An Experimental Study of the Washburn Equation for Liquid Flow in Very Fine Capillaries

LEONARD R. FISHER
CSIRO Division of Food Research, P.O. Box 52, North Ryde, N.S.W. 2113, Australia

AND

PROSPER D. LARK
Department of Physical Chemistry, School of Chemistry, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033, Australia

Received July 12, 1978; accepted December 5, 1978

The Washburn equation describes the flow of a liquid under its own capillary force in a horizontal tube. The equation has been tested and shown to be adequate in the range of capillary radii from 3 to 400 μm, but tests for smaller capillaries have indicated anomalously high flow rates. This communication reports tests of the Washburn equation for capillary radii down to about 0.1 μm for the flow of water in glass capillaries and 0.20 μm for cyclohexane in glass capillaries. No evidence was found for systematic deviations from the Washburn equation by cyclohexane, or for water flowing in capillaries with radii above 0.3 μm. For water flowing in narrower capillaries there is an abrupt decrease in flow rates and bubbles are observed in the flowing liquid. The presence of the bubbles accounts for the decreased flow rates because of the Jamin effect (caused by the difference between advancing and receding contact angles).

INTRODUCTION

The progress of a liquid flowing under its own capillary pressure in a horizontal cylindrical capillary is theoretically described (1) by the Washburn equation:

\[ l^2 = \frac{(\gamma rt \cos \theta)}{(2\eta)} \]  

[1]

in which \( l \) is the length of the liquid column at time \( t \), \( \eta \) is the viscosity of the liquid, \( r \) is the radius of the capillary, \( \gamma \) is the liquid–vapor interfacial tension, and \( \theta \) is the contact angle between the liquid and the capillary wall. Equation [1] is derived from Poiseuille's law (2) for viscous flow by assuming that the pressure drop (\( \Delta P \)) across the liquid–vapor interface is given the Laplace–Young equation (3, 4) for a hemispherical interface:

\[ \Delta P = 2\gamma \cos \theta / r. \]  

[2]

The proportionality between \( l^2 \) and \( t \) was first noted by Bell and Cameron (5). Equation [1] was first derived by Lucas (6). The necessary conditions for the validity of Eq. [1] have been listed by Oliva and Joye (7). The more important conditions are that flow should be nearly laminar (for Poiseuille's law to be applicable) and that a hemispherical meniscus shape should be maintained during flow. The first condition is fulfilled provided that the Reynolds number (\( Re \)) is less than about 1,200. For the present case the Reynolds number is given by

\[ Re = \frac{\gamma r^2 \rho \cos \theta}{(4\eta^2)}, \]  

[3]

where \( \rho \) is the density of the liquid. Equation [3] is derived by differentiation of Eq. [1] and substitution into \( Re = r(\frac{dl}{dt}) \rho / \eta \). In the present experiments the Reynolds number never exceeded 1.0 once the liquid...
had progressed along the tube sufficiently to establish laminar flow.

The effects of variations in the second condition (hemispherical meniscus shape) are virtually impossible to calculate, but it is assumed that the slower the flow the closer to hemispherical will be the meniscus, as long as effects due to a wetting film near the meniscus do not supervene. Thus the smaller the capillary radius, the more closely Washburn equation should be obeyed.

The Washburn equation for the case of a liquid/vapor interface has been tested many times (1, 5–15) and its general validity has been confirmed in the range $r = 3–400 \mu m$. Fedyakin (15) has claimed that liquids exhibit low surface tensions and viscosities when flowing in capillaries with $r < 0.1 \mu m$.

The aim of the present study is to test the Washburn equation systematically for capillary radii down to those studied by Fedyakin (15). We have covered a range of radii from $r \approx 0.1 \mu m$ to $r = 14 \mu m$ for the flow of two liquids—water and cyclohexane—in Pyrex glass capillaries.

The rate of flow determined experimentally for cyclohexane agrees with that predicted by the Washburn equation (with the measured value of $\theta = 8 \pm 2^\circ$) within experimental error over the whole range of capillary radii studied. However, the rate of flow of water is only compatible with the Washburn equation if a velocity-independent dynamic contact angle of about $30^\circ$ is assumed. This contact angle is in accord with those found by other workers (16) for water on freshly prepared fused silica surfaces.

There is also a dramatic decrease in the rate of flow of water in capillaries with radii less than about $0.2 \mu m$. Bubbles were observed in the water flowing in these capillaries, so the decreased rate of flow can be explained in terms of the Jamin effect (i.e., the effect of the difference between advancing and receding contact angles). This effect is opposite to that claimed by Fedyakin (15).

EXPERIMENTAL

Capillaries were prepared from Pyrex tubing of various internal diameters (0.2–5 mm). The tubing was washed in hot detergent solution, rinsed thoroughly with distilled water, and finally washed with triply glass-distilled water which had been filtered through a 0.1-$\mu m$-pore-diameter membrane filter (Sartorius, Catalog No. SM11309). The tubing was then placed in a dust-proof enclosure and annealed in a glass-blower's oven at 550°C to remove any trace of organic contamination.

Clean, dry capillaries were obtained by melting a central section of tube in an oxygen–coal gas flame and drawing the tubing out to some 10 m in length. Up to 10 sections of about 100 mm length were immediately flame-sealed from the middle section of this longer capillary.

Capillary flow was observed with a Nomarski interference microscope. The Pyrex capillaries (refractive index about 1.48) were immersed in standard immersion oil (refractive index 1.516) and viewed with a $\times 100$ Reichert interference objective of 1.25 numerical aperture. Measurements were made with a Reichert ×8 micrometer eyepiece. Since oil immersion was necessary to observe the capillaries, a special support was used (Fig. 1) to prevent contamination of the ends of the capillary by immersion oil.

An experiment was begun by breaking open the ends of a capillary with grease-free tweezers. The capillary was placed on the special support and brought into focus somewhere near its center. A drop of the liquid under study was then placed on one end of the capillary and the time for the meniscus to reach the position defined by an eyepiece cross-hair measured with a stopwatch. The liquid drop was fed through a glass syringe fitted with a 0.1-$\mu m$-pore-diameter membrane filter (Sartorius Catalog No. SM11309) in a stainless-steel holder.

Capillary diameters were measured with a
micrometer eyepiece at several points along the capillary. For most of the smaller capillaries ($r < 5 \, \mu m$) the diameter was also measured using a Jeol JSM-U3 or JSM-T20 scanning electron microscope. The capillaries were mounted (end-on) on an SEM microscope stub and coated at an angle of 30° with a layer of gold approximately 10 nm thick. Heavier coatings were found to obscure the hole in the capillary. The SEM magnification was calibrated with polystyrene latex beads of known size (particle diameter 0.796 μm, SD = 0.0083, Dow Chemical Co., Midland, Mich.).

Agreement between diameters measured by interference microscopy and those measured by SEM was always within 2% for diameters greater than 4 μm. Below this diameter the scatter of the SEM measurements (about the fitted line for $P^2/\tau$ vs $r$) increased rapidly, while the diameters measured by interference microscopy showed much less scatter. Thus we have only used the diameters as measured by inter-

![Diagram](image)

**Fig. 1.** Microscope slide arrangement used to study capillary flow.

![Graph](image)

**Fig. 2.** $P^2/\tau$ vs $r$ for cyclohexane. (©) Experimental points; (—–) theoretical line from Washburn equation, assuming $\theta = 8^\circ$; (---) least-squares regression line constrained to pass through the origin; (•••) tolerance bands such that there is 95% confidence that 95% of the points should lie within the bands.
ference microscopy. We are presently examining the reasons for the scatter of the SEM measurements [see also Ref. (17)].

Examination by SEM showed that some capillaries were noncircular. If the ratio of the maximum to minimum diameters was greater than 1.1, the results for that capillary were discarded.

TREATMENT OF DATA

The experimental results for cyclohexane and water are given in Figs. 2 and 3, respectively. The results are plotted as $I^2/t$ vs $r$. This should give a straight line passing through the origin with a slope of $(\gamma \cos \theta / (2\eta))$ if the Washburn equation is obeyed. The experimental points have been corrected for the variation of viscosity with temperature by multiplying the experimental value of $(I^2/t)$ by $\eta(T)/\eta(20^\circ C)$, where $T$ is the actual (room) temperature at which the experiment was performed. Since the range of experimental temperatures was 17 to 24°C, the correction factor was always between 0.93 and 1.07. No correction was made for the variation of $\gamma$ with temperature, since $\gamma(T)/\gamma(20^\circ C)$ was always between 0.99 and 1.01. The error in $I^2/t$ arises from the error in timing ($\pm 0.2$ sec) and the error in the measurement of $I$ ($\pm 0.2$ mm). For capillaries with $r < 10 \mu m$ the combined relative error in $I^2/t$ was always less than 1%.

The principal errors in optical micrometry are resolution ($\pm 0.2 \mu m$) and scale-reading errors ($\pm 0.1 \mu m$). Some optical and observational systematic errors (including the Mach effect) have also been found in micrometry (18, 19), but it has been shown that the Nomarski interference system does not suffer from these defects (20). Thus we estimate the error in $r$ measured by optical micrometry to be $\pm 0.2 \mu m$. This is in fair agreement with the standard error of estimate in $r$ of $\pm 0.3 \mu m$ found for both sets of experimental data.

The relative error in $r$ is usually much greater than the relative error in the corresponding value of $I^2/t$. Thus, for the pur-
poses of statistical treatments, we have used the model

\[ r = b\left(\frac{t}{t}\right) + e, \]  

where \( b \) is the slope of the least-squares regression line constrained to pass through the origin and \( e \) is an error term \((21)\). Values of \( e \) are taken as random independent values from a normal distribution. An examination of the residuals from the fitted regression line supports this latter assumption.

The errors attached to values of \( b \) in the discussion section give 95% confidence intervals for the true slopes based on this model \((21)\).

RESULTS

(a) Cyclohexane

The relevant parameters \((22)\) for the calculation of the theoretical slope at \(20^\circ\text{C} \) are \( \eta = 0.00102 \text{ Pa sec}, \gamma = 2.55 \times 10^{-2} \text{ N m}^{-1} \). The contact angle, \( \theta = 8 \pm 2^\circ \), was estimated by a drop volume method \((\text{L. R. Fisher, in press})\). The theoretical slope of a plot of \( \frac{t}{t} \) vs \( r \), calculated from these parameters, is \((1.24 \pm 0.005) \times 10^4 \text{ mm sec}^{-1}\).

The slope of the least-squares line through the experimental points and constrained to pass through the origin (Fig. 2) is \((1.21 \pm 0.05) \times 10^4 \text{ mm sec}^{-1}\). [An unconstrained regression line through the data points has a slope of \((1.18 \pm 0.06) \times 10^4 \text{ mm sec}^{-1}\) and an intercept on \( r \) of \( = (0.025 \pm 0.094) \mu \text{m}. \) Thus the assumption that the data fit a straight line constrained to pass through the origin is justified to within experimental error.]

Thus, within the limits of experimental error, the Washburn equation holds for cyclohexane in Pyrex glass capillaries with radii greater than \(0.2 \mu \text{m}\).

(b) Water

From the parameters \( \eta = 0.0010 \text{ Pa sec}, \gamma = 7.27 \times 10^{-2} \text{ N m}^{-1} \) \((22)\), and \( \theta = 0^\circ \), the theoretical slope of a plot of \( \frac{t}{t} \) vs \( r \) is \((3.63 \times 10^4 \mu \text{m sec}^{-1})\).

The slope of the least-squares line constrained to pass through the origin (Fig. 3) is \((3.13 \pm 0.09) \times 10^4 \text{ mm sec}^{-1}\). The 12% difference between this and the theoretical slope, assuming \( \theta = 0^\circ \), is significant at better than the 0.1% level of significance. [An unconstrained regression line through the data points has a slope of \((3.11 \pm 0.12) \times 10^4 \text{ mm sec}^{-1}\) and an intercept on \( r \) of \( = (0.025 \pm 0.094) \mu \text{m}. \) Thus the assumption that the data fit a straight line constrained to pass through the origin is justified to within experimental error.]

For capillary radii below about \(0.3 \mu \text{m}\) bubbles were observed in the flowing liquid. In all three cases, the values of \( \frac{t}{t} \) were at least four times smaller than those predicted by the Washburn equation. These data are given in Table I.

DISCUSSION

(a) Cyclohexane

The slope of a plot of \( \frac{t}{t} \) vs \( r \) agrees with that predicted by the Washburn equation for

\begin{table}
\centering
\begin{tabular}{|c|c|c|}
\hline
\( r \) \((\mu \text{m})\) & \text{Experimental} \((<)\) & \text{Theoretical} \((\text{assuming } \theta = 0^\circ)\) \\
\hline
0.35 & \( < 3.1 \) & 12.7 \\
0.27 & \( < 0.28 \) & 9.80 \\
0.27 & \( < 0.28 \) & 9.80 \\
0.25 & \( < 0.26 \) & 9.08 \\
0.25 & \( < 0.25 \) & 9.08 \\
0.25 & \( \sim 0.5 \) & 9.08 \\
0.20 & \( < 0.037 \) & 7.26 \\
0.20 & \( 0.40 \) & 7.26 \\
0.14 & \( 1.04 \) & 5.08 \\
\hline
\end{tabular}
\caption{Values of \( \frac{t}{t} \) for Water in Capillaries with \( r > 0.35 \mu \text{m} \)}
\end{table}

Values quoted as "less than" \((<)\) are derived from experiments where the liquid had progressed for such a short distance along the capillary during the time of the experiment that the liquid reservoir had to be removed, and flow thus halted, before the meniscus could be observed by our microscopic technique.
the flow of cyclohexane in initially dry Pyrex glass capillaries to within experimental error (±5%) over the whole range of capillary radii examined \((r = 0.21-14 \mu m)\). We thus conclude that the conditions of the Washburn equation are maintained in this range to within experimental error. In particular, the hemispherical meniscus shape is maintained and the advancing contact angle is less than 18°.

We note here that Good (13) has proposed a minor correction to the Washburn equation. This correction is less than 2% for both water and cyclohexane on glass, and our results are not sufficiently accurate to test an effect of this magnitude.

(b) Water

The flow of water in initially dry Pyrex glass capillaries obeys Washburn-type behavior in that a plot of \(l^2/t \) vs. \(r\) is linear and passes through the origin. However, the slope of the theoretical plot for \(\theta = 0°\) differs significantly from that of the line of best fit through the experimental points. The slopes can be made to agree if it is assumed that \(\theta = 30°\). We conclude from this that the advancing contact angle of water flowing in freshly prepared fused Pyrex glass capillaries is significantly different from zero, and is also velocity independent to within experimental error. A nonzero contact angle for water on freshly fused silica has been reported by other workers (16).

The presence of bubbles in water flowing under its own capillary pressure in very fine glass capillaries \((r \approx 0.3 \mu m)\) requires explanation. The bubbles would decrease the flow rate by the creation of a series of liquid plugs, with the advancing contact angle for each plug greater than the receding contact angle [the Jamin effect (23)].

At present we have no reasonable explanation for the origin of the bubbles. It might be thought that the water is degassing under the negative pressures experienced by it at these capillary radii. However, we have repeated our experiments with thoroughly freeze-thaw degassed water and have observed the same phenomena. We have also carefully examined the conditions listed by Oliva and Joye (7) and find that all are fulfilled in our experiments.

The decrease in flow rate is opposite to the effect claimed by Fedyakin (15). However, Fedyakin’s experiments were performed with capillaries which were closed at one end, so that flow eventually ceased when the pressure of the compressed gas in the capillary became equal to the Laplace pressure across the meniscus. The presence of bubbles in the flowing liquid would probably not have been noticed by Fedyakin’s techniques and would complicate the interpretation of his results, including his indirect method of estimating capillary diameters.

We conclude that the Washburn equation for the case of liquid/vapor menisci is obeyed by both water \((for \ r > 0.3 \mu m)\) and cyclohexane \((for \ r > 0.2 \mu m)\). For water in capillaries with \(r < 0.3 \mu m\), bubbles appear in the flowing liquid and decrease the flow rate because of the Jamin effect (23).

ACKNOWLEDGMENTS

We acknowledge the assistance of Dr. C. Nockolds, of The University of Sydney, and Dr. T. Little, of the CSIRO Division of Textile Physics, in obtaining the SEM results. The comments of Dr. J. M. Haynes of the University of Bristol and Dr. G. E. Hibberd of the Bread Research Institute of Australia have been greatly appreciated. We thank a referee for providing valuable additional references.

REFERENCES


Journal of Colloid and Interface Science, Vol. 69, No. 3, May 1979