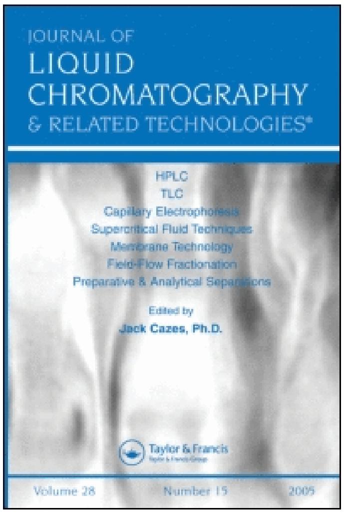

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SEDIMENTATION-FLOTATION FOCUSING FIELD-FLOW FRACTIONATION IN CHANNELS WITH MODULATED CROSS-SECTIONAL PERMEABILITY. I. THEORETICAL ANALYSIS

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ABSTRACT

A new-shaped cross-section of a channel with modulated permeability used in Sedimentation-Flotation Focusing Field-Flow Fractionation is proposed. The shape of the resulting velocity profile inside the channel is described as a function of the geometric channel characteristics. Basic separation parameters such as retention, efficiency and the related resolution are discussed. The principle of a channel with modulated permeability can also be applied to other subtechniques of Field-Flow Fractionation.

INTRODUCTION

Field-Flow Fractionation (FFF) is a separation method conceptually proposed by Giddings (1) who, together with his coworkers, elaborated the theory, the experimental techniques and a number of applications for the purpose of separating macromolecules and particles.

The principle of the method bases upon the simultaneous influence of concentration and flow inhomogeneities. The separation is due to differences

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in the migration velocity of the solute species separated in a narrow channel of rectangular cross-section through which a fluid is flowing. The physical field applied perpendicularly to the channel longitudinal axis, for instance, a thermal, electrical or magnetic field or gravitational forces, etc., produces a concentration gradient across the channel, commonly along the direction of the forces of the field. The streamline velocity of the fluid passing through the channel also changes across the channel. This velocity gradient is caused by viscosity effects associated with flow processes.

In our preliminary communication (2) we described the principle of a new separation method called Sedimentation-Flotation Focusing Field-Flow Fractionation (SFFFFF). This new method is based on the well-known physical phenomenon owing to which suspended particles or dissolved macromolecules sediment or float in the density gradient of the liquid phase. The sedimentation-flotation processes cause the solute of a given density to concentrate to a layer wherein the density of the environment is the same as that of the solute. Diffusion processes or the Brownian migration act in the opposite direction tending to disperse the concentrated solute zone that was formed. After a while dynamic equilibrium is reached, the solute flux due to sedimentation-flotation forces being just equilibrated by the flux resulting from dispersive processes and, as a result, the solute is focused to a narrow zone whose concentration distribution corresponds to the local density gradient. Upon attaining this dynamic equilibrium or even in the course of equilibration, the liquid in the narrow fractionation channel moves in a direction perpendicular to the density gradient

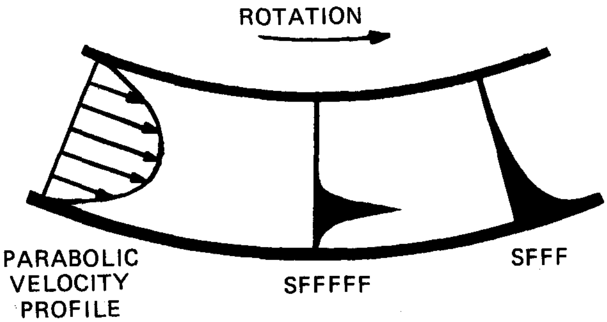

FIGURE 1. Section of the rotating channel with parabolic velocity profile. The concentration distribution across the channel is Gaussian in case of sedimentation-flotation focusing field-flow fractionation (SFFFFF) and exponential in case of sedimentation field-flow fractionation (SFFF).

formed. Under laminar flow conditions a steady velocity profile is produced and the solute zone moves along the channel with a linear velocity corresponding to the streamline velocity in the relevant coordinate. In our initial proposal (2) we supposed that the channel across which a density gradient and, consequently, a concentration distribution of the solute is formed, was narrow enough and that the velocity profile generated was parabolic as shown in Figure 1. This figure compares, at the same time, the Gaussian concentration distribution of the solute for SFFFFF and the exponential distribution for the classical Sedimentation Field-Flow Fractionation method (SFFF) (3).

This paper examines the theoretical aspects of SFFFFF for the case of a separating channel with modulated cross-sectional permeability that leads to a more complex distribution of the streamline velocities inside the channel. When chosing the appropriate shape of the cross-section, improved separation characteristics can be achieved by means of the SFFFFF method.

ANALYSIS

The distribution of the streamline velocities of a unidirectional steady flow in a channel of given cross-section can be expressed by solving the general equation

$$\frac{\delta^2 u}{\delta y^2} + \frac{\delta^2 u}{\delta z^2} = - \frac{G}{\mu} \qquad (1)$$

where u is the linear streamline velocity along the x-axis, y and z are coordinates in the plane of the channel cross-section, $G = \Delta P/L$ is the pressure gradient throughout the channel length L, and μ is the viscosity of the fluid. The analytical solution of Equation (1) for a given shape of the channel cross-section is known for certain simple cases only (4). One of the latter is a channel of rectangular cross-section. The positions of the walls of a rectangular channel are determined by the coordinates $y = \pm b$ and $z = \pm c$, $c > b$, where $a = c/b$ is called aspect ratio. Since the expression

$$u - \frac{1}{2} G \; (b^2 - y^2) \; / \mu \qquad (2)$$

is an even function of the both variables y and z that satisfies the Laplace equation and is zero for $y = \pm b$, it can be written as the Fourier series for y of the form

$$\sum_{n \text{ odd}} A_n \cosh \frac{n \pi z}{2b} \cos \frac{n \pi y}{2b} \qquad (3)$$

while the coefficients A_n can be found from the boundary condition for $z = \pm c$, This results in a relatively complex function describing the shape of the velocity profile in the coordinates y and z of a rectangular channel (5). An approximate simplified solution (5) suited to describe the shape of the velocity profile, if $c \gg b$ and $a \gg 1$, respectively, is given by

$$U = (1 - Y^2) \left[1 - \frac{\cosh(\sqrt{3}\, a\, Z)}{\cosh(\sqrt{3}\, a)}\right] \qquad (4)$$

where $U = u/u_{max}$ (u_{max} is the maximum streamline velocity in the channel centre), $Y = y/b$ and $Z = z/c$.

Figure 2 demonstrates the course of the dependence of U on Z for Y = 0 and for two different values of a = 20 and 100. It is obvious from the figure that the velocity profile formed in the plane of the z and x axes is flat in the central part while it is steeply bending near the side walls of the channel only. The higher the value of a, the steeper the curvature that begins relatively nearer to the wall. On the other hand, the velocity profile formed in the plane of the x and y axes or in parallel planes is parabolic as shown in Figure 3 for illustration.

Let us examine now the changes of the velocity profile in the plane of the x and z axes or in parallel planes in the case of the channel being of other than rectangular cross-section so that its permeability may change continuously along the z axis. We shall consider two cases that may be of practical importance: a channel whose two longer walls consist of planes containing the angle α (see Figure 4a), and a channel whose two longer walls consist of parabolic surfaces (see Figure 4b).

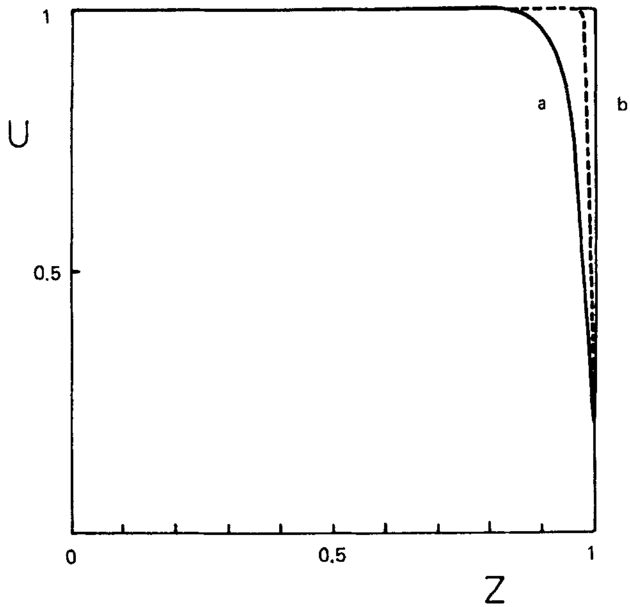

FIGURE 2. Velocity distribution in a rectangular channel. Aspect ratio a: a = 20 b: a = 100.

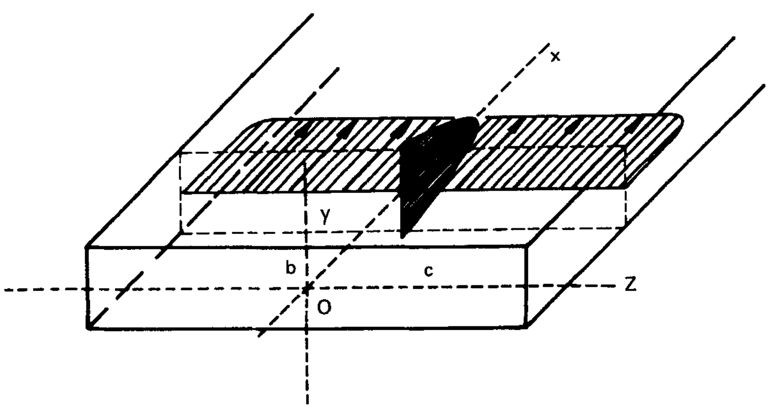

FIGURE 3. Schematic illustration of velocity distributions in a rectangular channel.

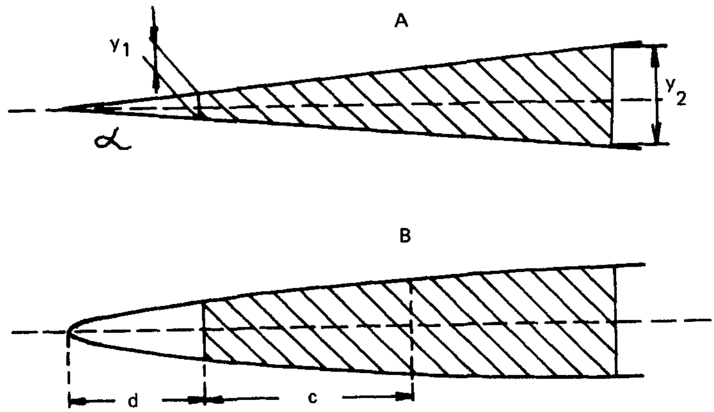

FIGURE 4. Cross-sections of two different model channels.

In case that channel permeability changes along the z axis, Equation (4) can be re-written as follows

$$U = \varphi(Z)\ (1 - Y^2)\left[1 - \frac{\cosh(\sqrt{3}\ a\ Z)}{\cosh(\sqrt{3}\ a)}\right] \quad (5)$$

where $\varphi(Z)$ is the permeability in the given point Z. In order to calculate and quantitatively express permeability in point Z, we can suppose with fair approximation that, in the close vicinity of point Z, relations describing the flow of a fluid between two parallel planes are valid and that, as a consequence, velocity U_Z in point Z, normalized relative to Z=0 is

$$U_Z = \frac{b^2(Z)}{b^2(0)}\ (1 - Y^2) \quad (6)$$

Therefore, linear velocity U is a function of the square of the distance of the channel walls in point Z. For instance, it holds for the velocity ratio in points A and B,

$$\frac{U_A}{U_B} = \left[\frac{b_A}{b_B}\right]^2 \tag{7}$$

In view of the above facts, the following relation holds for a channel formed by two planes containing a given angle α i.e. for a channel geometrically determined by the length ratio of the two shorter walls y_1 and y_2 (see Figure 4a) and by the aspect ratio,

$$U^* = \left[1 + Z \left(\frac{y_2 - y_1}{y_2 + y_1}\right)\right]^2 (1 - Y^2) \left[1 - \frac{\cosh(\sqrt{3}\, aZ)}{\cosh(\sqrt{3}\, a)}\right] \tag{8}$$

where U^* is the normalized velocity $U^* = U/U_{Z=0}$ ($U_{Z=0}$ being the velocity for Z=0).

The aspect ratio in Equation (8) is also a function of the coordinate Z. Since variability a(Z) affects the resulting form of the function $U^* = U(Z)$ only in the marginal parts when Z is approaching ± 1, constant values of a for calculating U^* in both marginal parts can be applied in Equation (8) without substantially affecting the course of the function $U^* = U(Z)$ in the important central part. Figure 5 shows the course of the functions $U^* = U(Z)$ for two different channels differing in the y_2/y_1 ratio, that means in the modulated permeability along the z-axis. The calculations were made for two different values of a = 20 and 100 in order to evaluate the influence of variability a(Z) on the results of the calculations. In this case, if the longer channel walls consist of two planes containing a given angle, the central parts of the velocity profiles are shaped like parabolic sections with the maximum velocity in the vicinity of one of the shorter side walls of the channel.

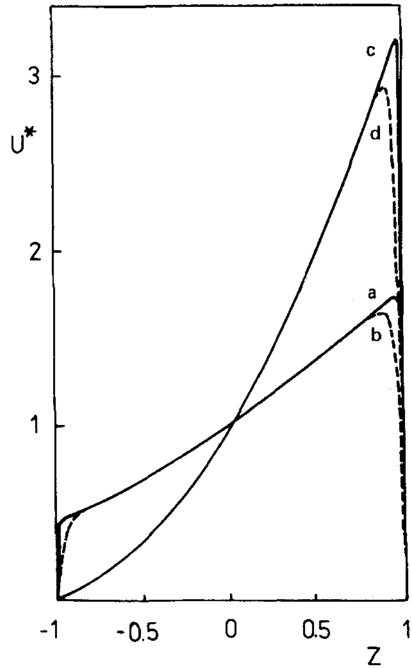

FIGURE 5. Normalized velocity distributions in channels with plane walls. a: $y_2/y_1 = 2$, $a = 100$, b: $y_2/y_1 = 2$, $a = 20$, c: $y_2/y_1 = 10$, $a = 100$, d: $y_2/y_1 = 10$, $a = 20$.

In case the channel consists of two surfaces parabolic in shape as shown in Figure 4b, the following relation holds instead of Equation (7)

$$\frac{U_A}{U_B} = \frac{c + d + c\,Z_A}{c + d + c\,Z_B} \tag{9}$$

and it holds for U^*

$$U^* = \left(\frac{cZ}{c+d} + 1\right)(1-Y^2)\left[1 - \frac{\cosh(\sqrt{3}\,a\,Z)}{\cosh(\sqrt{3}\,a)}\right] \tag{10}$$

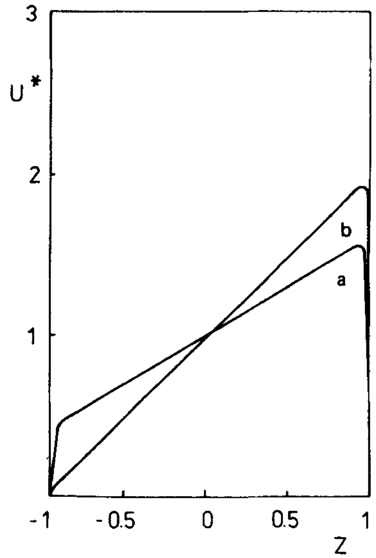

FIGURE 6. Normalized velocity distributions in channels with parabolic walls. a: c = 1.5, d = 1, a = 100, b: c = 49.5, d = 1, a = 100.

where d is the distance from the apex of the parabola to the shorter of the side walls (see Figure 4b).

The central part of the velocity profiles in the planes parallel to the x and z axes is linear in this case (as schematically depicted in Figure 6). The velocity profiles in the planes parallel to the plane where the x and y axes are situated are parabolic again.

RETENTION

If centrifugal forces are applied across the channel along the z axis, a steady-state or quasi-stationary density gradient can be formed in the two or multicomponent system of the liquid phase under appropriate conditions. For the thermodynamic equilibrium, this system should satisfy the condition

$$M_i\ (1 - \bar{v}_i\ \rho(Z))\ \omega^2 r\ dr - \sum_k\ (\delta\mu_i/\delta c_k) dc_k = 0 \quad (11)$$

The quantities M_i, $\bar{v}_i$, μ_i, and c of Equation (11) are molecular weight, partial specific volume, the chemical potential and the concentration of the i-th component, respectively, while r is the distance from the axis of rotation, $\rho(Z)$ is the density of the system at coordinate Z and ω is the rotational velocity of the centrifuge rotor. If the substance to be separated - the solute - is injected into the channel as a short puls, solute migration along the z axis takes place due to the density gradient. The concentration distribution of the solute at equilibrium or at steady-state condition along the z axis in the channel can be described with the aid of a Gaussian function of the form, for instance,

$$c(Z) = c_{max}\ \exp\left[- \frac{V\ \omega^2 Z_{max}}{2\ RT}\ \frac{d\rho}{dZ}\ (Z_{max} - Z)^2 \right] \quad (12)$$

where c(Z) is the concentration in the coordinate Z, V is the molar volume of solute, R is the gas constant, and T is the absolute temperature. The coordinate Z_{max} corresponds to the maximum concentration of the solute, that means to the position where the solute density equals the density of the environment in the liquid phase. Equations (11) and (12) and the way of deriving them were discussed in detail in a previous paper by the author (2).

If two or more different solutes differing in density are simultaneously present in the channel, their concentrating is effected due to sedimentation-flotation forces in various coordinates Z_{max}, in accordance with the course of the dependence of the liquid-phase density on coordinate Z. As soon as the liquid phase begins to move along the channel in the direction of the x axis, a velocity profile is formed along the z axis, that means along the density gradient or in the direction of the separation of the individual solutes. As a consequence, various solutes will be entrained at different linear velocities along the x axis, and this leads to their effective separation as can be seen from the schematic illustration in Figure 7. The individual separated solute species are detected at the channel outlet by means of a suitable detector, in a similar way as in chromatography.

EFFICIENCY

In chromatography, separation quality is generally characterized by the height equivalent to the theoretical plate H. If supposing, again, that, in the channel coordinate Z, H can be described with the aid of relations valid for two parallel infinite planes and that the starting solute concentration along the y axis is homogeneous, it holds (6)

$$H = 2\,D/\bar{u}(Z) + w^2(Z)\,\bar{u}(Z)/105\,D \qquad (13)$$

where D is the diffusion coefficient of the solute, $w(Z) = 2b(Z)$ is the distance of the channel walls along the y axis in the coordinate Z, and $\bar{u}(Z)$ is the average velocity of the liquid flowing in the channel at the coordinate Z. The highest efficiency, that means

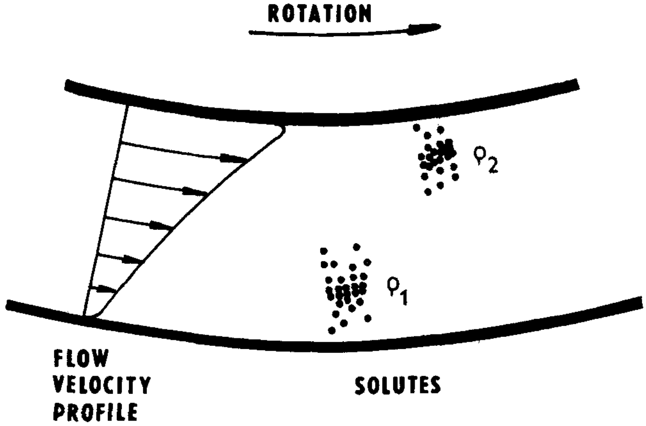

FIGURE 7. Separation by SFFFFF of two solute species in a rotating channel with modulated cross-sectional permeability.

minimum values of H, can be attained in the minimum of the function described by Equation (13). This minimum can be found in putting the first derivative of $dH/d\bar{u}(Z)$ equal to zero

$$\frac{dH}{d\bar{u}(Z)} = - \frac{2D}{\bar{u}^2(Z)} + \frac{w^2(Z)}{105\ D} = 0 \tag{14}$$

The optimum velocity $\bar{u}_{opt}$

$$\bar{u}_{opt} = \frac{D}{w(Z)} \sqrt{210} \tag{15}$$

corresponds to the minimum of this function.

The minimum value of H_{min} is given by the relation

$$H_{min} = \frac{2\ w(Z)\ \sqrt{210}}{105} = 0.276\ w(Z) \doteq \frac{w(Z)}{4} \tag{16}$$

RESOLUTION

The chromatographic resolution R_s of two solutes 1 and 2 has been defined by the known equation

$$R_s = \frac{2(t_{R1} - t_{R2})}{t_{W1} + t_{W2}} \tag{17}$$

where t_{Ri} are the retention times of solutes 1 and 2, and t_{Wi} are the widths of the elution curves of solutes 1 and 2 expressed in time units. Alternatively, an expression in elution volume units instead of time t, can be used in Equation (17). The height equivalent to the theoretical plate can be written as

$$H = \frac{\sigma^2}{L} \tag{18}$$

where L is the length of the channel and σ is the standard deviation of the elution curve given in units of length. For a Gaussian elution curve it holds that $4\sigma = W$, where W is the width of the elution curve expressed in units of length. In view of Equations (16) and (18) it holds

$$W_{min} = 2\sqrt{w(Z)L} \tag{19}$$

The trivial relation $u(Z) = L/t(Z)$ is valid for the linear velocity of the fluid phase. By substituting from Equations (7) and (19) into Equation (17) and by rearrangement we arrive at

$$R_s = \left[\frac{1 - \left(\frac{b_1}{b_2}\right)^2}{1 + \left(\frac{b_1}{b_2}\right)^{1.5}}\right] \left(\frac{L}{2b_1}\right)^{0.5} \qquad (20)$$

Equation (20) demonstrates which parameters describing the geometric and dimensional characteristics of the channel and to which quantitative degree decide on the resolution attainable when separating two solutes. Thus, resolution increases with the root of the channel lenght-to-thickness ratio in a given coordinate Z where the centre of the focused concentrated zone of the solute is situated. Or, a higher resolution can be attained if elongating the channel and decreasing its dimension along the y axis. The term in square brackets at the right-hand side of Equation (20) demonstrates to which degree the difference in channel widths in the positions of the centres of the zones of the separated solutes 1 and 2, affects the resolution. If denoting the term in square brackets in the right-hand side of Equation (20) as ψ , we can rewrite Equation (20) as follows

$$R_s = \psi \left(\frac{L}{2b_1}\right)^{0.5} \qquad (21)$$

Figure 8 shows the plot of the dependence ψ on the b_1/b_2 ratio. As is evident from the figure, the value of ψ increases with the decreasing b_1/b_2 ratio, asymptotically approaching unity. This means, in practice, that increasing the b_1/b_2 ratio is meaningful only up to a certain value; above this value, no substantial improvement in resolution can be attained.

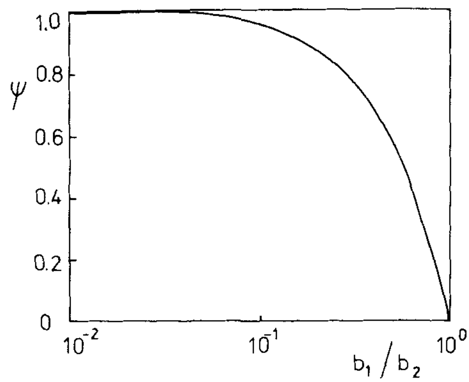

FIGURE 8. Dependence of resolution parameter ψ on ratio b_2/b_1.

EXPERIMENTAL

A very simple apparatus was constructed to demonstrate the formation of the flow velocity profile in a channel with modulated cross-sectional permeability. Two strips of PVC foil of different thickness (0.15 and 0.45 mm) were placed longitudinally between two glass plates of 2.5 x 1 x 30 cm so as to form a channel of trapezoidal cross-section. The dimensions of the channel were 1.5 x 30 cm, the thickness increasing from 0.15 to 0.45 mm. One of the ends of the channel was tightened and provided with stainless steel capillary tube for the inlet of solvent (ethanol). The whole system was clamped between two perspex plates and tigthened with several screws. The experiment proper was made by injecting a short pulse of ethanol-soluble dye into a steady stream of solvent flowing down the channel. The zone produced of the dye was recorded photographically at various phases of its development. These phases are shown in Figure 9. At the wall on the broader side of the channel the zone moves faster.

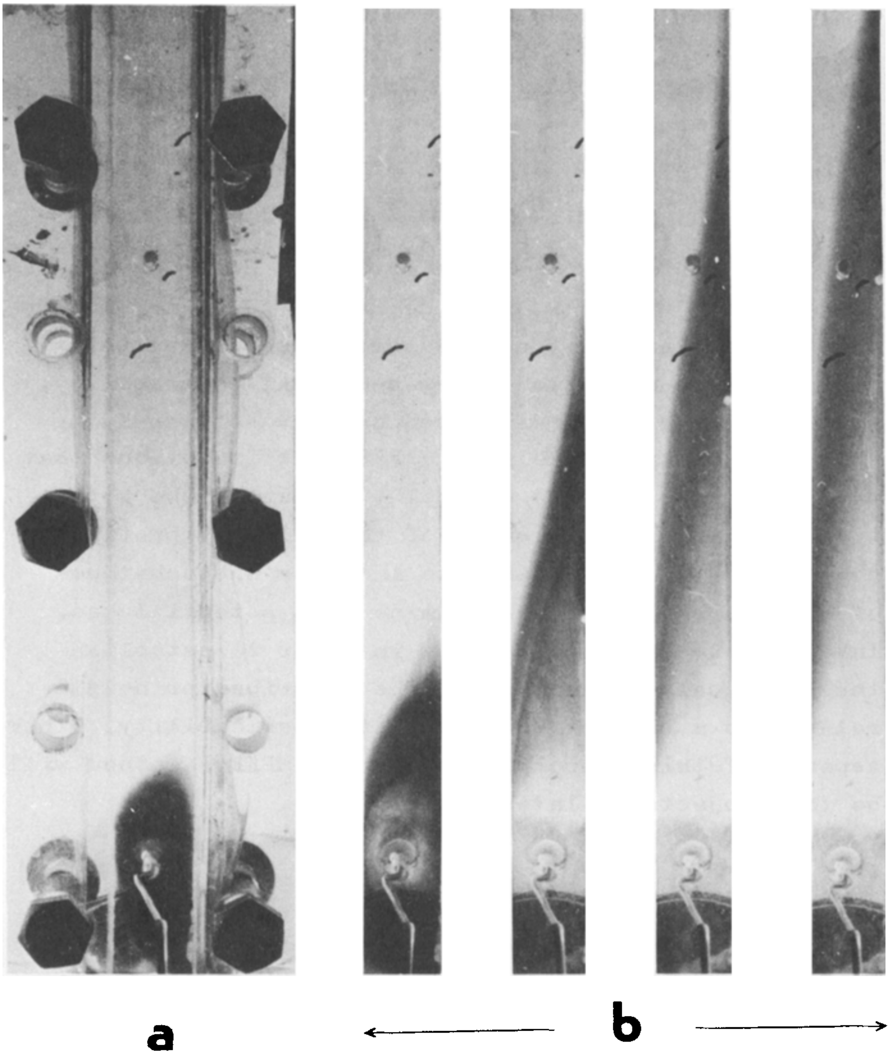

FIGURE 9. Development of the zone shape in the channel of trapezoidal cross-section.
a - top view on the channel at the moment of injection of dye
b - section of the channel with various phases of the zone movement.

The shapes of the front and the rear of the zone both correspond to a parabolic field of velocities in the core of the channel, which agrees with the theoretical analysis.

CONCLUSION

In this first part of a series of contributions dealing with SFFFFF we have demonstrated in theory the basic potentials that can be accomplished when using channels with modulated cross-sectional permeability. Even though we have restricted ourselves to applying this channel type solely to SFFFFF, it is obvious that the properties of this channel - as far as the potential formation of the shape of the velocity profile is concerned - can also find use in other subtechniques of FFF. We shall further examine this potential use. Investigations are continuing in order to establish the practical utilization of the described principle related to a channel with modulated permeability. Other aspects of this principle and of the SFFFFF method will be the subjects of later papers.

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