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Non-uniform accessibility and the use of hydrodynamic electrodes for mechanistic studies: a comparison of wall-jet and rotating disc electrodes

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The merits of non-uniformly accessible electrodes for discriminating between electrode reaction mechanisms are established. In particular a comparison of the theoretical behaviour of the uniformly accessible rotating disc electrode and the highly non-uniformly accessible wall-jet electrode towards a wide range of different types of electrode process shows that mechanistic resolution is better achieved with the latter electrode geometry.

1. Introduction

The use of hydrodynamic electrodes for the study of electrode reaction mechanisms has now reached an advanced stage of sophistication. A diverse range of electrode types has been developed and evaluated together with the associated theory so that it is possible to investigate most of the familiar mechanism types, such as EC, EC′, ECE or DISP, using any of the dropping mercury, rotating disc, channel, or wall-jet electrodes [1, 2]. Whilst it is established that the microelectrode, by virtue of its exceptionally high rates of mass transport, is the electrode of choice for the investigation of very fast reactions [3], a separate question arises as to which electrode type is the most mechanistically discriminating. That is to say, to what extent can closely similar electrode reaction mechanisms be best resolved? We have suggested previously [4] that hydrodynamic electrodes which have a high degree of non-uniform accessibility may be superior in this respect.

The importance of non-uniform accessibility can be understood as follows. In the case of a hydrodynamic electrode mechanistic conclusions are reached on the basis of the variation with one or more of the following as a function of the rate of mass transport (for example, flow rate, rotation speed, drop time, etc): (i) the transport-limited current, as measured by the "effective" number of electrons transferred, n_{eff}; (ii) the halfwave potential, in the case of a reversible electron transfer; and (iii) the waveshape as revealed, say, by Tafel analysis.

In all cases this variation depends on the competition between mass transport and heterogeneous charge transfer. To exemplify this and the role of uniformity of access, consider the case of an ECE process:

$$A +/- e^- = B \quad \text{(i)}$$

$$B \longrightarrow C \quad \text{(ii)}$$

$$C +/- e^- = G \quad \text{(iii)}$$

This is studied by examining the variation of n_{eff} with mass transport rate. Here n_{eff} is controlled by whether B is lost by transport into bulk solution ($n_{eff} \rightarrow 1$) or undergoes further electron transfer at the electrode ($n_{eff} \rightarrow 2$). The essential point is that, at a non-uniformly accessible electrode, the variation in n_{eff} with mass transport occurs more gradually than at a uniformly accessible electrode since in the region(s) of high mass transport, the steepness of the concentration gradients (thin diffusion layer) will promote the loss of the intermediate B, whereas in the region(s) of low mass transport B is encouraged to undergo further electron transfer because the shallow concentration gradients (thick diffusion layer) discourage transit of the intermediate away from the electrode surface. In contrast at a uniformly accessible electrode the loss of B is simply controlled by whether it is sufficiently long-lived to cross the (uniform) diffusion layer, resulting in a sharp transition in the effective number of electrons transferred as the rate of mass transfer is changed. These contrasting effects are illustrated in Fig. 1 for the particular cases of the rotating disc electrode (uniformly accessible) and the channel electrode (non-uniformly accessible). In essence, non-uniformly accessible electrodes will be more sensitive in distinguishing between similar mechanisms.

Generalisation of the above argument leads to the recognition that non-uniform accessibility is a desirable property of a hydrodynamic electrode designed for mechanistic work and we have previously pointed out the merits of channel electrodes in this respect [4, 5]. However, the electrode which has the greatest degree of non-uniform accessibility of any electrode geometry yet proposed is the wall-jet electrode [6–13]. In this a narrow jet of electrolyte impinges normally on the surface of a much wider planar electrode and spreads out radially over that surface; the fluid outside the jet being at rest [6]. Fig. 2 shows schematically the pattern of fluid flow.

The comparison of the non-uniformity of access of different electrode systems may be achieved by identi-

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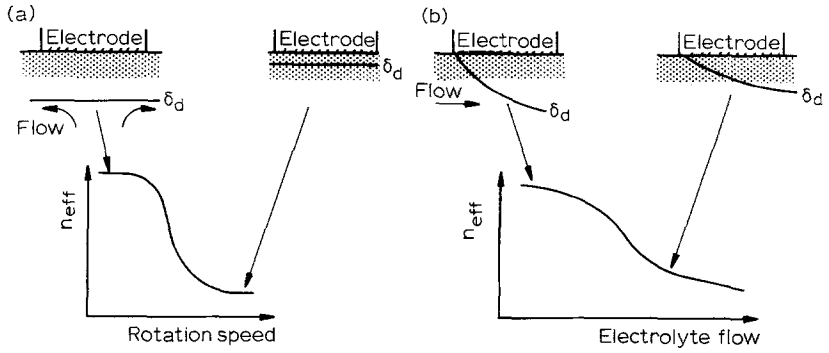

Fig. 1. (a) A rapid transition in the numbers of electrons transferred (n_{eff}), for an electrode reaction such as an ECE process which has electroactive intermediates, is observed at a uniformly accessible electrode, such as the rotating disc, when the diffusion layer becomes sufficiently thin for the intermediate (shown stipplied) to survive long enough to cross it. (b) A more gradual transition is seen at a non-uniformly accessible electrode such as the channel electrode depicted, where some intermediate escapes (upstream electrode edge) and some is always trapped (downstream electrode edge), due to the shape of the diffusion layer.

fying how the diffusion layer thickness, δ_d, varies over the electrode surface. This quantity is defined by the following equation for an electrode (area A) of arbitrary geometry

$$\delta_d = AFD[X]_\infty / I \quad (1)$$

where I is given by the appropriate transport-limited current equation for each electrode type, D is the diffusion coefficient of the electroactive species X which has a bulk concentration of $[X]_\infty$. The high non-uniformity of the wall-jet is shown by the fact that in this geometry δ_d varies as $r^{5/4}$ where r is measured radially from the centre of the electrode (see Fig. 2). In contrast the rotating disc is uniformly accessible ($\delta_d \propto r^0$) and the channel electrode is intermediate in behaviour having a diffusion layer thickness which increases merely as the cube root of the distance along its length.

The aim of this paper is to compare the characteristics of the rotating disc (RD) and the wall-jet electrodes (WJEs) for a wide range of electrode reaction mechanisms and thus explore the validity of the conclusions reached above as to the relative superiority of highly non-uniformly accessible electrodes for mechanistic work. We also attempt, for each mechanism, to quantify the ranges of rate constants for which each electrode type is applicable.

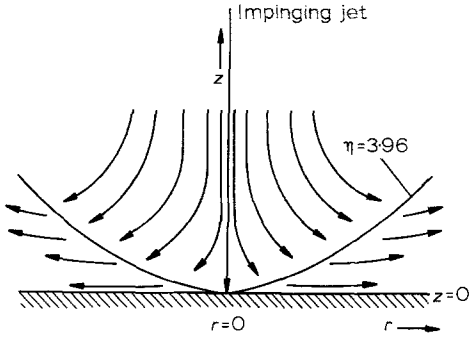

Fig. 2. The flow pattern at the wall-jet electrode. The contour $\eta = 3.96$ represents a boundary dividing flow towards the electrode from that moving away.

2. Theory

We have recently established a general computational method for the solution of mass transport problems involving wall-jet electrodes and shown how this may be extended for processes involving coupled homogeneous kinetics [14]. The method is based on the backwards implicit (BI) method [15, 16] and uses an "expanding grid" to facilitate efficient computations. Results were found to be in good agreement both with approximate analytical theory [12] where that was available, and with experiment [14].

The applications of the BI theory to the problems described below involve no new theoretical or computational developments and constitute a direct application of reference [14] or, in the case of waveshape/halfwave potential theory, reference [17]. We thus direct the reader to these references for details of the wall-jet calculations used to generate the results quoted below. In the following these are compared with the corresponding theoretical behaviour for rotating disc electrodes as reported in the literature.

3. Results and discussion

We first consider the form of the "working curves" describing the theoretical response of wall-jet and rotating disc electrodes for a diverse range of electrode process. A useful basis on which to compare the behaviour of the two electrodes is to first identify the diffusion layer thicknesses of the two electrodes:

$$^{RDE}\delta_d = 0.643 W^{-1/2} v^{1/6} D^{1/3} \quad (2)$$

where W is the disc rotation frequency (Hz), v is the solution kinematic viscosity ($cm^2\ s^{-1}$) and D is the diffusion coefficient of the electroactive species, and

$$^{WJE}\delta_d = 1.976 D^{1/3} R^{5/4} a^{1/2} V_f^{-3/4} k_c^{-1} \quad (3)$$

where the WJE has an electrode radius R, a jet radius a and the constant k_c (determined by experiment to be close to 0.9) quantifies the flow to the electrode [12, 14]. Unwin has shown [18] that for uniformly or approximately uniformly accessible electrodes (including the channel electrode) working curves for

one electrode type may be deduced from those of another merely by interchanging the relevant diffusion layer thicknesses. Application of this exercise to the RDE and WJE should then reveal the consequences of the high non-uniform accessibility of the latter in that the two working curves will not transform in this way.

3.1. *ECE mechanism*

This electrode reaction mechanism has been defined above in Reactions (i) to (iii) in which C is more easily reduced/oxidised than A. Such a process results in transport-limited currents which show a transition between two-electron and one-electron behaviour as the flow rate (V_f/cm^3 s^{-1}) or rotation speed (W/Hz) is increased. The theory describing the effective number of electrons transferred, n_{eff}, has been given for the RDE [19] and BI theory may be used to generate the corresponding behaviour at the WJE. In the former case n_{eff} is dependent on the parameter,

$$^{ECE}K_{RDE} = k(v/D)^{1/3}W^{-1} \quad (4)$$

where k is the first-order rate constant describing equation (ii) and D is the diffusion coefficient of the species A and B (assumed equal).

In the wall-jet case the analogous parameter is,

$$^{ECE}K_{WJE} = 7.975kR^{5/2}aV_f^{-3/2}k_c^{-2}v^{5/6}D^{-1/3} \quad (5)$$

If we interchange the diffusion layer thicknesses as suggested by the Unwin transformation [18], i.e. substitute Equations 2 and 3 into Equations 4 and 5, we find that,

$$\log_{10}\{^{ECE}K_{WJE}\} = \log_{10}\{^{ECE}K_{RDE}\} - 0.073 \quad (6)$$

Figure 3 shows the ECE working curves in the form of plots of n_{eff} versus either $\log_{10}\{^{ECE}K_{WJE}\}$ (as generated from backwards implicit (BI) calculations) or $(\log_{10}\{^{ECE}K_{RDE}\} - 0.073)$ (as taken from the literature [19]). If the WJE were behaving as an approximately uniformly accessible electrode the two curves shown would be superimposed [18]. The marked deviation reflects the non-uniformity of the wall-jet electrode. More importantly in respect of mechanistic resolution the transition of n_{eff} from 1 to 2 occurs much more gradually in the case of the WJE than the RDE and this implies a greater sensitivity of the former towards the identification of this mechanism. Note that the range of n_{eff} values shown in Fig. 3 (and in Fig. 4 below) is restricted since for $n_{eff} \sim 2$ the BI calculations become very expensive in terms of computer time [14]: nevertheless the experimentally pertinent range of n_{eff} is covered.

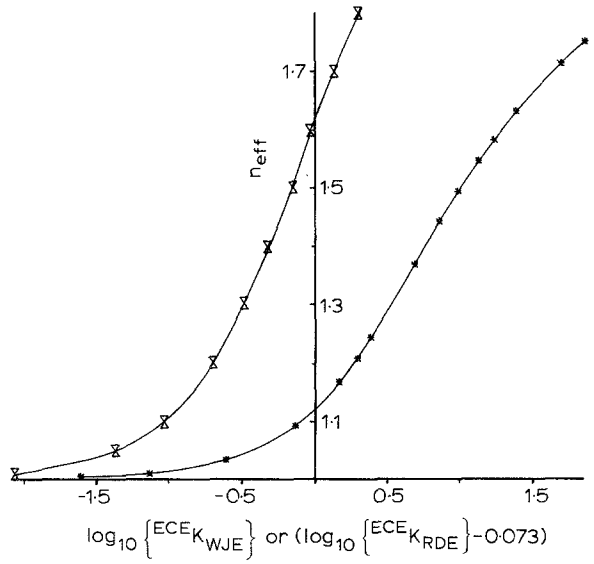

Fig. 3. A plot of n_{eff} against $\log_{10}\{^{ECE}K_{WJE}\}$ (*) or $(\log_{10}\{^{ECE}K_{EDE}\} - 0.073)$ (⋈) for the ECE mechanism.

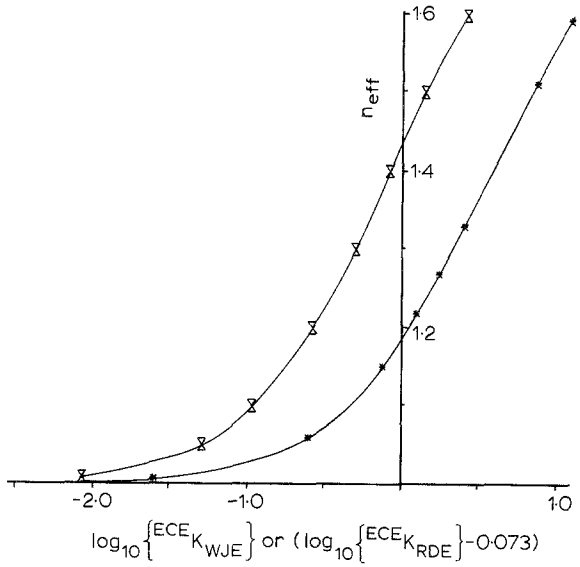

Fig. 4. A plot of n_{eff} against $\log_{10}\{^{DISP1}K_{WJE}\}$ (*) or $(\log_{10}\{^{DISP1}K_{RDE}\} - 0.073)$ (⋈) for the DISP1 mechanism.

3.2. *DISP1 mechanism*

This reaction mechanism is defined by

$$A +/- e^- = B \quad (iv)$$

$$B \longrightarrow C \quad (v)$$

$$B + C \xrightarrow{fast} A + G \quad (vi)$$

The scheme is closely related to the ECE mechanism and the relevant normalised rate constants $^{DISP1}K_{RDE}$ and $^{DISP1}K_{WJE}$ are also given by Equations 4 and 5 except that k now refers to Reaction (v). An equivalent equation to Equation 6 relates the two normalised rate constants under Unwin transformation and Fig. 4 shows working curves relating n_{eff} to these parameters – in the case of the WJE data this was computed as outlined above; the RDE data is taken from the literature [19]. Again it is found firstly that the curves are not superimposed (as a consequence of the non-uniformity of the WJE) and secondly that the wall-jet is a more sensitive test of the mechanism.

3.3. *EC′ mechanism*

This reaction mechanism is defined by

$$A + e^- = B \quad (vii)$$

$$B + Z \xrightarrow{k'} A + \text{products} \quad (viii)$$

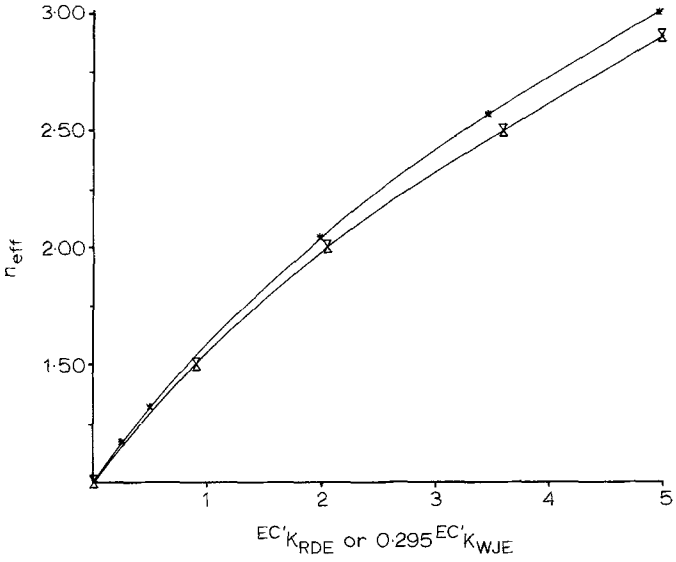

Fig. 5. A plot of n_{eff} against $^{EC'}K_{RDE}$ (⋈) or $0.295^{EC'}K_{WJE}$ (*) for the EC′ mechanism.

The products of the homogeneous step are taken to be electro-inactive at the potential of interest and the concentration of B is assumed to be much less than that of Z so that the chemical step can be assumed to be first order. The effective number of electrons transferred under transport-limited conditions has, in the case of the RDE, been shown [20] to depend on the parameter,

$$^{EC'}K_{RDE} = k''[Z]_\infty(8.032)^{-2/3}(v/D)^{1/3}W^{-1} \quad (7)$$

where $[Z]_\infty$ is the bulk concentration of Z. The corresponding quantity for the wall-jet is readily shown to be

$$^{EC'}K_{WJE} = 7.975k''[Z]_\infty R^{5/2}aV_f^{-3/2}k_c^{-2}v^{5/6}D^{-1/3} \quad (8)$$

Interchanging diffusion layer thicknesses leads to the result,

$$^{EC'}K_{RDE} = 0.295^{EC'}K_{WJE} \quad (9)$$

Figure 5 shows n_{eff} plotted against $^{EC'}K_{RDE}$ or $(0.295^{EC'}K_{WJE})$, the former curve being calculated by using backwards implicit theory and the latter being taken from the literature [20]. The non-uniformity of the WJE is again revealed by the non-superimposition of the curves.

3.4. *EC mechanism*

This mechanism is defined (for a reduction) by the scheme:

$$A + e^- = B \quad (ix)$$

$$B \xrightarrow{k^*} \text{products} \quad (x)$$

where the products are assumed to be electro-inactive and the A/B couple to be electrochemically reversible (E_0). The process can be studied through the shift in halfwave potential ($E_{1/2}$) as a function of the rate of mass transport [21–23]. This can readily be shown to depend on the normalised rate constants $^{EC}K_{WJE}$, (defined as in Equation 5 except that k^* replaces k) and

$$^{EC}K_{RDE} = k^*(8.032)^{-2/3}(v/D)^{1/3}W^{-1} \quad (10)$$

Figure 6 shows the variation of

$$\Delta\theta_{1/2} = (F/RT)(E_{1/2} - E_0) \quad (11)$$

with the appropriate parameter for either the WJE or the RDE. Again the form plotted on the x-axis is suggested by the relationship between the two normalised rate constants generated by interchanging diffusion layer thicknesses. Figure 6 reveals a slightly enhanced sensitivity of the WJE over the RDE in respect of the EC mechanism.

3.5. *EC2 mechanism*

This mechanism is again defined by Reactions (ix) and (x) except that now the decomposition of B is assumed to be second order (with rate constant k^{**}). Again the following kinetics cause a transport-dependent shift in the halfwave potential and the controlling parameters are identical to those introduced for the EC mechanism except that k^* is replaced by $k^{**}[A]_\infty$, where $[A]_\infty$ is the bulk concentration of A.

Figure 7 shows the working curves analogous to

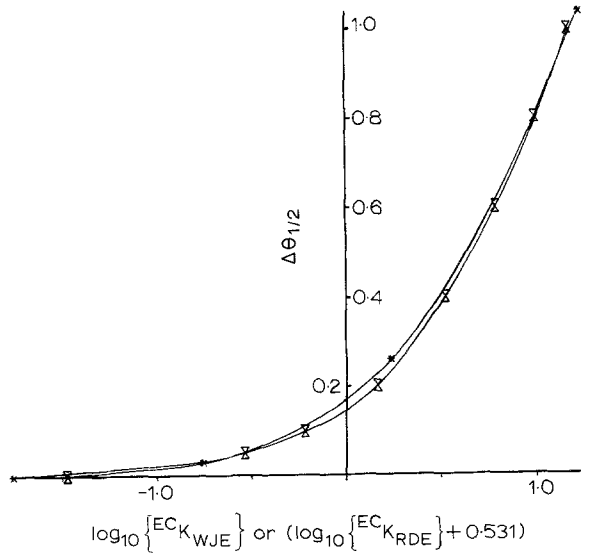

Fig. 6. A plot of $\Delta\theta_{1/2}$ against $\log_{10}\{^{EC}K_{WJE}\}$ (*) or $(\log_{10}\{^{EC}K_{RDE}\} + 0.531)$ (⋈) for the EC mechanism.

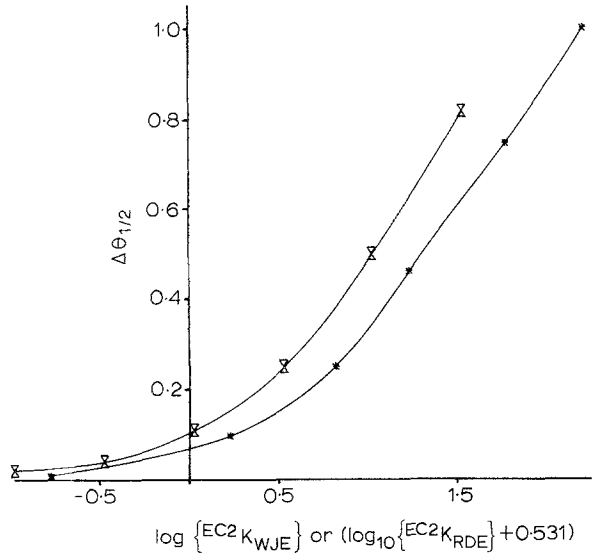

Fig. 7. A plot of $\Delta\theta_{1/2}$ against $\log_{10}\{^{EC2}K_{WJE}\}$ (*) or $(\log_{10}\{^{EC2}K_{RDE}$ + 0.531) (⋈) for the EC2 mechanism.

Figure 6. In this case the wall-jet non-uniformity is apparent. Notice that if a value of E_0 is available then Figs 6 and 7 permit the identification of the mechanism and the deduction of k^* or k^{**}, provided that a measurable shift in halfwave potential is found, by using the working curves to turn the experimental data into a knowledge of normalised rate constant as a function of either rotation speed or volume flow rate and then examining whether this relationship is as expected on the basis of the equations defining the relevant normalised rate constant. If however the experimentalist has no knowledge of E_0, and the following kinetics are too fast to be "outrun" by increasing the mass transport rate, then mechanistic and kinetic conclusions have to be found by fitting shifts in $\Delta\theta_{1/2}$ (i.e. $\Delta\Delta\theta_{1/2}$) with mass transport directly to working curves using trial rate constants. This relies on having data corresponding to the "transition" region of the working curve where the curve changes from being essentially independent of the normalised rate constant to following an asymptotic dependence of the form $\Delta\theta \propto \log_{10}$ (normalised rate constant). It can be seen that the WJE shows a larger such transition region, especially for the EC2 process, than does the RDE and thus is both more sensitive to identifying the mechanistic type and gives access to a wider range of rate constants than can be so measured using the RDE.

3.6. *Discussion*

The working curves generated for the different mechanisms reveal the predicted greater sensitivity of the non-uniformly accessible WJE over the RDE in respect of mechanistic resolution. Thus the ECE/DISP1 curves show a more gradual transition between the two- and one-electron limits, the EC′ curve displays a larger range of n_{eff} values for corresponding changes in normalised rate constants and the EC/EC2 curves a wider "transition" region between asymptotic and no dependence on the normalised rate constant.

In addition from the working curves we can deduce the range of rate constants accessible in each mechanism by both electrode types if we assume that the rotating disc operates in the frequency range $0.5 < W < 50$ and that the wall-jet has flow rates (in $cm^3\ s^{-1}$) constrained by $10^{-4} < V_f < 1$ and a radius, R, between 0.1 and 0.4 cm. For ECE or DISP processes this leads to a working range of $10^{-3} < k < 10^3$ (in s^{-1}) for the WJE in comparison to $5 \times 10^{-3} < k < 10$ for the RDE. In the case of EC′ reactions the WJE can examine processes faster than those for which $k''[Z]_\infty = 10^{-5}\ s^{-1}$ whereas the RDE is applicable to EC′ reactions with $k''[Z]_\infty > 10^{-1}\ s^{-1}$. EC and EC2 reactions for which $10^{-4} < k^*(k^{**}[A]_\infty) < 10^3$ (in s^{-1}) can be studied at a WJE (if E_0 is unknown) in contrast to the range $10^{-2} < k^*(k^{**}[A]_\infty) < 10$ for the RDE. Alternatively if E_0 can be found the WJE can be applied to EC processes with $k^*(k^{**}[A]_\infty) > 10^{-5}\ s^{-1}$. Consideration of the above numbers leads one to recognise that the WJE is applicable to a wider range of rate constants than is the RDE and that the working range is extended in both the slower and faster directions.

4. Conclusions

The WJE shows the following advantages over the RDE when examined comparatively for the purposes of mechanistic study:

(i) The electrode response as a function of the rate of mass transport is such as to give the WJE a greater sensitivity in respect of mechanistic resolution. This is more marked for ECE, DISP and EC2 mechanisms than for EC and EC′ processes.

(ii) Rather faster processes are amenable to study at the WJE particularly if extremes of electrolyte flow rate and electrode geometry are exploited.

(iii) Very slow processes can be examined with a WJE.

Whilst the merits of the non-uniform electrode reveal themselves in the above it is worth pointing out that difficulty of electrode fabrication will probably limit the size of practical electrodes which retain the wall-jet hydrodynamics to those of radii in excess of 0.1 cm. Thus microelectrodes in this geometry are unlikely to be realisable so that the principal merit of WJEs will lie in the optimal mechanistic resolution accessible to systems of intermediate kinetics. Finally is should be mentioned that for quasi-reversible systems (not discussed above) distorted voltammetric waveshapes will be observed for which modified theory is required [24].

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