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WETTING OF BINARY POWDER MIXTURES

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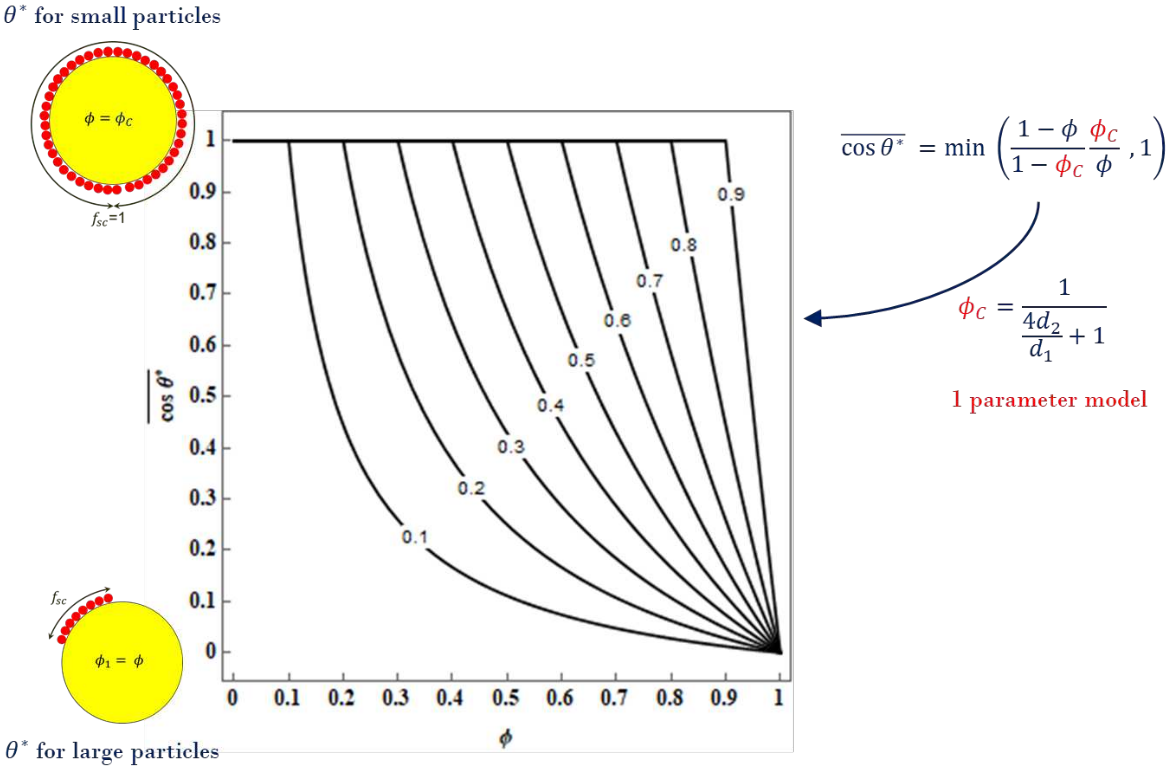
Abstract

The wetting process involved when a liquid droplet comes into contact with a mixture of particles is a complex phenomenon which is often understood by reference to Cassie-Baxter theory. However, various authors have applied the Cassie-Baxter theory for the prediction of contact angles on two-component mixtures without success. We hypothesise that the main difficulty in applying the Cassie-Baxter theory to mixtures is that if the particles differ in size, it is possible for the small particles to coat the large particles, so reducing the available surface area of the large particles. This leads to the view that bulk volume fractions are not good estimates of surface fractions of the components within the mixture. We argue that the Cassie-Baxter theory over represents the influence of large particles and that below a certain critical volume fraction they exert no influence. We present a simple geometrical model that relates the critical surface coverage volume fraction to the Sauter mean particle size of the binary mixture components. As a consequence, the wetting behaviour can be determined from the bulk volume fractions and the calculated critical surface coverage volume fraction, by means of a simple geometric model. We show that the simple model describes the five two-

components systems reported here and a further four systems reported in the literature, irrespective of whether the larger or small particles are hydrophobic/hydrophilic. With this model, it is possible to predict the wetting behaviour of mixtures of particles that coat each other using very simple characterisation methods, so reducing the development time in the creation of formulations in the pharmaceutical industry.

Graphical Abstract: Surface coverage wetting model



Keywords

Contact angle, Wetting, Surface coverage

1. Introduction

We review the applicability of the Cassie-Baxter theory [1,2] of the prediction of liquid contact angles on surfaces made from two-component mixtures consisting of hydrophilic/hydrophobic particles [3,4]. Cassie-Baxter theory was derived on the basis that contact angles are determined by the interactions within the interfacial contact area of the liquid and solid surface [1,2]. To validate their theory, Cassie-Baxter studied systems in which the components were not free to rearrange and so the surface fraction of each component was fixed and simple to determine. However, several authors have questioned the validity of the Cassie-Baxter theory and suggested that the three-phase contact line alone and not the interfacial contact area is important in determining the contact angle behavior [5–10]. This result was attributed to the difference in behavior of solid and liquid molecules. At the three-phase contact line, solid molecules are not mobile and cannot contact to obey area minimization when a liquid droplet is placed on them. Put simply, the laws of liquids cannot be directly applied to solids. The aim of our paper is to highlight the misconceptions and restrictions of Cassie-Baxter theory in predicting contact angles on surfaces made from two-component particulate mixtures. Consequentially, we put forward a new theory which is supported by detailed experimental investigations that allows the prediction of contact angles on two-component particulate mixtures.

2. Background

When a liquid droplet comes into contact with a solid surface, the liquid droplet wets the constituent particles. This wetting phenomenon is determined by the interactions between the molecules of the two phases coming into contact, forming a three-phase contact line, where the liquid, powder bed surface and vapour co-exist. The three-phase contact line will continue to advance to an equilibrium contact angle (θ_E) in which the liquid droplet takes the shape that minimizes the total free energy of the system, (see Figure 1).

A well-known relation for θ_E was developed by Young (1805) assuming an idealized smooth and homogeneous solid surface and that the liquid droplet does not spread further after reaching its equilibrium contact line radius [11]. A liquid is said to wet a surface if $\gamma_{SV} - \gamma_{SL} \geq$

γ_{LV} ($\cos\theta \leq 1$) and be non-wetting if $\gamma_{SV} < \gamma_{SL}$ ($\cos\theta$ is negative). However, in reality solid surfaces are not ideal, particularly pharmaceutical powders where there are several factors that affect the measured apparent contact angle (θ^*) such as contact line surface heterogeneities, chemical composition of the liquid and solid surface [1,2,12,13].

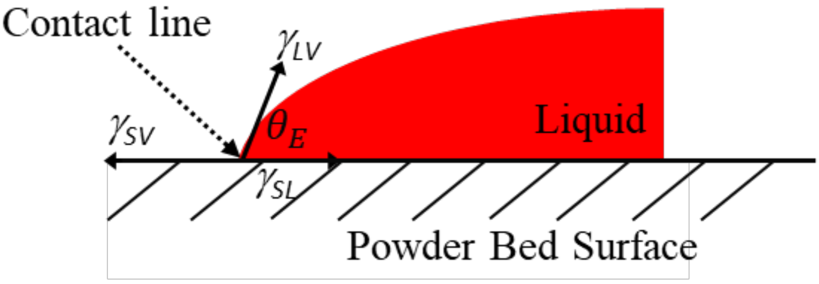


Figure 1. Cross sectional contact angle profile of a liquid droplet on a solid surface at a three phase contact line

Wenzel (1936) first related the θ^* to solid surface heterogeneities (roughness) assuming that the liquid droplet fills the grooves of a rough solid surface completely [12]. Wenzel's theory suggests that for $\theta^* > 90^{\circ}$, surface roughness enhances its wetting behaviour since there is a greater net energy decrease to induce spreading. However for $\theta^* < 90^{\circ}$, the non-wetting behaviour of a solid surface is exaggerated with surface roughness. However, Wenzel's theory was conceived for homogeneous, one-component solid systems.

In the pharmaceutical industry, solid systems are however frequently mixtures [4,14–16, 21]. For two-component mixtures of fibres in a cloth, Cassie-Baxter related the θ^* with the wetted fraction of surface area of a solid based on the assumption that the cloth surface is smooth and consists of a grid of cylinders, using the following expression [1]:

$$\cos\theta^* = f_1 \cos\theta_1^* + f_2 \cos\theta_2^*$$

$$f_1 + f_2 = 1$$

Equation 1

where θ^* is the apparent equilibrium contact angle, f_1 and f_2 are the area fractions of fibres 1 and 2 with apparent contact angles of θ_1^* and θ_2^* respectively.

There are a number of limitations in seeking to applying Cassie-Baxter to powders: a) in practise real solid surfaces do not consist of cylindrical particles and have complex pore structures in which the liquid droplet ‘may’ spread on the solid surface and fill the pores in any direction depending on the contact angle formed [17,18] and b) Cassie-Baxter studied systems in which the components were not free to rearrange and so the surface fraction of each component was fixed and simple to determine. In seeking to apply their result to mixtures of particles it has to be assumed that the surface fraction of each component is equal to the known volume fraction; a situation that arises naturally if particles can rearrange in the surface of the mixture i.e. in 2D, but not vertically i.e. in 3D. Then Equation 1 is rewritten as:

$$\cos\theta^* = (\phi)\cos\theta_1^* + (1-\phi)\cos\theta_2^*$$

Equation 2

$$1-\phi = \frac{cos\,\theta^* - cos\,\theta_1^*}{cos\,\theta_2^* - cos\,\theta_1^*} = \overline{cos\,\theta^*}$$

Equation 3

where ϕ is the volume fraction of particles of type 1 and $\overline{\cos\theta^*}$ is the normalized wetting parameter.

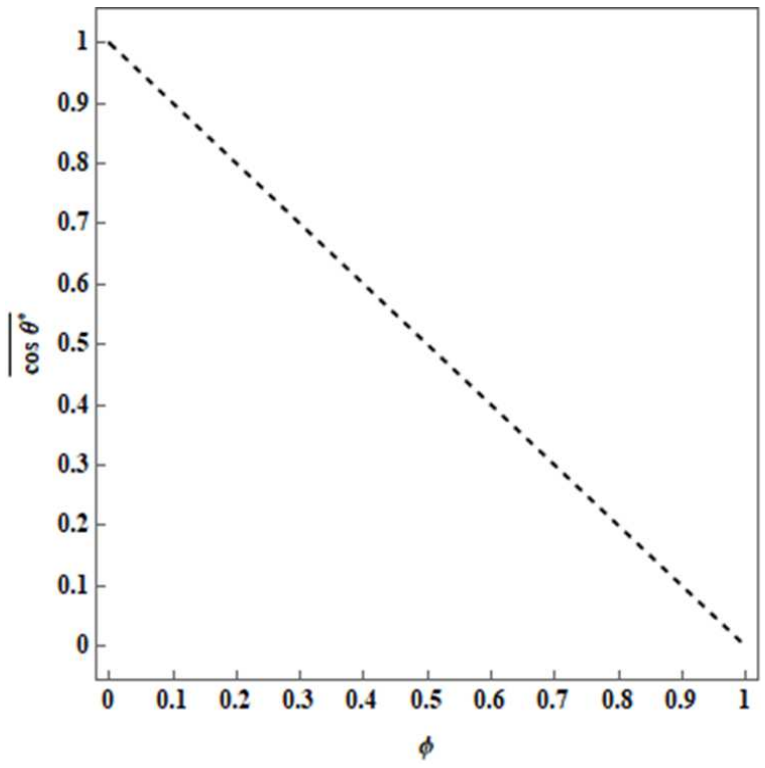


Figure 2. Relationship between the normalized contact angle and the volume fraction of particles of type 1 according to Cassie-Baxter, from Equation 3.

Figure 2 shows how the normalized wetting parameter ($\overline{\cos\theta^*}$) depends on the volume fraction of particles of type 1. The implication of Equation 3 is that a plot of $\overline{\cos\theta^*}$ versus the volume fraction (ϕ) of the particles in the powder mixture, gives a linear relationship (see Figure 2). This shows that as ϕ increases there is a corresponding reduction in the value of $\overline{\cos\theta^*}$.

However, in this paper we will hypothesise that there is a non-linear relationship between $\overline{\cos\theta^*}$ versus ϕ if the particles differ in size, as it is possible for the small particles to coat the large particles thus changing the apparent contact angle.

3. <u>Revised Theory</u>

We propose a model that considers a two-component powder system consisting of particles of differing chemical composition, using the following assumptions to complete the derivation:

1. Particles are treated as spheres.
2. The presence of air is neglected.
3. The solid surface is smooth.

We consider a unit volume of a mixture in which the volume fraction of large particles is ϕ.

Volume fraction of large particles

$$v_1 = \phi_1 = \phi$$

Equation 4

Volume fraction of small particles

$$v_2 = \phi_2 = 1 - \phi$$

Equation 5

From this, the surface area per unit volume, s_1 of the large particles is:

$$s_1 = \frac{6\phi}{d_1}$$

Equation 6

The projected area of small particles, p_2 is given by:

$$p_2 = \frac{3(1-\phi)}{2d_2}$$

Equation 7

If small particles cover the large ones, surface coverage of larger particles by small particles is related to s_1 and p_2 by:

$$f_{sc} = \frac{projected\ area}{surface\ area}$$

Equation 8

where f_{SC} is fractional surface coverage of larger particles by the small

Substituting Equation 6 and 7 into 8 gives:

$$f_{SC} = \frac{1}{4}\frac{(1-\phi)}{\phi}\frac{d_1}{d_2}$$

Equation 9

If we equate Equation 9 to $f_{SC} = 1$ and denote the volume fraction of larger particles at which this occurs as the critical surface coverage, ϕ_C substituting $\phi = \phi_C$ then solving for ϕ_C, yields the critical value fraction at which larger particles are completely covered by the small particles, rearrangement gives:

$$\phi_C = \frac{1}{\frac{4d_2}{d_1} + 1}$$

Equation 10

The value of d_1 and d_2 can be easily determined allowing ϕ_C to be predicted without conducting extensive analysis.

Equation 9 and 10 are solved to give the proposed surface coverage, f_{SC} as:

$$f_{SC} = \frac{1-\phi}{1-\phi_C}\frac{\phi_C}{\phi} \qquad \text{if } \phi \geq \phi_C$$

Equation 11

In the style of Cassie-Baxter we expect:

$$\cos\theta^* = (1-f)\cos\theta_1^* + f\cos\theta_2^*$$

Equation 12

$$\overline{\cos\theta^*} = f = \min\left(f_{SC}\ ,1\ \right)$$

$$\text{If } \phi > \phi_C \text{ then } f_2 = f_{SC}, f_1 = 1 - f_{SC}$$

$$\text{If } \phi \leq \phi_C \text{ then } f_2 = 1, f_1 = 0$$

Equation 13

$$\overline{\cos\theta^*}\ = f = \min\left(\frac{1-\phi}{1-\phi_C}\frac{\phi_C}{\phi}\ ,1\ \right)$$

Equation 14

Figure 3 shows the behaviour of $\overline{\cos\theta^*}$ from mixtures which is predicted using Equation 14. We see from Figure 3 that Equation 14 predicts a non-linear relationship between the $\overline{\cos\theta^*}$ and ϕ. We have shown that non-linear relationship of $\overline{\cos\theta^*}$ behavior on ϕ arises because small particles coat the large particles.

For a given mixture, if ϕ of large particles is greater than ϕ_c, the contact angle behavior changes considerably as there is partial surface coverage of larger particles by the small (see Figure 3). However, if ϕ of large particles is less than or equal to ϕ_c then complete ‘full’ surface coverage of the larger particles by the small is achieved, so the mixture behaves entirely as though it had the properties of small particles.

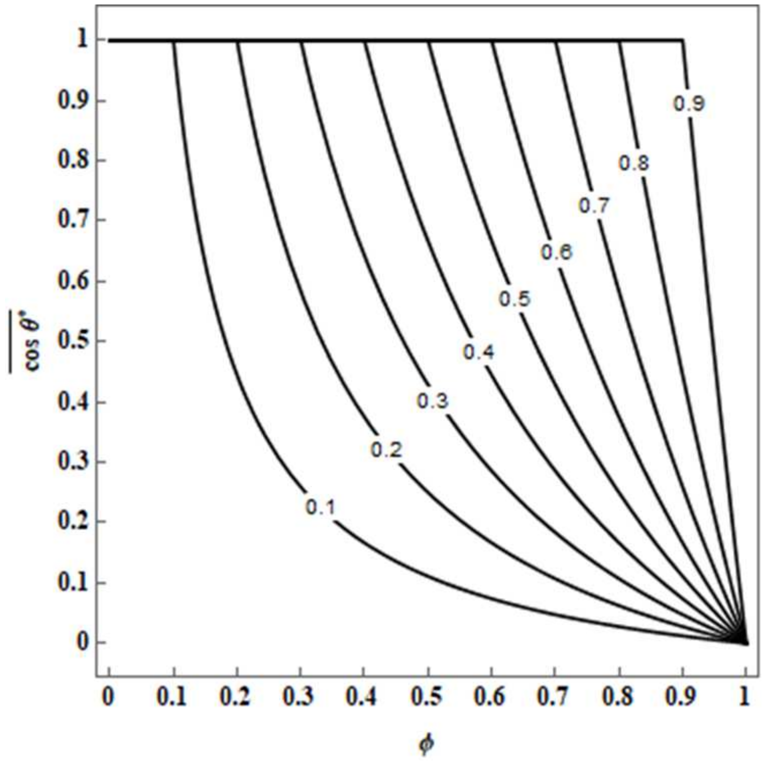


Figure 3. The normalized wetting parameter profiles of mixtures with volume fraction of large particles, ϕ, predicted from Equation 14 with the critical surface coverage volume fraction of large particles, ϕ_C, in the range of 0.1 - 0.9, in increments of 0.1.

Conceptually, Equation 14 is a simple geometrical model that relates the available surface fraction to the underlying bulk volume fractions of the components. This geometrical model depends only on the ratio of particle sizes, which in turn can be described by a ϕ_C at which complete surface coverage of the larger particles by the small is achieved. This approach allows that particles rearrange in 3D (prior, in this case, to being formed into a smooth solid surface), because upon mixing small particles coat larger particles which is in contrast to Cassie-Baxter theory that assumes that the “particles” (actually fibres) lie on the surface. We describe here a series of experiments to test the existing Cassie-Baxter theory and the proposed surface coverage theory described above (for predicting contact angle behaviour of surfaces formed from particulate mixtures). These experiments are intended to introduce a new contention, relating surface coverage to wetting behaviour.

4. Experiments

Single liquid droplet experiments were conducted to measure the θ^* on the solid surface. The solid surface was comprised of a wide range of hydrophilic and hydrophobic particles given in Table 1.

Table 1: Properties of hydrophilic and hydrophobic particles

Primary Particles	Supplier(s)	True Density[1] (kg/m^3)	Sauter mean diameter, $d_{3,2}$ (µm)	Measured θ^*[2] (°)
Micronized Lactose	DFE Pharma	1530	1.2	45
Lactose 100M	DFE Pharma	1150	4.5	20
Lactose 200M	DFE Pharma	1540	22	22
Lactose 350M	DFE Pharma	1390	6.0	35
Calcium Carbonate	Bernegger GmbH	2700-2900	6.5	98
Ethyl cellulose (sieved)	Dow chemical company	1130	6.2	90
Magnesium Stearate	Ligamed	1140	2.5	120
Stearic Acid (sieved)	Merck	0.2980	2.7	105

To prepare the solid surface, the two-component hydrophilic and hydrophobic mixtures given in Table 2 were pre-mixed in a Roto Junior mixer (Zanchetta). For all two-component mixtures, the different particle densities of the primary powders were accounted for so as to maintain the same overall volume of the solid in the batch. Powder compacts were then prepared using a 3300 single column universal system (Instron) at the rate of 1 mm/s until a cut off load of 450 N (0.64 MPa) is achieved. In this manner powder compacts of diameter 30

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[1] True density values were obtained from the suppliers

[2] Contact angle values measures using liquid binder 1.0 wt.%

mm were produced. The porosity was reported to be approximately ~35-40 % for each compact formed under these conditions [3]. Analysis was carried out using powder compacts in order to produce powder beds of more ‘regular’ structure to allow a comparative study and ultimately make sure that results observed can be attributed to wetting effects as opposed to these effects acting in combination with internal macrovoids [17].

Table 2: Two-component mixtures used

Primary Particles	Particle Description	Mixture	Reference
Lactose 200M Magnesium Stearate	Large Hydrophilic/ Small Hydrophobic	M-1	[3]
Lactose 200M Stearic Acid	Large Hydrophilic/ Small Hydrophobic	M-2	Present work
Micronized Lactose Ethyl Cellulose	Small Hydrophilic/ Large Hydrophobic	M-3	Present work
Lactose 350M Calcium Carbonate	Small Hydrophilic/ Large Hydrophobic	M-4	Present work
Lactose 100M Ethyl ellulose	Small Hydrophilic/ Large Hydrophobic	M-5	Present work
Microcrystalline Cellulose Phenacetin	Large Hydrophilic/ Small Hydrophobic	M-6	[22]
Limestone Tea	Small Hydrophilic/ Large Hydrophobic	M-7	[19]
Di-calcium phosphate dihydrate Jet milled Aspirin	Similar size Hydrophilic/ Hydrophobic	M-8	[21]
Glass Beads	Similar size Hydrophilic/Hydrophobic	M-9	[23]

Particle size analysis was carried out before and after compaction of the primary powders using laser diffraction (Malvern Mastersizer 2000). Similar results were obtained for the particle size before and after compaction (original particles recovered) as the powders were compressed under slight compression, producing weak powder compacts, thus suggesting that there was minimal deformation in the points of contact between the particles, however if deformation did exists, it is very minimal that the shape of the particles was only slightly affected.

The liquid binder was comprised of Hypromellose (Pharmacoat) (Shin-Etsu) as three solutions: 1.0 wt.%, 2.5 wt.%, 5 wt.% prepared by dissolving the solid binder in water at 25 ˚C under constant agitation. To these solutions the soluble component, (10 g/100 ml) was added to make saturated solution in order minimise dissolution during experiments. The liquid binder viscosity and interfacial tension were measured using a rotational rheometer (Malvern) and Wilhelmy plate tensiometer (Kilbron) respectively. A summary of the liquid binder properties is given in Table 3. The effect of the concentration of the liquid binder is investigated on the contact angle behavior as in the pharmaceutical industry viscosity is a critical parameter as it determines the strength of the liquid bridge between the particles which affects the resultant granule and final tablet properties.

Table 3: Properties of the liquid droplets

Binder	Concentration (wt.%)	Viscosity $(\mathbf{mPa \cdot s})$	Surface Tension (mN/m	Droplet volume (µl)
Hypromellose	1.0	3.67±0.08	44±1.40	15
	2.5	6.10±0.12	46±0.70	
	5.0	13.17±0.15	44±0.67	

The contact angle measurements of the binary mixtures were then measured by a sessile drop method First Ten Angstroms FTA 125 goniometer [19]. The sessile drop method was used to measure the contact angle by using a video camera positioned from the side, adjusting the lighting to obtain good contrast between the droplet and the background [20]. The liquid binder droplets of 15 µl were slowly deposited from an electronic pipette onto the solid surface at 25 ºC and the maximum θ^* formed between the liquid droplet and the solid surface was captured using a camera (Photron) and determined directly using image analysis. The maximum θ^* is the "advancing" contact angle. The contact angle values reported here are average of 10 measurements which were taken from different areas of the solid surface. Analysis is further extended to experimental data reported in the literature which focuses on two-component particulate mixtures.

5. Results and Discussion

Initial experiments were conducted to assess the dependence of contact angle on binder concentration. Figure 4 shows the effect of binder concentration on the $\overline{\cos\theta^*}$ vs ϕ profiles for the particulate mixture M1. Here, Cassie-Baxter Equation 3 and surface coverage wetting model Equation 14 are fitted to the $\overline{\cos\theta^*}$ vs ϕ profiles and the fitted parameters are given in Table 4. The surface coverage model provides for an abrupt transition in $\overline{\cos\theta^*}$.

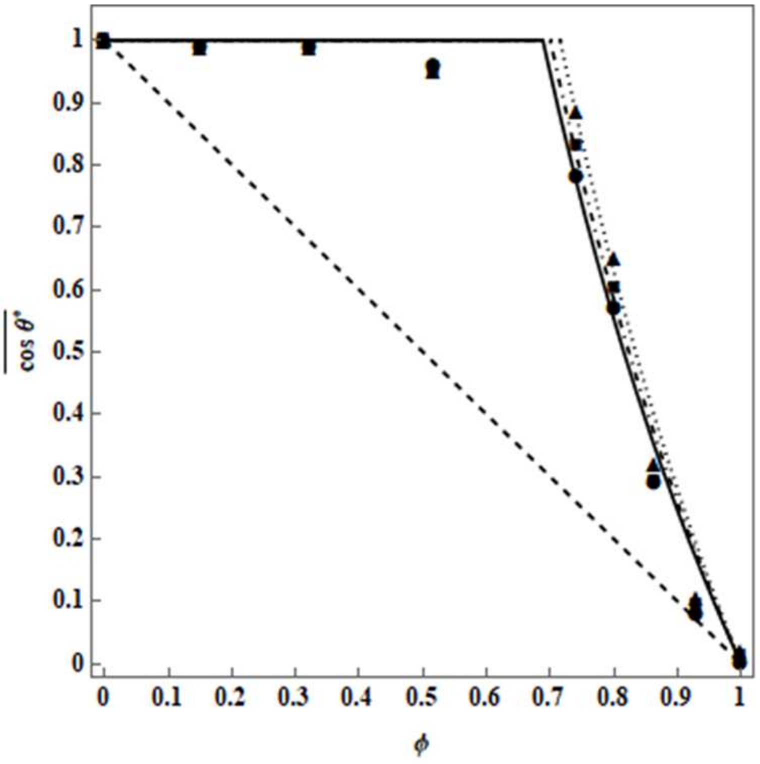


Figure 4. Effect of liquid binder concentration on the relationship between $\overline{\cos\theta^*}$ and ϕ for mixture M-1. The symbols correspond to the measured $\overline{\cos\theta^*}$ for ● 1.0 wt.%, ■ 2.0 wt.% and ▲5.0 wt.% binder. The solid, dot-dashed and dashed (tiny) line correspond to the fitted data of Equation 14. The dashed line corresponds to the expected Cassie-Baxter relationship Equation 3.

We see from Figure 4 that as ϕ decreases, there is a corresponding increase in the values of $\overline{\cos\theta^*}$ as small particles coat the large particles until ϕ_c is reached and the large particles are fully coated and the contact angle is constant at the value of the small particles. We observe essentially identical characteristics in $\overline{\cos\theta^*}$ behaviour when the liquid binder concentration is changed, see Figure 4 and Table 4. That is, changing the liquid binder concentration has little effect on the $\overline{\cos\theta^*}$ profile, despite substantial changes in viscosity because the surface tensions associated with the liquid change little, see Table 3.

Table 4: The fitted parameters for two-component mixture M-1.

Liquid binder concentration (wt.%)	1.0	2.5	5.0	Global Fitting
ϕ_c	0.688	0.699	0.715	0.702
Standard Error	0.0082	0.0085	0.0077	0.005
t-statistic	83.44	82.92	93.22	140
P-value	$4.75\text{x}10^{-13}$	$4.99\text{x}10^{-13}$	$1.96\text{x}10^{-13}$	$5.72\text{x}10^{-39}$

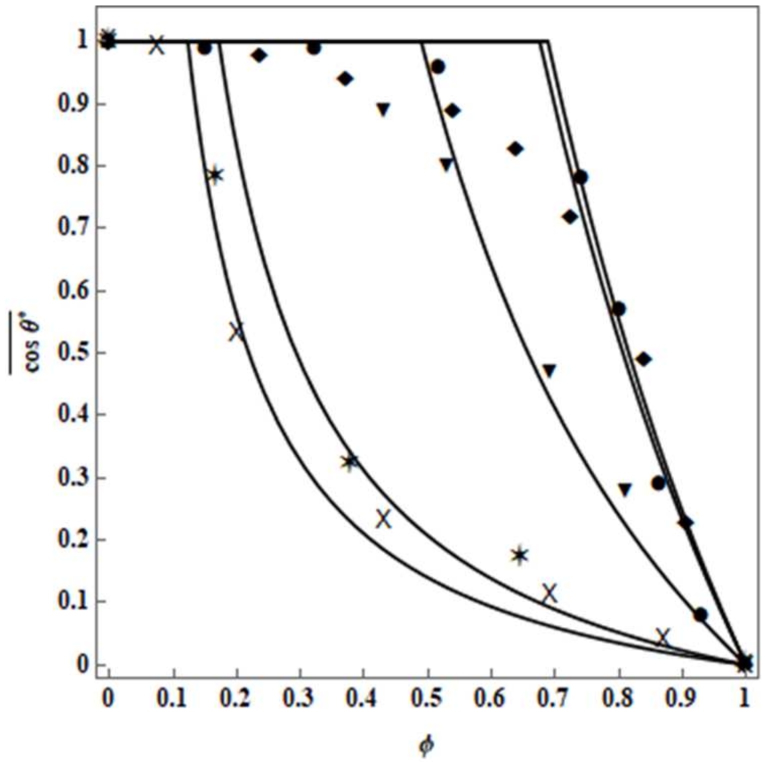


Figure 5. Effect of particle size on the relationship between $\overline{\cos\theta^*}$ and ϕ for mixture M-1 (●), M-2 (□), M-3 (□) M-4 (□), and M-5 (×) . The solid lines correspond to the fitted data of Equation 14.

The $\overline{\cos\theta^*}$ behaviour observed is in agreement with the implications from the surface coverage wetting model Equation 14, where $\overline{\cos\theta^*}$ behaviour is expected to increase non-linearly as ϕ decreases, as small particles coat the large particles (see Table 6). The non-linear relationship observed between $\overline{\cos\theta^*}$ versus ϕ does not follow the trend expected from the

Cassie-Baxter Equation 3. In each case, Equation 14 gives an excellent prediction of $\overline{\cos\theta^*}$ behaviour.

Figure 5 shows the effect of primary particle size on the $\overline{\cos\theta^*}$ vs ϕ profiles for the different mixtures. The effect of primary particle size on the $\overline{\cos\theta^*}$ vs ϕ profiles was also investigated on a further four particulate mixture systems reported in literature, (see Figure 6). Here, Cassie-Baxter Equation 3 and surface coverage wetting model Equation 14 are fitted to the $\overline{\cos\theta^*}$ vs ϕ profiles and the fitted parameters are given in Table 5.

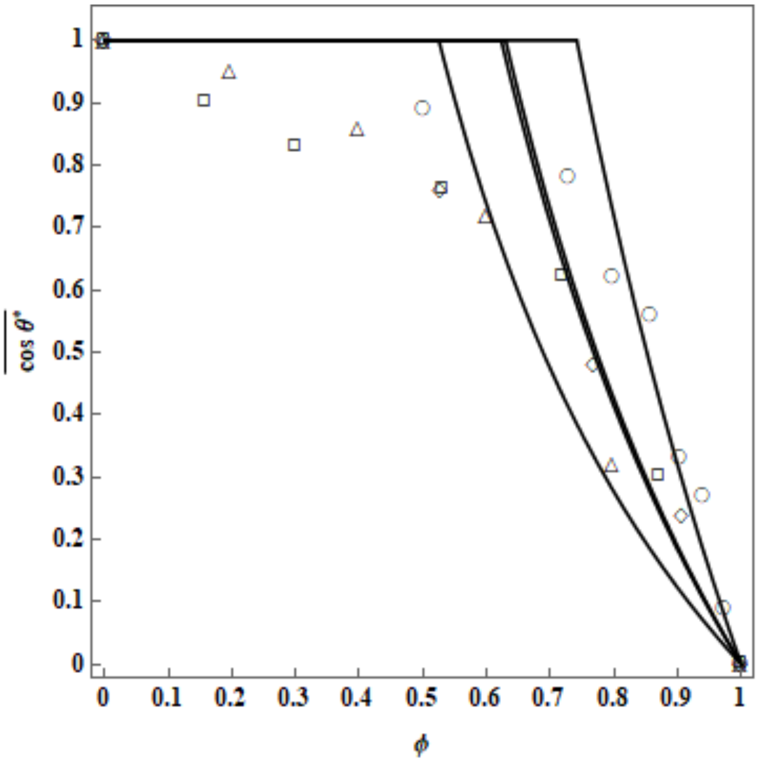


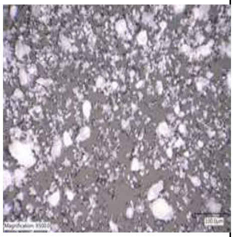
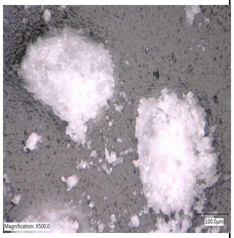
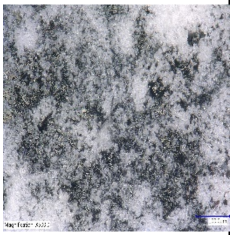
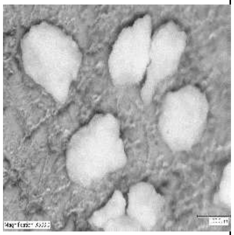
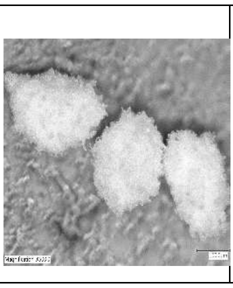
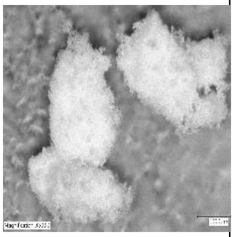
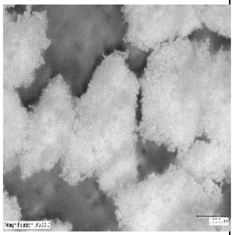
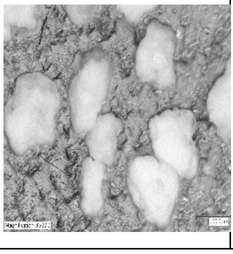
Figure 6. Analysis of experimental data reported in literature for mixtures M-6 (○), M-7 (□), M-8 (△), M-9 (⍰). The solid lines correspond to the fitted data of Equation 14 and the dashed line correspond to the expected Cassie-Baxter relationship.

It is evident that changing the primary particle size, particularly the ratio of the particle size of the two components, has a marked effect on $\overline{\cos\theta^*}$ behavior since it is this ratio that determines the extent to which surface coverage of large particles by small particles is possible, (see Figures 5-6 and Table 6).

Table 5: The fitted parameters for various two-component mixtures.

Mixture	ϕ_c	Standard Error	t-statistic	P-value
M-2	0.675	0.02	31.98	$9.95x10^{-10}$
M-3	0.489	0.02	30.24	$7.42x10^{-7}$
M-4	0.171	0.05	3.81	1.89x10-2
M-5	0.123	0.006	22.11	$5.59x10^{-7}$
M-6	0.742	0.02	34.77	$5.12x10^{-10}$
M-7	0.630	0.06	11.40	$3.38x10^{-4}$
M-8	0.623	0.044	14.05	$8.11x10^{-6}$
M-9	0.525	0.022	23.749	$2.47x10^{-6}$

Table 6. Microscopic images of particles

Lactose 200M particles	**Magnesium Stearate particles**	**Binary Mixture (coated particles) [M1]**		
				
Micronized Lactose particles	**Ethyl Cellulose particles**	**Binary Mixture (coated particles) [M3]**		
				
Lactose 100M particles	**Ethyl Cellulose particles**	**Binary Mixture (coated particles) [M5]**		
				

According to the surface coverage theory presented earlier, the critical volume fraction, ϕ_c, should depend only on the ration of the particle sizes in the two-component mixture via Equation 10. In Figure 7 the fitted values of ϕ_c are shown as a function of size ratio, as in Equation 10. It is apparent that the experimental data conform entirely to the theory. This means that $\overline{\cos\theta^*}$ behavior can be predicted from the particle size ratio without conducting extensive and expensive pharmaceutical research and development studies.

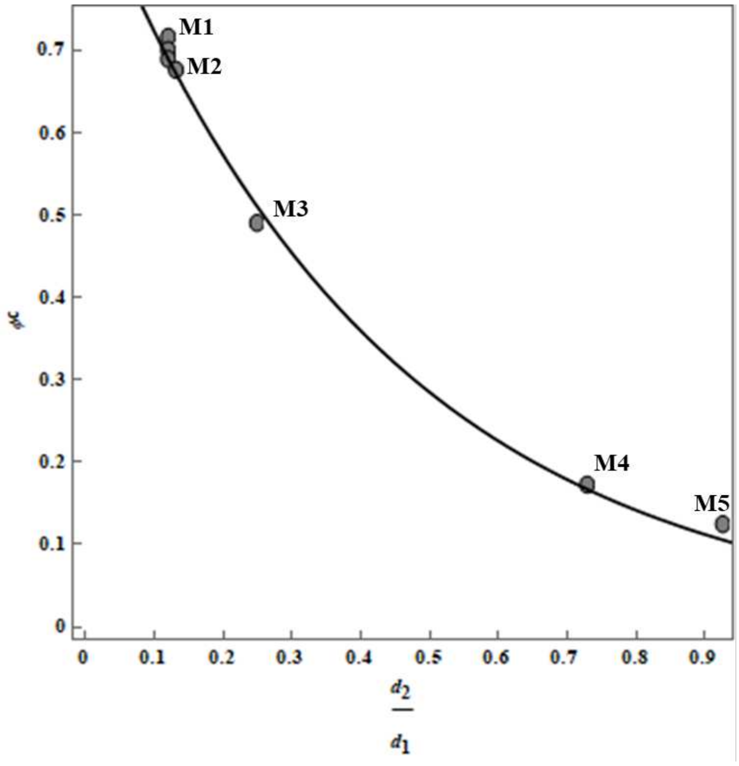


Figure 7. Effect of particle size ratio of different mixtures on ϕ_c. The line is the result predicted, without adjustable parameters, by Equation 10.

In the pharmaceutical industry, mixtures consist of components with different particle sizes, making surface coverage of one constituent over another inevitable, providing substantial motivation for the present work (see Table 6). The authors are aware that small particles usually agglomerate, and that the degree of dry coating of larger particles with smaller particles is process dependent [14,16]. However, quantification of the agglomeration effect and the extent of this influence is not within the scope of this study. In our experiments we have chosen to work on compresses formed from the binary mixtures for reasons of accuracy of measurement, rather than on loose powder beds as might be found at the point of binder addition in a granulation process. Our contention is that the proposed relationship, based on surface coverage of particles, will be useful in describing wetting of powder systems and in understanding the significant deviations from the Cassie-Baxter relationship reported in many publications. For potential future additional benefits, the surface coverage wetting model presented here may be further enhanced by unifying it with the works of Cassie-Baxter as our model required that any sort of particles will coat larges particles to a certain extent, whereas some solids might not interact in this way.

6. Conclusion

This paper considers the dependence of wetting behaviour of surfaces formed from binary mixture of particles having different sizes and wetting behaviours. Cassie and Baxter studied systems in which the components were not free to rearrange and so the surface fraction of each component was fixed and simple to determine. In seeking to apply their result to mixtures of particles it has to be assumed that the surface fraction of each component is equal to the known volume fraction; a situation that arises naturally if particles maintain a random spatial distribution, but not if some process, such as surface coating, yields a non-random spatial distribution.

In contrast, we propose that if the particles differ in size, it is possible for the small particles to coat the large particles, so reducing the available surface fraction of the large particles. In this paper we propose a simple geometrical model that relates the available surface fraction to the underlying bulk volume fractions of the components. This geometrical model depends only on the ratio of particle sizes, which in turn can be described by a critical component volume fraction at which full coverage of the larger particles by the small is achieved. We observe that with this correction, we are able to describe the wetting of two-component hydrophobic/hydrophilic systems using a range of binder solutions. We find that changing the binder concentration has little effect, despite substantial changes in viscosity.

By contrast, changing the size of the solid phase particles, and particularly the ratio of sizes of the two components, has a marked effect, since it is this ratio that determines the extent to which surface coverage of large particles by small is possible. Although many models that predict contact angle behaviour have been presented in literature, to the author’s knowledge, this surface coverage wetting model represents the first quantitative model that predicts wetting based on surface coverage of one solid by another. The objective in developing this model is to enable a simple approach to theoretical prediction, which is expected to be of value in particle wetting applications pertaining to various industries. This is especially so in the pharmaceutical industry, where wetting knowledge of solid surfaces is important in formulation development, to enable effective design of product that achieves the desired properties.

Nomenclature

Greek

Symbol	Meaning
$\boldsymbol{d}$	Sauter mean diameter
$\boldsymbol{f}$	Area fraction of components
$\boldsymbol{f_{sc}}$	Fractional surface coverage of large particles by small particle
$\boldsymbol{p_2}$	Projected area of small particles
$\boldsymbol{s_1}$	Surface area of larger particles
$\boldsymbol{\theta}$	Liquid-solid contact angle
$\boldsymbol{\theta}^*$	Apparent contact angle
$\overline{\boldsymbol{\cos\theta}^*}$	Normalized wetting parameter
$\boldsymbol{\phi}$	Volume fraction of larger particles
$\boldsymbol{\phi_1}, \boldsymbol{\phi_2}$	Volume fraction of particle types 1 and 2
$\boldsymbol{\phi_C}$	Critical volume fraction
$\boldsymbol{\gamma}$	Surface tension

Subscripts

Symbol	Meaning
1	Of particle type 1, the larger particle
2	Of particle type 2, the smaller particle
E	Equilibrium
S	Solid
L	Liquid
V	Vapour

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