JOURNAL OF APPLIED ELECTROCHEMISTRY **20** (1990) 793–797

# An electrochemical method for the measurement of the heterogeneous kinetics of the uptake of a reactive dye by a cotton cloth

R. G. COMPTON, M. WILSON

*Physical Chemistry Laboratory, South Parks Road, Oxford University, Oxford OX1 3QZ, Great Britain*

Received 29 September 1989; revised 15 December 1989

The heterogeneous kinetics of the reaction between a dichlorotriazinyl reactive anthraquinone dye and a cotton cloth under alkaline conditions are investigated using a novel electrochemical technique based on a channel electrode flow cell. The reaction is found to be first order in the surface concentration of the dye and a rate constant is reported. The general applicability of the method to the study of the kinetics of binding of dyestuffs is emphasized.

## 1. Introduction

We have recently [1–4] introduced a novel, general method for the investigation of the heterogeneous kinetics of processes taking place at the solid/liquid interface. The method involves pumping solution through a thermostated cell, under laminar flow conditions, along a rectangular duct (Fig. 1) and over the substrate which forms part of one wall of the channel. An appropriate electrochemical sensor (the 'detector electrode') is located immediately downstream of the substrate and this monitors, either potentiometrically or amperometrically, the amount of reactant which survives the passage over the substrate. Thus the current flowing, or potential established, at this electrode provides an indication of how much reaction has taken place at the substrate surface. The well-defined flow [5] permits the precise modelling of convective-diffusion within the cell, provided that a heterogeneous kinetic rate law (to specify a boundary condition at the reacting interface) and a chemical model of any solution processes are defined. In this way the detector electrode response and its solution flow rate dependence can be calculated. Comparison of theory and experiment allows selection between candidate rate equations, thus giving mechanistic information. Moreover, since the flow cell can provide high rates of mass transport to the reacting interface it is possible to probe rates of surface processes that would be too fast to measure with other experimental methodologies.

In our previous work we have applied the channel flow cell methodology to the reaction of $H^+$ with calcite [1, 3, 4] and to the bleaching of a coloured cloth with aqueous bromine [1, 2]. In this paper we extend the range of applications and demonstrate that the kinetics of the rate of uptake of reactive dyes by fabrics is opened up to quantitative study by this experimental approach. In particular we consider the reaction of the dichlorotriazinyl dye shown in Fig. 2 with a cotton surface under alkaline conditions. The reaction involves the nucleophilic displacement of chloride ions by deprotonated OH groups on the cotton as shown in Fig. 3. The anthraquinone moiety in the dye facilitates amperometric detection and the heterogeneous rate law for the dyeing reaction is deduced.

## 2. Experimental details

### 2.1. *The flow cell and flow system*

Experiments were carried out using the flow cell shown in Fig. 4, which is constructed in Perspex. The channel itself is 40 mm long, 6 mm wide and approx. 0.5 mm deep. A precise value for the latter quantity may be deduced from the slope of a plot of transport limited current against (flow rate)$^{1/3}$ obtained from a species of known diffusion coefficient in the absence of any complications due to homogeneous or heterogeneous kinetics (see below). The deeper duct sections at each end of the channel serve to equalise the pressure, and ensure 'plug flow' across the channel width.

A cover plate bears the substrate: in this case a piece of cotton cloth, onto which is deposited, using a rubber based glue, a copper foil electrode. The latter is electroplated with mercury before use by means of a standard protocol [6]. Upstream of the detector electrode is a strip of silver foil which acts as a pseudo-reference electrode. Both electrodes are about 1.5 mm long. The substrate and detector electrode are masked with thin PTFE tape, as shown in Fig. 4, so that once the cell is assembled, the width of the exposed substrate and electrodes is ~4 mm. Since the channel is 6 mm wide, the interface is then well inside the region in which the flow is of a plug nature in the *z*-direction (deviations from plug flow occur over distances of the order of the channel depth). The length of the exposed substrate is typically 4 mm.

The channel is formed by mating the channel unit and cover plate through the application of mechanical pressure. The o-ring around the channel acts as a seal.

0021-891X/90 $03.00 + .12

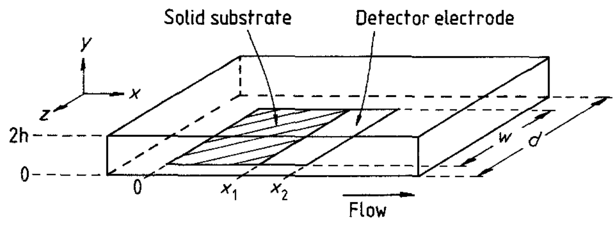

Fig. 1. Schematic flow cell strategy for the investigation of heterogeneous kinetics using the channel electrode flow cell.

Once assembled, the leading edge of the substrate has to be located sufficiently downstream so that Poiseuille flow is fully established. A distance of 1 cm is more than adequate [7].

The flow system into which the cell was plumbed, has been described fully [8] and consisted of a glass reservoir and several metres of 1.5 mm bore PTFE tubing, jacketted with an argon purged tube to prevent the ingress of (electroactive) oxygen. A platinum gauze counter electrode was located immediately downstream of the cell. Connections between the PTFE tubing, the cell, and the counter electrode were formed with silicone rubber tubing. Deoxygenated electrolyte was gravity fed from the reservoir via one of several calibrated glass capillaries capable of a total flow range of $1 \times 10^{-4}$ to $3 \times 10^{-1}\,cm^3\,s^{-1}$. The adjustment of the rate of flow within each range was achieved by varying the height between the reservoir and the tip of the capillary, where the electrolyte ran to waste.

Electrical contact to the working and reference electrodes was facilitated by extending the foils beyond the edge of the cover plate as illustrated in Fig. 4. Thermostating of the experiments was achieved by locating the cell and about 1 m of the preceding tubing within an air–thermostat, allowing temperature control to 25.0 ± 0.1° C.

### 2.2. *Electrochemical instrumentation*

An Oxford Electrodes potentiostat of conventional design was used for all voltammetric measurements and current-voltage curves were recorded on a Gould series 6000 X-Y recorder. Rotating disc experiments were conducted using an Oxford Electrodes rotating–disc assembly and motor controller. This permitted rotation speeds in the range 1–50 Hz to be utilised. The mercury RDE was prepared by electroplating a polished copper disc [6] and was insulated with Teflon.

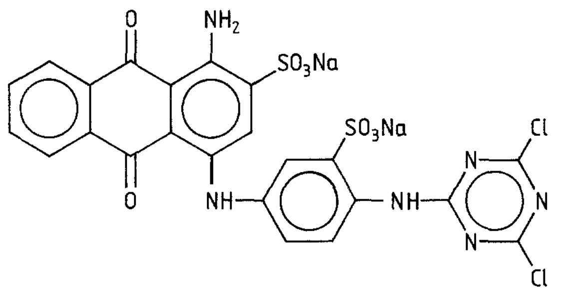

Fig. 2. The structure of the dichlorotriazinyl reactive anthraquinone dye studied.

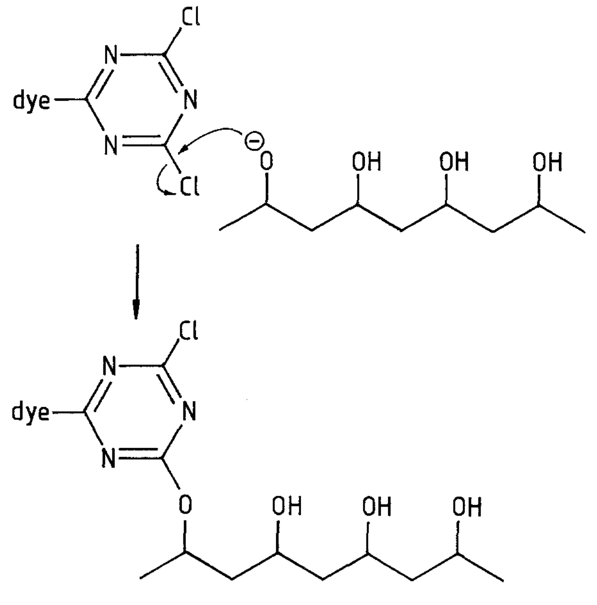

Fig. 3. The schematic reaction of a dichlorotriazinyl dye with a cotton (cellulose) surface.

All potentials were measured against either a saturated calomel electrode or a silver pseudo-reference electrode.

### 2.3. *Materials*

Solutions were made up with triply distilled deionised water (resistivity > $10^7\,\Omega\,cm$). Cotton cloth was scour/bleached unmercerised flat-woven Indian Head cotton supplied by, and the dichlorotriazinyl reactive anthraquinone dye (Fig. 2) prepared by, ICI Colours and Fine Chemicals (Manchester, UK). The latter was supplied as a solid mixed with a phosphate buffer (10% wt/wt buffer/dye) stabiliser. The buffer contained potassium dihydrogen phosphate and sodium hydrogen phosphate and sodium hydrogen phosphate in a 2 : 1 molar ratio. Solutions were typically made up by adding the solid to a 0.1 M solution of (AnalaR) Sodium carbonate to produce solutions of concentrations in the range 0.3–1.0 mM in the dye. The pH of these solutions was approximately 11.2.

## 3. Results and discussion

Preliminary experiments were conducted at a mercury plated rotating disc electrode to establish the behaviour of the dye towards electrochemical reduction. Figure 5 shows a typical current–potential (*I–E*) curve obtained for the reduction of a 1 mM solution of the dye in a 0.1 M $Na_2CO_3$. This is attributable to the one electron

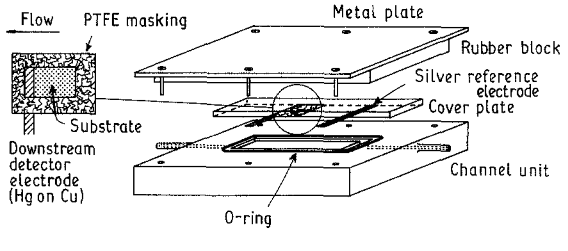

Fig. 4. Perspex channel flow cell for the study of the heterogeneous kinetics of dyeing.

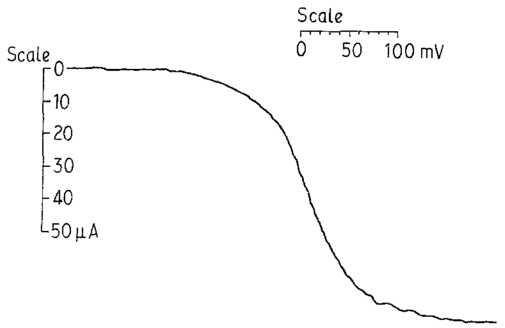

Fig. 5. A typical current–potential curve for the reduction of the dye at a mercury plated rotating disc electrode. The half wave potential occurs at −0.766 V (with respect to SCE).

reduction of the anthraquinone moiety and the limiting current was found to have a rotation speed dependence in agreement with the Levich equation:

$$I_{\mathrm{lim}} = 0.62nFAD^{2/3}v^{-1/6}[A]_0\omega^{1/2} \qquad (1)$$

where $n$ is the number of electrons transferred, $A$ (cm$^2$) is the area of the electrode, $D$ (cm$^2$ s$^{-1}$) is the diffusion coefficient and $[A]_0$ (mol cm$^3$) the bulk concentration, of the electroactive species, $v$ (cm s$^{-1}$) is the kinematic viscosity and $\omega$ (Hz) the rotation speed. The slope of the Levich plot in Fig. 6 enabled the deduction of a value of $3.5 \times 10^{-6}$ cm$^2$ s$^{-1}$ for $D$. This value was found to be essentially unchanged when the dye concentration was reduced to 0.33 mM. This suggested that the dye was largely unaggregated under the conditions studied. This inference was supported by the observation that the size of the diffusion coefficient is almost exactly that predicted, assuming the dye to be unassociated, by the relationship between diffusion coefficient and molecular weight established by Hillson and McKay [8] from a polarographic study of a large number of dyestuffs (see Fig. 7). Diffusion corrected Tafel analysis – a plot of $E$ against $\log_{10}[(I^{-1}) - (I_{\mathrm{lim}}^{-1})]$ as shown in Fig. 8 – gave a slope of 58 mV (decade)$^{-1}$ indicating the reduction to be electrochemically reversible [9].

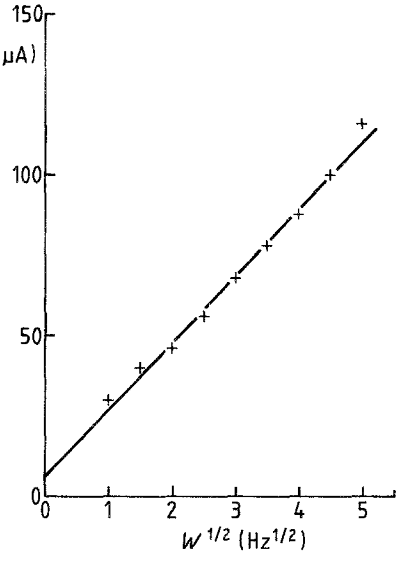

Fig. 6. A Levich plot showing that the limiting current for the reduction of the dye depends on the rotation speed according to Equation 1.

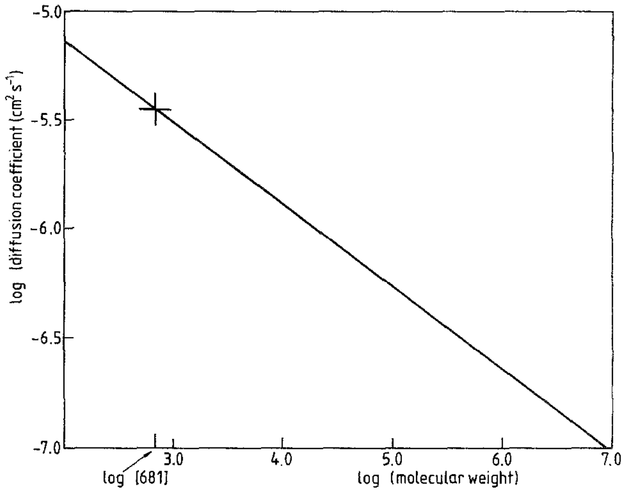

Fig. 7. The measured diffusion coefficient (+) obeys the relationship between diffusion coefficient and molecular weight deduced by Hillson and McKay [8] (depicted by the solid line), if it is assumed that the dye is monomeric.

We consider next the experiments carried out with the channel flow cell. These were again conducted in 0.1 M $Na_2CO_3$ and care was taken to make all kinetic measurements within 10 min of the solution being made up in the light of the known (slow) hydrolysis of the dichlorotriazinyl moiety [10]. Firstly experiments were performed with the cell plumbed into the flow system 'in reverse' so that the dye flowed over the detector electrode before it passed over the cotton cloth. Under these conditions the transport limited current for the reduction of the dye showed the expected cube root dependence on flow rate [5]:

$$I_{\mathrm{lim}} = 1.165FD^{2/3}(\tilde{U}/h)^{1/3}wx_1^{2/3}[A]_0 \qquad (2)$$

where $w$ (cm) is the width and $x_1$ (cm) the length of the electrode, $\tilde{U}$ (cm s$^{-1}$) is the mean solution velocity in

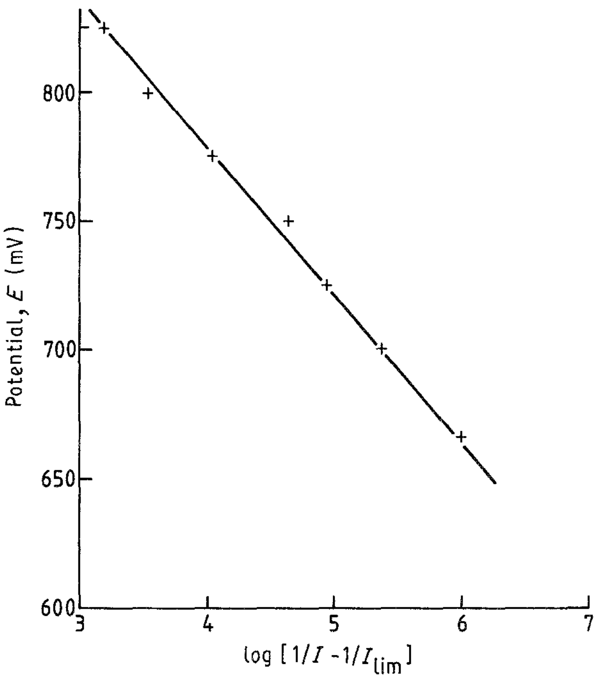

Fig. 8. A diffusion corrected Tafel plot showing the reduction of the dye is electrochemically reversible.

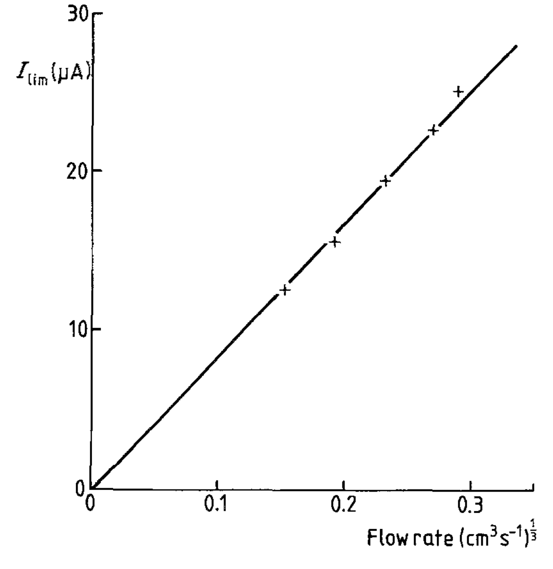

Fig. 9. Limiting current/flow rate data for the reduction of the blue dye obtained by flowing solution over the detector electrode before it passed over the cloth. Good agreement with Equation 2 is evident.

the channel. The latter is related to the volume flow rate, $V_f$, by $V_f = \bar{U} \times 2h \times d$ where $d$ is the width of the channel. This procedure allowed a precise value of the cell depth, ($2h$) to be found since $D$ was known from the rotating disc measurements. Figure 9 shows typical results in the form of a Levich plot.

Figure 10 shows analogous results to Fig. 9, except that the cell orientation has been reversed and the solution flows over the cloth before reaching the detector electrode. The solid line shows the results obtained with the cell in the previous orientation. Clearly there is reaction of the dye at the cloth surface which reduces the amount of dye reaching the electrode in the former case. The ratio of the currents flowing in the two cases at a given flow rate gives a measure of the shielding factor [1, 4],

$$S_f = \frac{\text{Limiting current with cloth upsteam}}{\text{Limiting current with cloth downstream}} \tag{3}$$

We have shown elsewhere [1, 4, 11] that, in the case of first order heterogeneous kinetics at the reacting interface, $S_f$ is a function of the following normalised rate constant:

$$\tilde{k} = k_1(2h^2 x_2 d/3D^2 V_f)^{1/3} \tag{4}$$

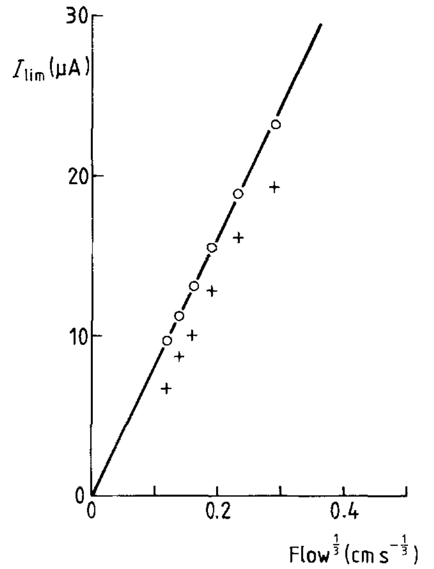

Fig. 10. Limiting current/flow rate data obtained at the detector electrode when the cotton cloth is located upstream (+). The solid line shows the corresponding behaviour when the cell is 'reversed' and the cloth is downstream of the detector.

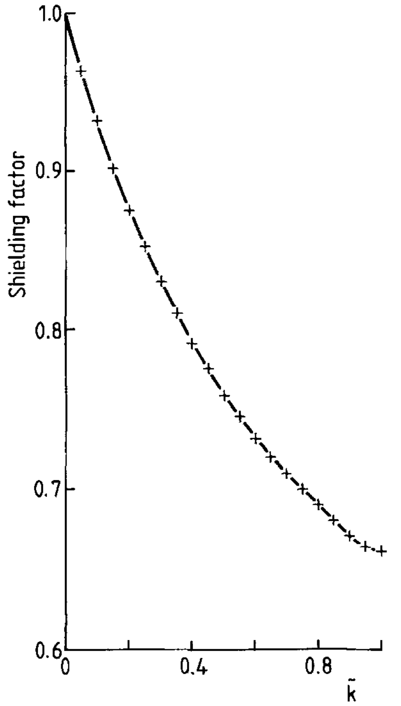

Fig. 11. Theoretical working curve showing the dependence of the shielding factor $S_f$ on $\tilde{k}$.

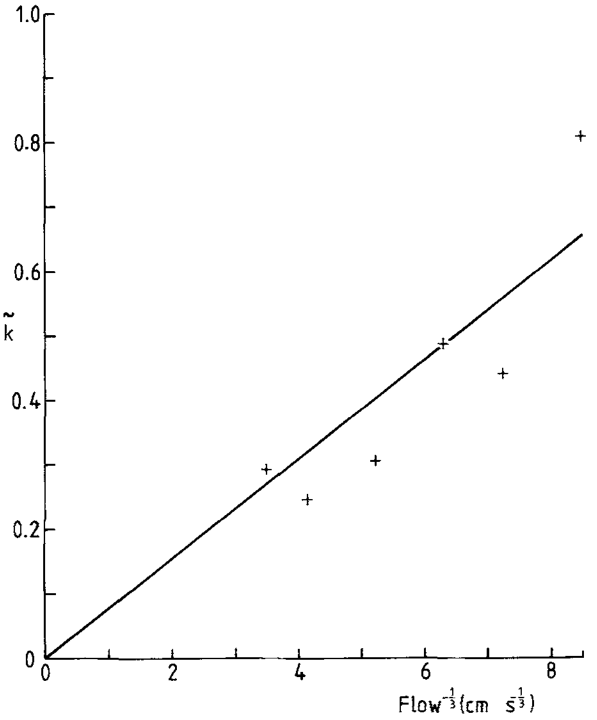

Fig. 12. The anaysis of $S_f$ data obtained from a 1 mM solution of dye in terms of a $\tilde{k}$ versus $V_f^{-1/3}$ plot.

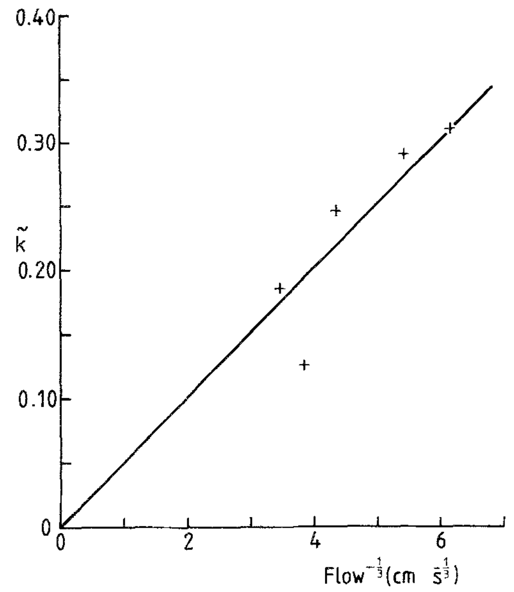

Fig. 13. The analysis of $S_f$ data obtained from a 0.5 mM solution of dye in terms of a $\tilde{k}$ versus $V_f^{-1/3}$ plot.

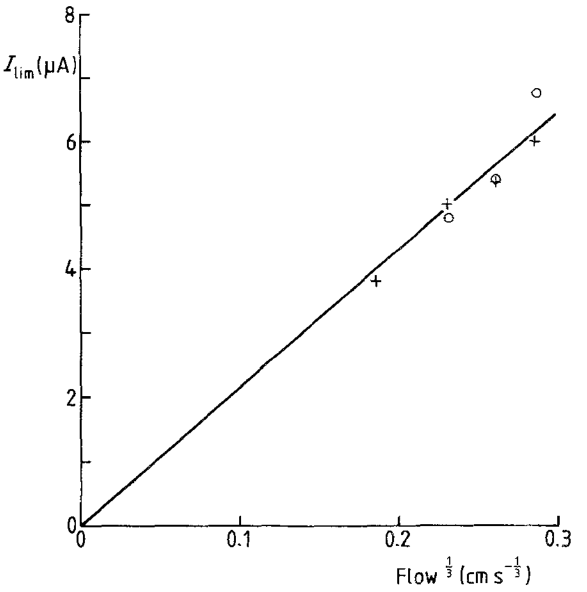

Fig. 14. Limiting current/flow rate plot showing data obtained with a hydrolysed solution of blue dye with the cloth (a) upstream (○), and (b) downstream (+), of the detector electrode.

where $x_2$ is the total length of the exposed cloth surface and the detector electrode and $k_1$ (cm s$^{-1}$) is the rate constant for the reaction at the substrate surface. Figure 11, calculated using the theory given in references [1] and [4], shows how $S_f$ depends on $\tilde{k}$ for the cell used to obtain the data shown in Fig. 10. It can be seen that fast rate constants and slow flow rates give small shielding factors. The 'working curve' in Fig. 11 facilitates the analysis of experimental results: $S_f$ values, at different flow rates, are converted into $\tilde{k}$ values which are then plotted against $V_f^{-1/3}$, as suggested by Equation (4). If the reaction is indeed first order in the surface concentration of the dye ([dye]$_0$) then a good straight line passing through the origin should be obtained, the slope of which permits the evaluation of $k_1$. Figure 12 shows the results of this exercise for the data shown in Fig. 10 from which we may deduce that first order kinetics operate:

$$\text{rate} = k_1[\text{dye}]_0 \qquad (5)$$

where $k_1 = 2.6 \times 10^{-4}$ cm s$^{-1}$.

Experiments were also made using a 0.5 mM solution of dye and the analysis of these is shown in Fig. 13. Again the inference of first-order kinetics is confirmed and the value of $k_1 = 2.2 \times 10^{-4}$ cm s$^{-1}$ deduced was in good agreement with that obtained at the higher concentration.

Finally experiments were made using a 1 mM solution of dye that had been left to hydrolyse over a period of two days. As can be seen from Fig. 14 no reaction with the cloth was found. This was attributed to the known hydrolysis of the dye to form the unreactive dihydroxytriazinyl compound [10].

In conclusion we have shown that the rate of reaction of a dichlorotriazinyl reactive anthraquinone dye with a cotton surface under alkaline conditions is controlled by a surface process which is first order in the surface concentration of the dye (Equation (5)). The rate constant is $(2.4 \pm 0.2) \times 10^{-4}$ cm s$^{-1}$. We thus conclude that the channel flow cell method is applicable to the quantitative study of the rate of uptake of reactive dyes by fabrics. We note that the method is not limited to reactants which may be detected amperometrically. The theory is readily extended [1–4] to allow for potentiometric [12] or non-electrochemical analysis such as by spectroscopic methods [3].

## Acknowledgement

We thank ICI Colours and Fine Chemicals (Blackley, Manchester) for their financial support.

## References

[1] P. R. Unwin, A. J. Barwise and R. G. Compton, *J. Colloid Interface Sci.* **128** (1989) 208.
[2] R. G. Compton, G. M. Stearn, P. R. Unwin and A. J. Barwise, *J. Appl. Electrochem.* **18** (1988) 657.
[3] R. G. Compton, K. L. Pritchard and P. R. Unwin, *J. Chem. Soc. Chem. Commun.* (1989) 249.
[4] R. G. Compton and P. R. Unwin, *Phil. Trans. R. Soc. Lond.* **A330** (1990) 1.
[5] *Idem*, *J. Electroanal. Chem.* **205** (1986) 1.
[6] P. J. Daly, D. J. Page and R. G. Compton, *Anal. Chem.* **55** (1983) 1191.
[7] V. G. Levich, 'Physicochemical Hydrodynamics', Prentice-Hall, Englewood Cliffs, New Jersey (1962).
[8] P. J. Hillson and R. B. McKay, *Trans. Faraday Soc.* **61** (1965) 374.
[9] W. J. Albery, 'Electrode Kinetics', Clarendon Press, Oxford (1975).
[10] D. Edwards, private communication.
[11] P. R. Unwin and R. G. Compton, *J. Electroanal. Chem.* **274** (1990) 249.
[12] R. G. Compton and K. L. Pritchard, *Phil. Trans. R. Soc. Lond.* **A330** (1990) 47.
[13] R. G. Compton, B. A. Coles, G. M. Stearn and A. M. Waller, *J. Chem. Soc. Faraday Trans.* **I**, 84 (1988) 2357.