The extent of errors associated with contact angles
II. Factors affecting data obtained using a Wilhelmy plate technique for powders

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Abstract

The reasons for error, and the magnitude of error that may be expected have been investigated for Wilhelmy plate contact angle measurements on compacted plates. A range of different materials have been considered, including a homologous series of powders (alkyl p-hydroxybenzoates), and α-lactose monohydrate (from three different suppliers). The effect of powder and plate storage conditions, the compaction force and dwell time used to prepare the plate, and the approach to defining the buoyancy slope of the Wilhelmy plate experiment have all been considered. The effect of compaction seems to be material dependent, some materials are unaffected by large changes in applied pressure, whilst others are particular sensitive to changes in the compaction process. Propyl p-hydroxybenzoate was especially sensitive to changes in compaction, such that even when trying to produce identical compacts, variability was noted for different days of plate preparation. Variability in measured contact angle was not associated with humidity equilibration, or time after the plate was made for the materials studied. The major cause of variability in the contact angle seemed to be the plate roughness. There is some concern that the plate roughness will not only affect the result by normal hysteresis effects, but also because the measured perimeter (external dimensions) will underestimate the true perimeter of a rough plate. Having noted many causes for concern with this technique, it was observed that standard deviations for the contact angles were smaller than for other contact angle techniques for powdered samples, however, accuracy and precision should not be confused.

Key words: Contact angle; Wilhelmy plate; Error; Compaction; Fractals

1. Introduction

Contact angle measurement on flat, smooth, homogeneous surfaces is simple and the reproducibility of the data obtained is extremely good.

Powder surfaces are not smooth and therefore contact angle measurement is more difficult. Despite this, contact angle measurement is still the most cited method for assessing the surface properties of pharmaceutical powders (e.g., Lerk et al., 1976; Zografi and Tam, 1976;Buckton and Newton, 1986; Parsons et al., 1992a).

Contact angle data for powdered systems allow

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an approach by which it is possible to estimate surface energy terms for materials, and thus predict interactions between different phases. Rowe (1989) has investigated the possibility that surface energy terms, derived from contact angle measurements on powdered systems, may be used to allow predictions concerning the most appropriate selection of a wet granulation binder for that material. Furthermore, Rowe (1990) has shown that the predictions of binder/powder interaction allow some correlation with the properties of the tabletted material. Parsons et al. (1992a) have considered how surface energy data can allow predictions concerning the performance of model inhalation aerosol systems. If contact angle data are to be used to make predictions about the interactions between drug powders and other formulation components, it is important that the reliability of the contact angle technique is understood. It has been noted that different contact angle methods for powdered systems will give a range of values for the contact angle (Buckton, 1993), but that it still may be appropriate to use any one of the techniques, provided that the data are only compared with other data which can be regarded as comparable. Consequently, it remains important to understand the critical features of each technique, and to have an understanding of the magnitude and the possible sources of errors. Parsons et al. (1992b) have considered the extent of errors associated with contact angles measured by liquid penetration

experiments, but the extent of errors for other contact angle approaches is less well documented. It is the aim of this study to explore the sources and the magnitude of errors for the Wilhelmy plate approach to the assessment of a contact angle between a powder and a liquid. The Wilhelmy plate approach has now been used on a few occasions for pharmaceutical powders, but its suitability has not been critically assessed.

2. Methods

2.1. Surface tension measurement of the probe liquids

The surface tensions of the liquids employed were measured and compared with literature values to ensure the purity of the liquids (Table 1). The surface tension was measured using the Wilhelmy plate technique, employing the Cahn Dynamic Contact Angle (DCA) analyser. The liquids used were purified water (reverse osmosis), ethylene glycol, propylene glycol, formamide, and diiodomethane, which were all selected due to their comparatively high surface tensions (i.e., low tendency to give zero contact angles on surfaces).

2.2. Contact angle measurement

Contact angles were measured for a homologous series of alkyl *p*-hydroxybenzoates (Apin). These included 4-hydroxybenzoic acid (Sigma) and the methyl, ethyl, propyl, butyl, benzyl, hexyl and heptyl derivatives. Angles were also measured on three different source batches of α-lactose monohydrate (from DMV, Meggle and Lactochem).

Contact angles were measured using the Wilhelmy plate technique (Cahn DCA). A schematic diagram of the apparatus is shown in Fig. 1. The apparatus is encased within a draught-free cabinet. Both the microbalance and the motorised platform were interfaced with a personal computer. The motorised platform could be raised at a constant pre-set speed, which for this work was set at 100 μm s^{-1}. Temperature was controlled at

Table 1
Surface tension values for all liquids employed

Liquid	γ_s (mN m^{-1}) [a]	γ_s^p (mN m^{-1})	γ_s^d (mN m^{-1})
Water [b]	72.0 70.0 ± 0.3	48.8	23.2
Ethylene glycol [b]	48.9 (48.8 ± 0.4)	15.5	33.4
Propylene glycol [b]	38.0 (37.5 ± 0.6)	9.4	28.6
Glycerol [c]	60.2 (59.2 ± 0.7)	29.2	31.0
Formamide [d]	58.0 (58.1 ± 0.3)	19.0	39.0
Diiodomethane [b]	50.4 (50.6 ± 1.0)	0	50.4
Bromonaphthalene [d]	44.0 (43.2 ± 0.7)	0	44.0

[a] Values in parentheses refer to data measured as described in section 2, to validate liquid purity.
[b] Zografi and Tam (1976).
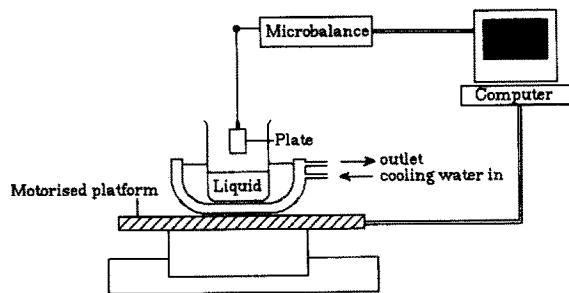[c] Parsons et al. (1992b).
[d] Van Oss et al. (1992).

Fig. 1. Schematic diagram of the Wilhelmy plate apparatus.

25 ± 0.5°C, by flowing water at constant temperature from a circulator (Gallenkamp) through a jacketed vessel. The powder plate was placed via a balance loop onto the arm of the microbalance. The test liquid was raised to make contact with the plate, and to continue to insert the plate into the liquid. Force readings were collected at 1 s intervals as a function of time and stage position. The force at zero depth of immersion (i.e., first contact between the plate and the liquid), F_{zdoi}, was then determined and the advancing angle was obtained using Eq. 1:

$$F_{zdoi} = p\gamma_{LV} \cos \theta / g \qquad (1)$$

where p is the plate perimeter, γ_{LV} denotes the liquid surface tension, θ is the contact angle and g represents the acceleration due to gravity.

Receding data were obtained by gradually removing the same plate from the liquid, by lowering the platform at the same speed as for the advancing experiment.

The operational reproducibility of the DCA instrument was checked each day using a glass plate for the surface tension measurement of water, and a teflon plate as a standard for contact angle measurement. Reproducibility was extremely good, and demonstrated that any variability detected in prepared powder compacts was due to the sample surface having changed, rather than being due to instrument error.

Compressed powder plates were produced using a highly polished rectangular punch and die assembly, which could be dismantled after com-

pression, to allow easy removal of the compact. The plates were prepared from 250 mg of powder which was spread evenly in the die, to attempt to minimise any variations in porosity in the compact. Plates were compressed using a Specac press which can apply forces up to 15×10^{-3} kN. The plates produced were all 1.07×2.00 cm and therefore the maximum pressure was 7.5×10^{5} kN m^{-2}. The compaction pressure and dwell time employed for each powder group were initially selected in order to optimise ease of production of the plates. A compaction pressure of 6×10^{5} kN m^{-2} was used for the hydroxybenzoates, and 1.5×10^{5} kN m^{-2} for the lactose samples, a 3 min dwell time being used in each case. The perimeter of the plate (p) was measured using a micrometer.

Prepared plates were stored for 2 days in a desiccator at 59% RH, 19°C prior to contact angle measurement. This equilibration was undertaken to minimise variation in storage conditions, which might affect the surface properties of the powder plates and therefore the resulting contact angle measurement (e.g., by analogy to the work of Hollenbeck et al., 1978).

The humidity of the chamber of the DCA analyser was monitored using a hair hygrometer as it was suspected that large fluctuations in humidity could also affect contact angle measurement. The humidity fluctuated between 40 and 50% RH.

2.3. Investigation of the effect of compaction pressure and dwell time on contact angle measurement

Four powders were considered in this study, propyl p-hydroxybenzoate, hexyl p-hydroxybenzoate, and α-lactose monohydrate. These powders were selected as they cover a wide range of measured contact angles.

Plates were prepared as described above, only using the range of compaction pressures and dwell times shown in Table 2. Water and ethylene glycol were used as probe liquids for contact angle measurement, with the exception of α-lactose monohydrate; for this powder, diiodomethane was used instead of water, due to the high aqueous solubility of lactose.

Table 2
Range of compaction pressures and dwell times used

Compaction pressure $(kN\ m^{-2} \times 10^5)$	Dwell time (min)
1	3
2	3
3	3
4	3
5	3
6	3
4	1
4	6
4	10

2.4. Determination of the effect of powder plate age on contact angle measurement

Plates of propyl *p*-hydroxybenzoate were prepared from powder under ambient conditions, and the formed plates (compacted using 6×10^5 kN m²) were stored at 59% RH, 19°C, for 1, 2, 3, 4, 5, 6, 14 and 28 days prior to contact angle measurement.

2.5. Pre-storage of the powder plate prior to compaction

Plates were prepared from propyl *p*-hydroxybenzoate powder which had been stored in a desiccator at 59%, 19°C, for at least 1 week prior to plate preparation. The plates were then stored for 2 days in the same desiccator, prior to measurement. Plates were prepared on a number of different days to check reproducibility.

2.6. Electron microscopy

Electron micrographs (Phillips XL20) were obtained for an example of each of the propyl *p*-hydroxybenzoate plates used in the study of the effect of compaction force, and also for a portion of each propyl *p*-hydroxybenzoate plate prepared from powder which had been pre-stored at 59% RH, 19°C.

3. Results and discussion

3.1. Variability in the buoyancy slope

The buoyancy slope of the DCA response should be a smooth flat line, however, in reality, the first few millimetres of the response were normally rough, presumably reflecting a similar roughness in the edge regions of the compacts, or perhaps differences in density towards the ends of the compact. Consequently, the data were analysed twice, by defining two different portions of the buoyancy slope (as shown in Fig. 2a and b). Method (a) was to consider the straight portion of the buoyancy slope, i.e., ignoring the first 4 mm, and method (b) was to consider only the first 4 mm of the buoyancy slope.

3.2. The effect of compaction pressure and dwell time on contact angle measurement

The reasons for carrying out this part of the study were two-fold. Firstly, to determine if it is
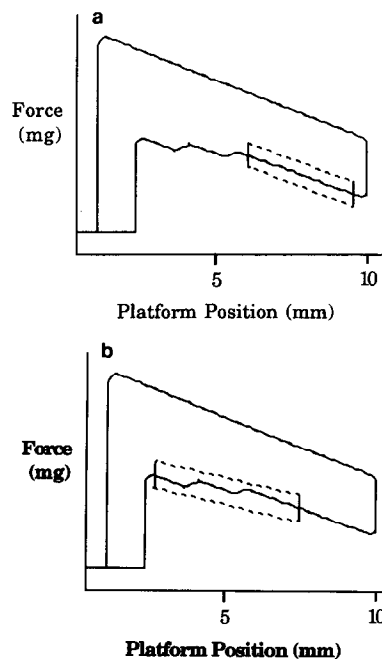

Fig. 2. (a) Portion of the buoyancy slope of the Wilhelmy plate trace used for method (a). (b) Portion of the buoyancy slope of the Wilhelmy plate trace used for method (b).

valid to compare contact angle measurements from powder plates which have been manufactured using different compaction pressures; and secondly, to establish whether compaction pressure significantly alters the surface free energy of tablets.

Previous work on the effect of compaction pressure on contact angle includes a study by Fell and Efentakis (1979), who reported that the effect of compaction pressure on contact angle measurement was unpredictable and depends on the material considered. Kiesvaara and Yliruusi (1991) recently undertook a similar study and also found that the effect of compaction force depended on the material under investigation. Buckton and Newton (1986) carried out a study, using five barbiturate powders. The contact angle measured on the barbiturates was found to decrease with increasing compaction pressure, until a threshold which they concluded corresponded to the minimum compaction pressure at which plastic deformation occurs. It was not possible to consider such a broad range of compaction pressures, as used by Buckton and Newton (1986), using the Wilhelmy plate method. This is because it is necessary to obtain a coherent plate for this technique as the compact must retain structural integrity when removed from the die; this is not required for the sessile drop method. Kiesvaara and Yliruusi (1991) calculated surface energies
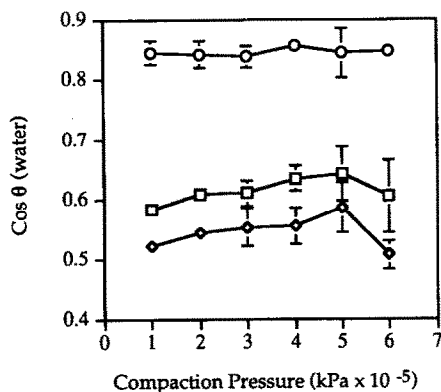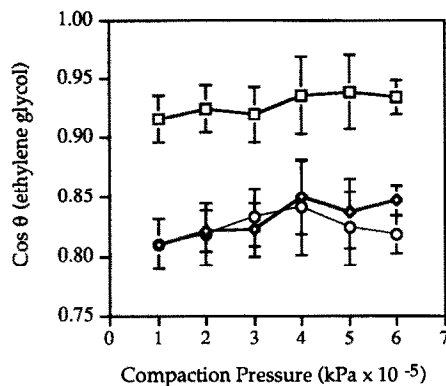

Fig. 4. cos θ as a function of pressure used to make the plate for angles measured on propyl p-hydroxybenzoates with ethylene glycol. ($\square$) Advancing, method (a); ($\diamond$) advancing, method (b); ($\bigcirc$) receding.

(geometric mean equation) from contact angle data obtained. Interestingly, they found that, although the surface energy was (for some materials) affected by compaction pressure, it was only the polar component that was affected. The dispersion component was not affected. This finding may relate to a re-alignment of molecules at the surface due to compaction.

Graphs showing the effect of compaction pressure on cos θ for water and ethylene glycol on propyl p-hydroxybenzoate are shown in Fig. 3 and 4, respectively. It is difficult to draw any definite conclusions due to the size of the standard deviations involved, particularly for data obtained using ethylene glycol. For example there is a significant difference between cos θ obtained, against water, using method (a) at 1×10^5 kN m^{-2} (0.584 ± 0.016) and at 4×10^5 kN m^{-2} (0.635 ± 0.021). However, there is not a significant difference between the cos θ value obtained at 1×10^5 kN m^{-2} and 5×10^5 kN m^{-2} (0.642 ± 0.045). However, the results obtained using water, for data analysed using methods (a) and (b), indicate that an increase in the compaction pressure results in an increase in cos θ (decrease in θ) up to a pressure of 5×10^5 kN m^{-2} (Fig. 3). This could be due to the decrease in surface roughness of the powder plates with increasing compaction pressure for this material. The surface of the powder plates prepared at increasing compaction

Fig. 3. cos θ as a function of pressure used to make the plate for angles measured for propyl p-hydroxybenzoate with water. ($\square$) Advancing, method (a); ($\diamond$) advancing, method (b); ($\bigcirc$) receding.

pressure were viewed using a scanning electron microscope (SEM). The resulting micrographs are shown in Fig. 5, and help explain the shape of Fig. 3. The micrographs show that the surface of the compacts become increasingly more smooth until a compaction force of 5×10^5 kN m^{-2}. Above this compaction pressure, there was an increase in the presence of particles at the surface of the plate. It was also noted that above this compaction pressure it became increasingly more difficult to dismantle the die. This may explain the increased presence of these particles at the surface of the powder plate and the large contact angle obtained for plates compressed at 6×10^5 kN m^{-2}. This phenomenon may also explain the unpredictable results obtained by previous workers (particularly since the range of compaction pressures used by workers is quite variable).

Compaction force and dwell time have little or no effect on the receding contact angle of propyl *p*-hydroxybenzoate (Fig. 3 and 4). Results obtained using ethylene glycol (see Fig. 4), analysed using method (a), show that the receding data ($\cos \theta$) are smaller than the advancing data. However, for results analysed using method (b), $\cos \theta$ (receding) is the same as the advancing data. Theoretically, it is impossible to accept that $\cos \theta$ is smaller for receding than advancing data and indicates that data analysed using method (a) give an anomalous result.

The standard deviations of $\cos \theta$ are larger for hexyl- than for propyl *p*-hydroxybenzoate. However, the results indicate that there is a relationship between $\cos \theta$ (against water) and dwell time (Fig. 6). There is no clear relationship between compaction pressure and $\cos \theta$. The receding angle is unaffected by compaction pressure or dwell time.

It was difficult to make any conclusions from the results for α-lactose monohydrate, because θ is very small and therefore the errors in measured angles are large. However, θ appears to be unaffected by compaction pressure (all surfaces giving contact angles of approx. $10 \pm 3°$ for ethylene glycol) and dwell time (not shown). This is consistent with the findings of Kiesvaara and Yliruusi (1991) who, using the sessile drop technique, also found that for α-lactose monohydrate θ was not sensitive to compaction pressure or dwell time during plate preparation.

The results indicate that the effect of compaction pressure on contact angle is material dependent. It has been suggested that surface roughness may be implicated for the propyl *p*-hydroxybenzoate samples. Alternative explanations to surface roughness effects include the nature of the material employed, in terms of its compressibility, i.e., the relative plasticity, elasticity or fragmentability of the powders, may also affect this relationship. For example, lactose is a fragmenting material and therefore the effect of increasing compaction pressure would be less likely to affect the surface properties of the compacts. However, the effect of increasing compaction pressure for materials which deform plastically may influence the surface properties of the compact more considerably (as proposed by Buckton and Newton (1986)).

An X-ray diffraction method which allows evaluation of the crystallite orientation at the surface of intact tablets has been reported (Fukuoka et al., 1987, 1991). At the surface of uncompacted powder, random orientation of crystallites was observed. Fukuoka et al. (1987) found, for salicylic acid, that during compaction, crystallites had a tendency to align in a particular orientation, preferentially at the surface of the tablet. The effect of compaction force was also investigated. Preferential crystallite orientation only occurred at low compaction forces. At higher compression forces, crystallite orientation was variable. Preferential orientation of crystallites may result in an increase or decrease in the contact angle, depending on the nature of the functional groups that are present at the surface of the tablet. If the crystallite orientation is such

Fig. 5. Scanning electron micrographs showing the effect of changes in compression on the surface of the formed plate. (a) Propyl *p*-hydroxybenzoate compressed at 1 kN m$^{-2} \times 10^5$; (b) propyl *p*-hydroxybenzoate compressed at 3 kN m$^{-2} \times 10^5$; (c) propyl *p*-hydroxybenzoate compressed at 5 kN m$^{-2} \times 10^5$; (d) propyl *p*-hydroxybenzoate compressed at 6 kN m$^{-2} \times 10^5$.
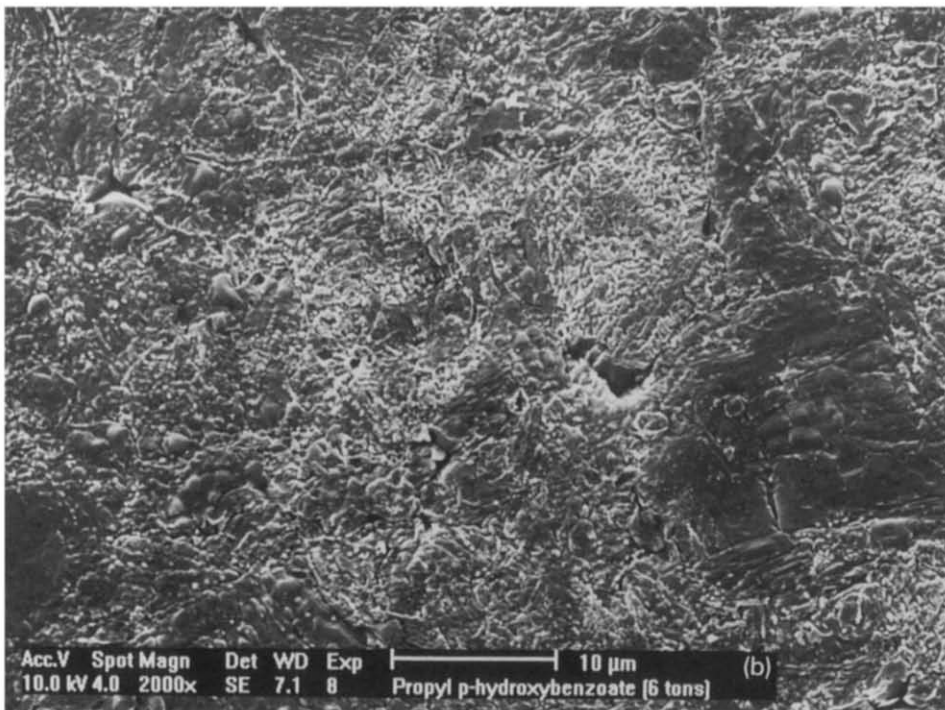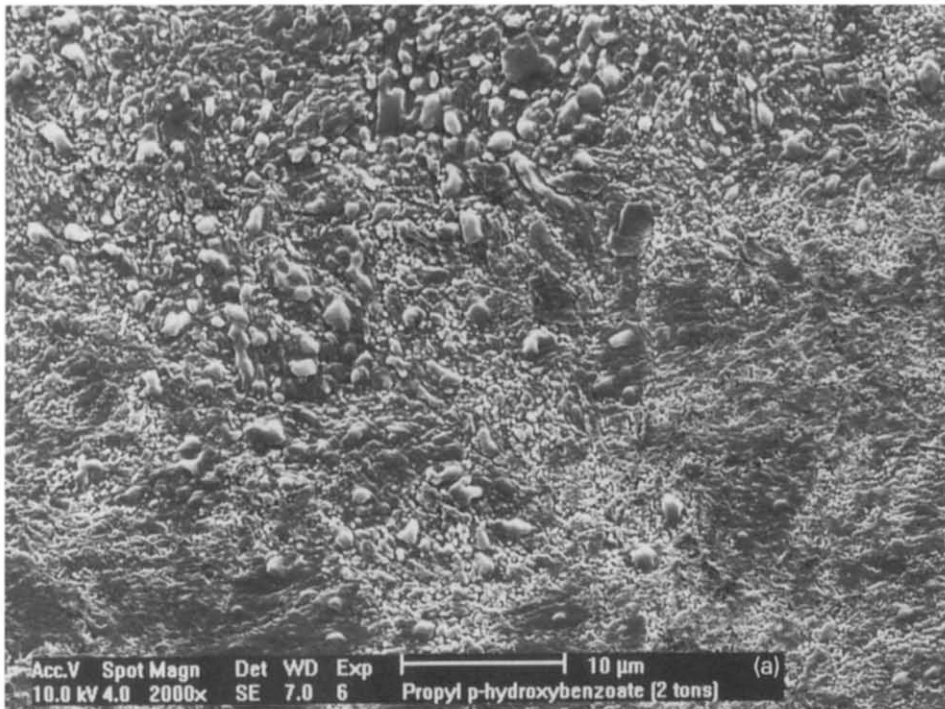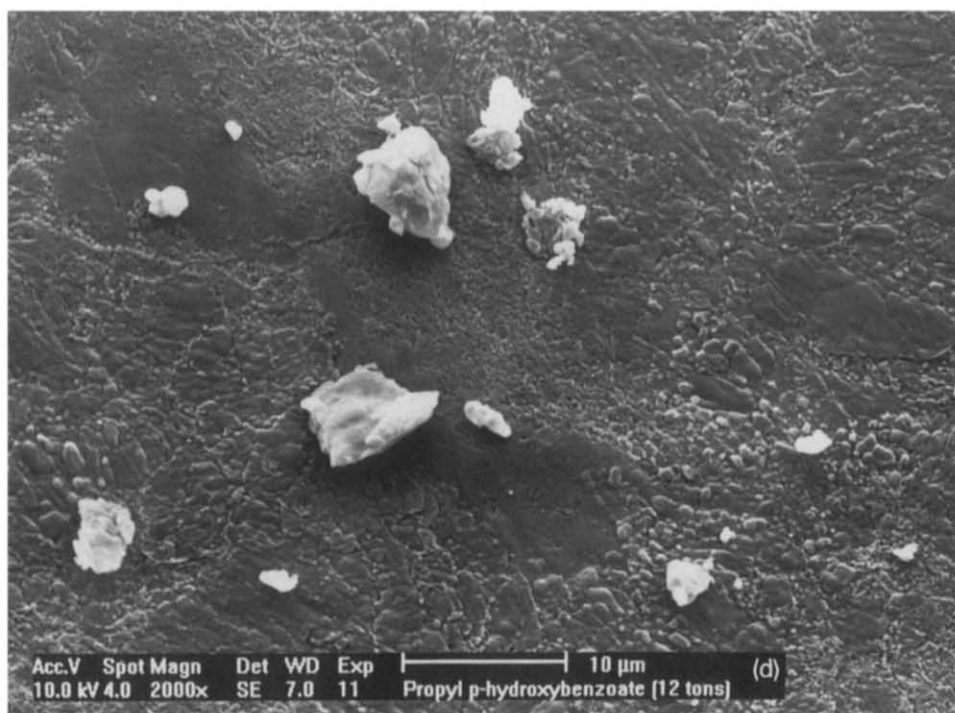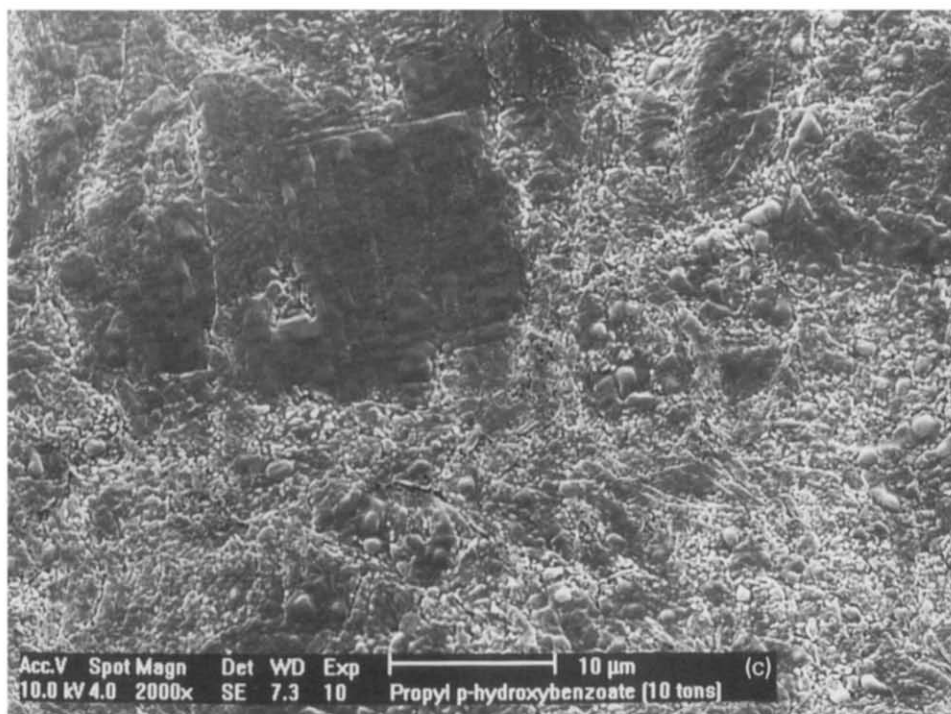
Fig. 5 (continued).

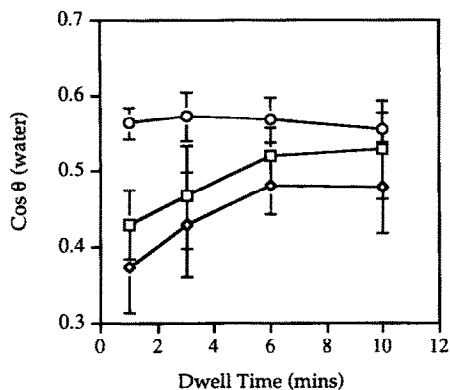Fig. 6. cos θ as a function of dwell time used to make the plate for angles measured on hexyl p-hydroxybenzoate with water. ($\square$) Advancing, method (a); ($\diamond$) advancing, method (b); ($\circ$) receding.

that there are several hydrophilic groups which are present at the surface, then this will result in a smaller contact angle. The presence of hydrophobic functional groups may result in a larger contact angle. It is also possible that orientation of molecules in regions of the surface which are amorphous will be significant, as the solid/liquid interfacial energy will be minimised due to the freedom of rotation of the molecules in the solid state. Such freedom of rotation would not exist if the solid surface were truly crystalline. It is probable that the effect of compaction on contact angle is due to the surface of certain materials becoming partially amorphous, and thus being able to align at the interface with the liquid.

3.3. The effect of powder plate storage on contact angle measurement

Propyl p-hydroxybenzoate was used as the model powder, as it was seen to show variations in contact angle as a function of compaction pressure. It was thought that such variability may recover as the compacted surface was allowed to age. Compacts were prepared at 6×10^5 kN m^{-2}, and stored at 59% RH, 19°C for varying periods post-compaction, prior to contact angle measurement. The data obtained are listed in Table 3.

The time of plate storage prior to contact angle measurement has no effect on θ. The re-sults, however, vary depending on the day the plates were produced. For example, θ values for plates prepared on day 1 (tested 1 and 3 days after preparation) are much smaller than those for plates prepared on day 5 (stored for 2 days). We are unable to explain why such differences should occur, as the plates were prepared and tested in the same way. This phenomenon does not occur with the majority of materials tested, but has been seen with other p-hydroxybenzoates. In reality, the extent of variation is comparatively small (compared with certain other methods of contact angle determination for powders), such that data obtained on different days can be pooled with confidence. That does not, however, remove the fact that the observation is indeed real, in that compacts made on any one day yield very reproducible values for contact angle, but if compacts are made on a different day, they will often be different from those made on the first day. An explanation for the variation in the value of contact angles from plates prepared on different days is that the surface of the compact is different depending upon the day on which it was prepared. To investigate this possibility, a study was undertaken using propyl p-hydroxybenzoate. Powder plates were prepared as before at 6×10^5 kN m^{-2}. Half of the plate was used for contact angle analysis and the surface of the remaining half was viewed under the SEM. Contact angle data are listed in Table 4 and the SEMs are shown in Fig. 7 (A–E). The contact angles determined for plates A and B were much greater than those for plates C–E, as well as being much

Table 3
Data obtained for propyl p-hydroxybenzoate for plates stored over different time intervals

No. of days stored	Day prepared	Day tested	cos θ vs water ($\pm$SD)
1	1	2	42.2±4.6
2	5	7	50.7±1.5
3	1	4	42.5±2.4
4	11	15	46.9±2.7
5	23	28	50.3±2.5
6	31	37	45.5±8.9
14	30	44	46.9±3.6
28	13	41	54.1±4.3

greater than the mean contact angle measure-
ment obtained previously (50.7 ± 1.5, Table 5).
The surfaces of plates A and B are rougher than
those of plates C–E. Thus, differences in the data
may be due to surface roughness. Whilst this
seems to clarify the reason for the differences in
measured contact angles, it does not explain why
plates prepared on different days are different in
nature. The experiments were controlled inas-
much as the powder was pre-stored at a defined
humidity, and then the compact was also stored
under the same conditions. The compaction pro-
cess was also controlled. The punch and die were
cleaned according to a standard procedure, and
regularly polished. There was no relationship be-
tween date of polishing and the measured contact
angle. We are unable to offer an explanation for
the changes in compaction behaviour, but reason-
ably can conclude that the contact angle mea-
surement is in this instance a good indicator of
variation in the nature of the compact.

3.4. General discussion on contact angle data

Data have been obtained for the alkyl p-hy-
droxybenzoates and three brands of α-lactose
monohydrate. Great care was taken to control
the conditions of plate manufacture for these
experiments. The conditions include the fact that
plates were prepared using an equal quantity of
powder and compressed in the same die at an
identical compression force, using the same dwell
time. Plates were stored at constant humidity and
temperature (59% RH, 19°C) for 2 days prior to
contact angle measurement. The DCA analyser
was checked for accuracy using a PTFE block on
a daily basis, and the temperature of the probe
liquid was maintained at 25°C. The only parame-
ter that could not be controlled was the humidity
of the testing chamber, however, this was moni-
tored using a hair hygrometer and, in general the
humidity did not alter significantly on a day to
day basis (40–50% RH). Several sets of data, for
propyl p-hydroxybenzoate, were obtained on dif-

Table 4
Contact angle data obtained for five individual powder com-
pacts of propyl p-hydroxybenzoate, for which half of the
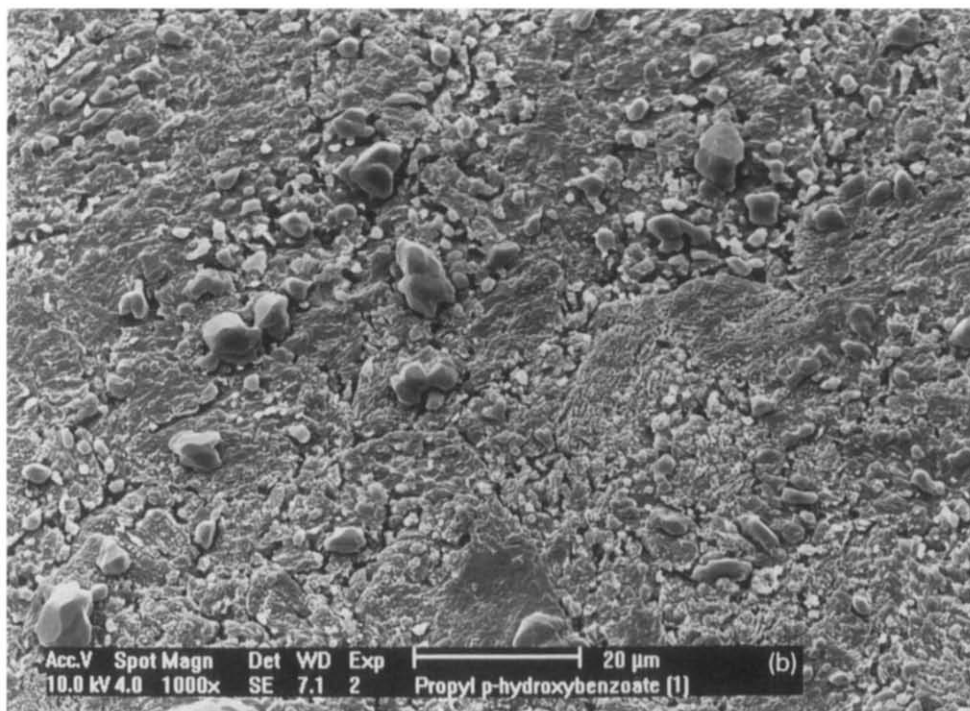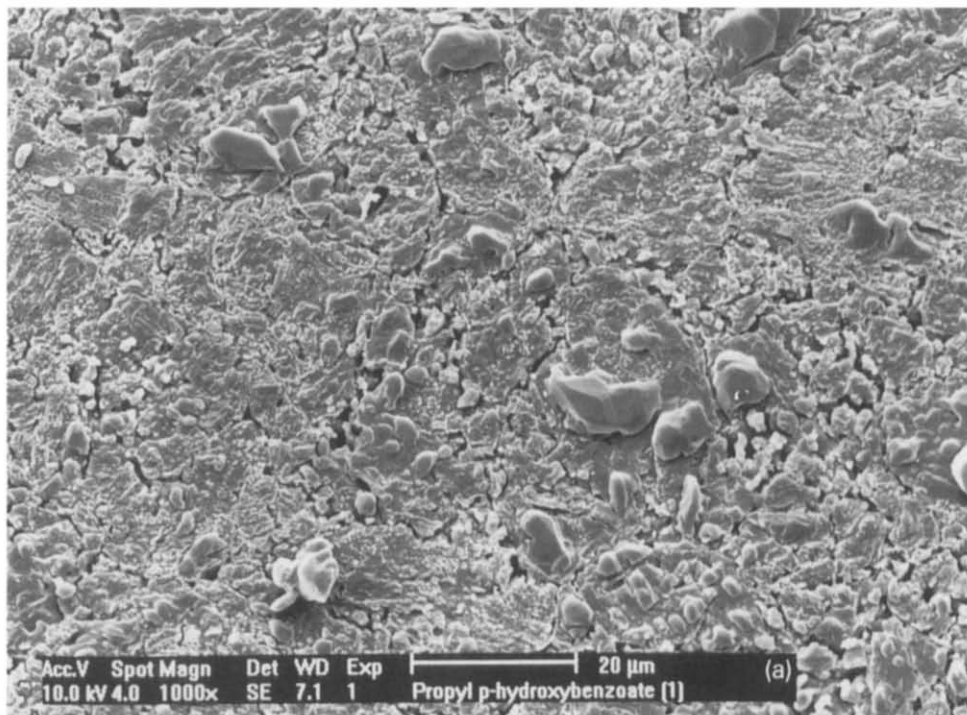compacts were studied using scanning electron micrographs
(see Fig. 7A–E)

Compact	θ_a (°)	θ_r (°)
A	71.5	41.8
B	66.3	35.3
C	41.3	33.7
D	47.1	34.5
E	53.9	33.9

NB: Plates were prepared on different days, and divided into
two halves. These represent examples of the range of contact
angles that had previously been measured.

ferent days. Where the humidity did vary, there
was no relationship between humidity and the
contact angle obtained.

3.5. Contact angle data obtained for the alkyl p-hydroxybenzoates

Advancing and receding data obtained for the
alkyl p-hydroxybenzoates are shown in Table 5.
Diiodomethane was found to spread ($\theta = 0$) over
the alkyl p-hydroxybenzoates. This theoretically
implies that the hydroxybenzoates have a high
surface energy (as zero contact angle is obtained
for such a high surface energy liquid). In reality,
however, such a high surface energy is unlikely
for such hydrophobic materials. The probability is
that the diiodomethane is penetrating into the
pores in the powder bed, and thus distorting the
apparent contact angle. The contact angle is cal-
culated using the perimeter of the plate as mea-
sured by micrometer. This is the external perime-
ter of the plate, but if the plate is porous, as all
compacts in this study will be, then the true
perimeter may increase in a manner related to
fractal geometry. Liquids of low viscosity will be
expected to penetrate more rapidly into pores,
and thus expose a larger fractal perimeter. Vis-
cous liquids may actually give more reliable data
as the rate of penetration into pores will be

Fig. 7. Scanning electron micrographs showing variation in the surface of compacts produced under identical conditions. Letters
A–E designate the micrographs taken of the other half of the compacts for which contact angle data are reported in Table 4.

Acc.V Spot Magn   Det WD Exp   20 µm   (c)
10.0 kV 4.0 1000x   SE   7.0 3   Propyl p-hydroxybenzoate (3)

Acc.V Spot Magn   Det WD Exp   20 µm   (d)
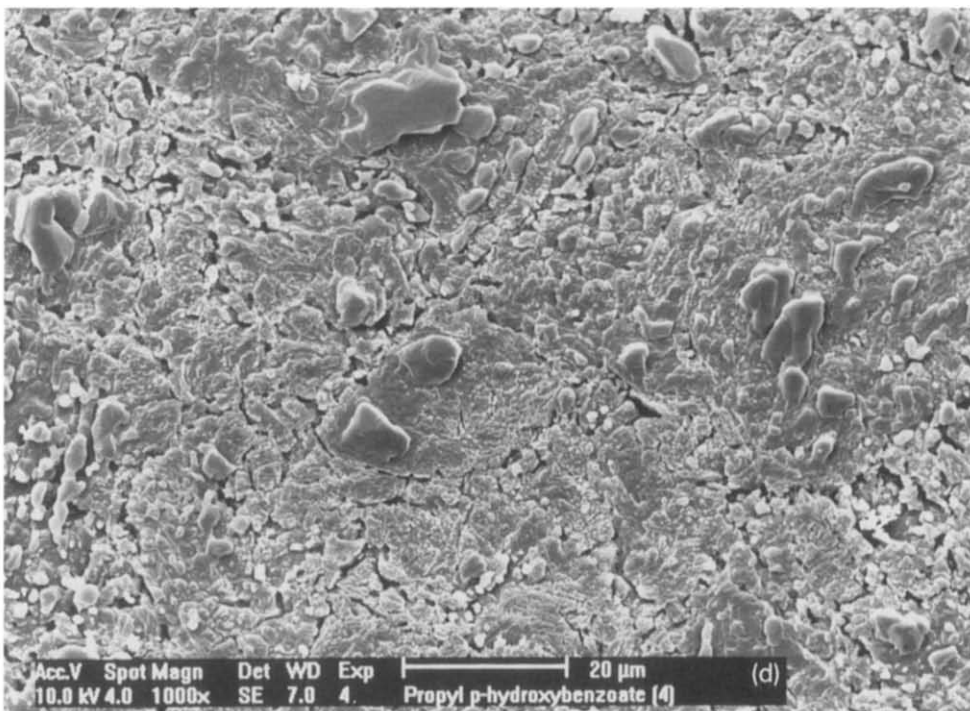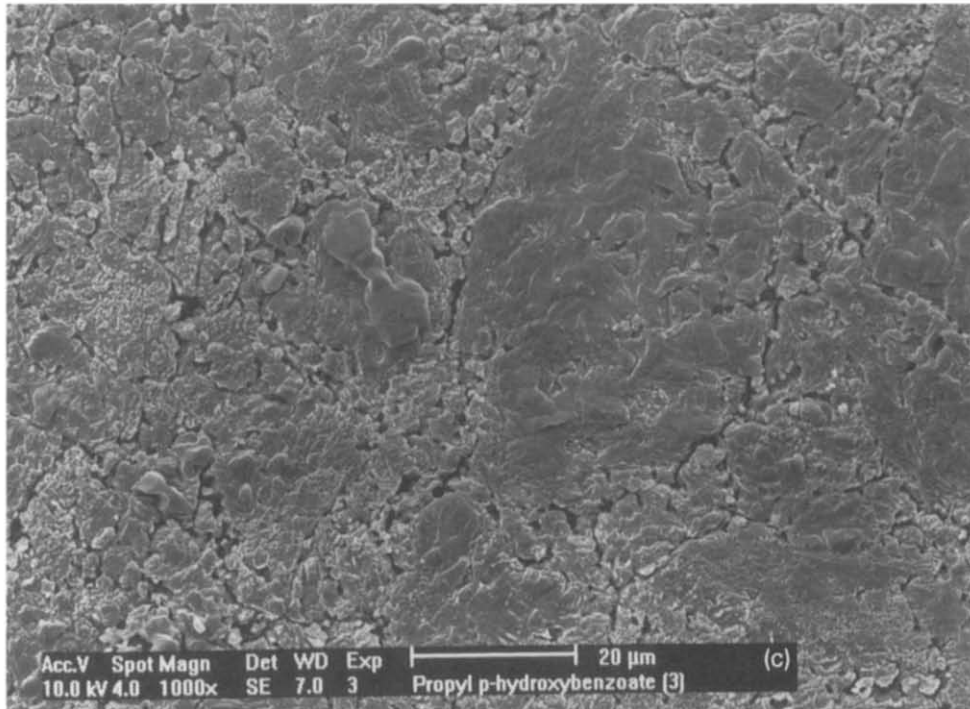10.0 kV 4.0 1000x   SE   7.0 4.   Propyl p-hydroxybenzoate (4)
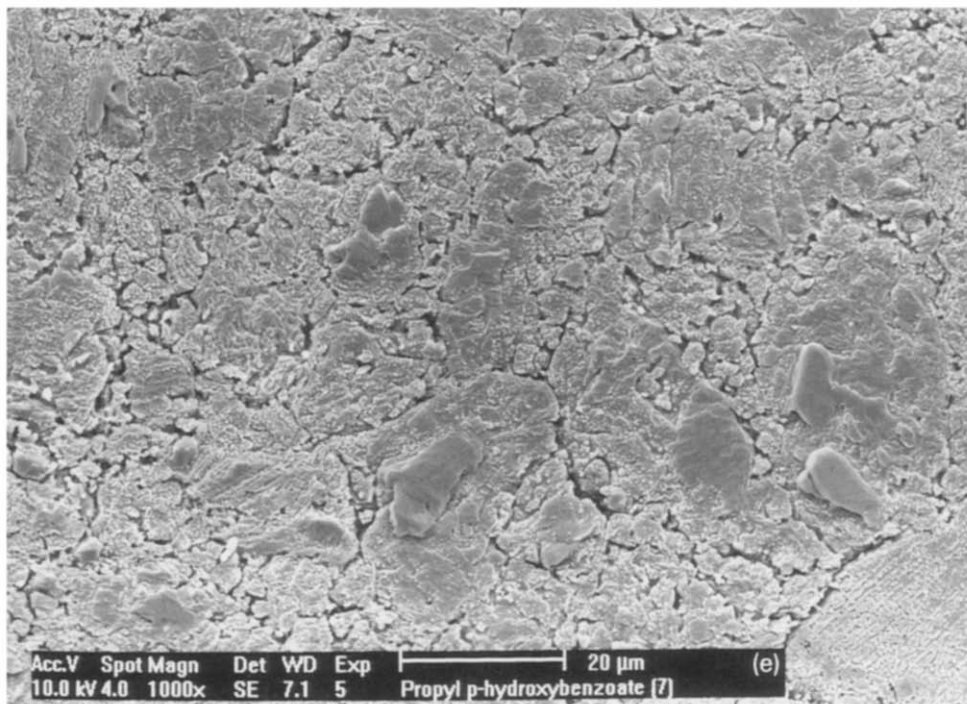
Fig. 7 (continued).

Fig. 7 (continued).

slower. An increase in true perimeter (due to fractal dimensions), over the measured perimeter, will give a contact angle which is artificially low. This is an error which is unique to the Wilhelmy plate approach for powdered systems. However, provided that liquids of similar viscosity are used, the contact angle data should allow comparisons between different powders.

3.6. Errors in θ and $\cos \theta$ values

If the data in Table 5 are considered in terms of θ, rather than $\cos \theta$, then in general the percent error in θ decreases as θ increases (although there are exceptions to the trend, due to the difficulty in producing smooth compacts of some of the higher members of the series). This

Table 5
Advancing data (method (a)) obtained for the alkyl p-hydroxybenzoates (contact angles in °)

Powder	θ (water)	$\cos \theta$ (water)	θ (EG/Form. [a])	$\cos \theta$ (EG/Form. [a])
4-HBA	46.0 ± 3.4	0.694 ± 0.042	16.0 ± 3.8 [a]	0.975 ± 0.009 [a]
Methyl	36.4 ± 4.3	0.804 ± 0.045	11.4 ± 2.2 [a]	0.971 ± 0.024 [a]
Ethyl	50.8 ± 1.4	0.623 ± 0.019	22.9 ± 2.3	0.921 ± 0.015
Propyl	50.7 ± 1.5	0.611 ± 0.021	20.0 ± 5.9	0.936 ± 0.033
Butyl	50.0 ± 3.2	0.642 ± 0.043	27.5 ± 2.6	0.886 ± 0.021
Benzyl	53.9 ± 1.4	0.589 ± 0.019	9.6 ± 4.1	0.984 ± 0.013
Hexyl	59.6 ± 3.2	0.506 ± 0.048	40.5 ± 1.7	0.760 ± 0.019
Heptyl	69.1 ± 0.3	0.357 ± 0.005	37.3 ± 3.6	0.791 ± 0.047

4-HBA, 4-hydroxybenzoic acid; EG, angle with ethylene glycol.
[a] Angle with formamide (Form.); ethylene glycol gave zero contact angle.

has been reported previously (e.g., Parsons et al. (1992a)) and is due to the shape of the cosine curve. As θ increases (to 90°) and cos θ tends to 1, so the gradient of the cosine curve decreases. Therefore, a given change in cos θ may result in a different change in θ, thus errors in θ indicate the magnitude of the angle as much as the experimental error.

The variability of the data reported here is lower than that obtained by Forster et al. (1991) who measured the contact angle of the alkyl *p*-hydroxybenzoates using the Wilhelmy plate method. Forster et al. (1991) employed a non-automated system and standard deviations for contact angle measurements for methyl, ethyl, propyl, butyl, amyl, hexyl and heptyl *p*-hydroxybenzoates were 7.9, 5.1, 5.8, 4.4, 4.7, 3.3, and 5.3, respectively. The improvement noted in the current data has occurred because the F_{zdoi} was determined by extrapolation of the buoyancy slope (undertaking least-squares analysis) rather than drawing the best straight line through the buoyancy slope, by hand. This automated method of analysing the data is less operator dependent and more accurate, therefore, the results obtained are more reliable.

The data are also more consistent than results obtained by Buckton and Newton (1986) using the sessile drop method. This is due to the difficulty of contact angle measurement, when using the sessile drop technique. Variability of the ses-
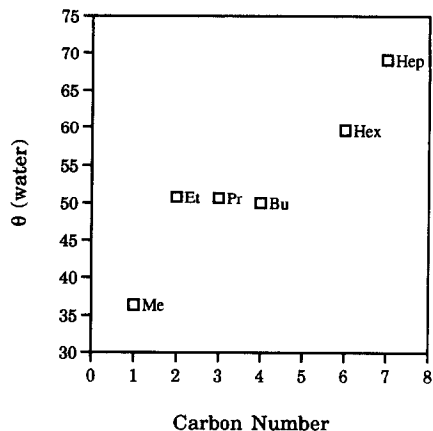

Fig. 8. The relationship between contact angle (water) and number of carbons in the alkyl chain of the alkyl *p*-hydroxybenzoates.

sile drop technique is outside of the scope of this study, but has been discussed by Buckton (1993).

Despite the improved reproducibility of the data, the results do not enable conclusions to be drawn about the difference in the wetting properties of some of these powders (see Table 5). For example, there is clearly a difference in the wetting properties of methyl *p*-hydroxybenzoate and hexyl *p*-hydroxybenzoate and between methyl *p*-hydroxybenzoate and ethyl *p*-hydroxybenzoate. However, we are not able to determine if there is a significant difference between ethyl, propyl, butyl and benzyl *p*-hydroxybenzoates. As these

Table 6
Advancing data (method (b)) obtained for the alkyl *p*-hydroxybenzoates (contact angles in °)

Powder	θ (water)	cos θ (water)	θ (EG/Form. [a])	cos θ (EG/Form. [a])
4-HBA	50.3 ± 3.1	0.639 ± 0.044	23.5 ± 2.1 [a]	0.933 ± 0.012 [a]
Methyl	39.0 ± 4.0	0.775 ± 0.044	17.1 ± 3.8 [a]	0.963 ± 0.015 [a]
Ethyl	56.0 ± 2.13	0.559 ± 0.0313	35.5 ± 3.33	0.815 ± 0.032
Propyl	56.3 ± 2.3	0.554 ± 0.032	45.6 ± 3.0	0.835 ± 0.028
Butyl	55.0 ± 2.9	0.572 ± 0.042	45.6 ± 2.4	0.700 ± 0.029
Benzyl	58.7 ± 2.8	0.519 ± 0.041	26.7 ± 2.1	0.893 ± 80.017
Hexyl	64.4 ± 4.4	0.432 ± 0.069	50.1 ± 1.4	0.642 ± 0.018
Heptyl	70.7 ± 3.1	0.320 ± 0.050	46.5 ± 2.8	0.687 ± 0.036

4-HBA, 4-hydroxybenzoic acid; EG, angle with ethylene glycol.
[a] Angle with formamide (Form.); ethylene glycol gave zero contact angle.

Table 7
Advancing data (method (b)) for α-lactose monohydrate (contact angles in °)

Lactose	θ (EG)	cos θ (EG)	θ (DIM)	cos θ (DIM)
Meggle	9.3 ± 3.0	0.986 ± 0.009	21.1 ± 6.7	0.929 ± 0.042
D.M.V.	12.5 ± 2.8	0.975 ± 0.009	14.9 ± 6.0	0.962 ± 0.026
Lactochem	9.3 ± 1.7	0.987 ± 0.005	10.9 ± 2.6	0.981 ± 0.010

four compounds have an increasing number of hydrophobic methylene groups on their side chain, theoretically it would be expected that θ would increase throughout the series. The relationship between θ (advancing and receding) against water as a function of carbon number is shown in Fig. 8.

Theoretically, methyl p-hydroxybenzoate should have a greater contact angle than 4-hydroxybenzoic acid, due to the extra hydrophobic, methylene group in its side chain. However, methyl p-hydroxybenzoate has a significantly lower contact angle than 4-hydroxybenzoic acid, ethyl, propyl and butyl p-hydroxybenzoates. This idiosyncratic behaviour of the methyl derivative must be a function of a different packing arrangement for that molecule in the crystal, making it significantly different from both the parent molecule, and the rest of the homologous series.

For α-lactose monohydrate contact angles were measured using ethylene glycol (EG) and diiodomethane (DIM). Results for α-lactose monohydrate analysed using method (a) gave a cos θ of 1. Therefore, data for this method of analysis are not shown (Table 7). It can be seen (Table 7) that the values obtained for the contact angles with both ethylene glycol and diiodomethane were identical within experimental error for each of the three lactose samples.

3.7. Comparison of methods (a) and (b) for determination of the contact angle

It is surprising that the standard deviation's obtained for both methods of analysis (a and b) are very similar (e.g., Tables 5 and 6). The first 4 mm of the buoyancy slope (used for method (b)) is invariably quite jagged and the portion of the buoyancy slope selected when using method (a) is generally very straight. The error in the data was, therefore, expected to be greater for method (b).

Use of method (b) to analyse contact angle data would, therefore, appear to be valid, when comparing the surface properties of powders. This is useful for the consideration of pharmaceutical powders which have a relatively high surface energy, such as lactose, providing the same method of analysis is employed for each powder.

It should also be noted that data analysed by method (a) frequently give a $\theta_a < \theta_r$, particularly for data obtained using ethylene glycol (e.g., see Tables 7 and 8), which is theoretically invalid. No work has been published concerning the correct portion of the buoyancy slope to use to determine F_{zdoi}. This is because there should not be non-lin-

Table 8
Receding contact angle data for α-lactose monohydrate

Lactose	θ (EG)	cos θ (EG)	θ (DIM)	cos θ (DIM)
Meggle	18.5 ± 4.1	0.946 ± 0.022	23.5	0.917
D.M.V.	22.6 ± 4.3	0.922 ± 0.028	32.2 ± 8.0	0.839 ± 0.074
Lactochem	19.3 ± 6.7	0.939 ± 0.034	31.7 ± 10.6	0.838 ± 0.082

EG, angle with ethylene glycol; DIM, angle with diiodomethane.

ear portions of the buoyancy slope. We have assumed that the straight portion of the buoyancy slope should be used. However, based on the data obtained here, method (b) would appear to be the most appropriate method of analysis.

4. Conclusions

The reproducibility of contact angle data obtained, for these pharmaceutical powders, is much greater than that of published data, due to the use of the automated Wilhelmy plate method. Reproducibility does not necessarily imply that the recorded value is a better reflection of the true contact angle than is obtained by other methods (there is a difference between precision and accuracy).

The effect of compaction pressure has varying effects on contact angle measurement depending on the material used. This is probably due to one of several reasons, however, surface roughness seems to be the most likely cause. For some materials, the contact angle was found to show variability depending upon the day when the compact was prepared. Despite attempts to control this variability, including control of pre-storage and post-storage conditions, the compaction process, and the conditions of the experiment, the variability remained for certain powders. It appears that the variability is a consequence of differences in plate roughness which occurred on different days for certain materials. It is probable that the variability in plate properties is an inherent compaction property of these specific powders, which will probably only occur infrequently (and which has not been observed with the majority of powders investigated).

The quality of the data cannot be improved by extensively controlling the method of contact angle measurement. This is probably due to the heterogeneous nature of powders and the 'rough' surface of the powder plates employed. It should be emphasised that this is not the case for idealised smooth surfaces.

The observations on different regions of the buoyancy slope mean that it is vital that workers state exactly how they obtained a contact angle value from a Wilhelmy plate experiment.

Despite the foregoing, contact angle measurement remains the most frequently cited method for measuring the surface energy of powders. Provided one is aware of the potential sources of error in measurement, the data obtained can still provide important information for use in formulation design.

Acknowledgement

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