3-DHBA (ClO₃⁻)]. The rate constant of this complex formation $K = 2.56 \cdot 10^6 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$, the activation energy $E_a = 15.9 \text{ kcal} \cdot \text{mol}^{-1}$ and the reaction activation entropy $\Delta S_a^\ddagger = -23.5 \text{ e.u.}$ have been calculated.

Keywords: voltammetry, catalytic current, molybdenum, thiosemicarbazone 2,3-dihydroxybenzaldehyde, chlorate of potassium.

Introduction

The influence of aromatic hydroxyl-containing compounds on the kinetics and mechanism of reactions in solutions involving molybdenum(VI), chlorate- [1-8] and bromate-ions [9] is rather different. So, in a solution with a small content of phenol and large enough concentrations of Mo(VI) and KClO₃ the maximum catalytic wave arises in the area of the potentials matching the second form of Mo(III) on electrode [2].

Catechol [1], 2,3-dihydroxybenzaldehyde (2,3-DHBA) [4] as well as mandelic acid (HMand) [3,5,6] stabilize certain forms of Mo(V) and Mo(III), formed during the polarographic stepwise reduction of Mo(VI) in solutions containing Na₂SO₄ as supporting electrolyte (pH 1 – 2.5). Two reduction waves for Mo(VI) complexes into Mo(V) and Mo(III) complexes were registered on polarograms. The presence of ClO₃⁻ ions proves a large increase of the catalytic current on the potentials of the first wave of reduction for Mo (VI). This effect allows an increasing of the sensitivity of the Mo(VI) determination.

The catalytic adsorptive voltammetry with accumulation [5-9] allows an additional increasing of the sensitivity for the molybdenum determination.

The present work is dedicated to the investigation of the nature of polarographic current in solutions containing Mo(VI), chlorate-ions and 2,3-dihydroxybenzaldehyde thiosemicarbazone (TSC 2,3-DHBA). The special attention is given to the influence of TSC 2,3-DHBA on the catalytic current in the system Mo (VI) – KClO₃, as well as to the comparison of these results with those obtained in the presence of Catechol [1], 2,3-DHBA [4] and HMand [3, 5-9].

Experimental part

The measurements of polarographic catalytic currents were carried out using the polarograph PU-1 (Russia) in the thermostated (25±0.1°C) three-electrode cell containing: the MDE (2.45 mg^{2/3} c^{-1/2}) working drop electrode (a), the saturated calomel electrode (SCE) as a reference electrode (b) and a platinum wire as an auxiliary electrode (c).

The pH values were determined with an universal pH-meter with a glass electrode.

The initial molybdenum(VI) solution was prepared from the chemically pure Na₂MoO₄·2H₂O salt. The purity of other reagents was of the analytical or chemically pure grades. The ligand standard solution (TSC 2,3-DHBA) with the concentration of 5·10⁻⁵ mol/dm³ was prepared as follows: an exact weighted amount of the reagent was placed in a 200 cm³ volumetric flask, then bidistilled water was added, the mixture was carefully mixed until the reagent full dissolution, filled up to the mark and mixed again. The aqueous solution of TSC 2,3-DHBA is unstable to light, thus every two day we prepared fresh solutions of this ligand.

Before the registration of the polarogram, the investigated solutions were deoxygenated by blowing off a current of the electrolytic hydrogen within 20 minutes.

Results and Discussion

In the Mo(VI) acid solutions at pH 1.0 – 2.5 in the presence of chlorate-ions on polarograms there are two catalytic waves. They correspond to the potentials of the first and the second reduction waves of Mo(VI) and testify the catalytic activity for both Mo(V) and Mo(III) species. In the presence of TSC 2,3-DHBA, the catalytic wave in the form of a big maximum, as well as for 2,3-DHBA [4], covers the area of potentials for the first and second waves. However under the conditions of the greatest display of catalytic effects and small concentrations of Mo(VI) (less than $5 \cdot 10^{-6}$ mol/dm³), the potential of maximum corresponds to the first catalytic wave in the system Mo(VI) - ClO₃⁻, i.e. its occurrence is associated with the formation of an active form of Mo(V).

The occurrence of a maximum and the current falling at potentials more negative than E_{\max} are associated with a decreasing of the concentration of Mo(V) active form in the near-electrode layer and transformation of Mo(V) into Mo(III). Moreover, in solutions containing Mo(VI), an oxidant (KClO₃) and an organic surface-active ligand (TSC 2,3-DHBA), the occurrence of a wave in the form of a big maximum may be associated with the adsorption of the ligand and /or its complexes with Mo(VI), on the mercury surface. In such a case the concentration in the near-electrode layer is more important, the speed of the chemical reaction is increasing. This process is determining the speed of the catalytic process entirely. It is necessary to note down that the catalyst complex particles are in the monomeric forme, when the molybdenum (VI) concentration in investigated solutions has been below $1 \cdot 10^{-4}$ mol/dm³. In order to explain the nature of the maximum, we have investigated the influence of pH, temperature, height of the mercury column above the capillary as well as the concentrations of TSC 2,3-DHBA, Mo(VI) and ClO₃⁻ ions on the magnitude of the maximal current I_p .

The catalytic nature of the current in the system Mo(VI) - TSC 2,3-DHBA - ClO₃⁻ is proved by a high value of the temperature factor equal to 7 % per degree.

The independence of the current magnitude in solutions of Mo(VI) complexes with TSC 2,3-DHBA and ClO₃⁻ on the height of the mercury column above the capillary confirms the volumetric-kinetic nature of the rate for the rate-determining reaction of the catalytic process.

The dependence of the I_p value from concentration of the oxidant (KClO₃), having the form of a curve with an inflection point and a saturation region (Fig. 1, curve 1) testifies about the formation of intermediate active complex (IAC).

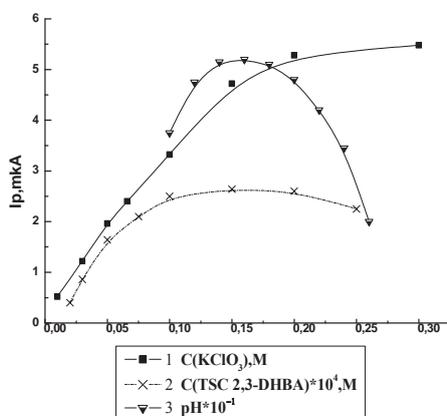


Fig.1. Dependence of I_p on the concentration of KClO₃, TSC 2,3-DHBA and pH: 0.2 M Na₂SO₄ + 0.05 M H₂SO₄ (pH 1.4-1.6). The concentrations: $1 \cdot 10^{-6}$ M Mo(VI) (curves 1, 2 and 3), $1.5 \cdot 10^{-5}$ M TSC 2,3-DHBA (1,3), 0.1 M KClO₃ (2) and 0.2 M KClO₃ (3).

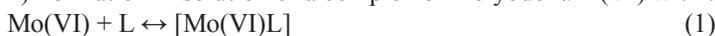
The curve of I_p dependence on the ligand concentration (TSC 2,3-DHBA) passes through a maximum (fig. 1, curve 2).

Initially the activating action of the ligand is increasing with the growth of concentration, reaches a peak and then decreases. The presence of the ligand in the coordination area of the catalyst gives rise to acceleration of the IAC formation. When in the coordination sphere of catalyst there are seats accepting the oxidant species KClO₃, the catalytic process is in progress. If, under certain conditions the ligand blocks completely the coordination seats around the catalyst, its activity decreases. The maximal value of the current has been observed at the ligand concentration equal to $1.5 \cdot 10^{-5}$ mol/dm³.

The optimal pH range is 1.5 – 1.6. The influence of the pH value (fig. 1, curve 3) may be connected with generation of a suitable for coordination form of the molybdenum and/or of the ligand, controlled by photolytic equilibria. Moreover, the ions of hydrogen participate in the redox reaction leading to the regeneration of depolarizer.

The dependence of the catalytic current magnitude on various concentration factors in solutions of Mo(VI) complexes containing 3-DHBA or TSC-2,3-DHBA has the similar character, and is explained by a common mechanism of the catalytic process in these systems. The general scheme of the catalytic process in such systems can be presented by following chemical and electrochemical reactions (for simplicity charges of particles are omitted):

1) Formation in solution of a complex of molybdenum (VI) with the organic ligand L



2) Reduction of the formed complex on electrode



3) Formation of an intermediate active complex with the oxidant species (ClO_3^-) and its adsorption on the electrode surface



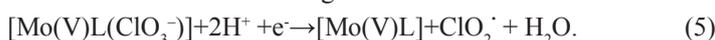
4) Redox-regeneration of the catalyst.

The IAC, formed according to the reaction (3), undergoes further changes leading to its disintegration in addition to the catalyst regeneration. As it has been shown by the authors [10] by studying the system $\text{Mo(VI)} - \text{H}_2\text{C}_2\text{O}_4 - \text{ClO}_3^-$, the redox regeneration of the catalyst can occur by two ways:

a) In the polarographically-active complex (PAC) $[\text{Mo(V)L}(\text{ClO}_3^-)]$ an electronic charge transfer from molybdenum on the oxidant (ClO_3^-) with a subsequent intracomplex oxidation and regeneration of the catalyst in its higher degree of oxidation, takes place



b) An electronic density shift in the PAC from the oxidant to molybdenum occurs and as a result the catalyst is regenerated in the lowest oxidation degree



The authors of [10] have shown that on the polarograms of molybdenum(VI) and $\text{H}_2\text{C}_2\text{O}_4$ in the presence of ClO_3^- ions, two waves can be observed, second wave being higher the first one. For small Mo(VI) concentrations and $\text{H}_2\text{C}_2\text{O}_4$ concentrations ($\approx 2.5 \cdot 10^{-3} \text{ mol/dm}^3$) only one peak on the polarograms, matching the catalytic current of reduction of complexes Mo(V) in Mo(III) is registered. For this reason authors considered that the catalyst regeneration occurs in its lowest degree of oxidation according equation (5). In our researches we have found, that for small ligand (concentrations $< 3 \cdot 10^{-5} \text{ mol/dm}^3$), one high sharp maximum corresponding to the first wave of reduction of the complex Mo(VI) to Mo(V) has been registered, and therefore it is more probable that the catalyst regeneration proceeds according to the first mechanism, i.e. the catalyst is regenerated in the highest oxidation state.

The investigation of Mo(VI)-Catechol- ClO_3^- [1, 2] and Mo(VI)-2,3-DHBA- ClO_3^- systems [4] show that for small concentrations of ligand ($< 5 \cdot 10^{-5} \text{ mol/dm}^3$) one sharp peak is observed on polarograms (see fig. 1, curve 3 [1]). With an increasing of the catechol or 2,3-DHBA concentrations, this peak becomes larger, without a clearly expressed top and the current decreases to more negative potentials. By a further increase of the ligand concentration ($> 5 \cdot 10^{-5} \text{ mol/dm}^3$) [4], the peak bifurcates and for concentrations more than $1 \cdot 10^{-4} \text{ mol/dm}^3$ the second maximum becomes slightly higher than the first one. It is quite likely, that this phenomenon is associated not only with an adsorption of complexes on the electrode surface as it was supposed in [6], but also with a regeneration of the catalyst in its lowest degree of oxidation. For TSC 2,3-DHBA the study of influence of higher concentrations on I_p is impossible because of its poor solubility.

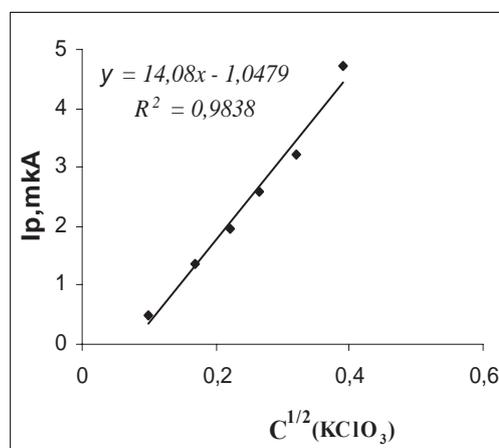


Fig.2. Dependence of I_p on $C^{1/2}(\text{KClO}_3)$ with $1 \cdot 10^{-6} \text{ M Mo(VI)}$, $1.5 \cdot 10^{-5} \text{ M TSC 2,3-DHBA}$, pH 1.45.

The reaction (3) is the rate limiting and consequently defines the rate of electrode process. The rate constant of PAC formation has been calculated according to Koutetski's equation $i_k/i_d=0,81\sqrt{nKC_s\tau}$ in solutions with the TSC 2,3-DHBA concentration of $1.5\cdot 10^{-5}$ mol/dm³ in the area of I_p linear dependence on $C^{1/2}(\text{KClO}_3)$ (fig.2), i.e. in conditions of a pseudo-ion-molecular reaction (where i_k is the catalytic current equal to I_p-I_d ; I_d – diffusion current of reduction of the complex Mo (VI) into Mo (V), recalculated for the Mo (VI) concentration of $1\cdot 10^{-6}$ mol/dm³, n – the number of electrons equal to 1; C_s – concentration of oxidant KClO_3 and τ is the dropping period of capillary, 3.6 s).

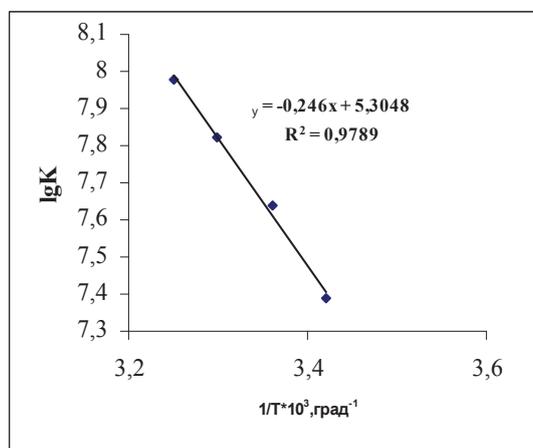


Fig.3. Dependence of log K on 1/T for $1\cdot 10^{-6}$ M Mo (VI), $1.5\cdot 10^{-5}$ M TSC 2,3-DHBA, pH 1.5.

From the function $\log K = f(1/T)$ (fig. 3) within the temperature range of 20 – 35°C the activation energy and entropy have been calculated according to [11]. The values of the PAC formation rate constant, as well as its activation energy and entropy are presented in Table 1.

Table 1

Kinetic and thermodynamic characteristics of catalytic processes in solutions of Mo (VI) with catechol, 2,3-DHBA, TSC 2,3-DHBA or HMand complexes and chlorate-ions

Ligand - activator	$K\cdot 10^6$, $\text{mol}^{-1}\cdot \text{dm}^3\cdot \text{c}^{-1}$	E_a , $\text{kcal}\cdot \text{mol}^{-1}$	ΔS_a^\ddagger , e. u.	References
Catechol	8.2	16,6	-26,0	1
2,3-DHBA	2.5	14,0	-28,3	4
TSC 2,3-DHBA	2.56	15.9	-23.5	-
HMand	220	14,3	-20,4	3

The found values of the rate constant for PAC formation [$\text{Mo(V) TSC 2,3-DHBA}(\text{ClO}_3^-)$], its activation energy and entropy testify about a high catalytic activity of systems. According to the activation influence, TSC 2,3-DHBA is close to catechol and 2,3-DHBA. The large negative values of entropy recognize the spatial difficulties arising at the introduction of ClO_3^- ions in the coordination sphere of Mo(V) complexes. As it can be seen from the values of activation entropy (Table 1), the involvement of ClO_3^- ions in the coordination sphere of Mo(V) complexes with HMand and TSC 2,3-DHBA occurs easier; therefore the activation action of this ligand is higher. On the polarograms of Mo(VI) complexes with TSC 2,3-DHBA and HMand in the presence of KClO_3 , the peaks have the highest I_p values. The minimum concentration of Mo(VI) ensuring the appearance of the peak on the polarogram is $4\cdot 10^{-8}$ mol/dm³ in the case of HMand while for TSC 2,3-DHBA this value is $2.5\cdot 10^{-8}$ mol/dm³.

The catalytic reaction in the system Mo(VI) - TSC 2,3-DHBA - ClO_3^- is very selective and can serve for the metal – catalyst determination of the molybdenum. The optimal conditions for this determination are following: $1.5\cdot 10^{-5}$ mol/dm³ TSC 2,3-DHBA, 0.2 M KClO_3 , 0.2 M Na_2SO_4 , 0.05 M H_2SO_4 (pH 1.4 – 1.6). The linearity of the function $I_p = f(C_{\text{Mo}})$ was observed in the concentration range $(0.25 - 10)\cdot 10^{-7}$ mol/dm³. For the Mo(VI) determination the presence of Tl (I), Cu (II), Pb (II), Mn (II), Zn (II), Co (II), Ni (II), Bi (III), Cr (III), Sn (IV), Te (IV), Se (IV) in the ratio 1:10; As (III), Sb (III), Fe (III), W (VI) in the ratio 1:1 do not interfere. The presence of large amounts of As (III), Sb (III), Fe (III)

and any amounts of V (V) and Cr (VI) leads to an increase of the Mo(VI) catalytic wave. The study of this influence is a purpose of our further research. At the ratio Mo(VI) : W(VI) > 1:1, I_p of molybdenum decreases, that is related, possibly, with an involvement of ligand in the complex formation with W(VI) and the formation of catalytic waves of tungsten.

Mandelic acid has been proposed for analytical purposes and is used owing to its good solubility and greater stability. Using the catalytic current of chlorate-ions, Mo (VI) in the presence of H Mand has been determined in lizimetric solutions and plants (tobacco leaves, hay beans ashes) [3]. The use of catalytic voltammetry with an adsorptive accumulation has allowed to authors [5-9] developing sensitive methods of the Mo (VI) determination in natural waters [5], while using tairon as a ligand – in river, well and artesian waters, in cucumbers, tomatoes and carrots [8]. The perspective to use the system Mo(VI) - TSC 2,3-DHBA - ClO_3^- for determination of molybdenum is attractive by its selectivity.

Conclusions

The polarographic catalytic currents in acid solutions, containing Mo(VI), chlorate-ions and 2,3-dihydroxybenzaldehyde thiosemicarbazone (TSC 2,3-DHBA) have been investigated, the schemes of the reactions proceeding in solution and on electrode were proposed. The increase of the catalytic current in the presence of ligand is explained by the formation in solution of an intermediate active complex $[\text{Mo(V) TSC 2,3-DHBA} (\text{ClO}_3^-)]$. The rate constant of this complex formation $K = 2.56 \cdot 10^6 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$, the activation energy $E_a = 15.9 \text{ kcal} \cdot \text{mol}^{-1}$ and the reaction activation entropy $\Delta S_a^\ddagger = -23.5 \text{ e.u.}$ have been calculated.

These values testify about the high catalytic activity of the studied system. The possibility of the molybdenum determination by means of the catalytic current has been shown.

Acknowledgments

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