International Journal of Pharmaceutics, 44 (1988) 1–8
Elsevier

IJP 01501

Review Article

The assessment, and pharmaceutical importance, of the solid/liquid and the solid/vapour interface: a review with respect to powders

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(Received 6 November 1987)
(Accepted 15 December 1987)

Key words: Surface energy; Wettability; Contact angle; Adsorption; Calorimetry; Vacuum microbalance; Liquid penetration; Compressed disc; Hysteresis; Immersion; Thermodynamics

Summary

The interaction of pharmaceutical powders with liquids and vapours (particularly water) is extremely important in many areas of physical pharmaceutical science. The surface energy of a solid can be assessed by contact angle measurements, although these have practical and theoretical limitations. The techniques of liquid penetration and measurement of drops on compressed discs will be reviewed. Problems of contact angle hysteresis, surface heterogeneities and rugosities as well as the dynamic nature of contact angles all hinder measurement. The application of thermodynamic measurements to the assessment of these interactions is described, using a vacuum microbalance and a microcalorimetric technique. This approach is theoretically valid and practically acceptable. To date it has yielded results which help to indicate the mechanism by which adsorption to the surface takes place.

Introduction

An important property of solids is that their surfaces are heterogenous. Heterogeneities can be of many types, for example, the electrical charge carried per unit area will differ at various points over the solid surface. Surfaces open to atmospheric conditions have been shown to acquire a greasy deposit, and although this deposit may be only one molecule thick it will dramatically alter the properties of the surface. It is also to be expected that gases and vapours will be located at various sites by the process of adsorption. It therefore follows that different faces of a microcrystalline powder may have different and arbitrary compositions, and under normal conditions should be regarded as dirty and undefined.

Attempts to characterise solid surfaces, such as powders, have been undertaken using descriptions of the morphology of the particles and the energetics of their surfaces (Parfitt and Sing, 1976).

Surface energy

The term surface energy of a solid is seldom used in pharmaceutical research. When describing wettability, it is most common to use a contact angle, which is the angle formed (measured

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through the liquid) by a liquid on a solid surface, which is in equilibrium with the vapour of that liquid. The 3-phase interface is an equilibrium between 3 interfacial energies – liquid/vapour(γ_{LV}), solid/liquid (γ_{SL}), and solid/vapour (γ_{LV}) – which are related to the contact angle by Young's equation (Young, 1805):

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \tag{1}$$

The liquid/vapour interfacial energy is the liquid's surface tension, and likewise the solid/vapour interfacial energy is the analogous surface energy of the solid. It is the surface energy of the solid that is characteristic of its surface. However, γ_{SV} is often described in terms of a general energetic parameter for the surface, the critical surface energy (γ_c), which is not related to any one vapour interaction and is calculated thus:

$$\gamma_c - \pi_e = \gamma_{SV} \tag{2}$$

where π_e is the film spreading pressure.

For a variety of reasons the definition of a contact angle as a complex equilibrium of energies at a 3-phase interface is still regarded as controversial, as is the Young equation.

The pharmaceutical importance of surface energy

The major interest is in terms of wettability: notably dissolution of solid oral dosage forms (e.g. Finholt and Solvang, 1968), wet granulation (Jaiyeoba and Spring, 1980), suspension formation (Heistand, 1964) and film coating of tablets (e.g. Harder et al., 1970). This alone makes its study valuable, but work in our laboratories (unpublished) suggests that surface energy has a role in product stability as well.

Surface energy measurement

Particularly in the pharmaceutical terms, solid interfacial interactions have been assessed by contact angle measurements. For flat solid surfaces (e.g. polymer films) this is possible by direct measurements of a drop on the surface. There are problems in terms of hysteresis, surface roughness, measurement technique and dynamic effects.

Contact angle hysteresis results from the heterogenous nature of solids. Young's equation would predict only one possible value, but in reality many values can be obtained between the maximum advancing contact angle and the minimum receding contact angle; this range being termed the hysteresis (Johnson and Dettre, 1969). The advancing angle can be measured by adding liquid to a drop on a surface from a syringe; during this process the volume of the drop changes and the base of the drop remains constant until the limiting value of the contact angle is obtained, then the contact angle remains constant and the drop volume and dimensions change. Equally, the receding angle can be measured by removing the drop with the syringe. Near-perfect smooth surfaces have shown no hysteresis at all (Ward and Neumann, 1974), whilst other systems, e.g. mercury on steel (MacDougall and Ockrent, 1942), have shown hysteresis of up to 154°C. Pease (1945) noted that the advancing contact angle is determined by low-energy components of the surface and as such could be regarded as the equilibrium contact angle for the non-polar regions, where as the receding contact angle could be regarded as the equilibrium contact angle for the polar regions of the surface.

The effect of rough surfaces can be seen diagrammatically in Fig. 1. Theoretical models of rough surfaces have been proposed by many workers (e.g. Neumann and Good, 1972; Eick et al. 1975) and the existence of many metastable contact angles between a maximum (advancing) and a minimum (receding) angle have been explained; unlike the situation where heterogeneities cause the hysteresis, no specific relevance can be attached to the values measured, i.e. no one angle can be regarded as an equilibrium angle for any part of the surface. Neumann et al. (1971) showed the critical size of rugosities to be in the region of 0.1 μm, below this they will not alter the measured angle; however, the type of system used and the shape of the rugosity will affect this value.

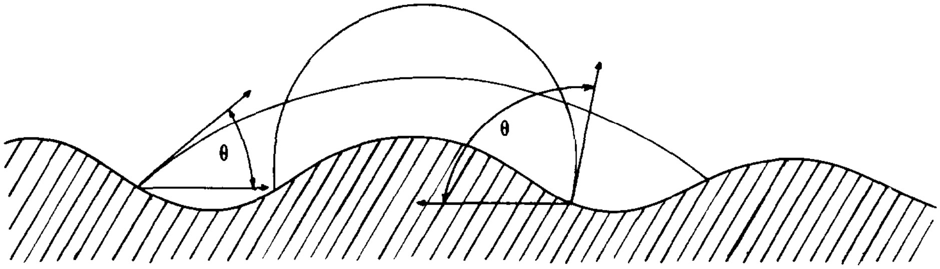

Fig. 1. The possible variation of contact angles due to rough surfaces.

Neumann and Good (1979) have reviewed measurement techniques for contact angle on smooth surfaces. Points that should be considered are drop size (contact angle may decrease with decreasing drop size), dynamic effects (contact angle will decrease rapidly with time after placing on surface, e.g. from 35° to 0° in 40 s for water on paracetamol; Stamm et al., 1984) and measurement technique. Measurement of the contact angle is open to operator error, a worthwhile method is to photograph the drop as soon as it contacts the solid and then construct the angle geometrically on the enlargement (Neumann and Good, 1979).

With powders there are problems as there is no continuous smooth surface on which to work; consequently, indirect techniques must be used. Two possibilities exist: firstly, preparation of compressed discs to obtain a smooth flat surface; and secondly, liquid penetration methods.

The powder compression method will result in either plastic deformation or fracture processes, these will alter the surface energy and thus defeat the object of the measurement (unless information is required on a tabletted product). This has been demonstrated by Buckton and Newton (1986a) who showed that as the compression force is increased the contact angle observed will decrease until a minimum value is obtained which is indicative of the surface energy of the deformed compacted surface. Preliminary data (Buckton and Newton, 1986b) showed that the surface energy of the flat face of a crystal was similar to that of the plastically deformed surface, and that it may be the crystal defects and edges that are responsible for the predominant hydrophobic nature of the powders studied.

If information is required on the surface energy of tabletted powders, then the use of compressed discs is of value and a number of established techniques are available to obtain the contact angle. Perhaps the easiest method is to saturate the bed with liquid and then place a small drop of liquid on the surface. The drop should be photographed immediately and then the angle should be measured by construction on the enlargement. Ideally, the drop should be added through a cabinet with optical glass sides, in which the vapour has been allowed to saturate. An alternative is to use an eye piece protractor mounted on the goniometer eye piece, the advantages being that results are instantly available (no need to wait for developing and printing) and it is cheaper. The disadvantages are that there is no permanent record of results to which further references can be made, and in cases where dynamic effects are marked, it will be difficult to measure the rapidly changing value. It is also possible to calculate to contact angle by measuring the maximum height of drop that can be formed on the compact surface, using the equations derived by Kossen and Heertjes (1965) and Heertjes and Kossen (1967), where for contact angles between 0° and 90°

$$\cos\theta = 1 - \sqrt{\frac{(Bh)^2}{3(1-z)\left(1-B(h)^2/2\right)}} \tag{3}$$

where h is the maximum height of the drop, z is the volume porosity and B is as in Eqn. 4, and ρ is the density of the liquid.

$$B = \frac{\rho \cdot g}{2\gamma_{LV}} \tag{4}$$

and for contact angles over 90°

$$\cos\theta = -1 + \sqrt{\frac{2}{3(1-z)}\cdot\left(\frac{2}{B\cdot h^2}-1\right)} \qquad (5)$$

Derivation of Eqns. 4 and 5 assumes the particles to be spherical, of equal size and homogeneously packed. The surface should be smooth. Derivations of these equations for rough surfaces have been suggested (Witvoet, 1971). Surprisingly, reproducible results with variation of less than 4° have been obtained for many pharmaceutical powders by this method (Lerk et al., 1976, 1977). The use of drop height and direct observation techniques have been compared (Fell and Efentakis, 1979); a reasonable degree of agreement was observed for powders with a range of contact angles between 59° and 121°. There is no similarity between contact angles measured on these tablets with their altered surface properties and those obtained by liquid penetration methods. In most instances the value obtained on a compressed disc is very much lower than that of the powder as measured by liquid penetration.

Liquid penetration experiments are undertaken on powders that are loosely packed into a tube and water (or other wetting liquid of choice) is passed through the bed. This can involve sucking the liquid up into the bed (e.g. Bartell and Osterhof, 1927) or passing liquid down through the column (e.g. adaptations of the Washburn (1921) method such as that of Studebaker and Snow, 1955). The advantage of passing liquid down through the bed is that even though the wetted bed will repack, liquid will still be presented to the dry bed, whereas when liquid is imbibed up into a bed repacking can result in breaking of the contact between the solid and the liquid.

The Washburn equation upon which these experiments are based:

$$\ell^2 = \frac{r\cdot\gamma_{LV}\cdot\cos\theta\cdot t}{2\eta} \qquad (5)$$

where ℓ is the distance of penetration after time t, of a liquid with viscosity η, and surface tension γ_{LV}, r being the capillary radius of the bed, assuming a model of a bundle of parallel capilaries), has been criticised, both in terms of the model used (Levine and Neale, 1979) and because the power to which ℓ should be raised will not always be two (Carli and Simioni, 1979).

Even if the Washburn equation is accepted, another problem exists; that is, with many pharmaceuticals an assessment of the interaction of water is required with a hydrophobic powder into which water will not penetrate. Many workers have, therefore, used alcohol/water mixtures and extrapolated to 0% alcohol to obtain a water value. This is not theoretically desirable because the binary mixture will tend to partition upon penetration, and by Raoult's Law the vapour which precedes the liquid will be preferentially rich in alcohol thus removing the basis for extrapolation to water. It would appear that the composition of the pre-wetting vapour is more important than the composition of the liquid mixture (Buckton and Newton, 1986c).

The possibility of measuring the contact angle, by liquid penetration, and using a Zisman plot (Fox and Zisman, 1950, 1952a and b), where the cosine of the contact angle is plotted as a function of the surface tension of the wetting liquid, and the resulting straight line is extrapolated to a value of surface tension where cosine of the contact angle equals one, has been explored. This critical surface tension value would be that of a liquid that would just spread on the surface of the solid and thus be equal to the surface energy of the solid. Such an extrapolation was not possible as the pure organic ligands do not produce a straight line, whilst alcohol/water binary systems produce different straight lines depending upon the choice of the alcohol (Buckton and Newton, 1986c). This demonstrates the lack of theoretical basis associated with this approach and should serve as a warning not to read too much into any results obtained by this method. However, liquid penetration results remain a good empirical indication of powder wettability (Buckton and Newton, 1985, 1986c).

A further problem that is encountered with standard contact angle measurements (direct or indirect) is that of adsorbed dirt, gas and vapour. At best the interaction becomes one of displacement from, and at worst direct interaction with, an undefined surface.

Alternative methods of assessing powder interfacial interactions

In many scientific fields it is usual to describe interfacial interactions in terms of thermodynamic parameters. Schröder (1984) demonstrated the thermodynamic relationships between adsorption and immersion, immersion and adhesion, immersion and contact angle/surface tension, and surface tension and immersion. However, the relationship between contact angle and the thermodynamic parameters relies on the Young equation, and it is acknowledged in the text (Schroder, 1984) that measurement of contact angles on powders is problematic. In defining the terms used above, adsorption should be taken to mean reversible physisorption, and its importance will be highlighted at a later stage; adhesion and immersion are best described by reference to one of the established models of the wetting process (Parfitt, 1973). By use of Young's Eqn. 1 and assuming a unit cube of solid (Fig. 2), adhesion creates a solid/liquid interface at the expense of a solid/vapour and a liquid/vapour interface, the work of adhesion (W_a) can be expressed as:

$$W_a = \gamma_{SL} - (\gamma_{SV} + \gamma_{LV}) = -\gamma_{LV}(\cos\theta + 1) \qquad (6)$$

Immersion involves the change of 4 solid/vapour interfaces to solid/liquid interfaces, with no change in liquid/vapour interfaces, thus the work of immersion (W_i) will be:

$$W_i = 4\gamma_{SL} - 4\gamma_{LV} = -4\gamma_{LV}\cos\theta \qquad (7)$$

To achieve spreading wetting, a solid/liquid is replaced by a liquid/vapour and a liquid/solid interface the work of spreading (W_s) becomes:

$$W_s = (\gamma_{SL} + \gamma_{LV}) - \gamma_{SV} = -\gamma_{LV}(\cos\theta - 1) \qquad (8)$$

For spontaneous wetting the system must need the addition of no work, that is for spreading cos $\theta + 1$ greater than 0, for immersion cos θ must be greater than 0 and for spreading cos $\theta - 1$ must be greater than 0. It follows that for all values of contact angle except 180°, adhesion will occur, for values below 90°, immersion will occur, but spreading is impossible without the aid of factors such as density.

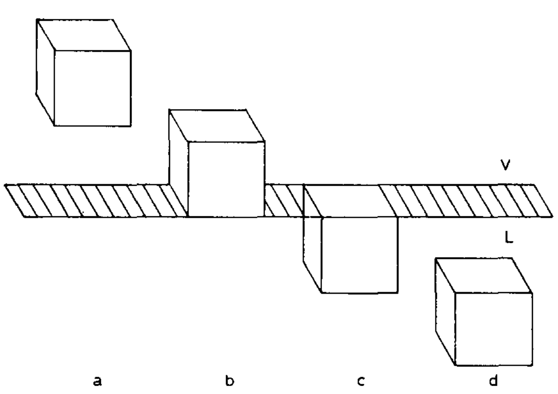

Fig. 2. The stages in the wetting process. a to b = adhesional wetting; b to c = immersional wetting; c to d = spreading wetting (After Parfitt 1973.)

As has been shown, the use of Eqns. 6–8 requires the measurement of a contact angle and use of Young's equation to obtain a free energy function. This is not acceptable for the reasons already noted and consequently alternative methods must be used. Use of a vacuum microbalance can give a measure of adsorption of vapour (weight increase per unit weight of powder) onto the uniformly vacuum-desorbed (and hence controlled) surface, and thus provide an equilibrium constant (K) for any chosen standard state. The Gibb's function is then available ($= -RT \cdot \ln K$ where R = gas constant, T = absolute temperature).

The enthalphy of adsorption can be obtained directly from microcalorimetry, by use of electrical calibration, where a parallel experiment of vapour adsorption onto a vacuum-cleaned surface is performed (correction for blanks is undertaken) (Buckton and Beezer, 1987). Following from this the entropy term is also available. As well as obtaining the thermodynamic parameters the kinetics of the process can be observed, this potentially provides information on mechanism of interaction. It is equally possible to use the vacuum microbalance to obtain the enthalpy of adsorption; this is achieved by measuring vapour uptake at a number of controlled temperatures and using a van't Hoff analysis. It is important to realise

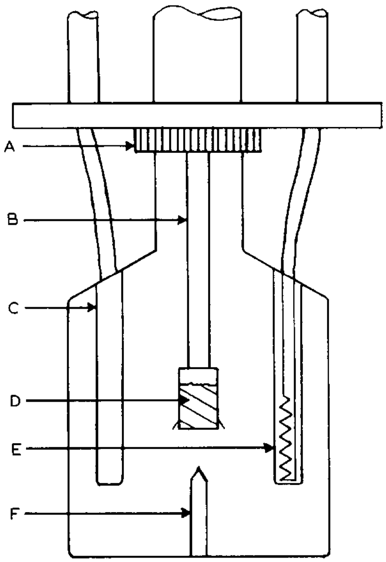

Fig. 3. Schematic representation of a breaking ampoule calorimeter vessel. A = locking nut; B = stirrer; C = thermistor; D = powder filled ampoule; E = heater; F = sharp projection.

that the enthalphy of adsorption obtained from the vacuum microbalance (isosteric) will be different to that obtained from the calorimeter, this will be explained below. Typical values for adsorption thermodynamics have been quoted by Schröder (1984) the isosteric enthalpy of adsorption will be independent of choice of standard state and in the region of -10 to -60 kJ/mol. All the others parameters will be open to variation depending upon the choice of standard state.

It is perhaps worthwhile to comment on the choice of methodology with regard to the microcalorimetry. Historically the breaking ampoule calorimeter has been used to measure powder/liquid interactions of pharmaceutical interest (Hansford et al., 1980; Storey, 1985). This method involves filling the powder in a thin walled glass ampoule which is then immersed in the thermostated liquid to facilitate equilibration. To initiate the process, the ampoule is broken by pushing it against a sharp projection from the base of the vessel by means of a remote operating mechanism. The system is shown diagrammatically in Fig. 3. Despite the action of a stirrer, hydrophobic powders will, at least to some extent, float when the liquid is water. A further problem with this technique is the inability to control the starting surface coverage of the powder. By application of Hess's Law (Fig. 4), it can be seen that a defined starting state and finishing state must be obtained in order to achieve meaningful results; use of 'as received' surfaces makes definition of the interaction impossible. The surface can be controlled by a variety of methods, such as sealing the ampoule under vacuum, sealing under controlled humidity etc. All attempts to ensure such control involve practical difficulties; for example, it is difficult to produce a glass ampoule that will withstand vacuum and still be weak enough to break easily in the calorimeter. There seems to be good reason to use a batch sorption cell which allows vacuum treatment of the surface before wetting. Such an experimental set up has recently been described (Fig. 5) (Buckton and Beezer, 1988) and consists of a sample in a stainless steel cell which can be exposed to vacuum, vapour and liquid.

The measurement of vapour adsorption is somewhat removed from the conventional view of measuring solid/liquid interactions; however, it can be justified along the lines of the BET theory (Brunauer et al., 1938); this describes initial ad-

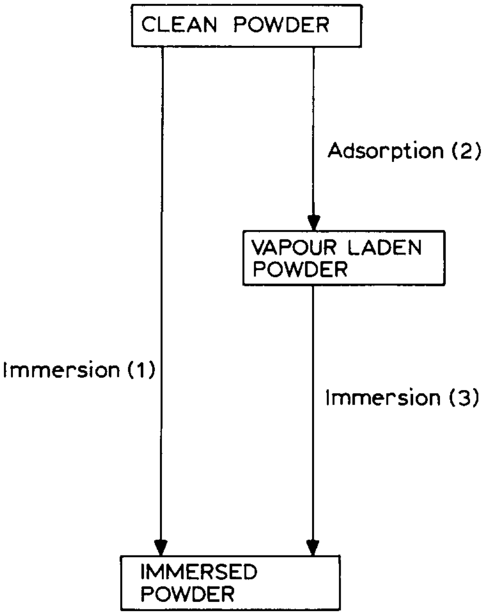

Fig. 4. Application of Hess's Law to the wetting process. Stage 1 = Stage 2 + Stage 3

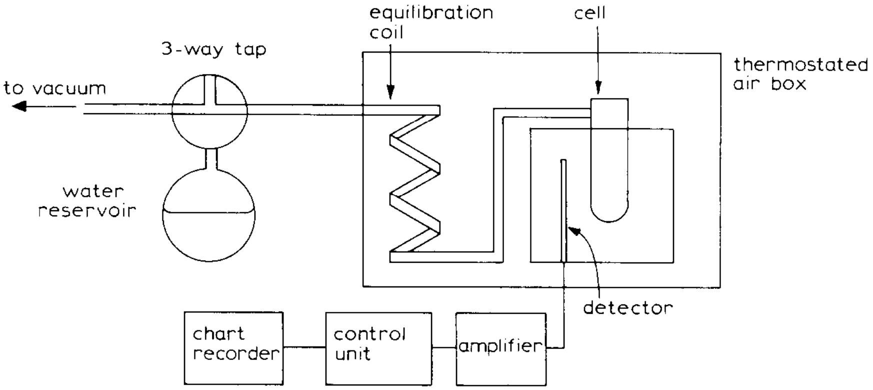

Fig. 5. Schematic representation of the batch microcalorimeter system to study vapour adsorption. (Reproduced with permission from the *International Journal of Pharmaceutics*; Buckton and Beezer, 1988.)

sorption of vapour as being the most significant stage in the interaction with subsequent adsorption onto the bound water being analogous to condensation. Immersion is the ultimate extension of this resulting in a rearrangement of water molecules to eventually take up the structure of liquid water. It seems that it is the ordering of water molecules that controls the wetting process. This view is derived from data obtained to date (Buckton and Beezer, 1988) which suggests that entropy, rather than enthalpy, may be the predominant factor in controlling wetting. In other words, the extent of water adsorption may be similar for different powders of different hydrophobic nature, but the prevailance of binding sites on the solid will alter how the water molecules are arranged and this will dominate the interaction. Clearly the results obtained from isosteric measurements will not differentiate between water bound in different ways and thus the enthalpy and entropy term may be misleading; however, the calorimetric technique which measures the enthalpy directly, gives proof that even though the total weight of vapour adsorbed is similar for different powders, the mechanism of binding is considerably different (giving a wide range of enthalpies and entropies for similar free energy values). Recent work to study the mechanism of water adsorption onto powders has used the technique of dielectric spectroscopy (Buckton et al., 1987). Here the ease of relaxation of the powder and water molecules in an alternating electrical field was studied. The changes of the inphase and out-of-phase responses, with changes of humidity and temperature, gives a measure of how much hinderance to dipole relaxation occurs, and thus an indication of how the local environment around each dipole changes, i.e. it looks at adsorption on a molecular level. Further work is needed in this field before mechanisms are fully understood.

Conclusions

The surface energetics of pharmaceuticals are of importance for a number of reasons. The measurement of interfacial interactions of powders is a complex business, because powders are small heterogeneous and often dirty surfaces. Certain empirical techniques exist to assess a contact angle for a powder. Liquid penetration has practical and theoretical limitations but offers a good ‘rule of thumb’ assessment of wettability.

Measurements on compressed discs are of use when considering tablets, but of little value when dealing with the powder.

The application of thermodynamic parameters to assessment of powder/vapour and powder/liquid interfaces provides scope for developing an understanding of such interactions. Experiments will need to be well controlled and results will always be difficult to interpret due to the complex nature of the surface under examination, which will tend to undergo polymorphic and energetic changes when mechanically treated or allowed to age.

References

Bartell, F.E. and Osterhof, H.J., Determination of the wettability of a solid by a liquid. *Ind. Eng. Chem.*, 19 (1927) 1277–1280.

Brunauer, S., Emmett, P.H. and Teller, E., Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.*, 60 (1938) 309–319.

Buckton, G. and Beezer, A.E., A microcalorimetric study of powder surface energetics. *Int. J. Pharm.*, 41 (1988) 139–145.

Buckton, G., Dissado, L.A., Hill, R.M. and Newton, J.M., The potential value of dielectric response measurements in the assessment of the wettability of powders. *Int. J. Pharm.*, 38 (1987) 1–7.

Buckton, G. and Newton, J.M., Assessment of the wettability and surface energy of a pharmaceutical powder by liquid penetration. *J. Pharm. Pharmacol.*, 37 (1985) 605–609.

Buckton, G. and Newton, J.M., Assessment of the wettability of powders by use of compressed discs. *Powder Technol.*, 46 (1986a) 201–208.

Buckton, G. and Newton, J.M., The significance of contact angles measured on surfaces that have undergone plastic deformation. In Gorrod, J.W., Gibson, G.G. and Mitchard, M. (Eds.), *Development of Drugs and Modern Medicine*, Ellis Horwood, Southampton, 1986, pp. 421–424.

Buckton, G. and Newton, J.M., Liquid penetration as a method of assessing the wettability and surface energy of pharmaceutical powders. *J. Pharm. Pharmacol.*, 37 (1986c) 329–334.

Carli, F. and Simioni, L., Limitations of the washburn equation in quantifying penetration rates. *J. Pharm. Pharmacol.*, 31 (1979) 128.

Eick, J.D., Good, R.J. and Neumann, A.W., Thermodynamics of contact angles II. Rough solid surfaces. *J. Colloid Interface Sci.*, 53 (1975) 235–248.

Fell, J.T. and Efentakis, E., Contact angle determinations on pharmaceutical powders: a comparison of two methods. *Int. J. Pharm.*, 4 (1979) 153–157.

Finholt, P. and Solvang, S., Dissolution kinetics of drugs in human gastric juice – the role of surface tension. *J. Pharm. Sci.*, 57 (1968) 1322–1326.

Fox, H.W. and Zisman, W.A., The spreading of liquids on low energy surfaces I. Polytetrafluoroethylene. *J. Colloid Sci.*, 15 (1950) 514–531.

Fox, H.W. and Zisman, W.A., The spreading of liquids on low energy surfaces II. Modified tetrafluoroethylene polymers. *J. Colloid Sci.*, 7 (1952a) 109–121.

Fox, H.W. and Zisman, W.A., The spreading of liquids on low energy surfaces III. Hydrocarbon surfaces. *J. Colloid Sci.*, 7 (1952b) 428–442.

Hansford, D.T., Grant, D.J.W. and Newton, J.M., Surface energetics of a hydrophobic powder. *J. Chem. Soc. Faraday I*, 76 (1980) 2417–2431.

Harder, S.W., Zuck, D.A. and Wood, J.A., Characterisation of tablet surfaces by their critical surface tension values. *J. Pharm. Sci.*, 59 (1970) 1787–1792.

Heertjes, P.M. and Kossen, N.W.F., Measuring the contact angles of powder–liquid systems. *Powder Technol.*, 1 (1967) 33–42.

Heistand, E.N., Theory of coarse suspension formulation. *J. Pharm. Sci.*, 53 (1964) 1–18.

Jaiyeoba, K.T. and Spring, M.S., The granulation of ternary mixtures: the effect of the wettability of powders. *J. Pharm. Pharmacol.*, 32 (1980) 386–388.

Johnson, R.E. and Dettre, R.H., In Matijevic (Ed.), *Surface and Colloid Science*, 2nd edn., Wiley, New York, 1969, pp. 85–153.

Kossen, N.W.F. and Heertjes, P.M., The determination of contact angles for systems with a powder. *Chem. Eng. Sci.*, 20 (1965) 593–599.

Lerk, C.F., Lagas, M., Boelstra, J.P. and Broersma, P., Contact angles of pharmaceutical powders. *J. Pharm. Sci.*, 66 (1977) 1480–1481.

Lerk, C.F., Schoonen, A.J.M. and Fell, J.T., Contact angles and wetting of pharmaceutical powders. *J. Pharm. Sci.*, 65 (1976) 843–847.

Levine, S. and Neale, G.H., Theory of the rate of wetting of a porous medium. *Trans. Faraday Soc.*, 71 (1975) 12–18.

MacDougall, G. and Ockrent, C., Surface energy relations in liquid/solid systems. 1. The adhesion of liquids to solids and a new method of determining the surface tension of solids. *Proc. R. Soc. Lond. Ser A*, 180 (1942) 157–173.

Neumann, A.W. and Good, R.J., Thermodynamics of contact angles, 1. Heterogenous solid surfaces. *J. Colloid Interface Sci.*, 38 (1972) 341–358.

Neumann, A.W. and Good, R.J., Techniques of measuring contact angles. In Good, R.J. and Stromberg, R.R. (Eds.), *Surface and Colloid Science, Vol. II*, Plenum, New York, 1979, pp. 31–91.

Neumann, A.W., Renzow, D.R., Reumuth, H. and Richter, I.E., *Fortscher Kolloide Polymere*, 55 (1971) 49–54 through Neumann and Good (1979).

Parfitt, G.D., *Dispersion of Powders in Liquids*, 2nd edn., Applied Science, England, 1973.

Parfitt, G.D. and Sing, K.S.W. (Eds.), *Characterisation of Powder Surfaces*, Academic, London, 1976.

Pease, D.C., The significance of the contact angle in relation to the solid surface. *J. Phys. Chem.*, 49 (1945) 107–110.

Schröder, J., On the thermodynamic functions of gas–solid adsorption and liquid–solid immersion and their relation to adhesion, contact angle and surface tension. *Prog. Org. Coatings*, 12 (1984) 159–180.

Stamm, A., Gissinger, D. and Boymond, C., Quantitative evaluation of the wettability of powders. *Drug Dev. Ind. Pharm.*, 10 (1984) 381–408.

Storey, D., Thermodynamics of the aqueous immersion of a series of imidazoles. *J. Pharm. Pharmacol.*, 37 (1985) 25P.

Studebaker, M.L. and Snow, C.W., The influence of ultimate composition upon the wettability of carbon black. *J. Phys. Chem.*, 59 (1955) 973–976.

Ward, C.A. and Neumann, A.W., On the surface thermodynamics of a two component liquid–vapour–ideal solid system. *J. Colloid Interface Sci.*, 49 (1974) 286–290.

Washburn, E.W., The dynamics of capillary flow. *Phys. Rev.*, 17 (1921) 273–283.

Witvoet, W.C., PhD thesis, Delft, The Netherlands, 1971.

Young, T., An essay on the cohesion of fluids. *Phil. Trans. R. Soc.*, 95 (1805) 65–87.