State of Adsorbed Halide Ions and Their Competitive Adsorption at Oxidized Pt Electrodes*

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The effects of strongly adsorbed Cl^-, Br^- and I^- on the initial and subsequent stages of surface oxidation of Pt anodes in aq. H_2SO_4 and $HClO_4$ are investigated over a wide concentration range, starting at the very low concentrations where significant effects are just detectable. A micrometer titration procedure is used which enables many data points to be obtained so that the forms of competitive adsorption isotherms for halide ion blocking of electro-deposition of OH and O species at Pt can be accurately determined. Related effects in blocking of H adsorption are also evaluated.

Methods are proposed for the analysis of the results in terms of lateral interaction effects. From this treatment, it is shown that adsorbed I^- in the oxide film loses almost all of its charge, as does Br^-, but Cl^- remains ionic and thus has much stronger interactions with itself and electrodeposited OH and O species in the developing oxide monolayer, than does Br^- or I^-. Thus, from the competitive adsorption behaviour, information on the electrosorption valence of Cl^-, Br^- and I^- can be obtained, as well as the form of the competitive adsorption isotherm for each of the halide ions.

I. INTRODUCTION

The state of ions, especially anions, at electrodes is of current interest in regard to their effects on other chemisorbed species such as »underpotentially« deposited H, metal atoms and oxygen species (OH and O) at noble metals[1-4]. With halide ions, there is strong competitive adsorption with respect to the states of H adsorbed at Pt[5,6] and the monolayer of surface oxide that can be formed at Pt at potentials above 0.75 V E_H[7].

The state of chemisorbed ions is dtermined by their so-called electro-sorption valency[8] that characterizes the magnitude of charge carried by an ion adsorbed at an electrode or of an electrodeposited atom such as H, metal M or oxide (OH or O) species. The interactions in a partial monolayer of ions and other chemisorbed, partially charged, species will be determined by the coverage of both types of species and by their electrosorption valencies[6,8]. Since the form of electrochemical isotherms is determined by this lateral

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interaction effect, some useful information on the electrical state of chemisorbed ions can be obtained by examining their competitive adsorption vis à vis other chemisorbed electrodeposited species such as H and OH or O at, for example, Pt electrodes. The chemisorption of the halide ions is also of interest in relation to the kinetics of their anodic discharge to form the respective halogen elements. These processes depend on (a) the strength of adsorption and coverage of the halide ion itself and (b) how the adsorbed halide ion affects the state of oxidation of the anode (noble metal) surface and hence its electrocatalytic properties[9] for steps in the halogen evolution reaction.

In the present work, the effects of chemisorption of Cl⁻, Br⁻ and I⁻ ions on the development of the surface oxide film at Pt in the potential range 0.75 to 1.2 ~ 1.4 V E_H has been quantitatively measured down to very low concentrations of the added halide ion in a supporting electrolyte of 0.1 M H_2SO_4 or 0.1 M $HClO_4$. The competitive adsorption of the halide ions, vis à vis anodic electrosorption of OH and O species at Pt, is evaluated over 4 ~ 5 decades of concentration of the halide ions by means of a micrometer titration procedure. The results thus obtained, over finely spaced concentration intervals enable the forms of the competitive adsorption isotherms to be rather precisely evaluated and the magnitudes of the lateral interaction energy parameter[10] to be deduced. The results indicate that there are some interesting differences of the electrosorption valence of Br⁻ and I⁻ in comparison with Cl⁻, when co-adsorbed with OH and O species at Pt.

II. EXPERIMENTAL

1. General Methods and Experimental Technique

Potentiodynamic experiments were carried out as decribed in previous papers[3,7]. A small, three-electrode cell was used with an H_2 reference electrode.

All solutions were made up in water twice distilled, followed by pyrodistillation, as described previously[11]. This procedure was shown in earlier work to give very satisfactory clean solutions as determined by various criteria described in ref. 11.

Solutions were outgassed by O_2-free, purified N_2.

All experiments were conducted at 298 ± 1 K.

2. Electrode

A Pt wire electrode, degreased in refluxed acetone, was sealed in a soft-glass tube. The mounted electrode was washed initially in 98% H_2SO_4 for 48 h. and then rinsed many times with hot pyrodistilled water before being immediately set in the cell. Such electrodes gave »clean« cyclic-voltammetry behavior[3,11] after 5—10 anodic/cathodic cycles between 0.05 and 1.4 V E_H.

3. Reference Electrode

All experiments were conducted with a Pt/H_2 reference electrode in the same solution. Potentials referred to in this electrode are denoted by E_H V.

4. Salts and Acids

B. D. H. »Aristar« grade $HClO_4$ and H_2SO_4 were used for preparing the supporting electrolyte solutions. As noted previously[11], this grade of the acids if found to be free from any significant traces of heavy metals or from other oxidizable or reducible impurities that might give rise to spurious diffusion-controlled currents in cyclic-voltammetry experiments. The B. D. H. $HClO_4$ is also agreeably free from traces of Cl⁻ ion, a point of importance in the present experiments.

A. C. S. analytical grade KCl, KBr and KI salts were recrystallized twice from the pyro-distilled water. In the case of KI, the recrystallizations were performed under N_2 and the resulting crystals kept in a dark vessel in N_2.

5. *Micrometer Titration Procedure*

In order to obtain detailed information on the progression of the anion adsorption effects, from initially very low concentrations, on the Pt surface oxidation process, a dilute solution of the halide salt in the acid supporting electrolyte was titrated, in successive aliquots, into the electrochemical cell by means of an accurate micrometer syringe. The solution was delivered through 1mm Teflon »spaghetti« tubing, terminating in a fine glass jet.

For each addition of the halide salt solution, a cyclic-voltammetry i vs V profile was run on two recorders in parallel: one to record separately a trace for each halide concentration for subsequent calculations; the other to build up a succession of superimposed traces to see the progressive effects of the added surface-active anion from the very lowest concentrations. The latter procedure was found to be very informative as will be seen from diagrams to be shown later.

Depending on the anion of the salt, the measurements were commenced at very low concentrations, $10^{-9} \sim 10^{-7}$ mol/dm³, since already significant effects can be detected at these very high dilutions.

Each experiment on a run of concentrations was preceded by recording the i-V profile for the Pt electrode in the supporting electrolyte solution. An initial i vs V profile, satisfactory by the standards previously published[3,11], was first recorded. This profile provided a reference surface oxidation isotherm for a range of potentials, against which i vs V profiles in the presence of various concentrations of halide ions could be compared.

A complete run covered $30 \sim 40$ separate concentrations of the added anion of the salt »$K^+ X^-$«.

6. *Evaluation of Results from the Experimental Measurements*

For each halide ion concentration, an anodic and cathodic potentiodynamic sweep was recorded at 0.025 V s⁻¹. From the progressive change of the shape of successive anodic i vs V profiles with increasing anion concentration, the general nature of the anion blocking effect on the initial stages of surface oxidation of the Pt electrode could be followed. Quantitatively, the extent of blocking of the electrodeposition of OH and O species was measured by integrating each i vs V profile over the surface oxide *reduction* region, allowing for the double-layer charging contribution. Related measurements of anion effects in the H-adsorption region at Pt could be obtained simultaneously.

III. RESULTS AND DISCUSSION

1. *State of Oxidized Surfaces of Pt Anodes*

In order to provide a basis for interpretation of the results to be described below, it will be desirable to summarize present knowledge on the state of electrochemically oxidized Pt surfaces. In acid (H_2SO_4 or $HClO_4$) media, surface oxidation of Pt commences detectably at $0.75 \sim 0.80$ V E_H, depending on the anion of these acids[1,3]. The first 15% of the monolayer of oxygen species, counted as OH (Pt + $H_2O \rightarrow$ Pt/OH + H^+ + e), is almost reversibly electrosorbed in acid media.[7] In alkali, pH $10 \sim 13$, this fraction is increased to ca. 30%.[3] Beyond the 15% in acid media, electrosorption of OH becomes progressively less reversible as coverage and anode potential increase due to OH/Pt rearrangement processes[7]. A monolayer of OH species (equivalent to the total H charge in the potential range 0.05 to 0.37 V E_H) is attained at 1.1 V E_H and the anodic i vs V profile up to this potential exhibits[3] peaks which have been ascribed to the successive formation of 3 distinguishable 2-dimen-

sional lattices of OH on the Pt surface lattice as has been found in LEED studies of monolayer oxidation of metals from the gas phase. Beyond ca, 1.1 V E_H, OH species are progressively oxidized to O species with increasing rearrangement of the OH + O monolayer and with eventual thickening of the film[12].

The competitive chemisorption of halide ions must be considered in the light of the above experimental knowledge and model of Pt surface oxidation.

2. General Effects in the Cyclic-Voltammetry i vs V Profiles

The first effects of added halide ions on the cyclic-voltammetry i vs V profiles for Pt in $HClO_4$ and H_2SO_4 can be detected at very low concentrations around 10^{-7}, 10^{-8}, and 10^{-9} M, respectively, for Cl^-, Br^- and I^-. Figures 1 and 2 show superimposed curves for Cl^- and for Br^- additions over a wide concentration range.

These figures show an interesting and important difference between the effects of Cl^- and Br^- on the surface oxidation part of the anodic sweep profile.
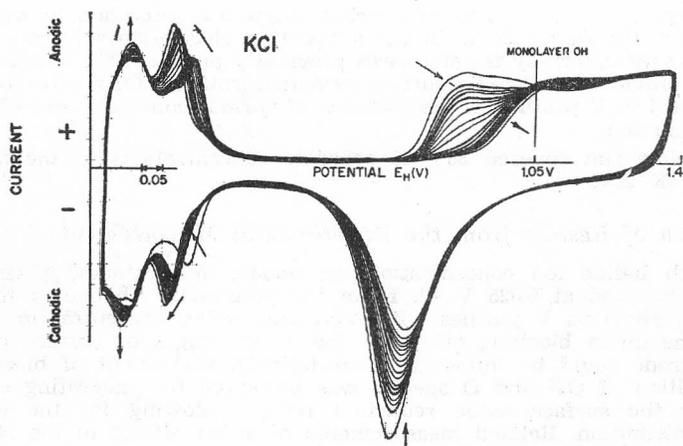

Figure 1. Series of cyclic voltammetry i vs V profiles for Pt in 0.1 m H_2SO_4 (298 K) at 25 mV s^{-1} with successive additions of Cl^- ion from 10^{-7} to 10^{-4} mol/dm³. Note monolayer OH coverage at Pt arises at ca. 1.1 V E_H, close to where isopotential point occurs. Arrows show directions of changes due to Cl^- additions, as KCl.
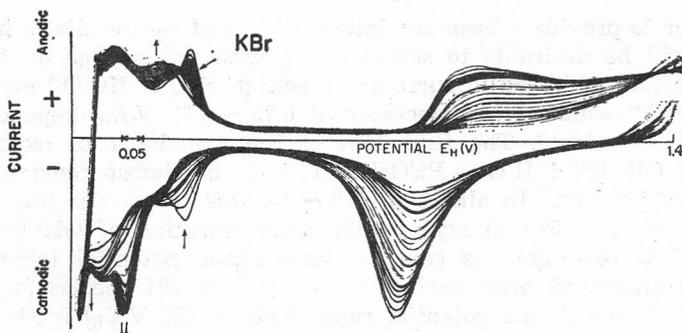

Figure 2. As in Figure 1. but for successive additions of Br^- ion (as KBr) from 10^{-8}—10^{-5} mol/dm³. Similar behaviour arises with I^- ion.

The addition of Cl⁻ first progressively blocks the initial stages of Pt surface oxidation with little effect beyond 1.1 V where the second stage of surface oxidation (PtOH → PtO + H⁺ + e) commences[7]. After addition of a substantial quantity of Cl⁻, a series of curves is built up (Figure 1) which shows an iso-sbestic type of point (»isopotential« point) at ca. 1.05 V, close to where other types of measurements[3,13] indicate the PtOH lattice monolayer is completed. The isopotential point corresponds to the crossing of curves where the i-V profiles pass from a blocked region (< 1.05 V) to a region beyond 1.05 V where currents higher than those on the initial reference curve pass.

With Br⁻ ion, a strikingly different behavior is seen (Figure 2): surface oxidation currents over the whole of the i-V profile in the anodic oxidation region are progressively lowered, except at the highest anodic potentials where Br₂ is eventually evolved. Thus Br⁻ evidently does not show any selectivity with regard to blocking the »PtOH« region in preference to the »PtO« region as Cl⁻ does. The effects of I⁻ are similar to those of Br⁻, except that problems with I₂ evolution and adsorption arise at lower potentials than do corresponding effects with Br⁻ for obvious reasons connected with the X₂/X⁻ standard potentials. The lowest concentration at which initial effects of the I⁻ ion can be detected is, however, some 8 times smaller than that for Br⁻ ion.

Figures 1 and 2 also show the effects of Cl⁻ and Br⁻ on the H underpotential deposition and ionization behavior at Pt in the potential range 0.37 — 0.05 V E_H. It is found* that isopotential points are also observed in the anion-induced redistribution of electrodeposited H amongst the four distinguishable states of H adsorption which can normally be resolved[11,14] in clean solutions below a monolayer at polycrystalline Pt wire electrodes.

3. Competitive Adsorption Isotherms for Halide Ion Effects on Surface Oxide Film Formation

From the data of individual curves corresponding to those of the sets shown in Figures 1 and 2 (and from similar experiments with I⁻), the extent of surface oxide blocking by the adsorbed halide ions can be plotted (Figures 3, 4) as a function of the log of the halide ion concentration, viz. its chemical potential/RT. The effects are represented in terms of the % surface oxide blocked (measured as charge for its reduction in the well-defined cathodic peaks). This % is referred to the oxide reduction charge measured in the initial, reference trace taken in the absence of added halide ion at the beginning of the experiment.

Figure 3 shows the competitive adsorption isotherms for % oxide blocked by the three halide ions. X⁻, as a function of log [X⁻] from measurements in 0.5 M H₂SO₄. Figure 4 shows a comparison of corresponding data for Cl⁻ adsorption effects in 0.1 M H₂SO₄ and 0.1 M HClO₄ which indicates that the Cl⁻ ion adsorption effect depends on the anion of the supporting electrolyte already present. Various evidence from published work[3,14] indicates that in H₂SO₄, the HSO₄⁻, ion is more strongly adsorbed at Pt than the ClO₄⁻ ion so that the adsorption of Cl⁻ is competitive not only with respect to electrosorption of deposited OH species but also to the anion already adsorbed form the

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* A paper discussing the significance of anion effects in the H region at low concentrations is in course of publication elsewhere[6]. Details will not be further discussed here.
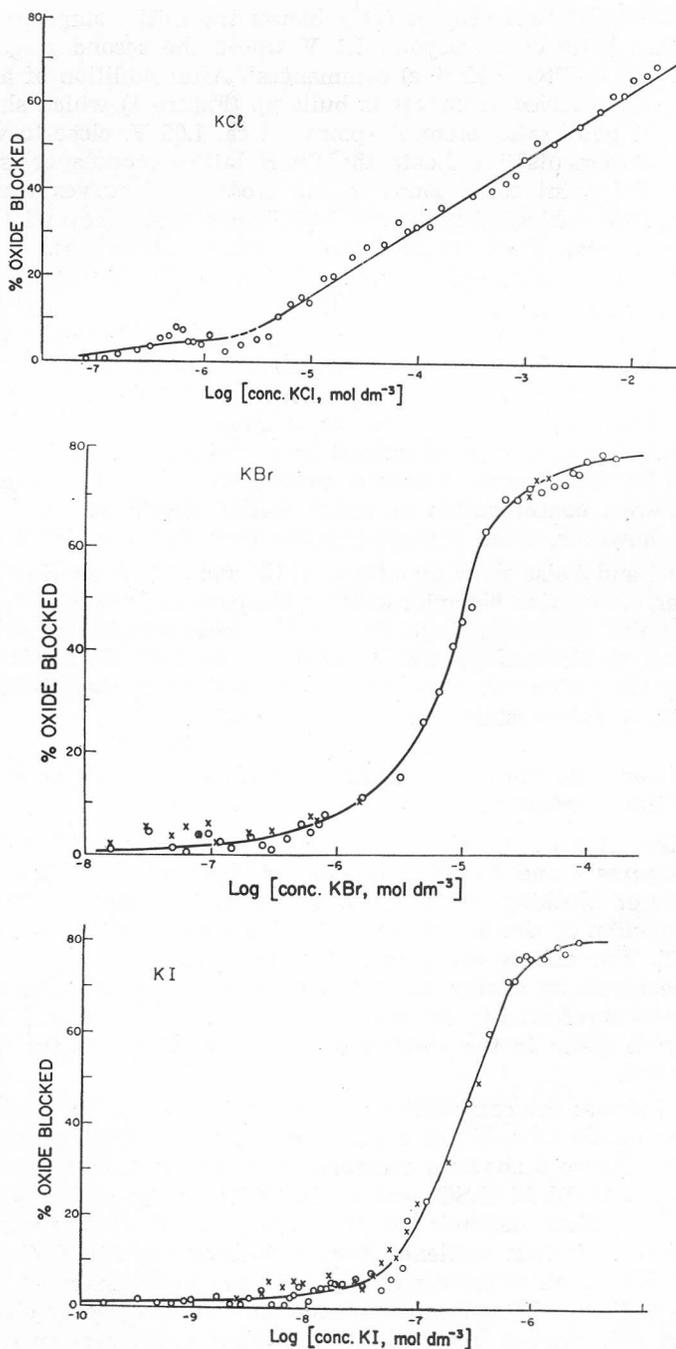
Figure 3. Percentage of surface oxide, measured as charge for its cathodic reduction, blocked by Cl⁻, Br⁻ and I⁻ ions as a function of log [X⁻] (data from curves such as those shown in Figures 1 and 2). Total surface oxide in X⁻ — free solution is that generated in a sweep to 1.4 V E_H in the case of Cl⁻ and Br⁻ and 1.2 V in the case of I⁻.
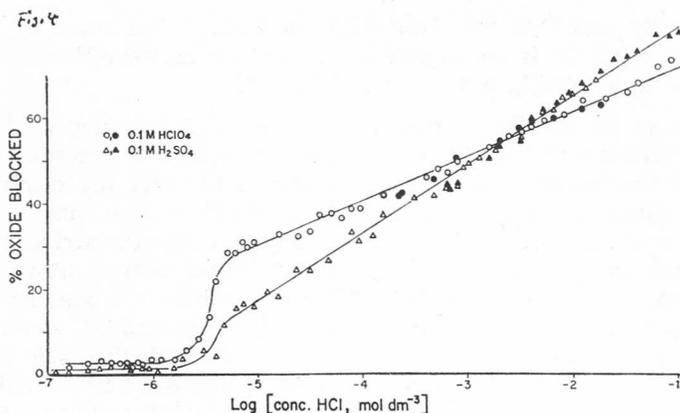
Figure 4. Comparison of % blocking of surface oxide formed at Pt in sweeps to 1.4 V E_H by added Cl⁻ ion (as KCl) in a 0.1 M H_2SO_4 and in a 0.1 M $HClO_4$ solution, 298 K (based on separate experiments from those of Figure 3).

supporting electrolyte. However, it is well known from anion effects in the H region[1,5] that halide ions are much more strongly adsorbed at Pt than are oxyanions.

It is seen from Figure 3 that at the highest halide ion concentrations the extent of oxide blocking does not approach 100% but rather 70—80%. This is presumably due to the limit of coverage that can be attainable by the adsorbed halogen atom/ion species due to residual repulsive interactions, hydration effects and the presence of adsorbed water at the electrode interface.

Comparison of the competitive adsorption isotherms of Figure 3 for Cl⁻, Br⁻ and I⁻ shows that the behavior of Cl⁻ is strikingly different from that of Br⁻ or I⁻. The Cl⁻ effect in aq. H_2SO_4 gives an excellent linear relation with log [Cl⁻] over four and a half decades of concentration change. This is one of the longest and most linear examples of logarithmic adsorption we are aware of in electrochemical systems. However, Br⁻ and I⁻ give more normal adsorption behavior in an expected S-shaped curve on the log plot.

The behavior shown in Figure 3 suggests that with Cl⁻ adsorption there are strong repulsive interaction effects in the surface oxide film with co--adsorbed Cl⁻, leading to the linear-log behavior. With Br⁻ and I⁻, on the other hand, such interaction effects are evidently smaller. An attempt to evaluate these interaction effects quantitatively is described later.

There are two points about these effects that need to be specially mentioned:

(a) It is unlikely that the behavior in Figure 4 should be explained in terms of a Temkin isotherm, i. e. through a broad range of adsorption energies as $0 < \Theta < 1$, associated with an *heterogeneous* surface with a continuous range of states. All the experimental evidence that has accumulated (e. g.[4,15,16]) on underpotential deposition of various species at Pt (H, OH and O, base metal atoms) shows that in electrochemical monolayer formation 4 ~ 7 *distinct* states of chemisorption arise in the monolayer rather than a range continuous in their adsorption energy distribution.

(b) With Br⁻ and I⁻ on the *same* electrode surface, the broad log adsorption behavior seen with Cl⁻ is *not* observed as it should be were the log adsorption behavior due to a Temkin heterogeneity factor.

Hence from (a) and (b) we conclude that the log behavior with Cl⁻ is due to strong interaction (rather than heterogeneity) effects — between the adsorbed Cl⁻ ions themselves and between adsorbed Cl⁻ and the electrodeposited OH species. Since Br⁻ and I⁻ differ only from Cl⁻ in their size, donicity and interactions with the water solvent, it is suggested that the striking difference in their behavior from that of Cl⁻ is due to some charge transfer in their chemisorption at Pt, $X^- + Pt \rightarrow Pt\, X^{(1-\gamma)e} + \gamma\, e_{Pt}$, where γ is the electrosorption valency factor[8]. With $\gamma \rightarrow 1$, Br⁻ and I⁻ adsorbed at Pt amongst electrodeposited OH and O species will thus have much attenuated electrostatic interactions with themselves and with OH and O species in the oxide film. With adsorbed Cl⁻, γ is evidently $\ll 1$ and thus strong electrostatic interactions, arise, due to the retained charge.

That I⁻ is adsorbed as neutral I atoms [cf. the converse effect with Na or Cs adsorption as W from the gas phase where it is well known that charge--transfer chemisorption occurs giving strong surface dipoles, Na⁺ W(-) or Cs⁺ W(-)] is also indicated from its effects on the upd *i-V* profiles in the H region at Pt: adsorption of I causes initially a uniform lowering of *all* the four peaks with their respective potentials remaining almost at the same values. Cl⁻ causes immediately a shift of these potentials to less positive values, due to interaction effects.

The conclusions are consistent with results from other experiments, e. g. by Hubbard[17], where the charge on adsorbed I was directly determined as approximately zero. Similar conclusions were reached by Bagotzky et al[5].

Figure 4 shows that the effect of added Cl⁻ ion depends on the anion of the supporting electrolyte already present. In HClO₄ solution, there is a marked transition region between the initial effects of added Cl⁻ and the subsequent effects at higher concentrations, for which a log relation in [Cl⁻] is established, as it is right from lowest concentrations in the case of H₂SO₄ solutions. In HClO₄ solutions, there is a sudden increase in the effectiveness of adsorbed Cl⁻ in blocking the OH deposition over a critical concentration range. This suggests that there may be a kind of ion exchange (Cl⁻ for ClO₄⁻) between Cl⁻ and ClO₄⁻ in the ad-layer at low Cl⁻ ion concentrations which does not occur with the more strongly adsorbed HSO₄⁻ ion.

4. *Treatment of Isotherms for Adsorption when Interaction Effects are Significant*

Interaction effects in monolayers at electrodes have usually been dealt with in terms of an isotherm of the form[10,18].

$$\frac{\Theta}{1-\Theta} = K \exp\left[\frac{VF}{RT}\right] \cdot \exp\left[-g\,\Theta\right] \cdot c \tag{1}$$

involving lateral dipole-dipole interactions or corresponding »induced heterogeneity«[19] associated with work-function changes. In eqn. (1) c is the adsorbate concentration, g the interaction parameter (cf. 10) and V is the metal-solution

potential difference; $K \exp \left[\dfrac{VF}{RT} \right]$ can be written as K_V, an electrochemical adsorption equilibrium constant, constant for a given measured potential. The overall »K« for the adsorption process is both potential and coverage dependent.

By evaluating the differential coefficient of Θ w. r. t. V in eqn. (1) and noting that for $\Theta = 1$ a charge q_1 for monolayer formation is required (210 μC cm^{-2} for OH on Pt), the pseudo-capacitance[20,21], $C_\emptyset = q_1 \left(\dfrac{\partial \Theta}{\partial V} \right)_c$ is obtained. As shown previously, $C_\emptyset$ as $f(V)$ exhibits a characteristically shaped peak having an half-width, $\Delta V_{1/2}$, related in a definite way[10] to the value of g in eqn. (1).

The present results apply to changes in the amount of OH and O species deposited over a range of potentials up to a given constant potential, the same in all experiments for a particular halide ion. The amounts of surface oxide produced under these conditions are determined by the coverage of co-adsorbed halide ions, which is dependent on the concentration or chemical potential μ_{X^-} of X$^-$ in solution.

It is of interest to show how the forms of the isotherms of Figure 3 and 4 can be treated quantitatively in terms of the value of g. This cannot be done in the usual way[10] from the $C_\emptyset$ function since a variation of the behaviour of the surface film with μ_{X^-} is involved rather than with V. However, the following approach for analysis of the competitive adsorption isotherms in terms of μ_{X^-} instead of V is proposed; two methods may be suggested as follows:

(a) *Treatment of the integral isotherm:* $\Theta_V = f(\mu_{X^-})$ (Figure 5).

Referring to eqn. (1), the concentrations (or activities) of X$^-$ which correspond to two arbitrary fractional coverages, say $\Theta = 0.25$ and $\Theta = 0.75$, can be evaluated, viz. $(c_{X^-})_{0.25}$ and $(c_{X^-})_{0.75}$. Then, for $\Theta = 0.25$,

$$\frac{0.25}{0.75} = K_V (c_{X^-})_{0.25} \exp [-0.25 \, g] = \frac{1}{3} \qquad (2)$$

and for $\Theta = 0.75$

$$\frac{0.75}{0.25} = K_V (c_{X^-})_{0.75} \exp [-0.75 \, g] = 3 \qquad (3)$$

Dividing eqn. (3) by eqn. (2) gives

$$9 = \frac{(c_{X^-})_{0.75}}{(c_{X^-})_{0.25}} \exp [-0.5 \, g] \qquad (4)$$

Hence g can be evaluated as

$$g = 2 \ln \frac{(c_{X^-})_{0.75}}{(c_{X^-})_{0.25}} - 2 \ln 9 \qquad (5)$$

from an experimental isotherm, assuming that the argument in the exp interaction term is linear in Θ. This has been assumed in various previous treatments of electrochemical adsorption[18,21] and finds a justification in Boudart's
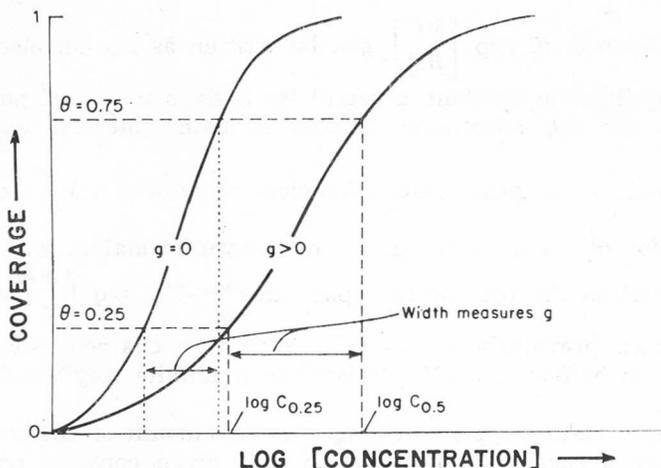
Fifure 5. Illustration of how the coverage attained at two different concentrations (log scale) enables (see eqn. 5) the g factor to be evaluated for ion adsorption involving lateral interactions (schematic).

model[19] of »induced heterogeneity« related to surface-potential changes and corresponding changes of the work-function of the adsorbent surface. Other terms such as $g\,\Theta^{3/2}$ or $\Theta^{1/2}$ have been treated in our earlier work[10].

(b) *Treatment of the isotherm in a different form:* $(\partial\,\Theta_V/\partial\,\mu_{X^-}) = f(\mu_{X^-})$. Eqn. (1), for constant V, can be written in the form

$$\frac{\Theta}{1-\Theta} = K_V \exp\left[\Delta\,\mu_{X^-}/RT\right]\cdot\exp\left[-g\,\Theta\right] \tag{6}$$

noting that for $c_{X^-} \doteqdot a_{X^-}$

$$c_{X^-} = \left[\exp\Delta\,\mu_{X^-}/RT\right] \tag{7}$$

where

$$\Delta\,\mu_{X^-} = \mu_{X^-} - \mu^{\circ}{}_{X^-} \doteqdot RT\ln C_{X^-} \tag{8}$$

Hence, eqn. (6) has a form analogous to eqn. (1) (with an exp in $\Delta\,\mu_{X^-}$ instead of VF). Then g may be evaluated in terms of an half-width parameters $\Delta(\Delta\,\mu_{X^-})$ instead of $\Delta\,V_{1/2}$, of the differential coefficient function, $(\partial\,\Theta/\partial\,\Delta\,\mu_{X^-})_V$. Thus, differentiating eqn. (6) w.r.t. $\Delta\,\mu_{X^-}$ for the case of $g = 0$ gives

$$(\partial\,\Theta/\partial\,\Delta\,\mu_{X^-})_V = \frac{1}{RT}\cdot\frac{K_V\exp\left[\Delta\,\mu_{X^-}/RT\right]}{(1 + K_V\exp\left[\Delta\,\mu_{X^-}/RT\right])^2} = D_\emptyset \tag{9}$$

where, for convenience, we have defined this differential coefficient of the isotherm as $D_\emptyset$. As with the corresponding $C_\emptyset$ function, this has the form of a peaked curve with a maximum at $\Theta = 0.5$ when eqn. (6) applies, and a characteristic half-width $\Delta(\Delta\mu_{X^-})_{1/2}$. An explicit expression of $(\partial\,\Theta/\partial\,\Delta\,\mu_{X^-})_V$ when $g \neq 0$ cannot be conveniently derived but numerical evaluation is easily performed. In terms of Θ, hower, the function $D_\emptyset$ is directly obtained as

$$D_\emptyset = (\partial\,\Theta/\partial\,\Delta\,\mu_{X^-})_V = \frac{1}{RT}\cdot\frac{\Theta(1-\Theta)}{1 + g\,\Theta(1-\Theta)} \tag{10}$$

The latter expression, with eqn. (6), can be used to derive half-widths of D_ϕ vs. $\Delta \mu_{X^-}$ profiles which enables a value of g for an experimental differential isotherm curve to be derived.

The significance of the half-width of the D_ϕ function in terms of $\Delta \mu_X$ profiles in relation to that of C_ϕ vs V curves is illustrated in Figure 6.
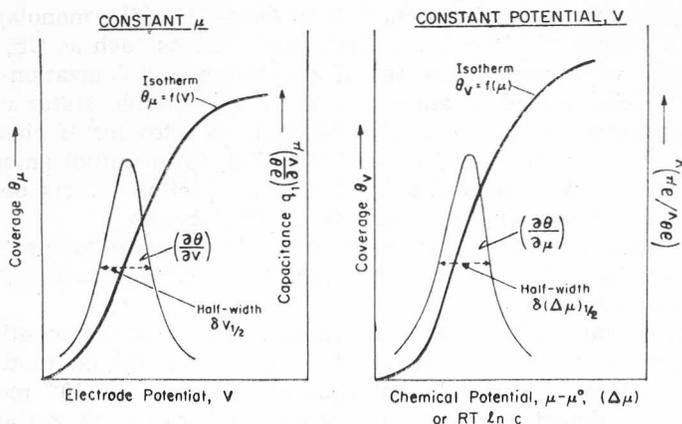

Figure 6. Schematic diagrams to show how half-widths of differential isotherms in $\Delta \mu_{X^-}$ are used to evaluate the interaction parameter g in comparison with the method (ref. 10) based on half-widths, $\Delta V_{1/2}$, of pseudocapacitance vs potential, V, profiles.

Applications of the two methods, (i) and (ii) above, were made to the analysis of the data in Figure 3 in order to obtain values of g from the observed dependence of blocking of OH/O coverage by the halide ions. For these cases, it is to be noted that the isotherms involved are competitive ones rather than direct adsorption isotherms, so the K_V constants represent the effects of *differences* of free energies of adsorption of OH/O species and X^- ions; correspondingly the $g \Theta$ term represents the *net* interaction energy between adsorbed X^- ions themselves and between these ions and the electrodeposited OH/O species, i. e. the dependence of the free energy of the anion-containing oxide film as a function of the surface concentration of co-adsorbed anions within it.

(c) *Values of the* g *parameter for* Cl⁻, Br⁻ *and* I⁻ *adsorption*

Application of the above treatments to the results presented in the Figures shown earlier in this paper gives the following values of the interaction parameter, g, according to the Frumkin-type isotherm expressed by eqn. (6). The approximate electrosorption valencies according to the equation $X^- + Pt \rightarrow$ $\rightarrow Pt X^{(1-\gamma)-} + \gamma$ e are also shown, as manifested by the properties of the ions adsorbed in an oxide film:

Ion	$g RT/kJ$ mol⁻¹		Electrosorption valence
Cl⁻	35 (H_2SO_4)	57 ($HClO_4$)	near zero
Br⁻	2.7		near 1
I⁻	1.8		near 1

These electrosorption valencies will not necessarily be the same on an »oxide-free« surface, e. g. as measured in the H-adsorption region at Pt, nor at other metals.

5. Competitive Adsorption Behavior in the H-Region at Pt

In conclusion, we shall refer briefly to the states of Cl^-, Br^- and I^- as indicated by their competitive adsorption vis a vis H at Pt over the potential range 0.05 to ca. 0.37 V E_H.

At Pt, underpotential deposition and ionization of atomic H occurs in $4 \sim 5$ distinguishable states from $\Theta_H = O$ to $\Theta_H = 1$ for the monolayer, corresponding to a charge of $210 \sim 220$ $\mu C/$real cm². Anions such as Cl^-, Br^-, SO_4^{2-} modify[5,14] the i vs V profile for the H deposition and ionization processes, so that the distribution of H amongst the distinguishable states is changed. This effect arises from (a) competitive blocking of sites for H chemisorption at the more positive potentials (0.25 — 0.35 V E_H); (b) eventual anion desorption at less positive potentials and (c) lateral interaction effects between adsorbed X^- ions and the surface moments of Pt-H bonds.

Here we wish to record that there are both some similarities and differences between the effects of Cl^-, Br^- and I^- on the upd profile for H and OH or O deposition at Pt.

In the H-region, both Cl^- and Br^- cause shifts of peak potentials to less positive potentials due to competitive blocking and lateral interaction effects, starting from almost the very lowest concentrations (10^{-7} — 10^{-8} mol/dm³) for which effects are detectable. I^-, on the other hand, causes at initial low concentrations, a progressive diminution of currents *almost uniformly* over the whole i vs V potentiodynamic profile, as I^- concentration is increased. In contrast to the effects of Cl^- and Br^- the peak potentials remain almost constant (Figure 7a, b).
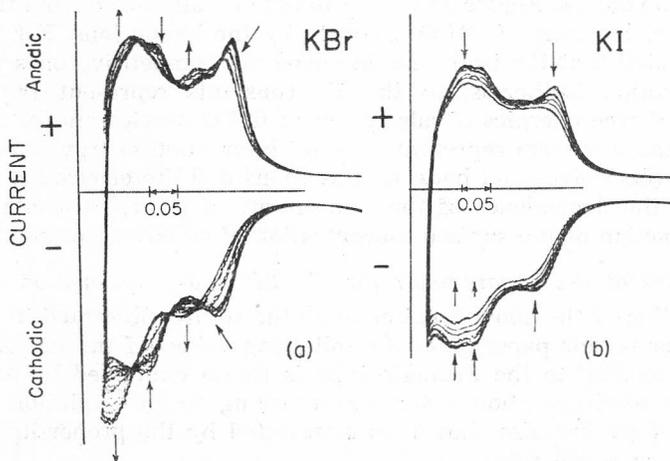

Figure 7: Comparison of effects of Br^- and I^- ions on the redistribution of adsorbed H as a function of potential at Pt, showing the neutral-atom-like effect of adsorbed I^- ion. (Based on curves similar to those of Figures 1 and 2 but with only the H region shown).

However, at higher concentration of I^-, the total amount of chemisorbed H becomes diminished to less than 40% of its initial value.

These results indicate that, in the H region, adsorbed Cl^- and Br^- behave similarly and their effects are those of species retaining their charges (hence the lateral interaction effects). I^-, on the other hand, behaves like an adsorbed

neutral atom (cf. 17) e. g. as is found with blocking of adsorbed H states at Pt by electrodeposited Hg atoms.

On the other hand, in the surface oxidation region at Pt, both Br^- and I^-, when adsorbed, behave similarly, like adsorbed neutral atoms and only the adsorbed Cl^- ion behaves as a species retaining most of its charge.

These results show (a) that Br^- and I^- adsorb at Pt with a large degree of charge-transfer to the metal; (b) that the electrosorption valency of these ions depends on the electrode potential and the 2-dimensional environment in which the adsorbed halide ion finds itself, viz. amongst polar OH or O bonds to Pt or amongst less polar H-Pt bonds; and (c) Cl^- ion strongly adsorbs but retains an appreciable fraction of its charge, so that relatively strong lateral interactions are manifested in the ad-layer giving rise to a remarkably linear--logarithmic adsorption isotherm over 4 decades of Cl^- ion concentration in the surface oxide blocking experiments.

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SAŽETAK

Stanje adsorbiranih halidnih iona i njihova kompetitivna adsorpcija na oksidiranim platinskim elektrodama

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Proučavan je utjecaj jako adsorbiranih halidnih iona, Cl^-, Br^- i I^- na početni i na daljnje stupnjeve površinske oksidacije platinskih anoda u sumpornoj i perklornoj kiselini. Upotrijebljen je mikrometrijski titracijski postupak, koji dozvoljava određivanje niza točaka na adsorpcijskoj izotermi i time daje mogućnost preciznog razlučivanja kompetitivnih adsorpcijskih izotermi za svaki od tih halidnih iona, koji blokiraju elektrodepoziciju OH i O na platinskoj elektrodi.

Predložena je i metoda za analizu rezultata, koja se zasniva na modelu lateralne interakcije adsorbiranih vrsta. Tako je pokazano da adsorbirani I^- i Br^- u oksidnom sloju gube naboj, dok Cl^- ostaje u ionskom obliku. Iz kompetitivnih adsorpcijskih izotermi izračunan je parametar interakcije, *g*, u Frumkinovoj izotermi, kao i elektrosorpcijska valencija za ta tri halidna iona.

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