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CONTACT ANGLE DETERMINATIONS ON PHARMACEUTICAL POWDERS: A COMPARISON OF TWO METHODS

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SUMMARY

Contact angle determinations have been carried out on pharmaceutical powders by two methods, the h–e technique (Kossen and Heertjes, 1965) and the direct measurement of the angle formed by a drop of liquid on the compacted powder. Despite the assumptions and variables involved, a reasonable degree of agreement between the two techniques is possible.

INTRODUCTION

Contact angle measurements on pharmaceutical solids give useful information on wettability. Most pharmaceutical solids occur as powders, and it is generally recognized that contact angle determinations on such systems must be made indirectly. Several methods are available (Washburn, 1921, Bartell and Osterhof, 1927, Kossen and Heertjes, 1965), and the technique of Kossen and Heertjes has been successfully adopted to study pharmaceutical powders (Lerk et al., 1976). Measurements have also been made by compressing the powder into a compact, and measuring the angle of a drop of liquid formed directly on the compact, a technique analogous to the methods used for determining contact angles on smooth surfaces. (Harder et al., 1970; Zografi and Tam, 1976; Nadkarni et al., 1975). The success of this method must depend on whether a smooth surface is formed by the act of compressing the powder. As the roughness and heterogeneous nature (e.g. pores) of a surface are known to affect the contact angle (Johnson and Dettre, 1969), it may be expected that factors such as compression pressure and particle size of the powder may influence the final result. This paper reports an investigation into a direct method of measuring contact angles on compressed powder surfaces, and compares the results with those obtained by the Kossen and Heertjes method.

MATERIALS AND METHODS

Materials

The solids used were acetylsalicylic acid B.P. (Monsanto), salicylic acid (Analar

B.D.H.), paracetamol and phenacetin (both reagent grade B.D.H.), phenylbutazone (Geigy), amylobarbitone B.P. (May and Baker), hexobarbitone (Ph. Ned. Brocacef, The Netherlands) and magnesium stearate (B.D.H.). They were either used as received or sieved (Alpine air jet sieve) to obtain size fractions it required. Teflon block (Plastics Ltd., Manchester, England), was prepared to give a smooth surface. Glass distilled water or the appropriate saturated solution was used as the test liquid.

Methods

Contact angles by the Kossen and Heertjes method were measured as described by Lerk et al. (1976) and Fell and Efentakis (1978). The pressure used to form the compacts was between 10 and 20 mN/m^2. Contact angles by direct measurement were obtained by projecting the magnified image of a liquid drop formed on the surface of the compacted powder, onto a screen. The contact angle was measured by tracing around the image of the drop, and using a protractor. Suitable magnification was obtained by placing the compact between the condenser and the X10 objective of a conventional microscope. The complete system of lamp, microscope and screen being mounted on an optical bench. Drops of suitable volume (0.004 ml) were carefully formed on the surface of the compact using an Agla syringe fitted with a fine needle. The needle was allowed to remain in the drop. Compacts were prepared by compressing an appropriate weight of powder in a 1.905 cm diameter flat faced punch and die system using a hydraulic press. The results are the means of at least 6 separate determinations.

RESULTS AND DISCUSSION

Initial experiments concerned with the direct measurement method, were carried out using water and polytetra fluoroethylene with a smooth surface to assess the reproducibility of the system and to compare the results with those of previous workers. The results

TABLE 1

CONTACT ANGLES OBTAINED BY DIRECT MEASUREMENT

Sat. = saturated solution

Compaction pressure mN/m^2	Material									
	Salicylic acid				Aspirin				Phenacetin Unfractionated	
	Unfractionated		45–63 μm		Unfractionated		45–63 μm			
	Water.	Sat.	Water.	Sat	Water.	Sat.	Water.	Sat.	Water.	Sat.
36	56°	100°	68°	102°	Penetrates		Penetrates		Penetrates	Penetrates
72	59°	94°	63°	94°	52°	68°	38°	70°	66°	92°
143	55°	79°	52°	77°	52°	68°	37°	72°	64°	76°
286	50°	72°	52°	75°	50°	67°	46°	70°	74°	79°
572	51°	67°	51°	70°	51°	66°	47°	69°	73°	77°

varied no more than ±3° from the mean value, 110°. Comparison of this result with those of 108° found by Fox and Zisman (1950), and 112–114° by Barnett and Zisman (1959) is favourable.

The results for various compounds determined directly using different compaction pressures and both saturated solutions and water are given in Table 1.

Unless the compaction procedure produces a perfectly smooth homogenous surface, it would be expected from previous studies that the degree of heterogeneity of the surface would influence the measured value of the contact angle. The variables chosen for investigation, compaction pressure and particle size, should influence both the factors given above. In addition, if water is used rather than a saturated solution, then dissolution of the surface may occur which could also change porosity and roughness.

In general the results indicate that the influence of compaction pressure is unpredictable, in some cases, increasing the pressure decreases the angle, in other cases it increases it. Particle size has an effect in the case of acetylsalicylic acid, but little effect with salicylic acid, whereas in all cases, the results with the saturated solutions are higher than those obtained with water.

The influence of surface roughness on the contact angle may be interpreted in terms of the equation suggested by Wenzel (1936).

$$\mathrm{Cos}\,\hat{\theta} = \mathrm{r}\,\mathrm{Cos}\,\theta_0$$

$\hat{\theta}$ is the observed contact angle on a surface of intrinsic contact angle θ_0. $r = A/A^1$ where A^1 is tthe apparent area of a plane having the same macroscopic dimensions and A is the true area taking into account the peaks and troughs of the rough surface. This equation predicts, therefore, that for true contact angles above 90°, roughening the surface will increase the contact angle, whereas for contact angles below 90°, the angle will be lowered on a rough surface. For contact angles of exactly 90°, the angle will remain the same.

If the angles measured by the h–e method were assumed to be correct, then a rough surface of salicylic acid would be expected to give a higher angle (θ by h–e method = 103°) whereas for acetylsalicylic acid and phenacetin lower angles would be expected (θ by h–e method = 73° for aspirin, 78° for phenacetin). Increasingly rough surfaces would be expected with the lowering of the compaction pressure and the use of a coarser particle size. For salicylic acid, higher angles are measured for saturated solutions at lower compaction pressures, but the angles for the higher compaction pressure are blow 90° and would suggest the reverse should be the case. The same is true for the phenacetin. The aspirin angles are constant for all compaction pressures, except for the 45–63 μm size fraction measured against water where increasing the compaction pressure increases the angle which is in keeping with the above arguments. Similar results were found for phenacetin against water.

Surface roughness can act as capillaries and it is suggested that there is a critical roughness above which the liquid will spread spontaneously over the surface (Johnson and Dettre, 1969).

$$\mathrm{r} = 1/\mathrm{Cos}\theta_0$$

where r = critical roughness for spontaneous wicking.

This may be the reason for the higher angles observed with the saturated solutions. Pure water will cause dissolution of the surface which may create capillary channels in the surface sufficient to cause wicking and hence lowering of the contact angle. A surface tension effect is not implicated as all the compounds lower the surface tension of water, and this would tend to lower the contact angle rather than raise it. The explanation of dissolution leading to wicking giving rise to a lower contact angle for water as opposed to the saturated solutions, is to some extent borne out by an examination of the solubilities of the materials. The greatest differences between the two angles occur for acetylsalicylic acid and salicylic acid which have solubilities of 1 in 300 and 1 in 460 respectively whereas phenacetin, for which the difference is rather less, has a solubility of 1 in 1310.

The porosity of the surface is an extreme case of surface roughness. If the liquid cannot penetrate into the pores, or into the bottom of a deep valley, the surface is said to be composite. In terms of contact angles, transition from a non-composite to a composite surface causes an increase in the contact angle (Johnson and Dettre, 1969). This may explain the high readings obtained with salicylic acid and phenacetin at low compaction pressures where the surface would be expected to be rougher and more porous. The phenomenon may well be time dependent, however, especially with phenacetin where penetration of the surface should occur. Although the measured angle was stable for at least 3 min, penetration may be extremely slow, and after a suitable period of time, the angle may reduce.

Comparison of the angles obtained by this method with those obtained by the h–e method is interesting. If the angles obtained from the saturated solutions at the higher pressures are compared, as these are stable, then the results for acetylsalicylic acid and

TABLE 2

A COMPARISON OF THE CONTACT ANGLES FOR SEVERAL COMPOUNDS AGAINST THEIR SATURATED SOLUTIONS DETERMINED BY THE h–e METHOD AND DIRECT MEASUREMENT

Material	Contact angle (degrees)	
	h–e	direct.
Aspirin	73	69
Phenacetin	78	77
Salicyclic acid	103	73
Paracetamol	59	60 [a]
Magnesium stearate	121	112
Amylobarbitone	102	85
Hexobarbitone	88	81
Phenylbutazone	109	82

[a] Penetration of the liquid drop occurred at all compaction forces; the measurement was made by adding liquid in increments to the initial drop and taking the reading immediately after each addition.

phenacetin show a fairly close agreement, whereas the salicylic acid result measured directly is much lower (Table 2). Also included in this table are the results from some other materials. Agreement is closer in some cases than in others, but neglecting salicylic acid, the rank order for the two methods is almost the same, except that the results from the direct measurement method are compressed into a narrower band. The greatest difference between the two results is in the case of salicylic acid. One possible explanation is that the higher pressures used in the direct measurement technique causes a change in crystal morphology leading to a lower contact angle. However, when the h–e method was carried out at 143 mN/m^2 a result of 100° was obtained, which is in good agreement with the results obtained at lower pressures.

It is also interesting to note that the results obtained for acetylsalicylic acid, phenacetin and magnesium stearate against water are in fairly close agreement to those obtained by Zografi and Tam (1976).

Despite the assumptions and variables involved in the two methods of determining contact angles, a reasonable degree of agreement between the results can be obtained. Penetration of the test liquid occurred in one case during the direct measurements, and this may be considered a drawback, although good agreement between the results was found.

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