Original articles

Kinetic regularities of electrochemical oxidation of the methionine anion on platinated platinum

E. V. Bobrinskaya✉, A. V. Vvedenskii, E. Yu. Sheremetova, A. I. Frolova

Voronezh State University,
1 Universitetskaya pl., Voronezh 394018, Russian Federation

Abstract

The purpose of this study was the determination of the kinetic regularities of the methionine electrooxidation process on the Pt(Pt) electrode in an aqueous-alkaline medium.

The main kinetic regularities of the methionine anion electrooxidation process were determined using by the methods of cyclic voltammetry, coulometry, and electrochemical impedance spectroscopy. The concentration of methionine in the alkaline solution before and after anodic oxidation was determined spectrophotometrically using spectrophotometer UNICO 2800. The measurements were carried out at room temperature both in an argon atmosphere and in an aerated aqueous solution. The results of voltammetric measurements were adjusted for the limiting oxygen recovery current and the charging current of the double electric layer.

The range of potentials of the electrochemical activity of the methionine anion on the Pt(Pt) electrode, the number of electrons involved in the anode process, and its kinetic scheme were determined. The main product of the electrooxidation of methionine in an alkaline medium on Pt(Pt) was the methionine sulfoxide anion. It was shown that the electrooxidation of the methionine anion on Pt (Pt) was carried out from the adsorbed state and was irreversible.

Keywords: Amino acid, Methionine, Platinum, Voltammetry, Electrooxidation, Anodic process

✉ Elena V. Bobrinskaya, e-mail: elena173.68@mail.ru

Condensed Matter and Interphases / Конденсированные среды и межфазные границы   2021;23(4): 459–467

E. V. Bobrinskaya et al.   Kinetic regularities of electrochemical oxidation of the methionine anion...

1. Introduction

For many years, special attention has been paid to methods for extracting platinum metals from ore-forming minerals. In particular, biotechnological methods based on the dissolution of platinoids by the metabolic products of heterotrophic metallophilic microorganisms. Amino acids and peptides are widely used for this purpose [1, 2]. It should be noted that amino acids are promising solvents in the process of microbiological leaching of gold-bearing raw materials; it is possible that this is also characteristic of platinum. This fact necessitates a more detailed study of the process of interaction of platinum with protein residues (in particular, with amino acids and short peptides), as well as clarification of the fundamental possibility of using substances of a protein nature as solvents of platinum. It is known that some amino acids affect the anodic dissolution of platinum, accelerating or slowing it down, but, in addition, the amino acid itself can be oxidized in the anodic process. Accordingly, it is important to take into account not only the direct anodic behaviour of platinum in alkaline solutions, but also specify the processes occurring with the amino acid.

Usually, the role of two functional groups $-NH_2$ and $-COOH$ is primarily studied during investigation of the electrooxidation process and adsorption of various amino acids on a platinum electrode [3–12]. Less information is available about the electrochemical and adsorption activity of amino acids containing other functional groups, for example, $-OH$ or $-S-CH$ [13–21]. On the other hand, studies [15, 19, 21] demonstrated that the presence of the $-S-CH$ group in the methionine molecule affects the regularities of its adsorption behaviour. Since during the electrooxidation of organic substances there is a correlation between adsorption and kinetic regularities of electrode processes, the purpose of this study was the determination of the kinetic regularities of the methionine electrooxidation process on the Pt(Pt) electrode in an aqueous-alkaline medium.

2. Experimental

The measurements were carried out at room temperature both in an argon atmosphere (chemically pure grade) and in an aerated aqueous solution by the cyclic voltammetry methods using a computerized potentiostatic complex IPC-Compact; frequency impedance spectra were obtained using the IPC Compact – FRA1 complex.

The methionine concentration in the alkaline solution before and after anodic oxidation was determined spectrophotometrically using a UNIKO 2800 spectrophotometer at wavelengths of 190–450 nm in quartz cuvettes with a thickness of 10 mm.

Potentiodynamic I,E-curves were obtained in a glass three-electrode cell with undivided cathode and anode spaces. It was preliminarily established that the separation of the spaces of the working and auxiliary electrodes practically does not affect the measurement results, however, it decreases the speed of the potentiostatic complex. The working electrode was platinum in the form of a grid, on which platinum black was electrolytically deposited. The auxiliary electrode was a smooth platinum mesh. The potential of the working electrode was measured relative to a saturated silver chloride reference electrode.

Before the experiment, the working electrode was treated with concentrated nitric acid for three minutes, washed repeatedly with bidistilled water, and then with a background 0.1 M NaOH solution.

Methionine solutions ($5 \cdot 10^{-3} \div 0.1$ M) was prepared from a weighed portion of a crystalline amino acid (Merck) in a background solution of sodium hydroxide (chemically pure grade) in bidistilled water. The fact that the introduction of an amino acid into the background solution is accompanied by a change in its acidity due to the occurrence of protonation/deprotonation reactions, changing the ratio between the main ionic forms of the amino acid was taken into account [22].

For the removal of possible electroactive impurities, before each measurement, the working electrode was treated with concentrated nitric acid (reagent grade), then repeatedly washed with distilled and rinsed with bidistilled water, and then subjected to potentiostatic anodic-cathodic activation in the background solution, changing the activation potential from +1.0 to –1.0 V, receiving 50 activation cycles.

The peak potential E_{max} of voltammetric $I,E(t)$-curve and the faradaic current at I_{max} are the main values experimentally measured

Condensed Matter and Interphases / Конденсированные среды и межфазные границы   2021;23(4): 459–467

E. V. Bobrinskaya et al.   Kinetic regularities of electrochemical oxidation of the methionine anion…

by linear voltammetry method. The results of voltammetric measurements were corrected for both the maximum current of oxygen reduction and the double layer charging current $I_{dl} = C_{dl}v$, where v is the potential scanning speed. Capacity value C_{dl} of the working electrode was evaluated by electrochemical impedance spectroscopy.

3. Results and discussion

For the determination of the potential range of the electrochemical activity of the methionine anion (Met⁻) on the Pt(Pt)-electrode, cyclic voltammograms were obtained both in the background solution and in the presence of Met⁻ both in aerated and deaerated solutions (Fig. 1).

In the absence of an amino acid on the Pt-electrode, three characteristic regions can be distinguished. In the hydrogen region (from −1.20 to −0.50 V) the processes of formation and ionization of adsorbed atomic hydrogen take place. Beyond the area of potentials from −0.50 to −0.20 V, in which only the currents of charging the double layer and the reduction of molecular oxygen were recorded, there was a region of oxygen adsorption, which began at $E > −0.20$ V. Processes with the participation of atomic oxygen are characterized by noticeable irreversibility: desorption of oxygen (for recoil curve) occurs at potentials corresponding to the charge of the double layer on the anodic branch of the voltammogram. Intensive release of molecular oxygen on the Pt-electrode started at $E > 0.6$ V.

The introduction of the methionine additive led to a noticeable increase in the current on the anodic branch of the cyclogram and the appearance of a peak at a potential of 0.60 V for aerated solution and 0.70 V for a deaerated solution, which was probably due to the electrooxidation of the amino acid. It should be noted that the change in the peak potential of electrooxidation with a change in the concentration of dissolved oxygen at a qualitative level indicates the involvement of oxygen-containing particles in the anodic process.

For the conformation of methionine electrooxidation in the range of the anodic peak potentials and for the determination of the number of electrons involved in this process, coulometric measurements were carried out, followed by spectrophotometric determination of the Met⁻ concentration in solution. It was found that the anodic peak potentials actually correspond to the process of electrooxidation of Met⁻, and two electrons take part in the anodic reaction (based on a current efficiency close to 100 %). Taking into account the results of coulometry, the total process of electrooxidation can be represented as follows:

$$2C_5H_{10}NSO_2^- + 2OH^- \rightarrow 2C_5H_{10}NSO_3^- + H_2O + 2\bar{e}.$$
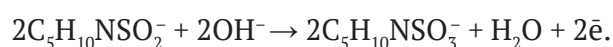
In this case, the main product of electrooxidation is methionine sulfoxide anion.

The identification of the kinetic limitations of the electrooxidation process requires diagnostic criteria allowing to detect the nature of the limiting stage of the electrochemical reaction, complicated by the adsorption of the reagent or product(s), and to establish the reversibility of
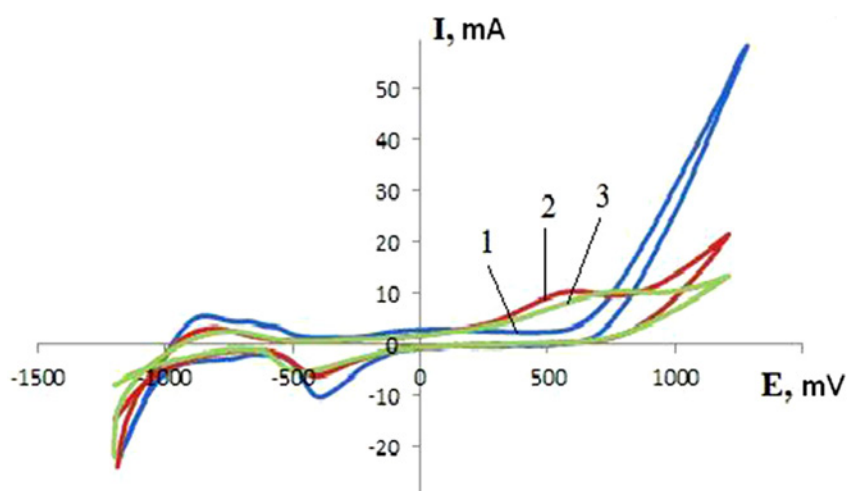
Fig. 1. Cyclic voltammograms obtained on a Pt-electrode at v = 0.005 V/s in an aqueous solution of 0.1 M NaOH (*1*) and 0.1 M NaOH + 0.01 M methionine without deaeration (*2*) and after deaeration of the solution (*3*)

Condensed Matter and Interphases / Конденсированные среды и межфазные границы   2021;23(4): 459–467

E. V. Bobrinskaya et al.   Kinetic regularities of electrochemical oxidation of the methionine anion...

the process. The method of linear voltammetry usually uses the current I_{max} in peak on the anodic branch $I,E(t)$-dependencies and the corresponding potential E_{max} as such criteria. Both parameters depend on the concentration of the amino acid, the pH of the background solution, and the potential scan rate.

The analysis of the experimental data shows that with an increase in the potential scanning rate, the current on both branches of the voltammogram increased. In this case, the anodic peak potential was noticeably improved, both under deaeration conditions and in an aerated solution. The decrease in the height of the oxygen desorption peak, as well as the shift towards the anodic side of the cathodic peak potentials, observed on the recoil curves, were most probably associated with the adsorption of the amino acid and (or) its oxidation products on the electrode. An increase in the concentration of the methionine anion led to a similar result. At the same time, the value of the current at the

peak and its position were practically invariant in relation to a change in the rotational speed of the platinum disk electrode (Fig. 2).

The obtained result indicates that the anodic peak current at $I,E(t)$-dependence was not associated with liquid-phase diffusion of reagents or products. It probably reflected the features of their adsorption accumulation on the electrode, which can be confirmed by analysing the diagnostic criteria of the linear voltammetry method [23–25].

The current and the anodic peak potential depend on the potential scan rate (v), the concentration of the methionine anion and the pH value, both in a previously deaerated solution and in a solution in equilibrium with the atmosphere. It was established that dependencies $I_{max} = f(v)$ are linear and, after correcting for the oxygen reduction current and the charging current of the electric double layer, they are extrapolated to the origin of coordinates (Fig. 3). This fact and the slope of this dependence close to one, indicate that the methionine electrooxidation
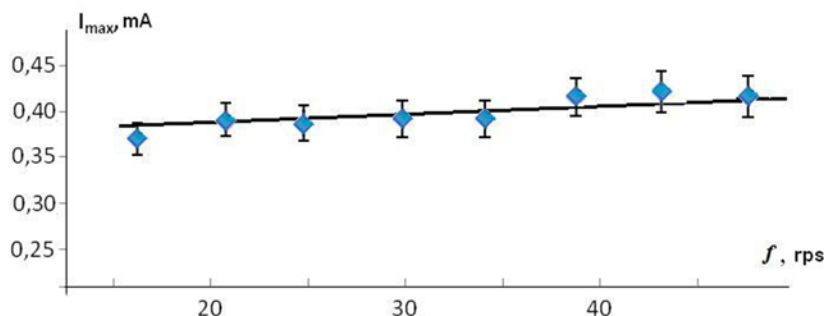

Fig. 2. The dependence of the peak current of electrooxidation in 0.10 M NaOH + 0.03 M Met⁻ solution, on the number of revolutions Pt of the rotating disk electrode; v = 0.10 V/s
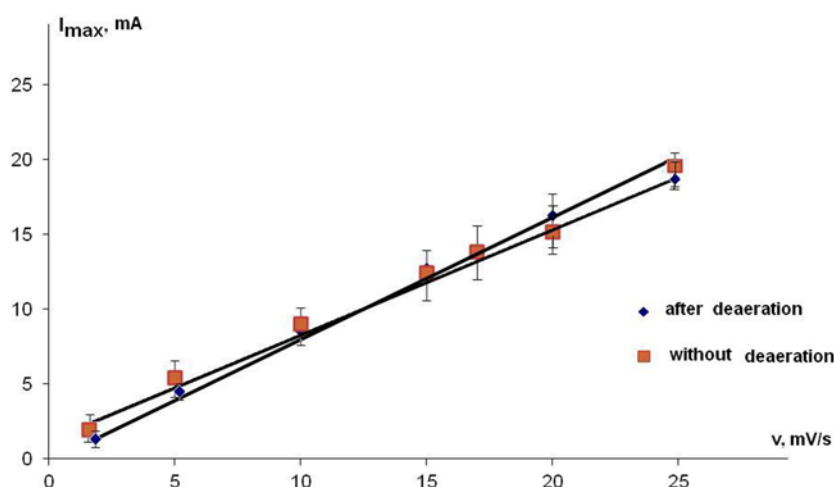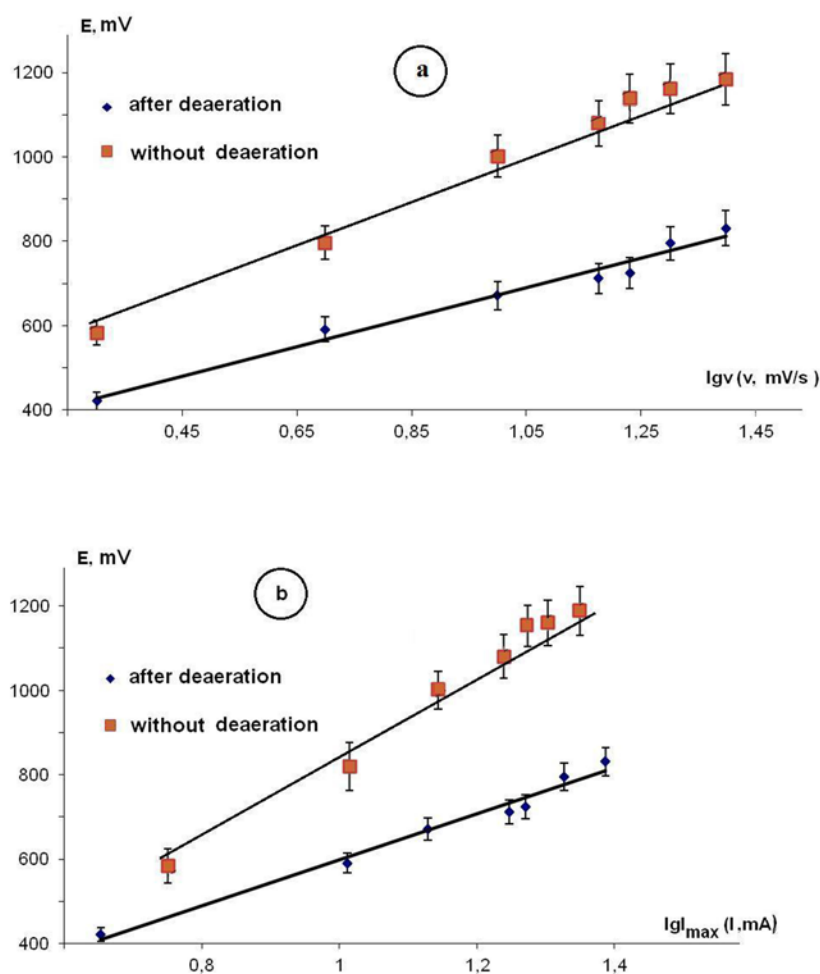

Fig. 3. Effect of the potential scanning rate on the value of the anodic peak current in a 0.10 M NaOH solution containing 0.01 M Met⁻

Condensed Matter and Interphases / Конденсированные среды и межфазные границы   2021;23(4): 459–467

E. V. Bobrinskaya et al.   Kinetic regularities of electrochemical oxidation of the methionine anion...

process is limited by the charge transfer stage and is irreversible. At the same time, the adsorbed particles are involved in the electrochemical reaction.
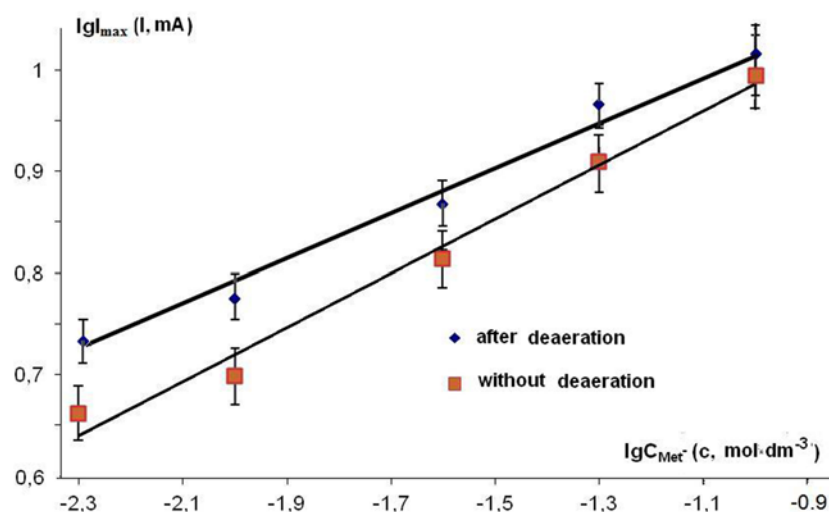
It can be assumed that the two-electron net process of methionine electrooxidation is a stepwise process. Considering that the dependencies $E_{max} - \lg v$ and $E_{max} - \lg I_{max}$ are linear (Fig. 4), and the value of $d \lg I_{max}/d \lg v$ parameter equals 0.21±0.052 (without deaeration of the solution) and 0.12±0.014 (after deaeration), then the stage of abstraction of the first electron is most likely the limiting stage of the anodic reaction of methionine electrooxidation. It should be noted that if the stage of transition of the second electron is taken as the limiting stage, then the slope of the corresponding dependence would be much smaller. In addition, the amplitude of the current on the voltammogram is affected

by both the concentration of the methionine anion and the concentration of OH⁻ ions. With an increase in the concentration of the methionine anion, the amplitude of the anodic peak current increases (Fig. 5), and the peak potential becomes more positive.

In this case, the value of the parameter $\dfrac{d \lg I_{max}}{d \lg C_{Met^-}} < 1$ and is 0.22 (after deaeration) and 0.27 (without deaeration). The latter means that the adsorbed particles are involved in the process of electrooxidation, as we assumed above. Another confirmation of this fact is the voltammograms obtained in the background electrolyte after washing the working electrode. The adsorption accumulation of methionine anions was carried out at potentials of 0.00; 0.20 and −0.25 V for 10 minutes. The obtained anodic

Fig. 4. Effect of the potential scanning speed (a) and the logarithm of the anodic peak current (b) on the position of the peak of electrooxidation in solutions containing 0.10 M NaOH+ 0.01 M Met⁻

Condensed Matter and Interphases / Конденсированные среды и межфазные границы   2021;23(4): 459–467

E. V. Bobrinskaya et al.   Kinetic regularities of electrochemical oxidation of the methionine anion...

Fig. 5. The dependence of the maximum current of electrooxidation on the concentration of Met⁻ anions at $v = 0.10$ V/s
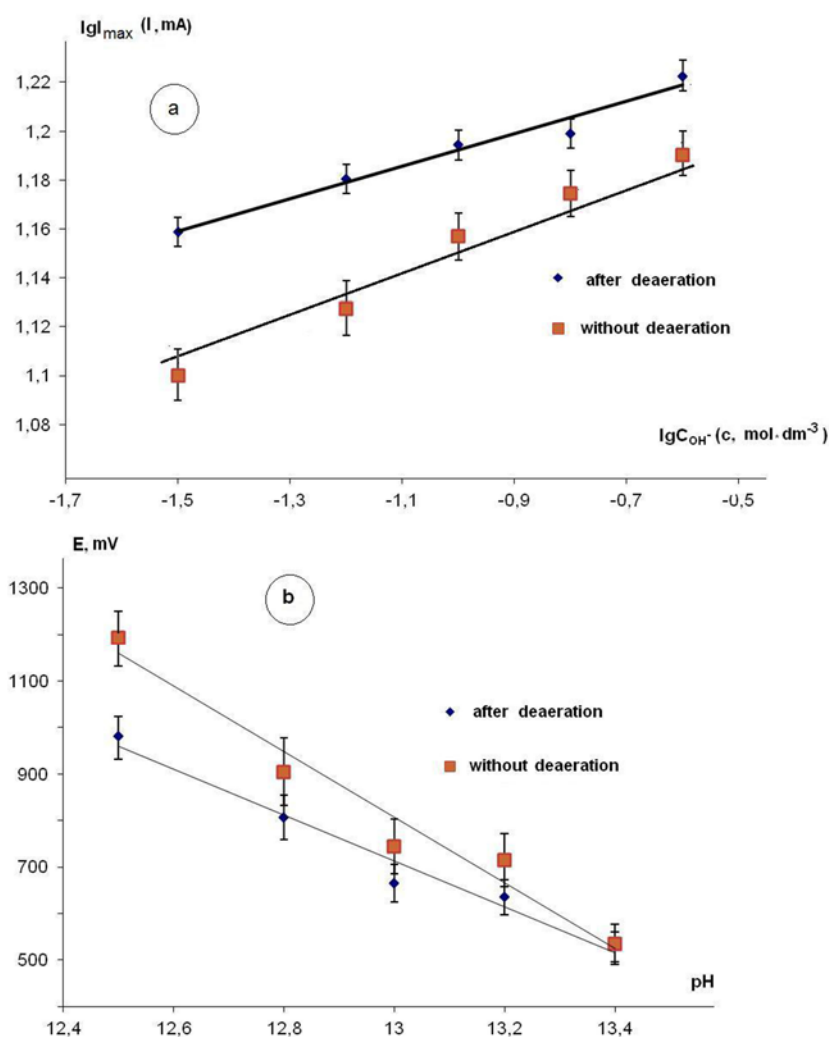
voltammograms in a 0.1 M NaOH solution before the adsorption accumulation of the amino acid (1) and after washing the electrode (2–4) are shown in Fig. 6.

The peaks of the amino acid electrooxidation were still registered on voltammograms obtained in the solution of the background electrolyte after washing the electrode. This indicates that the electrooxidation of Met⁻ on the Pt-electrode is carried out from the adsorbed state and represents the so-called "surface" electrochemical reaction. In addition, the adsorption of methionine on platinum is most likely irreversible.

Since hydroxyl ions are also involved in the process of electrooxidation of methionine anions, data on the effect of their concentration (at a constant concentration of Met⁻) on the rate of the anodic process were obtained. An increase in pH led to an increase in the amplitude of the maximum of electrooxidation and a shift in its potential in the cathodic direction, regardless of the degree of aeration of the working solution (Fig. 7). The value of the $d\lg I_{max}/d\lg C_{OH^-}$ parameter is not zero, but noticeably less than one, and in both cases amounts to 0.10±0.03 (Fig.7a), which means that adsorbed OH⁻-ions were involved in the anodic process.
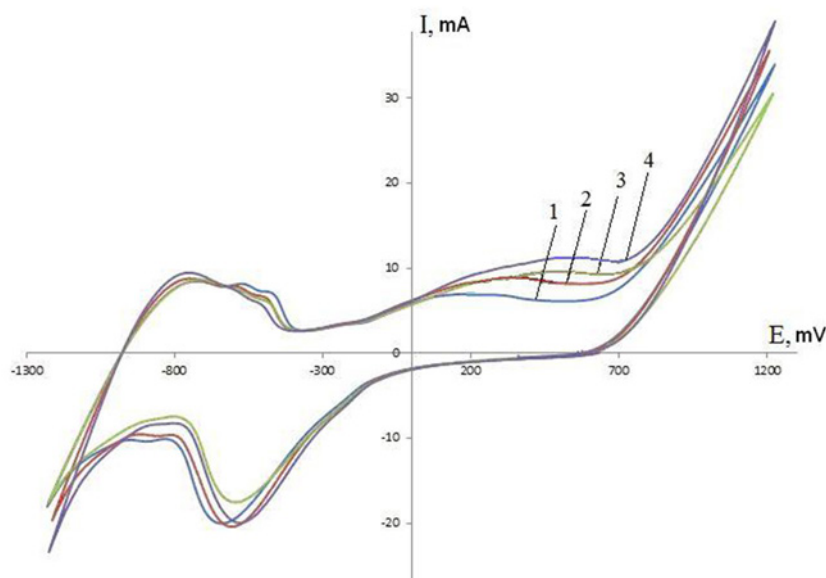
Fig. 6. Cyclic voltammograms obtained on Pt electrode at $v = 0.01$ V/s in an aqueous solution of 0.1 M NaOH before (*1*) and after adsorption accumulation and electrode washing: (*2*) – 0.00 V; (*3*) – −0.25 V; (*4*) – 0.20 V

Condensed Matter and Interphases / Конденсированные среды и межфазные границы   2021;23(4): 459–467

E. V. Bobrinskaya et al.   Kinetic regularities of electrochemical oxidation of the methionine anion...

Fig. 7. Change of the current (a) and peak potential (b) of electrooxidation depending on the pH of the solution containing 0.01 M Met⁻ at v = 0.10 V/s

Finally, since the kinetic parameter $\dfrac{d\lg I_{max}}{d\lg C_{Met^-}} > 0$, and with an increase in pH, the potential of the anodic maximum shifts to the negative values, it can be assumed that the dominant adsorbed form is the Red-form, which means that the methionine anion exhibits higher surface activity on platinum than the products of its electrooxidation.

4. Conclusions

The methionine anion exhibits significant electrochemical activity at the Pt(Pt) electrode. Two electrons are involved in the anodic process of electrooxidation, according to coulometric analysis with subsequent spectrophotometric determination of the methionine content in the solution. The most probable product of electrooxidation is methionine sulfoxide. The results of linear voltammetry indicate that, regardless of the degree of aeration of the working solution, charge transfer is the limiting stage of the methionine electrooxidation process. The process of methionine electrooxidation is kinetically irreversible and proceeds with the participation of adsorbed Met⁻ and OH⁻ ions. The Red-form, i.e., methionine anions, is the dominant adsorptive form in the electrooxidation reaction.

Authors contributions

A. V. Vvedenskii – scientific leadership, research concept, development of methodology, final conclusions. E. V. Bobrinskaya – conducting research, writing an article, editing the text.

Condensed Matter and Interphases / Конденсированные среды и межфазные границы   2021;23(4): 459–467

E. V. Bobrinskaya et al.   Kinetic regularities of electrochemical oxidation of the methionine anion...

Sheremetova E. Yu., Frolova A. I. – conducting research.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

References

1. Arens V. I., Chernyak A. S. Khimiya i microbiologiya v sfere gornogo dela [Mining chemistry and microbiology]. *Mining informational and analytical bulletin (scientific and technical journal)*. 2006:8: 304–313. Available at: https://elibrary.ru/item.asp?id=9496289 (In Russ.)

2. Tumanova E. A., Lozhkin V. I., Chebykin E. P., Korolev S. A., Safonov A. Yu. Electrochemical dissolution of platinum in the presence of some amino acids. *Russian Journal of Electrochemistry*. 1999;35(12): 1327–1330. Available at: https://elibrary.ru/item.asp?id=13330275

3. Huerta F., Morallón E., Quijada C., Vázquez J. L., Berlouis L. E. A. Potential modulated reflectance study of the electrooxidation of simple amino acids on Pt (111) in acidic media. *Journal of Electroanalytical Chemistry*. 2000;489(1-2): 92–95. https://doi.org/10.1016/s0022-0728(00)00202-3

4. Huerta F., Morallon E., Cases F., Rodes A., Va´zqueza J. L., Aldaz A. Electrochemical behaviour of amino acids on Pt (h,k,l). A voltammetric and in situ FTIR study. Part. 2. Serine and alanine on Pt (111). *Journal of Electroanalytical Chemistry*. 1997;431(2): 269–275. https://doi.org/10.1016/S0022-0728(97)00212-X

5. Marangoni D. G., Wylie I. G. N., Roscoe S. G. Surface electrochemistry of the oxidation reactions of a- and b-alanine at a platinum electrode. *Bioelectrochemistry and Bioenergetics*. 1991;25(2): 269–277. https://doi.org/10.1016/0302-4598(91)87008-5

6. Horányi G., Rizmayer E. M. Study of the adsorption of glycine on platinized platinum electrodes by tracer methods. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*. 1975;64(1): 15–19. https://doi.org/10.1016/s0022-0728(75)80275-0

7. Ogura K., Kobayashi, M., Nakayama, M., Miho M. Electrochemical and in situ FTIR studies on the adsorption and oxidation of glycine and lysine in alkaline medium. *Journal of Electroanalytical Chemistry*. 1998;449(1-2): 101–109. https://doi.org/10.1016/s0022-0728(98)00015-1

8. Xiao, Sun S.-G., Yao J.-L., Wu Q.-H., Tian Z.-Q. Surface-enhanced Raman spectroscopic studies of dissociative adsorption of amino acids on platinum and gold electrodes in alkaline solutions. *Langmuir*. 2002;18(16): 6274–6249. https://doi.org/10.1021/la025817f

9. Vvedenskii A. V., Bobrinskaya E. V., Kraschenko T. G., Vitnova O. A., Kuleshova N. E. Kinetics of anodic oxidation of anions of mono-and dicarboxylic aminoacids on Pt. *Proceedings of Voronezh State University. Series: Chemistry. Biology. Pharmacy.* 2013;2: 19–25. Available at: https://elibrary.ru/item.asp?id=20400913 (In Russ., abstract in Eng.)

10. Kraschenko T. G., Vvedenskii A. V., Bobrinskaya E. V., Kuleshova N. E. Kinetics of electrochemical oxidation of anion glycine on gold. *Kondensirovannye sredy i mezhfaznye granitsy = Condensed Matter and Interphases.* 2014;16(1): 42-49. Available at: https://elibrary.ru/item.asp?id=21490889 (In Russ., abstract in Eng.)

11. Tumanova E. A., Safonov A. Yu. Adsorption of some amino acids and dipeptides on the platinum electrode. *Russian Journal of Electrochemistry*. 1998;34(2): 153–159. Available at: https://elibrary.ru/item.asp?id=13289291

12. Bakanina U. N., Zhukova E. A., Abdullin I. F., Turova E. H., Budnikov G. K. Voltammetric study of some amino acids on platinum, gold, copper, and nickel electrodes. *Russian Journal of General Chemistry*. 2000;70(6): 837–840. Available at: https://elibrary.ru/item.asp?id=13360186

13. Huerta F., Morallón E., Vázquez J. L., Aldaz A. Electrochemical behaviour of amino acids on Pt(hkl). A voltammetric and in situ FTIR study: Part IV. Serine and alanine on Pt(100) and Pt(110). Journal of Electroanalytical Chemistry. 1999;475(1): 38–45. https://doi.org/10.1016/S0022-0728(99)00337-X

14. Kong D.-W., Zhu T.-W., Zeng D.-M., Zhen C.-H., Chen S.-P. In- situ FTIR spectroscopic studies of adsorption and oxidation of L- serine on Pt electrodes in neutral solutions. *Chemical Journal of Chinese Universities*. 2009;30(10): 2040–2044. Available at: http://www.cjcu.jlu.edu.cn/EN/Y2009/V30/I10/2040

15. Reynaud J. A., Malfoy B., Canesson P. Electrochemical investigations of amino acids at solid electrodes. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*. 1980;114(2): 195–211. https://doi.org/10.1016/s0022-0728(80)80447-5

16. Horányi G. A direct and indirect radiotracer study of the adsorption of serine at a platinized platinum electrode. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*. 1991;304(1-2): 211–217. https://doi.org/10.1016/0022-0728(91)85503-h

17. Mescheryakov V. V., Popova S. S., Raspopova G. A., Bobrova V. A. Eleceokhimicheskoe povedenie aminokislot na Pt-electrode [Electrochemical behavior of amino acids on the Pt electrode]. In: *Actual problems of electrochemical technology: Collection of*

Condensed Matter and Interphases / Конденсированные среды и межфазные границы   2021;23(4): 459–467

E. V. Bobrinskaya et al.   Kinetic regularities of electrochemical oxidation of the methionine anion...

articles by young scientists. Saratov: Sarat. state tech. un-t Publ.; 2000. pp. 244–249. (In Russ.)

18. Gu Y.-J., Sun S.-G., Chen S.-P., Zhen C.-H., Zhou Z.-Y. Adsorption of Serine on Pt single-crystal electrodes in sulfuric acid solutions. *Langmuir*. 2003;23(19): 9823–9830. https://doi.org/10.1021/la034758i

19. Popova S. S., Okisheva N. A., Ryabukhova T. O. Adsorbtsionno-elektrokhimicheskoe povedenie aminokislot na grafitirovannom mednom Cu(C)-elektrode [Adsorption-electrochemical behavior of amino acids on graphitized copper Cu (C)-electrode]. *Bulletin of the Technological University*. 2016;19(9): 155–157. Available at: https://www.elibrary.ru/item.asp?id=25948195 (In Russ.)

20. Shaidarova L. G., Ziganshina S. A., Budnikov G. K. Electrocatalytic Oxidation of cysteine and cystine at a carbon-paste electrode modified with ruthenium(IV) oxide. *Journal of Analytical Chemistry*. 2003;58(6): 577–582. https://doi.org/10.1023/a:1024124421268

21. Reynaud J. A., Malfoy B., Canesson P. Electrochemical investigations of amino acids at solid electrodes. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*. 1980;114(2): 195–211. https://doi.org/10.1016/s0022-0728(80)80447-5

22. Tukavkina N. A. *Bioorganicheskaya khimiya* [Bioorganic chemistry: textbook for universities]. Moscow: Drofa Publ.; 2005. 542 p. (In Russ.)

23. Galus V. *Teoreticheskie osnovy elektrokhimicheskogo analisa* [Theoretical Foundations of Electrochemical Analysis]. Moscow: Mir Publ., 1974. 552 p. (In Russ.)

24. Bard A. J., Faulkner L. R. Electrochemical methods: fundamentals and applications. New York: John Wiley & Sons; 2001. 833 p.

25. Laviron E. The use of polarography and cyclic voltammetry for the study of redox systems with adsorption of the reactants. Heterogeneous vs. surface path. *J. Electroanal. Chem.* 1995;382(1-2): 111–127.

Information about the authors

Vvedenskii Alexander Viktorovich, DSc in Chemistry, Professor, Professor at the Department of Physical Chemistry, Voronezh State University, Voronezh, Russian Federation; e-mail alvved@chem.vsu.ru. ORCID iD: https://orcid.org/ 0000-0003-2210-5543.

Elena V. Bobrinskaya, PhD in Chemistry, Associate Professor at the Department of Physical Chemistry, Voronezh State University, Voronezh, Russian Federation; e-mail: elena173.68@mail.ru. ORCID iD: https://orcid.org/0000-0001-7123-4224.

Elena Yu. Sheremetova, second year master's student, Faculty of Chemistry, Voronezh State University, Voronezh, Russian Federation.

Angelina I. Frolova, fifth year student, Faculty of Chemistry, Voronezh State University, Voronezh, Russian Federation.