Penetration of Liquids into Filter Paper Used in Paper Chromatography[*]

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(Received August 21, 1958)

The velocity of liquids ascending in filter paper, which is hung in a closed vessel and whose lower end is dipped in a liquid, is interesting from two viewpoints. The one is as the basis of the paper chromatography, in which the knowledge on the mechanism of the ascending of the developer liquid in a filter paper and on the properties of the filter paper seems to be fundamental to understand the physico-chemical details in the process of paper chromatography. The other standpoint is as a part of the studies of the penetration of liquids into porous materials. The latter, for example, the penetration of detergent solutions into clothes, is important when we consider the treatment of textiles in water.

The phenomenon can be treated by assuming that the penetration of liquids is due to the capillary force under the

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[*] Presented before the Himeji Meeting held by the Chemical Society of Japan on May 31, 1958.

resistance by the viscosity and the hydrostatic pressure. Many theoretical and experimental investigations have already been made from this standpoint. Brittin[1] and Ikeda and Soeya[2] studied the ascending of liquids in capillary tubes. Lucas[3], Peek and McLean[4] and Fujita[5] studied the penetration into filter paper. Wolkowa[6] studied the penetration of liquids into a tube packed with powdered material. Carman[7] also studied the layer of powders on the basis of Kozeny's theory.

According to these investigations, the velocity of ascending, $\mathrm{d}h/\mathrm{d}t$, is given by[3,4]

$$\mathrm{d}h/\mathrm{d}t=(1/8\eta h)(2r\gamma\cos\theta-r^2h\rho g) \qquad (1)$$

and the equation for the initial stage of penetration is[3,4,6]

$$h^2=kt \qquad (2)$$

with $$k=r\gamma\cos\theta/2\eta \qquad (2a)$$

In the present paper, a model of laminar capillary gaps will be used besides the model of tubular gaps already used by investigators cited above. Moreover, parameters will be used to take into account the winding of the gaps and the adsorption of liquids by the fibre. Finally, the penetration of liquids into the filter paper actually used in the paper chromatography will be studied.

Experimental

Organic Liquids.—Ethanol was boiled for 4 hours on a water bath with calcium oxide and distilled. The fraction distilled out at 78°C was dehydrated with sodium metal and distilled to collect the fraction at 78°C. Finally, it was again distilled on calcium oxide and the fraction of 78°C was used.

Benzene of the guaranteed reagent grade was distilled and the fraction at 80°C was used.

Acetone of the extra pure reagent grade was distilled and the fraction at 56.3°C was used.

Carbon tetrachloride of the extra pure reagent grade was treated with potassium hydroxide solution in an alcohol water mixture (KOH: H_2O: Alcohol $=1:1:2$) and shaken on a water bath for 30 min. at 50∼60°C. Then it was washed with water, dehydrated with sodium metal and distilled to collect the fraction at 76.7°C.

Method of the Measurement. — Toyo filter paper No. 50 (for chromatography) was cut in pieces of 1 cm. in width and 25 cm. in length, and marked every 1 cm. with a pencil to show the distance from one end. A piece of the filter paper was hung in a measuring cylinder of 200 cc. closed with a cork stopper. In the cylinder, 10 cc. of liquid for study was placed in advance. The filter paper was hung so that its lower end was just 1 cm. below the surface of the liquid. The time when the front of the liquid passed every pencil mark was measured by a stop watch. All measurements were made in a thermostat held at 20°, 30° or 40°±0.02°C.

Theoretical Consideration of the Penetration

It may be natural to assume that liquid goes up in a piece of filter paper owing to the capillary force, under the resistance by the viscosity and the hydrostatic pressure. The shape of the capillary gap may be assumed to be one dimensional (tube like) or two dimensional (laminar).

In the case of the one dimensional gap, the amount of the liquid which penetrates into the gap per unit time, Q (cc./sec.), is given by Poiseuille's law,

$$Q=(\pi r^4/8\eta l)p \qquad (3)$$

where η is the viscosity of the liquid, r the radius of the gap, p the pressure difference and l the length of the capillary filled with the liquid. The value of l may be different from the height of the liquid penetrated, because the capillary may be curved or wound. Therefore, the factor f is introduced here to indicate the degree of winding of the capillary by the equation,

$$f=l/h \qquad (4)$$

where h is the height to which the liquid has gone up.

Now, the pressure difference p is the difference of the pressure by the surface tension and the hydrostatic pressure by the gravity,

$$p=(2\gamma\cos\theta)/r-h\rho g \qquad (5)$$

where γ is the surface tension of the liquid, θ is the advancing contact angle and ρ is the density of the liquid and g is the constant of the gravity. At the equilibrium, $h=h_\infty$ and $p=0$, so that

$$h_\infty=2\gamma\cos\theta/r\rho g \qquad (6)$$

Then, another factor must be introduced here. If it is assumed that a fraction of the liquid which penetrates into the filter paper, α, is absorbed in fiber and $(1-\alpha)$ remains in the capillary gap, then,

$$(1-\alpha)Q=\pi r^2(\mathrm{d}l/\mathrm{d}t)=\pi r^2 f(\mathrm{d}h/\mathrm{d}t) \qquad (7)$$

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[1] W. E. Brittin, *J. Appl. Phys.*, **17**, 37 (1946).

[2] Y. Ikeda and T. Soeya, *J. Phys. Soc. Japan*, **4**, 306 (1949).

[3] R. Lucas, *Kolloid-Z.*, **21**, 105 (1917); **23**, 15 (1918).

[4] R. L. Peek and D. A. McLean, *Ind. Eng. Chem., Anal. Ed.*, **6**, 85 (1934).

[5] H. Fujita, *J. Phys. Chem.*, **56**, 625 (1952).

[6] Z. W. Wolkowa, *Kolloid-Z.*, **67**, 280 (1934).

[7] P. C. Carman, *J. Soc. Chem. Ind.*, **57**, 225 (1938); **58**, 1 (1939).

Integrating this equation with Eqs. 2 and 4,

$$t/\tau = -h/h_\infty - \ln(1-h/h_\infty) \tag{8}$$

is obtained, where

$$\tau = 8\eta f^2 h_\infty/(1-\alpha) r^2 \rho g \tag{9}$$

On the other hand, if the gap is two dimensional and its width is w and the half distance of the gap is a, $(w \gg a)$, then Eqs. 3, 5, 6, 7 and 9 should be replaced by

$$Q = (2wa^3/3\eta l)p \tag{3a}$$

$$p = \gamma \cos\theta/a - h\rho g \tag{5a}$$

$$h_\infty = \gamma \cos\theta/a\rho g \tag{6a}$$

$$(1-\alpha)Q = 2awf\mathrm{d}h/\mathrm{d}t \tag{7a}$$

and

$$\tau = 3\eta f^2 h_\infty/(1-\alpha)a^2\rho g \tag{9a}$$

respectively. However, the final equation 8 holds also in this case, although the interpretation of the constants h_∞ and τ is different from the former case. The assumption of two-dimensional gaps seems to be more reasonable than the one-dimensional gaps in the case of the filter paper.

On the basis of Eq. 8, it is easily seen that h^2 is proportional to the time, t, at the initial stage of the penetration,

$$h^2/t = 2h_\infty{}^2/\tau \quad (h/h_\infty \ll 1) \tag{9}$$

which agrees with Eq. 2 if $2h_\infty{}^2/\tau$ is equal to k.

According to the experimental data, the h^2-t curve is, however, straight only in the very initial range. The curve is not straight in the later stage. It is, therefore, desirable to expand Eq. 8 in a power series. It can be done in two ways:

$$h^2/t = (2h_\infty{}^2/\tau)\{1-(2/3)(h/h_\infty) - (1/18)(h/h_\infty)^2 - \cdots\cdots\} \tag{11a}$$

and

$$t/h^2 = (\tau/2h_\infty{}^2)\{1+(2/3)(h/h_\infty) + (1/2)(h/h_\infty)^2 + \cdots\cdots\} \tag{11b}$$

These equations show that the plot of h^2/t or t/h^2 against h should be almost linear if h is sufficiently small compared to h_∞. These equations also show that the deviation from the linearity should be smaller in h^2/t than in t/h_2, because the coefficient of the term of $(h/h_\infty)^2$ is smaller in Eq. 11a than in Eq. 11b. This is shown in Fig. 1, where curve I shows Eq. 11a and curve II shows Eq. 11b. The straight lines I′ and II′ are the initial slope of these curves. The symbols a and b show the deviation of curves I or II from the linearity by 1% and 5%, respectively.

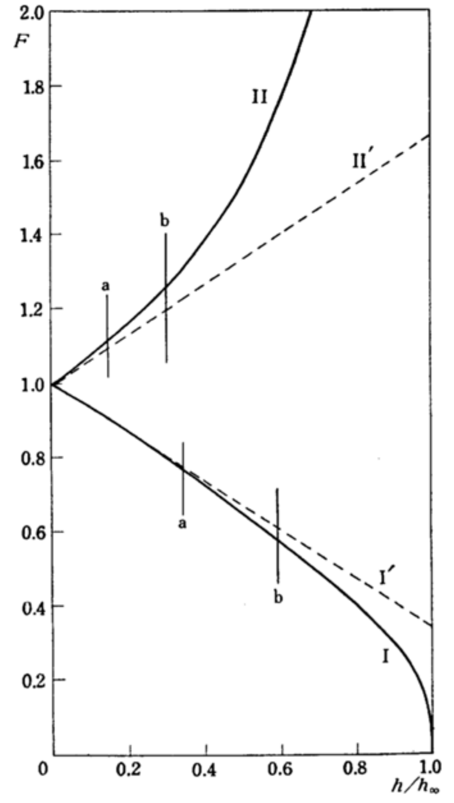

Fig. 1. Theoretical curves and their deviation from the linearity.

I: $F = (\tau/2h_\infty{}^2)(h^2/t)$
I′: $F = 1-(2/3)(h/h_\infty)$
II: $F = (2h_\infty{}^2/\tau)(t/h^2)$
II′: $F = 1+(2/3)(h/h_\infty)$
a: 1% deviation
b: 5% deviation

On the basis of the fact that curve I can be approximated by a straight line I′ in a fairly wide range of (h/h_∞), it is proposed to plote experimental values of (h^2/t) against h. The initial slope of this plot will give the values of A and B in the equation

$$h^2/t = A - Bh \tag{12}$$

and A and B are related to h_∞ and τ by the relations:

$$h_\infty = 2A/3B \tag{13}$$

and

$$\tau = 8A/9B^2 \tag{14}$$

as easily derived from Eq. 11a.

Results and Discussion

The height of the ascent of water and ethanol against time is shown in Fig. 2. The curves in this figure are the theoretical curves by Eq. 8, using the values of h_∞ and τ obtained by (h^2/t) vs. h plots on the basis of Eqs. 12, 13 and 14. These values are shown in Table I together with the

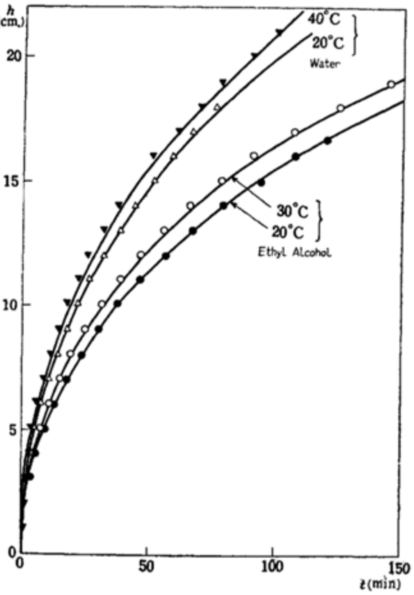

Fig. 2. The $h-t$ plot for water and ethanol.

TABLE I
CONSTANTS FOR THE PENETRATION OF WATER AND ETHANOL

	Water		Ethanol	
	20°C	40°C	20°C	30°C
A (cm²/min.)	5.45	6.10	3.10	3.87
B (cm./min.)	0.070	0.075	0.044	0.069
h_∞ (cm.)	51.9	54.2	47.5	37.4
τ (min.)	990	965	1460	722
x (μ)	14.3	13.1	6.09	7.50
y (μ)	1.65	1.37	1.59	1.84

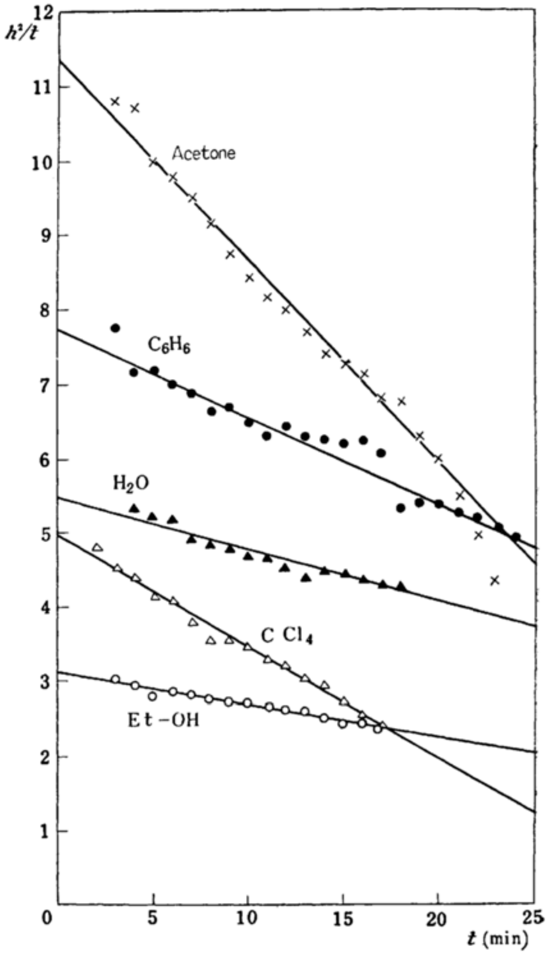

Fig. 3. The $h^2/t-h$ plot for acetone, benzene, water, carbon tetrachloride and ethanol.

TABLE II
CONSTANTS FOR THE PENETRATION OF SEVERAL LIQUIDS AT 20°C

	Acetone	Benzene	Water	CCl_4	Ethanol
A (cm²/min.)	11.37	7.71	5.45	4.95	3.10
B (cm./min.)	0.271	0.117	0.070	0.150	0.0435
η (c. p.)	0.323	0.647	1.009	0.970	1.200
γ (dyne/cm.)	23.70	28.88	72.75	26.77	22.27
ρ	0.7901	0.8788	0.9982	1.594	0.7893
x (μ)	10.9	7.65	14.3	7.78	6.09
y (μ)	2.06	1.82	1.65	1.88	1.59
$\cos\theta$	0.559	0.797	0.426	0.783	(1.00)
θ	55.0°	37.2°	64.8°	38.5°	(0°)
Two dimensional gap (a=6.09 μ)					
f (α=0.16)	2.71	3.06	3.38	2.95	3.50
f (α=0)	2.96	3.34	3.69	3.22	3.83
One dimensional gap (r=12.2 μ)					
f (α=0.16)	3.33	3.75	4.15	3.63	4.30
f (α=0)	3.64	4.10	4.54	3.96	4.70

values of A and B of Eq. 12.

In order to eliminate the factors depending on the properties of the liquid penetrating and in order to obtain the parameters depending mostly on the properties of the filter paper, two quantities, x and y, are introduced, both of which are proportional to the half distance, a, in the case of two-dimensional gap and are proportional to the radius, r, of the gap in the case of the one-dimensional gap. That is,

$$x=\gamma/\rho g h_\infty = a/\cos\theta \text{ or } r/2\cos\theta \qquad (15)$$

and

$$y=(3/2)(\eta B/\rho g)^{1/2}=(1-\alpha)^{1/2}a/f \text{ or } (3/8)^{1/2}(1-\alpha)^{1/2}r/f \qquad (16)$$

The values of x and y are cited in Table I. The values of x for water and ethanol are different from each other, while the values of y are approximately the same for both water and ethanol.

The relationship between (h^2/t) and h are shown in Fig. 3 for acetone, benzene, water, carbon tetrachloride and ethanol at 20°C. The linearity expected from Eq. 12 is satisfied. The values of A and B obtained from this linearity are listed in Table II. Using the values of the viscosity, surface tension and density of these liquids listed also in Table II, the values of x and y are calculated and shown in the same table. It is seen that the value x varies widely depending on the nature of the liquid, while the value of y is roughly the same.

According to Eq. 15, the difference of the value of x should be due to the difference of the contact angle. If the contact angle is assumed to be zero in the case of the smallest value of x, that is the case of ethanol (this corresponds to the assumption that $a=6.09\,\mu$ or $r=12.2\,\mu$), then, the largest possible values of $\cos\theta$ and the smallest possible values of the advancing contact angle, θ, are calculated as shown in Table II. For fat-free filter paper, it is said that the value of θ was zero for many liquids[4], but it is not so for the filter paper used in the actual paper chromatography.

In order to make further estimation, the value of α is assumed to be as follows. In the case of water, the amount of water contained in 1 cm^2 of the filter paper was 0.0165 g./cm^2, and the weight of the dried filter paper was 0.0133 g./cm^2. Therefore, the amount of water contained in 1 g. of the filter paper was 1.24 g. On the other hand, the amount of water adsorbed by 1 g. of the fiber of the filter paper may be about 0.2 g., referring to the data by Marshall and Peters[8]. Therefore, the value of α is assumed to be 0.16. If a liquid other than water is adsorbed less in the fiber, the value of α should be smaller than this. The values of f calculated under this assumption were listed in Table II. Assuming the value of $a=6.09\,\mu$ in the case of two-dimensional gap model, the mean value of f is 3.12 if $\alpha=0.16$ and 3.41 if $\alpha=0$. In the case of one-dimensional gap model of $r=12.2\,\mu$, the mean value of f is 3.85 if $\alpha=0.16$ and 4.21 if $\alpha=0$. Therefore, the length of the gap is three to four times larger than the length of the filter paper.

The value of $6.09\,\mu$ for the half distance of the gap seems to be reasonable, because the diameter of fibers of the filter paper measured under a microscope was about $15\,\mu$. In this connection, it may be good to point out the generally accepted fact that the dimension of the gap obtained by the measurement of the permeability of liquid is usually five to fifteen times greater than the value obtained by the measurement of the permeability of particles.

Summary

The penetration of liquid into a piece of filter paper hung vertically above a liquid is studied theoretically and experimentally. The height of the ascent of the liquid is proportional to the square root of the time at the initial stage of the penetration, but the proportionality does not hold in a wide range of time. The equation which describes this relationship between the height and time has been derived. The values of the parameters in the equation have been determined for acetone, benzene, water, carbon tetrachloride and ethanol. It is concluded that the capillary gap in the filter paper is about $6\,\mu$ in the half distance and the length of the gap is about 3 times larger than the length of the filter paper, if the gap is assumed to be two dimensional.

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[8] W. J. Marshall and R. H. Peters, *J. Soc. Dyers and Colourist*, **63**, 446 (1947).