

Electrosynthesis in systems of two immiscible liquids and a phase transfer catalyst

IV. Electrosynthesis using thin film contactor cells

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The cell described in the previous paper has been applied to the synthesis of 2,5-dimethoxyphenylacetate from 1,4-dimethoxybenzene under both potentiostatic and galvanostatic conditions. The desired product is oxidized under similar conditions to the starting material and the known methods of chemical reaction engineering have been used to model the reaction scheme and to define the optimum conditions for the synthesis. Under both potentiostatic and galvanostatic conditions, the highest yield of 2,5-dimethoxyphenylacetate is about 70%.

Glossary

C	concentration (mol cm^{-3})
C_0	initial concentration (mol cm^{-3})
E	electrode potential of any convenient scale (V)
F	the Faraday (C mol^{-1})
I	total current (A)
k	first order rate constant for electron transfer (cm s^{-1})
k^0	first order rate constant for electron transfer when $E = 0$ (cm s^{-1})
k_m	mass transfer coefficient (cm s^{-1})
n	equivalents per mole
R	gas constant ($\text{V C K}^{-1} \text{mol}^{-1}$)
T	temperature (K)
t	time (s)
V	volume of organic phase (cm^3)
x	conversion
z_A, z_B etc	no. of electrons
β	electrochemical transfer coefficient
ϕ	fractional yield of product based on the initial concentration of reactant
λ	ratio of rate constants.

1. Introduction

It has been shown in the previous paper [1] that two-phase electrolysis may be carried out using thin

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film contactor electrodes. These electrodes (rotating in the vertical plane) are covered by a thin film of the organic phase (thickness ~ 0.05 cm) and the electrochemical reaction takes place within this phase. The major part of the region between the working and counter electrodes consists of the aqueous solution; the organic phase is made sufficiently conducting by using a phase transfer catalyst (tetrabutylammonium cations) and this catalyst transfers anions which are consumed in the anodic acetoxylation of 1,4-dimethoxybenzene used as a model reaction.

The voltammetric behaviour of the electrodes has been explained using a simple model of a film with plug flow in the direction of rotation, mass transfer to the electrode taking place through a thin stagnant sublayer. It has been shown that two simple limiting conditions can be defined for the operation of this electrode. At low substrate and high phase transfer catalyst concentrations the electrochemical reaction (and, in the limit, mass transfer through the stagnant layer) becomes rate controlling especially at low rotation rates; on the other hand, at high substrate and low phase transfer catalyst concentrations and at high rotation rates there is mixed control by both the interfacial reaction and current flow through the film.

In this paper we examine potentiostatic oxidations under the first set of conditions and galvanostatic syntheses under the second set of conditions. The potentiostatic oxidations can be interpreted using the analyses from 'Chemical Reaction Engineering [2]' for the series reactions in scheme (a) [1]. The electrochemical reaction engineering for the galvanostatic conditions used for preparative reactions with this cell is developed for the specific case of the series reaction (a) [1]. Simple limiting conditions have been used for both the potentiostatic and galvanostatic syntheses so as to simplify the modelling. The extension of the models and their application to a wider range of conditions will be published elsewhere [3].

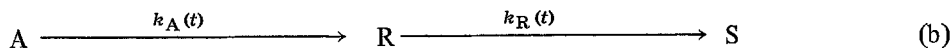
2. Experimental procedure

The cell and electrodes were similar to those described in the previous paper [1] except that both sides of the working electrode were used in the syntheses. The aqueous solution in all experiments consisted of 1.4 mol dm^{-3} sodium acetate with 1.4 mol dm^{-3} acetic acid saturated with sodium sulphate; appropriate concentrations of the phase transfer catalyst tetrabutylammonium hydrogen sulphate were added to the aqueous phase, the majority of the cation (60%) being extracted by the methylene chloride phase.

Appropriate amounts of the substrate 1,4-dimethoxybenzene(I) [and in some experiments 2,5-dimethoxyphenylacetate(II)] scheme (a) [1] were added directly to the organic phase. This phase was analysed for the starting material (I) and product (II) using gas chromatography. A dual column, FID system was used. The columns were 2 m in length and 1.75 mm internal diameter and were packed with 5% Carbowax 20M. Analyses were carried out at 550 K with a nitrogen carrier gas flow rate of $25 \text{ cm}^3 \text{ min}^{-1}$. Additional experimental details are given in the figure legends.

3. Comparison of the reaction engineering under galvanostatic and potentiostatic conditions

We abbreviate the reaction scheme (a) [1] by the conventional form



1,4-dimethoxybenzene (I) 2,5-dimethoxyphenyl acetate (II) higher acetoxyated products

where R is the desired product and $k_A(t)$ and $k_R(t)$ are the rate constants for the slow pseudo first order oxidations of A and R (cm s^{-1}). Although each of the steps in scheme (b) must consist of a set of elementary reactions, we assume here that the steps following the first electron transfer (for example, the second electron transfer, proton loss and combination of a cation with the acetate anion; these steps not necessarily being in this order) are fast so that scheme (b) is an adequate model. The rate constants k_A and k_R will be constant in potentiostatic experiments and, as a special case,

are equal to the mass transfer constant k_m (see below). In the galvanostatic experiments we assume that the reactions are sufficiently slow that we can neglect the effects of mass transfer on the surface concentrations of (I) and (II): this assumption will clearly be inadequate at long times [high conversions of (I)]. For galvanostatic syntheses the rate constants k_A and k_R will be time dependent.

It will be apparent that under the conditions used [1] the electrode itself behaves as a plug flow reactor while the bulk of the organic phase is a well stirred tank, recycle taking place between the tank and plug flow reactor. The general analysis of this system will be given elsewhere [3]; here we confine attention to low conversions per pass in the plug flow reactor so that we can simplify the model for the whole system to that of a batch process. We can write

$$V \frac{dC_A}{dt} = -\Omega k_A(t) C_A = -\Omega k_A^0 \left[\exp \frac{\beta_A z_A E(t) F}{RT} \right] C_A \quad (1)$$

$$V \frac{dC_R}{dt} = \Omega k_A^0 \left[\exp \left(\frac{\beta_A z_A E(t) F}{RT} \right) \right] C_A - \Omega k_R^0 \left[\exp \left(\frac{\beta_R z_R E(t) F}{RT} \right) \right] C_R \quad (2)$$

$$I = n_A F \Omega k_A^0 \left[\exp \left(\frac{\beta_A z_A E(t) F}{RT} \right) \right] C_A + n_R F \Omega k_R^0 \left[\exp \left(\frac{\beta_R z_R E(t) F}{RT} \right) \right] C_R \quad (3)$$

where I is the total current (A), V the volume of the organic phase (cm^3), Ω the area of the electrode where the reaction occurs (cm^2), k_A^0 and k_R^0 are the rate constants (cm s^{-1}) of the two steps in scheme (b) at the potential $E(t) = 0$ (any convenient scale), β_A and β_R are the transfer coefficients of the two reactions which involve z_A and z_R electrons respectively (we assume $z_A = z_R = 1$), while $n_A F$ and $n_R F$ Faradays per mole are transferred in the two steps.

In view of the similarity of the reactant (I) and product (II), the voltammetric curves for the two oxidations are expected and found to be closely similar, Fig. 1. We can therefore make the simplifying assumptions

$$\beta_A z_A = \beta_R z_R = \beta z \quad (4)$$

$$n_A = n_R = n = 2 \quad (5)$$

We first of all investigate the time independent plots of the fractional yield

$$\phi \left(\frac{R}{A} \right) = \frac{C_R}{C_{A,0}} \quad (6)$$

as a function of the degree of conversion

$$X_A = 1 - \frac{C_A}{C_{A,0}} \quad (7)$$

where $C_{A,0}$ is the initial concentration. Dividing Equation 2 by Equation 1 and using Equation 4 we obtain

$$\frac{dC_R}{dC_A} = -1 + \frac{k_R^0 C_R}{k_A^0 C_A} \quad (8)$$

Integrating Equation 8 with the initial condition

$$C_R = 0 \text{ when } C_A = C_{A,0} \quad (9)$$

we obtain

$$C_R = \frac{k_A^0}{k_A^0 - k_R^0} \left[C_A^0 \left(\frac{C_A}{C_{A,0}} \right)^{k_R^0/k_A^0} - C_A \right] \quad (10)$$

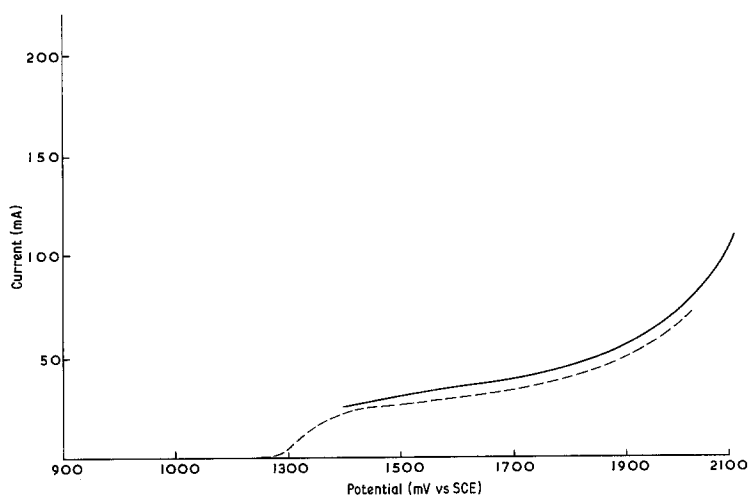


Fig. 1. Polarization curves for the substrate and product. Aqueous phase; 1.4 mol dm^{-3} CH_3COOH , 1.4 mol dm^{-3} CH_3COONa , saturated with Na_2SO_4 , 0.1 mol dm^{-3} Bu_4NHSO_4 . Organic phase; CH_2Cl_2 , — 10 mmol dm^{-3} 1,4-dimethoxybenzene, --- 10 mmol dm^{-3} 2:5-dimethoxyphenyl acetate. Rotation speed 10 rpm.

The special case $k_A^0 = k_R^0$ gives

$$C_R = C_A \ln \left(\frac{C_{A,0}}{C_A} \right) \quad (11)$$

With Equations 6 and 7 and writing

$$\lambda = \frac{k_R^0}{k_A^0} \quad (\text{or } \frac{k_R}{k_A} \text{ for potentiostatic syntheses}) \quad (12)$$

we obtain from Equation 10

$$\phi \left(\frac{R}{A} \right) = \frac{1}{1-\lambda} [(1-X_A)^\lambda - (1-X_A)] \quad (13)$$

and from Equation 11

$$\phi \left(\frac{R}{A} \right) = (X_A - 1) \ln (1 - X_A) \quad (14)$$

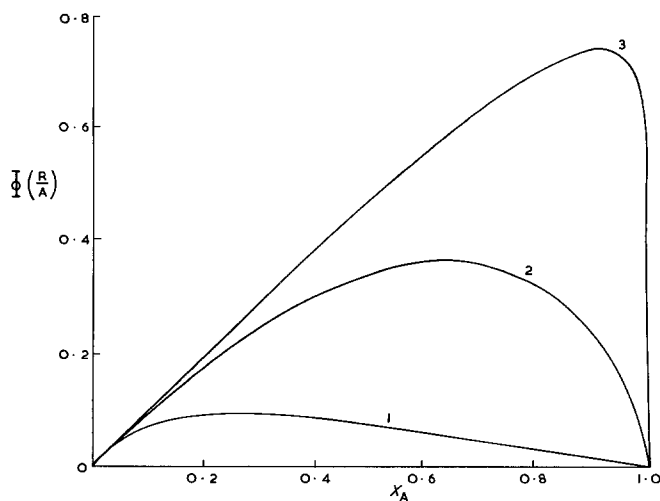


Fig. 2. Plots of fractional yield $\phi(R/A)$ as a function of X_A according to Equations 13 and 14. 1, $\lambda = 8$; 2, $\lambda = 1$; 3, $\lambda = 0.125$.

It will be apparent that, provided assumption 4 holds, Equations 8, 13 and 14 apply equally to galvanostatic and potentiostatic conditions (except that in the latter case k_A^0 and k_R^0 are replaced by k_A and k_R , see Equation 12). Figure 2 shows plots of $\phi(R/A)$ as a function of X_A for a number of values of the rate constant ratio λ .

The time dependent solutions of Equations 1-3 can also be obtained. Defining dimensionless parameters related to time

$$T_1 = \frac{It}{nFVC_{A,0}} \quad (15)$$

for galvanostatic experiments and

$$T_2 = \frac{\Omega k_A t}{V} \quad (16)$$

for potentiostatic experiments, we obtain solving Equations 1 and 2 for the latter case the known results

$$\phi\left(\frac{R}{A}\right) = \frac{1}{1-\lambda} [\exp(-\lambda T_2) - \exp(-T_2)] \quad (17)$$

with the special case

$$\phi\left(\frac{R}{A}\right) = T_2 \exp(-T_2) \quad (18)$$

for $\lambda = 1$. For galvanostatic conditions we combine Equations 1-3 to give

$$\frac{dC_R}{dt} + 2 \frac{dC_A}{dt} = -\frac{I}{nFV} \quad (19)$$

so that, with the generalization of Equation 9 to

$$C_R = 0, C_A = C_{A,0} \quad t = 0 \quad (20)$$

we obtain

$$\phi\left(\frac{R}{A}\right) = 2X_A - T_1 \quad (21)$$

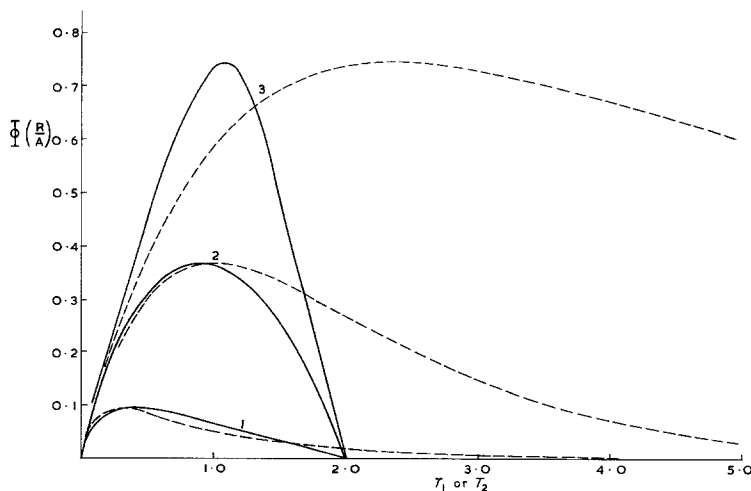


Fig. 3. Plots of fractional yield $\phi(R/A)$ as a function of parameters T_1 (galvanostatic conditions: Equations 22 and 23) and T_2 (potentiostatic conditions: Equations 17 and 18). — galvanostatic, --- potentiostatic. 1, $\lambda = 8$; 2, $\lambda = 1$; 3, $\lambda = 0.125$.

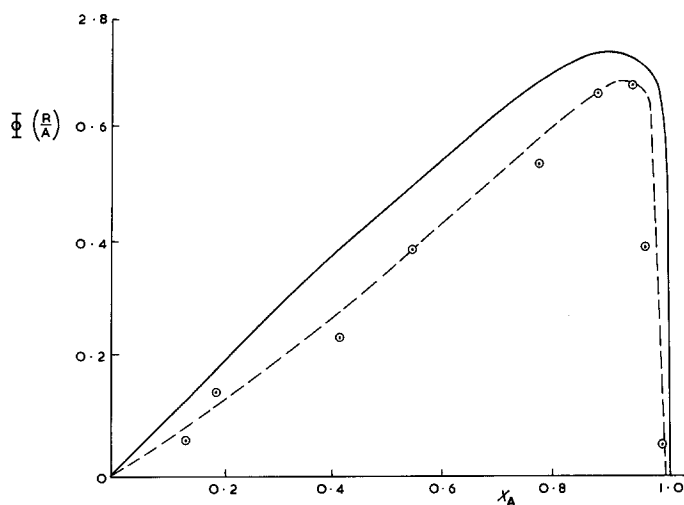


Fig. 4. Comparison of theoretical time independent plot for $\lambda = 0.125$ with an experimental curve under galvanostatic conditions. Aqueous phase; $1.5 \text{ mol dm}^{-3} \text{ CH}_3\text{COOH}$, $1.5 \text{ mol dm}^{-3} \text{ CH}_3\text{COONa}$, saturated with Na_2SO_4 , $0.1 \text{ mol dm}^{-3} \text{ Bu}_4\text{NHSO}_4$. Organic phase: 0.1 mol dm^{-3} 1,4-dimethoxybenzene in CH_2Cl_2 . Rotation speed = 150 rpm. Current density = 15.7 mA cm^{-2} .

The fractional yield of product R as a function of T_1 is obtained directly by combining Equation 21 with Equation 13 and with Equation 14 for the special case $\lambda = 1$:

$$\phi\left(\frac{R}{A}\right) = \frac{1}{1-\lambda} [(1-X_A)^\lambda - (1-X_A)] = 2X_A - T_1 \quad (22)$$

$$\phi\left(\frac{R}{A}\right) = (X_A - 1) \ln(1 - X_A) = 2X_A - T_1 \quad (23)$$

Figure 3 shows plots of the fractional yield of R for various values of λ both for potentiostatic (Equations 17 and 18) and galvanostatic (Equations 22 and 23) conditions, the data being plotted against the parameters T_2 and T_1 respectively. It can be seen that whereas the maximum yields achieved do not depend markedly on the manner of operation, the shape of the plots are highly dependent on the nature of the control variable especially for low values of λ .

4. Results and discussion

Figure 4 gives a comparison of the theoretical time independent plot for $\lambda = 0.125$ with an experimental result for a galvanostatic synthesis using conditions which meet as closely as possible the requirements of the model used. It is evident that whereas the oxidation broadly fits the scheme of a series reaction

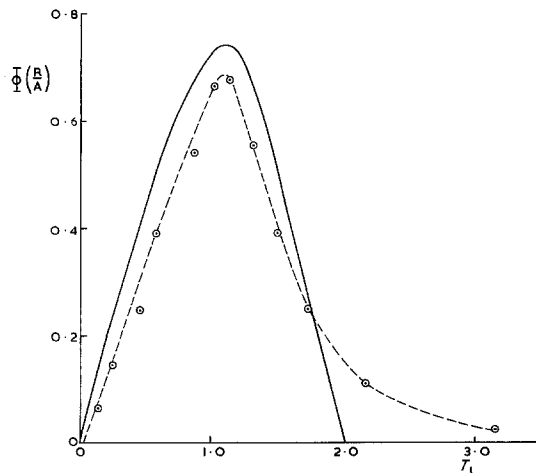


Fig. 5. Comparison of theoretical and experimental curves for galvanostatic conditions $\lambda = 0.125$. Fractional yield $\phi(R/A)$ versus T_1 . Experimental conditions as in Fig. 4.

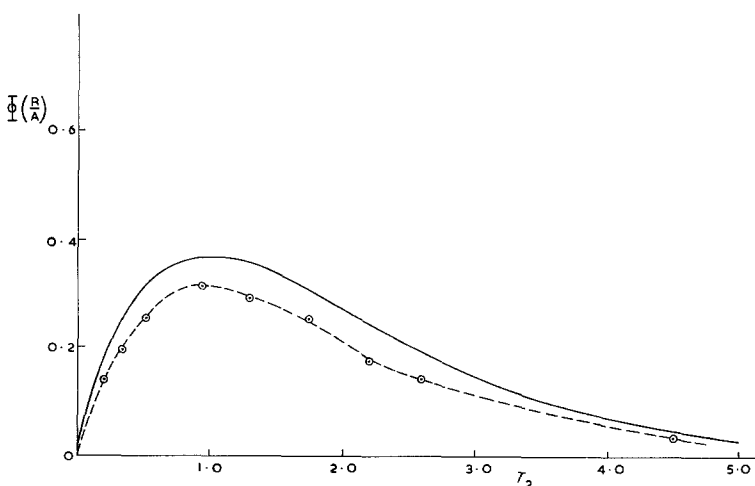


Fig. 6. Comparison of theoretical and experimental curves for potentiostatic conditions $\lambda = 1$. --- experimental curve, — theoretical curve. Aqueous phase: $1.5 \text{ mol dm}^{-3} \text{ CH}_3\text{COOH}$, $1.5 \text{ mol dm}^{-3} \text{ CH}_3\text{COONa}$ saturated with Na_2SO_4 , $0.3 \text{ mol dm}^{-3} \text{ Bu}_4\text{NHSO}_4$. Organic phase; 10 mmol 1,4-dimethoxybenzene in CH_2Cl_2 . Rotation speed 10 rpm . Potential 150 mV versus SCE.

(b) (a closer fit could be obtained by adjusting λ) there are nevertheless significant differences between the observed and predicted behaviour especially in the curvature of the plots at $X_A < 0.85$. These differences are brought out more clearly in plots against the dimensionless parameter T_1 , Fig. 5: the maxima are too sharp to be accounted for in terms of the simple model. Further work is clearly required to investigate: (i) the effects of lifting the restriction of assumption 4; (ii) the inclusion of the effects of mass transfer through the stagnant sub-layer (iii) the effect of the preferential adsorption of substrate or product on the $\phi(R/A)$ plots. The marked deviation between the experimental and predicted results at high T_1 is clearly due to the oxidation of water and/or acetate anion in a parallel reaction which becomes increasingly important as the substrate (I) and product (II) are consumed. It should be noted that the potential of the electrode/solution interface must rise under galvanostatic conditions (with the restriction of assumption 4 it is possible to derive results which do not explicitly include this parameter).

The marked difference between galvanostatic and potentiostatic syntheses can be seen by comparing Figs. 5 and 6. The particular potentiostatic oxidation illustrated was carried out on the mass transport limited current plateau for the oxidation of both the substrate and product, Fig. 1, which satisfies the condition

$$k_A \simeq k_R = k_m \text{ (i.e., } \lambda = 1 \text{)} \quad (24)$$

in view of the similarity of the dimensions of the two species. In plotting the experimental data the parameter T_2 was determined from the position of the maximum (using Equation 18) rather than from Equation 16 as the exact value of k_m is not known. Comparison of the experimental and predicted data in these figures shows that the major differences between the potentiostatic and galvanostatic mode of operation can be adequately explained using simple reaction engineering models.

5. Conclusions

It has been shown that the models of chemical reaction engineering can be extended to cover galvanostatic operation. The particular reaction used to test the performance of the thin film contactor cell, the anodic acetoxylation of 1,4-dimethoxybenzene, has been shown to conform broadly with a series (consecutive) reaction. Plots of the fractional yields as a function of conversion or of time both under potentiostatic and under galvanostatic conditions can be used as diagnostic criteria of the reaction mechanism. Although the experimental results conform in outline with the simple model proposed, it is evident that this model requires considerable elaboration.

It has been shown that the maximum yield obtained in this reaction is nearly independent of the mode of operation; the maxima (on time dependent plots) are broader for potentiostatic than for galvanostatic conditions, so that timing is less critical for such batch syntheses in potentiostatic

experiments. The time independent plots show that high selectivities can be obtained up to relatively high conversions for this test reaction.

References

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