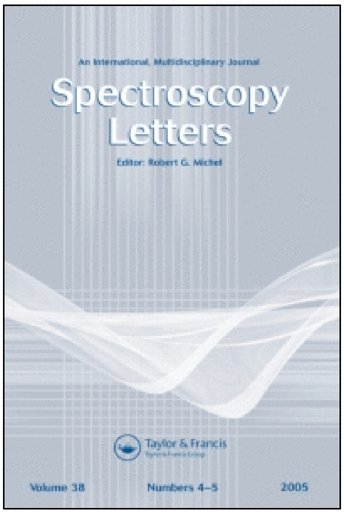

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In Situ FTIR Spectroscopic Characterization of Adsorbed Species on Carbon Electrodes. I. Phosphate, Sulfate and Perchlorate Ions in Aqueous Solution

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IN SITU FTIR SPECTROSCOPIC CHARACTERIZATION OF ADSORBED SPECIES ON CARBON ELECTRODES. PART I: PHOSPHATE, SULFATE AND PERCHLORATE IONS IN AQUEOUS SOLUTION

Keywords: *In situ* FTIR spectroscopy, adsorption, electrochemistry and glassy carbon electrode.

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ABSTRACT

Electrochemical adsorption studies on a glassy carbon electrode using FTIR spectroscopy are reported for the first time. The nature of adsorption for a series of tetrahedral anions from aqueous solution is reported.

INTRODUCTION

In recent years it has been shown that spectroscopic measurement of species generated at an electrode can be an extremely powerful tool for elucidating reaction pathways in electrosynthesis. Although FTIR spectroscopy has been used fairly extensivelv to detect organ-

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ic radicals in non-aqueous media,[1] similar studies in aqueous media are rare[2,3] due to the high infrared absorption of water. Moreover, all the in situ IR and FTIR studies reported so far have been concerned with optically non-absorbing electrodes made of shiny metals. However, syntheses of industrial importance are carried out at electrodes made of materials such as carbon, lead, cadmium, or finely divided metal oxides, preferably in aqueous media. To see if FTIR is capable of giving useful information under industrial conditions, a study was made of solution and surface species at a carbon electrode in various aqueous electrolyte systems. In this first paper we report the base case, i.e. no addition of electroactive material. Other cases will be reported later.[4]

EXPERIMENTAL

Materials and Reagents

A phosphate buffer of pH 8.0, a 0.1 M solution of sodium sulfate, and a 0.1 M solution of sodium perchlorate were used as test solutions. All were made up with doubly distilled, deionised water. A saturated calomel electrode (IBM) was used as a reference. The counter electrode was a ring of platinum wire, and the working electrode was a disc of glassy carbon mounted on a steel rod.

The disc was 1 cm. in diameter to match the IR beam size. Before use the electrode was polished with micropolishing gamma alumina (0.05 micron, Union carbide) and then cleaned ultrasonically.

Spectroscopic and Electrochemical Equipment

Potential step input waveforms were provided by a Model 173 potentiostat and Model 175 function generator (both PARC), synchronization between the application of the potential step and the beginning of the data collection being controlled by a Hewlett-Packard 9816 computer. IR spectra were recorded on a Nicolet 7199 FTIR spectrometer equipped with a KBr supported germanium beam splitter and a type B, 77°K cooled mercury-cadmium telluride solid state detector. Interferograms were signal averaged to enhance the signal to noise ratio. Final spectrum reported is the difference between 100 averaged spectra (4 cm^{-1} resolution) at the two potentials. No smoothing was used since it was found to distort the spectrum and change the relative intensities of bands. Instead zero filling of the interferograms was found to be more satisfactory. The reflection attachment used was a modified version of the apparatus described by Harrick,[5] Fig. 1a. The converging beam from the interferometer was reflected by a plane mirror M1 to the plane mirror M2 of a retroreflector placed such that any desired angle of incidence could be obtained at the cell window. The cell window and electrode formed the second element of the retroreflector. The two reflectors were placed at an angle of 97.5° with respect to each other in order to accommodate the beam focus of the Nicolet optics. After transmission through the cell window, the beam was reflected by the electrode, transmitted through the window again (Fig. 1b), collected by the spherical mirror M3 and directed to the focussing optics of the detector by the plane mirror M4. Light was polarized by a silicon Brewster angle polarizer (Harrick Scientific) mounted before the detector so that only light polarized parallel to the plane of incidence reached the detector. The entire reflectance accessory was mounted on an x-y-z positioner. The cell was mounted

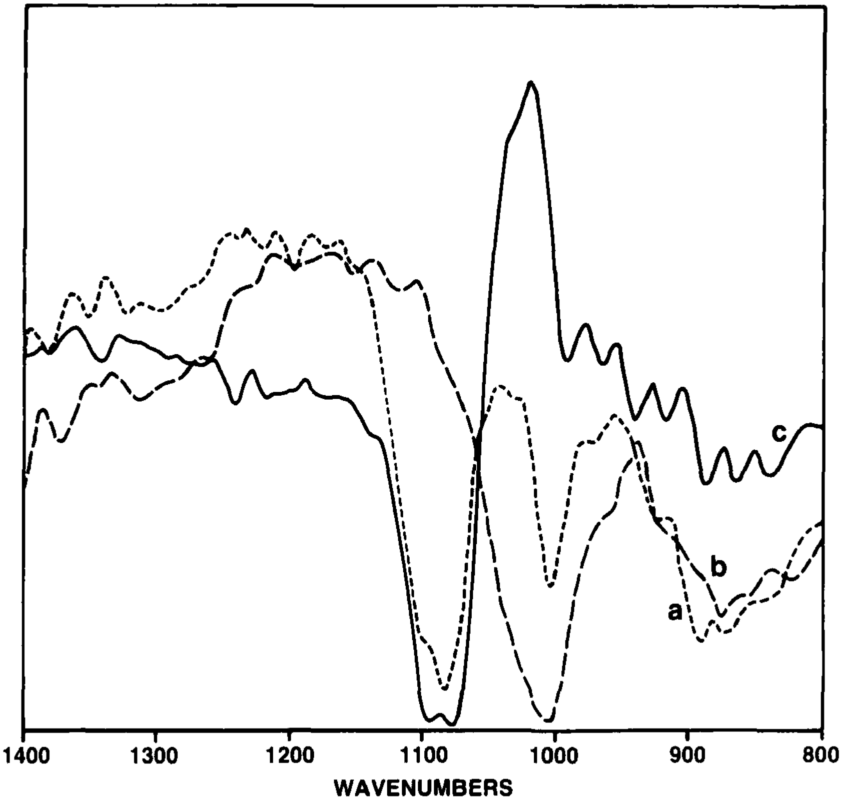

Figure 1. **a. Schematic diagram of the optical system.**
b. Reflection at the Brewster angle and the path of the IR beam through the cell.

on a separate x-y-z positioner to facilitate alignment. The cell itself was very similar to the one described earlier.[1,3] For surface work, the electrode surface was brought very close to the window such that only a thin layer (<u>ca</u>. one micron) of solution was sampled by the IR beam and the contribution of the bulk species to the observed spectrum was minimized. For studies on solution species, the electrode was moved back to allow a larger volume of the bulk solution to be sampled. The thickness of the solution layer could be precisely controlled by a micrometer screw attached to the electrode stem.

With the electrode either forward or back, four co-added interferograms were collected at each of two set potentials, E1 or E2. The cycle was repeated 25 times until two sets of 100 co-added interferograms were obtained, which were transformed into single beam spectra, R1 and R2, where R1 and R2 are the intensities of the reflected light at potentials E1 and E2 respectively. This procedure minimizes differences due to changes in the electrode surface with time. The final results were displayed as $\Delta R/R$[6,7] where $\Delta R/R = (R1-R2)/R1$.

RESULTS AND DISCUSSION

The basic theory concerning the absorption of electromagnetic radiation by thin layers on reflective substrates has been developed by Greenler[6] and Hansen.[8] A review of this theory as it applies to the present study is found in McIntyre.[7] In the case a metallic surface for which the reflectivity, R, is near or equal to unity, only the component of p-polarized radiation (parallel to the incident plane) which is also normal to the electrode surface has a non-zero value (Fig. 11, Ref. 7). This holds for all angles of incidence at the reflecting surface, which means that only dipoles normal to the electrode can be excited at a shiny metal electrode; this condition has been invoked by a number of workers[1-3,9,10] to deduce the orientation of molecules adsorbed at the electrode surfaces. The situation is different for partially reflecting substrates such as carbon. Porter, et al.[11] have estimated the real and imaginary indices (n and k) of carbon to be about 2.9 and 1.25 repectively in the infrared region, in which case any component of light polarized parallel to the electrode surface has a nonzero value at the electrode surface, so that both perpendicular and parallel dipoles are sensed. However, under the conditions of our experiment (about 45° angle of incidence at the electrode and the majority of the light polarized in the plane of incidence by the Brewster angle reflection) theory shows that the contribution from parallel dipoles is small, so that the spectra still give information principally about dipoles perpendicular to the electrode. Clearly, as McIntyre's calculations show, changing the angle of incidence changes the discrimination between the two orientations.[7] The experiment can therefore be designed to vary the sensitivity towards the two different dipole orientations, limited only by the geometrical constraints of the sample cell and the overall intensity of light reflected from the surface. This will be pursued in later papers.[4]

The single beam IR spectra of the phosphate solution at electrode potentials of -1.0 and +1.0 V and their difference spectrum are shown in Figure 2. Peaks I and II in the difference spectrum are due to species present at -1.0 and +1.0 V respectively. At the positive potential the infrared spectrum shows two bands at around 1000 and 1080 cm^{-1}, whereas only the band at 1000 cm^{-1} is present at the negative potential. Free phosphate ion, which belongs to the point group Td, has two IR-active fundamentals

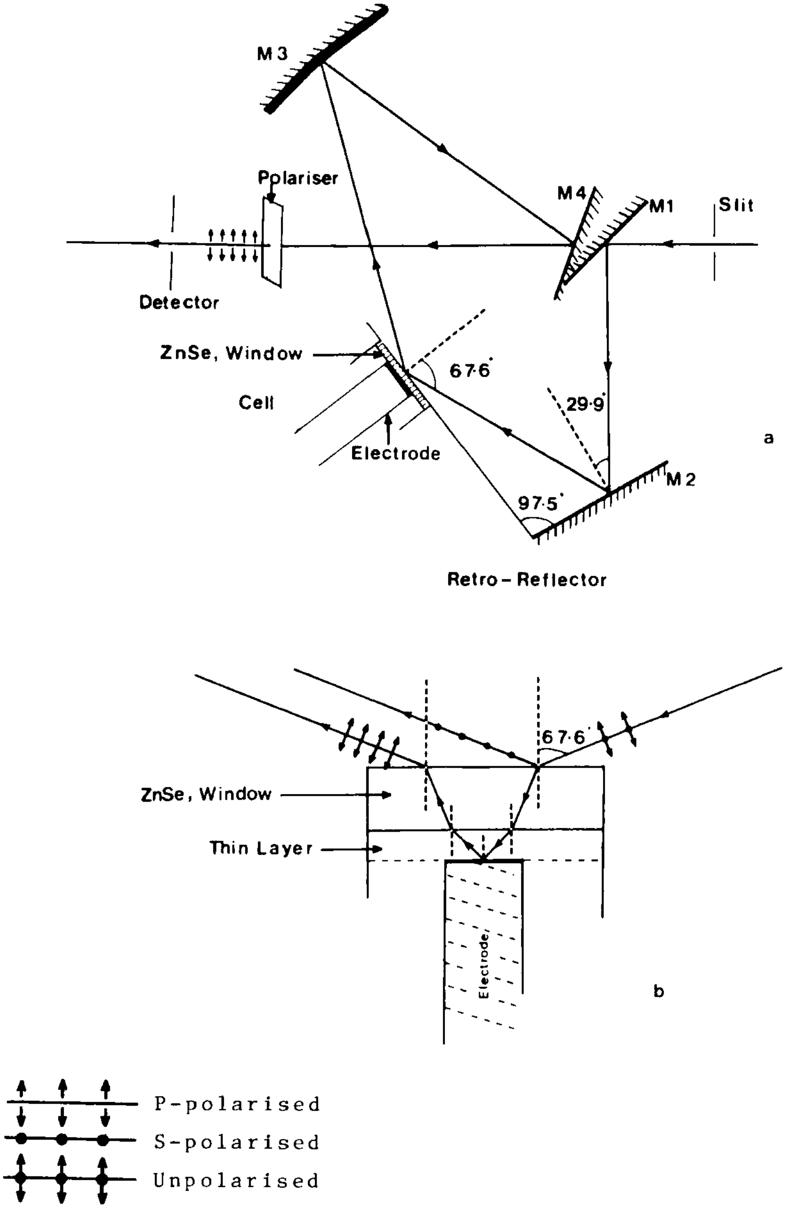

Figure 2. Spectra of aqueous phosphate solution at the carbon electrode through ca. one micron path of solution. a). Single beam spectrum at +1.0V. b). Single beam spectrum at -1.0V. c). Difference spectrum between (a) and (b).

of F2 symmetry (ν_3 and ν_4).[12] The band at 1000 cm^{-1} corresponds to the ν_3 vibration of the P-O asymmetric stretch of the free phosphate ions in solution. The ν_4 vibration, expected around 500 cm^{-1}, was not observed because of the total optical absorption by water in that region. At +1.0 V the additional band observed at 1000 cm^{-1} is probably due to the ν_3 vibration of adsorbed phosphate ion. The intensity of this band did not change with time but increased with increasing anodic potential without any shift in position. This indicates that the same species was present at all anodic potentials but that the surface concentration was a function of the applied potential, which is what would be expected for the adsorption of a negative ion on a positive electrode. If the change in intensity were due merely to an increase in concentration in the double layer, then such a large frequency shift would not be expected. The spectral evidence, therefore, points towards adsorption of phosphate on the electrode. Similar observations have been made of the adsorption of phosphate on platinum,[3] but this is the first observation on carbon. The shift of the ν_3 band to higher frequency on adsorption without any measurable splitting of the band indicates that the tetrahedral symmetry of phosphate is essentially retained. Similar results were obtained with sulphate ions, the ν_3 band shifting from ca. 1100 cm^{-1} to ca. 1200 cm^{-1}, however no shift was observed with perchlorate. This again suggests that the spectral shift is due to adsorbtion, since there is electrochemical evidence[13,14] that phosphate and sulphate are commonly adsorbed, but that perchlorate is not.

CONCLUSIONS

For the first time, there is direct infrared spectral evidence that phosphate and sulphate ions are adsorbed on carbon electrodes from aqueous solution at positive potentials. Perchlorate apparently is not, which has long been suspected from other evidence. The further implication of this observation is that it is possible to monitor adsorbed species and reactive intermediates on commercial electrode materials with FTIR spectroscopy, even through aqueous media.

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