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THE DYNAMIC DIFFUSION CONSTANT WITHIN FLUID FLOW IN AN OPEN STRAIGHT TUBE WITH AN ELLIPTICAL CROSS-SECTION

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SUMMARY

The concept of the dynamic diffusion constant within fluid flow in an open tube with a circular cross-section, elaborated by Westhaver and Taylor, is extended to the case of an open tube with an elliptical cross-section.

INTRODUCTION

There has been, of late, a surge of interest in the application to chromatography of tubes with a non-circular cross-section, and it was thought that the extension of the work on diffusion in round tubes to tubes with an elliptical cross-section would serve to give as well an insight in the behavior of fluids in tubes with still another cross-section, such as a rectangular cross-section.

When a miscible sample is introduced instantaneously and uniformly in a cross-section of a carrier fluid flowing in accordance with Poiseuille law within an open, straight tube with a circular cross-section and without a retentive layer for the sample on its wall, several distinct phases follow the injection.

During an initial phase the sample diffuses isotropically within the carrier, and the variance of its distribution with respect to the tube axis, the x-axis, increases linearly with time.

This first phase is followed by a second phase during which the sample is given by the carrier the paraboloidal distribution typical of Poiseuille flow. During this second phase the overall distribution of the sample within the tube is essentially uniform over the x-abscissa reached by the sample, and its variance increases quadratically with time.

Then occurs a third phase during which the sample near the wall, having diffused into the high carrier velocity gradient in that region, tends to catch up with the main body of the sample which has travelled at a higher speed, and builds up a hump in the rear of the formerly rectangular sample spread. A computer simulation of this phase, and of the following phase, during which the hump, having grown enough to overtake the front of the distribution, continues to have three inflexion points in its leading edge, was made[1] to obtain an insight into a fluid behavior for which there has not been an analytical treatment so far.

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Eventually a fifth phase is ushered in by the coalescence of the three inflexion points of the leading edge into one, so that the overall sample distribution begins to suggest the gaussian distribution which is approached asymptotically as time goes on.

As this fifth phase develops, the sample behaves more and more as if its spreading were determined by a diffusing process characterized by the dynamic diffusion constant D_1

$$D_1 = D + \frac{v_0^2 r_0^2}{48\,D} \tag{1}$$

calculated by Westhaver[2] and Taylor[3], and in which D, v_0 and r_0 are the static diffusion constant, the average carrier velocity and the inner tube radius, respectively.

The purpose of this study is the extension of eqn. 1 to the case when the tube cross-section is elliptical.

DISCUSSION

For the calculation of D_1 for the elliptical case, a first task consists in determining the velocity distribution within the carrier for the linear (Poiseuille) case. Toward this end we note first that we must then have

$$v_y = v_z = 0 \tag{2}$$

these two vanishing velocities being within the plane normal to the x-axis, in which the elliptical inner wall is determined by

$$\frac{y^2}{a^2} + \frac{z^2}{b^2} = 1$$

where a and b are the semi-main axes of the elipse. Eqn. 2 is an immediate conclusion from the assumed linearity of the flow process, because v_y and v_z being measured normally to the main flow could depend only upon an even power of that flow.

Next we express the negligible incompressibility of the fluid with the relation

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} = 0 \tag{3}$$

wherefrom, by virtue of eqn. 2:

$$\partial v_x / \partial x = 0 \tag{4}$$

We then write the six classical equations connecting the velocity components of a fluid of viscosity μ with the tensions τ_x, τ_y, τ_z, τ_{xy}, τ_{xz} and τ_{yz} on an elementary cube of fluid. We have first

$$\mu\left(\frac{\partial v_x}{\partial x} - \frac{\partial v_y}{\partial y}\right) = \tau_x - \tau_y = 0 \tag{5a}$$

$$\mu\left(\frac{\partial v_y}{\partial y} - \frac{\partial v_z}{\partial z}\right) = \tau_y - \tau_z = 0 \tag{5b}$$

wherefrom

$$\tau_x = \tau_y = \tau_z = -p(x) \tag{6}$$

the last equation expressing the condition that the essential pressure drop is in the x-direction.
We have also

$$\mu\left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x}\right) = \tau_{xy} \tag{7a}$$

$$\mu\left(\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x}\right) = \tau_{xz} \tag{7b}$$

$$\mu\left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y}\right) = \tau_{yz} \tag{7c}$$

and by virtue of eqn. 2:

$$\mu(\partial v_x/\partial_y) = \tau_{xy} \tag{8a}$$

$$\mu(\partial v_x/\partial z) = \tau_{xz} \tag{8b}$$

$$\tau_{yz} = 0 \tag{8c}$$

Next, we write that there are no field forces acting on the fluid, *i.e.*, since

$$f_x + \frac{\partial \tau_x}{\partial x} + \frac{\partial \tau_{xy}}{\partial y} + \frac{\partial \tau_{xz}}{\partial z} = 0$$

and

$$f_x = 0$$

we have

$$\frac{\partial \tau_x}{\partial x} + \frac{\partial \tau_{xy}}{\partial y} + \frac{\partial \tau_{xz}}{\partial z} = 0 \tag{9}$$

and, by virtue of eqn. 7:

$$\frac{\partial \tau_x}{\partial x} = -\frac{\mathrm{d}p}{\mathrm{d}x} = -\mu\left(\frac{\partial^2 v_x}{\partial y^2} + \frac{\partial^2 v_x}{\partial z^2}\right) \tag{10}$$

This last equation, together with the boundary condition that v_x vanish at the tube walls, permits to determine the general form of v_x:

$$v_x = 2v_0\left(1 - \frac{y^2}{a^2} - \frac{z^2}{b^2}\right) \tag{11}$$

And we obtain with eqn. 10:

$$-\frac{\mathrm{d}p}{\mathrm{d}x} = 4\mu v_0\left(\frac{1}{a^2} + \frac{1}{b^2}\right) \tag{12}$$

Integration of eqn. 11 over the entire ellipse gives the total fluid flow F:

$$F = \pi ab v_0 \tag{13}$$

For a pipe of length l we obtain for the total pressure drop, for a given flow F

$$\frac{p}{l} = -\frac{dp}{dx} = \frac{4F}{ab}\mu\left(\frac{1}{a^2}+\frac{1}{b^2}\right) \tag{14}$$

whence, for the hydrodynamic or pneumatic resistance R of the pipe

$$R = \frac{p}{F} = \frac{4\pi l}{\pi}\left(\frac{1}{a^3 b}+\frac{1}{ab^3}\right) \tag{15}$$

which, for $a=b=r_0$, reduces to the classical value for the resistance of a round pipe.

The derivation of the dynamic or effective diffusion constant D_1 starts with the observation that, were there no flow, the one-dimensional diffusion equation

$$D\frac{d^2c}{dx^2} = \frac{dc}{dt} \tag{16}$$

where c designates the concentration of sample within the solute, admits the solution:

$$c(x, t) = e^{-\frac{x^2}{4Dt}}/\sqrt{t} \tag{17}$$

Accordingly, we shall postulate that, when the fluid flow has the average velocity v_0, we may replace x by $x-e-v_0t$ in eqn. 17 [$e=e(y,z)$]

$$c(x, y, z, t) = e^{-\frac{(x-e-v_0t)^2}{4D_1 t}}/\sqrt{t} \tag{18}$$

and examine under what condition the concentration so expressed is approached asymptotically by the physical model.

We replace c from eqn. 18 in the three-dimensional diffusion equation:

$$D\Delta^2 c = \frac{dc}{dt} = \frac{\partial c}{\partial t} + \vec{v}\times \text{grad } c = \frac{\partial c}{\partial t} + zv_0\left(1-\frac{y^2}{a^2}-\frac{z^2}{b^2}\right)\frac{\partial c}{\partial x} \tag{19}$$

This substitution yields:

$$D\Bigg[-\frac{1}{2D_1 t\sqrt{t}} + \frac{(x-e-v_0t)^2}{4D_1^2t^2\sqrt{t}} + \frac{(x-e-v_0t)^2(\partial e/\partial y)^2}{4D_1^2t^2\sqrt{t}}$$

$$+\frac{(x-e-v_0t)(\partial^2 e/\partial y^2)}{2D_1 t\sqrt{t}} - \frac{(\partial e/\partial y)^2}{2D_1 t\sqrt{t}} + \frac{(x-e-v_0t)^2(\partial e/\partial z)^2}{4D_1^2t^2\sqrt{t}} +$$

$$+\frac{(x-e-v_0t)(\partial^2 e/\partial z^2)}{2D_1 t\sqrt{t}} - \frac{(\partial e/\partial z)^2}{2D_1 t\sqrt{t}}\Bigg] = \frac{v_0(x-e-v_0t)}{2D_1 t\sqrt{t}} +$$

$$+\frac{(x-e-v_0t)^2}{4D_1t^2\sqrt{t}} - \frac{1}{t\sqrt{t}} - 2v_0\left(1-\frac{y^2}{a^2}-\frac{z^2}{b^2}\right)\left(\frac{x-e-v_0t}{2D_1 t\sqrt{t}}\right) \tag{20}$$

Equating separately the terms with the common $1/t\sqrt{t}$ factor leads to the equation

$$D_1 = D\left[1 + \left(\frac{\partial e}{\partial y}\right)^2 + \left(\frac{\partial e}{\partial z}\right)^2\right] \tag{21}$$

and the identical equation is obtained by equating separately the terms in $(x-e-v_0t)^2/4D_1t^2\sqrt{t}$.
Equating separately the terms in $(x-e-v_0t)/2D_1t\sqrt{t}$ yields the other equation:

$$\frac{\partial^2 e}{\partial y^2} + \frac{\partial^2 e}{\partial z^2} = \frac{v_0}{D}\left(1 - 2\frac{y^2}{a^2} - 2\frac{z^2}{b^2}\right) \tag{22}$$

This equation, together with the boundary condition that $\partial e/\partial n$ vanish at the wall along a normal to it, serves to determine e. This last condition demands, by virtue of Green's theorem, that the integral of the right-hand side of eqn. 22 over the ellipse area vanish, which can be verified to be the case, owing to the selection of v_0 as the coefficient of t in $x-e-v_0t$.

It can be verified by inspection that

$$e = \frac{v_0}{12D\,(a^2+b^2)}\left[-2\,(a^2+2b^2)\,y^2 - 2\,(2a^2+b^2)\,z^2 + \right.$$
$$\left. + \left(1+2\frac{b^2}{a^2}\right)y^4 + 6y^2z^2 + \left(1+2\frac{a^2}{b^2}\right)z^4\right] \tag{23}$$

fulfills eqn. 22 and the boundary conditions.

We are now in a position to determine D_1 from eqn. 21 by the device of using the average value of $(\partial e/\partial y)^2$ and $(\partial e/\partial z)^2$ over the ellipse. This device constitutes the approximation required to determine the value of D_1 which will determine the value of c which is reached asymptotically after increasingly greater times. The physical interpretation of the right-hand side of eqn. 21 is that the first member of the bracket yields the entropy increase due to longitudinal diffusion of the sample along the x-axis while the other two terms represent the diffusion of the sample in the two radial directions.

In the determination of the average values of $(\partial e/\partial y)^2$ and $(\partial e/\partial z)^2$ use can be made of the formula giving the average value of $y^{2m}z^{2n}$ over the ellipse, which is

$$\overline{y^{2m}z^{2n}} = \frac{(2m)!\,(2n)!}{2^{2m+2n}m!\,n!\,(m+n+1)!}\,a^{2m}b^{2n}$$

and we obtain

$$D_1 = D + \frac{v_0^2\,(5a^4 + 12a^2b^2 + 5b^4)}{576D\,(a^2+b^2)} \tag{24}$$

which, as it should, gives Westhaver and Taylor formula when $a=b=r_0$.

It could be of interest for chromatographic applications to extend eqn. 24 to the case of tube walls with a retentive layer, but it will be immediately realized that a uniform layer will lead to the use of elliptic functions.

CONCLUSIONS

When, *e.g.*, $a \gg b$ eqn. 24 can be approximated by

$$D_1 \approx D + (5v_0a^2/576D) \tag{25}$$

and when eqn. 25 is compared with eqn. 1, it can be seen that the dynamic diffusion constant D_1, and therefore also the HETP of an open tube without a retentibe layer on the wall, will be the same as if the elliptical tube had been replaced by a round tube with a radius r_0 equal to:

$$r_0 = \sqrt{\frac{5}{12}}\,a \approx 0.645a \tag{26}$$

On the other hand, the resistance to flow, given by eqn. 15, can be written approximately:

$$R = \frac{4\mu l}{\pi} \cdot \frac{1}{ab^3} \tag{27}$$

Eqns. 26 and 27 lead us therefore to the conclusion that in elliptical tubes, and therefore also in tubes with a rectangular cross-section, the HETP, namely the quantity which we would like to be as small as possible, is determined essentially by the largest dimension of the elliptical cross-section, whereas the resistance to flow, namely another quantity which we would like to be as small as possible, is determined mostly by the inverse cube of the smallest dimension of the ellipse.

It is concluded therefore that tubes with an elongated cross-section such as a highly excentric ellipse or a very elongated rectangle, will have an inferior chromatographic behavior when compared to round tubes.

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