

On the Adsorption and Reduction of the Herbicide Picloram on Mercury and Carbon Electrodes

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At concentrations higher than $2 \cdot 10^{-4}$ M, and below pH 3, the cyclic voltammograms of picloram (=4-amino-3,5,6-trichloropyridine-2-carboxylic acid) on Hg electrodes show two prepeak systems (named I and II attending to the proximity to the main reductions peak), which can be attributed to the weak adsorption of reactant and the strong adsorption of the product at the electrode surface. The system II is due to the uncharged form of picloram, and system I to the picloram protonated at the pyridine N-atom. Small amounts of the surfactant *Triton X-100* (= α -[4-(1,1,3,3-tetramethylbutyl)phenyl]- ω -hydroxypoly(oxyethane-1,2-diy1)) cause the disappearance of system I, the shift of system II, and also affect the intensities and widths of anodic and cathodic peaks but not the charge passed in each peak. Thus, the adsorption process responsible for the appearance of system I is inhibited by the presence of *Triton*; by contrast, the process corresponding to system II is only modified by the surfactant, becoming an electrochemical process occurring at the potentials corresponding to system II, which is more reversible than that observed in the absence of *Triton*. The addition of *Triton* permitted the analysis of the main reduction process. Convolution voltammetry of the main reduction peak is consistent with the loss of a Cl-atom in equilibrium which occurs after a reversible electron transfer and is followed by the reductions of both species present in the equilibrium (*Scheme 2*). This is also the reduction mechanism on a glassy carbon electrode but the electron transfer on the carbon electrode increases with respect to the mercury electrodes; in addition, the loss of the Cl-atom does not take place on the electrode surface. From the recording of differential capacity – potential curves, it was concluded that picloram is adsorbed on the carbon electrode; but this adsorption is too weak to induce the appearance of prepeak systems.

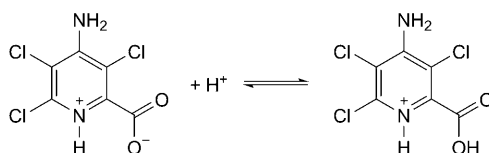
Introduction. – Salts of picloram (=4-amino-3,5,6-trichloropyridine-2-carboxylic acid) are widely used to control annual weeds on crops and other agricultural tasks such as control of knapweed, locoweed, bitterweed, snakeweed, leafy spurge, larkspur, mesquite, prickly pear, *etc.* Picloram is a crystalline organic solid with a chlorine-like odor. It is a systemic herbicide registered by EPA that can cause both short-term health effects, as damage to the central nervous system, and long-term effects, as liver damage. Picloram is the most persistent of the pyridine herbicides: *ca.* 10–30% of the original amount of herbicide is detected one year after its application [1]. It may leach to groundwater because of its low adherence to soil. Its degradation in the environment occurs mainly by microbial metabolism; the degradation products have not yet been identified. The maximum allowed level of picloram in drinking water according to the EPA is 0.5 mg l^{-1} because higher levels of the pesticide can cause damages to the human central nervous system, loss of weight, diarrhoea, and weakness.

Previous studies on the electroreduction of compounds having similar structures [2] indicate that the loss of Cl-atoms depends of the structure of the compound. This conclusion is based in the comparison of the reductions of 6-chloropicolinic acid (=6-chloropyridine-2-carboxylic acid; 6C1P) and clopyralid (=3,6-dichloropyridine-2-carboxylic acid), where no evidence of the loss of a Cl-atom was found, with that of picloram, which on a mercury pool electrode produced 4-amino-3,5-dichloropyridine-2-carboxylic acid, together with di- and trichlorinated pyridinealdehydes [3].

In the natural environment, the dynamics and the accumulation/degradation mechanisms of hydric pollutants is of high interest. Electrochemical studies of these dynamics can contribute to the knowledge of the natural deactivation of contaminants, the reductive way being a possible degradation route in those specific natural aquatic environments where the mechanism of photolytic detoxification does not act. Moreover, the knowledge of the electrochemical behavior of these substances is essential to develop elimination methods or technologies to decrease their toxicity [4]. In our laboratories, such reductive processes are being investigated [5–7].

For picloram, a pK value of dissociation of the carboxylic acid group of 2.20 ± 0.03 was determined [8], and the pK corresponding to the protonation of the pyridine ring was found to be 3.4 [8–11] (*Scheme 1*).

Scheme 1

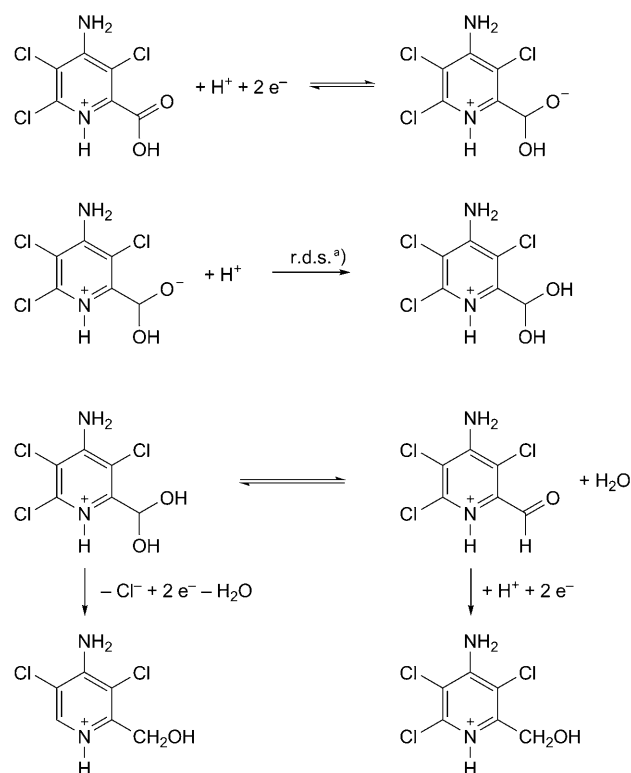


The overall reduction process of picloram on mercury electrodes involves the uptake of four electrons, showing one or two reduction waves in DC (direct current) polarography depending of the medium pH, whereas DP (differential pulse) polarograms exhibits two or three peaks. As shown in *Scheme 2*, the reduction of the species protonated at the heterocyclic N-atom corresponds to a chemical reaction in equilibrium placed after a reversible electron transfer and followed by the reductions of both species appearing in the equilibrium.

The acidic components of the buffer are involved in the rate-determining step, and the protonation of the pyridine ring involving the carboxylate ion is essential in the reduction processes. The peak 3 corresponds to the reduction of the protonated picloram carboxylate.

In the course of the investigation of the reduction of picloram on mercury electrodes, two prepeak systems were detected [12]. Such prepeaks originate from an electrode reaction in which the reactant is weakly adsorbed and the product is strongly adsorbed [13–15], the rate-controlled adsorption of the product being evidenced [16]. At sufficiently high concentrations of picloram, these prepeak systems were found in the potentials ranges -0.6 to -0.8 V (system I, close to the main reductions peak) and 0 to -0.4 V (system II). Above pH 3, the disappearance of the prepeak systems was found to be related to the dissociation of the carboxylic acid group. The electrochemical parameters showed that the species responsible for the appearance of system II must be

Scheme 2



a) Rate-determining step.

the uncharged form of picloram, whereas that responsible for the appearance of system I must be the picloram protonated at the pyridine N-atom.

The aim of this paper was the study of both the electroreduction and adsorption processes in the presence of a surfactant and on a carbon electrode, to establish the influence of these variables on the processes.

Experimental. – In all cases, *Merck* anal.-grade reagents were used without further purification. The working concentration of picloram was $2 \cdot 10^{-4}$ M, with the exception of the experiments in which the influence of this variable was studied. Solns. of 0.1M in both acetic and phosphoric acids were used as supporting electrolytes. Stock solns. of picloram were stored in the dark at 277 K to avoid decomposition. Ionic strength was adjusted to 0.4M with solid NaCl, and the pH was adjusted with solid NaOH. All potentials were measured against a *Metrohm-6.0733.100* Ag | AgCl | KCl_{sat} electrode.

Measurements were made on a *CHI650A* electrochemical workstation from *IJCambria* coupled to an *EF-1400* controlled-growth mercury electrode from *BASi*. The glassy carbon electrode was from *IJCambria* (area = 38.5 mm²). Measurement of differential-capacity curves were made by recording impedance–potential curves and obtaining the capacity from the imaginary component of the impedance. The recordings were made at very low rates (20 mV min⁻¹), to reach the equilibrium.

Solns. were purged with purified N₂ and the temp. was kept at 298 ± 0.1 K. All other experimental conditions are given in [8][12].

Results and Discussion. – *Fig. 1* shows the cyclic voltammograms of picloram in the absence and in the presence of *Triton X-100*. In the absence of the surfactant, and at concentrations higher than $2 \cdot 10^{-4}$ M, two prepeak systems were found in the voltammogram: in the potential range -0.6 to -0.8 V, close to the main reductions peak (in the following, peak 1), appears a system named system I, and in the potential range 0 to -0.4 V, which is far from both peak 1 and system I, appears a system named system II [8]. Under these conditions, these prepeak systems can be attributed to the weak adsorption of reactant and the strong adsorption of the product at the electrode surface. Above pH 3, the prepeak systems I and II were not found in the voltammograms and, since the p*K* value corresponding to the dissociation of the carboxylic group is around 2.2, the behavior must be related to this acid–base equilibrium. The values of the adsorption half-peak width, the separation between the adsorption prepeaks and the diffusion peak (peak 1), the ratio between the intensities of these peaks, and the experiments performed in aprotic media showed that the species responsible for the appearance of the peak system II must be the uncharged form of picloram, whereas that responsible for the appearance of system I must be the picloram protonated at the pyridine N-atom [12].

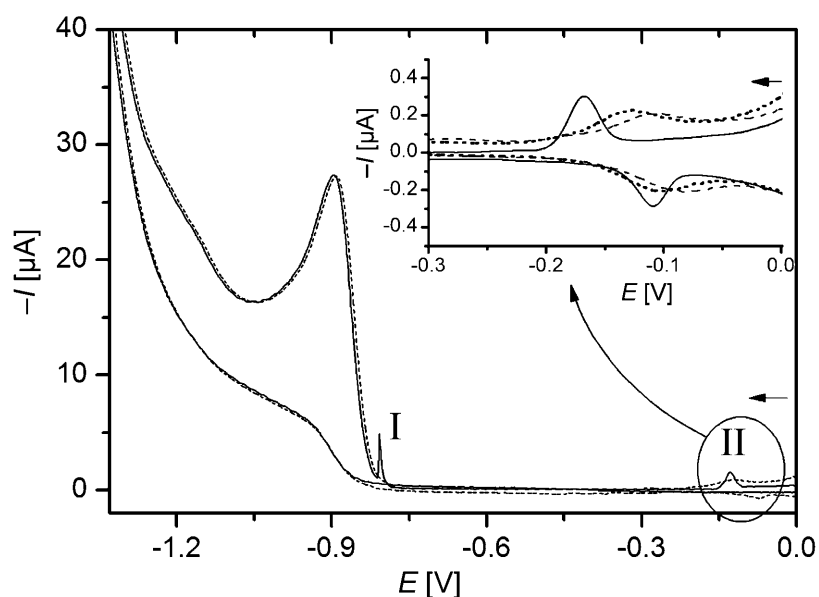


Fig. 1. Cyclic voltammogram on the HDME (hanging-drop mercury electrode) of $1.36 \cdot 10^{-3}$ M picloram at pH 1.5 in the absence of *Triton X-100*. Scan rate 1.0 V s^{-1} . *Inset:* Cyclic voltammograms in the potential region of system II at different *Triton X-100* contents: (—) 0%, (···) 0.01%, (---) 0.05%. Scan rate 0.5 V s^{-1} . Arrows indicate the start of the scan.

In the presence of a small amount of *Triton X-100* (even at 0.01%), system I disappeared irrespective of the scan rate used, and system II shifted towards more positive potentials. At the same time, both the anodic and cathodic peaks of system II decreased in intensity and increased in width, as is shown in *Fig. 1*. The charge passed in

each peak (anodic or cathodic) of system II was obtained by integration of the $i-E$ curves; the background voltammogram (recorded in the absence of picloram) was subtracted from the picloram voltammogram. These charges were independent of both the *Triton* content and the scan rate, at scan rates below $\nu = 2 \text{ V s}^{-1}$. In addition, the separation between the peak potentials of the anodic and cathodic peaks of system II decreased with respect to that found in the absence of surfactant. In fact, this separation is lower than 60 mV at scan rates below 1 V s^{-1} , as can be seen in *Fig. 2*.

From the above facts, it can be concluded that the adsorption process responsible for the appearance of system I (*i.e.*, that corresponding to picloram protonated at the pyridine N-atom) is inhibited by the presence of *Triton* but that corresponding to system II is only modified by the presence of the surfactant. Indeed, the reversibility of the electrochemical process occurring at the potentials corresponding to system II is higher than that observed in the absence of *Triton*. This last conclusion arises from the low value of the separation between the peak potentials of the anodic and cathodic peaks with respect to that obtained in the absence of surfactant.

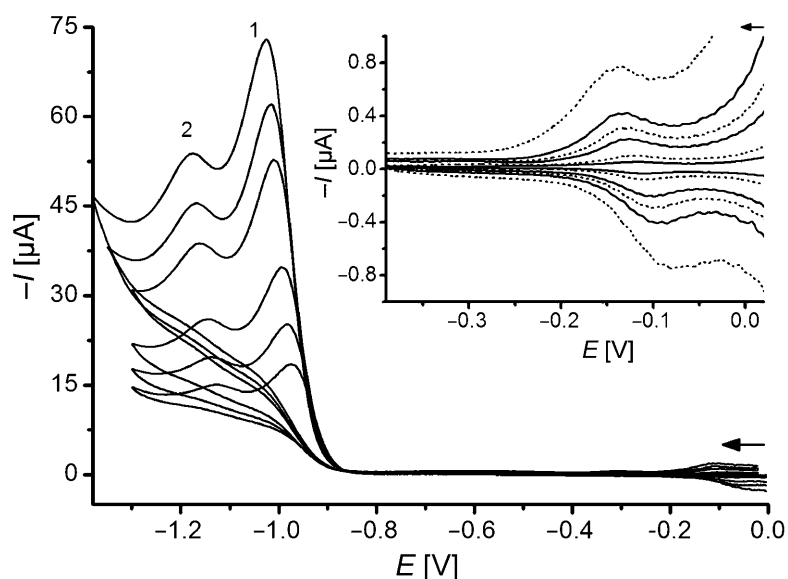


Fig. 2. Linear-sweep cyclic voltammetry on the HDME of $2 \cdot 10^{-4} \text{ M}$ picloram in the presence of 0.05% Triton X-100 at *pH* 1.6. Scan rates [V s^{-1}] 0.1, 0.2, 0.5, 1.0, 2.0, and 5.0. *Inset:* Cyclic voltammograms in the potential region of system II. Arrows indicate the start of the scan.

Fig. 2 also shows cyclic voltammograms of the main reduction process: two well-defined peaks were found in the presence of surfactant. This is in contrast with the results obtained in the absence of *Triton*, when two overlapped peaks were obtained [8]. The plot of $\log i_p$ vs. $\log \nu$ for the first reduction peak was roughly linear, having a slope near 0.5. The plots of E_p vs. $\log \nu$ of the cathodic peaks are shown in *Fig. 3*.

Below scan rates of 1 V s^{-1} , the slope of this plot for both reduction peaks was $-30 \text{ mV decade}^{-1}$, in agreement with EC-type reduction processes.

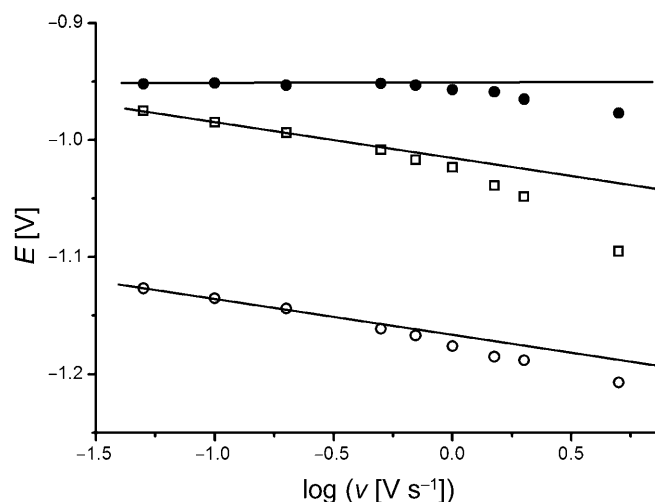


Fig. 3. Linear-sweep cyclic voltammetry on the HDME of $2 \cdot 10^{-4}$ M picloram in the presence of 0.05% Triton X-100 at pH 1.6. Plot of E_p vs. $\log \nu$ for the main reduction peaks: Peak 1 (\square) and Peak 2 (\circ). Results of convolution of peak 1 (\bullet): plot of $E_{1/2}$ vs. $\log \nu$.

Convolution voltammetry [17–22] was used to analyze the direct scans of the voltammograms by computing the integrals of Eqn. 1, where I is the actual current, J the convoluted current, ν an integration variable, and t is related to the potential through the scan rate. Thus S-shaped curves were obtained having a limiting value J_L independent of the mechanism of the electrochemical reaction, according to Eqn. 2, where n is the number of electrons involved in the process, A the electrode area, and D and c_0 the diffusion coefficient and the bulk concentration of the depolarizer, respectively.

$$J = \pi^{-1/2} \int_0^t \frac{I(\nu)}{(t-\nu)^{1/2}} d\nu \quad (1)$$

$$J_L = nFAD^{1/2}c_0 \quad (2)$$

Diagnostic criteria can be established with logarithmic analyses based on Eqn. 3 [18][22], where $f(I, J)$ is a function of both the convoluted and nonconvoluted currents J and I , respectively, and b a value that depends on the type of mechanism, in a similar way as the logarithmic analysis slope in DC polarography. With this equation, reversible (equilibrium) and irreversible electrochemical processes E_r and E_i , respectively, can be characterized, besides processes complicated by chemical reactions, such as EC (electrocoagulation) processes in which a chemical reaction occurs after the electron transfers and constitutes the rate-determining step.

$$E = E_{1/2} + b \ln[f(I, J)] \quad (3)$$

Since no reoxidation peaks were observed for the main reduction peaks, the direct scans of the first peak appearing in the voltammograms were analyzed by *Eqn. 3* and the $f(I_p, J)$ corresponding to irreversible, E_i , or EC processes. In all cases, the best linear analyses were obtained when the $f(I_p, J)$ corresponding to E_i or EC processes was used. The value of the logarithmic-analysis slope allowed to distinguish between the following processes: for a two-electron irreversible process E_i where the rate-determining step is the electron transfer, the slope must be around $39 \text{ mV decade}^{-1}$, whereas for the EC_i process, the slope must be of around $30 \text{ mV decade}^{-1}$. The experimental b values were of *ca.* $33 \text{ mV decade}^{-1}$ indicating that the process is of the EC_i type. Moreover, the half-wave potential was independent of the scan rate, as shown in *Fig. 3* indicating that this analysis is correct.

It was shown that the overall reduction process in the absence of *Triton* corresponds to an EC(E) four-electron process [8]. In this mechanism, there is a chemical reaction in equilibrium (actually the loss of Cl-atom) placed after a reversible electron transfer and followed by the reductions of both species appearing in the equilibrium (see *Scheme 1*). The values of the ratio between the convoluted limiting current of peak 1 (J_{L1}) to the overall convoluted limiting current (J_{LT}), J_{L1}/J_{LT} , are dependent of both the rate and equilibrium constants of the intermediate chemical reaction, and independent of the scan rate. The J_{L1} values can vary from a minimum value corresponding to a two-electron process, if the dehydration of the hydrated aldehyde obtained after the first two-electron transfers is very slow, and a maximum value corresponding to four electrons, when the said dehydration is very fast (it must be taken into account that the reduction of the free aldehyde takes place at less negative potentials than the reduction of the hydrated molecule). So, J_{L1}/J_{LT} must be comprised between 0.5 and 1. At 0.1% of *Triton* content, the value of this ratio was *ca.* 0.7, and this value was independent of the scan rate at $v \leq 2 \text{ V s}^{-1}$ and slightly lower than the value obtained in the absence of surfactant, which was close to 0.65 [8].

With the aim to investigate if the electrochemical processes change from one electrode to another, the reduction of picloram was also studied on a glassy carbon electrode. As for the reduction on mercury electrodes, the voltammograms in acidic media showed two overlapping peaks, and no signals were found above pH 4.5. *Fig. 4* shows the evolution of the voltammograms with the scan rate. The inset of the figure corresponds to the entire scan to show that no prepeak systems were found at any accessible potential value. The same results were obtained at any scan rate used.

As it can be seen, the second peak is less well-defined than in the precedent case. Nevertheless, the convolution analysis of the direct scans of the voltammograms shows that the ratio between limiting currents was *ca.* 0.7, and independent of the scan rate at $v \leq 2 \text{ V s}^{-1}$. This means that the electrochemical reduction process is of the same type as on mercury electrodes. In addition, this result indicates that the loss of the Cl-atom has the same rate and equilibrium constants in the three cases studied, this means that this chemical reaction does not take place on the electrode surface, and the kinetics and thermodynamic parameters of the Cl-release are independent of the applied potential.

The half-wave potentials obtained by the convolution analysis are independent of the scan rate, as was expected for the type of processes studied, but the b values decreased with respect to those obtained on mercury electrodes to *ca.* $-48 \text{ mV decade}^{-1}$. This is compatible with an increase of the irreversibility of the electron

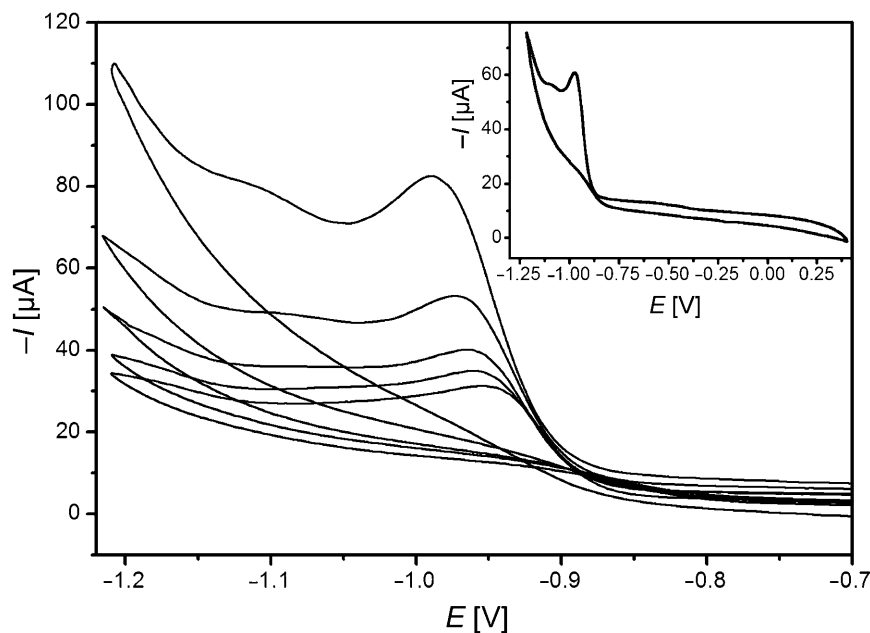


Fig. 4. Linear-sweep cyclic voltammetry of $2 \cdot 10^{-4}$ M picloram on the carbon electrode in the absence of Triton X-100 at pH 1.5. Scan rates [V s^{-1}] 0.1, 0.2, 0.4, 0.7, and 1.0. Inset: Voltammogram showing a wide range of potentials at 0.7 V s^{-1} .

transfer on the carbon electrode with respect to the mercury electrodes. Nevertheless, the electrochemical process remains essentially unchanged as can be inferred from the dependences of the voltammograms from both the pH and reactant concentration.

The effect of the surfactant on the adsorption process on the mercury electrode was clearly established from the voltammetric results. The adsorption of picloram on the carbon electrode was not evident in the voltammograms, and so it was investigated by recording differential capacity–potential curves in NaClO_4 solutions, and by using the glassy carbon electrode. Under these conditions, the pH is higher than 4.5 and, as stated above, no faradic processes occur. The curves corresponding to both the differential capacity of the picloram solution and the supporting electrolyte differ even in the potential range in which is included the zero charge-potential of the electrolyte–electrode system. This indicates that picloram is adsorbed on the carbon electrode in the zone of potentials where the electrode is charged (both positively and negatively), but the species responsible of the apparition of systems I and II are not adsorbed on carbon with sufficient strength to induce the appearing of such prepeak systems.

Conclusions. – The presence of *Triton X-100* causes the disappearance of system I, the shift of system II, and also affects the intensities and widths of the anodic and cathodic peaks but not to the charge passed in each peak. Thus, the adsorption process responsible for the appearance of system I is inhibited by the presence of *Triton*, but that corresponding to system II is only modified by the surfactant, the reversibility of

the electrochemical process occurring at the potentials corresponding to system II being increased compared to that observed in the absence of *Triton*.

The results of convolution voltammetry of the main reduction peak are consistent with a loss of a Cl-atom in an equilibrium occurring after a reversible electron transfer and followed by the reductions of both species appearing in the equilibrium. This is also the reduction mechanism on a glassy carbon electrode but the electron transfer on the carbon electrode increases with respect to the mercury electrodes. In addition, the loss of the Cl-atom does not take place on the electrode surface. From the recording of differential capacity–potential curves, it was concluded that picloram is adsorbed on the carbon electrode; but this adsorption is too weak to induce the appearance of prepeak systems.

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REFERENCES

- [1] S. Meru, K. Liber, K. Stonefiel, K. Solomon, G. Stephenson, *Arch. Environ. Contam. Toxicol.* **1990**, *19*, 572.
- [2] M. C. Corredor, J. M. Rodríguez Mellado, *Electrochim. Acta* **2004**, *49*, 1843; M. C. Corredor, J. M. Rodríguez Mellado, *J. Electroanal. Chem.* **2006**, *586*, 98; M. C. Corredor, J. M. Rodríguez Mellado, M. Ruiz Montoya, *J. Electrochem. Soc.* **2006**, *153*, E33.
- [3] J. M. Rodríguez Mellado, M. C. Corredor, L. Pospíšil, M. Hromadová, *Electroanalysis* **2005**, *17*, 979.
- [4] R. Marín Galvín, M. Ruiz Montoya, M. J. Higuera, R. Pérez, J. M. Rodríguez Mellado, *Water, Air, Soil Pollut.* **2005**, *165*, 347.
- [5] M. J. Higuera, M. Ruiz Montoya, J. M. Rodríguez Mellado, *Electrochem. Commun.* **1999**, *1*, 184; M. J. Higuera, M. Ruiz Montoya, R. Marín Galvín, J. M. Rodríguez Mellado, *J. Electroanal. Chem.* **1999**, *474*, 174; R. Ortiz, M. J. Higuera, R. Marín Galvín, J. M. Rodríguez Mellado, *J. Electrochem. Soc.* **2001**, *148*, E419; M. J. Higuera, R. Marín Galvín, J. M. Rodríguez Mellado, M. Ruiz Montoya, *Electrochem. Commun.* **2002**, *4*, 30.
- [6] J. M. Rodríguez Mellado, R. Marín Galvín, M. J. Higuera, M. Ruiz Montoya, in 'Trends in Heterocyclic Chemistry', Ed. Council of Scientific Research Integration, Trivadrurum, India, 2002, vol. 8, pp. 155–167 and refs. cit. therein.
- [7] J. M. Rodríguez Mellado, M. Ruiz Montoya, R. Marín Galvín, *Electroanalysis* **2004**, *16*, 1972.
- [8] M. C. Corredor, J. M. Rodríguez Mellado, M. Ruiz Montoya, *Electrochim. Acta* **2006**, *51*, 4302.
- [9] V. V. Volk, E. C. Y. Kuo, 'Contributing Report from Oregon State University to Western Regional Research Project W-o2: Pesticide Mobility and Degradation in Soil-Water Systems', Denver, Colorado, 1970.
- [10] A. Albert, 'Ionization Constants of Heterocyclic Substances', in 'Physical Methods in Heterocyclic Chemistry', Ed. A. R. Katritzky, Academic Press, New York, 1963.
- [11] M. W. Cheung, J. W. Bigger, *J. Agric. Food Chem.* **1974**, *22*, 202.
- [12] J. M. Rodríguez Mellado, M. C. Corredor, M. Ruiz Montoya, L. Pospíšil, M. Hromadová, *J. Electrochem. Soc.* **2005**, *152*, E379.
- [13] A. J. Bard, L. R. Faulkner, 'Electrochemical Methods: Fundamentals and Applications', John Wiley & Sons, New York, 1980.
- [14] R. H. Wopschall, I. Shain, *Anal. Chem.* **1967**, *39*, 1514.
- [15] E. Laviron, *J. Electroanal. Chem.* **1974**, *52*, 355.
- [16] M. H. Hulbert, I. Shain, *Anal. Chem.* **1970**, *42*, 162.
- [17] C. P. Andrieux, L. Nadjo, J. M. Savéant, *J. Electroanal. Chem.* **1970**, *26*, 147.
- [18] J. C. Imbeaux, J. M. Savéant, *J. Electroanal. Chem.* **1973**, *44*, 169.

- [19] J. M. Savéant, D. Tessier, *J. Electroanal. Chem.* **1975**, *61*, 251; J. M. Savéant, D. Tessier, *J. Electroanal. Chem.* **1975**, *65*, 57; J. M. Savéant, D. Tessier, *J. Electroanal. Chem.* **1977**, *77*, 225.
- [20] K. B. Oldham, *Anal. Chem.* **1972**, *44*, 196; K. B. Oldham, *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 1099.
- [21] G. D. Zoski, K. B. Oldham, P. J. Mahon, T. L. E. Menderson, A. M. Bond, *J. Electroanal. Chem.* **1991**, *297*, 1.
- [22] R. S. Nicholson, I. Shain, *Anal. Chem.* **1964**, *36*, 706.

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