

An Electrochemical Approach to Quantitative Analysis of Herbicides and to the Study of Their Interactions with Soils Components

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1. Introduction

Triazine herbicides are an important group of pesticides. Most of these compounds derived from the heterocyclic shown in Figure 1. It has three nitrogen atoms in positions 1, 3 and 5 and different substituents in position 2, 4 and 6. These triazines have a protonation - deprotonation site on the nitrogen atom labeled 5 in Figure 1. Substituents of different compounds are shown in table 2.

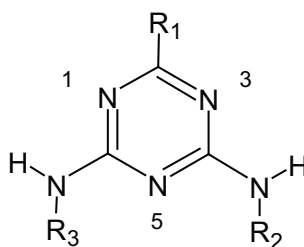


Fig. 1. Chemical structure of s-triazine core, substituent in R_1 : Cl, SCH_3 or OCH_3 ; R_2 and R_3 : hydrocarbons chains.

These herbicides have been extensively applied to pre and post-emergence weed control. Many studies were focused on ecological and health hazards of these compounds and their toxic effects are very well known. For this reason, the use of some triazine pesticides has been banned in some countries or their permitted levels in drinking water is very low, so that analytical procedures for quantitative determination of several triazines, as well as their degradation products, at low levels are often requested.

In this sense, several analytical techniques have been developed, like HPLC (Katsumata et al., 2006), CG-MS, capillary electrophoresis (Frías et al., 2004), solid-phase micro-extraction coupling with GC, LC, ion mobility spectrometry (Garcia Galan et al., 2010; Mohammadi et al., 2009; Sanchez Ortega et al., 2009; Quintana et al., 2001) and with HPLC (Zhou et al.,

2009; See et al., 2010), immunosensors (Bahnd et al., 2005) and multi-biosensor based on immobilized Photosystem II (Touloupakisa et al., 2005; Dong et al., 2009), micellar electrokinetic chromatography (Zhang et al., 2008), tandem techniques (Beale et al., 2009; Tsang et al., 2009; Lacina et al., 2010) cyclic voltammetry (Fuchiwaki et al., 2009; Zapardiel et al., 2000) and differential-pulse polarography (Ignjatovic et al., 1993; Kubo et al., 2008; Vaz et al., 1996) on solid electrodes, photosynthetic electron transport (PET) electrochemical biosensors (Campàs, et al., 2008; Preuss & Hall, 1995), PET colorimetric detection (Brewster & Lightfield, 1993; Shao et al., 2002) and adsorptive stripping voltammetry in dispersed media (Pedredo et al., 1995).

In the last years, the environmental pollution by pesticides has become in a serious problem especially in aquatic ecosystems, due to their heavy use in agriculture and to their persistence. The half-lives of herbicides vary from weeks to several months and, under environmental conditions, they are usually degraded to compounds with better water solubility. Indeed, the most important physicochemical properties of these pesticides and their degradations products are the solubility in water and the capacity to be retained by soils (Aelion & Mathur, 2001; Besse-Hogan et al., 2009). So that, the use of agricultural chemicals requires knowledge of their stability and transformation in the environment as well as their influence on micro-organisms. These s-triazine herbicides and some of their degradation products are used by water and soil microbes as a source of energy (alkyl fragments) and nitrogen (amine fragments) (Lyapchenko et al., 2004). For this reason, not only the development of new sensitive and selective analytical techniques for the determination of s-triazine herbicides and their metabolites in the environment, but also the recognition of their interactions with different elements, especially with heavy metals cations and organic compounds present in soils, are important problems in modern s-triazine chemistry. The study of complex formation or adsorption behavior between herbicides and cations or organic molecules contained in soils is an important topic because it determines pesticide mobility, its bioavailability and its effectiveness. Regarding to the interaction with inorganic species, Al(III) is a cation present in most soils, and several authors have studied its complexes with different herbicides in aqueous solutions or in complex model systems, which closely simulate those found in soils by using pure montmorillonite or montmorillonite covered by different amounts of OH-Al species (chlorite-like complexes) as adsorbents (Sannino et al., 1999). Several methods were employed in these investigations: macroscopic and molecular scale techniques, potentiometric titration data combined with EXAFS, ATR-FTIR and NMR, as well as spectroscopic data (Jonsson, 2007).

The present chapter is focused in the progress made in the s-triazine quantification as well as in the study of their interactions with inorganic compounds of soils employing electrochemical methods applied at the interface between two immiscible electrolyte solutions (ITIES) (Juarez & Yudi, 2003; Juarez & Yudi 2008; Juarez & Yudi 2009).

The interface between two immiscible electrolyte solutions and the transport of different ions across it are an important branch of electrochemistry because of their importance in the examination of heterogeneous kinetics and potential analytical applications (Reymond et al., 2000). This methodology is used as an appropriate electroanalytical technique for quantitative determination of organic ions. The possibility of working in an oil/water system overcomes problems such as the low solubility of many organic compounds, like the case of s-triazines, in water. Moreover, the traces quantification of pesticides in different kind of samples requires pre-concentration techniques. In the past few years, new

techniques were developed like liquid-liquid extraction, solid phase extraction, molecular imprinted polymers and carbon nanotubes, among others. These pre-concentration procedures were employed before the quantification of the pesticide, coupled to different techniques like GC-MS, capillary electrophoresis, non-aqueous capillary electrophoresis and micellar electrokinetic capillary chromatography (Katsumata et al., 2006; Sambe et al, 2007; Zhou et al., 2006; Carabias-Martínez et al, 2006; Hu et al., 2009; Pinto et al., 2010; See et al., 2010). In this sense, the use of a combined procedure consisting in a previous pre-concentration stage, followed by square wave voltammetry at a water/1,2-dichloroethane interface has achieved to improve the detection limit for s-triazines quantification (Juarez & Yudi, 2009). The pre-concentration of the analyte in the organic phase is possible due to its high solubility and partition coefficient in this solvent.

On the other hand, voltammetry at ITIES has proven to be a valuable tool to elucidate the stoichiometry of complex formation (Reymond et al., 1998; O'Dwyer & Cunnane et al., 2005; Azcurra et al., 2003; Caçote et al., 2004; Rahman et al., 2001; Yudi et al., 1992) and to identify and evaluate successive complex formation at the interface (Kakiuchi & Senda, 1991; Kakiuchi, 1993; Reymond et al., 1998). With the purpose of contributing to the knowledge of the interaction between Prometryne and soils components, the complex formation of the herbicide PROM with Al(III) cation at the water / 1,2 - dichloroethane interface, has been studied and the results are presented in this chapter (Juarez & Yudi, 2008).

2. Methodology

2.1 Liquid-liquid Interfaces

The interface between two immiscible electrolytes is one with its own dynamics. The structure of double layer in these interfaces has been studied since 1939. Over the years, the information obtained was used to develop a clearly defined model of the liquid-liquid interface (Girault, 1987). Surface tension measurements (Girault & Schiffrin, 1983) and capacitance (Samec et al., 1983) provides access to important interfacial parameters. The model proposed from these results, considers an interfacial area on which the molecules of both solvents are mixed. The penetration of ions in the solvent mixture zone (ZMS) depends on their hydrophobicity or hydrophilicity (Girault & Schiffrin, 1984). Figure 2 schematizes two immiscible solutions (α and β) with an ion X^{z+} in common. Under these conditions a potential difference is generated determined by the Nernst-Donnan equation (Koryta, 1979):

$$\Delta_{\alpha}^{\beta} \phi = \left[\mu_{X^{z+}}^0(\alpha) - \mu_{X^{z+}}^0(\beta) \right] / z_X F + \frac{RT}{z_X F} \ln \left[\frac{a_{X^{z+}}^{\alpha}}{a_{X^{z+}}^{\beta}} \right] \quad (1)$$

$$\Delta_{\alpha}^{\beta} \phi = - \Delta G_{tr, X^{z+}}^{0, \alpha \rightarrow \beta} / z_X F + \frac{RT}{z_X F} \ln \left[\frac{a_{X^{z+}}^{\alpha}}{a_{X^{z+}}^{\beta}} \right] \quad (2)$$

where ϕ is the internal potential, $\mu_{X^{z+}}^0(\alpha)$ and $\mu_{X^{z+}}^0(\beta)$ are the standard chemical potentials, z_X is the ion charge and $a_{X^{z+}}^{\alpha}$ and $a_{X^{z+}}^{\beta}$ are the X^{z+} activities in both phases α and β , respectively. $\Delta G_{tr, X^{z+}}^{0, \alpha \rightarrow \beta}$ is the Free Energy difference of solvation for the X^{z+} ion in α and β , respectively, which is related to the standard transfer potential of X^{z+} ion according to equation 3.

α	β
B_1A_1	B_2A_2
XA_1	XA_2

Fig. 2. B_1A_1 and B_2A_2 : base electrolytes in α and β phases, respectively. X^{z+} : transferable cation between both phases.

$$\Delta_{\alpha}^{\beta} \varphi_{x^{z+}}^o = - \frac{\Delta G_{tr, X^{z+}}^{o, \alpha \rightarrow \beta}}{z_x F} \quad (3)$$

In absence of current flux, the equilibrium condition is established and the potential difference, $\Delta_{\alpha}^{\beta} \varphi_{eq}$, is determined by equation 1. If a potential difference greater than the equilibrium potential is applied, by an external source, to the system, two processes occur: the charging of the double layer and the ion transfer through the interface. Figure 3 shows the voltammetric profiles obtained when a linear potential sweep is applied at the aqueous/organic interface in presence and absence of a semi hydrophobic X^{z+} cation. The transfer of base electrolyte, between the two phases, limits the potential window (grey line). Within this potential window, the interface behaves as an ideal polarizable electrode. The presence of semi hydrophobic X^{z+} ions, in the system, gives rise to positive and negative current peaks when their transfer from aqueous to organic phase, and vice versa respectively, occurs at potential values within the limits of potential window, as can be seen in black line in Figure 3.

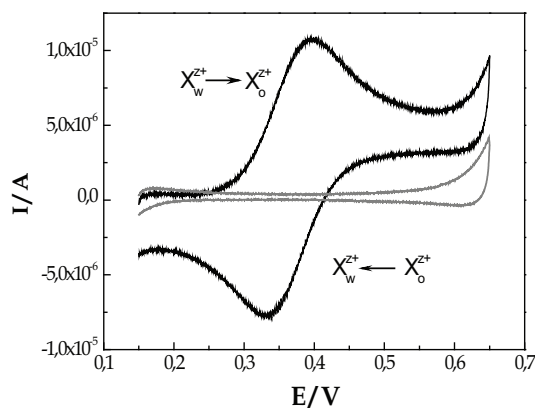


Fig. 3. Voltammetric profiles obtained when a linear potential sweep is applied at the interface between two immiscible solutions: (grey) Base electrolytes present in both phases; (black) base electrolytes and a semi hydrophobic cation. w : aqueous phase, o : organic phase.

2.2 Charge transfer reactions between liquid / liquid interfaces

One of the characteristics of the ITIES is the diversity of charge transfer reactions which can be studied by electrochemical methodologies (Girault, 1993). These charge transfer reactions can be classified into three main categories:

- Direct ion transfer,
- Assisted ion transfer,
- Electron transfer.

2.2.1 Direct ion transfer

In this case, an ion present in the aqueous phase is transferred to the organic phase (or vice versa) according to equation 4, favored by polarizing the interface.



From a phenomenological point of view, an ion transfer reaction includes three major steps (Reymond, 2000):

1. mass transfer from the bulk of one phase to the interface (mainly diffusion),
2. electrochemical ion transfer reaction,
3. mass transfer in the other phase away from the interface.

When a linear potential sweep is applied and a reversible diffusion controlled ion transfer from the aqueous to the organic phase occurs, the current - time dependence is given by (Nicholson & Shane, 1964; Bard & Wiley, 1980):

$$I(\tau) = zFAc_X^{w*} D_X^{w1/2} \left(\frac{zFv}{RT} \right)^{1/2} \pi^{1/2} \chi(\tau) \tag{5}$$

where c_X^{w*} is X^{z+} concentration in the bulk of aqueous solution, A is the interfacial area in cm^2 , D_X^w is the diffusion coefficient in aqueous phase, $\tau = (zF/RT)vt$, t is time, v is the sweep rate in Vs^{-1} , z is the ion charge F , R and T are the Faraday constant, the universal constant and the temperature, respectively, and $\chi(\tau)$ is the current function. When the current signal reaches a maximum value, $\pi^{1/2} \chi(\tau)$ is equal to 0.4463 and the peak current is proportional to X^{z+} concentration, to the square root of D_x and v , according Randles-Sevcik equation (Bard & Wiley, 1980):

$$I_p = 0.4463zFAc_X^{w*} D_X^{w1/2} \left(\frac{zFv}{RT} \right)^{1/2} \quad 25^\circ C \tag{6}$$

The peak potential, $\Delta\phi_p$, is related to standard transfer potential according to equation 7:

$$\Delta\phi_p - \Delta\phi_{1/2} = \Delta\phi_p - \Delta\phi^{o'} + \frac{RT}{zF} \ln \left(\frac{D_w}{D_o} \right)^{1/2} \tag{7}$$

Where $\Delta\phi_{1/2}$ is the half-wave polarographic potential and D_w and D_o are the diffusion coefficients of X^{z+} in both phases.

2.2.2 Facilitated ion transfer

In the case of a highly hydrophilic ion, its transfer from the aqueous to the organic phase does not occur within the potential window due to the high positive value of free energy for this process. However, this transfer can occur when a ligand present in the organic phase

acts as a complexing agent for the ion. In this way, the ion-ligand complex formation in organic phase, decreases the free energy for ion transfer.

Depending on the different concentration ratios and association constants, different types of facilitated ion transfer reactions can be envisaged, as described below (Girault, 1993).

ACT (aqueous complexation followed by transfer): Complex formation occurs in aqueous phase, previous to charge transfer.



TOC (transfer followed by complexation in the organic phase): Complex formation occurs in organic phase after the ion transfer.



TIC/TID (transfer by interfacial complexation/dissociation): Heterogeneous charge transfer occurs by interfacial complex formation or dissociation.



Equation 11 describes the reversible half-wave potential for a facilitated transfer process when the following conditions are fulfilled:

- $c_L < c_{X^{z+}}$ (the ligand concentration is lower than cation concentration).
- High Partition coefficient for the ligand, so that its aqueous phase concentration is negligible.
- High complex formation constant, so that the free ion concentration in organic phase is negligible (Girault, 1993).

$$\Delta_o^w \phi_{1/2}^{tr} = \Delta_o^w \phi_{X^{z+}}^0 + \left(\frac{RT}{z_X F} \right) \ln \left[\frac{D_{L(o)}}{D_{XL_s^{z+}(o)}} \right]^{1/2} + \left(\frac{RT}{z_X F} \right) \ln \left[\frac{K_{XL_s^{z+}}^o}{c_{X^{z+}}^w} \right] \quad (11)$$

Where $\Delta_o^w \phi_{X^{z+}}^0$ is the standard transfer potential of free X^{z+} ion, D_L and $D_{XL_s^{z+}}$ are the diffusion coefficients of ligand and complex, respectively in organic phase, $K_{XL_s^{z+}}^o$ is the complex constant formation in organic phase and $c_{X^{z+}}^w$ is the ion free concentration in aqueous phase. This expression allows obtaining $K_{XL_s^{z+}}^o$ from the variation of $\Delta_o^w \phi_{1/2}^{tr}$ with X^{z+} concentration in water.

Moreover, equation 12 relates the half-wave potential with cation and ligand concentration, in aqueous and organic phase respectively. From the slope values of $\Delta\phi_{1/2}$ vs $\ln c_L$ plots, it is possible to obtain the complex stoichiometry, providing $c_{X^{z+}}^w$ is constant (Homolka et al., 1982; Samec et al., 1982):

$$-\frac{RT}{zF}(s-1)\ln c_L^o = \Delta\phi_{1/2} - \Delta\phi^o + \frac{RT}{zF}(\ln c_{X^{z+}}^w + \ln s) + \frac{1}{2} \ln \frac{D_{L(o)}}{D_{X^{z+}(w)}} - (s-1)\ln 2 \quad (12)$$

Where s is the complex stoichiometry and the other parameters have the same meaning. The $i /$ time variation for a facilitated transfer process is given by (Homolka et al., 1982):

$$I(\tau) = s^{-1} z F A C_L^o D_L^{1/2} \left(\frac{z F v}{RT} \right)^{1/2} \chi(\tau) \tag{13}$$

The current function takes different values depending on the stoichiometry of the complex formed. Table 1 resumes the parameters of this function at the peak potential.

Parameter	Stoichiometry (cation: ligand)		
	1:1	1:2	1:3
$z(\Delta\phi_{P1} - \Delta\phi_{1/2}) / V$	0.02825	0.0710	0.0988
$z(\Delta\phi_{P2} - \Delta\phi_{1/2}) / V$	-0.03075	-0.0161	-0.0135
$z \Delta\phi_P / V$	0.0590	0.0871	0.1123
χ_{P1}	0.4463	0.3533	0.3033
χ_{P2}	-0.2760	-0.2206	-0.1910
$ \chi_{P2} / \chi_{P1}$	0.618	0.625	0.630

Table 1. Parameters of adimensional current function, $\chi(\tau)$ at the peak potential calculated for a reversible charge transfer and different complex stoichiometry, P1 and P2 correspond to positive and negative peaks respectively.

2.2.3 Electron transfer

The first evidence of electron transfer at liquid/liquid interfaces were found by Guainazzi *et al* (Girault, 1993; Guainazzi, 1975). They could reduce Cu(III) in aqueous phase to Cu(0) using hexacarbonylvanadate tetrabutylammonium in 1,2- dichloroethane. Moreover, Samec *et al.* (Samec et al., 1977) measured the oxidation current of ferrocene in nitrobenzene by the ferric/ferrous reduction in aqueous phase. Also, electron interfacial transfer has been applied for the electropolymerization in liquid/liquid interfaces, with the purpose of studying the polymerization mechanism, permeability of polymers to ions and new synthetic routes. (Gorgy et al., 2002; Cheng & Corn, 1999; Rieger et al., 2006; Johans et al., 2002; Marecek et al., 2005; Maeda et al., 2001; Cheng et al., 2000; Fantini et al., 2003)

The equation describing the electron transfer process when hemicouples are present at each phase (α and β), is given by:



2.3 Voltammetric techniques

A briefly explanation of the basic voltammetric techniques, cyclic voltammetry (CV) and Square Wave Voltammetry (SWV), applied to liquid/liquid interfaces is carried out below.

The polarization of liquid/liquid interfaces requires the use of four electrodes system similar to the electrochemical cell shown in Figure 4.

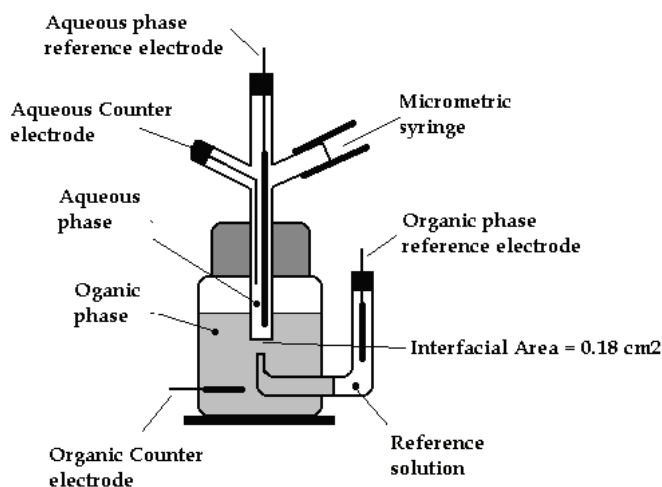
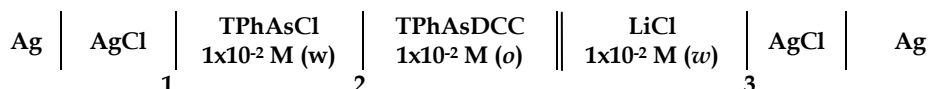


Fig. 4. Glass cell employed for electrochemical measurements.

In this system two Ag/AgCl reference electrodes are immersed in each phase to control the applied potential, ΔE , and two Pt counter electrodes allow the current flowing along the system.

In this way, the electrochemical cell containing only the base electrolytes, can be schematized as follows:



TPhAsDCC is tetraphenyl arsonium dicarbollycobaltate salt employed as organic base electrolyte in 1,2-dichloroethane and TPhAsCl is tetraphenyl arsonium chloride salt dissolved in water and employed as reference solution for the Ag/AgCl electrode corresponding to the organic phase. The contact between these two solutions generates an ideal non-polarizable interface (labeled 2 in the scheme) and a potential difference ($\Delta\phi_{INP}$) dependent of TPhAs⁺ concentration in both phases is established.

The Galvani potential difference ($\Delta_o^w\phi$) at the o/w interface is related to the applied potential (ΔE) by the following equation:

$$\Delta_o^w\phi = \Delta E + \Delta E_{ref}^w - \Delta E_{ref}^o + \Delta\phi_{inp} \quad (16)$$

Where ΔE_{ref}^w and ΔE_{ref}^o are the potential differences at interfaces 3 and 1 in the cell scheme and $\Delta\phi_{INP}$ is the difference potential at the non-polarizable interface 2.

The potential-time profiles for the electrochemical techniques employed in this case are shown in Figure 5.

Cyclic and SW voltammograms were recorded using an Autolab (Eco-Chemie, Utrecht, Netherlands) equipped with a PSTAT 30 potentiostat and the GPES 4.3 software package. Typical SW instrumental parameters, unless otherwise stated, were: square-wave frequency $f=8-40\text{Hz}$, square-wave amplitude $E_{SW}=35\text{ mV}$ and scan increment $dE=3\text{mV}$.

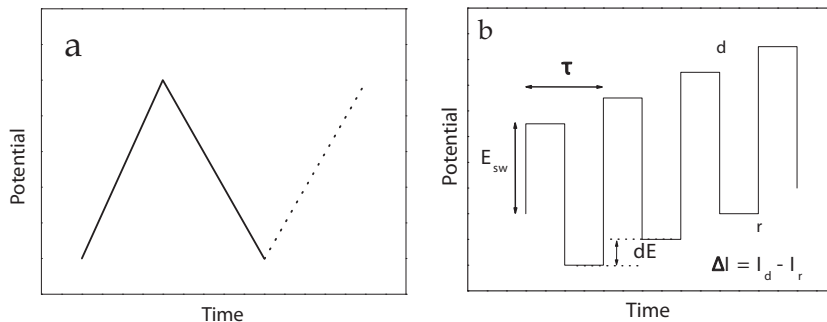


Fig. 5. a- Potential –time profile for Cyclic Voltammery. b- Potential-time profile for Square Wave Voltammery.

The base electrolyte solutions were 1.0×10^{-2} M LiCl (Merck p.a.) in ultrapure water and 1.0×10^{-2} M tetraphenyl arsonium dicarbollyl cobaltate (TPhAsDCC) or tetrapentyl ammonium tetrachlorophenyl borate (TPnATPhB) in 1,2-dichloroethane (DCE, Dorwill p.a.). The pH of the aqueous phase was adjusted within the range of 1.50 – 8.00 by addition of HCl (Merck p.a.) and LiOH (Merck p.a.) respectively. All the herbicides employed were of analytical grade. Table 2 resumes the physicochemical properties of the s-triazines studies.

Compound	Substituent			MW g.mol ⁻¹	pK _a	Water solubility mg.L ⁻¹	log P
	R1	R2	R3				
ATR	Cl	C ₂ H ₅	C ₃ H ₇	215.68	1.68	30	2.70
PRO	Cl	C ₃ H ₇	C ₃ H ₇	230.09	1.85	5	2.91
PROM	SCH ₃	C ₃ H ₇	C ₃ H ₇	241.37	4.05	33	3.34

Table 2. Physicochemical parameters for s - triazines. ATR: Atrazine. PRO: Propazine. PROM: Prometryne

3. Results

3.1 Electrochemical behavior of Triazines

As first step, the study of electrochemical behavior of s-triazines herbicides at a water/DCE interface was performed. Figure 6 shows the voltammetric response for the three s-triazines studied: Atrazine (ATR), Propazine (PRO) and Prometryne (PROM). In all cases a reversible ion transfer is observed. The positive peak potential, E_p^+ and the difference peak potential, $\Delta E_p = E_p^+ - E_p^- = 0.060$ V, were constant with sweep rate, v . The positive peak current, I_p^+ , is proportional to $v^{1/2}$, as expected for a reversible diffusion controlled mechanism. The differences in currents values observed in the figure would be arising from different equilibrium concentrations of each species at the present pH conditions. Taking into account the partition coefficient (P) and acid constant (K_a^w) values for the herbicides (table 2) and pH conditions, it is possible to obtain the fraction of the protonated, HX^+ , and neutral species, X , of the herbicides ($\alpha_{HX^+}^w, \alpha_X^w$) in water and the fraction of neutral species into the organic

phase (α_X^o). For the present pH values (0.80 and 0.88), α_X^o is equal to 0.983 and 0.987 for ATR and PRO respectively. In the case of PROM $\alpha_X^o = 0.686$ and $\alpha_{HX^+}^{w} = 0.313$ at pH 1.05. In this case, both species coexist at this pH and different transfer mechanisms can take place which determine the current values.

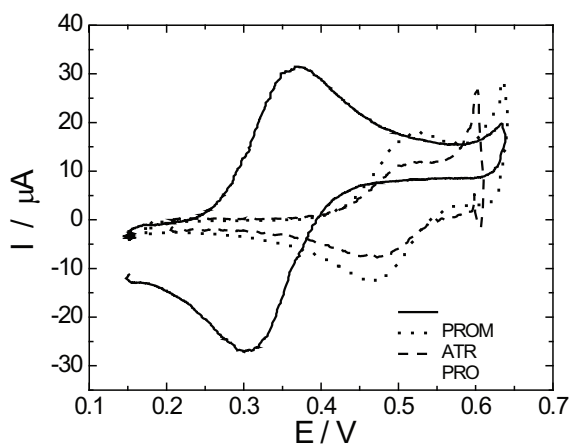


Fig. 6. Cyclic voltammogram obtained at $v = 0.050 \text{ Vs}^{-1}$ for ATR, PRO and PROM. Aqueous phase composition (apc): $1.00 \times 10^{-2} \text{ M LiCl} + 5.00 \times 10^{-4} \text{ M s-triazine}$ (— PROM, pH = 1.05; --- PRO, pH = 0.88; ATR, pH = 0.80). Organic phase composition (opc): $1.00 \times 10^{-2} \text{ M TPhAsDCC}$. Reprinted from *Electroanalysis* 15(2003)1481, A.V. Juarez and L.M.Yudi, Copyright (2003) with permission from Wiley.

There are two possible mechanisms that could be responsible for the voltammetric response observed as described by eq. 4 and 10: direct transfer of the protonated herbicide or H^+ transfer from aqueous phase, facilitated by the herbicide present in the organic phase. As can be deduced from the eq. mentioned above, the dependence of peak potential and current with experimental conditions (such as herbicide concentration, pH) allows the determination of the mechanism. In that sense, the dependence of $\Delta_o^w \phi_{1/2}^{tr}$ and I_p with both, herbicide concentration and pH was analyzed.

A facilitated proton transfer mechanism (reaction 10) is favored when the species X predominates over HX^+ (i.e. at $\text{pH} \gg \text{p}K_a^w$ conditions) and when this neutral species is highly soluble in organic phase. In this way, the necessary condition under which the facilitated proton transfer occurs can be written as (Homolka et al., 1984):

$$K_a^w \cdot P_X / c_{H^+}^w \gg 1 \quad (16)$$

where $c_{H^+}^w$ is the bulk concentration of the proton in the aqueous solution. If $c_{H^+}^w$ is higher than that of the neutral triazine (X) in the organic phase, the charge transfer process is controlled by the diffusion of X towards the interface. In this case, the reversible half-wave transfer potential, $\Delta_o^w \phi_{1/2}^{tr}$, is given by equation 11 (Homolka et al., 1984). Then, a linear variation of $\Delta_o^w \phi_{1/2}^{tr}$ with pH (slope = 0.059 V) is predicted for a facilitated proton transfer mechanism provided the condition $c_{H^+}^w \gg c_X^o$ is fulfilled.

Figure 7 shows the variation of $\Delta_o^w \phi_{1/2}^{tr}$ with pH for ATR (a), PRO (b) and PROM (c) at several sweep rates. In all systems, the herbicide was added to the aqueous phase. In the case of ATR and PRO, a linear dependence is observed in the whole range of pH analyzed. This is an indication that facilitated proton transfer is occurring in both cases, although the s-triazines were dissolved in aqueous phase, at $\text{pH} < \text{p}K_a^w$. Under these experimental conditions, a direct transfer of HX^+ species from the aqueous to the organic phase would be expected. Nevertheless, according to equation 16, the condition is fulfilled in the whole pH range studied. So, whatever the phase in which ATR or PRO are dissolved, the partition equilibrium favors the transfer of the neutral species to the organic phase. From this phase, they act as proton acceptor and facilitate the transfer to the organic phase (reaction 10). From the intercept value in Fig. 7 and equation 11, the dissociation constant of protonated herbicide in the organic solvent, K_{XIZ}^o , can be calculated. In this way, $K_a^o = 4.60 \times 10^{-9}$ and 7.03×10^{-9} were obtained for ATR and PRO, respectively. These values are approximately 10^6 folds lower than those for aqueous phase, as expected due to the low permittivity of organic media. In the case of PROM, the behavior is quite different, because it has a K_a^w value lower than the other herbicides. For $\text{pH} > 2.00$ a facilitated proton transfer is observed, similar to the case of ATR and PRO. While an inflection is observed in Figure 7 at $\text{pH} 2.00$, below this value, $\Delta_o^w \phi_{1/2}^{tr}$ is independent of pH demonstrating a change in the transfer mechanism.

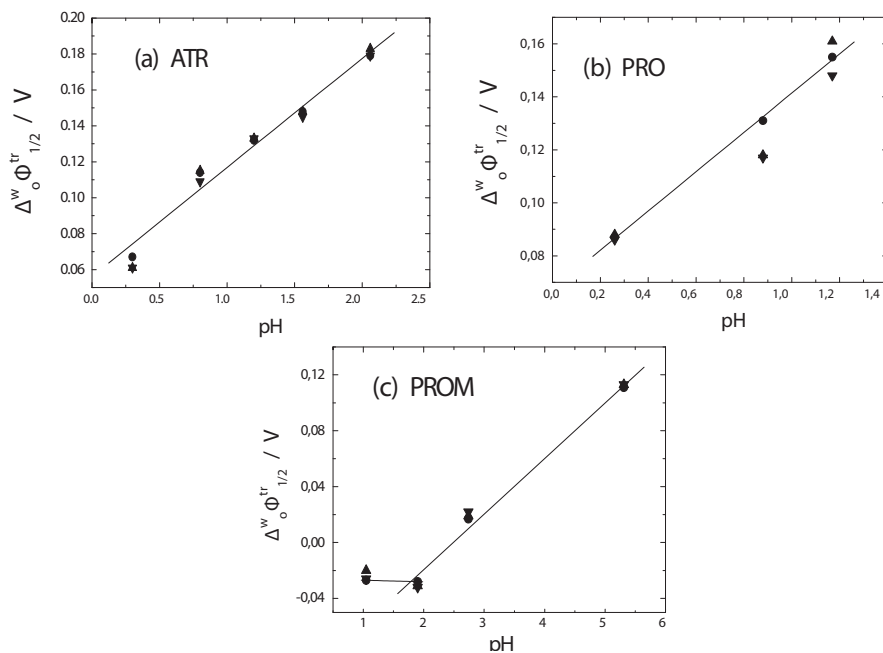


Fig. 7. Plot of $\Delta_o^w \phi_{1/2}^{tr}$ vs. pH for s-triazines: (a) ATR; (b) PRO; (c) PROM. $\Delta_o^w \phi_{1/2}^{tr}$ values were obtained at different sweep rate: (▼) 0.010 Vs⁻¹; (●) 0.050 Vs⁻¹; (▲) 0.100 Vs⁻¹. apc: 1.00×10^{-2} M LiCl + 5.00×10^{-4} M s-triazine. opc: 1.00×10^{-2} M TPAsDCC. Reprinted from Electroanalysis 15(2003) 1481, A.V. Juarez and L.M.Yudi, Copyright (2003) with permission from Wiley.

On the other hand, from plots of I_p^+ vs triazine concentration is possible to obtain the diffusion coefficients of the herbicides in the organic phase, as predicted by eq. 13, if a linear relationship is obtained. For this purpose, the experimental conditions were selected to ensure that the facilitated proton transfer is the occurring mechanism, so that, in all cases the pH values ensure the condition of $\alpha_X \cong 1$. Figure 8 shows the plots of I_p^+ vs concentration obtained for the three herbicides. As can be seen, a linear relationship is obtained with correlation coefficients 0.999, 0.992 and 0.996 for ATR, PRO and PROM respectively, in the concentration ranges $2.50 \times 10^{-5} \text{ M} < c_{\text{Triaz}} < 2.50 \times 10^{-4} \text{ M}$ (PRO and PROM) and $2.50 \times 10^{-5} \text{ M} < c_{\text{Triaz}} < 5.00 \times 10^{-4} \text{ M}$ (ATR). From the slope values obtained from these curves, D_X values equal to 1.56×10^{-6} , 8.83×10^{-7} and $2.90 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ were calculated for ATR, PRO and PROM respectively (equation 13).

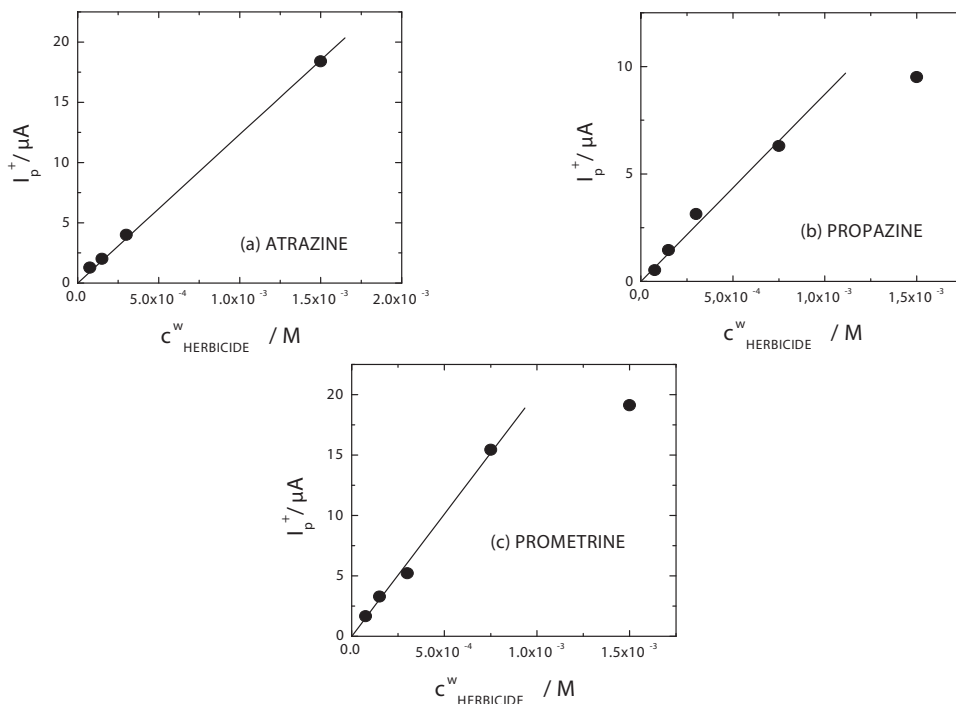


Fig. 8. Plot of I_p^+ vs. triazine concentration: (a) ATR, pH 1.20; (b) PRO, pH 1.20; (c) PROM, pH 2.00. $v = 0.050 \text{ V s}^{-1}$. Reprinted from *Electroanalysis* 15(2003) 1481, A.V. Juarez and L.M.Yudi, Copyright (2003) with permission from Wiley.

The results obtained demonstrate that quantitative analysis of ATR and PRO can be carried out at a liquid – liquid interface provided these species partition in the organic phase and the pH of aqueous phase satisfy the condition $c_{H^+}^0 \gg c_X^0$. In this case, facilitated proton transfer is the electrochemical process responsible for the faradaic current, which is proportional to s - triazine concentration in organic phase. For PROM quantification two experimental conditions could be used: at $\text{pH} \geq 2.00$, peak current is proportional to PROM concentration in organic phase as described above for ATR and PRO, while at $\text{pH} < 2.00$

protonated PROM in aqueous phase and neutral PROM in organic phase coexist, as can be expected for the fraction values calculated. Then, both processes could be occurring and determining the peak current value. For this reason, the latter experimental condition is not the best to carry out PROM quantification.

3.2 Prometryne quantification

From the results shown in the previous section, employing cyclic voltammetry technique, the detection limit (DL) obtained for the herbicides studied was 2.50×10^{-5} M. This value is not lower enough for trace quantification. In that sense a more sensitive electrochemical technique is required. For these purpose, square wave voltammetry (SWV) experiments were carried out at liquid/liquid interfaces (Juarez et al., 2005).

As mentioned above, PROM facilitates proton transfer from the aqueous to the organic phase under the condition $\text{pH} \geq 2.00$. PROM has a high partition coefficient, $\log P = 3.34$, which promotes the partition equilibrium to the organic phase where it acts as a proton acceptor.

3.2.1 Calibration curves before and after pre-concentration procedure

The calibration curve of PROM before pre-concentration experiments was plotted employing ΔI_p values from SWV experiments at $f = 8$ Hz and $\text{pH} 2.50$. From this curve it was possible to determine a linear range from 1.00×10^{-6} M to 5.00×10^{-4} M with a correlation coefficient of 0.9999. The detection limit (DL) reached under these experimental conditions was 1.50×10^{-6} M, determined from standard deviation of a set of three replicates.

The DL value obtained is lower than that employing I_p values from cyclic voltammetry experiments, but it is not lower enough to determine trace levels of PROM. For this reason, a pre-concentration treatment was developed. This procedure consists in concentrate the herbicide in the organic phase before the electrochemical measurements were performed. For this purpose, 500.00 mL of aqueous phase containing different concentration of PROM was stirred with three aliquots of 10.00 mL of DCE. The resulting 30.00 mL of organic solution was evaporated at room temperature in a rotary evaporator to reduce the volume to 2.0 or 3.0 mL. Then, 5.00 mL of solution was prepared with this extract and TPhAsDCC adding DCE up to the final volume. The pH of herbicide aqueous solution was fixed at 8.00 to ensure that the neutral form of the analyte predominates, and to favor a complete extraction to the organic phase. The concentration range was 1.0×10^{-8} M to 2.40×10^{-7} M in aqueous solution (corresponding to a range of 1.00×10^{-6} M to 2.40×10^{-5} M in organic phase after the extraction). The variation of ΔI_p with the herbicide concentration in aqueous phase is shown in Figure 9. A linear range from 8.0×10^{-8} M to 2.4×10^{-7} M was obtained. The correlation coefficient was 0.9858 and $\text{DL} = 1.0 \times 10^{-7}$ M was determined from standard deviation of a set of three replicates. As can be seen, the pre-concentration treatment allows an increase of the analytical signal.

It is important to remark that the extraction procedure of the herbicide not only decreases the detection limit, but also allows the possibility of purification of the samples. This advantage can be very useful in the analysis of real samples, because they could have interferents or other hydrophilic contaminants which would not transfer to the organic phase. Thus, it is possible to isolate the herbicide from the real aqueous matrix to the organic phase for its quantification.

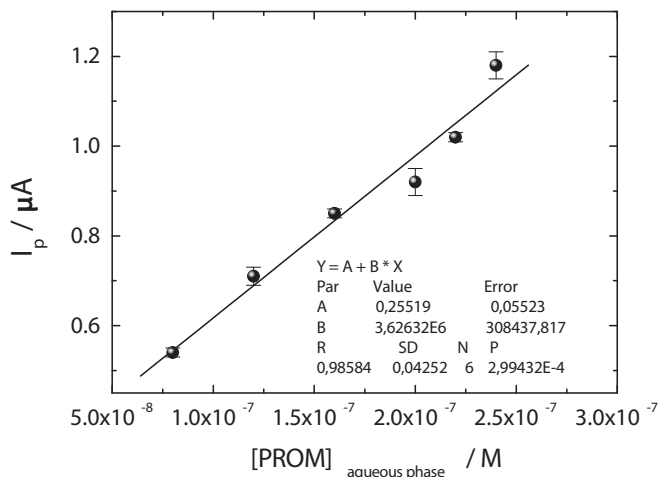


Fig. 9. Calibration curve of PROM employing pre-concentration treatment. apc: LiCl 1.00×10^{-2} M, pH 2.00; opc: TPhAsDCC 1.00×10^{-2} M + x PROM. This organic phase was obtained from pre-concentration of PROM aqueous solutions in the concentration range: 1.0×10^{-8} M - 2.4×10^{-7} M (showed in x-axis). SWV parameters: $f = 8$ Hz, $E_{sw} = 35$ mV, $dE = 3$ mV. Reprinted from *Electroanalysis* 21(2009)767, A.V. Juarez and L.M.Yudi, Copyright (2009) with permission from Wiley.

3.2.3 Standard addition method

The addition of standards was carried out on a pre-concentrated sample obtained from an aqueous solution containing 1.0×10^{-8} M PROM. Different aliquots of a 2.00×10^{-3} M PROM solution to the organic pre-concentrated phase were made. Figure 10 shows the square wave voltammograms obtained after the additions of the standard solution. The ΔI_p values obtained after each addition are shown in Figure 11 as a function of PROM added concentration. The correlation coefficient obtained from linear regression was 0.997. From x -axis intercept, a 1.0×10^{-6} M initial concentration in the organic pre-concentrated phase was determined. Certainly, this concentration value corresponds to PROM 1.0×10^{-8} M in the original aqueous phase. So that, these results allow concluding that standard addition method is appropriated for the quantification of PROM in pre-concentrated samples.

3.3 Prometryne-Al(III) interactions

The interaction between herbicides and soils compounds affect the adsorption, transport and degradation processes and, in consequence the fate of the herbicides in the environment. Al(III) is a cation present as important inorganic component of soils, so that its interaction with PROM was analyzed employing cyclic voltammetry at liquid/liquid interfaces.

As mentioned in methodology section, equations 11 and 12 relate the transfer potential with stoichiometry and complex formation constant. The analysis of transfer potential and current allows elucidating the charge and stoichiometry of the complex formed (Homolka et al., 1982; Samec et al., 1982; Reymond et al., 1998; Iglesias et al., 1998; O'Dwyer & Cunnane, 2005; Katano et al., 2000; Azcurra et al., 2003; Dassie et al., 1999; Caçote et al., 2004; Rahman et al., 2001; Yudi et al., 1992) as well as to obtain thermodynamic (Samec et al., 1982;

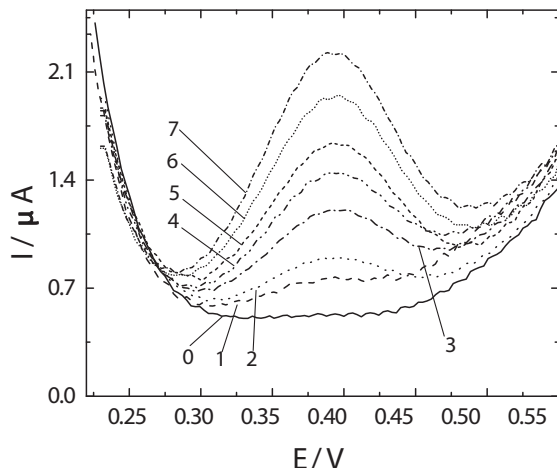


Fig. 10. SWV voltammetric profiles obtained after standard addition of a PROM 2.00×10^{-3} M solution to the organic pre-concentrated phase. apc: LiCl 1.00×10^{-2} M, pH 2.00, f 8 Hz. opc: TPhAsDCC 1.00×10^{-2} M + PROM (obtained by pre-concentrating a 1.0×10^{-8} M PROM aqueous solution), with the following aggregates: 0: 0 μ L; 1: 10 μ L; 2: 20 μ L; 3: 30 μ L; 4: 40 μ L; 5: 50 μ L; 6: 60 μ L; 7: 70 μ L. SWV parameters: f = 8 Hz, E_{sw} = 35 mV, dE = 3mV. Reprinted from *Electroanalysis* 21(2009) 767, A.V. Juarez and L.M.Yudi, Copyright (2009) with permission from Wiley.

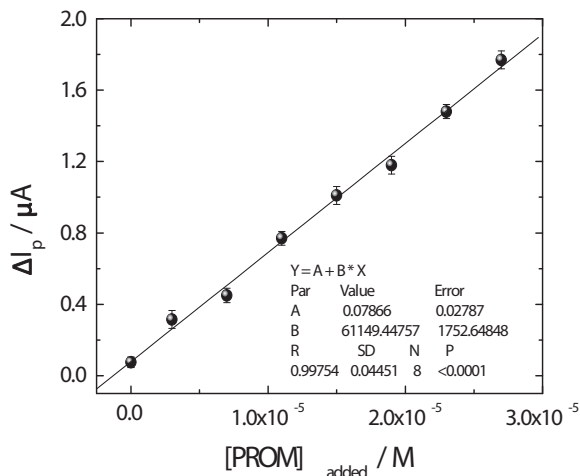


Fig. 11. Variation of ΔI_p with PROM concentration for standard addition experiments. The experimental conditions are the same than those in Fig. 8. Reprinted from *Electroanalysis* 21(2009) 767, A.V. Juarez and L.M.Yudi, Copyright (2009) with permission from Wiley.

Reymond et al., 1998; Iglesias et al., 1998; Caçote et al., 2004; Yudi et al., 1992; Koryta, 1979; Ferreira et al., 2006; Dassie & Baruzzi, 2002) and kinetic data (Samec et al., 1982; Seno et al., 1990; Sabela et al., 1994; Beatti et al., 1995; Shao & Mirkin, 1997, Homolka et al., 1984) of

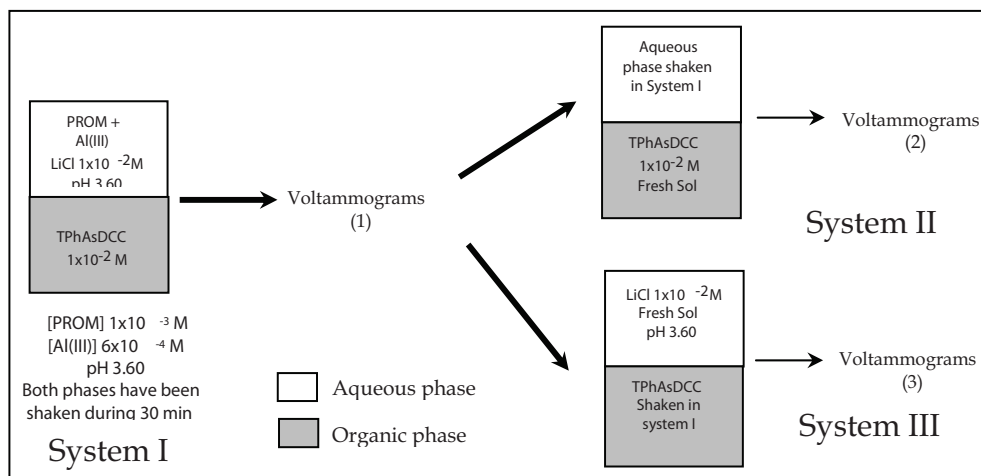
facilitated ion transfer. The global process of the X^{z+} ion transfer is given by equation 10. In this way, experiments changing ion and ligand concentration can be used for studying transfer mechanism as well as charge and stoichiometry of the complex and also, the complex formation constant.

With the aim of elucidating the complex formed between Al and PROM, experiments at different pH values: 1.50, 3.60, 4.50 and 5.30 were carried out. The relation Al:PROM was 3:1 in all cases. From the analysis of voltammetric response obtained at these pH values it was concluded that a competition between Al(III) and H^+ takes place: at low pH values, H^+ transfer prevails while at high pH values the facilitated transfer of Al(III) is observed.

When the Al:PROM relation changes, the complex formed in the organic phase depends on the cation and PROM concentration. Thus, depending on the PROM concentration, two different processes were observed: when the ligand concentration is lower than the concentration of the both cations, H^+ transfer is the only process observed at pH values between 1.50 and 4.50. It is worthwhile to note that even when the Al(III) concentration is higher than the H^+ concentration, H^+ transfer prevails. This fact indicates a higher formation constant value for $HPROM^+$ with respect to Al(III)-PROM. On the other hand, if the ligand concentration is higher than the H^+ and Al(III) concentrations, the transfer of both cations is observed. In this case, the voltammograms obtained shows two overlapped waves. One of the process is due to Al(III) transfer facilitated by PROM.

3.3.1 Determination of the Al(III) transfer mechanism

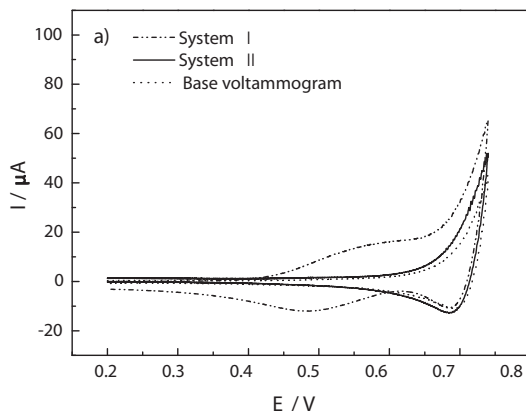
Scheme 1 shows one of the experiments carried out with the purpose to establish the transfer mechanism of the Al:PROM complex.



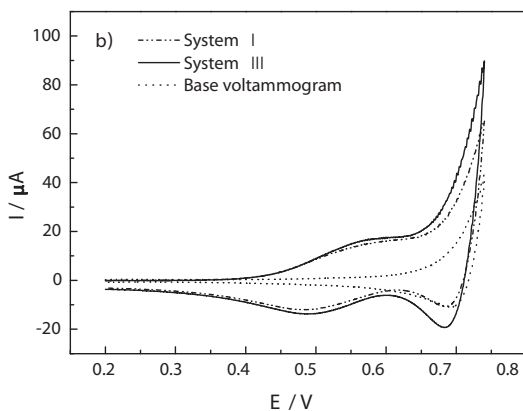
Scheme 1. An experiment carried out for determination of transfer mechanism. Reprinted from *Electrochim. Acta*, 54 (2008) 530, A.V. Juarez and L.M.Yudi, Copyright (2008) with permission from Elsevier.

Both solutions of system I were shaken to establish the partition equilibrium and then, the electrochemical measurement was taken. After this, both phases were separated and electrochemically analyzed. Figure 12 compares the voltammograms obtained for system I

(see scheme 1) with those obtained for system II (Figure 12 (a)) and III (Figure 12 (b)). From these results, it is possible to conclude that the total amount of PROM in the system prevails in the organic phase after agitation, even in the presence of Al(III) in the aqueous phase, and that cation transfer occurs by a facilitated mechanism. This mechanism is confirmed by the analysis of voltammetric parameters (I_p^+ , E_p^+ and ΔE_p).



a) (---) Voltammogram for base solutions: apc: 1.00×10^{-2} M LiCl, pH = 3.60. opc: 1.00×10^{-2} M TPhAsDCC. (·-·-·) Voltammogram for System I: apc: 1.00×10^{-2} M LiCl + 6.00×10^{-4} M $\text{Al}(\text{NO}_3)_3$ + 1.00×10^{-3} M PROM, pH = 3.60. opc: 1.00×10^{-2} M TPhAsDCC. (—) Voltammogram for System II: apc resulting from the agitation of system I, opc: 1.00×10^{-2} M TPhAsDCC.(fresh solution).



b)(---) Voltammogram for base solutions: apc: 1.00×10^{-2} M LiCl, pH = 3.60. opc: 1.00×10^{-2} M TPhAsDCC. (·-·-·) Voltammogram for System I: apc: 1.00×10^{-2} M LiCl + 6.00×10^{-4} M $\text{Al}(\text{NO}_3)_3$ + 1.00×10^{-3} M PROM, pH = 3.60. opc: 1.00×10^{-2} M TPhAsDCC. (—) Voltammogram for System III: apc: 1.00×10^{-2} M LiCl, pH = 3.60 (fresh solution). opc: resulting from the agitation of system I. Sweep rate= 0.050 Vs^{-1} . Reprinted from *Electrochim. Acta*, 54 (2008) 530, A.V. Juarez and L.M.Yudi, Copyright (2008) with permission from Elsevier.

Fig. 12. Voltammetric profiles corresponding to the experiment described in scheme 1.

3.3.2 Determination of the complex stoichiometry

With the aim to determine the stoichiometry of Al:PROM complex, experiments changing the ligand concentration were performed. Figure 13 shows the voltammetric response obtained. The pH value was fixed at 4.50, and the cation concentration was higher than ligand concentration employed to avoid H^+ competition. Under these experimental conditions, the dependence of current with ligand concentration is given by eq. 13, whenever, a reversible diffusion controlled transfer occurs. As can be seen, the peak current increased with PROM concentration and E_p^+ shifts to more negatives values as predicted by equations 12 and 13. To carry out these experiments it was necessary to change the organic electrolyte, and TPnATCIPhB was employed because it allows increasing the positive limit of the potential window. In this way, a better determination of the peak potential of Al(III) transfer could be done. As a consequence of the increase in the positive limit, a second process was observed around $E = 0.800$ V as the concentration of ligand increased. This process could be likely due to H^+ facilitated transfer.

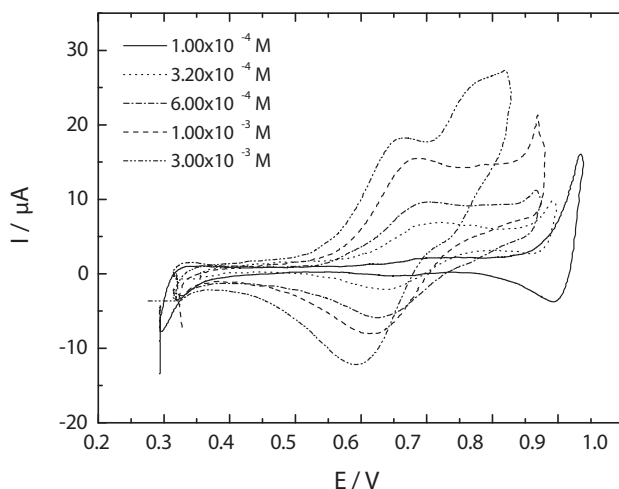


Fig. 13. Voltammetric profiles corresponding to Al(III) facilitated transfer by PROM at different concentrations of ligand. Apc: 1.00×10^{-2} M LiCl + 1.00×10^{-2} M $Al(NO_3)_3$, pH = 4.50. opc: 1.00×10^{-2} M TPATPhCIB + x M PROM, x = (—) 1.00×10^{-4} M; (····) 3.20×10^{-4} M; (---) 6.00×10^{-4} M; (-·-·-) 1.00×10^{-3} M; (- - - -) 3.00×10^{-3} M. Sweep rate = 0.050 Vs $^{-1}$. Reprinted from *Electrochim. Acta*, 54 (2008) 530, A.V. Juarez and L.M.Yudi, Copyright (2008) with permission from Elsevier.

Plots of I_p vs square root of sweep rate are linear as predicted by eq. 13 for this kind of ion transfer. With the purpose to calculate the stoichiometry and the charge of the complexes, the slopes of these plots at different ligand concentrations were obtained. Figure 14 compares the theoretical slope values obtained for different complexes and the experimental values obtained in this case. From the analysis of this figure, it is possible to conclude that PROM:Al(III) complex stoichiometry changes with the ligand concentration, while the charge of the transferred species is constant and equal to 2. The charge and stoichiometry complex can also be deduced from eq 12. From the analysis of E_p vs log [PROM] variation

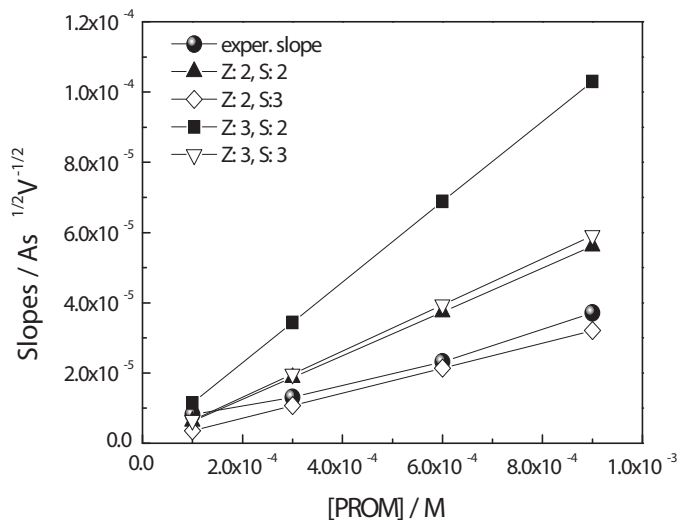


Fig. 14. Plot of experimental and theoretical slope values $I_p/v^{1/2}$ vs. [PROM]. Experimental slope: (●). Theoretical slopes for the following values of z and s : (▲) $z: 2, s: 2$; (◇) $z: 2, s: 3$; (■) $z: 3, s: 2$; (▽) $z: 3, s: 3$. Aqueous phase composition: 1.00×10^{-2} M LiCl + 1.00×10^{-3} M $Al(NO_3)_3$, pH = 4.50. Organic phase composition: TPhAsDCC 1.00×10^{-2} M + PROM n M. Sweep rate = 0.050 Vs⁻¹. Reprinted from *Electrochim. Acta*, 54 (2008) 530, A.V. Juarez and L.M. Yudi, Copyright (2008) with permission from Elsevier.

(not shown), a slope value equal to 0.062 V/dec was obtained, in a concentration range between 3.20×10^{-4} M to 1.00×10^{-3} M. This value approximates to the theoretical value corresponding to a complex with a charge +2 and a stoichiometry of 1:3 (Homolka et al., 1982).

4. Conclusions

This chapter resumes the results obtained from the electrochemical study of *s*-triazines herbicides at liquid-liquid interfaces. These herbicide compounds (Atrazine, Propazine and Pometryne) can be quantitatively analyzed from the electrochemical transfer current at the water/1,2-dichloroethane interface.

Regarding to the transfer of ATR and PRO, a facilitate proton transfer from aqueous phase trough the interface to form the protonated species in the organic phase was observed. In these cases, transfer potential varies with pH as predicted by theory and peak current is proportional to triazine concentration in organic phase and independent of the pH (for $c_{H^+}^w > c_L^0$ conditions). For these two species it was possible to calculate the acid dissociation constant in organic phase, K_a^o , from the intercepts in the graph of $\Delta_o^w \phi_{1/2}^{tr}$ vs pH. The values obtained were 4.60×10^{-9} and 7.03×10^{-9} for ATR and PRO, respectively.

PROM behavior is quite different and depends on the pH values. At low pH values, the transfer of protonated PROM from aqueous to organic phase can occur. Under these conditions, the peak potential is independent on the pH and peak current is proportional to protonated fraction of PROM, which decreases as pH increases up to pH = 2.00. Above this

value, the process change to a facilitated proton transfer, showing a behavior similar to that observed for ATR and PRO.

Calibration curves for these species, employing cyclic voltammetry, show detection limits of 2.50×10^{-5} M. This limit must be lowered to be able to apply this electrochemical methodology to the analytical determination of ATR, PRO and PROM in waste water or soil samples. However, the experimental conditions found so far were used to apply square-wave voltammetry technique at a liquid - liquid interface.

In that sense, the electrochemical response of PROM, employing SWV technique at liquid-liquid interface, was studied. The detection limit found was 1.50×10^{-6} M. This DL value is still very high for trace determinations of PROM required in environmental studies compared with other available techniques. However, one of the advantages of this system is the possibility of pre-concentrate the herbicide in the organic phase. Extraction procedures to the organic phase are possible due to the high partition coefficient of PROM and high solubility in 1,2-DCE. The aqueous:organic volume ratio equal to 500:30 and the later reduction of the volume of the organic phase enriched with PROM, by a factor of 6, yield an overall pre-concentration factor of 100. The detection limit could be lowered to 1.0×10^{-7} M under these experimental conditions. The concentration ranges from 1.0×10^{-6} to 5.0×10^{-5} M, without pretreatment, and between 8.0×10^{-8} to 2.4×10^{-7} M, carrying out the pre-concentration procedure previous to electrochemical measurement, were used for the calibration curves.

On the other hand, the standard addition method is highly efficient in this kind of systems and presents several advantages like less use of reactive and easy sample manipulation. A linear response in the concentration range between 1.0×10^{-6} to 2.7×10^{-5} M with correlation coefficient of 0.997 was obtained. The lower concentration value, in this case, corresponds to an aqueous PROM solution 1.0×10^{-8} M.

It is worthwhile to discuss the practical aspect of the procedure here proposed. In this sense, the extraction and pre-concentration methods developed by other authors (Herzog et al., 2008; Berduque & Arrigan, 2006; Berduque et al., 2005; Collins et al., 2008; Kim & Amemiya, 2008) have several practical advantages over the present procedure, as the use of low organic phase volume, among others. Nevertheless, the results obtained in this study justify evaluating the possibility of carrying out PROM pre-concentration following the thin film approach (Kim & Amemiya, 2008) or the electrochemistry modulated liquid - liquid extraction procedure (Berduque & Arrigan, 2006; Berduque et al., 2005; Collins et al., 2008; Kim & Amemiya, 2008).

Regarding to the study of the interaction between PROM and Al(III) at the water /1,2-DCE interface, it was possible to determine the charge and stoichiometry of the complex formed. A facilitated Al(III) transfer through the liquid - liquid interface takes place, depending on pH and PROM concentration. From the analysis of the experimental results, a competition of H^+ and Al(III) for the ligand is observed. At low pH values ($pH < 2.00$), only H^+ transfer occurs, a pH higher than 4.50 only Al(III) is transferred, and at intermediate pH values, the transfer of both cations takes place. To determine the stoichiometry of the Al:PROM complex, the experiments were carried out at pH 4.50 because no H^+ transfer was observed under these conditions. From the experimental results, we conclude that the stoichiometry depends on PROM concentration: 1:3 at $C_{PROM} \geq 3.00 \times 10^{-4}$ M and 1:2 for $C_{PROM} < 3.00 \times 10^{-4}$ M, while the charge of the transferred species is $2+$. Therefore, the ion forming the complex with the herbicide, at pH 4.50, is $Al(OH)^{2+}$. This statement is supported by the fact that $Al(OH)^{2+}$ is one of the predominant species at this pH value.

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Herbicides are much more than just weed killers. They may exhibit beneficial or adverse effects on other organisms. Given their toxicological, environmental but also agricultural relevance, herbicides are an interesting field of activity not only for scientists working in the field of agriculture. It seems that the investigation of herbicide-induced effects on weeds, crop plants, ecosystems, microorganisms, and higher organism requires a multidisciplinary approach. Some important aspects regarding the multisided impacts of herbicides on the living world are highlighted in this book. I am sure that the readers will find a lot of helpful information, even if they are only slightly interested in the topic.

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