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SHORT COMMUNICATION

Natural convection at planar and mesh electrodes in the ferro-ferricyanide system

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1. Introduction

A recent paper by Shemilt and Sedahmed [1] has presented results of natural convection mass transfer measurements at horizontal screen electrodes using the copper deposition technique. In the discussion of their results Shemilt and Sedahmed refer to an earlier paper by the present writer [2] in which natural convection at vertical nickel mesh cathodes was investigated using the ferricyanide reduction technique. In that paper it was observed that the data points when plotted in the usual logarithmic (Sh) versus $[(Sc)(Gr)]$ form showed a distinct tendency for results from a single electrode to lie slanted across the best straight line fit thus displaying an additional dependence on concentration (or $\Delta\rho$) in addition to that accounted for in the Grashof number. This can be easily seen by reference to Fig. 3 of [2], the situation being artificially remedied by the modification of the Grashof number by a factor $\Delta\rho/\rho_i$, thus producing the improved correlating plot of Fig. 4 [2]. Shemilt and Sedahmed comment that due to their higher concentrations no such concentration dependency affects their screen electrode results. However, it can now be shown that this 'concentration dependency' is non-existent and arises from a calculation error that can now be corrected.

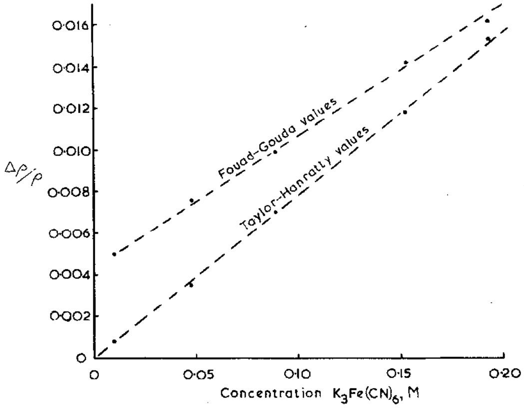

Fig. 1. Plot of $\Delta\rho$ against concentration for equimolar $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ in 2 N NaOH according to Fouad and Gouda [4] and Taylor and Hanratty [3].

2. Corrected values of density difference

Taylor and Hanratty [3] have recently presented results of natural convection mass transfer experiments at horizontal cylinders again using the cathodic reduction of ferricyanide ions as the test reaction. In their calculations Taylor and Hanratty have diagnosed and corrected an error in the calculation of $\Delta\rho$ previously made by Fouad and Gouda [4]. Fig. 1 shows the values of $\Delta\rho$ as a function of ferricyanide ion concentration in 2 M NaOH swamping electrolyte as calculated according to Fouad and Gouda and by Taylor and Hanratty. It also reveals the considerable magnitude of the discrepancy especially at low concentrations where at a concentration of 0·01 M the Fouad–Gouda values are approximately seven times greater than those of Taylor–Hanratty. Fouad and Gouda [4] had correlated data points for free convection by the equation

$$(Sh) = 0{\cdot}45\,[(Sc)(Gr)]^{0{\cdot}25} \qquad (1)$$

but Taylor and Hanratty's revision raises the results to be just 8% short of the well-accepted laminar natural convection equation of Wilke *et al.* [5]

$$(Sh) = 0{\cdot}67\,[(Sc)(Gr)]^{0{\cdot}25}. \qquad (2)$$

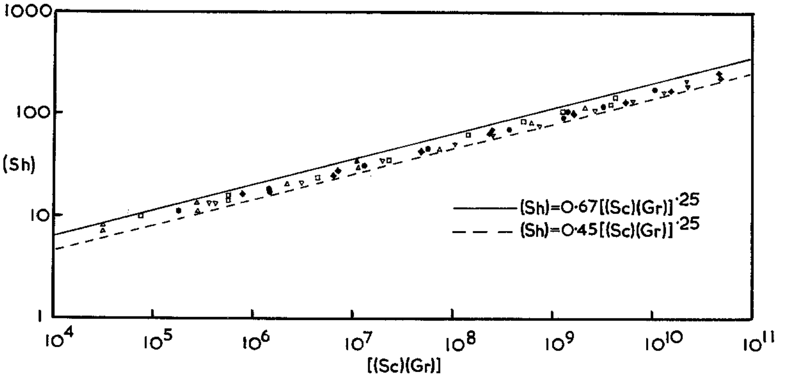

Fig. 2. Recalculated results for natural convection mass transfer at vertical meshes using $\Delta\rho$ values of Taylor and Hanratty [3]. △ 0·01 $K_3Fe(CN)_6$ concentration (M) respectively; □ 0·02; ● 0·05; ▼ 0·10; ◇ 0·20.

3. Application to mesh electrode

The present writer's earlier treatment of vertical mesh electrodes [2] had inadvertently followed the $\Delta\rho$ values of Fouad and Gouda, and when the Taylor–Hanratty values are used the previously observed concentration dependency of the *(Sh)*–[*(Sc)*(*Gr*)] plot disappears since the low concentration points are raised considerably. The correlating plot using the revised $\Delta\rho$ values is shown in Fig. 2 and it can be seen that additional concentration dependency no longer exists and the data show typical scatter and lie above the previous correlating line (1) and below that of Equation 2.

4. Further mesh electrode results

The present note provides an opportunity to report further previously unpublished work on vertical mesh electrodes due to di Gesso [6] who worked with different mesh geometries, and in particular with greater and smaller aperture counts than those used previously by the present writer [2], namely 80 x 80 apertures per inch and 25 x 25 apertures per inch. Di Gesso also used a taller range of electrodes and electrolyte concentrations of 0·01 and 0·28 M electrolyte. Experimental points of di Gesso are shown in Fig. 3 and data for the finer (80 x 80) mesh are seen to lie considerably below the previous data for a 40 x 40 mesh, whilst the data for the coarser (25 x 25) mesh lie higher. This can be attributed to the difficult access of fluid to the small apertures of the fine mesh and more ready access to the larger apertures, the mass transfer coefficients being in all cases calculated on the basis of the total electrode surface area.

5. Anomalous results for flat plates

Finally, whilst discussing natural convection in the ferricyanide system, attention is drawn to anom-

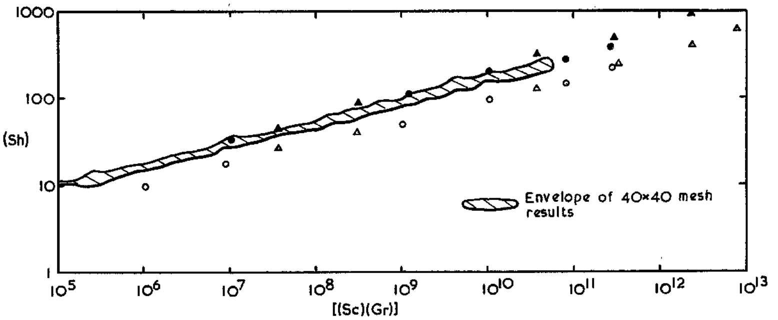

Fig. 3. Plot of *(Sh)* against [*(Sc)*(*Gr*)] for mesh electrode results of di Gesso [6]. ▲ 25 X 25 mesh count (apertures/ inch); 0·28 $K_3Fe(CN)_6$ concentration (M) respectively; ● 25 X 25; 0·01; △ 80 X 80; 0·28; ○ 80 X 80; 0·01.

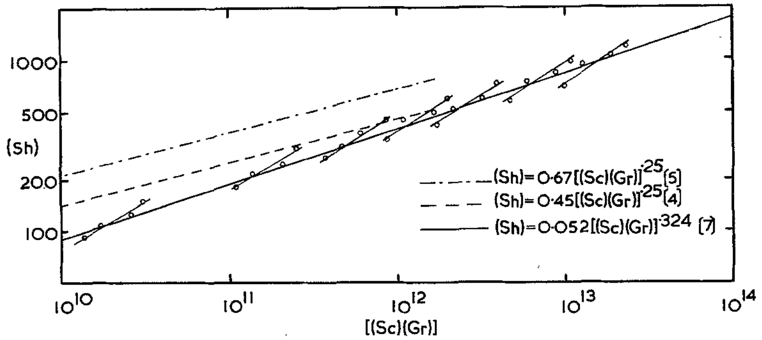

Fig. 4. Comparison of smooth plate results of Fouad and Zatout [7] with correlating equations of Fouad and Gouda [4] and Wilke *et al.* [5].

alous results presented by Fouad and Zatout [7] in a paper on mass transfer rates at rough surfaces. As part of this work the authors performed natural convection experiments at vertical smooth nickel plates and one would expect that results should agree with the data of Fouad and Gouda [4] as described by Equation 1 in the appropriate $[(Sc)(Gr)]$ range. However, a plot of Fouad and Zatout's smooth plate data as in Fig. 4, reveals that they lie considerably below Equation 1 and even further below Equation 2 as well as showing the concentration-dependent slant across the quoted correlation line.

$$(Sh) = 0{\cdot}052\,[(Sc)(Gr)]^{0{\cdot}324}. \qquad (3)$$

Revision of the Grashof numbers in accordance with the Taylor–Hanratty $\Delta\rho$ values tends to remove the apparent concentration dependence and moves all the data towards Equation 2, but the puzzling difference between these results and the earlier work of Fouad and Gouda remains.

References

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