Amperometric Detection of Periodate Using a Graphite Electrode Modified with a Novel α-Keggin-Type Silicotungstic Acid Salt and Determination of Ethylene Glycol in Antifreeze Fluids

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Abstract

A novel, water-insoluble, salt of α-Keggin-type silicotungstic heteropolyacid with hexadecylpyridinium cation ($SiW_{12}Hex$) was synthesized. The salt was immobilized onto the surface of spectroscopic graphite electrodes through physical adsorption from acetone solution to produce chemically modified electrodes (SiW_{12}Hex-CMEs). Some preliminary electrochemical data of soluble silicotungstate salts as well as of the modified electrode are given. Parameters such as the roughness of the electrode surface, the surface coverage and pH effect were investigated. The modified electrode was employed for the amperometric detection of periodate through its electrocatalytic reduction to iodate at −0.40 V (vs. Ag/AgCl) at pH 4.5 and for the indirect determination of ethylene glycol in antifreezing fluids. Linear plots of cathodic current versus the ethylene glycol concentration in the range of 0.2–5 mM ethylene glycol were obtained. An accuracy better than 2.1 % and a reproducibility (relative standard deviation) of 1.9 % ($n = 10$) for a 5×10^{-4} M standard solution of ethylene glycol were achieved. The recovery was 98–101 %.

Keywords: α-Keggin-type silicotungstates salt, Periodate electrocatalytic reduction, Ethylene glycol, Antifreeze fluids

1. Introduction

Catalysis by early transition metal-oxygen anion clusters (polyoxometalates or polyoxoanions) is a rapidly growing area, as a consequence of i) the unusual versatility of these catalysts, ii) the ability of one or more addenda ions in some structural families of polyoxometalates (mostly in α-Keggin-type anions) to be substituted by *d*-electron transition metal ions and of iii) their compatibility with the most attractive oxidants, e.g., O_2 and H_2O_2. A large number of articles dealing with the catalytic properties of heteropolyacids (HPAs) have been published and are comprehensively summarized in several reviews [1, 2].

HPAs are composed primarily of the early transition metal cation, M (most commonly W^{VI}, Mo^{VI}) and a central heteroatom, X (Si, P, Ge, etc.). The most investigated of all structural types is the α-Keggin-type heteropolyanions of formula $[X^{n+}M_{12}O_{40}]^{(8-n)-}$. Their structure comprises a central XO_4 tetrahedron surrounded by 12 metal oxygen octahedra joined in 4 M_3O_{10} edge sharing groups [3]. The heteroatom, X^{n+}, can be one of over half the *d* block elements and many of the *p* block elements. These complexes exhibit rich and well-elaborated substitution chemistry in which one or more of the d^o addenda ions can be replaced with other d^o early transition metal (*d*-electron transition metal ions, or organometallic or organic groups) [1].

A considerable number of reactions and particularly those of the monosubstituted HPA catalysts with the α-Keggin-type structure have been studied. The monosubstituted catalysts of formula $[M_s^{n+}XM_{11}O_{39}]^{(7-n)}$ where X = P or Si; M_s = Co, Mn, Cu, Fe(III), Cr, Ni, or Ru; and M = Mo or W are the most thoroughly studied [1, 4]. On the other hand, tri- and tetra-substituted HPAs catalysts have not been studied as extensively as the monosubstituted catalysts and the key reason for this is undoubtedly that the multisubstituted catalysts are harder to synthesize in pure, unequivocally characterized form [5].

Unsubstituted or substituted HPAs have been extensively used in many industrial applications, mainly in connection with O_2 or H_2O_2 as oxidants, for the bleaching of commercial pulp [6], oxidation of methane [7], hydrogen sulfide [8], alkylphenols [9], etc. Electrocatalytic reductions of nitrite and nitrate to ammonia [10], of H_2O_2 [11] and of bromate [12, 13] have also been reported.

Even though there is a continuing and increasing interest in the research of the electrocatalytic properties of HPAs, the work devoted to their application in the development of chemically modified electrodes is limited. The key reason for this is the high solubility of HPAs in aqueous solutions. Some attempts for the immobilization of HPAs onto electrode surface have been achieved through electrochemical deposition [14–15], as a dopant in a conductive polymer matrix [12] and layer by layer molecular self-assembly process based on electrostatic attraction as the driving force [16].

The aim of this article is to explore the construction of chemically modified electrodes (CMEs) based on a novel, water-insoluble salt of α-Keggin-type silicotungstic HPA with hexadecylpyridinium cation ($SiW_{12}Hex$) that was synthesized in our laboratory. As revealed by the cyclic voltammetry experiments, $SiW_{12}Hex$ retains the electrocatalytic behavior of the original HPA and exhibits well-defined redox waves. The resulting electrodes were employed for the amperometric detection of periodate through its electrocatalytic reduction to iodate. This approach provides the feasibility for a reliable, relatively fast and easy to perform determination of ethylene glycol in antifreeze fluids by measuring the excess of periodate after its reaction with the glycol.

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2. Experimental

2.1. Chemicals

Ethylene glycol, sodium *meta*-periodate, silicotungstic acid hydrate (99 + %, $H_4SiO_4 \cdot 12WO_3 \cdot xH_2O$) and acetone (99 + %) were supplied by Aldrich (Gillingham, Germany) and used without further purification. Hexadecylpyridinium chloride salt was purchased from Sigma (St. Louis, USA). Stock solution of sodium periodate (0.100 M; 1.07 g of $NaIO_4$ in 50 mL of distilled water) was kept in an amber vial. Stock solution of ethylene glycol (0.100 M; 0.3104 g in 50.0 mL of the working buffer solution) was standardized iodometrically and stored in a well-stopped vial.

2.2. Apparatus

All electrochemical experiments were conducted with a computer-controlled potentiostat, the Autolab electrochemical analyzer (Eco Chemie, Utrecht, The Netherlands). Cyclic voltammetry experiments were performed with a voltammetric cell (VC2, BAS, West Lafayette, IN) using a graphite rod (RWOOO1, 6.15 mm Ø, Ringsdorf-Werke, Germany) as the working electrode, a Ag/AgCl (3 M KCl) reference electrode (BAS). All potentials reported hereafter are referred to the potential of this electrode. A Pt wire (60 mm × 1 mm) was used as the auxiliary electrode (BAS). The supporting electrolyte was a 0.25 M phosphate buffer in 0.5 M KCl (0.050 M in amperometry experiments) at pH 3–7.5 deareated with a gentle stream of nitrogen.

2.3. Procedure

The applied potential for the amperometric measurements was set at −0.40 V. An aliquot of 9.4–x mL of the buffer solution (50 mM phosphate, pH 4.5 in 50 mM KCl) was added in a conical thermostated at 25 °C cell (equipped with the same electrodes as in cyclic voltammetry experiments) and the background current was allowed to decay to a stable value under mild stirring using a 12 mm magnetic stirring bar. Then, 0.60 mL of sodium periodate stock solution (final concentration 6.00 mM) was transferred into the electrochemical cell and a new baseline was recorded. Standards or unknown samples ($x = 0.02$–0.50 mL) of ethylene glycol were injected and the decrease of the current was recorded by means of an interface card. The steady state current was measured (± 0.1 μA) after a 5 min reaction period.

The surface coverage Γ of the modifier and the total effective area of the graphite working electrode were determined with cyclic voltammetry and double step chronocoulometry experiments, respectively [17].

2.4. Synthesis and Characterization of SiW_{12}Hex

2.49 g hexadecylpyridinium (0.0069 mol) is dissolved in 100 mL of warm (50 °C) distilled water; the solution is filtered and then poured dropwise into a 100 mL aqueous solution of 5.00 g (0.0017 mol) silicotungstic acid, under stirring. The mixture is allowed to stand for 60 min, is cooled, filtered through a Gooch 3 crucible and then washed with distilled water. The precipitate is dried for two days under vacuum and over P_4O_{10}. SiW_{12}Hex is taken at a 78 % yield as a crystalline white powder. The overall reaction is described by the Equation 1.

$$H_4[(SiO_4)(WO_3)_{12}] \cdot xH_2O + 4C_{21}H_{38}NCl \cdot H_2O \rightarrow (C_{21}H_{38}N)_4[(SiO_4)(WO_3)_{12}] + 4HCl + xH_2O \quad (1)$$

The complex is insoluble in water and soluble in acetone. The molecular weight of the product, $C_{84}H_{152}N_4SiW_{12}O_{40}$, is 4092.43 and its melting point >320 °C. Elemental analysis: C 24.65 %, H 3.74 % and N 1.37 % (theoretical values: 24.59, 3.78, and 1.36 %, respectively. By digesting the solid compound under flame, the residue $SiO_2 \cdot 12WO_3$ was found to be 69.45 % (theoretical value: 69.38). These results were also verified by gravimetric thermal analysis experiments performed by a Jupiter STA449 (NETCSZ, Germany) thermobalance.

2.5. Preparation of the Modified Electrodes

Spectroscopic graphite rods were polished on fine emery paper (Struers, Austria, grit No 800), then polished against a lens cleaning tissue (No 105 Whatman) and finally they were thoroughly washed with double-distilled water. They were dried at 60 °C for 30 min, heated in a muffle furnace at 700 °C for 90 s (to remove any small particles from the surface area) and allowed to cool in a desiccator. To avoid electrical contact between the sides of the electrodes and the solution, the sides of the working electrodes were covered with Parafilm before the electrochemical experiment.

The surface modification was made by direct adsorption of SiW_{12}Hex by pippeting 10 μL of a solution of SiW_{12}Hex in acetone (1.5×10^{-4} M; 0.0025 g in 4.0 mL acetone). After evaporation of the solvent the surface of the electrode was thoroughly washed with distilled water. The surface coverage (Γ) was calculated from cyclic voltammetric measurements 1.41 nmol cm^{-2}.

3. Results and Discussion

3.1. Voltammetric Behavior of Soluble SiW_{12}

Most electrochemical studies that have been performed up to now evaluate the voltammetric behavior of HPAs in a strong acidic media of sulfuric or hydrochloric or perchloric acid [11–13, 18]. Under these conditions the cyclic voltammograms of SiW_{12} exhibit five reduction waves in the approximate electron ratios 1 : 1 : 2 : 8 : 12, under specific experimental conditions, namely the concentration of the redox compound (>10^{-3} M) and the anodic value of the applied potential window [19]. However, HPAs in general exhibit a clear electrochemistry at slight acidic to near neutral media as well, and this has been well documented in the case of soluble iron substituted polyoxotungstates by Anson and his co-workers [10]. From the analytical point of view this pH range is of great interest as it is more compatible to the majority of catalytic reactions where HPAs can be involved.

As illustrated in Figure 1, cyclic voltammetry of a 2 mM SiW_{12} solution in 0.25 M phosphate buffer in 0.5 M KCl, pH 6.5 and pH 4.5 produced two well-defined reversible peaks of a diffusional controlled pattern, where the potential peak separation of each couple obeys a one-electron reduction mechanism, in accordance with literature results [19]. In accordance with previous studies [19], for concentrations of SiW_{12} lower than 1 mM, ill-defined

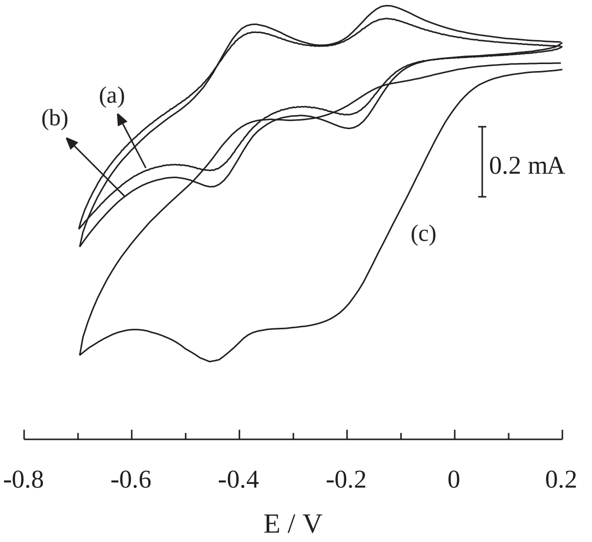


Fig. 1. Cyclic voltammograms of 2 mM silicotungstates in 0.25 M phosphate buffer in 0.5 M KCl, at (scan a) pH 6.5 and (scan b) pH 4.5. Scan c illustrates the catalytic reduction of 4 mM periodate at pH 6.5, injected in the same solution as in scan a. Scan rate: 250 mV s^{-1}.

peaks were recorded. Reduction waves were located at -0.182 and -0.440 V, respectively, and the corresponding potential peak separation was calculated at $\Delta E_{p_1} = 56$ and $\Delta E_{p_2} = 54$ mV, very close to the theoretical value of 60 mV for a one-electron reduction mechanism under diffusional control.

Formal potentials of $E^{o}_{sol,1} = -0.155$ and $E^{o}_{sol,2} = -0.412$ V, respectively, were calculated by taking the mean of the position of the anodic and cathodic peak in each redox couple. The peak potentials were almost unaffected by pH within the studied pH range (see also below the behavior of the immobilized modifier).

The electrocatalysis by the soluble SiW_{12} observed in a phosphate buffer solution, pH 6.5 containing 4 mM periodate is demonstrated in Figure 1 (scans a and c). Addition of periodate to the SiW_{12} solution and subsequent scanning over the same potential range (scan c) resulted in a large increase in current in the cathodic region because the periodate present in the solution oxidized the products produced during the reduction steps. As the oxidized form in each step is regenerated from the reaction of the corresponding reductive forms with periodate there is a significant increase in the cathodic current and a corresponding decrease in the accompanying oxidation in the anodic region. The increase of the catalytic current intensity is directly proportional to the concentration of periodate. To the best of our knowledge, this electrocatalytic reduction of periodate by SiW_{12} has not been previously reported and it could be utilized for the development of amperometric periodate sensors. However, SiW_{12} itself is not a suitable modifier, because of its high solubility, and other forms of it should be used to maintain electrocatalytic action and meet the analytical standards of CMEs.

3.2. Voltammetric Behavior of SiW_{12}Hex-CMEs

As illustrated in Figure 2, a continuous leaking of the modifier (silicotungstic acid) from the surface of the electrode was observed within 20 successive scans, leading to the reduction of the cathodic current up to 90 % of its original value. In order to overcome this problem the water insoluble hexadecylpyridinium sillicotungstate was employed as electrode surface modifier.

As it has been documented in previous studies the morphology of the surface of the graphite electrode is very important for the voltammetric and analytical characteristics of the CMEs [17, 20]. Polishing with emery paper of grit 1200 had been found to be the most appropriate when mediators with a molecular weight of 326 [17] and 856 [21] daltons have been used. In this study, three emery papers of grit 500, 800 and 1200 were tested. Best results, in terms of the intensity of the faradaic currents and the pattern of the reduction waves, were obtained when electrodes were treated with emery paper of grit 800. The high molecular weight of the mediator (4092 daltons) can explain these results. A bulky molecule is better adsorbed into the wide and deep cavities produced when graphite electrodes are polished with an 800 grit emery paper, rather than into the smaller ones produced when finer emery paper was used. For rougher emery papers, immigration phenomena of the mediator inwards to unoccupied (labyrinthic environment) adsorption sites can explain the poor voltammetric behavior of the immobilized mediator. Emery paper of grit 800 was selected for polishing the electrodes in further experiments.

Different concentrations of SiW_{12}Hex in the range of 1×10^{-5}–2×10^{-4} M were tested for the modification of the graphite electrodes. In all cases a 10 μL aliquot of the corresponding solution in acetone was pipetted onto the electrode surface. As in the case of soluble SiW_{12} the concentration of the modifier must exceed a certain value. A minimum concentration of 6×10^{-5} M SiW_{12}Hex ($\Gamma = 0.45$ nmol cm^{-2}) must be applied for obtaining a clear voltammetric pattern. As can be seen in Figure 3A curve b, (3×10^{-5} M SiW_{12}Hex, $\Gamma = 0.27$ nmol cm^{-2}) the first reduction wave is ill-defined and the second one is missing. On the other hand (Figure 3A curve a), well-defined reduction waves were recorded when a 6×10^{-5} M SiW_{12}Hex solution was applied. This behavior is possible due to the short lifetime (unstable chemical nature) of the intermediate product. This hypothesis is further proved by the cyclic voltammograms illustrated in Figure 3B. In such a low concentration of

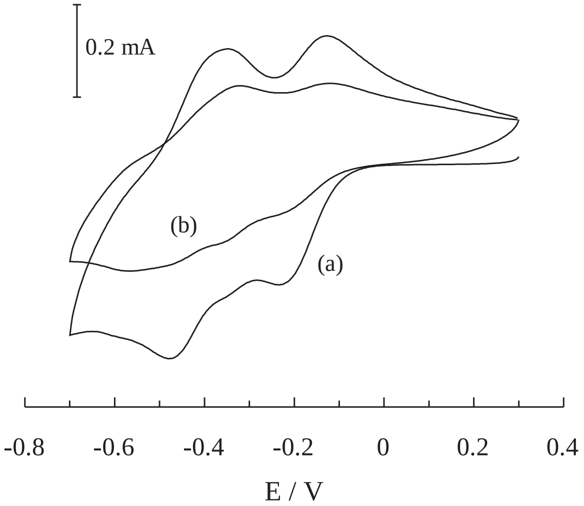


Fig. 2. Successive cyclic voltammograms of a CME prepared by pipeting 10 μL of a silicotungstic acid solution in acetone (153 mg/5 mL). Scan a (fifth scan) and scan b (twenty fifth scan). Buffer: 0.25 M phosphate buffer in 0.5 M KCl, pH 6.5; scan rate: 250 mV s^{-1}.

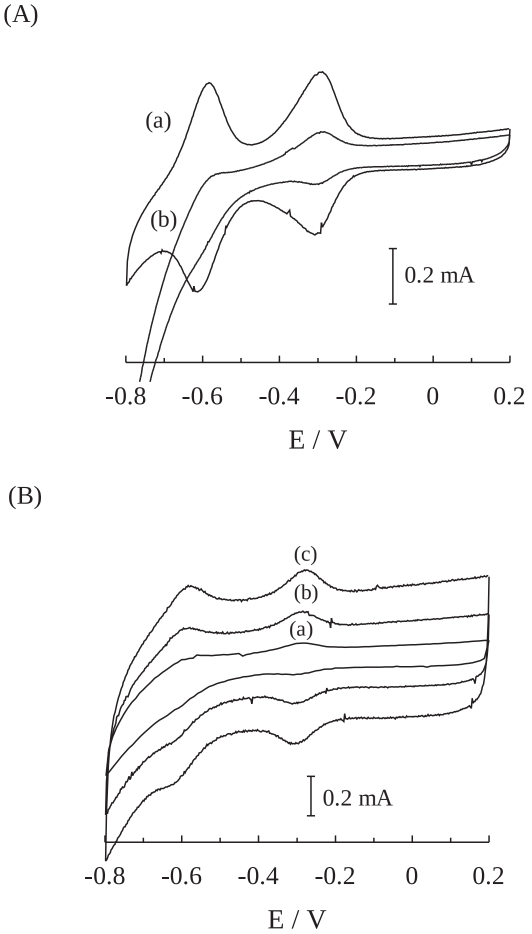


Fig. 3. Cyclic voltammograms of SiW_{12}Hex-CMEs in 0.25 M phosphate buffer in 0.5 M KCl, pH 5.5 at A) various surface coverages: a) 0.45 nmol cm^{-2} and b) 0.27 nmol cm^{-2}; scan rate: 1500 mV s^{-1}, and B) different scan rates: a) 1500 mV s^{-1}, b) 3000 mV s^{-1} and c) 6000 mV s^{-1}; surface coverage: 0.13 nmol cm^{-2}.

1×10^{-5} M SiW_{12}Hex ($\Gamma = 0.13$ nmol cm^{-2}), even the first wave is scarcely visible and cannot be detected at a scan rate of 1500 mV s^{-1} (scan a). Its pattern improves upon the increase of the scan rate to 3000 (scan b) and 6000 mV s^{-1} (scan c). This behavior is indicative of a highly reversible and very fast redox reaction (see below). On the other hand, the second reduction wave is scarcely visible even at high scan rates (3000 and 6000 mV s^{-1}), while at a scan rate of 1500 mV s^{-1} no faradaic current is observed. It should be pointed out that the applied scan rate is relatively high for studying the electrochemical behavior of immobilized mediators, since most of them behave as quasireversible or totally irreversible at scan rates higher than 300–500 mV s^{-1}.

Formal potentials of $E^{o}_{ads,1} = -0.374$ and $E^{o}_{ads,2} = -0.550$ V were calculated for the adsorbed species, at pH 4.5. Comparison of these values with those obtained using soluble redox compound showed, that the conjuction of silicotungstate with hexadecylpyridinium causes an altering in electronic structures of oxidized and reduced forms (electron transfer products) of the mediator. In most cases, the shift of E^{o} can be attributed to interactions between the immobilized chemical and the underlying graphite structure. In this work, the contribution of the adsorption seems to be negligible since no important shift (about 20 mV) of the value of E^{o} was observed when silicotungstates were immobilized onto the graphite electrode (compare scans a in Figures 1 and 2).

Figure 4A illustrates cyclic voltammograms obtained with SiW_{12}Hex-CMEs in a 0.25 M phosphate buffer in 0.5 M KCl, pH 5.5. CMEs were prepared with 8×10^{-5} M solution of SiW_{12}Hex in acetone that corresponds to a surface coverage of 0.74 nmol cm^{-2}. Values of peak potential separation (ΔE_p) range from 18 to 25 mV (mean values for both waves) for scan rates up to 700 mV s^{-1}, while for high scan rates (>4500 mV s^{-1}) values of ΔE_p moderate between 70 and 100 mV.

An additional parameter that verifies the facile charge transfer kinetics of the adsorbed mediator is the extended linearity of the peak height (I_p) with the scan rate v. As illustrated in Figure 4B, the I_p of each wave is proportional to the scan rate up to 4500 mV s^{-1}, typical behavior for a surface-confined molecule. Above 4500 mV s^{-1} the peak height follows a $v^{1/2}$ dependence (data not shown) indicating a mass transport limited within the modifier films.

The (apparent) electrochemical rate constant k^{o} was calculated from Tafel diagrams according to the method described by Laviron [22]. Figure 5 illustrates the procedure used for evaluating these kinetic parameters for the first (Figure 5A) and the second (Figure 5B) wave. Detailed description of the calculations is given in a previous work [23]. Mean values of k^{o} were found 100 ± 20 s^{-1} and 90 ± 18 s^{-1} for the first and the second wave, respectively. These values indicate very fast kinetics for both reductive species and explain the excellent behavior of the mediator at scan rates as high as 10 000 mV s^{-1}. The (apparent) electrochemical rate constants k^{o} of commonly used mediators ranged from 4 to 20 s^{-1} [17 and references cited therein].

The pH dependence on the electrochemical behavior of the adsorbed mediator was studied within the pH range 3 to 7.5 and similar results to those of the soluble mediator were obtained. Formal potentials for both waves were constant within the range 4.5 to 7.5 (Table 1). This behavior is rather indicative of a redox mechanism where no hydrogen ion participates. At pH 3 a third reduction wave appears at -0.792 V and can be attributed to a further reduction of two atoms of tungsten from the oxidation state VI to the oxidation state V. This two-electron reduction wave is in accordance with the literature [19] (see above) and was produced only in acidic media (pH < 4).

3.3. Electrocatalytic Reduction of Periodate

Whereas periodate reduction is totally irreversible at bare graphite electrode, its electrocatalytic reduction mediated by the adsorbed SiW_{12}Hex is quite different (Figure 6A and B). An enhancement of the cathodic peak current for periodate appeared (Table 1 and Figure 6) is indicative of the electrocatalytic action of SiW_{12}Hex. The fact that periodate attenuated the reduction peak of $E^{o}_{ads,1}$ and $E^{o}_{ads,2}$ supports this point. The electrochemical procedures that explain the enhancement of the cathodic current in the presence of periodate have already been developed (see caption of Figure 2). As illustrated in the inset graph of Figure 6B, the catalytic current produced by the mediated reduction of periodate is proportional to the concentration of the latter.

The overall electrocatalytic mechanism may be described by Scheme 1.

Although the catalytic rate is slight higher at pH 3 (Table 1), further experiments were conducted at pH 4.5 in order to avoid complications associated due to protonation of IO_4^-. Furthermore, the selected pH value seems to be more suitable for the

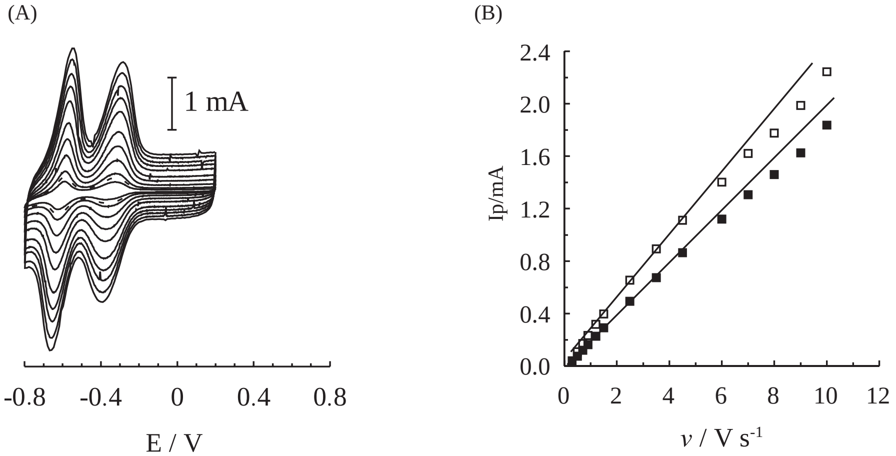


Fig. 4. Cyclic voltammograms of SiW_{12}Hex-CMEs in 0.25 M phosphate buffer in 0.5 M KCl, pH 5.5 at A) different scan rates: scans represent the experimental data for scan rates of 0.7, 0.9, 1.2, 2.5, 3.5, 4.5, 6, 7, 8, 9, and $10\,V\,s^{-1}$ in an order of increasing current; surface coverage: $0.74\,nmol\,cm^{-2}$. B) Variation of I_p with the scan rate; (□) first and (■) second reduction waves.

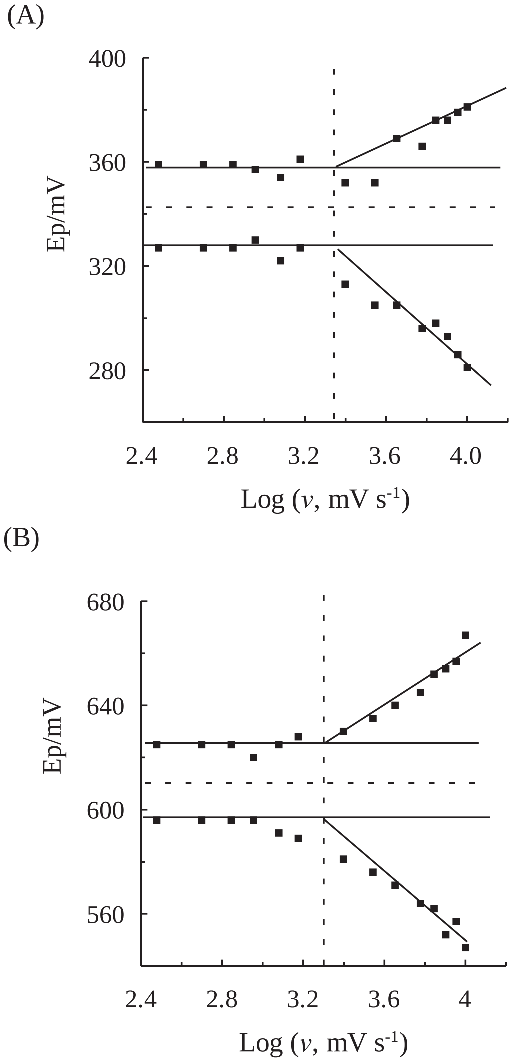
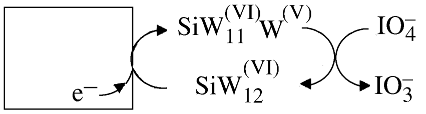


Fig. 5. Dependence of E_p on log(v). Buffer: 0.25 M phosphate buffer in 0.5 M KCl, pH 5.5; surface coverage: $0.74\,nmol\,cm^{-2}$. Graphical determination of the electrochemical rate constants of A) $SiW_{12}^{(VI)} \leftrightarrow SiW_{11}^{(VI)}W^{(V)}$ and B) $SiW_{11}^{(VI)}W^{(V)} \leftrightarrow SiW_{10}^{(VI)}W_2^{(V)}$ redox reaction.

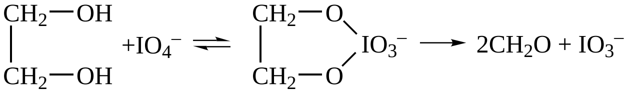


Scheme 1. Schematic representation of the electrocatalytic mechanism for the mediated reduction of periodate taking place during the first redox wave. At the second wave $SiW_{12}^{(VI)}$ and $SiW_{11}^{(VI)}W^{(V)}$ should be replaced by $SiW_{11}^{(VI)}W^{(V)}$ and $SiW_{10}^{(VI)}W_2^{(V)}$, respectively.

analytical applications of periodate sensor since the most analytically useful periodate reactions with organic analytes occur at the pH range 4–6 [24] (see below).

3.4. Application to the Determination of Ethylene Glycol

The determination of ethylene glycol was carried out indirectly as described in Section 2.3. The reaction between periodate and ethylene glycol proceeds through the reversible formation of a shortliving periodate ester [25] and it is described by the following equation:



$$\begin{matrix} CH_2-OH \\ | \\ CH_2-OH \end{matrix} + IO_4^- \rightleftharpoons \begin{matrix} CH_2-O \\ | \\ CH_2-O \end{matrix}\!\!>IO_3^- \longrightarrow 2CH_2O + IO_3^-$$

The consumption of periodate is determined by measuring the excess of the periodate concentration after the oxidation of the organic compounds. Titrimetric methods [25–27] are usually used. Some instrumental methods using spectroscopy [28], ion-selective electrode [24] and chemiluminescence [29] have also been reported.

The spectrophotometric method suffers serious interference from iodate, the absorption from reaction products, and the probability of further oxidation of HCHO and HCOOH in the light beam. The chemiluminescence method showed fairly good agreement with a reference method, however 7 % interference by the products of the reaction was reported.

Parameters such as the concentration of periodate and the working pH were optimized. The different analytical conditions

Table 1. Formal potentials of adsorbed $SiW_{12}Hex$ and catalytic currents of 2.5 mM periodate mediated by adsorbed $SiW_{12}Hex$.

	pH 3	*pH 4.5*	*pH 5.5*	*pH 6.5*	*pH 7.5*
1st wave ($E^{o}_{ads,1}$, mV)	−378	−349	−376	−371	−370
2nd wave ($E^{o}_{ads,2}$, mV)	−614	−595	−613	−611	−619
3rd wave ($E^{o}_{ads,3}$, mV)	−792	–	–	–	–
Catalytic current (mA)	0.714	0.648	0.587	0.476	0.432

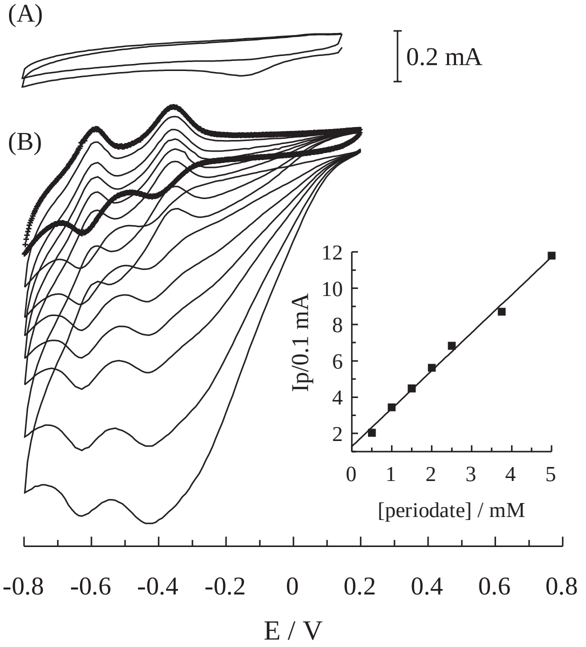


Fig. 6. A) Cyclic voltammograms (first and second scan) of 10 mM periodate on bare graphite electrodes in 0.25 M phosphate buffer in 0.5 M KCl, pH 4.5. B) Cyclic voltammograms illustrating the catalytic reduction of different concentrations of periodate at $SiW_{12}Hex$-CMEs in 0.25 M phosphate buffer in 0.5 M KCl, pH 4.5. Surface coverage: 1.41 nmol cm^{-2}; scan rate 0.7 V s^{-1}; (bold line) in the absence of periodate, (regular lines) in the presence of 0.5, 1.0, 1.5, 2.0, 2.5, 3.75, and 5.0 mM periodate in an order of increasing catalytic current. Embedded graph shows the linear relationship of the pure catalytic current (corrected by the background current) with the concentration of the oxidant.

were implemented with a standard solution of 0.5 mM ethylene glycol. A concentration of 6 mM IO_4^- was selected, as a compromise between a satisfactory reaction rate and an acceptable sensitivity. Higher concentrations of IO_4^- resulted in a less sensitive determination, as the remaining concentration of IO_4^- was the measured species. Lower concentrations of IO_4^- resulted in a more sensitive configuration, however linearity was limited in a shorter concentration range. The pH dependence for the ethylene glycol response was investigated in the range 3–7 (data not shown). Best results in terms of sensitivity were obtained in the range 4–5. A pH value 4.5 was used for further experiments.

Under the optimum conditions a linear calibration plot, $I/A = f$ ([analyte/mM]), was constructed applying the least-squares method. A linear relationship was obtained between the response and the ethylene glycol concentration in the range 0.2–5 mM with a correlation coefficient $r = 0.998$. The detection limit was 20 µM ethylene glycol for a signal-to-noise ratio of 3 ($S/N = 3$).

Table 2. Determination of ethylene glycol in diluted samples of in anti-freeze fluids.

Sample	*Proposed method (mM)*	*Titrimetric method (mM)*	*Relative error (%)*	*Recovery [a] (%)*
Glycoshell	3.01	3.06	1.7	98
Antifreeze coolant	1.47	1.50	2.0	99
Paraflu	2.33	2.38	2.1	101

[a] Addition of 1 mM ethylene glycol standard solution.

The proposed method was applied for the determination of ethylene glycol in commercially available antifreeze fluids. A sample volume of 40–200 µL from a 20-fold diluted commercial product was used. The results in Table 2 show that the amperometric determination of ethylene glycol with the proposed sensor is accurate to < 2.1 % with a relative standard deviation of 1.9 % ($n = 10$, 0.5 mM ethylene glycol). The determination is relatively fast with a throughput of 8–10 samples h^{-1}.

The selectivity of the proposed method is limited by the selectivity of the periodate reaction (Malaprade reaction), i.e., the oxidative cleavage of vicinal glycols. Some of the tested samples may contain diethylene glycol in a percentage lower than 5 %, however, no interference effect was observed since the proposed method is sensitive only to vic-glycols. No problems were caused by the fluorescent dyestuffs, which are present in minute amounts in the commercial anti-freeze fluids. Almost zero deviation was recorded when 2 mM iodate and 2 mM formadehyde were pipetted in the amperometric cell after the addition of 6 mM periodate.

The operational stability of the sensor was verified by performing successive measurements of 0.5 mM ethylene glycol solution and was found to retain almost 90 % of its initial activity after 40 injections.

4. Conclusions

Although periodate anion can hardly be considered as an analyte of interest, periodate monitoring devices are valuable analytical tools because of the interesting periodate chemistry. Periodate reactions with many classes of organic compounds (vicinal glycols, polyhydroxy compounds, α-hydroxy-amino compounds, etc.) are known to proceed smoothly, selectively and stoichiometrically at mild pH and temperature conditions, and at low concentrations. On the other hand, many of periodate reactions are catalyzed by traces of various metals and can be used for the development of very sensitive catalytic analytical schemes. Therefore, a reliable, interference-free periodate sensor can be found as a plethora of analytical applications. Hitherto, direct monitoring of periodate anion could only be achieved potentiometrically by using various periodate ion-selective electrodes and extensive work has been done on this field during the last two decades [30].

The modified $WSi_{12}Hex$ graphite electrode described in this work can also be used as an amperometric sensor for monitoring periodate reactions and it can find similar applications. Its proportional response toward periodate compared to the logarithmic response of periodate ion-selective electrodes can be proved as an advantage, particularly when this sensor is going to be used in flow-injection analytical systems.

5. References

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