**Preferred citation:** D.H. Everett, J.M. Haynes and R.J.L. Miller. Kinetics of capillary imbibition by fibrous materials. In **Fibre-Water Interactions in Paper-Making**, *Trans. of the VIth Fund. Res. Symp. Oxford*, *1977*, (Fundamental Research Committee, ed.), pp 519–534, FRC, Manchester, 2018. DOI: 10.15376/frc.1977.1.519.

# KINETICS OF CAPILLARY IMBIBITION BY FIBROUS MATERIALS

D. H. EVERETT, J. M. HAYNES and R. J. L. MILLER, School of Chemistry, University of Bristol, Bristol BS8, 1TS, England

**Synopsis** A simple gravimetric technique for determination of the rate of capillary imbibition of wetting liquids by porous solids is described, and illustrated with results obtained with a wide variety of liquids on a range of glass-fibre filter papers.

Application of the familiar Washburn equation to the results yields an 'imbibitionequivalent' pore size. Although, in the case of fibrous materials, it may be difficult to relate this to any real geometrical property, it nevertheless provides a practically useful description of the materials' behaviour.

The effects of prewetting on subsequent imbibition are explored.

#### Introduction

PRACTICAL interest in capillary imbibition stems from the numerous technological applications of the phenomenon, involving a great variety of porous media, under a wide range of conditions. A desire to understand and control the process, and to manipulate it for practical benefit, is natural. At the same time, a detailed description of the process raises some interesting problems concerning capillarity and the structural characteristics of porous media, and this is especially true where fibrous materials, such as paper and woven fabrics, are concerned.

The structure of the pore space formed by random packing of solid particles (whether spheres or fibres) can be described statistically. This is of limited help in analysing the imbibition process in such structures, however, because of the difficulties that still remain in determining meniscus configurations and hydro dynamic flow resistance in pores of irregular shape. Thus, to attempt to find a completely fundamental solution is a hopeless task. For this reason, it is preferable to begin with very simple geometrical models, amenable to reasonably exact treatment, and to introduce complications only when necessary.

Under the chairmanship of Prof. M. Judt

We shall show later that it is possible to describe an arbitrary pore structure in very simple model-equivalent terms, in a way that serves a practical need.

# The Lucas-Washburn equation

ALTHOUGH observations of the equilibrium elevation of liquids in fine capillaries are of considerable antiquity, and the equation of incompressible laminar flow in cylindrical tubes was given by Poiseuille in 1843,<sup>(1)</sup> the two were not united in a description of the kinetics of capillary imbibition until the work of Lucas in 1918<sup>(2)</sup> and Washburn in 1920.<sup>(3)</sup>

At equilibrium, a liquid of surface tension  $\sigma$  and density  $\rho$  in a tube of radius r will attain a height  $h_{eqm}$  greater than that attained in a tube of infinite radius, given approximately by

$$h_{\rm eqm} = (2\sigma\cos\theta)/r\rho g,$$
 . . . (1)

where g is the gravitational acceleration, and  $\theta$  the contact angle between the liquid and the material of the tube. A small correction, dependent on meniscus shape, is negligible provided that  $h_{\text{eqm}} \gg r$ , or  $r \ll (2\sigma \cos \theta/\rho g)^{1/2}$ . For  $\theta > \pi/2$ ,  $h_{\text{eqm}}$  is negative, and capillary depression is observed.

If, during the approach to equilibrium, the liquid has reached a height  $h(=\alpha h_{eqm})$  at time t, with h = 0 at t = 0, then a simple application of Poiseuille's Law yields

$$\ln (1-\alpha)^{-1} - \alpha = r^2 \rho g t / 8 \eta h_{eqm} \qquad . \qquad . \qquad (2)$$

where  $\eta$  is the viscosity of the liquid. This is the *Lucas–Washburn* equation.

When  $\alpha$  is very small ( $h \ll h_{eqm}$ ) a simpler form results from an expansion of the logarithm up to terms in  $\alpha^2$ :

This will be known here as the *Washburn* equation, and k (units of length/ (time)<sup>1/2</sup>) is the *specific Washburn constant*.

The derivation of these two equations involves the following assumptions-

- (i) the meniscus curvature is uniform, and is always equal to that obtaining at equilibrium;
- (ii) the surface tension always retains its equilibrium value;
- (iii) convergent flow at the tube entrance, and circulatory flow behind the moving meniscus, contribute negligibly to the flow resistance;
- (iv) laminar flow prevails elsewhere;
- (v) the acceleration of the fluid is always small.

Uniformity of meniscus curvature in liquid-liquid displacement in cylindrical tubes has been confirmed over a wide range of velocities by direct observation.<sup>(4, 5)</sup> This implies further that the radial pressure gradients arising from circulatory flow near the meniscus are negligible. It was also observed, however, that the curvature of the moving meniscus, whilst uniform, may, nevertheless depart considerably from its static equilibrium value, due to dependence of contact angle on the velocity of the contact line. This variation of curvature is always in such a direction as to oppose flow. More complex conditions will prevail in capillaries of non-uniform cross-section: a point to which we shall return.

The possibility that the surface tension may depart appreciably from its equilibrium value could be of serious significance when the imbibition of macromolecular surfactant solutions is considered. For pure liquids, however, the effect should be altogether negligible.

Convergent flow at the tube entrance has recently been considered analytically, and shown to be unimportant at realistic imbibition velocities.<sup>(6)</sup> Similarly, departures from the steady-state condition due to finite acceleration (to which attention was first drawn in 1921<sup>(7)</sup>) are significant only in the very earliest stages of imbibition.<sup>(8,9)</sup> The assumption of laminar flow is also justified at all practical imbibition rates in cylindrical tubes, though once again this assumption must be re-examined in the case of capillaries of nonuniform section.

An equation of the Washburn type can be obtained without reference to an explicit model of the pore system, by postulating a constant driving force proportional to surface tension (equivalent to assumptions (i) and (ii) above), and obedience to Darcy's law in the liquid-filled regions (equivalent to assumptions (iii)–(v)).<sup>(10)</sup> Because no model is used, the pore radius is not explicitly involved, although it will be included implicitly in the permeability constant.

An equation of the form

## $h^2 \propto t$

is also obtained by treating imbibition as a one-dimensional diffusion process.<sup>(11)</sup> In this case, the properties of the pore system *and* of the imbibing liquid are incorporated in the 'diffusion coefficient'.

It therefore appears that even though the Washburn equation is derived on the basis of a very simple model, it is not strictly necessary for the real pore system to resemble the model in order that Washburn kinetics may be followed.

### Gravimetric technique

ALTHOUGH the progress of imbibition into porous media can often be studied visually, the method is limited to observations of the position of the wetting front on external surfaces. Within the solid, average fluid saturation over a defined volume can be obtained, for example, from measurements of the attenuation of gamma radiation from a suitably collimated source, provided that the fluid differs in gamma-ray absorption coefficient from the porous solid, and that the porosity is uniform.<sup>(12)</sup> Other problems can arise, however, when the wetting front is diffuse, or irregular. An alternative possibility is therefore to follow the gain in weight of a porous sample as imbibition proceeds, since by this means any irregular advance of the wetting front is averaged over the whole cross-section.

The method will first be analysed for a simple model, to illustrate the principles involved. Let a straight cylindrical capillary tube of radius r be suspended vertically, and at time t = 0 let its lower end be placed in contact with a plane liquid surface. Let the liquid form a contact angle  $\theta$  with the inner surface of the tube, and  $\pi/2$  (or greater) with the outer surface. We need to calculate the vertical force required to hold the tube stationary, at some time t when the meniscus has risen to a height h in the tube (Fig. 1, a-c). It must be remembered that for  $h < h_{eqm}$ , the liquid is in motion, both inside the tube and in the vicinity of the tube entrance. The problem can be treated in various ways.

At the plane h = 0, the tube with its liquid contents can be regarded as being joined by a capillary bridge of area  $\pi r^2$ , to a reservoir of liquid bounded by a plane surface and consequently at the ambient pressure  $P^0$ . The liquid in





the tube immediately above h = 0 is at a different pressure, first because of the curvature of the meniscus, and second because of the pressure gradient associated with the flow. The first contributes a term  $(2\sigma \cos \theta)/r$ . To evaluate the second, the Poiseuille equation is used to express the volumetric flow rate Q entering the tube:

$$Q = \frac{\pi r^4 \Delta P}{8\eta h}$$

where  $\Delta P$  is the pressure gradient causing flow. But

$$Q = \pi r^2 \frac{\mathrm{d}h}{\mathrm{d}t}.$$

Hence

$$\Delta P = \frac{8\eta}{r^2} \cdot h \frac{\mathrm{d}h}{\mathrm{d}t}$$
$$= \frac{8\eta h^2_{\mathrm{eqm}}}{r^2} \cdot \frac{\alpha}{\mathrm{d}t} \frac{\mathrm{d}\alpha}{\mathrm{d}t}$$

Differentiating equation (2),

$$\Delta P = h_{\text{eqm}} \rho g(1-\alpha)$$
$$= \frac{2\sigma \cos \theta}{r} \cdot (1-\alpha).$$

Hence, the net force on the capillary tube is

Thus, the net force is equal to the weight of liquid suspended, irrespective of whether or not the equilibrium capillary rise height has been reached.

The same result can be obtained if we consider the solid to be exerting a force of  $2\pi r\sigma \cos \theta$  on the meniscus, and the moving liquid to be exerting a viscous force of  $8\eta hQ/r^2$  on the solid. There are difficulties, however, in imagining the solid to exert a tractive force on the liquid, and these are aggravated when we extend the idea to a recent suggestion by Good,<sup>(13)</sup> that an additional driving force is present if the solid ahead of the advancing meniscus is not at adsorption equilibrium with the saturated vapour of the imbibing liquid. Good correctly points out that a gradient of spreading pressure will exist ahead of the meniscus if equilibrium is not attained, but he then equates this directly to a driving force without suggesting a plausible mechanism whereby such a force could be transmitted to the liquid.

The imbibition process can also be regarded as being driven by stored surface energy, proportional to the difference between the surface tensions of the solid before and after wetting, i.e. the adhesion tension. This is partly used in raising the potential energy of the elevated liquid, and partly in overcoming viscous drag. The Lucas–Washburn equation has been derived in this way.<sup>(14)</sup> We note that in a more elaborate formulation it would be possible to include such effects as energy stored elastically in a deformable solid, and energy lost irreversibly in spontaneous changes of meniscus configuration in pores of non-uniform cross-section.

In all these considerations, we have neglected the rate of change of total momentum in comparison with the other forces acting in the system; this is permissible at all but the earliest stages of flow.

#### Experimental

A RECTANGULAR strip ( $120 \times 30$  mm) of glass-fibre filter paper was suspended with its long axis vertical from an electronic microbalance (CI Electronics, Mark IIC), and a reservoir of the liquid to be imbibed was raised so that it met the lower edge of the paper at time t = 0. The servo-system of the balance ensured that the balance beam remained stationary, and hence that the depth of immersion of the paper strip did not change, as the weight changed. (In some of the experiments a chain balance was used to achieve the same result manually, but this required considerable dexterity from the operator.) The electrical output of the balance was recorded continuously, and by adjusting the sensitivities of balance and recorder the anticipated total weight change on imbibition could be made to correspond approximately to full-scale deflection; individual readings could then be made with an uncertainty of less than 1 per cent of this figure. The balance could accept a total load of 1 g and could detect weight changes with a maximum sensitivity of 1 µg, which was more than adequate for our purpose.

Whatman filter papers GF81, GF82, GF83 and ST81 were used. The first three differ in fibre diameter and packing density, whilst the last is prepared by surface treatment of GF81 to produce a hydrophobic surface.

Various methods were investigated for cleaning the three untreated papers. Wet methods (e.g. washing in conc. HNO<sub>3</sub> or in 100-vol  $H_2O_2$  solution, rinsing and drying over  $P_2O_5$ ) produced irreversible changes in the structure of the fibre mat. A dry method (baking for 4 h at 450° C in a stream of oxygen) left the structure unchanged, but had no effect on the imbibition kinetics of any of the liquids studied. It was therefore concluded that the paper as supplied contained no impurities of consequence to imbibition studies, and all further work was done with uncleaned paper, which was, however, handled only with forceps.

In other experiments (to be described more fully elsewhere) model pore systems of various kinds were suspended from the balance. These included single glass capillary tubes, and strips of woven fabric and of wire mesh. The organic liquids used for imbibition were all of laboratory reagent (or, if available, analytical) grade, and were used without further purification. Water was freshly distilled. Surface tensions, viscosities and densities were taken from tables and corrected to the experimental temperature when necessary.

For some experiments, GF81 strips were partially prewetted with di-n-butyl phthalate (DBP) before imbibition. Prewetting of from 5 to 85 per cent of the pore space was performed by saturating the strips in solutions of various concentrations of DBP in benzene and allowing the benzene to evaporate slowly. The degree of prewetting was determined from the gain in weight of each strip.

#### Results

FIG. 2 shows results for the imbibition of iso-propanol in GF81 paper, plotted as weight gain,  $\Delta w$ , against the square root of elapsed time. The plot is accurately linear over most of the range, and since similar linearity was shown by all the other liquids, their results can be expressed simply as the slope  $k_w = d(\Delta w)/d(t^{1/2})$  of such a plot. In Fig. 3,  $k_w$  is shown as a function of the square root of the ratio of surface tension to viscosity, for eleven different liquids in GF81 paper. ( $k_w$  is divided by liquid density, to convert it to a volume basis.) Similar results are shown for various liquids in the other three papers.

Imbibition of DBP into GF81 partially prewetted with DBP also gave linear Washburn plots: the rate constants are shown as a function of x, the fraction of the pore space presaturated, in Fig. 4.

## Discussion

In general terms, the process of capillary wetting is driven by the reduction in surface energy that it achieves, of which the geometrical aspect is conveniently expressed in terms of a reduction  $\Delta A^{\text{eff}}$  in effective area:

$$\Delta A^{\rm eff} = \Delta (A_{\rm lv} - A_{\rm sl} \cos \theta)$$

Here, A is an interfacial area, and subscripts s, 1 and v refer to solid, liquid and vapour phases. During the wetting process  $A_{s1}$  evidently increases from an initial value of zero to reach ultimately the total area of the solid. The available energy is used up partly in overcoming viscous resistance and in increasing the gravitational energy of the liquid—the two effects considered in the Lucas–Washburn equation. In pores of non-uniform section, however, energy is also dissipated irreversibly in spontaneous interfacial movements. These arise from microscopic capillary instabilities, and show up as changes in both  $A_{1v}$  and  $A_{s1}$ .

To calculate these changes is quite difficult even in simple model pores, and quite impossible for structures as complicated as a paper. An alternative



Fig. 2—Weight uptake of isopropanol in 30 mm wide strip of GF/81 paper

possibility is to determine the amount of irreversible work from the hysteresis in the moisture content/suction relationship, which arises from the same cause. The prediction of wetting rates from the moisture characteristic will not be pursued here, however, but we shall instead discuss the results in terms of the simple Washburn equation.

The pore structure of these papers differs in many respects from the simple capillary model discussed earlier. The pores are extremely irregular in cross-



Fig. 3—Washburn rate-constants for various liquids in four different papers (30 mm wide strips)

Key to liquids used: 1 di-n-butyl phthalate

- 2 n-octanol
- 3 n-pentanol 4 n-butanol
- 5 iso-propanol 6 ethanol
- 7 methanol
- 8 n-octane
- 9 n-heptane
- 10 water
- 11 acetonitrile



Fig. 4—Effect of presaturation on wetting rate (di-n-butyl phthalate in GF/81 paper)

section, they show a wide spectrum of sizes and shapes, and they are interconnected. Moreover, because the solid fibres are preferentially contained in the plane of the paper, the pore system will be anisotropic. Even so, we have avoided the further difficulties, presented by more typical papers, of specific interactions between water and cellulose fibres, and structural and surfacechemical modifications arising from the incorporation of fillers, surface coating and sizing.

The existence of a range of pore sizes is to be expected in any non-regular array of particles or fibres, and this is apparently confirmed in the distributions of pore size obtained by such techniques as mercury porosimetry and maximum bubble pressure, both of which have been applied to papers (e.g. ref.<sup>(15)</sup>). It is important to realise that such measurements not only involve the approximation of representing pores of irregular cross-section by circular cylinders, but also imply assumptions about the way in which pores of different size are interconnected. The mercury penetration curve, for example, is usually interpreted by assuming the pores to be purely parallel-connected. The maximum bubble pressure, on the other hand, gives the diameter of the smallest constriction in a sequence of pores connected in series. For the special case of pores penetrating the thickness of a paper sheet, these cases may be not too dissimilar. For capillary penetration in the plane of the paper, however, series-connected networks will dominate. In the simplest case of pores of only two sizes, these will best be modelled, in terms of Fig. 1, not by two parallel



Fig. 5—Measured concentration profile for di-n-butyl phthalate in GF/81 paper

capillaries of different diameter, but by a single capillary whose diameter alternates randomly between the two sizes with an average periodicity much shorter than the overall length. Even so, the effect of parallel interconnections will not necessarily be negligible, and may be manifested as a diffuseness of the wetting front.

This is illustrated by measurements of the distribution of liquid in a partlywetted paper, made by removing a strip from the balance during an imbibition experiment and cutting it quickly into lengths of about 10 mm. The liquid used was dibutyl phthalate, whose low vapour pressure and relatively high viscosity minimised saturation changes during these operations. The weight per unit area of each section, compared with that of the dry paper, enables the liquid concentration to be obtained as a function of height (Fig. 5). The region BC of uniform concentration gives the saturation uptake, in  $mm^3 mm^{-2}$ , which is presumed to be typical for each paper irrespective of the liquid used. The region AB includes the extra volume of liquid raised as a meniscus at the contact between the strip and the free liquid surface. The nonuniform region CD represents a somewhat diffuse wetting front. At the level of individual pores, there is little opportunity (during imbibition) for saturations between zero and 100 per cent to occur: the wetting front in a single capillary is perfectly sharp. To the extent that parallel, rather than serial connections are allowed between pores of different sizes, however, the wetting front will develop diffusely.

Measurements of the saturation distribution at different stages of imbibition showed that the diffuse region CD was practically constant in shape as it moved up the paper strip. Imbibition thus consisted essentially of the extension of the uniform region BC along the strip. This provides experimental justification for applying the gravimetric method to such a complex pore structure. In terms of the Lucas–Washburn model, the driving force arises at menisci within the diffuse region CD, and is essentially invariant in time. The viscous resistance is exerted predominantly in the uniform region BC. The rate of weight change is directly proportional to the rate of extension of the uniform region. Moreover, since the ultimate capillary rise in these papers is several times greater than the length of the strips used, Equation (3) is obeyed over most of the experimental range, as in Fig. 2. This is convenient, since added constant terms in the measured weight, corresponding to regions AB and CD, are difficult to incorporate in Equation (2).

According to Equation (3),

$$k = \left(\frac{\sigma \cos \theta}{\eta} \cdot \frac{r_{\rm imb}}{2}\right)^{1/2} \qquad . \qquad . \qquad (5)$$
$$= \frac{1}{bS_{0}\rho} \cdot k_{w},$$

where

- $k_w = d(\Delta w)/dt^{1/2}$  (mgm sec<sup>-1/2</sup>), the Washburn coefficient;
  - b = width of paper strip (mm);
- $S_o = \text{saturation uptake (mm^3 mm^{-2})};$
- $\rho =$ liquid density (mgm mm<sup>-3</sup>); and
- $\Delta w$  = weight gained (mgm) relative to an arbitrary zero.

When  $k_w$  is evaluated from data (as in Fig. 2) for a series of liquids in a given paper, and plotted against  $(\sigma/\eta)^{1/2}$  for each liquid, a linear relationship is found (Fig. 3), the only significant deviation being the result for water, which is imbibed more slowly than expected. The only property of the liquid not specifically accounted for in Fig. 3 is  $\theta$ , its contact angle against the solid. Water is known to be highly susceptible to organic contamination which can both reduce  $\sigma$  and increase  $\theta$ , and the observed deviation could thus have been due to inadequate precautions against such contamination. This effect is shown more clearly by the hydrophobic (but organophilic) paper ST/81, into which water was not imbibed at all  $(d(\Delta w)/dt^{1/2} = 0)$ , because  $\theta > \pi/2$ .

The slopes of the plots of  $k_w$  against  $(\sigma/\eta)^{1/2}$  in Fig. 3 are, according to equation (5), proportional to the square root of a pore 'radius'. These values are listed as  $r_{\rm imb}$  in Table 1. The geometrical interpretation of  $r_{\rm imb}$  is obscured by two different features of the pore structure, namely the non-circularity of the pore section, and its non-uniformity from point to point along the pore. The radius appearing in equations (2) and (5) remains after cancellation between terms in  $r_1^2$  and  $1/r_2$ , where  $r_1$  is a radius controlling hydraulic resistance and  $r_2$  is inversely proportional to meniscus curvature. For cylindrical pores,  $r_1$  and  $r_2$  are equal to the geometrical radius, but although for non-cylindrical pores they can, in principle, be related by means of 'shape factors' to an actual geometrical length (as in the Kozeny–Carman equation, for instance), it should be noted that the shape factors are not necessarily the same for  $r_1$  and  $r_2$ , and cannot therefore be cancelled along with r.

One effect of pore non-uniformity arises because the capillary pressure and the flow resistance will be averaged in different ways as liquid moves along a pore of periodically-varying 'radius'. Thus,  $\langle r_1 \rangle^2$  and  $\langle r_2 \rangle^{-1}$  are defined in different ways. The variation of  $r_2$  along the pore also leads to a series of metastable values of  $h_{eqm}$  in equation (1), which is a fundamental reason for capillary hysteresis, as in mercury penetration and related phenomena. For these reasons, the identification of  $r_{imb}$  with any definable geometrical property of the pore structure is impracticable for all but the simplest models. Nevertheless,  $r_{imb}$  might be expected to be roughly proportional to the fibre radius at constant packing density, and inversely proportional to some function of the packing density at constant fibre radius.

The problem is further illustrated by comparing the values of  $r_{imb}$  and  $r_{perm}$  in Table 1. The latter are derived from water permeabilities (normal to the sheet) quoted by the manufacturer. By considering the pores as parallel

Paper	$r_{ m imb}/\mu{ m m}$	$r_{ m perm}/\mu m$	$S_{o}/mm^{3} mm^{-2}$
GF81	0.87	1.26	0.315
GF82	0.74	1.78	0.727
GF83	0.83	1.04	0.290
ST81	0.17		0.084

non-interconnected cylinders running straight through the sheet, it is easy to show from Poiseuille's equation that

where  $\kappa$  is the specific permeability coefficient, and the porosity can be taken as approximately unity in such open structures as these. Although the two radii are of similar magnitude in each case, they do not place the samples in the same order of pore size.

Although neither  $r_{imb}$  nor  $r_{perm}$  is a 'real pore size', each represents a real property of the paper. Because the imbibition process obeys equation (3) quite accurately, it follows that if  $r_{imb}$  is known for a given paper, the kinetics of the imbibition process can be predicted for *any* wetting liquid with similar accuracy. The determination of  $r_{imb}$  thus offers a useful means of characterising the imbibition properties of a material by means of a single number, even if it cannot be related to an actual pore size. Although it is still of interest to seek both empirical and theoretical correlations with other properties, model-dependent quantities such as  $r_{imb}$  can evidently serve a practical purpose as they stand.

The results on prewetted strips (Fig. 4) are of interest because prewetting is commonly used as a practical means of controlling imbibition, e.g. in plastering, where it is used to limit the amount of water withdrawn from wet plaster being applied to a porous substrate. The results show that as the fraction x of the pore volume that is prewetted increases, the rate of weight uptake generally decreases. The small increase in the rate constant at values of xbelow 0.1, which is believed to be real, may be due to a change of the pore structure caused by the prewetting liquid drawing the fibres into more parallel orientations by capillary attraction.

The reduction in k with increasing x is due in part to the fact that only the fraction (1-x) of the pore space remains active for imbibition. The ratio k/(1-x) increases continuously with x (Fig. 6). If the pores are modelled as parallel capillaries of different sizes, this might indicate that the mean active pore size increases as x increases, suggesting that prewetting occurs preferentially in the finest pores, as would be expected. On the other hand, if the pores are thought of as a series-interconnected sequence, then the length of each pore filled by prewetting liquid will be traversed by the advancing meniscus in effectively zero time, but will thereafter contribute to the viscous resistance in the usual way. The apparent time-scale for imbibition will thus be scaled by a factor (1-x), and the effective rate-constant will be

$$k' = k(1-x)^{-1/2}$$
 . . . (7)

Fig. 6 also shows k' as a function of x, and its relative constancy seems to in-



Fig. 6—Effect of presaturation on wetting rate—reduced rate constants as defined in text

dicate that the effective pore size for imbibition is unchanged by prewetting, i.e. that the finer pores are not preferentially filled. Further study is needed to discover whether the approximate constancy of k' is a general property, or whether it results from the particular pore-size distribution of this paper.

#### Conclusions

THE imbibition of wetting liquids into fibrous materials such as paper follows the Washburn equation, and leads to a useful measure of pore size. The gravimetric technique described here provides a convenient method for continuously following the progress of imbibition, although the regularity with which the Washburn equation is obeyed means that a simple one-point measurement would be equally suitable for routine characterisation of paper samples. Measurements of this kind could also be used to compare the wetting power of various liquids for the same porous solid.

Although it is very difficult to relate pore sizes measured in this way to the real geometry of a fibre mat, it would nevertheless be valuable to seek empirical relationships to such variables as fibre diameter and packing density.

The effect of pre-wetting is to reduce the rate constant for subsequent imbibition. The results do not, however, provide unambiguous evidence for the idea that presaturation occurs preferentially in the finer pores, since the interpretation depends on the model adopted for the interconnectivity of pores.

#### References

- 1. Poiseuille, J. L. M., Ann. Chim., 1943, 7, 50
- 2. Lucas, R., Kolloid Zeits., 1918, 23, 15
- 3. Washburn, E. W., Phys. Rev., 1921, 17, 273
- 4. Blake, T. D., Everett, D. H. and Haynes, J. M., in *Wetting* (S.C.I. Monograph 25), 1967, 164
- 5. Blake, T. D., Ph.D. Thesis, University of Bristol, 1968
- 6. Levine, S., Neale, G. H., Reed, P. and Watson, E. J., Paper presented at 50th American Chemical Society Colloid Symposium, Puerto Rico, 1976
- 7. Bosanquet, C. H., Phil. Mag., 1921, 45, 525
- 8. Levine, S. and Neale, G. H., J.C.S. Faraday II, 1975, 71, 12
- Szekely, J., Neumann, A. W. and Chuang, Y. K., J. Colloid Interface Sci., 1971, 35, 273
- 10. Denton, J. M., J. Chromatog., 1965, 18, 615
- 11. Rudd, D. F., J. Phys. Chem., 1960, 64, 1254
- 12. de Swart, J. G. and Groenevelt, P. H., Soil Sci., 1971, 112, 419
- 13. Good, R. J., J. Colloid Interface Sci., 1973, 42, 473
- 14. Levine, S. and Neale, G. H., Paper given at Society of Chemical Industry Symposium 'Wetting, Spreading & Adhesion', Loughborough, 1976
- Corte, H., Fundamentals of Papermaking Fibres, Ed. F. Bolam, Technical Section of the British Paper and Board Makers' Association, Kenley, Surrey, England, 1958, 301–331

# **Transcription of Discussion**

# Discussion

Mr J. A. Bristow Dr Haynes, I wondered why you didn't mention the problem of evaporation of the adsorbing liquid and I should like to ask a question about the experimental technique. Are your samples enclosed in some sort of container so that the air around them is stationary and saturated with the vapour of the liquid you are studying?

*Haynes* We took rudimentary precautions against evaporation by surrounding the paper strip with a shield. This served both to reduce the effect of random draughts in the laboratory on the recorded weight, and also to surround the sample with a more-or-less vapour-saturated air space. However, since we were using mostly fluids of rather low volatility, evaporation was not a problem.

Dr M. B. Lyne For cellulose fibres, and probably for glass fibres, the contact angle depends on the roughness of the fibre. For wetting liquids the contact angle is smaller with rough surfaces. Did you take this into account? Also, you mention various capillary radii that you calculated using the Lucas-Washburn equation. How did you measure the contact angle?

*Haynes* It was pointed out by Gibbs that if a solid surface has a geometric discontinuity, such as a sharp edge, then a range of contact angles, satisfying Young's equation, can be stably maintained by a fluid interface. When a three-phase line moves across a rough solid surface it will tend to linger at such places, the contact angle changing while the three-phase line stays still. The term canthotaxis describes the anchoring of a meniscus at an edge in this way. Between arrests, the three-phase line moves abruptly from one asperity to another, giving a readily-observable twinkling appearance at the edge of a slowly spreading drop. The occurrence of this phenomenon on paper surfaces is vividly illustrated in the films made in Professor Mason's group at PPRIC. Irreversible meniscus movements (often known as Haynes

Under the chairmanship of Prof. M. Judt

jumps, after the British soil physicist who observed a similar effect 50 years ago) are an important contributory cause of wetting hysteresis. It is rather difficult, however, to incorporate them in simple model descriptions of wetting kinetics of the kind being discussed here. In answer to your second question, contact angles were not measured, but were assumed to be close to zero in all cases.

Dr E. Back In your Table 1, you show a difference in pore size perpendicular to the surface of the paper and in the plane of the paper. These measurements were made using different methods. If they are made using the same method, for instance with liquid penetration, the ratio of pore radii comes out the other way round. If this comparison is carried out with different liquids for papers which contain rosin size or natural resins this ratio does not come out the same way. This is because the resin alters the contact angle and moreover the resin is not uniformly distributed through the sheet, but occupies discrete sites on the fibre. Could you say something about this?

*Haynes* All I can say is that pore anisotropy, and non-uniform distribution of additives, are additional features which must be incorporated in any complete study of wetting problems.

*Mr J. R. Parker* I would like to underline what Dr Haynes said about the difficulty in relating the results of imbibition experiments to any specific dimension of a porous material. With regard to Table 1 the permeability normal to the paper surface is much less than that for flow parallel to the plane of the paper. Had the radii both been calculated for flow in the same direction, then the ratio  $r_{\rm imb}/r_{\rm perm}$  could probably have been 0.5 or less.

An explanation for this discrepancy can be found by assuming that the capillaries are one-dimensional but of non-uniform cross section as in the third example shown in Fig. 2 (1) of the paper by Schubert. The rate of viscous flow will be determined mainly by the minimum radius of such a capillary and also by the position of the meniscus. The radius of the capillary at this point will determine not only the pressure due to capillarity but also the cross-sectional area of the advancing fluid. Thus the instantaneous rate of rise varies inversely to the cube of the radius at the meniscus. It follows that the effective mean radius of the capillary for imbibition is not only less than that for permeable flow but also is less than that of any physical dimension found in the model.