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Comments on the paper entitled In situ studies of adsorption of organic compounds on platinum electrodes, by J. O'M. Bockris and K.T. Jeng

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INTRODUCTION

The paper [1] describes results of experimental and theoretical studies of adsorption of several organic compounds on polycrystalline platinum by the use of radiotracer, ellipsometry and FT-IR techniques. The present comments concern the papers assumptions, research strategy, and methodology. Specific points that will be made below are: (1) since adsorption reversibility was not documented, the application of isotherms for adsorption characterization was not justified; (2) the difference in the roughness factor did not make for a fair comparison of adsorption measurements by various methods employed; (3) in consequence of the choice of hydrochloric acid as the supporting electrolyte, chloride-adsorbate substitution rather than the postulated water-adsorbate exchange, was predominantly observed; (4) adsorption of water and the value of the pzc of platinum affect the desting of the organic adsorbates in a way different from that implied in the discussed work.

Alternative conclusions to those proposed by Bockris and Jeng are given at the end of the comments.

PRINCIPAL ASSUMPTION

The principal assumption upon which the model of adsorption is proposed is made on page 567 of ref. 1. Here, it is written: "The adsorption process is assumed to exist in a reversible or quasi-reversible condition and a thermodynamic or statistical treatment is applicable." With perhaps the exception of 1-naphthamine (see below), this is contrary to what is found in the literature about adsorption of the studied compounds on platinum [2,3]. In fact, the room temperature adsorption has been reported to be spontaneous and, if not prevented by competing

surface contaminants or morphological surface constraints, goes to completion. This leads to essentially irreversible adsorption, or an immobile product [2]. The conditions for reversibility could have been tested by checking whether decreasing the bulk concentration of adsorbates diminished their surface concentration. Alternatively, evidence that surface/bulk surface exchange had been fast might have sufficed to demonstrate the reversibility. An outcome of the experiments of this type is reported on page 557. Here, it is stated that: "The adsorbed species is found to be difficult to exchange with non-labeled species, as indicated by radiotracer experiments." This suggests that the adsorption was largely, or completely, irreversible.

In contrast, the procedure recommended by chemical thermodynamics to carry out a quasi-reversible process is to run the reactions infinitely slowly in such a way that each step could be reversed at any time during the progress of reaction. Such a procedure is difficult to adapt to electrochemical adsorption experiments, and was not employed in ref. 1.

The above comments indicate that the adsorption model developed on pages 566–579 is not based on a solid thermodynamic footing. Consequently, this model is concluded to be inappropriate.

RESEARCH STRATEGY

Methods and surfaces

Comparisons were made [1] between surface concentrations obtained by ellipsometry, FT–IR and radiotracer techniques. While smooth surfaces were used for measurements with the optical methods, the surfaces used for the radiotracer work were rough. Such rough surfaces were prepared by electrodeposition of platinum on gold films pre-evaporated on a glass scintillator surface [4,5], and the roughness factor of such surfaces was as high as 63 (page 549). In order to allow for the comparisons, an assumption had to be made that surface properties of all the electrodes used were the same. However, the morphological differences between the electrode surfaces of different roughness may be one of the reasons why the deviations between FT–IR and radiotracer data, and between ellipsometry and radiotracer data, occurred. (It should be noted that the radiochemical and FT–IR data were normalized to the same maximum coverage [6].) Whereas, in general, all the techniques give similar output on a qualitative level, especially in the double layer range, an overall quantitative agreement was rarely found (Figs. 6 and 8). In fact, at some potentials, the deviations approached 500% (see the cases of phenol and 1-naphthonic acid adsorption (Figs. 6(b) and 6(f)). If the extreme deviations are due to the polymerization of some molecules, as proposed on page 557, it is hard to understand why some techniques are, and others are not, sensitive to such a polymerization. Even more significantly, one can argue that polymerization is active on the rough surface but is not on the smooth one. Therefore, only the data obtained with morphologically equivalent, preferably smooth [7] surfaces should be compared and the results of such comparisons considered conclusive.

Notably, the application of rough electrodes may explain why the rate of adsorption of the highly surface-active compounds was so sluggish (the time of attaining the saturation coverage at the bulk concentration of 10^{-2} M was close to 1 h, Fig. 10). The explanation proposed here is that the surfaces applied were heterogeneous in the sense that some surface sites were located "deeper" and some "shallower" in the platinum deposit. Consequently, the access of the adsorbate molecules to some surface sites was more difficult than to others, and the rate of adsorption was determined, to a large extent, by the transport of adsorbate molecules through the micropores in the deposit. The results of a procedure that would permit one to factor-out morphological effects of unknown magnitudes from the data, namely, those of the extrapolation of the rate measurements to a unit roughness, were not reported in the article under discussion.

Chloride interference

Hydrochloric acid was exclusively used as a supporting electrolyte in this work. However, the electrolyte anion, chloride, is well known to adsorb very effectively on platinum electrodes [8-10], up to 0.5 monolayer of surface chloride on the equivalent surface [8]. Since bonding of chloride to platinum is stronger than water to platinum, the reported processes should be viewed in terms of a competitive chemisorption between two active surfactants: surface chloride and an organic adsorbate. While electrochemical adsorption is always a competitive process, using two surfactants in solution instead of the studied one significantly complicates the experiment outcome. A recommended and intuitively obvious procedure in adsorption studies is to use supporting electrolytes containing weakly adsorbing anions (for instance, perchlorate or fluoride). The work in such electrolytes discloses the properties of the studied adsorbate most clearly. However, the possible difficulties with chloride as a competing adsorbate were not even mentioned as a problem of these investigations.

MODEL OF ADSORPTION

Water adsorption and system pzc

As a consequence of chloride adsorption, see above, the surface was largely depopulated of water molecules. Despite this fact the desorption of water, rather than that of chloride, was the main discussion topic of this paper. Even more importantly, considerations based upon water replacement led to the proposed water-substitution model of adsorption. That is, a model was proposed assuming a substitution of water which was grossly under-represented on the surface prior to adsorption of the organic material.

However, even if the perchlorate- or fluoride-based solvents were used for the investigations, the manner in which the water adsorption process was treated is hardly acceptable. Water interacts with platinum through very weak surface

chemical forces, as evidenced by its desorption to vacuum at ca. 170 K [11]. At room temperature, especially around the pzc, the molecular water adsorption in liquid water must display characteristics of a dynamic surface system. Consequently, it can be replaced easily by most known organic adsorbates. True, water decomposition products, surface hydrogen and oxygen, have a fundamental effect on adsorption processes on platinum electrodes [12]. However, without such a decomposition, water plays no major role in determining the destiny of electrochemical chemisorption of practically all compounds studied in the article under discussion. Notably, the bond energy for such adsorbates may be higher than 25 kcal^{-1} mol (100 kJ mol^{-1}), see below, (the value of 25 kcal mol^{-1} was specified on page 580). In such a case, the contribution from water desorption to the total adsorption energy balance should be small.

As a corollary to the above remarks, one needs to point out that extreme care is needed when bond energies of organic adsorbates on catalytic surfaces in gas phase are used for modeling electrochemical adsorption. Since the electric charge released upon adsorption at a constant electrode potential was not measured in ref. 1, it is unknown how many of the systems studied actually became adsorbed via a dissociative process. If some multiple, covalent Pt–C bonds are formed as a result of more than one C–H bond cleavage, the surface bond energies may be even higher than 200 kJ mol^{-1}. For instance, the bond energies for single dehydrogenated molecules of ethylene and acetylene have been calculated to be 184 and 280 kJ mol^{-1}, respectively [13]. Therefore, the net bond energy for those C_n molecules that are involved in the dissociative chemisorption depends on the number of covalent bonds created per one adsorbed molecule, on the degree of electron π donoring, and on the additivity principle applicable to a given multiple bonding state (see discussion in ref. 13).

Products of water decomposition on platinum

In the paper under discussion, a reference is made to adsorption on mercury (page 576), suggesting that adsorption on platinum is energetically similar to that on Hg. Further, in accordance with the mercury-model of adsorption, it is assumed that surface concentrations are predominantly controlled by the extent of deviation of adsorption potential from the electrode pzc. However, while the adsorption/desorption processes on mercury are determined mainly by interfacial electrostatics, the adsorption on platinum is driven by the strong chemical interactions between the adsorbate and the surface. Equally importantly, adsorption/desorption processes on platinum in aqueous media are controlled by the presence of adsorbed hydrogen and oxygen (or some oxygen-containing species derived from a partial water decomposition) on the electrode surface [12]. Both H- and O-adsorbates are capable of surface reactions with the adsorbate, leading to its reactive, or substitutive, desorption. In the absence of specific adsorption of anions, the electrode potential range where platinum is free of the H- and O-species is no broader than ca. 400 mV. Therefore, a flattened, pseudo-bell shaped Γ vs. E curve most

frequently represents the electrode potential dependence of an organic adsorbate [12]. Many of the expected pseudo-bell-shaped plots are seen in Fig. 5 of the discussed work. In view of the above discussion. the role of the pzc of platinum in the interpretation of such plots could be viewed in terms of the H- or O-species formation. and stabilization. on platinum [12.14]. That is, some excess negative charge is needed to stabilize hydrogen adsorbed on platinum at room temperature (compared with dry platinum surfaces [15]). and splitting of water to smaller. reactive fragments requires a positive surface charge. However. the mercury-derived designation of the pzc as the variable directly controlling electrode surface populations on platinum is not an appropriate procedure in interpreting adsorption results obtained with this latter metal.

It is interesting to note [2.3] that for reversible adsorption processes on platinum. the Γ vs. E plots show an "inverse" potential dependence to that predicted by the model proposed in the article under discussion. Namely. the surface concentration increases. not decreases. with the change in the electrode potential in the positive direction above the pzc. Such a coverage–potential relationship has previously been obtained for adsorption of acetic acid and several amino acids on platinum [16–19]. for which the adsorption processes have been proven reversible (mobile. ref. 2). Notably. this inverse potential relationship is also seen in Fig. 6(i)
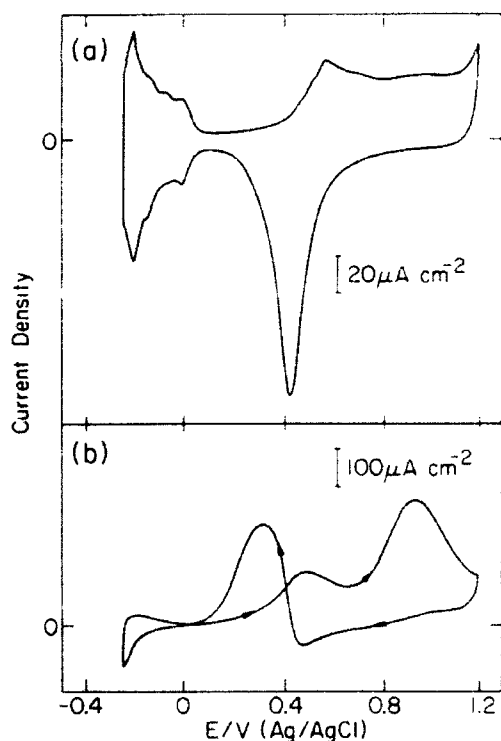

Fig. 1. Cyclic voltammetry of a smooth polycrystalline platinum electrode in 0.1 M $HClO_4$ containing 10^{-2} M of n-butanol. Scan rate = 50 mV s^{-1}.

for 1-naphthamine, which suggests that this compound is adsorbed reversibly. One may therefore conclude that the modeling of electrochemical adsorption by the use of reversible chemical thermodynamics for 1-naphthamine is legitimate [3]. Avoidance of issues such as those scrutinized above, as well as not making any reference to the categorization of adsorption processes on platinum [2,3], is concluded to be a major shortcoming of ref. 1.

CASE OF 1-BUTANOL

Another key statement that is inaccurate is made on page 556: " The adsorption maximum usually occurs in the double layer region where the electrochemical reaction is thought to be absent." To some extent, the concluded lack of electroactivity is contradicted by the voltammetric data in Figs. 6(a), (c)–(e), (h)–(k), (m) and (p), which give evidence for some surface electro-oxidation processes. Our voltammetric results obtained for 1-butanol on smooth platinum and in chloride-free electrolyte are shown in Fig. 1 of the present work. The data are clearly indicative of 1-butanol electro-oxidation: see the positive current in the potential
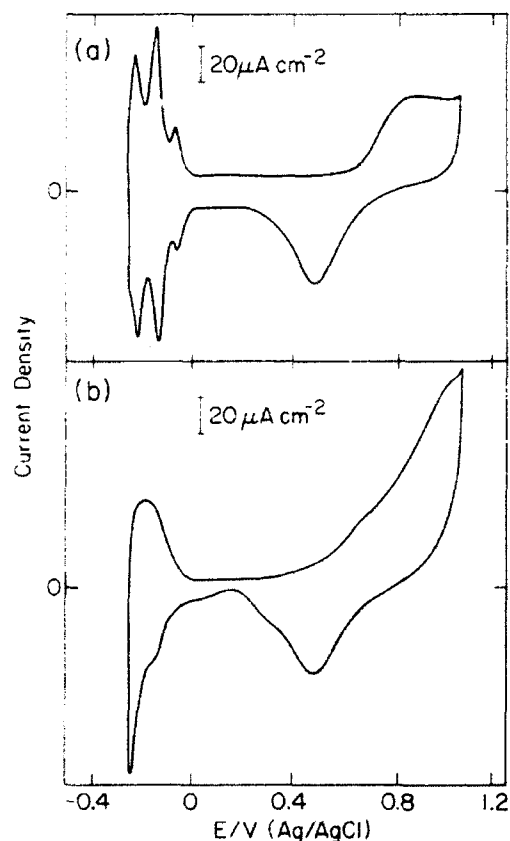
Fig. 2. Cyclic voltammetry of a polycrystalline platinum electrode in 0.1 M $HClO_4$ and 0.01 M NaCl containing 10^{-2} M n-butanol. Scan rate = 50 mV s^{-1}.

range from 0.05 to 0.60 V on the positive going scan, and from 0.55 to 0.05 V on the negative going scan (vs. Ag/AgCl electrode, [Cl⁻] = 1 M). In addition to the observations illustrated in Fig. 1, Fig. 2 of this work shows how much the voltammetric pattern is distorted by the surface and/or solution chloride. The double layer oxidative activity is virtually suppressed (see the different sensitivities between Figs. 1(b) and 2(b)) and a complicated surface reaction, most probably with participation of chloride, occurs in the oxygen region.

CONCLUSIONS

In view of the above discussion it is concluded that the model of adsorption, that is, the understanding of the interactions of the studied compounds with platinum, was based on insufficiently documented experimental material. Neither was the work supported by realistic assumptions concerning surface energetics. As a consequence, the postulated model of adsorption is concluded to be incorrect.

Below, a list of conclusions is proposed based upon the inspection of the data of the discussed [1], and previous [2,3,12,14] work. In the perspective of the present author these conclusions offer an alternative model of adsorption.

(1) In the double layer range, the compounds studied were either adsorbed associatively or decomposed to fragments; this was followed by the generation of an oxidation current. The current depended on the electrode potential and bulk concentration of the compounds studied, and was also affected by chloride chemisorption.

(2) The surface processes studied were suitable for analysis using a categorization of adsorption on platinum into three groups: surface coordination, catalytic decomposition to CO products, and a weak reversible chemisorption [3]. (See also ref. 2 where division of adsorption into two groups was proposed.)

(3) Undissociated surface water was largely removed from the surface by chemisorbed chloride and did not play a noticeable role in the adsorption energetics of a prevailing number of the species examined.

(4) Since the adsorption processes studied were essentially irreversible [2,3] (with the probable exception of 1-naphthamine), the concept of adsorption isotherms was inapplicable for the data treatment. In consequence, the interfacial thermodynamics were similarly inapplicable.

(5) The rate of adsorption was determined predominantly by the transport of the adsorbate molecules through the micropores in the platinum electrodeposit.

(6) The bond energy of the adsorbates studied varied from several to 200 kJ mol⁻¹ (or more), which covers the range of bond chemisorption energy involved in the corresponding gas phase adsorbates [13]. Consequently, in the prevailing number of cases examined, water desorption processes would have little effect on the adsorption energetics, even if the measurements were carried out in a chloride-free electrolytic solution.

(7) To factor-out morphological effects from adsorption–strength relationships requires a re-run of the radiochemical experiments with smooth surfaces. Only

then can a definite statement on the order of adsorption strength be proposed. Likewise, such new data would allow for a comparison, and an integral discussion, or the data obtained by the three surface techniques selected for this research [1].

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