PERKIN 2

The electrochemical reduction of indigo dissolved in organic solvents and as a solid mechanically attached to a basal plane pyrolytic graphite electrode immersed in aqueous electrolyte solution

Alan M. Bond,[a] Frank Marken,[b] Emma Hill,[b] Richard G. Compton *,[b] and Helmut Hügel[c]

[a] *Department of Chemistry, Monash University, Clayton, Victoria 3168, Australia*
[b] *Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford, UK OX1 3QZ*
[c] *RMIT, Department of Applied Chemistry, Bundoora, Victoria 3083, Australia*

The electrochemical properties of solid materials such as organic compounds, irrespective of their electrical conductivity, can be studied *via* the use of submicron sized particles mechanically attached to electrode surfaces immersed in aqueous media containing different electrolytes. In this study the reduction of solid indigo in buffered and non-buffered aqueous media has been investigated. Data are compared to those obtained from a voltammetric study of indigo dissolved in dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF) and in pyridine and the interpretation of results is facilitated by *in situ* EPR, *in situ* UV–VIS spectroscopy and atomic force microscopy (AFM) studies. For the reduction of solid indigo two distinct types of reduction processes, 'surface-type' and 'bulk-type', have been observed. The latter process has been found to be associated with the reductive dissolution of indigo. The 'surface-type' responses which occur in a microphase at the electrode/solid/solution interface are reversible $2H^+$-$2e^-$ reduction and oxidation processes with a corresponding 60 mV shift in half wave potential per pH unit in buffered electrolyte media over the pH range 4 to 11. The 'bulk-type' reduction process is proposed to be associated with the electroinsertion of cations into the solid indigo particles, thereby producing a reduced material and causing the loss of material from the electrode surface under convective flow conditions. The electrochemical solubilization of indigo occurred in non-buffered aqueous media even at neutral pH values.

Introduction

An understanding of the nature of the heterogeneous processes that occur at solid/liquid interfaces is important in many areas of chemistry.[1–4] For example, the heterogeneous chemistry of the vat dye dissolution process, which involves the conversion of the water insoluble dye into the water-soluble leuco form by reduction, is the major factor in determining the cost efficiency and environmental compatibility of dyeing.

A vast range of vat dyes have been synthesised although the natural dye indigo, which is studied in this paper, is still used in textile dyeing because of its favourable properties.[5] The reduction of water insoluble indigo to its water soluble form is commonly undertaken in a batch process at elevated temperature in aqueous alkaline media.[6] Typically, a dithionite salt ($Na_2S_2O_4$) is used as the reducing agent, although electrochemical approaches to the reduction process have been proposed.[7] The rate for the heterogeneous indigo reduction process depends on a range of variables[8] but may be regarded as a relatively complex surface confined dissolution process.[9] Several electrochemical studies have been reported on indigo and related dyes. However, parameters such as the particle size and the redox potential for the reduction of the dye dissolved in pyridine could not be correlated with the rate of dissolution.[8] Furthermore the potential for the onset of the oxidation of an aqueous solution of the leuco dye at a platinum electrode, the 'leuco potential',[8] apparently does not correlate with the dissolution rate. Thus, information obtained by studying dissolved material appears to have only limited relevance to the solid state reactions. This implies that electrochemical studies on the solids themselves may be necessary to unravel mechanistic details of the dissolution process.

Recently a new electrochemical tool for the investigation of electrochemical processes has been introduced which uses nanogram quantities of solid particles of an electroactive material mechanically attached to an electrode surface.[10,11] Distinct signatures for the solid state electrochemistry of various minerals have been reported[12] and studies have been extended to insoluble, non-conducting materials[13] and solid–solid phase transformations.[14] In this study the new technique is applied to an investigation of the complex reductive dissolution process of indigo in aqueous media. Importantly, it is proposed that parameters readily obtained from this type of solid state voltammetry may enable the rate and mechanism of reductive dissolution of vat dyes to be rationalized.

Experimental

Chemicals

Indigo (Aldrich) was used either as purchased or after sublimation at 290 °C under argon. Aqueous electrolyte solutions were prepared using KCl, NaCl, $CaCl_2$ (all BDH, AnalaR), $NaClO_4$, LiCl (both Aldrich) and water of a resistivity not less than 18 MΩ cm obtained from an Elgastat system (High Wycombe, Bucks, UK). Britton–Robinson buffer solution contained 0.04 mol dm^{-3} boric acid (BDH), 0.04 mol dm^{-3} acetic acid (BDH), and 0.04 mol dm^{-3} phosphoric acid (Aldrich) adjusted to the required pH by addition of conc. aqueous NaOH or NH_4OH. Pyridine and *N*,*N*-dimethylformamide (HPLC grade, Aldrich) were dried by passing through a column of activated alumina (Aldrich, Brockman-I, neutral). Dimethyl sulfoxide (anhydrous, Aldrich) was used as purchased. The supporting electrolyte in organic solvents was NBu_4PF_6 (Fluka, electrochemical grade) and benzoic acid (BDH) was used as a proton source. All solu-

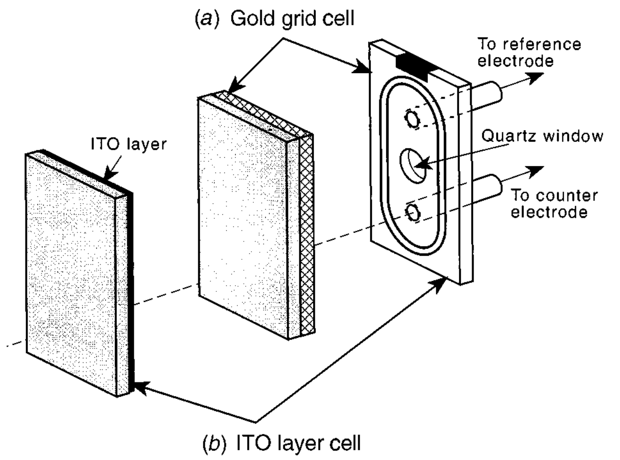

Fig. 1 Thin layer transparent electrochemical cells with (*a*) a gold grid electrode for solution experiments and (*b*) an ITO electrode coated on glass for electrochemical experiments using solids

tions were thoroughly degassed with argon for at least 20 min prior to experiments.

Instrumentation

For voltammetric experiments, an Oxford Electrodes potentiostat connected to a Lloyd P3 recorder was used. Electrodes used were a 3 mm diameter glassy carbon disk (BAS, West Lafayette, IN), a 50 µm diameter Pt disk (Microglass Instruments, Melbourne, Australia), a 1 mm diameter Pt disk and a 4.9 mm diameter basal plane pyrolytic graphite disk (pyrocarbon, Le Carbone Ltd., Sussex, UK) mounted in a Teflon holder. The reference electrode was a saturated calomel electrode (SCE) (Radiometer). UV–VIS spectra were recorded on a double beam scanning spectrophotometer (ATI Unicam, Cambridge, model UV2-100). For EPR studies a Bruker ER 200D with TE_{102} cavity and a field-frequency lock was used in conjunction with the previously described Compton–Coles cell.[15] Analysis of the electrode surface topography by AFM (atomic force microscopy) were carried out using a TopoMetrix TMX 2010 Discoverer system in the contact mode (typically 3 Hz scan rate) with TopoMetrix standard AFM probes (no. 5200).

Procedure

The methodology used for the preparation of electrode surfaces modified by mechanically attaching solid materials has been described elsewhere[13] and consists simply of rubbing a clean basal plane pyrolytic graphite electrode surface onto a sample of 1–3 mg compound on a piece of filter paper. Commercially available indigo as well as freshly sublimed indigo (290 °C, argon) were found to give essentially identical types of modification and voltammetric behaviour.

Cells for *in situ* spectroelectrochemical studies were a transparent thin layer cell with a gold minigrid (64% open area, Goodfellow, Cambridge, UK) electrode[16] [Fig. 1(*a*), optical path length 0.5 mm] and for the study of solid indigo a transparent indium tin oxide (ITO, Phosphor Products Co. Ltd., Upton, Dorset, UK) electrode in a channel cell [optical path length 0.6 mm, Fig. 1(*b*)]. The solid in the spectroelectrochemical study was transferred to the electrode surface by rubbing a thin layer with a cotton bud onto the electrode surface.

Results and discussion

Voltammetry of indigo in the solution phase

While the main interest in this paper is the study of the redox chemistry of solid indigo, solution phase data can provide useful background information. However, in spite of the importance of indigo as a commercial product and the significance of its redox properties for the dyeing process, few mechanistic details are known about the reduction and oxidation of indigo even in the solution phase. In contrast, derivatives of indigo have been extensively studied in the solution phase.[17–20] Only very polar organic solvents and/or elevated temperatures allow solution phase voltammetric studies of low concentrations of indigo to be undertaken. Further, the species present in the deep blue solution of indigo in organic solvents such as pyridine has been proposed to be dimeric or of higher associated form[21] rather than the indigo monomer which is known to possess a red colour in the gas phase.

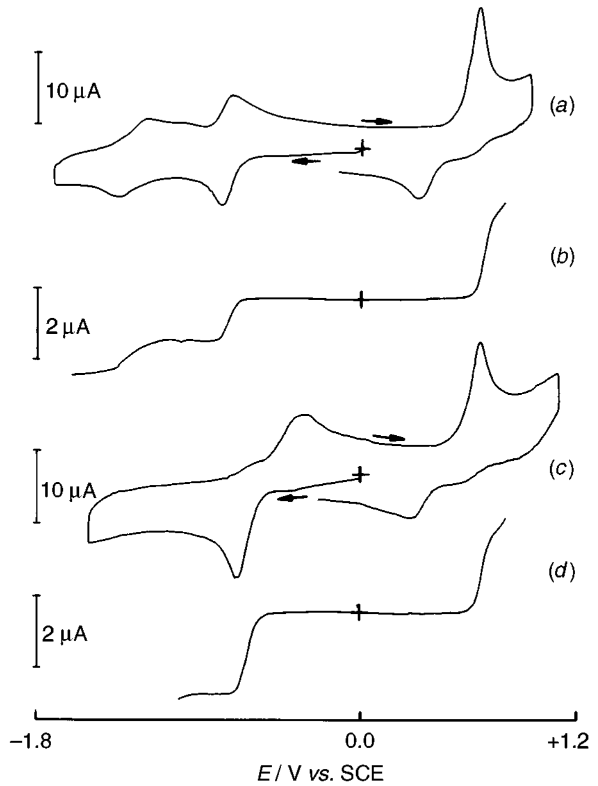

Fig. 2 Cyclic voltammograms obtained for reduction and oxidation of a solution of 0.5 mmol dm^{-3} indigo in DMSO (0.1 mol dm^{-3} NBu_4PF_6, $T = 20$ °C) in the absence (*a*,*b*) and in the presence (*c*,*d*) of 10 mmol dm^{-3} benzoic acid. Voltammograms (*a*) and (*c*) obtained using a 3 mm diameter glassy carbon disk electrode (scan rate 200 mV s^{-1}), and voltammograms (*b*) and (*d*) obtained using a 50 µm Pt microdisk electrode (scan rate 10 mV s^{-1}).

A brief study on the electrochemistry of indigo in pyridine solution has been reported previously.[8] For comparison purposes, results obtained from cyclic voltammetry and from microdisk voltammetry for the reduction and oxidation of a 1.1×10^{-4} mol dm^{-3} solution of indigo in pyridine are included in Table 1. Dimethyl sulfoxide (DMSO) was found to be a more suitable solvent and voltammograms at macro- and microelectrodes obtained in a 5×10^{-4} mol dm^{-3} solution of indigo in DMSO containing 0.1 mol dm^{-3} NBu_4PF_6 as the supporting electrolyte are shown in Fig. 2. The reduction of indigo at a 3 mm diameter glassy carbon electrode occurs in two well separated and chemically reversible steps. The first well defined reduction step with $E_{1/2}{}^{\text{red},1} = -0.73$ V *vs.* SCE (data summarized in Table 1) corresponds to a diffusion controlled process. Comparison with the redox chemistry of related indigo derivatives[17–20] allows this reduction to be assigned to the one electron process presented in Fig. 3(*a*). The second reduction process with $E_{1/2}{}^{\text{red},2} = -1.26$ V *vs.* SCE is more complicated (Fig. 2). However, this redox process is reversible in the chemical sense and is assigned to a second one-electron reduction of indigo. The assignment as a one electron process is confirmed by microelectrode voltammetry where two sigmoidal shaped reduction responses with approximately equal limiting currents

Table 1 Data[a] for the electrochemical reduction and oxidation of indigo dissolved in organic solvents

Concentration (solvent)/10^{-4} mol dm^{-3}	Electrode	$E_{1/2}^{\mathrm{red},1}$/V	(ΔE_p/ $E_{3/4}$-$E_{1/4}$)/ mV	$E_{1/2}^{\mathrm{red},2}$/V	(ΔE_p/ $E_{3/4}$-$E_{1/4}$)/ mV	$E_p^{\mathrm{ox,anod.}}$/V	$E_p^{\mathrm{ox,cath.}}$/V	$E_{1/2}^{\mathrm{ox}}$/V	$E_{3/4}$-$E_{1/4}$/ mV
	3 mm gc[b]	−0.78	60	−1.26	120	0.41	0.09		
1.1 (pyridine)	50 µm Pt[c]	−0.76 (0.6 nA)	56	−1.29 (0.5 nA)	90	—	—	0.69 (1.1 nA)	110
	3 mm gc[b]	−0.73	80	−1.17	240	0.70	0.08[d]		
2.4 (DMF)	50 µm Pt[c]	−0.72 (1.8 nA)	58	−1.26 (1.7 nA)	150	—	—	0.84 (3.0 nA)	65
	3 mm gc[b]	−0.73	70	−1.26	180	0.64	0.32		
5.0 (DMSO)	50 µm Pt[c]	−0.73 (1.2 nA)	38	−1.30 (0.9 nA)	110	—	—	0.69 (2.3 nA)	56

[a] Potentials reported in V *vs.* SCE (T = 22 °C). [b] 3 mm diameter glassy carbon electrode, scan rate 200 mV s^{-1}. Half wave potentials, $E_{1/2}$, calculated as the midpoint between E_p^{ox} and E_p^{red}. [c] 50 µm diameter Pt disk electrode, scan rate 10 mV s^{-1}; measured limiting current values are given in brackets. [d] Strongly dependent on the presence of traces of water.

Table 2 Data[a] for the electrochemical reduction and oxidation of indigo dissolved in organic solvent media containing 10 mmol dm^{-3} benzoic acid

Concentration (solvent)/10^{-4} mol dm^{-3}	Electrode	$E_p^{\mathrm{red,cath.}}$/V	$E_p^{\mathrm{red,anod.}}$/V	$E_{1/2}$/V	$E_{3/4}$-$E_{1/4}$/V	$E_p^{\mathrm{ox,cath.}}$/mV	$E_p^{\mathrm{ox,anod.}}$/V	$E_{1/2}^{\mathrm{ox}}$/V	$E_{3/4}$-$E_{1/4}$/ mV
2.4	3 mm gc[b]	−0.57	−0.35			0.45[d]	0.72		
(DMF)	50 µm Pt[c]	—	—	−0.64 (3.2 nA)	70	—	—	0.82 (3.0 nA)	68
5.0	3 mm gc[b]	−0.69	−0.32			0.27	0.67	—	
(DMSO)	50 µm Pt[c]	—	—	−0.63 (2.2 nA)	60	—	—	0.68 (2.2 nA)	57

[a] Potentials reported in V *vs.* SCE (T = 22 °C). [b] 3 mm diameter glassy carbon electrode, scan rate 200 mV s^{-1}. [c] 50 µm diameter Pt disk electrode, scan rate 10 mV s^{-1}; measured limiting current values are given in brackets. [d] Strongly dependent on the presence of traces of water.

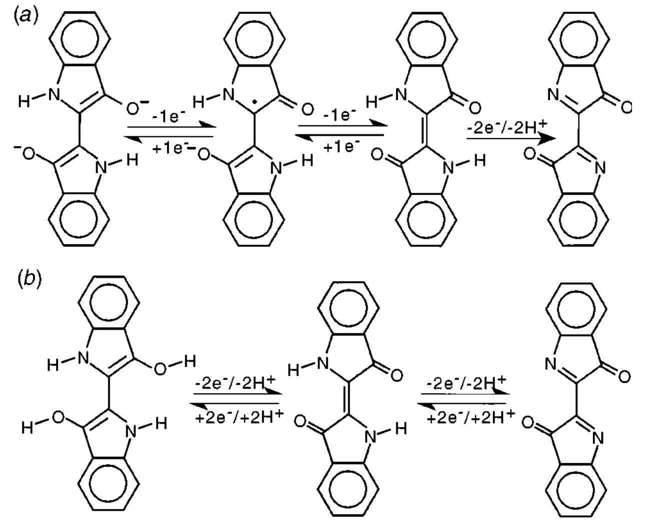

Fig. 3 Mechanistic scheme for the reduction and oxidation of indigo dissolved in organic solvents in the absence (*a*) and in the presence (*b*) of protons

corresponding to two one-electron reduction steps are detected [see Fig. 2(*b*)].

The irreversible oxidation of indigo dissolved in DMSO can be detected at E_p^{ox} = 0.64 V *vs.* SCE at a glassy carbon electrode. A product response is detected at 0.32 V *vs.* SCE on the reverse scan [Fig. 2(*a*)]. The limited current observed at a microelectrode is approximately twice the value observed for the reduction process (Fig. 2, Table 1) and therefore can be attributed to an overall two electron process. The mechanism for the oxidation process can be inferred from a study of the oxidation of indigo carmine,[17] a sulfonated derivative of indigo. In the absence of nucleophiles a two electron oxidation accompanied by the loss of two protons occurs [Fig. 3(*a*)] but in the presence of nucleophiles other complex follow-up reactions occur.

The presence of 10 mmol dm^{-3} benzoic acid in DMSO has a pronounced effect on the reduction processes. At macroelectrodes as well as at microelectrodes only one reduction response corresponding to a two electron process was observed [Fig. 2(*c*) and (*d*), Table 2]. This reduction occurs at a potential positive of that of the reduction in the absence of acid, $E_{1/2}^{\mathrm{red}}$ = −0.62 V *vs.* SCE, and both reduction and oxidation processes show very similar features in the presence of a proton source.

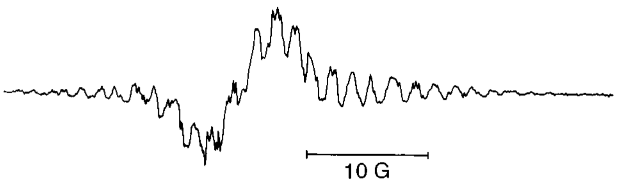

Fig. 4 EPR spectrum of the paramagnetic species generated electrochemically in a solution of 0.24 mmol dm^{-3} indigo in DMF (0.1 mol dm^{-3} NBu_4PF_6). A potential of E = −1.0 V *vs.* SCE was applied under no flow conditions.

The reduction of indigo in *N*,*N*-dimethylformamide (DMF) solution at a 3 mm diameter glassy carbon disk electrode also proceeds in two steps with $E_{1/2}^{\mathrm{red},1}$ = −0.73 V *vs.* SCE and $E_{1/2}^{\mathrm{red},2}$ = *ca.* −1.2 V *vs.* SCE (voltammetric data summarized in Table 1). Two reduction processes in DMF solution have also been reported for the reduction of thioindigo[18] ($E_{1/2}^{\mathrm{red},1}$ = −0.45 V *vs.* SCE, $E_{1/2}^{\mathrm{red},2}$ = −1.10 V *vs.* SCE) and of *N*,*N*′-diacetylindigo[19] ($E_{1/2}^{\mathrm{red},1}$ = −0.40 V *vs.* SCE, $E_{1/2}^{\mathrm{red},2}$ = −0.95 V *vs.* SCE). The rather negative potential for the first reduction process in the case of natural indigo reflects specific inter- and/or intra-molecular hydrogen bonding and aggregation.

Further proof for the presence of indigo aggregates rather than monomers comes from the detection of an electron paramagnetic resonance (EPR) signal in DMF solution for the electrochemically generated indigo radical anion (Fig. 4). The potential applied to generate the radical was held between the two reduction processes at E = −1.0 V *vs.* SCE. The spectrum is very complex and asymmetric, consistent with the presence of a range of species, rather than only a monomer.

The effect of 10 mmol dm^{-3} benzoic acid added into a solution of indigo in DMF is very similar to the effect described for the solution of indigo in DMSO. One reduction response corresponding to a two electron-two proton mechanism with E_p^{red} = −0.57 V *vs.* SCE was detected [Fig. 3(*b*)]. Essentially the same effect has been described for reduction of thioindigo[18] (E_p^{red} = −0.42 V *vs.* SCE) and for *N*,*N*′-diacetylindigo[19] (E_p^{red} = −0.48 V *vs.* SCE) in the presence of benzoic acid.

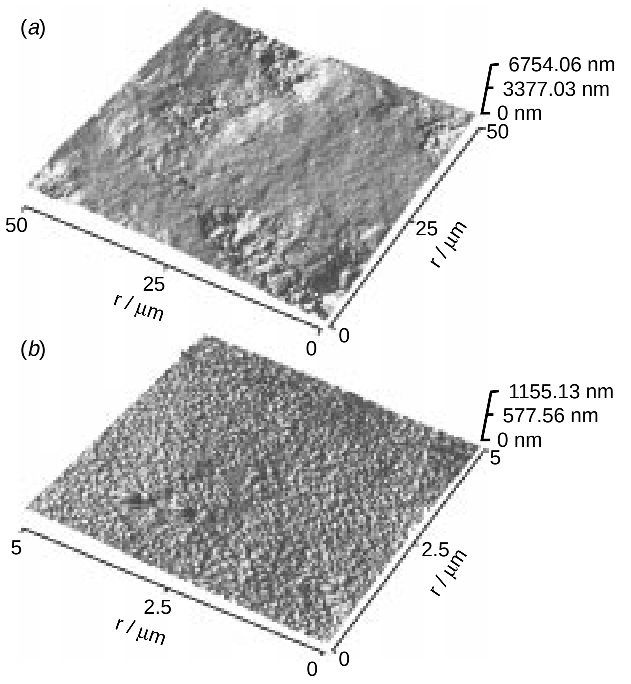

Fig. 5 AFM images of (*a*) a clean basal plane pyrolytic graphite electrode and (*b*) a basal plane pyrolytic graphite electrode with indigo mechanically attached to the surface. Note different scale between the two images.

Voltammetry of solid indigo

(a) Buffered aqueous environment. Commercially available indigo is a fine powder which readily adheres to a graphite surface to produce a shiny, dark blue surface. The AFM images of a basal plane pyrolytic graphite electrode with and without particles of indigo mechanically attached to the surface are shown in Fig. 5. On a flat part of the modified graphite surface, indigo particles of submicron dimensions can be detected in agreement with similar images obtained for decamethylferrocene by scanning electron microscopy.[22] Electrochemical reaction of the solid indigo will therefore occur at arrays of randomly spaced microscopically small particles.

The voltammetry of solid indigo mechanically attached to a basal plane pyrolytic graphite electrode and immersed in an aqueous solution in which indigo is insoluble is distinctively different from the solution behaviour reported above in DMSO. In Fig. 6 voltammetric responses for the reduction of indigo in aqueous Britton–Robinson buffer at various pH values are shown. On the first negative potential scan a large, symmetrically shaped and irreversible reduction response ($E_p^{red} = -1.0$ V *vs.* SCE at pH 5) is observed. On the reverse potential scan and in subsequent cycles two chemically reversible processes are detected ($E_{1/2} = -0.34$ V and at $E_{1/2} = 0.41$ V *vs.* SCE at pH 5). On repeated cycling the main and initial symmetrically shaped reduction response, labelled process 1, diminishes rapidly in height and disappears, whereas the chemically reversible responses, labelled process 2 and 3, remain. Although some aspects of these two processes are reminiscent of those found for solution phase diffusion controlled reactions, they also are similar to cases described recently[13] and are believed to be processes confined to the electrode surface (see later).

Data in Fig. 6 show that all three processes observed in the voltammetry of solid indigo are systematically affected by the pH of the aqueous solution environment. A plot of the peak potential, E_p^{red}, of process 1 and the half wave potentials, $E_{1/2}$, for processes 2 and 3 *vs.* the solution pH is shown in Fig. 7. The slope of the $E_{1/2}$ *vs.* pH plot for processes 2 and 3 is -60 ± 3 mV per pH unit. In contrast, the peak potential for process 1 undergoes a small pH dependent shift in the opposite, positive, direction with increasing pH.

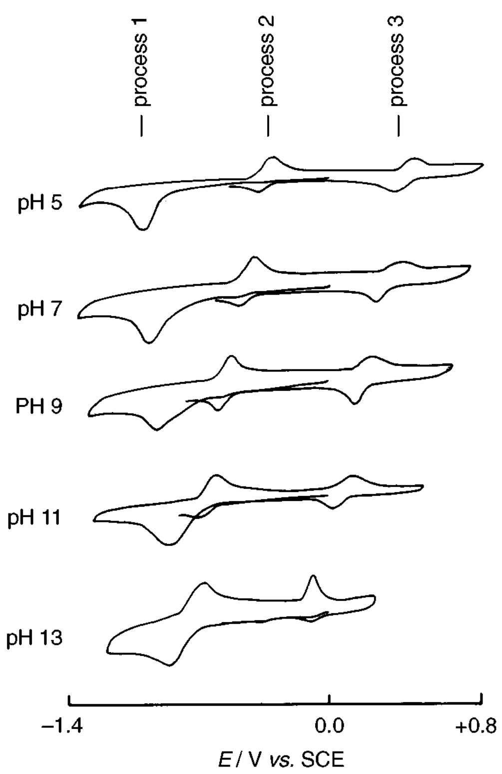

Fig. 6 Cyclic voltammograms obtained for microcrystalline indigo mechanically attached to a 4.9 mm diameter basal plane pyrolytic graphite electrode immersed in an aqueous solution of Britton–Robinson buffer at pH 5 to 11 and in 0.1 mol dm^{-3} NaOH at pH 13 (scan rate 100 mV s^{-1}, $T = 20$ °C)

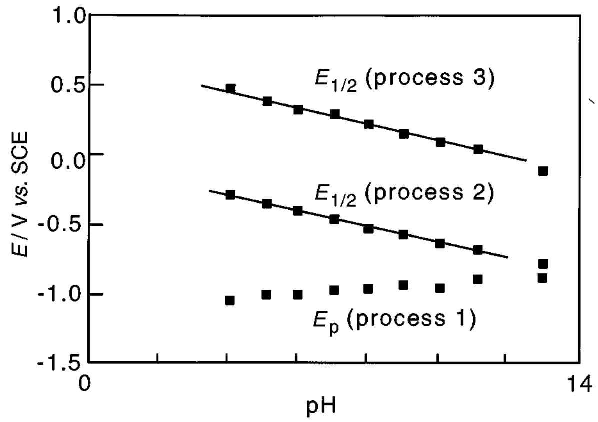

Fig. 7 Plot of $E_{1/2}$ (processes 2 and 3) and E_p (process 1) observed by cyclic voltammetry of microcrystalline indigo mechanically attached to a basal plane pyrolytic graphite electrode at various pH values (conditions as in Fig. 6)

Process 1 can be labelled as a 'break-in' reaction[23] with a voltammetric characteristic similar to that described recently for the reduction of solid heteropolymolybdate salts. At the reduction potential, the reduced form of the solid lattice 'opens' and electroinsertion of a cationic guest species occurs in order to achieve charge neutralization. Either Na^+ present in the buffer solution or protons together with water molecules are possible guest species when solid indigo is reduced. However, the relatively small dependence of the peak potential on pH suggests that Na^+ is the cationic species predominantly involved in the charge neutralization process, although rapid Na^+/H^+ ion exchange processes[24] may follow the electrochemical reaction step. A schematic representation of the processes that are postulated to occur in the presence of protons is given in Fig. 8. The very negative electrode potential ultimately leads to irreversible reduction of the surface of the microcrystalline solid when the lattice forces of the solid are

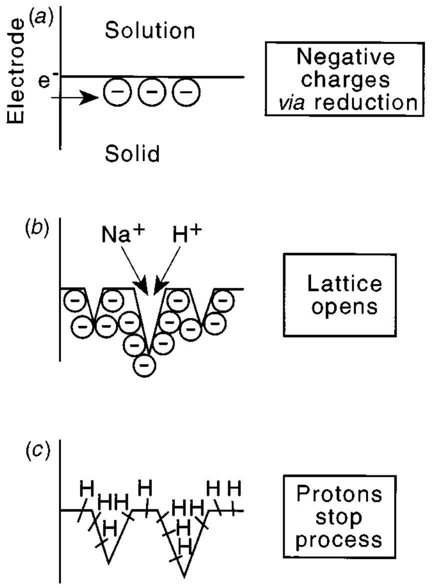

Fig. 8 Schematic representation of the redox processes at the three phase boundary electrode/solid/electrolyte solution

overcome. Insertion of cations and subsequent ion exchange equilibration achieves charge neutrality and yields the final product.

Processes 2 and 3, which became easily detectable after the first reduction of the solid occurred, are readily identified. The product from the solid state reduction process is leuco-indigo in its doubly protonated form. The reversibility of process 2 and the shift of the reversible potential with pH over most of the pH range studied allows the process to be described as the $2e^-$-$2H^+$ conversion between indigo and its leuco form [reaction (1)].

$$\text{Process 2: Indigo}_{\text{solid}} + 2e^- + 2H^+ \rightleftharpoons \text{leuco-Indigo}_{\text{solid}} \tag{1}$$

Analogously, over most of the pH range studied, process 3 may be identified as the reversible $2e^-$-$2H^+$ oxidation of indigo yielding dehydroindigo (structure shown in Fig. 3) [reaction (2)].

$$\text{Process 3: Indigo}_{\text{solid}} \rightleftharpoons \text{dehydro-Indigo}_{\text{solid}} + 2e^- + 2H^+ \tag{2}$$

A comparison with Fig. 3 shows that the processes 2 and 3 are essentially identical to the processes involved in the oxidation and reduction of indigo in solution in the presence of acid. In the DMSO solution phase the separation of the peak potentials for the oxidation and the reduction is 1.30 V whereas for the processes in aqueous environment the separation between the half wave potentials for oxidation and reduction are merely 0.74 V apart. What is remarkable is the high degree of reversibility for the solid state confined processes indicative for a minimum of structural change. A possible interpretation is that the highly polar aqueous environment allows the process to proceed reversibly without deaggregation. The type of structure of solid indigo[25] which is dominated by hydrogen bridges may also contribute to this effect.

The nature of process 1 is more difficult to identify. The peak potential for this reduction process shifts to more positive potential with *ca.* 19 ± 2 mV per pH unit increase. Therefore the presence of protons appears to inhibit the process. When Britton–Robinson buffer solution is prepared with ammonium cations replacing sodium only process 1 is strongly affected [Fig. 9(*a*)]. In the presence of NH_4^+ the process occurs at more positive potentials and gives a much broader response. These experimental findings strongly suggest the following formal description for process 1 [reaction (3)].

$$\text{Process 1: Indigo}_{\text{solid}} + e^- + \text{Cat}^+ \longrightarrow \text{Indigo}^-\text{Cat}^+_{\text{solid}} \tag{3}$$

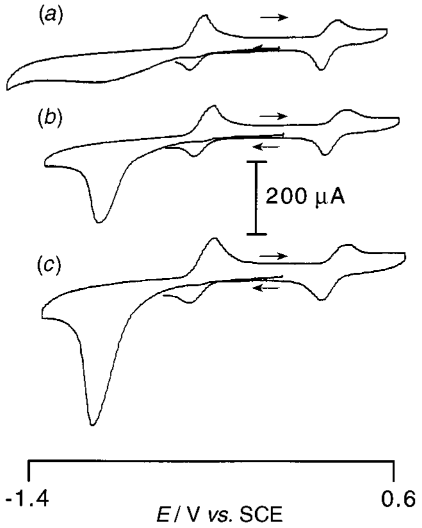

Fig. 9 Cyclic voltammograms (scan rate 200 mV s^{-1}, $T = 20\,°C$) obtained for indigo mechanically attached to a 4.9 mm diameter basal plane pyrolytic graphite electrode placed in aqueous Britton–Robinson buffer at pH = 7. (*a*) Buffer solution containing only NH_4^+ as cation. (*b*) Buffer solution containing Na^+ as cation. (*c*) Conditions as in (*a*) but electrode is rotated at 600 rpm.

The concentration of cations, Cat^+, such as Na^+ directly at the surface of the solid, is affected by the proton concentration and therefore protons will shift the response to more negative potentials. A very similar effect in the solid state voltammetry of salts of heteropolymolybdate anions has been described recently.[23] The broad voltammetric wave observed for NH_4^+ cation insertion is consistent with its acidic and therefore self-inhibiting character (see later). A further important feature of process 1 is the detection (process 2, Fig. 6) of leuco-indigo as a product so that disproportionation and protonation must be associated with this reaction.

Important additional information about the redox processes involved in the electrochemical conversion of solids mechanically attached to graphite electrodes can be obtained from rotating disk voltammetry. For solution processes a characteristic change in shape of the diffusion controlled voltammogram from a peak shaped (static electrode) to a sigmoidal shaped (rotating electrode) wave occurs. A fully solid confined process, however, will be independent of the convective flow induced by rotation of the electrode. Many other situations with only partial control by the rate of transport in solution or with accompanying dissolution reactions are possible and can be studied. Indigo mechanically attached to a basal plane pyrolytic graphite electrode surface and immersed in aqueous buffer solutions (pH 5 to 11) shows well defined voltammetric responses essentially identical in shape to the voltammograms obtained under no-flow conditions [Fig. 9(*b*) and (*c*)]. Therefore, under these conditions a fully solid-confined redox reaction can be proposed.

The voltammograms obtained at pH 13 or higher (Fig. 6) are more complex than indicated by reaction (1) (process 2) and (3) (process 1). At high pH values processes 1 (Na^+ dependent) and 2 (H^+ dependent) merge to give one chemically reversible response. In Fig. 10 it can be seen that this response decays slowly upon continuous cycling the potential. A more pronounced decay of the current response can be observed when the oxidation process is included in the cycle [Fig. 10(*b*)]. However, an important change occurs upon rotating the basal plane pyrolytic graphite electrode with indigo mechanically attached. In Fig. 10(*c*) it can be seen that the reduction becomes almost irreversible — a strong indication for a dissolution process which is coupled to the reduction and which allows material to escape from the electrode into the solution phase. Judged by the presence of a small peak on the reverse scan the dissolution

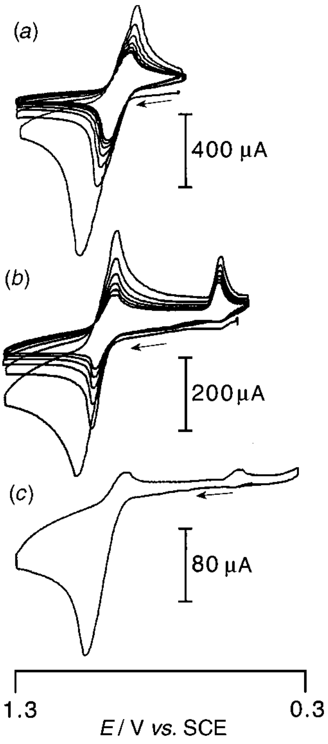

Fig. 10 Cyclic voltammograms obtained for indigo mechanically attached to a 4.9 mm diameter basal plane pyrolytic graphite electrode placed in aqueous 0.1 mol dm^{-3} NaOH. (*a*) Scan rate 200 mV s^{-1}; (*b*) scan rate 100 mV s^{-1}; (*c*) scan rate 50 mV s^{-1}, electrode rotated at 600 rpm.

process is slow and does not proceed to completion within the relevant experimental timescale which is determined by the scan rate. In a study of the reaction of solid indigo with a chemical reducing agent it was noted that at room temperature the formation of an intermediate reduction product occurred with a subsequent dissolution.[8] The electrochemical reduction is consistent with this suggestion.

The fact that processes 1 and 2 merge and dissolution of indigo begins to be detectable at pH values between 12 and 13 suggests a significant change in the reaction pathway. From the data at low pH, reduction of indigo directly to the protonated form of leuco-indigo occurs [process 2, reaction (1)] similar to the case of dissolved indigo in organic solvents in the presence of acid. On the other hand, at very high pH the mono-anionic and the di-anionic forms of reduced indigo may be expected to become stable. Approximate pK_a values for leuco-indigo in aqueous environments obtained by extrapolation of data obtained for various sulfonated forms of indigo led Etters[26] to propose that the hypothetical acid–base equilibrium constants for indigo monomers are pK_{a1} = 8 and pK_{a2} = 12.7. These values suggest that a change in mechanism should occur already at pH 8. But the observed change in mechanism of the reduction of indigo occurs between pH 12 and 13 and involves a transition from a 2e$^-$-2H$^+$ process most likely to a 1e$^-$ process. No transition from a 2e$^-$-2H$^+$ to a 2e$^-$-1H$^+$ process was detected voltammetrically for the solid. The reason for this is unknown, although it may be speculated that the pK_a of indigo in an associated state should be significantly different to the pK_a of a single molecule in solution.[27] From the experimental data described in this study it can be deduced that p$K_{a1,solid}$ > 12.

(b) Non-buffered aqueous environment. With regard to the well defined pH dependent voltammetric characteristics of solid indigo a surprising result can be observed in non-buffered aqueous environments. In Fig. 11(*a*), a cyclic voltammogram obtained for the reduction of solid indigo mechanically attached to a basal plane pyrolytic graphite electrode and immersed in aqueous 0.1 mol dm^{-3} NaCl (pH 6.3) is shown.

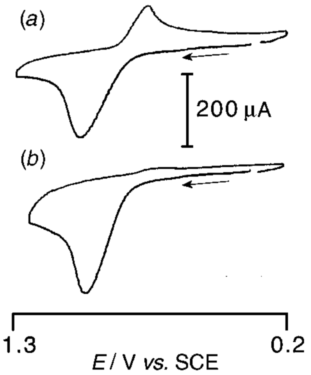

Fig. 11 Cyclic voltammograms obtained for indigo mechanically attached to a 4.9 mm diameter basal plane pyrolytic graphite electrode placed in aqueous 0.1 mol dm^{-3} NaCl solution (*a*) static and (*b*) rotating the electrode at 600 rpm (scan rate 100 mV s^{-1}).

The voltammetric response is significantly different from that obtained in buffered media at pH values around 6.3. The 'break-in' response now commences at a much less negative potential and the features of the oxidation process have changed. Significant changes in homogeneous chemical reaction steps accompanying electron transfer steps resulting from the presence of buffer in the solution phase are well known.[28] For pH sensitive heterogeneous processes even larger effects can be anticipated since protons have to diffuse from the bulk solution to the solid/liquid interface. In the case of indigo, a process involving proton consumption upon reduction is proposed to occur so that a pH gradient develops. Thus, at the solid/solution (electrolyte) interface the solution can temporarily become very alkaline. The detected voltammogram indeed has features very similar to the one obtained at pH = 13 in aqueous 0.1 mol dm^{-3} NaOH (Fig. 6). Furthermore, the rotating disk voltammogram obtained for the reduction of solid indigo mechanically attached to a basal plane pyrolytic graphite electrode and immersed in 0.1 mol dm^{-3} NaCl [Fig. 1(*b*)] gives clear evidence for the dissolution process with a significant loss of reversibility of the process. Thus indigo is transferred into the solution phase in an environment in which the neutral as well as the reduced forms are completely insoluble! A blue colour developed at the same time at the Teflon shroud holding the electrode at the level of the solution surface. A further important feature in the solid state voltammetry of indigo is the effect of the electrolyte concentration, which for the case of the electro-insertion of the electrolyte cation into the solid reduced material commonly causes a well defined 60 mV per decade concentration (activity) shift in the reduction potential.[29] For the case of the reduction of indigo mechanically attached to a basal plane pyrolytic graphite electrode this shift does not occur and the 'onset-potential' for the reduction wave always remains at −0.65 V *vs.* SCE.

Furthermore, in the presence of aqueous electrolyte solutions other than NaCl such as 0.1 mol dm^{-3} LiCl, 0.1 mol dm^{-3} $CaCl_2$, or 0.1 mol dm^{-3} NEt_4Cl the reduction processes are not greatly affected and show the same features. This low dependence on electrolyte concentration and identity is in marked contrast to results obtained in other voltammetric studies of microcrystalline forms of solid metal complexes,[30] TCNQ[14] and decamethylferrocene,[22] and suggests that only a very weak interaction of the electroinserted cationic species occur with the reduced indigo. These voltammetric characteristics are consistent with those expected for a dissolution process. It is important to note that the observed effect is a dynamic one associated with a considerable pH gradient. In a buffered environment or under equilibrium conditions the cation dependent process 1 will occur (see above).

The dissolution (or, more accurately, solubilization) of indigo mechanically attached to graphite electrodes at nearly neutral

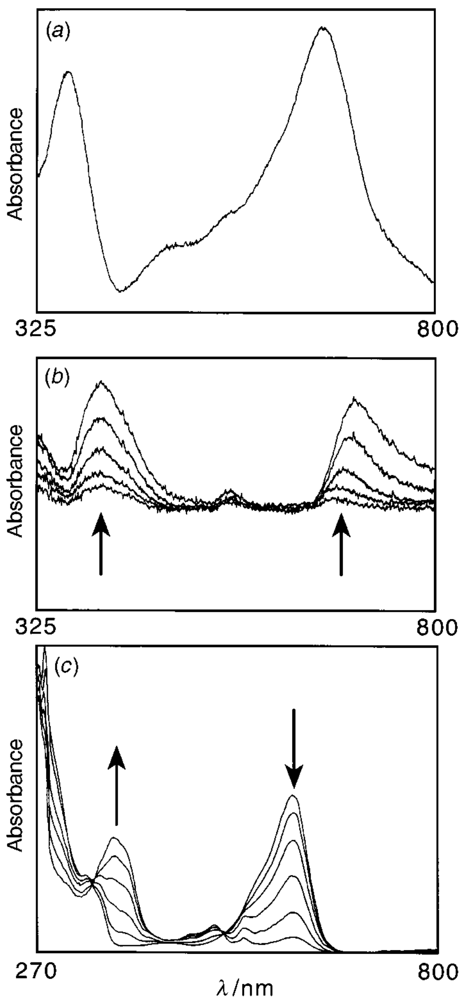

Fig. 12 (*a*) UV–VIS absorption spectrum of indigo mechanically attached to an ITO electrode and immersed in aqueous 1.28 mol dm^{-3} NaCl electrolyte solution. (*b*) Changes in the UV–VIS absorption of indigo on ITO when a potential of −1.0 V *vs.* SCE is applied (curves correspond to 5 s, 30 s, 2 min, 10 min and 30 min electrolysis). (*c*) *In situ* UV–VIS spectroelectrochemical monitoring of the reduction of 2.4×10^{-4} mol dm^{-3} indigo in DMF (0.1 mol dm^{-3} NBu_4PF_6, 10 mmol dm^{-3} benzoic acid) (applied potential −1.0 V *vs.* SCE).

pH in aqueous 0.1 mol dm^{-3} NaCl solution is a remarkable process with many unknown features such as the reaction stoichiometry and the identity of the products of the reduction process. Therefore a spectroelectrochemical method has been employed in order to obtain more information. Spectroelectrochemical monitoring of the dissolution reaction is possible at transparent indium tin oxide (ITO) electrodes using the cell shown in Fig. 1(*b*) when placed inside a UV–VIS spectrometer. The thin layer of solid sample is located in the beam path and changes in absorbance induced by a redox reaction may be monitored.

The voltammetric response of indigo mechanically attached to an ITO electrode and placed in unbuffered aqueous 1.28 mol dm^{-3} NaCl electrolyte solution was found to be very similar to the response observed for the reduction of indigo mechanically attached to a graphite electrode. A well defined process exhibiting a reduction response with $E_p^{red} = -0.85$ V *vs.* SCE and a corresponding oxidation with $E_p^{ox} = -0.64$ V *vs.* SCE on the reverse scan is observed at a scan rate of 100 mV s^{-1}. Since the blue colour associated with the indigo being attached to the transparent electrode remains after voltammetric reduction, it may be concluded that only a fraction of the electroactive material present, probably the smallest sized particles in direct contact with the electrode material and electrolyte solution undergo reduction.

In Fig. 12(*a*), a UV–VIS spectrum obtained for indigo mechanically attached to an ITO electrode is shown. Two absorption maxima at 360 nm and 666 nm are detected in agreement with literature reports.[31] This spectrum obtained before electrochemical reduction was used as the background and only the background corrected absorbance was measured during the course of the electrochemical experiment. On reducing solid indigo mechanically attached to an ITO electrode and immersed in 1.28 mol dm^{-3} NaCl electrolyte solution (potential stepped to −1.0 V *vs.* SCE) three new features are detected [Fig. 12(*b*)]. An increase in absorbances is detected mainly at 410 nm and at 700 nm and a small change in absorbance occurs at 550 nm.

In situ monitoring of the change in UV–VIS spectra of indigo dissolved in DMF in the presence of 10 mmol dm^{-3} benzoic acid upon reduction can be achieved when electrolysis of indigo dissolved in DMF is undertaken at a gold microgrid electrode in the optically transparent cell shown in Fig. 1(*a*). Fig. 12(*c*) includes the UV–VIS spectrum of 2.4×10^{-4} mol dm^{-3} indigo in DMF (0.1 mol dm^{-3} NBu_4PF_6). The most prominent absorption maxima are observed at wavelengths of 611 nm and 288 nm (partially obscured by absorption due to benzoic acid). The reduction *via* a $2e^-$-$2H^+$ process can be seen to proceed cleanly with two well defined isosbestic points and generation of a prominent product absorption band having a wavelength of 375 nm [Fig. 12(*c*)]. The spectra observed after reduction in the presence of a proton source are in close agreement with those described for other derivatives of indigo.[19]

Comparison of the UV–VIS spectra obtained in DMF solution [Fig. 12(*c*)] with those observed for the reduction of the solid in aqueous 1.28 mol dm^{-3} NaCl suggest that a simple conversion with one observed product does not occur. Rather, the absorption band observed for the solid in an aqueous environment at 410 nm is likely to correspond to the band at 375 nm observed in DMF solution for leuco-indigo. The absorption band observed for the reduction of the solid at 700 nm has characteristics very similar to the absorption of indigo itself. Therefore it is proposed that both indigo and leuco-indigo are the products of the reduction process. An overall one electron redox process with a follow-up disproportionation reaction step may be formulated as follows [reactions (4) and (5)].

$$\text{Indigo}_{\text{solid}} + e^- + \text{Na}^+ \rightleftharpoons \text{Indigo}^-\text{Na}^+{}_{\text{solid}} \qquad (4)$$

$$2\,\text{Indigo}^-\text{Na}^+{}_{\text{solid}} + H_2O \longrightarrow \text{leuco-Indigo} + \text{Indigo} + 2\,\text{NaOH} \qquad (5)$$

The small absorbance band detected at 550 nm in the solid state spectroelectrochemical experiment [Fig. 12(*b*)] is possibly associated with the presence of the intermediate Indigo^--$\text{Na}^+{}_{\text{solid}}$ but at present it is not possible to confirm this mechanism.

Conclusions

It has been shown that both the solution voltammetry and the solid state voltammetry of indigo are associated with complex kinetic phenomena coupled to the electron transfer at the electrode surface. In solution indigo is aggregated and reduction as well as oxidation are coupled to deaggregation processes. Voltammetry for the solid mechanically attached to graphite electrodes and immersed in aqueous media allows ‘surface type’ processes associated with proton uptake and expulsion to be observed. These processes (processes 2 and 3) are closely related to the corresponding responses observed for indigo dissolved in an organic solvent in the presence of protons. The uptake of cations into the microcrystalline solid was proposed for the process 1 in buffered aqueous media and the reduction process in non-buffered media. The latter ‘bulk-type’ process has been shown to be associated with the reductive dissolution of indigo.

The study of redox processes at solid/liquid interfaces of non-conducting materials such as indigo offers important new insights into the processes involved in a wide range of important surface chemistry. Solid state voltammetry of small quantities of samples mechanically attached to suitable electrode surfaces is an important tool valuable especially when coupled to analytical methods such as IR, EPR or UV–VIS spectroscopy.

Acknowledgements

We thank the EC for financial support (contract no. CHRX CT94 0475) under the Human Capital and Mobility Scheme, the EPSRC and Zeneca for a CASE studentship for E. H. and the Royal Society for awarding a University Research fellowship to F. M.

References

1 A. W. Adamson, *Physical Chemistry of Surfaces*, 5th edn., Wiley, New York, 1990.

2 R. J. D. Miller, G. L. McLendon, A. J. Nozik, W. Schmickler and F. Willig, *Surface Electron Transfer Processes*, VCH, Weinheim, 1995.

3 See, for example, J. O'M. Bockris and S. U. M. Khan, *Surface Electrochemistry*, Plenum Press, New York, 1993.

4 J. V. Macpherson and P. R. Unwin, *Prog. React. Kin.*, 1995, **20**, 185.

5 R. H. Peters, in *Textile Chemistry*, vol. 3, The Physical Chemistry of Dyeing, Elsevier, Amsterdam, 1975.

6 (*a*) F. R. Latham, in *Cellulosics Dyeing*, ed. J. Shore, Soc. of Dyers & Colorists, 1995; (*b*) U. Baumgarte, *Textilvered.*, 1969, **4**, 821.

7 (*a*) T. Bechtold, E. Burtscher, D. Gmeiner and O. Bobleter, *J. Electroanal. Chem.*, 1991, **306**, 169; (*b*) T. Bechtold, E. Burtscher, A. Amann and O. Bobleter, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1068.

8 T. Vickerstaff, *The Physical Chemistry of Dyeing*, Oliver and Boyd, Edinburgh, 1954 and references cited therein.

9 K. Y. Tam, R. G. Compton, J. H. Atherton, C. M. Brennan and R. Docherty, *J. Am. Chem. Soc.*, 1996, **118**, 4419 and references cited therein.

10 F. Scholz and B. Lange, *Chem. Soc. Rev.*, 1994, 341.

11 A. M. Bond and F. Scholz, *Langmuir*, 1991, **7**, 3197.

12 F. Scholz and B. Lange, *Trends Anal. Chem.*, 1992, **11**, 359.

13 A. M. Bond, R. Colton, F. Daniels, D. R. Fernando, F. Marken, Y. Nagaosa, R. F. M. Van Steveninck and J. N. Walter, *J. Am. Chem. Soc.*, 1993, **115**, 9556.

14 A. M. Bond, S. Fletcher, F. Marken, S. J. Shaw and P. G. Symons, *Faraday Trans.*, 1996, **92**, 3925.

15 R. G. Compton and A. M. Waller, in *Spectroelectrochemistry Theory and Practice*, ed. R. J. Gale, Plenum Press, New York, 1988, p. 349f.

16 M. B. G. Pilkington, B. A. Coles and R. G. Compton, *Anal. Chem.*, 1989, **61**, 1787.

17 G. Beggiato, G. Casalbore-Miceli, A. Geri and D. Pietropaolo, *Ann. Chim.*, 1993, **83**, 355.

18 (*a*) L. R. Yeh and A. J. Bard, *J. Electroanal. Chem.*, 1976, **70**, 157; (*b*) L. R. Yeh and A. J. Bard, *J. Electroanal. Chem.*, 1977, **81**, 319; (*c*) L. R. Yeh and A. J. Bard, *J. Electroanal. Chem.*, 1977, **81**, 333.

19 K. S. Schanze, L. Y. C. Lee, C. Gianotti and D. G. Whitten, *J. Am. Chem. Soc.*, 1986, **108**, 2646.

20 M. Shucheng, N. Jianmin, M. Hua and C. Lu, *Anal. Lett.*, 1992, **25**, 899.

21 J. Fabian and H. Hartman, *Light Absorption of Organic Colorants*, Springer Verlag, Berlin, 1980, ch. 10.

22 A. M. Bond and F. Marken, *J. Electroanal. Chem.*, 1994, **372**, 125.

23 A. M. Bond, J. B. Cooper, F. Marken and D. M. Way, *J. Electroanal. Chem.*, 1995, **396**, 407.

24 J. S. Shaw, F. Marken and A. M. Bond, *J. Electroanal. Chem.*, 1996, **404**, 227.

25 (*a*) E. A. Gribova, G. S. Zhdanov and G. A. Gol'der, *Sov. Phys. Cryst.*, 1956, **1**, 39; (*b*) P. Süsse, M. Steins and V. Kupcik, *Z. Kristall.*, 1988, **184**, 269; (*c*) P. Süsse and A. Wolf, *Naturwissenschaften*, 1980, **67**, 453.

26 J. N. Etters, *J. Soc. Dyers Colour.*, 1993, **109**, 251.

27 W. Stumm, *Chemistry of the Solid-Water Interface*, Wiley, New York, 1992.

28 See, for example, J. Heyrovsky and J. Kuta, *Principles of Polarography*, Academic Press, New York, 1966.

29 J. S. Shaw, F. Marken and A. M. Bond, *Electroanalysis*, 1996, **8**, 732.

30 A. M. Bond, R. Colton, F. Marken and J. N. Walter, *Organometallics*, 1994, **13**, 5122.

31 See, for example, (*a*) J. Weinstein and G. M. Wyman, *J. Am. Chem. Soc.*, 1956, **78**, 2387; (*b*) F. Gordon and P. Gregory, *Organic Chemistry and Colour*, Springer Verlag, Berlin, 1985, p. 208f.

Paper 7/01003F
Received 11*th February* 1997
Accepted 23*rd May* 1997