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Electrolytic mass transport at a rotating outer cylinder electrode with developing axial flow in the annulus

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Mass transport in an experimental horizontal electrochemical reactor with a rotating outer cylinder and axial flow in the annulus has been investigated, and appropriate dimensionless relationships for the estimation of mass transport rates have been developed by employing statistical regression analysis of experimentally measured flow rates and current density.

Nomenclature

c_o	active ion concentration in electrolyte bulk
c_a	supporting electrolyte concentration in electrolyte bulk
D	electrolyte diffusivity
d_e	equivalent diameter
F	Faraday's constant
I	electric current
i_c	cathodic current density
Nu	Nusselt number
L	electrode length
Pe	Peclet number ($Re \cdot Sc$)
R_1	inner cylinder radius (outer)
R_2	outer cylinder radius (inner)
R^2	square of the multiple correlation coefficient
Re	Reynolds number ($2v(R_2-R_1)/\nu$)
Sc	Schmidt number (ν/D)
Sh	Sherwood number ($2i_c(R_2-R_1)/zFDc_o$)
Ta_m	modified Taylor number ($R_2\omega(R_2-R_1)^{3/2}/\nu R_1^{1/2}$)
v	axial electrolyte velocity
z	valency ($z = 2$ in the current case)
ν	electrolyte kinematic viscosity
ω	rotation speed

1. Introduction

Mass transport at a rotating cylindrical surface in axial forced flow in the annulus formed by a rotating and a stationary concentric cylinder has hitherto received only limited attention in the literature. Combined rotational and axial flow in a heat-transfer orientated study [1] has been shown to have a stabilizing effect on laminar flow. Kataoka *et al.* [2–4] have studied the interrelationship between the axial movement of Taylor vortices and local rates of heat and mass transfer in terms of Stuart's theory [5, 6]. The latter have shown that in purely laminar flow, the average Sherwood number increases with increasing Re, but it decreases with increasing Re if there are Taylor vortices present in the flow pattern. Their data range, $0 \leqslant Re \leqslant 50$ and $30 < Ta < 60\,000$ does not extend to the region of relatively large axial velocities. Flower *et al.* [7, 8] correlated experimental data for air flowing axially in a long annulus between a rotating inner cylinder and a stationary coaxial outer tube via the regression relationship:

$$Sh = Ta^{0.52}Sc^{0.33}Re^{-0.10}. \quad (1)$$

Legrand *et al.* [9] used large electrodes mounted on two concentric cylinders in an electrochemical flow reactor (inner electrode rotating) and correlated their experimental results by the relationships

$$Sh = 0.38\,Ta_m^{1/2}Sc^{1/3} \qquad 25 < Re < 300 \quad (2a)$$

$$Sh = 0.12\,Re^{1/3}Ta_m^{2/5}Sc^{1/3} \qquad 300 < Re < \sim 800 \quad (2b)$$

for a Taylor number range of 200 to 1600. In a recent study using three distinct gap widths,

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Legrand and Coeuret [10, 11] found that for $Re < 300$ mass transport is independent of Re and that above $Re \sim 300$ up to about $Re = 800$ the quantitative influence of axial flow depends on the actual gap width (although the Re exponent of 1/3 and the Ta exponent of 0.47 remain unchanged). To the authors' knowledge no such relationships have yet been obtained in the case of a rotating *outer* cylinder where mass transfer occurs at its inner surface, with axial flow in the annulus.

The purpose of the study described in this paper was two-fold. First, practical electrochemical reactors do *not* have hydrodynamic entry sections which allow the full development of a particular hydrodynamic regime; in consequence, mass transport relationships based on laboratory data obtained under fully developed flow regime conditions can be applied only in an approximate sense. Second, when the axial flow component is large, relative to rotation-generated Couette-flow, laminar Taylor vortex models do not apply. An experimental study [12] was, therefore, undertaken to obtain mass transport data in a bench-scale apparatus designed with these arguments in mind, in order to establish appropriate dimensionless mass transport relationships which may serve as design equations for concentric cylindrical electrochemical reactors employing a rotating outer surface and developing axial flow in the annulus.

2. Experimental procedure

The concentric cylinder cell is shown in Fig. 1 and the overall flow chart of the apparatus in Fig. 2. The cathode was the inner face of a smooth 5.40 cm o.d., 5.08 cm i.d., 30 cm long pure copper tube. The anode was the outer surface of a 3.50 cm o.d., 3.18 cm i.d., 35 cm long pure copper tube. The electrodes were placed concentrically and sealed to two grooved discs with rubber O-rings. Each disc had a 5 mm diameter hole to allow flow of the electrolyte. A pulley was mounted onto the outer tube to rotate the cathode; several pulley transmission ratios could be effected with respect to the single pulley mounted on the shaft of an electric motor. The entire assembly was mounted on a steel support. The inner tube was plugged at both ends by two PVC cylinders set tightly against the inner surface of the tube. The active geometric electrode areas were 478.9 cm^2 (cathode) and 328.9 cm^2 (anode); the cross-sectional area of the annulus was 10.7 cm^2.

The electrolyte was circulated by a conventional pump between the cell and a reservoir, containing about 25 dm^3 of solution, which served as a large capacity buffer for the reactor inlet concentration and temperature. The axial flow rate was controlled by three control valves and a bypass circuit around the tank, and was measured by a calibrated rotameter. The rotation rate of the outer tube was set by means of two sets of pulleys (diameter ratio 1.1 and 1.5) and a belt drive between the tube and a resistance-controlled electric motor whose rotation speed varied between 0 and 35 rpm. The rotation rate was previously calibrated in terms of the motor–transformer setting and was frequently checked by a stopwatch during experiments.

Direct current for electrolysis was provided by a conventional regulated power supply with an output range of 0 to 7.5 V and a current range of 0 to 3 A. The variation of current with potential was obtained by a standard potential increase method. A calibrated current shunt was used to minimize electric noise. Polarization curves were plotted on an X–Y recorder, while current and

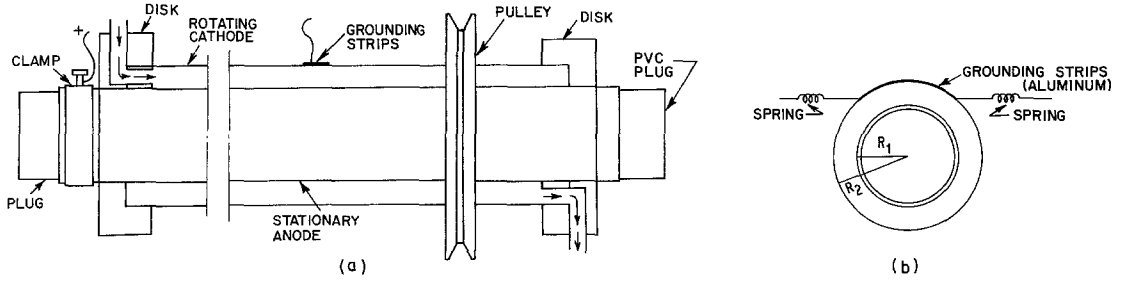

Fig. 1. Sketch of the experimental reactor (a) side view, (b) front view.

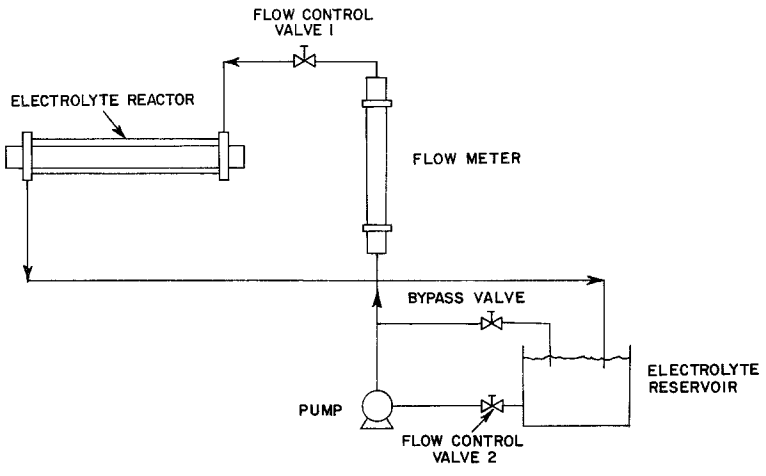

Fig. 2. Overall flow chart of the experimental apparatus.

potential were separately monitored using high-accuracy digital voltmeters.

Before each experiment the electrodes were polished with fine grain emery paper, washed and rinsed with water, de-ionized water and a small amount of alcohol. The dried electrodes were carefully assembled, electrolyte circulation was started and nitrogen was bubbled into the electrolyte to remove all the air (duration about one hour). Immediately before electrolysis, a low density current was passed through the cell for a short period of time in order to obtain a thin, fresh uniform copper deposit on the cathode to serve as a starting surface. In a number of preliminary experiments the most convenient method of connecting the cathode to the external current feed was established, since simple carbon brushes failed to keep a perfectly uniform contact. Finally several 1 cm wide aluminium strips, clamped to the rotating electrode as shown in Fig. 1b via spring loading, proved satisfactory.

The electrolyte composition was determined by standard electrogravimetric/spectrophotometric means [13] and preset before each series of experiments.

The experimental runs were carried out under conditions of (a) pure axial flow; (b) pure rotational flow; (c) combined axial–rotational flow. Table1 summarizes the range of experimental variables.

3. Analysis and discussion

The following definitions were used in the establishment of dimensionless regression relationships:

$$Re \equiv \frac{2v(R_2-R_1)}{\nu} \tag{3}$$

$$Sc \equiv \frac{\nu}{D} \tag{4}$$

$$Ta_m \equiv \frac{R_2\omega}{\nu}\frac{(R_2-R_1)^{3/2}}{R_1^{1/2}} \tag{5}$$

$$Sh = \frac{2i_c(R_2-R_1)}{zFDc_o}. \tag{6}$$

In defining Sh, the transference number of copper ions was neglected, inasmuch as their numerical values calculated by the Fenech–Tobias formula [14] are below 0.001 at the experimental

Table 1. The range of experimental variables

Concentration (mol dm^{-3})	
Cupric sulphate, c_o	0.001 936–0.017 39
Sulphuric acid, c_a	1.882–2.352
Axial flow rate	
v (cm s^{-1})	0.30–25
Re	32–3200
Rotation flow rate	
ω (rad s^{-1})	0.526–3.560
Ta_m	50–350
Electrolyte temperature (° C)	23–24
Electric current, I, (A)	0.060–3.10
Cathode current density	
i_c (A m^{-2})	1.253–64.7
Mass transport coefficient	
$k_m = \frac{i_c}{2Fc_o}$ (cm s^{-1})	2.97×10^{-4}–14.3×10^{-4}

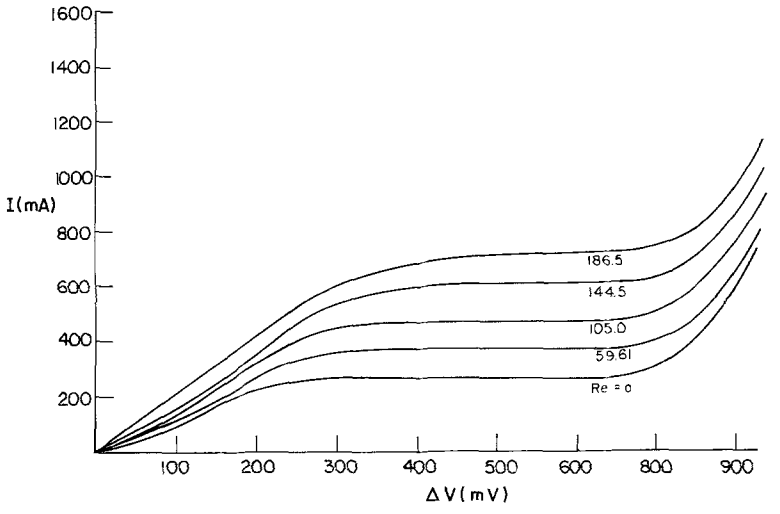

Fig. 3. Typical polarization curves in pure axial flow ($Ta_m = 0$).

electrolyte compositions. The density, viscosity and diffusivity of the electrolytes used were estimated by appropriate relationships [14] valid at 22° C and corrected to experimental temperatures according to the methods given by Reid *et al.* [15] or by interpolating the tabulated values of Eisenberg *et al.* [16]. The regression analysis was performed via conventional least-squares fitting [17], applied to 293 experimental runs (not counting replica runs).

3.1. *Pure axial flow*

Figure 3 illustrates typical polarization curves obtained (using analog recorders) in the absence of rotation, i.e. in the case of pure axial flow in the annulus. The *Re*-exponent in the regression relationship

$$Sh = 0.84 Re^{0.60} Sc^{1/3}; \qquad R^2 = 0.955 \tag{7}$$

shown in Fig. 4 agrees closely with the VanShaw–Reiss–Hanratty exponent of 0.58 [18] in the instance of turbulent flow at the entry region, and with the 0.60 exponent reported for developing turbulent flow [19–21]. The experimental results of this study indicate that the essentially tangential injection of flow into the annulus is a relatively strong turbulence-promoter; in laminar flow 0.5 [22] or 0.333 [21] would be the expected value of the *Re*-exponent (it is instructive to note

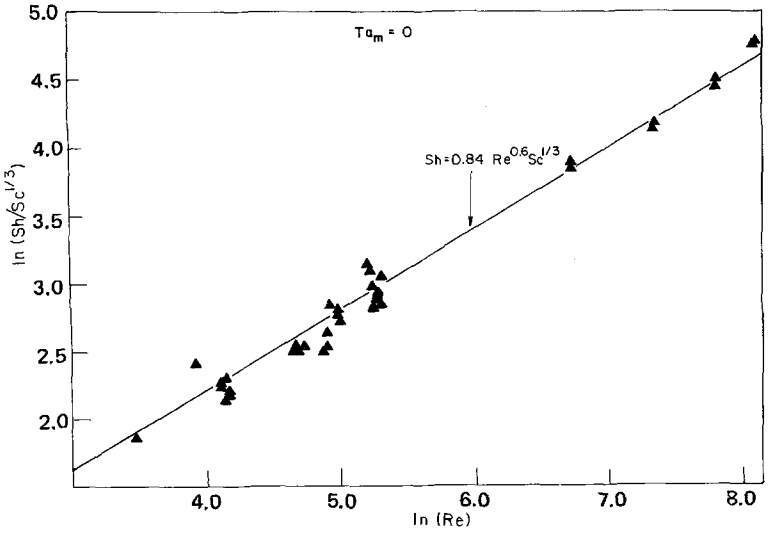

Fig. 4. Mass transport rates in pure axial flow ($Ta_m = 0$).

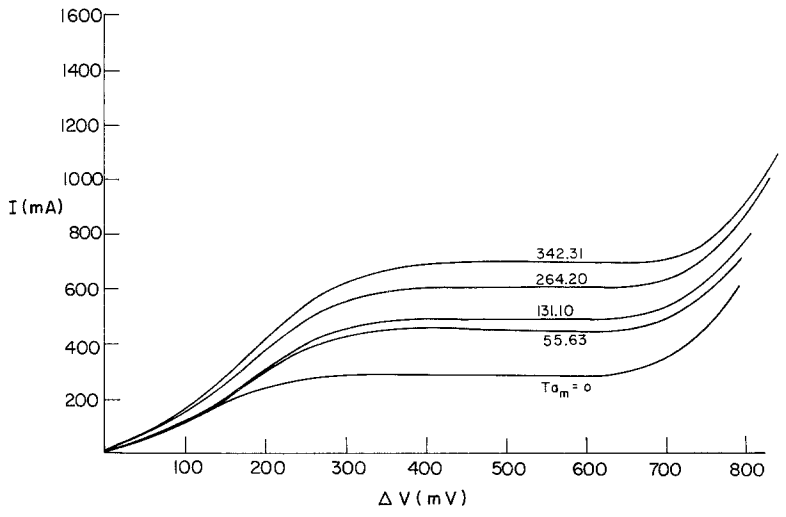

Fig. 5. Typical polarization curves in pure rotational flow ($Re = 0$).

that in the system used with the inner radius of the entry and exit tubes being 2.5 mm, the ratio of the average entry and exit velocities to the average velocity in the annulus is about 55; in Bazan's and Wragg's systems the hydrodynamic entry lengths are, respectively, 22 and 125 times larger than the electrode length).

3.2. *Pure rotational flow*

Typical polarization curves obtained in the absence of axial flow are shown in Fig. 5; a careful analysis of *all* experimental data leads to the construction of Fig. 6, depicting three distinct flow regimes: pure laminar flow, laminar Taylor-vortex flow and an intermediate transition flow region. These findings are qualitatively quite similar to the results of Becker and Kaye in heat transfer [1] and of Cornet and Kappesser [23]. In pure laminar flow the average mass transport rate is essentially independent of the rotation speed:

$$Sh = 8.953 Sc^{1/3} \tag{8}$$

inasmuch as the numerical value of the Ta_m exponent, 0.003 92, is statistically indistinguishable from zero, using a conventional t-test. In the laminar Taylor-vortex region the regression

$$Sh = 5.529\, Ta_m^{0.217} Sc^{1/3}; \qquad R^2 = 0.927 \tag{9}$$

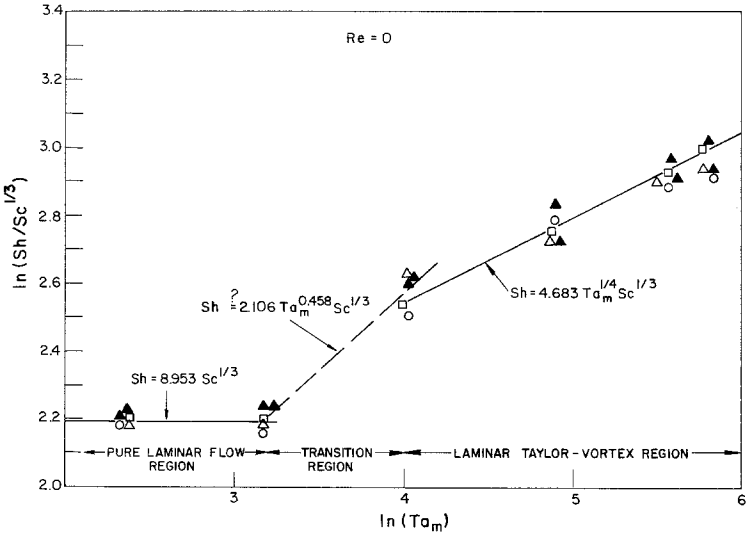

Fig. 6. Mass transport rates in pure rotational flow ($Re = 0$).

compares closely to the Becker–Kaye Ta_m exponent of 0.241. Since the generation of a laminar vortex requires a relatively small torque input, a rotating wire electrode as the limiting case of a small-radius rotor can be taken as an acceptable model; its current–rotation relationship [24–25], $i \propto \omega^{1/4}$, suggests that 0.25 should be the expected exponent. Also, since a laminar vortex is symmetric about the rotation axis, the associated centrifugal force may be considered, for the sake of argument, to be analogous to the gravity force in free convection whose analysis at both vertical and horizontal surfaces (e.g. [14, 26]) clearly indicates a Ra-exponent of 1/4. Hence, one would expect a Ta_m-exponent of 1/4 in the laminar-vortex regime. If the data are fitted with 1/4 stipulated as the corresponding regression parameter, the resulting relationship

$$Sh = 4.683\, Ta_m^{1/4} Sc^{1/3}; \qquad R^2 = 0.903 \tag{10}$$

has a slightly lower linear correlation coefficient and Equation 10 may replace Equation 9 without a significant loss of accuracy.

In the transitional zone, Becker and Kaye fitted their experimental data by a similar relationship whose Ta_m-exponent had a numerical value of 0.367. There is, however, considerable doubt whether Sh (or Nu)/Ta_m data can be related linearly on logarithmic scales in the transition zone [27]. In the present work, experimental data exhibited poor reproducibility in this zone and were omitted from Fig. 6. The dotted straight line drawn across the terminal points of the previous two zones:

$$Sh = 2.106\, Ta_m^{0.458} Sc^{1/3} \tag{11}$$

has a large R^2 value (0.96) but the physical validity of this relationship is doubtful.

In a rigorous analysis, pure rotational flow may be characterized by five hydrodynamic regimes [28] whose widths (in terms of Ta_m) mainly depend on which cylinder is rotated. At any rate, the laminar regime is wider when the outer cylinder is rotated [29]; the smaller the annulus gap : outer radius ratio the wider the laminar regime. Thus rotating outer cylinder systems are better suited for creating laminar and laminar-vortex regimes than rotating inner cylinder systems.

3.3. *Combined axial and rotating flow*

In the case of combined axial and rotating flow, the enhancing effect of the rotation speed on mass transport is observed only in a limited range, as shown in Fig. 7 and the corresponding regression relationship (Fig. 8)

$$Sh = 2.97\, Re^{1/3} Ta_m^{0.095} Sc^{1/3}$$
$$32 < Re < 1600 \tag{12}$$
$$50 < Ta_m < 270.$$

The high linear correlation coefficient ($R^2 = 0.939$) reflects the counterbalancing tendency of the experimental points scattered below and above the diagonal in this relatively narrow range. It is seen in Fig. 7 that the limiting current density at $Ta_m = 342$ is almost equal to that at $Ta_m = 264$. At $Ta_m > 342$ an increase in the rotation speed is expected to have either no effect or a reducing effect on mass transport [4] although no direct measurement could be made in the present apparatus.

It is instructive to compare the foregoing results to the observations of Legrand and Coeuret [10, 11] in the case of inner rotating cylinders mounted on an annulus and equipped with an adequate hydrodynamic entry portion for fully developed axial flow. For $Re < 300$, mass transport depends solely on the square-root of Ta, at a given Sc, whereas for $300 < Re < 500$ and at a diameter ratio of 1.43 (which is very close to the current experimental value of 1.45), Sh is linearly related to the $Re^{1/3}Ta^{0.47}$ product [10, 11]. The Legrand–Coeuret correlations predict Sh values about 0.18 to 0.5 times less than experimentally observed in the $32 < Re < 300$ range, and about 0.1 to 0.18 times less for $Re > 300$, when applied (with appropriate precautions taken for converting Ta_m values to Ta values) to experimental conditions in this work. It appears, therefore, that hydrodynamic conditions established by specific liquid entry arrangements and electrode length to reactor length ratios are predominant factors for mass transport rates, inasmuch as such numerical discrepancies cannot be assigned solely to the question of which cylinder is rotating. At axial flow rates corresponding to $1600 < Re < 2300$ the experimental data cannot be correlated by a simple dimensionless relationship, indicating most

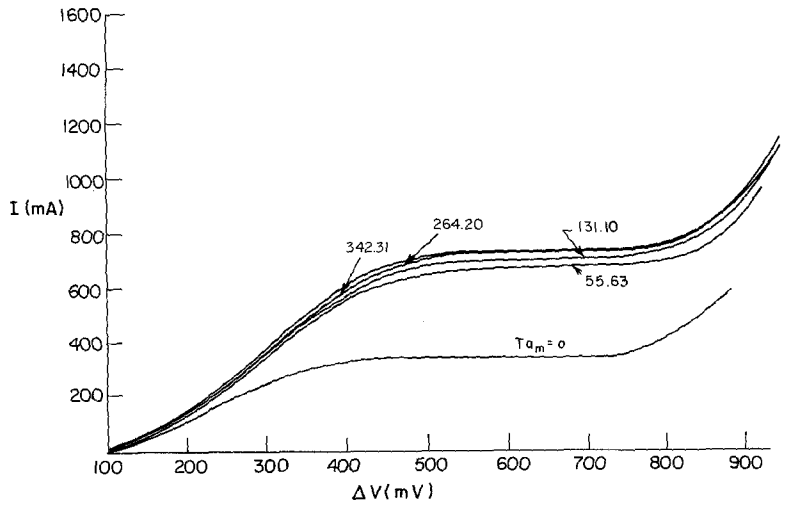

Fig. 7. Typical polarization curves in combined axial and rotational flow ($Re = 59.61$).

likely a transitional zone whose nature is not well understood at present. At $Re > 2300$, experimental limiting current densities exhibit a somewhat fluctuating tendency in duplicate experiments as shown in Table 2. Similar scatter at high associated fluid speeds has been reported elsewhere in the literature (e.g. [30]). The relatively low linear correlation coefficient ($R^2 = 0.795$) of the regression relationship

$$Sh = 2.42 Re^{1/2} Sc^{1/3} \qquad Re > 2300 \tag{13}$$

reflects these experimental difficulties. However, it may be stated with a sufficiently large statistical reliability [12] that the contribution of Couette flow to mass transport is negligible for $Re > 2300$ at least under current experimental conditions. These results indicate that at high axial flow rates Taylor vortices disappear and the rotational flow component exerts no distinguishable effect on mass transport. This finding may be contrasted with the results of Legrand obtained under opposite conditions, where due to very large rotation rates the axial flow component had a negligible effect on mass transport at high Ta_m (e.g. Fig. 4 [9]; Fig. 2 [10, 11]). It appears, therefore, that mass transport becomes solely axial-flow dependent at high axial flow rates and solely rotational-flow dependent at high rotation speeds, although direct quantitative comparison cannot be made at this time between rotating-inner and rotating-outer electrodes. In any event, for a practical electrochemical reactor very high rotation and/or very high axial flow rates are of limited importance.

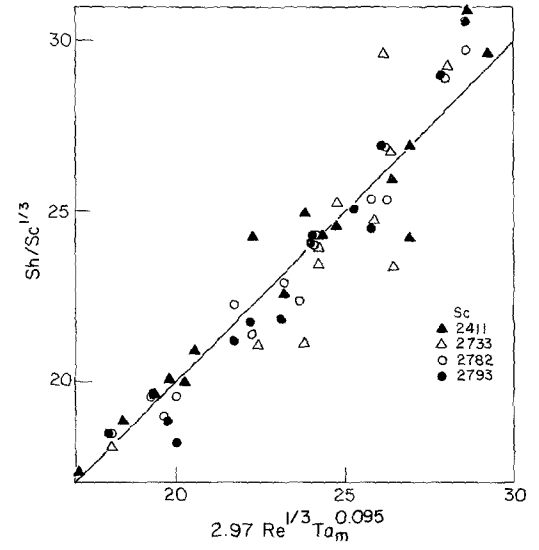

Fig. 8. Mass transport rates in combined axial and rotational flow ($32 < Re < 1600$; $50 < Ta_m < 270$).

3.4. *The effect of free convection*

The contribution of free convection to the mass transport rate was estimated by an interaction parameter analysis [31, 32] using experimental limiting current data and limiting current estimation methods for purely free and purely forced convection. The numerical results indicate that forced convection is mostly predominant; only in a single subset of experimental observations

Table 2. The variation of experimental Sherwood numbers with the Reynolds number in replica runs at high axial flow rates

Set number	*Replica number*	Re	Sc	$Sh/Sc^{1/3}$ *(experimental)*	$Sh/Sc^{1/3}$ *(Equation 12)*
1	1	2394	2275	108.58	
	2			111.16	118.40
	3			115.11	
			Average	111.62	
2	1	2395	2273	120.32	
	2			120.32	118.48
	3			124.88	
			Average	121.84	
3	1	2394	2279	120.52	
	2			122.49	118.40
	3			122.49	
			Average	121.83	
4	1	3195	2273	146.18	
	2			146.18	136.79
	3			147.70	
			Average	146.69	
5	1	3194	2275	126.82	
				128.19	136.77
				129.48	
			Average	128.16	

was the free convection effect found not negligible. The Acrivos fourth-power model [31] predicts throughout the experimental data the unimportance of free convection in the laminar flow range (its rigour is questionable beyond the purely laminar flow regime since it is based on laminar flow theory).

4. Concluding remarks

The dimensionless mass transport relationships obtained in this study may be used for the prediction of average mass transport rates at rotating cylindrical outer electrodes in electrolysers where the electrode length and axial reactor length are (essentially) identical. Further studies will be required for a full understanding of exact convection patterns and the variation of *local* mass transport coefficient with electrode geometry; here, electrochemical flow visualization techniques (e.g. [33]) may offer distinct advantages.

Acknowledgement

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References

[1] K. M. Becker and J. Kaye, *J. Heat Transfer* **84** (1962) 97.
[2] K. Kataoka, H. Doi and T. Hongo, *J. Chem. Eng. (Japan)* **8** (1975) 472.
[3] K. Kataoka, *ibid.* **8** (1975) 271.
[4] K. Kataoka, H. Doi and T. Komai, *Int. J. Heat Mass Transfer* **20** (1977) 57.
[5] J. T. Stuart, *J. Fluid Mech.* **4** (1958) 1.
[6] *Idem, ibid.* **9** (1960) 353.
[7] J. R. Flower, N. Macleod and A. P. Shahbenderian, *Chem. Eng. Sci.* **24** (1969) 637.
[8] J. R. Flower and N. Macleod, *ibid.* **24** (1969) 651.
[9] J. Legrand, P. Dumargue and F. Coeuret, *Electrochim. Acta* **25** (1980) 669.
[10] F. Coeuret, Private communication.
[11] J. Legrand and F. Coeuret, *Int. J. Heat Mass Transfer* (in press).
[12] Z.-H. Gu, M.A.Sc. thesis, University of Waterloo (1981).
[13] A. I. Vogel, 'Quantitative Inorganic Analysis', 3rd edn, Lowe and Brydone (1961).
[14] E. J. Fenech and C. W. Tobias, *Electrochim. Acta* **2** (1960) 311.
[15] R. C. Reid, J. M. Prausnitz and T. K. Sherwood, 'The properties of Gases and Liquids', 3rd edn

McGraw-Hill, New York (1977).
[16] M. Eisenberg, C. W. Tobias and C. R. Wilke, *J. Electrochem. Soc.* **103** (1956) 413.
[17] N. Draper and H. Smith, 'Applied Regression Analysis', Wiley, New York and Chichester (1966).
[18] P. Van Shaw, L. P. Reiss and T. J. Hanratty, *AIChE J.* **9** (1963) 362.
[19] G. Wranglen and O. Nilsson, *Electrochim. Acta* **7** (1962) 121.
[20] C. S. Lin, E. B. Denton, H. S. Gaskill and G. L. Putnam, *Ind. Eng. Chem.* **43** (1951) 2136.
[21] T. K. Ross and A. A. Wragg, *ibid.* **10** (1965) 1093.
[22] J. C. Bazan and A. J. Arvia, *Electrochim. Acta* **9** (1964) 667.
[23] I. Cornet and R. Kappesser, *Trans. Inst. Chem. Engs.* **47** (1969) 1194.
[24] T. Kambara, T. Tsukamoto and I. Tachi, *J. Electrochem. Soc. (Japan)* **18** (1950) 356.
[25] *Idem, ibid.* **18** (1950) 386.
[26] C. Schütz, *Int. J. Heat Mass Transfer* **6** (1963) 873.
[27] E. Brundrett, Private communication (in course of graduate lectures on viscous fluid flow, Univ. of Waterloo, 1981).
[28] T. Mizushira, The electrochemical method in transport phenomena, in 'Advances in Heat Transfer', Vol. 7. Academic Press, London and New York (1971) p. 87.
[29] G. I. Taylor, *Proc. Roy. Soc.* **A157** (1936) 546.
[30] K. N. Astill, *Trans. ASME J. Heat Transfer* **86** (1964) 383.
[31] T. Z. Fahidy and S. Mohanta, Mass transport in electrochemical systems, in 'Advances in Transport Processes', Vol. 1. (Edited by A. J. Mujumdar) Wiley-Eastern, New Delhi, India (1980) pp. 83, 264.
[32] S. Mohanta and T. Z. Fahidy, *Electrochim. Acta* **21** (1976) 143.
[33] M. S. Quraishi and T. Z. Fahidy, *J. Electrochem. Soc.* **127** (1980) 666.