DIMENSIONAL ANALYSIS FOR HYDRODYNAMIC ELECTROCHEMICAL SYSTEMS

J.L. Guiñón, R. Grima, J. García-Antón,
V. Pérez-Herranz
Universidad Politécnica de Valencia*
E-46071 Valencia, Spain

Electrochemical engineering as an independent subject has been well established since the early 1970s, and today it can be found in the curriculum of a number of chemical engineering departments. There are several books which can be used as introductory-level textbooks for a senior-level undergraduate course[1-4] and other books that can be used at the graduate level by those who want to delve deeper into the subject.[5-10]

According to Ibl,[11] the mass transport for hydrodynamic electrochemical systems is characterized by a correlation between dimensionless groups of the form

$$Sh = f(Re, Sc) \qquad (1)$$

where Sh, Re, and Sc are the Sherwood, Reynolds, and Schmidt dimensionless numbers, respectively (see Table 1). A complete table of type (1) equations, generally empirical, for mass transport rate in selected electrode geometries commonly occuring in an electrochemical reactor can be found in a monograph by Fahidy.[7]

The rigorous derivation of these correlations often requires complicated differential equations that are based on fundamental transport and conservation equations where analytical resolution is only possible in a few examples of electrodes with simple geometry in which the boundary conditions are well determined. This occurs, for instance, with a rotating disk (RDE). This device is frequently used to determine kinetic parameters, diffusivity of ionic species, and as a diagnostic to determine if the electrode reaction is controlled by mass transport.

The expression for the mass-transport rate at

* *Departamento de Ingeniería Química y Nuclear,
E.T.S.I. Industriales, P.O. Box 22012*

a RDE is given by the Levich equation[12]

$$Sh = 0.62 \, Re^{1/2} \, Sc^{1/3} \qquad (2)$$

Then, substituting the values of the dimensionless numbers (Table 1), we obtain the following equation for the limiting current density:

$$i_l = 0.62 \, n \, F \, D_A^{2/3} \, \nu^{-1/6} \, \omega^{1/2} \, C_A \qquad (3)$$

The Levich equation serves many purposes since it is valid under laminar flow up to a Reynolds number of $2 \cdot 10^5$. The global theoretical treatment of the Levich equation can be found in the original sources as well as (partially) in some monographs,[8,10,13] but its derivation in the classroom is cumbersome and therefore it is usually avoided. Most books give only the final equation. In teaching electrochemical mass transport we have noticed that the students are not always able to remember the Levich equation because it includes variables raised to uncommon exponents.

In this paper we will relate a simple derivation of the Levich equation based on the application of dimensional analysis and will propose a laboratory exercise to solve the above problem.

BACKGROUND

The applicability of dimensional analysis requires prior knowledge of the various parameters affecting the problem. This knowledge is gained from analysis of the system or from experiments. Thus, in an electrochemical system with electrodes in motion, the Navier-Stokes hydrodynamic equa-

TABLE 1
**Dimensionless Groups in
Electrochemical Hydrodynamic Transport**

Group	Name	Mechanism Ratio
$Sh = K_c \dfrac{L}{D} = i_l \dfrac{L}{nFC_A D}$	Sherwood number	effective mass transport/mass transport by molecular diffusion
$Sc = \dfrac{\nu}{D}$	Schmidt number	momentum transport/mass transport by molecular diffusion
$Re = u \dfrac{L}{\nu} = \omega \dfrac{L^2}{\nu}$	Reynolds number	inertia forces/viscous forces

tion (Eq. 4), the convection-diffusion equation (Eq. 5), and the relationship between flux and current density (Eq. 6) should be fulfilled.

$$\frac{Du}{Dt} = -\frac{1}{\rho}\nabla P + \nu\nabla^2 u + g \tag{4}$$

$$-\nabla J_A = \frac{\partial C_A}{\partial t} = D_A\nabla^2 C_A - u \cdot \nabla C_A \tag{5}$$

$$i_1 = -nFD_A\left(\frac{\partial C_A}{\partial y}\right)_{y=0} \tag{6}$$

Equation (6) applies when migration is negligible due to the fact that the solution contains an excess of supporting electrolytes.[3,4,10] Assuming that pressure forces and gravity force fields are absent, $\nabla P = 0$ and $g = 0$, and under conditions of steady-state, $du/dt = 0$ and $dC_A/dt = 0$. With these assumptions, and using the variables of Eqs. (4-6), we assume that at the RDE the current density is a function of Faraday's constant F, the diffusion coefficient D_A, the concentration of species C_A, the kinematic viscosity ν, the angular velocity $\omega = u/R$, and the disk radius, R. Hence, the following functional relationship may be written:

TABLE 2
**Kinematic Viscosity of Several Aqueous Electrolytes***

	H_2O	0.1 M HCl	0.1 M KCl	0.1 M KNO_3	0.1 M HNO_3
$\nu\ 10^2$, cm^2/s	1.004	1.008	0.995	0.992	1.002
$\nu^{-1/6}$, $s^{1/6}/cm^{1/3}$	2.153	2.151	2.156	2.157	2.154

Handbook of Chemistry and Physics, CRC Press, Inc., Florida

José L. Guiñón is professor of chemical engineering at Polytechnical University of Valencia. His major research focus has been in the areas of chemical equilibrium, surface analysis, and electrochemical engineering

José García-Antón is an associate professor of chemical engineering at Politechnical University of Valencia. His research interests are primarily in the areas of surface analysis, corrosion, and electrochemical engineering.
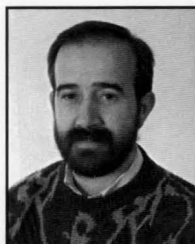
Valentin Pérez-Herranz received his chemical engineering degree in 1989. He is currently doing research and working for his PhD in the area of pulsating electrochemical reactors.

Rosario Grima is a chemical technician. She collaborates in the teaching and research of the chemical engineering department at Polytechnical University of Valencia. (Photo not available.)

$$i_1 = \Phi\left(F, D_A, \nu, \omega, C_A, R\right) \tag{7}$$

According to dimensional analysis, Eq. (7) can be expressed as a power series:

$$i_1 = K_1 F^a D_A^b \nu^c \omega^d C_A^e R^f \tag{8}$$

where a, b, c, d, e, and f are constant exponents, and K_1 is a dimensionless constant of proportionality. Since Eq. (8) has to be dimensionally consistent, the left- and right-hand terms must have the same dimensions. By substituting the appropriate dimensions for each variable in Eq. (8), we obtain

$$L^{-2}QT^{-1} = K_1\left(QM^{-1}\right)^a\left(L^2T^{-1}\right)^b\left(L^2T^{-1}\right)^c\left(T^{-1}\right)^d\left(ML^{-3}\right)^e(L)^f \tag{9}$$

To be dimensionally consistent, the sum of the exponents on each fundamental unit must be the same on both sides of the equation:

$$\sum \text{ of the exponents for } L: -2 = 2b + 2c - 3e + f$$
$$\sum \text{ of the exponents for } M: 0 = -a + e$$
$$\sum \text{ of the exponents for } Q: 1 = a$$
$$\sum \text{ of the exponents for } T: -1 = -b - c - d \tag{10}$$

The linear equation, Eq. 10, can be solved by taking into account that $a = e = 1$. Then, we obtain

$$1 = 2b + 2c + f$$
$$-1 = -b - c - d \tag{11}$$

Many mathematical solutions are possible with Eq. 11, depending upon the values of b, c, d, and f. Since there are two equations in four unknowns, they can be solved for two of the unknowns in terms of the other two. Since the kinematic viscosity of the aqueous electrolytes is almost constant (see Table 2), it is more meaningful to take the diffusion coefficient and the disk radius as independent variables. Solving for c and d in terms of b and f gives

$$c = (1 - 2b - f)/2$$
$$d = (1 + f)/2 \tag{12}$$

By substituting the values of exponents in Eq. (8), we obtain

$$i_1 = K_1 F D_A^b \nu^{(1-2b-f)/2} \omega^{(1+f)/2} C_A R^f \tag{13}$$

Since there are seven variables and four primary dimensions in Eq. (8), there should be (7-4=) three dimensionless groups. Mass transport is usually characterized by the Sherwood, Reynolds, and Schmidt dimensionless numbers given in Table 1. Thus, the terms of Eq. 13 may be collected in groups:

$$\frac{i_1 R}{FC_A D_A} = K_1\left(\frac{\omega R^2}{\nu}\right)^{(1+f)/2}\left(\frac{\nu}{D_A}\right)^{1-b} \tag{14}$$

The value of f may be obtained experimentally by keeping

A, v, ω, and C_A constant and measuring the variation of current, I, with the disk radius for a given ion. Analogously, the value of b may be obtained experimentally by keeping A, v, and C_A constant and measuring the variation of current, I, with diffusion coefficient D_A, using various ions.

Once we have obtained the values of f and b, we can obtain the value of c (the exponent of the kinematic viscosity) and d (the exponent of the angular velocity) from Eq. (12).

The value of the constant, K_1 can be obtained from the intercept at the origin, p, of the plot of log I versus log D_A

$$K_1 = \frac{10^p}{FAv^{-1/6}\omega^{(1+f)/2}C_A R^f} \qquad (15)$$

EXPERIMENTAL

Equipment and Procedure

The I-E curves were recorded with a Metrohm E-626 polarecord. The working electrode was a rotating disk electrode with platinum surface of 2.72 mm in diameter or a glassy carbon surface 3.08 mm in diameter, connected to a Metrohm 628 rotation unit. The reference electrode was an Ag-AgCl electrode with 3M potassium chloride solution, and the auxiliary electrode was a platinum wire. Dissolved oxygen was removed from the solutions by bubbling nitrogen for ten minutes. Prior to each polarization experiment, the RDE was repolished with 0.05 μm alumina. All experiments were carried out at 25°C with the help of a Selecta Frigitern S-32 thermostat.

The measurements of the electrode diameter (±0.01 mm) were obtained with a Shimadzu M microhardness tester, and the electrode rotation velocity was tested with a Movistrob revolutions counter.

Chemicals

All chemicals were reagent grade. The following solutions were prepared: 1mM in KI; $K_3Fe(CN)_6$, $K_4Fe(CN)_6\cdot 3H_2O$, and 0.1M in KCl; and 1mM Fe^{+3} (from iron titrisol^R, standard solution, Merck) and 0.1 M in HNO_3.

RESULTS AND DISCUSSION

Figure 1 shows a typical polarization curve of a given species at a certain rotation speed. To measure the limiting current, one should select a working potential in a region over which the plateau of the wave, a, is fairly parallel to the residual current, b, cor-
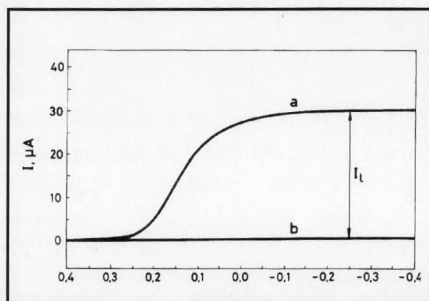

Figure 1. Polarization curves at a platinum RDE at 10^3rpm
 a. $10^{-3}M\ Fe(CN)_6^{-3} + 10^{-1}M\ KCl$
 b. $10^{-1}M\ KCl$

responding to the supporting electrolyte. In Figure 1, this may be anywhere between -0.1 V and the end of the wave at -0.4 V.

Table 3 shows the results obtained with several ions at the platinum and the glassy-carbon RDE. The differences in current are obviously due to the different electrode surfaces. Current density values are almost equal for a given ion in both electrodes, although these values are slightly higher for platinum than for glassy carbon. These results show that for a given species in laminar flow, the flux (*i.e.,* the average current density, Eq. 6) is independent of disk diameter, so the exponent of the disk radius is f=0.

The difference in limiting current observed for the various ions (Table 3) is due to the different values of the diffusion coefficient (see Eq. 6). The diffusion coefficient may be described by the Stockes-Einstein equation

$$D_A = \frac{kT}{6\pi r\mu} \qquad (16)$$

where

   k Boltzmann constant
   T absolute temperature
   μ viscosity of the solution
   r radius of the diffusing ion.

Hence, in an experiment with the same supporting electrolyte, the limiting current is inversely proportional to the hydrated radius of the electroactive species, the current density decreasing from iodide ion to ferric ion.

As indicated above, it is necessary to have the values of the logarithm of the diffusion coefficient in order to determine the exponent in the Levich equation. The diffusion

TABLE 3
Limiting Current of Various Ions at a Rotating Disk Electrode
- Rotation speed of the electrode, 10^3 rpm
- Pt-electrode surface, 5.80×10^{-2} cm^2
- C-electrode surface, 7.44×10^{-2} cm^2

ion	electrolyte	I Pt, μA	I C, μA	i Pt, μA/cm^2	iC, μA/cm^2
I^-	0.1 M KCl	53	67	914	900
$Fe(CN)_6^{-3}$	0.1 M KCl	30	35	517	470
$Fe(CN)_6^{-4}$	0.1 M KCl	26	32	448	430
Fe^{+3}	0.1 M HNO$_3$	23.5	29.5	405	396

TABLE 4
Diffusion Coefficient, cm^2/s, at 25°C

Ion	$\lambda°/Z^{[15]}$	$D_\lambda 10^6$	Electrolyte	$D_{exp}10^{6[16]}$	μ(c.P)	$(\mu\cdot D_{exp})10^6$
I^-	76.8	20.50	0.1M KCl	17.20	0.9979	17.16
$Fe(CN)_6^{-3}$	33.6	8.97	0.1M KCl	7.63	0.9979	7.61
$Fe(CN)_6^{-4}$	27.6	7.37	0.1M KCl	6.32	0.9979	6.30
Fe^{+3}	22.6	6.03	0.1M HNO$_3$	5.20	0.9964	5.18

coefficient can be calculated from the equivalent conductance at infinite dilution, λ^0, by means of the Nernst equation[14]

$$D_\lambda = \frac{RT}{ZF^2}\lambda^0 = 2.67 \times 10^{-7}\frac{\lambda^0}{Z}, \quad \frac{cm^2}{s} \text{ at } 25°C \quad (17)$$

or it can be obtained from experimental data in the literature, D_{exp}. Table 4 shows the values of the diffusion coefficient obtained either way.

The difference in the values of D_λ and D_{exp} is due to the fact that the former corresponds to infinite dilution, whereas the latter corresponds to a given concentration of supporting electrolyte. In fact, the best way to compare various experimental data for D_i in solutions with different supporting electrolytes is by means of the mobility product $\mu D_i/T$.[16] But under our experimental conditions, at constant temperature and taking into account that the viscosities of the supporting electrolytes are very similar, the values of D_i and μD_i are almost identical, as can be seen in Table 4.

Figures 2 and 3 show that the plots of log I versus log D_A actually have a linear variation. These figures show the

absolute current instead of the current densities for a better comparison at a specific value of the diffusion coefficient. Table 5 shows the results of the corresponding regression lines by least-squares. The slope obtained is closer to the theoretical value, 2/3, when using D_λ values than when using D_{exp} values, probably due to the fact that the latter come from different authors. On the other hand, the slope values are more accurate for platinum RDE than for glassy-carbon RDE.

Substituting the values f=0 and b=2/3 into Eq. (12), we obtain values of c=-1/6 and d=1/2 for the exponents of the kinematic viscosity and the angular velocity, respectively.

In Figure 4, experimental data of I versus $f^{1/2}$ is plotted for I^- and $Fe(CN)_6^{-3}$ respectively at platinum RDE. Least-square treatment of the data yields a straight line with the following equations:

For $10^{-3}M$ KI

$$I_1(\mu A) = 1.836\,f^{1/2}(rpm)^{1/2} - 4.36 \quad r = 0.9986 \quad (18)$$

For $10^{-3}M$ $K_3Fe(CN)_6$

$$I_1(\mu A) = 0.786\,f^{1/2}(rpm)^{1/2} + 3.59 \quad r = 0.9942 \quad (19)$$

Similar results are obtained at the glassy-carbon RDE. In the plot of I versus $\omega^{1/2}$ (or $f^{1/2}$), the deviation from a straight line intersecting the origin shows some kinetic step involved in the electron transfer reaction rather than being totally controlled by mass transport.[13]

The value of constant K_1 in the Levich equation can be obtained from the intercept at the origin in the plot of log I versus log D_A. By taking these values from Table 5 and substituting values of

TABLE 5
Results of Regression Line by Least-Squares in Plot of log I vs. log D at Rotating Disk Electrode
Theoretical slope: b = 2/3 = 0.666

RDE	line	Slope b	Difference (%)	Intercept	Coefficient p
Pt	logI-v-logD$_\lambda$	0.675	1.3	0.8362	0.9991
Pt	logI-v-logD$_{exp}$	0.685	2.8	0.8756	0.9988
Glassy-C	logI-v-logD$_\lambda$	0.692	3.9	0.9090	0.9922
Glassy-C	logI-v-logD$_{exp}$	0.702	5.3	0.9494	0.9922
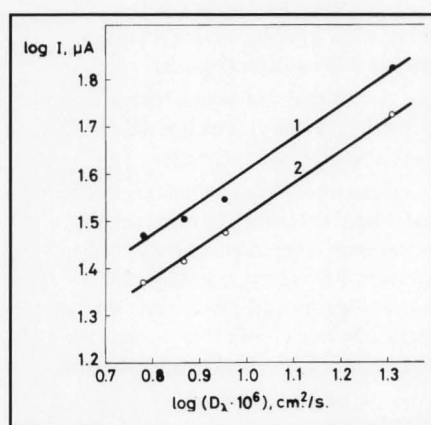
Figure 2. Plot of log I vs log D_λ of $10^{-3}M$ Fe^{+3}, $Fe(CN)_6^{-4}$, $Fe(CN)_6^{-3}$, and I^-. Diffusion coefficient values calculated from the equivalent conductance at infinite dilution.
(1) Glassy-carbon RDE **(2)** Platinum RDE. Rotation speed of electrode, f=10^3 rpm.
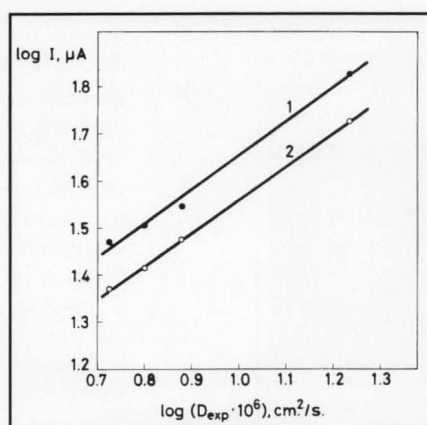

Figure 3. Plot of log I vs log D_{exp} of $10^{-3}M$ Fe^{+3}, $Fe(CN)_6^{-4}$, $Fe(CN)_6^{-3}$, and I^-. Experimental diffusion coefficient values.
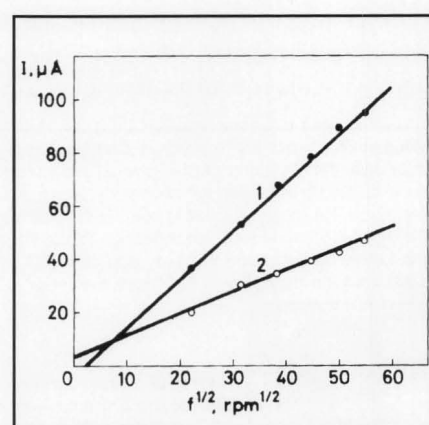**(1)** Glassy-carbon RDE. **(2)** Platinum RDE. Rotation speed of electrode, f = 10^3 rpm.

Figure 4. Plot of current as a function of the rotation speed at platinum RDE. **(1)** $10^{-3}M$ I^- **(2)** $10^{-3}M$ $Fe(CN)_6^{-3}$

Hydrodynamic Electrochemical Systems

$$F = 96487; \quad A_{Pt} = 5.80 \times 10^{-2} cm^2 s^{-1};$$
$$A_C = 7.44 \times 10^{-2} cm^2; \quad v = 10^{-2} cm^2/s;$$
$$v^{-1/6} = 2.15 \, s^{1/6}/cm^{1/3}; \quad f = 10^3 \, rpm;$$
$$\omega = 104 \, s^{-1}; \quad \omega^{1/2} = 10 \cdot 2 \, s^{1/2}$$

we obtain the values of the constant K_1. Table 6 shows that the K_1 values are closer to the theoretical value (0.62) when the plot of log I versus log D_{exp} is used than when log I versus log D_λ is used. The plot is also more accurate for platinum than for glassy-carbon electrodes. In other papers reporting glassy-carbon RDE data, a value of about 0.57 for K_1 was observed.[17]

The differences are even less if we take into account that the value of the Levich constant depends on the number of terms taken in the velocity expression. Thus, when two terms are included, the result is[18]

Levich constant:

$$K_1 = \frac{1}{1.6125 + 0.5704 \left(\dfrac{D_A}{v} \right)^{0.36}} \qquad (21)$$

By substituting typical values

$$v_{KCl} = 9.95 \times 10^{-2} \, cm^2/s \quad \text{and} \quad D = 6.10^{-6} \, cm^2/s$$

a value of $K_1 = 0.60$ is obtained, versus a value of 0.62 when the second term in Eq. (21) is neglected. The slight difference of K_1 from the theoretical values is due to the use of different electrode materials (platinum, glassy-carbon, etc.) depending on whether the surface state catalyzes the electrode reaction rate to a greater or a lesser extent.[14]

CONCLUSIONS

This electrochemical engineering experiment involves basic principles of mass transfer at an RDE. Although the experimental technique was developed as a research experiment, it is possible to offer it to students in an undergraduate laboratory. The interpretation of the experiment requires the use of dimensional analysis, which is a well-established tool available to engineering students. The students must handle values of theoretical and experimental diffusivity coefficients and compare the results obtained with two types of electrodes—platinum and glassy-carbon. Students have shown great interest in this teaching project.

TABLE 6
Experimental Values of Constant K_1 in the Levich Equation
Theoretical Value: $K_1 = 0.62, 0.60$

line	Pt-RDE	Glassy C-RDE
logI-v-logD_λ	0.56	0.52
logI-v-logD_{exp}	0.61	0.57

NOMENCLATURE

A	electrode surface, cm^2
C_A	solution concentration, mM
ρ_s	solution density, g/cm^3
D_A	diffusion coefficient, cm^2/s
f	frequency, rpm
F	Faraday constant, 96487 C/equiv.
g	gravity, 9.8 m/s^2
i_1	limiting current density, $\mu A/cm^2$
I_1	limiting current, μA
J	mass flux, $mol/cm^2 s$
K_1	Levich constant
L	characteristic length, cm
n	number of electrons transferred in reaction
P	pressure, $dyne/cm^2$
R	disk radius, cm
t	time, s
u	velocity, cm/s
ω	angular velocity, radians/s
λ^0	equivalent conductance at infinite dilution, $cm^2 s$/equiv.
v	kinematic viscosity of solution, cm^2/s

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