A reaction model for the electrochemical production of p-anisidine

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The work examines the possibility of a simple reaction model describing a complex organic electrosynthesis, such as the formation of p-anisidine. The experimental results obey the linear relationships of the model and in consequence the kinetic constants obtained in this way define reaction behaviour. The paper demonstrates how such a model can play a useful role in the design of pilot plant experimentation. Results from a parallel plate cell fit prediction from the model.

Nomenclature

$[X]$ Concentration of species X $(\mathrm{kmol\,m^{-3}})$

b Slope of Tafel plot $(\mathrm{mV^{-1}})$

E Electrode potential (mV)

F Faraday $(\mathrm{C\,g\text{-}equiv^{-1}})$

$\mathscr{F}$ Faraday based on k-equiv $= 10^3 F$ $(\mathrm{C\,k\text{-}equiv^{-1}})$

i_A Partial current density for the primary reaction $(\mathrm{A\,m^{-2}})$

i_B Partial current density for the consecutive secondary reaction $(\mathrm{A\,m^{-2}})$

i_H Partial current density for the parallel secondary reaction $(\mathrm{A\,m^{-2}})$

i Total current density $= i_A + i_B + i_H$ $(\mathrm{A\,m^{-2}})$

k Reaction rate constant $(\mathrm{A\,m^{-2}}$ per $\mathrm{kmol\,m^{-3}})$

k_H Rate constant for the parallel secondary electrode reaction $(\mathrm{A\,m^{-2}})$

k_L Individual mass transfer coefficient $(\mathrm{m\,s^{-1}})$

N Flux $(\mathrm{kmol\,m^{-2}\,s^{-1}})$

r Reaction rate $(\mathrm{kmol\,m^{-2}\,s^{-1}})$

Suffixes

A Appertaining to primary electrode reaction or species A

B Appertaining to consecutive secondary electrode reaction or species B

b In the bulk of the electrolyte

H Parallel secondary electrode reaction

s Near the electrode surface

1. Introduction

p-Anisidine, like p-aminophenol, can be prepared by the reduction of nitrobenzene in an acidic medium and both compounds are of industrial interest. Work on the production of p-aminophenol has been extensively reported in the literature [1–5] but the electrochemical synthesis of p-anisidine is mentioned only in one patent [6]. The reaction is carried out in a methanol environment and the overall stoichiometry is described by

$$C_6H_5NO_2 + CH_3OH \longrightarrow C_6H_4(NH_2)OCH_3 + O_2$$
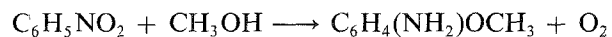
The reaction proceeds via phenylhydroxylamine as the intermediate, which by direct rearrangement can lead to the formation of p-aminophenol as a small but significant by-product. Chemical yield can also be adversely affected by the further reduction of phenylhydroxylamine to aniline.

The intention of the present work was to develop a reaction model which could be used to help in the design and interpretation of pilot plant experimentation. It must be emphasized that a reaction model is essentially different from a reaction mechanism in that all that is required from the former [7] is a prediction of the dependence of current density, i, on electrode potential, E, reactant concentration, mass transfer coefficient, k_L, and possibly some other factors such as, for instance, temperature or pH. Models are therefore specific forms of the function, $i = f(E, \mathrm{conc.}, k_L, \dots)$. In the case of multiple reactions occurring on the electrode, each should, if possible, be modelled individually and this has been done in the present work.

2. Experimental details

2.1. Electrolytic cells

Three types of cell were used in this work: a rotating disc electrode (RDE), a small glass H-cell and a wide gap parallel plate cell made of polypropylene. All these cells had copper cathodes.

The RDE set up was fully computerized [8] and capable of working at 55° C, the temperature at which all experiments were performed.

The area of the planar copper cathodes in the H-cell, which has been described elsewhere [9], varied between 0.25 and 12 cm^2, the anode being a graphite rod. Catholyte and anolyte (each 250 cm^3 in volume)

were separated by an Ionac MC-3470 cationic membrane (supplied by Sybron Chemicals Inc. Birmingham, NJ 08011, USA). A magnetic follower in the catholyte was replaced by a stirrer when results demonstrated the former to be unsatisfactory.

The parallel plate cell has also been described in a previous publication [5]. Cathode dimensions were $7.5 \times 30\,cm^2$, and as before the catholyte and anolyte were separated by an Ionac MC-3470 membrane, and the anode was of graphite. Ionac was used since it proved more effective than Nafion (supplied by DuPont Co. Wilmington, DE 19898 USA) in preventing transfer of nitrobenzene into the anolyte.

2.2. Materials

The nitrobenzene, sulphuric acid and methanol were B.D.H. 'AnalaR' grade. Reagent grade methanol and singly distilled water were used for cleaning the system. Materials used for analysis were HPLC grade and water was glass-double-distilled. All liquids were routinely filtered through $0.45\,\mu m$ filters before use.

The cathode was made from 99 % pure copper sheet, and the anode from HPC grade graphite.

2.3. Procedure

The cathode was prepared prior to each run by using first emery paper and then fine 'wet-and-dry' paper until the surface was clean, bright and free from scratches. The cathode was then degreased with acetone, rinsed with methanol and dried. The graphite anode was carefully rubbed with emery paper to remove any loose surface and rinsed with methanol.

Since operating procedures for RDEs and small H-cells are well established, only the technique used with the parallel plate cell will be described here. When the latter had been assembled and installed, anolyte and catholyte (both 10 % by volume sulphuric acid in methanol) were circulated and the current switched on as soon as the electrodes were covered in electrolyte to prevent an otherwise rapid corrosion of the copper cathode. When the system had reached the operating temperature of 55° C, circulation was stopped and a measured amount of nitrobenzene was added to the catholyte holding tank to give a concentration of $41\,g\,l^{-1}$. The dissolution of the nitrobenzene had been dissolved, the valve in the lyte to and from the tank via a return line. Once the nitrobenzene had been dissolved, the value in the return line was closed and the run started. All experiments were carried out amperostatically. Flow rates and current were controlled manually. Current, cell voltage, electrode potential, coulombs passed, flowrate and temperature were recorded.

2.4. Analysis

By-products were identified by mass-spectroscopy and confirmed by high performance liquid chromatography (HPLC). Nine compounds were identified by this
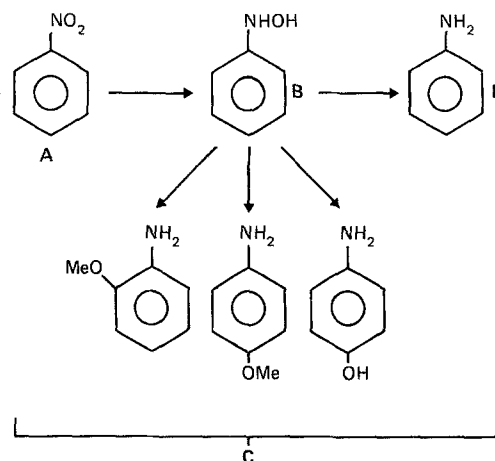

Fig. 1. The major reactions.

means. Of these four were major products, namely p-aminophenol, o- and p-anisidine and aniline. The remaining species (azoxybenzene, hydrazobenzene, p-methoxyhydrazobenzene, p-methoxyazobenzene and azobenzene) accounted for less than 10 % of the nitrobenzene consumed.

The major products were routinely analysed using HPLC. The mobile phase consisting of a 40:60 mixture of methanol and water was buffered to a pH of 6.0 using phosphates. The column was a Waters 'Novapak' C18 reverse phase and peaks were measured by UV absorbance at 254 nm. Further details of the analysis will be found in reference [10].

3. Results and discussion

3.1. The reaction model

For the purpose of the model, as shown in Fig. 1, nitrobenzene (A) is considered to be reduced by a four-electron step to phenylhydroxylamine (B) which undergoes chemical rearrangement and chemical reaction to form the p-aminophenol and anisidine, referred to collectively as C. B, however, is susceptible to further reduction giving rise to a consecutive secondary reaction in which an additional two electrons are transferred resulting in the formation of aniline. Hydrogen discharge will also occur, and although it may prove to be of little importance from a process point of view, it is essential to the stability of the computer model (see Section 4) that it is included as a component of the model. Minor products were excluded from the model.

From the discussion so far one can draw up the reaction scheme shown in Fig. 2.

With the assumption that no accumulation occurs at the electrode surface of the reacting species A_s, B_s and D_s (see Fig. 2), a coulombic balance and the assumption of a Tafel relationship leads to [10] Equation 1 for the primary reaction

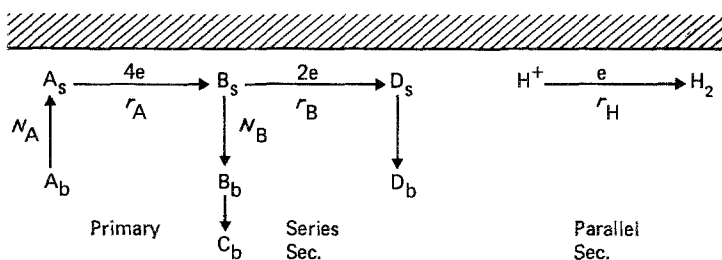$$i_A = \frac{[A]_b}{\dfrac{1}{4\mathscr{F}k_L} + \dfrac{1}{k_A\,e^{-b_A E}}} \tag{1}$$

Fig. 2. The reaction scheme.

The assumptions [12] that the diffusion of B away from the electrode is faster than the chemical step B → C, that as a first approximation the build up of B in the bulk of the electrolyte is negligibly small (in practice $[B_b]$ represented some 10 to 15 % of $[C_b]$) and that a Tafel relationship can be employed for i_B, the partial current density for the consecutive secondary reaction, leads to the equation

$$i_B = \frac{i_A k_B \, e^{-b_B E}}{4\mathscr{F}k_L + 2k_B \, e^{-b_B E}} \qquad (2)$$

The current density for the parallel secondary reaction is expressed by the Tafel equation

$$i_H = k_H \, e^{-b_H E} \qquad (3)$$

$$i = i_A + i_B + i_H$$

$$= \left(\frac{[A]_b}{(4\mathscr{F}k_L)^{-1} + (k_A \, e^{-b_A E})^{-1}} \right)$$

$$\times \left(\frac{4\mathscr{F}k_L + 3k_B \, e^{-b_B E}}{4\mathscr{F}k_L + 2k_B \, e^{-b_B E}} \right) + k_H \, e^{-b_H E} \qquad (4)$$

In order to produce a reaction model it is, therefore, necessary to obtain numerical values for constants k_A, k_B, k_H, b_A, b_B and b_H. These constants were determined largely from preparative runs carried out galvanostatically in the H-cell at 55° C, which were supplemented by a few polarization runs performed with a rotating disc also at 55° C. The results of the latter are shown in Fig. 3 and demonstrate that the background current density, i_H, is a negligible fraction of i, the total current density, and in consequence we can write that $i = i_A + i_B$.
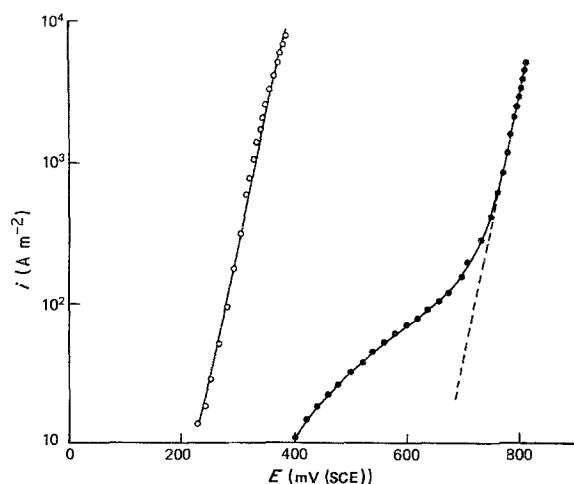
3.2. The determination of the kinetic constants

3.2.1. Value of b_A. The value of b_A was determined by confining attention to behaviour at low cathodic potentials. Under these circumstances, firstly,

$$4\mathscr{F}k_L \gg k_A \, e^{-b_A E}$$

and, secondly, as the preparative runs revealed, i_B is small compared to i_A, allowing the approximation

$$i = i_A$$

In this region, therefore, Equation 1 reduces to

$$i = k_A [A]_b \, e^{-b_A E}$$

or

$$\ln (i/[A]_b) = \ln (k_A) - b_A E \qquad (5)$$

The plot in Fig. 4, using results obtained with the RDE at 40 Hz gives a value for the slope, b_A, of 0.0339 mV^{-1}. An approximate value for k_A could not be determined by extrapolating Fig. 4 since the highly polished surface of the RDE was quite different from that of a copper electrode that was being used in prolonged synthesis.

3.2.2. Values of b_B *and* k_B. By dividing Equation 1 by Equation 2 and rearranging, one obtains the expression

$$\ln \left(\frac{i_A}{i_B} - 2 \right) = \ln \left(\frac{4\mathscr{F}k_L}{k_B} \right) + b_B E \qquad (6)$$

A plot of $\log_e [(i_A/i_B) - 2]$ against E would therefore have a slope b_B and an intercept from which k_B can be determined, provided a value of k_L, the mass transfer coefficient appertaining to the cell, is known.

In order to make use of Equation 6 values of i_A/i_B were calculated on the basis of the following argument. With reference to Fig. 2 products can be divided
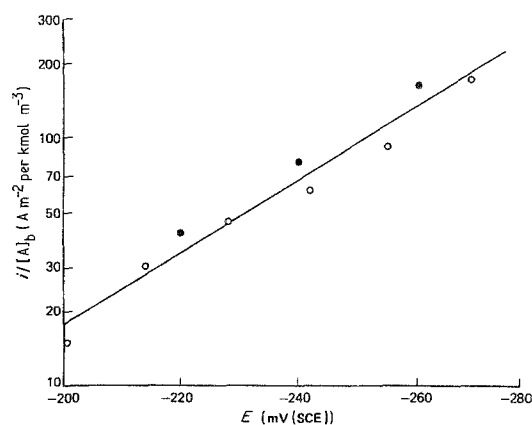

Fig. 3. Polarization curves using a RDE. O $[A]_b = 0.3 \, \text{kmol m}^{-3}$, ● $[A]_b = 0 \, \text{kmol m}^{-3}$.

Fig. 4. Plot for the determination of b_A. O $[A]_b = 0.3 \, \text{kmol m}^{-3}$, ● $[A]_b = 0.03 \, \text{kmol m}^{-3}$.
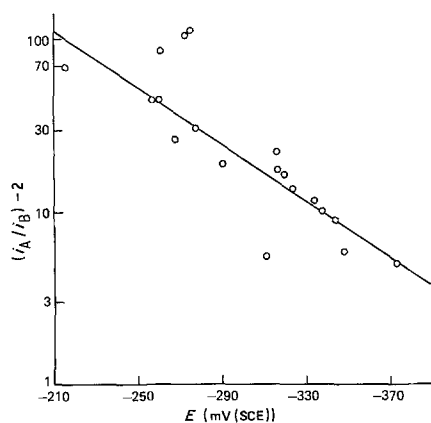
Fig. 5. Plot for the determination of k_B and b_B.

into those that require the transfer of four electrons and aniline, which requires the transfer of six. From a mass balance, referring again to Fig. 2,

$$r_A = N_B + r_B \qquad (7)$$

i.e. r_A = production rate of low-electron products + production rate of aniline. Hence

$$i_A = 4\mathscr{F} \times \text{production rate of all products.}$$

Since errors in the analysis of products are unavoidable it will be more appropriate to write

$$i_A \propto 4\mathscr{F} \times \text{measured production rate of all products}$$

Similarly $i_B \propto 2\mathscr{F} \times$ measured production rate of aniline. Thus

$$\frac{i_A}{i_B} = \frac{2 \times \text{measured rate (all products)}}{\text{measured rate (aniline)}}$$

A plot of Equation 6 is presented in Fig. 5. The slope gives a value for b_B of $0.019\,\text{mV}^{-1}$ and the intercept leads to a value of k_B of $1.029\,\text{A m}^{-2}$ per kmol m^{-3}. The value of k_L employed in the determination of k_B was $1.6 \times 10^{-5}\,\text{m s}^{-1}$ and was determined by a limiting current technique using copper deposition from aqueous acidic copper sulphate, the observed value being adjusted for differences in viscosity and diffusivity when applied to the organic system.

3.2.3. Value of k_A. Equation 1 can be rearranged as

$$Y = k_A[A]_b\, e^{-b_A E} \qquad (8)$$

where

$$1/Y = 1/i_A - 1/(4\mathscr{F} k_L[A]_b).$$

From a least squares plot of Equation 8 k_A is found to be $0.217\,\text{A m}^{-2}$ per kmol m^{-3}. Values of i_A were calculated from

$$i_A = i/(i_B/i_A + 1)$$

using the ratios i_B/i_A determined previously, as described in Section 3.2.2.

3.2.4. Values of k_H and b_H. The kinetic constants for hydrogen evolution were determined from the background polarization curve of Fig. 3 which gave values for k_H and b_H of $4.89 \times 10^{-10}\,\text{A m}^{-2}$ and $0.0368\,\text{mV}^{-1}$ respectively.
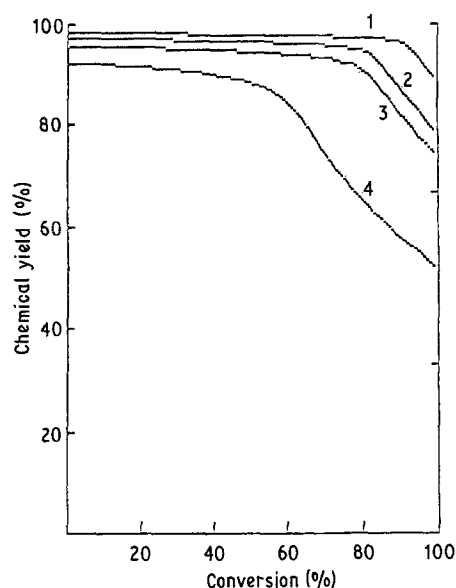

Fig. 6. Effect of conversion, current density and flow rate on the chemical yield in a narrow gap pilot plant cell. 1, $20\,\text{cm s}^{-1}$: $1000\,\text{A m}^{-2}$; 2, $20\,\text{cm s}^{-1}$: $2000\,\text{A m}^{-2}$; 3, $5\,\text{cm s}^{-1}$: $1000\,\text{A m}^{-2}$; 4, $5\,\text{cm s}^{-1}$: $2000\,\text{A m}^{-2}$.

3.3. The final equations of the reaction model

We are now in a position to fill in numerical values in Equations 1 to 3

$$i_A = \frac{[A]_b}{(4\mathscr{F} k_L)^{-1} + (0.217\, e^{-0.0339E})^{-1}}\,\text{A m}^{-2} \qquad (1)$$

$$i_B = i_A\left(\frac{1.02\, e^{-0.019E}}{4\mathscr{F} k_L + 2.04\, e^{-0.019E}}\right)\,\text{A m}^{-2} \qquad (2)$$

$$i_H = 4.89 \times 10^{-10}\, e^{-0.0368E}\,\text{A m}^{-2} \qquad (3)$$

4. Application of the model

In the design of pilot plant experimentation it is useful to be able to predict how the system would react to a change in key process parameters. Typically one would wish to know, say, the effect of mass transfer, current density and conversion on chemical yield or perhaps the effect of conversion on pilot plant running time. Such data are very easily generated by computer once a reaction model such as the one above has been established, provided of course that the mass transfer characteristics in terms of flow rate are known.

As an illustration, the present reaction model has been applied to a hypothetical pilot plant comprising a single module plate and frame cell, cathode area $0.1\,\text{m}^2$, and a catholyte capacity of $5\,\text{l}$. Mass transfer coefficients, in m s^{-1}, were calculated from the equation

$$k_L = 2.0 \times 10^{-4} v^{0.6} \qquad (9)$$

where v is the superficial velocity of flow in m s^{-1} through the catholyte compartment. The equation is specific to the chemical system of interest and would apply to a narrow gap cell with a mesh turbulence promotor. Fig. 6 shows the chemical yield as a function of conversion, flow velocity and current density. It highlights the catastrophic drop in chemical yield
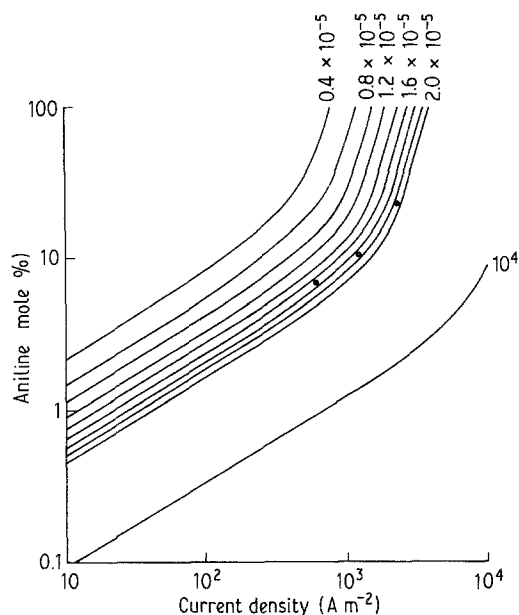
Fig. 7. Variation of aniline production with current density, with k_L as a parameter.

Fig. 8. Effect of conversion, current density and flowrate on pilot plant run time. 1, 20 cm s^{-1}: 1000 A m^{-2}; 2, 20 cm s^{-1}: 2000 A m^{-2}; 3, 5 cm s^{-1}: 1000 A m^{-2}; 4, 5 cm s^{-1}: 2000 A m^{-2}.

at high conversions, if low velocities, i.e. low mass transfer coefficients, are employed.

The importance of mass transfer is again emphasized by Fig. 7 the curves for which were determined from the reaction model and show how the relative production of aniline for a given current density is dependent on the magnitude of the mass transfer coefficient. The three points represent the actual performance of the parallel plate cell mentioned in Section 2.1. They fall along a line which would suggest a mass transfer coefficient of between 1.5–1.8 × 10^{-5} m s^{-1}, which is consistent with a predicted value of 1.0 × 10^{-5} m s^{-1} calculated using a correlation for unbaffled cells due to Mamoor [11]. Bearing in mind that entrance effects [11, 12] introduce a measure of uncertainty into the prediction of mass transfer rates, this agreement between model and observation is encouraging.

As a further illustration of the usefulness of a reaction model, Fig. 8 demonstrates how the run time of the pilot plant would be affected by conversion, current density and flow rate. Once again mass transfer coefficients have a marked effect, and for low values the last 10% of conversion occupies virtually half the run time, important information when planning the usage of the pilot plant.

Due to a question of confidentiality comparison with actual pilot plant results which were not obtained in the author's laboratories was not possible.

5. Conclusions

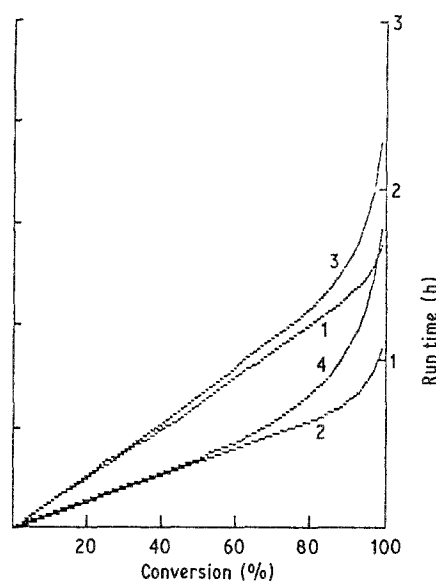The proposed reaction scheme for the reduction of

nitrobenzene in acidic methanol has led to a model which is capable of correlating observed results. Some further confirmation of the model has been provided by results in an unbaffled wide gap parallel plate cell.

Acknowledgements

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