E2-29: Cyclic voltametric studies of platinum surfaces

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Interfacial electrochemistry of platinum electrodes is very complicated. Formation of surface oxide and subsequent reduction followed by hydrogen adsorption together with desorption are some significant surface processes of platinum electrodes. These processes depend on experimental conditions such as solution pH, temperature, nature of the electrolyte, nature of the medium and the crystallographic behaviour of the surface.

Platinum metal has been used in a number of important processes. Use of platinum as a catalyst in several organic and inorganic reactions, and to synthesize anti-tumour organoplatinum complexes are among them. In this study, the electrochemical behaviour of platinum surfaces in aqueous and mixed aqueous/nonaqueous media is reported as an attempt to understand the reactivity of platinum electrodes.

Sodium hydroxide and sodium chloride were analytical grade and used as received. Analytical grade acetonitrile and acetone were used to prepare mixed solvent systems without any further purification. Electrolyte solutions were prepared with freshly distilled water and dearation was accomplished by sparging with nitrogen in all experiments.

A saturated calomel electrode (SCE), platinum disk (Bioanalycical systems, USA) and Pt wire were used as reference, working and counter electrodes, respectively. All potentials were reported with respect to the SCE. Cyclic voltametry was performed with an Oxford Instruments potentiostat and recorded on a Yew Instruments X-Y recorder.

Cyclic voltametric experiments of a platinum disk electrode in 0.1 M NaCl solution under nitrogen saturated conditions were conducted starting from different potentials. Hydrogen adsorption and desorption peaks do not appear when the starting potential is not positive enough for surface oxidation. This suggests that a clean platinum surface should be available for hydrogen adsorption. Surface cleaning can be accomplished by scanning from a sufficiently positive potential to the negative direction so that the oxide formed on the surface is reduced resulting in a clean surface. This was observed when cyclic voltametric experiments were started at a potential higher than +0.8 V.

More interestingly, 2 reduction peaks centred at +0.4 V and -0.2 V were observed at pH 7 during the potential scan from +1.0 V to -0.9 V, in contrast to the single peak observed in phosphate buffer at similar pH values. These 2 peaks can be assigned for the reduction of 2 types of platinum complexes; platinum-oxide and platinum-chloride complexes. These complexes are formed during the positive potential scan and undergo reduction reactions at respective potentials during the negative scan resulting in a fresh surface. Similar processes were also observed in acetone/water and acetonitrile/water mixed solvent systems.

Platinum electrochemistry in aqueous medium is complicated in the presence of chloride anions. Platinum-oxide and platinum-chloride complexes are formed at anodic potentials, and these complexes undergo reduction at distinct potentials resulting in a fresh platinum surface. Such studies would be important to understand the reactivity of platinum surfaces.