

Electrochemical Processes of Cadmium, Copper, Lead, and Zinc in the Presence of *N*-(2-Hydroxyethyl)piperazine-*N'*-3-Propanesulfonic Acid (HEPPS): Possible Implications in Speciation Studies

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Abstract

The influence of *N*-(2-hydroxyethyl)piperazine-*N'*-3-propanesulfonic acid (HEPPS) on the redox processes of cadmium, copper, lead and zinc was investigated by differential pulse anodic stripping voltammetry (DPASV), differential pulse polarography (DPP) and cyclic voltammetry (only for copper, lead and zinc). Depression of the metals peak current recorded by DPASV, DPP, and CV (only for copper and lead) were observed. HEPPS did neither complex cadmium or zinc nor modified the reversibility of the metals electrochemical DPASV and DPP (only for zinc) responses, but complexed copper and lead and modified the reversibility of the copper electrochemical DPASV and DPP responses, under the experimental conditions used. Stability constants for copper-HEPPS and lead-HEPPS systems were calculated by potentiometric titrations (pH measurements) using the SUPERQUAD computational program.

Keywords: *N*-(2-Hydroxyethyl)piperazine-*N'*-3-propanesulfonic acid, Heavy metals, Differential pulse anodic stripping voltammetry, Differential pulse polarography, Cyclic voltammetry, Potentiometry, Stability constants

1. Introduction

Heavy metals speciation studies are usually carried out at a constant pH. Many classical compounds used to buffer solutions near neutrality have important chemical and/or biological limitations [1]. *N*-Substituted aminosulfonic acids were introduced and studied by Good and collaborators since 1966 [1–3]. These authors performed the synthesis of those compounds and determined their second acid dissociation and some metal (magnesium, calcium, manganese, and cupric) ions-buffer complexation constants. More recently, Roy et al. [4] calculated the thermodynamic constants of some substituted aminopropanesulfonic acids from 5 to 55 °C and Azab et al. [5] studied the medium effect on the apparent second stage dissociation constants of some zwitterionic buffers.

These compounds have been widely used for various purposes including for heavy metal speciation studies [6–11].

Recent electrochemical studies performed with several Good's pH buffers showed that, under the experimental conditions used, 3-(*N*-morpholino)-2-hydroxypropanesulfonic acid (MOPSO), and 3-(*N*-morpholino)propanesulfonic acid (MOPS) modify the reversibility of copper electrochemical DPASV response [12], due to surface coverage of the electrode by those compounds, and piperazine-*N,N'*-bis(2-ethanesulfonic acid) (PIPES), *N*-(2-hydroxyethyl)piperazine-*N'*-2-ethanesulfonic acid (HEPES) and *N*-(2-hydroxyethyl)piperazine-*N'*-2-hydroxypropanesulfonic acid (HEPPSO) complex lead [13], suggesting that these pH buffers seems not suitable for speciation studies of those metal ions.

The pH buffer under study in this work, *N*-(2-hydroxyethyl)piperazine-*N'*-3-propanesulfonic acid (HEPPS) is also a Good's pH buffer, with a $pK_a(2) = 8.0$ and a useful pH range between 7.3 and 8.7 [14]. Information about the influence of HEPPS on the voltammetric responses of cadmium(II), copper(II), lead(II) and zinc(II) was not found in the literature.

Therefore, a systematic study of the suitability of HEPPS for these heavy metal speciation studies (determination of the different chemical forms of an element), by voltammetric techniques, deserve analytical and environmental interest. The strategy used in this article was, at first, to study the voltammetric behavior of these heavy metals in the presence of HEPPS by differential pulse anodic stripping voltammetry (DPASV). This technique was selected because it is one of the most widely and powerful direct analytical method of speciation used owing to its high detection power and the wide information that can be obtained from the experimental results [15]. In addition, differential pulse polarography (DPP) and cyclic voltammetry (CV) experiments were carried out for better understanding of how HEPPS affects the charge transfer processes of copper, lead and zinc at the electrode/electrolyte interface. Stability constants of copper-HEPPS and lead-HEPPS complexes were determined by potentiometric titrations (POT) (pH measurements) using the SUPERQUAD computational program. Alternating current voltammetry (ACV) was also performed to verify if HEPPS adsorbs at the working electrode under the experimental conditions used.

2. Experimental

2.1. Apparatus

Voltammetric and polarographic measurements were performed using a microAutolab voltammeter (Eco Chemie) connected to a Metrohm 663 VA stand equipped with a multimode electrode as a working electrode, employed as HMDE in DPASV and CV experiments and as DME in DPP. A Ag/AgCl(s), 3 M KCl electrode, as reference electrode, and a glassy carbon electrode, as a counter electrode, were used. The system was controlled by a personal computer.

Potentiometric titrations (pH measurements) were conducted with a PC-controlled system assembled with a Crison MicroPH 2002 pH meter, a Crison MicroBU 2030 micro burette, a Philips GAH 110 glass electrode and a Orion 90-02-00 (double junction) reference electrode with the outer chamber filled with KNO_3 0.1 M.

2.2. Reagents and Material

To avoid metal contamination, all glass and plastic material was cleaned by soaking in 20% HNO_3 for at least 24 hours and then rinsing several times with water.

All solutions were prepared with distilled and deionized water with a resistivity $>14 \text{ M}\Omega \text{ cm}$.

Cadmium, copper, lead and zinc stock standard solutions of, respectively, 8.90×10^{-3} , 1.57×10^{-3} , 4.83×10^{-3} and $1.53 \times 10^{-3} \text{ M}$, for voltammetric experiments, were supplied from Merck (references 19777.0500, 1.9786.0500, 19776.0500, 1.19806.0500, respectively). Intermediate solutions (cadmium: $8.90 \times 10^{-5} \text{ M}$; copper: $1.57 \times 10^{-5} \text{ M}$; lead: $4.83 \times 10^{-5} \text{ M}$ and zinc: $1.53 \times 10^{-5} \text{ M}$) were prepared weekly by dilution of stock standard solutions in high purity water.

Nitric acid, copper, and lead stock solutions of 2.802×10^{-2} , 4.98×10^{-2} and $4.83 \times 10^{-2} \text{ M}$, respectively, for potentiometric titrations were prepared and standardized as described elsewhere [13]. A nitric acid solution diluted tenfold from the stock standard solution was used as titrant for potentiometric titrations.

HEPPS was obtained from Sigma (reference E-9502). Stock solutions (1 M) were prepared by dissolving the buffer in high purity water and adjusting the pH with a sodium hydroxide solution.

Other chemicals were of analytical reagent grade.

2.3. Procedure

All measurements were carried out on 20 mL of the working solution, at room temperature (ca. 20°C) and 25°C for voltammetric and potentiometric experiments, respectively, in background solutions 0.1 M potassium nitrate (KNO_3), unless ACV experiments which were performed in 0.5 M KNO_3 .

For voltammetric determinations, the dissolved oxygen was previously removed from the solution by bubbling oxygen-free

nitrogen through the cell for 10 minutes. For potentiometric titrations, all solutions were magnetically stirred and a stream of oxygen-free nitrogen was bubbled into the cell during all the time of the experiment.

DPASV, DPP, and CV experiments were performed for solutions with a fixed metal ion concentration and variable HEPPS concentrations at pH 7.5. DPP and CV determinations were only carried out for copper, lead and zinc; for further details of the procedures and conditions adopted see Table 1. Metal adsorption onto cell materials becomes a dramatic problem in trace analysis when working at high pH is required [16, 17]. Computer simulated metal species (free and hydroxo complexes) diagram constructed by imposing a regularly variation of pH between 4.0 and 9.0, at a fixed metal ion concentration, $7.0 \times 10^{-7} \text{ M}$, showed that the formation of hydroxo complexes was relevant for pH values higher than 6.0, for copper and lead, 7.0, for zinc and 8.0 for cadmium. Therefore, in DPASV experiments the first aliquot of buffer was only added when constant current was obtained with the metal solution to certify that the current reduction was not due to metal losses owing to adsorption on the cell walls [16, 17].

For ACV, the frequency and amplitude of the sinusoidal signal imposed were, respectively, 75 Hz and 10 mV; the current (I_{ac}) was measured at a phase angle of 90° . The plots of capacitive current versus potential were recorded for HEPPS concentrations between 2.0×10^{-3} and 0.07 M. The total potential range scanned in an experiment was from 0 to -1.3 V .

All voltammetric experiments were repeated at least two times.

Potentiometric measurements for determination of copper-HEPPS and lead-HEPPS stability constants were carried out with $6.53 \times 10^{-3} \text{ M}$ HEPPS and $5.00 \times 10^{-3} \text{ M}$ metal (prepared by appropriate direct dilution of the standard metal solution) in 0.1 M KNO_3 , using nitric acid as titrant. The experiments were done for pH values lower than 7.0, to avoid precipitation of metal hydroxide. Due to the lower buffer capacity of the solution, the addition of metal lowered the pH to 5.869 (copper) or 5.728 (lead) (first point of data acquisition). The pH of the independent titrations varied between the previous values and 5.593 and 5.404 for copper and lead, respectively. The glass electrode was calibrated in terms of $-\log [\text{H}^+]$ using two buffer solutions with pHs 6.784 and 3.883, with the ionic strength adjusted to 0.1 M [18]; therefore the pH meter read $[\text{H}^+]$ and not a_{H^+} . The potential was recorded when $\Delta E \leq 0.1 \text{ mV/min}$.

Table 1. Experimental conditions used for DPASV, DPP and CV determinations. Metal ions concentrations of 2×10^{-5} and $1 \times 10^{-4} \text{ M}$ were used for DPP and CV experiments, respectively. HEPPS concentrations between 4×10^{-3} and $8 \times 10^{-2} \text{ M}$ were used for both techniques. For DPASV, a deposition time of 150 s (120 s with stirring and 30 s of equilibrium) was used for all metal ions. For DPP, a drop time of 1 s and a final potential of -1.2 V were used. Pulse duration of 60 ms, pulse height of 50 mV and a scan rate of 5 mV/s were used in both techniques. For CV, a scan rate of 20 mV/s was used.

Technique	Metal			
	Cd	Cu	Pb	Zn
<i>DPASV</i>				
Metal concentration (M)	3.6×10^{-7}	3.2×10^{-6}	1.9×10^{-7}	6.1×10^{-7}
HEPPS concentration range (M)	$4 \times 10^{-4} - 8 \times 10^{-2}$	$1 \times 10^{-3} - 8 \times 10^{-2}$	$4 \times 10^{-4} - 8 \times 10^{-2}$	$4 \times 10^{-4} - 8 \times 10^{-2}$
Initial and deposition potential (V)	-0.90	-0.40	-0.70	-1.2
<i>DPP</i>				
Initial potential (V)	-	0.3	-0.2	-0.7
<i>CV</i>				
Initial and final potential (V)	-	0.3	0	-0.7
Switching potential (V)	-	-0.3	-0.6	-1.3

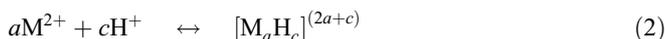
2.4. Calculations

For determination of stability constants of copper-HEPPS and lead-HEPPS systems, potentiometric data (pH measurements) were treated by the SUPERQUAD program; this program calculates the formation constants by minimization of an error-square sum based on measured electrode potentials. More details about the whole numerical approach involving the use of the SUPERQUAD are described elsewhere [19].

The presence of three component equilibrium of the general form was assumed:



together with the following two component equilibria:



where M an HL represents the metal (copper or lead) and the acid form of HEPPS, respectively; c represents the number of protons, if positive, or hydroxides, if negative. Second acid dissociation constant of HEPPS [14] and copper or lead hydrolytic species [20] compiled from the literature were introduced as fixed parameters for the computational fitting of the equilibrium described by (Equation 1) (Table 2). The best fit, i.e., the system with the smallest deviation, σ , was assumed to be correct.

3. Results and Discussion

Independent DPASV titrations of each metal ion with HEPPS were done with [buffer]/[heavy metal] molar concentration ratios between 1.1×10^3 and 2.2×10^5 , for cadmium, 312 and 2.5×10^4 , for copper, 2.1×10^3 and 4.2×10^5 , for lead, and 656 and 1.3×10^5 , for zinc. Peak current (I_p), peak potential (E_p) and peak width at half height ($w_{1/2}$) for each metal and HEPPS were recorded.

For cadmium and zinc, the values of E_p and $w_{1/2}$ were constant with increasing HEPPS concentration and similar to those

obtained in the absence of the pH buffer (data not shown), suggesting that HEPPS does neither complex these metal ions ($\Delta E_p = 0$ for all the HEPPS concentration range tested; $\Delta E_p = E_{p0} - E_p$, where E_p and E_{p0} represent the peak potential recorded in the presence and in the absence of the pH buffer, respectively) [15, 21, 22] nor affect the reversibility of the metals oxidation reaction (inhibition of metal oxidation tends to broaden the peak and lower I_p [23]), under the experimental conditions tested. Additionally, a decrease of peak current was observed with both metals for HEPPS concentrations higher than 0.01 M (Figure 1) (reduction $\leq 12\%$, for cadmium, and $\leq 30\%$, for zinc) probably due to its adsorption at the mercury working electrode (for more details see below).

On the other hand, DPAS voltammetric behavior of copper and lead were significantly different from those described above for cadmium and zinc. From Figure 1, it can be seen that for HEPPS concentrations higher than ca. $4 \times 10^{-3} M$ more marked decrease of peak current (peak reduction of ca. 70%, for copper, and ca. 85%, for lead, for 0.08 M HEPPS) were observed for both metals ions. These peak current reductions were accompanied with a cathodic shift in peak potential (see a typical example for copper in Figure 2) due to complexation of those metal ions by HEPPS (for lead, data not shown). Lead and copper complexation was also verified with HEPPSO, PIPES and HEPES [13, 24, 25]. For both metal ions, $w_{1/2}$ values increased for HEPPS concentrations ≥ 0.02 and 0.04 M for lead and copper (Fig. 3), respectively, showing that this pH buffer increased the irreversibility of those metal ions oxidation at the mercury electrode, under the experimental conditions tested. This effect was not verified with the other metal ions tested (cadmium and zinc in this work) and with lead and similar pH buffers (PIPES, HEPES and HEPPSO) [13]. However, MOPSO and MOPS also modified the reversibility of copper electrochemical DPASV and DPP (only MOPSO) responses [12].

Recently, surface active behavior of other similar zwitterionic Good's pH buffers (piperazine- N,N' -bis[2-hydroxypropanesulfonic acid], POPSO, [25], PIPES, HEPPSO, and HEPES, [26]), was described. It was anticipated that the reduction of peak height recorded by DPASV with all metals and HEPPS was

Table 2. Stability constants of copper-HEPPS and lead-HEPPS and statistic parameters of the adjustment obtained by SUPERQUAD program. For the meaning of β_{abc} see Section 2.4.; figures in parentheses are the computed standard deviation and refer to the last digit of the value; statistical parameters: χ^2 and σ statistic should be lower than 12.6 and 5, respectively [19]; n : number of experimental points used in the adjustment of the stability constants values.

System	a	b	c	$\log \beta_{abc}$	σ	χ^2	n
<i>Constants used as known parameters [14,20]</i>							
Hydrogen-ion hydroxide	0	0	-1	-13.854			
Copper-hydroxides	1	0	-1	-7.80			
	1	0	-2	-13.68			
Lead-hydroxides	1	0	-1	-7.80			
	1	0	-2	-17.2			
Proton-HEPPS	0	1	1	7.5			
<i>Adjusted constants</i>							
<i>Copper-HEPPS</i>							
I	1	1	0	2.47(7)	16.52	8.0	26
	1	2	0	6.22(7)			
I	1	1	0	2.88(3)	4.97	8.55	22
II	1	1	0	2.88(2)	4.95	7.78	18
III	1			2.94(3)	1.93	3.09	23
<i>Lead-HEPPS</i>							
I	1	1	0	3.049(3)	2.07	5.11	18
II	1	1	0	3.299(3)	2.46	6.00	16
III	1	1	0	2.887(5)	3.22	4.16	19

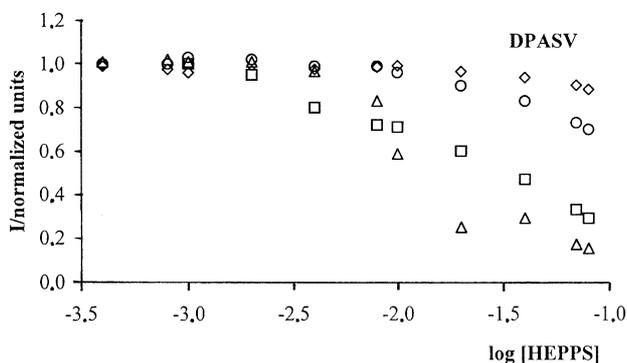


Fig. 1. Dependence of relative current responses (I_p/I_{p0}) of 3.6×10^{-7} M of cadmium (◇), 3.2×10^{-6} M of copper (□), 1.9×10^{-7} M of lead (△) and 6.1×10^{-7} M of zinc (○) on the logarithm of HEPPS pH buffer concentrations, in 0.1 M KNO_3 at pH 7.50, measured by DPASV. I_{p0} refers to a solution without buffer. For experimental details see Table 1.

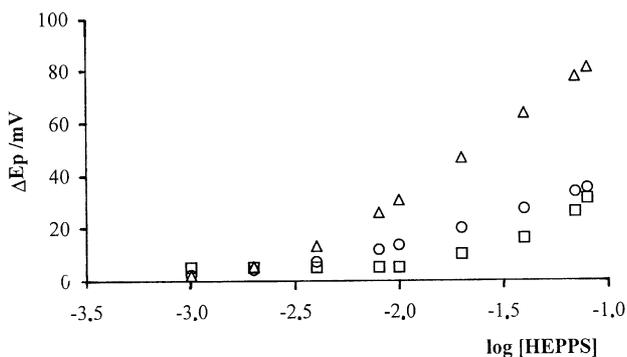


Fig. 2. ΔE_p values versus HEPPS concentration for 1×10^{-6} M of copper recorded by DPASV (□) and simulated according to model A (△) and model B (○) from potentiometric data at pH 7.5. For further details see Section 3.

probably due to adsorption of the pH buffer at the mercury electrode. In fact, I_p lower than I_{p0} can be due to other factors than adsorption; formation of labile complexes with diffusion coefficients lower than that of the free metal ion or of inert complexes [21] and occurrence of surface concentration effects [27, 28] also provoke reduction of the peak current. Peak current reductions are not due to the formation of inert complexes because for HEPPS concentration up to 2×10^{-3} M, corresponding to a large excess of ligand, there was no reduction of the peak current (Fig. 1). For chemical inert complexes, the E_p in the presence of ligand should remain constant with the same value as in the absence of ligand but the peak current should decrease even under conditions of ligand deficiency [22], as a consequence of the slow and negligible dissociation of the complexes [21]. The formation of labile complexes with diffusion coefficients lower than that of the free metal ion seems also not probable because in another work [29], we confirmed that the diffusion coefficients of lead labile complexes, whose ligands are simple structures as HEPPS, were equivalent to the diffusion coefficient of the free metal ion. These peak current reductions could not also be due to the occurrence of surface concentration effects, because, when reduction occurred, $|\text{HEPPS}|/|\text{heavy metal}|$ molar concentration ratios higher than 1000 were, in general, present [27, 28]. To investigate if the peak current reductions were due to adsorption of HEPPS on the mercury working

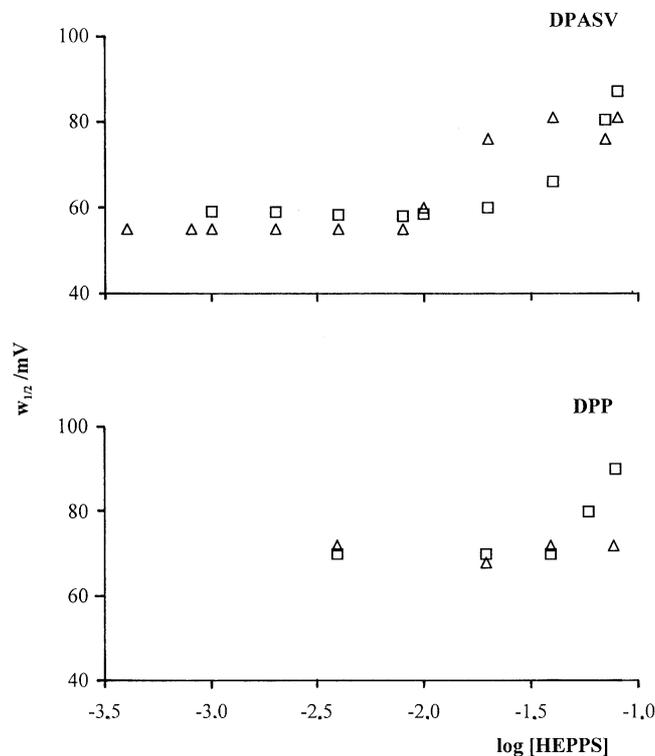


Fig. 3. Dependence of peak width at half height ($w_{1/2}$) of copper (□) and lead (△) recorded by DPASV and by DPP on the logarithm of HEPPS pH buffer concentrations, in 0.1 M KNO_3 at pH 7.5. For experimental details see Table 1.

electrode, $I_{ac} = f(E)$ curves were recorded by ACV, with a phase angle of 90° , between 0 and -1.3 V for pH buffer concentrations between 2×10^{-3} and 0.07 M. A phase angle of 90° was chosen because I_{ac} is then capacitive in nature and proportional to the double layer capacity, C_s [21]. C_s generally decreases in the presence of adsorption, leading to a diminution of I_{ac} current [21]. Figure 4 shows a typical example obtained with increasing concentration of HEPPS. This figure shows that the zero charge potential ($p_{zc} \cong -0.42$ V) was shifted in the direction of positive values, which occurs when there is adsorption of cations [30], accompanied with a depression of I_{ac} , proving that this pH buffer adsorbs at the mercury working electrode. This depression was very slight for the first HEPPS concentration tested, 2×10^{-3} M (curve b), being progressively more pronounced up to 4×10^{-2} M HEPPS (curve e). For 7×10^{-2} M HEPPS, the $I_{ac} = f(E)$ voltammetric curve (curve f) was superimposed with the one obtained for 4×10^{-2} M HEPPS (curve e), at almost all the potential range scanned, suggesting that the mercury electrode should be fully covered by HEPPS from at least 4×10^{-2} M of HEPPS upwards. Figure 4 also shows that there is no desorption up to -1.3 V, probably because adsorption was due to the piperazinic ring, being ca. 76% protonated and consequently positively charged. Even though this situation is not very common, this behavior was also described for other surfactants [12, 31, 32]. Peak current reductions (Figs. 1 and 5) observed for HEPPS concentrations $\geq 4.0 \times 10^{-3}$ mol/L, followed the depression of I_{ac} (Fig. 4), indicating that metal peak currents decreased with increasing surface coverage of the electrode. However, adsorption of HEPPS seems not to be the only cause for copper or lead peak current decrease as cadmium and zinc should also show a similar trend (no desorption was

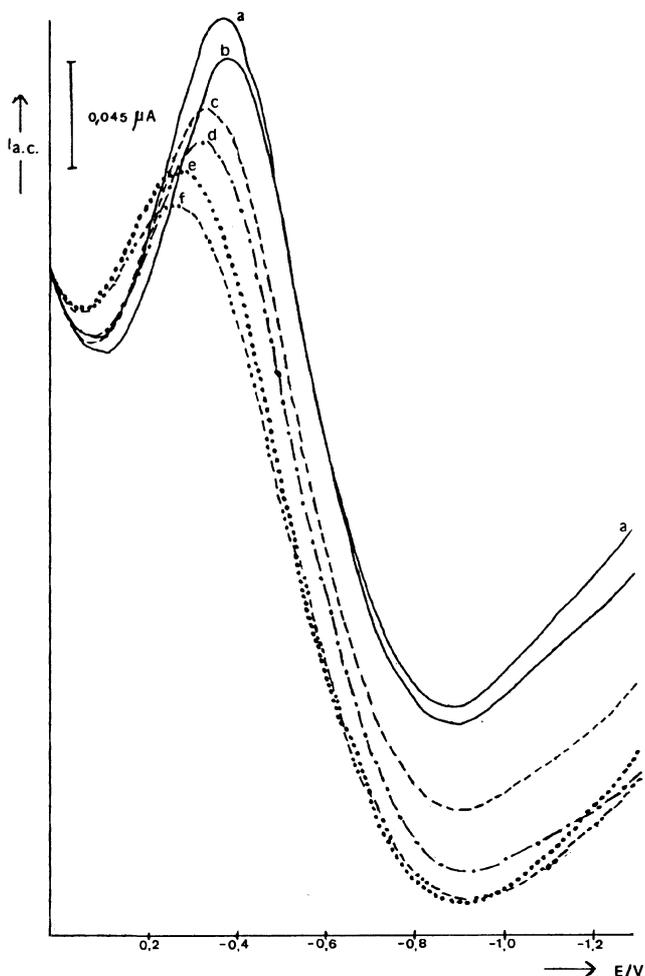


Fig. 4. AC voltammograms for HEPPS solutions in 0.5 M KNO_3 at pH 7.5: amplitude = 10 mV; frequency = 75 Hz; scan rate = 5 mV/s; $\phi = 90^\circ\text{C}$. [HEPPS] = a) 0.0 M; b) 2.0×10^{-3} M; c) 8.0×10^{-3} M; d) 1.0×10^{-2} M; e) 4.0×10^{-2} M; f) 7.0×10^{-2} M.

observed below -1.3 V). As during the reoxidation, copper or lead are complexed at the surface mercury electrode by HEPPS, this effect decreases the peak current which is accompanied with a cathodic shift of the peak potential [21]. For cadmium and zinc this phenomenon did not occur because these metals do not complex with the adsorbed pH buffer.

It is well known that the presence of electroinactive, surface-active substances adsorbed at an electrode/electrolyte interface, can affect diagnostic parameters in stripping voltammetry [23]. Sorption can affect peak current in two ways: by preventing metal deposition (a sorbed organic layer may hinder metal ion diffusion to the surface or retard chemical steps prior to electron transfer) and by changing the reversibility of the metal oxidation reaction [23, 33, 34]. These inhibitory effects depend on both the characteristics of the voltammetric technique and the nature of the particular metal ion [35]. For better understanding of how HEPPS affects the charge-transfer processes at the electrode/electrolyte interface on copper, lead and zinc DPASV responses, additional experiments performed by DPP and CV were done. The metals reduction process was studied by DPP and by CV (cathodic scan). For studying the metals oxidation process, the anodic scan obtained by CV was used. Typical effects of HEPPS on the redox processes (I_p/I_{p0}) at the working mercury electrode are presented in Figure 5. The figure shows that HEPPS reduces

drastically copper (ca. 60%, for cathodic scan recorded by CV, and ca. 70% for DPP and anodic scan recorded by CV, for 0.08 M HEPPS) and less for lead and zinc (peak reduction was only observed by DPP) DPP and CV responses. For lead, the HEPPS inhibitory effect was equivalent for both scans recorded by CV ($\leq 15\%$) and more pronounced by DPP ($\leq 21\%$) (Fig. 5). Zinc peak reduction recorded by DPP (Fig. 5) followed a similar behavior to that described above by DPASV (Fig. 1). In addition, no cathodic shift in peak potential and no increase in $w_{1/2}$ values were observed by DPP. On the other hand, in the presence of lead and copper, a cathodic shift of the peak potential was recorded for both metal ions (data not shown). No additional peaks were recorded at the potential range scanned for all the three metal ions (data not shown), evidencing that no fully inert zinc-HEPPS complex or quasilabile lead (or copper)-HEPPS complexes were formed [33]. These results are in agreement with those obtained by DPASV and confirms that HEPPS does not complex zinc but forms labile complexes with copper and lead. For copper, an increase of $w_{1/2}$ values was also observed for HEPPS concen-

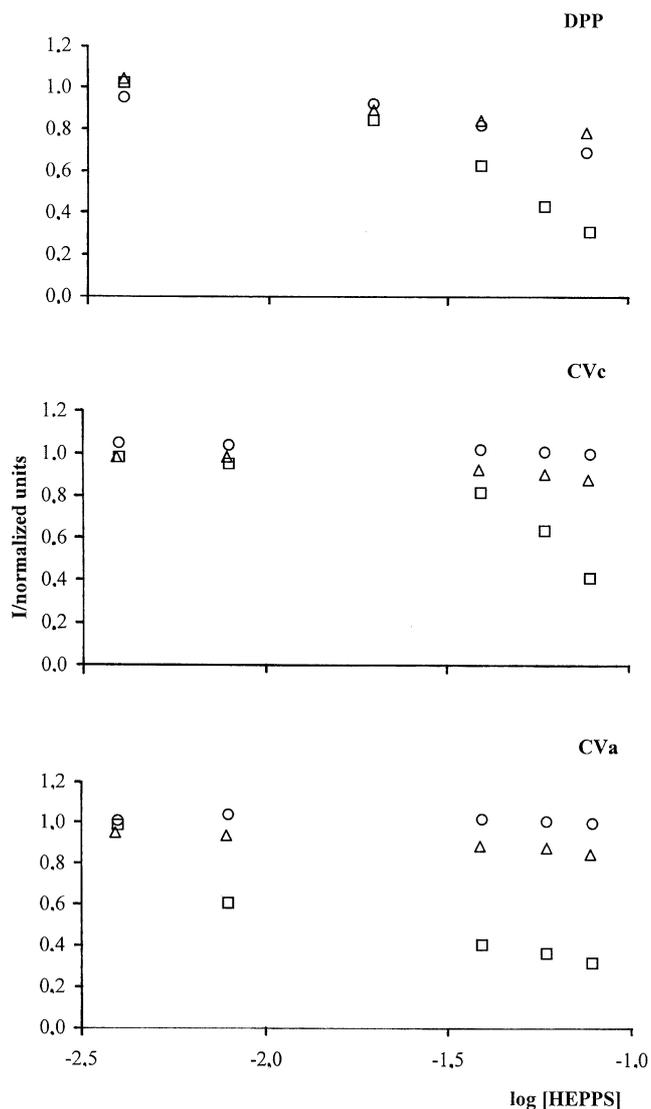


Fig. 5. Dependence of relative current responses (I/I_0) of copper (\square), lead (Δ), and zinc (\circ) recorded by DPP and by CV [cathodic (CVc) and anodic (CVa) waves] on the logarithm of HEPPS concentrations in 0.1 M KNO_3 at pH 7.5. For experimental details see Table 1.

trations $\geq 5.8 \times 10^{-2}$ M (Fig. 3). DPP and CV (both scans) results gave evidence that HEPPS adsorption on the working mercury electrode surface affects the charge-transfer of both (oxidation or reduction) processes for copper and lead ions.

Speciation of labile metal complexes in natural waters based on the shift of peak potentials depends on the degree of reactivity of the oxidized metal with the ligand of interest in the reaction layer. Therefore, metal speciation is evaluated indirectly and supposes that the system is electrochemically reversible [36]. As pH buffers are usually used at higher concentrations, the increase of $w_{1/2}$ values (Fig. 3) provoked by HEPPS show that this pH buffer is not suitable for lead or copper speciation studies by DPASV or DPP (only for copper), under the experimental conditions used in this work, when HEPPS concentration $\geq 2.0 \times 10^{-2}$ and 4.0×10^{-2} M, respectively, is present.

In order to calculate the stability constants of copper-HEPPS and lead-HEPPS systems, potentiometric data (pH measurements) were refined using the SUPERQUAD program. The data were modeled initially with only a ML specie. To this simple model was added protonated specie, MHL, or ML_2 , sequentially. Inclusion of other species only worsened the fit (ML and ML_2) (see an example for copper in Table 2) or were rejected (MHL) during the refinement process. Even though in DPASV experiments, all the conditions for application of the De-Ford-Hume method were not fulfilled for the copper-HEPPS system (the system did not behave electrochemically reversible), this methodology was used to get additional evidence that the ML species was the only one with real existence even for higher |pH buffer|/|heavy metal| molar concentrations ratios. For this purpose, the following simulations were performed: in a first attempt, conditional stability constants at pH 7.5 (pH used in DPASV experiments) were calculated from the copper-HEPPS stability constants determined by potentiometry. After that, ΔE_p were simulated for the HEPPS concentration range tested in DPASV experiments using the De-Ford-Hume equation [37] (Fig. 2). This figure shows that for HEPPS concentrations higher than 4×10^{-3} M, corresponding to |HEPPS|/|copper| molar concentration ratios >1250 , ΔE_p values simulated for model A (ML and ML_2) were much higher than those obtained by DPASV experiments and the ΔE_p values simulated for model B (ML) were closer to those determined by DPASV (Fig. 2), suggesting that all of the metal complex equilibria could be explained satisfactorily with ML . For lead-HEPPS system, values of ΔE_p simulated for model B were also closer to those recorded by DPASV (data not shown). These results corroborate that HEPPS complexes of copper or lead are in the proportion of 1:1. Results obtained for copper and lead with three independent potentiometric titrations assuming a 1:1 complex are reported in Table 2. From the overall titrations performed, an average (and standard deviation) of $\log K_{11} = 2.90 \pm 0.04$ ($n = 3$), for copper-HEPPS system, and of $\log K_{11} = 3.1 \pm 0.2$ ($n = 3$), for lead-HEPPS system, were calculated.

4. Conclusions

The present work describes the influence of HEPPS on the electrochemical behavior of copper, cadmium, lead and zinc recorded by DPASV, DPP and CV (only for copper, lead and zinc).

Due to pH buffer adsorption at the working mercury electrode, DPASV peak current reduction was verified for all the metal ions tested, being this phenomenon more marked for copper and lead (reduction ca. 70 %, for copper, and ca 85 %, for lead, for 0.08 M HEPPS). Peak current reduction was also observed by DPP and CV (both scans) for copper (more marked effect) and lead.

HEPPS did not complex cadmium or zinc but complexed copper and lead [$\log K_{Cu-HEPPS} = 2.90$ and $\log K_{Pb-HEPPS} = 3.1$ determined by potentiometric titrations (pH measurements)] and modified the degree of reversibility of copper, recorded by DPASV and DPP, and lead, determined by DPASV, under the experimental conditions used.

These results indicate that HEPPS seems not suitable for copper or lead speciation studies by DPASV and DPP (only copper).

5. Acknowledgements

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