

Electrochemical Characterization of β -Alkyl Substituted Porphyrins and Mn(III) Complexes in Alkaline Solution

Nadezhda M. Berezina,^{a@} Maria E. Klueva,^b and Mikhail I. Bazanov^a

^aIvanovo State University of Chemistry and Technology, Research Institute of Macroheterocyclic Compounds, 153000 Ivanovo, Russia

^bIvanovo State Medical Academy of the Ministry of Healthcare of the Russian Federation, 153000 Ivanovo, Russia

@Corresponding author E-mail: sky_berezina@rambler.ru

A comparative study of electrochemical and electrocatalytic properties of 3,7,12,18-tetramethyl-2,8,13,17-tetraethylporphyrine ($H_2TMeTEtP$, Etio IV), 2,3,7,8,12,13,17,18-octaethylporphyrin (H_2OEtP) and their complexes ((Cl)MTMeTEtP, (Cl)MOEtP, $M=Mn(III)$) was conducted by cyclic voltammetry in 0.1 M KOH. The sequence and areas of electrochemical processes were established. Values of the half-wave potentials of the first and second electroreduction processes of the π -electron macrocycle system as a whole were correlated with the increase in the length of alkyl substituents. The positive effect of increasing length of a functional substituent at β -positions in a porphine molecule on the electrocatalytic activity of the compounds in the oxygen reduction reaction (ORR) was established.

Keywords: Voltammetry, porphyrins, manganese complexes, electroreduction, molecular oxygen.

Электрохимические превращения β -алкилзамещенных порфиринов и Mn(III)-комплексов в щелочном растворе

Н. М. Березина,^{a@} М. Е. Ключева,^b М. И. Базанов^a

^aФГБОУ ВО Ивановский государственный химико-технологический университет, НИИ химии макрогетероциклических соединений, 153000 Иваново, Россия

^bГБОУ ВО Ивановская государственная медицинская академия Министерства здравоохранения Российской Федерации, 153000 Иваново, Россия

@E-mail: sky_berezina@rambler.ru

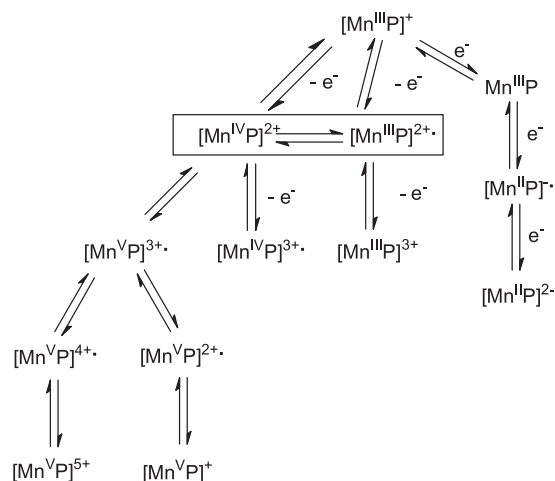
Методом циклической вольтамперометрии проведено сравнительное исследование электрохимических и электрокаталитических свойств 3,7,12,18-тетраметил-2,8,13,17-тетраэтилпорфина ($H_2TMeTEtP$, Этио IV), 2,3,7,8,12,13,17,18-октаэтилпорфирина (H_2OEtP) и комплексов ((Cl)MTMeTEtP, (Cl)MOEtP, где $M=Mn(III)$), в 0.1 M растворе KOH. Установлены очередность и области протекания электрохимических процессов. Значения потенциалов полуволн первого и второго процессов электровосстановления π -электронной системы макроцикла в целом коррелируют с увеличением длины алкильных заместителей. Установлено положительное влияние увеличения длины функционального заместителя в β -положениях молекулы порфина на электрокаталитическую активность соединений в реакции ионизации молекулярного кислорода.

Ключевые слова: Вольтамперометрия, порфирины, комплексы марганца, электровосстановление, молекулярный кислород.

Introduction

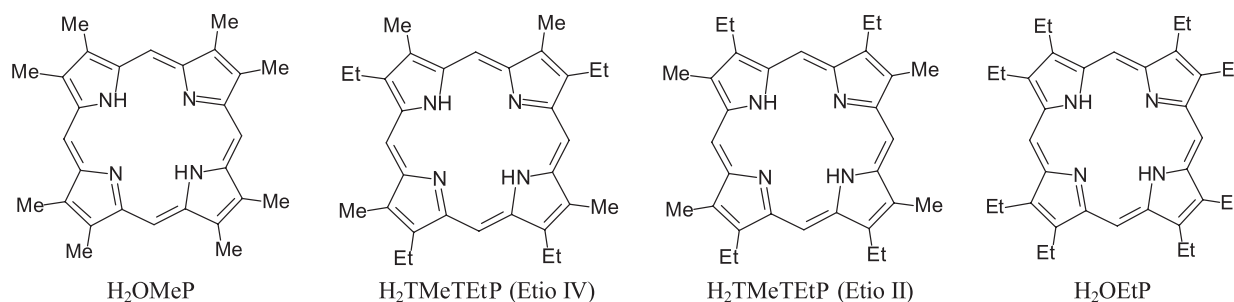
The study of the physicochemical and catalytic properties of macroheterocyclic compounds of the porphyrin is of great scientific and practical interest at present time.^[1] A special place can be occupied by manganese complexes. Manganese porphyrins (MnP) and their derivatives are characterized as stable forms with metal oxidation states of 2+ to 5+. Early electrochemistry and spectral properties of Mn^{III} and Mn^{II}-porphyrins in non-aqueous media were reported in detail.^[2-11] The high valent manganese porphyrins (Mn⁴⁺ and Mn⁵⁺) are highly reactive. Nonetheless, a number of the type [Mn^{VI}(O)P],^[12-14] MnO[P]⁺,^[15] [Mn^{VI}(OMe)₂P],^[16] [Mn^{VI}(X)P]₂O,^[17-18] where X=N₃⁻ or NCO⁻, [Mn^V(N)P]^[17,19-20] have been stable and spectrally characterized.

The vast majority of Mn-porphyrins electrochemistry in non-aqueous media involved reactions of Mn^{III} derivatives, most of which are easily reduced to their Mn^{II} form followed more negative potentials by a possible formation of the π -anion radical and then dianion depending upon the structure of the macrocycle and solvent. Moreover, the Mn^{III} complexes can be oxidized both on a macrocycle and a metal center, giving either Mn^{III} π -cation radicals and dications, or Mn^{IV} and Mn^V π -cation porphyrin radicals. The most general scheme of electrochemistry for Mn-porphyrins is given in Scheme 1.^[11]



Scheme 1.

The potentials and site of electron transfer for each electrode reaction of the studied manganese(III) porphyrins were found to depend upon either porphyrin ring basicity or planarity, the counterion on Mn^{III} and the steric effects



of axial ligands, the nature of the solvent and the experimental conditions.

In this study, the results of the electrochemical and electrocatalytic behavior of H₂TMeTEtP, H₂OEtP and complexes with Mn^{III} in a water-alkaline solution were presented.

Experimental

Synthesis of β -alkyl substituted porphyrins and their complexes (Mn^{III}TMeTEtP, Mn^{III}OEtP) was carried out by methods described in ^[21]. Porphyrin ligands were given by professor A.S. Semeikin.

Measurements were carried out in a three-electrode electrochemical cell YASE-2 (Russian: ЯСЭ-2). Ag|AgCl,KCl(sat) and platinum electrodes were used as the reference and counter electrodes, respectively. Values of potentials were shown vs. Ag/AgCl. The working electrode represented a graphitized carbon rod. The working end of the rod (0.64 cm²) was deposited with a layer (0.2–0.3 mm) of an active mass, prepared in ethanol, including the carbon (TEC – technical elemental carbon P-514 (State Standard N 7885-86) with the ash content 0.45 %), the fluoroplastic suspension (6 % FP-4D) and the studied compound in the mass ratio of 7:2:1. The final heating of the active mass was carried out at 573 K for one minute.

The measurements were performed by a potentiostat-galvanostat «P-30J». First of all, the saturation of an electrolyte with argon (99.99 %) was conducted by bubbling (0.14 mL·s⁻¹) for 40 minutes. Next, the working electrode was dipped in the electrolyte and cyclic *I*,*E*-curves were recorded in the potential range of 0.5÷–1.5 V. Selection of the potential range was carried out by changing the min anode potential value from 0.5 V to –0.9 V in step by 0.2 V. After completing the measurement under argon, the gaseous oxygen was bubbled through the solutions for 60 minutes. Potentials of cathodic (*E*_c) and anodic (*E*_a) peaks for observed processes with the participation of studied compounds were fixed with the accuracy of ±0.01 V.^[22] The experimental results and the calculated data are presented in the Tables 1-3 and Figures 1-4.

Results and Discussion

The interested regularities were established for the studied porphyrins, in agreement.^[23] The character of cyclic voltammograms in argon depended on the range of the potential measurements. The change in the min anode value (Figure 1) allowed to trace the appearance of a cathode wave for the first electrochemical process. This ultimately makes it possible to obtain conditions both for the reversible course observed processes and for their separate study. These results allowed to select the experimental conditions for the measuring of cyclic voltammograms and to obtain the reliable data of porphyrins redox behavior.

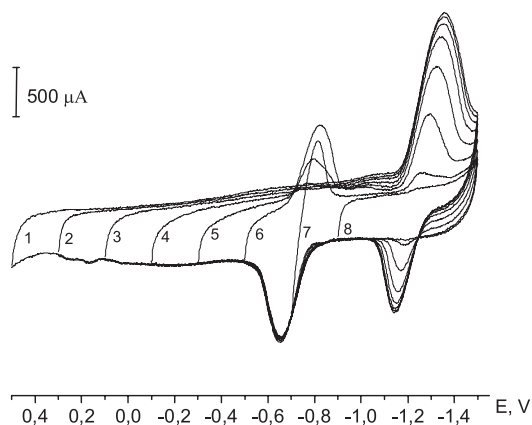


Figure 1. Cyclic voltammograms of $H_2TMeTEtP$ (Etio IV) at the minimal potential anode value. Range of measurement, V : 1 – (0.5 \div –1.5); 2 – (0.3 \div –1.5); 3 – (0.1 \div –1.5); 4 – (–0.1 \div –1.5); 5 – (–0.3 \div –1.5); 6 – (–0.5 \div –1.5); 7 – (–0.7 \div –1.5); 8 – (–0.9 \div –1.5) $v=20\text{ mV}\cdot\text{s}^{-1}$ in Ar.

The voltammograms of porphyrin ligands electroreduction were measured at different scan rates (v) in the range 5 \div 100 $\text{mV}\cdot\text{s}^{-1}$ (Figure 2) under conditions of reversible processes.

Data (Figure 2 and Table 1) show a shift of the cathode maxima (E_c) to the negative region, while anode ones (E_a) – to the region of positive potential values with an increase in the scan rate. The half-sum values of the cathode and anode peaks ($E_{1/2}$) were varied insignificantly (Table 1). The $E_{1/2}$ values are $-0.77\pm 0.01\text{ V}$ and $-1.27\pm 0.01\text{ V}$ for the first and second electroreduction processes of $H_2TMeTEtP$ (Etio IV), respectively. The nature of the observed maxima was clear. The first process involved the addition of an electron to the π -electron system of a macrocycle and the formation of a monoanionic (radical) form of the compound during the second a dianion in the scheme: $P\leftrightarrow P^{\cdot-}\leftrightarrow P^{2-}$ was form.

A significant decrease of the ΔE_p parameter was observed for both the first and second stages of the macrocycle electroreduction with decreasing of v . This indicated

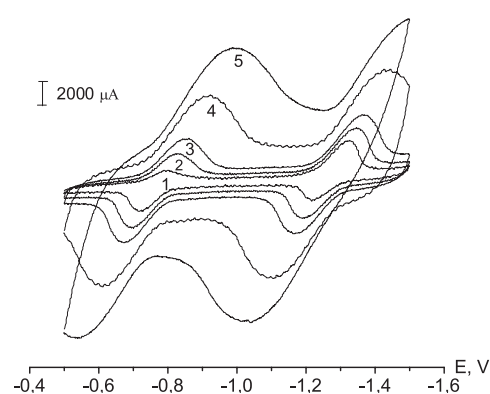


Figure 2. Cyclic voltammograms of $H_2TMeTEtP$ (Etio IV) at the scan rate, $\text{mV}\cdot\text{s}^{-1}$: 1 – 5, 2 – 10, 3 – 20, 4 – 50, 5 – 100.

that a decrease in v led to a more reversible (quasireversible) process. The ΔE_p values of the I and II processes are 0.31 and 0.33 V at high scanning rates, respectively, and are close to that obtained for the series of the phthalocyanine compounds of relative structure.^[24]

The values of the $\delta E_n/\delta \log v$ parameters for processes I and II are 150 mV and 130 mV for cathode and 150 mV and 145 mV for anode in the range of scanning speed from 10 to 100 $\text{mV}\cdot\text{s}^{-1}$, indicating their irreversible character. The changes in I_a/I_c ratio and αn from v confirm the above.

A comparison of the electrochemical behavior of a number of β -alkyl substituted porphyrin ligands (Table 2), investigated earlier and in the present study, allowed to distinguish the following number of regularities. The values of the half-wave potentials of the first and second electroreduction processes of the π -electron macrocycle system as a whole correlated with the increase in the length of alkyl substituents. The replacement of eight methyl groups by ethyl (H_2OEtP) resulted in a shift of $E_{1/2}$ for the I and II processes by 50 and 90 mV, respectively. The transition from H_2OMeP to $H_2TMeTBuP$ led to an even more significant change of $E_{1/2}$. The introduction of four electron-donating butyl groups into the β -position of the macrocycle of the $H_2TMeTBuP$ molecule led to a de-

Table 1. Parameters of electroreduction processes for an electrode modified by $H_2TMeTEtP$ (Etio IV), Ar, 0.1 M KOH.

v , $\text{mV}\cdot\text{s}^{-1}$	Process $L\leftrightarrow L^{\cdot-}$						
	E_c , V	E_a , V	$E_{1/2}$, V	ΔE_p , V	$\delta E_p/\delta \log v$, mV	I_a/I_c	αn
5	-0.79	-0.73	-0.76	0.06		1.90	0.98
10	-0.83	-0.70	-0.77	0.13		1.36	0.45
20	-0.86	-0.67	-0.77	0.19	Cat (150) An (150)	1.13	0.31
50	-0.92	-0.61	-0.77	0.31		0.99	0.19
100	-0.99	-0.53	-0.76	0.46		0.94	0.13
Process $L^{\cdot-}\leftrightarrow L^{2-}$							
5	-1.33	-1.22	-1.28	0.11		0.55	0.54
10	-1.35	-1.19	-1.27	0.16		0.75	0.37
20	-1.37	-1.17	-1.27	0.20	Cat (130) An (145)	0.92	0.30
50	-1.43	-1.10	-1.27	0.33		1.22	0.18
100	-1.50	-1.03	-1.25	0.47		1.10	0.13

$$E_{1/2} = (E_c + E_a)/2; \Delta E_p = E_a - E_c$$

$$I_a/I_c - \text{ for reduction, } I_c/I_a - \text{ for oxidation at constant } v; \alpha n = 0.059/\Delta E_p.$$

Table 2. Electrochemical parameters of redox process (*v*, vs. Ag/AgCl) for electrodes with ligands at *v* = 20 mV·s⁻¹, 0.1 M KOH, Ar.

Compounds	Process I			Process II			$E_{1/2}(\text{O}_2)$, V
	E_c^I , V	$E_{a^2}^I$, V	$E_{1/2}^I$, V	E_c^{II} , V	$E_{a^2}^{II}$, V	$E_{1/2}^{II}$, V	
H ₂ OMeP [23]	–	–	–0.77	–	–	–1.31	–0.30
H ₂ TMeTEtP (Etio II) [23]	–0.79	–0.71	–0.75	–1.48	–1.19	–1.34	–0.26
H ₂ TMeTEtP (Etio IV)	–0.86	–0.67	–0.77	–1.37	–1.17	–1.27	–0.26
H ₂ OEtP	–0.78	–0.68	–0.73	–1.28	–1.17	–1.22	–0.26
H ₂ TMeTBuP (Etio II) [23]	–0.77	–0.58	–0.68	–1.20	–1.03	–1.12	–0.21
TEC	–	–	–	–	–	–	–0.35

crease in the redox potentials of the reduction by 90 mV and 190 mV. Thus, an increase in the length of the alkyl substituents (electron donating ability) in the series of H₂OMeP, H₂TMeTEtP, H₂OEtP to H₂TMeTBuP compounds promotes (further) the processes of electroreduction of compounds at lower potentials.

The introduction of the gaseous oxygen into the electrolyte led to the appearance of an additional maximum in the potential range of 0.0÷–0.5 V, which is associated with the ORR (Figure 3), while the current peaks of I and II processes were conserved.

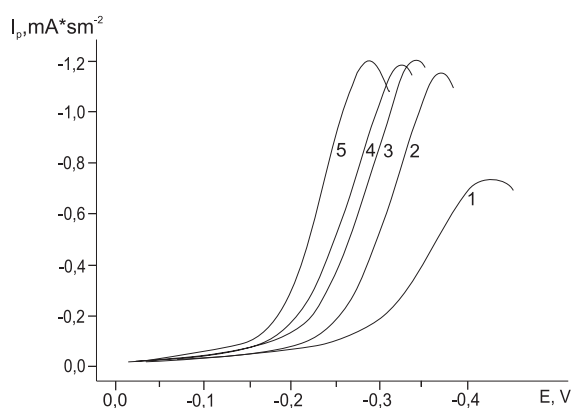


Figure 3. Fragment of the cathode part of *I*, *E*-curve of ORR. The time of bubbling is 30 minutes. *v*=20 mV·s⁻¹. 1 – without catalyst (TEC), 2 – H₂OMeP, 3 – H₂TMeTEtP (Etio IV), 4 – H₂OEtP, 5 – H₂TMeTBuP.

Analysis of the electrocatalytic activity of β -alkyl substituted porphyrins in ORR was carried out according to the *I*, *E*-curves (Figure 3, curves 2-5, Table 2) corresponding to the limiting saturation of the electrolyte with gaseous O₂. The growth of the electrocatalytic activity was due to the effect of depolarization. It was manifested by the shift of the electroreduction wave of molecular oxygen (as well as the values of $E_{1/2}(\text{O}_2)$) to positive values. These simultaneously led to an increase in the current of the O₂ electroreduction process at a fixed value of the potential.

The growth of the electrolytic action for ligands is observed with an increase in the length of the alkyl substituent in the series, according to the increase of the O₂ electroreduction potential ($E_{1/2}(\text{O}_2)$, V): TEC(–0.35) > H₂OMeP(–0.30) > H₂TMeTEtP(–0.26) ≥ H₂OEtP(–0.26) > H₂TMeTBuP(–0.21).

The conclusion that the change of the ligand structure can significantly affect on the electrocatalytic activity of

porphyrins in the ORR for alkaline solutions was consistent with the results of studies in non-aqueous media.^[25]

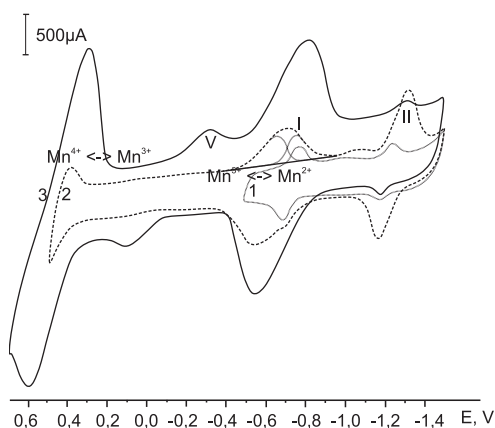


Figure 4. Cyclic voltammograms of H₂OEtP (1) ($\Delta E = -0.5 \div -1.5$ V) and (Cl)Mn^{III}OEtP (3) ($\Delta E = 0.7 \div -1.5$ V).

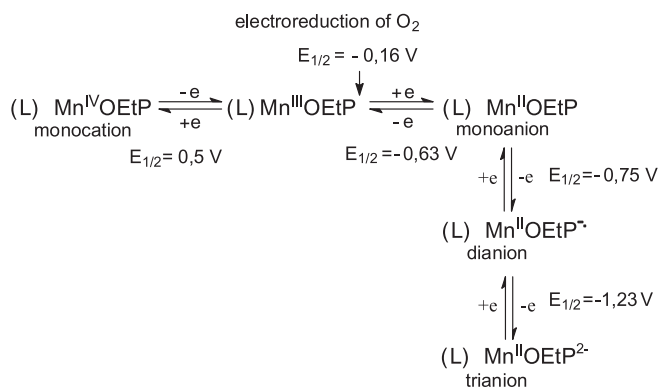
In cyclic voltammograms of β -alkyl substituted MnP (Figure 4) the range of potential was associated with the processes of electroreduction of the π -electron macrocycle system (I and II) with $E_{red/ox}^I = -(0.68 \div 0.77)$ V and $E_{red/ox}^{II} = -(1.12 \div 1.31)$ V, respectively; metal-centered redox process with $E_{red/ox} = (0.36 \div 0.63)$ V (Mn⁴⁺ ↔ Mn³⁺), and $E_{red/ox} = -(0.73 \div 0.55)$ V (Mn³⁺ ↔ Mn²⁺) (Table 3).

The potentials of I and II processes for (Cl)Mn^{III}OEtP and (Cl)Mn^{III}TMeTEtP practically coincide with the porphyrin ligands. The identical nature of these processes at the sequential addition of electrons to the π -electron system of the porphyrin macrocycle was demonstrated. It was required to increase the min anode value of the potential to +0.7 V (Figure 4, curve 3) to completely record the electrochemical process associated with the transformation of the metal (Mn⁴⁺ ↔ Mn³⁺). The Mn³⁺ ↔ Mn²⁺ process was removed from the broadened cathode and anode peaks lying in the potential range from –0.4 to –1.0 V by dividing into two components, one of which related to the Mn^{III} reduction ($E_{1/2} = -0.63$ V and –0.64 V), the second was to the process I ($E_{1/2} = -0.75$ V).

The introduction of molecular oxygen into the electrolyte led to the appearance of a cathode peak due to the course of the electroreduction of oxygen for electrodes with Mn porphyrins. The $E_{1/2}(\text{O}_2)$ values (Table 3) for (Cl)Mn^{III}OEtP and (Cl)Mn^{III}TMeTEtP were –0.16 V and –0.15 V, respec-

Table 3. Electrochemical parameters of redox process (ν , vs. Ag/AgCl) for electrodes with complexes at $\nu = 20 \text{ mV}\cdot\text{s}^{-1}$ in 0.1 M KOH in Ar.

Compounds	$M^{4+} \leftrightarrow M^{3+}$ ${}^*M^{3+} \leftrightarrow M^{2+}$		Process I		Process II		$E_{1/2}(\text{O}_2)$, V			
	E_c , V	E_a , V	$E_{1/2}$, V	E^I_c , V	E^I_a , V	$E^I_{1/2}$, V		E^{II}_c , V	E^{II}_a , V	$E^{II}_{1/2}$, V
(Cl)Mn ^{III} OEtP	0.38 *−0.70	0.63 *−0.55	0.51 *−0.63	−0.79	−0.70	−0.75	−1.30	−1.17	−1.23	−0.16
(Cl)Mn ^{III} TMeTEtP (Etio IV)	0.36 *−0.73	0.62 *−0.55	0.49 *−0.64	−0.81	−0.68	−0.75	−1.31	−1.16	−1.23	−0.15

**Scheme 2.**

tively, which indicated their rather high electrocatalytic effect. This can be associated with both an increase in the donor ability of functional substituents and with the involvement of a metal in the process of ORR. And the second factor was more significant.

Conclusions

Cyclic voltammetric measurements showed that complexes gave a metal-centered oxidation and metal-center reduction with two ligand-centered reduction processes. Thus, all the studied processes on the complexes can be represented in Scheme 2.

It is evident that cationic and anionic forms are possible during the anodic-cathodic polarization of electrodes with β -alkyl substituted Mn^{III} complexes in the aqueous-alkaline solution. The process of adsorption and ORR are carried out on neutral forms of complexes.

Acknowledgements. This work was performed with financial support of Russian Science Foundation, the agreement no. 14-23-00204-П.

References

- Shaposhnikov G.P., Kulinich V.P., Maizlish V.E. *Modified Phthalocyanines and Their Structural Analogues* (Koifman O.I., Ed.), Moscow: Krasand, 2012. 480 p. (in Russ.) [Шапошников Г.П., Кулинич В.П., Майзлиш В.Е. *Модифицированные фталоцианины и их структурные аналоги* (Койфман О.И., ред.), М.: Красанд, 2012. 480 с.]

- Felton R.H. In: *The Porphyrins* (Dolphin D., Ed.), New York: Academic Press, 1978. Ch. 3.
- Fuhrhop J.-H. In: *Porphyrins and Metalloporphyrins* (Smith K., Ed.), New York: Elsevier, 1975. Ch. 14.
- Kadish K.M., Cornillon J.-L., Yao C.-L., Malinski T., Gritzner G. *J. Electroanal. Chem.* 1987, 235, 189–207.
- Van Caemelbecke E., Kutner W., Kadish K.M. *Inorg. Chem.* 1993, 23, 438–444.
- Autret M., Ou Z.P., Antonini A., Boschi T., Tagliatesta P., Kadish K.M. *J. Chem. Soc., Dalton Trans.* 1996, 2793–2797.
- Mu X.H., Schultsz F.A. *Inorg. Chem.* 1995, 34, 3835–3837.
- Meunier B. *Chem. Rev.* 1992, 92, 1411.
- Lee J., Hunt J.A., Groves J.T. *J. Am. Chem. Soc.* 1998, 120, 6053–6061.
- Rodgers K.R., Goff H.M. *J. Am. Chem. Soc.* 1988, 110, 7049–7060.
- Kadish, K.M., Caemelbecke E.V., Royal G. *Electrochemistry of Metalloporphyrins in Nonaqueous Media*. In: *The Porphyrin Handbook* (Kadish K.M. et al., Eds.), San Diego: Academic Press, 2000, Vol. 8, Ch. 55, p. 1–114.
- Arasassingham R.D., He G.-X., Bruce T.C. *J. Am. Chem. Soc.* 1993, 115, 7985–7991.
- Collins T.J., Powell R.D., Slebodnick C., Uffelman E.S. *J. Am. Chem. Soc.* 1990, 112, 899–901.
- Arasassingham R.D., Bruce T.C. *Formation and Alkene Epoxidation by Higher-Valent Oxo-Metalloporphyrins* (Barton D.H.R., Ed.), New York: Plenum Press, 1993.
- Groves J.T., Stern M.K. *J. Am. Chem. Soc.* 1988, 110, 8628–8638.
- Camenzind M.J., Hollander F.J., Hill C.L. *Inorg. Chem.* 1982, 21, 4301–4308.
- Hill C.L., Hollander F.J. *J. Am. Chem. Soc.* 1982, 104, 7318–7319.
- Schardt B.C., Hollander F., Hill C.L. *J. Chem. Soc., Chem. Commun.* 1982, 104, 3964–3972.
- Buchler J.W., Dreher C., Lay K.-L., Lee Y.J.A., Scheidt W.R. *Inorg. Chem.* 1983, 22, 888–891.
- Bottomly L.A., Neely F.L. *J. Am. Chem. Soc.* 1989, 111, 5955–5957.
- Klueva M.E., Lomova T.N. *Mendeleev Commun.* 2002, 2(8), 238–239.
- Do Ngoc Minh, Berezina N.M., Bazanov M.I., Semeikin A.S., Glazunov A.V. *Macrocyclic Chem.* 2015, 8, 56–64.
- Antipin I.S., Antina E.V., Bazanov M.I. et al. In: *Advances in Porphyrin Chemistry* (Golubchikov O.A., Ed.) StPSU: НИИ Химии, 2007, Vol. 5, pp. 273–291 (in Russ.) [Антипин И.С., Антигина Е.В., Базанов М.И. и др. В кн.: *Успехи химии порфиринов* (Голубчиков О.А., ред.), СПбГУ: НИИ Химии, 2007, Т. 5, с. 273–291].
- Коча А., Динчер Н.А., Кочак М.В., Гуй А. *Russ. J. Electrochem.* 2006, 42(1), 31–37.
- Kuzmin S.M., Chulovskaya S.A., Parfenyuk V.I. *J. Porphyrins Phthalocyanines* 2015, 19, 1053–1062.

Received 02.05.17

Accepted 30.06.17