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Polyelectrolyte-Cu(II) interactions studied by cyclic voltammetry

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SUMMARY

The polymer-metal ion interactions were studied by cyclic voltammetry. These were carried out with poly(acrylic acid)-Cu(II) and poly(vinylsulfonic acid)-Cu(II) systems at different pH. At low pH, the polymer was adsorbed on the electrode surface increasing the irreversibility of the Cu^{2+}/Cu(s) redox system. At pH 2.7, it was possible to demonstrate that the interaction between Cu(II) and poly(vinylsulfonic acid) is basically electrostatic and with poly(acrylic acid) a complex formation also exists.

INTRODUCTION

The polymers have gained great importance in the electrochemistry field. Polymer layers are electrodeposited on metal substrates for corrosion protection [1]. Polymers are also incorporated as additives into industrial plating baths to improve the electrical and mechanical properties of the metal deposited [2-4]. In both applications, besides adsorption of macromolecules at the electrode surface, polymer-metal ion interactions are involved [4-7]. Consequently, it is necessary to investigate them in order to optimize process design and control.

The polymer-metal ion interaction may be only electrostatic or moreover, include the coordinate bonds, where the functional groups linked to the backbone are the ligands. The type of interaction depends on the chemical nature of the functional group and metal ion, whereas the magnitude of the interaction depends on the variables such as: molecular weight, ionic strength, and pH of the solution.

The interaction of polyelectrolyte with metal ions has been studied intensively over decades. The effect of counterions on ionic polymers in solutions has been described theoretically in terms of electrostatic interactions by the counterion condensation theory developed by Manning [8]. About complex formation with macromolecular ligands, complete reviews have been published [9-11].

However, the application of voltammetric techniques to the study of polyelectrolyte-metal systems is relatively recent [12]. On the basis of theoretical model that does not consider adsorption phenomena, pulse polarography has mainly been used. Although cyclic voltammetry (CV) is a very versatile electrochemical technique [13], it has been seldomly applied to study the polymer-metal systems [7].

The interaction between poly(acrylic acid) (PAA) and Cu(II) has been studied by potentiometry, viscosimetry, and UV-vis spectroscopy [14-18]. There exists a strong evidence that the carboxylic acid groups as dissociated form, coordinate with copper ions yielding a polychelate.

Poly(vinylsulfonic acid) (PVSA), whose pendant functional groups correspond to a stronger acid than that of carboxylic acid does not act as ligands to metal ions. Therefore, PVSA-Cu(II)

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interactions must be only electrostatic, but there is no experimental evidence that demonstrates this fact.

One of the most employed techniques to study the polymer-metal ion interactions is the Liquid-phase polymer-based retention (LPR), which has been approved by IUPAC [19-20]. By using this technique, a study of interactions between poly(sodium 4-styrensulfonate) and metal ions was carried out [21]. It was observed that the capacity of polymers to retain metal ions increased as the pH increased. The same is observed with the concentration and size of the macromolecules. Nevertheless, it was not possible to establish the interaction type: electrostatic or polychelate formation.

Therefore, the aim of this paper is to study by CV the polymer-metal ion interactions and to investigate if it is possible to distinguish between one electrostatic and complex formation. The poly(vinylsulfonic acid) and poly(acrylic acid) are used as ion exchanger and complexing polymer, respectively, and Cu(II) as metal ion.

EXPERIMENTAL

Solutions were prepared from distilled water. $Cu(NO_3)_2 \cdot 3H_2O$ p.a. UCB; KNO_3 p.a. Merck; PAA Aldrich (M_w 250.000, aqueous solution 35wt.%); PVSA Aldrich (aqueous solution 25 wt%). The polyelectrolytes were used as received.

The concentrations of the polymers were calculated considering the molar mass of the repeating units. The voltamperometric studies were carried out in aqueous solution for the following systems: (a) Cu(II) in absence of polyacid; (b) Cu(II)-PVSA, and (c) Cu(II)-PAA. In all the runs, the pH tested were 1.0, 2.7, and 5.0, except for the Cu(II)-PAA system which was assayed only up to pH 2.7. At higher pH a precipitate was observed. The polymers are stable in presence of HNO_s during the CV experiments. This was corroborated electrochemically: a solution of each polymer in 1M KCl was allowed to achieve an oxidation potential of 1.0V versus the normal electrode of hydrogen. It was not observed any response of current.

All the voltammograms reported were obtained using a three electrode potentiostatic system, BAS CV-50W, at room temperature. The cell was kept in an inert atmosphere by means of ultrapure nitrogen gas. A Pt disk sealed in a soft glass rod was used as a working electrode. Platinum wire was used as counter electrode. All the potentials are referred to Ag/AgCl, 3M NaCl electrode.

To achieve reproducibility of the data, after working with the polyelectrolyte solution, it was necessary to clean the surface of the electrode with 2 M HNO_3 previous polishing with diamond (1 µm) and alumina.

In all the runs, the Cu(II) concentration was $1 \cdot 10^{-2}$ M, scanning rate 0.100 $V \cdot s^{-1}$ and the number of cycles 10. 1 M KNO_3 was used as support electrolyte. The pH was adjusted by adding aqueous solution of HNO_3 and KOH. The pH measurements were done with pH-meter VWR model 8005.

RESULTS AND DISCUSSION

The poly(acrylic acid) (PAA) and poly(vinylsulfonic acid) (PVSA) were used as polyelectrolytes to study the interactions with Cu(II) by cyclic voltammetry.

Firstly, it was determined that the window potential ranged between 0.800 and -0.200 V. At pH 1.0 and potential more negative than -0.200 V the reduction of H^+ was observed, whereas at potentials more positive than 0.800 V the oxidation of H_2O occurred. Within the window potential of both polymers no oxidation-reduction process was observed.

$1\cdot10^{-2}$ M Cu(II) system in absence of polyacid

In the voltammogram for the Cu(II) ions, a cathodic peak around -0.050 V and the conjugated anodic peak at 0.072 V were observed (see Table 1 (a)). The redox couple involved in this response is Cu(II)/Cu(0). To corroborate this hypothesis, an electrolysis at constant potential (0.0 V) was carried out. A deposit of metallic copper on the electrode surface was obtained.

The voltammetric response is independent of the pH as no important differences among the voltammograms at pH 1.0, 2.7, and 5.0 exist (see Table 1 (a)).

Table 1 (a) shows that at pH 2.7 and 5.0 as the number of cycles increases a shift of either Ep_c or Ep_a to positive values (the $\Delta E_{1/2}$ value between the tenth cycle and first cycle is 0.015 V) (see Fig. 1, curve 1, for pH 2.7) is observed. This is attributed to that between one and another cycle, imperfections on the electrode surface are produced (due to uncompleted dissolution of deposited copper), decreasing the overpotential for nucleation.

Table 1. Results of the voltammograms recorded to the different systems under several pH conditions

PH	Cycle No	Ep_c (V)	ip_c (μA)	Ep_a (V)	Ip_a (μA)
a) $1\cdot10^{-2}$ M Cu(II) in absence of polyacid					
1.0	1	-0.052	-70	0.075	231
	10	-0.055	-65	0.102	209
2.7	1	-0.049	-76	0.072	236
	10	-0.037	-74	0.090	238
5.0	1	-0.052	-80	0.072	233
	10	-0.034	-80	0.087	244
b) $1\cdot10^{-2}$ M Cu(II) in presence of $1\cdot10^{-2}$ M PVSA					
1.0	1	-0.070	-50	0.087	187
	10	–	–	0.105	142
2.7	1	-0.052	-71	0.075	224
	10	-0.052	-63	0.096	209
5.0	1	-0.064	-79	0.081	222
	10	-0.070	-81	0.078	219
c) $1\cdot10^{-2}$ Cu(II) M in presence of $1\cdot10^{-2}$ M PAA					
1.0	1	-0.115	-45	0.093	159
	10	–	–	0.111	93
2.7	1	-0.115	-43	0.111	120
	10	–	–	0.138	37

$1{\cdot}10^{-2}$ M Cu(II) system in presence of $1{\cdot}10^{-2}$ M PVSA

Fig. 1, curves 2, 3, and 4 show the voltammograms of the PVSA-Cu(II) system at pH 1.0, 2.7 and 5.0, respectively, and in Table 1 (b) are summarized some results.

The pH dependency of the voltammetric response is very interesting. At pH 1.0, curve 2, the irreversibility of the system increases as Ep_c is shifted to the negative values and Ep_a towards more positive potentials. Moreover, a diminution of the current intensity of the respective peaks was observed. All these effects increase as the number of cycles increase. At the tenth cycle (Fig. 1 (B)) a reduction of Cu(II) to Cu(0) is completely mass transfer process controlled. But at pH 2.7, curve 3, the response is not different of that of Cu(II) system in absence of polyacid. At pH 5.0, curve 4, the result is practically the same, only at the first cycle the ΔE_p is slightly higher (0.145 V > 0.121 V) and at the tenth cycle Ep_c and Ep_a are shifted to negative values.

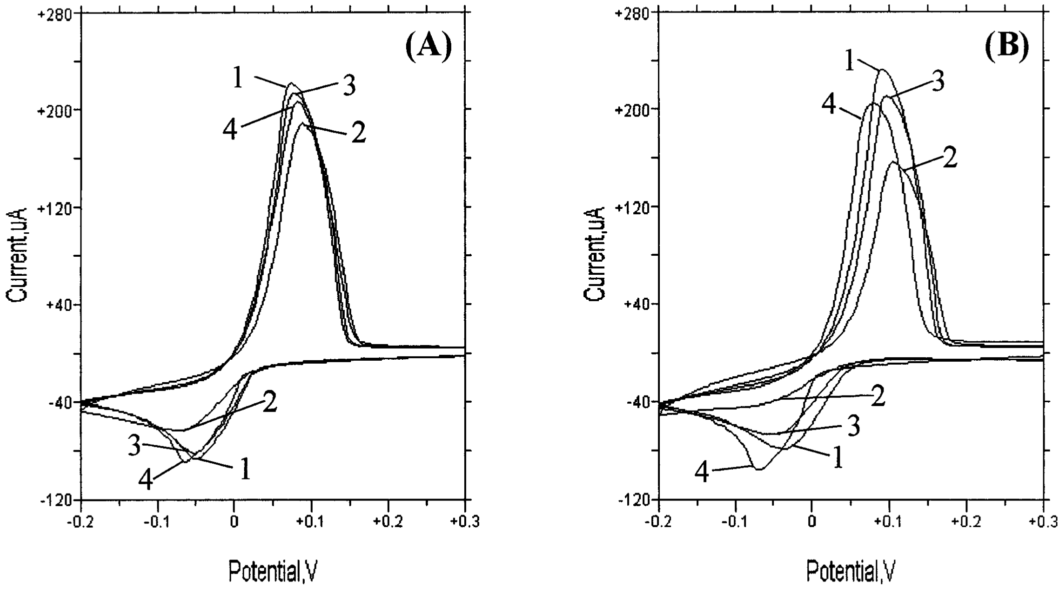

Fig. 1. Voltammograms of $1{\cdot}10^{-2}$ M Cu(II) in absence of PVSA at pH 2.7 (**1**) and in presence of $1{\cdot}10^{-2}$ M PVSA at different pH: (**2**) 1.0; (**3**) 2.7; (**4**) 5.0. (**A**) First cycle, (**B**) Tenth cycle.

This general behavior can be explained if it is postulated that the polyelectrolyte is adsorbed on the electrode surface (negatively charged) through hydrogen bridge bonds as shown in Fig. 2. Similar results have been reported with poly(ethylene glycol) and copolymers of maleic acid [6, 7].

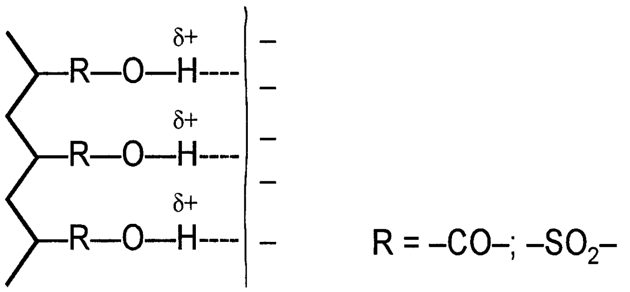

Fig. 2. Schematical description of the polyacid adsorption on the electrode surface.

The adsorbed polyelectrolyte hinders the access of the Cu(II) ions to the active sites of the electrode. The metal ions diffuse through the network formed by the polymer chains to the lower number available active sites. At pH 2.7, practically all the sulfonic groups are dissociated, hence the polyelectrolyte adsorption does not occur as the hydrogen bridge bonds are not possible and the polymer chains will be repelled by the electrode.

According to the previous data [21] it is assumed that at pH 5.0 the PVSA-Cu(II) interactions are maximum. However, this interaction is slightly observed in the voltammetric response. Therefore, it is possible to postulate that this interaction is an electrostatic type and is annulled by shielding effect produced by the support electrolyte.

$1{\cdot}10^{-2}$ M Cu(II) system in presence of PAA

Figure 3, curves 2 and 3, shows the voltammograms of the PAA-Cu(II) system at pH 1.0 and 2.7, respectively. Table 1 (c) summarizes the results.

In general, the presence of PAA increases noteworthy the irreversibility of the system as the cathodic peak tends to disappear and the anodic peak is shifted to positive values, decreasing in intensity.

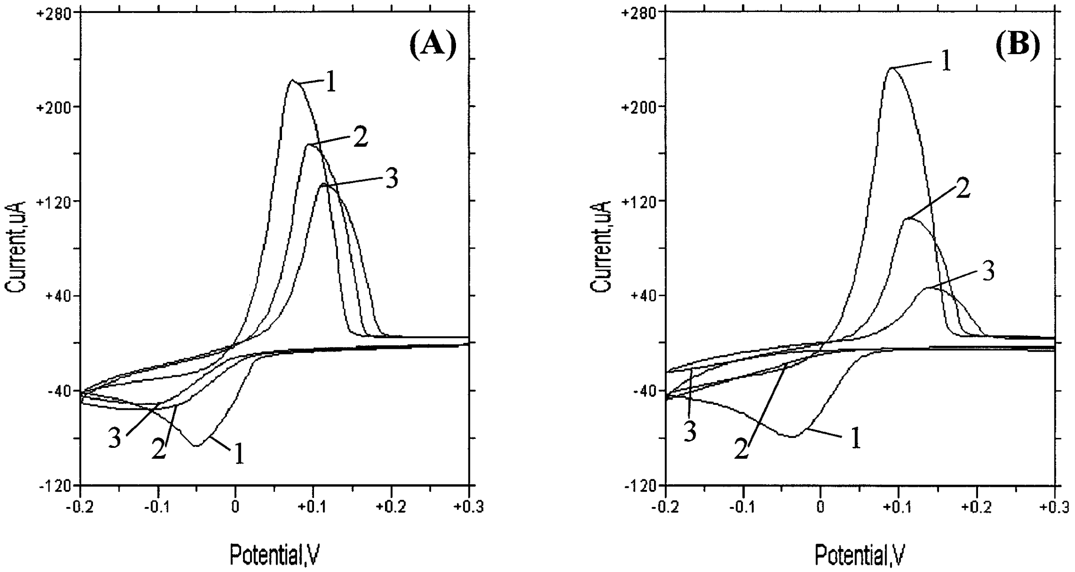

Fig. 3. Voltammograms of $1{\cdot}10^{-2}$ M Cu(II) in absence of PAA at pH 2.7 **(1)** and in presence of $1{\cdot}10^{-2}$ M PAA at different pH: **(2)** 1.0; **(3)** 2.7. **(A)** First cycle, **(B)** Tenth cycle.

The results at pH 1.0 are explained assuming that the polyelectrolyte is strongly adsorbed on the electrode surface. At this pH, the carboxylic acid groups are completely protonated. Even at the first cycle (Fig. 3 (A), curve 2) it is observed that the current is controlled by the mass transfer. The evolution of the voltammetric profile indicates that the polymer is not adsorbed and the thickness of the polymer increases as the cycle number increases.

The results at pH 2.7 (Fig. 3, curve 3) show a more irreversible behavior than that at pH 1.0. It is evident that the only explanation of the polyelectrolyte adsorption on the electrode is not enough to explain these results. Hence, it is necessary to consider the polymer-metal ion complex formation.

The carboxylic acid groups are weak acids and at pH 2.7 are partly protonated and the other ones are dissociated. Accordingly, it is postulated that the polyelectrolyte is adsorbed through the acid groups, adopting a conformation with the anionic groups oriented to the solution. These groups form coordinated bonds with Cu(II), as to achieve the electrode surface, they must cross the polymer chain barrier and overcome the retention strength of the carboxylate groups.

Fig. 4 shows that a decrease of the PAA concentration does not produce change in the voltammetric response of the system. The voltammograms obtained at different [PAA]/[Cu] ratios (0.1-1.0) are practically overlapped. This result corroborates that the polymer-metal ion interactions present in this electrochemical process are not produced in the solution, but in the polymer adsorbed layer on the electrode.

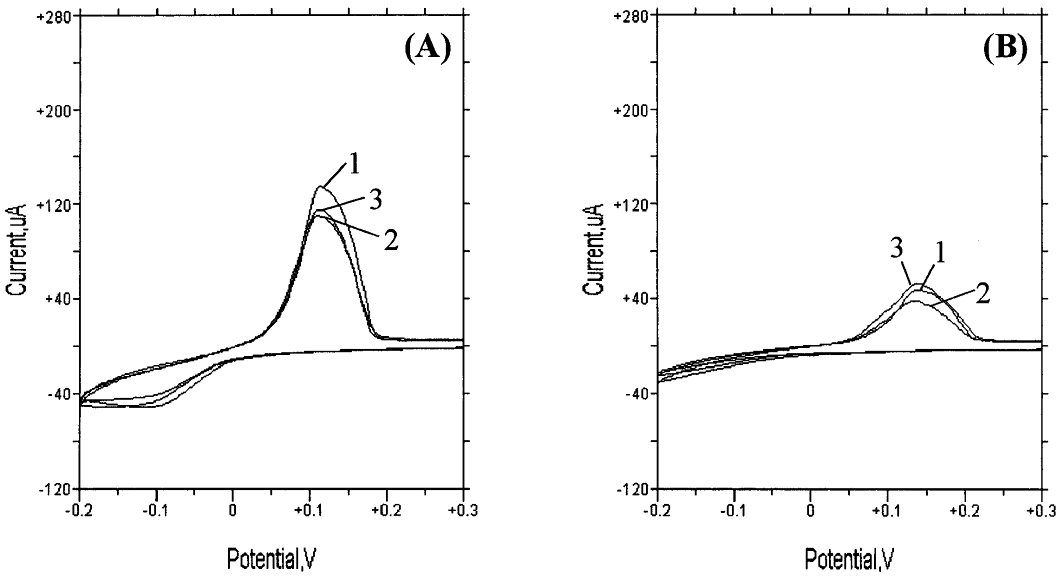

Fig. 4. Voltammograms of $1 \cdot 10^{-2}$ M Cu(II) in presence of PAA at pH 2.7 at [PAA]/[Cu] ratios: **(1)** 1/1; **(2)** 0.2/1; **(3)** 0.1/1. **(A)** First cycle. **(B)** Tenth cycle.

CONCLUSIONS

The polyelectrolyte-Cu(II) interactions were investigated using the poly(acrylic acid) and poly(vinylsulfonic acid). The presence of polyacids modifies the electrochemical behavior of Cu(II) ions in aqueous medium. The magnitude of this effect depends on the chemical properties of the polyelectrolyte as acid strength and chelating capability.

At low pH, when the major part of the functional groups are as acid form, the polyelectrolyte was adsorbed on the electrode surface.

At pH 2.7 the PVSA adsorption was not favored and no specific interaction between the polyelectrolyte and the Cu(II) ions was observed. But at the same pH, the weak acid polylectrolyte is adsorbed on the surface electrode and also forms a polychelate. These processes are clearly appreciated by the voltammograms, concluding that the cyclic voltammetry is a very efficient technique to investigate and identify the polymer-metal ion interaction type in an aqueous medium.

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