# IMBIBITION AND FLOW OF COMMON SOLVENTS IN CHROMATOGRAPHY PAPER

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The results reported here offer quantitative information on the properties of a commercial type of chromatography paper (Whatman No. 4) in the presence of various solvents.

## EXPERIMENTAL

### *Material*

*Thickness of paper.* According to the manufacturer, the thickness was 0.007 inch, or 0.18 mm. Our caliper measurements averaged 0.22 mm.

*Weight.* The weight ranged from 8.4 to 9.6 mg per $cm^2$. The imbibition and flow measurements given below were all corrected to a standard weight of 9.0 mg per $cm^2$.

*Density.* Strips measuring 5 × 10 cm were soaked in various solvents for three days at room temperature, then weighed in the solvents. The calculated density ranged from 1.54 to 1.57 in six common solvents; in water, it was 1.59. These differences are probably too close to the experimental error of the method to be meaningful.

### *Imbibition*

A one-liter jar was half filled with fluid and placed under a balance. The jar was completely closed except for a small hole at the top to permit passage of a thin wire. A sheet of paper covering most of the inside wall of the jar and dipping in the fluid ensured vapor saturation. A vertical paper strip, 1 × 5 cm, was hung from the end of the wire, which was fastened to the beam of the balance. The paper strip was first completely immersed, then raised by a simple device to positions at 0.5 or 1.0 cm intervals, without otherwise disturbing the assembly. Five to nine weighings were made, each of which was the sum of three values: the weight in air of the wet part of the strip above the fluid level, the weight in fluid of the immersed part of the strip, and the surface tension along the perimeter of the strip.

The calculated weight in fluid of the immersed part was subtracted from these figures. The differences obtained, which ranged from about 50 to 200 mg, were plotted against the paper height above the fluid. A straight line could be closely fitted to them, the mean deviation of the points being about 1 mg. The slope of the line gave the weight of moist paper per $cm^2$, and the intercept with the axis of the ordinates the effect of the surface tension of the fluid.

A few minutes were usually enough to ensure constant weighings and there was no suggestion that the degree of imbibition varied much during the time needed for a series of weighings; this was shown by repeating the weighings, this time lowering the paper gradually. With water and a longer paper strip, the weight:$cm^2$ ratio remained constant as high as 15 cm above fluid level.

The results are shown in Table I. The first column gives the volume of fluid carried by 1 $cm^2$ of paper, *i.e.*, moist weight minus dry weight, divided by the density

TABLE I

IMBIBITION, SURFACE TENSION, AND CORRECTED FLOW RATES $U_0$ IN WHATMAN PAPER NO. 4
Strips 1 cm wide. Surface tensions ($\gamma$) from QUAYLE[1].

| | *Imbibition* $mm^3/cm^2$ | *Surface tension obs. dynes/cm* | $\gamma$ | $U_0$ *ml/h* | | $U_0$ *found/* $U_0$ *calc.* |
|---|---|---|---|---|---|---|
| | | | | *1st day* | *2nd day* | |
| Water | 22.0 | 52 | 72 | 0.228 | 0.231 | 1.00 |
| Methanol | 16.7 | 23 | 22.2 | 0.263 | 0.276 | 0.91 |
| Ethanol | 16.5 | 23 | 22.5 | 0.125 | 0.123 | 0.82 |
| *n*-Butanol | 13.6 | 25 | 23 | 0.042 | 0.044 | 0.68 |
| Acetone | 16.6 | 23 | 23 | 0.372 | 0.380 | 0.68 |
| Ether | 14.4 | 18 | 16.5 | 0.423 | 0.445 | 0.61 |
| Chloroform | 12.4 | 28 | 27.1 | 0.274 | 0.285 | 0.47 |
| Carbon tetrachloride | 13.8 | 27 | 26 | 0.162 | 0.173 | 0.44 |
| Benzene | 11.9 | 29 | 28.4 | 0.177 | 0.193 | 0.59 |
| Pyridine | 19.6 | 39 | 37.7 | 0.246 | 0.266 | 1.10 |

of the fluid. It is fairly clear that polar solvents produced the highest imbibition. The second column gives the observed surface tension, acting on an estimated boundary length of 2.04 cm, the perimeter of the cross section of the strip; the third column, standard values for $\gamma$ from the literature. Except for water, which gave a low tension, the agreement is fairly good; the paper strip behaved as if it had been a solid plate.

*Rate of flow of water*

The first step consisted of the demonstration that a strip of filter paper, bent in the shape of a siphon, actually operated like one. The apparatus used is illustrated in Fig. 1.

A strip of aluminum foil was bent at right angles in the shape of an open frame. The bottom part held a small glass cup, 3 ml in capacity. The vertical sides were provided with holes, or notches, at various heights, to hold a glass pin, which passed through two holes in the paper strip. The sawed-off bottom of a small test tube, bearing a transversal slit, was placed at the bottom of the cup to hold the end of the paper in position. The assembly was hung from a balance with the help of a thin wire and enclosed in a partially filled jar. Proper precautions (described before) were taken to avoid evaporation. It was thus easy to vary $h$, the difference in height between the two levels; $h'$, the height of the paper loop above $h$; and $a$, equal to $2h' + w$, the length of the paper loop above $h$.

The paper strips were cut lengthwise, *i.e.*, in the machine direction; they were 0.5 cm in width and marked off with a pencil at 0.5 cm intervals. The same strip

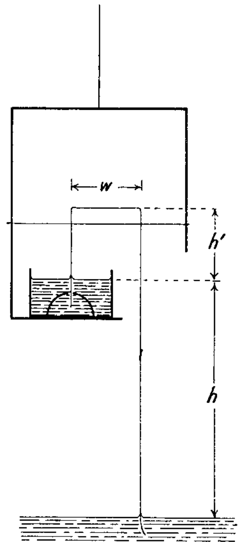


Fig. 1. Apparatus used for flow rate measurements (schematic).

was employed for each series of determinations. Weighings were made hourly in the course of a day. The rate of flow usually increased slightly in the first hour, then decreased very slowly in proportion to the drop in height in the cup. The average length of $a$ and $h$, and the average temperature, were noted. The values were then corrected for the viscosity difference between the temperature of the experiment and 20°, and for the width and weight of the paper, and expressed as ml per hour per cm width.

If the system operates like a true capillary siphon, the fluid delivered per unit time, $U$, should be proportional to the pressure head $h$, and inversely proportional to the total length $a + h$:

$$\frac{U_0}{U} = \frac{h + a}{h}; \qquad \frac{1}{U} = \frac{1}{U_0} + \left(\frac{a}{U_0} \cdot \frac{1}{h}\right)$$

in which $U_0$ is the value of $U$ when $a = 0$ or $h = \infty$. Plotting $1/U$ *versus* $1/h$ should give a straight line, the slope of the line should be proportional to $a$, and $U_0$ be a constant characteristic of the paper for a given solvent.

The results from a series of measurements in which $h$ was the dependent variable are shown in Fig. 2. Theoretical expectations regarding the effect of varying the length $h$ are confirmed by the linearity of the relation. In the first three experiments, the lines intercept the vertical axis close to $1/U = 4$. The value of $U_0$ would thus be about 0.25 ml per hour per cm width.

In these three experiments, the value of $a$ calculated from the slope is 1.95, 3.5 and 9.2 respectively, in fair agreement with the actual value. The results from Expt.

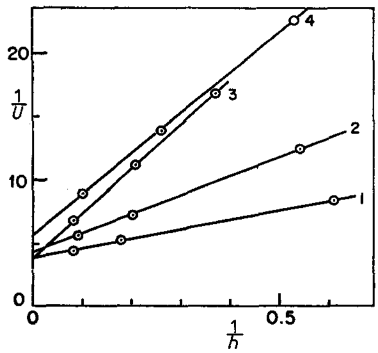


Fig. 2. Flow of water. Abscissae: reciprocal of pressure head in cm. Ordinates: reciprocal of flow in ml per hour per cm width. Expt. 1: length of loop $a$ 2.2 cm, height $h'$ 0.85 cm. Expt. 2: $a$ 4.2 cm; $h'$ 1.5 cm. Expt. 3: $a$ 8.6 cm; $h'$ 0.45 cm. Expt. 4: $a$ 8.1 cm; $h'$ 3.0 cm. Values corrected to 20°.

No. 4 were slightly discrepant and suggested that the height of loop might introduce a complicating factor.

This point was investigated by running a series of measurements in which the pressure head $h$ was kept constant at 2.5, while the loop, 1.5 cm in width $w$, varied

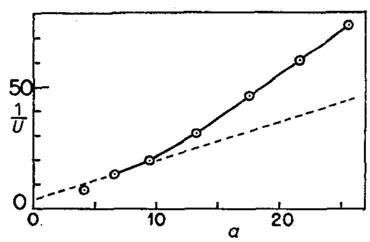


Fig. 3. Flow of water. Abscissae: length of loop in cm. Ordinates: reciprocal of flow in ml per hour per cm width. Dotted line: theoretical values for $U_0 = 0.25$.

in height $h'$ from about 1 to 12 cm. The results (Fig. 3) show a marked deviation from theory for the higher values of $a$; the output was reduced by 40 % when the loop was 12 cm high.

*Rate of flow of organic fluids*

The experiments with water, illustrated in Fig. 2, were repeated with methanol. The results were essentially the same, *i.e.*, the same close linear relation was obtained between $1/U$ and $1/h$; however, the intercept of the lines with the axis of ordinates showed a wider scatter. Therefore, in order to minimize the danger of errors due to the loop, the latter was made as short, the total length as long, as conveniently possible. The measurements were as follows: $h' = 0.8$ to 1.3 cm; $w = 1.5$ cm; $a = 2\,h' + w =$

3.5 cm approximately; $h = 33$ cm. The paper strips were 1 cm in width and cut in succession out of the same sheet.

Weighings were made at hourly intervals for one day, the apparatus left standing overnight, the cup refilled, and weighings made again the second day. They were corrected as above to yield $U$; $U_0$ was then equal to $U \times \frac{33 + 3.5}{33}$. These values are given in Table I (4th and 5th columns). The flow was usually slightly faster on the second day. The last column shows the ratio between observed flow (average of first and second day) and that expected if the differences in rates between water and other fluids had been solely due to differences in density and viscosity. There is a clear relation between rate of flow and polarity.

## DISCUSSION

The purpose of the present study was to estimate the amounts of various fluids imbibed by Whatman paper No. 4 and the rate of flow of these fluids under the effect of gravity. The nature of the work precluded high accuracy. The results are reported primarily for their order of magnitude and their comparative significance, since no such information appears to exist in the literature.

CASSIDY[2] has reviewed previous work in this field, devoted mostly to the study of capillary ascent of fluids in paper. He remarks about the "extremely complicated system and many variables" offered by filter paper. In view of the difficulty of defining a standard state of the material to which measurements might be referred and of deciding by what preparatory means such a state should be reached, it seemed warranted here, especially considering the preliminary nature of the results, to use the paper as it came from the manufacturer.

It must be stated that the characteristics of the paper in the presence of the fluids appeared very stable. It was not observed that preliminary treatment such as drying at 100°, exposure to vapors or contact with any of the fluids had a permanent effect on the properties of the material. Slow changes are, of course, not ruled out and the results are considered significant only within the limits of the experimental conditions.

The measurements of imbibition require little comment. It is unlikely, in view of the close linear relation between the height and the weight of the wet strips, that an important "weight profile" existed, such as is observed during the capillary ascent of fluid in paper[2,3*]. The distribution of fluid seems to have been even up to a height of at least 5 cm, the polar fluids being definitely more strongly imbibed.

The measurements of flow offered unexpected difficulties. Attempts to make the paper start from the bottom of a container were fruitless because of the impossibility of devising a satisfactory joint. Hence the need for a "loop" and for the demonstration that the system acted like a true siphon. This was given, within limits, for water.

* In the course of this work, it was noticed that the equation describing initial fluid rise in capillary tubes, as given by BIKERMAN[4], differs from that of LIGENZA AND BERNSTEIN[5] by the factor 2. Dr. W. R. THOMPSON, who was kind enough to read this manuscript, has pointed out (one-page note No. 41759, available in Bruning reproduction) the error made by the latter authors.

Furthermore, the close linearity of the relation between $1/U$ and $1/h$ suggested that, with water and methanol at least, there was no important weight profile in the descending part of the strip.

The loop effect was not studied with other fluids. In the flow measurements reported in Table I, conditions were such that this effect cannot have been considerable, so that the values given for $U_0$ come probably close to what they would be if it were possible to reduce the loop to zero length. In the last column, the relation between polarity and the ratio of observed to expected flow is quite striking.

In the early part of the work, flow measurements were made on strips 0.5 cm in width, and these gave usually higher values than those reported here. As the strip is widened, the rate would probably tend to a minimum per cm width; as the strip is lengthened, the rate tends to a maximum. It would thus represent a sort of constant of the paper for each fluid studied.

The results may be compared with those of KRESS AND BIALKOWSKY[6] on paper swelling: 90% by volume in water, 62% in methanol, 40% in ethanol, 4% in butanol. In the present instance, one $cm^2$ of paper had a volume of 22 $mm^3$, of which 5.7 $mm^3$ was occupied by 9 mg of cellulose and 16.3 $mm^3$ by air. Bound fluid would thus have occupied volumes of 5.1, 3.5, 2.3, and 0.2 $mm^3$ respectively, leaving (after subtraction from the first column in Table I) 16.9, 13.2, 14.2, and 13.4 $mm^3$ of free fluid in the open spaces. These figures only help to visualize the problem and are too imprecise to warrant much speculation. If polar fluids produce not only greater swelling but also relatively more rapid flow, this might be ascribed to some change in the shape of the fibers; becoming less ribbon-like and more cylindrical, these might cause the open spaces to be less ramified and thus offer less resistance to the movement of fluid. Differences in relative flow rates of 1 to 2, such as were observed here, could be due to differences in the capillarly bed too small to be correlated with the information yielded by measurements of imbibition.

## SUMMARY

The properties of a commercial chromatography paper (Whatman No. 4) were studied with water and nine organic fluids. Imbibition was greater with the more polar fluids and ranged from 22.0 $mm^3/cm^2$ for water to 11.9 $mm^3/cm^2$ for benzene. Measurements of flow rates under the influence of gravity showed that, the more polar the fluid, the smaller the resistance to flow offered by the paper. The rate of water was 0.23 ml per hour per cm width at 20°.

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