Ionic Mass Transfer by Natural Convection at a Horizontal Cylinder with an Imposed Axial Temperature Distribution

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Foi investigada experimentalmente a transferência simultânea de massa e calor pela convecção livre em um eletrodo cilíndrico horizontal com um gradiente de temperatura axial, utilizando a técnica eletroquímica da corrente limite de difusão. O sistema eletroquímico foi composto por ferro-ferricianeto de potássio, com um eletrólito de suporte de hidróxido de sódio, para que no cátodo cilíndrico a concentração e o flutamento térmico tivessem efeitos opostos. Padrões de fluxo convectivo resultaram da superimposição repentina da transferência de massa em uma situação de transferência de calor constante, observados utilizando-se fotografia de Schlieren. Variando-se vagarosamente a temperatura do cilindro, foi possível alcançar uma situação na qual em alguma distância axial ao longo do cilindro as forças de flutamento devido às diferenças de temperatura e concentração fossem igualmente equilibrados, como foi mostrado na fotografia de Schlieren. Uma estrutura de apoio teórico para as experiências foi desenvolvida considerando-se as magnitudes relativas dos termos fornecidos nas equações de Navier-Stokes correspondentes às forças de flutamento produzidas pelos efeitos térmicos e de concentração.

Simultaneous heat and mass transfer by free convection at a horizontal cylinder electrode with an imposed axial temperature gradient was experimentally investigated using the electrochemical limiting diffusion current technique. The electrochemical system was made up of potassium ferri-ferrocyanide, with a supporting sodium hydroxide electrolyte so that at the cylindrical cathode the concentration and thermal buoyancy had opposite effects. Convective flow patterns which resulted from the sudden superimposition of mass transfer on a steady heat transfer situation were observed using Schlieren photography. By gradually varying the temperature of the cylinder, a situation was reached where at some axial distance along the cylinder the buoyancy forces due to temperature and concentration differences were equally balanced, as revealed in the Schlieren image. A supporting theoretical framework for the experiments was developed by considering the relative magnitudes of the source terms in the Navier-Stokes equations corresponding to the concentration and thermally driven buoyancy forces.

Keywords: *natural convection, heat and mass transfer*

Introduction

This work is concerned with simultaneous heat and mass transfer in natural convection in an electrochemical system in which the concentration and thermal buoyancy effects are opposed.

Several reports in the literature^{1,2,3,4} have focused attention on the experimental and theoretical aspects of this phenomenon in systems in which heat and mass transfer produces aiding flow and/or opposed flow.

More recently⁵, convective patterns have been observed for mass transfer at cuboids using Schlieren photography in the copper sulphate-sulphuric acid-water system. Combined natural convection at horizontal cylinders where concentration and thermal buoyancy effects were either aiding⁶ or opposed⁷ has also been studied. The purpose of these investigations was to present visual evidence of the convective plumes above or below cylinders, and to obtain correlations for simultaneous heat and mass transfer measurements. In the case of plates and cylindrical electrodes,

with uniform and constant temperature, a combined Grashof number for heat and mass transfer has been successfully used in the correlations to account for thermal and concentration buoyancy effects⁶.

In the current investigation, combined natural convection has been studied at a horizontal cylinder electrode with an imposed axial temperature gradient. The convective flow patterns which were obtained were observed and filmed using the Schlieren method. The purpose of the present work is to find the position, in terms of axial distance along the cylinder, where the buoyancy forces due to temperature and concentration differences are equally balanced, and to explain this position in terms of the fundamental buoyancy force terms in the Navier-Stokes equations.

Experimental

The experiments were performed using the limiting diffusion current method. The electrochemical system was equimolar potassium ferri-ferrocyanide with 0.5 M NaOH as the supporting electrolyte. At the cathode, due to the cathodic reduction of the ferricyanide ion to ferrocyanide, a density increase is produced resulting in downward convection. An opposite thermal effect is produced by heating the electrode.

All experiments were carried out with simultaneous heat and mass transfer, where the concentration and thermal buoyancy effects were opposed.

The experimental cell

The electrochemical cell consisted of a rectangular tank with transparent sides, the base and two sides of which were made from plexiglass and the other two sides from glass.

A nickel cylinder cathode was centrally mounted in the solution in a horizontal position. One end of the cylinder was isolated with a plexiglass plate and the other was equipped with internal electrical heating. This heating was produced by a resistance wire wrapped around a ceramic core and was installed into the end of the cylindrical cathode. A variable transformer was used to supply power to the resistance wire to raise the temperature along the cathode to the desired profile value and to establish a gradient of temperature along the cylinder. Thermocouples were installed and soldered in small holes drilled along the surface of the nickel cylinder, with the junctions positioned on the exposed surface at five locations (0 mm, 10 mm, 32 mm, 50 mm, 83 mm).

The temperature of the bulk liquid was measured by a mercury-in-glass thermometer and also by thermocouples at different positions in the solution. The anode consisted of two large thin nickel sheets, measuring 25 cm high by 15 cm wide. Three different lengths of cathodes were used, 10 mm, 50 mm and 83 mm, each 22 mm in diameter.

The cell was positioned in a Schlieren optical system which facilitated the visualization and photographic recording of any changes in the refractive index of the solution above and/or below the electrodes arising from changes in the concentration or temperature of the solution.

Experimental procedure

Two kinds of experiments were carried out: 1) experiments where the initial temperature profile along the cylinder surface was uniform and equal to the bulk electrolyte temperature, and was then increased with electrolysis proceeding; and 2) experiments with a fixed initial temperature profile along the cylinder surface, higher than the bulk electrolyte temperature. In the latter the temperature was gradually decreased with electrolysis proceeding until a uniform temperature equal to the bulk electrolyte temperature was achieved.

Prior to each test run, the cathode surface was carefully resurfaced and polished and then placed in the cell.

The electrical circuit consisted of a stabilized power unit, a multirange ammeter, a high impedance voltmeter and a Y-t recorder which measured the current flowing in the circuit via the potential difference produced across a variable known resistance.

The temperatures indicated by the thermocouples were recorded every two minutes, from the initial to the final time, using a selector (Grant type SQ8-4K). The two electrolyte concentrations of equimolar ferri-ferrocyanide in 0.5 M NaOH chosen were 0.01 M and 0.1 M.

The potential difference was fixed at a value corresponding to the limiting current conditions. Current and temperature were recorded continuously. As soon as convection became visible above and/or below the cylinder electrode, the various stages of development of the flow structure were filmed.

Theory

In natural convection, the flow arises due to the temperature and concentration differences leading to density differences in a body force field. Therefore, the heat and mass transfer and fluid flow processes are inseparably linked and cannot be independently determined.

The driving buoyancy force for the vertical flow arises from the difference between the body forces within the fluid and the force due to the hydrostatic pressure gradient in the ambient medium. By applying a double Taylor series expansion to the ambient conditions, the coefficient of thermal volumetric expansion β_T for $\beta_T < 1$ is given by:

$$\beta_T = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P \quad (1)$$

where P , T and ρ denote the pressure, temperature and fluid density, respectively.

The density difference, due to an interaction between the gravitational body force and the hydrostatic pressure, can be approximated as a pure temperature effect, given by the equation

$$\rho_a - \rho = \beta_T \rho_a (T - T_a) \quad (2)$$

The quantities ρ_a and T_a are reference values.

Likewise, the governing relations for the natural convection mass transfer process are obtained for a low concentration of the diffusing species, for constant fluid properties and using the Boussinesq approximation as applied to density variation with concentration (C). This approximation is obtained in a manner similar to that for heat transfer, for $\beta_C \ll 1$:

$$\beta_C = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial C} \right)_{T,P} \quad (3)$$

For combined heat and mass transfer, the buoyancy term in the momentum equation is due to the combined effects of thermal and mass diffusion. For $\beta_C \ll 1$ and $\beta_T \ll 1$, the Boussinesq approximation can be employed:

$$g(\rho_a - \rho) = g\rho_a\beta_T(T - T_a) + g\rho_a\beta_C(C - C_a) \quad (4)$$

where g is the gravitational acceleration.

The vertical component of the Navier-Stokes equations can then be written as:

$$u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = \nu \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) + g\beta_T(T - T_\infty) + g\beta_C(C - C_\infty) \quad (5)$$

where u, v and x, y denote the x - and y -direction volume-averaged velocity components and coordinates, respectively. ν is the kinematic viscosity of the fluid, and the subscript ∞ refers to bulk fluid.

The second and third terms on the right side of Eq. 5 represent the buoyancy forces arising from temperature and concentration variations in the field.

Results and Discussion

Two kinds of experiments were carried out, as mentioned above. Figures 1a, 1b, 1c and 1d show the Schlieren photographs for the first case where the initial temperature profile is uniform and equal to the bulk electrolyte temperature, 21 °C, in which the cylinder is gradually heated to reach an axial temperature gradient where the temperature difference between the ends of the cylinder (ΔT) increased from 0.0 °C to 8.0 °C.

For Fig. 1, the length of the cylinder was 83 mm and the experiment was carried out for 0.1 M Ferri/0.1 M Ferrocyanide/0.5 M NaOH. Figure 1a shows the downward convective mass flow at steady state (time $t = 85$ s), where the

temperature along the cylinder was equal to the temperature of the bulk electrolyte (21 °C). Figure 1b shows the downward convective mass flow and the upward convective heat flow after heating the cylinder electrode to obtain a ΔT of 1 °C. In Fig. 1c the temperature at the base of the cylinder (T_5) was raised to 27 °C resulting in $\Delta T = 6$ °C. In Fig. 1d, T_5 is 29 °C with $\Delta T = 8$ °C. The heating was then stopped and Fig. 1e shows the convective flow patterns due to heat and mass transfer when T_5 decreased to 27 °C and Fig. 1f when T_5 decreased to 21 °C. In Fig. 1b and Fig. 1d the cylinder electrode has the same axial temperature gradient as in Fig. 1a and in Fig. 1f. Although the flows are similar, they are not equivalent because the sequence of events leading to their establishment was different. Similar results were obtained in the other experiments carried out using this method.

The other kind of experiment involved a fixed axial temperature gradient and a sudden superposition of mass transfer. The convective flow patterns with the same axial temperature gradients were different from those observed in the first case. When the heat transfer was present, especially at higher temperature gradients, it was difficult to observe the convection patterns due to the mass transfer contribution. The mass transfer appeared later and had relatively little influence on the overall flow structure.

In both cases it was observed that the steady limiting current increased when the temperature level on the surface of the cathode increased, and vice versa.

Figure 1. Schlieren photographs of opposed heat and mass transfer for 0.1 M Ferri/0.1 M Ferro/0.5 M NaOH, $L = 83$ mm and with an axial temperature gradient of

a) $\Delta T = 0$ °C, $t = 85$ s	d) $\Delta T = 8$ °C, $t = 1286$ s
b) $\Delta T = 1$ °C, $t = 375$ s	e) $\Delta T = 6$ °C, $t = 1454$ s
c) $\Delta T = 6$ °C, $t = 970$ s	f) $\Delta T = 0$ °C, $t = 1806$ s

Figures 2a, 2b and 2c shows Schlieren photographs with a cylinder electrode 10 mm in length for 0.01 M equimolar ferri-ferrocyanide in 0.5 M NaOH. Figure 2a ($t = 365$ s), corresponds to convective flow due to mass transfer in the steady state with a uniform cylinder temperature equal to the bulk electrolyte temperature of 22 °C. In Fig. 2b ($t = 618$ s) and Fig. 2c ($t = 665$ s) an axial temperature gradient of $\Delta T = 1$ °C is present.

In order to reach the situation where at some axial distance along the cylinder the buoyancy forces due to temperature and concentration differences were equally balanced, the flow field was first established using mass transfer and then disturbed by slowly heating the cylinder to attain the desired axial temperature profile. This was most conveniently observed for cylinders of 50 mm and 83 mm in length.

Figure 3 shows the temperature profiles obtained by heating, during the electrolysis, of a solution of 0.01 M Ferri/Ferrocyanide/0.5 M NaOH with a cylinder electrode 83 mm in length. The initial temperature profile was uniform and equal to the bulk electrolyte temperature (22 °C). In Fig. 3 the temperature profiles obtained by heating without electrolysis are superimposed. It was observed that

Figure 2. Schlieren photographs of opposed heat and mass transfer for 0.01 M Ferri/0.01 M Ferro/0.5 M NaOH, $L = 10$ mm, with an axial temperature gradient of a) $\Delta T = 0$ °C, $t = 365$ s; b) $\Delta T = 1$ °C, $t = 618$ s; c) $\Delta T = 1$ °C, $t = 665$ s.

Figure 3. Temperature profiles obtained by heating from an initial uniform temperature profile with the initial temperature equal to the bulk temperature (22.0 °C), for three different times.

the presence of mass transfer modifies the temperature distribution along the cylinder. The thermal effects generate a flow in the opposite direction of that produced by the mass transfer and, as a consequence, the temperature distribution in the area where the net buoyancy forces are zero has a greater slope than that obtained without electrolysis.

Figures 4c and 4d shows the corresponding Schlieren photographs of the flow for which the temperature profiles are shown in Fig. 3. These photographs were taken at 600 and 2220 s with $\Delta T = 6$ and 8 °C, respectively. Figures 4a and 4b shows the Schlieren photographs of the flow at the beginning of the same experiment, at 306 seconds with a uniform cylinder temperature equal to the bulk electrolyte temperature of 22 °C, and at 445 seconds, with an imposed axial temperature difference of $\Delta T = 2$ °C, respectively.

Data correlation

A correlation of the data was attempted on the basis of an additive combined Grashof number (GR_m). This equation takes account of the sign (direction) of the two component parts of GR_m , in which the mass transfer Grashof number (Gr_m) and the adjusted heat transfer Grashof number (Gr_h) are added to one another:

$$GR_m = Gr_m + (Sc / Pr)^{1/2} Gr_h \quad (6)$$

where Sc = Schmidt number and Pr = Prandtl number. However, at equal (or near equal) and opposite values of Gr_m and $(Sc/Pr)^{1/2} Gr_h$, GR_m becomes zero or has a very low value and cannot adequately represent the simultaneously occurring upward and downward flows, and the associated mass transfer rate.

The analysis of the situation was then approached by a consideration of the terms in the Navier-Stokes equation which correspond to the external force:

Figure 4. Schlieren photographs of opposed heat and mass transfer for 0.01 M Ferri/0.01 M Ferro/0.5 M NaOH, $L = 83$ mm, with an axial temperature gradient of

a) $\Delta T = 0$ °C, $t = 306$ s
b) $\Delta T = 2$ °C, $t = 445$ s

c) $\Delta T = 6$ °C, $t = 600$ s
d) $\Delta T = 8$ °C, $t = 2220$ s

$$g\beta_C \Delta C + g\beta_T \Delta T \quad (7)$$

The position along the surface of the cylinder (P), where buoyancy forces deriving from temperature and concentration gradients cancel each other out, can be deduced from Eq. 7. In the analysis, the sign (direction) of the mass and heat convection terms were taken into account, and the net buoyancy force was calculated. Values for the physical properties of the ferri/ferrocyanide redox system used in Eq. 7 were taken from Sarac *et al.*⁸. In general, in dilute solutions, the theoretical values obtained from Eq. 7 permit the approximate location of the position P to be identified.

Table 1 shows the values of the net buoyancy force at different temperatures in the 0.01 M Ferro-Ferricyanide/0.5 M NaOH solution with a bulk electrolyte temperature of 22 °C. In Table 1 the temperature at the surface along the cylinder electrode varies from 22 °C, equal to the bulk electrolyte temperature, to 31 °C. With these values a change in the sign of the net buoyancy force is produced between 25 and 26 °C. The temperature on the cylinder surface at the point of null net buoyancy force is $T_{P-N-S} = 25.7$ °C. This temperature was obtained by interpolating the values of Table 1. The heat transfer dominates and the convective flow is upward when the electrode surface temperature is higher than T_p . When the electrode temperature is lower than T_p the mass transfer dominates and the convective flow is downward.

Figure 5 shows a schematic diagram of the displacement of the thermal convective flow, at three different times corresponding to the run for which temperature profiles are shown in Fig. 3, with the corresponding Schlieren photographs in Figs. 4c and 4d and the values of the net buoyancy forces in Table 1.

The displacement of the convective heat flow for each time was measured from the Schlieren photographs obtained during the experiment for 600, 1200 and 2220 s. The position P in Fig. 5 is the position of zero net buoyancy

force as indicated by the Schlieren photographs. This value was obtained at 23.6 °C, and this corresponds to the temperature where all the temperature profiles (Fig. 3) undergo a change in slope.

The front of the thermal flow advanced more than predicted by the external force term of the Navier-Stokes equation. The position on the electrode where the net buoyancy force is zero, obtained by Eq. 7, is indicated in Fig. 5 by P_{N-S} .

The difference may be attributed, in part, to the fact that the prediction does not take account of the existence of thin boundary layers at the surface over which the buoyancy term changes appreciably.

To further quantify this effect and to cover a wider range of concentrations it would be necessary to solve a system of equations which, in addition to the Navier-Stokes equations, would include the equations of mass transport and energy and the equation of continuity.

Conclusions

The photography and measurement of the position on a cylinder with an imposed axial temperature gradient, at which opposed convective flows due to heat and mass transfer were equally balanced, was successfully carried out.

This position could be moved by changing the basic conditions of the experiment. By increasing the cylinder temperature, the competing convective flow due to mass transfer could be displaced until it apparently disappeared.

The development of the convective flow patterns depended strongly on the way in which the temperature and concentration differences were imposed, giving visual evidence of a number of apparent flow regimes. Prior establishment of a profile of temperature along the cylinder electrode produced an appreciable delay in the appearance of mass transfer convection patterns subsequent to the electrode surface being raised to its working potential.

Table 1. Variation of the net buoyancy force for unit mass of fluid $N = g\beta_C \Delta C + g\beta_T \Delta T$, with the electrode surface temperature for the 0.01 M Ferri/0.01 M Ferrocyanide/0.5 M NaOH system and the electrolyte temperature at 22 °C.

T (°C)	N
22	-0.01053
23	-0.00776
24	-0.00493
25	-0.00204
26	0.00089
27	0.00387
28	0.00693
29	0.01002
30	0.01335
31	0.01695

Figure 5. Schematic diagram of the displacement of the thermal convective flow corresponding to the temperature profiles shown in Fig. 3, and to the Schlieren photographs of Fig. 4c and 4d.

As simultaneous heat and mass transfer by free convection became established, corresponding modifications to each of the transfer processes were observed, so that the axial profile of temperature along the cylinder was modified by the superposed mass transfer process, and the limiting diffusion current was modified by changes in the temperature level.

The terms representing external forces in the Navier-Stokes equations can be used at low concentration to give an approximation of the position along the cylinder, where the concentration and thermally driven buoyancy forces are equally balanced.

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