

## СИНТЕЗ И ЭЛЕКТРОХИМИЧЕСКИЕ СВОЙСТВА Fe (III)-ЭТИОПОРФИРИНА II И ЕГО 5,15-БИС(ПИРИД-3-ИЛ)-ПРОИЗВОДНОГО

Н.М. Березина, Do Ngoc Minh, М.И. Базанов, А.С. Семейкин, А.А. Максимова

Надежда Михайловна Березина\*, Михаил Иванович Базанов, Александра Александровна Максимова  
Кафедра аналитической химии, Ивановский государственный химико-технологический университет,  
просп. Шереметевский, 7, Иваново, Российская Федерация, 153000  
E-mail: sky\_berezina@rambler.ru\*, bazanov@isuct.ru

Александр Станиславович Семейкин

Кафедра органической химии, Ивановский государственный химико-технологический университет,  
просп. Шереметевский, 7, Иваново, Российская Федерация, 153000  
E-mail: semeikin@isuct.ru

Do Ngoc Minh

Institute of Marine Economy and Engineering, Ba Ria - Vung Tau University, Truong Cong Dinh Str., 83,  
Vungtau, 790000, Vietnam  
E-mail: dongocminh@mail.ru

*В работе синтезированы и охарактеризованы 3,7,13,17-тетраметил-2,8,12,18-тетраэтилпорфин железо (III) ацетат [(AcO)FeTMeTEtP] и 5,15-бис(пирид-3-ил)-3,7,13,17-тетраметил-2,8,12,18-тетраэтилпорфин железо (III) ацетат [(OAc)OFe(Py-3)<sub>2</sub>TMeTEtP]. Методом циклической вольтамперометрии изучены электрохимические свойства и электрокаталитическая активность комплексов в реакции электровосстановления молекулярного кислорода в 0,1M растворе KOH. Проведен сравнительный анализ по влиянию комплексообразования, а также функционального замещения в молекуле (введение одного или двух пиридинильных фрагментов в мезо-положения макроцикла) на электрохимические параметры и активность алкилзамещенного и пиридилзамещенного порфиринов в реакции ионизации молекулярного кислорода. Исследование электрохимического поведения комплексов близкого строения в рассматриваемых условиях показало существенное влияние пиридинильного заместителя на изучаемые свойства. Полученные в нашей работе экспериментальные и литературные данные показали, что для (AcO)FeTMeTEtP и (AcO)Fe(Py-3)<sub>2</sub>TMeTEtP характерны редокс-процессы с участием как порфиринового макрокольца ( $L \leftrightarrow L^{\cdot-}$ ,  $L^{\cdot-} \leftrightarrow L^{2-}$ ), так и металла ( $Fe^{3+} \leftrightarrow Fe^{2+}$ ,  $Fe^{2+} \leftrightarrow Fe^+$ ). Обнаружено, что для (AcO)FeTMeTEtP, (Cl)Fe(Py-3)HMeDEtP и (AcO)Fe(Py-3)<sub>2</sub>TMeTEtP процесс электровосстановления центрального иона металла  $Fe^{3+} \leftrightarrow Fe^{2+}$  протекает при дополнительном введении в систему молекулярного кислорода. Результаты исследования электрокаталитической активности тетрапиррольных соединений в водно-щелочной среде позволяют сделать заключение о положительном влиянии как комплексообразования, так и введения электронодонорных алкильных заместителей в порфириновый макроцикл на процесс электровосстановления молекулярного кислорода. Каталитическая активность изученных соединений в реакции ионизации кислорода возрастает согласно снижению потенциала электровосстановления  $O_2$  [ $E_{1/2}(O_2)$ ] в ряду:  $H_2TMeTEtP < (AcO)FeTMeTEtP < (AcO)Fe(Py-3)_2TMeTEtP$ .*

**Ключевые слова:** порфирины, Fe-комплексы, вольтамперометрия, электровосстановление, молекулярный кислород

## SYNTHESIS AND ELECTROCHEMICAL CHARACTERISTICS OF Fe (III)-ETIO PORPHYRIN II AND ITS 5,15-BIS(PYRID-3-YL) DERIVATIVE

N.M. Berezina, Do Ngoc Minh, M.I. Bazanov, A.S. Semeikin, A.A. Maksimova

Nadezhda M. Berezina\*, Mikhail I. Bazanov, Aleksandra A. Maksimova

Department of Analytical Chemistry, Ivanovo State University of Chemistry and Technology, Sheremetevsky ave., 7, Ivanovo, 153000, Russia

E-mail: sky\_berezina@rambler.ru \*, bazanov@isuct.ru

Aleksandr S. Semeikin

Department of Organic Chemistry, Ivanovo State University of Chemistry and Technology, Sheremetevsky ave., 7, Ivanovo, 153000, Russia

E-mail: semeikin@isuct.ru

Do Ngoc Minh

Institute of Marine Economy and Engineering, Ba Ria - Vung Tau University, Truong Cong Dinh st., 83, Vungtau, 790000, Vietnam

E-mail: dongocminh@mail.ru

*In this work acetato(3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphinato)iron (III) [(AcO)FeTMeTEtP] and acetato[5,15-bis(pyrid-3-yl)-3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphinato]iron(III) [(OAc)OFe(Py-3)<sub>2</sub>TMeTEtP] have been synthesized and characterized. Electrochemical properties and electrocatalytic activity of complexes in oxygen electroreduction reaction in 0.1M KOH aqueous solution were studied by the cyclic voltammetry. The comparative analysis of the effect of complex formation, as well as functional substitution in the molecule (the introduction of one or two pyridyl fragments into meso-positions of the macrocycle) on the electrochemical parameters and activity of alkyl-substituted and pyridyl-substituted porphyrins in oxygen electroreduction reaction were carried out. The research of electrochemical behavior of complexes with close structure in experimental conditions has showed that a pyridyl substituent significantly affects the studied properties. The published data and obtained in our work have showed that (AcO)FeTMeTEtP and (AcO)Fe(Py-3)<sub>2</sub>TMeTEtP are characterized by redox processes involving both the porphyrin macrocycle ( $L \leftrightarrow L^{\cdot-}$ ,  $L^{\cdot-} \leftrightarrow L^{2-}$ ), and metal ( $Fe^{3+} \leftrightarrow Fe^{2+}$ ,  $Fe^{2+} \leftrightarrow Fe^+$ ). It should be noted that the process of electroreduction of the central metal ion ( $Fe^{3+} \leftrightarrow Fe^{2+}$ ) proceeds under additional introduction of oxygen into the system for the (AcO)FeTMeTEtP, (Cl)Fe(Py-3)HMeDEtP and (AcO)Fe(Py-3)<sub>2</sub>TMeTEtP. The results of investigation of the electrocatalytic activity of tetrapyrrole compounds in an aqueous-alkaline medium allows one to make a conclusion about the positive effect of complexation and the introduction of electron-donor substitutes in the porphyrin macrocycle on the electroreduction process of molecular oxygen. The electrocatalytic activity of the studied compounds in the oxygen ionization reaction were increased, according to the decrease in the half-wave potential of O<sub>2</sub> [E<sub>1/2</sub>(O<sub>2</sub>)] in the series: H<sub>2</sub>TMeTEtP < (AcO)FeTMeTEtP < (AcO)Fe(Py-3)<sub>2</sub>TMeTEtP.*

**Key words:** porphyrins, Fe-complexes, voltammetry, electroreduction, molecular oxygen

### Для цитирования:

Березина Н.М., До Нгос Минх, Базанов М.И., Семейкин А.С., Максимова А.А. Синтез и электрохимические свойства Fe (III) - этиопорфирина II и его 5,15-бис(пирид-3-ил)-производного. *Иzv. вузов. Химия и хим. технология.* 2018. Т. 61. Вып. 2. С. 29–34

### For citation:

Berezina N.M., Do Ngoc Minh, Bazanov M.I., Semeikin A.S., Maksimova A.A. Synthesis and electrochemical characteristics of Fe (III) - etio porphyrin ii and its 5,15-bis(pyrid-3-yl) derivative. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2018. V. 61. N 2. P. 29–34

### INTRODUCTION

Octaalkylporphyrin derivatives are the first synthetic porphyrins which have been investigated in

detail by means of different electrochemical methods [1]. The electrochemical behavior of these compounds is that they are stepwise oxidized or reduced at the

$p$ -conjugated system to give  $\pi$ -cation radicals, dication and  $\pi$ -anion radicals, dianions. For metalloctaethylporphyrins containing metal ions  $Zn^{2+}$  and  $Mg^{2+}$ , the  $\pi$ -conjugated system undergoes electrochemical conversions, but in the case of Fe (III)-, Co (II)-, Mn (III)-complexes electrochemical processes both at the  $\pi$ -conjugated system and at the central metal ions are observed. The first comprehensive comparison of electrode reactions involving the formation of  $\pi$ -anion radicals and  $\pi$ -cation radicals was described in the work. According to this work, electrochemistry of twenty-five octaethylporphyrins with different metal ions has been investigated by cyclic voltammetry in BuCN (valeronitrile) for oxidation, and in DMSO (dimethylsulfoxide) for reduction. It was found that the potential difference  $E_{1/2}$  between the first oxidation stage with the formation of the  $\pi$ -cation radical and the first reduction stage to obtain the  $\pi$ -anion radical is  $2.25 \pm 0.15$  V. This value is close to the theoretically calculated value of the energy difference between HOMO and LUMO (2.18 V), from which the electron is removed or to which it is attached for most metalloporphyrins [2]. Additionally, the potential difference  $E_{1/2}$  between the first and second reduction stages is  $0.42 \pm 0.05$  V, and the potential difference  $E_{1/2}$  between the first and second oxidation stages is  $0.29 \pm 0.05$  V. These potential differences do not depend on the degree of oxidation of the central metal ion.

Electrochemical properties of porphyrin alkyl-derivatives: 2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphine ( $H_2TMeTEtP$ ), octamethylporphine ( $H_2OMeP$ ), 2,8,12,-18-tetramethyl-3,7,13,17-tetrabutylporphine ( $H_2TMeTBuP$ ) and its Co complex in composition with technical elemental carbon (TEC) in a KOH aqueous solution have been described in [3]. The free ligands are characterized by two electroreduction processes of tetrapyrrol macrocycle to form  $\pi$ -anion radical and dianion. In the case of Co-complex an additional process of oxidation of the central metal ion Co(II) is observed. It was also found that by increasing length of alkyl substituents, the redox potentials of the observed processes are shifted to the anode region of potentials, i.e. a decrease in the induction effect on the macrocycle contributes to its reduction.

In the present work the results of studying electrochemical behavior and electrocatalytic activity of (OAc)Fe(III)-complexes (Fig. 1) in oxygen reduction reaction in aqueous alkaline solution were presented for the first time. The comparative characteristics of the effect of complex formation, as well as functional substitution in the molecule (the introduction of one or two pyridyl fragments into *meso*-positions of the macrocycle) on the electrochemical parameters and activity of alkyl-substituted and pyridyl-substituted porphyrins were carried out.

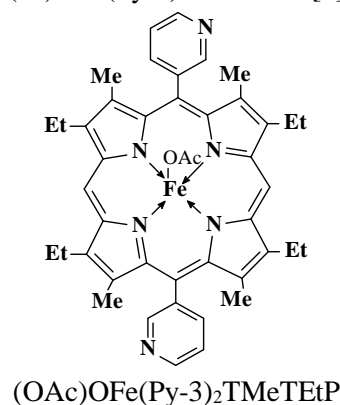
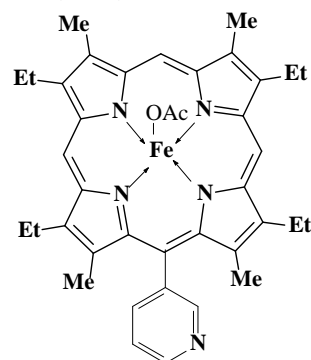
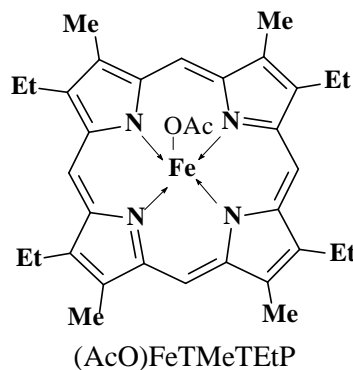
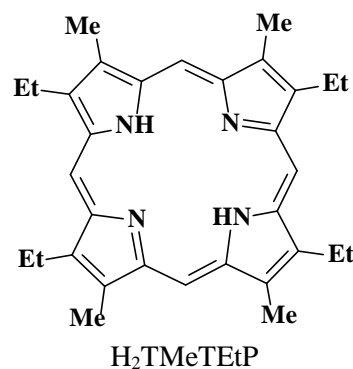


Fig. 1. Structure of porphyrins  
Рис. 1. Структурные формулы порфиринов

#### EXPERIMENTAL

Porphyrin-ligands were synthesized according to [4,5]. Metal complexes (AcO)FeTMeTEtP and (OAc)OFe(Py-3)<sub>2</sub>TMeTEtP were synthesized according to the methods described below.

*Acetato(3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphinato)iron(III) [(AcO)FeTMeTEtP]*. 500 mg of iron powder was added to a solution of 50 mg (0.081 mmol) of the ligand H<sub>2</sub>TMeTEt in 5 ml of CH<sub>3</sub>COOH. The reaction mixture was boiled for 2 h, cooled, and the powder was filtered off. 20 ml of water was added to the obtained solution that was neutralized with an ammonia solution. The precipitate was filtered off, dissolved in chloroform, chromatographed (Al<sub>2</sub>O<sub>3</sub>, eluent: chloroform). Yield – 0.030g (50%). Mass-spectrum (MALDI): [M<sup>+</sup>-CH<sub>3</sub>COO] – 532.26 (calc. 532.53). (AcO)FeTMeTEtP [ $\lambda$  (nm), (lg $\epsilon$ ), CHCl<sub>3</sub>]: 399 (4.94); 491 (4.25); 536 (3.99); 634 (3.92).

(OAc)OFe(Py-3)<sub>2</sub>TMeTEtP was synthesized analogously. Yield – 0.030g (44%). [ $\lambda$  (nm), (lg $\epsilon$ ), CHCl<sub>3</sub>]: 406 (4.70); 514 (3.87); 586 (3.73).

The purity and individuality of the compounds were monitored by thin layer chromatography (Silufol C60, eluent – CHCl<sub>3</sub>), and also US-VIS spectra (spectrophotometer SF-56).

Electrochemical measurements were performed by the method [6] in the three-electrode cell YASE-2. A saturated silver chloride electrode (Ag/AgCl) and a platinum electrode were used as the reference and counter electrodes, respectively. The working electrode was a graphite one. The working surface (0.64 cm<sup>2</sup>) was deposited with a layer (0.2-0.3 mm) of an active mass,

which was prepared in an ethyl alcohol, involved the carbon support (TEC – technical elemental carbon P-514 (GOST 7885-86) with the ash content 0.45%), the fluoroplastic suspension (6% FP-4D) and studied substance in weight ratio 7:2:1.

The measurements were carried out by using the potentiostat-galvanostat «J-31P». Potentials of cathodic (E<sub>c</sub>) and anodic (E<sub>a</sub>) peaks for observed processes involving studied compounds were fixed with the accuracy of  $\pm 0.01$  V. The values of redox potentials were determined as the average in a series of 5-6 parallel experiments. The obtained experimental results and calculated data are presented in Table and in Fig. 2, 3.

## RESULTS AND DISCUSSION

### *Electrochemical properties in an inert medium*

When an electrolyte is purged with argon, on the cyclic voltammetric curves for electrodes modified with H<sub>2</sub>TMeTEtP and (AcO)FeTMeTEtP two general sequential processes of electroreduction of the macrocycle [process I (L  $\leftrightarrow$  L<sup>-</sup>) and process II (L<sup>-</sup>  $\leftrightarrow$  L<sup>2-</sup>), Table], related to the attachment of electrons to the  $\pi$ -system of a macrocyclic ligand, are observed (Fig. 2). For the metal complex (AcO)FeTMeTEtP, additional processes (Fe<sup>3+</sup>  $\leftrightarrow$  Fe<sup>2+</sup> and Fe<sup>2+</sup>  $\leftrightarrow$  Fe<sup>+</sup>), localized on the metal atom, were found (Fig. 2).

*Table*

### **Electrochemical parameters of redox processes (vs Ag/AgCl) and the process of oxygen electroreduction in 0.1M KOH solution. $\nu = 20$ mV·s<sup>-1</sup>**

**Таблица. Электрохимические параметры редокс-процессов (vs Ag/AgCl) и процесса электровосстановления кислорода в 0,1M растворе KOH.  $\nu = 20$  мВ·с<sup>-1</sup>**

Compounds	E <sub>1/2</sub> , V				E <sub>1/2</sub> (O <sub>2</sub> ), V
	Fe <sup>3+</sup> $\leftrightarrow$ Fe <sup>2+</sup>	Process I L $\leftrightarrow$ L <sup>-</sup>	Fe <sup>2+</sup> $\leftrightarrow$ Fe <sup>+</sup>	Process II L <sup>-</sup> $\leftrightarrow$ L <sup>2-</sup>	
H <sub>2</sub> TMeTEtP (Etio II) [3]	-	-0.74	-	-1.35	-0.26
(AcO)FeTMeTEtP	-0.49	-0.61	-0.86	-1.27	-0.20
(Cl)OFe(Py-3)HMeDEtP [7]	-0.29*	-0.53	-0.71	E <sub>c</sub> (-1.03)	-0.15
(OAc)OFe(Py-3) <sub>2</sub> TMeTEtP	-0.38*	-0.62	-0.81	E <sub>c</sub> (-1.11)	-0.18
(OAc)OFe(Py-4) <sub>2</sub> TMeTEtP [8]	-0.69	-	-	-0.87 -1.04**	-0.18
TEC	-	-	-	-	-0.30

Notes: \* – values of potential at oxygen introducing into the system, \*\* – L<sup>2-</sup>  $\leftrightarrow$  L<sup>3-</sup>, E<sub>1/2</sub> = (E<sub>c</sub> + E<sub>a</sub>)/2

Примечания: \* – величины потенциала при введении кислорода в систему, \*\* – L<sup>2-</sup>  $\leftrightarrow$  L<sup>3-</sup>, E<sub>1/2</sub> = (E<sub>c</sub> + E<sub>a</sub>)/2

The first stage of electroreduction (AcO)FeTMeTEtP under the considered conditions proceeds at more positive potentials, in comparison with the ligand. The redox potential (E<sup>II</sup><sub>1/2</sub>) of the second reduction process (L<sup>-</sup>  $\leftrightarrow$  L<sup>2-</sup>) is shifted by 80 mV into the positive region, that indicates an increase in the reducing ability of transition metals complexes (in this case, iron).

According to the obtained and previously published data (Table), the introduction of one electroactive substituent into the *meso*-position of the porphin

leads to the fact that it possible to (Cl)OFe(Py-3)HMeDEtP is reduced in the second stage, compared with (AcO)FeTMeTEtP.

The electrochemical behavior of the bis-pyridyl complex (AcO)Fe(Py-3)<sub>2</sub>TMeTEtP and the *mono*-pyridyl analog (Cl)Fe(Py-3)HMeDEtP is practically identical in the number of stages of the electrochemical processes, with some weakness of the reducing properties for the bis-pyridyl complex (Fig. 2, Table), in contrast to the complex AcOFe(Py-4)<sub>2</sub>TMeTEtP.

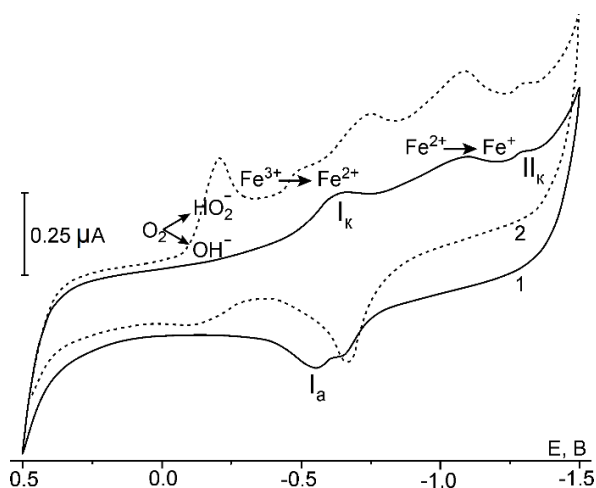


Fig. 2. CV-curves of (AcO)FeTMeTEtP in Ar (—) and O<sub>2</sub> (---) at 20 mV·s<sup>-1</sup>

Рис. 2. Циклические вольтамперограммы (AcO)FeTMeTEtP в Ar (—) и O<sub>2</sub> (---) при 20 мВ·с<sup>-1</sup>

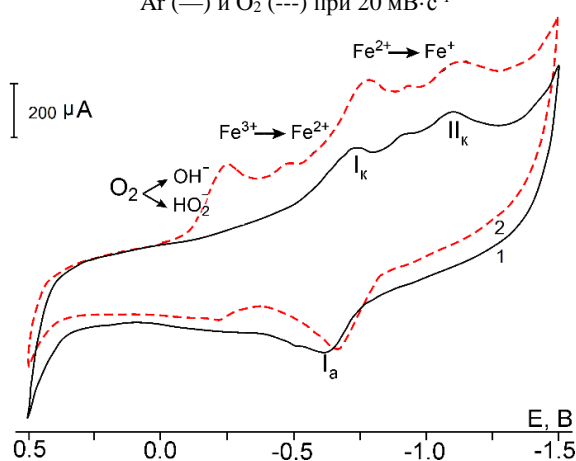


Fig. 3. CV-curves for the electrode containing complex (AcO)Fe(Py-3)<sub>2</sub>TMeTEtP at a scanning rate of 20 mV·s<sup>-1</sup> in argon (1) and at the complete saturation (2) with oxygen

Рис. 3. Циклические вольтамперограммы для электрода, содержащего комплекс (AcO)Fe(Py-3)<sub>2</sub>TMeTEtP при скорости сканирования 20 мВ·с<sup>-1</sup> в аргоне (1) и при полном насыщении кислородом (2)

For the complex (AcO)Fe(Py-3)<sub>2</sub>TMeTEtP, the following features can be noted:

- The process of electroreduction (electrooxidation)  $Fe^{3+} \leftrightarrow Fe^{2+}$  is fixed only in the case of additional introduction of molecular oxygen into the electrolyte. The observed value  $E_{1/2} = -0.38$  V and the reversibility parameter of this process  $\Delta E = 0.21$  V indicate a less expressed ability to reduce the central metal ion with additional introduction of the second pyridyl fragment into the molecule of the porphyrin ligand. The same conclusion can be drawn for the second stage of electroreduction of the central metal ion ( $Fe^{2+} \leftrightarrow Fe^{+}$ ), where for Fe (III) complex containing the bispyridyl, the value  $E_{1/2} = -0.81$  V is shifted to region of negative values by 100 mV, compared with the *mono-*

pyridyl analog [for the complex (Cl)Fe(Py-3)HMeDEtP it is -0.71 V]. It should be noted that these changes could be affected not only by the amount of pyridyl fragments in the molecule of the porphyrin compound, but also by the nature of the extra ligand (for complex (Cl)Fe(Py-3)HMeDEtP - chloride ion, for (AcO)Fe(Py-3)<sub>2</sub>TMeTEtP – acetate ion).

- The first stage of electroreduction (electrooxidation) of the porphyrin macrocycle is also characterized by a shift of the redox potential ( $E_{1/2} = -0.62$  V) to the negative range by 90 mV, compared with (Cl)Fe(Py-3)HMeDEtP ( $E_{1/2} = -0.53$  V). The second stage of electroreduction is also characterized by a displacement of the peak potential in the region of negative values by 80 mV.

It should be noted that for the (AcO)FeTMeTEtP, (Cl)Fe(Py-3)HMeDEtP, (AcO)Fe(Py-3)<sub>2</sub>TMeTEtP, the process of electroreduction of the central metal ion ( $Fe^{3+} \leftrightarrow Fe^{2+}$ ) proceeds under additional introduction of oxygen into the system.

*Electrocatalytic properties in ionization reaction of molecular oxygen*

In order to conduct an analysis of the electrocatalytic activity (AcO)FeTMeTEtP in the electroreduction reaction of molecular oxygen, *I*,*E*-curves (Fig. 2, 3, curve 2), corresponding to the saturation of the electrolyte with oxygen, were obtained. The increase in the catalytic activity of the investigated compounds leads to the depolarization effect, which is demonstrated in the displacement of the electroreduction wave of molecular oxygen and the half-wave potential [ $E_{1/2}(O_2)$ ] into the region of positive values in comparison with the system without a catalyst. Comparing the values of  $E_{1/2}(O_2)$  (Table), we can conclude that the catalytic activity of the studied compounds in the electroreduction reaction of molecular oxygen increases in the series:  $H_2TMeTEtP < (AcO)FeTMeTEtP < (AcO)Fe(Py-3)_2TMeTEtP$ .

The conducted investigation of the electrocatalytic activity of tetrapyrrole compounds in an aqueous-alkaline medium allows one to make a conclusion about the positive effect of complexation and the introduction of electron-donor substitutes in the porphyrin macrocycle on the electroreduction process of molecular oxygen. It should be noted that the additional introduction of pyridyl substituents into the macrocycle leads to an increase in the electrocatalytic effect in comparison with the macroheterocycle (AcO)FeTMeTEtP.

## CONCLUSION

The comparative analysis of the obtained in our work and published data (Table) showed that (AcO)FeTMeTEtP and (AcO)Fe(Py-3)<sub>2</sub>TMeTEtP are

characterized by redox processes involving both the porphyrin macrocycle ( $L \leftrightarrow L^{\cdot-}$ ,  $L^{\cdot-} \leftrightarrow L^{2-}$ ), and metal ( $Fe^{3+} \leftrightarrow Fe^{2+}$ ,  $Fe^{2+} \leftrightarrow Fe^+$ ). It has been established that complexation leads to the fact that the process of electroreduction of the tetrapyrrole macrocycle proceeds more easily, and the electrocatalytic activity of the compounds in the electroreduction reaction of molecular oxygen significantly increases.

*The work was carried out within the framework of Research Institute of Macroheterocyclic Compounds and supported by the grant of the President of the Russian Federation № МК-249.2017.3.*

## ЛИТЕРАТУРА

1. **Kadish K.M., Caemelbecke E.V., Royal G.** Electrochemistry of metalloporphyrins in nonaqueous media. In: The Porphyrin Handbook. Eds. K.M. Kadish et al. Academic Press: San Diego. 2000. V. 8. Chapter 55. P. 1-114.
2. **Тарасевич М.Р., Давыдова Е.С.** Неплатиновые катодные катализаторы для топливных элементов со щелочным электролитом (обзор). *Электрохимия*. 2016. Т. 52. № 3. С. 227-256.
3. **Базанов М.И., Петров А.В.** Электрохимические и электрокаталитические свойства производных порфина и его структурных аналогов. В кн.: Успехи химии порфиринов. Под ред. О.А. Голубчикова. СПб.: НИИ химии СПбГУ. 2007. Т. 5. С. 273-292.
4. **Иванова Ю.Б., Семейкин А.С., Глазунов А.В., Мамардашвили Н.Ж.** Пиридилзамещенные порфирины II. Синтез и основные свойства дипиридилпорфиринов. *Журн. орг. химии*. 2010. Т. 46. № 6. С. 918-923.
5. **Lyubimova T.V., Syrbu S.A., Semeikin A.S.** Synthesis of porphyrins from  $\alpha$ -unsubstituted dipyrromethanes. *Macroheterocycles*. 2016. V. 9. N 1. P. 59-64. DOI: 10.6060/mhc150977s.
6. **Do N.M., Berezina N.M., Bazanov M.I., Gyseinov S.S., Berezin M.B., Koifman O.I.** Electrochemical behavior of a number of bispyridyl-substituted porphyrins and their electrocatalytic activity in molecular oxygen reduction reaction. *J. Porph. Phthal.* 2016. V. 20. N 5. P. 615-623. DOI: 10.1142/S1088424616500437.
7. **Березина Н.М., Базанов М.И., До М.Н., Семейкин А.С.** Электрохимические свойства 5-(3'-пиридил)-2,3,7,8,12,18-гексаметил-13,17-диэтилпорфирина и его комплексов с Cu (II), Co (II) и Fe (III). *Изв. вузов. Химия и хим. технология*. 2012. Т. 55. Вып. 11. С. 45-50.
8. **Do Ngoc Minh, Berezina N.M., Bazanov M.I., Semeikin A.S., Glazunov A.V.** Electrocatalytic Reduction of Oxygen on Graphitized Carbon Electrode Modified with 5,15-bis(pyrid-4-yl)-3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphine and Its Cu (II), Fe (III) Complexes. *Macroheterocycles*. 2015. V. 8. N 1. P. 56-64. DOI 10.6060/mhc140714b.

## REFERENCES

1. **Kadish K.M., Caemelbecke E.V., Royal G.** Electrochemistry of metalloporphyrins in nonaqueous media. In: The Porphyrin Handbook. Eds. K.M. Kadish et al. Academic Press: San Diego. 2000. V. 8. Chapter 55. P. 1-114.
2. **Tarasevich M.R., Davydova E.S.** Non-platinum cathodic catalysts for fuel cells with alkaline electrolyte (review). *Russ. J. Electrochem.* 2016. V. 52. N 3. P. 193-219. DOI: 10.1134/S1023193516030113.
3. **Bazanov M.I., Petrov A.V.** Electrochemical and electrocatalytic properties of porphyrin derivatives and its structural analogues. In: *Uspexhi khimii porfirinov*. Ed. O.A. Golubchikov. SPb.: NII Khimii St. Petersburg State University. 2007. V. 5. P. 273-292.
4. **Ivanova Yu.B., Semeikin A.S., Glazunov A.V., Mamardashvili N.Zh.** Pyridyl-Substituted Porphyrins: II. Synthesis and Basic Properties of Dipyridylporphyrins. *Russ. J. Org. Chem.* 2010. V. 46. N 6. P. 917-923. DOI: 10.1134/S1070428010060230.
5. **Lyubimova T.V., Syrbu S.A., Semeikin A.S.** Synthesis of porphyrins from  $\alpha$ -unsubstituted dipyrromethanes. *Macroheterocycles*. 2016. V. 9. N 1. P. 59-64. DOI: 10.6060/mhc150977s.
6. **Do N.M., Berezina N.M., Bazanov M.I., Gyseinov S.S., Berezin M.B., Koifman O.I.** Electrochemical behavior of a number of bispyridyl-substituted porphyrins and their electrocatalytic activity in molecular oxygen reduction reaction. *J. Porph. Phthal.* 2016. V. 20. N 5. P. 615-623. DOI: 10.1142/S1088424616500437.
7. **Berezina N.M., Bazanov M.I., Do M.N., Semeikin A.S.** Electrochemical properties of 5-(3'-pyridyl)-2,3,7,8,12,18-hexamethyl-13,17-diethylporphyrin and its complexes with Cu (II), Co (II) and Fe (III). *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2012. V. 55. N 11. P. 45-50 (in Russian).
8. **Do Ngoc Minh, Berezina N.M., Bazanov M.I., Semeikin A.S., Glazunov A.V.** Electrocatalytic Reduction of Oxygen on Graphitized Carbon Electrode Modified with 5,15-bis(pyrid-4-yl)-3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphine and Its Cu (II), Fe (III) Complexes. *Macroheterocycles*. 2015. V. 8. N 1. P. 56-64. DOI 10.6060/mhc140714b.

*Поступила в редакцию 23.10.2017*

*Принята к опубликованию 25.01.2018*

*Received 23.10.2017*

*Accepted 25.01.2018*