A phenomenological theory of electrosorption

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ABSTRACT

A phenomenological theory of electrosorption is presented based upon notions of local charge and local electronic polarisability (Friedel oscillations). The strong link between the extent and nature of ionic and molecular adsorption at an electrode surface and the uv-absorption properties displayed by such molecular entities in an aqueous solution is emphasised. The theory may be used to predict, in certain cases the extent of ionic adsorption at the potential of zero charge (PZC) and, also, to rationalise recent results pertaining to metal underpotential deposition (UPD) processes on single crystal electrodes.

1. Introduction

The precise nature of the interphase between an electronic conductor and an electrolyte remains, even after almost a century of intensive scientific research, the central problem in electrochemical science [1]. This assertion is made in the full knowledge that the distribution of charges and solvent molecules within the interphasial region and their dependence upon potential, charge, pH and ionic strength will fundamentally determine all measurements/transformations carried out via an electrochemical process. However, even a cursory glance at the copious amounts of literature relating to the thermodynamics and kinetics [2–5] of electrified interfaces will reveal that the situation is not straightforward.

One of the most contentious issues arising from these studies may be summarised as follows:

What are the forces involved in the specific adsorption of ions and, in particular, how are these ions bonded to an electrode surface?

A working definition of specific adsorption has been put succinctly by Bockris et al. [1]:

"*The specific adsorption at the interface between an electronic and ionic conductor is the adsorption which is in excess or deficit of the amount which would be expected to be present in the interface from simple Coulombic considerations.*"

That is, there is an added dimension to the bonding involved in specific adsorption over and above any electrostatic interaction and which, as yet, remains unresolved. In this paper, an attempt will be made to address some of the difficulties which exist concerning physical models of specific adsorption and its major themes, of ionic hydration [6,7], "contact" adsorption [8], partial charge transfer [9,10] and donor-acceptor properties of metal-ion pairs [11].

This paper will be in three parts: first, an exposition will be given of a new model of adsorption based upon local electronic polarisability and local charge; predictions based upon this model will then be tested against past, present and newly-emerging data pertaining to specific adsorption. Second, the consequences of extending the model in a general way to adsorption processes associated with underpotential deposition will be examined. Finally, the relative success of the new model for the interpretation and prediction of electrosorption behaviour with respect to presently-accepted notions of specific adsorption will be discussed. It is hoped that a coherent, semi-quantitative picture of adsorption at electrode surfaces may thus emerge.

2. Experimental

A limited number of electrochemical experiments were performed in support of the present study. These involved cyclic voltammetric measurements of Pt{111} and PtPd{111} bulk alloy single crystal electrodes. The experimental apparatus together with the preparation procedures used for manufacturing single crystal electrodes have all been described previously as has the sources and purity of all reagents used [12–14]. All electrolytes were prepared using pure water obtained from a Milli-Q water system [12] and the flame-annealing method of Clavilier [15] was utilised to produce clean, well-defined electrode surfaces. All copper underpotential deposition measurements used a copper wire in contact with the electrolyte as a reference electrode.

3. Results and discussion

3.1. The basic elements

3.1.1. The ion

Fig. 1(a) shows schematically what happens when a negative point charge approaches a metallic conductor [16].

As the test charge approaches the metal surface in vacuum, charge oscillations are established extending both across the surface and into the bulk and these are referred to as Friedel oscillations [17,18]. In an analogous situation whereby an anion approaches a metal electrode, because of the dipoles and monopoles that are present in the electrical double layer, it may be envisaged that the amplitude of the Friedel oscillation at the surface may be enhanced/stabilised by these species as depicted in Fig. 1(b) in which charge displacement takes place laterally across the surface of the electrode with polarised water dipoles or monopoles stabilising displaced charge. The concept of electronic substrate mediated interactions is already well established in surface science studies of adsorption at single crystal surfaces [19]. Similarly for a cation, the same configuration may be attained but with the polarised water molecules orientated in the opposite direction (Fig. 1(c)). This may be thought of as a monopole or dipole stabilised Friedel oscillation.

In this representation, the degree of ion adsorption will depend upon three factors:

(i) the polarisability of the ion;
(ii) the ability of the polarised solvent molecule to stabilise displaced charge;
(iii) the ability of the metal to localise charge at the ion adsorption site (amplitude of the Friedel oscillation).

Factor (i) is a function of several variables but both ab initio calculations [20–23] and experimental measurements [24–27] of the polarisability of halide ions have demonstrated that, indeed, the polarisability of the halides increases in the order:

$$F^- < Cl^- < Br^- < I^-$$
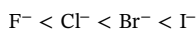
which also happens to reflect the strength of specific adsorption displayed by these ions. However, when oxyanions are considered, the correlation of specific adsorption with polarisability breaks down. According to experiments using well-ordered Pt{111} electrodes, the relative shift in the potential of the "butterfly peak" [28] is a function of the strength of specific adsorption. If this is correct, the order of specific adsorption should be:

$$ClO_4^- \approx F^- < HSO_4^- \leq H_2PO_4^- < Cl^- < Br^- < I^-$$
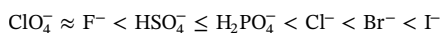
Similarly, calculations of the polarisabilities of the oxyanions in the gas phase indicate that they exhibit far greater polarisabilities than gas phase chloride ions [29,30], as expected since oxyanions contain many more constituent atoms! Hence, specific adsorption seems not to be explicable in terms of simple molecular polarisation. However, if one assumes that the total polarisability of an oxyanion is comprised of individual contributions from each of the N–O, S–O and P–O bonds (i.e. a localisation of polarisability defined by total polarisability divided by number of N–O, S–O or P–O bonds) then the values obtained do fit the electrochemical trend [29]. One of the factors which does influence the polarisability of a molecule or ion is the difference in energy between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [30]. A proxy for this energy difference is the uv-absorption maxima of the aqueous ion. Therefore, it was thought interesting to plot the specific adsorption of the halides [31] versus their uv absorption maxima in aqueous solution [27] (Fig. 2).

As expected, a monotonic increase in specific adsorption is observed as ν_{max} increases. If one now uses this curve to read off the specific
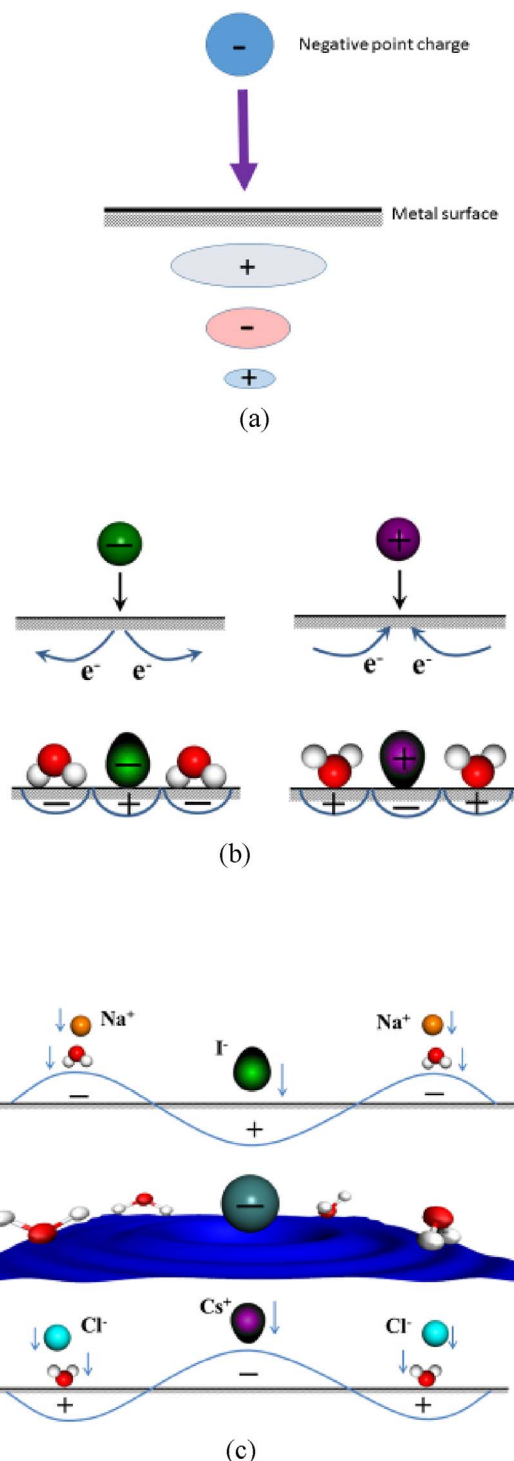

(a)

(b)

(c)

Fig. 1. (a) Charge oscillations as a result of a test charge approaching a metal surface in vacuum. (b) The same situation assuming electronic substrate mediated interactions for ions approaching an electrode surface. (c) Enhancement of amplitude of Friedel oscillation for case of cations and anions. The ovoid shape of the iodide and caesium ions represents the magnitude and direction of the polarisation induced by the local charge at the surface. The magnitude of the local Friedel oscillation amplitude is in turn represented by the sign and size of the 'segment' in (b) at the surface.

adsorption of bisulphate and dihydrogen phosphate ions based on their uv-absorption maxima in aqueous solution, excellent agreement is found with that predicted by the trend outlined above.

In reference [31], a log-log plot of specific adsorption versus ionic radius was used to support a model of ionic hydration/contact