Shear Enhanced Transport in Oscillatory Liquid Membranes

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The development of improved separation processes will play a major role in the successful commercialization of new products manufactured by genetically altered organisms, solving continuing problems such as waste treatment and improving the overall competitiveness of the chemical industry. The objective of separation processes is to selectively remove a component from a mixture and concentrate it into a nearly pure form at reasonable rates, reliably and at an acceptable cost. While numerous separation schemes exist, lack of selectivity, low throughputs, long down times for recharging, and difficulties with handling thermally or chemically labile material are still limitations. As a consequence, recognizing their profound impact on the process industries, there is considerable room for improved separation schemes.

One separation technique which has a great deal of unrealized potential is the use of liquid membranes. Noble and Way (1987 a) note that these membranes potentially provide both high selectivity and high solute flux through the use of chemical complexing agents which act as carriers, can be used for a reaction-separation device, and allow for the concentration of the product. In addition, cost of the liquid and carriers should not be a problem since relatively small amounts are used to impregnate the membranes and losses should be minimal. Economic analyses and pilot plant studies described by Noble and Way (1987 b) indicate that in its present state, liquid membrane technology should be competitive with liquid extraction for a number of processes. However, despite its promise, as of mid 1986 only one full-scale commercial venture used liquid membrane technology (Noble and Way, 1987 b).

The lack of use of liquid membrane technology in the separations industry may be ascribed largely to the difficulties of translating laboratory devices into large scale processes. Because of costs and difficulties associated with creating and breaking stable emulsions, liquid surfactant membranes seem to be an attractive alternative to traditional processes only when species must be extracted to very low levels, such as recovery of metal ions or removal of organic compounds from water to be discharged into the environment. Supported liquid membranes avoid many of the problems of emulsions, however they suffer from difficulties associated with solvent stability within the membrane and from relatively low solute transport rates. The use of membranes of increased thickness improves solvent and membrane stability, but greatly reduces transport rates. Process reliability considerations further limit their use due to a need for short recharging intervals.

In this paper, a novel procedure for dramatically increasing solute fluxes through supported liquid membranes, which should be readily realizable both in the laboratory and in process size equipment, is described. The imposition of a periodic pressure gradient transverse to the membrane is shown to increase the effective diffusivity of large molecules through the membrane by as much as two orders of magnitude or more, effectively eliminating the resistance to mass transport provided by the bulk of the liquid membranes. The enhancement provided by this periodic motion is superficially similar to that found in Taylor-Aris dispersion for steady flow in that the dispersion arises from the diffusion of the solute between streamlines with differing velocities. However, the relative enhancement can be "tuned" by adjusting the frequency to an optimal value which should allow for a degree of selectivity, particularly in the concentration of solutes from much smaller solvent molecules. In fact, as will be shown below, it is possible in principle to cause the effective diffusivity of a large molecule to actually be greater than that of a much smaller species.

The dramatic increase in transport rates should allow for wider application of liquid membranes because the thinness of the support will no longer be the overriding consideration. Better membrane stability would be easily achieved by using a greater membrane thickness without significantly affecting transport rates, and the increased inventory of solvent + carrier should enable much longer operation times. In addition, if membranes which have a three-dimensional pore structure are used, it may be possible to regenerate these membranes continuously by pumping additional solvent and carrier into the membrane perpendicular to the transport direction.

Transport Enhancement:

The enhancement in the mass transfer rate provided by the proposed device relies on convection provided by an oscillatory shear flow. A pressure differential applied across the membrane which is periodic in time will induce a flow, essentially an up and down (or back and forth) motion in the pores, without disrupting the membrane since there is no *net* convection through the membrane at the end of one period of oscillation. For the purposes of the present discussion, a membrane will be viewed as a bundle of circular tubes, making the pertinent physical problem axial transport in a circular tube. Because the enhancement in transport under consideration here results from the shearing motion of the fluid—which occurs during flow in both a tube and in a random pore structure—rather than actual inertia-induced fluid mixing, this model should contain the essential features of the physics which would occur in a membrane. However, the solution and analysis are much simpler for the assumed geometry and make it possible to clearly describe the mechanism which leads to enhancement.

A complete solution to the problem of oscillating flow in a tube has been available for almost 30 years (Aris, 1960) but the potential applications to enhancing diffusion for large molecules in liquid membranes and, as will be seen below, the substantial degree of selectivity which can occur has apparently not been previously realized. Therefore it is of interest to present the solution, explain the underlying physical phenomena and explore its consequences toward the transport of molecules through small pores.

The mechanism leading to enhanced transport can be seen by examining axial transport for the laminar pipe flow depicted in Figure 1. Transport in the direction of motion (z-direction) can be achieved either by molecular diffusion in the z direction or by diffusion in the r direction to a faster moving streamline, followed by convection. For *steady* flow, considering transport relative to the plane of no net flow, the ratio of the effective diffusion coefficient, K, to the intrinsic diffusion coefficient, D is given by Aris (1956) as

$$\frac{K}{D} = 1 + \frac{a^2 u^2}{48 D^2} \tag{1}$$

where a is the tube radius and U is the average velocity. If the molecular diffusivity is sufficiently large, (i.e. $D \sim aU$) radial concentration gradients will not form and little enhancement will result. However, if D is very small, axial transport will be greatly enhanced due to the parabolic velocity profile shape in which the certerline velocity is 2 times the average velocity. It should be noted that the necessity of having a net flow occur limits its use of this phenomena for separation operations.

For *periodic* tube flows, quite a different result is observed. If we impose a periodic oscillation such that $u = U\cos\omega t$, then the degree of enhancement which occurs is given by Joshi et al., (1983) as

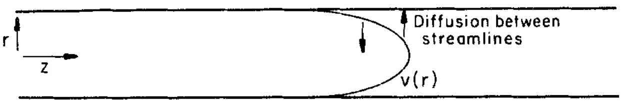

Figure 1. Schematic of Taylor Dispersion.

$$\frac{K}{D} = 1 + h(\alpha, \sigma)\left(\frac{\Delta x}{a}\right)^2 \tag{2}$$

where

$$h(\alpha, \sigma) = \frac{\alpha^3}{4(1-\sigma^{-2})}\,\frac{T_3(\alpha) - \dfrac{T_2(\alpha)T_3(\beta)}{\sigma^{1/2}T_2(\beta)}}{\alpha^2 T_1(\alpha) - 4\alpha T_4(\alpha) + 4T_2(\alpha)}$$

and

$$\begin{aligned} T_1(\xi) &= \mathrm{ber}^2\xi + \mathrm{bei}^2\xi \\ T_2(\xi) &= (\mathrm{ber}')^2\xi + (\mathrm{bei}')^2\xi \\ T_3(\xi) &= \mathrm{ber}\,\xi\,\mathrm{ber}'\xi + \mathrm{bei}\,\xi\,\mathrm{bei}'\,\xi \\ T_4(\xi) &= \mathrm{ber}\,\xi\,\mathrm{bei}'\,\xi + \mathrm{ber}'\,\xi\,\mathrm{bei}\,\xi \\ \beta &\equiv \alpha\sigma^{1/2} \end{aligned}$$

which is written in terms of the Womersley number $\alpha = a(\omega/\nu)^{1/2}$ where a is the tube radius, ω is the angular frequency, ν is the kinematic viscosity, the Schmidt number $\sigma = \nu/D$, and the dimensionless tidal displacement is $\Delta x/a$. In this expression the functions ber(ξ) and bei(ξ) are Kelvin functions, related to the Bessel function I_0 by $I_0(\xi i^{1/2}) = \mathrm{ber}\,\xi + i\,\mathrm{bei}\,\xi$.

The influence of periodic flow on mass transport in conduits, first examined by Aris (1960) for arbitrary Reynolds and Schmidt numbers in circular conduits, has recently received renewed attention. In particular, it has been investigated theoretically by Watson (1983), experimentally for fluids with $\sigma = O(1)$ by Joshi et al. (1983), and in connection with energy transport in tubes of circular cross-section by Kurzweg and de Zhao (1984). The data presented by Joshi et al. (1983) for transport of methane through air show agreement with the theoretical expression given above, with substantial enhancement of the transport rate being found. It must be noted however that for the value of the Schmidt number used in the experiments, $\sigma \sim 1$, the required oscillation frequency was sufficiently great that inertia effects became important, somewhat limiting the degree of enhancement. This arises for their values of σ and α, because the shear flow in the tube and therefore the flow area in which enhancement occurs, is confined to a narrow region near the walls. Under some circumstances enhancement is also limited by transition from laminar to turbulent flow.

Such limitations do not arise in the transport of larger molecules through the more viscous fluids used in liquid membranes. In the past, researchers have examined transport in tubes as a function of the Womersley number for fixed values of the Schmidt number. For the situation of interest here, the Schmidt number is on the order of 10^6 or more, thus it is no longer appropriate to examine the mass transfer as a function of α and σ independently, but rather as a function of $\beta = \alpha\sigma^{1/2} = (\omega a^2/D)^{1/2}$. Since the ratio $\alpha/\beta = \sigma^{-1/2} \ll 1$ for liquid membrane systems, the Womersley number is small even for large values of β and inertia effects are small. We will thus focus our attention on this limit; i.e. the limit as $\alpha \rightarrow 0$ and $\sigma \rightarrow \infty$, but where the product $\beta = \alpha\sigma^{1/2}$ is order one. From Eq. 2 we obtain

$$\frac{K}{D} = 1 + \left(\frac{\Delta x}{a}\right)^2 \left(1 - \frac{4}{\beta}\frac{T_3(\beta)}{T_2(\beta)}\right). \qquad (3)$$

Note that the degree of enhancement is proportional to $(\Delta x/a)^2$, and that the enhancement is a function of the dimensionless frequency of oscillation β. Physically, this parameter represents the square root of the ratio of the characteristic molecular diffusion time across the tube to the period of oscillation. A plot of the enhancement of mass transport for tubes as a function of frequency is given in Fig. 2. The augmentation approaches a maximum value at high dimensionless frequencies, however since the Schmidt number for liquid membrane systems ν/D is on the order of 10^6 or greater, the high frequency limit can be achieved under creeping flow conditions.

It is appropriate to consider at this point typical parameters which might be used in the implementation of this mode of transport enhancement in a fluid membrane system. Consider a liquid membrane phase with a viscosity of .1Pa · *s* and a solute with diffusion coefficient of 10^{-12} m^2/s, typical values for a large molecule diffusing through oil. To achieve a high degree of augmentation we require a value of β of about 10 (70% of the maximum augmentation for a given tidal oscillation) and $\Delta x/a$ also on the order of 10, yielding a relative increase in the transport rate of about 70—nearly two orders of magnitude. In order for the membrane to be stable with this magnitude of tidal oscillation, we shall require that the length L of the membrane be much greater than Δx, say $L/\Delta x = 10$, requiring $L/a = 100$. For a thick membrane with a length of 1mm and pore radii of 10 μm, this parameter range can be achieved with an oscillatory frequency of 1 radian/*s* (.16 Hz) and a maximum pressure differential (calculated assuming Poiseuille flow) of only 400 Pa. It should be noted that this pressure is much less than the typical capillary pressure of 10^4 Pa for this pore radius, thus the membrane will not be disrupted. While this membrane is quite thick (leading to increased stability), its predicted mass-transfer-resistance is that of a membrane only 1/70 as thick, or about 14 μm. Of course, we have neglected end effects in this calculation, thus the actual resistance to mass transfer will be somewhat higher, depending on the exact geometry of the end regions. The mass transfer should still be substantially improved, however, with the resistance to transfer of the bulk of the membrane effectively eliminated. For a pore size of 1 μm and thickness of 100 μm the same relative enhancement can be obtained at a frequency of 16 Hz and a pressure differential of 4×10^4 Pa, still readily achievable and less than the capillary pressure for this pore size.

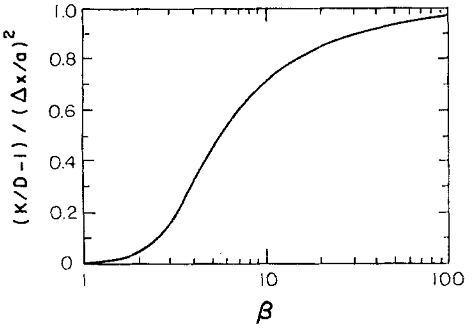

Figure 2. Degree of enhancement as a function of β.

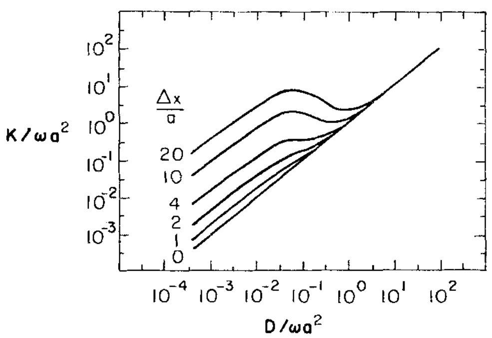

Figure 3. Plot of effective diffusivity vs. molecular diffusivity.

It is important to note that for a fixed frequency and pore radius the degree of enhancement is a function of molecular diffusivity, with the transport rate of molecules with low diffusivities being augmented to a greater degree than those with higher diffusivities. Molecules for which $\beta \ll 1$ receive essentially no augmentation in transport since they diffuse across the tube during a time which is much shorter than the period of oscillation, and thus simply move back and forth in the tube with the average velocity of the fluid. In Fig. 3, a plot of the dimensionless effective diffusivity *vs.* the dimensionless molecular diffusivity and a range of values of $\Delta x/a$ is shown. The family of curves is seen to exhibit a maximum if $\Delta x/a$ is greater than about 4 leading to the rather surprising result that it is actually possible to cause a large, low diffusivity molecule to travel faster than a smaller high diffusivity component. For example, if $\Delta x/a$ is 10, a component with a dimensionless molecular diffusivity of 10^{-1} will experience an effective diffusivity of 2 while a molecule with a molecular diffusivity which is 10 times greater will not be enhanced. The net result will be that the *larger* molecule will have a higher effective diffusivity by a factor of 2. For greater values of $\Delta x/a$, an arbitrary degree of relative enhancement can be obtained. In addition, changing the frequency of oscillation or the pore radius will make it possible to locate the minimum effective diffusivity (e.g., the region where the second derivative is positive) at any desirable value of the intrinsic diffusivity. As a consequence, if a facilitated transport system is being used to concentrate a solute from a smaller solvent, or if a carrier species is being used to aid in separation of two similar components, the frequency of oscillation can be adjusted to augment the transport of the large complexes without significantly increasing the rate of solvent transport. This feature of the solution for transport in tubes, which has not been previously recognized, has the potential to greatly increase the selectivity of liquid membranes.

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Notation

a = tube radius
D = molecular diffusivity

K = effective diffusion coefficient
L = length of pore
U = average velocity

Greek letters

α = Womersley number $a(\omega/\nu)^{1/2}$
β = $a(\omega/D)^{1/2}$
Δx = amplitude of tidal oscillation
ν = kinematic viscosity
σ = Schmidt number ν/D
ω = angular frequency of oscillation

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