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The Flow of a Solution into a Tube Filled with Solvent: Mathematical Derivations

We have recently given a set of equations[1] which yield the effluent concentration of a solution B introduced into a tube in which a solution A is flowing. Three experimental cases were considered and in each the flow concentration of B in the effluent was obtained in function of the volume of solution B injected and of the total amount of fluid collected. In the present paper, we wish to find the flow rates of solutions A and B at the outlet and their total output with time, and limit ourselves to the simplest experimental case, that in which the amount of solution B injected is unlimited. The more complicated cases could be approached by the same procedure.

We assume, as in the past, that the two solutions are of the same density and the same viscosity, and that the time is short enough to render negligible the effect of molecular diffusion of one solution into the other.

We first consider the flow of solution B. Instead of following the original procedure for the derivation of the Poiseuille equation, in which the integration of

$$V = \frac{P\,(R^2 - r^2)}{4\,\eta\,L} \tag{1}$$

is carried out from $r = 0$ to $r = R$, we integrate from $r = 0$ to $r = z$, where z is the radius of the paraboloid at its intersection with a transverse plane at the end of the tube (Figure). (In equation (1), V is the velocity of an annulus of diameter r and thickness dr; P is the pressure, R the diameter of the tube, L its length, η the viscosity.) From equation (1) we have

$$r^2 = R^2 - \frac{4\,\eta\,L\,V}{P} = R^2 - \frac{4\,\eta\,L^2}{P\,t} = z^2 .$$

Calling Q_B/t the instantaneous amount of solution delivered:

$$\frac{Q_B}{t} = \frac{2\,\Pi\,P}{4\,\eta\,L}\int_0^z (R^2 - r^2)\,r\,dr .$$

Carrying out the integration:

$$\frac{Q_B}{t} = \frac{\Pi\,P\,R^4}{8\,\eta\,L} - \frac{2\,\Pi\,\eta\,L^3}{P\,t^2} . \tag{2}$$

Equation (2) gives the instantaneous rate of discharge of solution B from the moment it reaches the end of the tube to infinity.

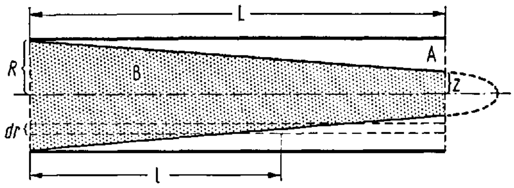

Diagram to illustrate conditions of flow.

The relative concentration c of solution B at the outlet is the ratio between Q_B/t and the total Poiseuille flow $Q_{A+B}/t = \Pi P R^4/8\eta L$:

$$\frac{Q_B}{Q_{A+B}} = 1 - \frac{16\,\eta^2\,L^4}{P^2\,t^2\,R^4} = c . \tag{3}$$

Writing $Q_{A+B}/\Pi R^2 L = U$ for the ratio between the total discharge and the capacity of the tube:

$$Q_{A+B} = U\,\Pi\,R^2\,L = \frac{\Pi\,P\,R^4\,t}{8\,\eta\,L}\,; \quad t = \frac{U\,L^2\,8\,\eta}{P\,R^2} .$$

Substituting this value of t in equation (3):

$$\frac{Q_B}{Q_{A+B}} = 1 - \frac{1}{4\,U^2} = c . \tag{4}$$

Equation (4) gives the relative concentration of B in the samples collected, referred to the relative amount of solution B introduced into the tube; it is the expression already obtained by a graphical procedure[1].

We now desire the total amount of solution A and solution B delivered at time t.

The instantaneous rate of delivery of solution A, Q_A/t, is obviously equal to the rate of total delivery $Q_{A+B}/t = \Pi P R^4/8\eta L - Q_B/t$ (equation (2)).

$$\frac{Q_A}{t} = \frac{2\,\Pi\,\eta\,L^3}{P\,t^2} . \tag{5}$$

This is integrated between $t = t_{L,0}$ (the time taken by the streamline on the axis, where $r = 0$, to reach the end of the tube) and any time t greater than $t_{L,0}$. From equation (1),

$$t_{L,0} = \frac{L}{V_{r=0}} = \frac{4\,\eta\,L^2}{R^2\,P}\,;$$

$$\int_{t_{L,0}} dQ_A = \frac{2\,\Pi\,\eta\,L^3}{P}\int_{t_{L,0}} \frac{dt}{t^2} = -\frac{2\,\Pi\,\eta\,L^3}{P\,t} + \frac{\Pi\,R^2\,L}{2} .$$

To this must be added the constant volume of solution A discharged between $t = 0$ and $t_{L,0}$. This is equal to:

$$\int_0^{t_{L,0}} dQ_A = \frac{\Pi\,P\,R^4}{8\,\eta\,L}\int_0^{t_{L,0}} dt = \frac{\Pi\,R^2\,L}{2} .$$

Hence, the total volume of solution A discharged is

$$Q_A = \Pi\,R^2\,L - \frac{2\,\Pi\,\eta\,L^3}{P\,t} . \tag{6}$$

Equation (6) gives the volume of solution A discharged in function of time; it is obviously valid only for $2\Pi\eta L^3/Pt \leq \Pi R^2 L/2$; for $t = \infty$, $Q_A = \Pi R^2 L$. In other words, solution A, the volume of which is $\Pi R^2 L$, is completely expelled from the tube only at infinite time.

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[1] J. Bourdillon, Exper. *19*, 250 (1963); *20*, 423 (1964).

In order to obtain the total amount of solution B discharged, we subject equation (2) to the same treatment:

$$\int dQ_B = \frac{\Pi\ P\ R^4}{8\ \eta\ L} \int_{t_{L,0}} dt - \frac{2\ \Pi\ \eta\ L^3}{P} \int_{t_{L,0}}^{t} \frac{dt}{t^2}\,.$$

Carrying out the integration and simplifying:

$$Q_B = \frac{\Pi\ P\ R^4\ t}{8\ \eta\ L} + \frac{2\ \Pi\ \eta\ L^3}{P\ t} - \Pi\ R^2\ L\,. \qquad (7)$$

Equation (7) is obviously valid only for $t \geq t_{L,0}$.

Let us finally consider the special case in which the amount of solution B introduced into the tube is equal to the capacity of the tube. Then, adding equation (6) to equation (7),

$$Q_A + Q_B = \frac{\Pi\ P\ R^4\ t}{8\ \eta\ L} = \Pi\ R^2\ L; \qquad t = \frac{8\ \eta\ L^2}{P\ R^2}\,.$$

Substituting t in equation (7) and dividing both sides by $\Pi R^2 L$,

$$Q_B = \frac{\Pi\ R^2\ L}{4}\,. \qquad (8)$$

Under these circumstances, the volume of solution B discharged is one quarter the volume of solution B injected.

Résumé. On offre un ensemble d'équations qui s'appliquent à l'écoulement laminaire de deux solutions A et B, de même viscosité, lorsqu'on introduit B dans un tube préalablement rempli de solution A.

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The Selective Esterification of the 5′-Hydroxyl of Thymidine

The usual procedure for the esterification of nucleosides[1-4] involves the use of protective groups for achieving selectivity. We now wish to report that the 5′-hydroxyl of thymidine can be selectively esterified by controlling the conditions of acylation. For this purpose, the use of a relatively large volume of solvent is necessary. The bulk and quantity of acylating agent and the amount of base present in the reaction mixture are also of significance, as selectivity is based on the emphasis of the greater reactivity of the primary hydroxyl in comparison with the secondary hydroxyl.

Thymidine-5′-phosphate was obtained as follows: Thymidine[5] (48.4 mg, 0.2 m*M*) was dissolved in acetonitrile (50 ml) containing pyridine (0.04 ml, 0.5 m*M*) by refluxing for 15 min. The solution was cooled to −10° and stirred while a solution of dibenzyl phosphorochloridate (104 mg, 0.35 m*M*) in acetonitrile (25 ml) was added dropwise over 4 h. After standing at room temperature for 12 h, the solution was concentrated and examined by paper chromatography. A single UV-absorbing zone (Rf 0.38 (A))[6] was discernible, and no thymidine (Rf 0.70 (A)) was present[7]. The product was isolated by evaporating the solution to dryness, dissolving the residue in chloroform (20 ml), washing the chloroform solution with water, drying and removing the solvent. Its identity as thymidine-5′-dibenzyl phosphate was established by its hydrolysis with crude snake venom in glycine buffer pH 9.0 to thymidine[8]. Hydrogenolysis[1] in the presence of Pd/C yielded thymidine-5′-phosphate (Rf 0.30 (A)).

For the preparation of *thymidine-5′-sulphate*, a solution of chlorosulphonic acid (100 mg, 0.85 m*M*) was added over a period of 4 h to a stirred solution of thymidine (200 mg, 0.82 m*M*) in acetonitrile (100 ml) containing pyridine (0.1 ml, 1.26 m*M*), cooled to −5°. After the reaction mixture had stood overnight at room temperature, it was evaporated to dryness and the residue dissolved in water (0.5 ml). Paper chromatography in solvent A revealed the presence of three UV-absorbing zones, Rf 0.34, 0.40, and 0.70; the fast-moving zone being due to thymidine. The optical densities of the eluates of these zones were in the ratio of 7.5:1.5:1.0 at 260 mμ. Fractionation of these products was done by chromatography on Whatman 3MM paper employing the same solvent system. The zones were separately eluted with water and lyophilized. The minor product (Rf 0.40 (A), 0.61 (B)) was identified as *thymidine-3′-sulphate* by comparison with material obtained unambiguously. The major product was therefore thymidine-5′-sulphate (Rf 0.34 (A), 0.53 (B)) and was isolated as the pyridinium salt. Found: C 44.28, H 5.07. $C_{10}H_{14}O_8N_2S \cdot C_5H_5N$ requires: C 44.87, H 4.74%.

Thymidine-3′-sulphate was obtained unambiguously by treating 5′-o-trityl thymidine (121 mg, 0.25 m*M*) in acetonitrile (75 ml) containing pyridine (0.1 ml) with chlorosulphonic acid (0.1 ml) at −5°. After allowing the reaction mixture to stand overnight, solvent was removed and the product detritylated by treating a solution in acetone-water (4:1) with 4*N* HCl (2 ml) at 15° for 1 h. Neutralization with triethyl amine evaporation of acetone and removal of triphenylcarbinol by extraction with ether yielded an aqueous solution containing thymidine-3′-sulphate. Pure thymidine-3′-sulphate could then be

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[1] F. R. ATHERTON, H. T. OPENSHAW, and A. R. TODD, J. chem. Soc. *1945*, 382.

[2] G. M. TENNER, J. Am. chem. Soc. *83*, 164 (1964).

[3] J. ARNOLD and T. D. PRICE, J. Am. chem. Soc. *84*, 1402 (1962).

[4] P. W. WIGLER and H. U. CHOI, J. Am. chem. Soc. *86*, 1636 (1964).

[5] All acylations carried out under strictly anhydrous conditions and carefully dried materials were used. Thymidine was recrystallized from CH_3CN. Acylating agents were freshly distilled.

[6] Descending paper chromatography. Solvent systems: A, *n*-butanol-acetic acid-water (4:1:5); B, isopropanol-water (4:1).

[7] Unreacted thymidine was present when lesser amounts of pyridine were used. Some diesterification occurred when pyridine content was increased to 0.1 m*M*.

[8] W. E. RAZZELL and H. G. KHORANA, J. biol. Chem. *234*, 2105 (1959).