An *in-situ* FTIR Study of the Adsorption Behaviour of Cyanide Ions on a Platinum Electrode

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In-situ FTIR studies of the adsorption behaviour of cyanide ions on a platnium electrode in aqueous K_2SO_4 solution indicate that cyanide is not adsorbed on the electrode, as reported for other metals; instead, CN^- appears to be oxidized to OCN^-, thereby liberating H^+ ions, which convert the SO_4^{2-} ions to HSO_4^-.

In recent years, the importance of FTIR spectroscopy in detecting electrogenerated species at electrode surfaces and electrode–electrolyte interfaces has been satisfactorily demonstrated.[1,2] However although the detection of organic radicals in non-aqueous media has been fairly well reported, similar studies in aqueous media are rare owing to water's high infrared absorbance. Further to our studies,[3] on the electrochemical adsorption behaviour of inorganic anions on both metallic and non-metallic electrodes in aqueous media, we report here the adsorption behaviour of cyanide ions on a platinum electrode in aqueous sulphate. There appears to be no evidence for the adsorption, at positive potential, of cyanide ions on the electrode surface, as reported on other metal electrodes.

Potential step-input waveforms were provided by a PARC Model 173 potentiostat and a Model 175 function generator. FTIR spectra were recorded on a Nicolet 7199 spectrometer with a retro-reflectance attachment. Details of the design and construction of the electrochemical cell and other relevant information have been given elsewhere.[1] The working electrode was a flat disc (diameter 1 cm) of polycrystalline platinum sealed at the end of a stainless steel rod. All measurements were made through a thin-layer solution (*ca.* 1 μm) of 10 mmol dm^{-3} KCN in 0.5 mol dm^{-3} aqueous K_2SO_4. Data collection was achieved by low-frequency potential modulation of the electrode surface.[1] Six co-added interferograms were collected after steady-state conditions had been reached at each of the two potential limits of −0.2 V (reference potential) and +0.4 V (sample potential) and stored separately. The cycle was repeated several times to obtain the desired S/N ratio. In order to eliminate the interference of solution species, a time interval was introduced between each cycle. The co-added interferograms collected at −0.2 and +0.4 V were Fourier transformed to single-beam spectra R_1 and R_2 respectively and the final results displayed as $\Delta R/R$, where $\Delta R/R = R_1 - R_2/R_1$. This is the normalized difference spectrum with all peaks extending to positive values of $\Delta R/R$ signifying decreased absorption at that wavelength at sample potential relative to the reference potential and *vice versa*.

Both FTIR and surface enhanced Raman spectroscopy (SERS) studies of the adsorption behaviour of cyanide ions in

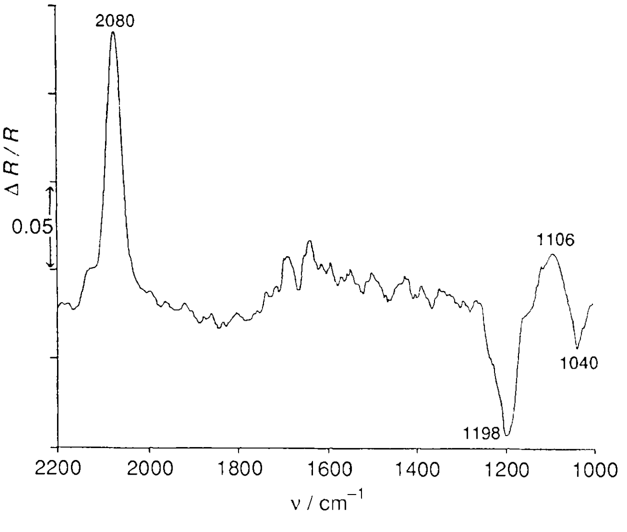

Fig. 1 Normalized difference spectrum of aqueous KCN solution in 0.5 mol dm^{-3} K_2SO_4 between −0.2 and +0.4V (referenced to SCE)

aqueous sulphate solution on Au and Ag electrodes have been reported[2] and it has been suggested that a band observed at 2100 cm^{-1} (in addition to the 2080 cm^{-1} band of free CN$^-$) could be attributed to adsorbed cyanide ions. The intensity of this band and therefore adsorption was found to increase as the potential was made more positive. However, to the best of our knowledge, no studies on the adsorption behaviour of cyanide ions on platinum have been reported.

The normalized difference spectrum of cyanide ions in sulphate solution is shown in Fig. 1. The band at 2080 cm^{-1} corresponds very well with the ν_{CN} of free cyanide and can be explained by the loss of free cyanide from the thin-layer solution at the interface. It is significant, however, that no bands due to adsorbed CN$^-$ (expected around 2100 cm^{-1}) are observed. However, free sulphate (point group Td) has only two fundamentals (ν_3 and ν_4) active in the infrared, which appear at 1104 and 613 cm^{-1}. Accordingly, the band at 1106 cm^{-1} directed upwards can be assigned to the vibration of free sulphate, which is depleted from the sampling area at +0.4 V. At the same time, the bands at 1198 and 1040 cm^{-1} in the downward direction are due to species generated at 0.4 V and could be assigned to the splitting of the ν_3 vibrations of sulphate ions adsorbed on the electrode surface through oxygen in a monodentate fashion.[4] However, the HSO$_4^-$ ion was also found to have absorptions centred on 1200 and 1036 cm^{-1} corresponding to its asymmetric and symmetric stretching frequencies. Consequently, an alternative and more likely explanation for the observed depletion of CN$^-$ and SO$_4^-$ ions from the region of the electrode surface and the appearance of new bands at 1198 and 1040 cm^{-1} at 0.4 V would be that the CN$^-$ is oxidised to OCN$^-$ at positive potential [eqn (1)].

$$CN^- + H_2O \longrightarrow OCN^- + 2H^+ + 2e \qquad (1)$$

The liberated H$^+$ ions could then lead to the conversion of SO$_4^{2-}$ to HSO$_4^-$ in the region close to the electrode surface giving rise to the bands at 1198 and 1040 cm^{-1}.

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