Reversible electrochemical pH-switching of luminescence in a *p*-sulfonatothiacalix[4]arene—terbium(3+) system

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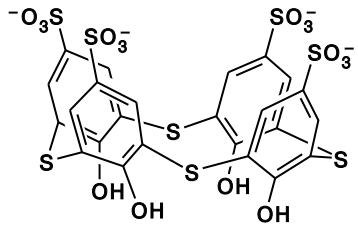
A quinone—hydroquinone system was used as a reversible electrochemical pH-switcher of luminescence in the *p*-sulfonatothiacalix[4]arene—terbium(3+) complex in an aqueous medium.

Key words: *p*-sulfonatothiacalix[4]arene, terbium(3+) complexes, luminescence, electrochemical pH-switching, cyclic voltammetry.

Supramolecular systems with photo-[1—9], redox,[10—21] and pH-switchable[22—25] properties, in particular, devices with switchable binding and switchable color and luminescence, are widely studied. In the earlier created pH-switching devices, switching occurs by the addition of acid and base. This results in an increase in the salt content with each cycle. Therefore, switching occurs only restrictedly and, hence, this variant of pH-switching cannot be used for the creation of practically useful devices. In this connection, it is important to develop another method of pH-switching when the reversible change in pH would be accompanied by the reversible change in the composition of the solution and functioning of such a system during unrestricted quantity of cycles.

It is known[26] that the oxidation of organic compounds is often associated with proton elimination, whereas the reduction is accompanied by the accumulation of protons. At the same time, there are organic redox pairs in which redox processes involving protons are chemically reversible, for instance, pairs quinone—hydroquinone or nitroso compound—hydroxylamine. Therefore, reversible electrochemical switching of the pH of the medium with the reversible change in the composition of the solution during electrolysis is principally possible. The only problem is the choice of the pH of the switcher with a set of properties required for each particular case.

Water-soluble *p*-sulfonatothiacalixarenes bind efficiently bulky complex cations at the upper sulfonate rim, whereas metal ions are bound at the lower phenolate rim.[2,3] Complexes of this type are used in the creation of devices with redox and pH-switching luminescence.[2,3] Now we report the results of investigation of the quinone—hydroquinone redox system as an electrochemical pH-switcher of luminescence in the complex of *p*-sulfonatothiacalix[4]arene (TCAS) with the Tb^{3+} ion.



TCAS

The Tb^{3+} ion itself does not luminesce, and its complex with TCAS, in which the metal ion is bound at the lower phenolate rim, possesses high luminescence. Binding and, therefore, luminescence, are pH-dependent. At pH 7 the Tb^{3+} ion is bound and the complex luminesces, whereas at pH 3 the metal ion is bound to a lesser extent and the luminescence is quenched.[3,27] Taking into account these data, we stated a problem of electrochemical pH-switching from 7 to 3 and back in a non-buffer aqueous solution containing 0.1 *M* $NaClO_4$ as a supporting electrolyte and a system $5 \cdot 10^{-4}$ *M* TCAS + $5 \cdot 10^{-4}$ *M* Tb^{3+} using the quinone—hydroquinone redox pair.

The cyclic voltammograms (CV) of quinone reduction and hydroquinone oxidation at pH 3.04 and 7.01 in the absence and in the presence of TCAS were preliminarily detected to determine the region of oxidation and reduction potentials. As it was expected, one peak of

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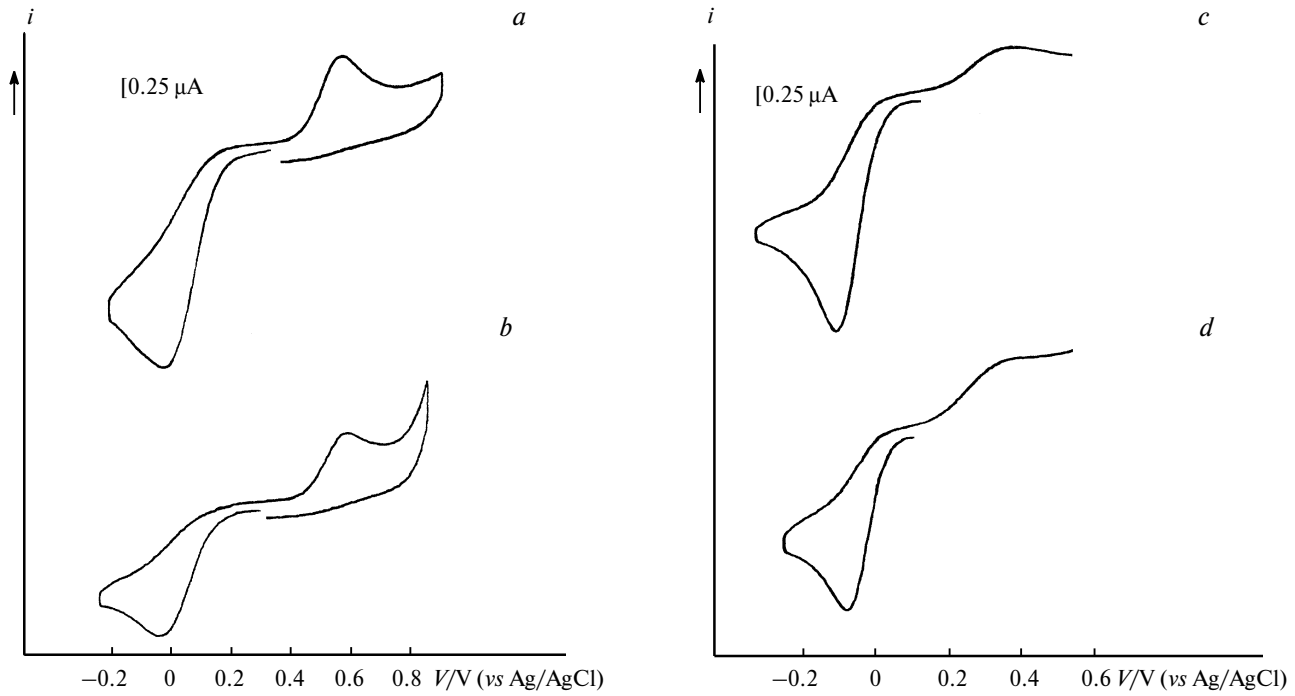

Fig. 1. Cyclic voltammograms at pH = 3.04 (*a*, *b*) and 7.01 (*c*, *d*) of quinone in the presence (*a*, *c*) and in the absence of TCAS (*b*, *d*) at the Pt electrode in an H_2O/0.1 *M* $NaClO_4$ medium; $C_{quinone} = 1.5 \cdot 10^{-3}$ mol L^{-1}, $C_{TCAS} = 2.0 \cdot 10^{-3}$ mol L^{-1}, $\upsilon = 100$ mV s^{-1}.

quinone reduction and one peak of hydroquinone reoxidation were detected on each CV of quinone (Fig. 1).

Typical dependences of the potentials of the reduction and oxidation peaks on pH are observed for the quinone—hydroquinone system. Especially high sensitivity is characteristic of the reoxidation peak of hydroquinone: in a highly acidic medium the peaks are shifted to anodic values. In the both solutions the introduction of TCAS decreases noticeably the current of the quinone reduction peak (i_p), which is controlled by the diffusion rate in all cases. This is indicated by the linear dependence of i_p on $\upsilon^{0.5}$. This decrease in the current in the presence of TCAS indicates, most likely, the binding of quinone with TCAS, which does not almost affect the reduction and reoxidation potentials (Table 1).

The CV morphology of hydroquinone almost corresponds to the CV curves of quinone with the only distinction that the peaks of hydroquinone oxidation and quinone rereduction are detected in this case and, correspondingly, the ratio of peak heights changes. Another distinction is that TCAS exerts no effect on the electrochemical behavior o hydroquinone. Therefore, unlike quinone, hydroquinone is not bound with TCAS.

Thus, in this pH range the chemically reversible reduction of quinone occurs with the transfer of two electrons, consumption of two protons, and formation of hydroquinone (Scheme 1). The reduction and oxida-

Scheme 1

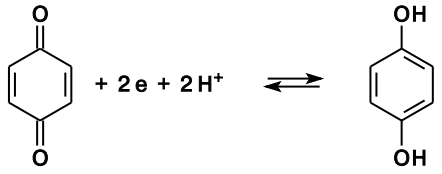

Table 1. CV data at the Pt electrode in an H_2O/0.1 *M* $NaClO_4$ for quinone and hydroquinone in the absence and presence of TCAS*

System studied	pH	$E_{p,red}$**	$E_{p,ox}$**	$I_{p,red}$	$I_{p,ox}$
		V		μA	
Quinone	3.04	−0.02	+0.57	1.65	0.65
	7.01	−0.06	+0.37	2.25	0.43
Quinone—TCAS	3.04	−0.03	+0.59	1.00	0.53
	7.01	−0.07	+0.38	1.70	0.40
Hydroquinone	3.04	+0.09	+0.54	0.43	1.63
	7.01	-0.11	+0.56	—	1.23
Hydroquinone—	3.04	+0.07	+0.55	0.50	1.63
TCAS	7.01	-0.11	+0.55	—	1.10

* The concentrations of quinone and hydroquinone are $1.5 \cdot 10^{-3}$ mol L^{-1}, $C_{TCAS} = 2.0 \cdot 10^{-3}$ mol L^{-1}, $\upsilon = 100$ mV s^{-1}.
** Relative to Ag/AgCl.

tion peaks are observed in the same potential region (see Table 1), where TCAS and Tb^{3+} are electrochemically inactive. From the viewpoint of oxidation and reduction potentials and pH-switching, the quinone—hydroquinone redox system is ideally suitable for electrochemical pH-switching in the TCAS—Tb^{3+} system.

Then we studied a possibility of electrochemical pH-switching of luminescence in the system $5.0 \cdot 10^{-4}$ *M* TCAS + $5.0 \cdot 10^{-4}$ *M* Tb^{3+} + $2.0 \cdot 10^{-3}$ *M* hydroquinone + $2.0 \cdot 10^{-4}$ *M* quinone *vs* 0.1 *M* $NaClO_4$. This initial solution, whose pH was adjusted with NaOH to 7.05, luminesces (Fig. 2). The concentration of protons equal to $1 \cdot 10^{-3}$ mol L^{-1} should be created in the solution to change pH from 7.0 to 3.0. This number of protons can be obtained by the oxidation of $5.0 \cdot 10^{-4}$ *M* hydroquinone. However, TCAS possesses some buffer capacity and, therefore, a high concentration of hydroquinone should be introduced into the solution. In addition, the diffusion current during electrolysis decreases with time according to the dependence $i \sim \tau^{-1/2}$ and, hence, prolonged electrolysis is needed for the complete processing of the substrate. In the next experiments, we took a fourfold amount of hydroquinone ($C = 2 \cdot 10^{-3}$ mol L^{-1}) and some amount of quinone ($C = 2 \cdot 10^{-4}$ mol L^{-1}) was added to the solution, although it is not necessary in the first oxidation step in the case of the initial solution.

The CV of the initial solution exhibits the peaks of both quinone reduction and hydroquinone oxidation (Fig. 3). The electrooxidation of the solution in a divided cell at the controlled oxidation potential of hydroquinone ($E \leq +0.4$ V) with the charge 1.37 times exceeding the theoretical value based on the proton concentration $C = 1.0 \cdot 10^{-3}$ mol L^{-1} results in (*i*) an increase in the quinone concentration with a simultaneous decrease in the hydroquinone concentration (see Fig. 3),

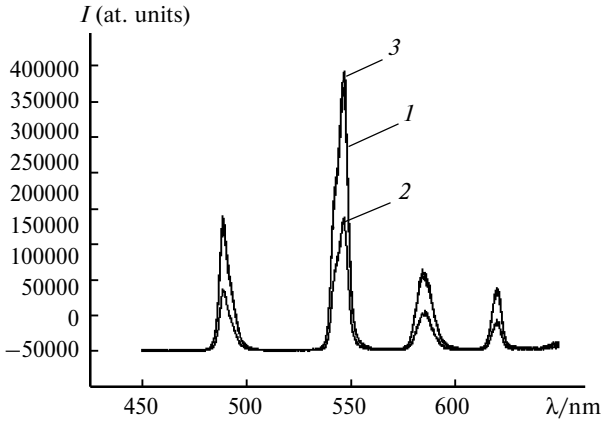

Fig. 2. Luminescence spectra of an aqueous solution $5.0 \cdot 10^{-4}$ *M* TCAS + $5.0 \cdot 10^{-4}$ *M* Tb^{3+} + $2.0 \cdot 10^{-3}$ *M* hydroquinone + $2.0 \cdot 10^{-4}$ *M* quinone + 0.1 *M* $NaClO_4$ at pH = 7.05 to (*1*) and after the cycle of electrochemical oxidation (*2*) and reversible reduction (*3*) (λ_{exc} = 330 nm).

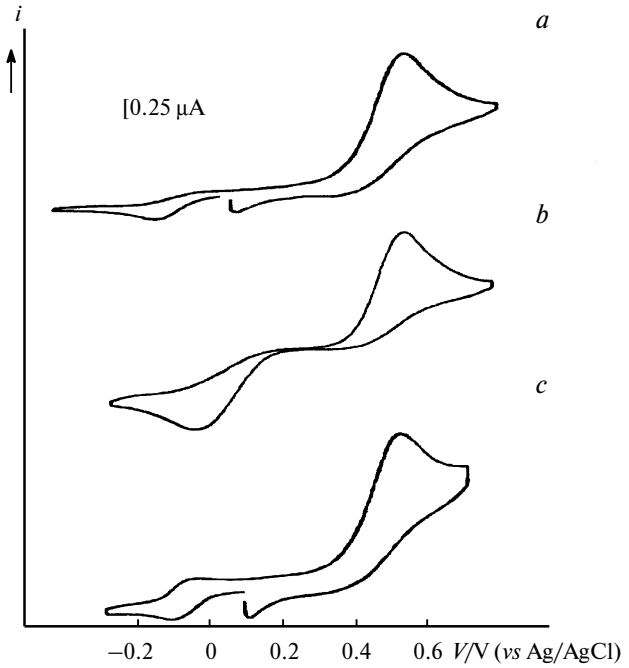

Fig. 3. Cyclic voltammograms of an aqueous solution containing $5.0 \cdot 10^{-4}$ *M* TCAS + $5.0 \cdot 10^{-4}$ *M* Tb^{3+} + $2.0 \cdot 10^{-3}$ *M* hydroquinone + $2.0 \cdot 10^{-4}$ *M* quinone + 0.1 *M* $NaClO_4$ before electrolysis, pH 7.05 (*a*); after electrochemical oxidation, pH 3.01 (*b*); after reversible electrochemical reduction, pH 7.14 (*c*).

(*ii*) a change in the pH to 3.01, and (*iii*) expected luminescence quenching (see Fig. 2). Therefore, the change in the pH and luminescence is due just to the oxidation of hydroquinone. The reverse reduction at the controlled potential of quinone reduction ($E \geq -0.1$ V), at the same current, and with the same charge returns the initial pH 7.14, luminescence (see Fig. 2), and the starting CV shape (see Fig. 3), indicating the entire reduction of the initial composition of the solution.

It should be mentioned that luminescence quenching after the electrochemical pH change from 7.05 to 3.01 is the same as for the chemical oxidation of the solution with hydrochloric acid in the system $5.0 \cdot 10^{-4}$ *M* TCAS + + $5.0 \cdot 10^{-4}$ *M* Tb^{3+} (Fig. 4).

Thus, using the reversible redox system quinone—hydroquinone, we succeeded to switch luminescence in a TCAS—Tb^{3+} system adequate to switching with the chemical change of pH. However, unlike the chemical variant, the electrochemical variant reversibly changes the composition of the solution. This result provides challenges for search for electrochemical pH-switchers for other systems and devices.

Experimental

p-Sulfonatothiacalix[4]arene tetrasodium salt (Na_4TCAS) in the cone conformation was synthesized according to a

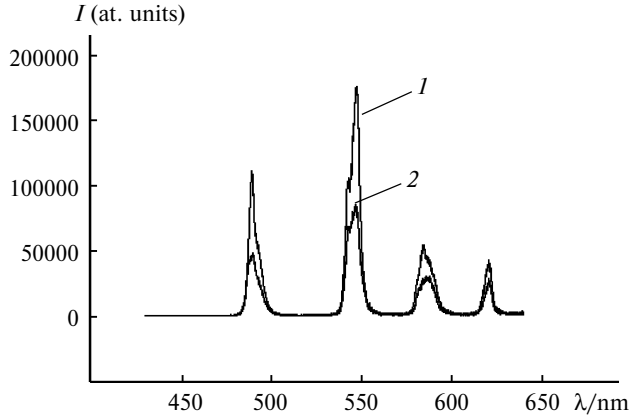

Fig. 4. Luminescence spectra of an aqueous solution of $5.0 \cdot 10^{-4}$ *M* TCAS + $5.0 \cdot 10^{-4}$ *M* Tb^{3+} at pH 7.05 (*1*) and after acidification with hydrochloric acid to pH 3.01 (*2*).

procedure described earlier.[28] In aqueous media this salt dissociates completely, and calixarene exists in solution as the tetraanion. In the presence of a large excess of a supporting electrolyte, counterions exert no noticeable effect on the ions under study and, therefore, they are not considered. Solutions for electrolysis were prepared by the dissolution of the compounds studied in a 0.1 *M* solution of $NaClO_4$ in bidistilled water and titration with a solution of hydrochloric acid or sodium hydroxide to the required pH value; pH of solutions were controlled with an I160 laboratory ionometer.

Solutions of $TbCl_3$ were standardized trilonometrically using xylene orange as indicator.[29]

Electrochemical measurements. Cyclic voltammograms were detected with a PI-50-1 potentiostat on an N 307/2 two-coordinate recorder with scan rates of 10, 20, 50, 100, and 200 mV s^{-1} under inert atmosphere. The working electrode was a disk Pt electrode (d = 0.5 mm) embedded into glass, and a Pt wire served as an auxiliary electrode. Prior to each measurement the working electrode was subjected to mechanical polishing. Potentials were measured and given relative to the reference electrode Ag/AgCl, 0.1 *M* KCl. Solutions were deaerated by argon bubbling in solution; T = 295 K.

Electrolysis was carried out in a glass three-electrode divided (porous glass membrane) cell on an electrode of the glassy carbon tissue (S = 11 cm^2) under an inert argon atmosphere in the galvanostatic regime (I = 0.5 mA, τ = 44 min) at controlled potentials of the corresponding peak. A Pt wire served as a counter electrode, and the reference electrode was a silver chloride electrode. The solution under study was poured into the working space (V = 12 mL), and the auxiliary space was filled with a supporting solution (0.1 *M* $NaClO_4$); T = 295 K.

Fluorimetric measurements. Luminescence spectra were recorded on an FL3-221-NIR spectrofluorimeter (Jobin Yvon) at 295 K using 1-cm quartz cells. Samples were deaerated by passing argon. The excitation wavelength was 330 nm, the slit was 2 nm, and the range of emission spectrum detection was 450—650 nm. The spectra were processed using the Microcal Origin 7.0 program.

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