Mass Transfer at a Microelectrode in Channel Flow

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Several recent papers have been devoted to numerical analysis of mass transfer from rectangular microband or circular microdisk electrodes placed in a parabolic channel flow. The numerical calculations typically show good agreement with experimental results. Frequently, the geometry and flow conditions are such that all the mass transfer occurs in a thin layer adjacent to the electrode, and such confinement simplifies the characterization of the transport to the problem of mass transfer in a shear flow. Analytical formulas are available for strip-shaped and disk-shaped geometries for both low and high Péclet numbers (the dimensionless wall shear rate) and are shown here to be in good agreement with the published experimental electrochemical results.

Introduction

Microelectrodes have become more commonly used in electrochemistry to probe kinetics of fast chemical reactions with rate constants on the order of 10^2-10^4 s^{-1}. Even faster reactions can be probed if the mass transfer rate is increased by forcing the solution to flow over the microelectrode. In recent studies by Booth *et al.*[1] and Compton *et al.*[2] numerical solutions of the steady state rate of mass transfer from a microelectrode in a channel flow have been reported and compared with experimental results (see also Rees *et al.*,[3,4] Tait *et al.*[5]). In this article we demonstrate that most of the experimental results are, in fact, in good agreement with existing analytical results, derived assuming the mass transfer rate is controlled by the shear rate near the boundary, which is consistent with the flow conditions utilized in the recent experiments. These analytical results are available in the fluid mechanics literature, and here we show how these results may be applied to microelectrodes in channel flow.

For a given ratio of the microelectrode dimension to the channel size, it is expected that at very low flow rates the effect of the upper boundary on the mass transfer is important. As the flow is increased, the downstream convection prevents rapid diffusion to the upper boundary, but the pressure-driven flow profile is parabolic, and numerical computations, such as those developed by Booth *et al.*[1] and Compton *et al.*,[2] are required to establish the rate of mass transfer as a function of flow rate. At sufficiently high flow rates, the reacted species is confined to a thin layer near the electrode, where the flow may be approximated by a linear shear flow. This high flow rate regime is common in the above-mentioned published experiments and corresponds to a limit where analytical progress has been made.

These physical arguments are made more precise below by considering the dual influences of a geometric parameter giving the ratio of electrode to channel size and a Péclet number characterizing the ratio of convective transport by the mean flow to diffusive transport. For the important high flow rate limit we demonstrate that mass transfer is characterized by a single dimensionless parameter, called the shear Péclet number, P_s, which is proportional to the local wall shear rate. We then summarize the analytical formulas and show that good agreement exists between the analytical solutions and the published experimental results over a wide range of P_s.

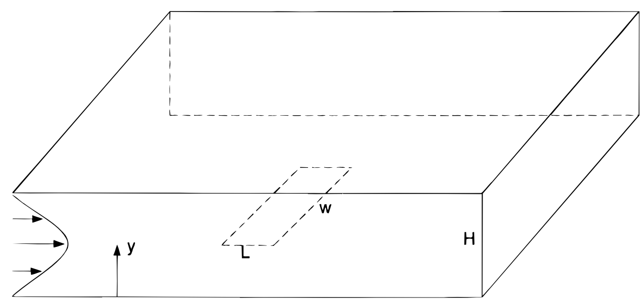

Figure 1. Parabolic channel flow over a microband electrode. For the case of a circular disk microelectrode, the disk radius is denoted by *a*.

The Transport Problem

We begin with an analysis of steady state mass transport from a rectangular microband electrode. Figure 1 illustrates the channel flow geometry. Typically, the width *w* of a microband electrode is much greater than its length *L* along the flow direction. For example, microband electrodes used in experiments by Compton *et al.*[2] have $w = 0.4$ cm, while *L* is on the order of micrometers. Provided that the channel width is much greater than *w*, the microband transport problem can be treated as two-dimensional. A solution containing chemical species C^+ flows over the electrode with steady laminar parabolic velocity $\mathbf{u} = u(\hat{y})\mathbf{e}_x$, where

$$\hat{u}(\hat{y}) = U\frac{\hat{y}}{H}\left(1 - \frac{\hat{y}}{H}\right) \tag{1}$$

Here a circumflex is placed over dimensional variables, $\hat{y} = 0$ corresponds to the bottom of the channel flow cell, *H* is the height of the channel cell,[6] and *U* is a characteristic velocity defined in the terms of the mean flow rate V_f by $U = V_f/6Hd$, where d is the channel width. It is assumed that the flow is undisturbed by any electrochemical reactions.

In the experiments, the electrode is maintained at a constant potential so that the reaction $C^+ + e^- \rightarrow C$ is carried to completion on the electrode surface. The chemical species C has diffusivity *D* and concentration in solution denoted by *c*. On the electrode, $c = [c]$, which represents a uniform concen-

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tration, while far away from the electrode $c \to 0$ and on the channel walls $\partial c/\partial \hat{y} = 0$. The steady state distribution of species C is then obtained by solving the convective−diffusion equation

$$\hat{u}(\hat{y})\frac{\partial c}{\partial \hat{x}} = D\left(\frac{\partial^2 c}{\partial \hat{x}^2} + \frac{\partial^2 c}{\partial \hat{y}^2}\right) \quad (2)$$

This transport problem may be characterized by two dimensionless parameters, the Péclet numbers, $P = UH/D$, representing the ratio of convective transport to diffusive transport, and L/H, the ratio of the electrode size to the length scale characteristic of velocity variations. An analogous nondimensional characterization applies for a circular microdisk with L replaced by the disk radius a. In typical electrochemical experiments, P is large and L/H is small. As an example, Compton *et al.*'s experiments with a 4 μm microband electrode have $P = 170{-}1200$ and $L/H \approx 0.01$. Both limits suggest that mass transfer from the electrode is confined to a thin region next to the electrode, and this is confirmed by the numerically calculated concentration profiles plotted for microdisk electrodes in Figures 4 and 5 of Booth *et al.*[1] Outside this narrow mass transfer layer the concentration is effectively undisturbed from its bulk value. Consequently, only the velocity profile nearest to the wall influences the mass transfer rate and the relevant velocity profile is then the shear flow $\hat{u} = S\hat{y}$, where S is the wall shear rate given by $S = U/H$.

It is then appropriate to nondimensionalize eq 2 by setting $y = \hat{y}/L$, $x = \hat{x}/L$, and $\hat{u} = SLy$. The convective−diffusion equation becomes

$$P_s y \frac{\partial c}{\partial x} = \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \quad (3)$$

where P_s is the shear Péclet number defined as $P_s = UL^2/HD = P(L/H)^2$. P_s represents the ratio of convective transport to diffusive transport within the thin mass transfer layer and completely characterizes the transport rate.

Discussion

When $P_s \ll 1$, diffusive transport dominates near the electrode, which implies that edge effects are significant and diffusion occurs evenly in all directions. The influence of convection on the rate of mass transfer to or from the electrode may be calculated analytically using the method of matched asymptotic expansions. In particular, we note that the diffusive solution (to the Laplace equation) has $c \sim r^{-1}$ as $r \to \infty$ in three dimensions, whereas $c \sim \ln r$ in two dimensions. Even when $P_s \ll 1$, convection becomes comparable to diffusion at a distance $L/P_s^{1/2}$ from the electrode. We may neglect the parabolic aspect to the flow profile and use analytical results for low Peclét number transport in shear flow, eqs 6 and 8 below, provided $L/P^{1/2} \ll H$. As a rule of thumb, it is reasonable to require the thickness of this far field region to be less than 1/10 of the channel height, corresponding to a 10% maximum difference in velocity between the actual parabolic flow profile and the assumed shear flow profile, in which case low Péclet number results derived for the shear flow problem are reliable if $1 \gg P_s > 100(L/H)^2$.

When $P_s \gg 1$, convection is balanced by cross-stream diffusion, which leads to the classic Lévêque problem:[7]

$$P_s y \frac{\partial c}{\partial x} = \frac{\partial^2 c}{\partial y^2} \quad (4)$$

This form of the equation indicates a mass transfer boundary layer with thickness $O(LP_s^{-1/3})$, which gives rise to a mass transfer rate from the surface proportional to $O(P_s^{1/3})$. A similarity solution exists for the Lévêque problem, and although in this high Péclet number limit edge effects and axial diffusion are negligible, they may be incorporated in more sophisticated analyses valid for moderate shear Péclet numbers (see eqs 7 and 9).

For microelectrode experiments, although the mean flow Péclet number P is large, the shear Péclet number P_s is usually moderate. Experiments performed by Booth *et al.*[1] and Compton *et al.*[2] have $0.01 < P_s < 200$. For these intermediate shear Péclet numbers,[8] the thickness of the mass transfer layer is set by the microband length L. Within the mass transfer layer, downstream diffusion is as important as cross-stream diffusion. The rate of mass transfer as a function of P_s in the above range can be approximated by constructing a finite P_s correction to the pure diffusion limit for $P_s < 1$ or a moderate P_s correction to the Lévêque result for $P_s > 1$. These asymptotic results are available in the fluid mechanics literature and are summarized in the next section.

Analytical Results for Low and High Shear Péclet Numbers

Strip Shapes. For microband electrodes, two sets of experimental data for $0.01 < P_s < 10$ are reported by Compton *et al*. The majority of the experiments correspond to low shear Péclet numbers P_s. We now summarize asymptotic results for low and high shear Péclet numbers and show that the experiments are well represented by these analytical results without having to resort to expensive numerical calculations. In general, it is convenient to report all results in dimensionless form, and it is common in the heat and mass transfer literature to describe the dimensionless flux as a Nusselt number, denoted N. For strip shapes the Nusselt number is defined as

$$N = \frac{I}{nF[c]Dw} \quad (5)$$

where I is the measured current, n the number of electrons transferred per reacting ion, F the Faraday constant, $[c]$ the electrode surface concentration of species c, D the diffusivity, and w the width of the electrode.

Ackerberg *et al.*[9] developed an asymptotic solution for mass transfer from a two-dimensional strip in a shear flow at low shear Péclet numbers.[10] The analysis distinguishes a region in the near field close to the electrode, where diffusion dominates, and a far field region which occurs at an approximate distance $O(L/P_s^{1/2})$ from the electrode, as discussed above. Matched asymptotic expansions are then used to develop the solution for $P_s < 1$:

$$N = \pi g(P_s)(1 - 0.04633P_s g(P_s)) + O(P_s g(P_s)) \quad \text{where} \quad g(P_s)^{-1} = \ln(4/P_s^{1/2}) + 1.0559 \quad (6)$$

At very low shear Péclet numbers the finite strip looks like a two-dimensional source, which is the origin of the $\ln(P_s)$ behavior.

Newman[7] derived a high shear Péclet number solution by treating the leading edge, the bulk, and the trailing edge of the strip separately. For $P_s > 1$, the surface flux is[11]

$$N = 0.8075P_s^{1/3} + 0.7058P_s^{-1/6} - 0.1984P_s^{-1/3} + O(P_s^{-2/3}) \quad (7)$$

In Figure 2 we have plotted the asymptotic results (6) and (7)

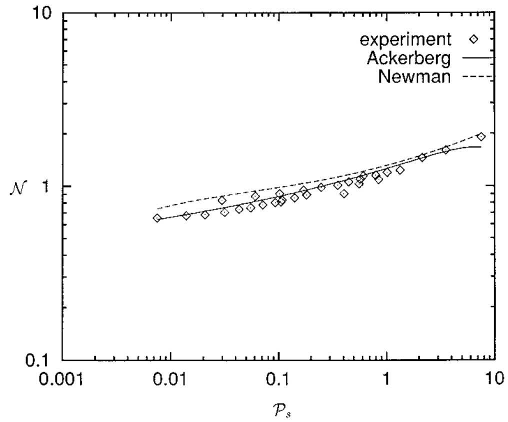

Figure 2. Dimensionless rate of mass transfer versus the shear Péclet number. Experimental data are obtained from Figure 13 from Compton *et al.*[2] and are compared with eqs 6 and 7.

along with published experimental data from Compton *et al*. In particular, we see that the low Péclet number expansion due to Ackerberg is in excellent agreement with almost all of the data (even for $P_s \approx 3$), and Newman's high Péclet number result begins to be effective for $P_s > 3$, as noted by Compton *et al*. Similar agreement of (6) with experimental data for the analogous heat transfer problem was reported by Ackerberg *et al*.[9]

Disk-Shaped Microelectrodes. For microdisk electrodes two sets of experimental data covering $0.6 < P_s < 200$ are reported by Booth *et al*. Here $P_s = Ua^2/HD$, and $N = I/nF[c]Da$, where a is the disk radius. Phillips[12] developed an asymptotic expression at low P_s by considering the circular disk in four parts, the leading edge, the bulk, the side edge, and the trailing edge:[13]

$$N = \frac{4 - 0.12268 P_s^{3/2}}{1 - 0.20281 P_s^{1/2}} \qquad P_s < 1 \tag{8}$$

Stone[14] developed a moderate P_s correction to the Lévêque problem based on a numerical solution using an integral equation approach which is valid for all P_s:[15]

$$N = 2.157 P_s^{1/3} + 3.55 P_s^{-1/6} \qquad P_s > 1 \tag{9}$$

In Figure 3 we have plotted the asymptotic results (8) and (9) along with published experimental data from Booth *et al.*[1] Phillips' result is in good agreement with the data even for $P_s \approx 4$ (this range of validity was previously indicated in the numerical study of Stone), and for higher P_s eq 9 lies within about 7−10% of the experimental results. The small discrepancy between experimental data at higher P_s and the asymptotic expression is larger than expected, although the asymptotics agree with the full numerical solution;[1] nevertheless, there is some discrepancy with the experiments which we are unable to explain.

Conclusion

Provided $P_s = UL^2/HD$ is not too small, the problem of mass transfer from a microelectrode in a channel flow can be reduced to the problem of mass transfer in a shear flow. Approximate asymptotic solutions developed for the problem of mass transfer in shear flow are then applicable for the calibration of microelectrodes.

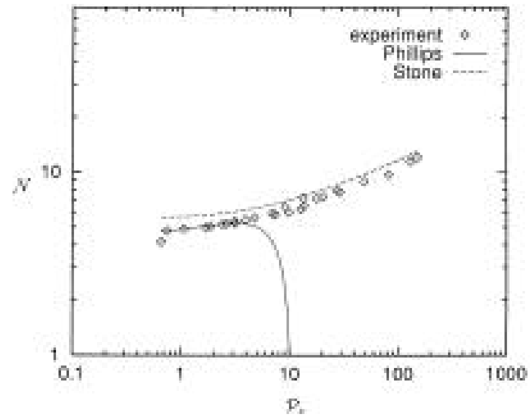

Figure 3. Dimensionless rate of mass transfer versus the shear Péclet number. Experimental data are obtained from Figures 6 and 7 of Booth *et al.*[1] and compared with eqs 8 and 9.

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References and Notes

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$$N = \frac{3^{1/3}}{2\Gamma(4/3)} P_s^{1/3} \approx 0.8075 P_s^{1/3} \tag{10}$$

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$$N = \frac{3(6^{1/3})\Gamma(1/3)}{5\Gamma(2/3)} P_s^{1/3} \approx 2.157 P_s^{1/3} \tag{11}$$

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