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Note

Dynamic contact angle measurement on materials with an unknown wet perimeter

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Abstract

Whilst contact angle measurements obtained using the Wilhelmy balance technique are accurate and reproducible for planar surfaces, their use for characterizing particulate materials is highly dependent upon accurate knowledge of the wet perimeter. This communication suggests that the approach of Pepin et al. [Int. J. Pharm. 152 (1997) 1] for wet perimeter determination using non-polar liquids may lead to erroneous conclusions. Alternative approaches for wet perimeter determination are suggested.

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Knowledge of the wetting properties of powder surfaces is essential for many industrial processes such as minerals separation, paint and ink manufacture, and pharmaceutical formulation. Whilst a number of approaches are available for powder wettability characterisation, there is no unequivocal method that provides accurate and reproducible data (Buckton, 1993; Muster, 2001). The Wilhelmy balance technique has demonstrated superior reproducibility for dynamic contact angle determination on planar surfaces (Neumann and Good, 1979). As a result, approaches based on the Wilhelmy balance method have been investigated as a means to determine dynamic powder contact angles or pharmaceutical powders (Chawla et al., 1994; Sheridan et al., 1994; Buckton et al., 1995). To date, pharmaceutical powder surfaces for Wilhelmy measurements have been created through the use of powder coated glass slides (Dove et al., 1999) and compression of powders into compacts (Buckton et al., 1995). However, for accurate contact angle measurement the wet perimeter needs to be accurately assessed. Pepin and coworkers have approached the issue of wet perimeter by spraying the rough surface with a thin film of hydrophobic glue, and used an extension of Fowkes (1964) equation describing interfacial tension to estimate the wet perimeter (Pepin et al., 1997–1999).

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Our experience has show that such an approach may result in misleading and often meaningless values of the wet perimeter. The following content highlights a discrepancy in the theory underlying wet perimeter determinations.

Fowkes (1964) suggested that the molecular interactions between a solid and a non-polar liquid could be estimated using a geometric mean relationship:

$$\gamma_{\mathrm{SL}} = \gamma_{\mathrm{SV}} + \gamma_{\mathrm{LV}} - 2\sqrt{\gamma_{\mathrm{LV}}^{\mathrm{d}}\gamma_{\mathrm{SV}}^{\mathrm{d}}} \tag{1}$$

where γ_{SV}, γ_{SL} and γ_{LV} are the surface tensions between the solid and vapour, solid and liquid and liquid and vapour phases, and γ_i^{d} is the dispersive component of the surface tension.

If combined with the Young equation, which describes the balance of surface tensions in terms of a three-phase contact angle, θ:

$$\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}} = \gamma_{\mathrm{LV}} \cos\theta \tag{2}$$

we obtain:

$$\gamma_{\mathrm{LV}}(\cos\theta + 1) = 2\sqrt{\gamma_{\mathrm{LV}}^{\mathrm{d}}\gamma_{\mathrm{SV}}^{\mathrm{d}}} \tag{3}$$

Therefore, in theory, the dynamic contact angle measured for two strictly non-polar solvents using the Wilhelmy approach will enable the wet perimeter to be obtained as

$$p = \frac{F_2 a - (F_1\gamma_{\mathrm{LV2}}/\gamma_{\mathrm{LV1}})}{\gamma_{\mathrm{LV2}}(1-a)} \quad \text{where } a = \left(\frac{\gamma_{\mathrm{LV2}}}{\gamma_{\mathrm{LV1}}}\right)^{0.5} \tag{4}$$

where p is the wet perimeter and F_i is the capillary force (Pepin et al., 1997).

The first precaution to be observed when using this approach is that the surface tension of the test liquids should be higher than that of the solid. Failure to comply with this may result in the perfect wetting (i.e. $\cos\theta = 1$) of the solid by one or both of the test liquids, and lead to an erroneous wet perimeter estimation. Therefore, non-polar liquids with a high surface tension are needed for general measurement. Diiodomethane and 1-bromonaphthalene are suitable choices with surface tensions of 50.8 and 44.4 mN m^{-1}, respectively.

The second requirement for a sensible wet perimeter determination is that a positive value for p is obtained, which occurs when

$$F_2 a > \frac{F_1\gamma_{\mathrm{LV2}}}{\gamma_{\mathrm{LV1}}}$$

$$\text{or where rearranged}: \left(\frac{\gamma_{\mathrm{LV1}}}{\gamma_{\mathrm{LV2}}}\right)^{0.5} > \frac{F_1}{F_2} \tag{5}$$

Assuming that the two liquids used for wet perimeter determination are (1) 1-bromonaphthalene and (2) diiodomethane, the value of F_1/F_2 must be less than 0.934. The capillary force values F_1 and F_2 are directly related to the contact angle through the relationship involving the wet perimeter and the liquid surface tension:

$$\cos\theta_i = \frac{F_i}{p\gamma_{\mathrm{LV}i}} \tag{6}$$

Therefore, for F_1 to be less than F_2 (to result in a F_1/F_2 ratio less than 1), the value of $\gamma_{\mathrm{LV2}} \cos\theta_2$ must exceed $\gamma_{\mathrm{LV1}} \cos\theta_1$. Now, we bring to mind the work of several authors (Zisman, 1964; Kwok and Neumann, 1999) who report on the systematic dependence of $\gamma_{\mathrm{LV}} \cos\theta$ on γ_{LV}, and it becomes evident that the value of $\gamma_{\mathrm{LV}} \cos\theta$ decreases with increasing γ_{LV}. Since $\gamma_{\mathrm{LV1}} < \gamma_{\mathrm{LV2}}$, the $\gamma_{\mathrm{LV1}} \cos\theta_1$ term will be greater than $\gamma_{\mathrm{LV2}} \cos\theta_2$, and therefore, F_1/F_2 must be greater than 1, and the value of p becomes negative and erroneous.

Alternative approaches for wet perimeter determination also have their own limitations. Physical methods such as microscopy (Buckton et al., 1995) and micrometer measurements do not account for localised porosities and roughness and therefore underestimate the perimeter. Current work (Muster et al., 2004) in our laboratories has shown that measurement of F during the immersion of a test sample into a series of “perfectly wetting” liquids (i.e. $\cos\theta = 1$) such as cyclohexane and hexane can provide a good estimate of p by utilising equation:

$$p = \frac{F}{\gamma_{\mathrm{LV}}} \tag{7}$$

This approach appears to be analogous to the use of “perfectly wetting” liquids in contact angle determinations using liquid penetration methods (Neumann and Good, 1979). Another alternative for wet perimeter determination was published by Miller et al. (1983), who claim that the maximum pull-out force can be correlated to the wet perimeter with relatively insignificant discrepancies. The latter method has received minimal attention in the literature but warrants further investigation.

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