



The bromine electrode. Part I: Adsorption phenomena at polycrystalline platinum electrodes

S. FERRO and A. DE BATTISTI*

Department of Chemistry, University of Ferrara, via L. Borsari 46, I-44100 Ferrara, Italy

(*author for correspondence, e-mail: dbtcll@unife.it)

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Abstract

A cyclic voltammetric study of the behaviour of Br^- and Br_3^- at Pt electrodes, in the potential range between hydrogen and oxygen evolution, is described. Different experiments were carried out, in the presence of Br^- alone, and with a mixture of Br^- and Br_3^- , in which the ratio between the species has been kept constant and equal to 1. The halide concentration was varied between 4×10^{-6} and 1×10^{-3} mol dm $^{-3}$, at constant ionic strength, in 1 M HClO_4 as well as in 1 M NaClO_4 adjusted to a pH of 2. Underpotential deposition of Br is observed at potentials as low as -0.125 V vs SCE. The adsorption parameters of Br species were determined from the adsorption/desorption peak pair in the hydrogen adsorption/desorption region, and from the oxide reduction peak data. In the absence of oxygen adsorption, a relatively high coverage of the electrode surface is attained. A Langmuir-type adsorption is observed under the different experimental conditions.

1. Introduction

Adsorption of anions at Pt electrodes is an important factor affecting the path of anodic reactions, like oxygen evolution and electrooxidation of organic substrates (e.g., methanol [1]). The strong chemisorption of Cl^- , for instance, a precursor stage of electrosorbed Cl-radicals, inhibits the surface oxide formation, causing an anodic shift of the oxygen evolution potential [2].

An analogous role has been ascertained for Br^- although, in this case, the available literature is far less rich. On the basis of the above considerations, it was thought of interest to carry out an investigation not only on the adsorption of Br^- but also of Br_2 and Br_3^- , primary products of its anodic oxidation, in view of further investigations of electron transfer for the $\text{Br}_3^-/\text{Br}^-$ redox couple, but also on the kinetics of Br^- -mediated anodic reactions.

Adsorption of bromine species at Pt surfaces has been studied both under ultrahigh vacuum (UHV) [3–5] as well as atmospheric conditions [6], and from aqueous solution [6–11]. Contradictory results have been obtained: Bertel and coworkers [3] considered the UHV adsorption of gaseous Br_2 on Pt(1 1 0), looking at the role of annealing temperatures and bromine coverages, that is, from 0.02 monolayers (ML) to about 0.5 ML. They reported that Br_2 adsorbs in pairs at room temperature; after annealing at temperatures higher than 375 K, the dimers undergo a gradual conversion into substitutionally (reconstructive) adsorbed bromine

atoms. While a conventional halogen adsorption should result in a metal-to-halogen charge transfer, implying a significant increase of surface work function (due to the dipole moment associated with the halogen adatoms), substitutional adsorption would suggest a smaller or reversed effect. Essentially in agreement were the results of Menzel et al. [4], who also found a halogen-induced reconstruction of the metal surface (after annealing at $T > 400$ K), with the formation of Pt–Br–Pt chains in which the metal-halogen bond is thought to be predominantly covalent.

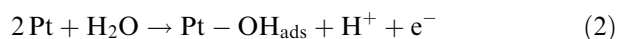
Analogous chains have been observed by Xu and Harrison [5], who examined the adsorption of Br_2 on Pt(1 1 1) at low temperatures, but dissociative adsorption was found even at 25 K. Chainlike structures form at a coverage ≥ 0.03 ML, together with the appearance of islands at coverages > 0.07 ML. In consideration of the very low temperature, the Br atoms, originating from the dissociation of Br_2 molecules, are suggested to be only transiently mobile; in addition, in order to justify the island formation, weakly bound Br_2 molecules would adsorb near or at preexisting Br atoms, which would act as preferential sites for Br_2 dissociation.

Under atmospheric conditions, exposing a Pt(1 1 1) surface to bromine vapour leads to coverages from 0.44 to 0.50 Br/Pt, as found by Feliu and coworkers [6]; such results seem consistent with the neutral character of the bromine adsorbates, a continuous variation in Br coverage toward saturation being a consequence of the high compressibility of the neutral adsorbate.

Finally, considering the adsorption from solution, a cyclic voltammetric study on Pt(1 1 1) immersed in aqueous $\text{CaBr}_2\text{--KBr--HBr}$ mixtures has been reported by Salaita et al. [7]; investigations were carried out at different pH, from 2 to 12. Interestingly, Br atoms were the main adsorbed species, as a result of a possible surface reaction, which has been schematized as follows [8]:



In the absence of bromides (or other potentially adsorbing anions) in solution, oxidation of the Pt surface results from the anodic reaction of water:



obviously, the electrochemical adsorption of Br^- and OH^- are competing redox processes, which may be dependent on pH and halogen anion concentration.

The competition between Br^- adsorption and surface oxide formation, at a polycrystalline Pt electrode, has been also considered by Conway et al. [9], in relation to the electrocatalysis of anodic Br_2 formation. Bromide adsorption data have been found to fit a Langmuir-type isotherm, suggesting low lateral repulsive interactions between the adsorbed species (i.e., the state of adsorbed Br^- is much more atomic than ionic, in substantial agreement with the above reaction scheme proposed by Salaita et al. as well as with the results obtained by Felici and coworkers [6]). At variance, a high electroadsorption valency of 0.95 ± 0.05 was found by Gasteiger et al. [10], which would indicate that, in the potential range from -0.25 to $+0.5 \text{ V}$ vs SCE. The bromide ion interacts with the Pt(1 1 1) surface retaining almost its charge. This result contrasts with the above reported estimation given by Conway and coworkers [9]; on the other hand, the expected bromide-to-platinum charge transfer could take place at potentials more positive than those considered in [10], also allowing the obtainment of a Br coverage larger than the value they found (i.e., half a monolayer).

In the present work, an experimental investigation has been carried out at a polycrystalline Pt electrode, in order to assess the interfacial behaviour of Br^- with respect to those of the mixture $\text{Br}^-/\text{Br}_3^-$ (from which also the adsorption of Br_2 should take place).

2. Experimental details

Cyclic voltammetric measurements were carried out by an Autolab PGSTAT20 digital apparatus equipped with a SCANGEN module, which allows the application of linear sweeps.

All reagents were of special purity grade and solutions were prepared in milliQ water ($\rho \geq 18 \text{ M}\Omega\text{cm}$); extra pure NaBr (Riedel-de Haën), HClO_4 (70%, Aldrich),

NaClO_4 monohydrate (Fluka) and Br_2 ($\geq 99.5\%$, Carlo Erba, pack of $10 \times 1 \text{ ml}$ glass tubes) were used as received. A platinum ring, a cylindrical platinum grid and a double-walled saturated calomel electrode (SCE), with an intermediate saturated NaNO_3 solution, were used as the working, counter and reference electrode, respectively.

Stock solutions of 1 M NaBr and 2 M NaBr/1 M Br_2 (i.e., equimolar $\text{Br}^-/\text{Br}_3^-$ solution) were prepared in two all-glass flasks and stored in the dark. A micrometer syringe (Hamilton) was used to inject controlled volumes of the chosen standard solution into the electrochemical cell (volume 50 ml); thus, a wide range of Br^- or $\text{Br}^-/\text{Br}_3^-$ ion concentrations could be covered in the same supporting electrolyte solution (1 M HClO_4 or 1 M NaClO_4 adjusted at a pH of 2 with HClO_4), starting from a concentration as low as $4 \times 10^{-6} \text{ M}$.

To clean the Pt electrode, repetitive scans, between the HER and the OER and in the presence of the supporting electrolyte only, were applied overnight; afterwards, both the cell and the electrodes were washed with milliQ water, prior to the addition of 50 ml of fresh supporting electrolyte solution. The latter was then degassed with argon and the electrode cycled again, until a reproducible signal was obtained (blank CV curve). Stirring was applied after each Br^- or $\text{Br}^-/\text{Br}_3^-$ mixture addition, in order to homogenize the test solution, while argon was allowed to fill the empty part of the cell during all measurements.

3. Results and discussion

The blank linear sweep cyclic voltammograms, obtained at Pt in 1 M HClO_4 (solid line) and 1 M NaClO_4 (pH 2, dotted line) are shown in Figure 1; curves were obtained at 100 mV s^{-1} , at room temperature, but at different times. From the evaluation of the UPD hydrogen accommodation, both the effective electrode surface area and the roughness factor ($R_f = \text{effective area}/\text{geometric area}$) were estimated [12]. Average values of 2.34 and 2.05 cm^2 , corresponding to R_f of 4.14 and 3.62, were

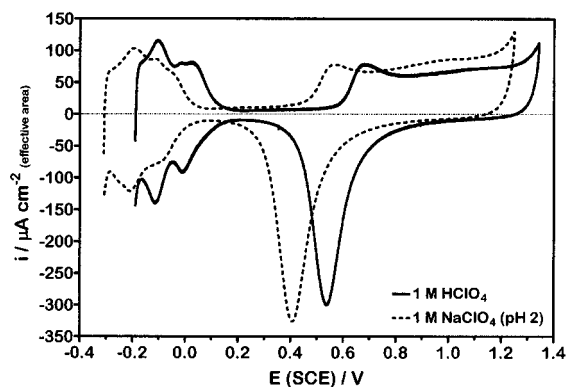


Fig. 1. Comparison of CV curves, obtained in 1 M HClO_4 (solid line) and 1 M NaClO_4 adjusted to a pH of 2 with perchloric acid (dotted line). Scan rate 0.1 V s^{-1} .

obtained in the two media (HClO_4 and NaClO_4 at pH 2), respectively. This difference may be related to surface modification due to the measurements to which the electrode was subjected before changing the pH.

Alternatively, the pH itself could play a role in the preferential stabilization of some crystal orientations, thus leading to small variations in terms of CV profile as well as regarding the electrochemically active surface area. In the following, results obtained in the more acidic supporting electrolyte will be discussed first.

As shown in Figure 2A, an addition of $0.2 \mu\text{l}$ of the $\text{Br}^-/\text{Br}_3^-$ stock solution (leading to a concentration of $4 \times 10^{-6} \text{ M}$) has a dramatic effect on the voltammetric behaviour of Pt: in particular, both the wave relative to Pt-OH formation and the corresponding reduction peak are significantly reduced. Changes are also visible in the hydrogen region: the less cathodic couple of peaks tends to disappear, while the more cathodic couple of signals is progressively amplified (in Figure 2, arrows indicate the change trend), as the $\text{Br}^-/\text{Br}_3^-$ concentration in solution is increased.

$\text{Br}^-/\text{Br}_3^-$ concentrations in the range from 0 to $100 \mu\text{M}$ and from $150 \mu\text{M}$ to 1 mM were investigated and results are shown in Figure 2A and 2B, respectively, maintaining the same window of polarization (at variance with the procedure used by Conway et al. [9], who changed the anodic inversion potential to less positive values while increasing the bromide concentration in solution to avoid Br_2 formation). As a result of this different

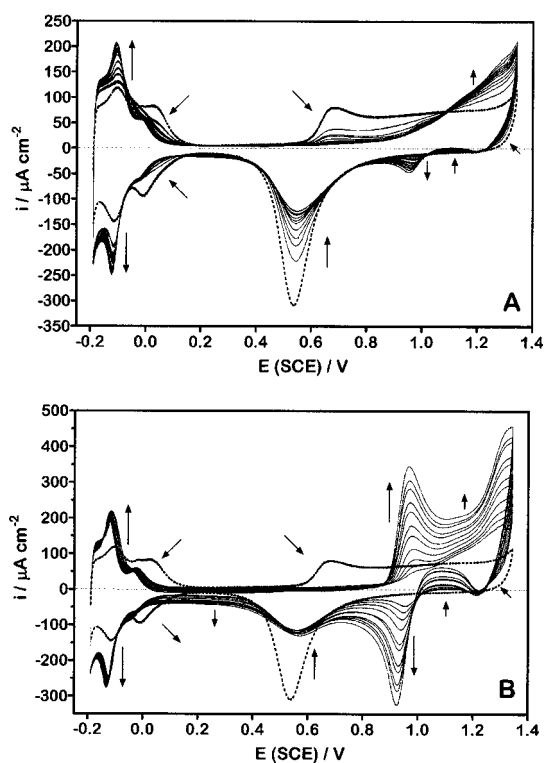


Fig. 2. CV curves recorded in 1 M HClO_4 , with increasing amounts of $\text{Br}^-/\text{Br}_3^-$ is solution: (a) from 4 to $100 \mu\text{M}$; and (b) from 150 to $1000 \mu\text{M}$. Scan rate 0.1 V s^{-1} . Arrows indicate the evolution of the profile as the Br-related species in solution is increased.

experimental approach, some features (listed below) appear particularly relevant.

1. Both the Br_2/Br^- redox couple (centered at about 0.944 V vs SCE) and that centered at about 1.29 V vs SCE (possibly related to the BrO^-/Br_2 redox equilibrium) become clearly evident as the $\text{Br}^-/\text{Br}_3^-$ concentration is increased.
2. The oxide reduction peak is significantly affected by the adsorption of the different Br-related species, but it never disappears, as a plausible consequence of the considered polarization window. To make the oxide reduction signal practically negligible, the anodic sweep has to be limited to 0.95 V vs SCE (i.e., just before the bromide oxidation peak, Figure 3). This choice was made by Conway et al. [9], who claimed that, under these conditions, the bromide adsorption and reaction takes place at an 'almost completely oxide-free' Pt surface. In contrast, under the conditions chosen in the present paper, the Pt surface cannot be considered free from oxygenated species, at the potentials required for a significant Br_2 formation.
3. As far as the hydrogen region is concerned, the presence of Br-related species at the Pt surface also clearly hinders the hydrogen adsorption, as indicated by the progressive disappearance (while shifting toward more cathodic potentials) of the couple of peaks initially centered at about 0.014 V vs SCE . On the other hand, that centered at about -0.11 V vs SCE has an opposite behaviour, being also related to the Br reductive desorption/'oxidative' adsorption [7].

Analogous data were obtained working with the Br^- stock solution (instead of the $\text{Br}^-/\text{Br}_3^-$ mixture). As shown in Figure 4, effects are less important than in the previous case, because of the 'simpler' composition of the solution. Comparison of Figures 2 and 4 clearly suggests that both Br^- and Br_2 (or Br_3^-) adsorb on the electrode surface. Since a very good agreement exists between the CV signal obtained at a given $\text{Br}^-/\text{Br}_3^-$ concentration with that at a threefold $[\text{Br}^-]$ (e.g., curves

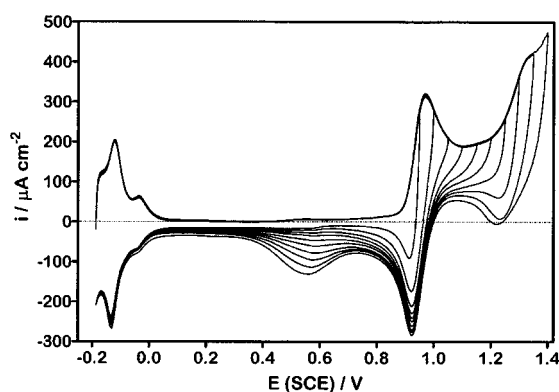


Fig. 3. CV curves recorded in 1 M HClO_4 , in the presence of $1 \text{ mM Br}^-/\text{Br}_3^-$ is solution, varying the anodic switching potential from 0.95 to 1.40 V vs SCE . Scan rate 0.1 V s^{-1} .

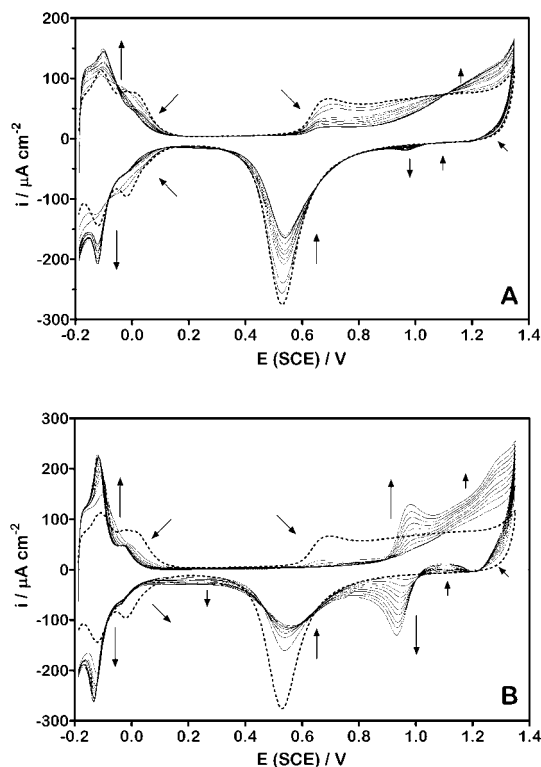


Fig. 4. CV curves recorded in 1 M HClO₄, with increasing amounts of Br⁻ in solution: (a) from 4 to 100 μM; and (b) from 150 to 1000 μM. Scan rate 0.1 V s⁻¹. Arrows indicate the evolution of the profile as the Br⁻ ion concentration in solution is increased.

recorded in the 100 μM Br⁻/Br₃⁻ and in the 300 μM Br⁻ overlap almost perfectly – Figure not given), it seems reasonable to assume that Br₂, and not Br₃⁻, undergoes dissociative adsorption and interacts with the electrode surface, together with the bromide anions. On the other hand, it is worth mentioning that the reaction Br⁻ + Br₂ → Br₃⁻ has an equilibrium constant $K_{\text{eq}} \approx 16$ [9], which points toward a solution composition approaching the nominal one.

With reference to Figure 2B, the negative current, measured in connection with the double layer section, during the anodic sweep, is noteworthy. The charging of the double layer is overcompensated by some kind of reduction process, tentatively attributable to the presence of Br₂ and/or Br₃⁻, whose reduction takes place significantly only when the concentration is relatively high (greater than ~200 μM). Since the same effect is notable in Figure 4B, in the absence of both Br₂ and Br₃⁻ (the bromine produced during the anodic sweep is likely to be completely reduced through the cathodic scan), the occurrence of a reaction like that schematized in Equation 1 cannot be ruled out.

From the variation of the oxide reduction peak current, with the adsorbing species concentration (this variation has been indicated as Γ), a detailed investigation of the adsorption phenomenon can be carried out. Analyses were made for the two operating conditions (the Br⁻/Br₃⁻ mixture and Br⁻ alone) and at the two pH. From the plot of $1/\Gamma$ against $1/c$, an estimate of Γ_{max}

was made, allowing the transformation of data in terms of θ , as shown in Figure 5 (the offset of axes is required for seeing the rising part of the curves). A quite good fit of the data was obtained supposing, as a first approximation, a Langmuir-type adsorption. Additionally, the maximum coverage by Br-related species was also estimated, dividing Γ_{max} by the height of the oxide reduction peak, in the presence of the pure supporting electrolyte (Γ_0). As provided in Table 1, values between 0.62 and 0.66 are found for that ratio, in substantial agreement with the estimations given by Bagotzky et al. [1] and Orts et al. [11].

In principle, considering the significant coverages attainable by Br-related species, the Langmuir isotherm should be better substituted by a relation taking into account the possible presence of lateral interaction [13]. Thus, the elaboration has been tentatively repeated hypothesizing a Frumkin-type isotherm (Equation 3 below), instead of the Langmuir one previously cited:

$$\frac{\theta}{1-\theta} = \beta c \cdot e^{-2a\theta} \quad (3)$$

where $\beta = \exp[-\Delta G_{\text{ads}}^{\circ}/RT]$ is the equilibrium constant for the adsorption phenomenon, c is the adsorbing species concentration and a is a parameter accounting for particle–particle lateral interaction (it is positive for attraction and negative for repulsion). Testing of the

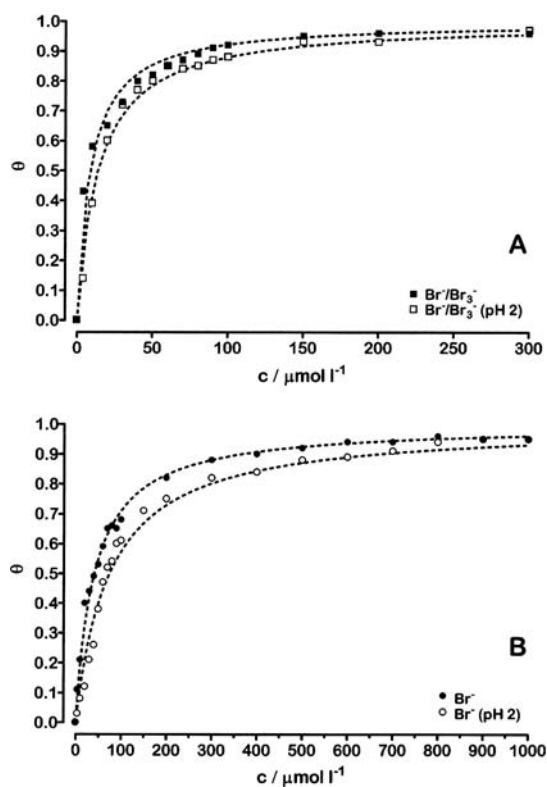


Fig. 5. Adsorption isotherms for Br-related species from (a) Br⁻/Br₃⁻ and (b) Br⁻ solutions, at the two investigated pH; data points fitted with Langmuir-type equations.

Table 1. Analysis of the oxide reduction peak dependence on the nature and concentration of Br-related species in solution (working potential: ~ 0.54 V vs SCE)

		Br ⁻ /Br ₃ ⁻		Br ⁻	
		1 M HClO ₄	1 M NaClO ₄ at pH 2	1 M HClO ₄	1 M NaClO ₄ at pH 2
Langmuir	Γ_{\max}/Γ_0	65.7%	63.3%	61.7%	63.1%
	$-\Delta G_{\text{ads}}/\text{kJ mol}^{-1}$	28.93	27.76	25.08	23.57
Frumkin	a	0.13	0.17	-0.18	0.29
	$-\Delta G_{\text{ads}}/\text{kJ mol}^{-1}$	27.88	27.26	25.58	22.73

Frumkin isotherm allowed the determination of its characteristic parameters (a and ΔG_{ads}), which have been collected in Table 1, together with that of the Langmuir isotherm (ΔG_{ads} [13]).

It is interesting to observe that a values quite close to zero were obtained, suggesting minor contributions for the lateral interactions. As a curiosity, a negative value was found for that parameter in the case of bromide adsorption from the 1 M HClO₄ medium, that is, the situation in which hydroxyl radicals are formed with major difficulty (due to the relation between the standard redox potential and the pH of the solution), together with a minimum for the ratio Γ_{\max}/Γ_0 . Both this value and that of a are related to the interactions existing among the different particles at the electrode surface; in particular, both Br- and O-related species should be considered. Assuming that a lower coverage of O-related species is present on the Pt surface at the more acidic pH (compared with the other situation, at the same electrode potential) and on the basis of the data in Table 1, the following statements seem to apply:

- (i) The accommodation of neutral Br-related species (Br[·] or Br₂) is limited by the presence of Pt-OH/Pt-O species on the Pt surface, because the latter reduces the accessible surface area. Since the O-related coverage increases as the pH is increased, an opposite behaviour is expected for the adsorption of Br₂.
- (ii) Accommodation of charged Br ^{δ -} species (where δ represents the residual charge, after the partial charge-transfer that allows the chemisorption process) cannot be excluded, in spite of the a value previously discussed. Such arrangement should also

be influenced by the above O-related species, their presence having a ‘positive effect’, as they screen/reduce the repulsions among the adsorbed Br ^{δ -} anions.

Analysing Figure 4 (but the same considerations hold for Figure 2) and considering the hydrogen region, CV curves show that the first couple of peaks, centered at about 0.014 V vs SCE and undoubtedly related to hydrogen adsorption, is progressively damped, in the presence of an increasing amount of Br⁻ (or of the Br⁻/Br₃⁻ mixture) in solution. In contrast, an opposite behaviour is found for the signals centered at about -0.11 V vs SCE, for which an analysis in terms of Langmuir and Frumkin isotherms was also carried out (Table 2). In that case, the examination was done separately considering both the anodic and the cathodic peaks, and assuming that constant hydrogen desorption/adsorption current contributions were present. Analogous problems did not exist with the oxide reduction peak.

As previously stated, the cathodic peak signal at about -0.13 V vs SCE has been assigned to the reductive desorption of Br, by Salaita et al. [7]; consequently, the related anodic peak at about -0.125 V vs SCE has to be attributed to an oxidative adsorption of Br-related species. The latter phenomenon represents an underpotential deposition of bromine, which necessarily affects the kinetics of the successive bromide anodic oxidation.

The difficulties in determining a correct value for the Br-related adsorption/desorption peak current are unfortunately the reason of the unreliability of some of the data in Table 2 (less convincing data have been

Table 2. Analysis of the hydrogen region dependence on the nature and concentration of Br- related species in solution (working potential regions: from -0.114 to -0.106 V vs SCE, and from -0.131 to -0.117 V vs SCE, for the anodic and cathodic signals, respectively)

		Br ⁻ /Br ₃ ⁻		Br ⁻	
		1 M HClO ₄	1 M NaClO ₄ at pH 2	1 M HClO ₄	1 M NaClO ₄ at pH 2
Anodic signal					
Langmuir	$-\Delta G_{\text{ads}}/\text{kJ mol}^{-1}$	26.08	24.53	(19.55)	27.26
Frumkin	a	0.39	-0.08	(-0.33)	(-3.29)
	$-\Delta G_{\text{ads}}/\text{kJ mol}^{-1}$	24.95	24.79	(20.43)	(20.10)
Cathodic signal					
Langmuir	$-\Delta G_{\text{ads}}/\text{kJ mol}^{-1}$	26.71	(15.74)	23.57	24.20
Frumkin	a	0.03	-0.47	-0.25	-0.34
	$-\Delta G_{\text{ads}}/\text{kJ mol}^{-1}$	26.50	28.97	24.16	25.12

reported in parentheses). A general remark can be given, based on the values of a : a minor, repulsive effect is generally found, making use of results on the adsorption/desorption of Br^- from the Pt electrode, in Br^- as well as $\text{Br}^-/\text{Br}_3^-$ solutions (at the two considered pH), suggesting a progressive uptake/release of charge on/from the surface-interacting particles.

For the case where the adsorption can be described by a Langmuir-type isotherm, the peak current density is proportional to the surface concentration, Γ_x , of the electroactive, generic adsorbate X [14]:

$$|i_p| = \frac{n^2 F^2 \Gamma_x}{4RT} v \quad (4)$$

where v represents the sweep rate, n is the number of electrons exchanged during the adsorption process, while F , R and T have their usual meaning. Once the peak current density has been obtained from the CV curve, an estimation of Γ_x can be obtained by Equation 4. The above analysis was carried out basing on both the oxide reduction peak and on the couple of signals centered at about -0.11 V vs SCE, and considering that only one electron is exchanged during the adsorption of Br- as well as O-related species (i.e., $\cdot\text{OH}$ radicals are formed, instead of $\text{O}\cdot$ radicals; alternatively, the ‘bridged structure’ of O species coordinated to two adjacent Pt atoms, recently proposed by Zolfaghari et al [15], could be considered). A qualitative examination of the data collected in Table 3 shows that, unsurprisingly, the surface concentration of O-related species, Γ_o , is higher at the less acidic pH. In the presence of Br^- or the $\text{Br}^-/\text{Br}_3^-$ mixture in solution, adsorption of Br-related species takes place at the electrode surface. Such adsorption competes with that of O-related species, if the electrode potential is sufficiently positive. In this case, the electrode surface becomes covered with both Br- and O-related species, the maximum surface concentration of the former being reported in the second row of Table 3.

The last two rows in Table 3 refer to the hydrogen region, and surface Br-related species concentrations have been estimated from both the anodic and the cathodic peak (couple centered at -0.11 V vs SCE), leading to values for $\Gamma_{\text{Br(H,a)}}$ and $\Gamma_{\text{Br(H,c)}}$, respectively. It is interesting to check the surface concentration of Br-related species (Γ_{Br}) starting, for example, from the adsorption in the hydrogen region (for the $\text{Br}^-/\text{Br}_3^-$ mixture in 1 M HClO_4 , $\Gamma_{\text{Br(H,a)}} \approx 6.5 \times 10^{14}$ at cm^{-2}) and following the potential as in the CV curve.

Increasing the electrode potential, adsorbed $\text{H}\cdot$ radicals are progressively oxidized, permitting the possible increase in Γ_{Br} . When the electrode potential is sufficiently positive to allow hydroxyl adsorption, Γ_{Br} decreases and reaches the value that has been estimated on the basis of the oxide reduction peak ($\sim 66\%$ of the maximum coverage, as shown in Table 1), due to the concomitant and competitive presence of both Br- and O-related particles at the electrode surface. Once the oxide reduction has taken place, the further adsorption of Br-related species is in competition with that of hydrogen; at the potential of the peak signal, $\Gamma_{\text{Br(H,c)}} \approx 8.4 \times 10^{14}$ at cm^{-2} . Looking at the role of the pH, a substantial increase in $\Gamma_{\text{Br(H,a)}}$ and $\Gamma_{\text{Br(H,c)}}$ is generally encountered, which seems in contrast with the possibly expected role of the proton. However, other cations can play a similar role (Ca^{2+} and K^+ , as discussed in [7], possibly Na^+ in this specific case), their incorporation in the Br adlayer appearing necessary for the achievement of high coverages, thus suggesting that the adlayer is not formed by neutral species.

4. Conclusions

The experimental results fully support the expectation of a strongly favoured adsorption of Br^- , based both on poor primary solvation of the anion and on its short-range interactions with the metal surface. At Pt surfaces, the latter leads to an early UPD of Br radicals, covering the electrode surface and preventing the formation of Pt–OH bonds, which is shifted towards more positive potentials. The strong interactions between bromine radicals and the Pt surface also accounts for Br_2 dissociative adsorption.

As shown in Table 3, Γ_{Br} values, when compared with Γ_o , are compatible with the attainment of a relatively high surface coverage. An extension of the polarization to the potential region where oxygen adsorption appears may reduce the coverage to about 2/3, that is, the value previously reported [1, 11]. At the Pt electrode, under these conditions, surface adsorption of different radical species takes place, which compete for the available surface but also interact with each other, also changing the energetics of adsorption through lateral interactions. Minor repulsions are present among the Br-related species (partially uncharged $\text{Br}^{\delta-}$ anions and/or bromine molecules, which are apparently subjected to dissociative

Table 3. Estimations of maximum O- and Br-related species surface concentration, as obtained from the CV peaks [14]

Surface concentration /at cm^{-2}	$\text{Br}^-/\text{Br}_3^-$		Br^-	
	1 M HClO_4	1 M NaClO_4 at pH 2	1 M HClO_4	1 M NaClO_4 at pH 2
Γ_o	2.0×10^{15}	2.1×10^{15}	1.8×10^{15}	2.1×10^{15}
Γ_{Br}	1.2×10^{15}	1.3×10^{15}	1.0×10^{15}	1.2×10^{15}
$\Gamma_{\text{Br(H,a)}}$	6.5×10^{14}	6.3×10^{14}	7.4×10^{14}	8.0×10^{14}
$\Gamma_{\text{Br(H,c)}}$	8.4×10^{14}	9.7×10^{14}	7.6×10^{14}	8.7×10^{14}

adsorption), as a possible consequence of the absorption of cations that neutralize the charge in the adlayer. In addition, while the weak adsorption of hydrogen is hindered by the presence of Br-related species in the solution, the strongly-adsorbed-type of hydrogen does not seem to be influenced by the Br adsorption, which possibly takes place at the same Pt surface sites.

As far as the anodic part of the CV profile is concerned, the results will serve as the basis for further investigation of the kinetics of the bromine electrode.

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