

1974

Optical Absorption Phenomena at Electrode Surfaces

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Recommended Citation

Tyson, Julian and West, T. S., "Optical Absorption Phenomena at Electrode Surfaces" (1974). *Nature*. 1277.

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Optical absorption phenomena at electrode surfaces

THERE has been a considerable expansion recently, in the application of optical techniques, such as internal reflection and specular reflection spectroscopy, ellipsometry, interferometry, holography and optical microscopy, to the study of adsorption phenomena in electrochemical reactions¹⁻³.

In general, these methods have been used to study the optical properties of the electrode material and of thin films adsorbed on to their surfaces. Internal reflection spectroscopy and specular reflection spectroscopy have both been used to monitor the surface concentration of an electroactive species⁴⁻⁶.

We describe here some preliminary observations of the optical absorption phenomena which occur above a platinum cathode surface when dilute aqueous solutions of metal cations containing a preponderant concentration of an indifferent electrolyte, such as an alkali metal halide, are electrolysed at low current densities and controlled potentials in a silica cuvette.

Well defined transient absorption spectra are obtained both 'on' the cathode surface and as much as 10^6 – 10^7 Å into the solution phase. The wavelengths of the absorption maxima of the transient absorption bands bear a close relationship to the shorter wavelength absorption lines of the same atomic species in a gas phase. Furthermore, the peak intensities of these transient signals are proportional, in each case, to the concentration of the free electroactive cations in solution. No corresponding signals are observed at the anode or in the absence of the electroactive species, or at potentials below that required to discharge the particular cation. The signals are most intense at grazing incidence on the cathode, but they are also found in the solution phase when the cathode is below the analysing light beam.

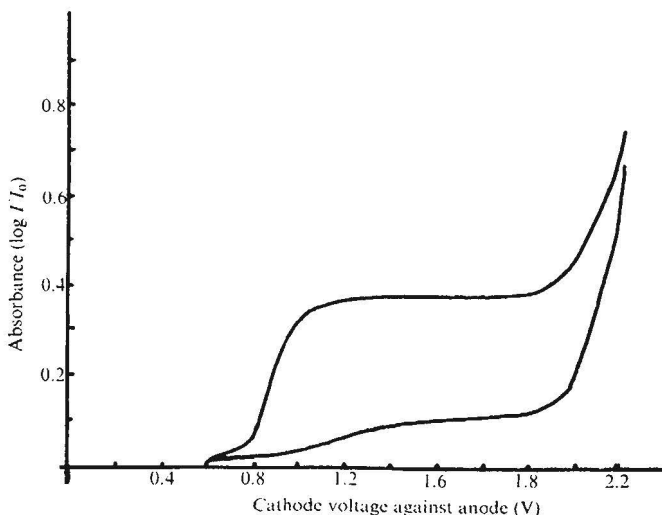


Fig. 1 Variation of absorbance (207 nm) with voltage. Upper curve, 5 p.p.m. Zn^{2+} in 0.03 M K_2SO_4 ; lower curve, 0.03 M K_2SO_4 only.

These observations suggest the transient existence of hydrated free atoms in the solution, close to the cathode surface. It is probable that these are formed by a process of electron tunnelling from the cathode with the formation of hydrated electrons which subsequently reduce the hydrated, or otherwise liganded, cations.

These experiments suggest to us the basis of a potentially useful analytical trace technique of hydrated (solvated) atomic absorption spectroscopy (T. S. West, Fourth International Conference on Atomic Spectroscopy, Toronto, unpublished). The technique may also prove useful for the examination of surface mechanisms in electrodeposition and electrochemistry in general.

A simple ultraviolet/visible spectrophotometer was built from a hydrogen lamp and power supply, a tungsten filament lamp, a monochromator, and a photomultiplier tube with a Branden-

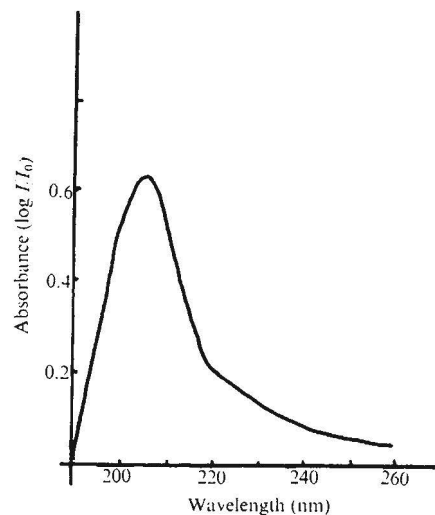


Fig. 2 Variation of absorbance with wavelength; 10 p.p.m. Zn^{2+} in 0.03 M K_2SO_4 at -1.4 V.

burg type 475R e.h.t. power supply. The output was monitored by a chart recorder. A 20-mm silica cell was used, with two platinum plate electrodes inserted. A potentiostatic waveform source was used as a signal generator. The alignment was such that a narrow collimated beam of light passed over the surface of the cathode, with the anode kept well clear of the light path. The cathode could be racked upwards or downwards in the light beam.

Each element was studied by using the highest possible potential difference in order to find a wavelength at which a maximum transient increase in absorbance was obtained. At that wavelength, the optimum electrode pretreatment conditions and potential difference were found, and, using these, the variations of absorbance with wavelength and with concentration of metal cation were obtained.

The stock solutions were diluted to give solutions of (typically) 10 parts per million (p.p.m.) in 0.03 M K_2SO_4 or 0.1 M KCl. A 5 cm³ aliquot was placed in the cell and de-aerated with oxygen-free nitrogen. The gain of the system was adjusted so that zero absorbance was registered, and a potential step (square wave) was imposed on the electrodes so that the electrode in the light path became the cathode. After the change in absorbance had been recorded, the cell was emptied (by suction) and the working electrode was washed with dilute base electrolyte while a high positive potential (up to 5.0 V) was applied—that is, it was cleaned by anodic stripping. If necessary, any surface oxide was reduced by reversing the polarity of the system.

Using this technique we studied the following metal ions: Cu^{2+} , Cd^{2+} , Fe^{2+} , Fe^{3+} , Pb^{2+} , Zn^{2+} , Co^{2+} and Ni^{2+} . On applying a potential difference between the electrodes a transient increase in absorbance was observed. This change in absorbance

has been interpreted as absorption of light by reduced species generated on or near the cathode surface.

A variation of absorbance with voltage was observed, in most cases, after a simple step function had been applied, that is, the potential difference was stepped from 0.0 V to the preset required value. Pulsed square wave functions were also used (both between zero and the required voltage and between positive and negative values) but, in general, these did not increase the magnitude of the absorbance obtained. The magnitude of the potential difference is limited by cathodic evolution of hydrogen (it was limited to about -2.2 V in 0.03 M K_2SO_4). At the absorption maximum, plots of absorbance against potential difference were obtained. These have the appearance of d.c. polarograms; as the potential difference is increased, the absorbance increases until a plateau region occurs. This persists as the applied potential difference is progressively increased until the background electrolyte begins to be reduced, or hydrogen is evolved, at which point a rapid increase in absorbance, resulting from scattering, is observed. Zinc typically has a plateau region of -1.1 to -2.0 V (Fig. 1).

With an oxidised cathode an increased signal was obtained at lower potential differences. At -2.0 V the nature of the pre-treatment had no effect on the magnitude of the absorbance signals observed for any of the cations.

With the background electrolyte alone, no absorbance was observed at wavelengths greater than 210 nm. Below this, a band with a maximum absorbance of about 0.25 (half bandwidth 10 nm) was observed at 197 nm.

Plots of absorbance against wavelength were made at the optimum observed conditions. Generally, these are, not unexpectedly, much broader than gas phase absorption lines and have a single maximum occurring in the ultraviolet. For example, zinc has a maximum at 207 nm and a half bandwidth of 16 nm (Fig. 2). The spectra for the other metals so far examined are broader.

Absorbance against concentration was plotted at the absorption maximum for each metal. Generally, the plots were linear, over a variety of concentration ranges. The zinc calibration was linear between 1 and 12 p.p.m.

The absorption typically reached its maximum value after approximately 30 s and then decayed to the initial value over a period of up to 2 min if the applied potential was maintained. The decay was more rapid if the potential difference reverted to zero at, or just after, the maximum absorbance had been reached.

The maximum absorbance was only maintained if an oscillating voltage function (both positive and negative going) was used at a frequency greater than 0.1 Hz.

Although some metals give rise to more intensely absorbing species, there is a concentration range for each metal so far studied, over which the absorbance is a linear function of concentration. This, together with the possibility of achieving selectivity with a suitable choice of wavelength and voltage, or with selective complexing and masking (as in the preconcentration step in voltammetric stripping analysis), points the way to analytical applications.

We thank the Science Research Council for the award of a research studentship to J. F. T.

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Received March 5, 1974.

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