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Conditions under which dispersion of a solute in a stream of solvent can be used to measure molecular diffusion

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It is shown that an assumption made in the author's previous discussion (Taylor 1953) can be presented as a result of analysis. The conditions under which an approximate solution of the equations for diffusion in a moving fluid can be used to interpret longitudinal dispersion of a solute in a stream of solvent flowing through a tube is given as

$$\frac{4L}{a} \gg \frac{Ua}{D} \gg 6\cdot 9.$$

Here U is the mean velocity, a the radius of the tube, D the coefficient of molecular diffusion. L is the length of tube over which appreciable changes of concentration occur.

INTRODUCTION

In a recent paper (Taylor 1953), I have discussed the dispersion of a soluble salt when injected into a stream of solvent flowing slowly through a tube. The distribution of concentration, C, of the soluble material depends on the balance between convection along the tube due to variation in velocity over the cross-section and radial molecular diffusion. Since the flow is laminar the velocity relative to the wall at a point distant r from the axis, $2U(1-r^2/a^2)$, where U is the mean speed of flow and a the radius of the section. It is convenient in the present discussion to define concentration and velocity relative to axes which move with the mean flow. Relative to these axes, the velocity u is

$$u = U(1-2z^2), \tag{1}$$

where $z = r/a$, and the equation for diffusion is

$$\frac{\partial^2 C}{\partial z^2} + \frac{1}{z}\frac{\partial C}{\partial z} + a^2\frac{\partial^2 C}{\partial x^2} = \frac{a^2}{D}\frac{\partial C}{\partial t} + \frac{a^2 U}{D}(1-2z^2)\frac{\partial C}{\partial x}, \tag{2}$$

where D is the coefficient of molecular diffusion. In general, the transfer of C along the tube by molecular diffusion is small compared with that produced by convection. It will be assumed therefore that $a^2\dfrac{\partial^2 C}{\partial x^2}$ is small compared with $\dfrac{\partial^2 C}{\partial z^2} + \dfrac{1}{z}\dfrac{\partial C}{\partial z}$. It will be seen later that the condition necessary for this to be true can be expressed in a simple manner. The transport equation will therefore be taken as

$$\frac{\partial^2 C}{\partial z^2} + \frac{1}{z}\frac{\partial C}{\partial z} = \frac{a^2}{D}\frac{\partial C}{\partial t} + \frac{a^2 U}{D}(1-2z^2)\frac{\partial C}{\partial x}. \tag{3}$$

Here $\partial/\partial t$ represents differentiation with respect to time at points fixed relative to axes moving with velocity U.

In the previous discussion the distribution of C in the case when $\partial C/\partial x =$ constant was found in the form

$$C = C_0 + \frac{a^2 U}{4D}\frac{\partial C_0}{\partial x}(z^2 - \tfrac{1}{2}z^4) \tag{4}$$

and $\partial C/\partial t = 0$, where C_0 is the concentration in the centre of the tube at $z = 0$.

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In problems of transport along a tube the mean concentration C_m over any section is more significant than C_0.

C_m is defined by
$$C_m = 2\int_0^1 Cz\,\mathrm{d}z, \tag{5}$$
and (4) may be modified to the form
$$C = C_m + \frac{a^2U}{4D}\frac{\partial C_m}{\partial x}\left(-\tfrac{1}{3}+z^2-\tfrac{1}{2}z^4\right) \tag{6}$$
by adding the constant which is necessary in order that (5) may be satisfied. As before, $\partial C/\partial t = 0$ in the case when $\partial C_m/\partial x$ is constant.

The expression (6) is a solution of (3) when $\partial C_m/\partial x$ is independent of x. The rate at which C is transported across a section is
$$Q = 2\pi a^2\int_0^1 Cuz\,\mathrm{d}z, \tag{7}$$
and inserting values of u and C from (1) and (6) it is found that
$$Q = -\pi a^2\left(\frac{a^2U^2}{48D}\right)\frac{\partial C_m}{\partial x}. \tag{8}$$
The rate of transfer of matter in a tube of radius a due to a diffusivity K is
$$-K\pi a^2\frac{\partial C_m}{\partial x}. \tag{9}$$
Comparing (8) and (9), it will be seen that the combined effect of longitudinal convection and radial molecular diffusion is to give rise to a transfer across planes which move with the mean speed of flow which is equal to that which diffusivity
$$K = \frac{a^2U^2}{48D} \tag{10}$$
would give to a stationary fluid.*

In the previous work (Taylor 1953) it was assumed that the same relationship between Q and $\partial C_m/\partial x$ will exist, to a first approximation, even when $\partial C_m/\partial x$ is not constant, so that the dispersion relative to axes moving with speed U could be discussed by means of the equation
$$\frac{\partial C_m}{\partial t} = K\frac{\partial^2 C_m}{\partial x^2}. \tag{11}$$
It was realized that such an approximation would only be likely to be valid when the time necessary for a radial variation in C to die down owing to radial diffusion was much shorter than the time necessary for an appreciable change in C to occur through longitudinal convection, and this condition was expressed by the condition (Taylor 1953, equation (16), p. 190)
$$\frac{L}{U} \gg \frac{2a^2}{3{\cdot}8^2D}. \tag{12}$$
Here L is the longitudinal extent of the region in which $\partial C/\partial x$ is appreciable.

* The factor $\frac{1}{48}$ has been obtained by Westhaver (1947) in a problem concerning the migration of ions in an electric field against a slow flow in a capillary tube.

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An alternative analysis leading to (11)

The intuitive method used in deriving (12) leaves much to be desired, and the nature of the assumption which justifies the critical step from (10) to (11) needs to be made clearer. For this purpose the effect of a small variation in $\partial C_m/\partial x$ on the distribution of C over a cross-section will be explored. By analogy with (6) it will be assumed that a solution may be taken in the form

$$C = C_m + \frac{a^2U}{4D}\frac{\partial C_m}{\partial x}\left(-\tfrac{1}{3}+z^2-\tfrac{1}{2}z^2\right)+g(z)\frac{\partial^2 C_m}{\partial x^2}, \tag{13}$$

where $g(z)$ represents the perturbation in C due to the existence of a small finite value for $\partial^2C_m/\partial x^2$. The problem is to determine $g(z)$ when $a^2U/4DL$ is small.

Substituting (13) in (6)

$$\frac{\partial^2 C_m}{\partial x^2}\left[g''(z)+\frac{1}{z}g'(z)-\frac{a^4U^2}{4D^2}\left(-\tfrac{1}{3}+\tfrac{5}{3}z^2-\tfrac{5}{2}z^4+z^6\right)\right]-\frac{a^2U}{D}(1-2z^2)\,g(z)\frac{\partial^3 C_m}{\partial x^3}$$
$$=\frac{a^2}{D}\frac{\partial}{\partial t}\left\{C_m+\frac{a^2U}{4D}\left(-\tfrac{1}{3}+z^2-\tfrac{1}{2}z^4\right)\frac{\partial C_m}{\partial x}+g(z)\frac{\partial^2 C_m}{\partial x^2}\right\}. \tag{14}$$

In order that (14) may be approximately of the same form as the diffusion equation it is necessary that

(i) the term $\dfrac{a^2U}{D}(1-2z^2)\,g(z)\dfrac{\partial^3C_m}{\partial x^3}$ may be small compared with the term in square brackets;

(ii) the terms containing $\partial C_m/\partial x$ and $\partial^2C_m/\partial x^2$ in the bracket on the right-hand side of (14) shall be small compared with the term containing only C_m;

(iii) the expression inside the square bracket in (14) shall be independent of z.

(i) and (ii) are true when the length a^2U/D is small compared with the length of tube in which significant changes in C_m occur.

The equation for diffusion with coefficient of diffusion K' is

$$K'\frac{\partial^2 C_m}{\partial x^2}=\frac{\partial C_m}{\partial t}. \tag{15}$$

Comparing (14) and (15) and using only the significant terms, the equation for $g(z)$ is

$$g''(z)+\frac{1}{z}g'(z)-\alpha\left(-\tfrac{1}{3}+\tfrac{5}{3}z^2-\tfrac{5}{2}z^4+z^6\right)=\frac{K'a^2}{D}, \tag{16}$$

where
$$\alpha=\frac{a^4U^2}{4D^2}. \tag{17}$$

The complementary function for (16) is

$$g(z)=A\ln z+B, \tag{18}$$

and $A=0$ since C is finite at $z=0$.

The expression
$$g(z)=Cz^8+Dz^6+Ez^4+Fz^2+B \tag{19}$$
is a particular integral of (16) if

$$C=\tfrac{1}{64}\alpha,\quad D=-\tfrac{5}{72}\alpha,\quad E=\tfrac{5}{48}\alpha,\quad F=\frac{K'a^2}{4D}-\tfrac{1}{12}\alpha. \tag{20}$$

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The condition at the boundary $z = 1$ is $\partial C/\partial z = 0$. Hence from (6)

$$g'(z) = 0 \quad \text{at} \quad z = 1. \tag{21}$$

Inserting this condition in (19)

$$F = -4C - 3D - zE \tag{22}$$

and inserting the values of C, D and E from (20) this leads to the equation which determines K', namely,

$$K' = \frac{4D}{a^2}\left(\tfrac{1}{12} - \tfrac{1}{16}\right) \quad \text{or} \quad K' = \frac{a^2U^2}{48D}. \tag{23}$$

Comparing (23) with (10) it will be seen that the same value is now obtained for the longitudinal diffusivity of the stream that was obtained making the intuitive assumptions.

To complete the calculation it is only necessary to determine the constant term B in (19).

In the definition of C_m given in (5) substitute the expression (13). This leads to

$$\int_0^1 zg(z)\,\mathrm{d}z = 0;$$

hence

$$\tfrac{1}{10}C + \tfrac{1}{8}D + \tfrac{1}{6}E + \tfrac{1}{4}F + \tfrac{1}{2}B = 0$$

or, using (20),

$$B = \frac{31}{64 \times 5 \times 9}\alpha,$$

and

$$g(z) = \frac{a^4U^2}{16D^2}\left\{\tfrac{1}{16}z^8 - \tfrac{5}{18}z^6 + \tfrac{5}{12}z^4 - \tfrac{1}{4}z^2 + \frac{31}{16 \times 5 \times 9}\right\}. \tag{24}$$

The distribution represented by (24) will contribute something to the integral (7) for the transport over a section but it will be of a lower order of magnitude than that given in (8) if the length $a^2U/4D$ is small compared with the length of tube over which C has an appreciable value.

Conditions under which measurements of C_m may be applied to obtain values of D

In my previous paper (Taylor 1953) it was suggested that measurements of K, made by measuring dispersion along a capillary tube, may be used for measuring the diffusion coefficient D using (10). In order that the expression $K = a^2U^2/48D$ may be used for a valid representation of dispersion in a tube, two conditions must be satisfied:

(i) In order that the longitudinal molecular diffusion may be negligible compared with the dispersive effect represented by K it is necessary that

$$D \ll \frac{a^2U^2}{48D},$$

or, approximately,

$$\frac{aU}{D} \gg \sqrt{48} \text{ or } 6{\cdot}9. \tag{25}$$

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(ii) $\dfrac{a^2U}{4D}\left(\dfrac{1}{L}\right)$ must be small. Here L is used to represent the distance in which greater part of the change in concentration takes place. L^{-1} may be taken as a mean of $\dfrac{1}{C_m}\dfrac{\partial C_m}{\partial x}$ in that region.

Combining (i) and (ii) the condition to be satisfied in experiments is

$$\frac{4L}{a} \gg \frac{Ua}{D} \gg 6{\cdot}9. \tag{26}$$

If ratios 10:1 are permitted between the terms of the inequalities (26) the following are permissible:

$$\frac{Ua}{D} = 69 \quad \text{and} \quad \frac{4L}{a} = 690. \tag{27}$$

Thus for a tube of radius 0·025 cm, such as that used in my previous experiments, the least value of L for which (10) could be used accurately is

$$L = \frac{690}{4} \times 0{\cdot}025 = 4{\cdot}3\,\text{cm}, \tag{28}$$

and to satisfy (27) when the diffusion coefficient was $1{\cdot}0 \times 10^{-5}$ the velocity U would have to be controlled at

$$U = \frac{69 \times 10^{-5}}{0{\cdot}025} = 0{\cdot}028\,\text{cm/s}.$$

In my previous paper (Taylor 1953, p. 196), experiments were described in which potassium permanganate $(1{\cdot}5 \times 10^{-5} > D > 0{\cdot}5 \times 10^{-5})$ was introduced at various rates into a tube 0·054 cm bore. The rates were 8·3, 6·7, 0·26, 0·0028 cm/s. Of these the first three satisfy the condition $Ua/D > 69$. The fourth does not satisfy this condition. At the other limit the first two do not satisfy the condition $L > 10\dfrac{Ua^2}{4D}$. The third nearly satisfies it if L is taken as the length of tube between the points where C is $\frac{1}{100}$ and $\frac{99}{100}$ of the full concentration. The fourth satisfies this condition. Thus only the third satisfies approximately both conditions, and in fact only the third was used in comparing the value of D, obtained from (10) with values given by previous observers.

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