Limitations of the Washburn equation in quantifying penetration rates

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Recently Cook et al (1977) proposed to calculate contact angles of hydrophobic drugs from penetration measurements employing mixtures of alcohol and water. They used the Washburn's equation to derive the contact angle values from the penetration data, finding that this value was dependent on the drug particle size. The authors suggested that this could be due to a Washburn's equation inadequacy. This is indeed the case: the quadratic relationship between the length (or volume) of penetration and time, established by the Washburn's equation, does not always hold.

The classical Washburn's equation is given by:

$$L^2 = \frac{R\gamma\cos\theta}{2\eta}t \qquad .. \qquad .. \qquad (1)$$

(where: L = length of penetration, R = capillary radius, θ = solid/liquid contact angle, η = liquid viscosity, t = time).

As the volume of penetrated liquid is directly proportional to penetration length, as first shown by Washburn (Washburn, 1921), equation 1 can be written in a simplified form as

$$V^n = K' L^n = K t \qquad .. \qquad (2)$$

(with n = 2, K' and K constants) or

$$V = K^m t^m \qquad .. \qquad .. \qquad (3)$$

(with m = 1/n = 0·5).

But recently it has been shown that m can assume values other than 0·5 (Schicketanz 1974; Carli & Simioni 1977).

Writing equation (3) in a logarithmic form we obtain:

$$\log V = m \log K + m \log t$$

Thus if we plot the penetration data (volume or length) vs time on a double logarithmic plot, m can be calculated from the slope of the linear portions of the curve. This means that before deriving the contact angle values from the penetration data one has to find out the correct m value to be introduced into equation 3.

Recently the authors (Carli & Simioni, in press) have shown that this m value assumes different values depending on the type of pore size distribution of the porous structure being penetrated; as it is reasonable to assume that powder beds of the same drug but with different particle size can produce different porous structure, i.e., pore size distribution, the value of the contact angle calculated via Washburn's equation could
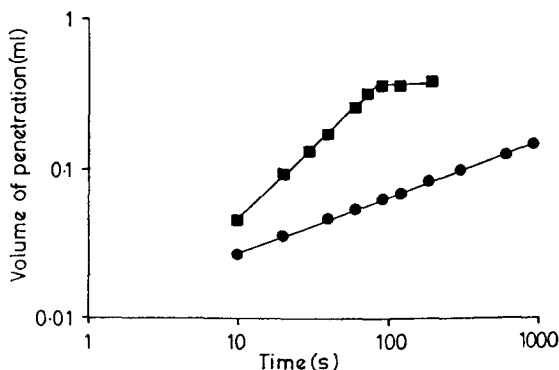
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Fig. 1. Double logarithmic plot of water penetration volume into quartz powder beds vs time. Each experimental point is the mean of four replicates, each replicate differing from the mean for no more than 10%. —■— Quartz particles smaller than 92 μm; —●— Quartz particles between 620 and 850 μm. Measurements were made with the simple Enslin apparatus (Schicketanz, 1974), using distilled water at room temperature. The powder bed area was of ~3 cm².

apparently depend on the particle size, m being considered constant and equal to 0·5.

An example of different m values originated by penetration data in beds of the same substance but with different particle size is shown in Fig. 1, which is the double logarithmic plot of water penetration rate into beds of two different sizes of quartz particles. The slopes of the two curves are different: the value of m for quartz particles smaller than 92 μm is $\simeq$1, whereas for particles between 620 and 850 μm is =0·38. (The upper curve levels off as complete saturation of the powder bed is already achieved at 100 s).

Therefore the assumption that m =0·5, as given by the Washburn's equation, may prove to be misleading.

June 19, 1978

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