NOTES

The Effect of Adsorbed Water Vapor on Liquid Water Flow in Pyrex Glass Capillary Tubes

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

$$l^2 = \gamma r t \cos\theta/(2\eta) \qquad [1]$$

in which l is the length of the liquid column at time t, η is the viscosity of the liquid, r is the radius of the capillary, γ is the liquid/vapor interfacial tension, and θ is the contact angle between the liquid surface and the capillary wall. In a recent communication (2) we showed that Eq. [1] is obeyed by both water and cyclohexane flowing in initially dry Pyrex glass capillaries with $r > 0.2$ μm. We now report experimental evidence that prior exposure of the capillaries to water vapor can cause a marked decrease in the flow rate of liquid water. Prior exposure of the capillaries to cyclohexane vapor had no effect on the flow rate of either liquid. From a comparison of the flow rates of water and cyclohexane in silica and Pyrex glass capillaries, we suggest that water adsorption on Pyrex glass creates an energetically heterogeneous surface, leading to contact angle variations which distort the advancing water meniscus and reduction of the flow rate of liquid water.

The capillaries were initially prepared in sealed 100-mm lengths, as previously described (2). Capillary diameters ranged from 5 to 70 μm. For exposure to water vapor, the capillary ends were broken off with grease-free tweezers and the capillaries placed on a Teflon support in an enclosed glass chamber. The relative humidity in the chamber was controlled by addition of a saturated solution of sodium chloride (equilibrium relative humidity $\approx 76\%$ (3)). This salt solution was used in preference to pure water so that minor temperature fluctuations would not raise the relative humidity to saturation and cause condensation of bulk water on the capillaries. The liquid flow rate in a capillary was measured within 1 min of the removal of the capillary from the chamber. Details of the methods for measuring flow rates and capillary radii are given in our earlier paper (2).

Sets of results for each combination of liquid, capillary type, and time of exposure of the capillary to water vapor were plotted as l^2/t vs r. From Eq. [1], each set of points plotted in this way should fall on a straight line passing through the origin and having a slope of $\gamma \cos\theta/(2\eta)$. The slopes of the least-squares regression lines, through each set of

points and constrained to pass through the origin, are given in Table I. The uncertainties quoted are 95% confidence intervals for the true slope, based on the model used in our earlier paper (2). Relaxation of the constraint that the regression lines pass through the origin, or addition of a quadratic term to our model, did not significantly improve the fit.

The most obvious feature of the results is that the rate of water flow in Pyrex glass capillaries is significantly reduced if the capillaries have first been exposed to water vapor, the magnitude of the effect generally increasing with the time of exposure. This effect could be caused by contamination, or by the effect of an adsorbed film on either the geometry or the surface properties of the capillaries. Contamination would change the surface tension γ and the contact angle θ in Eq. [1], but is an unlikely explanation since no effect was found with identically treated silica capillaries. A sufficiently thick film of adsorbed water would lower the value of r in Eq. [1]; however, such a thick film is unlikely to be present, since, in the case of cyclohexane, the flow rate is unaffected by prior exposure of the capillaries to water vapor. Nor is it likely that a highly viscous "boundary layer" of water at the water/Pyrex interface is affecting the flow. The balance of the evidence (4) is against the existence of such long-range ordering, and in any case a boundary layer of constant thickness would cause curvature in plots of l^2/t vs r, which are in fact linear (Table I).

The adsorbed water must therefore be affecting either the surface energy or roughness of the Pyrex glass. A change in either of these surface properties could affect the contact angle θ, and hence, according to Eq. [1], affect the flow rate of liquids through the capillaries. An increase in roughness alone would reduce the flow rate of both liquid water and liquid cyclohexane, which is not in accordance with the observations.

Probably, then, a change in the energy of the Pyrex surface is responsible for the decreased water flow rates. Good and his co-worker have shown both theoretically (5, 6) and experimentally (7, 8) that liquid flow rates will be up to 10% higher in capillaries whose surfaces are initially free of adsorbed vapor than in Pyrex glass capillaries whose surfaces are covered with an equilibrium wetting film. However, a freshly fused Pyrex glass surface is hydro-

TABLE I

Effect of Prior Exposure of Capillaries to Water Vapor on the Flow Rate of Liquid Water or Liquid Cyclohexane

Capillary type	Time of exposure (t) to water vapor (hr)	Liquid	Slope of regression line of l^2/t vs r (mm sec^{-1} × 10^3)^a
Pyrex glass	0	Water	23.8 ± 2.8
	20		17.5 ± 1.2
	48		17.9 ± 2.9
	120		12.0 ± 0.9
Silica	0	Water	15.1 ± 1.6^b
	20		14.5 ± 1.9
	48		14.9 ± 0.7
	120		17.5 ± 4.0
Pyrex glass	0	Cyclo-	12.4 ± 0.05
	170	hexane	12.7 ± 0.2

^{a} Intervals are the 95% confidence intervals for the true slope (2).

^{b} This value is lower than that for water in dry Pyrex glass capillaries, reflecting the fact that fused silica is more hydrophobic than fused Pyrex glass (10).

phobic,[1] and so the question of the formation of an equilibrium wetting film does not arise. It is, nevertheless, possible that water adsorption on annealed Pyrex glass will create an energetically heterogeneous surface. A freshly fused Pyrex glass surface which has been annealed for a few hours at a temperature between 530 and 760°C shows some phase separation into silica and sodium borate (9–11). The silica surface consists mostly of siloxane bridges (12), and hydrolysis of siloxane bridges is so slow that a fused silica surface remains hydrophobic even after 8 weeks' exposure to water vapor. Reaction of water vapor with sodium borate may be expected to be much faster, and it is thus reasonable to assume that fused Pyrex glass surfaces will quickly become energetically heterogeneous and remain so for many weeks, while a silica surface remains energetically homogeneous.

How could an energetically heterogeneous surface reduce the flow rate of liquid water? Three mechanisms suggest themselves. The first is that the advancing contact angle is increased, but this seems unlikely. Indeed, it seems more likely that the presence

[1] Contact angles measured from microphotographs were 30 ± 6° for both advancing and receding angles; cf. values of 38 ± 3° and 24 ± 3° for water on quartz which has been heat-treated at 800°C (R. N. Lamb and D. N. Furlong, personal communication).

of hydrophilic patches formed during annealing would decrease the contact angle. The second possibility is that rapid fluctuations of the contact angle could provide an additional mechanism for energy dissipation. However, the dissipation rate is unlikely to bear the same relation to l, t, and r as it does for viscous flow, and hence the linearity between l^2 and t would be lost. Thus the Washburn equation would cease to hold if this additional energy dissipation mechanism is significant. The third possibility is that the meniscus is distorted from its hemispherical shape in its passage over the patchwise heterogeneous surface. It has been shown theoretically (13) that a patchwise heterogeneous surface can cause contact angle variations along the three-phase contact line even if the patches have dimensions as small as 1 nm. The lack of effect on liquid cyclohexane flow supports one or the other of the last two hypotheses, since the contact angle of cyclohexane on both low- and high-energy surfaces is close to zero, so that contact angle fluctuations should not be significant.

We therefore conclude that prior adsorption of water vapor reduces the flow rate of liquid water by creating an energetically heterogeneous surface, which probably distorts the moving meniscus from its equilibrium hemispherical shape. Further speculation is not justified by the present data. It is worth noting, however, that Pyrex glass is often used in studies of capillary flow—for example, packed glass spheres are often used as models for the study of liquid penetration in porous materials (e.g., (14)). The results presented here suggest that the effect of adsorbed water vapor should be heeded in the interpretation of such experiments.

REFERENCES

1. Washburn, E. W., *Phys. Rev.* **17**, 374 (1921).
2. Fisher, L. R., and Lark, P. D., *J. Colloid Interface Sci.* **69**, 486 (1979).
3. "Handbook of Chemistry and Physics," 53rd ed. Chem. Rubber Co., Cleveland, Ohio. 1972–1973.
4. Clifford, J., *in* "Water: A Comprehensive Treatise" (F. Franks, Ed.), Vol. 5, p. 75. Plenum, New York, 1975.
5. Good, R. J., *Chem. Ind.*, 600 (1971).
6. Good, R. J., *J. Colloid Interface Sci.* **42**, 473 (1973).
7. Good, R. J., and Lin, N.-J., *J. Colloid Interface Sci.* **54**, 52 (1976).

8. Good, R. J., and Lin, N.-J., in "Colloid and Interface Science" (M. Kerker, Ed.), Vol. III, p. 277. Academic Press, New York, 1976.

9. Nordberg, M. E., *J. Amer. Ceram. Soc.* **27**, 299 (1944).

10. Seward, T. R., Uhlmann, D. R., Turnbull, D., and Pierce, G. R., *J. Amer. Ceram. Soc.* **50**, 25 (1967).

11. Hair, M. L., in "Clean Surfaces: Their Preparation and Characterization for Interfacial Studies" (G. Goldfinger, Ed.). Dekker, New York, 1970.

12. Pashley, R. M., and Kitchener, J. A., *J. Colloid Interface Sci.* **71**, 491 (1979).

13. Neumann, A. W., in "Wetting, Spreading and Adhesion" (J. F. Padday, Ed.), p. 3. Academic Press, New York, 1978.

14. van Brakel, J., and Heertjes, P. M., *Nature (London)* **268**, 44 (1977).

LEONARD R. FISHER[2]

CSIRO Division of Food Research
P.O. Box 52, North Ryde
New South Wales 2113, Australia

PROSPER D. LARK

Department of Physical Chemistry
School of Chemistry
University of New South Wales
P.O. Box 1, Kensington
New South Wales 2033, Australia

[2] To whom correspondence should be addressed.