
Diffusional Dispersion of a Pulse Injection into a Laminar Stream

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In most conventional experimental diffusion methods, direct diffusional displacement is relied upon to give concentration profiles for measurement. Long periods of time may be required when small diffusivities are involved, such as in liquids. The method of pulse injection actually magnifies the displacement so that less time is required to give adequate dispersion for measurement. An added advantage is that the convective diffusivity

$$K = R^2\, U^2/48\, D \qquad (1)$$

first postulated by Taylor (1953), is inversely proportional to the molecular diffusivity so that the smaller the molecular diffusivity the larger the magnification of diffusional displacement. This is especially significant in the study of liquids since liquid diffusion coefficients are about four orders of magnitude smaller than those for gases.

For convective transport to be dominant over molecular transport in a laminar flow system, Taylor (1954) stated that

$$K = D + R^2\, U^2/48\, D \qquad (2)$$

Later, Aris (1956) showed that the true effective diffusivity was the sum of the molecular diffusivity and Taylor convective diffusivity.

$$K = D + R^2\, U^2/48\, U \qquad (3)$$

This result, of course, removes Taylor's restriction imposed by equation (2). Aris' study also showed that any initial distribution of solute injected into a laminar stream of solvent tends to become more symmetrical and the distribution tends toward normality.

At least two investigators (Chang, 1966; Giddings and Seager, 1962) have advantageously used the pulse injection method to obtain gaseous diffusivities. The magnification of dispersion in laminar flow of gases allowed them to significantly decrease the time required for a single determination of diffusivity. In liquids, the magnification of dispersion during laminar flow is even greater than for gases, so a large reduction in time required is to be expected when applying the pulse injection method to liquid systems.

Briefly, in this method a thin band of solute is injected into a laminar solvent stream flowing through a tube. The injected band is made as thin as possible to approximate a plane source and the radial concentration is made as uniform as possible. The longitudinal concentration profile is measured at some distance downstream from the injection point and is used to calculate the liquid diffusivity.

MATHEMATICAL DEVELOPMENT

By defining a moving coordinate system such that

$$y = x - Ut \tag{4}$$

the following system may be characterized mathematically by the normal distribution given in Crank (1956)

$$C = (B/\sqrt{t}) \text{ Exp } [-y^2/4Kt] \tag{5}$$

which is a solution of the differential equation

$$\partial C/\partial t = K \, (\partial^2 C/\partial y^2) \tag{6}$$

for a plane source in one dimension.

In equation (5), the arbitrary constant, B, may be evaluated by stipulating that the total amount of solute, M, remain constant,

$$M = \int_{-\infty}^{+\infty} C \, dy = 2B \, (\pi K)^{1/2} \tag{7}$$

Substituting for B, equation (5) becomes

$$C = [M/2 \, (\pi K t)^{1/2}] \text{ Exp } (-y^2/4Kt) \tag{8}$$

Equation 8 may now be compared to a Gaussian curve (normal distribution)

$$n \, (x) = (1/\sigma\sqrt{2\pi}) \text{ Exp } [- \, (x-\mu)^2/2\sigma^2] \tag{9}$$

where μ = mean of the distribution, and σ^2 = variance of the distribution. Noting that $y = x - Ut$, we see that $\mu = Ut$ and that

$$2\sigma^2 = 4Kt \tag{10}$$

so

$$K = \sigma^2/2t \tag{11}$$

It may be shown that the width, w, of the Gaussian curve, at half its maximum height is related to the variance in the following manner

$$w = 2\sigma \, (2 \ln 2)^{1/2} \tag{12}$$

Then

$$\sigma^2 = w^2/(8 \ln 2) \tag{13}$$

From equation (11), we have

$$K = w^2/(16\ t\ ln\ 2) \qquad (14)$$

Combining equations (8) and (14)

$$D + R^2\ U^2/48\ D = [w^2/(16\ t\ ln\ 2)] \qquad (15)$$

Solving for D, we have

$$D = [w^2/(32t\ ln\ 2)]\ \left\{1 \pm \{1 - (64/3)\ [(RU\ t\ ln\ 2)/w^2]^2\}^{1/2}\right\} \qquad (16)$$

Then, in order to evaluate the molecular diffusivity one may simply inject a small band of solute into a solution flowing in a straight circular tube. By measuring the mean velocity in the tube and the width of the resultant distribution at half height after a time, t, one may then calculate the diffusion coefficient from equation (16).

As noted by Chang (1966) and Giddings and Seager (1962), the total dispersion of a pulse by independent processes is given by

$$d^2\ \text{total} = d^2\ \text{column} + d^2\ \text{extra effect}\ (1) + d^2\ \text{extra effect}\ (2) + \ldots \qquad (17)$$

If we use a long tube initially and then a short reference tube, we may utilize equation (17) to "back out" end effects that may distort the dispersion of the solute and give faulty data. Equation (16) then becomes

$$D = [(w^2_1 - w^2_2)/32\ (t_1 - t_2)\ ln\ 2]\ \left\{1 \pm (1 - (64/3)\ [RU\ (t_1 - t_1)\ ln\ 2/w^2_1 - w^2_2)]^2\}^{1/2}\right\} \qquad (18)$$

The above analysis was made for a straight tube and corrections are necessary when a coiled tube is used. As pointed out by Giddings (1960), the correction varies inversely with the square of the coil radius and is proportional to the tube radius raised to the fourth power so the use of small diameter tubing is desirable.

CHOICE OF ROOTS

It is observed that equation (18), which is the final expression for calculating the diffusivity D, has a multiplicity of roots since it was obtained as the solution to a quadratic equation. One must be able to choose the correct root; and the procedure is the same as that shown by Giddings and Seager (1962), who showed that the positive root should be chosen up to a critical velocity, $U_c = \sqrt{48}\ (D/R)$, after which the negative root should be used. They showed graphically that there was no velocity effect on the diffusivity; and indeed there is none, other than disruption of the experiment which occurs at the onset of turbulent flow.

APPLICABILITY OF METHOD

Since the foregoing analysis was based on a solution of Fick's second law (equation 6), any restriction on that law must also apply to any system on which the resultant equations are used. Moreover, as stated previously this analysis was made for a straight tube and is subject to the corrections mentioned for coiled tubes.

Since data is most easily obtained by measuring the concentration profile at a point as the injected pulse passes, one must be careful that the dispersion does not change appreciably while passing.

This condition is met by the following restriction

$$K/UL < 0.01 \qquad (19)$$

which Levenspiel and Smith (1957) showed to be sufficient for alleviating skewness in the normal distribution obtained at the point of measurement.

In previous applications to gaseous diffusion (Chang, 1966; Giddings and Seager, 1962), this technique has shown excellent reproducibility of data and produced results comparable to those obtained by conventional methods. It is felt that similar success can be attained in liquid diffusion studies once a program is initiated to develop the potential of the pulse injection method for liquids. The only real difficulty might arise in obtaining an analytic method acceptable for measuring concentration in the system one wishes to study.

ACKNOWLEDGMENT

Financial support was provided by the National Science Foundation through Research Grant No. GK-1023. Graduate fellowship support was also provided by the National Science Foundation.

NOMENCLATURE

B	Arbitrary constant	t	Time
C	Concentration	w	Width at half height of Gaussian curve, length units
D	Molecular diffusivity		
K	Effective diffusivity	x	Distance relative to fixed coordinates
M	Total amount of solute		
$n(x)$	Normal distribution	y	Distance relative to moving coordinates
R	Radius of experimental tube		
U	Mean velocity of flow	μ	Mean of normal distribution
d	Width at half height of Gaussian curve, time units	σ	Standard deviation of normal distribution, length units

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