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Wall-jet electrodes: the importance of radial diffusion

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Existing models for mass transport to wall-jet electrodes (WJE) are critically re-evaluated in the light of some new calculations and experiments which relate to steady state and transient currents observed at wall-jet ring disc electrodes both in the presence and absence of homogeneous chemical kinetic complications. Specifically, it is concluded that in many cases quantitative descriptions are only realisable if transport to the electrode is described as having a significant contribution from radial diffusion in addition to the radial convection and normal diffusion that are usually only considered. This greatly increases the complexity of the mathematical solution of problems of interest and may prove an important limitation of WJEs *vis-a-vis* alternative hydrodynamic electrodes for other than analytical purposes.

1. Introduction

The wall-jet electrode (WJE) is a well defined hydrodynamic electrode in which the flow is due to a jet of liquid which impinges normally on to a planar electrode surface and spreads out radially over that surface, the fluid outside the jet being at rest [1]. Recent work has shown WJEs to have considerable application in both single electrode and double electrode (wall-jet ring disc electrode, WJRDE) mode. Specifically two broad classes of electrochemical interest arise. First, these electrodes have been developed for use with such techniques as anodic stripping voltammetry [2–5], flow injection analysis [6, 7] and HPLC detection [8]; in all of which its sensitivity, robustness and ease of practical application for online usage have been considered advantageous. Second, the gross non-uniform accessibility of the electrode with its concomitant sharply varying current density confers on the electrode the capacity for powerful resolution of mechanistic electrochemical problems [9]. In this latter context a general computational approach has been developed for single electrodes which has enabled the derivation of theory for, first, the transport limited current/flow rate behaviour for simple electron transfers [10], and for ECE, DISP and EC′ processes [10, 11], and, second, current–voltage voltammetric wave shapes for, say, EC and EC_2 mechanisms [9, 12] which permit the half wave potential/flow rate characteristics of electrode processes of interest to provide mechanistic and kinetic information.

More recently we have extended our computations to simulate (i) steady state experiments at WJRDEs with and without homogeneous chemical kinetic complications, and (ii) transient measurements at both WJEs and WJRDEs. These calculations have been compared with experiment [13–15]. In broad terms good agreement is found for relatively fast flow rates (typically above $0.05\,cm^3\,s^{-1}$) for practical electrodes. For example, investigation of homogeneous first order kinetics [9] using steady state collection efficiency measurements gave excellent agreement with independently measured values when conducted at high flow rate, but at lower flows significant and systematic deviations were seen. Again, potential step measurements using a single electrode gave chronoamperometric responses exactly as predicted by theory in the light of independently measured diffusion coefficients, provided experiments were conducted under conditions of high mass transport. These deviations were tentatively ascribed to a radial diffusion contribution which had not been taken into account in the theory. In this paper we consider this problem quantitatively. Theoretical results are presented which take explicit account of radial diffusion effects on currents at single electrodes and the experimental double electrode investigations are extended to the transient mode. The latter permits the most critical possible test of theory against experiment since it is to be intuitively expected that radial diffusion effects will be greatest for (a) double electrode experiments where the ring 'sees' much more stagnant solution than does the disc and (b) transient conditions where radial concentration gradients are enhanced at short times.

2. Theory

In this section the theory for the transport limited current at WJE taking explicit account of the existence of radial diffusion is presented. The form of the convective diffusion equation relevant to the WJE geometry under steady state conditions for an electroactive

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species A is:

$$V_r \frac{\partial[\mathrm{A}]}{\partial r} + V_r \frac{\partial[\mathrm{A}]}{\partial z} = D \frac{\partial^2[\mathrm{A}]}{\partial z^2} + D \frac{\partial^2[\mathrm{A}]}{\partial r^2} \quad (1)$$

where D is the diffusion coefficient, V_z the convective flow velocity in the normal (z) direction, and V_r the convective flow velocity in the radial (r) direction. To solve this equation the broad general strategy previously described [10, 16] is adopted which works with an expanding finite-difference grid characterized by the parameters J, K. These respectively describe the numbers of 'boxes' in directions normal and radial to the electrode surface [10]. We again work with a normalized concentration g^A, defined by:

$$g^A_{j,k} = [\mathrm{A}]/[\mathrm{A}]_{\mathrm{bulk}} \quad (2)$$

where $[\mathrm{A}]_{\mathrm{bulk}}$ is the concentration of the electroactive species flowing in to the wall-jet cell and the subscripts j ($0 < j < J$) and k ($0 < k < K$) denote the position on the finite-difference grid. With this notation the boundary conditions relevant to the mass transport controlled discharge of A are:

$$g^A_{0,k} = 0 \qquad k = 1, 2, \ldots K \quad (3)$$

$$g^A_{J-1,k} = 1 \qquad k = 1, 2, \ldots K \quad (4)$$

$$g^A_{j,0} = 1 \qquad j = 1, 2, \ldots J \quad (5)$$

The derivatives in equation (1) are approximated to their finite-difference form as before [10] where, for example:

$$\frac{\partial^2[\mathrm{A}]}{\partial r^2} = \frac{g^A_{j,k+1} - 2g^A_{j,k'} + g^A_{j,k''-1}}{(\Delta r^2)} \quad (6)$$

where k' and k'' denote interpolated normalized concentrations generated via the protocol defined in [10]. This leads to the following finite-difference equation:

$$\frac{V_r(j, k+1)}{\Delta r}\{g^A_{j,k+1} - g^A_{j,k'}\} + \frac{V_z(j, k+1)}{\Delta z} \times \{g^A_{j+1,k+1} - g^A_{j,k+1}\} = \frac{D}{(\Delta z)^2}\{g^A_{j+1,k+1} - 2g^A_{j,k+1} + g^A_{j-1,k+1}\} + \frac{D}{(\Delta r)^2}\{g^A_{j,k+1} - 2g^A_{j,k'} + g^A_{j,k''-1}\} \quad (7)$$

It will be noted that the radial diffusion component has been centred one grid point behind that of the axial component to facilitate easy and economical computation. Extended test computations based on transient expanding grid backward implicit finite-difference theory [14, 16] showed this to be a valid procedure. Applying the boundary conditions (3–5) to Equation 7 leads to $(J - 1)$ simultaneous equations which can be expressed in the form of a $(J - 1) \times (J - 1)$ matrix as defined by Equation 33 in [10]. Using the notation of that paper leads to the following matrix elements:

$$d^A_j = g^A_{j,k'}\{1 - 2\varepsilon^r_{j,k+1}\} + g^A_{j,k''-1}\{\varepsilon^r_{j,k+1}\} \quad (8)$$

$$d^A_{J-1} = g^A_{J-1,k'}\{1 - 2\varepsilon^r_{J-1,k+1}\} + g^A_{J-1,k''-1}\{\varepsilon^r_{J-1,k+1}\} + \{\varepsilon^z_{J-1,k+1} - \lambda_{J-1,k+1}\} \quad (9)$$

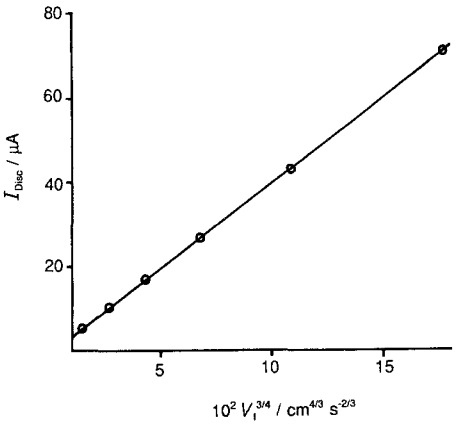

Fig. 1. Comparison of the computed disc current/flow rate behaviour for the WJE geometry specified in the text (a) without radial diffusion shown by the solid line and (b) with radial diffusion (○). A diffusion coefficient of 1×10^{-6} cm^2 s^{-1} was assumed in these calculations.

$$u^A_j = g^A_{j,k+1} \quad (10)$$

$$a^A_j = -\varepsilon^z_{j,k+1} \quad (11)$$

$$b^A_j = 2\varepsilon^z_{j,k+1} - \varepsilon^r_{j,k+1} - \lambda_{j,k+1} + 1 \quad (12)$$

$$c^A_j = \lambda_{j,k+1} - \varepsilon^z_{j,k+1} \quad (13)$$

where

$$\varepsilon^z_{j,k+1} = \frac{D\Delta r}{(\Delta z)^2 V_r(j, k+1)} \quad (14)$$

$$\varepsilon^r_{j,k+1} = \frac{D}{(\Delta r) V_r(j, k+1)} \quad (15)$$

and the parameter λ has been defined previously [10].

3. Theoretical results

Using the theory outlined above, steady state transport limited currents including radial diffusion effects were computed on a Sun IPC SPARC workstation and convergence examined by varying J and K. A WJE of the following typical geometry was investigated: radius $R = 0.164$ cm, cell constant $k_c = 0.9$ [17] and jet diameter $a = 0.0345$ cm. A wide range of volume flow rates in the range $10^{-1} > V_f/\mathrm{cm^3\,s^{-1}} > 5 \times 10^{-3}$ were investigated and compared to the case of no radial diffusion by putting the parameter ε^r (Equation 15) equal to zero. All computations were made for an aqueous solution with kinematic viscosity 0.0089 cm^2 s^{-1}.

Figure 1 shows the disc current calculated as a function of flow rate for the case of no radial diffusion. As can be seen the disc current depends accurately on $V_f^{3/4}$ as predicted by the analytical theory of Albery [17]. Also shown in Fig. 1 is the corresponding current for the case including radial diffusion: the latter gives a negligible effect (< 0.5%). To further probe this effect a range of diffusion coefficients (10^{-5}–10^{-6} cm^2 s^{-1}) were next employed to test the behaviour of the disc current with and without radial diffusion. Figure 2 compares the disc current calculated as a function of diffusion coefficient for a fixed flow rate of 2×10^{-3} cm^3 s^{-1} for the two cases. Note again that, in the absence of radial diffusion, the simulations confirm

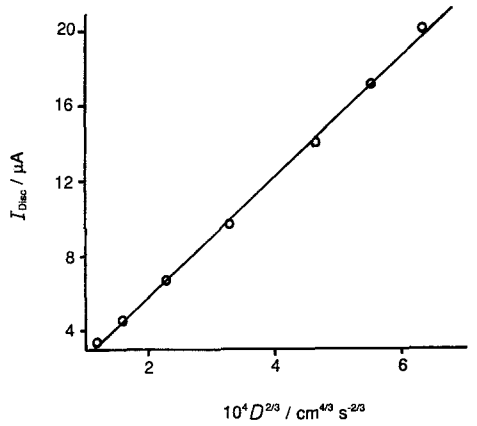

Fig. 2. Comparison of the computed disc current/diffusion coefficient behaviour for the WJE geometry specified in the text (a) results without radial diffusion are noted by the solid line and (b) with radial diffusion (o). A fixed flow rate of 2×10^{-3} cm^3 s^{-1} was assumed in these calculations.

the analytical prediction that the limiting current depends on ($D^{2/3}$). However, comparison of the two cases again provides excellent evidence that radial diffusion has a negligible effect on the observed disc current for an electrode with typical experimental flow cell geometries. This can be understood in terms of the following observations. First, it might be expected that radial diffusion effects would dominate in the regions where the solution is most stagnant. From the point of view of the disc current this would be near the outer radius of the electrode. However, in this region of the wall-jet the radial concentration gradients are necessarily low and so the effect upon the current is negligible. Second, the $r^{5/4}$ variation of the diffusion layer thickness suggests that the radial concentration gradients are largest near the centre of the disc near $r = 0$. However, the contribution of normal flux, which provides the electrode current, at any radius r is weighted by a $2\pi r(dr)$ factor reflecting the area of an annulus at that point. Thus, although the normal concentration gradient is very small for large radii, a dominant amount of the limiting current is drawn from the disc edges. In this region the radial concentration gradient is almost zero and, hence, no radial diffusion effects are seen. However, it may be anticipated for double electrode experiments, where a ring electrode is used to make amperometric measurements on species electrogenerated at the disc, that significant effects may appear, since the very act of amperometric detection on the second electrode must induce a radial concentration gradient. This problem is addressed in section 5.

4. Experimental details

Experiments were carried out using a WJRDE of platinum, with a disc radius of 0.164 cm, inner ring radius 0.175 cm and outer ring radius 0.189 cm contained in a large volume WJ cell described previously [15]. A platinum gauze auxiliary electrode was contained within the cell and the tip of a radiometer K401 SCE reference electrode placed in the flow stream just before entry to the WJ cell in order to minimize uncompensated ohmic drop. The nozzle diameter was 0.0345 cm and the nozzle-electrode distance was 0.3 cm. Test solutions contained 2 mM $K_4Fe(CN)_6$ or $K_3Fe(CN)_6$ in 0.4 M K_2SO_4 supporting electrolyte, prepared from analytical grade reagents and tri-distilled water. A pharmacia P-3 variable flow rate peristaltic pump was used to drive solution through the cell, pump pulsation being damped by a glass ball capacitor and 5 m length of 1 mm i.d. Teflon tubing placed before the cell. Volume flow rates were varied between 0.03 and 0.12 cm^3 s^{-1} and measured gravimetrically. Experiments were performed at 25 ± 1°C.

Diffusion coefficients for ferro- and ferri-cyanide ions were determined from diffusion limited wall-jet disc current measurements at +0.45 V and +0.10 V/SCE respectively, and from disc electrode transients as described previously [14, 15]. The values obtained were 6.2×10^{-6} and 6.8×10^{-6} cm^2 s^{-1}, respectively.

A conventional style potentiostat was employed, together with a variable frequency square wave generator to apply the potential steps. In potential step experiments with ferrocyanide in bulk solution, the potential was stepped from +0.10 V (no electrode reaction) to +0.45 V/SCE (mass transport limited current). In experiments involving ferricyanide in bulk solution the initial potential was +0.45 V, which was then stepped to +0.10 V.

Current transients were recorded on a Gould Advanced OS4020 digital storage oscilloscope, triggered by the first potential step, and then transferred to a Hewlett Packard 7035B x–y recorder. The oscilloscope was calibrated using an external source.

5. Results and discussion

In section three it was demonstrated theoretically that radial diffusion effects are negligible for steady state disc measurements for electrodes of practical geometries. It was also predicted that amperometric measurements using ring disc electrodes would be much more susceptible to interference. It may be anticipated that, because of the high transient radial concentration gradients which can occur in potential step experiments, that the most sensitive experiment in order to probe radial diffusion processes in the WJ-geometry is via chronoamperometric ring measurements made in response to disc potential steps. In particular, a previous report has already demonstrated experimentally the presence of such complications in disc transient measurement conducted with flow rates below 0.5 cm^3 s^{-1} [15].

Transient measurements at a platinum–platinum WJRDE are next reported for two systems: (a) the electrooxidation of potassium ferrocyanide, and (b) the electroreduction of potassium ferricyanide in aqueous solution. In both cases a volume flow rate of 0.11 cm^3 s^{-1} was used: for such fast flows both steady state and transient disc experiments are known to be free from radial diffusion effects. Figure 3 shows the measured ring current as a function of time resulting from a potential step on the disc electrode (at time

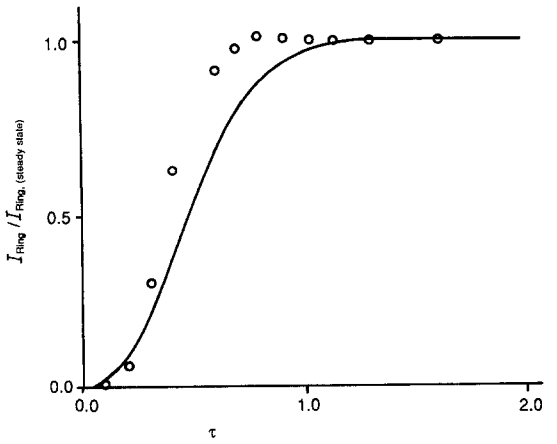

Fig. 3. Ring current transient as a function of normalized time (see text) for the oxidation of ferrocyanide at the disc, (O). The solid line shows the theoretical transient computed form the no radial diffusion model.

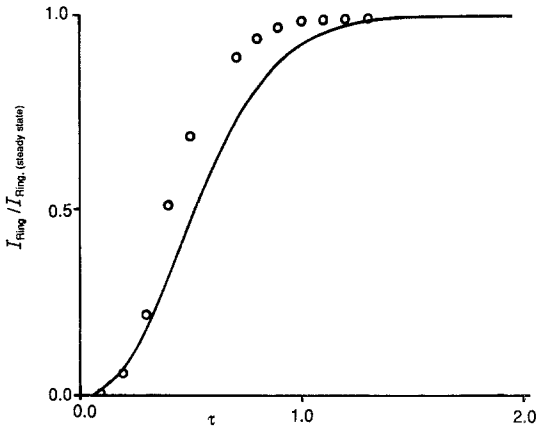

Fig. 4. Ring current transient as a function of normalised time (see text) for the reduction of ferricyanide at the disc, (O). The solid line shows the theoretical transient computed form the no radial diffusion model.

$t = 0$) between values corresponding to no current flowing and to the transport controlled oxidation of ferrocyanide. Throughout the measurement the ring electrode was potentiostatted at a value corresponding to the transport controlled reduction of ferricyanide. The current is shown normalised to its steady state value and is plotted against the normalised time parameter τ (linearly related to real time t and defined in [14]). The current passes through a small maximum before reaching its steady state value. It has been shown elsewhere [9] that this is a direct consequence of the inequalities of the diffusion coefficients of the ions being discharged at the electrode and those being formed. However, using a theory which neglected radial diffusion, such maxima were only predicted to occur for ratios of diffusion coefficients, $D_{product}/D_{reactant}$ markedly different from unity. In the present case steady state measurements (see section 4) revealed this ratio to be 1.1. Figure 3 shows the full theoretical transient computed for the experimental electrode geometry employed and using the measured steady state diffusion coefficients of ferro- and ferri-cyanide. The absence of a measurable theoretical maximum is apparent and, moreover, it is clear that theory greatly over estimates the time taken for the ring current to reach its steady state value. Both of these observations point to the contribution of significant radial diffusion to the mass transport problem under consideration.

Figure 4 shows analogous experimental ring current data for the case where ferricyanide is reduced to ferrocyanide at the disc and the latter species is quantitatively 'collected' at the ring. Again Fig. 4 shows, in addition to the experimental points, the theoretical transient deduced from the no-radial diffusion model. The latter significantly under-estimates the rate of ring response, pointing to major radial diffusion induced by the large radial concentration gradients arising from the amperometric double electrode experiment. Finally, it should be noted that experimental ring transients can be slowed down due to adsorption of electrogenerated material at the disc surface [18]; if such effects are present in the ferrocyanide/ferricyanide system studied here then the effects of radial diffusion will be even greater than implied by Figs 3 and 4.

6. Conclusions

Wall-jet electrodes are valuable hydrodynamic tools for the electroanalytical chemist. However, comparison of experiment with theory is only currently possible for measurements conducted under mass transport conditions which can be accurately described by a model which includes axial convection and normal diffusion, but specifically excludes radial diffusion. The work described in this paper and elsewhere [13, 15] demonstrates that such experiments must be carried out above a certain minimum electrolyte flow rate. The value of this critical flow rate is strongly dependent on the nature of the experiment. For steady state measurements at a single disc electrode almost any experimentally realisable flow rate is adequate. Transient measurements dictate faster flow rates (see above) as do double electrode experiments [19]. The combination of transient measurements and double electrodes is particularly sensitive to radial diffusion effects: in the work described above even flow rates as fast as $0.1\,cm^3\,s^{-1}$ were insufficient to out run radial diffusion. Due caution should be exercised when conducting hydrodynamic voltammetry in this electrode geometry.

References

[1] M. B. Glauert, *J. Fluid Mech.* **1** (1956), 625.
[2] H. Gunasingham, K. P. Ang, C. C. Ngo, *Anal. Chem.* **57** (1985) 505.
[3] C. M. A. Brett and M. M. P. M. Neto, *J. Electroanal. Chem.* **258** (1989) 345.
[4] C. M. A. Brett and A. M. C. F. Oliveira Brett, *ibid.* **262** (1989) 83.
[5] C. M. A. Brett, A. M. C. F. Oliveira Brett and J. L. C. Pereira, *Electroanalysis* **3** (1991) 683.
[6] J. G. Douglas, *Anal. Chem.* **61** (1989) 922.
[7] H. Gunasingham, K. P. Ang., C. C. Ngo, *Analyst* **133** (1988) 1533.
[8] H. Gunasingham, B. T. Tay and K. P. Ang, *Anal. Chem.* **56** (1984) 2422.
[9] R. G. Compton, A. C. Fisher and G. P. Tyley, *J. Appl. Electrochem.* **21** (1991) 295.
[10] R. G. Compton, C. R. Greaves and A. M. Waller, *ibid.* **20**

(1990) 575.
[11] R. G. Compton, A. C. Fisher and G. P. Tyley, *ibid.* **21** (1991) 2.
[12] *Idem., ibid.* **20** (1990) 912.
[13] C. M. A. Brett, A. M. C. F. Oliveira Brett, R. G. Compton, A. C. Fisher and G. P. Tyley, *Electroanalysis* **3** (1991) 631.
[14] A. C. Fisher, R. G. Compton, C. M. A. Brett and A. M. C. F. Oliveira Brett, *J. Electroanal. Chem.* **318** (1991) 53.
[15] C. M. A. Brett, A. M. C. F. Oliveira Brett, A. C. Fisher and R. G. Compton, *J. Electroanal. Chem.* **334** (1992) 57.
[16] A. C. Fisher and R. G. Compton, *J. Phys. Chem.* **95** (1991) 7538.
[17] W. J. Albery and C. M. A. Brett, *J. Electroanal. Chem.* **148** (1983) 201.
[18] W. J. Albery and M. L. Hitchman, 'Ring-Disc Electrodes', Oxford University Press, Oxford (1976) Chapter 10.
[19] R. G. Compton, A. C. Fisher, M. H. Latham, C. M. A. Brett and A. M. C. F. Oliveira Brett *J. Appl. Electrochem.* **21** (1991) 2.