PAPER GEOMETRY AND FLOW VELOCITY IN PAPER CHROMATOGRAPHY*

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The velocity of solvent flow in paper chromatography is often an important variable influencing the resolution and indirectly the R_F value of solute zones[1]. The influence of velocity on resolution has not been fully studied in paper chromatography, but theories of the chromatographic process[2] as well as experiments in the basically similar method of gas chromatography[3] show that flow velocity is important. Unlike column chromatography the flow rate cannot be controlled by an applied pressure since in most cases the driving forces for flow are capillary in nature. Three methods are currently available for controlling solvent velocity in a given paper–solvent system at a specified temperature. These are (1) the application of external forces such as centrifugal and gravitational, (2) the addition of surface-active agents to alter the capillary driving forces (this will also influence the chromatographic process to a greater or lesser extent), and (3) the use of different paper geometries such as wick system. The latter method, which is the subject of this communication, has been used especially with circular (horizontal) chromatography with wicks[4]. The general problem has been discussed by MÜLLER *et al.*[5].

An accurate picture of solvent flow in paper is given by assuming that the movement of solvent is governed by the diffusion equations in which the diffusion coefficient is a function of solvent concentration[1]. The equation (Fick's second law) is consequently nonlinear and difficult to solve. If, in addition, one adds the complications of variable geometry, the problem becomes amenable only to extended machine calculations. An approximate theory is presented here which avoids these difficulties, and still gives reasonably quantitative predictions of flow rate.

D'ARCY found that the flow velocity, or flux, in a porous media is proportional to the pressure gradient[6]

$$q = -c\frac{dP}{dz} \qquad (1)$$

where q is the mass flux of solvent per unit width, W, of paper strip. The total flux, q_0, equals qW and hence

$$q_0 = -cW\frac{dP}{dz} \qquad (2)$$

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Integrating along the strip from the solvent source at z_0 to the solvent front at z_f, we have

$$-P = \frac{q_0}{c} \int_{z_0}^{z_f} \frac{\mathrm{d}z}{W(z)} \tag{3}$$

where P is the capillary pressure change from the saturated to the dry paper. Combining this equation with the assumption that the rate of advance of the front is proportional to the flux, *i.e.*, $\mathrm{d}z_f/\mathrm{d}t = bq$, and integrating, we have

$$\int_{z_0}^{z_f} \left[W \int_{z_0}^{z_f} \frac{\mathrm{d}z}{W} \right] \mathrm{d}z_f = \tfrac{1}{2} \varkappa \, (t - t_0) \tag{4}$$

where capillary flow begins at t_0, which, in most cases, is arbitrarily set equal to zero. The flow rate coefficient, $\varkappa$, equals $-2bcP$, and is a function of the paper–solvent system. Eqn. (4) is derived on the basis that the flux is constant at every cross section, and that the solvent concentration is uniform throughout the paper. Such an assumption is in error in view of the known concentration gradients[1], but it is necessary in order to obtain mathematical solutions in closed form.

Eqn. (4) has been integrated for the following geometries:

1. Rectangular strips, $z_f^2 = \varkappa t$, the well known parabolic flow equation[5,7,8].
2. Tapered strips with $W = a + mz$, $z_0 = 0$, m either positive or negative,

$$\left(\frac{a}{m} + z_f\right)^2 \left[\ln\left(1 + \frac{mz_f}{a}\right) - \tfrac{1}{2}\right] + \tfrac{1}{2}\left(\frac{a}{m}\right)^2 = \varkappa t \tag{5}$$

3. Strip with width discontinuity, $W = a$ for $z = 0$ to l, $W = \varepsilon a$ for $z = l$ to ∞ ($\varepsilon < 1$). Allowing for the compression of the streamlines a distance h before the discontinuity, we obtain for $z_f > l$

$$\begin{aligned} z_f^2 - g\,(z_f - l) &= \varkappa t \\ g &= 2\,(l - h)\,(1 - \varepsilon) \end{aligned} \tag{6}$$

or, in terms of the dimensionless parameters, $\tau = t\varkappa/l^2$ and $y = z_f/l$

$$y^2 - \frac{g}{l}\,(y - 1) = \tau \tag{7}$$

4. Radial flow in which the solvent source is located a distance z_0 from the center of the disc

$$z_f^2 \ln \frac{z_f}{z_0} - \tfrac{1}{2}\,(z_f^2 - z_0^2) = \varkappa t \tag{8}$$

5. Radial flow with a rectangular wick of length L and width a (other wicks such as strings have an effective width proportional to their cross sectional area). Under usual operating conditions we have $L \gg a$ and $z_f \gg a$. With these assumptions an approximate solution to eqn. (4) is

$$z_f^2 = \frac{\varkappa a}{2\pi L}\, t \tag{9}$$

This is parabolic flow in which the flow rate coefficient, $\varkappa_r = \varkappa a/2\pi L$, is significantly less than that for rectangular flow, $\varkappa$. As shown by the form of $\varkappa_r$, the flow rate in radial-wick systems can be very easily controlled by varying the length to width ratio.

Data on the above examples were taken using water on Whatman No. 1 paper at a temperature of 30° ± 0.5°. The use of horizontal flow eliminated gravitational effects. The value of $\varkappa$ was determined using rectangular flow. The experimental

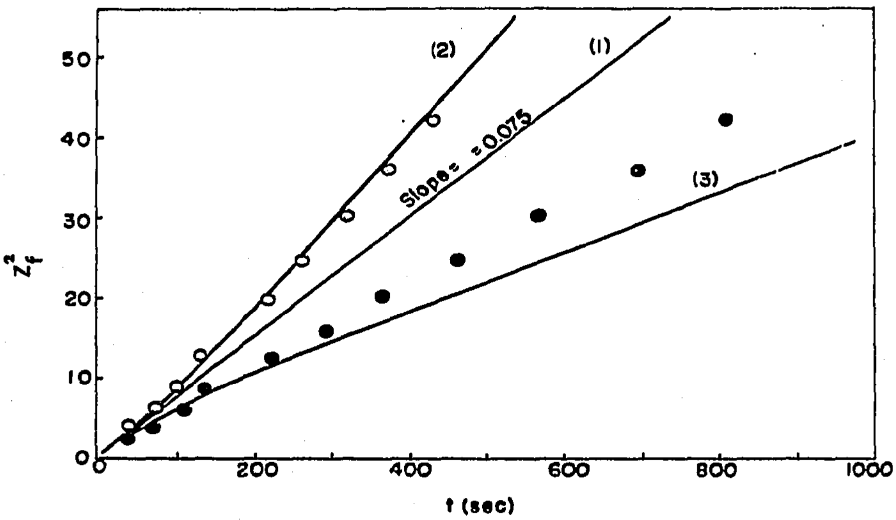

Fig. 1. Flow in tapered strips. (1), rectangular strips; (2), experimental and calculated converging flow (a = 2.0 cm, m = — 0.231); (3), experimental and calculated diverging flow (a = 0.32 cm, m = 0.258).

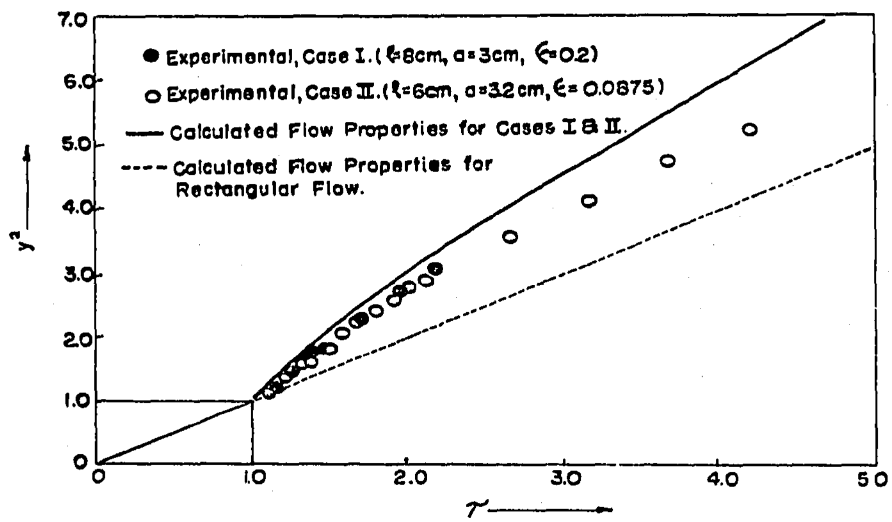

Fig. 2. Flow characteristics with discontinuous width. The width of the shoulder, a (1 — ε)/2 has been used for h.

and calculated results are shown in Figs. 1–4. The agreement is satisfactory in view of the assumptions made.

Several points are of particular interest in discussing the results obtained here. First, it can be seen that in all cases of diverging flow (tapered strip with $m > 1$, radial and radial-wick) the front advances more rapidly than predicted while with converging flow (tapered strip with $m < 1$, width discontinuity) the observed velocity is less than calculated. This can be explained in terms of the concentration gradients. Solvent flux is actually divided into two roles, one being the movement of the solvent front as predicted here, and the other being the progressive saturation of the paper, a factor not accounted for in the present theory. In diverging flow, with a

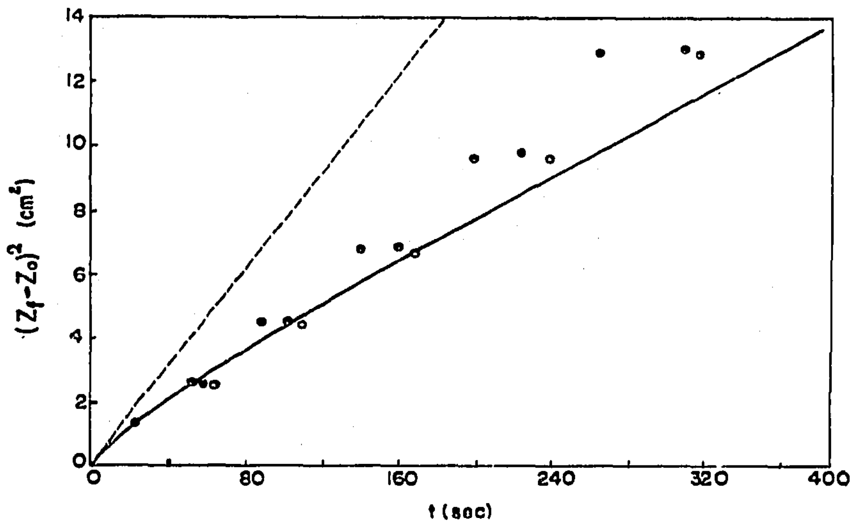

Fig. 3. Radial flow with $z_0 = 0.50$ cm. The solid line is calculated for radial flow and the dotted line for rectangular flow, both with $\varkappa = 0.075$ cm² sec⁻¹.

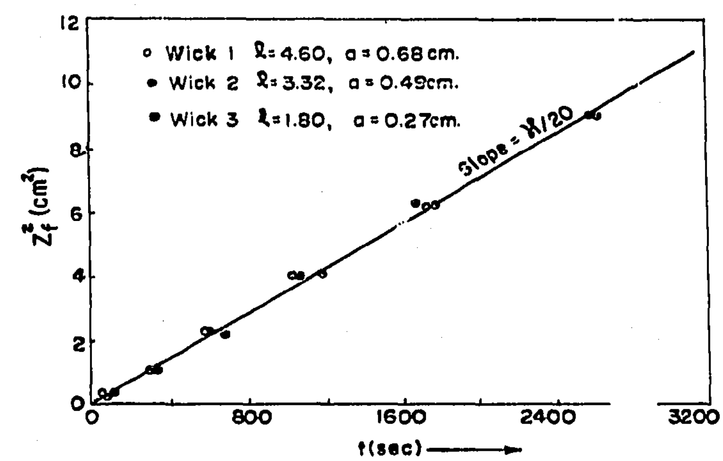

Fig. 4. Radial flow with wick dimensions approximately, $2\pi\, l/a = 42$.

relatively wide solvent front, a disproportionate amount goes to the former. This leads to an increased frontal velocity. In converging flow a lesser amount is available for advancing the front, and the decreased velocity results.

In the case of radial flow with wicks a very satisfactory straight line is obtained plotting z_f^2 against time. Furthermore, significant changes in length and width leave the effect of the wick unchanged as long as the length–width ratio is constant. As in other cases of diverging flow, the frontal velocity is larger than predicted. The measured $\varkappa_r$ is $\varkappa/20$ rather than $\varkappa/42$. The use of a large range of wick sizes has shown that the experimentally measured $\varkappa_r$ is approximately $\varkappa a/\pi L$, twice as large as the calculated value, $\varkappa a/2\pi L$. This rule can be effectively used in predicting and controlling flow velocity.

The results obtained here show that with a wick source, the area enclosed by the moving front increases linearly with time. This is verified in the work of HENDRICKSON, BERUEFFY AND MCINTYRE[9], and by LE STRANGE AND MÜLLER[10].

SUMMARY

The flow of liquids in paper has been described on the assumption that paper is either saturated or dry. With this assumption a simple mathematical treatment can be carried out. It is shown how the use of different paper geometries can be used to control flow velocity. Since paper can be partially saturated certain deviations from experimental data are noted. These deviations are qualitatively predictable. On the basis of the analysis and the experimental results provided here, reasonably accurate predictions of the flow velocity can be made.

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