INTRODUCTION

Modern techniques for preparation and electron spectroscopic characterization of surface structure and composition in ultra-high vacuum (UHV) have ushered in an era of rapid progress for gas-solid surface studies. These advanced techniques have great potential usefulness in the science of electrochemistry. Specifically, low-energy electron diffraction (LEED) provides data from which electrode surface and adsorbed layer crystallographic structure can be determined. This represents a substantial advance for the science of electrochemistry in which surfaces of undefined structure on polycrystalline or bulk single-crystalline material have been the norm. Furthermore, Auger electron spectroscopy (AES) quantitates the elemental composition of the surface and adsorbed layer, including interfacial impurities. Thermal desorption mass spectrometry (TDMS) provides data regarding the molecular constitution and thermal stability of the adsorbed material. A growing number and variety of other techniques also highly useful for study of electrode surfaces have become available although not exploited for the present study.

An understanding of how solvents and electrolytes interact with electrode surfaces is of both fundamental and practical importance. A majority of polar compounds chemisorb on metal surfaces, and electrode reactions are inherently sensitive to these chemisorption phenomena. Adsorption of solvent can be controlled by surface pretreatment in solution. Electrode

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reactions in particular are strongly influenced by halogens and halides. Accordingly, studies of adsorbed materials such as solvents and electrolytes by LEED and related methods will yield facts concerning structures, chemical composition and stability which will be informative to electrochemists.

The present article describes studies of the structures formed by typical polar solvents and other electrolytic materials such as I₂ and hydrogen halides on well-defined platinum single crystal surfaces in ultra-high vacuum. By combining effusion beam dosing with efficient pumping, dosages spanning the range from UHV to pressures approaching the vapor pressure of the pure liquid were included. The structure of the adsorbed layer was studied by LEED, elemental composition by Auger spectroscopy and thermal stability by thermal desorption mass spectrometry.

EXPERIMENTAL ASPECTS

Electrode surfaces were prepared and exposed to electrolyte vapor in a UHV system using a nozzle-beam doser at pressures low enough to allow use of electron techniques but high enough to approach the equilibrium vapor pressure of the electrolyte. A brief review of the UHV techniques employed in this study (LEED, AES and TDMS), together with a short description of the UHV system and material requirements are given below.

Brief Review of UHV Techniques

Low-energy electron diffraction provides data from which surface crystallographic structure can be determined, including the structure of the first few atomic layers of the substrate and any adsorbed material which might be present. The symmetry of the diffraction pattern is a direct consequence of the periodic arrangement of the atomic or molecular constituents in the surface of the crystal. In a diffraction experiment the elastic component of a scattered electron beam (which contains the primary diffraction information) can be separated from the inelastic components by a post-acceleration technique illustrated in Figure 1. The elastic component which has penetrated the cathodic grid system is accelerated (+7000 eV potential) onto a fluorescent screen causing light emission where the electron hits. In this study, LEED patterns were photographed by means of a Nikkormat camera on high-speed black-and-white film. An exposure of 30s at f5.6 was generally optimal at the beam currents stated in the figure captions. Patterns were observed throughout an incident energy range from 10 to 250 eV in order to locate all constituent spots.

Auger electron spectroscopy yields spectral data indicative of the identity and quantity of elements present in the surface