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Polarographic and Voltammetric Determination of meso-Tetrakis(4-sulfonatophenyl)porphyrin Tetrasodium Salt at Mercury Electrodes*

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Dedicated to the memory of Professor Jaroslav Heyrovský on the occasion of the 85th anniversary of the invention of polarography.

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The electrochemical behavior of *meso*-tetrakis(4-sulfonatophenyl) porphyrin tetrasodium salt (TPPS4) was investigated in aqueous media of BR buffer in pH range 2-12. Modern electroanalytical methods, i.e DC tast polarography (DCTP) and differential pulse polarography (both at a dropping mercury electrode), differential pulse voltammetry, adsorptive stripping voltammetry, and cyclic voltammetry (all at a hanging mercury drop electrode) were used for this purpose. TPPS4 gives three cathodic signals for pH 2 - 12, first of them corresponding to a two electron quasireversible process. From these signals, the first two are suitable for the determination of TPPS4 using both polarographic methods with limit of determination about $2 \cdot 10^{-6}$ mol L^{-1} in BR buffer, pH 10. At concentration higher than $3 \cdot 10^{-6}$ mol L^{-1}, the calibration curve of the first signal deviates from the linear course due to formation of aggregates of TPPS4 in solution. The lowest limit of determination, $5.1 \cdot 10^{-7}$ mol L^{-1} was achieved by AdSV due to strong adsorption of TPPS4 at the electrode surface. However, for concentrations higher than $1 \cdot 10^{-6}$ mol L^{-1}, the strong adsorption prevents the use of HMDE for voltammetric measurements conducted at low scan rates due to deformation of voltammetric curves and non-linearity of calibration dependences. On the other hand, at higher scan rates used in CV the linear dynamic range for voltammetric determination of TPPS4 is $4 \cdot 10^{-7}$ - $1 \cdot 10^{-5}$ mol L^{-1}.

Key words: meso-Tetrakis(4-sulfonatophenyl)porphyrin tetrasodium salt, porphyrins, DC tast polarography, differential pulse polarography, differential pulse voltammetry, adsorptive stripping voltammetry, cyclic voltammetry

1. INTRODUCTION

Porphyrins are a family of very special molecules involved in a group of important biological processes [1–3] and they have a number of unique features [4-7]. The porphyrin cycle is present in: a) chlorophylls, in which it is related to energy transformation in photosynthesis; b) in hemoglobin, where it is associated with oxygen transport during respiration; and c) in cytochromes and other enzymes, which are related to the catalysis of redox reactions. Porphyrins are flat macrocycles, formed by four pyrrole rings, with π–π conjugation [8] but with a number of possible conformational arrangements [9]. The specific function of each porphyrin is determined by the variety of their substituents and by their capacity for coordination with many metallic ions or atoms. Porphyrins with specific structures can also be prepared in the laboratory for use as catalytic agents [10,11], photosensitive and optical materials [12-14], for molecular electronics [15,16], and for medical purposes and mimetic studies [17].

Analytical chemistry is other area, where porphyrins have found a variety of applications [see reviews 18,19]. *Meso*-tetraphenylporphyrine (TPP), which is known as a sensitizer of photodynamic effect, used for example for treatment of tumor disorders or atherosclerosis [20,21], and its derivative *meso*-tetrakis(4-sulfonatophenyl)porphyrin tetrasodium salt (TPPS4, see structure in Fig. 1) are widely used due to relatively easy preparation of both and hydrophilic properties of TPPS4. The electroanalytical applications of porphyrins including TPP and its derivatives can be found in various measurement techniques. In voltammetry, electrodes modified by porphyrin films deposited at electrode surface enable sensitive determination of different metals [22-25] with increased selectivity. Modified electrodes can be also used as amperometric detectors in flowing liquid methods. In these methods, complexes between transition metal cations and porphyrins (metalloporphyrins) are used for modification of electrode, because they are selective to other coordinating anions (i.e., ZnTPPS4 on glassy carbon electrode was used for FIA determination of sulphite and nitrite in water samples containing phenols [26]; CuTPP mixed with carbon paste is suitable for the determination of hydrazine [27]). Coordinating interaction with extra ligands enables also the use of metalloporphyrins as electroactive components of membranes of ISE in potentiometry. For this purpose, metalloporphyrins can be immobilized in PVC films, electropolymerized on polysiloxane, carbon or on Ag or Pt electrode [19]. Typically, membranes based on TPP complex with Mn^{2+}, In^{3+} [28] or Ga^{3+} [29] show some selectivity towards chlorides or fluorides; TPPS4 deposited with water-soluble polypyrrole on a 2-aminoethanethiol modified Ag electrode was used for the determination of iodide [30]. The coupling of biocatalytic effect of metalloporphyrins with electrochemical transducing of recognition event in biosensors attracts growing attention; the electrocatalysis of electrooxidation of thiocholine by CoTPP was used for amperometric detection of acetylcholinesterase [31]. The complexation ability of TPP and its derivatives has found its use also in HPLC, they are used for the determination of transition metals [18,19,32] and as stationary phases in immobilized metal ion chromatography for the separation

of organic compounds, i.e., aromatic carboxylates and sulphonates, polycyclic aromatic hydrocarbons [18,19,33,34], and fullerenes [35,36].

Our group is interested in other derivatives of TPP – porphyrines derived from 5,10,15,20 tetrakis(pentafluorophenyl)porfyrin, where one to all (4) pentafluorophenyls are replaced by glycosylated steroids. These derivatives might show many interesting properties (in addition to Sorret band, fluorescence etc.), like ion complexation, molecular and chiral recognition, formation of self-assembling systems, incorporation into cell membranes and ion channels formation, but they could also find use in vast fields of complex-formation chemistry, construction of UV-Vis/NIR sensors, in research of basic processes in photochemistry and photobiology. They can be also investigated as possible agent for photodynamic therapy and for phototoxic and anti-viral applications. Depending on the number and type of substituents (glycosylated steroids), they can posses properties similar to TPPS4, which is used as a model substance in studies concerning chemical and photochemical studies and assemblies of porphyrins in aqueous solutions in absence or presence of different complexing agents (cyclodextrines, nucleic acids, proteins, and other biomolecules) [37,38]. Therefore, in the present work we chose this compound as a model substance and investigated its electrochemical behavior at mercury electrodes using modern electroanalytical methods: DC tast polarography (DCTP) and differential pulse polarography (DPP) at a classical dropping mercury electrode (DME) and differential pulse voltammetry (DPV), adsorptive stripping voltammetry (AdSV), and cyclic voltammetry (CV) at hanging mercury drop electrode (HMDE).

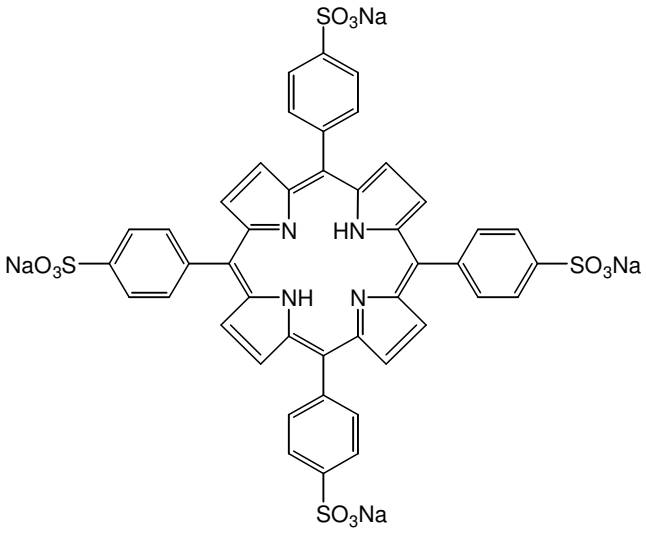

Figure 1. Structural formula of TPPS4.

2. EXPERIMENTAL PART

2.1. Reagents and materials

$1 \cdot 10^{-3}$ mol L^{-1} stock solution of TPPS4 was prepared by dissolving 0.1238 g of pure compound (98%, Fluka) in 100 mL of deionized water. More diluted solutions of TPPS4 were prepared by the dilution of the stock solution with water. All solutions were stored in the darkness. It followed from the

spectrophotometric study that the stock solution was stable for at least 240 days [39]. Britton-Robinson buffers (BR buffers) were prepared in a usual way, i.e. by mixing a solution of 0.04 mol L^{-1} in phosphoric acid, 0.04 mol L^{-1} in acetic acid, and 0.04 mol L^{-1} in boric acid with the appropriate amount of 0.2 mol L^{-1} sodium hydroxide solution. All chemicals were obtained from Sigma. Deionised water was produced by Milli-Q_{plus} system (Millipore, USA).

2.2. Apparatus

An EcoTribo polarograph controlled by PolarPro software, version 5.1 (both EcoTrend Plus, Prague, Czech Republic) served for electrochemical measurements. The measurements were carried out in a three-electrode cell comprising classical DME or miniaturized hanging mercury drop electrode (HMDE) of the UMμE type (EcoTrend Plus, Prague), a platinum wire auxiliary electrode, and saturated Ag/AgCl reference electrode. The parameters of the classical DME used in DC tast and DP polarography were as follows: At a mercury reservoir height of h = 64 cm, the flow rate was m = 1.93 mg s^{-1} and the drop time was τ = 3.7 s (at an applied voltage of 0 V in 0.1 mol L^{-1} KCl). Work with the DME was carried out at a polarization rate of 4 mV s^{-1} and controlled drop time of 1 s. For DPV and AdSV at HMDE, the maximum drop size attainable obtained by opening the valve for 200 ms, with a surface of 1.076 mm^2, and polarization rate of 20 mV s^{-1} were used. The modulation amplitude in pulse methods (DPP at DME, DPV and AdSV at HMDE) of –50 mV with pulse duration of 80 ms was used. pH measurements were carried out using a Jenway 4330 conductivity and pH meter (Jenway, United Kingdom) with combined glass electrode.

2.3. Procedures

The following procedure was applied to obtain polarograms and voltammograms of TPPS4: A required amount of aqueous TPPS4 solution was placed in a 10 mL volumetric flask, 5 mL of BR buffer of the required pH were added and the solution was filled to the mark with deionized water. The investigated samples were deoxygenated by bubbling with nitrogen for 5 min. Each determination was repeated 3 times, and the results were averaged. Calibration curves were evaluated by applying the least squares linear regression method. The statistical parameters of calibration dependences (i.e., slope, intercept, limit of determination (LOD)) were calculated according to Oppenhelmer [40], Schwartz [41], and Ebel [42] using statistic software ADSTAT version 2.0 (Trilobyte, Czech Republic). This software uses confidence bands (α = 0.05) for calculation of LOD. It corresponds to the lowest signal for what relative standard deviation is equal 0.1 [ref. 43].

3. RESULTS AND DISCUSSION

3.1. DC tast polarography

DC tast polarograms of TPPS4 show two cathodic waves at intervals pH 2 - 12, first of them corresponds to a quasireversible electrode reaction (Fig. 2), as proved by cyclic voltammetry (see

further). Half-wave potentials of the first wave $E^{I}_{1/2}$ shifts towards negative potentials with the increasing pH, this shift can be described in the range of pH 2.5-12.0 by following equation:

$E^{I}_{1/2}$ [V] = –0.067 pH – 0.216 (R = –0.9997)

In BR buffer of pH 2 anomalous behavior was observed: The first wave does not fit on linear $E_{1/2}$ vs. pH dependence (see Fig. 3). This anomaly is connected with the use of BR buffer, pH 2. When it was substituted by 0.01 mol L^{-1} Na_2HPO_4 and the pH was adjusted to 2.0 with 0.05 mol L^{-1} H_3PO_4, similarly as in 0.05 mol L^{-1} H_3PO_4, pH 1.3 and BR buffer pH 2.5, no anomaly was observed. The origin of this phenomenon is not clear at the moment.

The best developed DC tast polarographic waves were obtained at pH 10, where concentration dependence was measured (Fig. 4). For the second wave, it is linear in the whole investigated range, $4 \cdot 10^{-6}$ - $5 \cdot 10^{-5}$ mol L^{-1}, for the first wave, the calibration curve deviates from the linear course at concentrations higher than $3 \cdot 10^{-5}$ mol L^{-1}. It is the same concentration as in the case of calibration curves measured by DC polarography in acetate buffer, pH 4 as proved by Shi and coworkers [44]. In this work, the deviation was ascribed to the formation of aggregates of TPPS4, induced by inorganic salts. When we measured the absorption of TPPS4 at its absorption maximum of $\lambda = 417$ nm, its absorbance in water obeys the Lambert-Beers´ law also to the concentration of $3 \cdot 10^{-5}$ mol L^{-1}, thus the aggregation occurs probably at this concentrations regardless of inorganic salt content in the solution. The addition of an organic solvent has no influence on the deviation of calibration dependence from the straight line, as we proved by measuring the absorbance of TPPS4 in 50 % methanolic solution.

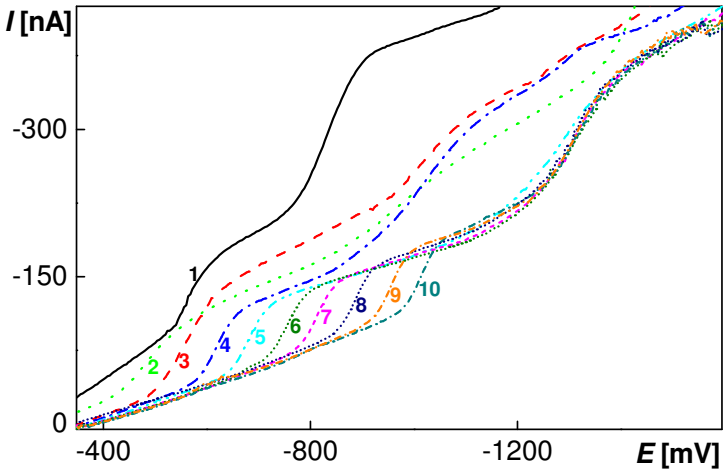

Figure 2. DC tast polarograms of TPPS4 (c = $5 \cdot 10^{-5}$ mol L^{-1}) in BR buffer of pH 2 (1), 4 (2), 5 (3), 6 (4), 7 (5), 8 (6), 9 (7), 10 (8), 11 (9), 12 (10).

3.2. Differential pulse polarography

The electrochemical behavior of TPPS4 using DPP at DME was studied analogously to DCTP in BR buffer, pH 2.5 – 12.0. It reflects the behavior in DCTP, thus the compound gives two peaks, the peak potential E^{I}_{p} of the first one shifts towards more negative potentials with increasing pH according to the following equation: E^{I}_{p}[V] = –0.066 pH – 0,189 (R = –0.9997). The peak potential of the

second peak is constant between pH 7.0 and 12.0. In BR buffer, pH 2, the anomalous behavior of TPPS4 can be seen again, as indicated at Fig. 5, where obtained DP polarograms are depicted. The best developed and most easily evaluated peaks were obtained again at pH 10, where calibration dependences were measured. In Fig. 6, the DP polarograms obtained in the lowest attainable concentration range are depicted. The height of the first and second peak is a linear function of TPPS4 concentration in the concentration range of $2 \cdot 10^{-6}$ - $3 \cdot 10^{-5}$ and $2 \cdot 10^{-6}$ - $5 \cdot 10^{-5}$ mol L^{-1} (see inset in Fig. 6), similarly to DCTP. The parameters of calibration curves are summarized for both polarographic techniques in Table 1.

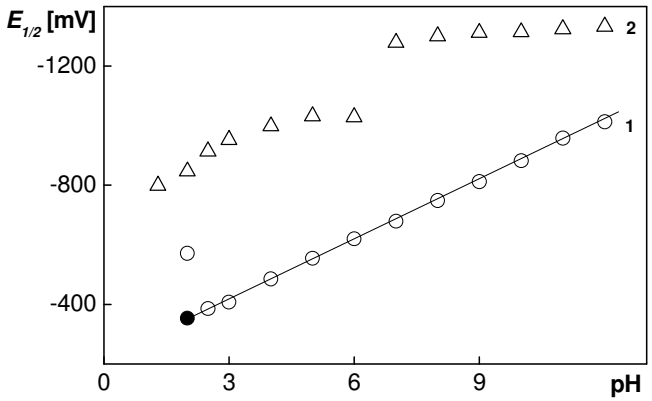

Figure 3. Dependence of the half wave potential $E_{1/2}$ of the first (1) and second (2) wave of TPPS4 ($c = 5 \cdot 10^{-5}$ mol L^{-1}) on pH of BR buffer (pH 2-12,○) and 0.01 mol L^{-1} Na_2HPO_4 (pH 2, ●) measured by DC tast polarography.

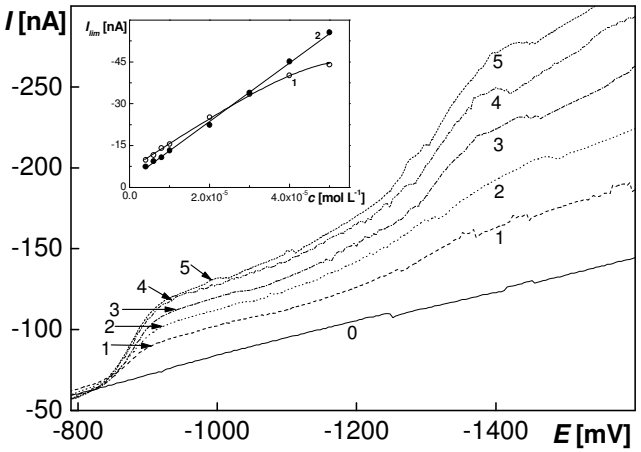

Figure 4. DC tast polarograms of TPPS4 in BR buffer, pH 10, analyte concentration: 0 (0), $1 \cdot 10^{-5}$ (1), $2 \cdot 10^{-5}$ (2), $3 \cdot 10^{-5}$ (3), $4 \cdot 10^{-5}$ (4), $5 \cdot 10^{-5}$ (5) mol L^{-1}. Inset is the calibration dependence of the first (1,○) and the second (2,●) wave.

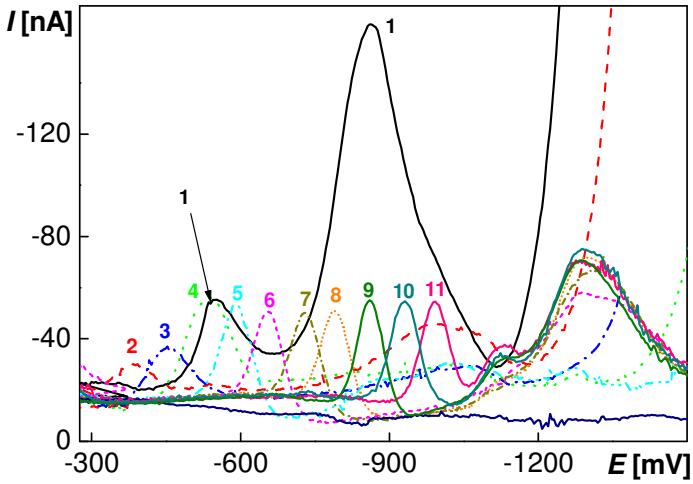

Figure 5. DP polarograms of TPPS4 (c = $5 \cdot 10^{-5}$ mol L^{-1}) in BR buffer pH 2 (1), 3 (2), 4 (3), 5 (4), 6 (5), 7 (6), 8 (7), 9 (8), 10 (9), 11 (10), 12 (11).

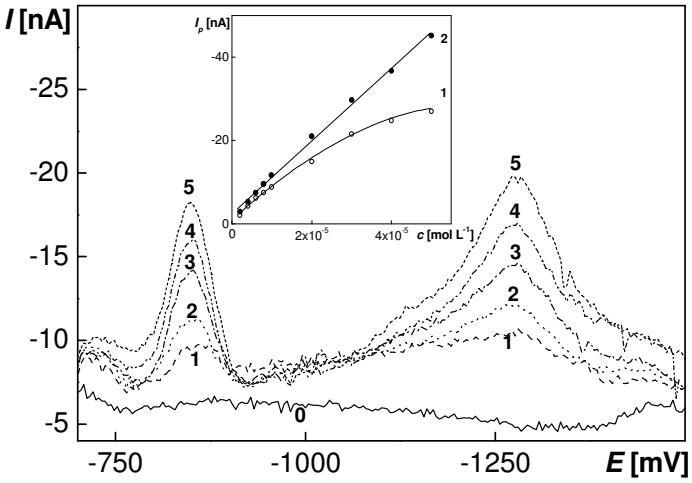

Figure 6. DP polarograms of TPPS4 in BR buffer pH 10; analyte concentration: 0 (0), $2 \cdot 10^{-6}$ (1), $4 \cdot 10^{-6}$ (2), $6 \cdot 10^{-6}$ (3), $8 \cdot 10^{-6}$ (4), $10 \cdot 10^{-6}$ (5) mol L^{-1}. Inset is the calibration dependence of the first (1,○) and the second (2,●) peak.

3.3. Differential pulse voltammetry and adsorptive stripping voltammetry

Also for DPV at HMDE, the influence of pH on recorded voltammograms was investigated for $5 \cdot 10^{-5}$ mol L^{-1} TPPS4 in BR buffer, pH 2.0-12.0. As in previous cases, the substance gives two peaks. However, they are not well developed and the calibration dependence measured in BR buffer, pH 5, in the concentration range of $(2\text{-}50) \cdot 10^{-6}$ mol L^{-1} is non-linear for both peaks and thus not suitable for

analytical purposes. As for the lower concentrations from this range the absorbance is proportional to TPPS4 concentration, we assume that the non-linear course is caused by aggregation of the substance at the electrode surface. This effect is at HMDE more pronounced than at DME with periodically renewed mercury drop.

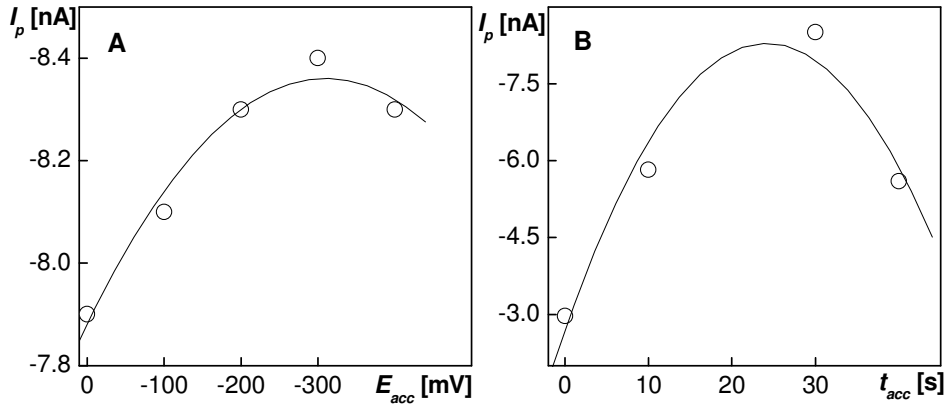

Figure 7. Dependence of the height of the AdSV peak (I_p) of TPPS4 ($c = 1 \cdot 10^{-6}$ mol L^{-1}) on potential of accumulation E_{acc} (A; $t_{acc} = 30$ s) and the time of accumulation t_{acc} (B; $E_{acc} = -300$ mV) in BR buffer pH 5.

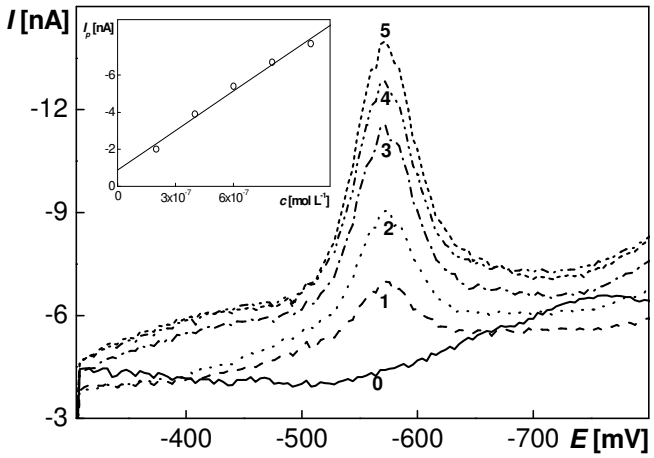

Figure 8. Adsorptive stripping voltammograms of TPPS4 at HMDE in BR buffer, pH 5, $t_{acc} = 30$ s, $E_{acc} = -300$ mV. The first peak was evaluated, TPPS4 concentration: 0 (0), $2 \cdot 10^{-7}$ (1), $4 \cdot 10^{-7}$ (2), $6 \cdot 10^{-7}$ (3), $8 \cdot 10^{-7}$ (4), $10 \cdot 10^{-7}$ (5) mol L^{-1}. Inset is the calibration dependence.

However, for lower concentrations, the adsorptive accumulation of TPPS4 can be used for its determination. At first, influence of the accumulation potential (E_{acc}) and time (t_{acc}) on the peak heights was investigated (Fig. 7) for the TPPS4 concentration of $1 \cdot 10^{-6}$ mol L^{-1}. The best developed and repeatable peaks were obtained in BR buffer, pH 5, at $E_{acc} = -300$ mV. 30 s was chosen as optimum accumulation time. Calibration curve measured under optimized conditions ($E_{acc} = -300$ mV and $t_{acc} =$ 30 s) are linear in the concentration range of $(2\text{-}10) \cdot 10^{-7}$ mol L^{-1} for the first peak, the second peak

cannot be evaluated. (Tab. 1). Voltammograms corresponding to this lowest attainable concentration range are depicted in Fig. 8 and the parameters are summarized in Table 1.

3.4. Cyclic voltammetry

In order to characterize the reduction pathways in aqueous media, the cyclic voltammograms of TPPS4 in acidic, neutral and alkali media were measured at HMDE. They were recorded from positive to negative potentials; the scan was reversed just before the onset of the background electrolyte decomposition current. At Fig. 9 the first cycles recorded in BR buffer, pH 4.0, 7.0, and 10.0 are presented. When more cycles were repeated, the peak heights increased slightly during the first five cycles, after that they have remained constant, which could be due to complete coverage of the electrode surface by the adsorbed TPPS4. There is observable the pair of quasireversible redox peaks p^{c1}/p^{a1} followed by indistinctive cathodic peaks p^{c2} and p^{c3} corresponding to an irreversible process. In pH 4 solution, the p^{c1} is deformed by another sharp cathodic signal, probably caused by the existence of streaming maxima of the first kind, which have been observed already for pH 2-6 using DPV at HMDE and disappeared after addition of 50 μl of gelatine to the measured solution. No other peaks were observed under repetitive cycling. For pH 7 buffer, the p^{c1}/p^{a1} pair is best developed with the peak potential difference $\Delta(E_p^{c1} - E_p^{a1}) = 22$ mV and the peak height ratio $I_p^{c1}/I_p^{a1} = 0.99$, thus the process tends to became reversible. On the bases of these results and analogy with other electrochemical studies we assume that the first reduction signal p^{c1}/p^{a1} is a quasireversible $2e^-$, $2H^+$ reduction of the π electron system of porphyrine skeleton. For aqueous media, it was proved by classical DC polarography [45,46] and further by studies of Zeng et al. [47] for BR buffer pH 6.8 and Shi et al. [44] in acetate buffer pH 4-6, who obtained two electrons by comparing experimentally obtained Q-t curves with calculated charge for the adsorbed reactant transferring two electrons. The adsorption of TPPS4 on the mercury surface in this case was proved by spectroelectrochemistry. The irreversible cathodic peak p^{c2} corresponds to the second peak observed by polarographic methods; the following peak p^{c3} is observable only at CVs obtained at pH 7.0 and 10.0, at pH 4.0 it is only insinuated in the onset of background electrolyte. However, to make a definitive conclusion regarding the number of electrons involved in these reactions would require a more extended mechanistic study.

Cyclic voltammetry was further used to investigate the character of the process. Therefore, cyclic voltammograms of TPPS4 ($c = 1 \cdot 10^{-5}$ mol L^{-1}) at HMDE were measured in BR buffer pH 7.0 and 10.0 at various scan rates (20, 50, 100, 200, 500, 1000 mV s^{-1}). An example showing the CVs of TPPS4 in BR buffer, pH 7, and corresponding dependences of the cathodic and anodic peak currents Ip^{c1}, Ip^{a1} on the square root of scan rates is depicted in Fig. 10. These dependences are linear as well as analogous dependences obtained for BR buffer, pH 10 which would suggest that these processes corresponding to reduction of the porphyrin skeleton are diffusion controlled. However, the high symmetry of observed peaks rather suggests that the limiting current is controlled by adsorption of the analyte at the electrode surface.

The signals obtained in CV can be also used for analytical purposes. In BR buffer, pH 7.0 and 10.0, the peak heights Ip^{c1}, Ip^{a1} at higher scan rates are directly proportional to the TPPS4

concentration in the range of $4 \cdot 10^{-7}$ - $3 \cdot 10^{-5}$ mol L^{-1}. In Fig. 11 cyclic voltammograms corresponding to the lowest attainable concentration range are depicted together with the concentration dependences, their parameters are summarized again in Table 1. The detailed investigation of rather complex reaction mechanism is under further investigation.

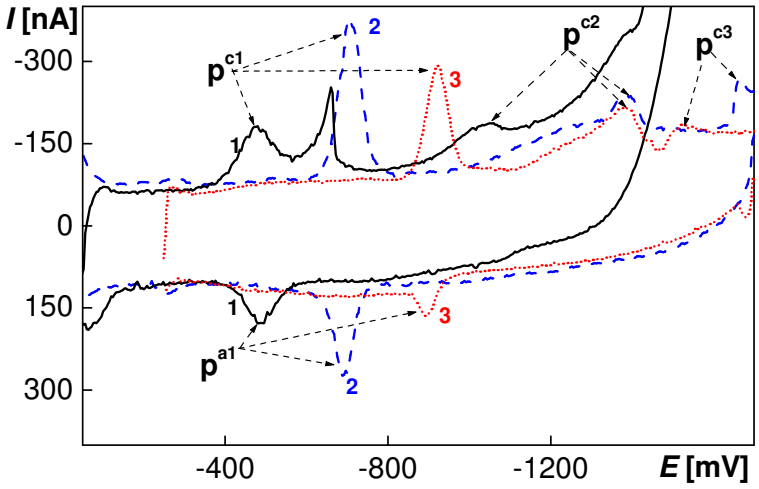

Figure 9. Selected cyclic voltammograms of TPPS4 (c = $1 \cdot 10^{-5}$ mol L^{-1}) at HMDE in BR buffer, pH: 4.0 (1; ——), 7.0 (2; ----) , and 10.0 (3;·····). The first scan presented, scan rate 500 mV s^{-1}.

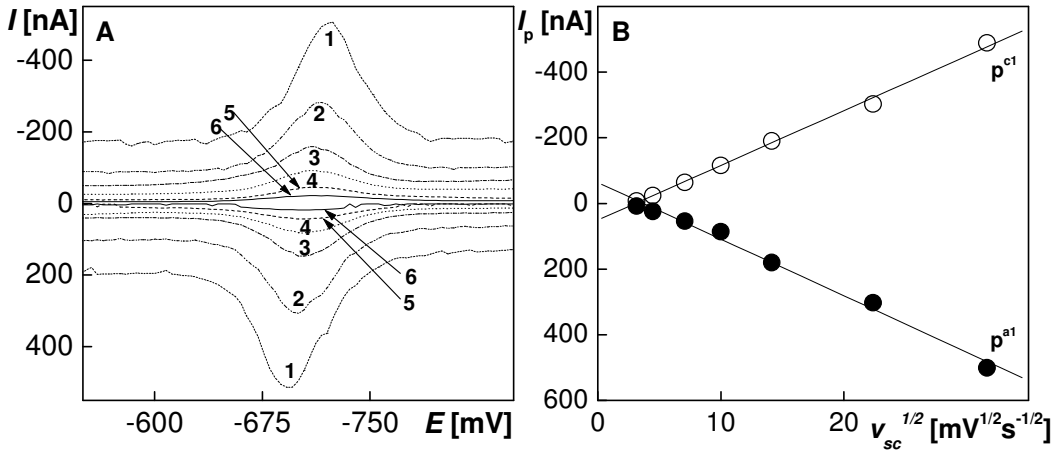

Figure 10. Cyclic voltammograms of TPPS4 (c = $1 \cdot 10^{-5}$ mol L^{-1}) in BR buffer pH 7.0, scan rate v_{sc} = 1000 (1), 500 (2), 200 (3), 100 (4), 50 (5) and 20 (6) mV s^{-1} (A) and corresponding dependence of the peak height I_p for the cathodic peak p^{c1} and anodic peak p^{a1} on the square root of the scan rate $v_{sc}^{1/2}$ (B). The first scan presented and evaluated.

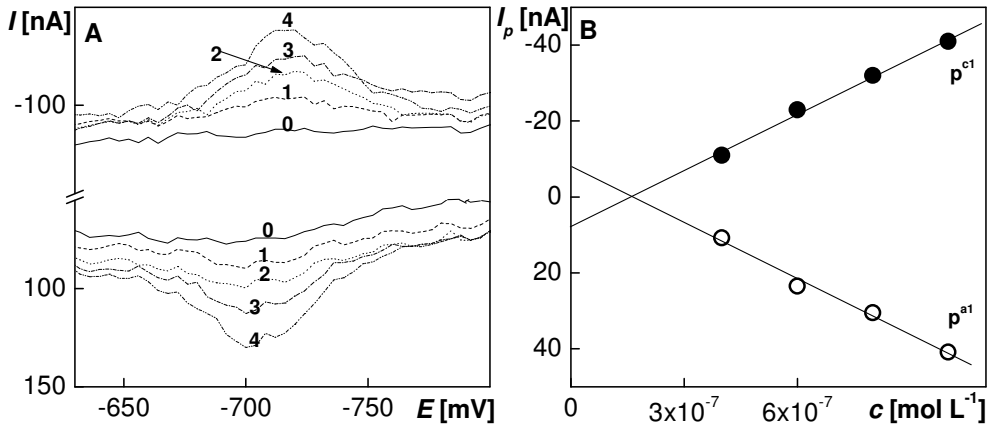

Figure 11. Cyclic voltammograms of TPPS4 in BR buffer, pH 7.0, scan rate 500 mV s^{-1}; *c* (TPPS4) = 0 (0), $4 \cdot 10^{-7}$ (1), $6 \cdot 10^{-7}$ (2), $8 \cdot 10^{-7}$ (3), $10 \cdot 0^{-7}$ (4) mol L^{-1} (A) and corresponding calibration dependence (B).

Table 1. Optimum conditions and parameters of calibration dependences for polarographic and voltammetric determination of TPPS4 at mercury electrodes.

Technique / electrode	**DCTP / DME**	**DPP / DME**	**AdSV / HMDE**	**CV / HMDE**
First peak				
Optimum conditions	BR buffer, pH 10	BR buffer, pH 10	BR buffer, pH 5; E_{acc} = –300 mV ; t_{acc} = 30 s	BR buffer, pH 7; v_{sc} = 500 mV s^{-1}
Linear dynamic range [mol L^{-1}]	$4 \cdot 10^{-6}$ - $3 \cdot 10^{-5}$	$2 \cdot 10^{-6}$ - $3 \cdot 10^{-5}$	$(2\text{-}10) \cdot 10^{-7}$	$4 \cdot 10^{-7}$ - $1 \cdot 10^{-5}$ [a,b]
Slope [mA mol^{-1} L]	–0.911	–0.667	–7.100	–22.94 [a]; –23.73 [b]
Intercept [nA]	–6.4	–1.8	–0.9	0.86 [a]; 2.24 [b]
R	0.9991	0.9967	0.9929	0.9948 [a]; 0.9863 [b]
LOD [mol L^{-1}]	$2.5 \cdot 10^{-6}$	$1.6 \cdot 10^{-6}$	$5.1 \cdot 10^{-7}$	$9.0 \cdot 10^{-7}$ [a] $8.0 \cdot 10^{-7}$ [b]
Second peak				
Linear dynamic range [mol L^{-1}]	$4 \cdot 10^{-6}$ - $5 \cdot 10^{-5}$	$2 \cdot 10^{-6}$ - $5 \cdot 10^{-5}$	----[c]	----[c]
Slope [mA mol^{-1} L]	–1.054	–0.871	----[c]	----[c]
Intercept [nA]	–2.6	–2.4	----[c]	----[c]
R	0.9995	0.9984	----[c]	----[c]
LOD [mol L^{-1}]	$2.1 \cdot 10^{-6}$	$1.3 \cdot 10^{-6}$	----[c]	----[c]

[a] The first cathodic peak p^{c1}; [b] The first anodic peak p^{a1}; [c] Second peak is difficult to evaluate
R – correlation coefficient, LOD – limit of determination

4. CONCLUSIONS

The electrochemical behavior of TPPS4 was investigated in aqueous media of BR buffer in pH range 2-12. TPPS4 offers three cathodic signals for pH 2 - 12, first of them corresponding to a two electron quasireversible process, which tends to became reversible in neutral media.

For the analytical purposes, new methods for the determination of TPPS4 were developed using DC tast polarography and differential pulse polarography at a classical dropping mercury electrode and adsorptive stripping voltammetry and cyclic voltammetry at hanging mercury drop electrode. The lowest limit of determination, $5.1 \cdot 10^{-7}$ mol L^{-1}, was achieved by AdSV due to strong adsorption of TPPS4 at the electrode surface. However, for concentrations higher than $1 \cdot 10^{-6}$ mol L^{-1}, the fast adsorption disables the use of HMDE for voltammetric measurements conducted at low scan rates due to deformation of voltammetric curves and non-linearity of calibration dependences. On the other hand, at higher scan rates used in CV, the linear dynamic range for voltammetric determination of TPPS4 is $4 \cdot 10^{-7}$ - $1 \cdot 10^{-5}$ mol L^{-1}. For higher concentration, both polarographic methods are applicable showing linearity of concentration dependences for the second cathodic peak to $5 \cdot 10^{-5}$ mol L^{-1}. The preceeding first cathodic peak is influenced by the aggregation of TPPS4 in the solution and thus at concentrations higher than $3 \cdot 10^{-5}$ mol L^{-1} the calibration dependence deviates from straight line. The possibility to use non-toxic silver solid amalgam electrode [48] for the determination of the tested substance is under investigation.

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