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The effect of surface treatment on the values of contact angles measured on a compressed powder surface

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Summary

Contact angles formed by a series of alkanes, water and glycerol have been determined on compressed discs of ten powders (Avicel PH-101, starch, magnesium stearate, and the following calcium salts: carbonate, phosphate, stearate, formate, acetate, lactate and gluconate), by use of the drop height method. The contact angles were assessed on untreated compacts, and on compacts which had been cleaned in a vacuum chamber and re-equilibrated with air saturated with the vapour of the wetting liquid. Under both sets of conditions the beds were saturated with the test liquid prior to measuring a maximum height drop. There was no correlation between the surface tension of the alkanes and their contact angle on the powders. The contact angles formed by the alkanes were not subject to significant change after vacuum treatment of the surface. Contact angles formed by polar liquids (water and glycerol) were higher after vacuum treatment. The difference in values was greatest for the most hydrophobic powders. To assess the implications that the different values of the contact angle may have on the predicted performance of the powders, the spreading coefficients were calculated to examine the interaction between the powders and two polymeric binders (HPMC and PVP). The values of contact angles before and after treatment, yielded values for the spreading coefficients that did not correlate with each other (i.e. different rank orders). However, in only one case (magnesium stearate) would the prediction of best choice of binder change on the basis of the two sets of data. Thus, the results demonstrate that the surface treatment and environmental conditions to which a powder has been exposed will change the measured contact angle, and may invalidate predictions that are made from such data.

Introduction

The wettability of pharmaceutical powders is of importance in the preparation, storage and use of formulated products (e.g. Buckton, 1990). Recently, a number of publications have demonstrated that it is possible to predict product performance and to optimise formulations, on the basis of the theoretical interactions between different phases. These interactions are calculated from surface energy and polarity data (e.g. Rowe, 1989a–c). Logically, accurate predictions will depend upon accurate measurements of contact angles. It has always been recognised that the methods by which a contact angle of a liquid on a

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powder is determined are imperfect, due to both practical and theoretical limitations that are associated with the available techniques.

In this work, contact angles have been measured on compressed powder surfaces. It is acknowledged that the process of forming a compact has the potential to cause surface deformation and, consequently, to alter the contact angle such that results may not reflect the properties of the original powder (Buckton and Newton, 1986). Despite this reservation, compressed powder samples offer the quickest, most straightforward, and thus the most regularly used, approach to the assessment of the wettability of powders. It is likely that many workers will attempt to use data from similar experiments to make predictions of product performance.

Theory

A contact angle (θ) represents an equilibrium of three interfacial forces (γ), and is described by Young's equation:

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

where the subscripts L, S, and V refer to the liquid, solid and vapour phases, respectively. Thus, the contact angle measurement should not be carried out in the presence of air, but in the presence of the vapour of the probe liquid. (This is equally true for the measurement of surface tension (γ_{LV})).

It is often argued that contact angles measured in air are valid, as they are more 'realistic' when the results are to be applied to systems that are made and used in the presence of air. This view would have more validity if the composition of air were uniform from day to day and from country to country, this is not the case; humidity levels, for example, can vary significantly.

This study compares the contact angles formed in air on untreated surfaces with values measured on vacuum cleaned surfaces in the presence of air that had been saturated with the vapour of the test liquid.

Materials and Methods

Materials

Ten powders were investigated, including five pharmaceutical excipients: magnesium stearate (Baxeden Chemicals), Avicel PH-101 (FMC Corp.), Starch 1500 (Colorcon Inc.), calcium carbonate (Thew Arnott Ltd) and calcium phosphate dihydrate (K&K Greef Ltd), and five other calcium salts (formate, acetate, lactate, gluconate and stearate) which, together with the liquids (GPR grade) were obtained from BDH.

Methods

Experimental design There are many options that may be considered with regard to design and control of a contact angle experiment. In this study the influence of vacuum 'cleaning' of the surface has been investigated. The cleaned surface is not necessarily completely clean, but will have equilibrated to a reproducible state, with many physically sorbed species being removed. Having obtained a cleaned surface, there are a number of options as to subsequent equilibration, these include adding (i) only the vapour of the test liquid, (ii) a carrier gas (e.g. nitrogen) saturated with the vapour of the test liquid, (iii) air saturated with the vapour of the test liquid. Each of these experiments has some merit and each may yield different results, which may provide useful information. Some of these experiments will be harder to manage than others, e.g. adding just the vapour of the test liquid would result in a pressure difference between the inside (the saturated vapour pressure of the liquid at that temperature) and the outside of the chamber, thus it would be difficult to manage the system in order to add the liquid drops.

In this work, an untreated surface was compared with results on a cleaned surface which had been equilibrated with air that had been saturated with the vapour of the test liquid. At the molecular level, a powder compact which is saturated with the test liquid will have a diffusion layer of air around it which will tend to be saturated with the vapour of the liquid. The experiments presented here, therefore, will predominantly relate to the effect of surface cleaning. The untreated surface will have adsorbates which were present prior to contact with the liquid, and which may or may not remain sorbed in the presence of the liquid and its vapour; the treated sample will not have such residual adsorbates prior to exposure to the test liquid (in vapour form), thus the interaction between the solid and liquid could change under these two conditions.

Any differences between the treated and untreated samples would reflect differences that could be expected between samples with different histories (i.e. exposure to different environmental conditions.

Procedure Powder compacts were prepared in the punch and die systems described by (Buckton and Newton, 1986), by use of a hand press. One set of discs were used as formed, and the other set were stored in a vacuum chamber to degas the surface, and then were equilibrated with air that was saturated with the vapour of the test liquid in situ. The vacuum (10^{-3} Torr) was produced using a rotary pump (Edwards, E2M5).

Liquid was added to the surface of the compacts from a micrometer syringe, and after saturation of the bed had been achieved, the maximum height of the drops of liquid that could be formed on the compact was measured. Measurements were undertaken either in air or in the environmentally controlled chamber, using a travelling microscope. Contact angles were calculated as described by Heertjes and Kossen (1967). The results are averages of three replicates on each of (at least) three different discs.

Results and Discussion

The values obtained for the contact angles are presented in Table 1.

The contact angles formed by the homologous series of alkanes do not correlate with the surface tension of the alkanes. Furthermore, the effect of vacuum treatment and saturation with vapour has very little effect on the recorded contact angles

TABLE 1

Contact angles of various liquids on the ten powders in compact form

Solid		Liquid					
		Hexane	Heptane	Octane	Decane	Water	Glycerol
Calcium formate	a	21	18	15	16	14	31
	t	21	18	15	16	41	65
Calcium acetate	a	24	27	30	22	27	49
	t	24	27	30	22	46	67
Calcium lactate	a	23	23	20	23	21	45
	t	20	23	20	19	36	74
Calcium gluconate	a	25	22	22	24	28	39
	t	27	23	23	24	41	62
Calcium stearate	a	48	37	39	34	75	79
	t	36	37	38	34	136	143
Avicel	a	12	25	23	19	28	54
	t	12	25	22	19	42	60
$CaHPO_4$	a	19	18	23	20	31	48
	t	24	20	24	22	38	59
$CaCO_3$	a	18	20	17	21	30	49
	t	23	22	17	23	35	67
Magnesium stearate	a	31	29	26	39	90	81
	t	34	31	27	39	145	108
Starch	a	28	22	23	24	42	52
	t	28	21	22	24	56	53

a, in air; t, after vacuum treatment.

formed by the alkanes. These findings are common for all ten powders.

Contact angles of water on the powders show significant differences when the untreated are compared to the vacuum treated surfaces. The largest changes in contact angles between the solid/air and solid/vapour values were for the most hydrophobic surfaces. Magnesium and calcium stearate had a difference of 54 and 61°, respectively, between the two values. These differences can be compared to the more hydrophilic solids, for example calcium carbonate had a difference of only 7° between the two water contact angles.

On an empirical basis, it would not be of great concern that the magnitude of the contact angles changed, if it were not for the fact that the ranking of the contact angles for the solids is different under the two experimental conditions. Notably, Avicel had a very low contact angle in the presence of air (lower than calcium carbonate for example), but in the presence of water vapour the angle was very much larger (higher than calcium carbonate). The low value for the equilibrium contact angle reported here for Avicel/water in air, is not dissimilar to the value of the dynamic contact angle for the same solid that was reported before (Zajic and Buckton, 1990) and can be regarded as a true reflection of the hydrophilic nature of this powder. It should not be surprising that the contact angle formed with water will be subject to change in different environmental conditions, Avicel shows a steep water sorption isotherm at humidities over 30% (e.g. Hollenbeck et al., 1978) and thus its surface properties will vary at each humidity. However, it may perhaps seem surprising that the contact angle is higher, rather than lower, on surfaces which are in equilibrium with the air saturated with vapour rather than an uncontrolled air/vapour mixture.

In general terms, the contact angles for glycerol (which was used as an alternative hydrophilic liquid) showed similar trends to those obtained for water. The contact angles formed after cleaning the surface and using air saturated with the vapour of the liquid were generally significantly higher than those obtained on the untreated powders. As with water the most hydrophobic powders showed large differences in contact angles under the two experimental conditions.

In systems in which the angle is significantly increased by the treatment process, it must be concluded that there are changes in the three interfacial forces (see Eqn 1). That is, the solid/vapour interfacial tension is smaller than the solid/air interfacial tension, and/or that the liquid/vapour is stronger than the liquid/air interfacial tension, and/or the solid/liquid interfacial tension is greater after treatment. The results obtained with both water and glycerol show that the treated samples are generally more hydrophobic than the untreated. As glycerol is not a very volatile liquid, it would be expected that the air saturated with glycerol vapour would not be significantly different to the ambient conditions. It follows that the change in the results obtained are more likely to be associated with the cleaning of the compact surface during vacuum treatment, rather than the change in the composition, and thus the properties, of the air.

As the treatment process results in surfaces that are more hydrophobic than the original samples, materials which are sorbed to the compact surface produce a less hydrophobic surface than that of the powder under test. Cleaning seems to remove these sorbed contaminants and decrease wettability (by water).

Implications for predictions based on contact angle data

Recent published work has considered interactions between different phases based on spreading coefficients (e.g. Rowe, 1989a–c). Spreading coefficients relate the polarity and surface energy of the solid to that of the phase with which it is to interact. The polarity and surface energy of the solid are obtained from the contact angles formed by two liquids each of known surface energy and polarity.

The surface energy and its polar (p) and dispersion (d) components have been calculated for the ten powders using the reciprocal mean theory (Wu, 1971), with the data for octane and water, before and after treatment (Table 2). The polar values change after vacuum treatment, but the dispersion values do not; this is a reflection of the

TABLE 2

The surface energies and their polar (p) and dispersion (d) components, calculated for the ten powders using the contact angle data for octane and water

		γ (mN/m)	γ^d (mN/m)	γ^p (mN/m)
Calcium formate	a	69.9	22.7	47.2
	t	56.9	22.7	34.2
Calcium acetate	a	64.6	20.6	44.0
	t	53.3	20.6	32.8
Calcium lactate	a	67.3	22.1	45.2
	t	59.7	22.1	37.6
Calcium gluconate	a	64.0	21.8	42.2
	t	53.3	20.6	32.8
Calcium stearate	a	35.2	18.8	16.4
	t	6.4	6.4	0
Avicel	a	64.1	21.7	40.8
	t	56.0	21.8	34.2
$CaHPO_4$	a	62.5	21.7	40.8
	t	58.5	21.6	36.9
$CaCO_3$	a	63.1	22.5	40.6
	t	60.4	22.5	37.9
Magnesium stearate	a	29.3	21.2	8.1
	t	3.8	3.8	0
Starch	a	56.1	21.7	34.4
	t	47.5	21.8	25.7

a, in air, t, after vacuum treatment.

relative changes in contact angles for octane and water before and after treatment.

Two spreading coefficients can be calculated for any two phases, that of phase 1 spreading over phase 2:

$$\lambda_{12} = 4\left[\frac{\gamma_1^p \cdot \gamma_2^p}{\gamma_1^p + \gamma_2^p} + \frac{\gamma_1^d \cdot \gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{\gamma_1}{2}\right] \tag{2}$$

and of phase 2 spreading over phase 1:

$$\lambda_{21} = 4\left[\frac{\gamma_1^p \cdot \gamma_2^p}{\gamma_1^p + \gamma_2^p} + \frac{\gamma_1^d \cdot \gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{\gamma_2}{2}\right] \tag{3}$$

Recently, spreading coefficients have been used to predict the interaction between polymeric binders (e.g. hydroxypropylmethylcellulose (HPMC), and polyvinylpyrrolidone (PVP)) and pharmaceutical powders (e.g. Rowe, 1989a; Zajic and Buckton, 1990). Two types of granule have been postulated based upon the two spreading coefficients (Rowe, 1989a,b). When the binder spreads over the powder a granule which is more dense is postulated, but when the powder would spread over the binder a more porous system is predicted. When neither spreading coefficient is positive, the system will not granulate or will form only poor weak granules.

Spreading coefficients have been calculated for all ten of the powders used in this study with HPMC and PVP. The aim was to ascertain the extent of error in the predictions that may be introduced by using contact angles measured in different conditions. The values of the spreading coefficients of the powder over the binder (λ_{12}) and the binder over the powder (λ_{21}) are presented in Table 3 for HPMC and Table 4 for PVP.

If the spreading coefficients of HPMC over the 10 powders for the results obtained in air, and the results obtained in the vapour of the liquid on the cleaned surface, both predicted the same performance, a linear relationship should exist between the two sets of spreading coefficients, which, if plotted, would pass through the origin. From the data in Tables 3 and 4, although a general trend is observed, there is no correlation between the two sets of spreading coefficient data. The PVP data also yield two sets of spreading coefficients which do not correlate. The results for starch are a

TABLE 3

Spreading coefficients for the powder over the binder (λ_{12}) and the binder over the powder (λ_{21}), for HPMC, using the contact angle data for water and octane, in air (a) and after vacuum treatment (t)

	λ_{12}		λ_{21}	
	a	t	a	t
Calcium formate	−25.2	−9.2	17.2	7.8
Calcium acetate	−19.0	−5.1	13.4	4.8
Calcium lactate	−22.3	−12.5	15.5	10.1
Calcium gluconate	−18.0	−9.0	13.3	7.6
Calcium stearate	9.2	6.2	−17.2	−77.8
Avicel	−18.1	−8.2	13.3	7.0
$CaHPO_4$	−16.0	−11.1	12.2	9.1
$CaCO_3$	−16.7	−13.3	12.7	10.7
Magnesium stearate	6.3	22.8	−31.9	−66.4
Starch	−8.3	0.3	7.2	−1.52

TABLE 4

Spreading coefficients for the powder over the binder (λ_{12}) and the binder over the powder (λ_{21}), for PVP, using the contact angle data for water and octane, in air (a) and after vacuum treatment (t)

	λ_{12}		λ_{21}	
	a	t	a	t
Calcium formate	−23.6	−5.3	8.9	1.3
Calcium acetate	−17.3	−1.8	4.7	−2.4
Calcium lactate	−20.2	−9.3	7.2	2.9
Calcium gluconate	−15.6	−5.6	5.2	0.6
Calcium stearate	14.6	8.1	−22.2	−86.3
Avicel	−15.8	−4.6	5.2	0.2
$CaHPO_4$	−13.5	−7.9	4.3	1.9
$CaCO_3$	−13.8	−10.1	5.2	3.5
Magnesium stearate	14.5	5.8	−34.1	−93.8
Starch	−4.8	5.1	0.2	−7.1

particularly good example of non-correlation (these are discussed despite the fact that it is obvious that starch would never be granulated with other binders), where there is a reversion in sign for λ_{12} and λ_{21} with both HPMC and PVP, when the results for the treated and untreated samples are compared; this would suggest that (theoretically) quite different types of granules would form if starch was granulated with HPMC or PVP in the presence (starch spreading on PVP/HPMC) or absence (PVP/HPMC spreading on starch) of air.

Despite these reservations, if the experiments are always carried out under the same conditions (i.e. treated or untreated surfaces), then only for magnesium stearate would the decision on choice of binder be changed. This is because the spreading coefficients obtained from results measured in air are always higher for HPMC than PVP (except for calcium stearate which, on the basis of these data, should be granulated with PVP) as are the spreading coefficients obtained from results measured after vacuum treatment (again except from calcium stearate). As mentioned above, only for magnesium stearate would the predicted best binder change, on the basis of the results obtained on untreated surfaces PVP would be the binder of choice for magnesium stearate, but HPMC would be preferred if the results from treated surfaces are considered.

Conclusions

The extent of surface contamination and atmospheric conditions that are present at the time of measurement will have a significant influence on the value of the contact angle obtained. The major influence is probably the adsorption of atmospheric contaminants onto the surface, but the composition of the vapour that is in equilibrium with the surface may have some effect. It cannot be assumed that a change in experimental conditions will result in an equal, or even proportionate, change in the value of the contact angle for different samples. These aspects require considerable further work, before the full significance can be assessed. Results of this work appear to suggest that the greatest change occurs in the polar interactions.

Predictions based on spreading coefficients are susceptible to changes in the contact angle data. In this work, the ranking of spreading coefficients, i.e. the ranking of predicted best to worst granulations, for any one polymer is not the same for systems measured in air compared with those measured on cleaned surfaces in the presence of air saturated with the vapour of the wetting liquid. However, in only one case did the prediction of best binder change form HPMC to PVP when the different experimental conditions were compared.

The environmental control during contact angle measurements and pretreatment of the powder should be improved, and the level of surface contamination present on a sample should be considered, if an improved understanding of powder/liquid interactions is to be developed.

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