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Potential step chronoamperometry at the wall-jet electrode: experimental

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Abstract

Experimental verification of the theory for the transient current response of a wall-jet electrode to a potential step is given. The systems studied are ferrocyanide and bromide oxidation in a specially designed large volume cell. Good and reproducible agreement between diffusion coefficients determined by this method and independent techniques is found. Optimized conditions, to avoid on the one hand the necessity of subtracting double-layer charging currents and on the other radial diffusion contributions, are defined.

INTRODUCTION

Potential step chronoamperometry is an important and useful experimental technique. By stepping the potential from one point on a voltammetric wave to another and monitoring the current response, diffusion coefficients can be determined without knowing the concentration of electroactive species or the number of electrons transferred. At hydrodynamic electrodes, in combination with limiting current measurements under steady-state conditions, both the diffusion coefficient and the concentration of electroactive species can be found. In other cases, interference from adsorption or film formation is minimized because of the short time-scale compared with the equivalent experiment at stationary electrodes. The first hydrodynamic electrode to be used for chronoamperometry was the uniformly accessible rotating-disc electrode [1]. A general theory of chronoamperometric transients at channel electrodes has recently been presented [2].

Wall-jet electrodes have frequently been applied in the analysis of flowing liquids [3]. We are currently exploring the use of wall-jet electrodes in kinetic determinations and mechanistic discrimination deriving from their highly non-uniform accessibility [4,5]. Thus, in the case of chronoamperometry, measurements can be carried out and the desired experiment performed without interrupting the solution flow. Additionally, there are no problems from reagent depletion or build-up of intermediates or products.

In a previous paper [6] we developed the theory of potential step chronoamperometry at a wall-jet disc electrode, where the potential was stepped from a value where the electroactive species does not react to one corresponding to the diffusion-limited current. Results of the theoretical calculations were presented in a normalized current transient as a function of dimensionless time, permitting the analysis of experimental data for electrodes of any geometry and for any solution flow rate as long as they satisfy the conditions for a wall jet and radial diffusion can be neglected.

In this paper the theory is experimentally verified and optimal conditions for the use of potential step chronoamperometry in the determination of diffusion coefficients at the wall-jet disc electrode are defined.

EXPERIMENTAL

Experiments were carried out using a wall-jet platinum disc electrode of radius 1.637 mm contained in a large volume Perspex wall-jet cell (Fig. 1) of internal diameter 8 cm and designed not to interfere with the wall-jet streamlines. The enclosed nature of the small volume wall-jet cells used previously [7] is not suitable for accurate verification of theory, owing to possible edge effects, although the small size presents advantages of robustness and portability for electroanalytical applications. The tip of a Radiometer K401 saturated calomel reference electrode (SCE) was placed in the flow stream just before the entry to the wall-jet cell. This arrangement was found to be successful in minimizing uncompensated ohmic drop, as the reference electrode is effectively located at the nozzle inlet (diameter, 0.345 mm) into the cell. The nozzle–electrode distance was 3 mm in all experiments. A platinum gauze auxiliary electrode was contained within the cell.

Test solutions were 2.01 mM $K_4Fe(CN)_6$ in 0.4 M K_2SO_4 supporting electrolyte and 1.51 mM KBr in 0.5 M H_2SO_4 supporting electrolyte, prepared from analytical reagents and triply distilled water. A Pharmacia P-3 variable-flow-rate peristaltic pump was used to drive solution through the cell; pump pulsation damping was provided by a glass ball capacitor and a 5 m length of 1 mm internal diameter Teflon tubing placed before the cell. Volume flow rates were varied between 0.01 and 0.12 cm^3 s^{-1} and measured gravimetrically. Experiments were performed at 25 ± 1°C.

A conventional potentiostat (Oxford Electrodes), modified to include a bounce-free flip-flop switch for the potential step, was employed. Current transients were recorded on a Gould Advance OS4020 digital storage oscilloscope, triggered by the potential step and then passed to a Hewlett-Packard 7035B *x–y* recorder. The storage oscilloscope was calibrated from an external source. A number of

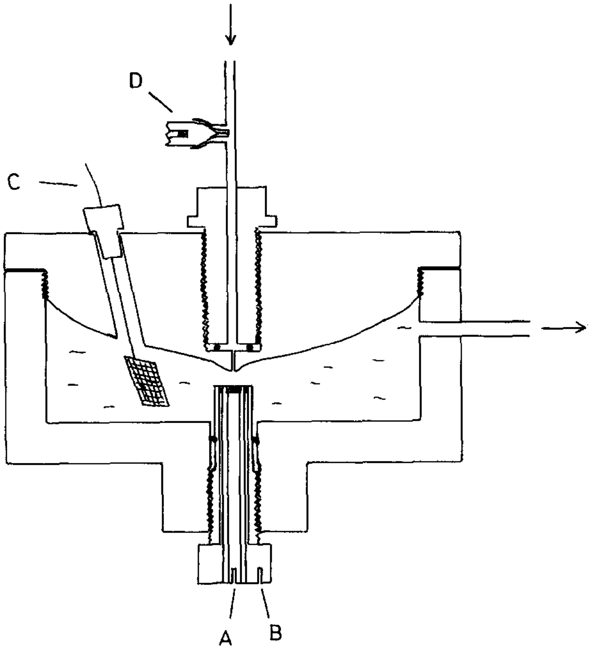

Fig. 1. Diagram of optimally contoured large volume wall-jet cell: A, disc electrode contact; B, ring electrode contact; C, Pt gauze auxiliary electrode; D, SCE reference. The cell body is made of Perspex.

transients were recorded for each experiment and the average values were used for analysis.

RESULTS AND DISCUSSION

The purpose of this study was to compare the shape of the normalized theoretical and experimental current transients and to determine the best conditions for performing the experiment. For these reasons it was decided to study an electroactive species of "typical" diffusion coefficient first in order to optimize the conditions. The oxidation of ferrocyanide in potassium sulphate electrolyte ($D \approx 0.6 \times 10^{-5}$ cm^2 s^{-1}) was chosen for this purpose.

For these experiments the potential was stepped from +0.10 V where no electrode reaction occurs to +0.45 V/SCE corresponding to the diffusion-limited oxidation to ferrocyanide ($E^{\circ\prime} = E_{1/2} = 0.225$ V/SCE, independent of flow rate). Transients were recorded at a number of flow rates. A typical example is given in Fig. 2.

In preliminary steady-state voltammetric experiments undertaken with the newly designed cell the limiting current, I_L was plotted as a function of $V_f^{3/4}$ where [8]

$$I_L = 1.597 k_c R^{3/4} \nu^{-5/12} D^{2/3} a^{-1/2} V_f^{3/4} c_\infty \qquad (1)$$

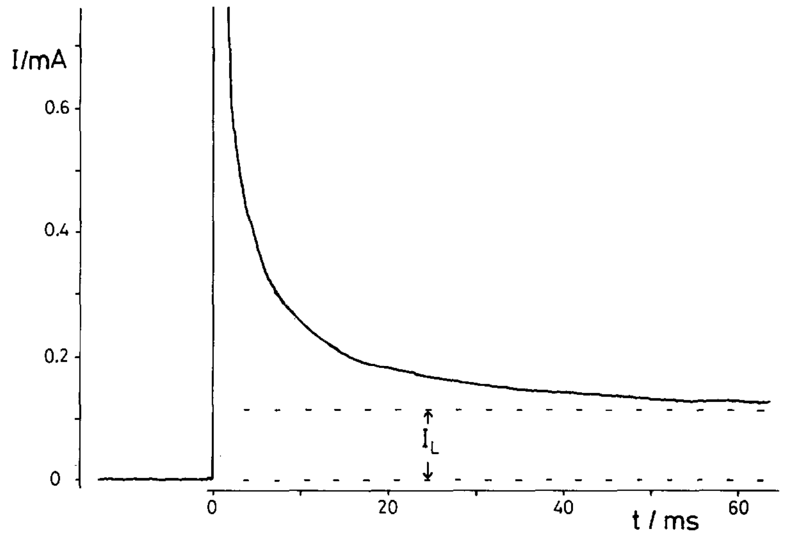

Fig. 2. Chronoamperogram for oxidation of 2.01 mM $K_4Fe(CN)_6$ in 0.4 M K_2SO_4 electrolyte at a wall-jet disc electrode (E stepped from 0.10 to 0.45 V): $V_f = 0.072$ cm^3 s^{-1}.

k_c is a numerical constant describing the momentum flux, R/cm is the electrode radius, ν/cm^2 s^{-1} is the kinematic viscosity, D/cm^2 s^{-1} is the diffusion coefficient, a/cm is the jet diameter, V_f/cm^3 s^{-1} is the volume flow rate of solution and c_∞/mol cm^{-3} is the bulk concentration of electroactive species. A good straight line with intercept close to zero was obtained and the best agreement with the accepted value of the diffusion coefficient (0.62×10^{-5} cm^2 s^{-1}), as found by other workers [7], was obtained with $k_c = 0.90$.

The normalized transient to which experimental data have to be fitted is shown in Fig. 3 as a normalized current I/I_L vs. τ where [6]

$$\tau = \left(271.6 \frac{k_c^2}{a\nu^{5/6}R^{5/2}} D^{1/3} V_f^{3/2}\right) t \tag{2}$$

For a given electrode, the only parameters that vary are ν, D and V_f, and for a given electroactive species only D and V_f vary. Thus in the latter case we can write (2) as

$$\tau = \left(pD^{1/3}V_f^{3/2}\right)t \tag{3}$$

where p is a system-dependent constant.

The effect of flow rate on the speed of transients for a given couple can be visualized by plotting $(I/I_L)V_f^{3/4}$ vs. $\tau V_f^{3/2}$, and this is shown in Fig. 4 for some typical flow rates. It is immediately apparent that at short times the real-time transients are virtually coincident, so that as much of the whole transient as possible needs to be recorded together with the current I_L at infinite time.

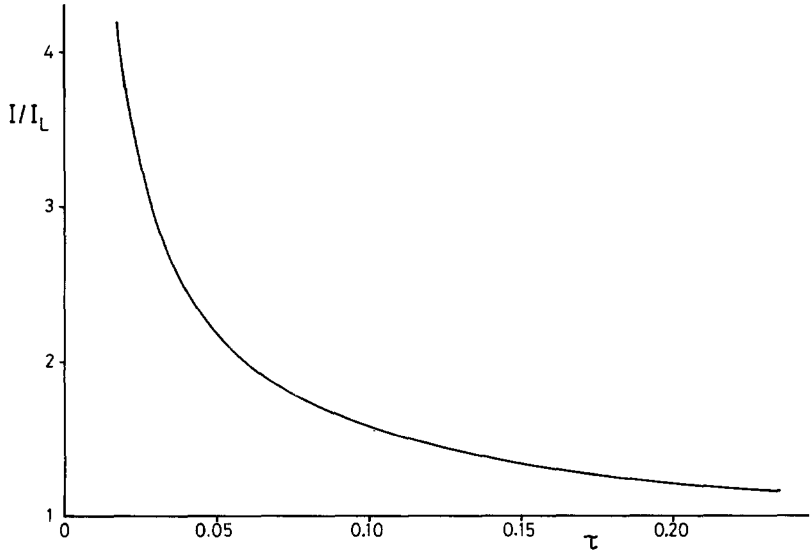

Fig. 3. Normalized theoretical chronoamperometric transient.

At short times the contribution due to double-layer charging should be subtracted from the current transient. Experiments conducted in the supporting electrolyte showed that the double-layer charging current was unimportant after 3 ms. In any case, this may suggest that lower flow rates should be employed in order to avoid any necessity of performing double-layer charging current subtraction, since then only a very small initial portion of the transient occurs at these short times.

We also recognize that the passage of a faradaic current gives rise to an induced charging current that may last up to 30 cell time constants [9]. It should be subtracted in order to give a pure faradaic transient, vindicating our protocol for precluding fast flow rates with concomitant fast chronoamperometric transients.

With a value of $\nu = 0.94 \times 10^{-2}$ cm^2 s^{-1} for 0.4 M K_2SO_4, measured using an Ostwald viscometer, we arrive at

$$\tau = \left(1.33 \times 10^4 D^{1/3} V_f^{3/2}\right) t \tag{4}$$

The current transients were fitted to the normalized theoretical transient, as in Fig. 5, and D was calculated from this expression.

Figure 6 shows a plot of $D^{1/3}$ against flow rate. This plot shows that above $V_f = 0.05$ cm^3 s^{-1} the diffusion coefficient obtained is virtually constant. The value of $(0.61 \pm 0.02) \times 10^{-5}$ cm^2 s^{-1} agrees well with that obtained by other experimental techniques, including limiting current measurements. Interestingly, the apparent diffusion coefficient increases at lower flow rates. This can probably be ascribed to a radial diffusion contribution, which is not taken into account in the

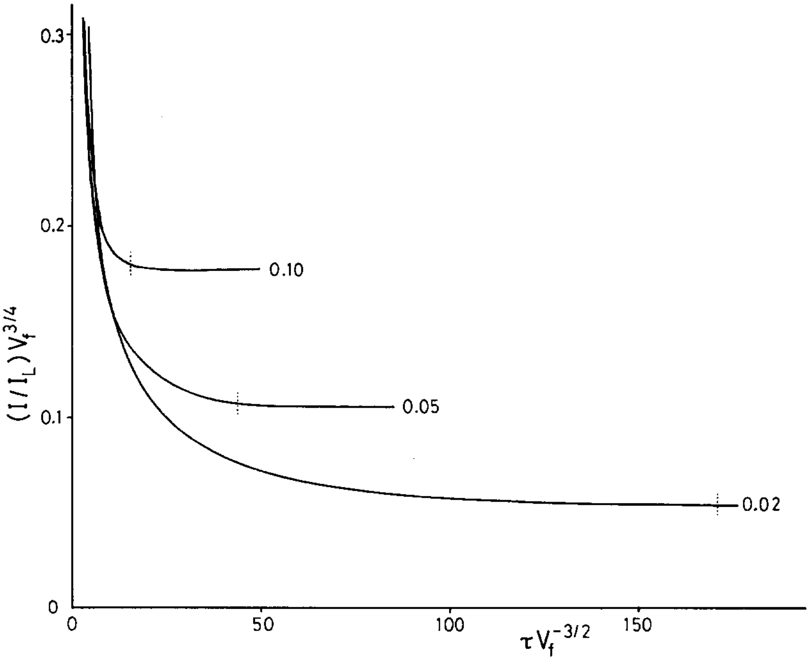

Fig. 4. Plot showing the effect of flow rate on real-time current transients for V_f values of 0.10, 0.05 and 0.02 cm^3 s^{-1}. For $D = 0.6 \times 10^{-5}$ cm^2 s^{-1}, 100 on the $\tau V_f^{-3/2}$ axis corresponds to approx. 0.5 s. The vertical bars indicate $I/I_L = 1.01$.

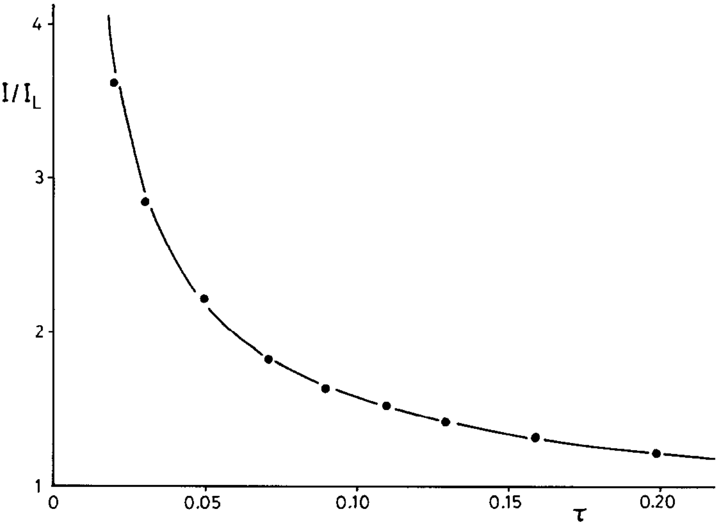

Fig. 5. Data from Fig. 2, shown by experimental points (●), fitted to the theoretical normalized transient (———). $\tau = 0.10$ corresponds to $t = 21.4$ ms.

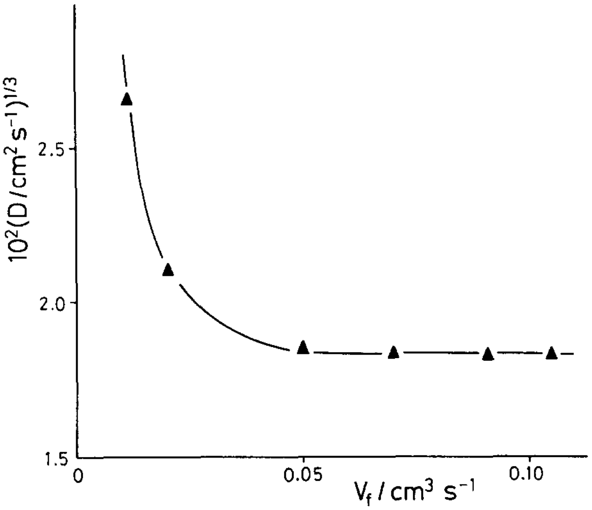

Fig. 6. Plot of calculated $D^{1/3}$ as a function of flow rate for ferrocyanide oxidation.

theory. The potential step is an inherently more sensitive probe of this than other slower techniques because of the high concentration gradients resulting from the potential step perturbation.

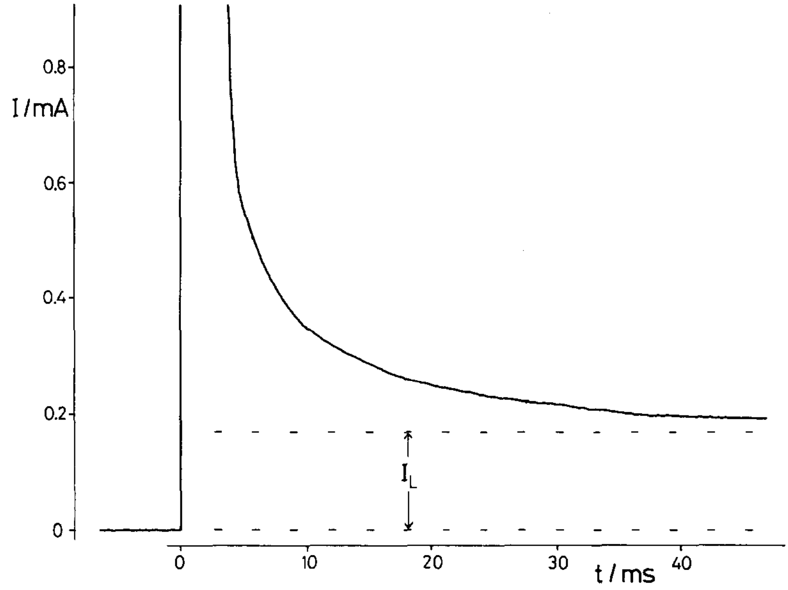

Fig. 7. Chronoamperogram for oxidation of 1.51 mM KBr in 0.5 M H_2SO_4 electrolyte (E stepped from 0.80 to 1.15 V): $V_f = 0.055$ cm^3 s^{-1}.

Using the optimized conditions for the experiment defined above, transients were recorded for bromide oxidation in 0.5 M sulphuric acid. The potential was stepped from +0.80 to +1.15 V/SCE ($E^{\circ\prime} = E_{1/2} = +0.93$ V). A typical example is shown in Fig. 7. The expression corresponding to (4) for this case, where $\nu = 0.95 \times 10^{-2}$ cm^2 s^{-1}, is

$$\tau = \left(1.32 \times 10^4 D^{1/3} V_f^{3/2}\right) t \tag{5}$$

Analysis of the transient gives $D = (1.80 \pm 0.04) \times 10^{-5}$ cm^2 s^{-1}, in excellent agreement with the literature value of 1.82×10^{-5} cm^2 s^{-1} [10]. Once again, and as for ferrocyanide oxidation, it was verified that higher values of D are found at lower flow rates.

In conclusion, theoretical predictions for potential step chronoamperometry at wall-jet electrodes have been experimentally verified. Whilst it is clearly true that the flow rate values used should not be too high, so as to avoid the necessity of subtraction of double-layer effects, radial diffusion appears to be important for flow rates of less than 0.05 cm^3 s^{-1}. Thus it is suggested that these experiments be carried out in the range 0.05–0.08 cm^3 s^{-1}.

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