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VOLTAMMETRIC RESPONSE OF FREE AND POLYMER ENTRAPPED BIS-(TRISALKOXY)-HEXAVANADATE

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ABSTRACT. The electrochemical behaviour of the dissolved and polymer entrapped trans-bis-(trisalkoxy)-hexavanadate (trans-BTHV) was studied by cyclic voltammetry performed at glassy carbon and carbon paste electrodes, in different experimental conditions (potential scan rate and pH). The free trans-BTHV showed a one pair of well defined peaks, corresponding to a 5 electrons quasi-reversible redox process. In the pH range 4.5 to 7 the voltammetric response of trans-BTHV, immobilized in AQ 55D polymer, consisted in two waves: a first one of 5 electrons at 0.15 V/SCE and a second one of 1 electron at –0.075 V/SCE (pH 6). In both cases, the dependence of peak current intensity on the potential scan rate proved that the redox process was controlled by diffusion.

INTRODUCTION

A modified electrode (ME) has been generally defined as a deliberate control of the molecular structure at the electrode surface, aimed at tailoring the electrode to meet specific applications. Thus, the IUPAC definition indicate that a ME is "an electrode made of a conducting or semiconducting material that is coated with a selected monomolecular, multimolecular, ionic or polymeric chemical film and by means of faradaic (charge-consuming) reactions exhibits chemical, electrochemical and/or optical properties of the chemical film" [1]. In the last years the CMEs became very attractive because of the wide range of their applications in electrochemical technology as well as in chemical analysis and energy conversion.

Modified electrodes can be prepared by several different techniques as follows: chemisorption, covalent binding or polymer film coating. Polymeric layers can be obtained starting from the preformed polymers (by dip coating, solvent evaporation or cross linking) or produced by *in-situ* polymerization (photo- or electrochemical polymerization) [1, 2]. Additionaly to the stability and to the long lifetime of the electrode, the most important advantage of ME with polymer matrix is that the multilayered coating provides a three dimensional reaction zone at the electrode surface, which gives rise to an increase in the flux of reactions that occur there, finally increasing the electrode sensitivity [3].

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Recently, considerable interest was focused on the preparation, investigation and development of inorganic polynuclear electrode materials, i.e. polyoxometalates. These offer large possibilities of composition variations with a direct applicability in many and various domains among electrocatalysis is the most relevant in the present context [4, 5, 6]. These mediators exhibit good stability, specific reactivity, fast redox transition leading to direct electron transfer, and facilitate the formal transfers of oxygen or hydrogen during electrode reactions [7].

Electrochemical characterization by cyclic voltammetry (CV) [6, 8, 9], cronopotentiometry [8] or UV - VIS spectroscopy [6] of some vanadium-containing heteropoly acids were reported. Muller and coworkers [10] taking in consideration that trisalkoxy-hexavanadate may be able to become an interesant redox catalyst depending on the variation of nature, position and number of trisalkoxy ligands, synthetised and characterized the cis- and trans- $(CN_3H_6)_2[V_6O_{13}\{(OCH_2)_3 CCH_2OH\}_2] * H_2O$.

The aim of this paper is the electrochemical characterization, of the free and polymer entrapped trans–bis-(trisalkoxy)-hexavanadates (trans-BTHV), by cyclic voltammetry at two electrode materials: glassy carbon (GC) and carbon paste (CP) electrode. The voltammetric response, recorded in different experimental conditions (potential scan rate and pH), was analysed in order to be attributed to a redox process and to estimate the characteristic electrochemical parameters. Consequently, a comparison of the redox responses of cis- and trans- BTHV was performed.

EXPERIMENTAL

Chemicals

Pure bis-(trisalkoxy)-hexavanadate (trans-$(CN_3H_6)_2[V_6O_{13}\ \{(OCH_2)_3C\text{-}CH_2OH\}_2]*H_2O$) (trans-BTHV) was a kindle gift of Dr. Muller (*Bielefeld, Fakultät fûr Chemie der Universität*) and was used without further purification. The polyoxometalate solutions were freshly prepared just before using by dissolving the appropriate amounts of the salt into the supporting electrolyte. All other reagent grade chemicals were obtained from *Reactivul-Bucureşti*.

The supporting electrolyte was a 0.25 M solution of K_2SO_4. Its pH value was adjusted with 1/15 M phosphate buffer in the pH range 5.5-7 and with diluted phosphoric acid in the pH range 1-5.5. The 1/15 M phosphate buffer (pH 7) was prepared by mixing the appropriate volumes of $Na_2HPO_4*12H_2O$ and KH_2PO_4 solutions.

The poly(ester-sulphonic acid) polymer (Eastman Kodak AQ 55D) was purchased as a 28% aqueous solution from *Eastman Kodak Co., France*. The graphite powder (99.9% purity) was obtained from *Fluka, Germany* and the paraffin oil from *Fischer Oil, USA*. A glassy carbon disk (Type 16, *Hochtemperature-Werkstoffe GmbH, Thierhaupten, Germany*) (ϕ= 3.5 mm) was used as a working electrode. The carbon paste electrode CPE was obtained as previously described [11, 12].

Electrochemical measurements

The electrochemical characterization of the polyoxometalate was carried out using an undivided three electrode electrochemical cell (10 ml capacity), equipped with a saturated calomel electrode (SCE) and a platine electrode (~ 1 cm^2) as reference and counter electrode, respectively. As working electrode were employed a carbon electrode (GC) (ϕ = 3.5 mm), a carbon paste electrode (CP) (ϕ = 6 mm) and a glassy carbon modified electrode (ME). A fresh and clean surface of the GC electrode was obtained by polishing the electrode with emery paper (400-450 and 600 grit, *Buehler, Lake Bluff. Ill, USA*).

All cyclic voltammetry measurements were performed with a home made cyclic voltammetry set-up, including a low current potentiostat (Polarograph LP7e, *Czechoslovakia*), and an acquisition data module (AT MOI - 16F*, National Instruments, USA*) controlled by a AT-486-DX PC - computer (*Olivetti, Switzerland*). The software was elaborate based on LabVIEW 3.1. package [13].

All experiments were conducted at ambient temperature (20 ± 2℃) and at atmospheric pressure. All potentials are quoted with respect to the SCE.

Preparation of the modified electrode

The trans-BTHV-modified glassy carbon electrode (ME), was obtained by deposition on the electrode surface of a polymer film containing the salt of trans-BTHV. Thus, on the surface of a freshly polished and thoroughly rinsed (distilled water) GC electrode was deposited a mixture containing 100 µl AQ 55D polymer and 4 mg trans-BTHV. In order to obtain a strongly adherent trans-BTHV-AQ 55D film, the coated electrode was allowed to dry for 2 h at 45℃.

RESULTS AND DISCUSSION

The voltammetric response of the dissolved cis-BTHV on gold electrode showed two waves placed at $\varepsilon^{o'}$ = 0 V/NHE and $\varepsilon^{o'}$ = 0.57 V/NHE [10]. The first one was attributed to a 5 e^- process corresponding to the following reaction:

$$V_6^{(IV)}O_7(OH)_6\{(OCH_2)_3CCH_2OH\}_2]^{2-} \rightarrow [V^{(IV)}V_5^{(V)}O_{13}\{(OCH_2)_3CCH_2OH\}_2]^{3-} + 6H^+ + 5e^- \qquad (1)$$

and the second one, involving 1 e^- transfer, was associated with:

$$[V^{(IV)}V_5^{(V)}O_{13}\{(OCH_2)_3CCH_2OH\}_2]^{3-} \rightarrow [V_6^{(V)}O_{13}\{(OCH_2)_3CCH_2OH\}_2]^{2-} + e^- \qquad (2)$$

In order to compare the electrochemical behaviour of cis-BTHV and trans-BTHV the cyclic voltammograms of the trans-BTHV in solution were recorded in the pH range of 1 - 7. Contrarily to the cis-BTHV, the voltammetric response of the trans- BTHV presents one pair of well defined peaks (A1/C1, figures 1A, 1B), irrespective of the electrode materials (GC and CP). The corresponding peak currents decrease with the increase of the pH value, due to the low stability of the trans-BTHV in neutral media.

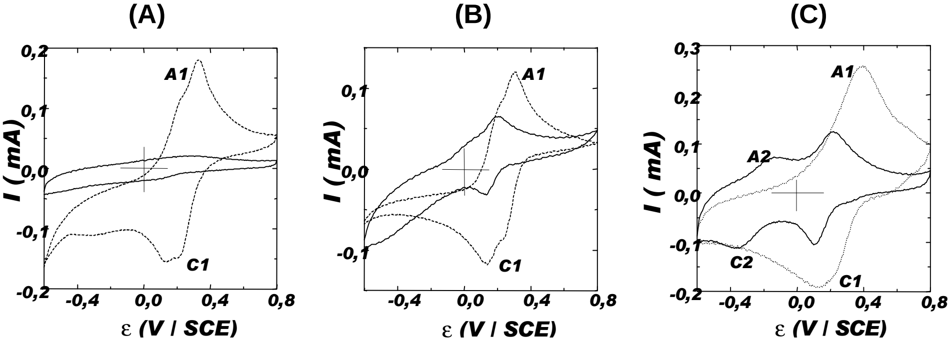

***Figure 1**. Voltammetric response of dissolved bis-(trisalkoxy)-hexavanadate at [GC (A), CPE (B)] and polymer entrapped in an Eastman AQ 55 D matrix (C). Experimental conditions: scan rate 75 mV/s; supporting electrolyte 0.25 M K_2SO_4, pH 2 (-- -- --) and pH 6 (-------); ambient temperature; starting potential - 0.6 V vs SCE.*

In the pH range 1-4, the trans-BTHV immobilized in a polymer matrix showed a similar voltammetric response to the dissolved compound. For higher pH values (4 - 7) a second wave (A2/C2) was observed (figure 1 C) in the lower potential domain, as was reported for dissolved cis-BTHV [10] at gold electrode.

The hight of A1/C1 wave suggested a 5 electrons redox process, corresponding to the reaction (1), while the A2/C2 wave was associated to an one electron transfer, described by the reaction (2).

The immobilization efficiency is proved by the following sequences of the A1/C1 peak currents: $(I)_{CP} < (I)_{GC} < (I)_{ME}$, observed at pH 2 and $(I)_{GC} < (I)_{CP} < (I)_{ME}$, noticed at pH 6. Moreover, at all pHs the redox response corresponding to the immobilized trans - BTHV was higher than that for dissolved compound.

In table 1 are presented the main electrochemical parameters of the A1/C1 voltammetric wave obtained from cyclic voltammograms recorded in the specified experimental conditions. The values of these parameters point out the redox process associate to the A1/C1 voltammetric wave as a quasi-reversible one, indifferent of the pH value or the immobilization state.

As a consequence of the immobilization, at pH 2, an increase of the electrochemical parameters ($\Delta\varepsilon_p$; $\varepsilon^{o'}$; ε_p - $\varepsilon_{p/2}$) was observed (table 1), suggesting the existence of some interactions between the trans-BTHV polyanion and the negatively charged polymer matrix. Contrarily, at pH 6, the decrease of $\Delta\varepsilon_p$, $\varepsilon^{o'}$and $(\varepsilon_p - \varepsilon_{p/2})_{anodic}$ values could be attributed to the protective effect of the polymer matrix on the polyanion stability.

Table 1.

Electrochemical parameters of the cyclic voltammetric response observed for dissolved (*) and polymer entrapped (**) trans-BTHV. Experimental conditions: see figure 1, v = 50 mV/s.

Elec-trode	**pH = 2**					**pH = 6**				
	$\Delta\varepsilon_p$ (mv)	$\varepsilon^{o'}$ (V)	*Ipa/Ipc*	$\varepsilon_p - \varepsilon_{p/2}$ (mV)		$\Delta\varepsilon_p$ (mv)	$\varepsilon^{o'}$ (V)	*Ipa/Ipc*	$\varepsilon_p - \varepsilon_{p/2}$ (mV)	
				anodic	cathodic				anodic	cathodic
GC*	221	0.111	0.92	126	-163	189	0.095	0.74	203	-
CPE*	180	0.090	1.17	139	-151	108	0.054	1.4	134	61
ME**	305	0.153	1.12	169	-217	110	0.055	0.54	69	90

As can be shown from reaction (1), the standard potential corresponding to the redox process associated to the peak A1/C1 should be pH dependent. Indeed, the cyclic voltammograms recorded at different pH values for free or immobilized trans-BTHV showed that the formal standard potential ($\varepsilon^{o'}$) (estimated as the average of the anodic and cathodic peak potentials) depends on the electrolyte pH (figure 2).

The number of protons (table 2) involved in the redox process, corresponding to the A1/C1 wave, were calculated from the slope $\varepsilon^{o'}$–pH dependence calculated for different electrodes, considering a 5 electrons transfer [10]. The obtained results revealed that in the 1 to 3.5 pH range 4 and 3 protons are involved in the redox process at GC, ME and CP electrodes, respectively. At pH > 4, the $\varepsilon^{o'}$ value became independent on the pH for all investigated electrodes.

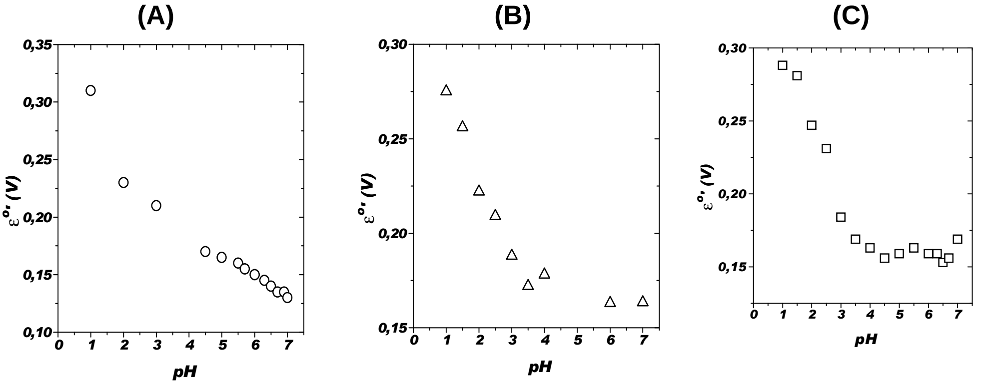

Figure 2. *pH dependence of formal potential of A1/C1 peak GC (❍), CP (Δ) and ME (*C*). Experimental conditions: see figure 1.*

Table 2.

The protons number estimation corresponding to the A1/C1 peak process at the pH 1 - 3.5, v = 75 mV/s.

Type of electrode	**GC**	**ME**	**CP**
slope = 0.059 (p/n)	0.053	0.048	0.037
p/n	4.5/5	4.1/5	3.1/5
r	0.98	0.98	0.997

It is interesting to remark that the intensity of the A1/C1 peak slightly increase with the pH decrease (figure 3), proving once again the effect of pH on the trans-BTHV stability.

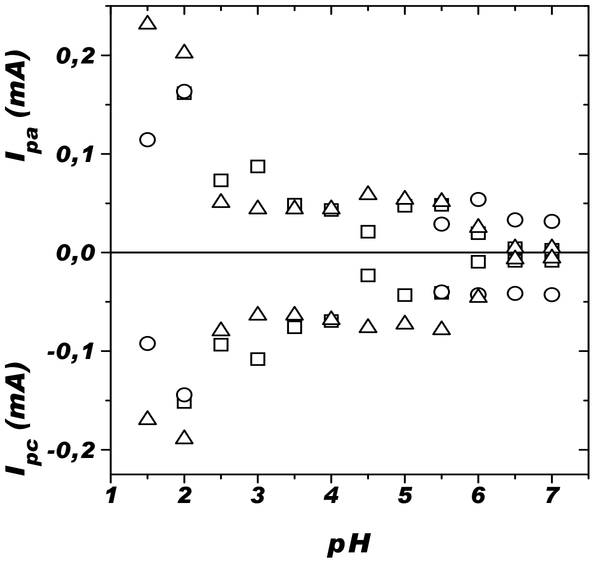

Figure 3. *Dependence the (A1/A2) peak currents on the pH: GC (❍), CP (Δ) and ME (*C). *Experimental conditions: scan rate, 75 mV/s; for other conditions see fig. 1*

As can be seen in figure 4, within the experimental errors, the peak currents corresponding to the A1/C1 wave depend linearly on $v^{1/2}$, proving a diffusion controlled process for all type of studied electrodes. This behaviour is expected for the dissolved trans-BTHV on GC and CP electrodes, while for ME proves that the trans-BTHV is freely diffusing within the AQ 55D-polymer matrix. In the same time, this finding offers a supplementary explanation for the low stability of the ME.

(A) **(B)** **(C)**

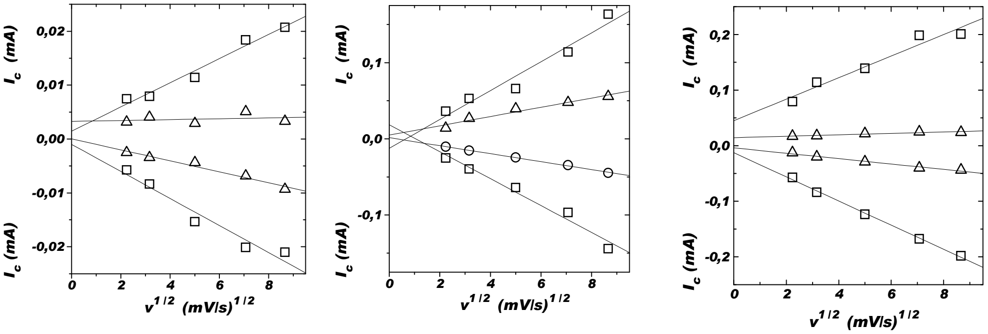

Figure 4. *Dependence of the peak currents (A1/A2)on the potential scan rate for GC (A), CPE (B) and polymer modified electrod ME (C) at pH 2 ( ), pH 6 (Δ). Experimental conditions: see fig. 1.*

CONCLUSIONS

All the experimental results obtained converge to prove the feasibility of electrochemical characterization of trans-bis-(trisalkoxy)-hexavanadate free and immobilized on glassy carbon, carbon paste and glassy carbon, respectively. Contrarily of cis-BTHV and irrespective of the electrode materials (GC and CP), the voltammetric response of the dissolved trans- BTHV presented one pair of well defined peaks, corresponding to a 5 electrons quasi-reversible redox process.

In the pH range 4.5 to 7 the ME with polyoxometalate showed a relatively stable voltammetric response of the trans-BTHV immobilized in AQ 55D polymer, consisting in two waves: a first one of 5 electons at 0.15 V/SCE and a second one of 1 electron at –0.075 V/SCE (pH 6).

For all investigated electrodes, the influence of the potential scan rate on the peak current intensity showed that the voltammetric response was controlled by diffusion.

The effect of pH on the formal standard potential of the 5 electrons wave, placed at ~ 0.1 V/SCE, allowed to estimate the number of proton involved in the redox process, showing a participation of 4 and 3 protons for GC, ME and CP electrodes respectively.

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