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The wall–jet electrode and its application to the study of electrode reactions with coupled homogeneous kinetics: the DISP1 reaction

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A wall–jet electrode cell suitable for mechanistic studies is described and used to study the reduction of fluorescein at mercury in aqueous base (pH 9.5 to 10.0). Limiting current–flow rate data are found to be in excellent agreement with theory derived for a DISP1 process.

1. Introduction

The wall–jet electrode (WJE) is a well-defined hydrodynamic electrode in which the flow is due to a jet of fluid which impinges normally onto a planar electrode surface and spreads out radially over that surface, the fluid outside the jet being at rest [1]. Though the WJE has been widely and enthusiastically adopted by electroanalytical chemists for a variety of techniques (anodic stripping voltammetry [2–4], flow-injection analysis [5–7] and HPLC detection) [8, 9], we have pointed out elsewhere that little, if any, use has been made of the WJE for the study of complex electrode reaction mechanisms and specifically those involving coupled homogeneous kinetics [10]. This is surprising since the electrode is highly non-uniformly accessible which is thought to be a desirable feature in achieving discrimination between closely similar electrode reaction mechanisms [11, 12].

In a previous paper [10] we developed a general computational method for solving mass transport problems involving wall–jet electrodes and in particular developed the theory for the transport-limited current–flow rate behaviour for simple electron transfer reactions, and for ECE and DISP1 processes [11, 12]. In the former case good agreement with existing analytical approaches was noted [13, 14]. In this paper we present experimental results which test the validity of the DISP1 theory and use the wall–jet electrode to study the mechanism of the reduction of fluorescein in aqueous base at pH 9.5 to 10.0. As a preliminary the design of a suitable cell for mechanistic studies is reported.

2. Design and construction of a wall–jet cell

Fig. 1 shows a schematic outline of the experimental wall–jet cell and its fittings. It consists of a main body of Perspex (of length 11 cm and diameter 10 cm) with an internal cavity into which were fitted three screw-in sections (Perspex cylinders of diameter 2.8 cm). The first of these contained the working electrode. This was made of a copper rod surrounded by an insulating covering of Teflon so that the section penetrating into the internal cavity was 1.0 cm in diameter. At the upper end of the copper rod, a thin circular disc (0.3 to 0.4 cm diameter) of either copper or platinum was attached and this acted as the working electrode (Fig. 1). The copper disc was mercury plated; the platinum disc was used directly as a working electrode after polishing. Obviously it would be possible to build a wide range of working electrode screw-in sections by simply attaching discs of the required metals as above.

The second screw-in section had a centrally drilled inlet hole and this acted as the jet (diameter 0.0345 cm). The third screw-in section supported the reference electrode (a commercial saturated calomel electrode, of diameter about 5 mm). O-rings were used to seal each of the screw-in sections into the cell, thus preventing any leakage. The volume of the solution in the cell under working conditions was about 20 cm^3.

It was found that one attractive feature of this design was that it did not suffer from air bubbles collecting inside the working chamber. The escape of bubbles was facilitated by the relatively large clearances between the screw-in sections and the cell body, by the large internal volume of solution within the cell, and by the positioning of the exit to the cell well above the jet exit (Fig. 1).

The solution entered the cell via a short Teflon tube and flowed through the jet, so that it impinged normally on the centre of the working electrode. The solution exit was positioned near the top of the cavity and another Teflon tube allowed connection to a flow system (see Section 3) which included the counter electrode and was capable of delivering a controlled and variable solution flow.

Perspex was chosen as a cheap and convenient-to-work material in which to build most of the cell. It had the merit of allowing visual inspection of the interior of the cell (useful for confirming the absence of air bubbles) but the limitation that only aqueous systems could be studied (as Perspex is softened by most

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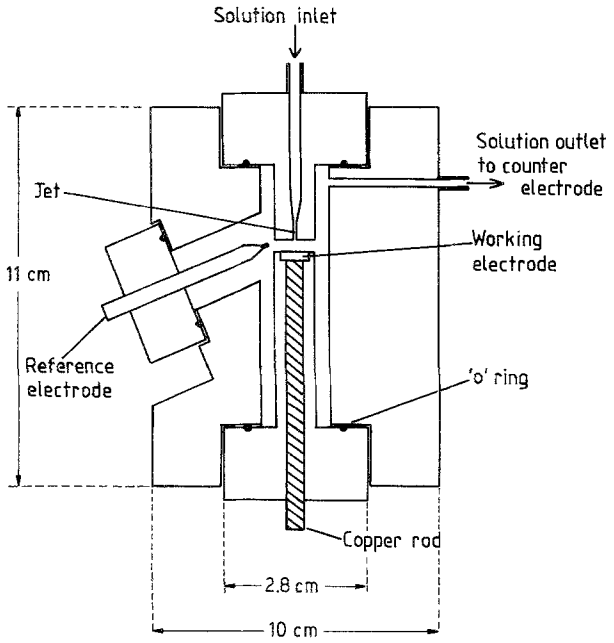


Fig. 1. The experimental wall-jet cell.

organic solvents). The design could be easily reproduced using a variety of other materials.

The separation between the working electrode and the jet exit, d_j, is an important consideration in the construction of a wall-jet cell in that it controls whether true wall-jet hydrodynamics are present. If the separation is too small, the jet interferes with the flow in the boundary layer and smaller currents than expected are found, especially at low flow rates [14]. However, if the separation is too large, the jet of solution spreads out before it hits the surface of the working electrode and again deviations from the desired hydrodynamics are seen [15]. Previous workers [14] have found the former to be the case if $d_j < 2$ mm and the latter if $d_j < 5$ mm. For the WJE described here, a separation of 2 mm was found to be sufficient to give excellent agreement with theory over a wide flow rate range (see below).

3. Experimental details

Two working electrodes were used. One was made of copper, the other of platinum. Both were polished to a mirror finish with successively finer diamond lapping compounds (Hyprez Sprays, Engis, England) down to 0.25 μm. The surface of the copper electrode was then mercury plated using a procedure described by Page *et al.* [16]. A mirror finish was finally obtained by applying a drop of triply distilled mercury to the electrode and then removing the excess. The copper electrode had a radius of 0.403 cm and the platinum electrode, 0.340 cm.

The reference electrode used throughout was a saturated calomel electrode (Radiometer, Copenhagen). The counter electrode was made of a platinum gauze (5 cm × 1 cm) and was located in the flow system downstream of the WJE cell.

Electrolyte solution was passed through the WJE cell using a gravity-fed flow system and a series of calibrated capillaries were employed to obtain a volume flow rate in the range 10^{-3} to 2×10^{-1} $cm^3 s^{-1}$. Solution flowed into the flow system from a reservoir, of approximate capacity 100 cm^3, fitted with a bubbler to deliver argon gas (British Oxygen Company) to deoxygenate the solution. The reservoir was connected to the inlet of the WJE cell by several metres of Teflon tubing of bore 1.5 mm (Altex, Anachem, Luton). Since this tubing is oxygen permeable it was encased in wider bore PVC tubing (8 mm) which was purged with argon. Joints to the cell were made using flexible silicone rubber tubing. Solution flowed out of the cell, past the gauze counter electrode, through a flow-control capillary, and then to waste. The WJE cell and the Teflon tubing were thermostatted in an air thermostat box, which consisted of a heater, fan and thermostat. This allowed the temperature of the cell to be maintained at 25 ± 0.5° C.

All solutions were made up with deionised water (of resistivity > 18 M ohm cm) obtained from an Elgastat Ultra High Quality Unit. The source and grade of the chemicals used were as follows: potassium chloride, sodium hydroxide, sodium hydrogen carbonate, maleic acid (all British Drug Houses, AnalaR grade), fluorescein sodium (BDH, LR grade), mercury (BDH, Aristar), potassium bromide (Fisons 99.5%) and potassium ferricyanide (Hopkins and Williams 99%).

4. Results and discussion

We consider first the behaviour of the cell when used to study simple electron transfer reactions. Albery and Brett [13] have derived an analytical theory for the flow rate dependence of the transport-limited current in this case

$$I_{lim} = 1.59\, k_c n F D^{2/3} v^{-5/12} V_f^{3/4} a^{-1/2} R^{3/4} [A]_0 \quad (1)$$

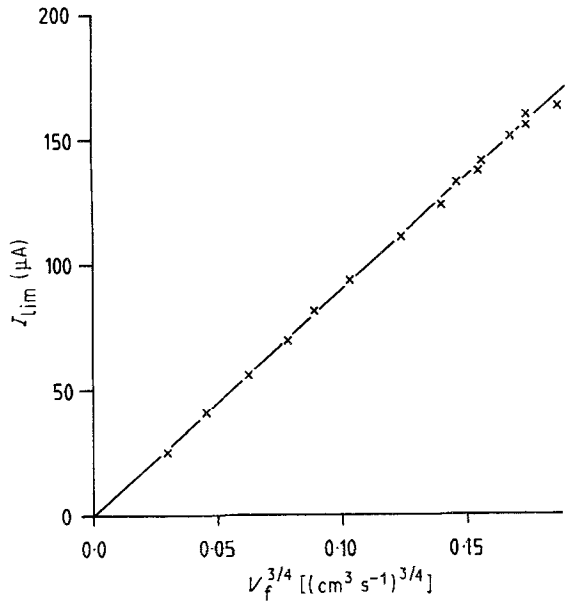


Fig. 2. A plot of I_{lim} versus $V_f^{3/4}$ for the reduction of a 10^{-3} mol dm^{-3} solution of potassium ferricyanide in an electrolyte of 0.5 mol dm^{-3} KCl–0.1 mol dm^{-3} NaOH at the platinum WJE.

Table 1. The systems studied to evaluate k_c

System	*Electrolyte*	*Electrode*	*Diffusion coefficient* ($cm^2 s^{-1}$)
H^+ reduction	0.5 mol dm^{-3} KCl	Hg	7.6×10^{-5} [18]
Br^- oxidation	1.0 mol dm^{-3} H_2SO_4	Pt	1.6×10^{-5} [19]
Maleic acid reduction	1.0 mol dm^{-3} HCl	Hg	8.2×10^{-6} [20]
Ferricyanide reduction	0.1 mol dm^{-3} NaOH–0.5 mol dm^{-3} KCl	Pt	7.6×10^{-6} [17]
Fluorescein reduction	0.1 mol dm^{-3} NaOH–0.5 mol dm^{-3} KCl	Hg	3.2×10^{-6} [21]

where k_c is a cell constant determined by experiment, v is the kinematic viscosity (cm^2 s^{-1}), F is Faraday's constant (C mol^{-1}), D is the diffusion coefficient of the electroactive species (cm^2 s^{-1}), V_f is the volume flow rate (cm^3 s^{-1}), a is the diameter of the jet (cm), $[A]_0$ is the bulk concentration of the electroactive species (mol cm^{-3}) and R is the radius of the electrode (cm).

Fig. 2 illustrates a typical I_{lim}–$V_f^{3/4}$ plot for the reduction of ferricyanide (of concentration 1×10^{-3} mol dm^{-3}) in an aqueous supporting electrolyte of 0.5 mol dm^{-3} KCl at high pH (0.1 mol dm^{-3} NaOH). The reduction was carried out at a platinum WJE and was found to occur with a half-wave potential of +0.3 V (vs SCE). Over the flow rate range investigated (0.009 to 0.15 cm^3 s^{-1}), a good straight line was obtained as predicted by theory. Using the value of $k_c = 0.90$, close to that recommended by Albery and Brett [13] a value of the diffusion coefficient of ferricyanide at 25° C was found to be 7.5×10^{-6} cm^2 s^{-1}. This is in excellent agreement with the literature value of 7.6×10^{-6} cm^2 s^{-1} [17]. It would appear therefore that the cell is operating with the desired hydrodynamics.

However, the work of Albery and Brett [13] suggested some uncertainty as to whether k_c was independent of the particular chemical system studied. Accordingly we examined a range of systems involving simple electron transfer to see whether they fitted Equation 1 with a common value of k_c. The systems studied and their supporting electrolytes are listed in Table 1.

In all these experiments the electroactive species was present at a concentration of 1×10^{-3} mol dm^{-3} and the supporting electrolyte concentrations and electrode materials used were as cited in Table 1. All of the reactions are simple one-electron transfers except in the case of maleic acid. The latter undergoes a two-electron–two-proton reduction at low pH; the rate of the proton transfers is so fast that they do not influence the overall rate of the electrode reaction [20].

Current–voltage curves were recorded for each system as a function of flow rate and in each case a linear dependence of I_{lim} on $V_f^{3/4}$ was found and a graph of ln $\{I_{lim}/(n[A]_0 V_f^{3/4})\}$ against ln(D) was plotted as shown in Fig. 3. The slope of the line drawn in this graph is 0.67 as suggested by theory. Thus good agreement with Equation 1 was seen and it may be concluded that k_c is solely dependent on the hydrodynamics of the system. A value of $k_c = 0.9 \pm 0.05$ was deduced and this is in very good agreement with values advocated elsewhere [13, 14].

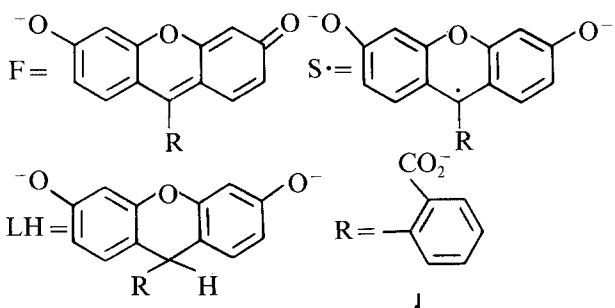
We turn next to the reduction of fluorescein (F) in carbonate buffer at pH 9.5 to 10.0. It has been shown that in this pH range the reduction is a two-electron process forming leucofluorescein (L) via a DISP1 mechanism [22, 23] in which Reaction 2 is the rate-limiting step.

$$F + e^- \longrightarrow S\cdot \quad (1)$$

$$S\cdot + H^+ \xrightarrow{k_1} SH\cdot^+ \quad (2)$$

$$SH\cdot^+ + S\cdot \longrightarrow F + LH \quad (3)$$

where



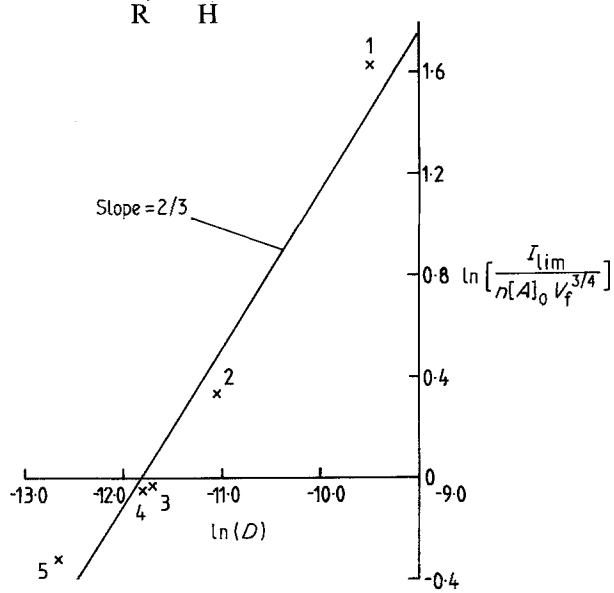


Fig. 3. The linear dependence of ln $\{[I_{lim}/n[A]_0 V_f^{3/4})]/[\mu A\, mol^{-1}\, dm^3 (cm^3 s^{-1})^{-3/4}]\}$ on ln (D/cm^2 s^{-1}).

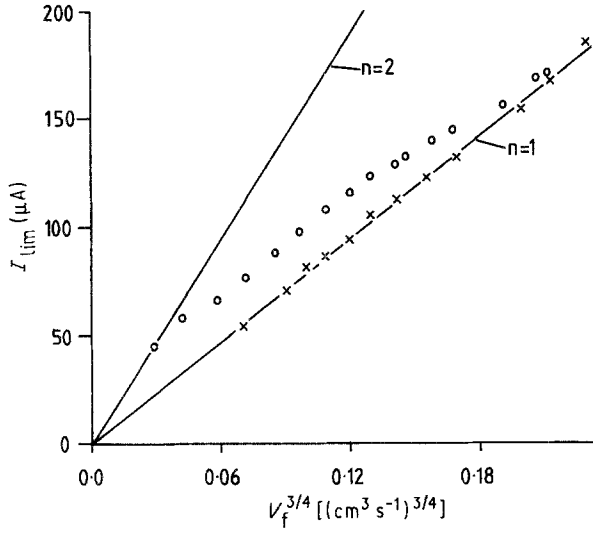


Fig. 4. The variation of I_{lim} with flow rate for the reduction of 10^{-3} mol dm^{-3} fluorescein (in 0.5 mol dm^{-3} KCl/0.1 mol dm^{-3} NaOH) at a mercury wall-jet electrode at (a) pH = 13 (x), and (b) pH = 9.65 (o).

This is in contrast to the behaviour at pH 13 where S• is stable on the electrochemical timescale [22, 23].

Fig. 4 shows I_{lim}-flow rate data obtained at pHs of 13 and 9.65. The expected simple one-electron behaviour is seen at the higher pH whereas at the lower pH a transition from one- to two-electron behaviour is seen as the flow rate is reduced. This transition reflects the fact that S• is swept away from the electrode surface at fast flow rates, limiting the electron transfer to one, whereas at low flow rates Reactions 2 and 3 take place in the vicinity of the electrode with the overall generation of L, the two-electron product. Figs 5 and 6 show plots of N_{eff}, the effective number of electrons transferred, deduced from plots such as Fig. 4, as a function of flow rate for two different pH values. These were compared with theory generated from the Expanding Grid Backwards Implicit Method [10]. This was used to generate N_{eff}–flow rate behaviour for various values of k_1 and the best fit to the experimental data found. It can be seen that this gives excellent agreement with the experimental data over the entire flow rate range. Values of $k_1 = 0.35\,s^{-1}$ (pH 10.0) and $k_1 = 0.90\,s^{-1}$ (pH 9.65) were deduced. These are in very good agreement with those previously deduced from *in situ* electrochemical ESR measurements [22].

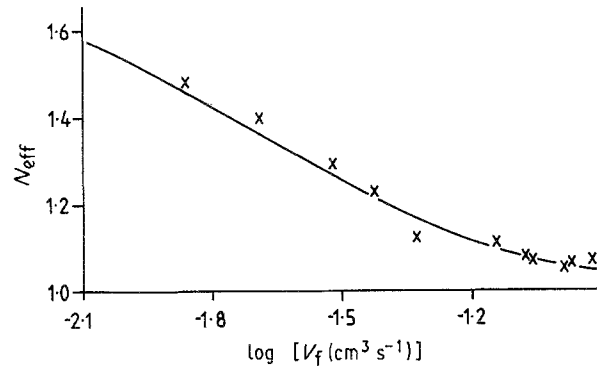


Fig. 5. The best fit between the experimental data for the reduction of fluorescein at pH 10.0 and the theoretical behaviour for a DISP1 process with a rate constant of $k_1 = 0.35\,s^{-1}$.

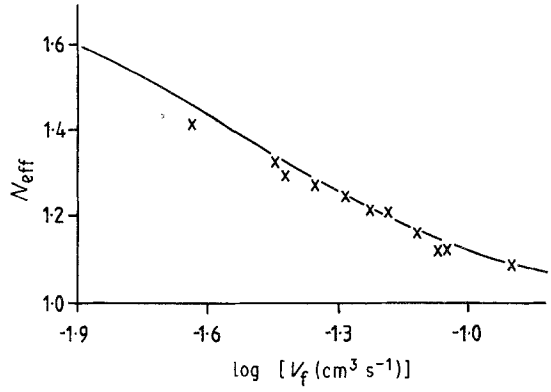


Fig. 6. The best fit between the experimental data for the reduction of fluorescein at pH 9.65 and the theoretical behaviour for a DISP1 process with a rate constant of $k_1 = 0.90\,s^{-1}$.

In conclusion we have demonstrated the validity of the theory previously derived for ECE/DISP1 processes at wall-jet electrodes [10], and confirmed that the reduction of fluorescein proceeds via a DISP1 mechanism.

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