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Effect of Micellar Media on Electrochemical Oxidation of Calix[4]resorcinolarenes

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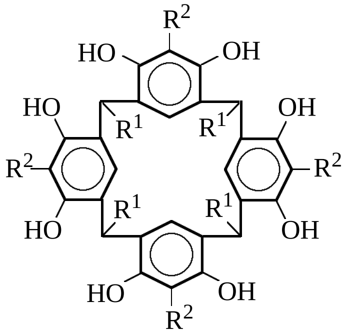
Abstract—Aminomethylated calix[4]resorcinolarenes in aqueous solutions of nonionic (Triton X-100) and ionic (cetyltrimethylammonum bromides) surfactants undergo selective oxidation controlled by the hydrophobicity of the substrates. In the inverted micellar system sodium bis(2-ethylhexyl) sulfosuccinate–decane–water after the percolation threshold, hydrophobized aminomethylated calix[4]resorcinolarenes undergo reversible one-electron oxidation to give the stable phenoxyl radical.

Biochemical processes catalyzed by enzymes occur in highly organized systems, such as cell membranes and subcellular particles [1]. Cell membranes can by mimicked by vesicles, microemulsions, and micelles, formed in surfactant solutions. In this connection much attention has been attached both to micellar systems as such and to various reactions in them [2]. Certain progress has been made toward understanding the mechanism of action of micellar systems and their influence on principal biochemical processes, such as transfer of phosphoryl and acyl groups and electron transfer [2, 3].

Considerable recent interest has been focused on macrocyclic phenols, calixarenes [4, 5], which, depending on the structure and nature of the solvent, can serve both as endo and as exo receptors [6], whereas functionalized calixarenes and their metal complexes, as models of active centers of enzymes [7–9].

Earlier we showed that intra- and intermolecular activation of reaction centers of calix[4]resorcinolarenes with amines imparts to these compounds catalytic activity in hydrolysis of phosphorus acid esters in aqueous micellar media [10] and in one-electron electrochemical oxidation of calixarenes themselves in molecular solutions (DMF, 2-propanol) [11].

In the present work we studied for the first time the effect of direct and inverted micellar systems on the electrochemical oxidation of calix[4]resorcinolarene **I**, as well as aminomethylated calix[4]resorcinolarenes **II**–**IV** and their structural unit, 2-dimethylaminomethyl-4-nonylphenol (**V**), by means of cyclic voltammetry and ESR spectroscopy combined with electrolysis.



I, $R^1 = C_9H_{19}$, $R^2 = H$; **II**, $R^1 = C_{11}H_{23}$, $R^2 = CH_2N(C_2H_5)_2$; **III**, $R^1 = C_9H_{19}$, $R^2 = CH_2N(CH_3)_2$; **IV**, $R^1 = CH_3$, $R^2 = CH_2NC_5H_{10}$.

In the inverted micellar system sodium bis(2-ethylhexyl) sulfosuccinate (**VI**)–decane–water [system (1)], the electrochemical oxidation pattern depends on the nature and hydrophobicity of substrates (calix[4]resorcinolarenes), presence or absence of NaOH, and temperature. Note that in this system we could study only hydrophobized calix[4]arenes **I**–**IV**, since their analogs ($R^1 = CH_3$) are insoluble even in the presence of NaOH. In view of this fact, as well as increased amphiphilicity of the substrates in the presence of NaOH, we expected that calix[4]resorcinolarenes would react with micelles to form either mixed micellar aggregates comprising compound **VI**, calix[4]resorcinolarene, and water, or associates in which substrates are bound with micelle surface.

At 17–21°C in system (1) both in the presence and in the absence of NaOH no oxidation peaks were

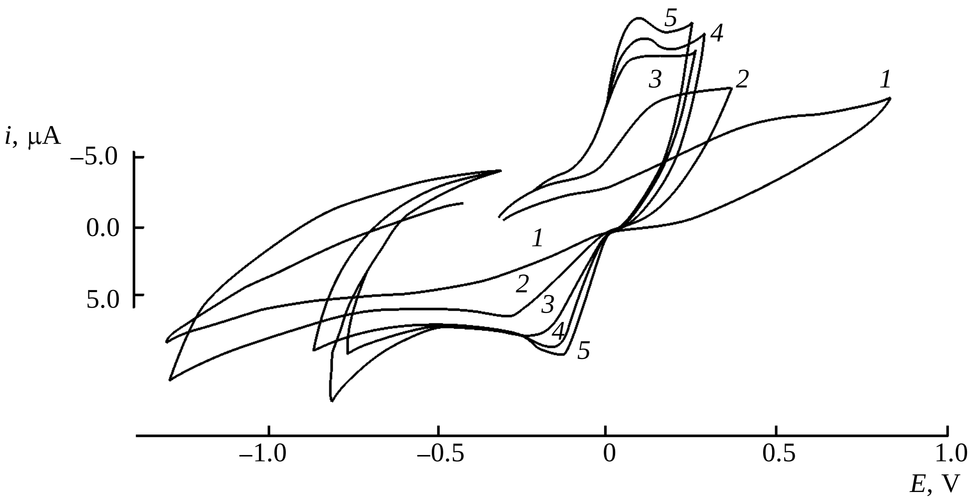


Fig. 1. Cyclic voltammograms of a 2.5×10^{-3} M solution of calixarene **II** in system (1) on a glassy carbon electrode. Temperature, °C: (*1*) 22, (*2*) 26, (*3*) 32, (*4*) 36, and (*5*) 42 (potential sweep rate 150 mV/s).

detected for compounds **I**, **II**, and **V**. The cyclic voltammograms showed a very flat current rise with potential, which got slightly steeper in the presence of NaOH (Fig. 1). This current rise is associated with oxidation of substrates, as evidenced by ESR data. When performing electrochemical oxidation of compound **II** directly in an ESR resonator (potential +1.0 V) at 10–21°C, we observed the ESR spectrum of the stable phenoxyl radical (Fig. 2), whose intensity linearly increased with time to attain a limiting value after 30-min electrolysis. It is known [12] that system (1) in the above temperature range has a low electrical conductivity. The background salt used (Et_4NBF_4) is poorly soluble in this system, cyclic voltammograms were recorded without *iR* compensarion, and, therefore, their patterns are explained by a high ohmic voltdrop in the reference electrode–working electrode circuit.

At 25–42°C system (1) exhibits the known phenomenon of electrical percolation, i.e. a sharp increase of electrical conductivity [12, 13]. As a result, we could observe well-defined oxidation peaks of compounds **I**, **II**, and **V**. With increasing temperature, the peak currents naturally increase, the peaks get narrower, and their potentials shift to lower values (see table and Fig. 1). The cyclic voltammograms in whole resemble the corresponding curves obtained in DMF/Et_4NBF_4 (0.1 M), but, because of the contribution of the ohmic *iR* component, they are slightly distorted even at the highest experimental temperature.

The cyclic volammograms of compounds **I** and **V** in the absence of NaOH show a single irreversible oxidation peak, while that of compound **II**, two oxidation peaks. The first peak is reversible, and the second, weaker peak is irreversible. The facilitated first electron transfer in calixarene **II** compared with **I** (ΔE_p 0.4 V at 42°C) and the reversibility of this process suggest oxidation, at first peak potentials, of zwitter ions of compound **II**, yielding the stable phenoxyl radical. The latter was detected by ESR spectroscopy in the course of electrolysis at first peak potentials directly in an ESR resonator (Fig. 2). The spectra of radicals generated at 10 and 40°C are similar to each

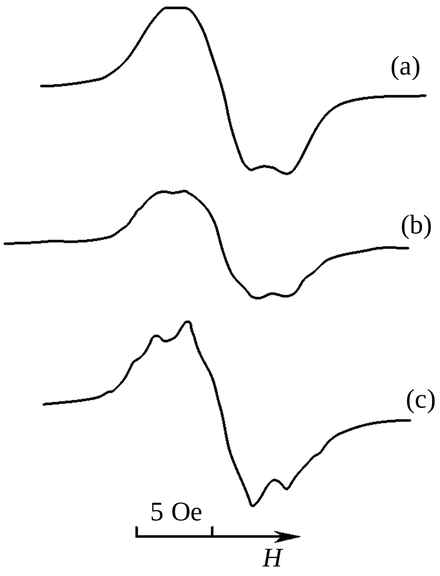


Fig. 2. ESR spectrum of the phenoxyl radical generated by electrochemical oxidation of a 2.5×10^{-3} M solution of calixarene **II** in system (1) on a glassy carbon electron at first peak potentials. Temperature, °C: (a) 10, (b) 30, and (c) 50.

Characteristics of oxidation peaks of calixarenes **I**–**IV** and phenol **V** on a glassy carbon electrode in system (1) after the percolation threshold

Comp. no.	$c \times 10^3$, M	$c_{NaOH} \times 10^3$, M	T, °C	E_p, V[a]	$(E_p - E_{p/2})$, mV	$i_p \times 10^6$, A
I	2.5	0	37[b]	0.57	150	2.8
	2.5	0	42	0.48	130	5.8
	2.5	10	26[b]	0.19	300	1.0
	2.5	10	31	–0.04	170	1.8
	2.5	10	36	–0.18	100	2.8
	2.5	10	42	–0.21	80	3.5
II	2.5	0	26[b]	0.17	140	4.0
	2.5	0	32	0.09	110	7.0
	2.5	0	36	0.09	110	7.0
	2.5	0	42	0.08	100	9.8
	4.0	16	24[b]	0.4	330	7.5
	4.0	16	37	0.17	150	10.5
IV[c]	2.5	0	22	–0.02	80	12.0
V	2.0	0	31[b]	0.76	270	6.2
	2.0	0	36	0.57	170	7.0
	2.0	0	42	0.51	130	8.5
	2.0	2.0	29[b]	1.26	470	4.5
	2.0	2.0	35	0.82	260	7.2
	2.0	2.0	42	0.65	180	9.0

[a] Relative to $Ag/AgNO_3$ (0.01 M) in MeCN. [b] The oxidation peak is ill-defined at lower temperatures. [c] In system (2).

other, but the latter spectrum is better resolved. The complex, five-component spectrum of the radical suggests that the principal hfs constants ($a_H \sim 1.5$, 1.6, and 3.3 Oe) are due to coupling with three protons, from the methylene bridges and the resorcinol nucleus.

Introduction into system (1) of a fourfold excess of NaOH with respect to substrates has almost no effect on the oxidation of compounds **II** and **V** and much facilitates the oxidation of calixarene **I** (ΔE_p 0.70 V). This means that in the system studied compound **I** undergoes deprotonation to give phenolate anions, and it is their oxidation which is observed at negative potentials. As to compounds **II** and **V**, then, as we showed earlier [14], aminomethylated derivatives of phenols and calix[4]resorcinolarenes involve strong intramolecular hydrogen bonds OH···N and form the zwitter ions $O^- N^+H$. As a result, their hydroxy groups have much higher pK values than in the corresponding parent compounds. The fact that NaOH additives have no effect on the oxidation potentials of calixarenes **II** and **V** suggests the zwitter-ionic form of the latter in system (1).

Note that in the range 25–42°C the oxidation peak currents of compounds **I**, **II**, and **V** in system (1) are of the same order as in DMF, where these compounds are present as monomeric species. In both media the peak current is determined by the diffusion rate of the substrate to the electrode surface. Compounds **I**, **II**, and **V** are insoluble in decane and water, and, consequently, in system (1) they are present, as noted above, on the surface of inverted micelles or form mixed micelles. The high electrical conductivity of the system after the percolation threshold is explained by that micelles form channels (clusters) containing aqueous phase and serving for ion transfer between electrodes [15, 16]. The fairly large oxidation currents of compounds **I, II**, and **V** suggest that cluster formation also favors electron transfer due to the high rate of diffusion (sliding) of these compounds along the channels or due to a relay-race (chain) mechanism of electron transfer, like that operating in enzymatic tissue oxidation processes [17].

The results obtained for the inverted micellar system 1 prompted us to study electrochemical oxidation of calix[4]resorcinolarenes in solutions containing direct micelles. As convenient objects for these studies we chose reversibly oxidized aminomethylated derivatives **II**–**IV**. It was found that the governing factor of the electrochemical oxidation of these compounds in DMF–water systems containing an nonionic [Triton X-100 (**VII**); system (2)] or a cationic [cetyl trimethylammonium bromide (**VIII**); system (3)] surfactant and a background electrolyte (Et_4NBF_4, 0.1 M) at 22°C is the length of the hydrocarbon radical R^1 at the methylene bridge of the calixarene. At a short radical (compound **IV**, $R^1 = CH_3$), a well-defined classical reversible oxidation peak is observed, while at longer radicals (compounds **III**, $R^1 = C_9H_{19}$, and **II**, $R^1 = C_{11}H_{23}$), no oxidation takes place on a glassy carbon electrode. The lack of oxidation peaks for compounds **II** and **III** in micellar systems (2) and (3) is probably explained by the fact that these compounds form, due to hydrophobic interactions, mixed micellar aggregates [10], which hinders their transport to the electrode surface. Compound **IV**, as we found in [10], in the systems studied form, by intramolecular hydrogen bonds, other aggregates sharply differing from those formed by compounds **II** and **III** in critical aggregation concentrations and reactivity. Because of the much lower binding constant, much calixarene **IV** is present in solutions in the monomeric form and can diffuse to the electrode surface and thus undergoes oxidation. It should be noted that in DMF in the presence of the background salt Et_4NBF_4 (0.1 M) compounds **II**–**IV** are oxidized similarly at the same potentials, reversibly, yielding the stable phenoxyl radical [11]. Thus, in direct micellar media one can selectively oxidize substrates which exhibit similar reactivity in molecular solutions.

EXPERIMENTAL

Compoud **I** was synthesized by the procedure [18], compounds **II**–**IV**, by the procedure [19], and compound **V**, by the procedure [20]. Compounds **VI**–**VIII** were used without preliminary purification. The electrochemical data were obtained in the micellar systems compound **VI**–decane–water and DMF (30 vol%)–water in the presence of surfactant **VII** or **VIII**. The background salt Et_4NBF_4 was purified by recrystallization from acetonitrile (0.1 M). The inverted micellar systems were prepared according to [12, 21] at fixed parameters: Z = [decane]/[**VI**] = 10.9 and W = $[H_2O]$/[VI] = 15.1. The concentrations of compounds **VII** and **VIII** were 10^{-2} M.

The cyclic voltammograms were recorded with a PI-50-1 potentiostat on an N-307/2 two-coordinate recorder. The potential sweep rate was 100 mV/s. The working electrode was a glassy carbon disc (diameter 2 mm) embedded into Teflon. The reference electrode was $Ag/AgNO_3$ (0.01 M) in MeCN (potential +0.3 V with respect to a saturated calomel electrode). Dissolved oxygen was purged off with argon or nitrogen.

ESR spectroscopy with electrochemical generation of active species were obtained on an apparatus combining a Radiopan SE/X-2544 ESR spectrometer coupled with a potentistat and an electrochemical cell, which allowed the electrochemical process to be performed directly in an ESR resonator. The working electrode was a platinum plate, the auxiliary electrode was a platinum wire, and the reference electrode was a silver wire. The solutions were dearated by triplicate freezing–pumping–thawing.

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