Measuring Diffusion Coefficients by Taylor's Method of Hydrodynamic Stability

Diffusion coefficients for liquid solutions can be measured using a hydrodynamic stability criterion first derived by G. I. Taylor. This method is used in the present work to determine diffusion coefficients for a range of solutes from small molecules to colloidal particles, at infinite dilution and at finite concentrations. The method is simple and accurate and seems to have wide applicability. Taylor's stability criterion can also be used to establish known, linear concentration gradients of several different solutes in one column of fluid, and one solute can be used to create a desired gradient of a second solute.

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Introduction

The dispersion technique for determining diffusion coefficients resulted from Taylor's (1954) analysis of longitudinal dispersion of a pulse of solute injected into a long capillary through which solvent flows by forced convection. Taylor's original analysis has been extended (Aris, 1956) and his experimental method for measuring diffusion coefficients has been refined (Osuano, 1972). The dispersion method has several advantages over other techniques for measuring diffusion coefficients, including the fact that convective effects are controlled and measurements can be made quickly. Disadvantages include the necessity of sophisticated instrumentation and fluid delivery systems, as well as limitations of the mathematical analysis to systems where the diffusion coefficient is constant.

In the appendix of his 1954 paper on dispersion, Taylor comments on the effects of gravity on dispersion in tube flow. With characteristic brevity, he explains the effect of gravity on dispersion and natural convection in a vertical tube and describes (in one paragraph) a second method that could be used to determine diffusion coefficients. He concludes with the intriguing observation, "Using this method I have obtained values of D which lie within the range of previous measurement." Our paper is concerned with this second dispersion method of Taylor's, which is based on hydrodynamic stability in a vertical tube.

Consider a long capillary closed at the bottom and filled with a fluid initially of uniform density that is in contact with a reservoir at its upper, open end, Figure 1. If the reservoir is filled with a second fluid whose density is greater because of an added solute, the interface between the two fluids is unstable and the more dense fluid from the reservoir plunges into the tube and displaces a rising counterflow of the lighter fluid. Solute in the descending plume diffuses radially into the rising solution so as to continually reduce the density of the descending fluid. Eventually the mixed fluids in the capillary are stabilized with respect to gravitational forces by this lateral diffusion process as well as by viscous damping. Taylor derived the following critical Rayleigh number for circular capillaries:

$$Ra_c \equiv \left(\frac{gb^4}{D\eta}\frac{d\rho}{dz}\right)_c = 67.94 \qquad (1)$$

where η is the fluid viscosity, ρ the density, g the gravitational acceleration, and b the tube radius. z is the vertical coordinate directed upward along the tube axis. The fluid in the capillary is stable to small perturbations when the density gradient is smaller than given by Eq. 1. The numerical value of Ra_c depends on the cross-sectional geometry of the capillary. Wooding (1959) published the details of Taylor's derivation and extended it to noncircular capillaries (1960).

What Taylor and subsequent researchers found experimentally is that the mixing by natural convection continues just to the point where Eq. 1 is satisfied at all points along the capillary; this result could not be predicted from the linearized stability analysis leading to Eq. 1. Thus, by contacting two solutions as in Figure 1, one can establish a linear density gradient in a vertical capillary that subsists for long times because of the slowness of Brownian diffusion, which tends to distort the gradient at the bottom. Because the density gradient is proportional to the

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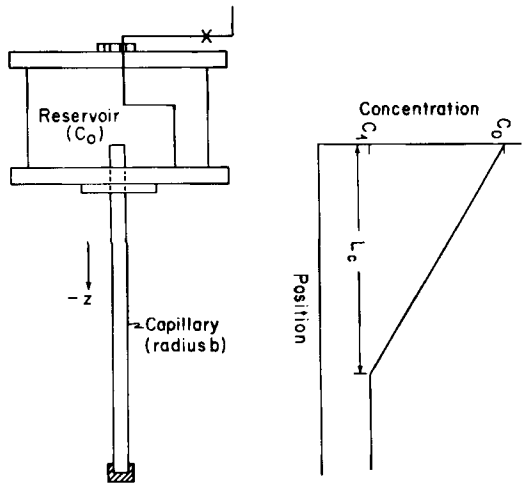

Figure 1. Capillary and reservoir configuration.
At right: stabilized solute concentration profile within capillary for small C_0.

solute concentration gradient, at least at low solute concentrations, measurement of the stabilized concentration gradient allows direct computation of D from Eq. 1, given the other physical parameters. Taylor's apparently crude experimental apparatus yielded an accurate value for D of potassium permanganate in water (Taylor, 1954, appendix).

To measure the critical density gradient one must relate solution density to solute concentration; this can be done for small changes in concentration with a linear expression:

$$\rho = \rho_1 + \alpha C \tag{2}$$

where ρ_1 is the density of the solution initially in the tube. Rearranging Eq. 1 gives

$$\left(\frac{dC}{dz}\right)_c = 67.94 \frac{D\eta}{\alpha g b^4} \tag{3}$$

If the physical properties on the righthand side of Eq. 3 are constant, the concentration profile within the capillary is linear, meaning that the solute has penetrated into the capillary to a well-defined distance L_c when convection has ceased, as shown in Figure 1. Measurement of L_c can be used with Eq. 3 to give the diffusion coefficient. Molecular diffusion effects, which tend to distort the linear solute profile near the bottom of the gradient, are negligible if $L_c \gg b$ and if L_c is determined within a reasonable time after the hydrodynamic stability condition is reached.

Wooding (1959, 1960, 1962) performed experiments with vertical tubes that were packed with impermeable particles to study hydrodynamic stability in porous media. He obtained data on the time course of the fluid mixing in the tubes by observing the motion of dyes placed in the reservoir (more dense) fluid. Wooding's observations and measurements represent the only published data on this problem, other than our own, of which we are aware.

In this paper we summarize our experiences using Taylor's stability method for determining diffusion coefficients in aqueous solution. We first comment on experimental details and data analysis and then present results of measurements extending from small molecules to colloidal particles. Next we consider the extensions of Taylor's method involving concentration-dependent diffusion coefficients and multiple gradients. We conclude with a discussion of advantages and limitations of this technique.

Experiment and Data Analysis

The apparatus consists of a precision-bore circular capillary of known radius and length greater than the maximum penetration depth of any experiment. These capillaries can be purchased in a variety of sizes down to 0.1 mm internal radius. Each capillary is fitted at one end with a syringe needle to facilitate filling and emptying; an epoxy is used to seal around the needle.

The capillary is filled with solution of solute concentration C_1 and connected to a reservoir, Figure 1, which is then slowly filled with solution of concentration C_0. The volume of fluid in the reservoir should be at least 100 times that in the capillary to maintain a constant reservoir concentration as fluid which is displaced from the capillary flows into the reservoir. The initial contacting of reservoir and capillary fluids should be done slowly, with minimum convective currents in the reservoir, to reduce the chance of the overshoot phenomenon discussed later. If the amount of solute is limited, one can fill the tube with the more concentrated solution, load the less concentrated solution into the reservoir, and invert the capillary/reservoir apparatus. For example, in one of our experiments ($b = 5 \times 10^{-4}$ m, $L = 3 \times 10^{-1}$ m, $C_1 = 10$ kg/m^3, and $C_0 = 0$) only a few milligrams of solute (the protein carbonic anhydrase) were necessary to perform one experiment (Lin, 1971). The preceding discussion assumes that the solute increases the density of the solution ($\alpha > 0$); if the opposite is true, the solute-rich fluid must lie below the solute-poor fluid.

A way of measuring the stable concentration gradient inside the capillary is required. We have used two methods. In the first (Lin, 1971) a traveling spectrophotometer was used to determine local values of solute concentration, $C(z)$, in the tube. These data were differentiated to obtain the stable gradient, and D was calculated from Eq. 3. Figure 2 shows such data for an experiment with a small, fluorescent solute molecule. These data verify the persistence of stability and show that Eq. 3 holds at all points within the capillary to which the more dense solution has penetrated.

The second method of determining the density gradient in the capillary is based on a mass balance of solute within the capillary and assumes that Eq. 3 holds at every point. Consider the case of $C_1 = 0$. Because the concentration profile must be linear if all physical parameters are constant, the diffusion coefficient can be calculated from the penetration depth L_c illustrated in Figure 1:

$$D_o = \frac{\alpha g b^4}{(67.94)\eta} \frac{C_0}{L_c} \tag{4}$$

The subscript o on D designates dilute conditions, since all physical properties were assumed independent of solute concentration.

The penetration depth is determined by removing the solution from the capillary and measuring the mean solute concentration

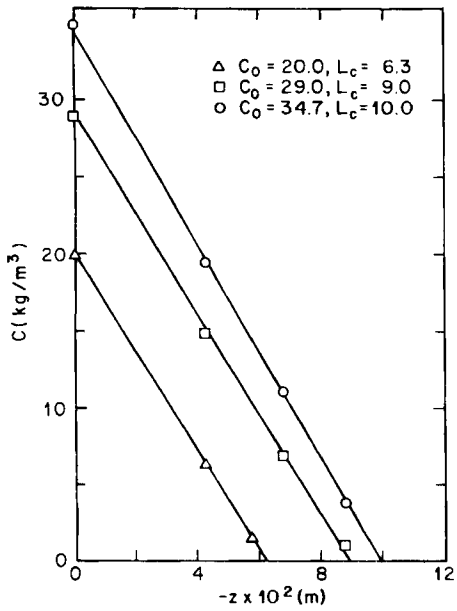

Figure 2. Measured concentration profile of quinine hydrochloride (α = 0.195) within a capillary (b = 0.05 × 10^{-2} m) at stable conditions.

C_1 = 0 for all data. C in kg/m³, L_c in 10^{-2} m (Lin, 1971).

$\overline{C}$ by an analytical technique. Mathematically, this mean concentration can be expressed as

$$\overline{C} = \frac{1}{L}\int_{-L}^{0} C dz \tag{5}$$

where L is the length of the capillary. Combining Eqs. 3–5 under the assumption that $L > L_c$, we have

$$L_c = 2L\frac{\overline{C}}{C_0} \tag{6}$$

Once L_c is determined, D_o is calculated directly from Eq. 4.

Both methods discussed above, measuring $C(z)$ or $\overline{C}$, require an analytical technique to measure solute concentration. This requirement can be avoided by using a second tracer solute, such as a dye, which is added to the reservoir fluid. If the amount of dye added is sufficiently small, such that $(\alpha^*/D^*)C_0^* \ll (\alpha/D)C_0$, where the asterisk refers to the dye, then it has no significant effect on the stable density profile. L_c is now given by Eq. 6 with $\overline{C}$ and C_0 replaced by $\overline{C}^*$ and C_0^*, respectively. A discussion of multicomponent solutions follows in the next section. Thus, it is easy to apply either of the two methods to solutes for which there is no good method of detection, as long as a dye or other tracer is found that does not interact with the solute.

Table 1 lists some results for D_o obtained in our laboratories using these methods. Note that the solutes span a broad range in molecular weight, from small molecules to colloidal particles covering three orders of magnitude in diffusion coefficient. In most of the experiments multiple columns were used, and in some cases capillaries of different radii were used for the same solute. The consistency among the D_o values for any one solute using capillaries of different radii, and the measured linearity of the profiles—Figure 2, for example—provides strong evidence for Taylor's conjecture that the stability condition is reached in

Table 1. Some Results for D_o in Aqueous Solutions at Low Reservoir Concentrations

	Exp. Value m^2/s	Avg. Lit. Value*
Sodium fluorescein†	8.2×10^{-10}	—
Quinine hydrochloride†	5.3×10^{-10}	—
Sucrose†	4.5×10^{-10}	4.5×10^{-10}
Bovine serum albumin†‡		
pH = 2.4, >0.1M IS	5.3×10^{-11}	4.8×10^{-11}
pH = 4.5, >0.15M IS	5.9×10^{-11}	6.0×10^{-11}
pH = 7.0, >0.1M IS	5.9×10^{-11}	6.0×10^{-11}
pH = 6.5, 0.1M IS	5.9×10^{-11}	6.0×10^{-11}
Bovine carbonic anhydrase†		
pH = 8.36, >0.1M IS	8.6×10^{-11}	8.8×10^{-11}
Latex (polystyrene) spheres, 910 Å dia.‡		
pH = 5.5, 0.01M IS	5.1×10^{-12}**	4.7×10^{-12}
pH = 5.5, 0.001M IS	5.1×10^{-12}**	4.7×10^{-12}

IS: ionic strength
All values corrected to 293 K by Walden's formula: $D_o\eta/T$ = constant.
*Sucrose: *International Critical Tables*
Bovine serum albumin: Wagener and Scheraga (1956); Dubin et al. (1967); Raj and Flygare (1974)
Bovine carbonic anhydrase: from sedimentation coefficient measured by Lindskog (1960)
Latex spheres: calculated from $D_o = kT/6\pi\mu a$ where a is particle radius; also measured by Dubin et al. (1967)
**±15% uncertainty in value of α
†Lin (1971)
‡Anderson et al. (1978)

the capillary and provides confidence that the stability method is reliable. In a few instances, most notably with the latex particles, we did observe overshoot of the penetration; that is, the reservoir fluid penetrated further than predicted from Eq. 3 and in a few cases reached the bottom of the capillary (this was visualized with the opaque latex solutions). However, by using several capillary/reservoir systems operating simultaneously and being careful to fill the reservoir slowly, we were able to obtain a reproducible set of values for D_o for the latex particles without too much difficulty.

To perform these experiments it is important to know how long the apparatus must be left undisturbed after the reservoir is loaded with solution. To study the approach to stability, Lin (1971) made time measurements of the concentration profile in the capillary. The solute was either sodium fluorescein or quinine hydrochloride, both of which fluoresce. The concentration profiles were measured with a fluorometer that could be moved along the capillary. At fixed z the solute concentration displayed oscillatory behavior superimposed on its gradual increase with time. Gradually these oscillations were damped until they were sufficiently small to be undetectable when the final, stable gradient was reached.

In an attempt to quantify the time required to reach a stable gradient, we define t_o as the time at which solute has penetrated to 63% of L_c. Table 2 shows results for three experiments with different solutes. The fluorescein experiments were most accurate, since the concentrations in the capillary were measured vs. time. In the other two experiments, the penetration was estimated visually vs. time. A natural time constant for each system should depend on the diffusion coefficient of the solute and the capillary radius, since the gravity-induced convection is diminished by lateral diffusion between the downward moving (solute-rich) and upward moving (solute-poor) fluids. Dimensional arguments lead

Table 2. Time t_o Required to Reach 63% of Stable Gradient in Capillary

System	t_o h	t_oD/b^2	$L_c \times 10^2$ m
Sodium sulfate* $D = 1.24 \times 10^{-9}$ m²/s, 298 K $b = 0.466 \times 10^{-2}$ m	13.	2.2	29.
Sodium fluorescein** $D = 8.2 \times 10^{-10}$ m²/s, 293 K $b = 0.0500 \times 10^{-2}$ m $C(z)$ measured vs time at fixed z	0.45	5.3	15.
Latex spheres, 910 Å dia.*** $D = 5.4 \times 10^{-12}$ m²/s, 298 K $b = 0.0279 \times 10^{-2}$ m	22.	5.5	10.

L_c: final depth of penetration of solute when stability was reached, Fig. 1
A first-order approach to stability limit was assumed to determine t_o in each case.
$C_1 = 0$ in all experiments
*Wooding (1959). Tube packed with impermeable glass spheres; void volume in column, 36%. Depth of penetration measured by following methylene blue dye as it moved down column.
**Lin (1971). $C(z)$ measured vs. time at fixed z.
***Anderson et al. (1978). $\bar{C}$(Eq. 5) measured vs. time.

to the prediction that $t_o \sim b^2/D$. Table 2 shows that t_oD/b^2 is approximately equal for fluorescein and the latex particles, even though their diffusion coefficients differ by more than a factor of 100. This ratio is about a factor of two different for Wooding's data on packed tubes. In Table 3 are listed times t_c allowed after initial contact between the capillary and reservoir fluids before measurements of the density gradient were made. These values were reached experimentally by trial and error, and should be considered conservative estimates of times required to reach the stable condition. Based on Table 3 we conclude that the time required to ensure that a stable gradient is reached in the capillary is approximated by

$$\frac{t_cD}{b^2} \approx 25 \tag{7}$$

Table 3. Time t_c to Reach Stable Conditions in Capillary

	t_c h	t_cD/b^2
Sodium sulphate* $D = 1.24 \times 10^{-9}$ m²/s, 298 K $b = 0.0483 \times 10^{-2}$ m	<3.	<46.
Sodium sulphate* $b = 0.466 \times 10^{-2}$ m, packed with glass spheres	<120.	<20.
Sodium fluorescein** $D = 8.2 \times 10^{-10}$ m²/s, 293 K $b = 0.0500 \times 10^{-2}$ m	<2.	<24.
Bovine serum albumin*** $D = 3.6 \times 10^{-11}$ m²/s, 277 K $b = 0.0292 \times 10^{-2}$ m	<24.	<36.
Latex spheres, 910 Å dia.*** $D = 5.4 \times 10^{-12}$ m²/s, 298 K $b = 0.0279 \times 10^{-2}$ m	<96.	<24.

Values shown represent conservative estimates.
All solutions were aqueous.
*Wooding (1959). Methylene blue dye used to determine penetration into capillary.
**Lin (1971)
***Anderson *et al.* (1978)

Extensions of the Method

Multicomponent solutions

We have extended the analysis of Wooding (1959) to multicomponent solutions by writing his Eq. 26 for each of the N solutes present in the solution. Assuming that the solution is dilute in all solute species, so there is no coupling between diffusion of the species, and letting the superscript (i) denote solute i, the marginal stability criterion becomes

$$\frac{gb^4}{\eta} \sum_{i=1}^{N} \frac{\alpha^{(i)}}{D^{(i)}} \frac{dC^{(i)}}{dz} = 67.94 \tag{8}$$

Glendinning and Russel (1980) have further extended the analysis to allow for diffusive coupling between solutes i and j of the form

$$\text{Flux of solute } i = -\sum_{j=1}^{N} D^{(ij)} \nabla C^{(j)} \tag{9}$$

where the $D^{(ij)}$ are constant coefficients. The stability criterion for this coupled system is

$$\frac{gb^4}{\eta} \sum_{i=1}^{N} \sum_{j=1}^{N} \alpha^{(i)} \{D\}_{ij}^{-1} \frac{dC^{(j)}}{dz} = 67.94 \tag{10}$$

where $\{D\}$ is the matrix of coefficients $D^{(ij)}$. In an uncoupled system $D^{(ij)} = 0$ if $i \neq j$, and $D^{(ii)} = D^{(i)}$, so that Eq. 10 reduces to Eq. 8.

The correctness of Eq. 8 has been demonstrated with aqueous solutions of a sugar (mannose) and an electrolyte (sodium dichromate) (Lowell and Anderson, 1982). Sodium dichromate absorbs light in the visible spectrum, and hence its color can be used to approximate L_c to about ±10% accuracy by direct visual observation of the penetration into the capillary. More precise determinations of L_c were made in these experiments by measuring the amount of mannose or dichromate in the tube after stability was reached and substituting the result in Eq. 6. The experiments were run with no solute initially in the capillary ($C_1^{(i)} = 0$) and the reservoir solutions were dilute. The penetration depth was predicted from Eq. 8 to be

$$L_c = \frac{gb^4}{(67.94)\eta} \left[\frac{\alpha^{(1)} C_0^{(1)}}{D^{(1)}} + \frac{\alpha^{(2)} C_0^{(2)}}{D^{(2)}} \right] \tag{11}$$

Since the physical properties for both solutes, including their diffusion coefficients, were known, our measurements could be compared with Eq. 11 to test the validity of Eq. 8. In all mixtures of the solutes, from pure mannose to pure dichromate, the data for L_c agree very closely with Eq. 11. These experiments demonstrate the feasibility of forming simultaneous gradients in a vertical tube.

Concentration effects

Wooding (1959) showed that Eq. 1 is valid locally in the capillary even if D is an exponential function of the solute concentration. We expect Eq. 1 to be a good approximation for any concentration dependence of D since the stability analysis considers only conditions over length scales of the order of the capillary radius and physical properties should be essentially constant at this length scale, especially near the stability limit

where radial gradients in the capillary are approaching zero. (Wooding conjectures that Eq. 12 might not provide the marginal stability conditions for a solute which is a "complex molecule" because the variation of D with C "may be rapid." We do not understand the basis of this remark.) Our assumption is that Eq. 1 can be rewritten to include explicit dependence of D and η on the solute concentration:

$$\frac{\alpha g b^4}{D(C)\eta(C)}\frac{dC}{dz} = 67.94 \tag{12}$$

Although we assume here that α is independent of C, a reasonable assumption for most liquid systems at moderate solute concentrations, it is a straightforward exercise to include possible concentration effects on this parameter as well. Direct measurement of $C(z)$ by a spectroscopic method would allow determination of $D(C)$ from Eq. 12, given independent data for $\eta(C)$.

It is also possible to use the material balance technique to gain information on $D(C)$ (Anderson et al., 1978). The mean solute concentration $\overline{C}$ is measured by removing the fluid from the capillary after stability has been reached. Combining Eqs. 5 and 12, we have

$$\overline{C} = \left[\frac{\alpha g b^4}{(67.94)L}\right]\int_{C_1}^{C_0}\frac{C dC}{D(C)\eta(C)} \tag{13}$$

If this expression is differentiated with respect to C_0, with C_1 held constant, there follows

$$D(C_0) = \left[\frac{\alpha g b^4}{2(67.94)L}\right]\frac{1}{\eta(C_0)}\left[\frac{\partial \overline{C}}{\partial (C_0^2)}\right]^{-1} \tag{14}$$

By numerically differentiating data for $\overline{C}$ vs. C_0, given the concentration dependence of η, the above expression can be used to evaluate D.

A less direct way of using Eq. 13 is to assume algebraic forms for $D(C)$ and $\eta(C)$ and substitute them directly into the above integral. For example, let us assume the following:

$$D = D_o(1 + kC) \tag{15a}$$

$$\eta = \eta_o(1 + mC) \tag{15b}$$

where η_o and m are known. Substitution of these expressions into Eq. 13 gives

$$\frac{1}{m-k}\ln\left[\frac{(1+kC_0)^{1/k}}{(1+mC_0)^{1/m}}\right] = \left[\frac{(67.94)L}{\alpha g b^4}\right]D_o\eta_o\overline{C} \tag{16}$$

The unknowns D_o and k are obtained by fitting Eq. 16 to the data for C vs. C_0. We have taken a similar approach (Anderson et al., 1978) to find first-order concentration effects on the diffusion coefficients of a protein (bovine serum albumin) and colloidal particles (910Å dia. latex spheres). Except possibly for light-scattering methods (Berne and Pecora, 1976), we feel these results for D_o and k would be very difficult to obtain by other methods.

Discussion

The experimental results cited here clearly substantiate Taylor's suggestion that the hydrodynamic stability condition provides a simple but accurate method for determining diffusion coefficients. Actually the transport property measured in this way is the product $D\eta$, a combination that appears frequently in theories of the liquid state; therefore, in a solution for which D is known, Taylor's method provides a means to determine the viscosity. However, this is also a disadvantage of Taylor's method when used to find the concentration dependence of diffusion coefficient, since $\eta(C)$ must be determined by separate experiments. We do not consider this to be a serious disadvantage since shear viscosity measurements are rather simple to perform, at least for solutions exhibiting Newtonian behavior.

Taylor's vertical capillary method is not the only example of using a hydrodynamic stability criterion for evaluating fluid properties. Thompson and Sogin (1966) studied Rayleigh instability in heated gas lyaers as a method for determining transport properties of gases at high temperature and pressure. Likewise, Liang and Acrivos (1970) measured critical Rayleigh numbers for heated layers of non-Newtonian fluids and thereby obtained values for the zero-shear viscosity.

The principal advantages of Taylor's vertical capillary method for determining diffusion coefficients, compared with conventional methods, are:

1. A wide range of diffusion coefficients is measurable (10^{-9} to 10^{-12} m^2/s)
2. Only a small amount of solute is required
3. A tracer can be used to find L_c, meaning that one does not need a detection system for the solute of interest
4. Obtaining the diffusion coefficient as a function of solute concentration requires simple numerical treatment of the data
5. The apparatus is simple and inexpensive

The major drawbacks to the method are:

1. A relatively long time is required to reach the stability limit, from about 3 h for molecular solutes to days for colloidal particles
2. Possible overshoot of the denser fluid can give a false gradient
3. α and η must be known by independent means

The first of these difficulties can be made less important by setting up multiple columns at once to obtain many points over one time period. As discussed before, the overshoot problem can be avoided by careful filling of the reservoir.

A final observation on Taylor's method is that it can be used to establish a relatively stable, linear concentration gradient over distances from centimeters to meters. There are a variety of mass-transfer related phenomena, such as chemotaxis (Lauffenburger, 1985) and diffusiophoresis (Anderson and Prieve, 1984), that are most conveniently studied under conditions of controlled concentration gradients. Taylor's vertical capillary can be used to generate a gradient of the desired solute species using a second, inert solute to establish the penetration depth.

Notation

b = capillary radius, m
C = solute concentration in capillary, kg · m^{-3}
C_0 = solute concentration in reservoir, kg · m^{-3}
C_1 = initial solute concentration in capillary, kg · m^{-3}
D = solute diffusion coefficient, m^2 · s^{-1}
g = gravitational acceleration, m · s^{-2}
L = length of capillary, m
L_c = penetration depth of solute into capillary, m
t = time after contacting fluids in reservoir and capillary, s
T = temperature, K
z = distance along capillary axis toward higher gravitational potential, m

Greek letters

α = constant, Eq. 2
η = solution viscosity, kg · m^{-1} · s^{-1}
ρ = solution density, kg · m^{-3}

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