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Mixed convection mass transfer studies of opposing and aiding flow in a parallel plate electrochemical flow cell

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Studies of combined natural and forced convection in a vertical parallel plate electrochemical cell in laminar conditions in cases of opposing and aiding flow are reported. In an ongoing project it was necessary to identify conditions in which natural convection had no significant influence on mass transfer rates at the cell walls so that data could be validly compared with purely laminar flow computational models. For the different electrode lengths investigated, natural convection dominated at low Reynolds number and there was no Reynolds number dependence. At high Reynolds number the data approached the laminar flow solution. At intermediate Reynolds number, however, there existed a distinct region where free and forced convection were significant. At high electrolyte concentrations data did not merge with laminar flow equations until $Re = 1000$ and low electrolyte concentration data for the large plate could not be compared with numerical predictions below Re of 250. An attempt was made to compare the data with those of other workers on combined forced and natural convection heat and mass transfer.

Keywords: *parallel plate cell*, *mass transfer*, *electrochemical technique*, *aiding flow*, *opposed flow*, *mixed convection*

Nomenclature

A	electrode surface area (m^2)
C	bulk species concentration ($mol\,m^{-3}$)
D	diffusion coefficient ($m^2\,s^{-1}$)
d_e	duct equivalent diameter (m)
F	Faraday constant ($96\,487\,C\,mol^{-1}$)
Gr	Grashof number ($gL^3\,\Delta\rho/\rho\nu^2$)
g	acceleration due to gravity ($9.806\,m\,s^{-2}$)
i_L	limiting electrolysis current (A)
K	mass transfer coefficient ($m\,s^{-1}$)
L	electrode length (m)
Ra	Rayleigh number ($Gr\,Sc$)
Re_{d_e}	Reynolds number ($d_e v\rho/\mu$)
Re_L	Reynolds number ($Lv\rho/\mu$)
Sc	Schmidt number (ν/D)
Sh_{d_e}	Sherwood number based on duct equivalent diameter (Kd_e/D)
Sh_L	Sherwood number based on length (KL/D)
v	fluid velocity ($m\,s^{-1}$)
z	electrons exchanged in electrode reaction
Greek letters	
$\Delta\rho$	density difference between bulk electrolyte and electrode interface ($kg\,m^{-3}$)
ρ	fluid density ($kg\,m^{-3}$)
ν	kinematic viscosity ($m^2\,s^{-1}$)
μ	dynamic viscosity ($kg\,s^{-1}\,m^{-1}$)

1. Introduction

Thermal buoyancy forces play a significant role in forced convection heat transfer when the flow velocity is relatively small and the temperature difference between the surface and the free stream is relatively large. The buoyancy force modifies the flow and the temperature fields and hence the heat transfer rate from the surface. The thermal buoyancy force may be either assisting or opposing the forced flow, depending on the forced flow direction and the surface temperature relative to the free stream temperature. Problems of heat transfer in channels by free convection or combined free and forced convection have been the subject of investigations for many years [1–5]. Mixed convection occurs in many heat transfer devices, such as the cooling system of a nuclear power plant, large heat exchangers and the cooling of electronic equipment. Tao [1] considered combined free and forced convection in fully-developed laminar flow in a vertical channel of constant axial wall temperature gradient with or without heat generation while Szewczyk [2] investigated the effects of free convection on a predominantly forced convection flow, as well as the forced convection effects on a predominantly free convection flow. The particular case of a two-dimensional upward or downward external flow superposed on the flow about a fixed heated vertical plate was considered. More recently, modelling and predictions of the local and average heat transfer coefficient for different types of cell geometries with assisting and opposing combined forced and natural convection have been studied by various workers [6–9]. Kobus and Wedekind [8]

0021-891X

attempted to obtain a closed-form integral model solution for combined forced and natural convection, for both assisting and opposing flows, and for a Prandtl number other than unity. They also extended the range of experimentally measured average heat transfer data for both assisting and opposing flows to both the pure forced and the natural convection asymptotes.

Such combined convection effects can also occur in the mass transfer context. Tobias and Hickman [10] investigated combined free and forced flow with horizontal flat plates in a horizontal duct. They made use of sectioned electrodes to observe the mass transfer at different positions along an electrode from the leading edge and also used upward and downward facing surfaces. Combined forced and free convection mass transfer was also studied by Wragg and Ross [11] and Wragg [12] in an annular flow cell for both aiding and opposed flow using the Cu/$CuSO_4$/H_2SO_4 electrochemical system.

The present work lies in the context of a multipartner programme for mass transfer and current density distribution determination in cells of complex geometry. To be able to compare experimental data with numerical modelling work at low laminar flow Reynolds numbers, especially in high Schmidt number systems like electrolytes, it is necessary to identify conditions in which natural convection has no significant influence on the mass transfer rates at the cell walls. It is only under these conditions that data can be validly compared with purely laminar flow computational models.

Mass transfer in cases of aided flow, where natural convection at the cathode was downward and codirectional with forced convection, and opposed flow, where forced convection was counter directional with natural convection, were investigated in a vertical parallel plate electrochemical flow cell. In the system under study, ferricyanide ions are reduced to ferrocyanide ions at the cathode which results in a density increase at the electrode/solution interface and a consequent downward buoyant flow in the region close to the vertical surface. When bulk forced flow is also present, the two types of convection may oppose or aid one another according to whether they are co- or antidirectional and the mass transfer rate will depend on the relative magnitude of the two flow types.

2. Experimental details

A vertical cell 2.03 m tall with an inlet section length of 1.03 m, and exit section length of 0.34 m was made in grey PVC to provide light proofing suitable for use with the ferri–ferrocyanide electrolyte in sodium hydroxide solution. The working cathode was a 0.35 m long nickel plate 0.1 m wide set in one wall of the channel while the anode was a 0.41 m long plate set opposite the cathode with an interelectrode spacing of 0.01 m. Figure 1 shows the flow rig, which consisted of a 100 dm^3 reservoir equipped with a cooling coil, a Beresford PV 121 chemical pump and rotameters covering a flow rate range of 0.02 litres per minute ($Re = 5$) to 220 litres per minute ($Re = 66\,000$). The flow rig was equipped with several drains and an emergency dump tank. Oxygen-free nitrogen was also provided to condition the electrolyte. The temperature in the reservoir was regulated by means of heat exchanger coils which were supplied with either cold or hot water.

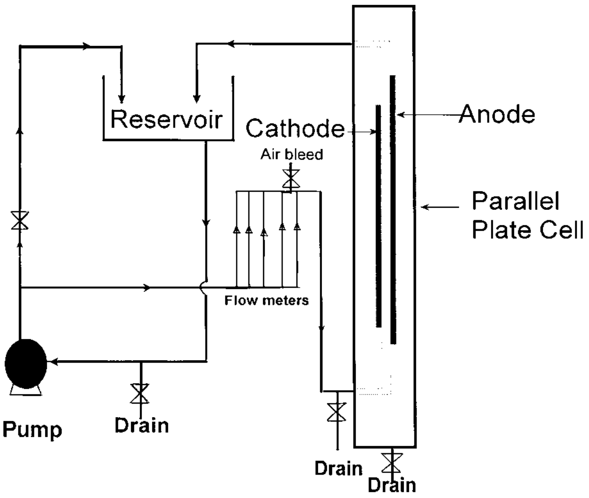

Fig. 1. Flow rig carrying the parallel plate cell.

A standard electrical circuit for measurement of cathodic limiting currents was used consisting of a stabilized power source, a multichannel ammeter and a high impedance voltmeter. The cathodic reaction was the reduction of $Fe(CN)_6^{3-}$ to $Fe(CN)_6^{4-}$ from a $K_3Fe(CN)_6$/$K_4Fe(CN)_6$/NaOH/H_2O electrolyte. Electrolyte density and viscosity values were taken from [13], and diffusivity of ferricyanide ion from the data of Bazan and Arvia [14]. To alter the density difference for natural convection $K_3Fe(CN)_6$ concentrations of 0.0055 M ($\Delta\rho = 0.449\ kg\,m^{-3}$), 0.0152 M ($\Delta\rho = 1.241\ kg\,m^{-3}$) and 0.15 M ($\Delta\rho = 12.2\ kg\,m^{-3}$), were used the $\Delta\rho$ values being taken from the work of Taylor and Hanratty [15]. The $K_4Fe(CN)_6$ concentration was the same as that of $K_3Fe(CN)_6$ and the NaOH concentration was 0.5 M. The temperature was controlled at 22 °C. Current–voltage curves giving well defined limiting currents were obtained for zero flow (pure natural convection) and for various values of channel Reynolds number in the range 15 to 1200. In this work there is particular interest in low Reynolds number flows so that the effect of natural convection is significant. The experimental arrangement is described in greater detail elsewhere [16]. Figure 2 shows the lengths of the plates used. Five different lengths were used for each concentration and the experiments were repeated at least twice for each concentration and length. Lengths of the plate required to be inactive were stopped off using Lacomit lacquer.

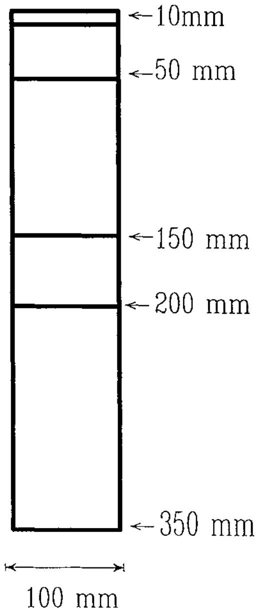

Fig. 2. Cathode plate showing electrode lengths used.

3. Results

Figure 3 shows a logarithmic plot of mass transfer coefficient against Reynolds number for an electrode length of 350 mm (the full plate) and three different concentrations for opposed flow. At low Reynolds number, natural convection dominates and there is little Re dependence; at high Reynolds number the data approach the modified Leveque solution for a fully developed laminar flow [17]. At intermediate Re there exists a region incorporating a minimum in K where free and forced convection are significant. At high concentration data do not merge with laminar flow equation until above $Re = 1000$. Even at 0.0055 M experimental electrochemical data for the large plate cannot be compared with numerical predictions below Re of approximately 250. Figure 4 shows data in the form of Sherwood number against $Re\,Sc\,d_e/L$ for the three different concentrations. The modified Leveque solution $[Sh = 1.789\ (Re\,Sc\,d_e/L)^{0.33}]$ is also shown on this plot. Modified implies that the Leveque solution takes account of the finite width of the plate and follows the method of Roušar *et al.* [17]. A plot such as Fig. 4 emphasizes the extreme extent of departure from laminar flow equations under conditions of significant natural convection. Figure 5 shows how the mean K value varies with cathode length for different Reynolds numbers. The expected decay of K with length occurs but the curves giving lowest K values are at Re 20 and 77 rather than zero. The explanation is that at a Reynolds number of zero, flow is by pure natural convection, while at Reynolds numbers of 20 and 77, forced convection opposes natural convection and, therefore, affects the velocity profile at the electrode surface. The effect is that mass transfer is higher under pure natural convection as compared to low

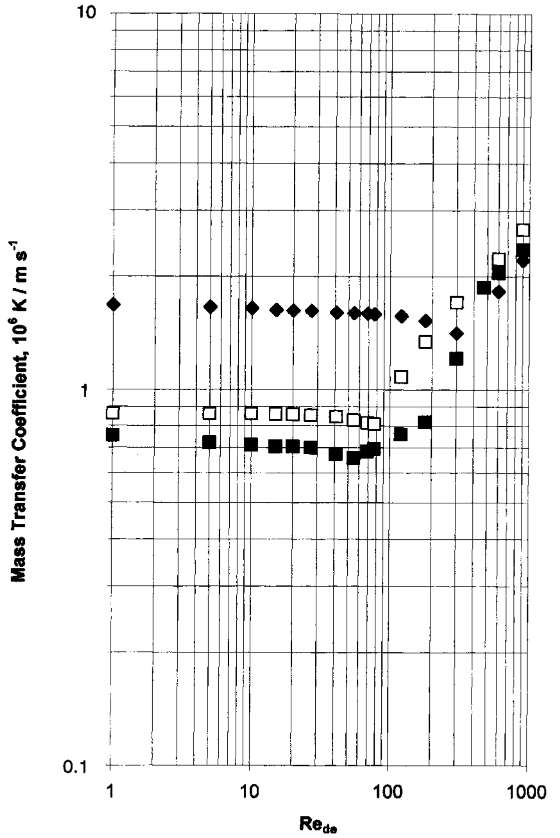

Fig. 3. Plot of mass transfer coefficient against Reynolds number for 350 mm cathode length at different electrolyte concentrations (opposing flow). Key: (■) 0.0055 M, (□) 0.0152 M, (◆) 0.15 M.

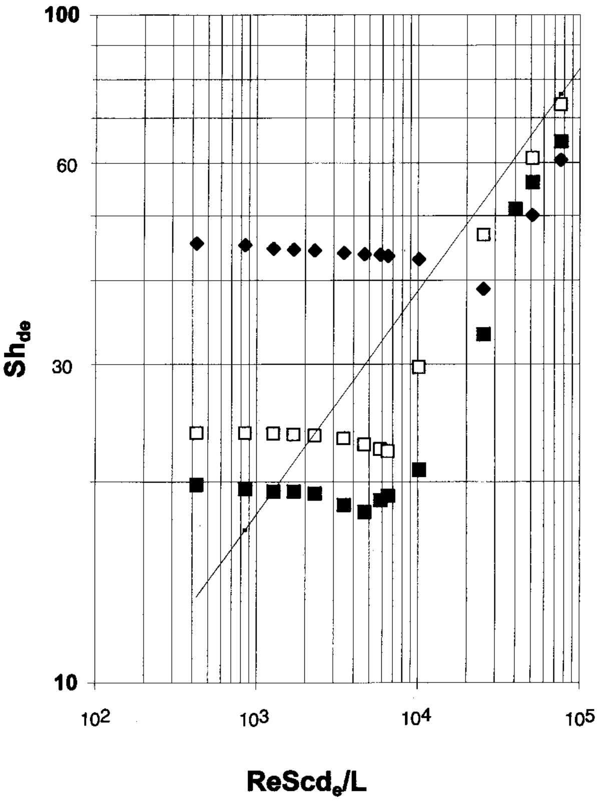

Fig. 4. Plot of Sherwood number based on d_e against $Re\,Sc\,d_e/L$ for 350 mm cathode length at different electrolyte concentrations (opposing flow). Key: (■) 0.0055 M, (□) 0.0152 M, (◆) 0.15 M; (——) Leveque $[Sh = 1.789\ (Re\,Sc\,d_e/L)^{0.33}]$.

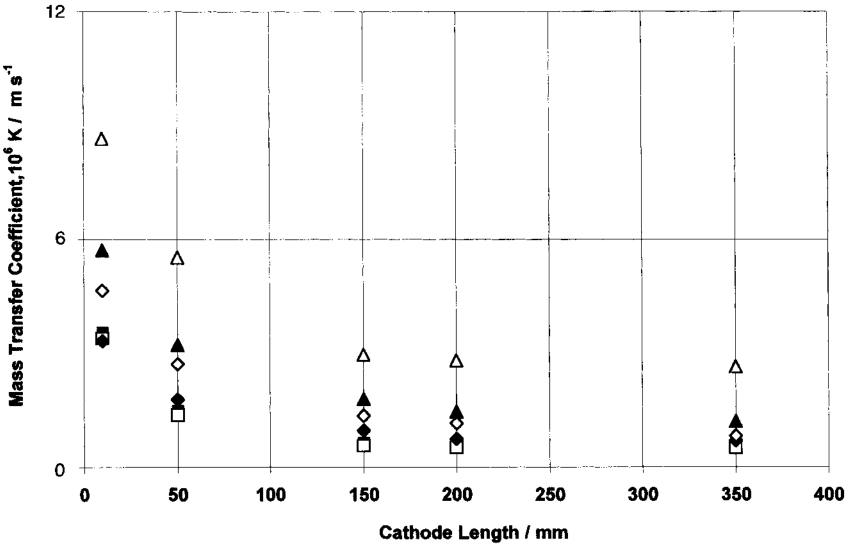

Fig. 5. Plot of mass transfer coefficient against cathode length at different Reynolds numbers for 0.0055 M electrolyte concentration with opposing flow: (■) 0, (□) 20, (◆) 77, (◇) 180, (▲) 300, (△) 1200.

Reynolds numbers. A plot of Sherwood number against $Re\,Sc\,d_e/L$ for the five different electrode lengths and at $C = 0.0055$ M is shown in Fig. 6. Apart from the 10 mm electrode all data are seen to be satisfactorily merging with the modified Leveque solution at $Re\,Sc\,d_e/L$ of approximately 10^6. The observed minimum is more sharply defined for shorter length electrodes. Results from pure natural convection are shown as Fig. 7 where there is also comparison with the well accepted correlating equation for vertical plates:

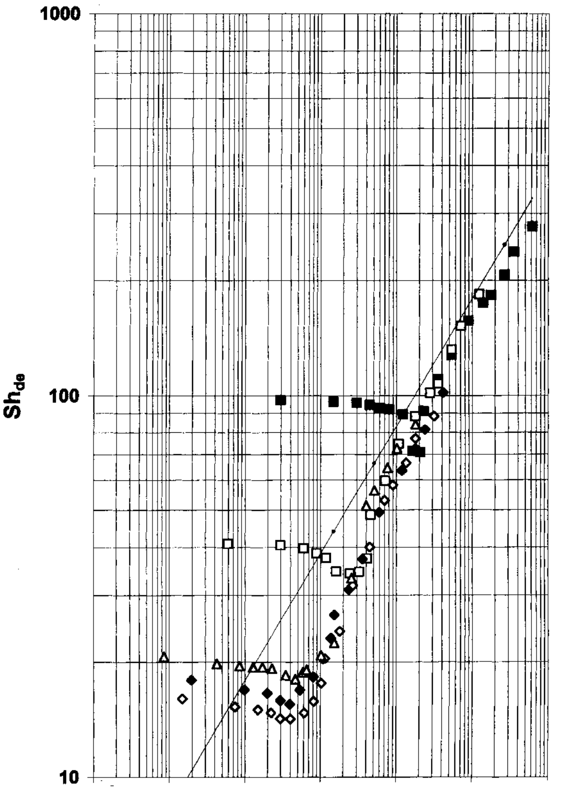

Fig. 6. Plot of Sherwood number $(K\,d_e/D)$ against $Re\,Sc\,d_e/L$ at different cathode lengths and electrolyte concentration of 0.0055 M (opposing flow): (■) 10, (□) 50, (▲) 150, (◆) 200 and (◇) 350 mm; (——) Leveque $[Sh = 1.789\,(Re\,Sc\,d_e/L)^{0.33}]$.

$$Sh = 0.67\,(Gr\,Sc)^{0.25}$$

The data lie a few per cent low which is consistent with the findings of other workers for natural convection using the ferro–ferricyanide system [18, 19].

Data for aiding flow, i.e. with forced flow from top to bottom in the channel, at an electrolyte concentration of 0.015 M for different electrode lengths are shown in Fig. 8. Here the curves are of a totally different form and do not go below the Leveque line. Figure 9 shows a comparison of the plots for aiding and opposing flows for combined forced and natural convective mass transfer with the Leveque equation. This Figure can be divided into three major regions based on the flow behaviour patterns. Free convection controls in region A, free and forced convection are both significant in region B, while forced convection controls in region C. It is therefore possible, by examination of experimental data, to define the limits beyond which either pure free or pure forced convection are effectively dominating.

Kobus and Wedekind [8] obtained a closed-form integral model solution for combined forced and natural convection, for both assisting and opposing flows in heat transfer using air as working fluid. They also extended the range of experimentally measured average heat transfer data for both assisting and opposing flows to both the pure forced and the natural convection asymptotes. Their data, compared with those of other workers, were presented in Fig. 4 of [8] as the ratio of Nusselt number to Reynolds number against Richardson number for a Prandtl number of 0.72.

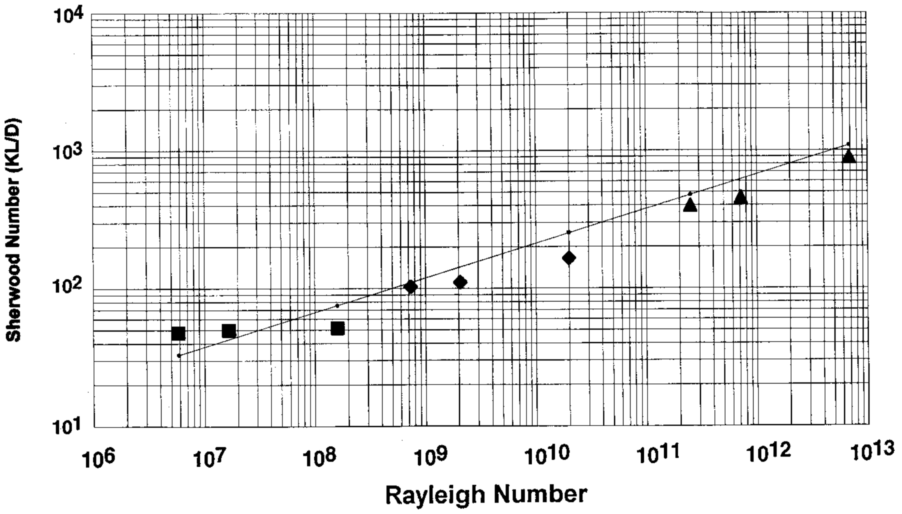

Fig. 7. Plot of Sherwood number (KL/D) against Rayleigh number for pure natural convection at 0.0055, 0.015 and 0.15 M electrolyte concentration. Key: (■) 10, (◆) 50 and (▲) 350 mm; (——) $Sh = 0.67\ (Gr\,Sc)^{0.25}$.

The present data for forced and natural convection mass transfer for aiding and opposing flows plotted as a function of Sherwood number against Richardson number for a 10 mm electrode length is depicted in Fig. 10. Three features are prominent; a forced convection asymptote at low Richardson number, a minimum in the case of opposed flow corresponding to mixed convection and a natural convection asymptote at high Richardson number. The forced convection limit is reached at Richardson number of zero and the free convection limit is reached as this parameter approaches infinity. Comparison of our data with those of Kobus and Wedekind [8] is also shown on this plot. This has been achieved by incorporating Sc and Pr to the power 0.33 for the mass and heat transfer data, respectively. The two sets of data show a close agreement. Kobus and Wedekind comment that experimental heat transfer data for combined forced and natural convection is only presently available for air, with a Prandtl number of 0.72. Their attempt to carry out similar experiments in water met with difficulties and no experimental data were produced. However, the present work shows quite clearly that data for combined convection can be readily and consistently produced in liquid systems with higher property numbers, in this case the Schmidt number being 1633.

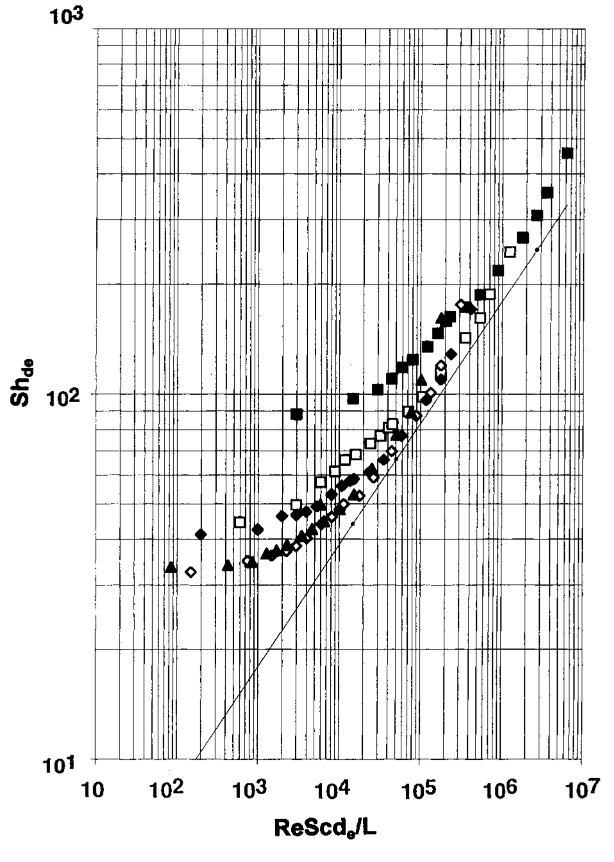

Fig. 8. Plot of Sherwood number ($K\,d_e/D$) against $Re\,Sc\,d_e/L$ for different cathode lengths with electrolyte concentration of 0.015 M (aiding flow): (■) 10, (□) 50, (◆) 150, (◇) 200 and (▲) 350 mm; (——) Leveque [$Sh = 1.789\ (Re\,Sc\,d_e/L)^{0.33}$].

A further comment on the work of Kobus and coworkers might be that their forced convection asymptote involving a Nu_x vs $Re_x^{0.5}$ relationship (where x is distance along surface) reflects the case for thermal and momentum transfer development from the same leading edge on a flat plate, whereas in their experimental work a fully developed duct flow was realized. In such a case the classical Leveque analysis leads to a Nu_x vs $Re_x^{0.33}$ asymptote.

In summary, this work highlights the importance of neglecting data at low Reynolds number when comparing with pure laminar flow numerical predictions for forced convective mass transfer in flow channels.

Acknowledgement

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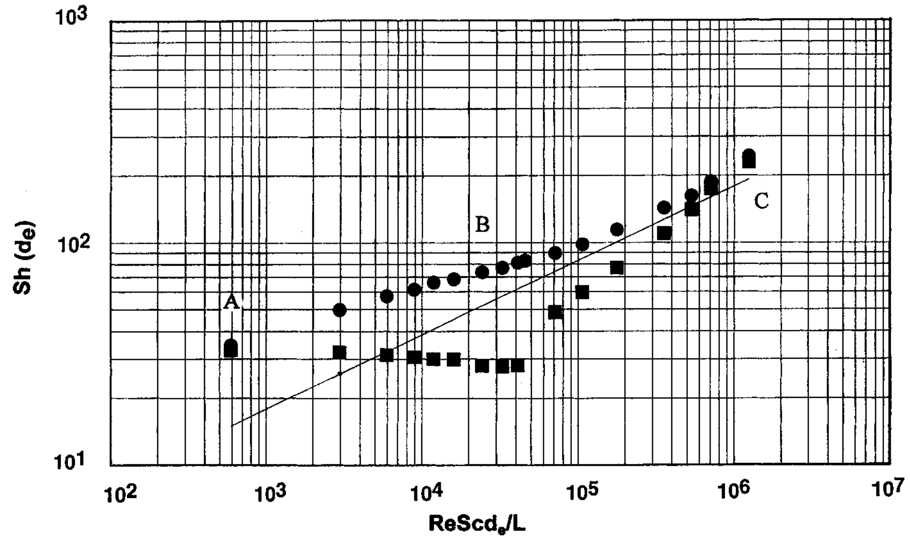

Fig. 9. Combined forced and natural convective mass transfer at electrolyte concentration of 0.015 M and 50 mm electrode length; a comparison of aiding (●) and opposing (■) flow. (——) Leveque [$Sh = 1.789\ (Re\,Sc\,d_e/L)^{0.33}$].

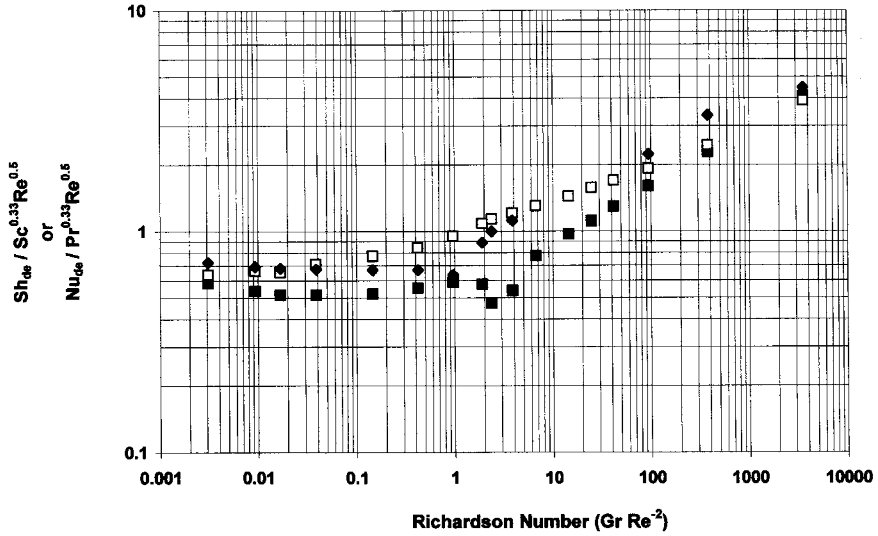

Fig. 10. Plot of ratio of $Sh/Sc^{0.33}\,Re^{0.5}$ against Richardson number for 10 mm cathode and 0.0055 M electrolyte concentration; and $Pr^{0.33}$ from data in Fig. 4 of [8]. Key: (■) opposing flow, (□) aiding flow, (◆) opposing flow data of [8], Fig. 4.

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