A Novel Rotated Disc Electrode and Time Lag Method for Characterizing Mass Transport in Liquid-Membrane Systems

DAVID A. GOUGH

and

JOHN K. LEYPOLDT

**Department of Applied Mechanics and
Engineering Sciences, Bioengineering Group
University of California at San Diego
La Jolla, CA 92093**

A time lag method is described for use with a membrane-covered, rotated disc electrode that allows determination of the partitioning and diffusivity of small molecules in hydrophilic gel membranes and membrane permeability from a single measurement. This new technique takes into account the concentration boundary layer in the solution adjacent to the membrane and reaction at the electrode surface of solutes that are diffusion- or kinetic-limited. Examples are given of the use of this method for characterizing mass transfer in a commercial cellulosic membrane with oxygen, hydroquinone, ferrocyanide, and glucose as solutes.

SCOPE

Polymeric membranes have found many applications in biomedical and industrial technology. Many separation processes such as reverse osmosis, hemodialysis, filtration, and blood oxygenation are based on membranes. There is a need to accurately characterize the transport of solutes in these membranes as a basis for design of more effective processes. If the membrane can be approximated as a homogeneous phase containing a linear distribution of solute, a parameter that describes diffusive transport of the solute within the membrane is membrane permeability, P_m, given by:

$$P_m = \frac{\alpha D_m}{\delta_m} \tag{1}$$

where α is the partition coefficient, D_m is the diffusion coefficient for the solute within the membrane, and δ_m is the membrane thickness.

In this formulation, membrane permeability depends on the product of two physical parameters, α and D_m, which must be measured independently and represent different mechanisms of transport control by the membrane. The partition coefficient is the equilibrium ratio of solute concentration in the membrane to that in the external phase, and can have an effect even in the absence of net transport through the membrane. The partitioning effect can be dominant where processes occur in the membrane that are a function of the local concentration, such as absorption or chemical reaction of the solute in immobilized enzyme systems (Filippusson and Hornby, 1970; Engasser and Horvath, 1976).

Conversely, the diffusion coefficient is a measure of the resistance to transport through the membrane once the solute has already entered and exited the membrane phase. If instantaneous equilibria across the membrane-solution interface can be assumed, D_m alone is the important transport parameter in the decay of transient phenomena in the membrane. Therefore, complete characterization, that could facilitate the design of new membranes, requires direct measurement of either α or D_m in addition to P_m and δ_m.

Accurate meaurement of the diffusion coefficient of small molecules within the membrane is complicated by transport in the layers of solution on either side of the membrane. In early studies, attempts were made to eliminate these concentration boundary layers by intensive stirring. However, it is now thought that complete elimination is impossible and that the effects of the solution layers must be taken into account (Smith et al., 1968; Malone and Anderson, 1977). A quantitative measure of the significance of the solution boundary layer effects in the measurement of membrane permeability is the mass transfer Biot number (Eckert and Drake, 1972):

$$Bi = P_s/P_m \tag{2}$$

where P_s is the permeability or mass transfer coefficient for the solution layer. For a membrane with gas phases on either side the Biot number is very large and hence boundary layer effects are negligible. However, for membranes in contact with liquid phases, the Biot number can vary over a range of values depending on flow conditions and solute and membrane properties.

In this communication, we demonstrate the use of a time lag method and a novel, membrane-covered rotated disc electrode for characterization of transport in hydrophilic gel membranes that may overcome these difficulties. The time lag method developed here is analogous to the well-known transient technique commonly used in gas-membrane systems where concentration boundary layer effects need not be considered (Barrer, 1951; Crank, 1975), but considers these effects in the solution phase. Notable assumptions made in the derivation are that transients in solution are fast compared to transients in the membrane and the electrochemical reaction kinetics are not altered by the presence of the membrane. The membrane-electrode apparatus and time lag method are used to analyze four model systems.

CONCLUSIONS AND SIGNIFICANCE

The model develped here suggests that the concentration boundary layer in the solution can make a significant contribution to total diffusional resistance, where the value of the Biot number is low or the reaction kinetics at the electrode surface are finite.

Experimental determinations of P_m and D_m for oxygen, hydroquinone, and ferrocyanide were made from which values of

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α were calculated. D_m for each solute was determined from analysis of the time lag, with P_m either approximated in the same experiment by the total steady state solute resistivity at high electrode rotation rate where the concentration boundary layer in solution has a relatively small effect, or measured more precisely in a separate experiment. Although some technical difficulties were encountered in producing a suitable step change of the bulk solute concentration, the results with the solution boundary layer taken into account compared favorably with results in the literature obtained by other methods.

In the case of glucose, where the process is partially limited by the kinetics of the reaction at the electrode surface which have not been previously quantified, the transport properties were estimated by comparison with the results of the above solutes and the transient analysis used to calculate values for the kinetic parameters.

The methods described here provide a useful means of characterizing transport and reaction of rapidly diffusable solutes in liquid-membrane systems, and form a basis for the development of novel membranes.

BACKGROUND

Of the many types of experimental apparatus for measuring membrane permeability, the most common is the batch dialyzer (Kaufmann and Leonard, 1968) or the diaphragm cell (Mills and Woolf, 1968) in which a membrane separates two stirred chambers. The chambers are initially charged with different amounts of diffusant, the concentration in the chambers measured as a function of time, and the total resistance to mass transfer, including the solution resistance then calculated from these quasi-steady state measurements. The distinction among various types of experimental systems based on these designs is in the stirring apparatus and in the analysis of the solution resistance. Several approaches to stirring have been enumerated (Spriggs and Li, 1976) and reviewed in detail elsewhere (Leonard et al., 1974; Klein et al., 1977).

In all of these previous designs, the solution mass transfer coefficient is nonuniform across the membrane, complicating the interpretation of data since only an average mass transfer coefficient can be determined and much of the detail may be lost. In addition, in most, the volume of the external cell in which the concentration is measured is generally much larger than the membrane volume, making accurate determination of the partition coefficient nearly impossible since sensitivity depends on the ratio of membrane volume to external cell volume (Spacek and Kubin, 1967). Hoogervorst (1978) has reported a method for determination of the partition coefficient in a liquid-membrane system despite the small ratio of membrane to cell volume, but does not take into account the effect of the solution boundary layer.

We have developed a novel, membrane-covered rotated disc electrode system that can be of use to characterize transport in hydrophilic gel membranes. As described in detail elsewhere (Gough and Leypoldt, 1979), a disc working electrode and a high impedance reference electrode are both mounted on a rotating shaft, over which the membrane is placed. With this configuration, any iR drop between the working and reference electrodes may be insignificant or correctable by conventional means so that the electrode potential is precisely controlled, and the current flux through the membrane between the disc and an external counter electrode can be made symmetrical and uniform across the disc surface.

Levich observed that mass transfer to the analogous classical rotated disc electrode without a membrane is unique in that the concentration boundary layer is of uniform thickness across the disc surface (Levich, 1962). Thus, the diffusant is uniformly accessible to the electrode at all points on the electrode surface. Further, the thickness of the concentration boundary layer is inversely proportional to the square root of rotation rate and can therefore be readily manipulated. With the proper current distribution, these properties also obtain for the membrane-covered, rotated disc electrode (Gough and Leypoldt, 1979), and for electrode processes that are partially reaction-limited (Levich, 1962; Gough and Leypoldt, 1980a).

We took advantage of these features in several previous studies. The effect of electrode rotation rate on the steady state diffusion current was first analyzed (Gough and Leypoldt, 1979). At low rotation rates, where the thickness of the concentration boundary layer in solution is relatively large, the solution mass transfer resistance is a major contribution to total diffusional resistance. Under these conditions, the diffusion current approaches the theoretical Levich current (Levich, 1962) that would be seen in the absence of a membrane. However, at high rotation rates, the diffusion current is limited by the membrane and the molecular permeability of the membrane can be readily characterized. This steady state method was used to determine the permeability of Cuprophane PT-150 to oxygen and hydroquinone (Gough and Leypoldt, 1980b) and to ferrocyanide (Gough and Leypoldt, 1979).

A transient method involving a step change of electrode potential was also used to determine the diffusion coefficient of oxygen and hydroquinone in the membrane (Gough and Leypoldt, 1980b). The technique was analyzed both for electrode processes that are completely diffusion-limited and partially reaction-limited. In that study the membrane-electrode system was also used to estimate some kinetic constants of glucose oxidation, which is a partially reaction-limited process where, in addition, under the conditons of that experiment the effective electrode surface area decreased with the logarithm of time.

A membrane-covered, rotated disc electrode has been previously used by other investigators in conjunction with a transient method to characterize transport parameters in membranes. Chien, Olson, and Sokoloski (1973) used a carbon rotated disc electrode covered by a Millipore VC membrane to study the transport of p-nitrophenol. In their electrode configuration, the disc electrode was polarized at constant potential with respect to the second, nonrotated combination reference/counter electrode. The transport parameters were qualitatively estimated at high rotation rates by an adaptation of the conventional time lag method, not considering the effects of the concentration boundary layer in solution. No attempt was made to rigorously describe the effects of electrode rotation rate or reaction kinetics.

THEORETICAL ANALYSIS

We now consider transient mass transfer in the membrane-covered, rotated disc electrode system following a step change of the bulk solute concentration. The disc electrode is covered by a membrane of thickness δ_m, rotated at constant angular frequency ω, and held at constant potential. As before (Gough and Leypoldt, 1979), we let $Z = 0$ at the membrane-solution boundary with Z being positive in the direction normal to and away from the membrane surface. Initially, the bulk solute concentration is C_1. At time $t = 0$, a specified amount of solute is rapidly injected into the bulk solution so that the final concentration becomes C_2. A description of the current is derived here as a function of time. For a thin membrane, the governing equation is:

$$\frac{\partial C_m}{\partial t} = D_m \frac{\partial^2 C_m}{\partial Z^2} \qquad - \delta_m \le Z \le 0 \qquad (3)$$

where C_m is the concentration and D_m, tthe diffusion coefficient for the solute in the membrane. We assume that the reaction at the electrode surface follows a first order kinetic law with a first order reaction constant k_1. The boundary condition at the electrode-membrane interface is then:

$$D_m \frac{\partial C_m}{\partial Z}(-\delta_m, t) = \frac{kC_m}{\alpha}(-\delta_m, t) \tag{4}$$

where α is the partition coefficient of the solute in the membrane and k is proportional to the rate constant k_1, with the proportionality factor being dependent on such factors as the electrode roughness and potential. The boundary condition at the membrane-solution interface is given by:

$$D_m \frac{\partial C_m}{\partial Z}(0, t) = \frac{D}{\alpha \delta_d}[\alpha C_2 - C_m(0, t)] \quad t > 0 \tag{5}$$

where D is the diffusion coefficient within the bulk solution and δ_d is the Levich diffusional boundary layer (Levich, 1962) given by:

$$\delta_d = 1.61\ D^{1/3}\nu^{1/6}\omega^{-1/2} \tag{6}$$

with ν, the kinematic viscosity of the bulk solution. Eq. 5 is expected to be a good approximation of this situation provided that transient phenonema in the solution damp out much faster than transients in the membrane following a step change of concentration. The initial condition can be obtained by solving the steady state analog of Eq. 3 with boundary conditions (Eqs. 4 and 5). Thus replacing αC_2 in Eq. 5 by αC_1, we obtain (Gough and Leypoldt, 1980a):

$$C_m(Z, 0) = \frac{\alpha C_1}{1 + \frac{\alpha D_m}{k\delta_m} + \frac{\alpha D_m \delta_d}{D\delta_m}}\left[1 + \frac{\alpha D_m}{k\delta_m} + \frac{Z}{\delta_m}\right] \tag{7}$$

Eqs. 3, 4, 5, and 7 are a complete statement of the problem and we proceed by introducing the following nondimensional variables and parameters:

$$\bar{C}_m = \frac{\alpha C_2 - C_m}{\alpha C_2} \tag{8}$$

$$y = 1 + \frac{Z}{\delta_m} \tag{9}$$

$$\tau = \frac{D_m t}{\delta_m^2} \tag{10}$$

$$Bi = \frac{D\delta_m}{\alpha D_m \delta_d} \tag{11}$$

$$h = \frac{k\delta_m}{\alpha D_m} \tag{12}$$

$$W = \frac{C_1}{C_2} \tag{13}$$

Eqs. 3 to 7 then become:

$$\frac{\partial \bar{C}_m}{\partial \tau} = \frac{\partial^2 \bar{C}_m}{\partial y^2} \qquad 0 \le y \le 1 \tag{14}$$

$$\frac{\partial \bar{C}_m}{\partial y}(0, \tau) - h\bar{C}_m(0, \tau) = -h \tag{15}$$

$$\frac{\partial \bar{C}_m}{\partial y}(1, \tau) + Bi\,\bar{C}_m(1, \tau) = 0 \tag{16}$$

$$\bar{C}_m(y, 0) = 1 - \frac{W}{1 + h^{-1} + Bi^{-1}}(y + h^{-1}) \tag{17}$$

Eqs. 14 to 17 can be solved by the application of integral transforms as described elsewhere (Ozisik, 1980). However, we treat here a case that is more common in practice in which the kinetics at the electrode surface are rapid compared to diffusion through the solution and membrane. The solution of the more general problem that includes reaction limitation at the electrode surface is analogous and, for the sake of algebraic convenience, is only stated below. Therefore, in the limit of very rapid kinetics, where $h \rightarrow \infty$, the boundary condition (Eq. 15) is replaced by:

$$\bar{C}_m(0, \tau) = 1 \tag{15a}$$

and the initial condition (Eq. 17) is replaced by:

$$\bar{C}_m(y, 0) = 1 - \frac{Wy}{1 + Bi^{-1}} \tag{17a}$$

The use of a finite sine transform is expedient for the above modified problem (Miles, 1971) and the solution is:

$$\bar{C}_m(y, \tau) = \frac{-y}{1 + Bi^{-1}} + 2(1 - W)Bi \sum_{k_n} \frac{(k_n^2 + Bi^2)\sin k_n}{k_n^2[k_n^2 + Bi^2 + Bi]} \exp(-k_n^2\tau)\sin k_n y \tag{18}$$

where the sum is over the roots of the following equation:

$$k_n \cot k_n + Bi = 0 \tag{19}$$

The change in flux at the electrode surface relative to the flux at time zero is:

$$\begin{aligned} j(\tau) &= \frac{\alpha D_m C_2}{\delta_m}\left\{\left(\frac{-\partial \bar{C}_m}{\partial y}\right)_{y=0} - \frac{W}{1 + Bi^{-1}}\right\} \\ &= \frac{\alpha D_m (C_2 - C_1)}{\delta_m}\left\{\frac{1}{1 + Bi^{-1}} - 2\,Bi \sum_{k_n} \frac{(k_n^2 + Bi^2)\sin k_n}{k_n[k_n^2 + Bi^2 + Bi]}\exp(-k_n^2\tau)\right\} \end{aligned} \tag{20}$$

Integrating $j(\tau)$ over the interval $t = 0$ to t gives the total flux of solute to the electrode during this period from which the total current flux can be obtained. Thus,

$$\begin{aligned} Q(t) &= nF\pi R^2 \int_0^t j(\tau)\,dt = \\ &\frac{nF\pi R^2 \alpha D_m (C_2 - C_1)}{\delta_m(1 + Bi^{-1})}\left\{t - \frac{2\delta_m^2(1 + Bi)}{D_m} \sum_{k_n} \frac{(k_n^2 + Bi^2)\sin k_n}{k_n^3(Bi + k_n^2 + Bi^2)}[1 - \exp(-k_n^2\tau)]\right\} \end{aligned} \tag{21}$$

where n is the number of electrons, F is the Faraday constant, and R is the electrode radius. As $t \rightarrow \infty$, $Q(t)$ approaches the line:

$$Q^\infty(t) = \frac{nF\pi R^2 \alpha D_m (C_2 - C_1)}{\delta_m(1 + Bi^{-1})}\left\{t - \frac{2\delta_m^2(1 + Bi)}{D_m} \sum_{k_n} \frac{(k_n^2 + Bi^2)\sin k_n}{k_n^3(k_n^2 + Bi^2 + Bi)}\right\} \tag{22}$$

It can be shown (Churchill, 1972) that:

$$2 \sum_{k_n} \frac{(k_n^2 + Bi^2)\sin k_n y}{k_n^3(k_n^2 + Bi^2 + Bi)} = \left[1 + \frac{1}{3(1 + Bi^{-1})^2} - \frac{1}{1 + Bi^{-1}}\right]y - \frac{y^2}{2} + \frac{y^3}{6(1 + Bi^{-1})} \tag{23}$$

Evaluating Eq. 23 at $y = 1$ and combining with Eq. 22 gives the following expression:

$$Q^\infty(t) = \frac{nF\pi R^2 \alpha D_m (C_2 - C_1)}{\delta_m(1 + Bi^{-1})}\left\{t - \frac{\delta_m^2}{6D_m}\left(3 - \frac{2}{1 + Bi^{-1}}\right)\right\} \tag{24}$$

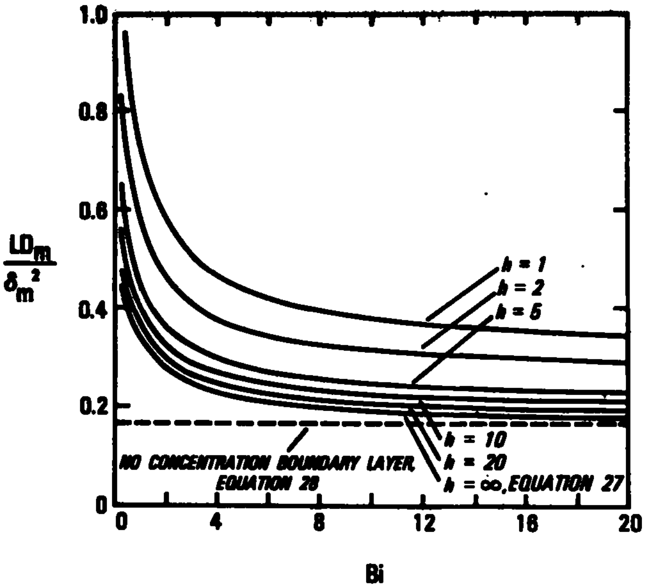

Figure 1. Effect of *Bi* and *h* on the dimensionless time lag.

This line has an intercept on the *t*-axis given by:

$$L = \frac{\delta_m^2}{6D_m}\left(3 - \frac{2}{1 + Bi^{-1}}\right) \tag{25}$$

The intercept L has been referred to as the time lag (Crank, 1975; Barrier, 1951). Eq. 25 shows the dependence of the time lag on the solution mass transfer coefficient or Biot number. As the Biot number becomes large, the solution mass transfer resistance diminishes and the time lag becomes:

$$\lim_{Bi \to \infty} L = \frac{\delta_m^2}{6D_m} \tag{26}$$

This is the usual expression that applies to a single membrane in the absence of an external concentration boundary layer (Crank, 1975). The more general problem with finite electrode kinetics (Eqs. 14 to 17) leads to the following time lag:

$$L = \frac{\delta_m^2}{6D_m}\left[3 - \frac{2 - \dfrac{6}{hBi}}{1 + h^{-1} + Bi^{-1}}\right] \tag{27}$$

The predicted effect of the Biot number and finite kinetics on the time lag is shown in Figure 1. The normalized time lag given by Eq. 27 is plotted as a function of the Biot number for various values of h. The dashed line represents the time lag without solution resistance and reaction limitation, as given by Eq. 26. For all values of h, the normalized time lag strongly depends on the Biot number at low Biot numbers and approaches a constant at high Biot numbers. With increasing values of h, the normalized time lag approaches the curve described by Eq. 25 where kinetics at the electrode surface are infinite.

It should be noted that Eq. 27 is symmetrical with respect to Bi and h, and that these parameters can be interchanged in Figure 1. The figure shows that the use of the time lag method in systems where there may exist a concentration boundary layer, without proper consideration of external mass transfer or possible kinetic limitations, could lead to a significant error in determination of the diffusion coefficient.

Other investigators working with the time lag method in gas-membrane systems have described results of transport in composite membranes (Barrie et al., 1963; Barrer, 1968) which should be useful for comparison here. Assuming no convective flow within the Levich diffusion boundary layer, the present system can be thought of as a composite solid. Adapting the previous authors' results in our notation yields a time lag, L_c, for a composite membrane of the form:

$$L_c = \frac{\dfrac{\delta_d^2}{D}\left(\dfrac{\delta_d}{6D} + \dfrac{\delta_m}{2D_m\alpha}\right) + \dfrac{\delta_m^2}{D_m}\left(\dfrac{\delta_d}{2D} + \dfrac{\delta_m}{6\alpha D_m}\right)}{\dfrac{\delta_d}{D} + \dfrac{D\delta_m}{\alpha D_m \delta_d}}$$

$$= \frac{\delta_m^2}{6D_m}\left(3 - \frac{2}{1 + Bi^{-1}}\right)\left[1 + \frac{\delta_d^2 D_m}{D\delta_m^2}\left(\frac{1 + 3Bi}{3 + Bi}\right)\right] \tag{28}$$

Eq. 28 reduces to the results obtained by Eq. 25 provided that:

$$\frac{\delta_d^2 D_m}{D\delta_m^2}\left(\frac{1 + 3Bi}{3 + Bi}\right) << 1 \tag{29}$$

or, that transient effects in the solution phase dissipate faster than those in the membrane.

EXPERIMENTAL

The design and construction of the rotated disc electrode has been discussed in detail by Gough and Leypoldt (1979). The working electrode was a platinized platinum disc of 0.5 cm² geometric area. The electrode roughness factor, R_f, or the ratio of true surface area to geometric area was approximately 240 and was checked routinely, especially during experiments with glucose. The roughness factor was intentionally fixed at this relatively low value to accentuate the effects of kinetic limitation.

Procedures for electrode polarization, estimation of the true surface area, and electrode platinization have been previously reported (Gough and Leypoldt, 1980a). Solutions were prepared from analyzed, reagent grade chemicals with deionized, distilled water and equilibrated during the experiment with pure argon. The permeability of the membrane has been previously characterized by conventional techniques with solutes other than those used in this study (Colton et al., 1971). The ionic permeability of the membrane has also been previously estimated (Gough and Leypoldt, 1979) and is greater than membrane solute permeability, assuring that the process was never limited by the passage of current through the membrane.

Experiments were conducted in the following manner. Rapid injections of small, known volumes of concentrated, deoxygenated solution containing solute were first made in absence of the membrane using a Luggin capillary reference electrode in order to develop an effective procedure for producing a step change of concentration. With some practice, a concentration change could routinely be produced that was rapid compared to the anticipated transit time in the membrane, as reflected by current recordings.

Conditions that promote a more effective concentration step are high rotation rates, low original volume, rapid injection through a small orifice to disperse the injectate, and introducing the solute directly below the electrode. With the membrane, five or more experiments were conducted with each solute at a given rotation rate. The recorded current was manually integrated and fit to a straight line by linear regression through points representing 2 to 4L. For a given solute, the Biot number was varied by using different rotation rates or multiple thicknesses of the membrane.

RESULTS

An example of the data for oxygen is given in Figure 2. The current density transient is shown with and without a membrane after a rapid injection of a specified volume of oxygenated buffer. In the upper tracing without the membrane, the current density typically rose to a sharp peak immediately after injection, then eventually reached a constant, steady state value after several seconds. With some skill, it was possible to reproducibly generate a response with rapid overshoot and return. But it was difficult by simple injection to produce a step change without the initial overshoot. There was no similar effect when deoxygenated buffer was injected, confirming that the current density peak was not merely due to a transient flux of electrolyte near the electrode surface, but rather to reaction of oxygen.

In the lower tracing taken under identical conditions but with a membrane, the current density rose slower than in the absence of the membrane and typically passed through a maximum that was slightly higher than the eventual steady state current density, then returned to steady state. The results of oxygen at lower rotation rates or with greater membrane thickness, or of hydroquinone and ferrocyanide all demonstrated the same characteristic shape, but in each case the initial rise was slower, reflecting lower total permeability. The conditions shown in this figure represent the shortest anticipated time lag used in the present study.

There are several possible sources of error in these experiments. First, the concentration change was not made in an ideal, sharp step. Without the membrane, the current typically rose to a sharp maximum, then fluctuated before attaining the final steady state value. A possible strategy for more accurately describing this behavior would be to model the concentration change as an initial linear increase followed by a linear decrease to the new, constant steady state level. However, in light of our present objectives the anticipated small error involved did not warrant such an effort. In addition to the possible inaccuracy caused by the nonideal concentration change, these results may be subject to errors that affect conventional time lag experiments (Siegel and Coughlin, 1970; Petropoulos and Myrat, 1977) related to the linear approximation of the integrated time lag curve at long times. Variations in repeated measurements were taken into account by determining the mean of five individual time lags at a given set of experimental conditions.

The results of oxygen, hydroquinone and ferrocyanide are summarized in Table 1. For each experiment specified by ω, δ_m and D, two different values of P_m were used in the calculations of Bi, α and D_m. For the results not in brackets, D_m was taken as the total steady state resistance to the solute at the specified rotation rate. These values should be considered as only approximate because the contribution of the concentration boundary layer in solution to the resistance was neglected.

The approach was nevertheless convenient since a second experiment in which P_m is determined exactly was not required. The values in brackets are based on a more accurate measurement of P_m by an independent experiment in which the steady state resistance to the solute was extrapolated to infinite rotation rate, thereby eliminating the contribution of solution resistance. By inspection, the relative difference between the bracketed and unbracketed values in each case is smaller than the respective standard deviation of the measured time lag, suggesting that the error introduced by this approximation is of minor consequence. The values of 1.0 or greater for α are probably not realistic, since α is expected to vary from approximately 0.6 to 1.0, increasing with decreasing molecular weight. These incorrect values probably correlate most closely with slight underestimates of D_m that result from the inaccuracy of the time lag measurement. The standard deviation in L, which became relatively greater with decreasing molecular weight and smaller values of δ_m, was related to solution mixing after solute injection.

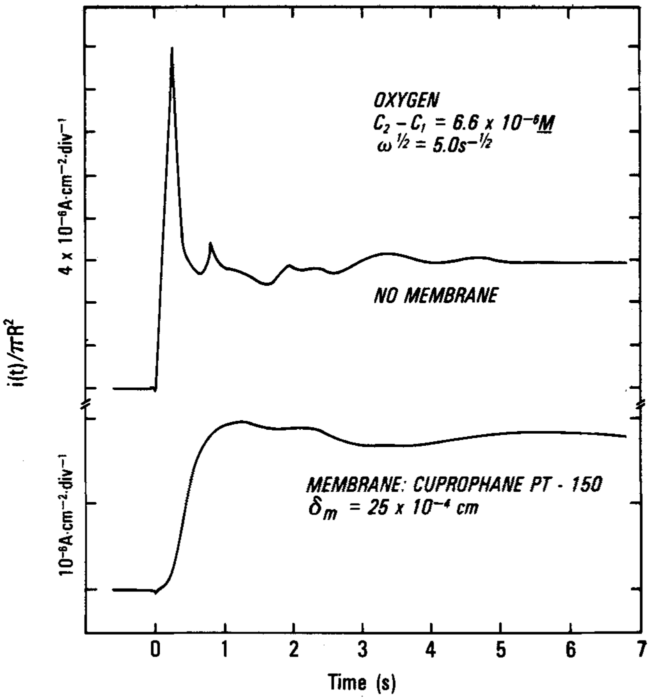

Figure 2. Examples of the data for diffusion-limited solutes.

In principle, this source of error could be further reduced by developing an improved solute injection technique, using thicker membranes, and averaging over a larger number of measurements. The results were also quite sensitive to the precision of estimate of membrane thickness, since this term is taken to the second power in the time lag equation. If the concentration boundary layer were not taken into account in

TABLE 1. SUMMARY OF SOLUTE TRANSPORT PROPERTIES IN CUPROPHANE PT-150 (VALUES IN PARENTHESES CORRESPOND TO P_m AT INFINITE ROTATION RATE)

Solute and Conditions	$L \pm$ S.D., s*	$\omega^{\frac{1}{2}}$, $s^{-\frac{1}{2}}$	D, ǂ $cm^2 s^{-1} \times 10^6$	δ_m, cm $\times 10^4$	P_m, cm $\cdot s^{-1} \times 10^4$	Bi	α	D_m, $cm^2 s^{-1} \times 10^7$	D_m, Literature†
Oxygen; 0.1N KCl, 0.01M phosphate buffer, pH 7.3, 37°C	0.46 ± 0.28	3.0	23.2	27	10.4(13.9)	3.14(2.35)	0.72(0.89)	39.2(42.2)	41.0
	0.56 ± 0.37	5.0		27	10.7(13.9)	5.09(3.92)	1.00(1.23)	28.8(30.5)	
	1.05 ± 0.10	5.0		50	5.70(6.90)	9.55(7.89)	0.60(0.71)	47.2(48.6)	
Hydroquinone; 0.1N KCl, 5×10^{-4} M H_2SO_4, 30°C	0.71 ± 0.29	5.0	11.6	27	5.60(6.37)	6.12(5.38)	0.69(0.77)	22.0(22.5)	24.1
Ferrocyanide; 1.N KCl, 0.01M phosphate buffer, pH 7.3, 30°C	2.61 ± 0.48	5.0	6.32	27	1.59(1.67)	13.7(12.9)	0.88(0.99)	4.54(4.56)	5.65
	5.76 ± 0.11	5.0		50	0.82(0.84)	27.9(25.9)	0.56(0.54)	7.28(7.77)	

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* Each value is an average of five measurements.
ǂ Gough and Leypoldt, 1980b.
† Gough and Leypoldt, 1980a.

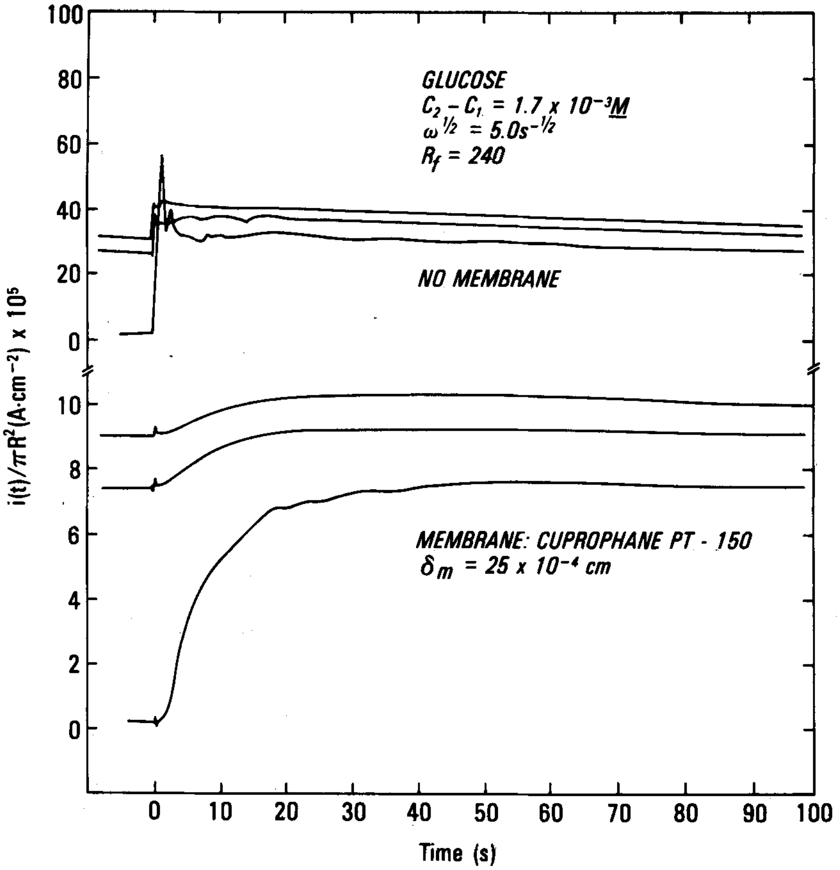

Figure 3. Examples of the data for glucose: segments of a continuous tracing superimposed.

these studies, the error introduced could be substantial. According to Eq. 25, as the value of the Biot number approaches 1.0, the resulting value for D_m could be under-estimated by as much as 50%.

Although there have been several previous studies on the permeability of Cuprophane PT-150, there are no data in the literature for these solutes with which the present results can be directly compared (other than our own obtained by a similar method, Gough and Leypoldt, 1980a; 1980b). However, in one study (Colton et al., 1971), a quasilinear relationship was found between the ratio D_m/D and solute molecular weight for a variety of solutes that may be useful for indirect comparison. In that study, P_m was determined from the membrane resistance to the solute, and α was estimated by a volumetric method, allowing the calculation of D_m. Most of the data represented higher molecular weight solutes where the solution resistance is relatively small. While the present results correlate reasonably well with these data, we suspect that our results may be more accurate for low molecular weight solutes.

Analysis of the results of glucose was more complicated. It has been previously shown (Lerner at al., 1979; Gough and Leypoldt, 1980a) that glucose oxidation at a platinized platinum electrode is a partially reaction-limited process. The consequences of this are shown with and without the membrane in Figure 3. In both sets of experiments, the electrode was first activated by prepolarization in the absence of glucose, then the measurement potential was applied and the background current allowed to reach steady state before the first glucose injection. As observed previously (Gough and Leypoldt, 1980b), the background current density was slightly anodic and independent of rotation rate or the presence of the membrane. A known amount of glucose was rapidly injected, causing the current density in the upper tracing without a membrane to rise sharply to a peak, then return to the new value. In this case, however the resulting current density did not reach a steady state, but decreased linearly with time, a phenomenon related to the complex mechanism of electrochemical glucose oxidation.

Two subsequent glucose injections followed directly and were recorded continuously, although the tracing for each injection was superimposed in this figure to make injection times coincide. The second and third injections with the same amount of glucose resulted in successively smaller current density increments, indicating that the process was clearly nonlinear with concentration and significantly reaction-limited. In the lower tracing, similar effects were observed with the membrane, although the net current density was substantially reduced. As above, the three transient current densities were recorded continuously and superimposed to the same starting time. The slight anodic background current density prior to the first injection was not time-dependent.

The first glucose injection gave rise to a characteristic transient that gradually reached a maximum then began to decay linearly. As without the membrane, the second and third injections of the same amount of glucose resulted in successively smaller current density increments, suggesting that this membrane does not provide enough resistance to transport to convert the process to clear diffusion-control. The constant slope corresponding to the current decay was subtracted from the current due to the transient in the membrane, and the resulting current integrated and used in the time lag calculation.

Since values of the kinetic constants for glucose oxidation that apply under these conditions are not known, the Biot number for glucose could not be determined directly from this experiment. As an alternative, therefore, we estimated the Biot number by linear interpolation on a basis molecular weight from the results of oxygen, hydroquinone, and ferrocyanide, and used that value to calculate the kinetic rate constants. In future experiments with other membranes, these values of the kinetic constants can be used to calculate a relative Biot number. The values used were: D, 9.0×10^{-6} cm$^2 \cdot$ s^{-1}; D_m, 1.2×10^{-6} cm$^2 \cdot$ s^{-1}; α, 0.75; and δ_m, $25. \times 10^{-4}$ cm, giving a value for Bi of 8.08. With the experimentally determined electrode roughness factor of 240, this led to values for h and k of 2.64 and 9.49×10^{-4} cm s^{-1}, respectively.

The kinetic behavior appears to be substantially different for different modes of electrode operation. In our previous study of glucose oxidation kinetics after a step change in electrode potential (Gough and Leypoldt, 1980a), the current decayed with the logarithm of time rather than linearly; the resulting comparable kinetic constants were lower than those reported here by approximately two orders of magnitude. These observations suggest that different reaction mechanisms may prevail at the same electrochemical potential due to the differences in experimental protocol.

Another useful comparison can be made between the present model and the composite solid model which gives a time lag expressed by Eq. 28. If the values obtained for the various solutes studied here are used in Eq. 29, the results for the left-hand term are: 1.55, 0.73, 0.62, 0.34, 0.22, and 0.10. All but the first of these values satisfies the inequality in Eq. 29. The composite solid model is based on diffusion only in the two membrane phases with no external concentration boundary layer, whereas in the present model there may exist convective diffusion in the solution layer but diffusion only in the membrane. Thus, if Eq. 28 were applied directly to our experiment, it would represent an upper limit for L where diffusion alone is possible. If the effects of convection could quantitatively be assessed, these values would be significantly reduced. The values for the left-hand side of Eq. 29 are an index of the comparability of these two models.

This study prepares the way for characterization of new membranes, including membranes that contain immobilized catalysts, and for investigations with other solutes.

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NOTATION

Bi = dimensionless transport parameter, Biot number
C_1 = bulk solute concentration before concentration step, mol/cm^3
C_2 = bulk solute concentration after concentration step, mol/cm^3
C_m = solute concentration in the membrane, mol/cm^3
$\bar{C}_m$ = dimensionless solute concentration in the membrane, mol/cm^3
C_s = solute concentration in solution, mol/cm^3
D = solute diffusion coefficient in solution, cm^2/s
D_m = solute diffusion coefficient in the membrane, cm^2/s
F = Faraday constant, C/mol
h = dimensionless kinetic parameter defined in Eq. 12
j = solute flux, mol/cm^2 · s
j_s = solute flux through the membrane, mol/cm^2 ·
k, k_1 = rate constants, cm/s
k_n = summation constant
L = time lag, s
L_c = time lag for composite membrane, s
n = number of electrons, mol^{-1}
P_m = membrane permeability, cm/s
P_s = solution permeability, cm/s
Q = total current flux, C
Q^∞ = total current flux at long times, C
R = electrode radius, cm
R_f = electrode roughness factor, cm^2/cm^2
t = time, s
W = ratio of concentrations defined in Eq. 13
y = dimensionless distance parameter
Z = distance from the membrane surface, cm

Greek Letters

α = solute partition coefficient
δ_d = concentration boundary layer thickness, cm
δ_m = membrane thickness, cm
ν = kinematic viscosity, cm^2/s
τ = dimensionless time-dependent parameter defined in Eq. 10
ω = angular rotation rate, rad/s

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