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Competitive transfer of H^+ and Al(III) ions facilitated by a Prometrine herbicide through a liquid/liquid interface

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ABSTRACT

The transfer of aluminium(III) across the water/1,2-dichloroethane interface facilitated by the herbicide Prometrine (PROM) was investigated using cyclic voltammetry. In the presence of PROM in the organic phase, the transfer of Al(III) and H^+ from the aqueous to the organic phase was observed and the competition between these two cations for the herbicide was analyzed at different pH values. At pH 4.50, it was possible to determine the formation of an Al(III):PROM complex in the organic phase, with a stoichiometry of 1:3 and a charge of 2^+, indicating that the species in the complex with PROM is $Al(OH)^{2+}$.

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1. Introduction

1,3,5-Triazine (s-triazine) derivates are very important compounds for agricultural applications due to their herbicidal properties and they are the most widely used in Europe and the USA. Triazine derivatives are stable in the soil for 3–12 months. These compounds are able to be incorporated into plants and inhibit photosynthesis enzymes. 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) [1].

Development of new sensitive and selective analytic techniques for the determination of s-triazine and their metabolites in the environment as well as the recognition of their interactions with different elements, especially with heavy metals cations present in soils, are important problems in modern s-triazine chemistry. The study of complex formation between herbicides and cations contained in soils is a relevant topic since it determines pesticide mobility, its bioavailability and effectiveness.

Voltammetry at liquid/liquid (L|L) interfaces has proven to be a valuable tool to elucidate the stoichiometry of complex formation [2–12], to identify and evaluate successive complex formation at the interface [13–15], and to obtain thermodynamic [3–5,10,12,16–18] and kinetic [3,19–24] data of facilitated ion transfer. Two different mechanisms have been proposed for the formation of metal cation complexes at liquid/liquid interfaces, giving rise to direct or facilitated ion transfer. The nature of cation and ligand, L, the stability constant of the complex formed and the partition coefficient of the ligand determine the operative mechanism. When the ligand L is hydrophobic and the stability constant of the complex ML_s^{z+} in the aqueous phase is low, the complex formation in this phase, followed by its direct transfer is negligible. Thus, the total process for metal ion M^{z+} transfer from the aqueous (w) into the organic (o) phase facilitated by the ligand L can be written as

$$M_{(w)}^{z+} + sL_{(o)} \rightleftarrows ML_{s(o)}^{z+} \quad (1)$$

Homolka et al. [24] demonstrated that this transfer mechanism is favored when the condition: $K_w^{dis} P_L / c_w^{M^+} \gg 1$ (where K_w^{dis} is the complex dissociation constant in water, P_L is the partition coefficient of the ligand and $c_w^{M^+}$ is the cation concentration in water) is fulfilled. These authors deduced the theoretical voltammetric profiles for this mechanism. From the dependence of peak parameters with ligand and cation concentrations, it is possible to calculate the stoichiometry and charge of the complex.

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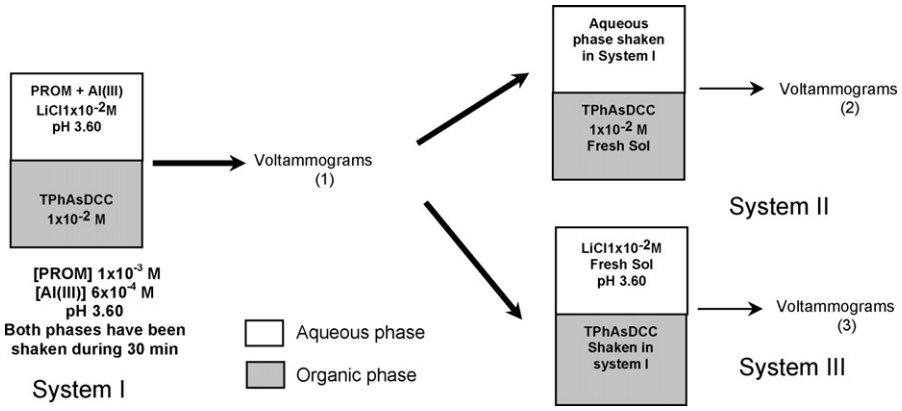

Scheme 1. An experiment carried out for determination of transfer mechanism.

In a previous paper, we studied the transfer of three s-triazine (Atrazine, Propazine and Prometrine (PROM)) across the water/1,2-dichloroethane interface [25]. A facilitated H^+ transfer mechanism from the aqueous to the organic phase was demonstrated by the analysis of the positive peak potential and peak current as a function of pH. This behavior was explained by taking into account the high partition coefficient value for these 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 [26]. The interaction of herbicides with metal ions and mineral surfaces may affect their mobility, degradation and bioavailability in the environment; however, these interactions are far from being thoroughly understood [27]. 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 [27].

The aim of the present paper is to study the interaction of the Al(III) cation and the herbicide Prometrine at the water/1,2-dichloroethane interface with the purpose of contributing to the acknowledgment of these complexes.

2. Experimental

The voltammetric experiments were performed in a four-electrode system using a conventional glass cell with 0.18 cm^2 interfacial area. Two platinum wires were used as counter electrodes, and the reference electrodes were Ag/AgCl. The reference electrode in contact with the organic solution was immersed in an aqueous solution of 1×10^{-2} M tetraphenyl arsonium chloride (TPhAsCl) (Sigma).

The base electrolyte solutions were 1×10^{-2} M LiCl (Merck p.a.) in ultrapure water and 1×10^{-2} M tetraphenyl arsonium dicarbollyl cobaltate (TPhAsDCC) or tetrapentylammonium tetrakis(4-chlorophenyl)borate (TPATPhClB) in 1,2-dichloroethane (1,2-DCE, Dorwil p.a.). TPhAsDCC was prepared by metathesis of tetraphenyl arsonium chloride (TPhAsCl, Sigma) and cesium dicarbollyl cobaltate (CsDCC, Lachema p.a.). Similarly, TPATPhClB was prepared by mixing an aqueous solution of tetrapentyl ammonium chloride (TPACl, Merck) with an ethanol:water (2:1) solution of potassium tetrakis(4-chlorophenyl)borate (KTPhClB, Aldrich). Each precipitate was recrystallized from a water:acetone or ethanol:acetone mixture, respectively, and then dried in an oven at 30 °C for 2 days.

The pH of the aqueous phase was adjusted within the range of 1.50–5.30 by addition of HCl (Merck p.a.) and LiOH (Merck p.a.), respectively.

The aqueous solutions of Al(III) were prepared from $Al(NO_3)_3$ of the highest purity (Sigma). The concentrations employed varied from 6×10^{-4} to 1×10^{-2} M.

The s-triazine used, PROM, was of the highest purity available (Riedel de-Haën). PROM was added to the aqueous or the organic (1,2-DCE) phase depending on the experiment. Aqueous PROM solutions were prepared in a concentration range between 1×10^{-4} and 1×10^{-3} M. All experiments were carried out after equilibrating the two phases by agitation employing equal volumes. In this way, a partition equilibrium was achieved before the start of the electrochemical experiment.

Cyclic voltammetry was performed using a four-electrode potentiostat, which eliminates the IR drop automatically by means of a periodic current-interruption technique [28]. A Hi-Teck Instruments waveform generator and a 10-bit Computer Boards acquisition card connected to a personal computer were also employed.

Scheme 1 describes one of the experiments carried out to establish the transfer mechanism.

First of all, equal volumes of the two phases were shaken (system I): the aqueous phase contained the herbicide PROM and Al(III), while the organic phase contained 1×10^{-2} M TPhAsDCC. The cell was filled with these solutions and CV experiments were carried out. After this, both phases were separated and new voltammograms were carried out with fresh organic or aqueous solutions (system II or system III, respectively). Finally, the results were compared.

3. Results and discussion

The pH effect on complex formation between Al(III) and PROM and its transfer through the water/1,2,-dichloroethane interface were analyzed. These results are shown in Fig. 1. In all experiments, the cation:ligand relationship was kept constant and equal to 3:1. The pH values analyzed were 1.50 (a), 4.50 (b) and 5.30 (c). In Fig. 1(a), a transfer process is observed at $E_p^+ = 0.380$ V. The peak potential difference $\Delta E_p = 0.060$ V was independent of the potential sweep rate *v*. This voltammetric response corresponds to the H^+ transfer process facilitated by PROM as previously demonstrated [25] from the analysis of E_p^+, ΔE_p and I_p^+ with pH and PROM concentration. This hypothesis is also verified comparing voltammograms in the presence of PROM with and without Al(III). As can be noted, identical profiles are obtained. Therefore, under these experimental conditions, PROM facilitates H^+ transfer but not Al(III) transfer,

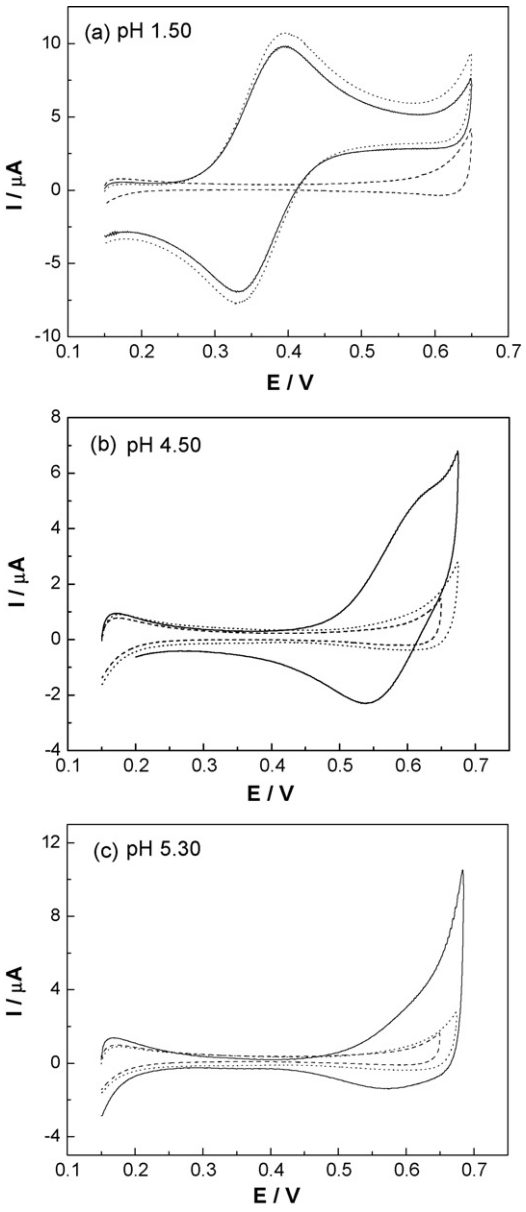

Fig. 1. Voltammetric profiles obtained in the presence of Al(III), H^+ and PROM at different pH. Aqueous phase composition: (a) pH 1.50 (– –) 1×10^{-2} M LiCl, (···) 1×10^{-2} M LiCl + 5×10^{-4} M PROM, (—) 1×10^{-2} M LiCl + 5×10^{-4} M PROM + 1.5×10^{-3} M $Al(NO_3)_3$; (b) pH 4.50, (– –) 1×10^{-2} M LiCl, (···) 1×10^{-2} M LiCl + 2×10^{-4} M PROM, (—) 1×10^{-2} M LiCl + 2×10^{-4} M PROM + 6.0×10^{-4} M $Al(NO_3)_3$; (c) pH 5.30, (– –) 1×10^{-2} M LiCl, (···) 1×10^{-2} M LiCl + 2×10^{-4} M PROM, (—) 1×10^{-2} M LiCl + 2×10^{-4} M PROM + 6.0×10^{-4} M $Al(NO_3)_3$. Organic phase composition: 1×10^{-2} M TPhAsDCC. Sweep rate = 0.050 V s^{-1}.

indicating that the protonation of PROM in the organic phase is thermodynamically favored with respect to the complex formation with Al(III). At pH 4.50, the H^+ concentration is lower than the Al(III) concentration and the facilitated transfer of Al(III) is the only process observed, as noted by the comparison of voltammograms recorded in the presence and absence of Al(III) in Fig. 1(b). Fig. 1(c) shows the response at pH 5.30. In this case, the facilitated transfer of Al(III) is also the only process found. However, at this pH value, the transfer occurs at a very high potential where Al(III) transference overlaps with the background current. Additionally, the current value for the process in Fig. 1(c) is lower than that shown in Fig. 1(b), which could be attributed to the presence of other hydroxylated species of Al(III) at this pH value, lowering the

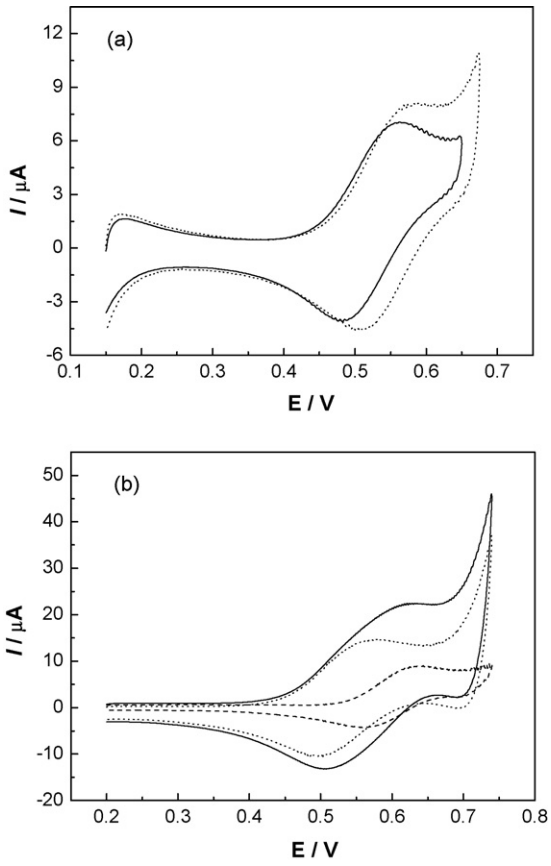

Fig. 2. Voltammetric profiles obtained at pH 3.60 in the presence of Al(III), H^+ and PROM. (a) Aqueous phase composition (a.p.c.): (···) 1×10^{-2} M LiCl + 2×10^{-4} M PROM; (—) 1×10^{-2} M LiCl + 2×10^{-4} M PROM + 6×10^{-4} M $Al(NO_3)_3$. Organic phase composition (o.p.c.): 1×10^{-2} M TPhAsDCC. Sweep rate = 0.100 V s^{-1}. (b) Cyclic voltammogram obtained in presence of PROM in organic phase. (···) a.p.c.: 1×10^{-2} M LiCl, o.p.c.: 1×10^{-2} M TPhAsDCC + 1×10^{-3} M PROM; (—) a.p.c.: 1×10^{-2} M LiCl + 6×10^{-4} M $Al(NO_3)_3$, o.p.c.: 1×10^{-2} M TPhAsDCC + 1×10^{-3} M PROM; (– –) voltammogram resulting from the subtraction of (—) and (···). Sweep rate = 0.050 V s^{-1}.

effective concentration of the cation available to form the complex with PROM.

At pH values between 1.50 and 4.50, a competition between H^+ and Al(III) for the ligand occurs. The complex formed in the organic phase depends on the cations and PROM concentration. Fig. 2(a) and (b) shows the results obtained at pH 3.60 and Al(III) concentration of 6×10^{-4} M. As noticed, different processes take place depending on the PROM concentration. When the ligand concentration is lower than the concentration of the cations, H^+ transfer is the only process observed. This behavior is evident in Fig. 2a, where voltammetric profiles in the presence and absence of Al(III) are compared. From the analysis of the E_p^+, ΔE_p and I_p^+ values for both signals, it can be concluded that the same process, namely H^+ transfer, occurs. Moreover, the difference between positive and negative potential, ΔE_p, is equal to 0.060 V. This value is obtained when the ion transferred is monovalent. 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. Indeed, the solid line in Fig. 2(b) contains two overlapped voltammetric waves. Although both transfer potentials are close

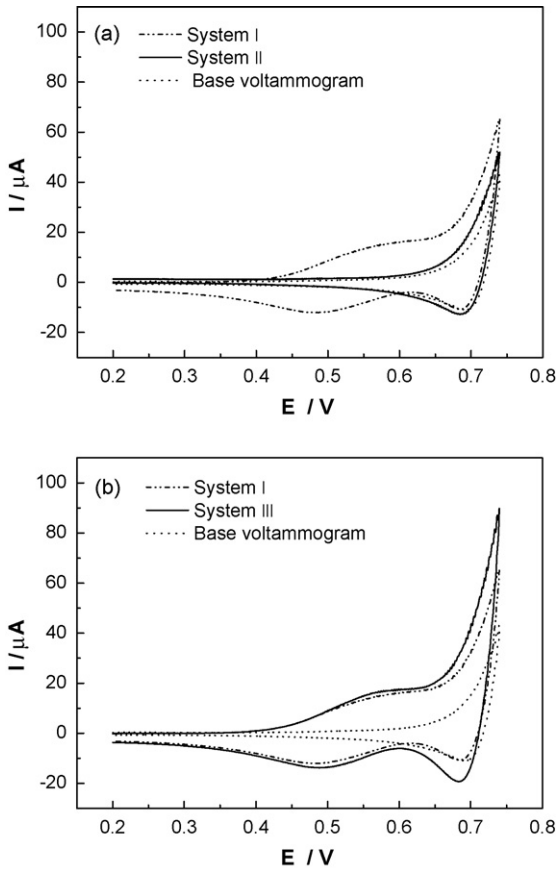

Fig. 3. Voltammetric profiles corresponding to the experiment described in Scheme 1. (a) (···) Voltammogram for base solutions—a.p.c.: 1×10^{-2} M LiCl, pH 3.60; o.p.c.: 1×10^{-2} M TPhAsDCC. (··–··–··) Voltammogram for system I—a.p.c.: 1×10^{-2} M LiCl + 6×10^{-4} M $Al(NO_3)_3$ + 1×10^{-3} M PROM, pH 3.60; o.p.c.: 1×10^{-2} M TPhAsDCC. (—) Voltammogram for system II—a.p.c. resulting from the agitation of system I; o.p.c.: 1×10^{-2} M TPhAsDCC (fresh solution). (b) (···) Voltammogram for base solutions—a.p.c.: 1×10^{-2} M LiCl, pH 3.60; o.p.c.: 1×10^{-2} M TPhAsDCC. (··–··–··) Voltammogram for system I—a.p.c.: 1×10^{-2} M LiCl + 6×10^{-4} M $Al(NO_3)_3$ + 1×10^{-3} M PROM, pH 3.60; o.p.c.: 1×10^{-2} M TPhAsDCC. (—) Voltammogram for system III—a.p.c.: 1×10^{-2} M LiCl, pH 3.60 (fresh solution); o.p.c.: resulting from the agitation of system I. Sweep rate = 0.050 V s^{-1}.

to each other, when the voltammograms in the presence (solid line) and absence (dotted line) of Al(III) are subtracted, a peak current at E = 0.610 V is defined as observed in Fig. 2(b) (dashed line). This second process can be due to Al(III) transfer facilitated by PROM.

3.1. Determination of the Al(III) transfer mechanism

With the purpose of elucidating the transfer mechanism of Al(III), the experiment described in Scheme 1 was executed. Both solutions of system I were shaken to establish the partition equilibrium and the electrochemical measurement was taken. After this, both phases were separated and electrochemically analyzed. Fig. 3 compares the voltammograms obtained for system I (see Scheme 1) with those obtained for system II (Fig. 3(a)) and system III (Fig. 3(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) and demonstrated in the following section.

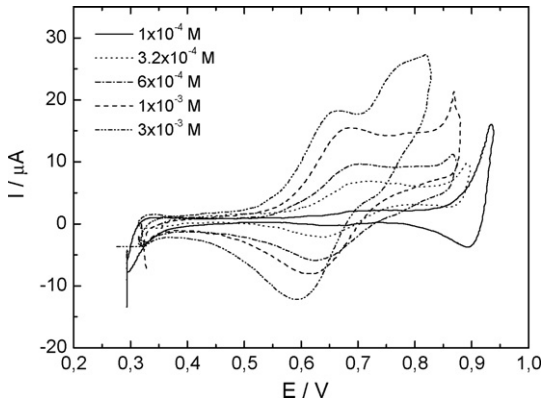

Fig. 4. Voltammetric profiles corresponding to Al(III) facilitated transfer by PROM at different concentrations of ligand. Aqueous phase composition: 1×10^{-2} M LiCl + 1×10^{-2} M $Al(NO_3)_3$, pH 4.50. Organic phase composition: 1×10^{-2} M TPATPhClB + x M PROM, (—) $x = 1 \times 10^{-4}$ M; (···) $x = 3.2 \times 10^{-4}$ M; (·–·–·) $x = 6 \times 10^{-4}$ M; (– –) $x = 1 \times 10^{-3}$ M; (··–··–··) $x = 3 \times 10^{-3}$ M. Sweep rate = 0.050 V s^{-1}.

3.2. Determination of complex stoichiometry

When a potential linear sweep is applied to the interface and the facilitated ion transfer is reversible and diffusion-controlled, the current is related to the ligand concentration (provided $c_M^w \gg c_L^o$) through [2]:

$$I(\tau) = s^{-1} z F A c_L^o D_L^{1/2} \left(\frac{zFv}{RT}\right)^{1/2} \chi(\tau) \quad (2)$$

where s is the stoichiometric number of the complex, z is the cation charge, A is the interfacial area, c_L^o is the ligand concentration in the bulk of the organic phase, D_L is the ligand diffusion coefficient in the organic phase, v is the sweep rate, and $\chi(\tau)$ is the current function. The current function depends on the stoichiometry of the complex formed [2].

Eq. (2) allows the determination of the stoichiometry and the charge of the complex from the slope of the I_p vs. $v^{1/2}$ plot.

On the other hand, Eq. (3) relates to the half wave potential with the ligand and metal concentration [2]:

$$E_{1/2} = E^0 - \frac{2.3RT}{zF}(\log\ c_M^w + \log s) - \frac{1}{2}2.3 \log\frac{D_L}{D_M} + 2.3(s-1)\log 2 + \frac{0.028}{z} - \frac{2.3RT}{zF}\log\left(\frac{D_w}{D_o}\right)^{1/2} - \frac{2.3RT}{zF}(s-1)\ \log c_L^o \quad (3)$$

From the slope of the $E_{1/2}$ vs. $\log c_L^o$ plot, the stoichiometry and the charge of the complex formed can be evaluated, keeping c_M^w constant.

With the purpose of determining the stoichiometry of the PROM:Al(III) complex, a pH value of 4.50 was chosen because no competition of H^+ and Al(III) occurs, in accordance with Fig. 1(b). Fig. 4 shows the voltammograms corresponding to different ligand concentrations for $c_M^w \gg c_L^o$ conditions. As can be seen, the peak current increases with PROM concentration and E_p^+ shifts to more negative values as predicted by Eqs. (2) and (3), respectively. From these experiments, it is possible to determine the complex stoichiometry according to Eq. (3). It should be noted that here a different organic base electrolyte was employed to avoid the overlap between the peak potential and the positive limit of the window observed when TPhAsDCC was used. Therefore, TPhAsDCC was replaced by TPATPhClB to increase the positive limit of the window from 0.750 to 0.920 V. 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.

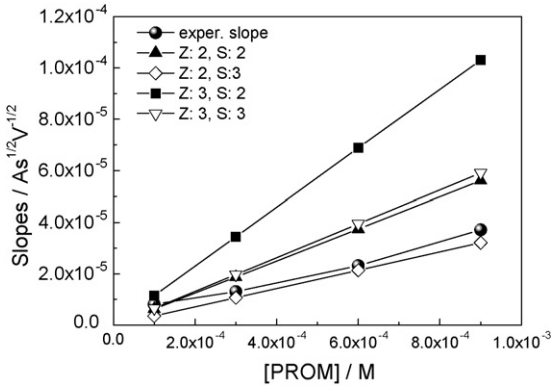

Fig. 5. Plot of experimental and theoretical slope values $I_p/v^{1/2}$ vs. [PROM]. Experimental slope: (●) theoretical slopes for the following values of z and s: (▲) z: 2, s: 2; (◊) z: 2, s: 3; (■) z: 3, s: 2; (▽) z: 3, s: 3. Aqueous phase composition: 1×10^{-2} M LiCl + 1×10^{-3} M $Al(NO_3)_3$, pH 4.50. Organic phase composition: 1×10^{-2} M TPhAsDCC + n M PROM. Sweep rate = 0.050 V s^{-1}.

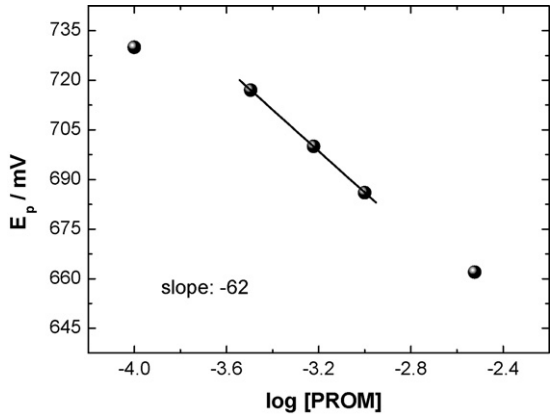

Fig. 6. Plot of E_p^+ vs. log[PROM]. Aqueous phase composition: 1×10^{-2} M LiCl + 1×10^{-2} M $Al(NO_3)_3$, pH 4.50. Organic phase composition: 1×10^{-2} M TPATPhClB + x M PROM. $v = 0.050$ V s^{-1}.

From the slope obtained from the variation of I_P with the sweep rate (Eq. (2)), the stoichiometry and the charge of the complex formed were calculated. Fig. 5 shows the comparison of the theoretic and experimental slopes values as a function of the ligand concentration. Theoretic values were calculated for different s and z values. From the analysis of this plot, it can be concluded that the PROM:Al(III) complex stoichiometry changes with ligand concentration: at low PROM concentrations, the slope value coincides with a stoichiometry corresponding to 1:2, while at high ligand concentrations, the stoichiometry is 1:3. The charge of the transferred species is 2 in both cases.

The stoichiometry and charge of the complex was also calculated from the slope of E_p^+ vs. $\log c_{PROM}$ plot, in accordance with Eq. (3). Fig. 6 shows this variation. The slope value calculated in the concentration range between 3.2×10^{-4} and 1×10^{-3} M is equal to −62 mV/dec, which approximates the theoretical value corresponding to a complex with a charge of +2 and a stoichiometry of 1:3 [2]. Experimental data corresponding to the lowest ($c_{PROM} = 1 \times 10^{-4}$ M) and the highest ($c_{PROM} = 3 \times 10^{-3}$ M) PROM concentration values were not included in the linear regression since, as shown above, in the former, a different stoichiometry is obtained, whereas in the latter the condition $c_M^w \gg c_L^o$ is not completely fulfilled.

4. Conclusions

Facilitated Al(III) transfer through a liquid–liquid interface depends on pH and PROM concentration. From the analysis of the experimental conditions employed, a competition of H^+ and Al(III) for the ligand is observed. At low pH values (lower than 2), only H^+ transfer occurs, at pH ≥ 4.50 only Al(III) is transferred, and at intermediate pH values, the transfer of both cations occurs. To determine the stoichiometry of the Al(III):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 $c_{PROM} \geq 3 \times 10^{-4}$ M and 1:2 for $c_{PROM} < 3 \times 10^{-4}$ 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. This study allows the conclusion that the presence of Al(III) in the aqueous phase does not favor PROM retention in this phase because no complex formation occurs in the aqueous phase.

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