Development of a Flow Microcalorimetry Method for the Assessment of Surface Properties of Powders

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Purpose. This study describes the development of a microcalorimetric flow cell which allows powder surface energetics to be probed my means of measuring their interaction with water vapour. Methods. A flow cell has been constructed and tested in an isothermal microcalorimeter to assess the interaction between water vapour and powder surfaces. The cell was constructed to mix two separate air streams (0% and 100% relative humidity respectively) to create any humidity at a standard flow rate. The powder sample was equilibrated in dry air and then exposed to sequential increments in humidity. Results. Adsorption isotherms were constructed from the cumulative heat as a function of humidity. It was possible to differentiate between different samples of α-lactose monohydrate (which appeared identical by contact angle determination). It was also possible to measure adsorption to two different alkyl p-hydroxybenzoates which were hydrophobic and of low surface area. Conclusions. This technique offers a very sensitive and versatile method of obtaining a reliable indication of powder surface energetics and as such is a major advance in the field.

KEY WORDS: isothermal microcalorimetry; adsorption; wetting; powders; lactose; batch variability.

INTRODUCTION

Surface properties of materials influence the ease of production, the physical and chemical stability and the ultimate use of many products (1). For powders there are major problems associated with contact angle techniques. Detailed criticisms of contact angle techniques for powders have been presented elsewhere (e.g. 1-6). In essence contact angles can be measured on powder systems after compaction of the material or by measuring fluid flow through a powder bed. The liquid penetration techniques are based on the Washburn equation which has been criticised (6) and have a tendency to overestimate the true contact angle (2). The use of sessile drops on compressed powders can be flawed due to the compaction process changing the surface nature (7) and because the surface must be pre-saturated with a saturated solution of the powder in the test liquid (1). The use of compacted wafer of powders as Wilhelmy plates also suffers from the fact that the powder is compacted. There is a tendency for contact angle values to be underestimates of the true wettability when studied by either of the compaction methods (4,5). Given the difficulties with contact angle methods, it is desirable to utilise other approaches to surface characterisation for powders, an alternative is to consider microcalorimetry. To date we have utilised a batch microcalorimetric approach (8,9), involving the application of a vacuum to the sample to produce a uniform defined starting point, then admitting water vapour from a remote reservoir. The interaction with a vapour is in many ways the best way to probe a surface as the first layer of adsorbed vapour molecules give the most significant information about the powder-probe interaction. The problems with the calorimetric method as used to date (e.g. 8) included the fact that vacuum treatment may affect the surface of the powder; that there were practical difficulties in maintaining the vacuum in the system; that the blank response for adding vapour into a vacuum was large in comparison with the test response; and that the system only allowed two states (dry and totally wet). The single point isotherm that was produced gave comparatively little information on the adsorption process. Furthermore, the system was unsuitable for certain materials which volatilised under vacuum, and for others which tended to exhibit deliquesence.

In this paper the development and use of a vapour flow cell is described,4 and its suitability for use on different types of powders is investigated.

EXPERIMENTAL

A flow cell was engineered as shown in Figure 1, such that it was all housed in the water bath of the calorimeter (25 ± 0.0002 °C), with the final measuring cell being housed in the measuring site of the instrument (Thermal Activity Monitor, Thermometric). Air is passed into a dry and a wet line, the dry line is desiccated (0% RH) and the wet line is passed through 2 humidification stages within the calorimeter. These two lines are mixed to give a controlled humidity and this is then passed into the measuring cell.5 The available space at the measuring site allows for a cylindrical cell of approximately 4 ml capacity. The flow cell was constructed from stainless steel, with tubes being secured in place with epoxy resin. All joints were sealed permanently to give air tight joints except the screw top to the powder cell, which had a O-ring fitting. Periodically the water reservoirs were emptied, flushed with alcohol then dried to minimise risk of bacterial growth.

Two variable speed peristaltic pumps (Gilson Milipuls) were used to provide the air supply for the wet and dry lines

4 The cell as used was based on the design that was invented by Professor Bakri at University of Grenoble (10). His cell has now been commercialised by Thermometric, so other workers would not need to construct their own cell in the manner described in this work.

5 There is a small difference between the cell here and the recent commercial product in that the vapour inlet here is at the bottom of the cell (i.e. in the powder bed), whilst the commercial cell has the inlet above the top of the powder sample. The advantage of this system is that all the powder will contact the inlet air, thus removing the risk of dead space in the cell and increasing the sample load that can be used. The advantage of the commercial system is that there will be less background noise due to the inlet air disturbing the powder bed.
Fig. 1. Diagrammatic representation of the flow cell used. The entire unit is housed in the water bath of the calorimeter. The test cell only is housed in the measuring site of the calorimeter. The two humidification cells yield air of 100% RH which is mixed in desired proportion with air of 0% RH in the mixing chamber.

respectively. The flow rate of air through the pumps was checked by displacement of water (previously saturated with air) from an inverted measuring cylinder. The humidity of the air exhausted from the thermostated cell was monitored by use of a calibrated humidity meter (Rotronic hygromet). The blank response for passing air of differing humidities through the empty cell was recorded. The effect of weight of sample was checked by measuring the response for differing loads of α-lactose monohydrate (Meggle).

Standard loads (1 g accurately weighed) were used for subsequent experiments on different sources of α-lactose monohydrate (Meggle, CMV and Lactochem) and methyl p-hydroxybenzoate and propyl p-hydroxybenzoate. These samples were selected as lactose was found to be impossible to measure using the old vacuum microcalorimeter system (due to a tendency to deliquescence at 100% RH) and methyl p-hydroxybenzoate had given problems with the old system (unpublished data) due to extreme hydrophobicity and low surface area for adsorption.

The surface areas of the powders were measured by nitrogen adsorption (Quantaorb), using a single point BET method. Results are means of duplicate samples. Whilst such single point determinations are not perfectly accurate, there use is acceptable here as the main function of the work is to demonstrate the possibilities of the calorimetric flow cell.

Contact angles were measured by use of the Wilhelmy plate approach (Cahn DCA) on rectangular compacts of powder of nominal dimensions 2 cm × 1 cm × 1 mm. Each compact contained a standard weight of powder and was prepared under a pressure of 4 × 10^5 kN m^-2 for 3 minutes, using a Specac press. Two test liquids of known surface energy (analytical grade, with purity checked by measurement of surface tension) were used in order to calculate surface energy terms for the powders. The surface energy (γ) and its polar and dispersion components (γ_p and γ_d respectively) were calculated for the lactose samples using Wu's harmonic mean approach (11).

RESULTS

Pump Calibration

The air pumping capability was found to give a reproducible flow rate as a function of pump speed. The peristaltic tubing was replaced if any deviation was noted in the humidity produced. The flow rate of 600 ml h^-1 was selected for routine use as it produced an air flow which readily resulted in 0% RH when using the dry line only. The humidity obtained at this flow rate for different combinations of the pump speed in the wet and dry pumps is shown in Figure 2, and was found to be linear over most of its range, however,

![Graph showing relationship between humidity (%) and dry speed (rpm)](image)

![Graph showing relationship between humidity (%) and wet speed (rpm)](image)

Fig. 2. The humidity produced in the flow cell by mixing air with total pump speed of 20 rpm (equivalent to 600 ml h^-1), from either the wet or dry lines.