Measurement of Transport Enhancement in Oscillatory Liquid Membranes

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As discussed by Noble and Way (1987), supported liquid membrane systems possess potential (as yet largely unrealized) for commercial separations of components in the liquid phase. Because of their ability to implement carrier species within a liquid membrane barrier, a great deal of chemically specific selectivity can be achieved. An undesirable side effect, however, is the generally low rate of transport that occurs for membranes which are thick enough to have structural integrity. Recently, Leighton and McCready (1988) suggested that enhancement to the transport of the solute (+carrier) species across the membrane of two or more orders of magnitude could be achieved by imposing an oscillatory pressure gradient on the liquid membrane system. The theoretical limit is an effective membrane thickness on the order of the pore *diameter*.

Enhancement of transport for large molecules in oscillatory shear flows was previously predicted by Horn and Kipp (1967) and Harris and Goren (1967) for high Schmidt numbers and has been experimentally investigated for small Schmidt numbers by Rice (1974) and Joshi et al. (1983). Because the enhancement is the result of the interaction of molecular diffusion in the radial direction and convection along the length of the pore, the degree of enhancement is actually greater for large species which have low diffusivities. Thus, it is ideally suited for membrane systems because careful choice of oscillation frequency allows enhancement of the diffusivities of large molecules such as carrier-solute complexes, while those of smaller solute or solvent species are not enhanced. This last feature is particularly useful in dilute systems where concentration of the solute is desired.

Because of the potential promise of oscillatory membranes, it is worthwhile to confirm that the predicted enhancement will actually occur in a supported membrane system. In this paper we describe our experiments to verify the theoretical predictions. A glass frit impregnated with a light hydrocarbon oil was used as a membrane that separated two chambers containing dilute solutions of phenol in water. The oscillatory flow in the membrane was produced by the use of a syringe pump. The data presented below demonstrate that enhancements in the rate of phenol transfer across the membrane of nearly 200 times the molecular diffusivity rates were achieved. Furthermore, the observed predictions of the dependence of the rate enhancement on the oscillation frequency and stroke volume agree with theoretical predictions. At the conditions of highest achieved enhancement, the effective thickness of the 2 mm membrane was approximately 12 μm.

Experimental Apparatus

The apparatus used in the oscillatory liquid membrane experiments is depicted in Figure 1. An oscillating syringe pump is coupled to the lower of two chambers separated by a liquid membrane. The membrane (depicted in Figure 1) consists of a coarse glass frit with an area of 2.84 cm^2 and a thickness of 2 mm, impregnated with the light isoparaffinic solvent, Exxon S100N. This fluid, which has a viscosity of 44 cp (44 mPa · s) at room temperature, was chosen since it has been used in the emulsified liquid membrane experiments of Li and Shrier (1972) and Ho et al. (1982). Phenol, which has a diffusivity of 0.65×10^{-6} cm^2/s in the oil phase and a partition coefficient of 0.52 between the oil and aqueous phases as reported Ho et al. (1982) was used as the tracer species. In order to make the oil impregnation stable, the glass frit was first treated with Scotchguard, a fluoroaliphatic resin in 1,1,1,-trichloroethane. The treatment involved drawing the Scotchguard, thinned with additional 1,1,1,-trichloroethane, through the support using vacuum. Impregnation with the oil phase was then accomplished by drawing the oil into the glass frit with a vacuum.

A series of experiments were performed to establish the stable

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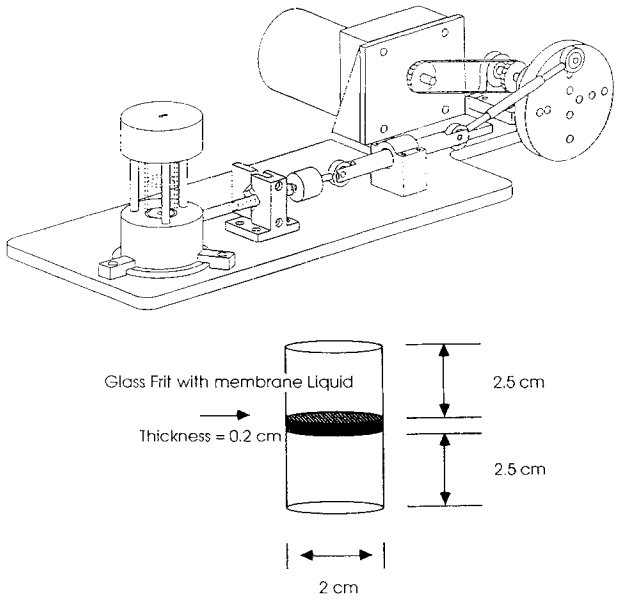

Figure 1. Experimental apparatus and liquid membrane cell.

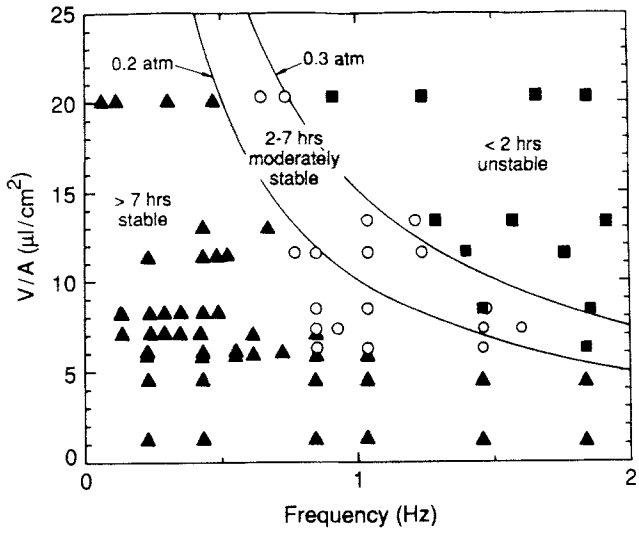

Figure 2. Membrane stability.

operating boundaries of the membrane system. Obviously, if the stroke volume were too large, the oil would be completely forced out of some of the pores, thus rupturing the membrane. Likewise, if the frequency of oscillation were too large, the pressure drop could be too high for the membrane to support, also leading to rupture. The stability experiments were conducted by loading water with a high concentration of green dye into the lower chamber at the start of the experiment. If the membrane ruptured during operation, the dye would be observed to penetrate into the upper chamber which initially contained clear water.

The transfer rate experiments were performed by initially filling the lower chamber with a 1% phenol solution. Dye was also always added to the lower chamber. Samples removed from the upper chamber, which initially contained distilled water, were analyzed using gas chromatography to determine the transfer rates. Experiments were done for stroke volumes ranging from 0.009 mL to 0.058 mL and for oscillation frequencies ranging from 0.021 Hz to 1.08 Hz.

Results

Figure 2 shows a graph of the membrane stability as a function of stroke volume and frequency. If rupture occurred, it was generally observed to first occur through only a few pores. Except for the most severe conditions where rupture occurred immediately, the rupture process appeared to be caused by the gradual displacement of membrane oil by water. If the values of the elapsed time until rupture are binned into <2, 2-7 and >7 hours, suggestive of unstable, moderately stable and highly stable membranes, respectively, the stability of the membrane is roughly defined by a hyperbola which, for Figure 2, represents a constant amplitude of the pressure drop. While the pressure drop across the membrane was not directly measured during the mass transfer experiments, it could be inferred from separate steady pressure drop/flow rate experiments conducted with water and cyclohexane on both the untreated and treated membrane support. The pressure difference corresponding to the transition from the highly stable to moderately stable state was calculated to be 0.2 atm and that from the moderately stable to unstable state to be about 0.3 atm. It should be pointed out that the amplitude of the oscillatory pressure drop at rupture is nearly an order of magnitude greater than the capillary pressure. The membrane is stable above the capillary pressure, because the *average* pressure drop is zero and the total volumetric flow of the fluid through the membrane support is controlled by syringe pump. In a practical system where a high degree of stability is required it may be possible to incorporate a thin layer of microporous material in the interior of the membrane support to form a capillary pressure barrier against rupture.

The concentration in the upper chamber both with and without oscillations showed a linear increase in phenol concentration with time. The experiments were conducted at each selected frequency and stroke volume for a sufficiently long period of time (2–10 hours) that a reliable rate of increase could be measured. Figure 3 shows the measured mass transfer coefficient made dimensionless with the mass coefficient observed with no oscillation as a function of the oscillation frequency for different stroke volumes. It is seen that the degree of enhancement due to oscillation is substantial (a factor of nearly 200 at highest frequency and stroke volume studied) and that it is an increasing function of frequency and stroke volume. The degree of enhancement was found to be repeatable for different trials, with the mass transfer coefficients from the separate impregnations usually lying within 20% of each other.

Analysis

In order to understand the results of these experiments it is necessary to model the interaction of diffusion and convection for oscillatory flow in a porous support. Unfortunately the structure of a glass frit is quite complex and does not lend itself easily to exact analysis. Indeed, the most general theoretical results to date apply only for straight conduits of constant (arbitrary) cross-section (Watson, 1983). In order to make a first approximation to understanding the enhancement in the mass transport in our membrane we shall assume that it is composed of a spaghetti-like bundle of circular tubes of constant

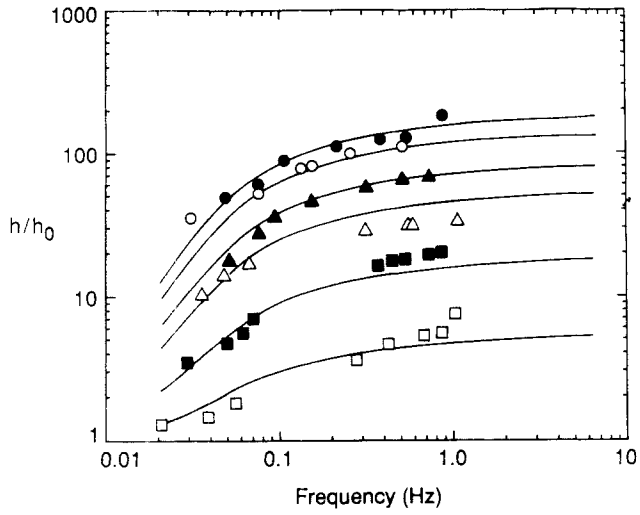

Figure 3. Comparison of observed enhancement with theory.

Stroke volumes were □9 μL, ■18 μL, △31 μL, ▲39 μL, ○50 μL, ●58 μL.

radii a and whose lengths are λL where L is the thickness of the membrane and λ is the tortuosity of the pores. In doing so we may apply the results of Leighton and McCready (1988) for straight tubes; however, we neglect all effects due to nonuniform radii between pores and the large variation in pore radii along fluid paths through the support. We shall also neglect the effects of the oscillatory meniscus flow near the surface of the membrane. Due to these approximations we expect the agreement between theory and experiment to be largely qualitative in nature.

For an imposed periodic oscillation of the form $\langle u \rangle = U \cos(\omega t)$ through a tube where $\langle u \rangle$ is the area average instantaneous velocity, Leighton and McCready (1988) showed (by use of the results of Joshi et al., 1983) that the relative degree of enhancement of transport at the high Schmidt number, low frequency limit (appropriate for liquid membrane systems) is given by:

$$\frac{K}{D} = 1 + \left(\frac{\Delta x}{a}\right)^2 \left[1 - \frac{4T_3(\beta)}{\beta T_2(\beta)}\right] \tag{1}$$

In this equation K is the effective diffusion coefficient, D is the molecular diffusivity, ω is the angular frequency, $\beta = a(\omega/D)^{1/2}$, and $\Delta x/a$ is the dimensionless tidal displacement. The functions $T_2(\beta)$ and $T_3(\beta)$ are defined as

$$T_2(\xi) = (ber')^2(\xi) + (bei')^2(\xi) \tag{2}$$

$$T_3(\xi) = ber(\xi)ber'(\xi) + bei(\xi)bei'(\xi) \tag{3}$$

where the functions $ber(\xi)$ and $bei(\xi)$ are Kelvin functions related to the Bessel function I_o by $I_o(\xi i)^{1/2} = ber(\xi) + i\, bei(\xi)$. It is convenient for the present approximate analysis to write Eq. 1 as

$$\frac{K}{D} = 1 + \left(\frac{K}{D} - 1\right)_\infty f\left(\frac{\omega a^2}{D}\right) \tag{4}$$

where the function $f(\omega a^2/D)$ may be determined from Eq. 1, and which approaches unity as the dimensionless frequency becomes large. This equation has been written in terms of the maximum theoretical enhancement at large frequencies:

$$\left(\frac{K}{D} - 1\right)_\infty = \left(\frac{\Delta x}{a}\right)^2 = \left(\frac{V}{\epsilon A L}\right)^2 \left(\frac{\lambda L}{a}\right)^2 \tag{5}$$

where V is the stroke volume, ϵ the void fraction, λ the tortuosity of the tubes, and A the area of the membrane. This last equality relates the tidal displacement and the maximum enhancement to the stroke volume (rendered dimensionless with the total volume of fluid in the pores) and the pore structure. For the treated glass frits used in this study, λ, a, and the void fraction ϵ, remain to be determined.

The void fraction of the support was measured by weight difference before and after wetting by various polar and nonpolar fluids to be about 0.18. It was found that the void fraction did not show a significant change due to the treatment with Scotchguard. We may further characterize the membrane structure by examining the mass transfer rate without oscillations h_o. Applying our model to this case, h_o is related to the structure by

$$h_o = \frac{\epsilon}{\lambda^2} \frac{D\alpha}{L} \tag{6}$$

where α is the partition coefficient and L is the membrane thickness. From a measured mass transfer coefficient with no oscillations of $1.34 \times 10^{-7} \pm 1.2 \times 10^{-8}$ cm/s and a void fraction of 0.18, we obtain an estimate of the tortuosity of 1.51. The only undetermined parameter remaining in the model is the pore radius.

In order to analyze our results we shall fit Eq. 4 and 5 to our data for all stroke volumes employed, using a single dimensionless pore length ($\lambda L/a$) and the pore radius a as adjustable parameters. As may be seen from Figure 3 the fit to the data is quite good. The radius calculated from the frequency dependence of the enhancement was found to be about 51 μm, in qualitative agreement with the scanning electron micrograph of the pore structure given in Figure 4. The best fit value of the dimensionless pore length was $\lambda L/a = 24.3$, significantly less than the value of 59.2 which would be predicted from the tortuosity calculated from the mass transfer coefficient with no oscillations and the pore radius estimated from the frequency response. This corresponds to an observed magnitude of the enhancement a factor of 5.9 below what would be expected from Eq. 5. While the causes of this deviation are uncertain, we speculate that it is in large part due to the large variation in pore diameter experienced by fluid elements as they flow through the complex support structure.

Although the maximum degree of enhancement in our experiments occurred under conditions where membrane life time was rather short (about 2 h), we expect that similar degrees of enhancement may be achievable with much greater membrane life times for diffusion of large molecular weight species. This should occur because large molecular weight species have much lower diffusivities which, in turn, allow the use of lower operating frequencies for the same dimensionless frequency and degree of enhancement. We found in our experiments that membrane stability is greatly increased at lower frequencies.

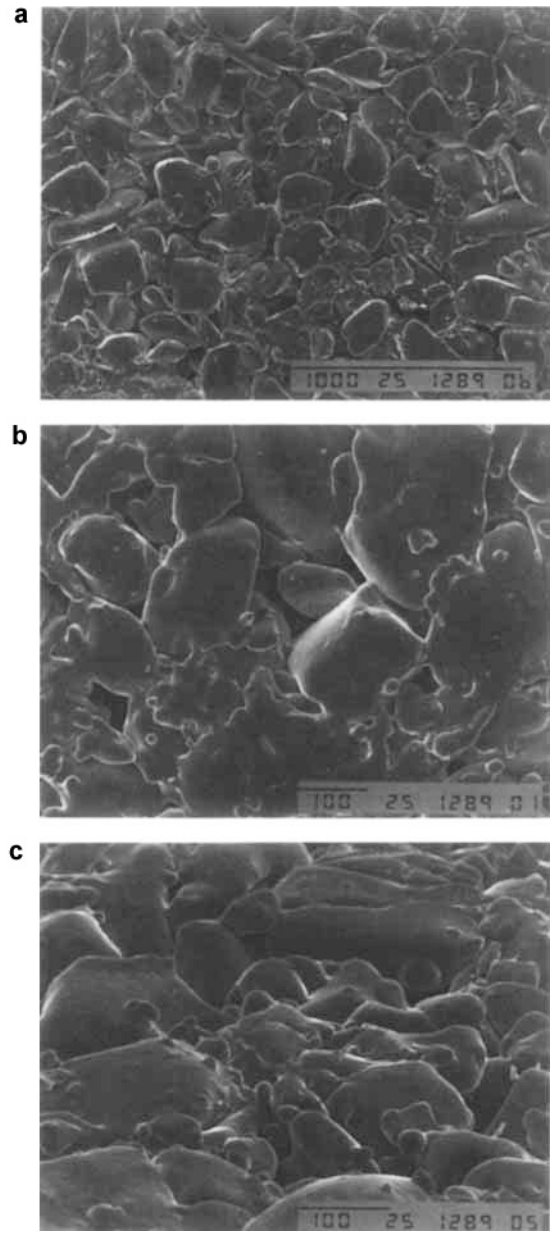

Figure 4. Membrane support.

Scanning electron micrographs of the surface of the membrane support are shown: a. zero incidence; b. zero incidence, higher magnification; c. 60° angle from zero incidence view reveals surface topology.

Stability may be further improved by the careful design of the membrane support.

The data presented above clearly demonstrate the significant enhancement in transfer which can be achieved by imposing an oscillatory flow on a liquid membrane system. Furthermore, while a glass frit is quite complex, the major qualitative features of the theory (e.g., dependence on frequency, pore radius, and the square of the stroke volume) are observed. The large deviation between the measured magnitude of the enhancement and that predicted from the model of the pore structure is not surprising given the simplicity of the model. The discrepancy does suggest, however, that the mass transfer rate can be dramatically improved over the already large values measured here if membrane supports with a larger void fraction and more uniform pore structure are employed.

Acknowledgment

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Notation

a = pore radius
A = membrane area
D = molecular diffusivity
h = mass transfer coefficient
h_o = mass transfer coefficient without oscillations
K = effective diffusion coefficient
L = membrane thickness
V = stroke volume

Greek letters

α = oil/water partition coefficient
$\beta = a(\omega/D)^{1/2}$
Δx = amplitude of tidal oscillation
ϵ = void fraction
λ = tortuosity
ω = angular frequency of oscillation

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