

Electrochemical and sonoelectrochemical monitoring of indigo reduction by glucose

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Abstract

The reduction of indigo (dispersed in water) to leuco-indigo (dissolved in water) is an important industrial process and investigated here for the case of glucose as an environmentally benign reducing agent. In order to quantitatively follow the formation of leuco-indigo two approaches based on (i) rotating disk voltammetry and (ii) sonovoltammetry are developed. Leuco-indigo, once formed in alkaline solution, is readily monitored at a glassy carbon electrode in the mass transport limit employing hydrodynamic voltammetry. The presence of power ultrasound further improves the leuco-indigo determination due to additional agitation and homogenization effects.

While inactive at room temperature, glucose readily reduces indigo in alkaline media at 65 °C. In the presence of excess glucose, a surface dissolution kinetics limited process is proposed following the rate law $dn_{\text{leuco-indigo}}/dt = k \times c_{\text{OH}^-} \times S_{\text{indigo}}$ where $n_{\text{leuco-indigo}}$ is the amount of leuco-indigo formed, $k = 4.1 \times 10^{-9} \text{ m s}^{-1}$ (at 65 °C, assuming spherical particles of 1 μm diameter) is the heterogeneous dissolution rate constant, c_{OH^-} is the concentration of hydroxide, and S_{indigo} is the reactive surface area. The activation energy for this process in aqueous 0.2 M NaOH is $E_A = 64 \text{ kJ mol}^{-1}$ consistent with a considerable temperature effects. The redox mediator 1,8-dihydroxyanthraquinone is shown to significantly enhance the reaction rate by catalysing the electron transfer between glucose and solid indigo particles.

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1. Introduction

Indigo is one of the oldest known dyes. The current consumption of the dye is enormous due to the popularity of blue jeans, which are dyed with indigo. The consumption of indigo and other vat dyes reaches about 33 million kg annually [1]. Before indigo can be used in dyeing processes, it needs to be reduced to its water soluble leuco form. The reduced form

has a high affinity for cellulose fibres, it is absorbed into the fibres, and when oxidized back to its blue form it stays within the fibre [2]. Industrially reduction is performed with sodium dithionite, which creates a problem due to environmentally harmful waste, because of the formation of products such as sulphites, sulphates and sulphur [3]. Alternatives for the commercial indigo dyeing process to replace dithionite are therefore desirable.

An approach to minimise waste is to employ direct [4,5] or indirect [6,7] electrochemical reduction with different redox mediators. The indirect electrochemical reduction uses mediators such as redox active iron complexes and anthraquinones to transfer electrons between electrode and dye molecule [8,9]. However, there are inherent limitations to

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the electrochemical approach. Thus, organic reducing agents have also been investigated as possible alternatives to sodium dithionite [10].

In this study the reduction of indigo with D-(+)-glucose is investigated quantitatively. Glucose and other reducing sugars have recently been suggested as possible “green” reducing agents for vat dyes but no mechanistic detail is known [11]. Glucose undergoes a complex degradation sequence in alkaline solutions and the reducing effect of glucose is known to be linked to a degradation intermediate rather than to glucose itself [12]. In alkaline media a complex sequence of degradation steps occurs [13–15] with dehydrated intermediates with extended π -systems being the most likely redox active reducing agents.

The colorimetric monitoring of solid indigo dye presents technical problems [16], and a voltammetric monitoring of the solution concentration of leuco-indigo would be much more accurate and easier to perform. Initially, in this study, a new methodology is developed to monitor the formation of leuco-indigo in aqueous alkaline solution by rotating disc voltammetry. Hydrodynamic methods such as sonovoltammetry and rotating disk voltammetry are compared. Next, the parameters affecting the glucose-based process are determined and a kinetic rate law is proposed based on a model of reductive dissolution of spherical indigo particles (Fig. 1). Anthraquinones have been recognized to stimulate indigo reduction by pure cultures of bacteria [17,18], and anthraquinone-rich madder powder was an invariable ingredient in the medieval indigo dye vat [19]. Here, we show a strong catalytic effect for the 1,8-dihydroxyanthraquinone redox mediator and that the presence of the redox mediator allows the indigo reduction process to be conducted with a lower alkali concentration.

2. Experimental

2.1. Reagents

Chemical reagents such as indigo (Fluka), NaOH (Aldrich), D-(+)-glucose (Sigma), and 1,8-dihydroxyanthraquinone (Sigma) were obtained commercially and used without further purification. Demineralised water was taken from an Elga purification system with at least 18 M Ω cm resistivity. Argon (BOC) gas was employed for de-aeration.

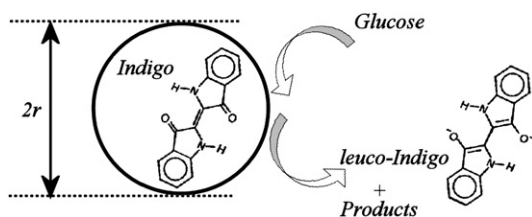


Fig. 1. Schematic representation of the reductive dissolution of indigo particles in the presence of glucose.

2.2. Instrumentation

For voltammetric studies a micro-Autolab II potentiostat system (EcoChemie, Netherlands) was employed with a Pt mesh counter electrode and a saturated Calomel (SCE) reference electrode (Radiometer, Copenhagen). A 3-mm diameter glassy carbon disk electrode (BAS, USA) was used as the working electrode in rotating disk and sonovoltammetric experiments. Experiments were conducted in a thermostated electrochemical cell (with a Haake B3 circulator) equipped with a rotating disk accessory. Sonovoltammetric experiments were conducted in an inverted voltammetric cell [20] and employing a Hielscher UP200s 24 kHz ultrasonic glass probe system. Experiments were conducted under constant de-aeration with high purity argon and at constant temperature of 65 ± 2 °C (338 ± 2 K) unless stated otherwise. Scanning electron microscopy (SEM) images were obtained with a JEOL JSM6310 system.

2.3. Procedure for the rotating disc voltammetric determination of leuco-indigo

A 0.2 M NaOH solution was thermostatted to 65 °C and indigo added after dispersion in a small volume of solution by treatment with 24 kHz ultrasound. Glucose was added under an atmosphere of argon and voltammograms were recorded as a function of time. The rotation speed in all experiments was 5.0 Hz and the mass transport controlled limiting current (which is directly proportional to concentration) [21] was measured for the leuco-indigo oxidation process (see text).

2.4. Procedure for sonovoltammetric determination of leuco-indigo

Power ultrasound can be employed as a hydrodynamic tool to increase the signal-to-background ratio for diffusion controlled redox systems and to remove effects of electrode surface fouling [22]. A 24 kHz ultrasound emitted from a glass horn probe is employed here as an alternative methodology to rotating disk voltammetry. An inverted cell [23] with the working electrode pointing up towards an ultrasonic horn probe is employed to measure mass transport limited currents for the leuco-indigo oxidation. Otherwise, the procedure is consistent with that used for rotating disk voltammetry monitoring of the leuco-indigo concentration (see text).

3. Theory

The dissolution of indigo in aqueous media is a heterogeneous process which is likely to involve a surface confined reaction step. The surface area of the particulate and highly water insoluble indigo is therefore controlling the rate of dissolution. Dissolution reactions have been treated in the literature for example for spherical [24] or for cylindrical particles [25]. Here, indigo particles are assumed to be spherical and uniformly sized (for simplicity) and the rate law for the

reductive dissolution of indigo to leuco-indigo in the presence of excess glucose is given by Eq. (1).

$$\frac{dn_{\text{leuco-indigo}}}{dt} = k' \times S_{\text{indigo}} \quad (1)$$

In this equation $n_{\text{leuco-indigo}}$ is the molar amount of leuco-indigo produced, k' is a chemical dissolution rate constant (in $\text{mol s}^{-1} \text{m}^{-2}$) and the surface area $S_{\text{indigo}} = 4\pi r^2$ (with r the approximate radius of the indigo particles). If a spherical indigo particle is assumed, the amount of indigo, n_{indigo} , in the suspension is determined by the radius r , the density ρ , and the molar mass M (Eq. (2)).

$$n_{\text{indigo}} = \frac{\rho}{M} \frac{4}{3} \pi r^3 \quad (2)$$

The rate of reductive indigo dissolution is then equivalent to the rate of leuco-indigo formation and given by the change in particle radius (Eq. (3)).

$$\frac{dn_{\text{leuco-indigo}}}{dt} = -\frac{\rho}{M} 4\pi r^2 \frac{dr}{dt} \quad (3)$$

Comparison of Eqs. (1) and (3) suggests an expression for the change in particle radius with time (Eqs. (4)–(6)).

$$k' \times S_{\text{indigo}} = -\frac{\rho}{M} 4\pi r^2 \frac{dr}{dt} \quad (4)$$

$$\frac{dr}{dt} = -k' \times \frac{M}{\rho} \quad (5)$$

$$r(t) = r_0 - k' \times \frac{M}{\rho} \times t \quad (6)$$

The concentration of leuco-indigo as a function of time is then obtained by combining Eqs. (2) and (6) (Eq. (7)).

$$\begin{aligned} n_{\text{leuco-indigo}}(r_0, t) &= n_{\text{indigo}}(r_0, 0) - n_{\text{indigo}}(r_0, t) \\ &= n_{\text{indigo}}(r_0, 0) - \frac{\rho}{M} \frac{4}{3} \pi \left(r_0 - k' \times \frac{M}{\rho} \times t \right)^3 \end{aligned} \quad (7)$$

The initial rate of leuco-indigo formation can be obtained by derivation (Eq. (8)).

$$\left(\frac{dn_{\text{leuco-indigo}}}{dt} \right)_{t=0} = k' \times 4\pi r_0^2 \quad (8)$$

Eq. (7) allows the change in leuco-indigo concentration with time to be plotted. Fig. 2 shows plots of the concentration of leuco-indigo generated for an amount of indigo particles equivalent to a 1.3 mM concentration with an assumed radius of $r_0 = 0.5 \mu\text{m}$. The molar mass $M = 0.262 \text{ kg mol}^{-1}$, and the density $\rho = 1451 \text{ kg m}^{-3}$ [26,27] were used. The rate constants employed were $k' = k \times c_{\text{OH}^-}$ which is equal to (i) $7.7 \times 10^{-9} \text{ m s}^{-1} \times 200 \text{ mol m}^{-3}$, (ii) $4.1 \times 10^{-9} \text{ m s}^{-1} \times 200 \text{ mol m}^{-3}$, and (iii) $2.0 \times 10^{-9} \text{ m s}^{-1} \times 200 \text{ mol m}^{-3}$. The predicted time dependence is consistent with the experimentally

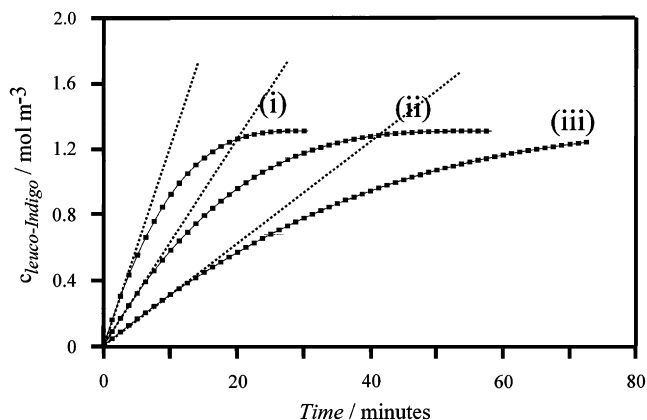


Fig. 2. Predicted plots of the concentration of leuco-indigo formed during reductive dissolution of indigo. Parameters are $r_0 = 0.5 \mu\text{m}$, $M = 0.262 \text{ kg mol}^{-1}$, $\rho = 1451 \text{ kg m}^{-3}$, and a rate constant of (i) $k' = 7.7 \times 10^{-6} \text{ m s}^{-1} \times 200 \text{ mol m}^{-3}$, (ii) $k' = 4.1 \times 10^{-6} \text{ m s}^{-1} \times 200 \text{ mol m}^{-3}$, (iii) $k' = 2.0 \times 10^{-6} \text{ m s}^{-1} \times 200 \text{ mol m}^{-3}$. The dashed line indicates the initial rate.

observed curves (compare with experimental data, vide infra) and both the initial rate and the end point plateau data are readily obtained. The initial rate (see dashed line) is the most convenient way of extracting the rate constant for indigo dissolution. The more linear shape in experimental data plots is caused by the effect of the non-spherical particle shape.

Fig. 3 shows the SEM image of typical indigo particles. These particles crystallise in small platelets. The rapidly growing edges of the platelets (during crystallisation) are likely to be more reactive also during reductive dissolution and

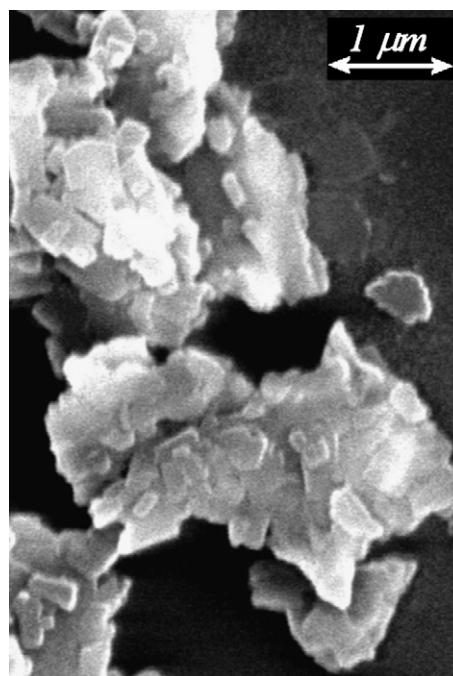


Fig. 3. Scanning electron micrograph for indigo crystals with typically 0.1–1 μm diameter employed in this study. The image was obtained after deposition of a small quantity of indigo particles suspended in distilled water onto a glass plate, evaporation of the water, and gold sputter coating.

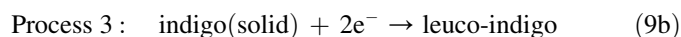
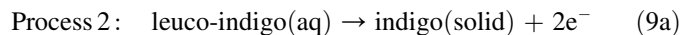
therefore the “active” surface area will be dominated by these edge areas rather than the plane area. Directed hydrogen bonding within the solid state structure is responsible for this effect [28]. This geometric anisotropy will dominate the rate of dissolution which then remains almost constant over the whole course of reaction. This results in an almost constant reaction rate (see Eq. (1)) and therefore in a much more linear increase in leuco-indigo concentration (in contrast to the more curved plots predicted based on the approximate sphere model). However, the use of the initial rate data (as employed here) will produce reliable rate constant data in both cases.

4. Results and discussion

4.1. The electrochemical response for glucose and indigo in alkaline aqueous solution

Initially, the electrochemical response for glucose at a glassy carbon electrode immersed in alkaline solution is investigated. Fig. 4 shows the oxidation response for a solution of 22 mM D-(+)-glucose in 0.2 M NaOH (65 °C) developing with time. A clear but broad oxidation response is observed at ca. -0.1 V vs. SCE (Process 1). Initially this process is absent but with time this response gradually increases indicating a chemical reaction which leads to the formation of a readily oxidisable intermediate from glucose.

Next after a delay of 20 min, indigo (equivalent to 1.33 mM) was added into the reaction mixture. Indigo is insoluble in this aqueous reaction mixture and forms a dark blue colloidal suspension. No direct reduction of indigo at the glassy carbon electrode surface is observed. Therefore, leuco-indigo formed due to chemical reduction of indigo can be observed very clearly. Immediately after indigo addition (see Fig. 4A(v)) a small anodic current (Process 2) and a new cathodic peak current (Process 3) are observed. Processes 2 and 3 are consistent with the oxidation and re-reduction of leuco-indigo in solution (Eq. (9)) with a midpoint potential of -0.75 V vs. SCE. This onset of the indigo reduction process occurs at a considerably more negative potential when compared to the oxidation of glucose and therefore the reduction of indigo by glucose may be expected to be kinetically very slow. The process is possibly due to the irreversible nature of the glucose oxidation. The peak for the cathodic process (Process 3) is associated with the “stripping” of a small amount of solid indigo from the electrode surface back into solution.



Voltammetric currents observed under rotating disc conditions (hydrodynamic conditions [29]) are governed by convection processes, and the mass transport controlled limiting current is directly proportional to the concentration of the reacting species in the bulk solution. That is, for Process 2 the observed limiting current is directly proportional to the concentration of

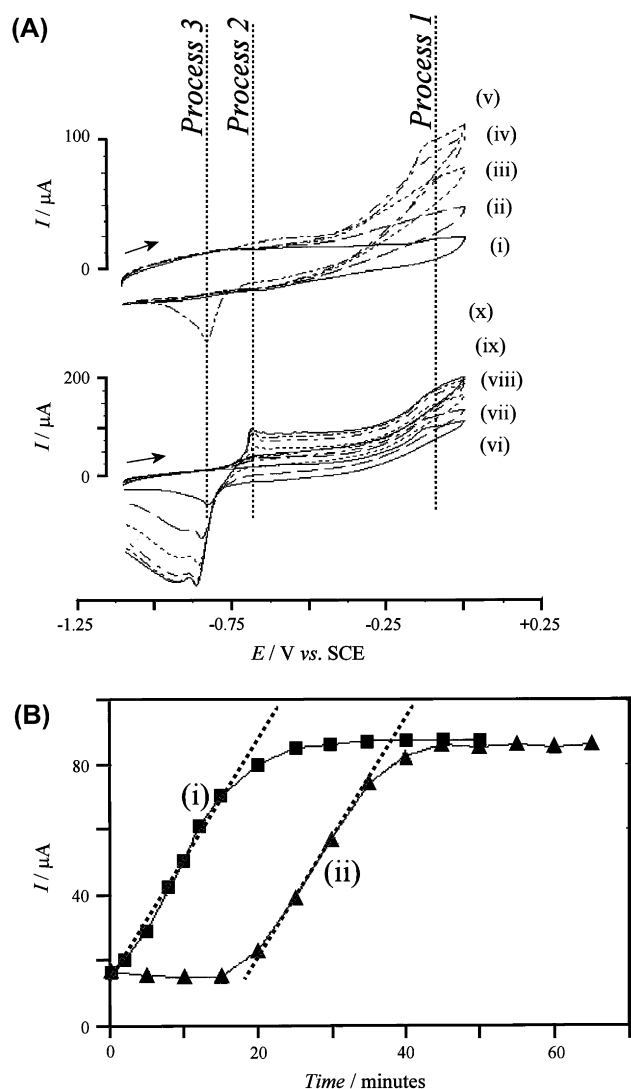


Fig. 4. (A) Cyclic voltammograms (scan rate 10 mV s^{-1} , rotation 5 Hz) for D-(+)-glucose (22 mM) in aqueous 0.2 M NaOH at $65 \text{ }^\circ\text{C}$ obtained at a rotating 3 mm diameter glassy carbon disk electrode. The current was monitored for (i) 0 min, (ii) 5 min, (iii) 10 min, (iv) 15 min after glucose addition. Next, indigo (1.33 mM) was added 20 min and further cyclic voltammograms are recorded at (v) 20 min, (vi) 25 min, (vii) 30 min, (viii) 35 min, (ix) 40 min, and (x) 45 min. (B) The plot shows the limiting current for the leuco-indigo reduction (Process 2) as a function of time. Plot (ii) shows data for the above experiment and plot (i) shows data for an experiment where indigo (1.33 mM) and D-(+)-glucose (22 mM) were added simultaneously into 0.2 M NaOH at the start of the experiment.

leuco-indigo. A plot of the limiting current as a function of time is shown in Fig. 4B. Curve (ii) corresponds to the experiment described above where a delay between glucose addition and indigo addition was applied. Curve (i) shows data for an experiment conducted under the same conditions except that both glucose and indigo were added simultaneously. Both plots show an approximately linear change in leuco-indigo concentration and in both cases the slopes (the initial rate) are very similar (see dotted line). The similarity of these slopes and lack of a lag in slope (i) suggest that the formation of leuco-indigo is kinetically limited and the formation of the

electroactive reductant derived from glucose is not crucial or rate determining under these conditions. A slow heterogeneous chemical step represented by the heterogeneous dissolution rate constant is likely. The final stage of the reaction where a current plateau is observed is consistent with the recolouration of the reaction mixture (the dark blue colour changes into yellowish-brown) and with the complete conversion of indigo to leuco-indigo. Exposure of the resulting solution to air immediately causes the formation of dark blue indigo from the dissolved leuco-indigo.

4.2. The effect of the solution composition on the rate of formation of leuco-indigo

The progress of the formation of leuco-indigo in the presence of glucose can clearly be followed by observing the mass transport controlled limiting current for the oxidation of leuco-indigo (Process 2). By varying the ratio of glucose to indigo further information about the stoichiometry of the process is obtained. Fig. 5 shows plots of limiting current data. Doubling the glucose concentration has no significant effect on the rate of leuco-indigo formation (Fig. 5A); while reducing the concentration of indigo from 5.7 to 2.9 to 1.3 mM (based on moles of insoluble solid per volume solution) clearly reduces the final amount of leuco-indigo produced (Fig. 5B). The rate of leuco-indigo formation is approximately the same when the glucose concentration is altered but it appears to be proportional to the amount of indigo present (or the surface area of indigo particles in suspension, see Eq. (1)). In all cases the time required for full conversion remains approximately the same.

When the NaOH concentration was increased from 0.1 to 0.5 M both the rate and extent of leuco-indigo reduction increased (Fig. 5C), and the rate equation given in Eq. (1) may be modified to give the following rate law (Eq. (10)).

$$\frac{dn_{\text{leuco-indigo}}}{dt} = k' \times S_{\text{indigo}} = k \times c_{\text{OH}^-} \times S_{\text{indigo}} \quad (10)$$

The rate expression (Eq. (10)) allows the individual rate constants k' to be determined as a function of hydroxide concentration and this allows $k = 4.1(\pm 0.3) \times 10^{-9} \text{ m s}^{-1}$ (at 65 °C) to be estimated. An additional effect observed in the presence of different NaOH concentrations is the change in the final limiting current. At lower hydroxide concentration clearly the final current plateau is reduced. However, it is very likely that this effect is introduced due to the diffusion coefficient of the resulting leuco-indigo in the aqueous electrolyte. A higher alkalinity may be better for preventing aggregation effects and for generally improving leuco-indigo solubility and diffusivity.

Additional experiments were carried out in order to explore the effect of other cations and ionic strength on the rate of the leuco-indigo formation. Both, replacing 0.2 M NaOH with 0.2 M KOH and the addition of 0.8 M NaCl to 0.2 M NaOH did not have any significant effect. Furthermore, when fructose was used instead of glucose similar rate data for the formation of leuco-indigo were obtained (data not shown).

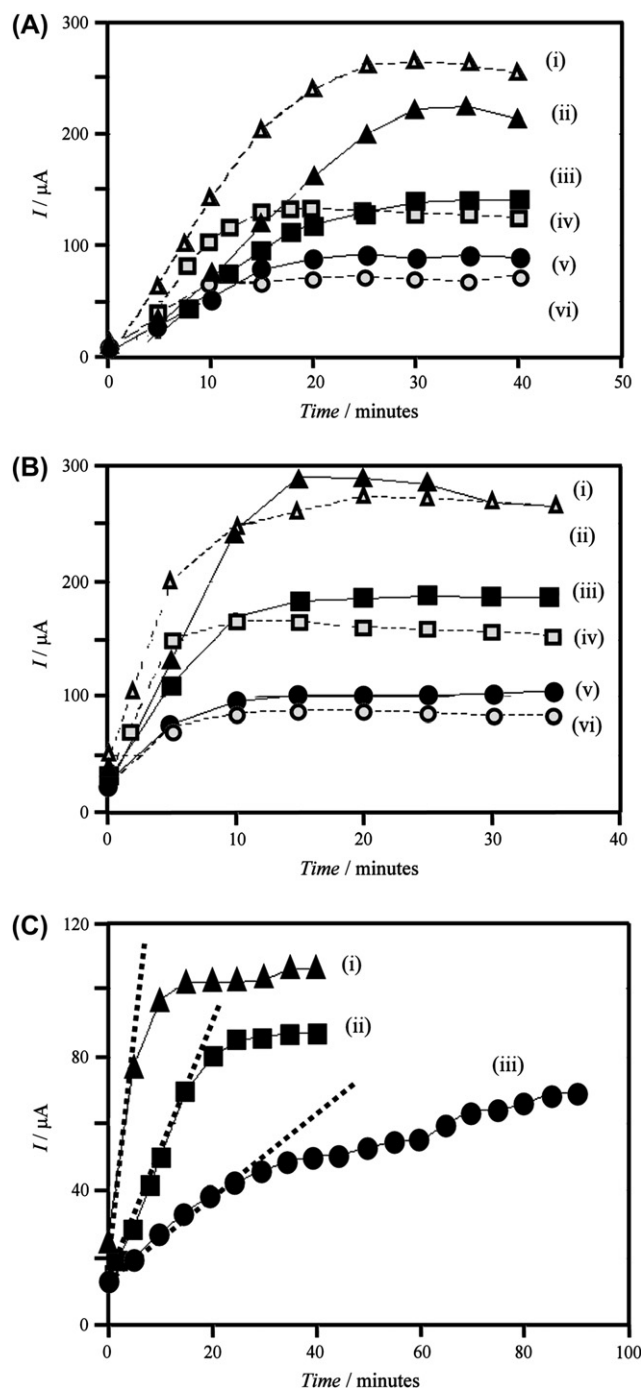


Fig. 5. Time course of the formation of leuco-indigo in the presence of glucose in aqueous NaOH with time monitored at a rotating 3 mm diameter glassy carbon disk electrode (see text). (A) The effect of glucose and indigo concentrations on the rate of leuco-indigo formation in 0.2 M NaOH: (i) 44 mM glucose, 5.7 mM indigo; (ii) 22 mM glucose, 5.7 mM indigo; (iii) 22 mM glucose, 2.9 mM indigo; (iv) 44 mM glucose, 2.9 mM indigo; (v) 22 mM glucose, 1.3 mM indigo; (vi) 44 mM glucose, 1.3 mM indigo. (B) The effect of glucose and indigo concentrations on the rate of leuco-indigo formation in 0.5 M NaOH: (i) 22 mM glucose, 5.7 mM indigo; (ii) 44 mM glucose, 5.7 mM indigo; (iii) 22 mM glucose, 2.9 mM indigo; (iv) 44 mM glucose, 2.9 mM indigo; (v) 22 mM glucose, 1.3 mM indigo; (vi) 44 mM glucose, 1.3 mM indigo. (C) The effect of the NaOH concentration on the rate of leuco-indigo formation: (i) 1.3 mM indigo, 22 mM glucose, 0.5 M NaOH; (ii) 1.3 mM indigo, 22 mM glucose, 0.2 M NaOH; (iii) 1.3 mM indigo, 22 mM glucose, 0.1 M NaOH.

4.3. The effect of temperature on the rate of leuco-indigo formation

Hydrodynamic cyclic voltammograms were measured at three different temperatures: 55 °C, 65 °C and 75 °C, and the plots of the limiting currents per time are shown in Fig. 6. The plots show quite clearly that temperature strongly affects the rate of indigo reduction with higher temperatures accelerating the reduction. The Arrhenius plot allows an estimate for the activation energy $E_A = 64 \text{ kJ mol}^{-1}$ to be obtained.

4.4. The catalytic effect of 1,8-dihydroxyanthraquinone on the rate of leuco-indigo formation

Both the relatively small magnitude of the dissolution rate constant and the high activation energy suggest that a slow chemical reaction step governs the reductive dissolution of indigo (see also Fig. 4B). Anthraquinone derivatives are known to act as electron transfer mediators in the electrochemical reduction of indigo [5,8]. In particular 1,8-dihydroxyanthraquinone is a very effective mediator for this reaction. Fig. 7 shows the effect of the 1,8-dihydroxyanthraquinone mediator (1,8-DHAQ) on the reduction of indigo

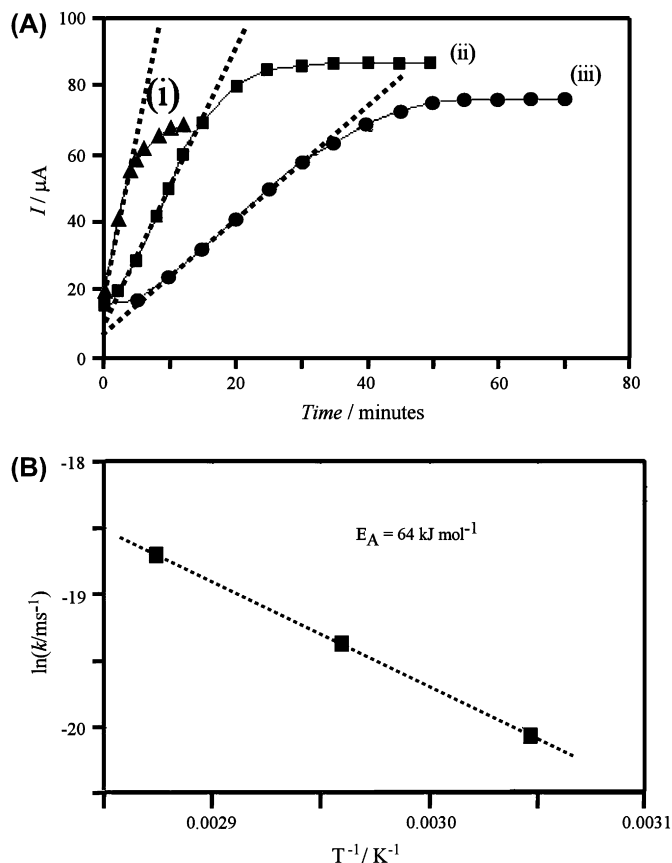


Fig. 6. (A) Indigo reduction with glucose at (i) 55 °C, (ii) 65 °C, and (iii) 75 °C in 0.2 M NaOH at 3 mm diameter glassy carbon rotating disk electrode (rotation speed 5.0 Hz). Compare with Fig. 2. (B) Arrhenius plot for the dissolution rate constant k ($7.7 \times 10^{-9} \text{ m s}^{-1}$ at 75 °C, $4.1 \times 10^{-9} \text{ m s}^{-1}$ at 65 °C, and $2.0 \times 10^{-9} \text{ m s}^{-1}$ at 55 °C).

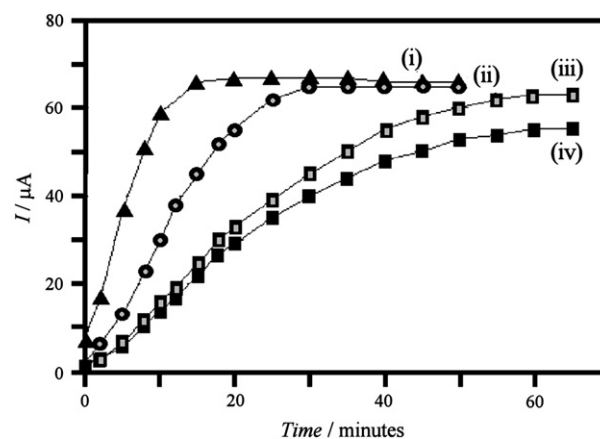


Fig. 7. Plots are shown for the limiting currents for leuco-indigo (3 mm diameter glassy carbon rotating disk electrode, rotation speed 5.0 Hz) for the reduction of indigo (1.3 mM) by glucose (22 mM) at a temperature of 65 °C with and without different concentrations of 1,8-DHAQ in 0.1 M NaOH: (i) 0.32 mM, (ii) 0.032 mM, (iii) 0.0032 mM, and (iv) no 1,8-DHAQ.

by glucose at 0.1 M NaOH. The 1,8-DHAQ mediator seems to have a strong catalytic effect on the reduction process. The reaction rate is increased even at lower NaOH concentrations. Successful leuco-indigo production is possible even in 0.05 M NaOH.

4.5. Sonoelectrochemical monitoring of the formation of leuco-indigo

Power ultrasound introduces strong agitation which can be exploited for hydrodynamic (sonovoltammetric) measurements. In addition power ultrasound applied to electrodes leads to surface cleaning effects and higher reproducibility [30]. The experimental set up for the use of a 24 kHz glass horn system is shown in Fig. 8. From the resulting current data the concentration of leuco-indigo can be monitored and the progress of the indigo reduction recorded. The rate parameters obtained in these measurements were virtually identical to those obtained with rotating disk methods. Fig. 8B shows typical plots. The final limiting current after complete reductive dissolution of indigo was increased when the horn-to-electrode distance was decreased due to the more intense agitation close to the horn system.

5. Conclusions

It has been shown that hydrodynamic voltammetry (rotating disc and sonovoltammetry) offers a convenient and reliable tool for the determination of leuco-indigo in an alkaline bath containing indigo and glucose precursors. The methodology allowed a rate law and rate constant to be determined. The sustainability of glucose as a reductant in indigo dyeing may be considered to be limited by the present demonstration of a high temperature requirement and a high alkalinity. However, the demonstration of a catalytic role for the anthraquinone derivative points the way towards improvements that

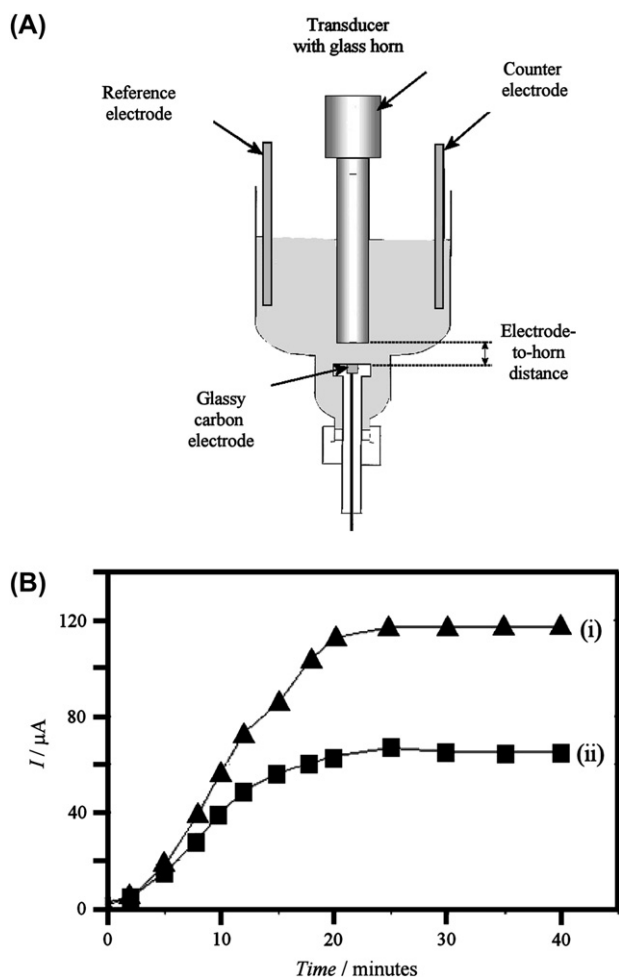


Fig. 8. (A) Schematic drawing of the experimental set up employing an ultrasonic horn system placed opposite to the glassy carbon working electrode. (B) Plots of the mass transport limited currents observed for the oxidation of leuco-indigo are shown for indigo (1.3 mM) reduction with glucose (22 mM) in 0.2 M NaOH when 24 kHz ultrasound is applied (at 65 °C). The distance between horn and 3 mm diameter glassy carbon electrode surface was (i) 10 mm and (ii) 24 mm.

could be brought about in the glucose-driven process by the identification of related compounds that combine an appropriate redox functionality and an ability to interact with the indigo particle surface.

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