CATALYTIC CATHODIC STRIPPING VOLTAMMETRY OF 5-PHENYL-1,3,4-OXADIAZOLE-2-THIOL IN THE PRESENCE OF NICKEL(II) AND COBALT(II) IONS

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Received February 19, 2004
Accepted July 8, 2004

5-Phenyl-1,3,4-oxadiazole-2-thiol (POT) and the systems Ni(II)-POT-acetate buffer, Co(II)-POT-acetate buffer were investigated by differential-pulse cathodic stripping voltammetry (DPCSV). The results of the voltammetric measurements show that POT gives a DPCSV signal at about –0.2 V vs Ag|AgCl. The presence of both POT and nickel(II) ions gives rise to a new peak at about –0.6 V; in the presence of cobalt(II) ions a new peak appears at –1.1 V. Based on published results obtained for other sulfur compounds in the presence of Ni(II) or Co(II) ions, the peak at –0.6 V is ascribed to catalytic reduction of Ni(II), and the peak at –1.1 V to hydrogen catalytic discharge. Optimum conditions have been found for the determination of POT by DPCSV. A linear dependence has been found only for the catalytic Ni(II) peak in the region 10^{-8}–10^{-7} M POT. The calculated limit of detection and limit of quantification are 3.4×10^{-9} and 1.1×10^{-8} mol l^{-1}, respectively.

Keywords: Cathodic stripping voltammetry; 5-Phenyl-1,3,4-oxadiazole-2-thiol; Nickel(II); Cobalt(II); Electrocatalysis; Electrochemistry; Thiols.

Thiols are of great interest in the field of biochemistry, pharmacology, and for chemical industry. The interest in electrocatalysts such as phthalocyanine derivatives, organic mediators, enzymes, or in the utilization of pyrocatechol as an electrochemical indicator of the presence of thiols, has stimulated investigations in this important area[1,2]. The well-known cathodic stripping voltammetry techniques based on the accumulation and reduction of mercury–thiol complexes have been extensively applied for this purpose. In addition, some thiols may catalyse reduction of metal ions such as nickel(II) or cobalt(II), giving rise to the so-called catalytic pre-wave (pre-peak). This results in a high sensitivity, allowing the detection of the catalyst at very low concentrations, as was demonstrated for cysteine and

doi:10.1135/cccc20041600

cystine[3], benzothiazole-2-thiol[4,5], D-penicillamine[6], glutathione[7], oxidized glutathione[8], thiocytosine[9], and mercaptopurine riboside[10].

5-Phenyl-1,3,4-oxadiazole-2-thiol (POT), like other important oxadiazoles, is known as a common condensation reagent[11]. Derivatives of POT are used as components of many drugs[12], insecticides[13] and fungicides[14], as well as ingredients of photographic emulsions[15]. To our knowledge, no reports have been published so far on the analytical use of voltammetric methods for the determination of POT. It is known from the literature that 2-phenyl-1,3,4-oxadiazole-5-thiol is electrochemically active in the pH range 4–6 [16]. In a water–alcohol solution, in an acidic buffer, its DC wave was recorded at –1.15 V. In the presence of cobalt(II), a new wave appeared. The signal corresponds to catalytic reduction of protons originating from the cobalt(II)–2-phenyl-1,3,4-oxadiazole-5-thiol complex adsorbed on the cathode.

The aim of this work was a voltammetric (DPCSV) study of 5-phenyl-1,3,4-oxadiazole-2-thiol and its cobalt(II) and nickel(II) complexes in aqueous solution.

EXPERIMENTAL

Reagents and Solutions

A fresh stock solution of 10^{-3} M POT (98%, Acros Organics) was prepared by dissolving a known amount of the compound in 0.1 M NaOH (3 ml) in a 50-ml volumetric flask and filling it up to the mark with water. This stock solution was then diluted as required. Solutions of Ni(II) and Co(II) nitrates were prepared by diluting standard solutions. 2×10^{-1} M acetate buffers were prepared by addition of sodium acetate to acetic acid. 2×10^{-1} M ammonium buffers were prepared by addition of HNO_3 (65%, Merck) to aqueous ammonia. 2×10^{-1} M MOPS buffers were prepared by addition of sodium hydroxide to 3-morpholinopropane-1-sulfonic acid (99.5%, Sigma). All chemicals were of analytical grade (POCh SA Gliwice, Poland, if not stated otherwise). The solutions were prepared with triply distilled water.

Instrumentation

A controlled-growth mercury drop electrode, CGMDE (Entech, Cracow, Poland) was used. All electrode potentials were referred to the Ag|AgCl (3 M KCl) reference electrode with a KNO_3 bridge. The counter electrode was a platinum wire.

The voltammetric experiments were performed with a microAutolab/GPES (general-purpose electrochemical system, version 4.7, Eco-Chemie) computer-controlled potentiostat. Differential-pulse cathodic stripping voltammetry (DPCSV) was carried out with a pulse amplitude of 20 mV.

Working Procedure

The general procedure used to record cathodic stripping voltammograms was as follows: 10 ml of the suporting electrolyte (a proper amount of buffer mixed with water) was placed in the voltammetric cell and the solution was purged with argon for 10 min, with the stirrer on. When an initial blank was recorded, the required volume of POT or metal ions was added with a micropipette. After a new mercury drop formed, accumulation was effected for the required time at the predetermined accumulation potential on stirring. At the end of the accumulation period, the stirrer was switched off and after 10 s a negative-going potential scan was started. When further amounts of POT or metal ions were added, the solution was deoxygenated for another 20 s before the voltammetric scans.

RESULTS AND DISCUSSION

DPCSV Studies of 5-Phenyl-1,3,4-oxadiazole-2-thiol

Effect of Deposition Parameters

The dependence of the POT peak current ($c = 5 \times 10^{-7}$ mol l^{-1}, $c_{\text{buf}} = 6 \times 10^{-2}$ mol l^{-1}, $t_{\text{d}} = 180$ s) on the deposition potential in acetate (pH 3.7, 3.9, 4.2), ammonium (pH 8.8) and MOPS (pH 6.6, 7.0, 7.5) buffers was studied over the range 0.3 to –0.3 V. New, well-shaped peak was recorded only in the acetate buffers. The highest peak was found at pH 3.9 and deposition potential between 0.15 and 0.05 V. The potential 0.075 V was chosen for the POT deposition.

Variation of the deposition time for a 5×10^{-7} M POT showed that the peak current increased linearly with the accumulation time and reached a plateau after a time period longer than 180 s. The deposition time 180 s was chosen for subsequent experiments, as it combines good sensitivity and a relatively short analysis time.

Effect of Buffer Concentration

An influence of acetate buffer concentration on POT (5×10^{-7} and 5×10^{-6} mol l^{-1}) at pH 3.9 was found (Fig. 1). Analogous measurements for 5×10^{-7} M POT were carried out in acetate buffers at pH 3.7 and 4.2. In each case, the peak height varied according to the buffer concentration. The influence of buffer concentration was also observed when 2×10^{-4} M EDTA was present in the sample. To preclude a probable influence of the capacity current, different waiting times (10 and 40 ms) were applied before pulse. In each case, the $I = f(c_{\text{buf}})$ dependence was parabolic. This dependence could be explained by an additional electrode reaction taking place during the deposition. The polarographic behaviour of thiols is generally believed to be due to the oxidation of mercury in their presence. The chemical reaction between the oxidized mercury and the thiol results in the formation of a mercury salt that is adsorbed on the surface of the electrode (reactions (*1*) and (*2*)).

$$Hg^+ + HSR \rightarrow HgSR + H^+ \quad (1)$$

$$2\ HgSR \rightarrow Hg + Hg(SR)_2 \quad (2)$$

During the negative scan, the reduction of the mercury(I) or mercury(II) takes place[17]. The fact that, for a given buffer concentration, the cathodic peak of thiol reaches its maximum, could suggest the production of species at the electrode according to the reaction (*3*).

$$Hg^+ + HSR \rightarrow HgSRH^+ \quad (3)$$

The possibility of formation of positively charged species such as Hg_2S^{2+} or $Hg_2S_2H^+$ at a positive deposition potential has been considered elsewhere[18].

Electrochemical properties of the adduct $HgSRH^+$ are probably different from those of HgSR. Recording the DPCS voltammograms of 5×10^{-7} and 5×10^{-6} M POT at different buffer concentrations and constant pH (Fig. 2), a cathodic peak with a subtle shoulder at a lower potential is observed for the

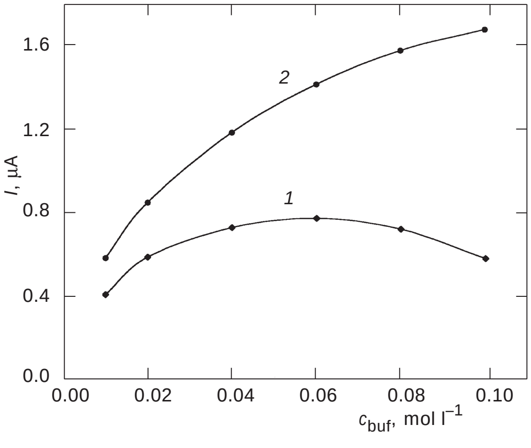

FIG. 1

Hg-POT peak current dependence on acetate buffer concentration: pH 3.9, E_d = 0.075 V, t_d = 180 s; 5×10^{-7} (*1*), 5×10^{-6} (*2*) M POT higher POT concentration (Fig. 2b), attributed to reduction of HgSR and $HgSRH^+$. Buffer is the proton donor and for each thiol, a range exists of the buffer concentration where the possibility of the adduct production is the highest. The experimental data suggest that the HgSR and $HgSRH^+$ are independently adsorbed at specific sites. The peak current is proportional to the surface concentration of the accumulated species. Unfortunately, the cathodic potential of the species is not constant but changes a little with varying POT concentration.

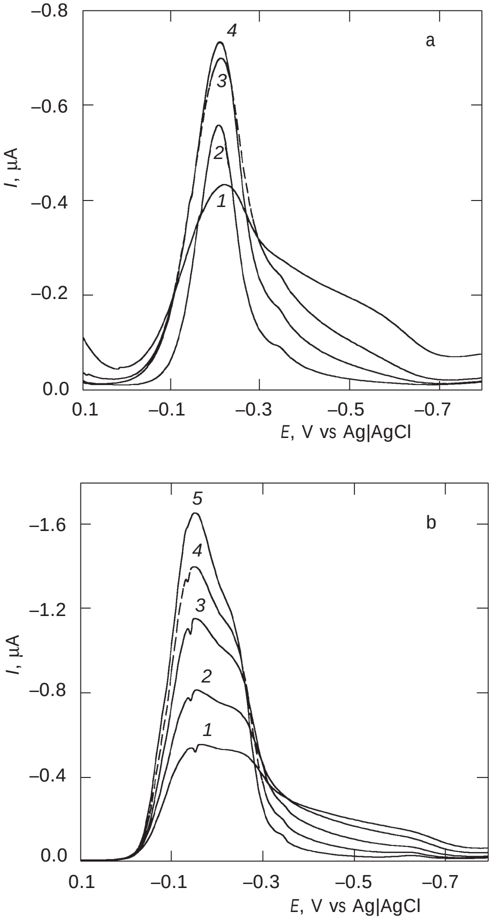

FIG. 2
DPCS voltammograms obtained for: a 5×10^{-7} M POT in 0.01 (*1*), 0.10 (*2*), 0.04 (*3*), 0.06 (*4*) M acetate buffer and b 5×10^{-6} M POT in 0.01 (*1*), 0.02 (*2*), 0.04 (*3*), 0.06 (*4*), 0.10 (*5*) M acetate buffer; pH 3.9, E_d = 0.075 V, t_d = 180 s

Effect of POT Concentration

The effect of POT concentration varying in the range 10^{-7}–10^{-6} mol l^{-1} on the Hg-POT peak current was studied for different deposition times. It was found that the height of these peaks increases non-linearly with the POT concentration. The reduction of mercury thiolate (Hg-POT) gives different peak shapes depending on the concentration of POT and the deposition time (t_d). When the time is short (45 or 60 s), only one cathodic peak is recorded and the peak potential shifts to positive values as the POT concentration increases. For deposition times longer than 60 s, the peak splits at a certain concentration and the second peak is recorded. A similar behaviour of glutathione was explained by some characteristics of the accumulation process in the MOPS buffer[5]. On the other hand, the kinetics of the disproportionation (Eq. (*2*)) appears to be the cause of the displacement of the peak potential with increasing t_d. At the same time, the kinetics depends on the molecular structure of the compound[17]. The obtained calibration graph precludes the possibility of POT determination by this method in a wide range of concentrations. The signal is directly proportional to the POT concentration only for short deposition times (45 or 60 s), but the sensitivity of the measurements is rather poor. When the deposition on the electrode surface takes longer than 60 s, the response to POT results in a calibration graph with a sigmoidal component.

DPCSV Studies of Ni(II)-5-phenyl-1,3,4-oxadiazole-2-thiol Complex

It is well known that some thiols catalyse reduction of Ni(II), producing a peak located at –0.6 V vs Ag|AgCl (3 M KCl)[9,19]. In this context, the effect of Ni(II) concentration on the Hg-POT peak was also investigated. The experiments were carried out in 0.06 M acetate (pH 3.9–5.5), ammonium (pH 7.8, 9.0), and MOPS (pH 6.6–7.4) buffers; the Ni(II) concentration varied from 5×10^{-6} to 1×10^{-4} mol l^{-1}. The deposition potential varied from 0.3 to –0.5 V. Figure 3 presents DPCS voltammograms for different concentrations of POT in the Ni(II) medium. The voltammograms indicate two main stripping peaks over the potential range from 0 to –1.5 V. Peak A is assigned as the catalytic Ni(II) pre-peak[20,21], peak B is the reduction peak of uncomplexed Ni(II). In Fig. 4 (curve 2), the additional peak C is recognized as a catalytic hydrogen discharge peak, which characterises Ni(II) complexes of sulfur-containing compounds[20]. Examination of the applicability of the DPCSV analysis of POT in the presence of Ni(II) indicated that peak A in Fig. 3 is well defined and sensitive for the determination of POT. The blank signal at pH 5.0 (acetate buffer) was the lowest, which was the decisive factor for choosing this buffer as the best. The deposition potential E_d = 0 V was used in further experiments. As expected, the catalytic Ni(II) pre-peak increased with the nickel concentration; the concentration 6 × 10^{-4} mol l^{-1} was used through this work. It combined good sensitivity and separation

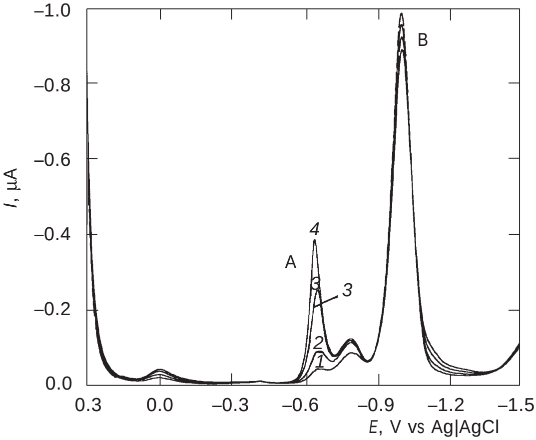

FIG. 3

DPCS voltammograms of blank (*1*), 2 × 10^{-8} (*2*), 6 × 10^{-8} (*3*), 1 × 10^{-7} (*4*) M POT in 6 × 10^{-4} M Ni(II) medium: 0.03 M acetate buffer; pH 5.2, E_d = 0 V, t_d = 90 s

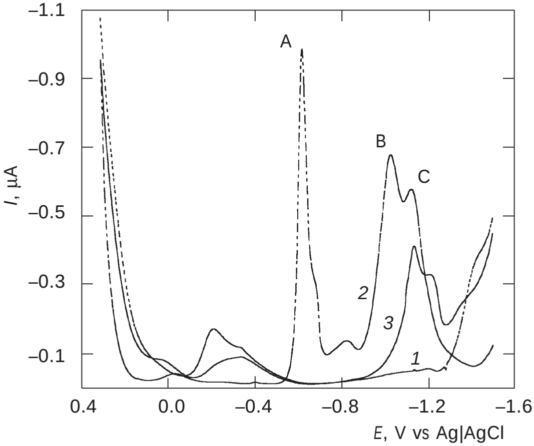

FIG. 4

DPCS voltammograms of 5 × 10^{-7} M POT (*1*) in 6 × 10^{-4} M Ni(II) (*2*) and 5 × 10^{-5} M Co(II) (*3*) containing media under optimum conditions at t_d = 90 s. For *1*: 0.08 M acetate buffer; pH 3.9, E_d = 0.075 V. For *2*: 0.03 M acetate buffer; pH 5.0, E_d = 0 V. For *3*: 0.08 M acetate buffer; pH 3.9, E_d = 0.3 V from the neighbouring reduction peak of Ni(II). The buffer concentration has also an influence on the sensitivity of the catalytic Ni(II) peak, and the optimum 0.03 M concentration was chosen. The deposition time was examined from 30 to 300 s and the plateau was recorded after 90 s. Therefore, t_d = 90 s was chosen for subsequent experiments.

Dependence of Catalytic Ni(II) Pre-peak on 5-Phenyl-1,3,4-oxadiazole-2-thiol Concentration

The possibility of the DPCSV determination of POT was tested in the concentration range 10^{-8}–10^{-6} mol l^{-1}. A linear dependence of catalytic Ni(II) pre-peak on the thiol concentration in the range 10^{-8}–10^{-7} mol l^{-1} was found (correlation coefficient 0.9997), the equation of the straight line being I [nA] = 3.54 × c [10^{-9} mol l^{-1}] – 28. The reproducibility of the procedure was assessed by six measurements of samples at the same concentration of POT. Reproducibility of the catalytic peak current at various POT concentrations is shown in Table I.

Precision and accuracy of the method were investigated by the determination of POT at three different concentrations in the linearity range. The results are presented in Table II.

The limit of detection (LOD) = 3.4×10^{-9} mol l^{-1} and limit of quantification (LOQ) = 1.1×10^{-8} mol l^{-1} of the procedures were calculated from the peak current, using the equations LOD = $3s\,m^{-1}$ and LOQ = $10s\,m^{-1}$, where s, the noise estimate, is the standard deviation of the peak current (five runs) of the sample and m is the slope of the calibration curve.

TABLE I
Reproducibility of the catalytic 6×10^{-4} M Ni(II) peak current (I) at various POT concentrations (c(POT)): 0.03 M acetate buffer; pH 5.02, E_d = 0 V, t_d = 90 s

c(POT), 10^{-9} mol l^{-1}	I, nA[a]	r.s.d., %[b]
20	42.4	4.9
60	182	5.3
100	327	1.2

[a] Average of six runs. [b] Relative standard deviation of the peak current.

TABLE II
Precision (r.s.d.) and accuracy obtained by DPCS voltammetry (5 runs)

c(POT), 10^{-9} mol l^{-1}	c(POT) found, 10^{-9} mol l^{-1}	r.s.d., %[a]	Accuracy, %[b]
20	19.92 ± 0.72[c]	2.93	–0.40
60	59.44 ± 3.38[c]	4.57	–0.93
100	100.39 ± 1.42[c]	1.14	0.39

[a] Relative standard deviation. [b] Accuracy = [(found – added)/added] × 100. [c] $t(S/n^{1/2})$, $p = 0.95$.

DPCSV Studies of Co(II)-5-phenyl-1,3,4-oxadiazole-2-thiol Complex

Taking into account the results of the DC polarography of 2-phenyl-1,3,4-oxadiazole-5-thiol in acid, the Co(II) containing medium[16], the influence of Co(II) on POT was examined by DPCSV (pH 3.9). New peaks were observed at –1.1 and –1.2 V (Fig. 4, curve *3*). The peak at –1.1 V lies in the potential range characteristic of the hydrogen catalytic discharge produced by a series of compounds in the presence of Co(II) and Ni(II)[9,21]; the peak at –1.2 V represents the diffusion-controlled Co(II) reduction. The optimum conditions for applicability of the catalytic hydrogen peak for determination of POT in the Co(II) medium have been found: subsequent experiments were performed in 0.08 M acetate buffer at pH 3.9, at deposition potential E_d varying from 0.3 to 0 V, and with 5×10^{-5} M Co(II). The possibility of thiol determination in the POT concentration range 10^{-7}–10^{-6} mol l^{-1}, using the catalytic hydrogen peak, was investigated at various deposition times (45–300 s). Unfortunately, when the deposition time was longer than 90 s, the sigmoidal component of the calibration graph was also included. Only for short deposition times, 45 and 60 s, the calibration plot was linear.

Comparing the catalytic hydrogen peak current, catalytic Ni(II) peak current and Hg-POT peak current recorded under optimized conditions and at the same deposition time (45 s or 60 s), the sensitivity of the catalytic Ni(II) peak is the highest. Only this peak allows to determine POT in the range 10^{-8}–10^{-7} mol l^{-1}.

CONCLUSION

It is possible to determine POT by DPCSV only in the presence of Ni(II). The optimum conditions for recording the best analytical signals have been found. Statistical validation has revealed that the method is free of significant systematic errors. In the case of the DPCSV response for the Hg-POT and catalytic hydrogen peaks, the obtained calibration graphs with sigmoidal components preclude using these signals for the determination of POT by the method. It has also been found that the concentration of the buffer affects the height of the DPCSV peaks of POT. The formation of positively charged species such as Hg-POT$^+$ (HgSRH$^+$) is the most likely explanation of this behaviour.

The authors thank Prof. C. Kinart for scientific discussions.

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