

EFFECTS OF ADSORBED HALIDE IONS ON THE CYCLIC-VOLTAMMETRY CURRENT - POTENTIAL PROFILES FOR Pb UNDERPOTENTIAL DEPOSITION AT Au

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Abstract. By means of cyclic-voltammetry experiments conducted in aq. HClO₄ solutions, the effects of adsorbed halide ions Cl⁻, Br⁻, and I⁻, on the *i* vs *E* UPD profiles of Pb at Au is studied down to very low concentrations. In the presence of specifically adsorbed halide ions, it has been found that the peaks for the initial process of Pb atoms deposition are substantially shifted to less positive potentials. Depending on the species, the effects on the upd profiles are different but it is generally observed that the effects are significant already at high dilutions of the UPD added species. For example, in the case of I⁻ the effects are already discernible at about 10⁻⁷M. Saturation effects for the different species are also attained at different concentrations. The most striking and interesting effect of added Cl⁻, and Br⁻ but not observed in the case of added I⁻, is the appearance of an extra peak in the anodic sweep at the most positive potential of the sweeps (ca. 0.40 to 0.55 V/E_H). A corresponding peak is observed on the cathodic sweep of the profile in the case of added Br⁻, but not in the case of added Cl⁻. Examples are discussed with Pb adatom blocking isotherms for a range of adsorbed anion concentrations; the type of competitive adsorption isotherm depends appreciably on the identity of the anion involved. For example, Cl⁻ gives linear-logarithmic behaviour in [Cl⁻], indicating strong lateral interactions while Br⁻ and I⁻ effects conform to Langmuir-type behaviour.

INTRODUCTION

Adsorbed anions usually have marked effects on the current-potential (*i* vs *E*) under-potential deposition (UPD) profiles of H at Pt [1-3], Pb at Au [4] or of the initial stages of surface oxidation of Pt or Au [3, 5]. The adsorption is competitive in nature between the species deposited and the adsorbed anions at the under-potentials so that (as with H) the same quantity of Pb is eventually deposited but over a different range of potentials and in different sub-states from those in the absence of the competitively adsorbing species. Previous work on the anion effects on the UPD of Pb at Au in aqueous solutions has shown that the order of strength of specific adsorption of anions is of the order F⁻ < ClO₄⁻ < HSO₄⁻ < Cl⁻ < OH⁻ < Br⁻ < B₄O₇²⁻ < I⁻ [6, 7]. Schmidt and co-workers [7] found that in the UPD of Pb on Au, the monolayer cathodic peak was shifted to more cathodic potentials by adsorbed anions in the increasing order NO₃⁻ < CH₃COO⁻ < Cl⁻ < Br⁻, with a similar order for Cl⁻ and Br⁻ being found by Kolb *et al.* [8]. Vicete and Bruckenstein [9] found in their investigations that Cl⁻ ion enhances the adsorption of Pb on Au. In the absence of Cl⁻ the monolayer cathodic peak is sharper, although it was slightly shifted to more negative potentials, as expected for competitive adsorption by an anion. Studies of adsorption of Cl⁻, Br⁻, and I⁻ ions at Pt have been made by bold and Breiter [10] and demonstrated that these ions are already significantly adsorbed at low concentrations.

In this paper we present the results on the effect of strongly adsorbing anions Cl⁻, Br⁻ and I⁻ on the *i* vs *E* UPD profiles of Pb on Au by means of the sensitive cyclic-voltammetry

technique. This is examined with respect to the shift of the peak potentials to more negative potentials in the presence of these anions. An important aspect of the work is the characterization of the competitive adsorption effects over a wide range of fairly closely spaced halide concentrations down to 10^{-7} M with Cl⁻ and Br⁻ and 10^{-8} M with I⁻. The results obtained were used to evaluate the isotherms for adsorption of halide ions and for competitive blocking of the Au surface by the halides during the competitive adsorption.

EXPERIMENTAL

General. The electrochemical measurements consisted mainly in determination of cyclic voltammograms in the presence of halide ions using a Wenking potentiostat and a Tacussel arbitrary function generator, GSATP, under condition of careful control of potential-sweep range and sweep-rate. Only by means of the sensitive cyclic voltammetry can the effects of adsorbed halide ions on the *i* vs *E* UPD profiles of Pb on Au be followed sensitively. The *i* vs. *E* profiles for Pb upd at Au in the absence of the halide ions was used as the reference point. High-purity techniques in dealing with cells and solutions were employed (as described below) when working with aqueous solutions.

Purity and purification of solvents and gases

Water. Pyrodistilled water, prepared as described in a previous publication [11], was used in the work on aqueous solutions as a reference system. The criteria for its satisfactory purity were as previously discussed [11].

Gases: Electrolytic H₂ and N₂ gases, used for the Pt/H₂ reference electrode and for deoxygenation of the solutions, respectively, were purified in a conventional gas train mainly to remove traces of O₂.

Hydrogen was passed through a gas train consisting of Mg(ClO₄)₂ as a desiccant, molecular sieves (BDH type 4A), an oven containing palladized asbestos and Cu turnings at 623 K, and finally activated charcoal traps cooled by liquid N₂.

N₂ gas was passed through an identical purification train except that only Cu turnings were used in the oven. The metallic surface of the Cu turnings at 623 K was periodically regenerated by passing H₂ through the oven until the Cu turnings regained their bright metallic surfaces after reduction of any oxide film that had been formed.

Cleaning of glassware. Before performing electrochemical experiments, the electrochemical cell and its glass component parts were soaked in fresh, concentrated chromic + sulphuric acid solution for *ca* 12 h. They were then rinsed several times with doubly distilled water and finally washed with hot pyrodistilled water. Identical cleaning procedures were applied periodically to the ancillary glassware for preparing salts or solutions, or for storing doubly-distilled and pyrodistilled water.

Working electrodes. These were made from Au wires of 99.999% purity, using Johnson Matthey "Grade 1" polycrystalline Au. Suitable lengths of these wires, usually of diameter 0.51 mm (0.02"), were first degreased overnight in refluxing acetone in a Soxhlet extractor. The Au wires were then flame-welded to much longer pieces of Ag wire to provide electrical contact and a droplet of (Pb-free) soft-glass was then melted on to the wire and sealed into the

end of a 6 mm diameter soft-glass tube leaving between 15 and 20 mm of wire protruding beyond the end of the tube. The Au-Ag contact was at least 15 mm above the glass seal. The soft glass had been previously cleaned in fresh chromic acid solution and rinsed several times, first with doubly-distilled water, then followed by pyrodistilled water. The completed electrodes were then washed and stored in fresh, concentrated H_2SO_4 , as indicated earlier.

An electrode of Au, relatively large in area, was also used as the counter electrode.

Hydrogen reference electrode. The hydrogen reference electrodes, which were used in the experiments conducted in aqueous medium, were prepared according to the procedure given by Ives and Janz [12], using a platinizing solution of 2% H_2PtCl_6 in 2 N HCl without the addition of lead acetate (cf. the recipe of ref. [13]) because of the possibility of introducing undesirable impurities into the working electrode electrolyte. The finished electrodes were rinsed several times with doubly distilled water and stored under pyrodistilled water. Potentials were checked from time to time against similar electrodes to detect any potential drift.

Electrochemical cell. A conventional two-compartment cell was used. The reference-electrode compartment was separate but it was connected to the solution and electrode in the working-electrode compartment by a Luggin capillary in the usual way. Solutions in the working-electrode compartment were deoxygenated by bubbling a slow stream of purified N_2 for 20-30 min before measurements were commenced.

The salts used in the present work were purified from the following starting materials by double recrystallization from pyrodistilled water, followed by vacuum drying: $\text{Pb}(\text{NO}_3)_2$, NaCl, NaBr and NaI. All solutions were prepared using pyrodistilled water [11]. H_2SO_4 and HClO_4 solutions were made up using the purest commercially available acids (BDH AristaR grade) which, as noted previously [14, 15], had been found to be of sufficiently high purity to be used directly, as demonstrated by highly sensitive cyclic-voltammetry results conducted at Pt electrodes [11].

Real surface area of Au electrodes. Unlike the situation with Pt electrodes whose real areas can be determined by UPD H accommodation measurements [16, 17], the real areas of Au electrodes cannot be evaluated by such a procedure. However, by means of a procedure of Michiri *et al.* [18] the charge required to electrodeposit O species in 0.5 M H_2SO_4 below the potential of the well-defined current minimum (so-called "Burshtein minimum"), immediately preceding O_2 evolution can be determined as $400 \mu\text{C}$ per real cm^2 , and this figure was assumed to be the charge required to electrodeposit a monolayer of O species, based on a charge of $2 e$ per site of O atoms. B.E.T. measurements were used by the above authors to provide calibration data for the Au electrode areas and their method was shown to be valid over a range of temperatures and sweep-rates. This procedure was used in the present work, with an allowance for double layer charging in the cyclic voltammetric curves.

Micrometer titration procedure. Although the effect of halide ions, especially Cl^- , on the upd of Pb at Au has been reported in the literature, e.g. in the refs. [4, 8, 9], these experiments were done either at only one or over a narrow range of Cl^- concentrations. Therefore, in order to obtain more useful information on the progression of the competitive adsorption effects of added halide ions on the UPD profiles of Pb at Au from very low concentrations, a dilute solution of the X^- salt was titrated in successive aliquots into the electrochemical cell by

means of an accurate micrometer syringe through a 1 mm Teflon 'spaghetti' tube, terminating in a fine glass jet.

Depending on the species to be added, the measurements were commenced at very low concentrations, 10^{-8} to 10^{-6} M, since significant effects were already detectable at high dilutions, especially in the case of I^- .

Before additions of any aliquots of X^- ion were made, an i vs E profile of the UPD of Pb at Au was first obtained in the absence of added ion; this curve was used as a reference against which i vs E profiles in the presence of various concentrations of halide ions could be compared.

After each addition of the solution of the halide salt into the electrochemical cell containing a known volume of working electrolyte solution, the solution was vigorously stirred by bubbling of N_2 . Cyclic-voltammetry sweeps at 50 mV s^{-1} were recorded 60 - 300 s after addition of the halide ion to allow time for adsorption equilibrium to be attained especially at low concentrations. Two X-Y recorders were employed in parallel: one to record separately the i vs E profile for each halide concentration for subsequent calculations, the other to build up a succession of superimposed i vs E profiles corresponding to each aliquot of the added solution, thus displaying the progressive effects of the added halide ions.

The micrometer titration procedure was also applied in order to record a series of individual and superimposed i vs E profiles for Au corresponding to different concentrations of the additions after successive additions of Cl^- , Br^- , and I^- had been made to the background electrolyte without a Pb salt being present. This gave a series of "control" or "background" curves.

RESULTS AND DISCUSSION

Effects of adsorption of halide ions on i vs E profiles for UPD of Pb at Au. The effects of added halide ions on the i vs E profile for UPD of Pb at Au in aq $HClO_4$ solutions can be detected at very low concentrations, around 10^{-5} , 10^{-6} and 10^{-7} M for Cl^- , Br^- , and I^- , respectively. A clean potentiodynamic i vs E profile for Pb UPD at Au obtained in aq 1M $HClO_4$ + 10^{-3} M $Pb(NO_3)_2$ solution from this work showing the various distinguishable Pb ad-states obtained that is used a reference is given in Figure 1. A series of superimposed cyclic-voltammograms, corresponding to various additive concentrations, following successive additions of Cl^- , Br^- or I^- in aq $HClO_4$, are shown in Figures 2, 3 and 4, respectively. The concentration ranges are indicated in each case and series of curves show the effects of progressive competitive adsorption of these halide ions on the UPD profile for Pb monolayer formation on Au.

Significant and interesting differences are seen between the effects of these added species, even at very high dilutions, as will be discussed below for the individual effects of the three halide ions.

Effects of Cl^- . The effects of Cl^- on the i vs E UPD profile of Pb at Au in aq $HClO_4$ (Figure 2) are significant and interesting. At very high dilutions, in the concentration range 10^{-7} to 10^{-6} M the initial effects are manifested as slight diminutions of the first cathodic peak. As the concentration of added Cl^- is increased, the first cathodic peak (C_{Pb1}) and the corresponding first anodic peak (A_{Pb1}) (Figure 2) are progressively shifted to more cathodic, i.e. less positive, potentials at the same time becoming sharper than the corresponding peaks in the absence of

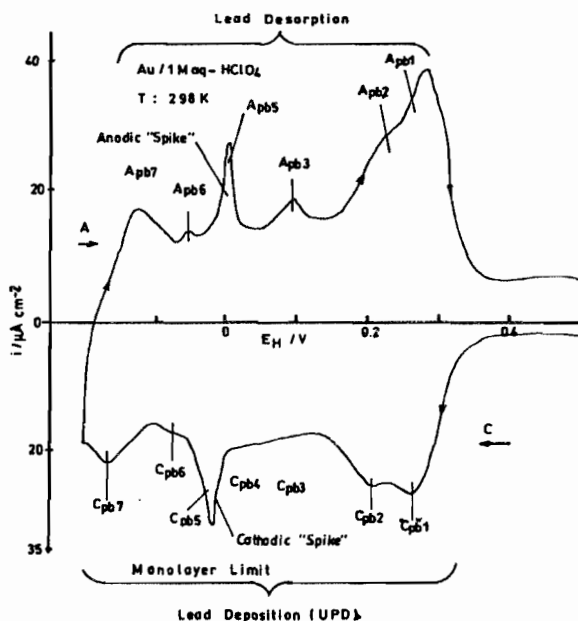


Figure 1. Potentiodynamic i vs E profile for Pb UPD at Au in aq 1 M $\text{HClO}_4 + 10^{-3}$ M $\text{Pb}(\text{NO}_3)_2$ solution at 298 K showing the various distinguishable Pb ad-states developed in a formation of a monolayer region. $s = 50 \text{ mV s}^{-1}$. (Used as the reference figure).

added Cl^- ion. The sharpening of the peaks in the presence of Cl^- suggests that with Cl^- adsorption, there are strong lateral interactions corresponding to repulsion between the adsorbed Cl^- and the electrodeposited Pb adatoms, and between the adsorbed Cl^- ions themselves. It is believed that adsorbed Cl^- on Au still retain some partial charge on adsorption [19]. A saturation level of the effects of Cl^- are detected at a concentration of about 10^{-2} M. The added Cl^- has only small effects on the other resolvable peaks in the i vs E profile.

The most striking and interesting effect of Cl^- (also observed in the case of Br^-) that was not observed in the case of I^- (see Figures 2 and 3), is the appearance of an extra peak (shoulder) in the anodic sweeps at the most positive potentials of the sweeps. This effect arises in the potential range ca 0.4 to 0.55 V/E_{H} , beyond the potential of the usual first anodic peak observed in "clean" solution. Important points to note about this peak are: it is observed only in the concentration range of approximately 10^{-5} to 10^{-3} M and its shape and size are concentration dependent; it shifts to less positive potentials with increasing Cl^- concentration until it becomes merged with the main anodic peak at higher concentrations; no corresponding peak arises on the cathodic side of the i vs E profile in the whole concentration range of Cl^- used in the present study.

A series of progressively restricted range sweeps were performed on the UPD i vs E profile for Pb at Au in aq HClO_4 containing 4×10^{-4} M Cl^- (Figure 5) in order to relate to which Pb ad-state on the cathodic sweep the extra anodic peak on the anodic sweep, due to Cl^- , corresponds. Examination of Figure 5 shows that this extra anodic peak, at more positive potentials than the usual anodic peaks, is not associated with the ad-state C_{pb1} . It starts to develop after the completion of the "spike" (ad-state C_{pb5}). It was also found that this extra

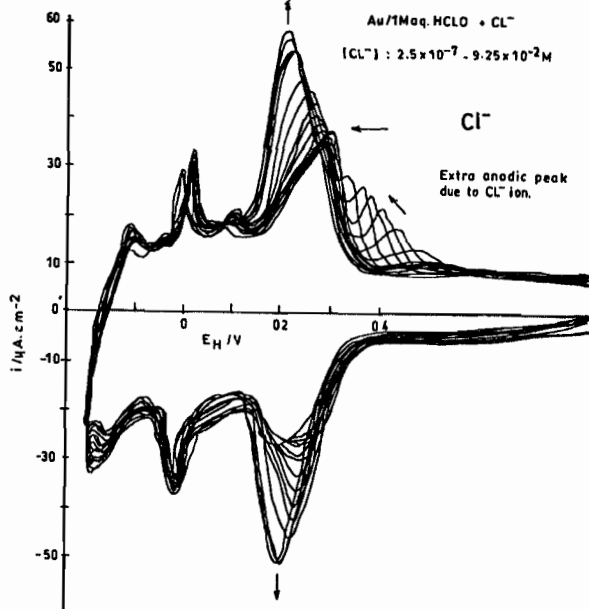


Figure 2. Series of superimposed cyclic i vs E profiles for Pb UPD at Au in aq 1 M HClO₄ + 10⁻³ M Pb(NO₃)₂ with successive additions of Cl⁻ ion from 2.5×10^{-7} to 9.25×10^{-2} M. Arrows show directions of change of curves with increasing [Cl⁻]; $s = 50 \text{ mV s}^{-1}$

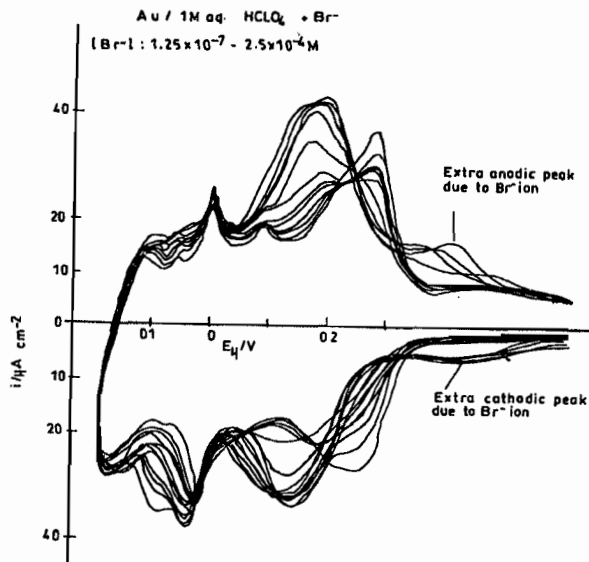


Fig. 3. Series of superimposed cyclic i vs E profiles for Pb UPD at Au in aq 1 M HClO₄ + 10⁻³ M Pb(NO₃)₂ with successive additions of Br⁻ ion from 1.25×10^{-7} to 2.5×10^{-4} M. Arrows show directions of change of curves with increasing [Br⁻]; $s = 50 \text{ mV s}^{-1}$.

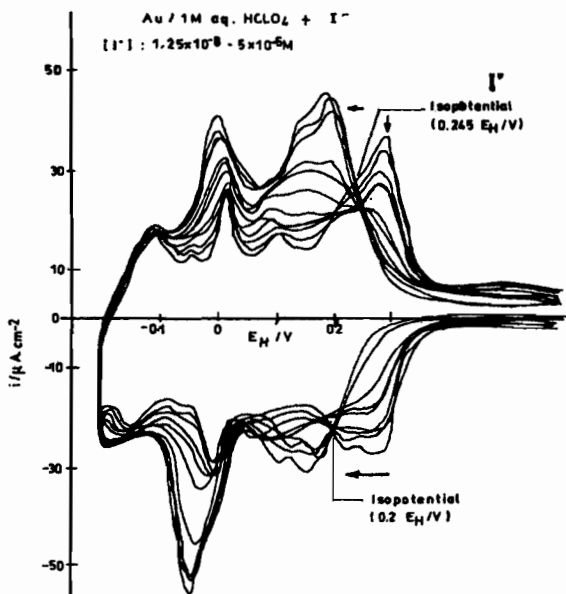


Figure 4. Series of superimposed cyclic i vs E profiles for Pb UPD at Au in aq 1 M HClO₄ + 10⁻³ M Pb(NO₃)₂ with successive additions of I⁻ ion from 1.25 × 10⁻⁸ to 5 × 10⁻⁵ M. Arrows show directions of change of curves with increasing [I⁻]. $s = 50$ mV s⁻¹

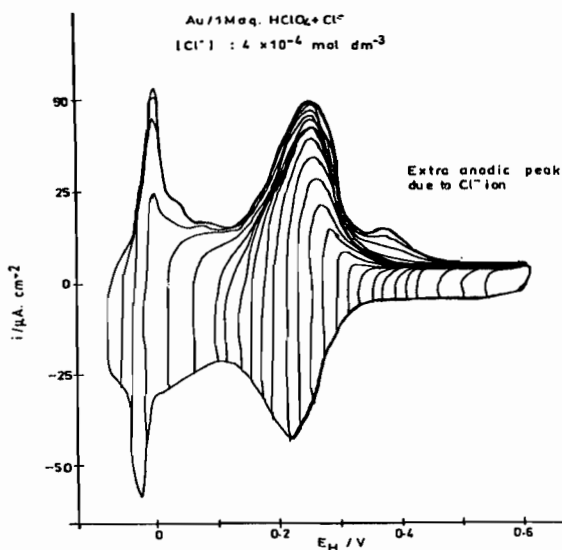


Figure 5. Series of progressively restricted cyclic-voltammetry i vs E profiles for Pb UPD at Au in aq 1 M HClO₄ + 10⁻³ M Pb(NO₃)₂ containing 4 × 10⁻⁴ M of Cl⁻ ion; $s = 50$ mV s⁻¹

peak was independent of stirring, an indication that it is not due to some impurity from the electrolyte solution or from the electrode.

It is interesting to note that this extra peak which corresponds to some form of Pb which desorbs at potentials more positive than those of the other anodic peaks does not correspond, at least, to C_{Pb1} which is the peak for the most tightly bound Pb at the Au electrode surface.

In the case of the series of the superimposed i vs E profiles obtained in aq $HClO_4$ with successive additions of Cl^- but without a Pb salt being added, no anodic or cathodic peak is observed at the same potential or over the same concentration range for which the extra anodic peak was observed in the case of Pb UPD at Au from aq $HClO_4$ in the presence of added Cl^- . It is not therefore an artefact arising from the effect of Cl^- on the background curve. The fact that this peak arises at more positive potentials, and is absent when the background electrolyte contains only Cl^- , leads us to propose that this peak is due to desorption of some kind of Pb adatoms, or possibly a Pb chloride complex, strongly interacting with the Au electrode substrate.

Vicente and Bruckenstein [9], in their studies of the UPD of Pb at Au in solutions containing various concentrations of Cl^- using a rotating disk electrode, found that the first cathodic peak arose at slightly more positive potentials in contrast to what is observed in the present work. Although the first cathodic peak in their [9] investigation became sharper, similar to what was observed in the present work, they found that the cathodic charge increased with increasing Cl^- concentration. They [9] also concluded that the Cl^- ion enhanced the Pb(II) ion adsorption and the adsorbed species in the UPD layer was probably a chloride complex of Pb, such as $PbCl^+$.

Girgis *et al.* [20] have reported results on Pb electrodeposition on Au from aq solutions of 0.2M ammonium acetate and 0.11M $PbCl_2$. They found that the presence of Cl^- had an appreciable effect on the i vs E UPD profile for Pb at Au. The first cathodic peak was shifted to more negative potentials, although the shift was smaller in acetate solution than that reported in Cl^- in supporting electrolytes of perchlorate or sulphate [8, 21]. They explained these observations in terms of involent of co-adsorption of acetate in the UPD phenomenon with Pb. Although Auger electron spectroscopy indicated the presence of small quantities of Cl in the first layers of Pb in the UPD film, no lead chloride reflections, i.e. due to bulk $PbCl_2$, could be detected by X-ray diffraction.

Vilche and Jüttner [22] have studied the effect of CH_3COO^- anion on the UPD of Pb at Cu(111) single-crystal in aq 0.5 M $NaClO_4$ solutions at various pH values. Their results [22] showed that in the presence of 0.01 M CH_3COO^- anion the first cathodic peak was shifted to more cathodic potentials. Addition of Cl^- , even at high dilutions, caused the first cathodic peak and the corresponding first anodic peak to shift to more negative potentials. These peaks also became sharper and increased in height, similar to what was observed in the present work.

Hubbard *et al.* [23] showed that adsorption of HCl from aqueous solution onto Pt(111) gives rise to a stable (3x3) adlattice. The LEED pattern of the electrodeposited layer was ordered and underwent a series of changes with increasing θ_{Pb} . Auger electron spectroscopy also indicated the presence of Cl^- in the topmost layer of the surface at all Pb coverages.

Since the polycrystalline Au surface is assumed to consist principally of (100), (110) and (111) faced regions [8], and with some populations of higher-index stepped terraces, and also from the results of Hubbard *et al.* [23], it seems likely that, at low coverages, Cl^- adsorbs onto one of these single-crystal facets, probably (111), to form a stable overlay lattice. Electrodeposition of Pb onto such a surface might be influenced by the preadsorbed, ordered Cl^- adlattice to form an ordered layer of co-adsorbed Pb adatoms. Such a stable Pb adlayer

would then tend to become desorbed only at more positive potentials. At very low or high Cl^- coverages, the favourable ordered adlattice may not be able to be formed and hence not influence the ordering of the electrodeposited Pb adatoms. This is, perhaps, why we do not observe the extra peak at low and high chloride concentrations.

The shifts in peak potentials of the first anodic peak (A_{Pb1}) due to Cl^- , observed by various workers using different electrolyte compositions, are summarized in Table I below.

Table 1. Shift in peak potential of the first anodic peak A_{Pb1} in the presence of added Cl^- ion.

[Cl ⁻]	E_p (mV)
0.11 M (in aq acetate solution)	-45 [20]
0.5 M (in acidified aq 0.1 M NaClO_4)	-75 [8]
10^{-2} M (in 1M aq HClO_4)	-90*

*Result of the present work.

Effects of Br⁻. Unlike the considerably different effects of Br^- and Cl^- on the initial stages of surface oxidation of Pt [3], the effect of Br^- on the i vs E profile for Pb at Au from aq 1 M HClO_4 solutions is rather similar to that of chloride (Figure 3). At low concentrations of added Br^- (approximately in the concentration range 10^{-7} to 10^{-6} M), it is observed that there is a progressive diminution of the first cathodic peak (C_{Pb1}) and the corresponding anodic peak (A_{Pb1}); at the same time, the two peaks shift to less positive potentials.

In the case of adsorbed Br^- ions, the first cathodic peak (C_{Pb1}) and the corresponding first anodic (A_{Pb1}) are less sharper than those obtained in the presence of adsorbed Cl^- ions. It should also be noted that even after shifting to more negative potentials due to Br^- ions, the main peaks retain more or less the same shape as those in the absence of added Br^- . These observations suggest that there are weak lateral repulsive interactions between the electrodeposited Pb adatoms and the adsorbed Br^- ions and between the adsorbed Br^- ions themselves. This is because Br^- are adsorbed as neutral atoms [19], unlike the case of adsorbed Cl^- which still retain some charge. A similar observation is also made in the case of adsorbed I^- because they also undergo complete charge transfer on adsorption (Figure 4) [19].

As the concentration of added Br^- increases in aq HClO_4 (Figure 3) an extra peak develops at more positive potentials (*ca* $0.4\text{V}/E_H$) both on the anodic and the cathodic sweeps of the i vs E profiles, although the extra peak on the cathodic side is less pronounced and its size is independent of the concentration of Br^- ions once it develops. The significant features about this peak are: it only develops at high Br^- concentration, it does not shift to less positive potentials with increasing Br^- concentration and it does not merge with the main anodic peak, a situation different from that due to Cl^- .

As explained in the case of adsorbed Cl^- , this extra peak could also be due to adsorption and desorption of some complex of lead with bromide, which strongly interacts with the Au electrode substrate.

It is also found that the effectiveness of competitive adsorption of Br^- is greater than that of Cl^- because the first cathodic peak is shifted to less positive potentials at lower concentrations than with Cl^- and reaches a saturation limit suddenly, i.e. at a critical concentration. Thus saturation effects are observed at a lower concentration in the presence of Br^- than that of Cl^- .

Like the effect of Cl^- , the UPD i vs E profiles for deposition and ionization of Pb remain in an overall way more or less symmetrical in the presence of Br^- , so that both Br^- adsorption and Pb deposition remain essentially reversible.

Effects of I^- . As Figure 4 shows, the effects of I^- on the i vs E UPD profile of Pb at Au are rather similar to those of Br^- at high dilutions. At low concentrations, the adsorption of I^- causes initially a lowering of the first cathodic peak with a small shift to more negative potentials. At the same time, the "spike" on the cathodic sweep broadens into a normal peak, and its height increases with added I^- concentration. This effect is different from that of Cl^- or Br^- (Figures 2 and 3). Unlike the effects of Cl^- or Br^- , the presence of I^- does not result in the formation of the extra peak (Figure 4) at the positive end of the anodic sweep.

In the case of adsorbed I^- , there is sudden increase in the effectiveness of competitive adsorption vs Pb deposition at a critical I^- concentration in solution which results in a sudden transition to saturation at a lower concentration (*ca.* 10^{-7} mol L^{-1}) than that for either Cl^- or Br^- required to reach corresponding saturation limits (in the case of Cl^- , the approach to saturation limit is not discontinuous (Figure 6).

Unlike the effects of Cl^- or Br^- , adsorbed I^- does not cause the first cathodic peak and the corresponding first anodic peak to be sharper. In fact the shifted first cathodic peak is evidently made up of two peaks (Figure 4); a similar situation is observed in the absence of I^- (compare with Figure 1). The increase in the effectiveness of the competitive adsorption of I^- , *vis a vis* Cl^- and Br^- , is manifested by blocking of Pb deposition at more positive potentials, a kind of "overpotential effect". This is indicated by the increase in the "spike" peak which is normally associated with continued Pb deposition beyond the normal level of monolayer coverage.

Effect of temperature on the adsorption of anions. The effect of temperature on the UPD i vs E profiles in the presence of adsorbed anions (Cl^- and Br^-) in aqueous HClO_4 was investigated at three temperatures; 278.5, 295 and 318 K. The absolute shifts in peak potential (in mV) of the first cathodic in peak potential (C_{pb1}) against log concentration of Cl are shown in Figs 9 and 10, respectively, at these three temperatures. Examination of Figure 9 shows that for a given concentration of Cl^- , to more negative potentials, at 295 and 318 K is approximately the same and that at 278.5 K is correspondingly lower at all Cl^- concentrations used in the present study.

For Br^- , except at the lowest concentration (10^{-6} mol L^{-1}), the shift in peak potential, to more negative potentials, increases with temperature rise at all concentrations of Br^- . A shift of the peak potential of the first cathodic peak to more negative potentials in the presence of added anions, which are known to cause such a shift, would imply that the adsorbability of these anions increases with temperature rise, an unexpected situation.

It has been found elsewhere [24] that the peak potentials of the UPD i vs E profiles for Pb at Au in aqueous HClO_4 are shifted to more negative potentials with temperature rise in the absence of strongly adsorbing anions such as Cl^- , Br^- , and I^- . Since the experiment was conducted with the reference electrode at the same temperature as the working electrode, it was concluded that such a shift was due to the negative temperature coefficient of the H_2 reference electrode. It is, therefore, likely that the observed shift in potentials in the presence of Cl^- and Br^- , with temperature rise is not due to these anions. We, therefore, conclude that temperature, at least in the present range studied, has no noticeable significant effect on the UPD i vs E profiles of Pb at Au.

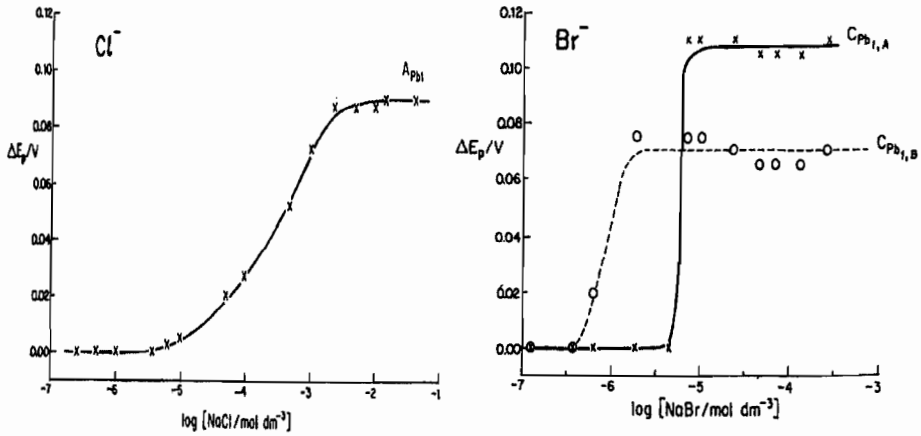


Figure 6. Shift in peak potential of the first cathodic peak (C_{pb1}) in the i vs E profile for Pb UPD at Au in aq 1 M $\text{HClO}_4 + 10^{-3}$ M $\text{Pb}(\text{NO}_3)_2$ as a function of $\log [\text{Cl}^-]$; data from curves in Figure 2.

Figure 7. Shift in peak potential of the first cathodic peak (C_{pb1}) in the i vs E profile for PbUPD at Au in aq. 1 M $\text{HClO}_4 + 10^{-3}$ M $\text{Pb}(\text{NO}_3)_2$ as a function of $\log [\text{Br}^-]$; data from curves in Figure 3.

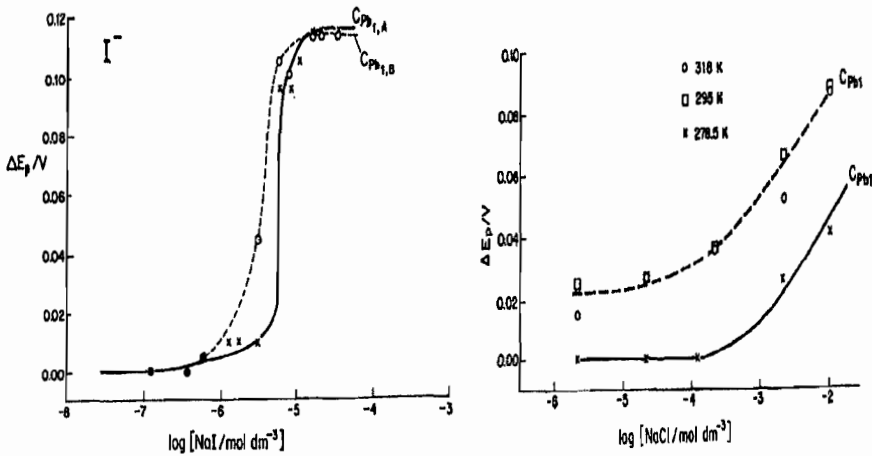


Figure 8. Shift in peak potential of the first cathodic peak (C_{pb1}) in the i vs E profile for Pb UPD at Au in aq. 1 M $\text{HClO}_4 + 10^{-3}$ M $\text{Pb}(\text{NO}_3)_2$ as a function of $\log [\text{I}^-]$; data from curves in Figure 4.

Figure 9. Shift in peak potential of the first cathodic peak (C_{pb1}) in the I vs E profile for Pb UPD at Au in aq 1 M $\text{HClO}_4 + 10^{-3}$ M $\text{Pb}(\text{NO}_3)_2$ as a function of $\log [\text{NaCl}]$; at three temperatures: 278.5, 295, and 318 K.

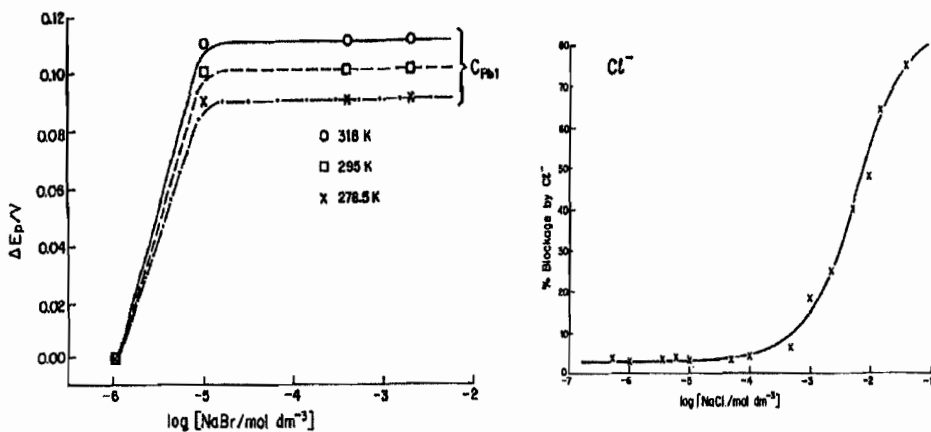


Figure 10. Shift in peak potential of the first cathodic peak (C_{Pb1}) in the i vs E profile for PbUPD at Au in aq 1 M $HClO_4$ + 10^{-3} M $Pb(NO_3)_2$ as a function of $\log[NaBr]$; at three temperatures: 278.5, 295, and 318 K.

Figure 11. Percentage blocking of Pb on Au in 1 M $HClO_4$ + 10^{-3} M $Pb(NO_3)_2$, measured as it's charge reduction by Cl^- as a function of $\log[Cl^-]$; data from curves in Figure 2.

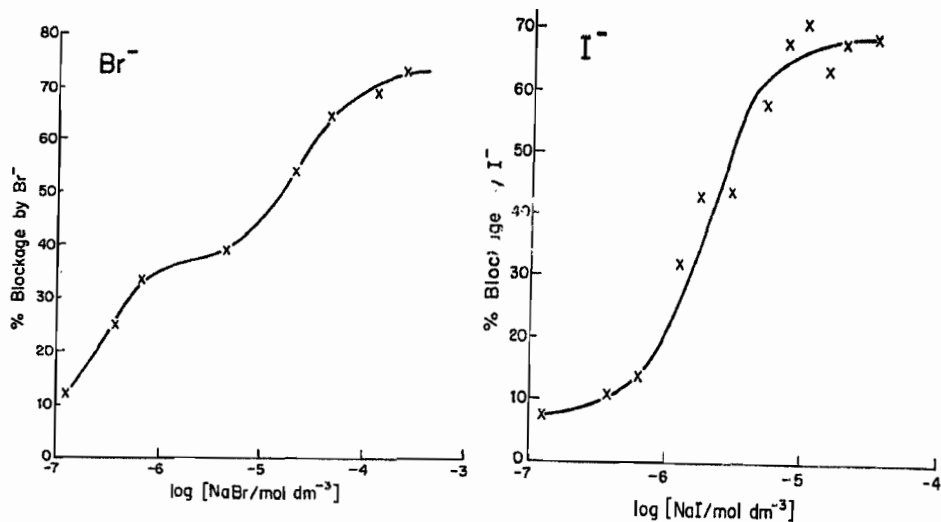


Figure 12. Percentage blocking of Pb on Au in 1 M $HClO_4$ + 10^{-3} M $Pb(NO_3)_2$, measured as it's charge reduction by Br^- as a function of $\log [Br^-]$; data from curves in Figure 3.

Figure 13. Percentage blocking of Pb on Au in 1 M $HClO_4$ + 10^{-3} M $Pb(NO_3)_2$, measured as it's charge reduction by I^- as a function of $\log [I^-]$; data from curves in Figure 4.

Competitive adsorption isotherms for adsorption of halide ion (X^-) with electrosorbed Pb adatoms. From the individual I vs E profiles corresponding to those of the sets shown in Figures 2 to 4, the absolute shifts in peak potential of the first cathodic peak, C_{pb1} , can be plotted as a function of the log of the concentration of the halide ion. The resulting relations are shown in Figure 6 to 8. The effects can be represented in terms of the % surface blocked by the halide ion X^- . The % blocking is calculated by fixing an arbitrary reference point, say $E_H = 0.2$, and then comparing the reduced charge for Pb deposition (due to competitive adsorption of the halide ion) to that corresponding to the UPD charge in the absence of added halide ion at the beginning of the experiment.

Figures 11 to 13 show such competitive adsorption isotherms for % blocking of Pb UPD by the halide ion X^- , as a function of $\log [X^-]$ from measurements in aq $HClO_4$.

The competitive adsorption isotherms of Figures 11 to 13, representing the effects of the halide ions X^- , show that the behaviour of Cl^- is different from that of either Br^- or I^- . The effect of chloride on the peak potential shift does not become significant until about 3 decades of Cl^- concentrations are covered and the effect really stretches over a wide concentration change, about 5 decades, before it reaches a saturation limit. Unlike the behaviour of Br^- and I^- , the transition towards saturation is not sudden but continuous, and the saturation effect is reached at a Cl^- concentration of 10^2 M, substantially higher than that for either Br^- or I^- . The effects of Cl^- on UPD Pb deposition observed here are, however, rather different from those of Cl^- at oxidised Pt reported by Conway and Novak [3]. For Pt surface oxide formation, the chloride blocking effect in aq H_2SO_4 gave an excellent linear relation with $\log [Cl^-]$ over four and a half decades of concentration change, actually somewhat similar to what is observed in the effect of Cl^- on Pb adatom deposition.

With Br^- and I^- , the plots are rather similar, although the concentration at which the effects become significant depends on the halide ion. The competitive adsorption isotherms of Figures 7 and 8 show that the effects become significant at concentrations of approximately 5×10^{-6} and 5×10^{-7} M for Br^- and I^- respectively. The striking similarity between the behaviour of Br^- and I^- is manifested in the shape of the log plot: they both give more normal (i.e. Langmuir-type) adsorption behaviour in an expected S-shaped curve on the log plot, unlike the wide stretch in the plot for the Cl^- effect. With Br^- and I^- there is, however, a sudden transition to a saturation effect, a feature not observed in the effects of Cl^- ion. This discontinuous transition could be due to a sudden rearrangement of the adsorbed Br^- or I^- and the electrodeposited Pb adatoms in the UPD layer possibly with change of electron distribution. The difference of shapes of the curves for the log plots is also probably associated with interactions in the UPD layer between the electrodeposited Pb adatoms and the co-adsorbed halide ions, X^- , depending on their partial charges in the adsorbed state, a point discussed under conclusion section.

The maximum shifts of the first cathodic peak due to competitive adsorption by Br^- and I^- are -115 and -120 mV, respectively (see Table 2).

Table 2. Maximum shift of the peak potential of the first cathodic peak (C_{pb1}) in the presence of added anions.

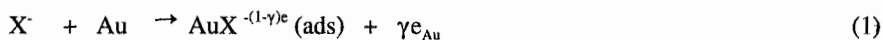
Added species	Shift in peak potential, mV
Cl ⁻	-110
Br ⁻	-115
I ⁻	-120

CONCLUSIONS

The sharpening of the peaks due to adsorbed Cl⁻ (Figure 2) and the shape of the adsorption isotherm (Figure 11) for competitive adsorption of Cl⁻ with Pb at Au, suggests that there are strong repulsive lateral interaction effects in the UPD Pb layer when adsorbed Cl⁻ is present, leading to the rather extended shift in peak potential or % blocking with increasing log [Cl⁻]. However, Br⁻ and I⁻ give a more normal (i.e. "Langmuir"-like) adsorption behaviour, i.e. in an "S-shaped" curve on the log plot.

Therefore with adsorbed Br⁻ and I⁻, the interaction effects in the UPD Pb layer are probably attractive (contrary to the situation with Cl⁻) and lead to 2-d phase formation in a co-operative phenomenon.

It is well known that I⁻ is adsorbed (at Au) as neutral I atoms [2, 3, 25] and this is also indicated indirectly from its effects on the UPD *i* vs *E* profiles for Pb at Au. Thus, the shifted cathodic peak (C_{pb1}) still resembles the peak in the absence of I⁻ in shape and size. We, therefore, conclude that the more extended logarithmic effect of [Cl⁻] is due to strong lateral interaction effects: repulsions between the adsorbed Cl⁻ ions themselves and other interactions between adsorbed Cl⁻ and the electrodeposited Pb adatoms that form a polar bond with surface Au atoms. Since Br⁻ and I⁻ differ only from Cl⁻ in their size, donicity, polarizability and interactions with the solvent, it is suggested that the striking difference in their behaviour *vis a vis* that of Cl⁻ is due to the difference in the degree of charge-transfer when chemisorption takes place at the Au electrode. This chemisorption process may be represented as



where γ is the electroadsorption valency factor [19].

With adsorbed X^- , it is evident that $\gamma \ll 1$ and thus strong electrostatic interactions arise in the Pb UPD layer due to the retained fractional charge. For Pb chemisorbed at Au in aq. HClO₄, $\gamma = 1.95$ [19]. For Br⁻ and I⁻ adsorbed at Au among electrodeposited Pb adatoms, will have much reduced electrostatic interactions with themselves and with neighbouring Pb adatoms in the UPD layer.

The adsorption behaviour observed is competitive rather than simple, so that interactions are between X^- and Pb_{ads}, as well as involving pre-adsorbed solvent molecules. As with H at Pt [3], the

same quantity of Pb is eventually electrodeposited as in the absence of adsorbed ions but over a different range of potentials and in different sub-states. The adsorption of the added halide ions is competitive in nature with the Pb adatoms rather than co-adsorption because the cathodic charge for deposition of a Pb monolayer increases in the presence of these ions.

It was noted earlier that the UPD i vs E profiles for the Pb deposition and ionization at Au remain more or less reversible in the presence of adsorbed anions so that both anion adsorption and Pb deposition remain essentially reversible. Evidently with Pb at Au, re-adsorption of Cl⁻ ions occur rapidly, following ionization desorption of Pb, as indicated by the cathodic shift of the C_{pbl} peak on an immediately following anodic sweep.

It is also observed, as noted earlier, that the UPD profiles for Pb at Au are most affected over the low Pb coverage region, as may be expected, since it is for such conditions that more surface is available for competing adsorption between the added anions and the UPD adatom species.

Solvent effects in electrochemical formation of adatom arrays of Pb on Au by the same workers has also been reported [26]. It was shown that the observed effects could arise from the "solvent-substitution" adsorption process, but also solvent-dependent, specific adsorption of anions can complicate the UPD behaviour.

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