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THE WALL-JET RING-DISC ELECTRODE

PART I. THEORY

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ABSTRACT

A theoretical treatment is presented for the wall-jet ring-disc electrode Velocity profiles for the radial and axial flow in the wall-jet system are derived A general treatment for transforming the convective diffusion equation into the same form as that for a rotating ring-disc electrode is presented This transformation means that the results of the rotating ring-disc electrode for the limiting currents the collection efficiency and diffusion layer titration curves can be applied directly to the wall-jet ring-disc electrode

INTRODUCTION

The term "wall-jet" described the flow due to a jet of fluid striking a plane surface at right angles and spreading out radially over that surface The fluid motion has been described by Glauert [1] for both laminar and turbulent flow Yamada and Matsuda [2] derived and tested experimentally an expression for the limiting current under laminar flow when a jet issuing from a small circular nozzle impinges normally on the centre of a disc electrode Applications of this system have included an electrochemical detector for a wide range of organic compounds as an alternative to spectrophotometric detection in HPLC [3,4] Pungor et al. [5–7] have studied the wall-jet electrode under turbulent flow. The stagnation region where the jet hits the electrode surface has been investigated by Chin and Tsang [8] and Chin and Chadran [9] have considered a ring-disc electrode with a jet impinging from a large nozzle, such that there is uniform flow to the disc

In this paper we consider the wall-jet ring-disc electrode (WJRDE) with small circular nozzle. We first describe the velocity profiles for the flow in the system We then present a general method of transforming the convective diffusion equation into the same form as that for the rotating ring-disc electrode. This allows us to obtain expressions for the limiting currents at the disc and ring electrodes, for the collection efficiency and for the description of diffusion layer titration curves

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WALL-JET VELOCITY PROFILES

The coordinates for the wall-jet ring-disc electrode are displayed in Fig 1b

We start by considering the variation of the velocity components, u in the radial direction and v in the direction normal to the wall electrode, with η, where η is a dimensionless parameter describing distance normal to the wall electrode Following Glauert [1] we have

$$\eta = \left(135M_f/32\nu^3r^5\right)^{1/4}z \tag{1}$$

where

$$M = k^4V_f^3/2\pi^3a^2 \tag{2}$$

ν is the kinematic viscosity, k is a constant determined by experiment to be 0 86 [2], V_f is the volume flow rate and a is the diameter of the jet

Glauert [1] showed that the radial velocity component u, is given by

$$u = \left(15M/2\nu r^3\right)^{1/2}f'(\eta) \tag{3}$$

where

$$f'(\eta) = (2g/3)(1 - g^3) \tag{4}$$

$$f(\eta) = g^2$$

and

$$\eta = \ln\left[(1 + g + g^2)^{1/2}/(1 - g)\right] + 3^{1/2}\tan^{-1}\left[3^{1/2}g/(2 + g)\right] \tag{6}$$

As g varies from 0 to 1, η varies from 0 to infinity

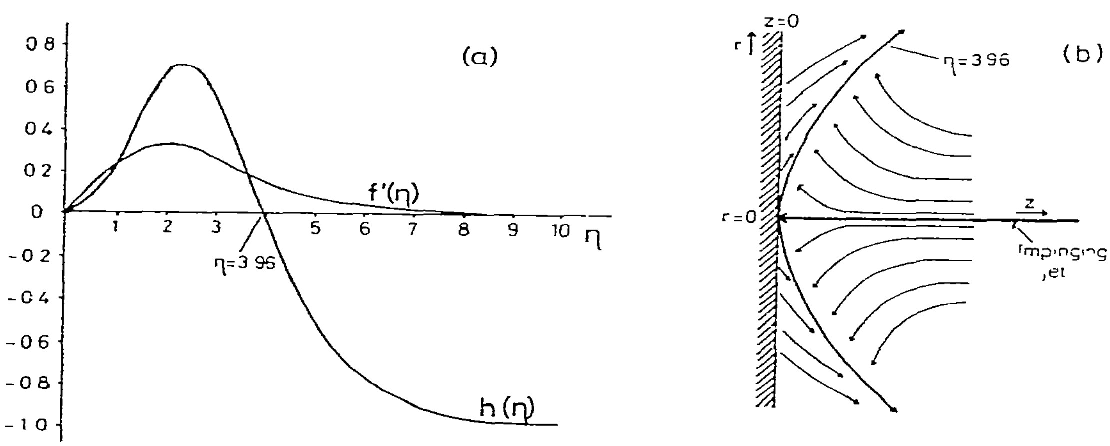

Fig 1 The velocity profiles for the radial velocity, $f'(\eta)$ and for the normal velocity $h(\eta)$ as a function of the dimensionless coordinate η given in eqn (1)

To find the velocity component in the direction normal to the electrode we use Glauert's result [1] for the stream function ψ

$$rv = -\partial\psi/\partial r \tag{7}$$

and

$$\psi = (40M\nu r^3/3)^{1/4} f(\eta) \tag{8}$$

From eqns (1), (7) and (8) we obtain

$$v = \tfrac{3}{4}(40M\nu/3r^5)^{1/4} h(\eta) \tag{9}$$

where

$$h(\eta) = (5/3)\eta f'(\eta) - f(\eta) \tag{10}$$

From eqns (3) and (9) it can be seen that both u and v decrease as r increases. In Fig 1a we show how u and v vary with η by plotting the function $f'(\eta)$ for u and $h(\eta)$ for v These functions were calculated by taking different values of g and using eqns (4), (5), (6) and (10). It can be seen that, as one might expect, the radial velocity component is zero at the wall, passes through a maximum at $\eta = 2\ 03$ and then declines back to zero. The behaviour of v is more interesting Starting from zero at the wall it rises at first with a parabolic dependence; it then passes through a maximum at $\eta = 2\ 31$ and drops back to zero at $\eta = 3\ 96$ For these values of η the flow is *away* from the wall For larger values of η, $h(\eta)$ is negative reaching a limiting value of -1 In this region flow is towards the wall There is therefore a vital boundary at $\eta = 3\ 96$ which divides the solution into a region where flow is away from the electrode from the region where flow is towards the electrode This boundary and schematic stream lines are depicted in Fig 1b The boundary should mean that the electrode only sees fresh solution that has just passed through the jet

We shall be particularly interested in the behaviour of u and v close to the electrode surface where $\eta \ll 1$. From eqns (1), (3), (4), (5), (6), (9) and (10) we find

$$g \simeq \tfrac{1}{3}\eta$$

$$u_{\eta\to 0} \simeq \tfrac{2}{9}(15M/2\nu r^3)^{1/2}\eta \tag{11}$$

$$v_{\eta\to 0} \simeq (7/36)(40M\nu/3r^5)^{1/4}\eta^2 \tag{12}$$

and

$$v_{\eta\to 0} \simeq (7/8)(z/r)u_{\eta\to 0} \tag{13}$$

Equation (13) arises from the continuity equation

$$\partial(ru)/\partial r + \partial(rv)/\partial z = 0 \tag{14}$$

We now generalise this relation for any ring-disc electrode If u has the general form

$$u_{\eta\to 0} = Cz/r^m \tag{15}$$

the from eqn. (14)

$$v_{\eta \to 0} = \tfrac{1}{2}(m-1)\, Cz^2/r^{m+1} \qquad (16)$$

and

$$v_{\eta \to 0} = \tfrac{1}{2}(m-1)(z/r)\,u_{\eta \to 0}$$

For a RRDE $m = -1$ while for a WJRDE, from eqns (1) and (11) $m = 11/4$. For a wall-jet electrode from eqns. (1) and (11)

$$C_{\mathrm{WJ}} = \left([5M]^3/216v^5\right)^{1/4} \qquad (17)$$

while for a rotating disc electrode [10]

$$C_{\mathrm{RD}} = 8.0W^{3/2}v^{-1/2}$$

where W is the rotation speed in Hz

THE CONVECTIVE DIFFUSION EQUATION

We now solve the convective diffusion equation describing transport of an electroactive species of concentration c to the ring-disc electrode

$$u\,\partial c/\partial r + v\,\partial c/\partial z = D\,\partial^2 c/\partial z^2 \qquad (18)$$

The radial diffusion term which is negligible has been omitted In solving eqn (18) we shall make use of the results for the rotating ring-disc electrode and present a general treatment for solving eqn. (18) where u and v are given by equations of the form of eqns. (15) and (16) respectively.

By defining the following dimensionless variables we can transform eqn (18) into a common form

$$\chi = (qC/D)^{1/3}\left(r_1^{-q/3}/r^{1/2(m-1)}\right)z \qquad (19)$$

$$\xi_p = (r/r_1)^q - (r_{p-1}/r_1)^q \qquad (20)$$

and

$$\gamma = (c - c_\infty)/c_\infty \qquad (21)$$

where

$$q = \tfrac{1}{2}(5-m) \qquad (22)$$

$$r_0 = 0$$

and where the subscript p defines the different zones of the ring-disc electrode with $p = 1$ for the disc, $p = 2$ for the gap and $p = 3$ for the ring

With these definitions eqn. (18) becomes

$$\chi\,\partial\gamma/\partial\xi_p = \partial^2\gamma/\partial\chi^2 \qquad (23)$$

The current at the disc ($p = 1$) or the ring ($p = 3$) electrode is given by

$$|i| = 2\pi nFD\int_{r_{p-1}}^{r_p} r(\partial c/\partial z)_{z=0}\mathrm{d}r$$

$$= 2\pi nFD^{2/3}C^{1/3}c_{\infty}r_1^{2q/3}q^{-2/3}\int_0^{\xi'_p}|(\partial\gamma/\partial\chi)_{\chi=0}|\mathrm{d}\xi_p \qquad (24)$$

where

$$\xi'_p = (r_p/r_1)^q - (r_{p-1}/r_1)^q \qquad (25)$$

and we have used eqns. (19) and (20). The valuable feature of this equation is that the currents on the ring and disc electrodes can be found from the integrals working from the common eqn (23). It is helpful here to define particular geometric parameters for the geometry of the ring-disc electrode which are related to the three values of ξ'_p We follow our original notation for the ring-disc electrode [11] For the disc·

$$\xi'_1 = 1.0 \qquad (26)$$

For the gap

$$\alpha = \xi'_2 = (r_2/r_1)^q - 1 \qquad (27)$$

For the ring

$$\beta = \xi'_3 = (r_3^q - r_2^q)/r_1^q \qquad (28)$$

From eqns. (15) and (22) for the rotating disc system $q = 3$ while for the wall-jet system $q = 9/8$.

LIMITING CURRENTS ON THE DISC AND RING ELECTRODES

We now use eqn (23) to calculate the limiting currents on either the disc or the ring electrode. The boundary conditions for γ are

$\chi \to \infty \qquad \gamma \to 0$

$\xi = 0 \qquad \gamma = 0$

$\chi = 0 \qquad \gamma = -1$

Laplace transformation of eqn (23) followed by solution of the differential equation in terms of an Airy function gives

$$\bar{\gamma} = -\mathrm{Ai}(s^{1/3}\chi)/s\mathrm{Ai}(0)$$

from which we obtain

$$\left(\frac{\partial\gamma}{\partial\chi}\right)_0 = \frac{-\mathrm{Ai}'(0)}{\mathrm{Ai}(0)\Gamma(2/3)}\xi_p^{-1/3}$$

Substitution shows that for the wall-jet disc electrode the current density varies with $r^{-5/4}$, the electrode is certainly not uniformly accessible. Integration gives

$$\int_0^{\xi'_p}(\partial\gamma/\partial\chi)_0\mathrm{d}\xi_p = 3^{1/3}(\xi'_p)^{2/3}/2\Gamma(4/3) \qquad (29)$$

For the rotating disc electrode it is satisfactory that substitution of eqn. (29) in eqn. (24) with $\xi_1' = 1$ and $q = 3$ gives the Levich equation. For the wall-jet disc electrode with $\xi_1' = 1$ and $q = 9/8$ we obtain

$$i_{D,L} = 1.59kn'FD^{2/3}\nu^{-5/12}V_f^{3/4}a^{-1/2}r_1^{3/4}c_\infty \qquad (30)$$

It is also satisfactory that this result is identical with that of Yamada and Matsuda [2] who obtained it by considering a general relation derived from the stream function.

For the ring electrode for either the rotating or the wall-jet systems we find from eqn. (24) and eqn. (29)

$$i_{R,L} = \beta^{2/3} i_{D,L} \qquad (31)$$

where β is defined in eqn. (28).

THE COLLECTION EFFICIENCY

We now consider the collection efficiency of the ring-disc electrode. We assume that the bulk concentration of the species generated on the disc is zero. So we redefine γ to be

$$\gamma = c/c_0$$

where c_0 is the concentration of the species on the disc surface. We assume that this concentration is uniform. This will be achieved either if the disc electrode is passing its limiting current when c_0 will equal the bulk concentration of the precursor, or if the electrochemical system is reversible. The case where the system is irreversible and the current is much less than the limiting current will be considered in a subsequent paper.

From eqn. (24) we can write for the collection efficiency, N_0,

$$N_0 = -\int_0^{\beta}(\partial\gamma/\partial\chi)_0 \mathrm{d}\xi_3 \Big/ \int_0^1 (\partial\gamma/\partial\chi)_0 \mathrm{d}\xi_1$$

The boundary conditions for γ are

All zones	$\chi \to \infty$	$\gamma \to 0$
Disc	$\chi = 0$	$\gamma = 1$
Gap	$\chi = 0$	$(\partial\gamma/\partial\chi) = 0$
Ring	$\chi = 0$	$\gamma = 0$

These boundary conditions are the same for both the rotating disc and wall-jet systems, so we can conclude straightaway that N_0 for the wall-jet system obeys the same relation as for the rotating ring-disc [11]

$$N_0 = 1 - \mathrm{F}(\alpha/\beta) + \beta^{2/3}[1 - \mathrm{F}(\alpha)] - (1+\alpha+\beta)^{2/3}[1 - \mathrm{F}\{(\alpha/\beta)(1+\alpha+\beta)\}] \qquad (32)$$

where

TABLE 1

Gap and ring parameters to be used in eqn. (32) for N_0

	α	β
Rotating ring-disc	$(r_2/r_1)^3 - 1$	$(r_3/r_1)^3 - (r_2/r_1)^3$
Wall-jet ring-disc	$(r_2/r_1)^{9/8} - 1$	$(r_3/r_1)^{9/8} - (r_2/r_1)^{9/8}$
Double channel [a]	$(l_2/l_1) - 1$	$(l_3/l_1) - (l_2/l_1)$

[a] Measuring from the upstream edge of the upstream electrode, the gap lies between l_1 and l_2 and the downstream edge of the collecting electrode is at l_3

$$F(\theta) = \frac{3^{1/2}}{4\pi} \ln\left\{ \frac{(1+\theta^{1/3})^3}{1+\theta} \right\} + \frac{3}{2\pi} \tan^{-1}\left(\frac{2\theta^{1/3} - 1}{3^{1/2}} \right) + \frac{1}{4}$$

and where α and β are defined in eqns. (27) and (28). Results for α and β are given in Table 1. It is interesting that double electrodes set in the side of a channel or of a tube also obey the same differential eqn. (23). Braun [12] showed that for these electrodes the collection efficiency is also given by eqn. (32) with the definitions of α and β given in Table 1. In Table 2 we compare collection efficiencies for common radius ratios for the wall-jet and rotating systems. It can been seen that the collection for the wall-jet system is about 60% lower than that for the rotating system. This is because, as discussed above, the current density is not uniform in the wall-jet system; more material is generated near the centre of the disc and is therefore lost through the thin diffusion layer to the bulk of the solution.

DIFFUSION LAYER TITRATION CURVES

In a diffusion layer titration curve a species such as Br_2 is generated on the disc electrode and collected on the ring. During its passage from the disc to the ring the Br_2 may react with the target species to be determined

Disc... $Br^- \rightarrow \frac{1}{2}Br_2 + e$

Solution... $Br_2 + X \rightarrow$

Ring... $\frac{1}{2}Br_2 + e \rightarrow Br^-$

The ring current as a function of the disc current has the shape shown in Fig. 2. Initially no ring current is seen because all the Br_2 is consumed by X before it reaches the ring. There is then a curved portion where the bromine dominated region spreads across the ring electrode. Eventually when the ring electrode is entirely in the bromine dominated region the ring current is a linear function of the disc current. For the RRDE we have shown [13] that the take off point occurs at

$$|i_D| = |i_X|/[1 - F(\alpha)] \quad (33)$$

TABLE 2

Comparison of collection efficiencies of WJRDE and RRDE

WJRDE						RRDE					
r_3/r_2	r_2/r_1					r_1/r_2	r_2/r_1				
	1.02	1.04	1.06	1.08	1.10		1.02	1.04	1.06	1.08	1.10
1.02	0.059	0.056	0.054	0.052	0.051	1.02	0.101	0.095	0.090	0.087	0.084
1.03	0.076	0.072	0.070	0.068	0.066	1.03	0.129	0.122	0.116	0.112	0.109
1.04	0.090	0.086	0.083	0.081	0.079	1.04	0.153	0.144	0.138	0.134	0.130
1.05	0.103	0.099	0.096	0.093	0.091	1.05	0.174	0.165	0.158	0.153	0.149
1.06	0.114	0.110	0.107	0.104	0.102	1.06	0.192	0.183	0.176	0.171	0.166
1.07	0.125	0.120	0.117	0.114	0.112	1.07	0.209	0.200	0.192	0.187	0.182
1.08	0.135	0.130	0.126	0.123	0.121	1.08	0.225	0.215	0.208	0.202	0.197
1.09	0.144	0.139	0.135	0.132	0.130	1.09	0.239	0.229	0.222	0.216	0.211
1.10	0.153	0.148	0.144	0.140	0.138	1.10	0.253	0.243	0.235	0.229	0.224

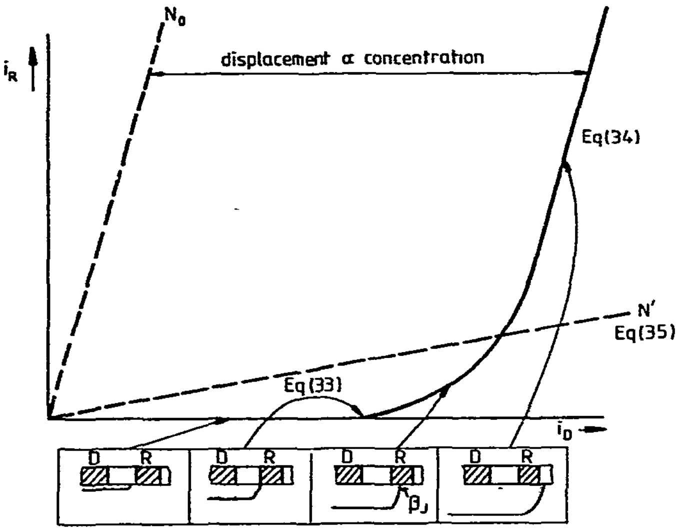

Fig. 2. Typical titration curve for a ring-disc electrode. The insets show the Br_2 dominated zone spreading out from the disc electrode.

and that the linear part is given by

$$i_R = N_0|i_D| - \beta^{2/3}|i_X| \tag{34}$$

where i_X is the limiting current on the disc that would be seen if the species X was electroactive.

In the curved portion we showed that the collection efficiency N' is given by:

$$N' = 1 - F\left(\frac{\alpha}{\beta_J}\right) - \frac{1+\alpha}{(1+\alpha+\beta_J)^{1/3}}\left[1 - F\left\{\frac{\alpha(1+\alpha+\beta_J)}{\beta_J}\right\}\right] \tag{35}$$

where

$$\frac{|i_X|}{|i_D|} = 1 - F(\alpha) - \frac{\beta_J^{1/3}}{(1+\alpha+\beta_J)^{1/3}}\left[1 - F\left\{\frac{\alpha(1+\alpha+\beta_J)}{\beta_J}\right\}\right]$$

and β_J describes the boundary on the ring electrode surface at $r = r_J$ between the Br_2 region and the X region:

$$0 < \beta_J = (r_J/r_1)^q - (r_2/r_1)^q < \beta \tag{36}$$

All of these expressions from eqns. (33) to (36) hold for the wall-jet ring-disc electrode using the definitions of α and β in Table 1 and of β_J in eqn. (36). The same results also hold for double channel electrodes.

The fact that N_0 for the wall-jet is less than that for the rotating system, means that the wall-jet ring-disc electrode is less sensitive than the rotating one. However the wall-jet electrode has three great advantages. First there are no rotating parts; the solution can be impelled through the jet by a pump or by gravity. Secondly there is a very small dead space; the solution is fired directly at the electrode. Thirdly the electrode has an ideal configuration for attachment to a chromatographic column. This means that for analytical applications such as diffusion layer titration curves the wall-jet system is to be preferred to the rotating system.

The theoretical results presented in this paper will be tested experimentally in the subsequent paper.

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