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Enhanced Diffusional Separation in Liquids by Sinusoidal Oscillations

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Abstract

A general analysis of the problem of enhanced diffusional separation of dilute liquid solutions contained within open ended capillary tubes and subjected to axial oscillations is presented. Results show that the mass diffusion flux of the various components is equal to the product of the molecular diffusion coefficient of the species in question, the magnitude of the species axial concentration gradient, the square of the ratio of the tidal displacement to the capillary radius, and a function of the Womersley number. The earlier results of Dryer are shown to be correct for small oscillation frequencies and tube diameters, but predict effective diffusion coefficients which are too low at higher Womersley numbers. Differential diffusion separation fluxes some six orders of magnitude larger than possible with the same geometry in the absence of axial oscillations appear to be achievable for typical aqueous solutions.

INTRODUCTION

In the late 1960s Lange and his colleagues (*1*) developed a method for separating components in dilute aqueous solutions by the use of an enhanced diffusion process involving the axial movement of liquids in and out of open ended capillary tubes while maintaining an axial concentration gradient for the species to be separated. Very large increases in effective diffusion coefficient over the values found in the absence of oscillations where observed. The physical mechanism for this enhanced diffusion is the very large increase in cross-sectional area which becomes available for diffusion by the formation of viscous

boundary layers along the capillary walls during the oscillation process. One of the curious results found was that the axial diffusion mass flow is independent of both the oscillation frequency and the tube radius.

More recently there have appeared several papers (*2–5*) which treat the general problem of enhanced diffusion produced by sinusoidal oscillations. These studies, which were apparently unaware of the earlier work of Dryer (*1*), clearly show that enhanced species diffusion in fluid mixtures is very much a function of oscillation frequency and capillary diameter. Indeed, recently we found (*6*) that enhanced diffusion by oscillations is a tuning process in the sense that for a given oscillation frequency and molecular diffusion coefficient, there will be one particular tube radius for which the diffusion mass flow is maximized. This critical radius corresponds approximately to the distance the diffusing species diffuses in the radial direction during one-half cycle of the oscillation period. The tuning effect has been used most recently to separate components within gas mixtures (*7*).

It is the purpose of the present paper to resolve the apparent discrepancy between the semiquantitative results of Ref. *1* on enhanced diffusion in liquids with a more rigorous analysis based on an approach similar to that used by Watson (*4*). We will confine our attention to enhanced diffusion in liquids only. This will allow considerable simplification in the analysis since a perturbation expansion in reciprocal powers of the Schmidt number (which is large for liquids) becomes possible. In the analysis we obtain not only the value of the enhanced diffusion mass flux for additives in dilute liquid solutions but also obtain the magnitude of the differential diffusion mass flow expected in the separation of multicomponent mixtures. The observation of Ref. *1* concerning independence of tube radius and oscillation frequency on diffusional mass flow is shown to be correct only as long as the Womersley number remains small.

FORMULATION OF THE PROBLEM

Consider a bundle of N open-ended capillary tubes of radius $r = a$, each of which are bent into the C shape configuration shown in Fig. 1 and connected to a two chamber reservoir separated by a movable piston. The average length of the capillary tubes is L, and their total cross section $A_0 = N\pi a^2$, when excluding wall cross-sectional area and assuming blocked interstitial spaces. The left chamber (2) is initially filled with a carrier fluid (water) while the right chamber (1) is filled with a dilute

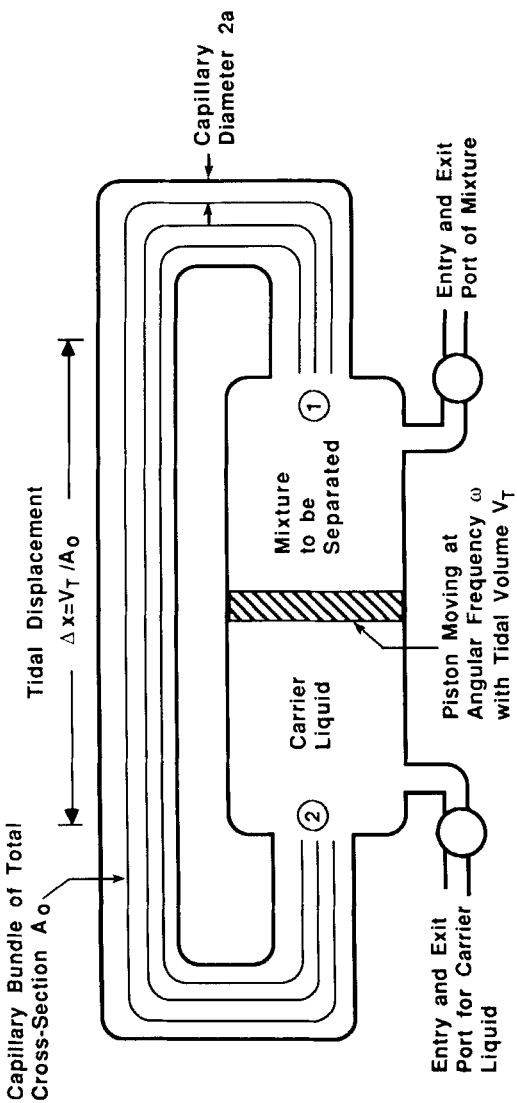

FIG. 1. Geometry of the problem under consideration.

solution containing both a light (L) and heavy (H) molecular weight additive within the same carrier fluid. The left and right halves of the capillaries are filled with the same fluid as found in the left and right chambers, respectively. At time $t = 0$ the fluid within the reservoir and capillaries is set into axial oscillations at angular frequency ω and at a displacement tidal volume V_T. In view of the fluid incompressibility, this motion leads to a tidal displacement within the capillary tubes of $\Delta x = V_T/A_0$ which is kept at less than $L/2$ in order to insure that there will be no direct convective interchange of fluids between the two chambers under the assumed laminar flow conditions. After a short transient, this type of oscillatory motion within the described configuration will lead to enhanced axial diffusional flows along the capillaries in the presence of essentially constant axial concentration gradients determined by the time-dependent concentration difference of each particular species in question between the two chambers.

Neglecting end effects, it is easy to show (see Ref. *8*) that the periodic axial laminar velocity profile within each of the capillaries will be

$$U(\eta,t) = \frac{-i\lambda U_0}{\alpha^2}\left[1 - \frac{J_0(\sqrt{-i}\alpha\eta)}{J_0(\sqrt{-i}\alpha)}\right]e^{i\omega t}$$

$$= U_0 f(\eta) e^{i\omega t} \tag{1}$$

where $\lambda = a^2|\partial p/\partial x|/\rho\nu U_0$ is the nondimensional pressure gradient maximum acting along the capillaries, $\alpha = a\sqrt{\omega/\nu}$ is the Womersley number measuring the ratio of inertia to viscous forces, ν is the fluid kinematic viscosity here taken as that of the carrier liquid, ρ is the fluid density, U_0 is a representative velocity, and $\eta = r/a$ is the nondimensional radial distance. Note that it is the real part of Eq. (1) which presents the actual axial velocity. Graphs for the real part of $U(\eta,t)$ for several different values of α have been obtained by Uchida (*9*). Suffice it here to point out that the time-independent portion $f(\eta)$ above reduces to the familiar Poiseuille parabolic profile as the Womersley number becomes much less than unity while it has the form of a constant velocity core bounded by a boundary layer of thickness $\delta = \sqrt{2\nu/\omega}$ at the tube wall for large α. An interesting alternative to the velocity field representation given by Eq. (1) is the Lagrangian displacement ξ for fluid elements within the capillaries. For the case of the fluid elements initially lined up at axial position $x = 0$, halfway between the tube ends, one has the Lagrangian displacement

$$\xi(\eta,t) = \int_0^t U(\eta,t)dt \tag{2}$$

which is plotted in Fig. 2 at time intervals of $\omega t = 30°$ for the particular case of $\alpha = 10$ in unit lenghts of $U_0\lambda/\omega\alpha^2$. Note that, even for this moderate value for the Womersley number, the profile departs considerably from the standard parabolic shape and shows signs of a boundary layer structure. We have also indicated in Fig. 2 the cross-stream averaged tidal displacement Δx. This can be defined as above or in the mathematical form

$$\Delta x = \frac{4U_0}{\omega} \left| \int_0^1 \eta f(\eta) d\eta \right| \tag{3}$$

which, on integration, yields

$$\Delta x = \frac{2U_0\lambda}{\omega\alpha^2} \left| 1 - \frac{2}{\sqrt{-i}\alpha} \frac{J_1(\sqrt{-i}\alpha)}{J_0(\sqrt{-i}\alpha)} \right| \tag{4}$$

and can in turn be expressed more conveniently as

$$\Delta x = \frac{\left|\frac{\partial p}{\partial z}\right|}{\frac{1}{2}\rho\omega^2} \left| 1 + \frac{2}{\alpha} F(\alpha) \right| \tag{5}$$

where $F(\alpha)$ is the complex function

$$F(\alpha) = F_R(\alpha) + iF_I(\alpha) = i\left[\frac{\text{ber}'\,\alpha + i\,\text{bei}'\,\alpha}{\text{ber}\,\alpha + i\,\text{bei}\,\alpha}\right] \tag{6}$$

with $J_0\sqrt{-i}\alpha) = \text{ber}\,\alpha + i\,\text{bei}\,\alpha$ representing the Kelvin functions and the prime denoting differentiation. An evaluation of function $F(\alpha)$ is given in Fig. 3 together with some numerical values obtained directly from tables given in Ref. *10*. The limiting forms of $F(\alpha)$ are

$$F(\alpha) = \begin{cases} -\frac{\alpha}{2} + i\frac{\alpha^3}{16}, & \alpha \ll 1 \\ -\frac{1}{\sqrt{2}} + i\left(\frac{1}{\sqrt{2}} - \frac{1}{2\alpha}\right), & \alpha \gg 1 \end{cases} \tag{7}$$

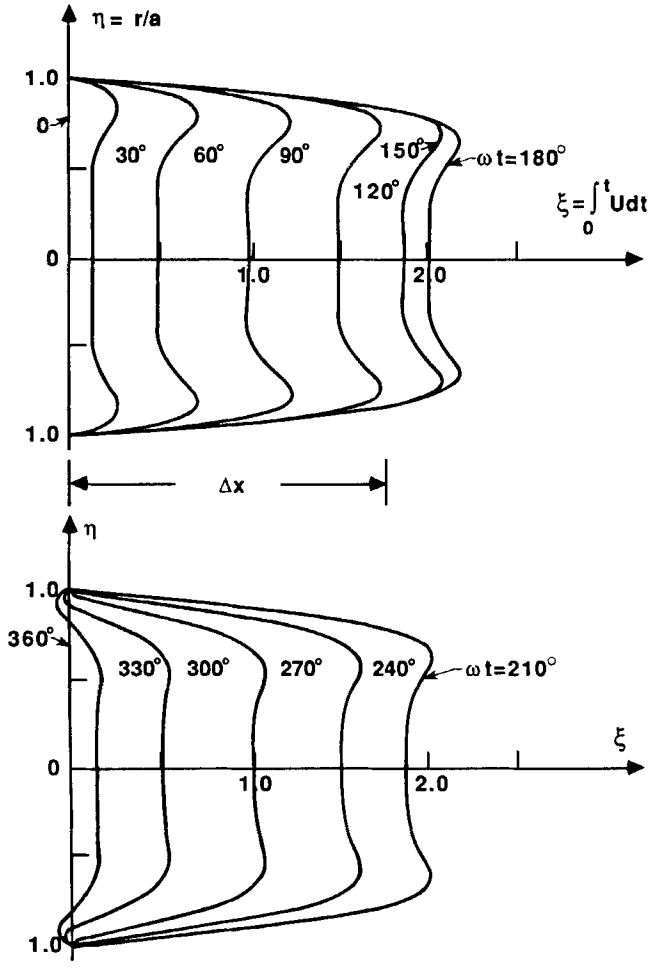

FIG. 2. Fluid element displacement at time intervals of $\omega t = 30°$ throughout the oscillation cycle. Here $\alpha = 10$, and values are expressed in length units of $U_0\lambda/\omega a^2$.

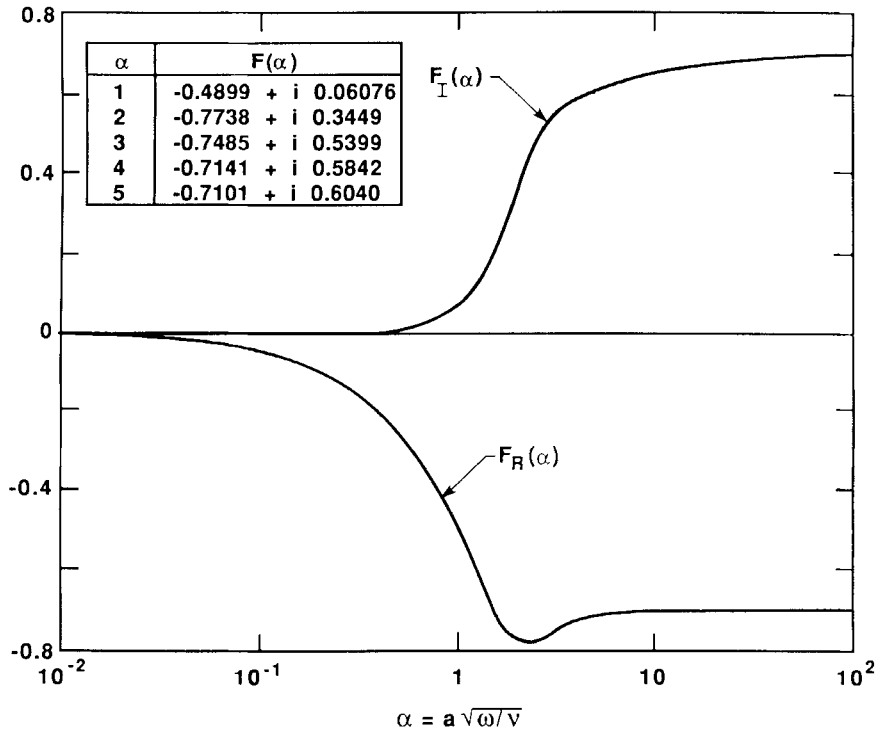

FIG. 3. Plot of the function $F(\alpha)$ as a function of Womersley number.

From this last result and Eq. (5), it follows that the tidal displacement is related to the maximum of the periodic pressure gradient by

$$\Delta x = \begin{cases} \left|\dfrac{\partial p}{\partial z}\right| \dfrac{1}{8}\alpha^2, & \alpha \ll 1 \\ \dfrac{1}{2}\rho\omega^2 \left(1 - \dfrac{\sqrt{2}}{\alpha}\right), & \alpha \gg 1 \end{cases} \tag{8}$$

Note, from Eq. (8), that the axial pressure gradient can become large for fixed tidal displacement as the oscillation frequency becomes large.

CONCENTRATION VARIATION AND TIME AVERAGED AXIAL DIFFUSION MASS FLUX

Having obtained the velocity and displacement fields within the oscillatory flow under consideration, we are now in the position to determine the concentration distribution for the light and heavy additives within the carrier fluid along the capillary bundle. The governing equation here is

$$a^2\left[\frac{\partial C}{\partial t} + U_0 f(\eta)e^{i\omega t}\frac{\partial C}{\partial x}\right] = D\left[\frac{1}{\eta}\frac{\partial}{\partial \eta}\left(\eta\frac{\partial C}{\partial \eta}\right) + a^2\frac{\partial^2 C}{\partial x^2}\right] \tag{9}$$

where $C(\eta,x,t)$ is the mass concentration in g/cm^3 of the particular species in question, x is the axial distance along the capillaries with $x = +L/2$ and $x = -L/2$ denoting the ends, and D is the appropriate mass diffusion coefficient. To solve this equation we make use of the locally valid Chatwin approximation (*2*),

$$C(\eta,x,t) = \gamma\{x + ag(\eta)e^{i\omega t}\} \tag{10}$$

where γ is the time-averaged local concentration gradient. Although this approximation is likely to be invalid near the capillary ends because of the convective mixing which occurs there with the fluid in the reservoir, it is still a reasonable approximation that in most of the central portion of the capillary $\gamma = \{C[(1)] - C[(2)]\}/L$, as we will assume later when estimating the differential diffusion mass flows between the two compartments of the fluid reservoir.

Although an exact solution of Eq. (9) subjected to restriction (10) is possible (see Refs. *4* or *7*), we can avoid many of the complications associated with such a solution by noting that one is here dealing with diffusion in liquids where the Schmidt number, defined as $S = \nu/D$, is about 1000 and hence a large parameter. Accordingly, the differential equation for $g(\eta)$, which has the form

$$\frac{d^2 g}{d\eta^2} + \frac{1}{\eta}\frac{dg}{d\eta} = S[i\alpha^2 g + f\mathrm{Re}] \tag{11}$$

can be solved by the regular perturbation expansion

$$g(\eta) = g_0(\eta) + \frac{1}{S}g_1(\eta) + \frac{1}{S^2}g_2(\eta) + \cdots \tag{12}$$

which cannot be made to satisfy the standard nonpenetration condition $dg/d\eta = 0$ at the wall, but should yield a very close approximation over the rest of the capillary cross-section. Such a perturbation expansion carried out to order 1/S yields the concentration

$$C(\eta,x,t) = \gamma\left\{x + a\left[-\frac{\lambda \mathrm{Re}}{\alpha^4 S} + \frac{i\mathrm{Re}f(\eta)}{\alpha^2}\left(1 + \frac{1}{S}\right)\right]e^{i\omega t}\right\} \tag{13}$$

and thus contains the Kelvin function terms only implicity through $f(\eta)$. The Reynolds number appearing in Eqs. (11) and (13) is defined as $\mathrm{Re} = U_0 a/\nu$.

The instantanious axial mass flux produced by the sinusoidal oscillations of fluid within the capillaries is, upon neglecting the small effect of direct axial diffusion, equal to

$$j(t) = 2\int_0^1 \eta[U_0 f(\eta)e^{i\omega t}]_R[C(\eta,x,t]_R d\eta \quad (\mathrm{g/s \cdot cm^2}) \tag{14}$$

On integrating this quantity over one cycle of the oscillations, the following, time-independent, mass diffusion flux is obtained:

$$j = a\gamma U_0 \int_0^1 \eta[f_R g_R + f_I g_I]d\eta \tag{15}$$

Substituting the values of $f(\eta)$ and $g(\eta)$ from Eqs. (1) and (13), respectively, and carrying out the indicated integration, yields

$$j = \left[\frac{\gamma D \mathrm{Re}^2 \lambda^2}{\alpha^7}\right]F_I \tag{16}$$

or, with the use of Eq. (5), the sought after and surprisingly simple result

$$j = \gamma D\left(\frac{\Delta x}{a}\right)^2 T(\alpha) \tag{17}$$

where

$$T(\alpha) = \frac{\alpha F_I(\alpha)}{4\left|1 + \frac{2}{\alpha}F(\alpha)\right|^2} \tag{18}$$

Applying the standard Fick's law to Eq. (17), one sees that this result is the same as saying that the oscillatory convention-diffusion process considered here is equivalent to enhanced axial diffusion through a quiescent fluid with an effective diffusion coefficient of

$$D_{\text{eff}} = D\left(\frac{\Delta x}{a}\right)^2 T(\alpha) \tag{19}$$

which can easily be orders of magnitude larger than D. This last result has the asymptotic forms

$$D_{\text{eff}} = D\Delta x^2 \begin{cases} \dfrac{1}{a^2}, & \alpha < 1 \\ \dfrac{1}{4a\delta}, & \alpha \gg 1 \end{cases} \tag{20}$$

where $\delta = \sqrt{2\nu/\omega}$ is again the viscous boundary layer thickness. A plot of Eq. (18) is found in Fig. 4. Note that the small α result indicates that the total effective diffusion mass flow $J = jA_0$ is indeed independent of tube radius and frequency as found by Dryer et al. (*1*), whenever the Womersley number is less than about 3. However, this conclusion no longer holds at large α where the time averaged mass flow and mass diffusion flux are proportional to the square root of oscillation frequency. This departure from earlier predictions has clearly to do with the existence of much thinner boundary layers occurring at higher α (see Fig. 2) than the simple parabolic profile assumption made in the semi-quantative analysis presented in Ref. *1*. To achieve large effective diffusion coefficients and hence large axial diffusion flux, it will be of advantage to run experiments at large values of $(\Delta x/a)$, large axial concentration gradients, and large Womersley numbers.

ENHANCED MULTICOMPONENT DIFFUSIONAL SEPARATION IN LIQUIDS

The result given by Eq. (17) can be used directly to determine the differential diffusional mass flow possible in the configuration shown Fig. 1. Assuming a dilute mixture of a light and heavier molecular additive in an aqueous carrier such that the hydrodynamic characteristics are essentially determined by the carrier, one has

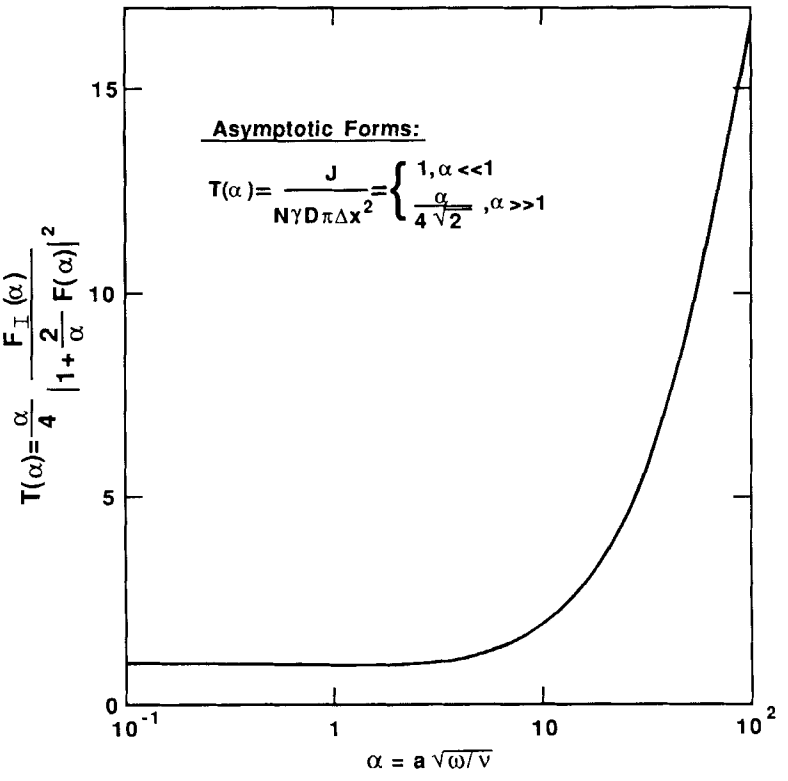

FIG. 4. Mass diffusion flux J as a function of Womersley number.

$$\Delta J = A_0(j_L - j_H) = [\gamma_L D_L - \gamma_H D_H]A_0\left(\frac{\Delta x}{a}\right)^2 T(\alpha) \qquad (21)$$

where the products γD is the product of the time-averaged axial concentration gradient which decreases in time and the molecular diffusion coefficient of the species indicated by the subscript L (light) or H (heavy). Whenever the diffusion coefficients, D_L and D_H differ from each other, which is generally the case when the two species differ in molecular weight, a partial enrichment of the heavier species will occur in the right chamber while the left chamber will become partially enriched in the lighter (and hence higher D) species. Note that to conserve total mass, the diffusional movement of the L and H species through the capillaries from the right to left chamber will be accompanied by a counterdiffusional flow from left to right of the carrier liquid.

Also, if the diffusion process is allowed to be continued for a very long time, the final state will be one of complete mixing with zero remaining separation. Accordingly, in a functioning separation device based on the present process the running time would be only about as long as needed to remove about half of the lighter species from the right chamber. At that point the enriched fluid would be drained from the system and the carrier fluid removed by absorption or freezing before moving the remaining fluid on to the next separation stage. To obtain commercially desirable large separation mass flows it would be of advantage to have a large total cross-section A_0 of the capillary bundle while at the same time keeping the individual radii r = a small.

As a sample calculation for obtainable differential mass flows, consider the case of a 1% concentration $C_L(\textcircled{1}) = C_H(\textcircled{1}) = 0.01$ g/cm^3 of two additives with $D_L = 1 \times 10^{-5}$ g/cm^3 and $D_H = 0.5 \times 10^{-5}$ g/cm^3 in an aqueous solution. Let the total cross-section be $A_0 = 100$ cm^2 and the individual capillaries have 2 mm diameter and 200 cm length. The tidal displacement is taken as 100 cm, the oscillation frequency as $\omega/2\pi = 10$ Hz, and the carrier kinematic viscosity is $\nu = 0.01$ cm^2/s. These conditions correspond to a Womersley number of $\alpha = 7.9$ and yield, via Eq. (21), $J_L = 0.08$ g/s, $J_H = 0.04$ g/s with a $\Delta J = 0.04$ g/s.

Although these mass flows are still quite small compared to normal convection flows, they are some 1.6×10^6 times larger than achievable for the same geometry in the absence of oscillations. The maximum oscillator pressure difference required between the capillary ends for the above example would be, according to Eq. (8), 39 atm. This is a quite large value but not inconsistent with the even higher pressure difference encountered in liquid chromatography. Note that we have also assumed in this sample calculation that the oscillatory flow remains laminar. Such may not always be the case at higher Womersley numbers and large $\Delta\chi\alpha$ (*11*).

CONCLUDING REMARKS

We have shown that separation in liquids can be accomplished at relatively high differential diffusion mass flow rates by oscillating liquid mixtures in capillaries while maintaining axial concentration gradients. The results show that the effective axial diffusion coefficient is equal to the product of the molecular diffusion coefficient of the species in question, the square of the ratio of the tidal displacement to the capillary radius, and to a montonically increasing function of Womersley number.

The process works with any carrier fluid and should be especially useful in the separation of high molecular weight species such as proteins and colloids, which are presently difficult to separate in large quantities by other means such as electrophoresis. In addition, this type of enhanced diffusional separation may find application for use in conjunction with other separation methods such as field-flow fractionation (*12*).

Acknowledgments

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