Electroanalysis, 3 (1991) 631–636

The Wall-Jet Ring-Disc Electrode: The Measurement of Homogeneous Rate Constants from Steady State Ring Currents

Christopher M. A. Brett and Ana Maria C. F. Oliveira Brett
Departamento de Química, Universidade de Coimbra, 3049 Coimbra, Portugal

Richard G. Compton,[1] Adrian C. Fisher, and Gwynfor P. Tyley
Physical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, UK

ABSTRACT

The wall-jet ring-disc electrode is shown to provide a convenient means determining homogeneous rate constants by means of ring current measurements as a function of disc currents and electrolyte flow rates. Theory is provided for the analysis of such "collection efficiency" experiments and applied to the specific case of the bromination of anisole, where good agreement with experiment is found. Advantages with respect to the rotating ring-disc electrode are pointed out.

INTRODUCTION

Double electrodes have found general applicability in the study of electrode reaction mechanisms, particularly as rotating ring-disc electrodes [1]. The general principle is that intermediates formed on a generating (disc, upstream, . . .) electrode are transported to a detector (ring, downstream, . . .) electrode where they undergo further electrochemical reaction. First, the nature of the intermediates may be inferred from their current-voltage characteristics on the latter electrode. Second, kinetic data may be found through the use of so-called "collection efficiency" measurements. In these experiments the generator potential is swept through the range of interest while the detector potential is held at some value corresponding to the transport limited oxidation/reduction of a selected intermediate. The "collection efficiency" is defined as

$$N = \frac{\text{generator current}}{\text{detector current}} = \frac{i_{\text{gen}}}{i_{\text{det}}}$$

and reflects the amount of the intermediate that "survives" the transit across the gap from the disc to the ring. Measurements of N as a function of the rate of mass transport allow the nature of the kinetics of the intermediate's decay to be established. To date most measurements have utilized either the rotating ring-disc electrode (RRDE) [1, 2] or occasionally double channel electrodes [3].

Wall-jet electrodes are finding increasing use in analysis [4], principally because of the advantages of on-line detection and fast sample throughput. Development of the associated theory is important. In the context of mechanistic investigations using single hydrodynamic electrodes, the wall-jet geometry has been shown to possess considerable advantages over other geometries, most notably because of its highly nonuniform current distribution [5]. The flow is the result of a jet of fluid that strikes a planar surface at right angles and spreads out radially over that surface; the fluid outside the jet is at rest [6]. The wall-jet ring-disc electrode (WJRDE) [7] consists of concentric disc and ring electrodes separated by a thin insulating gap.

Wall-jet ring-disc electrodes show a number of advantages over RRDE's in mechanistic investigations. The flow-through nature of the wall-jet cell means that constant concentrations of reagents and products are found, and the buildup of intermediates and products of the electrode reaction that may influence the mechanism is prevented (chemostatic conditions); at the RRDE these conditions cannot be realized. Additionally the WJRDE is more highly sensitive to variations in mass transport than the RRDE (higher flow rate than rotation speed dependence). As is the case for the single wall-jet electrode, greater mechanistic discrimination should arise from the highly nonuniform current distribution compared with the equivalent rotating double electrode.

In this paper a general method for the description of kinetic processes at the WJRDE is developed. This theory can be readily extended to cover kinetically more complex systems. The particular case where the intermediate

---

[1] To whom correspondence should be addressed.

1040-0397/91/$3.50 + .25

decays with first order kinetics is shown to be in good agreement with experiment.

THEORY

We consider the following general process occuring at a WJRDE:

Disc: A + e = B
Solution: B → Products
Ring: B → A + e

B undergoes reaction by first order kinetics (an EC process, rate constant k_{EC}/s^{-1}). The convective diffusion equations relevant to the WJRDE geometry under steady state conditions are:

$$v_r \frac{\partial a}{\partial r} + v_z \frac{\partial a}{\partial z} = D \frac{\partial^2 a}{\partial z^2}$$

$$v_r \frac{\partial b}{\partial r} + v_z \frac{\partial b}{\partial z} = D \frac{\partial^2 b}{\partial z^2} - k_{EC} b$$

where v_r is the radial solution velocity (*r*-direction) and v_z is the velocity in the direction normal to the electrode surface (*z*-direction), $a = [A]$, $b = [B]$ and D is the diffusion coefficient of A and B (assumed equal). Radial diffusion has been neglected. The basis of this approximation has been developed elsewhere [7] and is discussed below. Further it is assumed that only A is present in bulk solution and all concentrations are normalized relative to this bulk value, $[A]_\infty$, viz. $g^A = [A]/[A]_\infty$ and $g^B = [B]/[A]_\infty$.

We have shown elsewhere [5, 8] how the backwards implicit finite difference method may be used to calculate full current-voltage curves at a single wall-jet electrode. In particular if the boundary conditions pertinent to the electrode surface are specified the concentration profiles of all kinetically significant species may be generated via a matrix formalism. We adopt essentially the same protocol in this work except that now boundary conditions for both A and B must be specified in each of the different surface zones of the electrode, i.e. the disc, the gap, and the ring. These are:

1. The disc: Identical conditions operate as for a single wall-jet electrode. Specifically we assume that A/B couple to be electrochemically reversible [8].
2. The gap: Here a "no-flux" condition operates and the surface boundary conditions become

$$D\left(\frac{\partial b}{\partial z}\right) = D\left(\frac{\partial a}{\partial z}\right) = 0$$

When placed into finite difference form these become

$$g^{A}_{0,k} = g^{A}_{1,k}$$
$$g^{B}_{0,k} = g^{B}_{1,k}$$

3. The ring: This surface is potentiostatted so that all the B arriving at it is reconverted to A. This entails the following boundary condition in finite difference form:

$$-\left(\frac{\partial a}{\partial z}\right) = \left(\frac{\partial b}{\partial z}\right)$$

Additionally,

$$g^{B}_{0k} = 0.0$$

These boundary conditions allow the generation of the necessary matrix elements so as to permit solution of the problem via the backwards implicit method. For the disc region these are the same as for an EC mechanism at the wall-jet electrode [8] and are dependent on the disc potential. For the gap region the matrix elements are the same as for the disc region except as follows:

$$d^{A}_{1} = g^{A}_{1,k'}$$
$$b^{A}_{1} = [\epsilon_{1k+1} - \lambda_{1k+1} + 1]$$
$$d^{B}_{1} = g^{B}_{1,k'}$$
$$b^{B}_{1} = [\epsilon_{1k+1} - \lambda_{1,k+1} + 1 + K_{1k+1}]$$

For the ring region the modified matrix elements required are:

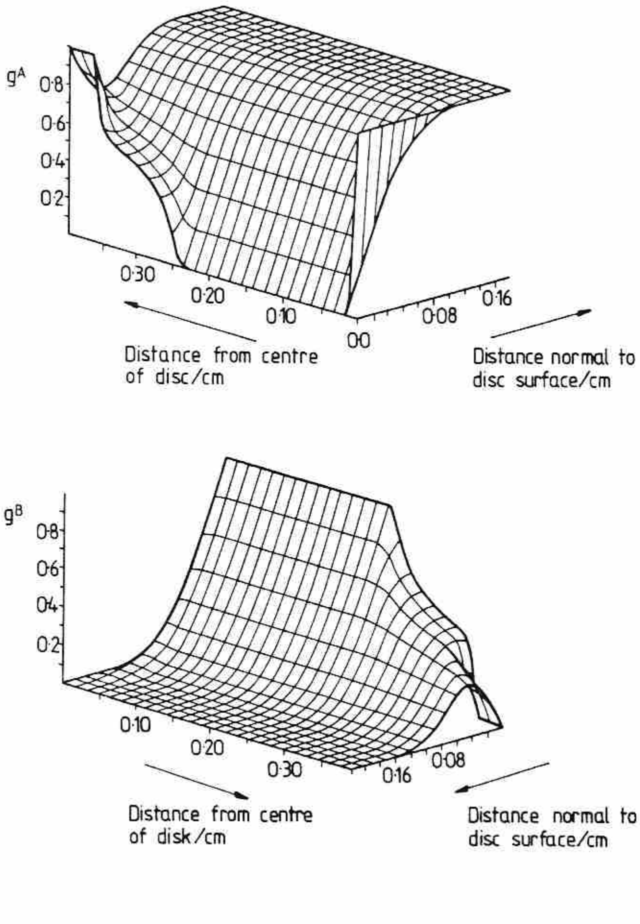
$$d^{A}_{1} = g^{A}_{1,k'} + \epsilon_{1,k+1} g^{B}_{1,k+1}$$
$$b^{A}_{1} = [\epsilon_{1k+1} - \lambda_{1k+1} + 1]$$
$$d^{B}_{1} = g^{B}_{1,k'}$$
$$b^{B}_{1} = [2\epsilon_{1k+1} - \lambda_{1k+1} + 1 + K_{1k+1}]$$

Considering the electrode as three distinct areas (disc, gap, and ring) the method of mathematical solution is first to solve the matrix equations for A and B for the disc region using the Thomas Algorithm [9]. This produces the concentrations of A and B at the boundary of the disc with the gap. These concentrations then permit the solution of the matrix equations for the gap. The results then provide "starting" concentrations so as to allow solution in the zone of the ring. The disc current can then be calculated as before [8] and the ring current analogously. Computations were carried out using programs written in Fortran 77 on a VAX 11/785 mainframe computer. Copies of the Fortran program can be obtained from the authors.

Model calculations were carried out for a WJRDE with the following parameters: disc radius = 0.35 cm, ring inner radius = 0.375 cm, disc outer radius = 0.40 cm, jet nozzle diameter = 0.0345 cm, $D = 2.0 \times 10^{-6}$ cm² s⁻¹, kinematic solution viscosity = 0.0089 cm² s⁻¹, electrolyte flow rate = 0.001 cm³ s⁻¹ and the experimental constant k_c = 0.9. In all calculations convergence was examined by varying the size of the computational grid used: In the absence of kinetics a grid of 200 × 10000 was sufficient to give convergence to three significant figures in the computed collection efficiency. This size increased with the magnitude of k_{EC}: For $k_{EC} = 0.1\ s^{-1}$ a size 500 × 10000 was needed because of the B concentration profile being constrained to within a smaller distance of the electrode. Typical results generated for the no kinetics case ($k_{EC} = 0$) can be seen in Figure 1. Figure 1a shows that, as expected, A is depleted in the vicinity of the disc electrode. This depletion is then partially relaxed in the zone of the gap as A diffuses from bulk solution. Finally the ring electrode regenerates A from B thus restoring the concentration of the former to its bulk value at, and near, the surface of the electrode. The introduction of kinetics produced corresponding profiles: Figure 2 relates to the specific case of the EC process with $k_{EC} = 0.1\ s^{-1}$ and were computed using the parameters specified above. The loss of A as compared to the no kinetics case, through homogeneous decay, is evident.

In the case of a simple electron transfer in the absence of homogeneous kinetics as analytical theory has been developed for the calculation of the collection efficiency [7]. It was found that the computed collection efficiencies for the no kinetics case quoted by Albery [7] agreed with the values calculated from analytical theory.

FIGURE 1. Concentration profiles within the wall-jet flow cell for the no kinetics case, calculated using the parameters specified in the text. (a) Concentration profile of A; (b) Concentration profile of B.



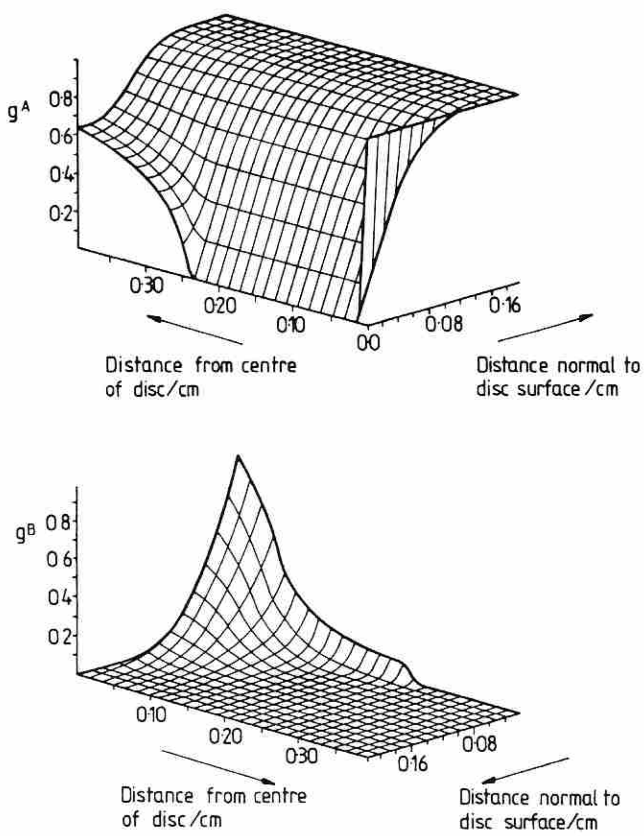


FIGURE 2. Concentration profiles with the wall-jet flow cell for the case where $k_{EC} = 0.1\ s^{-1}$, calculated using the parameters specified in the text. (a) Concentration profile of A; (b) Concentration profile of B.

The variation of disc current and ring current as the disc potential was varied was next examined. Figure 3 shows plots of ring current against disc current for various rate constants, $k_{EC} = 0$, 0.1, and $0.5\ s^{-1}$ with the same parameters as above except for an electrolyte flow rate of $0.05\ cm^3\ s^{-1}$. As expected, a linear relationship is observed and the slopes of the lines correspond to the measured collection efficiency under these conditions.

Figure 4 shows how the collection efficiency as deduced from the slopes of the lines such as those shown in Figure 3 varies with flow rate for the cell geometry specified above; the example used is for $k_{EC} = 0.1\ s^{-1}$. Clearly, as the flow rate is reduced more B is lost before it arrives at the ring electrode and thus the collection efficiency falls. Figure 5 shows the variation of collection efficiency with rate constant at a fixed flow rate. As expected, the collection efficiency falls as the rate constant increases because of the depletion of B as it is transported to the ring electrode.

Plots such as Figures 4 and 5 may be used directly for the analysis of experimental data gathered at a WJRDE of known geometry. Alternatively, and with greater generality, a "working curve" may be generated for a specific electrode geometry. This utilizes the fact that the under the

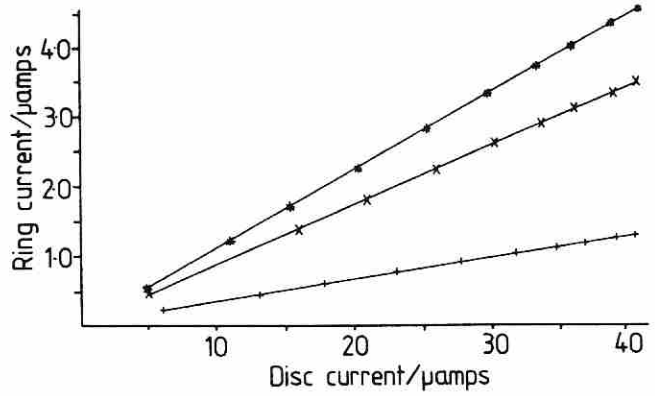


FIGURE 3. A plot of ring current (microamps) against disc current (microamps) for the EC mechanism with k_{EC} = 0 (*), 0.1 (×) and 0.5 (+) s^{-1}.

mass transport model specified above the collection efficiency for a given electrode is a unique function of a dimenionless rate constant *K*, defined in reference [8], where *K* is proportional to (disc radius)$^{5/2}$ and inversely proportional to (electrolyte flow rate)$^{3/2}$. Figure 6 shows such a working curve, which relates to the electrode geometry utilized in the experiments described below.

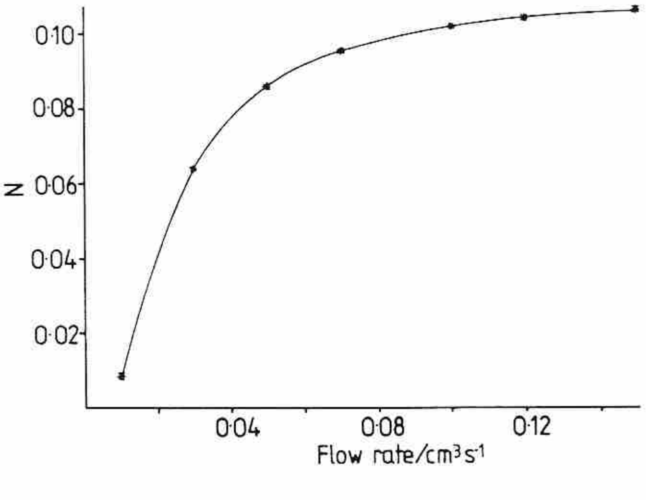
EXPERIMENTAL

The theory developed in the previous section was tested using the bromination of anisole according to the scheme:

Disc: $Br^- \rightleftarrows \frac{1}{2}Br_2 + e$
Solution: $CH_3OC_6H_5 + Br_2 \rightarrow CH_3OC_6H_4Br + HBr$
Ring: $\frac{1}{2}Br_2 + e \rightarrow Br^-$

Experimental conditions were similar to those used at the RRDE[10], i.e. [NaBr] = 0.5 M; [$HClO_4$] = 10^{-3} M; [anisole] = 0.92 and 1.47 × 10^{-3} M. Preliminary experiments were conducted using ca. 1 mM NaBr.

FIGURE 4. A plot of the variation in collection efficiency with flow rate ($cm^3\ s^{-1}$) for the case where k_{EC} = 0.1 s^{-1}.



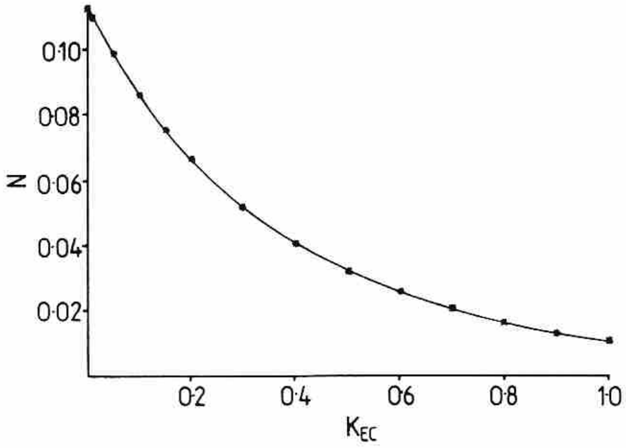


FIGURE 5. A plot of the variation in collection efficiency with k_{EC} at a fixed flow rate of 0.05 $cm^3\ s^{-1}$.

A platinum-platinum WJRDE in Kel-F sheath of the following dimensions was employed: disc radius 1.637 mm; inner ring radius 1.745 mm; outer ring radius 1.888 mm. This ring-disc electrode was polished with successively finer grades of alumina down to 0.3 μm. The electrode was inserted into a wall-jet cell of the type previously described [7], the nozzle diameter of which was 0.345 mm. The experimental value of the cell constant k_c was found to be 0.86. The reference electrode was an Ag/AgCl wire in 1.0 M KCl located within a separate compartment. Solution was driven through the cell by a Pharmacia P-3 three channel peristaltic pump. Pump pulsations were minimized by a hollow glass ball and a 5 m length of Teflon tubing. Flow rates were calibrated gravimetrically for each experimental collection efficiency measurement. Experiments were conducted at constant temperature (25°C).

Anisole was distilled in a nitrogen atmosphere under reduced pressure. All reagents were analytical grade and solutions were made with triply distilled water.

Collection efficiencies were measured using an Oxford Electrodes galvano/potentiostat to three significant figures. The ring electrode was potentiostatted at +0.45 V vs. Ag/AgCl reference.

RESULTS AND DISCUSSION

Preliminary electrochemical experiments using the Br_2/Br^- couple in the medium described above (except for the absence of anisole) showed that the wall-jet disc electrode behaves as expected. Specifically, the transport-limited current, i_{lim}, showed the predicted [7] dependence on flow rate and gave a diffusion coefficient for Br^- in good agreement with the literature [11] and mass transport corrected Tafel analysis of the current (i)/voltage curves—plots of electrode potential vs. $\log_{10}(p - p^{-1})$ where $p = (i_{lim}/i)^{1/2}$—gave slopes of 59 mV per decade as expected for a reversible electrode process of the stoichiometry

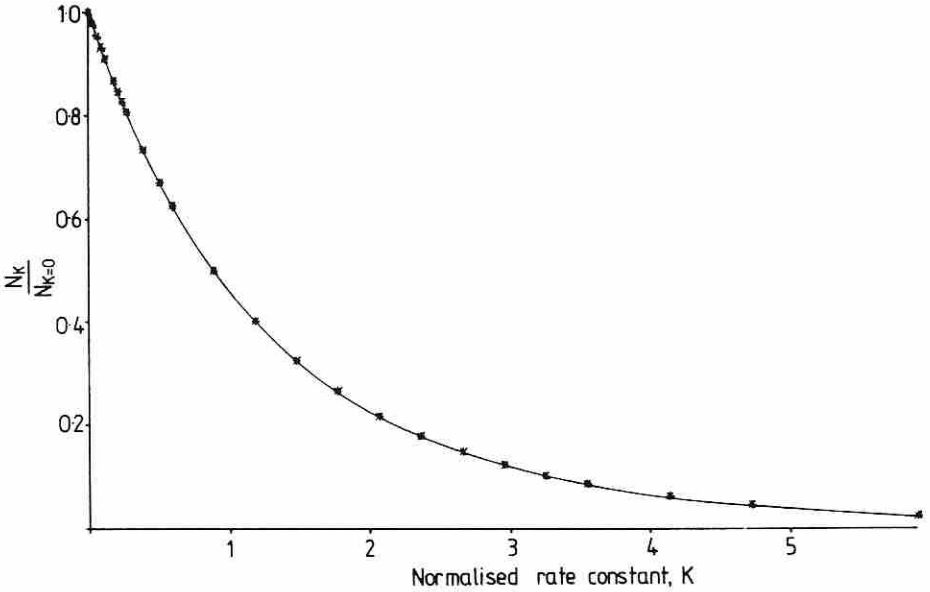


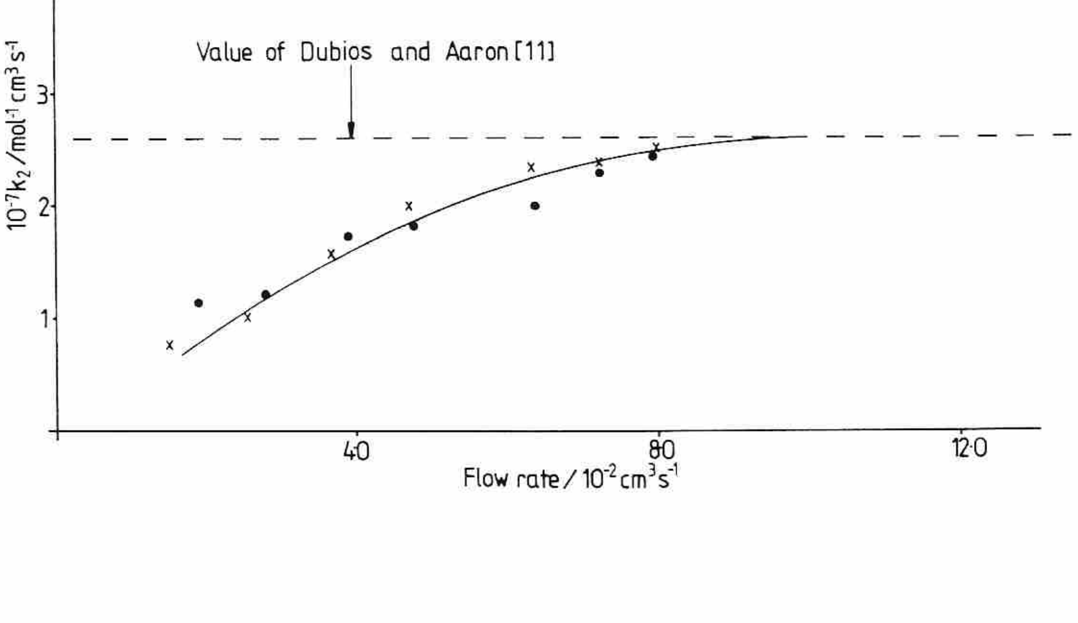
FIGURE 6. A working curve showing the dependence of the collection efficiency on K. The electrode geometry is specified in the text.

in question. The collection efficiency of the double electrode was determined to be 0.130; this compares well with the theoretical value of 0.127 [7].

Kinetic collection efficiencies, N_k, were determined as described above and plots of ring current, i_R, vs. disc current, i_D, obtained as a function of electrolyte flow rate (0.015→0.080 $cm^3 s^{-1}$). Disc currents up to maxima of the order of 10 μA were employed to ensure psuedo-first order conditions. i_R was found to be accurately linear with i_D over this range, and the slopes of the plots were used as a direct measure of N_k. These values of N_k were analyzed using a working curve similar to that shown in Figure 6, other than that it was generated for the geometry and cell constant specified in the preceding section. This procedure enabled the normalized rate constant, *vide supra*, to be calculated as a function of flow rate. Normalized rate constant values were then converted into the corresponding true pseudo-first order rate constants. The second order rate constant, k_2, for the bromination of anisole was deduced from the latter from a knowledge of [anisole] and the speciation of the Br_3^-/Br_2 system, following the protocol developed by Albery [10].

Figure 7 shows the variation of k_2 with flow rate. Also included is the value deduced by Dubois and Aaron [12]. It can be seen that the WJRDE determination is in good agreement with [12] at high flow rates, but that at lower flow rates the electrochemical method provides an underestimate of the rate constant. This systematic behavior can

FIGURE 7. A plot of second order rate constant, $k_2/mol^{-1}\ cm^3\ s^{-1}$ vs. flow rate/$cm^3\ s^{-1}$ for the bromination of anisole from WJRDE measurements: [anisole]: 0.92 × 10^{-3} M (×), 1.47 × 10^{-3} M (○). Other conditions as specified in text.



be interpreted as a consequence of the simplified model of the cell hydrodynamics presented above, in which diffusive transport was assumed to take place solely in a direction normal to the electrode. Such an approximation has previously been found to give good agreement with experiments conducted at single wall-jet electrodes. However, in the double electrode experiments described here it may be expected that radial diffusion plays a not insignificant role at very low flow rates. This is because of the large radial concentration gradients that necessarily arise at the gap/ring interface when collection efficiency experiments are being undertaken allied to those arising from the intrinsic nonuniformity of the wall-jet geometry as compared to, for instance, the rotating ring-disc electrode configuration, compounded by the relatively high diffusion coefficient of the bromide ion.

In conclusion it can be seen that the WJRDE provides a simple method for the determination of homogeneous rate constants and that the theory given above provides a satisfactory basis for the analysis of experimental results so long as sufficiently fast flow rates are utilized. The algorithm used in the numerical theory is completely general, and thus the theory described in this paper can be readily extended to the kinetics of more complex real systems. A particular advantage of the wall-jet approach over the RRDE and most other electrochemical methods is that determinations are conducted under chemostatic conditions, since spent reagent flows cleanly to waste in the wall-jet flow cell.

REFERENCES

1. W. J. Albery and M. L. Hitchman, *Ring Disc Electrodes,* Clarendon Press, Oxford, 1971.
2. K. B. Prater and A. J. Bard, *J. Electrochem. Soc. 117* (1970) 335.
3. A. C. Fisher and R. G. Compton, *J. Appl. Electrochem., 21* (1991) 208.
4. C. M. A. Brett and M. M. P. M. Neto, *J. Electroanal. Chem. 258* (1989) 345.
5. R. G. Compton, C. R. Greaves, and A. M. Waller, *J. Appl. Electrochem. 20* (1990) 575.
6. M. B. Glauert, *J. Fluid Mech. 1* (1956) 625.
7. W. J. Albery and C. M. A. Brett, *J. Electroanal. Chem. 148* (1983) 201.
8. R. G. Compton, A. C. Fisher, and G. P. Tyley, *J. Appl. Electrochem., 20* (1990) 912.
9. L. Lapidus and G. Pinder, *Numerical Solutions of Partial Differential Equations in Science and Engineering,* Wiley, New York, 1982.
10. W. J. Albery, M. L. Hitchman, and J. Ulstrup, *Trans. Faraday Soc. 64* (1968) 2831.
11. R. Landberg, W. Greissler, and S. Muller, *Z. Chem. 1* (1961) 169.
12. J. E. Dubois and J. J. Aaron, *Compt. Rend. 258* (1964) 2313.