Determination of a Mass-Transfer Coefficient Using the Limiting-Current Technique

Keith Scott[‡] and Justo Lobato[*],[†]

Department of Chemical and Process Engineering, University of Newcastle upon Tyne, Merz Court, NE1 7RU, UK, and Faculty of Chemistry, Department of Chemical Engineering, University of Castilla- La Mancha. Campus Universitario s/n 13004 Ciudad Real, Spain, jlobato@correo.inqu-cr.uclm.es

Abstract: In this work, mass-transfer coefficients of a cross-corrugated plate have been determined by the limiting-current technique. A simple Microsoft Excel spreadsheet has been created, which allows students to correlate data. Students will be able to calculate the mass-transfer coefficient of different processes, for example, cross-flow membrane filtration processes or membrane reactors. The possibility of using the spreadsheet with different correlations and to discriminate between them is also validated by comparing the model results with published experimental data available in the recent literature. It is possible as well to study the influence of different turbulence promoters on the flow.

Introduction

The process industries produce a wide variety of chemicals and components, which presents the manufacturer with a need for separation, concentration, and purification of a range of materials. The last 30 years have seen the introduction of a range of separations based on one simple concept: a membrane to supplement or replace techniques of distillation, adsorption, extraction, crystallization, etc. Membrane separation technology is in a state of rapid growth and innovation. Over the last 40 years and particularly in the last two decades, numerous different separation processes have emerged in which synthetic membranes play a prominent role. The performance of a membrane is defined in terms of two simple factors, flux (mass transfer) and selectivity [1]. Examples of the application of membrane processes are reported in the literature [1, 2].

Electrochemical techniques, in particular mass-transfer measurements by the limiting-current method, provide convenient and accurate means for the determination of local and average transport rates. Applying analogies between momentum, heat, and mass transport, electrochemical measurements provide insight into the fundamental aspects of transport and are convenient for obtaining transport-rate correlation. These are useful for design purposes in nonelectrochemical systems such as cross-flow membrane processes and membrane reactors.

Many different approaches can be used to improve the flux in cross-flow filtration processes [3]. The most common method is the introduction of turbulence promoters in the flow channel. This approach increases the flux by improving the mass transfer away from the membrane. Turbulence promoters of various configurations have been studied, including volume displacement rods in tubular membranes; static mixers in tubular membranes; turbulence promoters attached to, or at some distance from, the membrane in tubular or flat membranes; fluidized beds in tubular membranes; and mesh screens in flat and spiral-wound membranes. Flux enhancement, however, is usually only achieved at the expense of significant increased frictional pressure drop. Most recently, attention has been drawn toward using corrugated membranes as turbulence promoters [4]. This is analogous to the use of corrugated plates in plate heat exchangers, which proved to increase the mechanical strength of the plate as well as the heat transfer rate [5].

Theory

The limiting-current technique is based on driving an electrochemical reaction to its maximum possible rate where it is limited by mass transport. The limit is indicated by a current plateau (the limiting current) on a current-versus-potential plot.

The ionic flux of species i, N_i, can be described with diffusion as the principal mechanism for transport of ions near the electrode:

$$N_i = -D_i \frac{dC_i}{dy}\bigg|_{y=0} \qquad (1a)$$

where D_i is the diffusion coefficient, C_i the concentration, and y is the coordinate perpendicular to the electrode surface. Because electrode reactions involving only one species are considered, the subscript i will henceforth be omitted, thus,

$$N = -D \frac{dC}{dy}\bigg|_{y=0} \qquad (1b)$$

The current density for an electrochemical reaction,

$$O + z e^- \rightarrow R \qquad (2)$$

---

[*] Address correspondence to this author.
[†] University of Castilla- La Mancha
[‡] University of Newcastle upon Tyne

is given by the following equation:

$$i = zFN \qquad (3)$$

where z is the number of electron associated with reaction and ι is the Faraday constant.

Concentration profiles in systems involving convection are not linear, and the concentration tapers off gradually to its bulk value, C_b. It is convenient to define an equivalent, Nernst-type, stagnant diffusion layer of thickness δ with a linear concentration profile such that the concentration gradient in eq 1b can be replaced by a linear difference, that is,

$$i \; = \; - zFD \; \frac{dC}{dy} \; = \; -zFD \; \frac{C_b - C_0}{\delta} \qquad (4)$$

C_0 represents the reactant concentration at the electrode. As the potential is further decreased, ions are consumed faster by the electrode reaction, resulting in a lower concentration at the electrode. Because δ, the boundary-layer thickness, is determined by the flow, and the bulk concentration is fixed, the decrease in C_0 brings about a higher current. Because the concentration at the electrode cannot be less than zero, there is a limit, which the current cannot exceed. This mass transport limiting current is determined by setting $C_0 = 0$ in eq 4 to obtain eq 5.

$$i_L \; = -zFD \; \frac{C_b}{\delta} \qquad (5)$$

The limiting current is an important design parameter because it represents the maximum rate at which an electrode reaction can proceed. Moreover, it provides a convenient technique for transport-rate studies, because mass transport coefficients can be readily and accurately calculated from the experimentally obtained current plateau. The mass transport coefficient, k, is defined by

$$N_i = k\Delta C = k(C_b - C_0) \qquad (6)$$

Representing the flux in terms of the current,

$$k \; = \; \frac{i_L}{nF(C_b - C_0)} \qquad (7)$$

The only parameter on the right that cannot be readily measured is C_0; however, at the limiting current, C_0 is zero [5], providing

$$k \; = \; \frac{i_L}{nFC_b} \qquad (8)$$

For mass transport by molecular diffusion, the pertinent variables are a characteristic length, diameter, d_h; the diffusivity, D; the velocity of the fluid, V_b; the mass density of the fluid, ρ, the viscosity of the fluid, μ; and the mass-transfer coefficient, k. If we carry out a dimensional analysis we find the significant dimensionless groups to be [6]

$$Sh = \frac{kd_h}{D} = \frac{i_L d_h}{niDC_b} \qquad (9)$$

$$Re = \frac{d_h V_b \; \rho}{\mu} \qquad (10)$$

$$Sc = \frac{v}{D} \qquad (11)$$

The Sherwood number (Sh) can be expressed in electrochemical systems in terms of the limiting current, eq 9. The Reynolds number (Re) is given by eq 10 and is a criterion of the kind of flow. A value of Re less than 2100 is indicative of laminar flow, above this value the flow is likely to become turbulent; so, an increase in either the velocity or the diameter can swing the flow from laminar to turbulent conditions. As the flow increases, the mass transport and heat transfer becomes faster and more turbulent. The equivalent diameter of the channels of the membrane, d_h, depends on the dimensions of the corrugation of the channels. The Schmidt number (Sc) is used in mass transfer in general and diffusion in flowing-system calculations. It is normally defined by eq 11 where v is the kinematic viscosity:

$$v = \mu/\rho \qquad (12)$$

The Chemical System. Deposition or redox-type electrode reactions are typically employed in the limiting-current technique. In redox reactions the product and reactant are in solution and the electrode surface remains unchanged. Problems associated with electrode contamination and subsequent poisoning are often present, and, therefore, the electrode must be carefully prepared and the electrolyte purified. Redox reactions involving gaseous products are not desirable because of difficulties in removing the gas bubbles from the electrode surface in a reproducible manner.

Cathodic reduction reactions that are most popular include copper deposition from acidified copper sulfate solution and the reduction of ferricyanide ion to ferrocyanide on platinum or nickel electrodes.

Electrode Design. Any electrochemical process consists of two half-cell reactions: reduction at the cathode and oxidation at the anode. For the limiting current measurements to be valid, the process must be rate-limited by the half-cell reaction at the electrode that is being monitored (working electrode), typically the cathode. The anode (counter electrode) must, therefore, be designed such that it provides the least interference with the process. This implies maintaining low anode polarization by providing low current density and sufficient convective flow at the anode. To ensure low anodic current densities, its area must be relatively high or preferably larger than that of the cathode. Proper cathode design is most crucial for obtaining well-defined and meaningful limiting current measurements. Because of the nonuniform transport rates typically observed over extended surfaces, long electrodes yield only average values. It is, therefore, advantageous to measure local transport rates and their distribution by means of segmented insulated electrodes or microelectrodes. In order that the segmented cathode approximates a continuous electrode, the segments must be coplanar and equipotential. To improve resolution, segments of different lengths can be employed as needed.
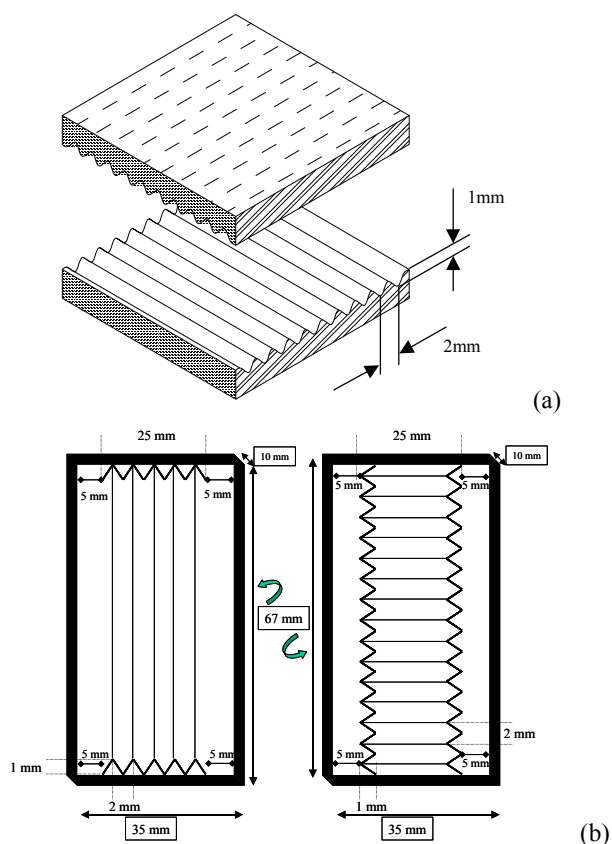
Figure 1. (a) Corrugated membrane plates (not to scale); (b) Dimensions of the membrane plates (not to scale).
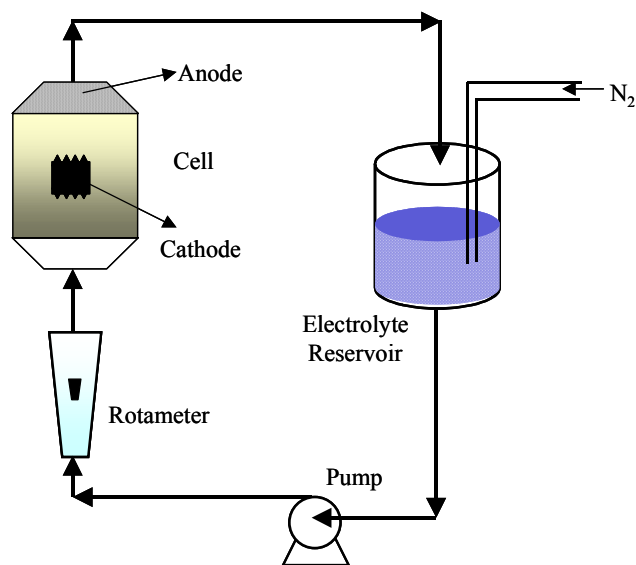

Figure 2. Flow-cell arrangement.

Typically, in regions where the current density varies rapidly, narrower segments are required.

Experimental

Before the experimentis begun, the instructor must explain the theoretical concepts of electrochemical reactions, mass-transfer coefficients, and the limiting current [7, 8].

Example: Determination of the mass-transfer coefficient of a cross-corrugated membrane. The cell was made of Perspex to support the corrugated membrane. The membranes were constructed of Perspex plates as shown in Figure 1, giving visibility throughout the unit. The corrugations of the membranes were 1 mm in height and 2 mm from peak to peak.

Figure 2 shows the layout of the apparatus, which consists of a 1-dm^3 reservoir of electrolyte feeding the cell via a centrifugal pump and returning to the reservoir. In order to remove the oxygen bubbles, nitrogen was purged through the electrolyte. An EG&G Princeton Applied Research VersaStat was used to conduct the electrolysis process using linear-sweep voltammetry. The data was logged using the EG&G Model 270 Research Electrochemistry Software (the potentiostat and the software were supplied by EG&G Princeton Applied Research Company, www.princetonappliedresearch.com).

The cathodic reduction of ferricyanide was used for this technique:

$$Fe(CN)_6^{-3} \ + \ e^- \ \rightarrow \ Fe(CN)_6^{-4} \qquad (13)$$
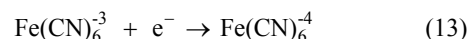
The electrolyte consisted of the following components: 0.3 M Na_2CO_3 (supporting electrolyte), 0.01 M $K_3Fe(CN)_6$ (ferricyanide to be cathodically reduced), 0.1 M $K_4Fe(CN)_6$ (ferrocyanide in excess). As the reaction is reversible, an excess of anodic reactant is required to ensure the limiting current is at the cathode. The ferri–ferrocyanide electrolyte decomposes through a reaction catalyzed by light, forming free cyanide ions; therefore, the electrolyte should therefore be kept in the dark and frequently analyzed.

The nickel cathode was hand-pressed into one of the plates to take the shape of the corrugations over a period of 5–10 min, and both it and the anode, also nickel, were polished with emery cloth [11]. The back of the cathode was previously coated with insulating paint, and an electrical connection was established at the side edge to avoid interference to the flow pattern. Nitrogen was bubbled through the electrolyte to expel dissolved oxygen.

At a constant flowrate, a slow linear potential sweep was applied to the cell, and the corresponding currents measured. As the reaction proceeded, the current increased to a maximum, the limiting current, where it remained constant as the cathodic potential increased. The limiting current plateau extended over a large range of potential, *V*, as shown in Figure 3. A further increase in potential caused the current to increase once more. At this point, as well as the ferricyanide reaction, hydrogen gas was evolved. Once the cell voltage range at which the limiting current occurred was identified, the process was repeated over a range of flowrates.

Large variations in the *Sc* number, eq 11, often required for transport studies, are best obtained by modifying the viscosity of the electrolyte, for example, by the addition of glycerin oil to the aqueous electrolyte. With no glycerin, *Sc* equals 1,483; 25% glycerin yields an *Sc* value of 4,997, and 35% glycerin gives an *Sc* value of 9,662.

Results and Discussion

Local mass-transfer rates were calculated directly from Faraday's law and correlated with the dimensionless numbers in eqs 9–11. The correlation depends largely on which flow regime exists in the cell, and it can be simple laminar flow, laminar flow with complications, free and mixed convection, turbulent forced convection, oscillating flows, stirred cells, convection by gas evolution, and particulate [10]. The system reported shows the use of corrugations to promote turbulence in regions of low flow, and is unusual in that the channels are made up of two identical surfaces, one rotated by 90° from the other. The flow between the corrugations was at one of two angles to the nickel-corrugated electrode (Figure 4): (1) at 0° to the corrugation at the electrode, that is, along the through of
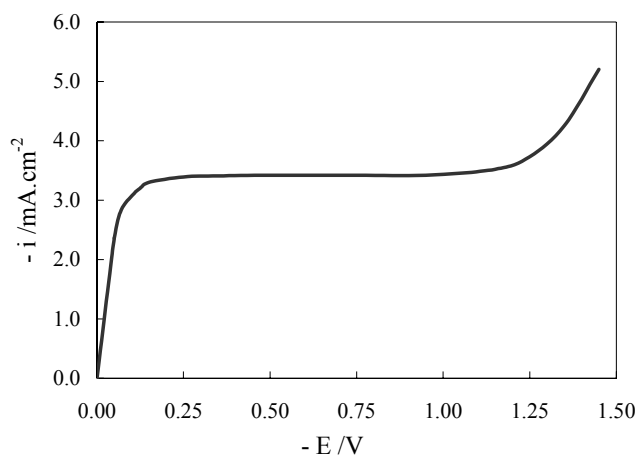
Figure 3. The limiting-current plateau region for ferricyanide reduction at corrugated nickel electrodes.
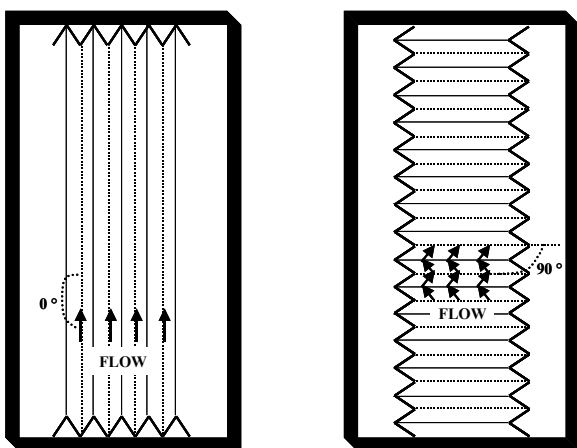
Figure 4. Angles between the corrugation and the flow direction: 0° and 90°.

the corrugation or (2) at 90° to the corrugation at the electrode, over the ribs of the corrugation.
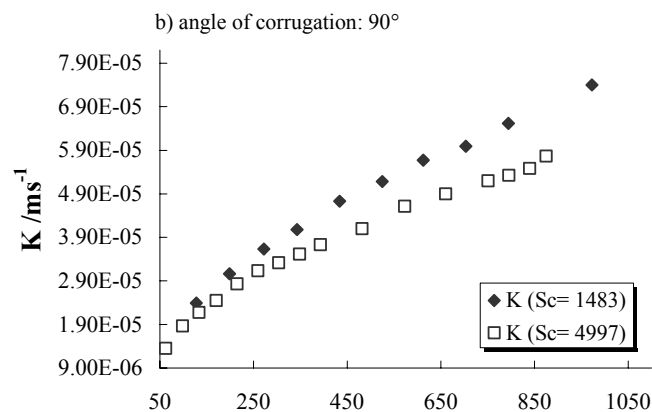
Mass-Transfer Coefficients. Figures 5a and 5b show the variation in mass-transfer coefficient with Reynolds number for the angles of flow to corrugation 0° and 90°, respectively, and with two different Schmidt numbers. For both angles of corrugation, 0° and 90°, the viscosity increases, that is, the Schmidt number decreases and the mass-transfer coefficient decreases. At very low values of the Reynolds number, below 450, however, there is no difference in the mass transport at the two Schmidt numbers studied. On the other hand, for both Schmidt numbers used, the mass-transfer coefficient is larger for corrugation at 90° than for 0° corrugation. It seems that the peaks and the troughs of the membrane with corrugation at 90° with respect to the flow enhances the mass transport.

Correlation of the Experimental Data. The work was done under laminar conditions, but fitted using equations for both laminar and turbulent conditions. The Leveque relationship is valid to correlate mass transfer along the surface of the membrane channels under laminar conditions ($Re < 2100$):

$$Sh = C \left(\mathrm{Re}\, Sc \frac{d_\mathrm{h}}{x} \right)^{0.333} \qquad (14)$$
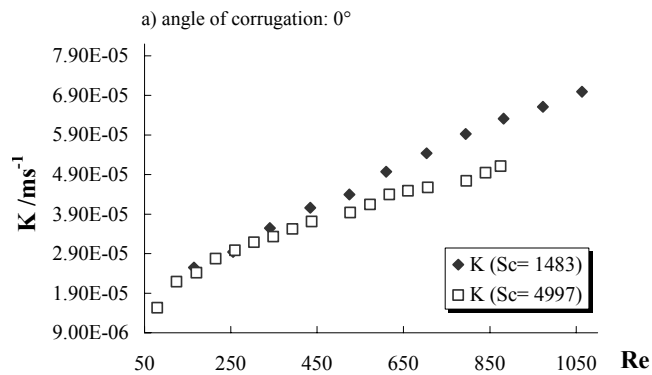
Figure 5. Mass-transfer coefficients and Reynolds numbers: (a) angle of corrugation = 0°; (b) angle of corrugation = 90°.

whereas the following equation, valid for mass-transfer entrance in turbulent channel flow [9], was used to correlate the data assuming turbulent conditions:

$$Sh = C\, Re^{0.58} Sc^{0.333} \qquad (15)$$

The experimental data obtained by the students is fitted to eqs 15 and 16 using a Microsoft Excel 7.0 spreadsheet (provided in the supporting material). The relative error in each data point is calculated using eq 16:

$$E(\%) = \left| \frac{Sh(\exp) - Sh(\mathrm{eq})}{Sh(\exp)} \right| \times 100 \qquad (16)$$

where $Sh(\exp)$ is the Sherwood number calculated from the experimental data and $Sh(\mathrm{eq})$ is the Sherwood number obtained using eqs 14 and 15.

Figures 6a and 6b show the experimental data for both Schmidt numbers studied and for an angle of corrugation of 90° together with the fits obtained from the Excel-based calculation using equations for both laminar and turbulent conditions. It should be noted that for both Schmidt numbers, 1483 and 4997, the experimental data fit better to the equation used for turbulent conditions than for the laminar-flow expression, as would be expected. The analysis of the data

Table 1. Constants for the Equations Used for Laminar and Turbulent Conditions and the Corresponding Average Error (%) for Different angles of corrugation and Schmidt numbers

Corrugation angle	Schmidt number	$Sh = C(Re\, Sc\, d/x)^{0.333}$		$Sh = C\, Re^{0.58} Sc^{0.333}$	
		C	E (%)	C	E (%)
0°	1483	1.391	10.2	0.213	2.0
0°	4997	1.379	6.8	0.227	4.3
90°	1483	1.519	17.3	0.243	2.8
90°	4997	1.433	12.1	0.255	4.6
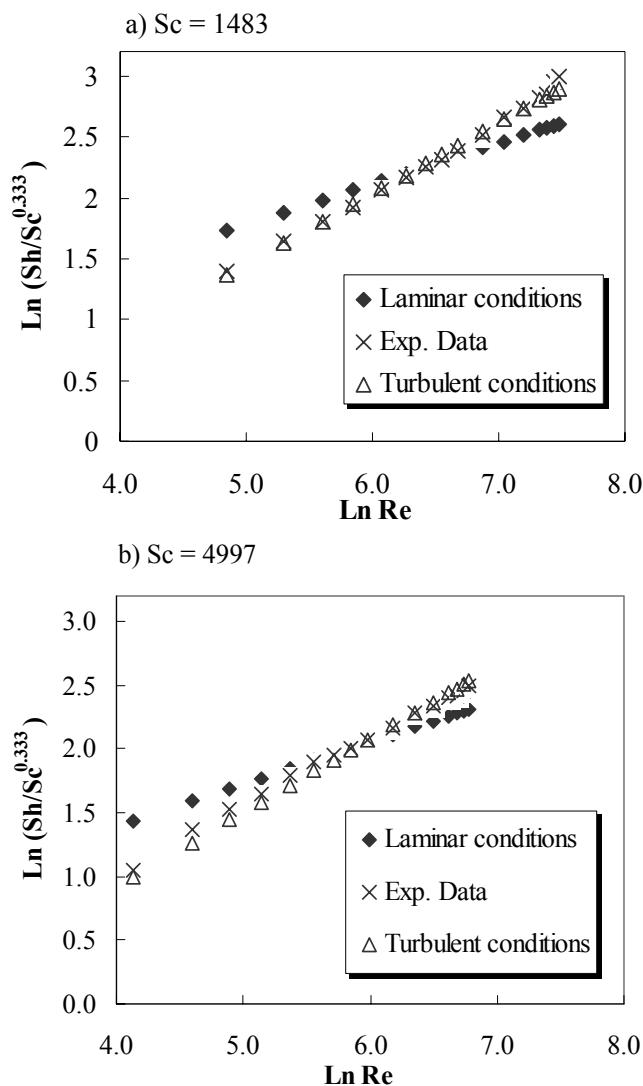
Figure 6. Experimental data and best fit of the equations assuming laminar and turbulent conditions; Angle of corrugation equals 90°. (a) $Sc = 1483$; (b) $Sc = 4997$.

showed that the laminar flow, thought to exist at low flow rates or Reynolds numbers (Re), does not occur. Actually, it is likely that the irregular flow path caused by the corrugations gives a more turbulent flow.

Table 1 shows the constant, C, obtained from the two equations, assuming laminar or turbulent conditions, and the corresponding average error (%) using the experimental data for the corrugation angles and Schmidt numbers (Sc) studied in this work. In all cases, there is a much better fit of the data to the equation assuming turbulent conditions, which gives an average error lower than 5%. When using the expression for the laminar regime, all the errors are higher than 10%, except

for 0° corrugation and a Schmidt number of 4997 where it is difficult determine if the conditions are laminar or turbulent.

Conclusions

Mass-transport coefficients at the surface of two separate cross-corrugated walls in a flowing liquid can be easily calculated using the limiting-current technique. The mass-transfer correlations show that the laminar regime expected to exist at low Reynolds numbers ($Re < 2100$) does not represent the flow behavior. It is more likely that the irregular flow path caused by the membrane corrugations enhances mass transfer to the extent that turbulent conditions apply.

There are many chemical processes that imply the use of high-viscosity substances (for example filtration of suspensions of oil in water), which means they exist in the low-flow regime (laminar flow, $Re < 2100$) and hence show low mass transport. These results show that corrugated membranes enhance the flow and the more advantageous turbulent regime (faster mass transfer) is reached, which suggests that these membranes can be used to study processes that are normally in the low regime.

This work is important for chemistry and chemical engineering students, and it is also very useful for postgraduates, because they can use this method to calculate mass-transfer coefficients in membranes, reactors, or similar systems.

Using this procedure, students learn to calculate mass-transfer coefficients from experimental data obtained in the laboratory. The instructor can propose several plates with different shapes or configurations and different corrugations (these are easy to make in the faculty workshop) to study the influence of each on the flux. The influence of temperature can also be studied. The experimental data obtained by the students can be fitted to the different equations available in the literature [9] using Microsoft Excel 7.0 spreadsheets.

Nomenclature

C_b: bulk reactant concentration (kmol m^{-3})
C_0: reactant concentration at the electrode (kmol m^{-3})
d_h: equivalent diameter (m)
D: diffusivity (m^{2}s^{-1})
i: current density (A m^{-2})
i_L: limiting current density (A m^{-2})
F: Faradays constant (96,501 C mol^{-1})
k: mass transfer coefficient (ms^{-1})
n: number of electrons to or from the electrode (in the ferri-ferrocyanide system is one)
Re: Reynolds number (dimensionless number)
Sc: Schmidt number (dimensionless number)
Sh: Sherwood number (dimensionless number)
T: temperature (K)

V_b: bulk velocity (ms^{-1})

x: distance from leading edge (m)

z: number of electrons associated with reaction (in the ferri-ferrocyanide system is one)

Greek letters

δ: thickness of the layer at the cathode (m)

μ: viscosity (k g^{-1}s^{-1})

ν: kinematic viscosity (m^2 s^{-1})

References and Notes

1. Scott, K.; Hughes, R. *Industrial Membrane Separation Technology;* Blackie Academic and Professional, Glasgow, **1996**

2. Hestekin J. A.; Bhattacharyya D.; Sikdar S. K.; Kim B.M. Membranes for Treatment of Hazardous Wastewater. In *Encyclopedia of Environmental Analysis and Remediation;* Meyers, R. A., Ed.; Wiley & Sons: New York, 1998**,** 2684–2708.

3. Shen, J. J. S.; Probstein, R. F.; *Ind. Eng. Chem., Process Des. Dev.* **1979,** *18* (3), 547–554.

4. Scott, K.; Mahmodd, A. J.; Jachuck, R. J.; Hu, B. *J. Membr. Sci.* **2000,** *17,* 31–16.

5. Racz, I. G.; Wassink, J. G.; Klaasen, R. *Desalination* **1986,** *60,* 213–222.

6. Kessler, D. P.; Greenkorn, R. A. *Momentum, Heat, and Mass Transfer Fundamentals;* Marcel Dekker: New York, 1999.

7. Scott, K. *Electrochemical Reaction Engineering,* Academic Press: Burlington, MA 1991.

8. Selman, J. R. *AIChE Symposium Series*, **1981,** 11 (204), 88–102.

9. Selman, J. R.; Tobias, W.C. *Adv. Chem. Eng.* **1978**, *10,* 211–318.

10. Nishmura, T.; Kunitsugu, H.; Nakagiri *Heat Transfer Japanese Res,* **1998,** *27* (7), 522–534.

11. Nickel foil was supplied by Goodfellow company, www.goodfellow.com (Accessed June 2002).