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MASS-TRANSFER MEASUREMENTS WITH THE TECHNIQUE OF ELECTROCHEMILUMINESCENCE

RALPH G. COLELLO and GEORGE S. SPRINGER
Massachusetts Institute of Technology, Cambridge, Massachusetts

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Abstract—When a potential is applied between two platinum electrodes immersed in a chemiluminescent solution a blue glow appears at the surface of the anode. The parameters affecting the intensity of the glow are investigated and the limiting current conditions are obtained. In low-Reynolds-number flows, local intensities of the glow are measured on flat plates and around the circumference of a circular cylinder by the current output of a photomultiplier tube. It is found that, at limiting currents, the intensity of the glow is proportional to the calculated mass-transfer rate to the surface of the anode, and a relationship is obtained between the current output and the mass-transfer rate for the experimental system employed.

NOMENCLATURE

A,	area [cm^2];
b,	height of flat plate model [cm^2];
c_0,	concentration of H_2O_2 on surface of model [g/cm^3];
c_∞,	concentration of H_2O_2 in free stream [g/cm^3];
$\hat{c}$,	specific heat [cal/g degC];
D,	diffusion coefficient of H_2O_2 in the solution [cm^2/s];
d,	diameter of cylindrical model [cm];
k,	thermal conductivity [cal/s cm degC];
h,	heat-transfer coefficient [cal/s cm^2 degC];
h_d,	mass-transfer coefficient [cm/s];
I,	measured light intensity [μA];
K,	proportionality constant defined by equation (1) [g/μAs];
L,	length of flat plate model [cm];
l,	characteristic length (see equation 6) [cm];
Nu,	Nusselt number ($= hd/k$);
Pr,	Prandtl number ($= \hat{c}\mu/k$);
Re,	Reynolds number ($= V_\infty d/\nu$);
Sc,	Schmidt number ($= \nu/D$);
Sh,	Sherwood number ($= h_d l/D$);
t,	elapsed time [s];
V_∞,	free stream velocity [cm/s];
W,	mass-transfer rate [g/s];
X,	distance from leading edge of flat plate model [cm];
ν,	kinematic viscosity [cm^2/s].

INTRODUCTION

IN THIS paper the application of an electrochemiluminescent (ECL) process to the measurement of mass-transfer rates is described. In the ECL process two electrodes are immersed in a chemiluminescent solution. When a voltage is applied between the electrodes a blue glow appears over the entire surface of the anode. This glow provides visual information about the behavior of the flow near the surface of the anode and, in particular, it indicates very well the position of separation [1, 2]. For appropriate conditions and applied potentials, in laminar flow the intensity of the glow is related to the mass-transfer rate of the active electrolyte to the surface of the anode [3]. Thus, if the anode is made in the shape of the model, this technique suggests the possibility of measuring local or average mass-transfer (and by analogy heat-transfer) rates to surfaces immersed in flowing liquids, while visualizing the behavior of the flow near the surface.

In the following the parameters affecting the ECL reaction and the intensity of the glow are investigated and the conditions for limiting currents are established. At limiting currents the current density in the electrode circuit is a maximum and the concentration of the active electrolyte at the surface of the anode is negligible compared to the free stream concentration [4]. Under limiting current conditions and in low-Reynolds-number flows, local intensities of the glow were measured on flat plates and around the circumference of a circular cylinder, including the separated region, by the current output of an uncalibrated photomultiplier tube. It is shown that the light intensities thus measured are proportional to calculated values of the local mass-transfer rates to the surface of the anode and a relationship between the current output and the calculated mass-transfer rate is obtained for the experimental system employed. In this paper the term "mass transfer" is used to denote the transport of ions or molecules by diffusion and convection.

EXPERIMENTAL APPARATUS

A schematic diagram of the apparatus used in the present experiments is shown in Fig. 1. The flow was provided by a circular flow chamber, driven by a synchronous motor. Variation in speed was achieved through the use of pulleys and gear reducers. The maximum flow

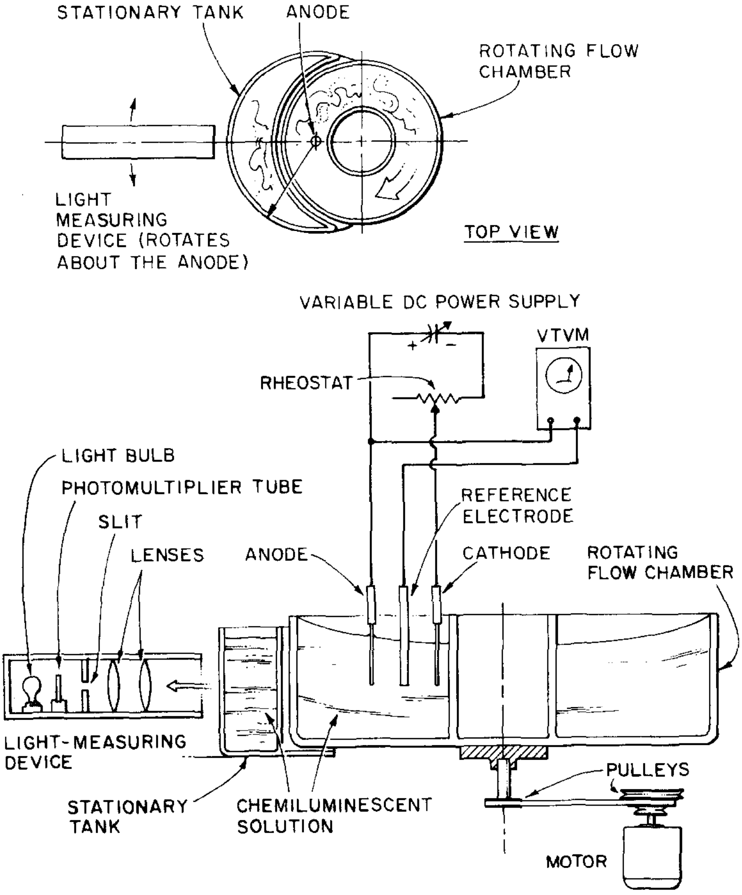

FIG. 1. Schematic of experimental apparatus.

velocity provided by this apparatus was about 45 cm/s.

The flow chamber was constructed from a 33-cm dia. Plexiglas cylinder. Concentric with the wall of the chamber was a 14-cm dia. Plexiglas cylinder. A suitably shaped stationary tank (Fig. 1), constructed of Plexiglas and filled with the chemiluminescent solution, was placed outside the rotating flow chamber. The purpose of this tank was to ensure that all measurements were made through the same amount of solution irrespective of the relative orientation of the model and the light-intensity measuring device.

Three electrodes were placed in the solution: an anode, a cathode and a saturated KCl–calomel electrode.

The ECL glow is produced at the anode. Therefore, it is necessary to make the anode in the shape of the model about which the glow is to be studied. In the present experiments, cylindrical and flat-plate models were used. The flat-plate models were bent along a circular arc approximating the shape of an undisturbed streamline.

The cathode was a flat plate bent along a circular arc and placed near the inner wall of the flow chamber. The anode and cathode were platinum and of approximately the same surface area in order to prevent bubbling of the solution.

A saturated KCl–calomel electrode in combination with a VTVM was used to measure the potential between the anode and the solution. The electrode circuit is shown in Fig. 1. A regulated d.c. voltage supply was connected in parallel with a 2-Ω rheostat and the anode and cathode.

In order to measure light intensity, two Kodak Aero-Ektar (f/2·5) lenses were placed back to back so that the two focal planes of the lens assembly were optically identical. A vertical slit about 0·038-cm wide and 1·27-cm long was set in one focal plane. A photomultiplier tube was mounted behind the slit. A linear relationship exists between the light input and current output for the photomultiplier tube used, so that the intensity of the ECL glow was directly proportional to the measured current. This assembly was mounted so that the anode was in the other focal plane. A light bulb was also placed behind the slit for focusing and for determining the area of the anode on which the light intensity was measured. The image of the slit on the anode was four times the area of the slit (0·193 cm^2).

For cylindrical models, the light intensity measurements were made by rotating the light measuring device about the axis of the cylindrical model (see Fig. 1). Light intensities from flat-plate models were measured with the light measuring device in a fixed position, and by moving the flat plate in the focal plane of the light measuring device.

The experiments were performed in a darkened room. No special care was taken to omit all extraneous light, since only relative light intensity measurements were required in the present experiments.

THE ELECTROCHEMICAL SYSTEM

The two major variables of the ECL process are the composition of the chemiluminescent solution and the applied potential. Experiments were performed to determine the effects of these variables on the light intensities and on the limiting currents.

The composition of the solution is given in Table 1. Distilled water is the solvent since tap water usually contains impurities which excite the chemiluminescent reaction, producing a bulk glow of the solution. Luminol is the chemiluminescent substance. It exhibits chemiluminescence above approximately pH 8 only, thus potassium hydroxide is added to adjust the pH of the solution. Hydrogen peroxide is the active electrolyte and is acting as the oxidizing agent. Potassium chloride is added to the solution as a supporting, inert electrolyte, in order to minimize the effects of ion migration on the mass transfer.

The concentration of each of the components of the solution given in Table 1 was varied to determine the effect of each on the light intensity. It was found that small variations in the concentrations of potassium chloride, potassium hydroxide and Luminol do not alter the light intensity appreciably. The concentration of hydrogen peroxide, however, is significant to the light intensity level (Fig. 2). It may be noted (Fig. 2) that at the points where the light intensities are a maximum the light intensity varies less for small changes in applied potential with decreasing concentrations of hydrogen peroxide. This is of importance since, as will be shown, the limiting current conditions are also attained at the potentials at which the light intensities are a maximum. For this reason the lowest hydrogen peroxide concentration shown in Fig. 2 (0·3 ml/l solution) was used in the remainder of this study.

Table 1. *Composition of chemiluminescent solution*

Substance	g/l of solution	Remarks
H_2O	—	solvent should be distilled
KCl	74·56	supporting electrolyte
KOH	1·68	adjust pH, Luminol exhibits chemiluminescence in alkaline solution only
H_2O_2*	0·0976	oxidizing agent, concentration strongly affects light intensity
Luminol†	0·15	chemiluminescent substance soluble in alkaline solutions only

* Corresponds to 0·3 ml of H_2O_2 (30% solution).

† Eastman Kodak Company Luminol = 5-amino-2,3-dihydro-1,4 phthalazinedione.

Kinematic viscosity of solution (85°F) $\nu = 0{\cdot}0078\ \text{cm}^2/\text{s}$.

Diffusion coefficient of H_2O_2 (85°F) $D = 1{\cdot}1 \times 10^{-5}\ \text{cm}^2/\text{s}$ (measured, see Appendix)

The experiments must be performed under limiting current conditions, i.e. when the concentration of the active electrolyte (H_2O_2) is approximately zero at the surface of the anode ($c_0 \simeq 0$). The limiting currents are reached when a small change in the applied potential does not alter the current significantly. For the hydrogen peroxide concentration used in this study (0·3 ml/l solution, Table 1) limiting current conditions are attained at an anode to solution potential of about 0·41 V (Fig. 3). The maximum light intensity for this solution also occurs at 0·41 V (Fig. 2). Thus, the solution given in Table 1, and an anode to solution potential of 0·41 V were used in all the following experiments. A variation in the free-stream velocity does not change the value of the applied potential at which the maximum light intensity and the limiting current occur, as is demonstrated by the results presented in Figs. 3 and 4.

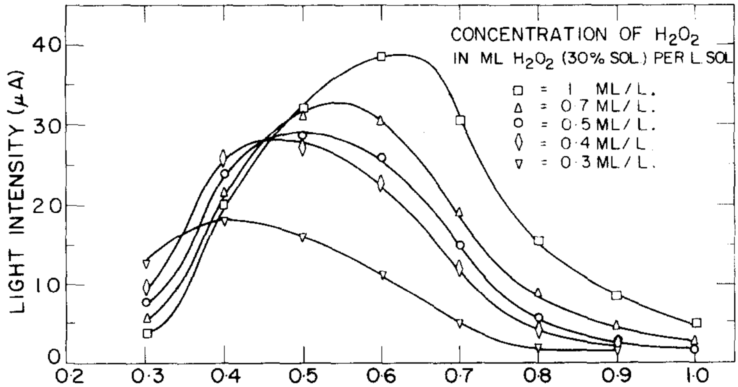

FIG. 2. Variation of light intensity as a function of anode to solution potential with various concentrations of hydrogen peroxide. Light intensity measured 5·08 cm from the leading edge of a flat plate. Free-stream velocity 40·2 cm/s.

Using a flat-plate model the current in the anode–cathode circuit was also measured without the active electrolyte (H_2O_2) in the solution (Fig. 3). This current is a measure of the extraneous current-producing reactions and is of importance when the current is used as a measure of the mass transfer [5–7]. In the present experiments, where the light intensity is used to measure mass-transfer rates, these reactions are of no concern in the actual measurements, but are of interest in the determination of the diffusion coefficient (see Appendix).

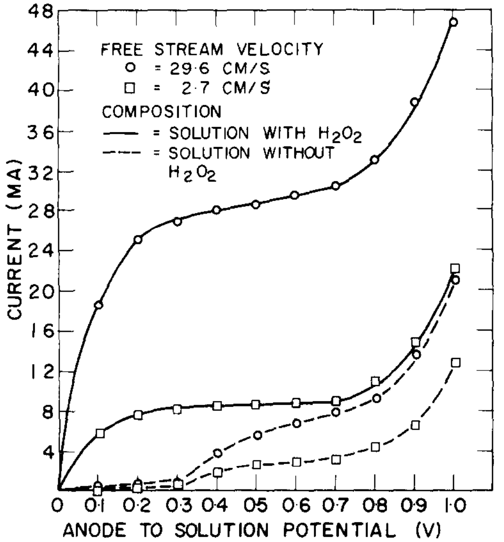

FIG. 3. Variation of current as a function of anode to solution potential using solution of Table 1 with and without hydrogen peroxide in the solution. Current measured using a flat-plate anode.

In the experiments performed in this investigation no special care was taken to prevent contamination of the solution from the air. The same solution was used for periods of up to 3 h with only minor changes in the measured light intensities.

MEASUREMENTS

The experiments of Springer [3] indicate that the intensity of the ECL glow is proportional to the calculated mass-transfer rate of the active electrolyte to the surface of the anode. This suggests the existence of a proportionality constant given by the equation

$$K = \frac{W/A}{I/A} \qquad (1)$$

where I is the light intensity as measured by a photomultiplier tube, W is the mass-transfer rate to the surface and A is the surface area. The absolute value of K depends, of course,

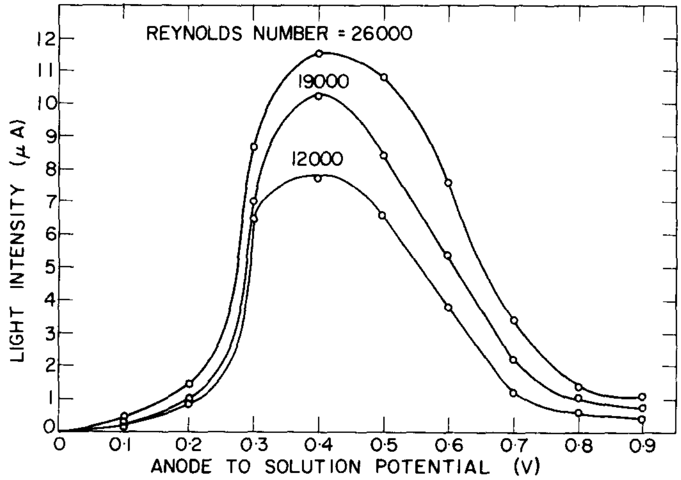

FIG. 4. Variation of light intensity as a function of anode to solution potential at different Reynolds numbers. Light intensity measured 5·08 cm from the leading edge of flat plate using the solution given in Table 1.

upon the operational characteristics of the experimental system. Special care was taken, therefore, to insure that there were no changes in the apparatus, or solution, during the following series of experiments.

Three experiments were performed to establish the existence of the proportionality constant (K) and to determine its value for the experimental system used. The first experiment dealt with a flat-plate model in steady laminar flow.

A flat-plate model (anode) was placed in the flow chamber, and the chamber was rotated until steady-state conditions were achieved. Then, the light intensity was measured as a function of distance from the leading edge of the plate. The results of the measurements are shown in Fig. 5.* The light intensity per unit area given in Fig. 5 (and also on the following figures) was obtained by dividing the current output of the photomultiplier tube (μ) by the area of the image of the slit on the anode (0·193 cm^2).

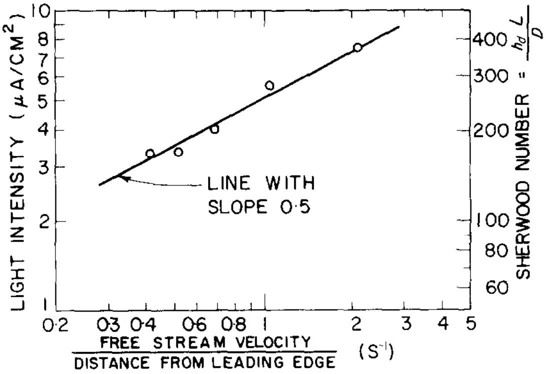

FIG. 5. Local light intensity and Sherwood number on a flat plate as a function of free stream velocity divided by the distance from the leading edge. Anode to solution potential 0·41 V. Solution given in Table 1. Free stream velocity 2·7 cm/s.

In order to determine K, an arbitrary value of V_∞/X was selected from Fig. 5 and for this V_∞/X the mass flux per unit area was calculated. At a distance X from the leading edge, the mass flux per unit area to the surface of a flat plate in steady laminar flow is, [8]

$$\frac{W}{A} = 0{\cdot}34\frac{Dc_\infty}{\sqrt{\nu}}\left(\frac{\nu}{D}\right)^{\frac{1}{3}}\left(\frac{V_\infty}{X}\right)^{\frac{1}{2}}. \qquad (c_0 \cong 0). \quad (2)$$

c_∞ is the free-stream concentration of the hydrogen peroxide in the solution, ν is the kinematic viscosity of the solution and D is the diffusion coefficient. The values of these parameters are listed in Table 1. V_∞ is the free-stream velocity. It is noted that if the intensity of the ECL glow depends on the mass-transfer rate only, then the light intensity must be proportional to $(V_\infty/X)^{\frac{1}{2}}$. That this is so under the present experimental conditions is borne out by the results in Fig. 5.

The mass flux calculated by equation (2) and the light intensity measured at the corresponding V_∞/X value, when substituted into equation (1), give $K = 7{\cdot}7 \times 10^{-9}$ g/μAs.

In the second experiment at time $t = 0$ the potential was suddenly applied to a flat-plate anode immersed in the standard solution. The bulk velocity of the solution relative to the plate was zero ($V_\infty = 0$). The experimental results are shown in Fig. 6. Assuming that the fluid extends from the plate (concentration $c_0 \simeq 0$) to infinity (concentration: c_∞), at any given time (t) the mass transfer rate to unit surface area of the plate is [9].

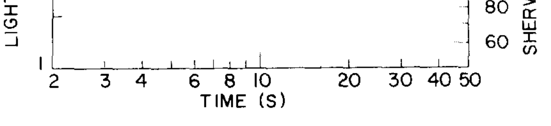

FIG. 6. Variation of light intensity and Sherwood number with time on a flat plate for zero bulk flow velocity ($V_\infty = 0$). Anode to solution potential 0·41 V. Solution given in Table 1.

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* In Figs. 5–8 the Sherwood numbers are also indicated. The Sherwood numbers were calculated after the value of K was determined, as will be explained later.

$$\frac{W}{A} = -\frac{Dc_\infty}{(\pi Dt)^{\frac{1}{2}}} \qquad (c_0 \cong 0). \qquad (3)$$

Equation (3) indicates that if the intensity of the glow is governed by diffusion only, then the light intensity must be proportional to $1/t^{\frac{1}{2}}$. The experimental results in Fig. 6 follow closely the line with the slope given by equation (3).

For the above experiment K was obtained by calculating W/A from equation (3) at an arbitrary time (t) and by measuring the light intensity at the corresponding time. Using equation (1), the value of K for this experiment was found to be $K = 8{\cdot}1 \times 10^{-9}$ g/μAs.

In a third experiment a circular cylinder (anode) was placed in steady, laminar flows normal to the axis of the cylinder. The results of the light intensity measurements around the circumference of the cylinder are shown in Fig. 7. The total light output for the cylinder was obtained (Fig. 8) by integrating numerically the data given in Fig. 7. The current density around the cylindrical model (anode) may be non-uniform due to the asymmetrical arrangement of the anode and the cathode. In this investigation the effects caused by this non-uniformity are neglected.

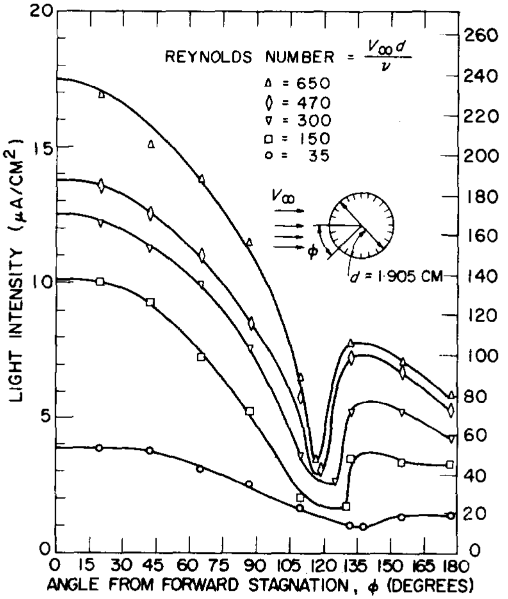

FIG. 7. Local light intensity and Sherwood number around the circumference of a circular cylinder at different Reynolds numbers. Anode to solution potential 0·41 V. Solution given in Table 1.

It is shown by McAdams [10] that the heat transfer to liquids flowing normal to a single cylinder may be estimated by the expression

$$Nu/Pr^{0{\cdot}3} = 0{\cdot}35 + 0{\cdot}56\,Re^{0{\cdot}52}. \qquad (4)$$

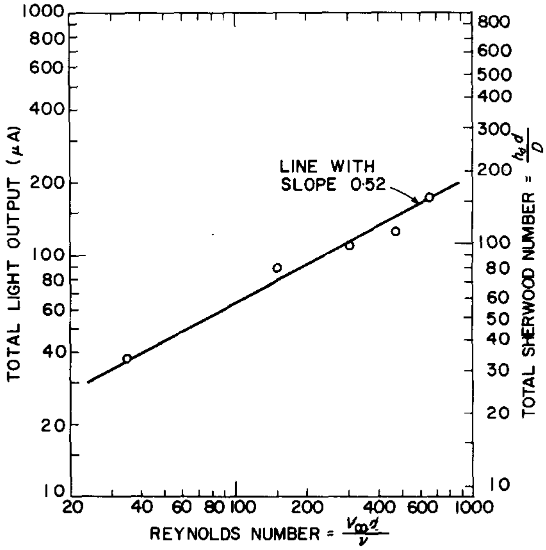

FIG. 8. Variation of total light intensity and total Sherwood number with Reynolds number for flows past a 1·905-cm-dia. circular cylinder. Anode to solution potential 0·41 V. Solution given in Table 1.

If the ECL process is governed by mass transfer then by analogy between heat and mass transfer the Prandtl number (Pr) may be replaced by the Schmidt number ($Sc = \nu/D$) and the Nusselt number (Nu) by the Sherwood number (Sh) giving

$$Sh = \frac{(h_d)d}{D} = \frac{(W/A)d}{Dc_\infty}$$

$$= [0{\cdot}35 + 0{\cdot}56\,Re^{0{\cdot}52}]\,Sc^{0{\cdot}3} \qquad (c_0 \cong 0) \quad (5)$$

where h_d is the mass-transfer coefficient, given by the equation $W/A = h_d(c_\infty - c_0)$. The Reynolds number ($Re$) is based on the diameter (d) of the cylinder. The measured light intensity vs. Reynolds number curve follows the line of slope 0·52 (Fig. 8), indicating again the proportionality between the mass flux and the intensity of the glow.

For the above experiment K was evaluated by calculating W/A from equation (5) for an arbitrary Reynolds number and by finding the light intensity from Fig. 8 at the corresponding Reynolds number, giving $K = 7{\cdot}2 \times 10^{-9}$ g/μAs.

On the basis of the previous three experiments for K the average value $K = 7{\cdot}67 \times 10^{-9}$ g/μAs was selected. Using this value, for any given light intensity the Sherwood number is calculated from the expression

$$Sh = \frac{(W/A)l}{Dc_{\infty}} = \frac{K(I/A)l}{Dc_{\infty}} \qquad (c_0 \cong 0). \qquad (6)$$

The Sherwood numbers indicated in Figs. 5–8 were computed by substituting either the length of the flat plate ($L = 7$ cm) or the diameter of the cylinder ($d = 1{\cdot}905$ cm) in the above expression for l.

A comparison is made now between the Sherwood numbers (mass transfer) determined for the cylindrical models in the present experiments and between the Nusselt numbers obtained by Eckert and Soehngen [11]. Eckert and Soehngen measured the heat transfer to cylinders in low Reynolds-number flows normal to the axis of the cylinder. The comparison is made at the lowest and highest Reynolds numbers used by Eckert and Soehngen. There is fair agreement between Eckert and Soehngen's and the present data (Fig. 9). The agreement is particularly good at low Reynolds numbers, and in the unseparated region.

In the experiments described in the foregoing no attempt was made to determine the conditions at which the reaction producing the ECL glow becomes limited by reaction kinetics at the surface. However, for the conditions encountered in the present experiments the results indicate a proportionality between the intensity of the ECL glow and the mass-transfer rate to the surface of the anode in low Reynolds-number flow. It is expected that further investigations will extend the results described above to high Reynolds-number flows.

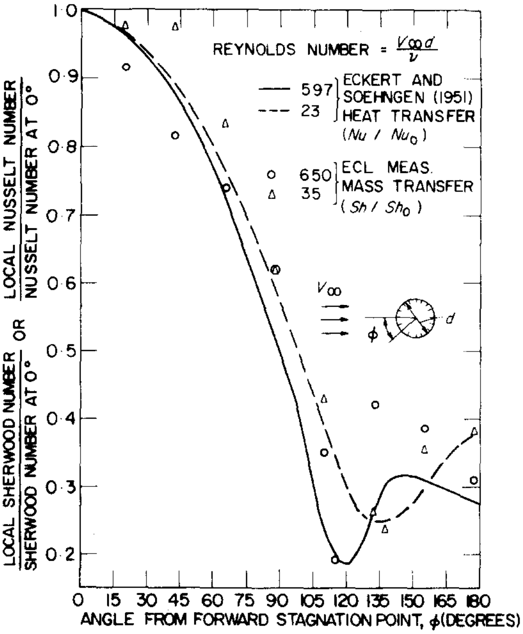

FIG. 9. Comparison between local Sherwood numbers and local Nusselt numbers around a circular cylinder. Nusselt numbers obtained by Eckert and Soehngen [11]. Local Sherwood numbers obtained in present investigation.

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Prior to the present investigation, experiments were performed in this Department by R. L. Alpert, F. L. Egendorf, M. Potash and F. O. Verlot, under the direction of Professor A. H. Shapiro, demonstrating the dependence of the electrochemiluminescent glow on the mass-transfer rate. The authors are grateful to Professor Shapiro for suggesting the problem and for making available to them the valuable information and experience gained from these experiments. They wish to thank Professor Shapiro also for his helpful suggestions during the course of this work.

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APPENDIX 1

The determination of the diffusion coefficient

In order to obtain the diffusion coefficient (D) for hydrogen peroxide in the standard solution, experiments were performed with a flat-plate anode in steady, laminar flow. At limiting-current conditions, the current is a measure of the mass-transfer rate according to the equation

$$W/A = i/AnF \qquad \text{(A1)}$$

where W/A is the mass flux per unit area to the surface, i is the current, F is Faraday's constant and n is the valence of the ECL reaction ($n = 2$).

In steady, laminar flow the total mass flux to a flat plate of height b and length L on which the surface concentration is uniformly zero ($c_0 \simeq 0$) is [8].

$$W = 0{\cdot}68\, Dc_\infty b \left(\frac{\nu}{D}\right)^{\frac{1}{3}} \left(\frac{V_\infty L}{\nu}\right)^{\frac{1}{2}}. \qquad \text{(A2)}$$

V_∞ is the free-stream velocity, c_∞ is the free-stream concentration of the hydrogen peroxide in the solution, and ν is the kinematic viscosity of the solution (Table 1).

Equations (A1) and (A2) give

$$D \cong \frac{1}{\nu^{\frac{1}{2}}} \left[\frac{i(\nu/V_\infty L)^{\frac{1}{2}}}{0{\cdot}68\, nFc_\infty L}\right]^{\frac{3}{2}}. \qquad \text{(A3)}$$

The diffusion coefficient was calculated from equation (A3) by measuring the current at three free-stream velocities, namely 40·2, 29·2 and 8·5 cm/s. The diffusion coefficient for each of these cases was found to be within ±3 per cent of the value given in Table 1 ($D = 1{\cdot}1 \times 10^{-5}$ cm^2/s). On the basis of the results given in Fig. 4 it was assumed in these calculations that the current due to extraneous, current-producing reactions could be neglected in comparison with the total current.

Résumé—Lorsque un potentiel est appliqué deux électrodes de platine immergées dans une solution chimiluminescente, une lumière bleue apparaît à la surface de l'anode. Les paramètres affectant l'intensité de la lumière sont étudiés et les conditions du courant limite sont obtenues. Dans les écoulements à faibles nombres de Reynolds, les intensités locales de la lumière sont mesurées sur des plaques planes et autour d'un cylindre circulaire à l'aide du courant de sortie d'un photomultiplicateur. On trouve que, aux courants limites, l'intensité de la lumière est proportionnelle à la vitesse de transport de masse calculée à la surface de l'anode, et l'on obtient une relation entre le courant de sortie et la vitesse de transport de masse pour le système expérimental utilisé.

Аннотация—При наличии потенциала между двумя платиновыми электродами, погруженными в хемилюминисцентный раствор, на поверхности анода появляется голубое свечение. Исследуются параметры, влияющие на интенсивность свечения. Получены условия предельного тока. Локальная интенсивность свечения при низких числах Рейнольдса на плоской плстине и контуре круглого цилиндра измерялась по выходному току трубки фотоэлектронного умножителя. Найдено, что при предельных токах интенсивность свечения пропорциональна расчетной скорости массопереноса на поверхности анода. Получена зависимость между выходным током и скоростью массообмена для данной эксперименталбной установки.