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Electrosynthesis in systems of two immiscible liquids and a phase transfer catalyst
III. Characterisation of thin film contactor cells

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An electrochemical version of a thin film contactor, based on a vertical rotating disc electrode, is described and applied to a two-phase electrolysis, aromatic substitution using phase transfer catalysis to supply the nucleophile. A simple model is used to develop a theoretical description of the cell and the resulting equations have been tested using the acetoxylation of 1,4-dimethoxybenzene as the anode reaction.

Glossary

a	radius of electrode (cm)
C	concentration (mol cm^{-3})
C^0	concentration at the surface of the electrode (mol cm^{-3})
C_i	concentration in the bulk organic phase (mol cm^{-3})
C_f	concentration in the mobile part of the film at $\theta = \pi$
E	electrode potential with respect to any convenient reference electrode (V)
E_{app}	electrode potential applied to the film (with respect to any convenient reference electrode) (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 (V C K^{-1} mol^{-1})
r	radial dimension of the film (cm)
T	temperature (K)
z	axial dimension (cm)
z_1	thickness of the stagnant region in the film (cm)
$z_{A,B,etc}$	no. of electrons
θ	radial position of the film (radians)
β	electrochemical transfer coefficient
ω	rotation rate (radians s^{-1})
ρ	resistivity of the film (Ω cm)

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1. Introduction

Electrosynthetic reactions in multiphase media (specifically anodic aromatic substitutions [1–4]) have been carried out using dispersions of an organic solvent (usually methylene chloride) in aqueous media. Current flow takes place mainly through the relatively conducting aqueous phase (thereby lowering power costs) while the synthetic reactions have been assumed to be confined to the organic phase; the function of the phase transfer catalyst is to transfer with anions into the organic phase both to confer adequate conductivity to this phase and to provide the coupling agent (e.g., CN^- or CH_3COO^-) for the intermediates generated from the aromatic substrates.

These reactions have normally been carried out in batch reactors using the intense stirring provided by Ultra-Turrax stirrers. The investigation of the mode of operation of anodes in two-phase electrolysis [5–7] has sought to answer the questions: (i) whether the anodes are covered by a film of the organic phase, (ii) whether the electrodes are contacted by a stream of droplets or indeed (iii) whether substrate is transferred to the electrode from droplets? Using the oxidation of ferrocene as a test reaction it has been concluded that (ii) is the likely explanation provided the droplets are sufficiently large. However, these oxidations have been carried out in the absence of phase transfer catalysts and the conditions therefore differ widely from those used in the synthetic experiments: in particular, reaction must be favoured at the edges of impacting droplets when no phase transfer agent is used.

It is, however, possible to design cells, Fig. 1, in which the anode is necessarily covered by a thin film (provided that there is a sufficiently high heat of wetting of the electrode by the organic phase). The two phases are now discrete but in other respects the design meets the same criteria as those required in synthetic reactions in dispersed phases: in particular, current flow is dominantly in the aqueous and the electrode reaction in the organic phase. This design of cell is, in fact, an application to

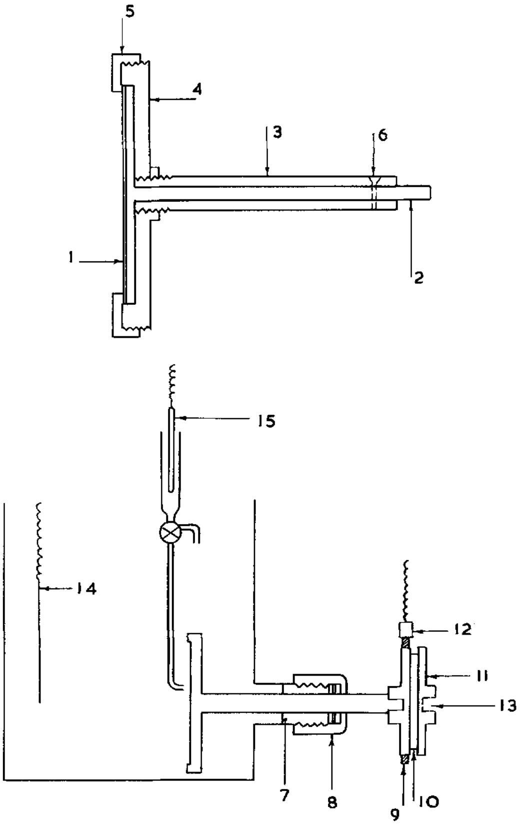


Fig. 1. Diagram of thin film contactor cell. 1, platinum disc; 2, brass back plate and shaft; 3, PTFE sleeve; 4, PTFE insulator; 5, PTFE holding ring; 6, countersunk screw holding PTFE sleeve; 7, PTFE bush; 8, quickfit screw and cap with PTFE washer and silicon rubber seal; 9, bronze slip ring; 10, rubber pad; 11, flexible coupling; 12, carbon brush; 13, to motor shaft; 14, stainless steel mesh counter electrode; 15, saturated calomel reference electrode.

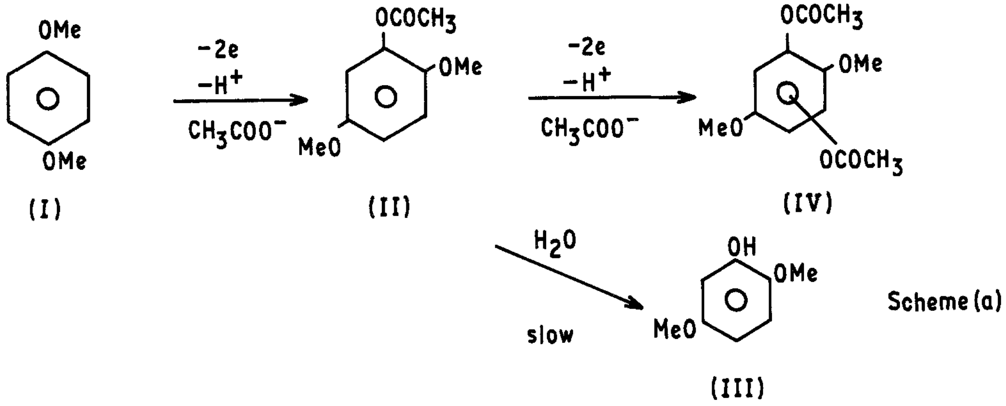
electrochemical processing of Thin Film Contactors (widely used in Chemical Engineering in Solvent Extraction systems, see e.g., [8]).

In this paper, we describe an investigation into the characterisation of the reactor while in the succeeding paper [9] we report work on electrosynthesis using this device.

2. Experimental procedure

The major part of the experiments described here was carried out using a 5.8 cm diameter platinum disc electrode half immersed in methylene chloride (lower phase) while the upper half was in the aqueous phase. Electrical contact was made externally to the shaft which passed through polytetrafluoroethylene (PTFE) compression seals in the glass body. The electrode was sealed into PTFE so that only the side opposite a stainless steel counter electrode served as the anode. The electrode could be rotated at rates between 1 and 250 rpm using variable speed motors. The Luggin capillary of the reference electrode was positioned in the aqueous phase close to the film on the anode.

The cells normally contained 250 cm^3 of both phases. The aqueous phase usually consisted of 1.4 mol dm^{-3} sodium acetate and 1.4 mol dm^{-3} acetic acid saturated with sodium sulphate; tetrabutylammonium hydrogen sulphate (the phase transfer catalyst) was added to the aqueous phase and, under the conditions of the experiment, ~ 60% of the cation was transferred (with acetate as the counter ion) into the organic phase. The acetoxylation of 1,4-dimethoxybenzene(I) to 2,5-dimethoxyphenylacetate(II):



Scheme (a)

was chosen as the test reaction both for the characterisation of the reactor and for the synthetic experiments [9]. Substrates (I) and (II) were added directly to the organic phase. This acetoxylation reaction is convenient since there is only a single primary reaction product, (II), which is relatively stable to solvolysis (less than 1% of phenol (III) is formed under the conditions used here).

Experiments reported here were carried out at ~ 300 K at constant potential.

3. Analysis of a simple model of the thin film contactor electrode

In this section we develop an analysis of the performance of the electrode using a highly simplified model. We assume that (see Figs. 2–4):

(i) The electrode region, $0 < r < a$, $0 < \theta < \pi$ is covered by a uniform film of liquid lying in the range $0 < z < z_2$ where r is the radial dimension (cm), a is the radius of the electrode (cm), z is the dimension perpendicular to the electrode (cm), z_2 is the thickness of the film (cm) and θ is the angle of emergence of the film from the reservoir of methylene chloride (rads). The thickness of the film is independent of θ and the rate of rotation ω (rads s^{-1}).

(ii) Within the film, the region $0 < z < z_1$ consists of a stagnant layer and its thickness z_1 is independent of r, θ and ω.

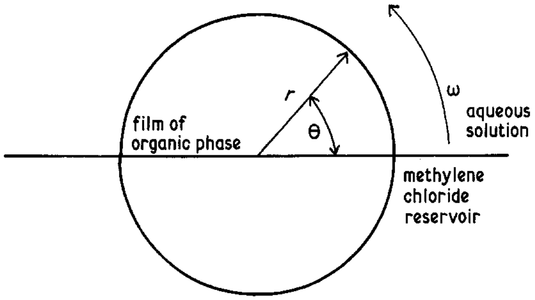


Fig. 2. Coordinate system for the analysis of the thin film contactor electrode.

(iii) The concentration of substrate in the region $z_1 < z < z_2$ is independent of z i.e., this layer of the film is well mixed and the velocity of the film in this region is independent of θ.

(iv) Concentration changes in the well stirred reservoir of the methylene chloride phase in the lower half of the cell are negligible.

(v) Ion transfer at the methylene chloride/aqueous solution interface is rapid.

(vi) The substrate is oxidized in a single first order rate determining reaction; the concentration of all other species involved in the reaction may be neglected.

(vii) Mass transfer through the stagnant layer of methylene chloride ($0 < z < z_1$) is governed by a mass transfer coefficient, k_m (cm s^{-1}); the value of k_m is independent of r and θ.

It will be shown that this very simple model is sufficient to account for the behaviour of the electrode under limiting conditions. However, it is clear that the model will have to be extended in order to account for the behaviour over a wider range of conditions (see below). Using this plug flow model for the film on the disc electrode and considering the accumulation of substrate A (1,4-dimethoxybenzene) in the volume element in the well stirred part of the film, see Fig. 4 and both the influx and outflux from this element due to convection and the outflux to the electrode via the stagnant layer, we can write

$$2r\,2\mathrm{d}\theta\,\mathrm{d}r\,(z_2-z_1)\,\frac{\partial C_A}{\partial t} = (z_2-z_1)\,\mathrm{d}r 2\pi\omega r\left(C_A - \frac{\partial C_A}{\partial \theta}\partial\theta\right)$$
$$-(z_2-z_1)\,\mathrm{d}r\,2\pi r\omega\left(C_A + \frac{\partial C_A}{\partial \theta}\mathrm{d}\theta\right) - 2\pi r\,2\mathrm{d}\theta\mathrm{d}r\,k_m\,(C_A - C_A^0) \quad (1)$$

where C_A^0 is the concentration of A at the surface of the disc. Equation 1 reduces to

$$\frac{\partial C_A}{\partial t} = -\omega\frac{\partial C_A}{\partial \theta} - \frac{k_m}{z_2 - z_1}(C_A - C_A^0) \quad (2)$$

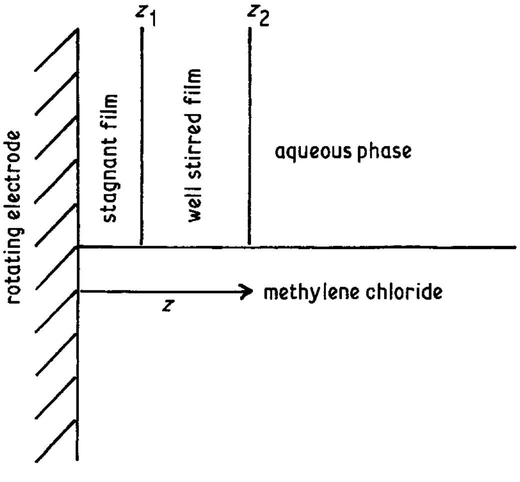


Fig. 3. Coordinate system for the stagnant and well mixed region of the thin film.

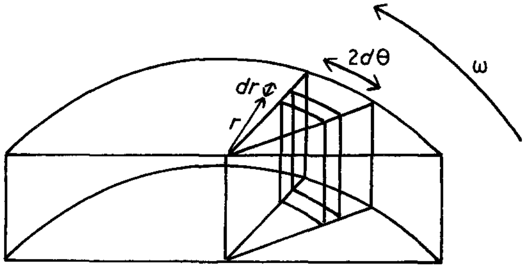


Fig. 4. Coordinate system used in the derivation of Equation 1.

In the steady state we have

$$\omega \frac{\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}\theta} = -\frac{k_{\mathrm{m}}}{z_2 - z_1}(C_{\mathrm{A}} - C_{\mathrm{A}}^{0}) \tag{3}$$

Assumption (vi) gives for the rate of the electrode reaction

$$k_{\mathrm{A}}^{0} C_{\mathrm{A}}^{0} \exp\left(\frac{\beta_{\mathrm{A}} z_{\mathrm{A}} E F}{RT}\right) = k_{\mathrm{m}}(C_{\mathrm{A}} - C_{\mathrm{A}}^{0}) \tag{4}$$

where β_{A} is the transfer coefficient of the anodic reaction in which z_{A} electrons are transferred (we assume $z_{\mathrm{A}} = 1$) E is the electrode potential on any convenient scale (V) and k_{A}^{0} is the rate constant of the electron transfer process when $E = 0$ (cm s^{-1}). We also need to take into account the voltage drop in the film and write

$$E = E_{\mathrm{app}} - n_{\mathrm{A}} F k_{\mathrm{m}} \rho z_2 (C_{\mathrm{A}} - C_{\mathrm{A}}^{0}) \tag{5}$$

where E_{app} is the voltage applied across the film (V) (with respect to the chosen reference electrode), ρ is the resistivity of the film (Ω cm) and $n_{\mathrm{A}}F$ is the charge transferred per mole of substrate (C mol^{-1}). Defining

$$\alpha = \frac{k_{\mathrm{m}}}{k_{\mathrm{A}}^{0} \exp \dfrac{\beta_{\mathrm{A}} z_{\mathrm{A}} E_{\mathrm{app}} F}{RT}} \tag{6}$$

$$\gamma = \frac{\beta_{\mathrm{A}} n_{\mathrm{A}} F^2 k_{\mathrm{m}} \rho z_2}{RT} \tag{7}$$

we have to solve

$$C_{\mathrm{A}}^{0} \exp[-\gamma(C_{\mathrm{A}} - C_{\mathrm{A}}^{0})] = \alpha(C_{\mathrm{A}} - C_{\mathrm{A}}^{0}) \tag{8}$$

and integrate (1) over the range $0 < \theta < \pi$. The total current is

$$I = \frac{n_{\mathrm{A}} F a^2 \omega}{2}(z_2 - z_1)(C_{\mathrm{A,i}} - C_{\mathrm{A,f}}) \tag{9}$$

where $C_{\mathrm{A,i}}$ is the concentration in the reservoir of methylene chloride (mol cm^{-3}) and $C_{\mathrm{A,f}}$ is the concentration in the mobile part of the film at the outlet $\theta = \pi$ (mol cm^{-3}).

Equation 8 has no general analytic solution but certain approximations give useful results for limiting conditions. For example, for low film resistivities and substrate concentrations, $\gamma(C_{\mathrm{A}} - C_{\mathrm{A}}^{0})$ and γC_{A} are small so that we obtain from 8

$$C_{\mathrm{A}} - C_{\mathrm{A}}^{0} \simeq \frac{(1 - \gamma C_{\mathrm{A}})C_{\mathrm{A}}}{1 - \gamma C_{\mathrm{A}} + \alpha} \simeq \frac{C_{\mathrm{A}}}{1 + \alpha} \tag{10}$$

Combining Equation 10 with Equation 3

$$C_{A,f} = C_{A,i} \exp - \left(\frac{\pi k_m}{\omega (z_2 - z_1)(1 + \alpha)} \right) \tag{11}$$

giving

$$I = \frac{n_A F a^2 \omega (z_2 - z_1) C_{A,i}}{2} \left[1 - \exp\left(\frac{-\pi k_m}{\omega (z_2 - z_1)(1 + \alpha)} \right) \right] \tag{12}$$

A further useful approximation can be obtained which will apply to the operation of the electrode at high substrate concentrations and rotation rates, low electrolyte concentrations and current densities such that there are appreciable concentration changes across the stagnant boundary layer. This is one set of conditions which will normally be used in synthesis. Provided that C_A^0 is close to $C_A/2$ we write

$$C_A^0 = \frac{C_A}{2} + \Delta C_A \tag{13}$$

where ΔC_A is small (but see further below) and, in any event lies in the range given by $C_A/2 - \Delta C_A < C_A^0 < C_A/2 + \Delta C_A$. Equation 8 then becomes

$$\left(\frac{C_A}{2} + \Delta C_A \right) \exp \left[-\gamma \left(\frac{C_A}{2} - \Delta C_A \right) \right] = \alpha \left(\frac{C_A}{2} - \Delta C_A \right) \tag{14}$$

Taking logarithms and subtracting $\ln (C_A/2)$ from both sides of the resulting equation

$$\ln \left(1 + \frac{2\Delta C_A}{C_A} \right) - \gamma \left(\frac{C_A}{2} - \Delta C_A \right) = \ln \alpha + \ln \left(1 - \frac{2\Delta C_A}{C_A} \right) \tag{15}$$

As $2\Delta C_A/C_A$ is small we expand the logarithmic terms and obtain*

$$\Delta C_A = \frac{\dfrac{C_A}{2} + \dfrac{1}{\gamma} \ln \alpha}{1 + \dfrac{4}{\gamma C_A}} \tag{16}$$

Therefore

$$C_A - C_A^0 = \frac{C_A}{2} - \frac{\dfrac{C_A}{2} + \dfrac{1}{\gamma} \ln \alpha}{1 + \dfrac{4}{\gamma C_A}} \tag{17}$$

Integrating Equation 3 with Equation 17 between 0 and π and $C_{A,i}$ and $C_{A,f}$ we obtain

$$4 \ln \frac{C_{A,f}}{C_{A,i}} + \gamma (C_{A,f} - C_{A,i}) = - \frac{\pi k_m (2 - \ln \alpha)}{2\omega (z_2 - z_1)} \tag{18}$$

For small concentration changes in the direction of rotation, (high rotation rates)

$$C_{A,f} - C_{A,i} = \frac{\pi k_m (2 - \ln \alpha)}{2\omega (4 + \gamma C_{A,i})(z_2 - z_1)} \tag{19}$$

Combining Equation 19 with Equation 9 we obtain

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* We note that the next non-zero term in the expansion is $16(\Delta C_A)^3/3\gamma C_A^3$ so that Equation 16 holds over an appreciable range of ΔC_A.

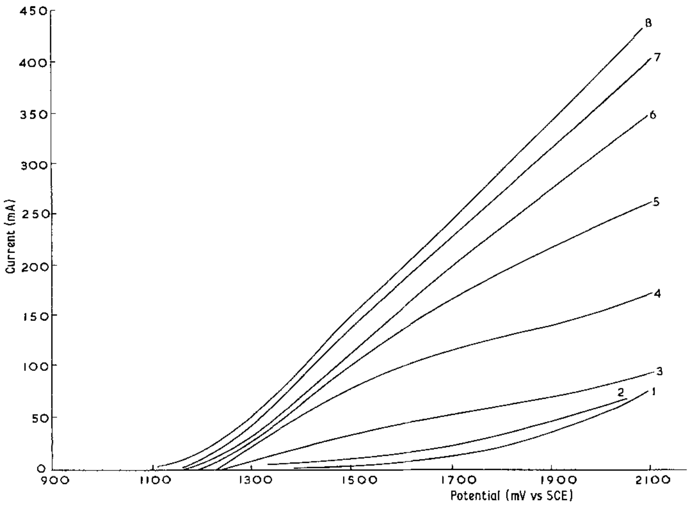

Fig. 5. Polarization curves for p-dimethoxybenzene in methylene chloride taken at the following concentrations. 1, Without substrate; 2, 0.1 mmol dm^{-3}, 3, 5.5 mmol dm^{-3}; 4, 10 mmol dm^{-3}; 5, 20 mmol dm^{-3}; 6, 30 mmol dm^{-3}; 7, 50 mmol dm^{-3}; 8, 100 mmol dm^{-3}. Aqueous phase; 1.4 mol dm^{-3} CH_3COOH, 1.4 mol dm^{-3} CH_3COONa, saturated with Na_2SO_4, 0.1 mol dm^{-3} Bu_4NHSO_4, rotation speed 100 rpm.

$$I \simeq \frac{\pi n_A F a^2 (2 - \ln \alpha) k_m C_{A,i}}{2(4 + \gamma C_{A,i})} \tag{20}$$

which can be written in the form

$$\gamma = \frac{8I}{\pi n_A F a^2 C_{A,i}} = \left(2 - \ln \frac{k_m}{k_A^0}\right) k_m + \frac{\beta_A n_A F k_m}{RT}\left(E_{app} - \frac{2I\rho z_2}{\pi a^2}\right) \tag{21}$$

4. Results and discussion

Figure 5 shows that with a fixed rotation rate and Bu_4N^+ concentration the polarization curves approach the limiting form of ohmic control (due to current flow through the film) with increasing concentration of substrate. This follows from Equation 5 for $E \ll E_{app}$ when

$$\frac{2I}{\pi a^2} \simeq n_A F k_m (C_A - C_A^0) = \frac{E_{app}}{\rho z_2} \tag{22}$$

Figure 6 shows the effect of electrolyte concentration on the ohmically controlled polarization plot. The film resistances derived are directly proportional to the independently determined bulk resistivities

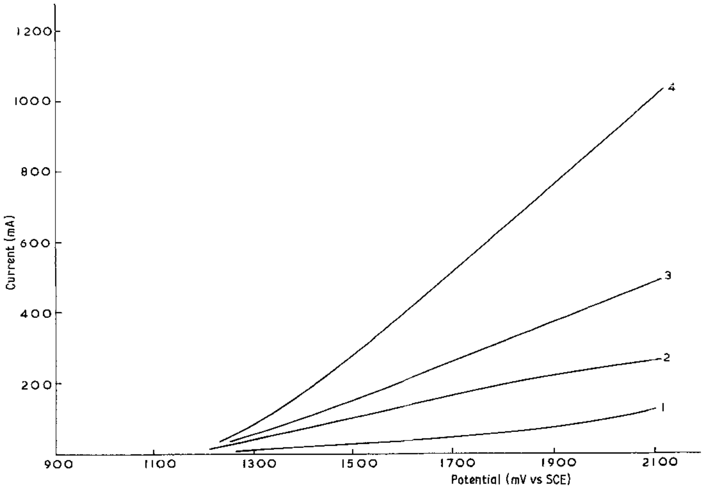

Fig. 6. The effect of Bu_4NHSO_4 concentration in the organic phase on the ohmically controlled polarization plots. 0.1 mol dm^{-3} p-dimethoxybenzene. 1, 0.01 mol dm^{-3} Bu_4N^+; 2, 0.05 mol dm^{-3} Bu_4N^+; 3, 0.1 mol dm^{-3} Bu_4N^+; 4, 0.3 mol dm^{-3} Bu_4N^+. Aqueous phase, 1.4 mol dm^{-3} CH_3COOH, 1.4 mol dm^{-3} CH_3COONa, saturated with Na_2SO_4. Rotation speed 100 rpm.

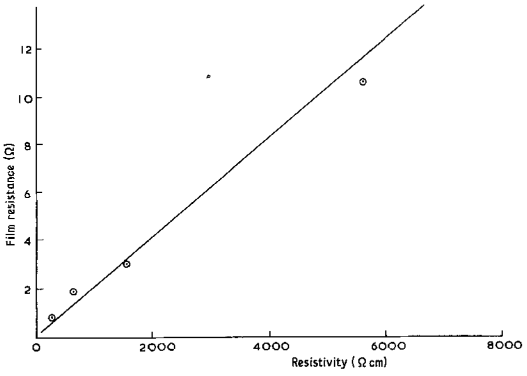

Fig. 7. The plots of film resistances derived from Fig. 6 against the independently determined resistivity of the organic phase.

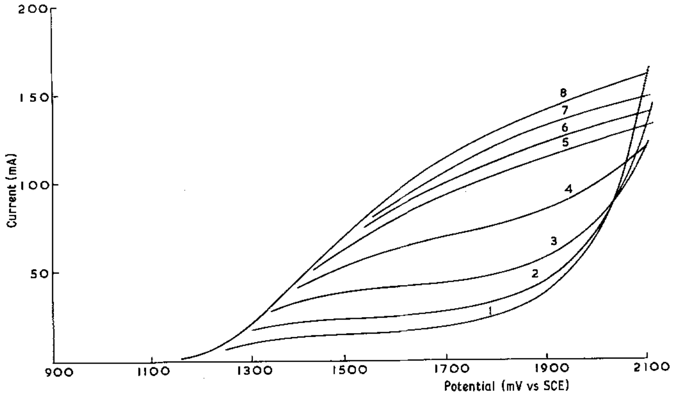

Fig. 8. The effect of rotation speed on the polarization plots. 1, 1 rpm; 2, 5 rpm; 3, 10 rpm; 4, 20 rpm; 5, 40 rpm; 6, 60 rpm; 7, 80 rpm; 8, 100 rpm. Aqueous phase; 1.4 mol dm^{-3} CH_3COOH, 1.4 mol dm^{-3} CH_3COONa, 0.05 mol dm^{-3} Bu_4NHSO_4 saturated with Na_2SO_4. Organic phase; 10 mmol dm^{-3} p-dimethoxybenzene.

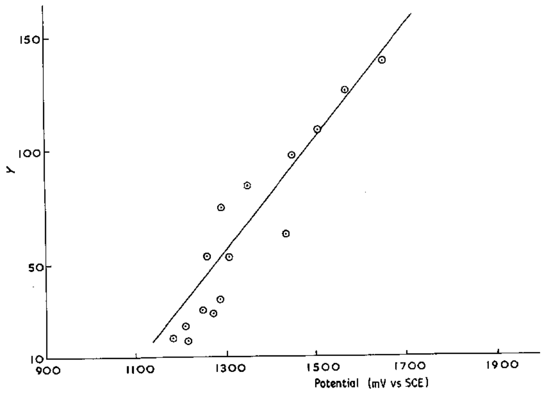

Fig. 9. Collapse of polarization data according to Equation 21, where $E = E_{app} - (2I\rho z_2/\pi a^2)$.

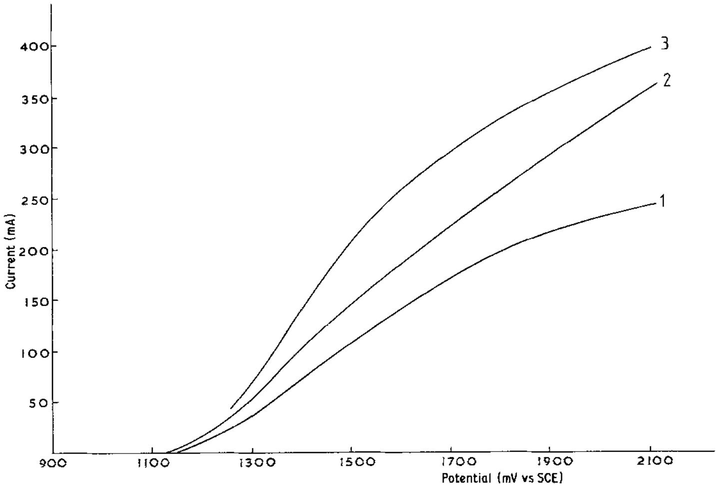

Fig. 10. Polarization data at high substrate concentrations and film resistivities. Aqueous phase; 1.4 mol dm^{-3} CH_3COOH, 1.4 mol dm^{-3} saturated with Na_2SO_4. Organic phase; 0.05 mol dm^{-3} Bu_4NHSO_4, 0.1 mol dm^{-3} p-dimethoxybenzene. 1, 80 rpm; 2, 40 rpm; 3, 8 rpm.

for the CH_2Cl_2 phase, Fig. 7, and the film thicknesses derived ($z_2 \simeq 0.05$ cm) are reasonable. There is no evidence for any additional resistance due to ion transfer at the methylene chloride/aqueous solution interface [10].

At low substrate concentrations Fig. 5 shows that the behaviour is close to that of a polarization curve in a single phase. Under these conditions Fig. 8 shows that at low ω the currents are proportional to the rotation speed while at high ω they approach a limit as is predicted by Equation 12.

The collapse of the data at high substrate concentrations and rotation rates according to Equation 21 is illustrated in Fig. 9. It is evident that the simple model proposed also holds under these limiting conditions. However, under conditions differing from these limits, measurements of the polarization curves show that further factors need to be taken into account in the modelling. For example, at high substrate concentrations, when the oxidation is far from mass transfer control, Fig. 10 shows that the currents increase with decreasing rotation rate and it is evident that changes in the film thickness with ω (and equally with θ) must be included in the further development of models of the electrode. Such modelling will also have to take into account rippling in the film.

5. Conclusions

It has been shown that an electrochemical thin film contactor electrode may be used for anodic two-phase oxidations where the organic phase is in the form of a thin film on the surface of the electrode. This electrode may be characterized by using voltammetric techniques. A simple model of a uniform film in contact with a stagnant layer and with plug flow in the direction of rotation has been shown to give a reasonable interpretation of the results under limiting conditions (low substrate and high electrolyte concentrations and low rotation rates; high substrate and low electrolyte concentrations and high rotation rates). However, it is evident that the model requires considerable elaboration to account for measurements under other than these simple limiting conditions.

In view of the demonstration of the role of a thin film of the organic phase on the electrode in these cells, it is likely that a similar film is also present when other cell and electrode configurations are used e.g., mesh electrodes with a dispersed organic phase.

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