Measurement of Diffusion Coefficients by Taylor's Method of Hydrodynamic Stability

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Taylor (1954) first suggested the measurement of diffusion coefficients using motion in a vertical liquid column subjected to an adverse density gradient in a gravitational field. The device in Figure 1 consists of a reservoir filled with concentrated solution and mounted above a long vertical capillary tube containing pure solvent or less dense solution. The tube is sealed at its lower end and is open at the upper end. Since the heavier solution in the reservoir is above the solvent (or less dense solution) in the capillary, equilibrium is expected to be unstable. The heavier solution would fall down into the solvent producing a downward current and the solvent so displaced would form a rising countercurrent. The solute in the downward current would then diffuse laterally into the rising current of solvent and so lose the excess density over that of the rising fluid at the same level. As the heavier liquid continues to penetrate down the tube, the density gradient, which is initially very large, becomes gradually smaller until the convective motion ceases altogether. At this stage, the system becomes stable under an adverse density gradient. The only means left for vertical transport of the solute is then molecular diffusion which is very slow. Taylor derived the following criterion at marginal stability:

$$\frac{g a_c^4}{D\eta}\frac{d\rho}{dz} = 67.94 \tag{1}$$

where D is the diffusion coefficient of the solute, η is the viscosity of the solution, ρ is the density, a_c is the inner radius of the capillary tube, and g is the acceleration due to gravity. z is the vertical coordinate directed upward along the tube axis. Generally, small concentration differences are maintained between the reservoir and the capillary so that the density of the solution may be related linearly to solute concentration. Let C_o and C_1 denote the mass concentrations of the solute in the reservoir and the capillary, respectively. Then, in this concentration range, the solution density, ρ, may be related to the solute concentration via the relationship:

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

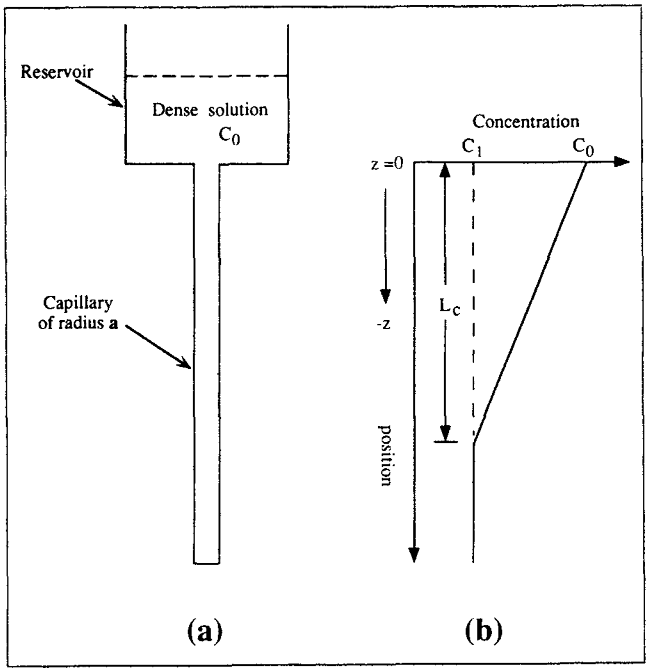

Figure 1. Capillary and reservoir configuration.
Right: solute concentration profile within capillary at marginal stability.

where ρ_1 is the density of the solution initially in the tube, and α $(= d\rho/dC)$ is the density coefficient of the solution in the concentration range $C_1 < C < C_o$. Combining Eqs. 1 and 2, we obtain:

$$\frac{dC}{dz} = 67.94 \frac{D\eta}{\alpha g a_c^4} \tag{2}$$

If therefore, the vertical gradient of solute concentration is measured after the currents have stopped, a measure of $D\eta/\alpha g a_c^4$ can be obtained directly from Eq. 2. Since η, α, and a_c can be measured independently, the technique provides a method for determining the diffusion coefficient D.

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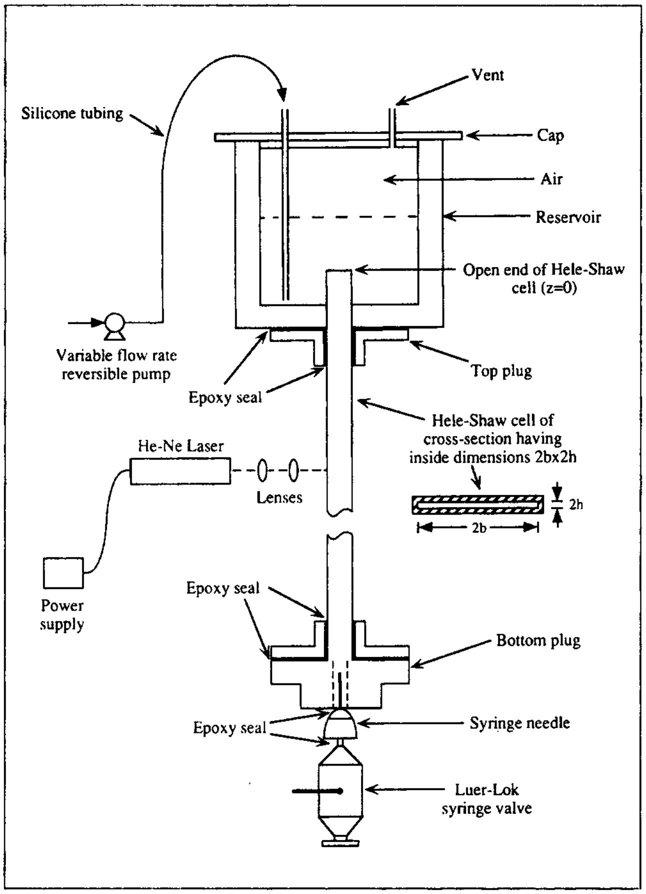

Figure 2. Hele-Shaw cell and reservoir arrangement for measuring the diffusion coefficient through stabilization of an inverse density gradient.

Mathematical rigor was added by Wooding (1959), and experimental verification was provided by Lin (1971) who demonstrated by fluorescence means that, at marginal stability, Eq. 1 is satisfied at all points along the capillary. Thus, when convection is complete, a linear density profile is established along the capillary as shown in Figure 1. In a typical experiment, therefore, one may observe how far down the tube the solute penetrates. If this distance is represented by L_C, then

$$\frac{dC}{dz}=\frac{C_o-C_1}{L_c} \tag{3}$$

so that D is simply calculated from

$$D(\overline{C})=\frac{\alpha g a_c^4 (C_o-C_1)}{67.94\,\eta(\overline{C})L_c} \tag{4}$$

where $\overline{C}$ is the mean concentration of the solute in the capillary $[=(C_o+C_1)/2]$.

The technique was used by Anderson and coworkers (1978, 1982) and more recently by Selim et al. (1993) to determine the diffusion coefficients for a range of solutes from small molecules to colloidal particles. An account of past work plus extensions of the method to multicomponent solutions was presented by Quinn et al. (1986).

The objective of this work is to adapt this experimental method to the case of a vertical channel of rectangular cross section. In Figure 2, 2b denotes the width of the channel and 2h its thickness. For a Hele-Shaw cell where $\beta \gg 1$ ($\beta = 2b/2h$), Wooding (1960) derived the following stability criterion:

$$\frac{\alpha g h^4}{D\eta}\frac{dC}{dz}=\lambda_h \tag{5}$$

where λ_h is given by

$$\lambda_h=\frac{3a_o^2}{\beta^2}\left\{1+\frac{12s}{a_o^5\beta}+\left(\frac{8a_o^2}{21}+\frac{108s^2}{a_o^{10}}\right)\frac{1}{\beta^2}+O(\beta^{-3})\right\} \tag{6}$$

In Eq. 6, $a_o=\pi/2$ and

$$s=\frac{1}{1^5}+\frac{1}{3^5}+\cdots\simeq 1.0045 \tag{7}$$

An experimental apparatus employing a Hele-Shaw cell connected to a reservoir is shown in Figure 2. The reservoir is a Plexiglas cylinder, 6.1 cm in height and 3.8 cm in diameter, and equipped with a plexiglas cap with an off-center bore through which a 2-mm slanted-tip glass tube is permanently connected. This tube is used to fill the reservoir with denser solution via a variable speed pump. The Hele-Shaw cell is precision-bore borosilicate glass, 90 cm long, purchased from Wilmad Glass Co. (Buena, NJ). Two Hele-Shaw cells with cross sections of different dimensions were used in this study.

The rectangular cross section of cell I has inside dimensions of 0.48653 cm in width and 0.0242 cm in thickness. Cell II is 0.7940 cm wide and 0.0392 cm thick. The tolerance in these dimensions quoted by the manufacturer is ±0.0001. Since the analysis of the data depends on h^4, this tolerance introduces about a ±1% uncertainty in the magnitude of the diffusion coefficient. The cell is open at the top and is sealed with epoxy to the bottom of the reservoir. The bottom of the cell is sealed to a Plexiglas plug through which a channel has been drilled. The channel opens on one end into the bottom of the cell, while the other end is fitted with a Luer-Lok microvalve to facilitate filling and emptying; an epoxy is used to seal around the microvalve.

The Hele-Shaw cell-reservoir arrangement was mounted on a rigid support designed to ensure verticality of the Hele-Shaw cell. The whole assembly was housed in a constant temperature air bath maintained at 25±1°C and was mounted on a vibration-free optical table (Mells-Groit). The filling of the Hele-Shaw cell without introducing air bubbles was accomplished by connecting the microvalve at the lower end of the cell to a silicone tubing and injecting less dense solution into the cell very slowly using a variable speed pump. Care was taken to ensure that the cell was completely filled to its top end without any liquid spillover on the floor of the reservoir. Immediately afterward, the reservoir was slowly filled with denser solution. Lin (1971) has shown that this step is important and careful (slow) filling of the reservoir usually prevents the "overshoot" problems encountered by Wooding (1962).

In all experiments, the solution level in the reservoir was at least 1 cm higher than the position of the top end of the Hele-Shaw cell so that disturbances at the air/liquid interface could not propagate into the cell. As soon as the dense solution covered the open end of the Hele-Shaw cell, free convection started. The system was allowed to sit a minimum period of time to ensure that hydrodynamic stability is reached. This was achieved by monitoring the penetration depth during the convection process. To monitor the penetration depth, a laser-excited fluorescent dye tracer (rhodamine 6G) was mixed with the denser fluid prior to its injection into the reservoir. This dye has an absorption band of 480-580 nm wavelength. Fluorescence is emitted in a broad band centered at about 590 nm wavelength and is excited by a green He-Ne laser at 554 nm. To excite the dye, a light beam from a 1 mW He-Ne (green) laser is passed through a set of cylindrical lenses which convert the 0.62 mm dia. beam to a horizontal slit of parallel rays, approximately 0.5 cm wide and 0.06 cm high.

The flat beam is next focused on the large side of the cross section of the Hele-Shaw cell. The laser and the lenses were mounted on one side of the capillary tube on a horizontal support. This support is connected to a vertical screw shaft which is driven by a reversible stepper motor controlled through a microcomputer. In this way, the laser optics assembly can be moved up and down the diffusion column using the stepper motor. During the convection process, the penetration depth of the dye may be located visually using a laser goggle which makes the orange fluorescent light from the dye visible, but not the green excitation light. When the penetration depth ceases to change with time, marginal stability is attained and L_c is measured using a cathetometer. It is important to note that both solute and tracer dye penetrate simultaneously to the same depth in the diffusion column during the convection process. This was verified experimentally by Lowell and Anderson (1982). Accordingly, the penetration depth of the dye is identical to that of the solute at all times.

Aqueous solutions of sucrose, β-alanine, urea, lithium chloride, potassium chloride, sodium chloride, sodium sulfate, and magnesium sulfate were used in the diffusion experiments. In preparing the reservoir solutions, a known weight of the solute was dissolved in a stock solvent to achieve the desired concentration C_o. The stock solvent consisted of rhodamine 6G (supplied by Kodak) dissolved in deionized and doubly-distilled water. The concentration of rhodamine 6G was maintained at about 5 ppm. For less dense solutions, no dye was added to the solvent. The chemicals used in preparing the solutions were of reagent-grade quality, and all solutions were used promptly after their preparation. Furthermore, to minimize any temperature-induced density differences, care was taken to ensure that both the reservoir and less dense solutions were at exactly the same temperature as each other and the apparatus before introduction into the system.

The introduction of a second tracer solute, such as a dye, into the reservoir fluid may give rise to a ternary system. However, if the amount of dye added is sufficiently small, it can be shown (Quinn et al., 1986) that the presence of the dye has no significant effect on the stable density profile of the binary system. At the concentration levels of 5 ppm for the dye used in the experiments, the effect of the dye is expected to be negligible. Under these circumstances, Eq. 5 is still valid and may be arranged to give the following expression for the diffusion coefficient of the solute:

$$D(\bar{C}) = \frac{\alpha g h^4 (C_o - C_1)}{\lambda_h \eta(\bar{C}) L_c} \tag{8}$$

For the two Hele-Shaw cells used here, $h = 0.0121$ cm and $\beta = 20.103$ for cell I and $h = 0.0196$ cm and $\beta = 20.255$ for cell II. Since $\beta \gg 1$, Eq. 6 may be used to find λ_h as 0.0177 and 0.0193 for cells I and II, respectively.

Equation 8 was used throughout to determine D as function of C for our solutes. The measurements were carried out at various concentrations. For each concentration, the experiment was repeated three or four times and the mean value was used for the diffusion coefficient. Reproducibility was better than 2% of the mean value. The data for any one experiment were taken with both cells, and the results for the diffusion coefficient showed no dependence on the cell thickness h. During the experiments, the concentration C_o in the reservoir was always 3 to 5% higher than the initial concentration C_1 in the Hele-Shaw cell. Viscosity and density data as the function of concentration were found from the literature. Several viscosity and density measurements were made, mainly at high solute concentrations, to supplement the information in the literature. The densities were measured in triplicate at 25°C in single-stem pycnometers, each holding 30 cm^3 of solution. Viscosity measurements were made with a Cannon-Fenske type viscometer at 25°C. In the diffusion experiments, the time t_c required to ensure that a stable density gradient is reached in the cell was found to satisfy the following criterion:

$$\frac{t_c D}{h^2} \simeq 36 \tag{9}$$

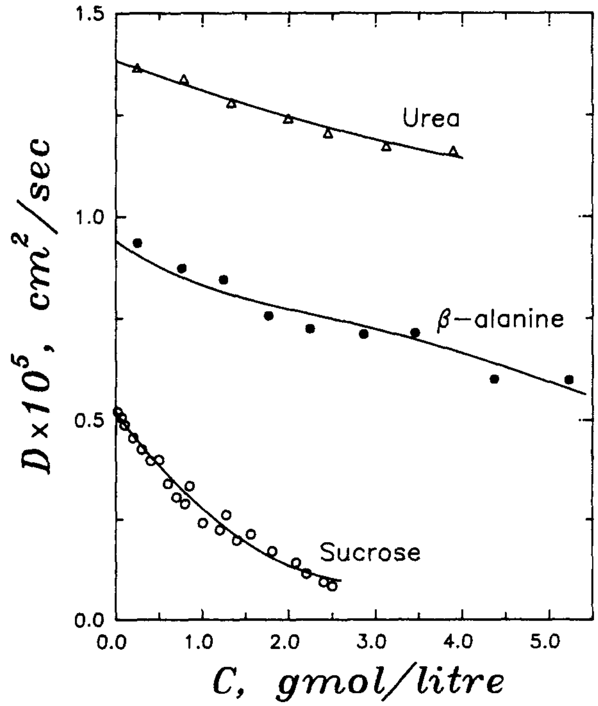

Figure 3. Diffusion coefficients of urea, β-alanine, and sucrose in water at 25°C.

Symbols represent observed results and solid curves literature values.

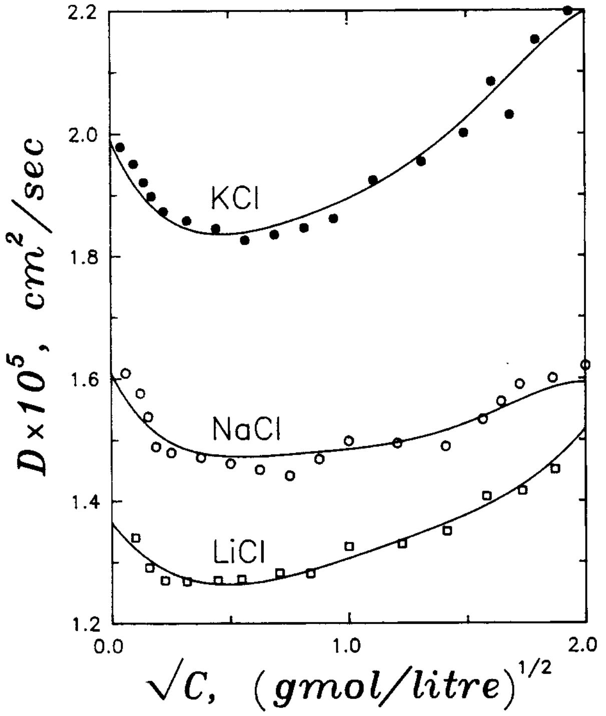

Figure 4. Diffusion coefficients of potassium chloride, sodium chloride, and lithium chloride in water at 25°C.

Symbols represent observed results and solid curves literature values.

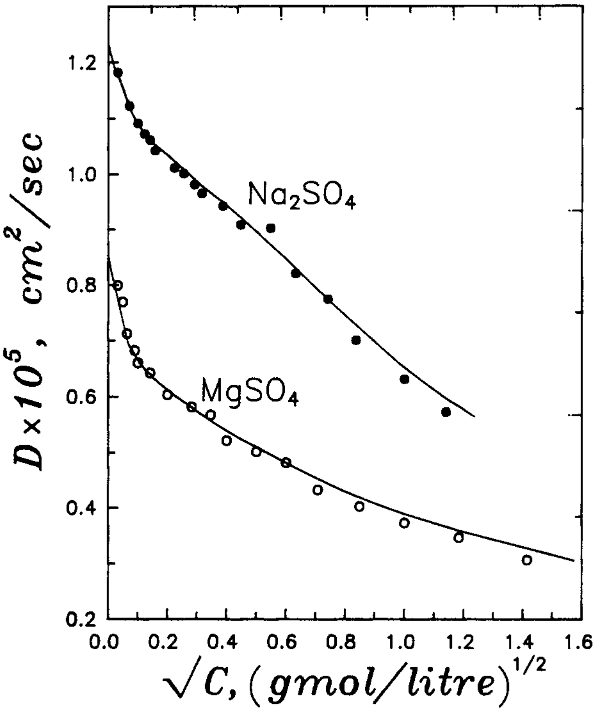

Figure 5. Diffusion coefficients of sodium sulfate and magnesium sulfate in water at 25°C.

Symbols represent observed results and solid curves literature values.

This ratio is about one and half times higher than the corresponding ratio for circular capillaries (Quinn et al., 1986).

The experimental data obtained with the Hele-Shaw cells are shown in Figures 3, 4 and 5. The symbols represent the data obtained in this study, while the solid curves (within about 0.2%) are from the data in the literature. Sources for the latter data are listed in Table 1. The present data agree quite well with existing literature values. The absolute average deviation of the data from the solid curves in the figures varies from 2 to 4%.

The two cells used to collect the present data had β values of 20.103 and 20.255 for cells I and II, respectively. To further study edge effects from the ends of the cell and their effect on the results, a third cell with $\beta = 25.036$ was constructed. Diffusion data for sucrose and sodium sulfate obtained with

Table 1. Sources of Diffusion Data

Solute	Source	Method
Sucrose	Gosting and Morris (1949) Irani and Adamson (1958) Henrion (1964)	Gouy interferometry Diaphragm cell Diaphragm cell
Urea	Gosting and Akeley (1952) Albright and Mills (1965)	Gouy interferometry Diaphragm cell
β-Analine	Donoian and Kegeles (1961) Albright (1966)	Gouy interferometry Diaphragm cell
LiCl	Harned and Hildreth (1951) Stokes (1950)	Conductance Method Diaphragm cell
KCl	Harned and Nuttal (1949) Gosting (1950) Stokes (1950)	Conductance method Gouy interferometry Diaphragm cell
NaCl	Harned and Hildreth (1951) Stokes (1950)	Conductance method Diaphragm cell
Na_2SO_4	Harned and Blake (1951) Wendt (1962) Rard and Miller (1979)	Conductance method Gouy interferometry Rayleigh interferometry
$MgSO_4$	Harned and Hudson (1951) Rard and Miller (1979)	Conductance method Rayleigh interferometry

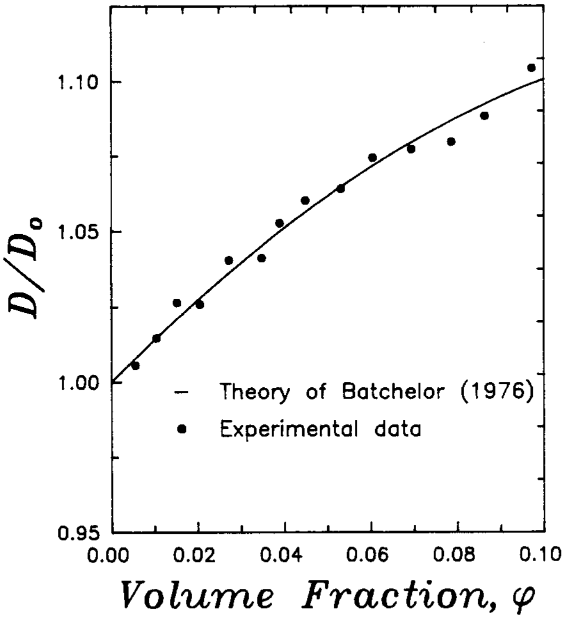

Figure 6. Experimental data for the diffusion coefficient of uncharged silica spheres vs. theoretical predictions of Batchelor (1976).

this cell were essentially identical to those obtained with the first two cells. This indicates that for $\beta > 20$, edge effects are negligible.

As an application, the method was used to measure the diffusion coefficient of colloidal particles. Monosize silica spheres were prepared according to the method of Stöber (1968) and were next sterically stabilized by chemisorption of stearic alcohol at their surface. Particle radius was 14.5 nm from electron micrographs of the coated particles. Further details regarding the preparation and characterization of the particles are available in Selim et al. (1993). The diffusion coefficient of the particles dispersed in cyclohexane was measured using the present method over the range $0 < \phi < 0.1$, where ϕ is the volume fraction of the particles in the suspension. The experimental results are shown in Figure 6. Theoretical predictions for the diffusion coefficient from Batchelor's theory (Batchelor, 1976) are also shown in the figure. The agreement between the experimental data and theoretical predictions is fairly good.

The results obtained from this study confirm Wooding's stability analysis for a Hele-Shaw cell (Wooding, 1960) and represent a novel use of Hele-Shaw cells in diffusion studies. The simplicity and acceptable accuracy of the technique justify its use for measurement of the diffusion properties of different solutes ranging from small molecules to colloidal particles. There are no compelling reasons, however, for using a rectangular cross section as opposed to a circular one. In fact, given the simplicity of the circular capillary, it is obviously the preferred geometry for this application. The optical clarity of the rectangular cross section, however, favors its use over the circular. In studying the convective flow which occurs, a rectangular cross section would obviate many of the reflection problems encountered with a circular tube.

Notation

a_c = capillary tube radius
b = half width of cell cross section
C = solute concentration
C_o = solute concentration in reservoir
C_i = initial solute concentration in capillary or Hele-Shaw cell
$\overline{C}$ = mean solute concentration in capillary or Hele-Shaw cell
D = diffusion coefficient at finite concentration
D_o = diffusion coefficient at infinite dilution
g = gravitational acceleration constant
h = half thickness of cell cross section
L_c = critical penetration depth
t_c = time to reach critical penetration depth
z = distance along capillary or Hele-Shaw cell toward higher gravitational potential

Greek letters

α = constant, Eq. 2
η = solution viscosity
λ_h = critical Rayleigh number for vertical Hele-Shaw cell
ρ = solution density

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