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Cylindrical tube and surface tension viscous flow models in the assessment of capillary flow and liquid contact angles in pharmaceutical powders

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Summary

The validity of the cylindrical tube (CT) model for the estimation of contact angles of irregular porous media using liquid penetration data is based on the linearity of l vs $t^{1/2}$ plots which assumes the same geometric contribution for liquids exhibiting different contact angles in the same medium. In recent criticisms it was observed that conformation of penetration data to $t^{1/2}$ dependence has also been predicted for systems other than cylindrical tubes, and a method for obtaining contact angles based on surface tension viscous flow (STVF) model and scaling concepts was proposed. To assess the validity of these proposals, the rates of liquid penetration of a homologous series of alkanes, alcohol and carboxylic acids into fifteen pharmaceutical powders (Avicel PH101, Starch 1500, magnesium stearate, calcium carbonate, calcium phosphate, calcium formate, calcium acetate, calcium lactate, calcium gluconate, calcium stearate, *p*-hydroxybenzoic acid, methyl *p*-hydroxybenzoate, ethyl *p*-hydroxybenzoate, propyl *p*-hydroxybenzoate and butyl *p*-hydroxybenzoate) were determined. Contact angles were obtained according to the CT model. Plots of l vs $t^{1/2}$ were linear as predicted by the CT model. Plots of reduced distance travelled as a function of reduced time, based on the STVF scaling concepts, did not superimpose on a single curve, an indication that the systems studied were in dissimilar states, exhibiting differing contact angles. On the other hand, contact angles obtained from STVF scaling concepts were similar, thus indicating that the systems are in similar states. This contradicts the results from plots of reduced distance vs time. The inability of both approaches to reach the same conclusion questions the validity of the universal application of the STVF model. The STVF model does not adequately describe liquid-powder systems which display finite and differing contact angles when different liquids are used on the same powder. This may be due to the differences in wettability and surface energetics inherent in such systems and not necessarily because of geometric factors.

Introduction

The contact angle formed between a liquid and a solid medium provide useful information on the wettability of the solid. Contact angles are usually obtained by direct observation of a drop of liquid on a flat surface and by measurement of the height of the drop. Pharmaceutical powders exist as finely divided irregular porous solids; as a result it is not possible to carry out assessment of their contact angle by direct methods. For such systems various methods giving an indirect deter-

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mination of contact angle such as measurement of drop height on compressed discs (Heertjes and Kossen, 1967) rates of liquid penetration into powder beds (Washburn, 1921; Studebaker and Snow, 1955) have been proposed. Of these methods, liquid penetration is the only procedure to maintain the powder in its original form. The technique is based on the assumption that a bed of porous powder is effectively a bundle of cylindrical capillary tubes (capillary tube model) with an average radius r. The kinetics of liquid penetration into such a bed can be described by the Washburn equation

$$l^2 = \frac{r\gamma \cos \theta}{2\eta} t \qquad (1)$$

where l is the distance travelled by the liquid front in time, t, θ denotes the contact angle while η and γ are viscosity and surface tension of the liquid, respectively. Eqn 1 has been used to estimate contact angles by Studebaker and Snow (1955) by comparing the penetration of a non-wetting liquid with that of a liquid exhibiting zero contact angle (i.e., perfectly wetting liquid) in the same porous bed. The assumption is made that if the packing of the powder bed is reproducible the values of r will be equal in identically prepared beds. Therefore, for a perfectly wetting liquid l, ($\cos \theta = 1$) and a non-wetting liquid 2, $\cos \theta_2$ can be obtained from

$$\cos \theta_2 = \frac{\gamma_1 \eta_2 \text{gradient}_2}{\gamma_2 \eta_1 \text{gradient}_1} \qquad (2)$$

where gradient is that of a plot of l^2 as a function of t. Implicit in this reasoning is the assumption that geometric condition is the same for liquids exhibiting different contact angles in the same medium. Miller and Miller (1956) have argued that media exhibiting different contact angles are in dissimilar states, so that no appropriate comparisons can be made between them. Yang and Zografi (1986) have criticized the use of Eqn 1 and its extension (Eqn 2) to estimate contact angles in porous media consisting of powders or compacts. According to these authors, the cylindrical tube model, upon which Eqn 1 is based, does not take into account several important features of liquid flow in media consisting of pores with irregular shapes. They argued that the meniscus at the liquid-vapour interface does not move continuously through such media, but exhibits a discrete jumping movement, known as the 'Haines jump' (Haines,1927). This jumping movement, and the interconnections between the tortuous micro channels in a porous powder result in capillary pressure hysteresis during emptying and filling of pores, as the liquid penetrates. The macroscopic gradients obtained from l^2 vs t plots are related to the microscopic liquid geometry of the powders and therefore are a hysteresis function of pressure. Furthermore, in the solution of Eqn 1 it is often assumed that all of the void space behind the wetting front is completely filled with liquid as penetration proceeds downwards, i.e., that flow is fully saturated. However, the degree of unsaturation is said to vary with different physical properties of the solid-liquid systems used, e.g., contact angles.

The validity of the use of the cylindrical tube model for studying capillary flow in irregular porous powder, is often based on the observation of linearity in the plots of l^2 vs t, as predicted by Eqn 1. This has been disputed by Yang and Zografi (1986) who pointed out that conformance of penetration data to a linear plot is in fact a general mathematical property of the solution of any nonlinear diffusion equation subject to the step function boundary conditions.

In view of these criticisms, Yang and Zografi (1986) have gone further to show "the extent of the deviation to be expected when one assumes that the cylindrical tube model is applicable as in the Studebaker and Snow method (1955)", by comparing contact angles obtained from liquid penetration data to those obtained from measurements of liquid drops on flat surfaces. Although the basis for direct comparison of contact angles from these completely different methods is questionable (because the contact angles from liquid penetration are dynamic and advancing contact angles while those from stationary drops on flat surfaces are static contact angles), they concluded that liquid flow in porous powders does not follow the cylindrical tube model and therefore, contact angles obtained from the method of Studebaker and Snow do not give physically correct values. In another study by Yang et al (1988b), an empirical relationship which could be used to scale liquid-powder systems exhibiting different contact angles was proposed from scaling concepts developed from the surface tension viscous flow (STVF) model of Miller and Miller (1955a,b, 1956). It has been suggested that the cylindrical tube model be replaced by STVF model (Yang et al., 1988a).

This paper examines the reservations raised by Yang and Zografi (1986) and assesses the validity or otherwise of the STVF model of Miller and Miller (1955a,b, 1956) and its extension by Yang et al. (1988a,b) to the elucidation of contact angles.

Materials and Methods

Materials

Choice of powder media

Three groups of powder media consisting of 15 pharmaceutical powders were selected for this work. Group 1 consists of pharmaceutical excipients commonly used in the pharmaceutical industry, e.g., Avicel PH101 (FMC Corp.), Starch 1500 (Colorcon Inc.), calcium carbonate (Thew Arnott Ltd.), dibasic calcium phosphate dihydrate (K&K Greef Ltd.) and magnesium stearate (Baxeden Chemicals). In group 2 are benzoic acid and the lower members of *para*-substituted esters of benzoic acid consisting of methyl, ethyl, propyl and butyl *p*-hydroxybenzoate (Nipa U.K.). All five members in this group belonged to a homologous series. Group 3 consists of calcium salts of straight-chain or OH-substituted dicarboxylic acids, i.e., calcium formate, calcium acetate, calcium lactate (OH substitution), calcium gluconate (OH substitution) and calcium stearate (BDH). These powders were chosen as models because of their application in the pharmaceutical industry and also because of differences in their physical and wetting characteristics.

Choice of liquid media

Three groups of a homologous series of liquids were used (GPR grade from BDH). These are: (1) the saturated straight-chain alkanes consisting of hexane, heptane, octane, decane and dodecane; (2) monohydric alcohols and (3) monocarboxylic acids. The alcohols were treated with molecular sieves to remove traces of water. The densities of the liquid were determined with a pycnometer. The viscosities and surface tensions were measured for the liquids after they had been saturated with each solid using a U-tube viscometer (British standard 188; 1957) and the Wilhelmy plate method at 20°C, respectively.

Methods

Liquid penetration

The time taken for a saturated solution to travel predetermined distances in a packed powder bed were measured at room temperature (20–25°C). The powders were packed in tubes of 12 cm length having a uniform internal diameter of 1.25 cm. The tubes were coated on the inner surface with a 2% v/v solution of dimethyldichlorosilane in carbon tetrachloride to prevent preferential wetting of the glass during measurement. Segregation of the powder bed was prevented by using a tube with a small internal diameter and a low packing height (never exceeding 5 cm). During measurement the powder bed was constantly illuminated with a fibre optic cold light source, thus preventing uneven flow due to heating of the penetrating liquid. If the liquid passage was not uniform, poor packing was suspected and the result was rejected. A minimum of five and a maximum of eight replicates were performed for each powder-liquid system.

Contact angle measurements on compressed discs

Powder compacts were prepared in the punch and die systems described (Buckton and Newton, 1986) by use of a hand press. Maximum height of the drops of liquid that could be formed on the compact was measured by use of a travelling microscope. These measurements were used to calculate the contact angles, according to the method of Heertjes and Kossen (1967). The results are averages of three replicate on each of (at least) three different discs.

Results and Discussion

Capillary tube (CT) and contact angle

A critical examination of Eqn 2 reveals the presence of a 'wetting factor'

$$\frac{\gamma_1}{\eta_1 \text{gradient}_1} \qquad (3)$$

and a 'non-wetting factor'

$$\frac{\eta_2 \text{gradient}_2}{\gamma_2} \qquad (4)$$

The wetting and non-wetting factors are a unique property of the powder, which depend on the history of the geometry of the powder bed and the ratio of the viscous and interfacial forces of the test liquids. They help to set the magnitude of cos θ for a given liquid-powder system.

Similitude and scaling of surface tension and viscous flow

Following the use of a theory of capillary flow, based on the physical laws of surface tension and viscous flow (Miller and Miller, 1955a) to determine contact angles of liquid-powder systems (Yang et al. 1988b), it was considered useful to carry out calculations using data from liquid penetration experiments in order to test its application to pharmaceutical systems.

Surface tension viscous flow theory

The simplest type of porous flow solution deals with saturated media in which all pores are completely wetted. For such system Darcy (1856) demonstrated an empirical proportionality between macroscopic flow rate and driving force

$$q = k\nabla H/l \qquad (5)$$

where $\nabla H/l$ is the hydraulic gradient, q denotes the volume of liquid flowing through a cross-sectional area per unit time or flux and k is the hydraulic conductivity. Miller and Miller (1955a,b, 1956) developed a model for capillary flow phenomena. This approach, known as the surface tension viscous flow model (STVF), was based on the assumption that for an unsaturated porous medium, the shapes of the liquid-air interface are governed by the classical laws of surface tension and contact angle, while the flow patterns within the liquid filled spaces obey the hydrodynamic laws of viscous flow. They concluded that the properties of the medium such as hydraulic conductivity (k), wetness (Φ) and diffusivity (D) are functionals, which depend on the pressure history but scale invariant to monotonic time scale distortion of that history. Such time invariant functionals were described as 'hysteresis functions' symbolized by the subscript H. From these arguments Darcy's law was obtained in the form,

$$v = k_{\mathrm{H}}(P)f - \nabla P \qquad (6)$$

where f represents body forces per unit volume (i.e., gravity) and v is the flow velocity. After accounting for the conservation of matter, a combined equation analogous to that of Richards (1931) can be obtained

$$+[k_{\mathrm{H}}(P)(\nabla P - f)] = \frac{\partial \Phi_{\mathrm{H}}(P)}{\partial} t \qquad (7)$$

These results were developed in a set of reduced variables obtained from similitude analysis, permitting direct comparison of similar flow systems. Two system parameters were introduced in the STVF theory. Firstly, a microscopic characteristic length (or characteristic pore size), $\emptyset$, for comparing media, and secondly a macroscopic characteristic length, l, for comparing entire flow systems. Detailed similitude was obtained for interface shapes and for microscopic flow patterns between two media whose solid geometries differed by a constant magnifying factor. Two such media were called 'similar'. When the interface geometries are also similar the two media are said to be in similar states. Although the similar media concepts have been tested and verified using soil materials exhibiting zero contact angle (Klute and Wilkinson, 1958) and in idealized systems (Yang et al., 1988b), they have not been applied extensively to pharmaceutical powders.

Condition for similar states

A condition necessary for two similar media to be in similar states is that the reduced film curvature should be the same. Another condition for similarity of states is that the contact angle at each point in one medium must match the contact angle at the corresponding point of the other medium. This limits comparison between systems to those having the same contact angle characteristics. It has been argued that the reduced solutions for two similar media with the same contact angle will be identical. If this is true, then it should be possible to 'telescope' reduced solutions of system parameters from similar media into one another. Thus, two similar media in similar states have identical values of l^* and t^*, where from the following scaling relationships

$$l^* = l/L \tag{8}$$

and

$$t^* = \emptyset\eta/\eta L^2 \tag{9}$$

$*$ is the reduced distance, l, travelled by the liquid front during liquid penetration, L is the macroscopic characteristic length which has been set at 1 cm in order to simplify the calculations (there is no inherent scale for macroscopic length since space time is self scaled in vertical one-dimensional flow systems). t^* is the reduced time, γ denotes the surface tension, $\emptyset$ is the average particle size and η represents the viscosity. This argument was used to test the application of STVF similar media theory to the powders used in this study. Plots of l^* vs t^* should yield curves which are superimposed on a single curve. The results shown in Fig. 1a and b are typical of all powders investigated in this work.The reduced curves for a homologous series of liquid do not telescope reasonably well into a single curve for all the powders investigated. Significant deviations start to occur after the liquids have moved a distance of 1 cm irrespective of time.

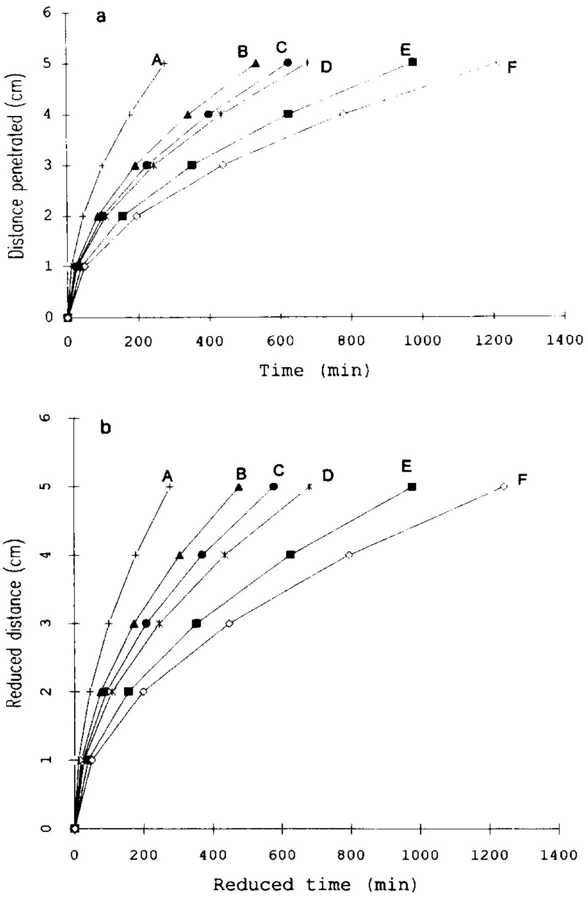

Fig. 1. Plots of (a) distance of liquid penetration vs time and (b) Plots of reduced distance of penetration vs reduced time for Avicel (A, methanol; B, ethanol; C, propanol; D, butanol; E, pentanol; F, hexanol).

According to Yang et al. (1988a,b) liquid-powder systems that exhibit different contact angle are necessarily in dissimilar states, since the liquids will occupy different stable positions in the pore openings at the same reduced system parameters. Therefore, the reduced microscopic geometries of these media will not be the same, and plots of reduced system parameters of various liquids and a particular powder combination will not telescope into a single curve.

The implications that arise from this reasoning are that the liquids used in this study have different contact angles and as a result the liquid-powder systems are in dissimilar states. Therefore, the use of the Studebaker and Snow (1955)

TABLE 1

Contact angles of various liquids on (a) calcium salts of dicarboxylic acids, (b) p-hydroxybenzoate (PHB) and its salts and (c) some pharmaceutical excipients, from compressed discs (C), from Eqn 2 (Studebaker and Snow, 1955) (S) and from Eqn 11 (Yang et al., 1988b) (Y)

Powder		Liquid					
		Hexane	Heptane	Octane	Decane	Dodecane	Water
(a) Calcium formate	S	44	66	57	47	51	0
	Y	75	76	75	75	74	75
	C	21	18	15	16	16	14
Calcium acetate	S	82	82	83	83	83	0
	Y	76	76	76	76	75	75
	C	24	27	30	22	26	27
Calcium lactate	S	82	83	83	83	83	50
	Y	76	76	76	76	76	76
	C	23	23	20	19	23	21
Calcium gluconate	S	0	33	24	29	32	83
	Y	76	76	76	76	76	76
	C	25	22	22	24	27	28
Calcium stearate	S	89	89	89	89	89	NP
	Y	76	76	75	75	66	NP
	C	48	37	39	34	36	75
(b) *p*-Hydroxybenzoate	S	0	33	53	42	26	53
	Y	75	75	75	75	74	44
	C	33	29	31	31	28	45
Methyl *p*-hydroxybenzoate	S	64	54	68	68	63	82
	Y	76	76	76	76	75	76
	C	32	33	34	35	37	50
Ethyl *p*-hydroxybenzoate	S	66	71	74	79	76	74
	Y	76	76	76	76	76	76
	C	30	30	27	28	33	41
Propyl *p*-hydroxybenzoate	S	11	0	55	50	25	36
	Y	76	76	65	76	75	76
	C	25	23	29	33	33	47
Butyl *p*-hydroxybenzoate	S	82	83	83	80	79	87
	Y	76	76	76	76	75	76
	C	20	23	28	26	26	36
(c) Avicel	S	29	23	38	0	35	77
	Y	73	74	74	72	70	75
	C	12	25	23	19	33	28
$CaHPO_4$	S	0	50	50	61	59	34
	Y	71	72	71	71	68	72
	C	19	18	23	20	26	31
$CaCO_3$	S	40	37	43	0	39	47
	Y	30	[a]	[a]	[a]	[a]	47
	C	18	20	17	21	27	30
Magnesium stearate	S	22	0	0.5	33	48	NP
	Y	74	74	74	73	73	NP
	C	30	29	26	39	37	90
Starch	S	20	36	34	0	22	90
	Y	72	73	72	69	65	74
	C	28	22	23	24	28	42

$\theta = 0$ for liquids assumed to be perfectly wetting; NP, no penetration; [a] Contact angle $\ll 0$ due to high values of reduced penetrability ($\sigma^* > 0.104$).

adaptation of the Washburn equation in determining contact angles is not correct (Yang and Zografi, 1986). To accept that these conclusions are correct, the contact angles determined from STVF scaling model must also predict that the liquid-powder systems are in dissimilar states.

Conditions for dissimilar states

It can be argued that for similar media in dissimilar states, i.e., liquids penetrating the same powder, which display finite contact angles ($\theta > 0$), contact angles calculated from reduced penetrability, σ^*, should be different for each liquid where,

$$\sigma^* = \frac{\sigma\eta}{\emptyset\gamma} \tag{10}$$

σ is the gradient of l vs $t^{1/2}$. There is no properly defined theoretical relationship between penetrability and contact angle. However, Yang et al. (1988b) have proposed an empirical relationship

$$\sigma^* = \left[1.151 \times 10^{-2} \cos(1.186\theta) - 5.419 \times 10^{-4} \cos(3.5523\theta)\right]^{1/2} \tag{11}$$

This was based on the assumption that contact angles on flat surfaces are most likely to be closer to the true contact angles than those obtained using Washburn equation. Eqn 11 was used to calculate the contact angles of the liquid-powder systems investigated (see Table 1a–1c). There is very little difference between contact angles for liquid-powder systems for the groups of homologous series of liquids used. Therefore, the liquid-powder systems considered are similar media in similar states, and following the reasoning of Yang et al. (1988b), the use of the Washburn equation to determine contact angles is valid. This is contrary to the conclusion that may be drawn from the fact that plots of reduced distance as a function of reduced time (Fig. 1b) do not superimpose on a single curve for any group of homologous series of liquids studied, i.e., that the liquid-powder systems are in dissimilar states.

This inability of the two approaches to reach the same conclusions despite the fact that both are founded on the STVF scaling concepts questions the validity of a universal application of the STVF scaling model to all liquid-powder systems. There is also the conceptual problem raised by Yang et al. (1988b) in the use of an empirical relationship (Eqn 11), derived solely on the assumption that contact angles obtained from flat surfaces can be used to extrapolate penetration rates in porous media. This is further exacerbated by the fact that cos θ obtained from compressed discs of powders are not equal in value to those from Eqn 11 (see Table 1a–c). Eqn 11 cannot be expected to give the correct values of finite contact angles and penetration rates for pharmaceutical powders. There is need to exercise caution in predicting the magnitude of contact angles that may be derived from liquid penetration data by use of contact angle data derived from liquid drops on flat surfaces. This view is supported by the results in Table 1a–c which show that experimentally determined values of contact angles are not similar for both methods.

Surface tension viscous flow model vs cylindrical tube model

From the results of the present experiments, and those of other workers (Klute and Wilkinson, 1958; Elrick et al., 1959) it seems that whenever the STVF theory has been applied under non-ideal conditions, i.e., liquids having finite contact angles and powders having a broad spectrum of shape and size distribution, deviations from theory have been observed. This observation does not invalidate the use of the cylindrical tube model in the determination of contact angles. Similar media concepts seem to be valid for liquid-powder systems where cos $\theta = 1$ or are equal and when the medium is homogeneous. Failure of the STVF model to describe adequately liquid-powder systems which display finite and differing contact angles when different liquids are used on the same powder may be due to the difference in wettability and surface energetics that is inherent in such systems and not necessarily because of geometric factors.

The reproducibility of liquid penetration rates in powder beds packed under the same conditions in this study, confirms the uniformity and reproducibility of packing and by implication the validity of the assumption of Studebaker and Snow (1955) that the unknown geometric factors associated with the porous powder can be cancelled out when results of two liquids on the same powder bed are considered. It follows therefore that after taking surface tension and viscosity into account, differences in penetration rates will be due to differences in wettability and surface energetics which are epitomized by the differences in contact angles.

These arguments together with the role played by the non-wetting factor ($\eta_2 \text{gradient}_2/\gamma_2$) in the determination of rank order of finite contact angles from liquid penetration data described earlier, indicate the validity of Studebaker and Snow's adaptation of the Washburn equation and opens to question the application of the STVF scaling model to liquid penetration data. In fact the non-wetting factor is similar to the scaling factor (Eqn 10) used by Yang et al. (1988b) to describe reduced penetrability, with the exception of their introduction of a characteristic microscopic length (i.e., particle size). Plots of η_2/γ_2 from the non-wetting factor in Studebaker and Snow's equation vs the scaling factor used by Yang et al. (1988b) indicate a linear relationship (Fig. 2), providing further evidence of their similarity.

Conclusion

It seems that the penetration gradient of the non-wetting liquid in Studebaker and Snow's equation has been inadvertently scaled, by the introduction of η_2/γ_2 in Eqn 2, thus accounting for the effect of surface tension and viscous forces. Furthermore, the possible geometric effects have been accounted for by using powder beds in similar states of packing. Therefore, the use of Studebaker and Snow's adaptation of the Washburn equation is appropriate and of value in the comparison of contact angles and the wettability of powders. However, it should be noted that values of contact angles obtained from Studebaker and Snow's method may be treated as relative contact angles except in the special case were cos $\theta = 1$ for the perfectly wetting liquid.

Whenever the STVF theory is applied to liquids having finite contact angles and powders having a broad spectrum of shape and size distri-

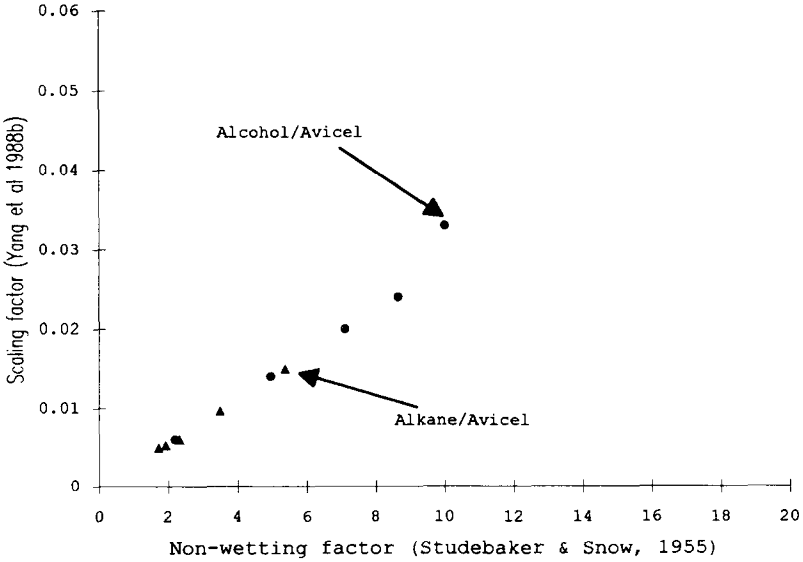

Fig. 2. Scaling factor from Yang et al (1988b) as a function of non-wetting factor from Studebaker and Snow (1955) for some liquid-powder systems.

bution, deviations from theory are observed, due to differences in wettability and surface energetics of the systems and not necessarily because of geometric factors.

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