IONIC MASS TRANSFER IN THE ELECTROLYSIS OF FLOWING SOLUTIONS. THE ELECTRODEPOSITION OF COPPER UNDER MASS-TRANSFER CONTROL ON TUBULAR ELECTRODES.*

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Abstract—Ionic mass transfer for the electrodeposition of copper from aqueous copper sulphate–sulphuric acid solutions has been studied on tubular stainless steel electrodes.

The following parameters were varied: rate of flow, copper ion concentration, viscosity, height and diameter of tubular electrodes, and temperature. The data can be correlated by the dimensionless equation

$$Sh = 0.647\ Re^{1/2}\ Sc^{1/3}.$$

The temperature coefficient of the kinetic mass-transfer constant is 1·2, corresponding to an experimental heat of activation of 3850 ± 200 cal/mol.

The solution of the momentum- and heat-transfer equations worked out by Eckert for flat plates, according to von Kármán's treatment, and recently extended by Wranglén to the analogous mass-transfer problem, can be applied under certain conditions to tubular electrodes.

Résumé—On a étudié le transfert ionique de masse dans l'électrodeposition des ions cuivre (II) sur des électrodes tubulaire d'acier inoxydable.

Les données expérimenteles furent obtenues en fonction des paramétres suivants: vitesse de circulation de l'électrolyte, concentration d'ions cuivre, viscosité de la solution, hauteur et diamètre des électrodes et température.

On a obtenu l'equation suivante:

$$Sh = 0,647\ Re^{1/2}Sc^{1/3}.$$

Les solutions des équations obtenues par Eckert pour le transfert de chaleur et de quantité de mouvement dans le cas de plaques planes en utilisant la méthode de von Kármán, et qui ont été aussi appliquées à des problèmes analogues de transfert de masse par Wranglén, sont applicables à des électrodes tubulaire sous certaines conditions.

Zusammenfassung—Es wurde die Stofftransportgeschwindigkeit bei der elektrolytischen abscheidung von Kupfer aus wässerigen schwelfsauren Kupfersulfat-Lösungen an röhrenförmigen Elektroden aus rostfreiem Stahl untersucht.

Es wurden die folgenden Parameter variiert: die Strömungsgeschwindigkeit, die Konzentration der Kupferionen, die Zähigkeit, die Höhe und der Durchmesser der röhrenförmigen Elektroden sowie die Temperatur. Die Messwerte können durch die dimensionslose Gleichung dargestellt werden:

$$Sh = 0,647\ Re^{1/2}\ Sc^{1/3}.$$

Der Temperaturkoeffizient der Stoffübergangszahl entspricht einer Aktivierungswärme von 3850 ± 200 cal/mol.

Die Gleichung kann unter gewissen Bedingungen theoretisch abgeleitet werden, indem man die von Eckert für das Wärmeübergangsproblem und von Wranglén für das Stoffübergangsproblem an ebenen Platten ausgearbeitete Lösung, unter Anwendung der von Kármán'schen Näherung für die Impuls- und Stofftransportgleichung, auf die röhrenförmige Zelle ausdehnt.

INTRODUCTION

IONIC mass-transfer processes under forced convection with laminar flow have been studied in several cases. The greatest attention has been paid to the rotating disk

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electrode, the theory of which was developed several years ago by Levich.[1] The streaming mercury electrode has also been considered in some detail by Rius, Llopis and Polo.[2] Lévêque[3] has also devised a streaming electrode intended for polarography and has obtained its kinetic equation. The three electrodes mentioned above are particularly interesting because the steady state forced convection is obtained by stirring the solution with the electrodes, keeping a laminar flow on their surface.

The case in which the electrodes are fixed and the electrolytic solution is streaming along the electrode surface under laminar flow has not received much attention. Lin, Denton, Gaskill and Putnam[4] have studied various electrochemical reactions involving mass transfer in the inner electrode surface of a concentric cell in order to obtain design information. In recent years Jordan and Javick[5,7] have considered a conical electrode placed into the stream of a flowing solution which has been successfully applied to voltammetry.   Wranglén[6] has published results for metal deposition on a horizontal flat plate that is simultaneously an electrode and a wall of the electrolysis cell.

We are investigating electrolytic reactions in flowing solutions employing different types of electrodes and flowing conditions. We have been studying tubular electrodes for two main purposes. First, it may be assumed that reproducible velocity and concentration profiles would result on the electrodes under certain flowing rates, and it would be useful to compare the mathematical solutions of momentum and heat transfer equations worked out for the horizontal flat plate to the tubular electrode. Secondly, if the equation for mass transfer is simple and experimental errors involved are low, it would be interesting to apply tubular cells with flowing electrolytes to hydrodynamic voltammetry studies. Therefore, if these cells are properly designed, they could be particularly useful for the kinetic study of electrochemical reactions. The mass-transfer equations obtained in the present work support these ideas, which are now under development.

EXPERIMENTAL

1. *The tubular electrolysis cell and the flowing solutions*

The electrolysis cell, Fig. 1, was made of a metal tube of which inner side was the working electrode. It was vertically mounted between two Pyrex glass tubes. The inside diameters of the three pieces were 1·70 cm. The end of the tubular pieces had been perfectly polished to give very good contact between them, eliminating any binding material which could have modified the actual diameter of the cell and altered the flowing conditions into the cell. The three pieces were held together by pressing one against the other with special holders. Polyethylene tubing was useful to keep the cell in position. Tubular electrodes were made of stainless steel; four of them were employed having the following heights:

electrode	height cm	area cm²
1	6·00	32·0
2	3·00	16·0
3	1·50	8·00
4	0·75	4·00

The counter electrode was the outer surface of a copper tube of much smaller diameter, 0·47 cm, placed at the axis of the cell. The reference electrode was placed in a special container and connected to the cell just above the working electrode, with a standard tapered joint. The potential of the working electrode was determined in three different positions as indicated in the figure. Solutions of 0·008 to 0·223 M $CuSO_4$ in *ca* 1·5 M H_2SO_4 were employed. To increase the viscosity and density of the solutions glycerine was added in some experiments. The solutions were continuously pumped through the cell from bottom to top by means of a rotating pump which had a stainless steel propeller and a Lucite body. The propeller was rotated by a 1/8 H.P. a.c. motor whose rate was conveniently
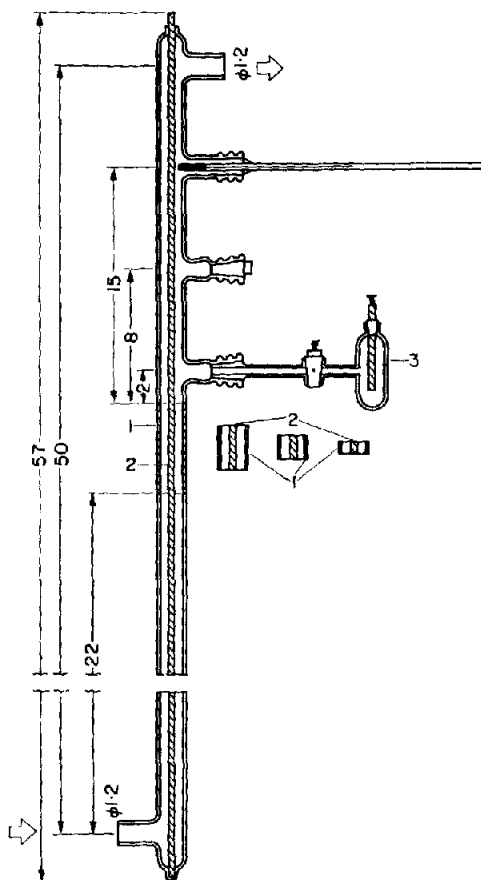
FIG. 1. Scheme of the tubular cell. 1 and 2: electrodes; 3: reference electrode; dimensions are in cm.

adjusted to get a constant solution flow. The propeller was adjusted in the body of the pump by means of Teflon gaskets and O-rings to eliminate any possible addition of impurities to the solution.

The solution was stored in a Pyrex glass container placed in a thermostat. A continuous flow of purified nitrogen was bubbled through the solution. Hence, dissolved oxygen was almost completely removed from the solutions. The rate of flow was determined by means of a flowmeter based on the measurement of pressure drop through tubes of different diameters. The change in pressure was read on a mercury manometer, previously calibrated. From the volumetric rate of flow Q, in cm^3/sec we obtained the average flow velocity, V, in cm/sec by

$$V = \frac{Q}{\pi(r_s^2 - r_i^2)},$$
(1)

where r_s and r_i are the external and internal electrode radii. Two flowmeters were employed to cover the range of rates of flow. A diagram of the whole set-up employed is shown in Fig. 2.

2. *Properties of the solutions and experimental conditions*

The compositions of the solutions was determined by chemical analysis. The copper ion content was measured electrolytically, the sulphuric acid concentration by titrating with standard sodium hydroxide solutions. Glycerine concentration was calculated from viscosity and density measurements applying the equations recently worked out by Fenech and Tobias[8] for that system.

The diffusion coefficients for copper ions in sulphuric acid solutions were taken from Gordon and Cole[9]. For the solutions containing glycerine they were calculated from the equations given by
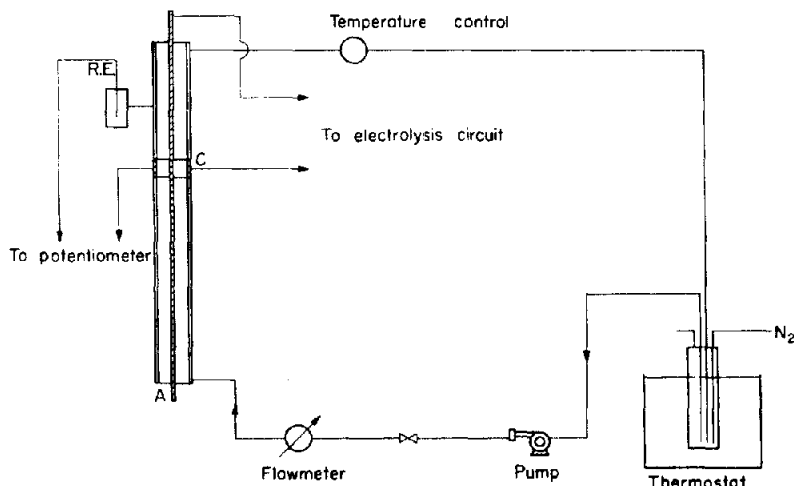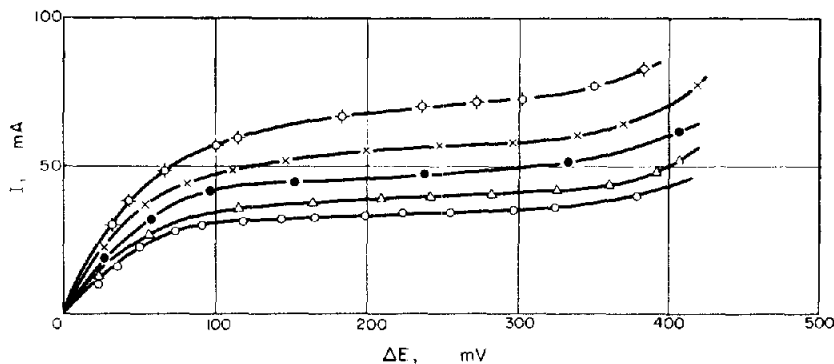
Fig. 2. Diagram of the hydrodynamic circuit.

Fig. 3. Experiments at 35°C.

$C_0 = 0.0076$ M; $C_a = 1.484$ M; $h = 6.00$ cm.

○: 9·3 cm/sec; △:11·3 cm/sec; ● : 14·6 cm/sec;

×: 17·8 cm/sec; --○--: 22·6 cm/sec.

Fenech and Tobias[8]. The viscosity of the solutions, which covered the range from 1.067×10^{-2} to 7.2356×10^{-2} cm²/sec, was determined by a Hoeppler viscometer.

Densities were measured picnometrically.

3. *Polarization curves*

The potential of the electrode was changed from zero to a value close to 500–600 mV by means of a potentiometric device as usually employed for electrolysis. Lead/acid batteries were employed as d.c. sources. The potential difference between the cathode and reference electrode was read with a Siemens–Halske potentiometer equipped with a suitable Weston galvanometer. The current intensity was read with a Siemens precision ammeter and in a few cases—for very low intensities—it was determined by measuring the potential drop on a standard resistor in series with the cell.

Polarization curves were obtained pointwise without interrupting the electrolysis current. Once a solution at a constant temperature was flowing through the cell, polarization curves were obtained at different rates of flow one after the other, starting each time from a zero potential difference between the electrodes.

RESULTS

Polarization curves for different solutions were obtained at temperatures ranging from 25 to 45°C and rates of flow from 6 to 50 cm/sec. Figs. 3, 4 and 5 show some
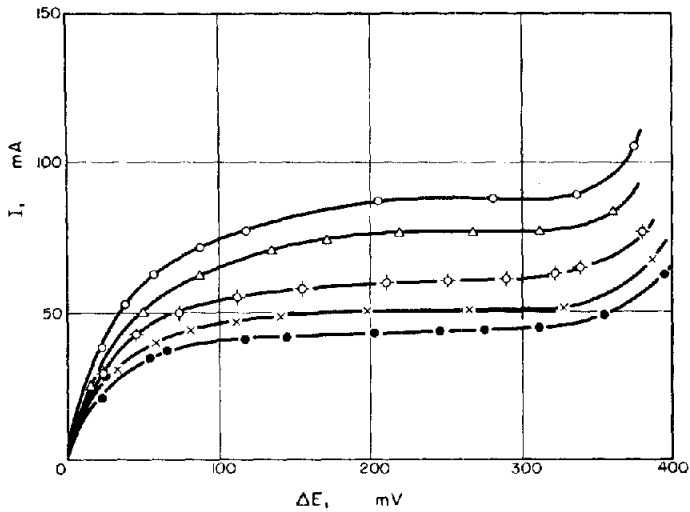
FIG. 4. Experiments at 45°C.

$C_0 = 0.0076$ M; $C_a = 1.484$ M; $h = 6.00$ cm.

● : 8·97 cm/sec; × : 11·5 cm/sec; -◯-: 14·8 cm/sec
△: 17·6 cm/sec; ◯: 20·5 cm/sec.
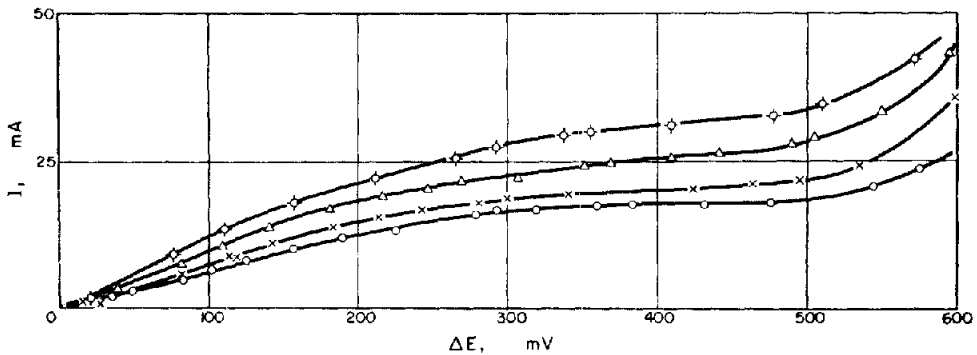
FIG. 5. Experiments with glycerine.

$C_0 = 0.0180$ M; $C_a = 1.480$ M; $h = 3.00$ cm.

$C_g = 6.15$ M; $t = 25$°C

◯: 30·5 cm/sec; × : 40·4 cm/sec; △: 52·9 cm/sec;
-◯-: 64·6 cm/sec.

typical polarization curves obtained for the electrodeposition of copper under different conditions. Tables 1 to 5 present the experimental data. The following nomenclature has been used:

No. number of the experiment; C_0, molar copper ion concentration; C_a, molar sulphuric acid concentration; C_g, molar glycerine concentration; D_0, copper ion diffusion coefficient in cm²/sec; ν, kinematic viscosity of the solution in cm²/sec; V, average velocity of flow in cm/sec; i_L, limiting current density in mA/cm²; ΔC_a, molar change of concentration of sulphuric acid; k, mass transfer constant in cm/sec; Sc, Re and Sh, respectively Schmidt, Reynolds and Sherwood numbers; d, diameter of the inner electrode, h, height of the tubular electrode (both in cm); and t, temperature.

TABLE 1. ELECTRODE 1; $d = 0.47$ cm; $h = 6.00$ cm; $t = 25°C$.

No.	V	i_L	$k \times 10^4$	ΔC_a	Re	Sh	$Re^{1/2} Sc^{1/3}$
$C_0 = 0.026$; $C_a = 1.403$; $D_0 = 6.32 \times 10^{-6}$; $\nu = 1.071 \times 10^{-2}$; $Sc = 1695$							
18	7.12	2.70	5.38	0.0112	4000	511	760
19	11.5	3.39	6.76	0.0112	6450	642	965
20	14.6	3.74	7.46	0.0112	8170	708	1087
21	17.7	3.92	7.81	0.0112	9930	742	1197
22	23.6	4.56	9.09	0.0112	13500	805	1407
$C_0 = 0.0076$; $C_a = 1.484$; $D_0 = 6.34 \times 10^{-6}$; $\nu = 1.067 \times 10^{-2}$; $Sc = 1634$							
33	8.10	0.675	4.46	0.0032	4555	422	805
34	10.4	0.898	6.08	0.0032	5790	575	906
35	14.3	1.07	7.22	0.0032	8070	683	1070
36	16.6	1.17	7.92	0.0032	8350	748	1151
37	19.8	1.31	8.91	0.0032	11150	843	1257
$C_0 = 0.1326$; $C_a = 1.459$; $D_0 = 6.11 \times 10^{-6}$; $\nu = 1.118 \times 10^{-2}$; $Sc = 1829$							
59	8.05	14.2	5.55	0.0557	4325	545	804
60	10.7	16.1	6.29	0.0557	5750	618	927
61	14.5	18.1	7.10	0.0557	7820	697	1082
62	19.1	20.3	7.95	0.0557	10270	782	1240
63	21.9	21.5	8.39	0.0557	11780	824	1324

TABLE 2. ELECTRODE 2; $d = 0.47$ cm; $h = 3.00$ cm; $t = 25°C$.

No.	V	i_L	$k \times 10^4$	ΔC_a	Re	Sh	$Re^{1/2} Sc^{1/3}$
$C_0 = 0.0746$; $C_a = 1.450$; $D_0 = 6.22 \times 10^{-6}$; $\nu = 1.093 \times 10^{-2}$; $Sc = 1755$							
67	6.87	9.37	6.57	0.0319	1884	314	523
68	10.7	11.6	8.09	0.0319	2935	388	654
69	15.1	13.8	9.61	0.0319	4145	463	777
70	18.3	15.4	10.7	0.0319	5037	516	856
71	22.9	17.9	12.4	0.0319	6280	600	956
78	7.12	8.25	5.73	0.0319	1954	277	523
79	15.1	12.8	8.93	0.0319	4145	430	777
80	22.6	19.1	13.2	0.0319	6200	639	950
$C_0 = 0.0279$; $C_a = 1.480$; $D_0 = 6.32 \times 10^{-6}$; $\nu = 1.072 \times 10^{-2}$; $Sc = 1725$							
84	7.12	3.45	6.41	0.0120	1993	304	546
85	12.2	4.52	8.39	0.0120	3427	398	703
86	15.1	5.07	9.42	0.0120	4230	447	781
87	18.4	5.67	10.5	0.0120	5140	502	861
88	22.6	6.66	12.4	0.0120	6325	588	955
$C_0 = 0.0110$; $C_a = 1.460$; $D_0 = 6.34 \times 10^{-6}$; $\nu = 1.067 \times 10^{-2}$; $Sc = 1712$							
93	7.12	1.42	6.67	0.0047	2000	315	535
84	10.2	1.69	7.98	0.0047	2880	377	642
95	15.1	2.03	9.57	0.0047	4245	452	780
96	18.4	2.37	11.1	0.0047	5160	527	858
97	22.6	2.51	11.8	0.0047	6350	558	953

INTERPRETATION

1. *Kinetic constant and temperature*

The limiting current was obtained from polarization curves and corrected, when necessary, for the residual current. When the ionic diffusion rate is the rate-determining step in the mechanism of the electrochemical reaction, i.e. when a large excess

TABLE 3. ELECTRODE 3; $d = 0.47$ cm; $h = 1.50$ cm; $t = 25°C$.

No.	V	i_L	$k \times 10^4$	ΔC_a	Re	Sh	$Re^{1/2} Sc^{1/3}$
$C_0 = 0.1370$; $C_a = 1.470$; $D_0 = 6.21 \times 10^{-6}$; $\nu = 1.097 \times 10^{-2}$; $Sc = 1718$							
119	7.12	24.7	9.36	0.0585	973	226	374
120	11.9	30.6	11.6	0.0585	1625	280	483
121	15.1	35.1	13.1	0.0585	2067	317	545
122	18.4	38.5	14.6	0.0585	2510	352	600
123	22.6	44.3	16.8	0.0585	3090	407	690
$C_0 = 0.0177$; $C_a = 1.470$; $D_0 = 6.33 \times 10^{-6}$; $\nu = 1.068 \times 10^{-2}$; $Sc = 1685$							
124	7.12	2.67	7.82	0.0076	1000	185	376
125	11.9	3.87	11.3	0.0076	1670	268	486
126	15.1	4.73	13.8	0.0076	2122	328	548
127	18.4	5.28	15.5	0.0076	2578	366	605
128	22.6	5.75	16.8	0.0076	3172	398	671
$C_0 = 0.0551$; $C_a = 1.460$; $D_0 = 6.25 \times 10^{-6}$; $\nu = 1.083 \times 10^{-2}$; $Sc = 1736$							
129	7.12	9.47	8.91	0.0235	986	214	378
130	11.9	12.0	11.3	0.0235	1648	271	488
131	15.1	14.3	13.5	0.0235	2093	323	551
132	18.4	16.5	15.6	0.0235	2542	373	607
133	22.6	19.2	18.0	0.0235	3130	432	672

TABLE 4. ELECTRODE 4; $d = 0.47$ cm; $h = 0.75$ cm; $t = 25°C$.

No.	V	i_L	$k \times 10^4$	ΔC_a	Re	Sh	$Re^{1/2} Sc^{1/3}$
$C_0 = 0.0436$; $C_a = 1.450$; $D_0 = 6.27 \times 10^{-6}$; $\nu = 1.080 \times 10^{-2}$; $Sc = 1725$							
134	7.12	8.90	10.6	0.0186	495	127	267
135	12.5	13.2	15.7	0.0186	870	187	353
136	15.1	14.9	17.8	0.0186	1051	213	389
137	18.4	16.4	19.5	0.0186	1280	234	430
138	22.6	18.1	21.6	0.0186	1570	258	475
$C_0 = 0.0860$; $C_a = 1.450$; $D_0 = 6.20 \times 10^{-6}$; $\nu = 1.095 \times 10^{-2}$; $Sc = 1767$							
139	7.12	19.9	12.0	0.0366	488	146	268
140	12.6	28.6	17.2	0.0366	865	208	356
$C_0 = 0.0222$; $C_a = 1.420$; $D_0 = 6.32 \times 10^{-6}$; $\nu = 1.070 \times 10^{-2}$; $Sc = 1695$							
144	7.12	4.02	9.42	0.0096	499	112	266
145	12.5	6.45	15.1	0.0096	876	179	352
146	15.1	7.78	18.2	0.0096	1060	216	388
147	18.4	8.20	19.2	0.0096	1290	228	428
148	22.6	9.56	22.4	0.0096	1585	266	475

TABLE 5. ELECTRODE 2; $d = 0.47$ cm; $h = 3.00$ cm; $t = 25°C$.

No.	V	i_L	$k \times 10^4$	ΔC_a	Re	Sh	$Re^{1/2} Sc^{1/3}$
$C_0 = 0.0183$; $C_a = 1.460$; $C_g = 2.84$; $D_0 = 3.21 \times 10^{-6}$; $\nu = 2.5467 \times 10^{-2}$; $Sc = 7940$							
149	33.3	2.28	6.46	0.0050	2260	604	950
150	52.6	2.82	7.98	0.0050	3490	746	1180
151	45.9	2.66	7.53	0.0050	2875	705	1070
152	60.0	3.25	9.20	0.0050	4370	860	1320
$C_0 = 0.0180$; $C_a = 1.480$; $C_g = 6.15$; $D_0 = 1.26 \times 10^{-6}$; $\nu = 7.2459 \times 10^{-2}$: $Sc = 57500$							
153	30.5	1.10	3.15	0.0026	917	751	1170
154	40.4	1.28	3.69	0.0026	1200	878	1340
155	52.9	1.59	4.58	0.0026	1870	1090	1670
156	64.6	1.95	5.62	0.0026	1474	1340	2000

of an inert electrolyte is present, the limiting current, I_L, is related to the concentration of the ionic species reacting on the electrode by

$$I_L = k \cdot A \cdot C_0 \cdot z \cdot F, \tag{2}$$

where k is the formal average kinetic constant for the whole area A of the electrode and C_0 is the bulk concentration of the reacting diffusing species; z and F have their usual significance. Equation (2) was employed to calculate the constant k.

The temperature dependence of k, as in other cases[10], can be also represented in the present case by an Arrhenius equation. From a plot of $\log k$ vs. $1/T$, where T is temperature in °K, a heat of activation of 3850 ± 200 cal/mol is obtained.

This figure was employed to calculate the limiting current density and the kinetic constant at 25°C when the constant temperature of the run differed from this temperature. Therefore, the following calculations have been referred to that temperature. Values of k corrected to 25°C are included in the tables.

2. The application of dimensional analysis

As shown elsewhere[11] and especially remarked by Ibl[12], dimensional analysis is a useful tool to relate the experimental variables of a diffusion-convection controlled electrochemical process.

The dimensional groups of interest for this case are

$$\text{Sherwood number: } Sh = \frac{k \cdot X}{D_0},$$

$$\text{Reynolds number: } Re = \frac{V \cdot X}{v},$$

$$\text{Schmidt number: } Sc = \frac{v}{D_0}.$$

where X is a characteristic length in cm.

The Sherwood number involves the mass-transfer kinetic constant and it can be taken as a ratio between the characteristic length and the thickness of the effective diffusion layer.

The Reynolds number relates driving forces acting on the liquid and viscous forces which tend to slow down the stream.

The Schmidt number relates the physico-chemical properties which determine momentum transfer by viscous effect due to velocity gradients and mass transfer by diffusion due to concentration gradients.

Sherwood and Reynolds numbers were defined in terms of electrode height, h, for reasons which will be referred to later.

For the present case a relationship of the form

$$Sh = K \cdot Re^x \cdot Sc^y \tag{3}$$

has to be established. The parameters K, x and y were calculated from the experimental data.

3. The kinetic constant and the rate of flow of the solutions

The formal average kinetic constant, calculated from equation (2), has been plotted as a function of the square root of the average flow velocity. Fig. 6 shows the
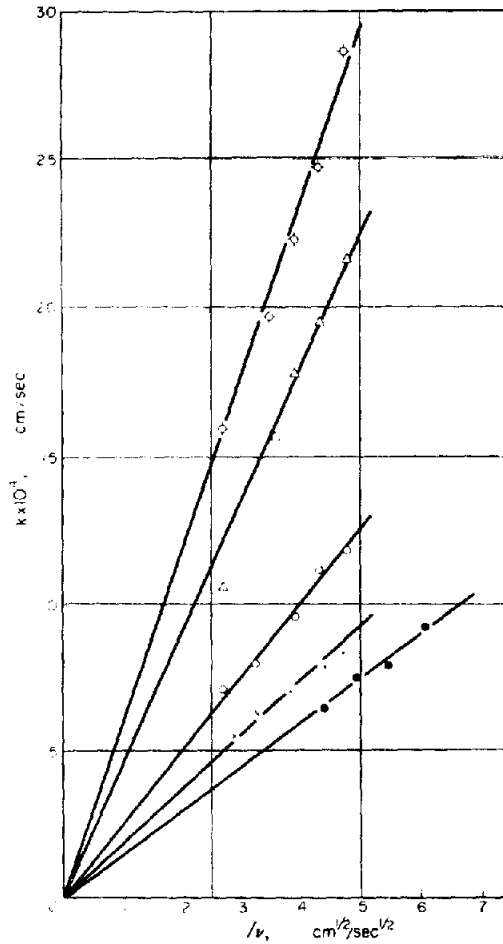
FIG. 6. Plot of k vs. $V^{1/2}$.

○: exp. 93 to 97; ●: exp. 149 to 152; ×: exp. 59 to 63

△: exp. 134 to 138; -○-: exp. 119 to 123.

linear relationship obtained; it suggests very reasonably that exponent x in equation (3) is 1/2.

4. The kinetic constant and the ratio involved in Schmidt number

It was important to find the relationship between the rate constant and Schmidt number, which was obtained with a tubular electrode of fixed dimensions, changing only the physical properties of the electrolytic solution. Copper sulphate—sulphuric acid solutions containing glycerol were employed to find the relationship. In these experiments the Schmidt ratio was varied between 1×10^3 and 50×10^3. A log–log plot of Sherwood vs. Schmidt numbers for constant Reynolds number is shown in Fig. 7. Straight lines of slope 1/3 have been drawn through the points and this number corresponds to the value of y in equation (3).
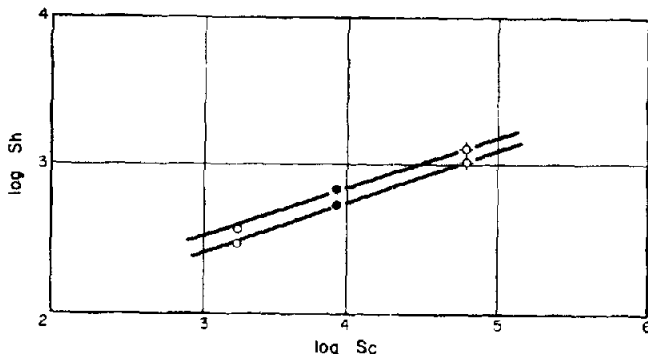
FIG. 7. Log–log plot of Sh vs. Sc numbers.

$\bigcirc$: $C_g = 0$; $\bullet$: $C_g = 2.84$ M; $-\oslash-$: $C_g = 6.15$ M.

5. *The correlation for the ionic mass-transfer process in the tubular cell*

Finally, to work out the general equation comprising all the variables involved in the process a further analysis is necessary, in which the average properties of the system have to be considered.

The final calculations of the dimensionless numbers would have to be done employing the average properties of the solutions, taking into account the fact that its concentration is not uniform when we are approaching the working electrode surface.

In the present case, when a steady electric current flows through the cell, the current is transported mainly by the inert electrolyte added to the solution. This inert electrolyte is carried to the electrode without discharging on it; hence its concentration increases on the electrode surface. Once a steady state is reached, the amount of inert electrolyte brought by migration is compensated by an equal amount which leaves the electrode by convection and diffusion. The steady state on the electrode surface may be expressed by

$$i_L . t_a = k_a . z . F . \Delta C_a. \tag{4}$$

This increment of concentration of the inert electrolyte, ΔC_a, on the electrode surface has to be considered in the evaluation of the average kinetamatic viscosity and diffusion coefficient. The equation which allows the calculation of ΔC_a by successive approximations is[14]

$$\Delta C_a = t_a \left(\frac{D_0}{D_a}\right)^{\frac{1}{2}} C_0, \tag{5}$$

where t_a is the transport number of the hydrogen ion and D_a its diffusion coefficient. For sulphuric acid solutions, D_a and t_a have been taken from the literature.[13] As is indicated in the tables the ΔC_a values in our experiments were small. Therefore, considering the experimental error involved in the determinations, the final values of Sherwood, Schmidt and Reynolds numbers were calculated without taking into account the average properties, but the bulk ones.

The general correlation worked out, from a least square calculation, for Sherwood, Schmidt and Reynolds numbers may be written:

$$Sh = 0.647 . Re^{1/2} . Sc^{1/3} \tag{6}$$

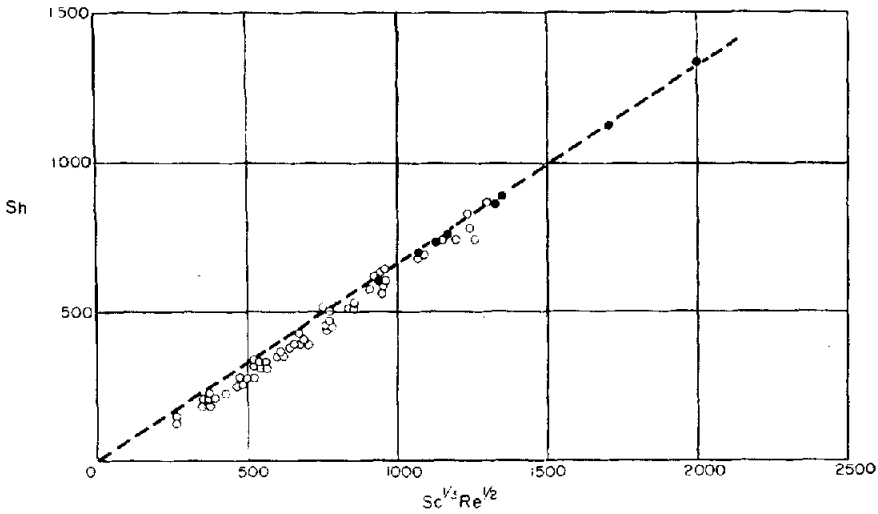A plot of Sh vs. $Re^{1/2} . Sc^{1/3}$ is shown in Fig. 8.

FIG. 8. Plot of Sh vs. $Sc^{1/3}$. $Re^{1/2}$. Dotted line was drawn with eq. (20).

The maximum experimental error involved in the equation (6) is 14 per cent, distributed as follows: Sherwood number, 9·5 per cent; Reynolds number, 3·5 per cent; Schmidt number, 1·7 per cent. The error in the limiting current is less than 4 per cent and that of the velocity of flow is estimated as 7 per cent.

6. The expressions for the limiting current density, the kinetic constant and the thickness of the Nernst diffusion layer

From equation (6) the following expressions are obtained:

$$i_L = 0·647 . h^{-1/2} . V^{1/2} . D_0^{2/3} . \nu^{-1/6}, \tag{7}$$

$$k = 0·647 . z . F . C_0 . h^{-1/2} . V^{1/2} . D_0^{2/3} . \nu^{-1/6}, \tag{8}$$

$$\delta_N = 1·56 . h^{1/2} . V^{-1/2} . D^{1/3} . \nu^{1/6}. \tag{9}$$

The dependence of δ_N with the electrode height is presented in Fig. 9.

DISCUSSION

The interesting feature of the present work is represented by equation (6), which expresses the rate of ionic mass transfer in the annular electrode of the tubular cell. An analogous equation has been derived recently by Wranglén[6,14] for a horizontal plate electrode along which the solution is flowing in a direction parallel to its surface, while the mass-transfer direction is normal to that surface. Wranglén has worked out the kinetic equation for ionic mass transfer by applying Eckert's[15,16] solution for the heat-transfer problem at a horizontal plate based on von Kármán's approximation.

This approach of the mass transfer problem can undoubtedly be extended to a vertical tubular electrode if the following assumptions are fulfilled: (a) the radius of curvature of the electrode is much larger than the effective diffusion layer thickness at the working electrode; (b) the mass transfer due to natural convection is negligible as compared to that by forced convection. Over the tubular electrode surface, two

processes occur simultaneously: mass transfer, in this case the rate-determining step of the electrochemical reaction, and momentum transfer which results as a consequence of viscous forces. If the above assumptions are made the general equation for mass transfer can be written as usual in orthogonal coordinates:

$$\frac{d}{dx}\int_0^L (C_0 - C_e).u.dy = D\left(\frac{dC}{dy}\right)_{y=0}, \tag{10}$$

where x is the flow direction and corresponds to heights measured on the electrode, y the mass-transfer direction, normal to x, C_0 the bulk concentration of the diffusing species, C_e its concentration on the electrode surface, u the local fluid velocity, and L the thickness of the layer within which diffusion takes place. The limits of the integral actually extend from zero to δ_d, the thickness of the diffusion boundary layer. It is assumed that no transport occurs in the z direction. The right hand side term of equation (10) expresses the rate of mass transfer per unit electrode area.

Similarly, the general equation for momentum transfer is

$$\frac{d}{dx}\int_0^{L'} u(u_s - u)\,dy = \nu\left(\frac{du}{dy}\right)_{y=0}, \tag{11}$$

where u_s is the flow velocity in the bulk of the solution and L' refers to the distance from the electrode surface in the y direction, where there is a velocity gradient. As before, the integration of equation (11) is from zero to δ_h, the thickness of the hydro-dynamical boundary layer.

The integration of equation (10) and (11) assuming cubic parabolic velocity and concentration profiles and that both the hydrodynamical and diffusion boundary layer originates at the same point of the surface, yields an equation which expressed in terms of dimensionless numbers and local properties of the solution, can be written

$$Sh_x = 0 \cdot 331\ Re_x^{1/2}.Sc^{1/3}. \tag{12}$$

When equation (12) is extended to the whole electrode area it becomes

$$Sh_h = 0 \cdot 662\ Re_h^{1/2}.Sc^{1/3}. \tag{13}$$

The general solution for the case in which the hydrodynamical boundary layer is not formed simultaneously with the diffusion boundary layer, is

$$Sh_x = 0 \cdot 331 . Re_x^{1/2}Sc^{1/3}\left[1 - \left(\frac{x_0}{x}\right)^{3/4}\right]^{-1/3} \tag{14}$$

Equation (14) has recently been considered by Wranglén and Nilsson[6] for the flat plate electrode. This equation reduces to equation (13) if $x_0 = 0$, where x_0 is the distance from the point of the surface where the hydrodynamical boundary layer originates to the point where the diffusion boundary layer begins to form.

Both equations (13) and (14) predict linear relationship between the mass-transfer kinetic constant and the square root of velocity of the solution ; k is inversely proportional to the square root of the electrode height, and directly proportional to the cube root of the ratio between kinematic viscosity and diffusion coefficient. Equation (13) is compared to the experimental data in Fig. 8.

That equation also allows the calculation of the effective thickness of the diffusion

boundary layer on the electrode. This has been done and compared to the experimental results in Fig. 9, where δ_N means the thickness of the Nernst diffusion layer assuming a linear concentration profile.

Our results indicate that the cylindrical surfaces of the electrode can be regarded as a plane to a first approximation.
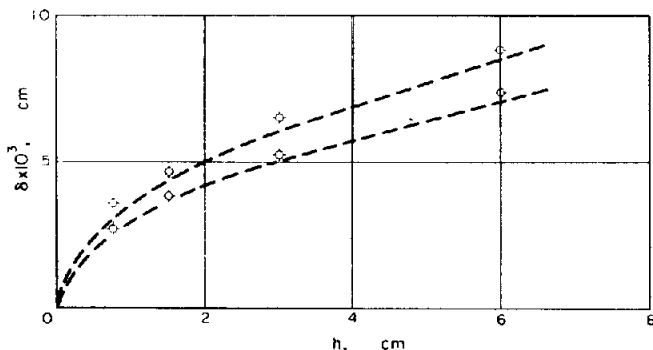

FIG. 9. The Nernst average diffusion layer plotted vs. electrode heights. Full line has been drawn with eq. (9).

$-\bigcirc-$: V = 21·6 cm/sec; $\bigcirc$: V = 15·1 cm/sec.

Nevertheless the actual situation in the cell we have studied is more complicated because the hydrodynamical boundary layers formed in the inner and outer walls of the tube become very thick, yielding even ahead of the leading edge of the working electrode, something like the well known Pouseuille parabolic velocity distribution observed in pipes after a certain distance from the entrance. Schlichting[17] has derived for parallel solid walls the following equation to calculate the distance d, at which the two hydrodynamic boundary layer merge:

$$d = 0.04 . a . Re, \tag{15}$$

where a is the distance between the walls and Re is the Reynolds number referred to the width of the channel.

Schlichting's equation was derived for two parallel solid walls in which the liquid inflow is parallel to the surface of the walls. The behaviour of our cylindrical surfaces can be regarded as that of plane surfaces and although in the present case the liquid enters the cell perpendicularly to the axis of the cylindrical tube, at least a rough approximation of d can be obtained with equation (15). In the present case a is about 0·6 cm; we thus obtain for $V = 20$ cm/sec, $v = 10^{-2}$ cm/sec, and $Re = 1200$, a value $d = 29$ cm. This value is about the same as the length of the inert interface used in our experiments, 22 cm. Therefore it is reasonable to assume that in this case the two hydrodynamical boundary layers have merged or have almost merged when the leading edge of the electrode is reached. This merging may explain why satisfactory agreement is obtained between experimental and calculated values without taking the inlet length into consideration (the first factor reduces δ, the second increases it).

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