An Interferometric Technique for the Study of Steady State Membrane Transport

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A membrane wedge interferometer was designed for obtaining steady state mass transfer data on liquid-membrane-liquid systems. Procedures were developed for analyzing the diffusive transfer process, and experiments were conducted on the ethyl alcohol-water-cellophane membrane system to obtain the type of data needed for elucidating mechanisms of membrane transport. The proposed technique provides an accurate method of studying membrane transport without the troublesome complications which characterize other methods.

SCOPE

The need for information concerning the fundamental aspects of mass transport in membranes is a pressing one, but theoretical understanding is often limited because of a lack of precise experimental data. In fact, it appears that the literature contains more theoretical models of membrane transport than accurate experimental measurements. This situation is understandable, since the available experimental techniques such as the batch dialyzer are subject to several important limitations which inhibit the critical evaluation of transport models. One of the main problems with the batch dialyzer method is that the mass transfer characteristics of the membrane must be isolated from the mass transfer resistances of the liquid phases near the membrane surfaces. Consequently, success in elucidation of the transport properties of the membrane is directly dependent on how accurately the complex velocity and concentration fields in the liquid phases can be characterized. It is apparent that there exists a need for alternative methods for the study of membrane transport.

Interferometric techniques which directly measure concentration profiles have been quite useful for the study of molecular diffusion in liquids. The opaque characteristics of membranes have inhibited such direct measurements of concentration profiles in membranes. However, interferometric measurement of the concentration distributions in the liquids surrounding the membrane is feasible, and, hence, it should be possible to determine the mass fluxes of the diffusing components at each membrane surface and the liquid phase concentrations of these substances at the two liquid-membrane interfaces. With this information, it then becomes possible to evaluate various models of transport in the membrane. The full potential of interferometric techniques has not been realized, since previous optical studies on membranes have involved unsteady state diffusion fields. The objective of this study is to develop a steady state interferometric method for studying membrane transport. This work includes the development of an experimental apparatus, experimental procedures, and data analysis procedures including internal consistency checks.

CONCLUSIONS AND SIGNIFICANCE

A membrane wedge interferometer was designed for measuring steady state mass transfer in liquid-membrane-liquid systems. With this apparatus, experiments can be conducted at a demonstrable steady state and without the complications of unknown liquid phase resistances. Procedures were developed for obtaining refractive index distributions from interference fringes and for determining mass fluxes, interfacial concentrations, and membrane thickness from these refractive index distributions. With this technique, the mass fluxes through the membrane can be checked for consistency by comparing results from the two sides of the membrane. The procedure developed here also eliminates the necessity for obtaining concentration data right up to the membrane-solution interface.

Experiments on the ethyl alcohol-water-cellophane membrane system were conducted to illustrate the experimental procedure and data analysis techniques. The results for this system indicate that cellophane is about an order of magnitude more permeable to water than to ethyl alcohol. This permeability difference can cause large convective velocities, and in one experiment the net mass transfer of ethyl alcohol was against its concentration gradient.

It was concluded that the membrane wedge interferometer provides an accurate method of studying membrane transport without the troublesome complications which characterize other methods. Since there appears to be no standard against which the data from a new membrane experiment can be compared, no definitive estimate of the accuracy of the technique is available. However, since this technique is based on proven optics, and since no significant assumptions or approximations are imposed on the analysis of the interferometric data, it is reasonable to believe that accuracy can be attained which approaches the 3% accuracy which has been attained for liquid diffusivity measurements with the wedge interferometer by Duda et al. (1969).

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The ability to describe and characterize membrane transport processes has become of increasing importance in both the biological and engineering sciences in the past several decades. In particular, membrane transport phenomena are of fundamental concern in many separation processes, such as reverse osmosis, and in many biomedical areas, such as the development of artificial organs. However, in spite of the tremendous research effort expended, progress in the elucidation of membrane transport phenomena has been impeded by the limitations of available experimental techniques for studying membrane transport systems.

The most common experimental apparatus for liquid-membrane-liquid transport studies is a batch dialyzer which consists of two stirred chambers separated by a membrane; mass fluxes through the membrane are determined by monitoring the composition changes of the liquids in the two chambers. Unfortunately, the batch dialyzer technique is subject to several inherent limitations. In the first place, isolation of the mass transfer characteristics of the membrane is complicated by resistances to mass transfer which exist in the liquid phases near the surfaces of the membrane. Consequently, success in the elucidation of the transport properties of the membrane is directly dependent on how accurately the complex velocity and concentration fields in the liquid phases can be characterized. A discussion of methods for determining the liquid phase and membrane resistances in batch dialyzers has been presented by Smith et al. (1968). Secondly, the experiment carried out in the batch dialyzer is not truly a steady state experiment. Hence, this technique may possess the shortcomings of any unsteady state membrane experiment, and these are discussed in detail below. Furthermore, the velocity fields in the liquid phases can cause deflection of the membrane which can have a significant effect on the membrane transport process. In addition, membrane stresses introduced by the stirring of the liquid solutions may require the use of membrane support materials to perform experiments on fragile membranes, and this procedure incorporates additional uncharacterized mass transfer resistances. Finally, in the batch dialyzer, local membrane characteristics are not isolated, and it is thus not possible to account for any microholes or punctures that give rise to erroneous permeabilities.

In light of these limitations, it is apparent that there exists a need for alternative methods for the study of membrane transport. One possibility that is particularly attractive is the utilization of interferometric techniques which have been widely used to analyze diffusional transport in liquid systems without membranes. The available interferometric methods can not, in general, be adapted to measure concentration profiles directly inside membranes, since these materials are typically opaque. However, interferometric measurement of the concentration distributions in the liquids surrounding the membrane is feasible, and, hence, it should be possible to determine the mass fluxes of the diffusing components at each membrane surface and the liquid phase concentrations of these substances at the two liquid-membrane interfaces. With this information, it then becomes possible to evaluate various models of transport in the membrane.

Bollenbeck and Ramirez (1974) have used a Rayleigh interferometer to determine concentration and mass flux data at a membrane surface, and Forgacs et al. (1975) have constructed a wedge interferometer for electrochemical investigations in membrane systems. These experimental investigations involve unsteady state diffusive transfer in the liquid-membrane-liquid system, and, thus, such interferometric systems are not particularly suitable for determining the steady transport characteristics of the membrane. If information on relaxation phenomena inside a membrane is required, then an unsteady or periodic experiment must be conducted. However, the majority of membrane studies are concerned with the steady state transport characteristics of the membrane, and utilization of an unsteady state experiment introduces troublesome complications. First of all, relaxation effects in the membrane and at the membrane-liquid interfaces may have a significant effect on the mass transfer in the membrane, hence complicating the analysis considerably. Such an effect will be evident when the characteristic time of the experiment is comparable to the characteristic time of the membrane material. Furthermore, analysis of membrane transport under steady state conditions leads to ordinary differential equations rather than partial differential equations which generally must be considered for unsteady state membrane transport. Finally, in an unsteady experiment, it may not be possible to formulate initial conditions for the entire system unambiguously. Clearly, then, there are advantages to be gained by conducting steady, rather than unsteady, membrane experiments.

In view of the difficulties encountered with previous membrane transport experimental techniques, a new method for the study of mass transfer through membranes has been developed. This method is a modification of the wedge interferometer technique which has been used for measuring binary diffusion coefficients in liquid systems (Duda et al., 1969). The wedge interferometer was modified so that liquid solutions could flow through two optical wedge cells in a direction parallel to a membrane separating the wedges, and the system was designed to operate with steady state mass transfer in a direction normal to the membrane. This experimental technique has several significant advantages over presently available methods of characterizing membrane transport:

1. The concentration driving force across the membrane and the associated mass fluxes can be determined without the complications of unknown liquid phase resistances.
2. The experiments can be conducted under a true and demonstrable steady state condition.
3. Transport data can be quickly determined over a wide range of concentrations simply by changing the compositions of the flowing liquid solutions, without disturbing the membrane.
4. Experiments with very fragile membranes can be performed without the complications associated with membrane support materials.
5. With this technique, it is possible to identify any nonhomogeneity or micropuncture in the membrane by direct observation of the interference patterns.

In this paper, we discuss the experimental apparatus and data analysis procedures and present results of a series of experiments with an ethyl alcohol-water-cellophane membrane system.

EXPERIMENTAL METHOD

Experimental Apparatus

The present modification of the wedge interferometer for membrane transport characterization is designed to permit measurement of the concentration field under steady state conditions. The basic optical wedge membrane cell consists of two identical wedges set side by side and separated by a membrane, as shown schematically in Figure 1. Also shown in Figure 1 are the various pieces of support apparatus needed to hold the membrane and

optical cells in place before positioning on the microscope stage. The optical plates were approximately 1.3 cm thick with a surface of 2.5 cm × 9 cm. The 2.5 cm × 9 cm faces of each plate were polished flat to one-quarter of a wavelength of helium-neon laser light, and one of these faces was coated with a multilayer optical coating which reflected approximately 85% of incident light. In addition, the 1.3 cm × 9 cm face of each plate which was in contact with the membrane was made as perpendicular to the two 2.5 cm × 9 cm faces as possible and also was polished optically flat. Both the plates and the coating were fabricated by Liberty Mirror Division of Libby-Owens Ford Co., Inc., Brackenridge, Pennsylvania.

The basic principle of the experiment is as follows. Two solutions of different composition flow at a constant flow rate from one end of each wedge to the other. Each wedge has three holes drilled through the top plate. The middle hole in each wedge is used to carry out reference free diffusion experiments which are used for interpreting interference fringes from membrane transport experiments, as is discussed below. The other two holes allow flow to be initiated through each wedge in a direction parallel to the membrane. The flow system used in conjunction with the optical wedge membrane cell is shown in Figure 2, which is a top view of the diffusion cell. The temperature and pressure in the wedge cells are effectively constant, but the concentration difference between the two flowing solutions initiates mass transfer across the membrane.

Analysis of the experiment is facilitated if there are no concentration gradients and velocity components in the diffusion field in a plane parallel to the membrane. If this can be achieved, there exists in such a diffusion field one-dimensional mass transport in a direction normal to the membrane. This situation can be obtained by separating the liquid phases adjacent to the membrane from the flowing solutions by utilizing an appropriate barrier material, as depicted in Figure 2. The barrier material must be rigid enough to eliminate any parallel velocity components in the liquid diffusion fields adjacent to the membrane and porous enough to allow sufficient mass transfer from the flowing solutions to maintain steady state conditions. Furthermore, it is also necessary that the barrier material be at least partially transparent so that interference fringes may be observed and followed through it. It was found that agar gel satisfied all of these requirements. One part of agar powder was added to 100 parts of distilled water, and the mixture was heated until it just started to boil, at which point the solution had become clear. The gel was then layered about 1 mm thick between two glass slides and allowed to solidify at room temperature. The top slide was then removed, and the layer of gel dried in an oven at 90°C for about 1 hr. The resulting gel layer was transparent and rigid enough to permit strips of the desired size (approximately 1 mm × 10 mm) to be cut for use as barriers. From concentration distributions derived from interference fringes measured with the wedge interferometer, it was concluded that there were insignificant concentration gradients parallel to the membrane in the liquid diffusion fields contained between the barriers and the membrane. Hence, the agar gel barrier provides a simple and effective means of obtaining one-dimensional mass transfer fields in the liquid solutions near the membrane surfaces.

A laser beam light source and a microscope and camera were used to generate and record the interference patterns. A helium-neon laser provided a 1.2 mm diameter beam of wavelength 6 328 Å which was collimated to within

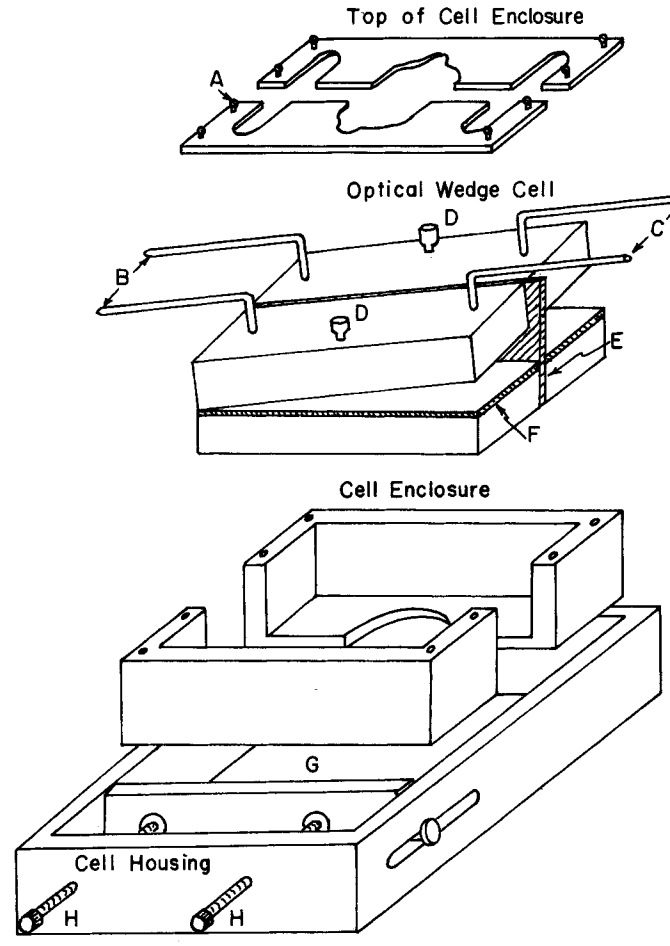

Fig. 1. Membrane wedge interferometer cell and support apparatus: A, wedge angle adjusting screws; B, inlet tubes; C, outlet tubes; D, holes for reference experiments; E, membrane; F, silastic spacer; G, sliding block; H, tightening screws.

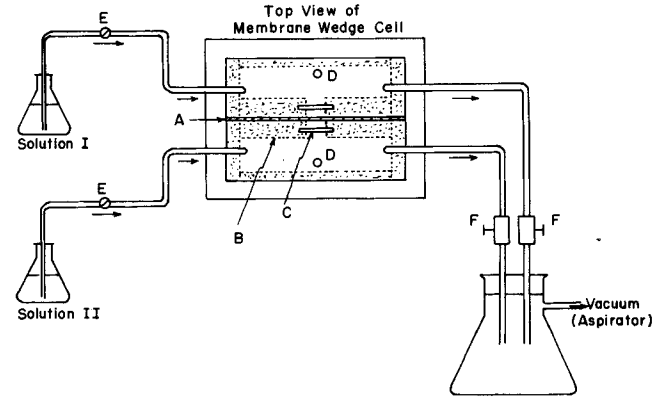

Fig. 2. Flow system for membrane wedge experiment: A, membrane; B, silastic rubber channel; C, agar barrier; D, holes for reference experiments; E, inlet valves; F, microneedle valves.

1 mrad, and this beam was expanded to about 1 cm diameter by an 8X collimator. The interference patterns were observed and photographed with a modified Unitron Model BN-12 Microscope. This microscope had several features which were extremely useful for the wedge membrane experiments. In particular, the inverted design gave a large working distance, so that the wedge apparatus fitted easily on the microscope stage. Also, the generated interference patterns could first be observed in a microscope mounted viewing screen before being photographed with a 35 mm camera. The total magnification for observation and photography was 10X, and the field of view

was about 2 mm × 4 mm. The photographs were generally taken with an exposure time of 1/60 s on ASA 400 Kodak Tri-X Pan black and white film.

Experimental Procedure

To assemble the membrane wedge cell, the bottom glass plates of the two wedges were placed on a flat glass sheet, and silastic rubber spacers were placed in position on these bottom plates. These spacers were cut from sheets that had previously been cast in the shape of a very thin wedge of approximately 0.2 mm at one end and 0.4 mm at the other. Thus, the silastic spacers placed in the wedge served not only to constrain the flow field but also to determine (approximately) the angle of the wedge. Once the spacers were positioned on the bottom plates, the agar gel barriers were put into place, and the top plates were then carefully added so as to form two optical wedges. This procedure was quite delicate, as it was necessary to align closely the top and bottom plates of each of the two wedges.

After each wedge with its closed diffusion cell was formed, the unpolished edges of each wedge were sealed with silicon rubber sealer to give a watertight seal. Then the two separate wedge assemblies were placed in the cell enclosures shown in Figure 1, and the tops of the cell enclosures were put into position. At this point, the wedges were filled with distilled water to remove trapped air bubbles, particularly inside the closed diffusion cells. A piece of swollen membrane (2 cm × 9 cm) was then placed on the polished edge of one optical wedge, and this wedge with the membrane was put into the cell housing shown in Figure 1. The other wedge was then introduced into the cell housing, and the membrane was sandwiched between the two wedges with the sliding block and the tightening screws. After the wedges were placed into the cell housing, the entire assembly was tightened with two thumb screws in order to produce an airtight system. The wedge angles were then adjusted by applying pressure to the top plates with the adjusting screws shown in Figure 1. Because the wedges were filled with pure water at this point, the criterion for the proper adjustment of wedge angles was that the generated interference fringes were evenly spaced and perpendicular to the membrane surfaces.

To start an experiment, all system valves were opened, and the flow of solutions I and II (Figure 2) was initiated by purging air from the system with an aspirator. Since these two solutions contained different concentrations of the two diffusing materials, mass transfer through the membrane was initiated because of the chemical potential difference between the flowing solutions. Flow of the liquid solutions through the wedges was driven by gravity with a constant head and was controlled by two microneedle valves located at the outlet tubes. The flow rate through each wedge cell was of the order of 10^{-3}-10^{-1} ml/s and was sufficiently rapid that the flowing solutions experienced insignificant concentration changes. This constancy of concentration, coupled with the negligible mass transfer resistances in the flowing liquids and the absence of flow induced velocity components in the closed diffusion cells, led to one-dimensional mass transfer normal to the membrane in the liquid regions adjacent to the membrane and in the membrane itself. In the experiments of this study, it was found that approximately 10 min. were sufficient for the attainment of a valid steady state condition, as could be verified by the constancy of the observed fringes with time. However, as an extra precaution, steady state interference fringes were photographed after the solutions had been flowing for about 4 hr.

The membrane used in this study was a commercial cellophane dialyzer membrane (#70158-1, Central Scientific Co.) with a dry thickness of approximately 0.02 mm. Ethyl alcohol and water were used as the diffusing species, since this binary system is well characterized in terms of solution density, refractive index, and mutual diffusion coefficient and since the cellophane membrane is permeable to some extent to both of these materials. Before it was placed in the wedge cell, the dry membrane was soaked in a large volume of distilled water at about 60°C for 2 hr. and then washed repeatedly with distilled water to remove all traces of any soluble substances that may have been inside initially. Binary solutions were made from 200 proof ethyl alcohol and distilled, deionized water. All experiments were carried out at room temperature (25° to 28°C).

Reference Free Diffusion Experiments

In the analysis of the interferograms obtained from the membrane wedge interferometer, it is shown below that direct measurement of the wedge geometry can be avoided by utilizing reference free diffusion experiments on each side of the membrane. Since the purpose of these reference experiments is effectively to eliminate the wedge geometry from the analysis of the interference fringes, these experiments are carried out immediately after a membrane transport determination so that the wedge configuration is not disturbed. The experimental procedure for the reference free diffusion experiments was as follows. After the interferograms for the membrane experiment were photographed, the inlet and outlet valves were closed and the hole for the reference experiments on each side of the membrane was opened. The outlet valve was then opened slightly, and about half of the solution on a given side of the wedge cell was emptied around the open reference experiment hole. Then a solution of different but known concentration was introduced into a given side of the wedge cell through the open reference experiment hole, and this solution was brought into contact with the solution left in the wedge. Thus, a free diffusion experiment was set up between the reference solution of known refractive index and the solution remaining in the wedge which was also of known refractive index. The interference fringes from this reference free diffusion experiment were then photographed, and the results were utilized in the data analysis decribed below.

Measurement of Membrane Thickness

In order to elucidate the mass transport process in a membrane, the mass fluxes and liquid phase concentrations at the membrane surfaces and the thickness of the membrane under transport conditions must be deduced from the experimental data. In principle, all of this information could be obtained from photographs of the diffusion field which show interference fringes in the liquid phases separated by an opaque membrane. However, because of limitations in the experimental optical system, it is not possible to obtain interference fringes right up to the membrane surface or to deduce the exact location and thickness of the membrane from such photographs. Photographs of the diffusion field show a black band in the center which is approximately 0.12 mm in width. Since the wet membrane thickness is only about one-third of this distance, portions of the liquid phases, as well as the membrane are included in this blind area. There are several possible explanations for the presence of the blind zone. The polished 1.3 cm × 9 cm faces may not be ground perfectly perpendicular to the polished 2.5 cm × 9 cm faces, the coatings on the 2.5 cm

× 9 cm faces may not be uniform right up to the membrane surfaces, and there may be slight misalignment of the top and bottom plates of the wedges.

The presence of the blind zone is a potential shortcoming of the proposed experiment. However, this difficulty can be resolved, as will be evident later, if an auxiliary experiment is used to determine the membrane thickness as a function of the concentration of a solution in which it is immersed. Small pieces of membrane were equilibrated at room temperature in ethyl alcohol-water solutions of several different concentrations for about a week. Two spots were then marked on opposite surfaces of these membrane pieces with a marking pen, and the membrane thickness was then measured microscopically by focusing on these spots. The experimental data on the concentration dependence of the membrane thickness in the concentration range 0 to 30 wt.% ethyl alcohol can be represented by the equation

$$L = 4.01 \times 10^{-3} - 3.68 \times 10^{-3}\,\omega_A + 3.54 \times 10^{-3}\omega_A^2 - 1.27 \times 10^{-3}\omega_A^3 \quad (1)$$

where L is expressed in centimeters.

Further details of the experimental apparatus and procedure are presented elsewhere (Min, 1975).

THEORY AND DATA ANALYSIS

We now describe the procedures utilized for the determination of concentration profiles in the liquid phases from the interference fringes and for the calculation of mass fluxes, interfacial concentrations, and membrane thickness from these concentration distributions.

Analysis of Interferograms

Figure 3 contains an example of a typical fringe in the liquid phase on one side of the membrane. In the region far away from the membrane, this fringe is parallel to the wedge axis, and the refractive index corresponds to that of the flowing solution n_∞. Analysis of such interference fringes is complicated by the fact that light does not propagate along a straight line when refractive index variations normal to the propagation direction are present. However, because the wedge cell is quite thin and because moderate refractive index gradients are utilized in this study, this effect can be shown to be negligible, and the fringes associated with the optical wedge approximately satisfy the following relationship:

$$nd = \frac{\nu\lambda}{2} \quad (2)$$

Clearly, the product of the refractive index and wedge thickness is constant along a given fringe and, hence, so is the product of the refractive index and the distance of the fringe from the wedge axis. Hence, along a fringe obtained from a membrane transport experiment, the refractive index at any position z from the membrane n_z can be related to the known refractive index of the flowing solution n_∞ by the equation

$$n_\infty(y_\infty + \phi) = n_z(y_z + \phi) \quad (3)$$

which can also be written as

$$\frac{n_z - n_\infty}{n_\infty} = \frac{y_\infty - y_z}{y_z + \phi} \quad (4)$$

Equation (4) is sufficient for the calculation of the refractive index distribution, since y_z, y_∞, and ϕ can be determined experimentally. However, measurement of ϕ is somewhat inconvenient, and, thus, a reference free diffusion experiment, which has been described above, is utilized to eliminate ϕ from the analysis.

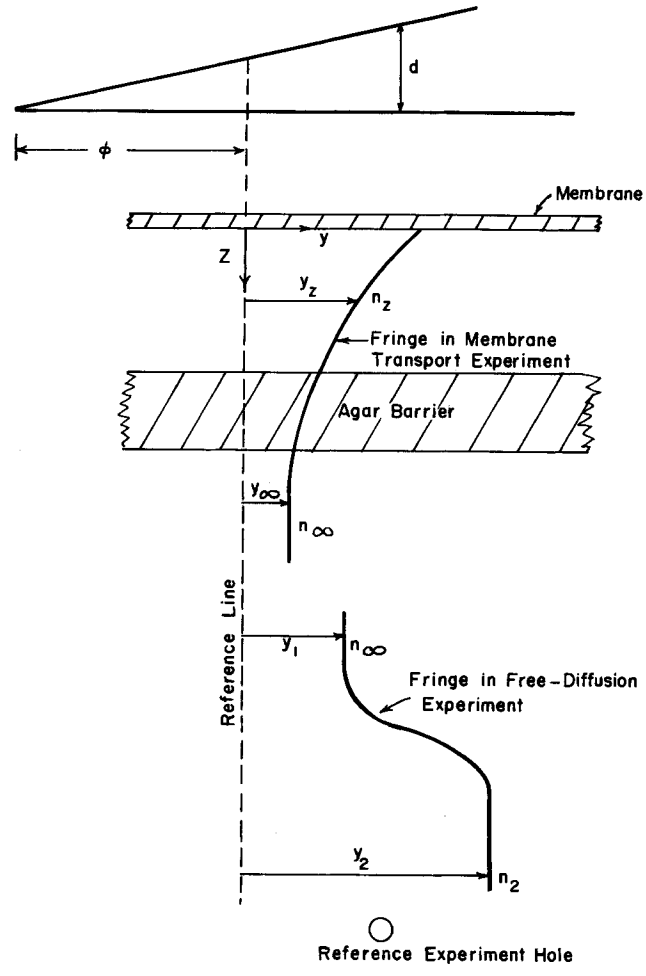

Fig. 3. Diagram of quantities used in the interpretation of an interferogram.

Along an interference fringe obtained from the free diffusion experiment (see Figure 3), we have the relationship

$$n_2(y_2 + \phi) = n_\infty(y_1 + \phi) \quad (5)$$

and, therefore, ϕ is given by

$$\phi = \frac{n_2 y_2 - n_\infty y_1}{n_\infty - n_2} \quad (6)$$

We note here that the same reference line is used to analyze each experiment. In principle, this could be achieved experimentally by etching or plating a line on the bottom plate of each wedge, extending from near the edge where the membrane is located to the hole for the reference experiment. This line would then appear in the photographs of interference fringes generated from the membrane transport experiment and also in the photograph of the free diffusion experiment and thus would serve as a convenient reference line for both types of fringes. However, because such a line is difficult to produce without disturbing the coating on the wedge plates, an alternate procedure was followed in this study. Specifically, after the interference fringes next to the membrane were photographed, the microscope stage was moved perpendicularly to the membrane until the reference run hole could be viewed through the eyepiece. The reference free diffusion experiment was then initiated, and the resulting interference fringes were photographed. The interferograms for both the free diffusion and membrane transport experiments were subsequently analyzed with

the edge of the interferogram photograph used as a reference. This edge would be the same distance from the wedge apex in all photographs as long as the microscope slide movement was maintained perpendicular to the membrane. Substitution of Equation (6) into Equation (4) gives

$$\frac{n_z - n_\infty}{n_2 - n_\infty} = \frac{y_z - y_\infty}{(y_2 - y_1)(1 + q)} \tag{7}$$

where

$$q = \left(\frac{y_z - y_2}{y_2 - y_1}\right)\left(\frac{n_\infty - n_2}{n_\infty}\right) \tag{8}$$

Although Equations (7) and (8) can be used directly to determine the refractive index distribution, it is convenient to take advantage of the fact that the magnitude of q is typically about 0.01 and to derive the approximate result

$$\frac{n_z - n_\infty}{n_2 - n_\infty} = \frac{y_z - y_\infty}{y_2 - y_1} \tag{9}$$

which is the first term of a series expansion. This equation is sufficiently accurate for most experimental purposes and has the advantage that it involves only two distance measurements ($y_z - y_\infty$ and $y_2 - y_1$), one from the photograph of the membrane transport experiment and one from the free diffusion photograph. Once the refractive index distributions were calculated for the ethyl alcohol-water solutions surrounding the membrane, they were converted to concentration distributions by using the following refractive index-mass fraction relationship:

$$n = 1.3330 + 5.8143 \times 10^{-2}\,\omega_A + 1.0739 \times 10^{-1}\,\omega_A{}^2 - 2.4350 \times 10^{-1}\,\omega_A{}^3 \tag{10}$$

This equation represents a least-squares polynomial fit of refractive index data (Washburn, 1930) for the ethyl alcohol-water system at 25°C in the concentration range 0 to 30 wt% ethyl alcohol.

Analysis of Diffusive Transfer

Since the experiment is devised so that there are no velocity components and concentration gradients in the closed diffusion cells in planes parallel to the membrane, the only nonzero components of the mass fluxes of the diffusing materials are in a direction normal to the membrane. Also, since the diffusion field is one dimensional and steady and since there are no chemical reactions, it follows from utilization of species continuity equations and jump species mass balances that the mass fluxes of ethyl alcohol and water, n_A and n_W, are the same everywhere in the liquid-membrane-liquid system. Finally, since the system is isothermal, since the effect of pressure gradients on the diffusion flux can be considered negligible, and since the membrane material is effectively insoluble in the surrounding liquid phases, the mass transfer process in each liquid phase can be described by an equation of the following form:

$$n_W = \omega_W(n_A + n_W) - \rho D\frac{d\omega_W}{dz} \tag{11}$$

Determination of n_A and n_W for each liquid phase is based on the utilization of Equation (11) in conjunction with the measured concentration distributions in the liquid phases. The method developed below allows for the determination of both n_A and n_W from data on only one side of the membrane and hence permits an independent check on the consistency of the flux calculations. Furthermore, the analysis involves integration rather than differentiation of the data, utilizes the complete measured concentration distribution, and does not require that the concentration profile be known right up to the membrane surface.

Integration of Equation (11) from $z = z_o$ where $\omega_W = \omega_{WO}$ to $z = z$ where $\omega_W = \omega_W$ gives

$$Y = (n_A + n_W)X - n_W \tag{12}$$

where

$$Y = \frac{\int_{\omega_{WO}}^{\omega_W} \rho(\omega_W) D(\omega_W)\, d\omega_W}{z - z_o} \tag{13}$$

$$X = \frac{\int_{z_o}^{z} \omega_W\, dz}{z - z_o} \tag{14}$$

The quantities Y and X can be determined directly from the measured mass fraction distribution and from the following equations describing the mass fraction dependence of ρ and D:

$$\rho = 9.9709 \times 10^{-1} - 1.9328 \times 10^{-1}\,\omega_A + 3.3922 \times 10^{-1}\,\omega_A{}^2 - 7.0370 \times 10^{-1}\,\omega_A{}^3 \tag{15}$$

$$D = 1.240 \times 10^{-5} - 3.380 \times 10^{-5}\,\omega_A + 3.948 \times 10^{-5}\,\omega_A{}^2 - 1.936 \times 10^{-5}\,\omega_A{}^3 \tag{16}$$

These equations are least-squares polynomial fits to density and diffusivity data (expressed in grams per cubic centimeter and square centimeters per second, respectively) for the ethyl alcohol-water system at 25°C in the concentration range 0 to 30 wt % ethyl alcohol (Perry, 1950; Hammond and Stokes, 1953). From Equation (12), it is evident that a plot of Y vs. X will give a straight line with a slope equal to $(n_A + n_W)$ and an intercept of $(-n_W)$. Such a plot can be made for each liquid phase, and, hence, two estimates of both n_A and n_W can be readily determined.

Unfortunately, the membrane thickness and the liquid phase concentrations at the liquid-membrane interfaces can not be determined directly from photographs of the diffusion field because of the presence of the blind zone discussed above. However, excellent estimates of these quantities can be deduced by applying the following integrated form of Equation (11)

$$z - z_o = \int_{\omega_{WO}}^{\omega_W} \frac{\rho(\omega_W)\, D(\omega_W)\, d\omega_W}{\omega_W(n_W + n_A) - n_W} \tag{17}$$

and by utilizing the following procedure:

1. Assume the membrane is located in the center of the blind area and estimate a membrane thickness.
2. Using known values of n_W and n_A and Equations (15) and (16) for ρ and D, calculate the liquid phase mass fractions of ethyl alcohol at the liquid-membrane interfaces utilizing Equation (17).
3. Calculate a new membrane thickness by using the average of the two ethyl alcohol interfacial mass fractions and applying Equation (1).
4. Repeat the procedure until the iterative calculation scheme for the membrane thickness and the interfacial mass fractions has converged.

The uncertainty of the membrane position and the utilization of an average mass fraction in Equation (1) for the calculation of membrane thickness led to errors of less than 5% in the liquid phase mass fractions at the membrane surfaces and in the membrane thickness. Finally, we note that, by using Equation (1), we are assuming that the swelling of the membrane during a transport experiment is approximately isotropic.

Table 1. Calculated Membrane Transport Data

Run number	Mass fractions, ω_A, in flowing solutions	Liquid phase mass fractions, ω_A, at liquid-membrane interfaces	$n_A \times 10^6$, g/cm² s	$n_W \times 10^5$, g/cm² s	Membrane thickness, mm
1	0.30	0.127	3.24	−1.22	0.0373
	0	0.0394	3.41	−1.32	
2	0.30	0.150	1.22	−1.52	0.0364
	0.05	0.0767	1.44	−1.30	
3	0.30	0.175	−0.850	−2.12	0.0354
	0.10	0.123	−1.55	−2.82	
4	0.20	0.0894	2.71	−1.47	0.0380
	0	0.0347	3.41	−1.70	
5	0.20	0.127	0.724	−1.58	0.0368
	0.05	0.0709	0.833	−1.98	

RESULTS AND DISCUSSION

The results of five experiments carried out on the ethyl alcohol-water-cellophane membrane system at room temperature are presented in Table 1. The same membrane was used in all five experiments so that membrane variations would not complicate the results. For each experiment, twenty fringe position measurements were read from the interferogram for each side of the membrane with an interval between points of approximately 0.005 cm. These measurements were then used to calculate mass fraction distributions in the manner described above. The mass fraction profiles for run 1 are presented in Figure 4, and the corresponding Y-X plots for this run are given in Figure 5. The points in Figure 5 were fit by a linear least-squares method, and two independent estimates for both n_A and n_W, deduced from the slopes and intercepts of the straight lines, are included in Table 1. Liquid phase mass fractions at the membrane-liquid interfaces and the membrane thickness, calculated by the scheme described above, are also included in Table 1. The data presented in this table represent the maximum information that can be deduced experimentally about the transport process when no measurements of the concentration distributions in the membrane are available. These data, coupled with liquid-membrane equilibrium measurements, can be used as a means of elucidating the membrane transport mechanism, but this is beyond the scope of the present paper and we do not pursue it here.

Comparison of the n_A and n_W values calculated from the liquid phases on both sides of the membrane shows an average deviation about a mean value of the flux of approximately 10% and a maximum deviation of 29%. The cause of these variations has not been ascertained. However, it is felt that the major source of error is associated with taking measurements from the interferogram photographs, owing to some lack of sharpness in the interference patterns. Another possible source of error is a small difference in the cross-sectional areas of the wedges in a direction normal to the membrane.

It is evident that the membrane is significantly more permeable to water than to ethyl alcohol. The water mass flux is from four to about twenty-five times as large as the mass flux of ethyl alcohol, and one consequence of this difference is illustrated by run 3. For this run, the amount of ethyl alcohol carried with the mass average velocity is larger than the diffusive contribution, and, in this particular experiment, ethyl alcohol undergoes net mass transfer against its concentration gradient.

In summary, it is fair to conclude that the membrane wedge interferometer provides an accurate method of studying membrane transport without the troublesome complications which characterize other methods. Since there appears to be no standard against which the data from a new membrane experiment can be compared, no definitive estimate of the accuracy of the technique is available. However, since this technique is based on proven optics, and since no significant assumptions or approximations are imposed on the analysis of the interferometric data, it is reasonable to believe that accuracy can be attained which approaches the 3% accuracy

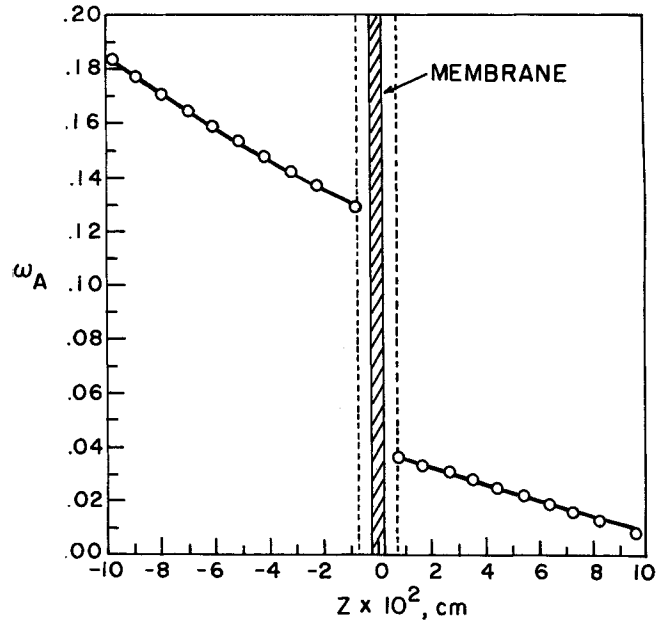

Fig. 4. Mass fraction profiles for run 1. Dotted lines represent extent of blind zone.

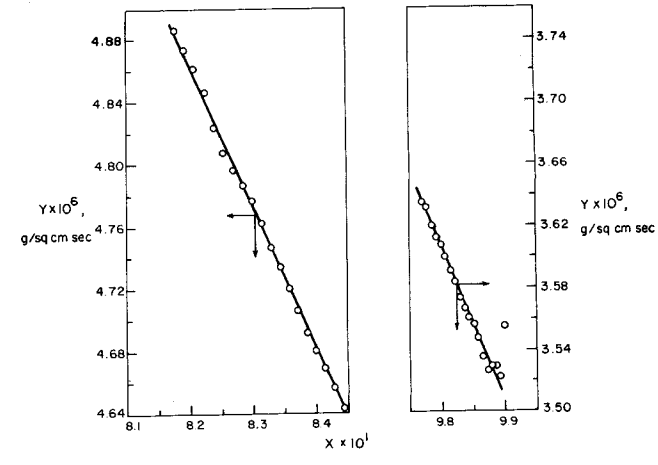

Fig. 5. Y-X plots for run 1.

which has been attained for liquid diffusivity measurements with the wedge interferometer by Duda et al. (1969). The only significant disadvantages of the technique are the fact that it is probably more difficult to carry out an experiment with this apparatus than with the equipment utilized in previous investigations and the fact that accurate diffusivity data must be available. However, such data can be generated from appropriately conducted free diffusion experiments by using the wedge interferometer.

ACKNOWLEDGMENT

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

NOTATION

d = wedge thickness
D = binary mutual diffusion coefficient
L = membrane thickness
n = refractive index
n_A = mass flux of alcohol with respect to a fixed reference frame
n_W = mass flux of water with respect to a fixed reference frame
n_z = refractive index along a fringe at position z
n_2 = refractive index of solution used for reference free-diffusion experiment
n_∞ = refractive index of flowing solution
q = quantity defined by Equation (8)
X = quantity defined by Equation (14)
y = distance variable parallel to membrane
y_z, y_1, y_2, y_∞ = fringe positions defined in Figure 3
Y = quantity defined by Equation (13)
z = distance variable normal to membrane
z_o = reference position in diffusion field

Greek Letters

λ = wavelength of monochromatic light
ν = integer
ρ = total mass density of binary liquid phase solution
ϕ = distance of reference line from wedge axis
ω_A = mass fraction of alcohol
ω_W = mass fraction of water
ω_{WO} = mass fraction of water at z_o

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Manuscript received August 1, 1975; revision received November 4, and accepted November 5, 1975.

Prediction of Transport Processes Within Porous Media: Diffusive Transport Processes Within Anisotropic or Isotropic Swarms of Nonspherical Particles

The effects of particle shape and orientation upon diffusive transport processes occurring within unconsolidated porous media are investigated analytically. By means of a generalization of an earlier presented geometric model, diffusivities are predicted for both anisotropic systems (represented by swarms of aligned oblate or prolate spheroids) and isotropic systems (represented by swarms of randomly orientated spheroids). Theoretical predictions are compared with experimental data reported in the literature.

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