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Effects of surface roughness on advancing and receding contact angles *

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Summary

The ability of liquid drops to advance and recede over a solid surface of varying surface energy and roughness, including drugs compacted into disks, has been investigated by measuring advancing and receding contact angles. For the relatively non-polar solids used in this study, roughness of the type encountered in pharmaceutical systems produces significant contact angle hysteresis by primarily affecting the receding angle. Despite the apparent random nature of the surface roughness of compacted disks, it is concluded that the concentric groove model by Shuttleworth and Bailey (Disc. Faraday Soc., 3 (1948) 16) best describes the effect of roughness qualitatively. In view of the relatively small effect of such roughness on advancing contact angles, it is concluded that such angles measured on highly compressed disks generally can be taken to be reasonable estimates of the intrinsic equilibrium contact angle.

Introduction

Many processes of pharmaceutical interest involve the wetting and spreading of a liquid over a solid surface with the displacement of air or a second immiscible liquid. Such processes include: dispersion of powders; disintegration and dissolution of solid dosage forms; and polymer film coating of tablets and granules. Two factors

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are important in determining the tendency for wetting to occur. One, is the surface energy of the solid–vapor interface, γ_{SV}, in relationship to the surface energies of the liquid–vapor, γ_{LV}, and solid–liquid, γ_{SL}, interfaces, as expressed by the Young equation, which relates intrinsic contact angle, θ_e, to those parameters:

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

The second factor is the geometry of the solid surface as represented by the degree and type of roughness of the surface or the degree and type of porosity. The first factor is an intrinsic property of the solid–liquid combination; the second depends on the previous treatment and handling of the solid sample.

To gain some insights into the intrinsic wettability of various pharmaceutical solids, e.g. drugs or excipients, contact angles have often been measured by placing a liquid drop on disks prepared by compression of powder under high pressure (Zografi and Tam, 1976). Although the powder is compressed until no difference in contact angle is noted, there remains the possibility that roughness of the surface caused by the compaction process and the discrete nature of the particles will have some influence on the observed angle. In a more practical situation, roughness of tablet surfaces could play a role in determining the wettability of coating liquids applied during the process of polymer film coating, particularly as it might affect the adhesion of the film to the solid surface (Rowe, 1978).

The effect of roughness on contact angles is best seen from the hysteresis which occurs when advancing contact angles, θ_A, are compared to receding contact angles, θ_R. The hysteresis, H, is defined as:

$$H = \theta_A - \theta_R \tag{2}$$

since θ_A is always greater than θ_R.

From theoretical studies of idealized rough surfaces with concentric grooves, of the type shown in Fig. 1A and 1B, it is generally assumed that the concentric layers of peaks and grooves act as energy barriers for the movement of an advancing and receding drop (Shuttleworth and Baily, 1948; Johnson and Dettre, 1964a; Huh and Mason, 1977). The equilibrium positions of the drop in both cases are assumed to be primarily dependent on the idealized slope angle, α_m, shown in Fig. 1, such that:

$$\theta_A = \theta_e + \alpha_m \tag{3}$$

$$\theta_R = \theta_e - \alpha_m \tag{4}$$

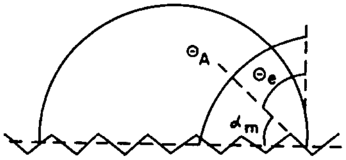
where θ_e is the intrinsic angle.

Although this is a highly idealized model, a few experiments have shown that contact angles do change with moderate roughness in the predicted direction (Bartell and Shephard, 1953; Dettre and Johnson, 1964; Neumann et al., 1971). If the roughness becomes great enough so as to essentially produce a porous surface, then in effect, one has a heterogeneous surface consisting of patches of solid and air, having fractional surface areas of f_s and f_a, respectively. In such cases, the observed contact angle θ_m, can be estimated from the Cassie-Baxter equation (Cassie and Baxter, 1944) where:

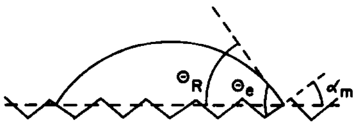
$$\cos \theta_m = f_s \cos \theta_e - f_a \tag{5}$$

This predicts an increase in the value of θ_m with increasing f_a, but does not predict hysteresis. At very high levels of roughness, indeed, θ_m, obtained from *both* advancing and receding contact angle measurement does increase (Dettre and Johnson, 1964).

Recent theoretical and experimental studies have shown that the spreading of a liquid over a rough surface is also highly dependent on the orientation and texture of the roughness, particularly the presence of sharp edges with > 0.05 μM step-heights in the case of concentric grooves. Huh and Mason (1977), for example, have shown theoretically that when a liquid front encounters a sharp edge, it will stick to that edge and an equilibrium contact angle will not be observed. Thus, in the process of advancing and receding liquids over a rough surface, intermediate states of a non-equilibrium nature may exist. This can give rise to 'stick-jump' phenomena or discontinuous movement of the drop, as well as the measurement of contact angles intermediate to θ_A or θ_R. Oliver et al. (1980) have demonstrated experimentally that this does occur with well-defined concentrically grooved surfaces. On the other hand, radial grooves which lie parallel to the movement of liquid provide channels for



(A) Advancing Drop



(B) Receding Drop

Fig. 1. Effect of roughness on contact angle for (A) advancing and (B) receding sessile drops, according to the model of Shuttleworth and Bailey (1948).

spontaneous capillarity, the extent of which depends on the degree of curvature in the channel. In a randomly roughened surface, such as with a tablet or compressed disk, therefore, it is possible that a drop would spread assymetrically, favoring some movement through parallel grooves.

With this perspective in mind, therefore, it seemed of some importance to explore more closely the effect of surface roughness on contact angle, where the roughness approximates the random type seen with pharmaceutical compacts. Studies were first carried out using chemically well-defined non-compacted solids (paraffin, polymethylmethacrylate and polytetrafluoroethylene) made in smooth and rough forms. Comparisons were then made with selected hydrophobic drugs prepared as compressed disks.

Experimental

Materials

The solids used in this study were: paraffin (PF); polymethylmethacrylate (PMMA); polytetrafluoroethylene (PTFE); griseofulvin; hydrocortisone; and indomethacin. PF was used in the form of sheets [1]; previous studies have shown the same contact angles as block paraffin (Zografi and Yalkowsky, 1974). PF samples used as received are referred to as 'smooth PF', while samples subjected to gentle surface abrasion are referred to as 'rough PF.' PMMA was used in two forms, a relatively smooth form [2] and one made rough by cutting through the cross-section of a cylindrical rod of PMMA [3]. Similarly, a smooth form of PTFE tape [4] was compared to a form made rough [5] in the same manner as with the rough PMMA. The three powdered drugs were compressed to form disks: griseofulvin [6] at 7000 and 25,000 PSI; indomethacin [7] at 25,500 PSI; and hydrocortisone [8] at 51,000 PSI.

Scanning electron micrographs [9] of these solid surfaces are given in Figs. 2 and 3. Gold and gold–platinum sputtered samples were subjected to voltages of 10 kV. From stereo-paired photographs it was estimated that no surface labeled 'smooth' exhibited steps or depressions greater than 0.4 μM, and usually much less, whereas those surfaces labeled 'rough,' had steps and depressions which covered the range of 5–20 μM. The three compressed disks all exhibited surfaces in the 'rough' category (> 1 μM).

It must be stressed that no attempt was made to quantitatively classify the extent and type of roughness. Rather, the emphasis was on choosing solids of reasonably

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[1] Parafilm M, American Can Company, Greenwich, CT.

[2] Acrylite, CY/RO Industries, Wayne, NJ.

[3] Glasflex Corporation, Stirling, NJ.

[4] University of Wisconsin Stores.

[5] University of Wisconsin Physics Shop.

[6] Griseofulvin USP, Schering Corporation, Kenilworth, NJ.

[7] Merck Sharp and Dohme, West Point, PA.

[8] Sigma Chemical Company, St. Louis, MO.

[9] JEOL JSM-35c Scanning Microscope.

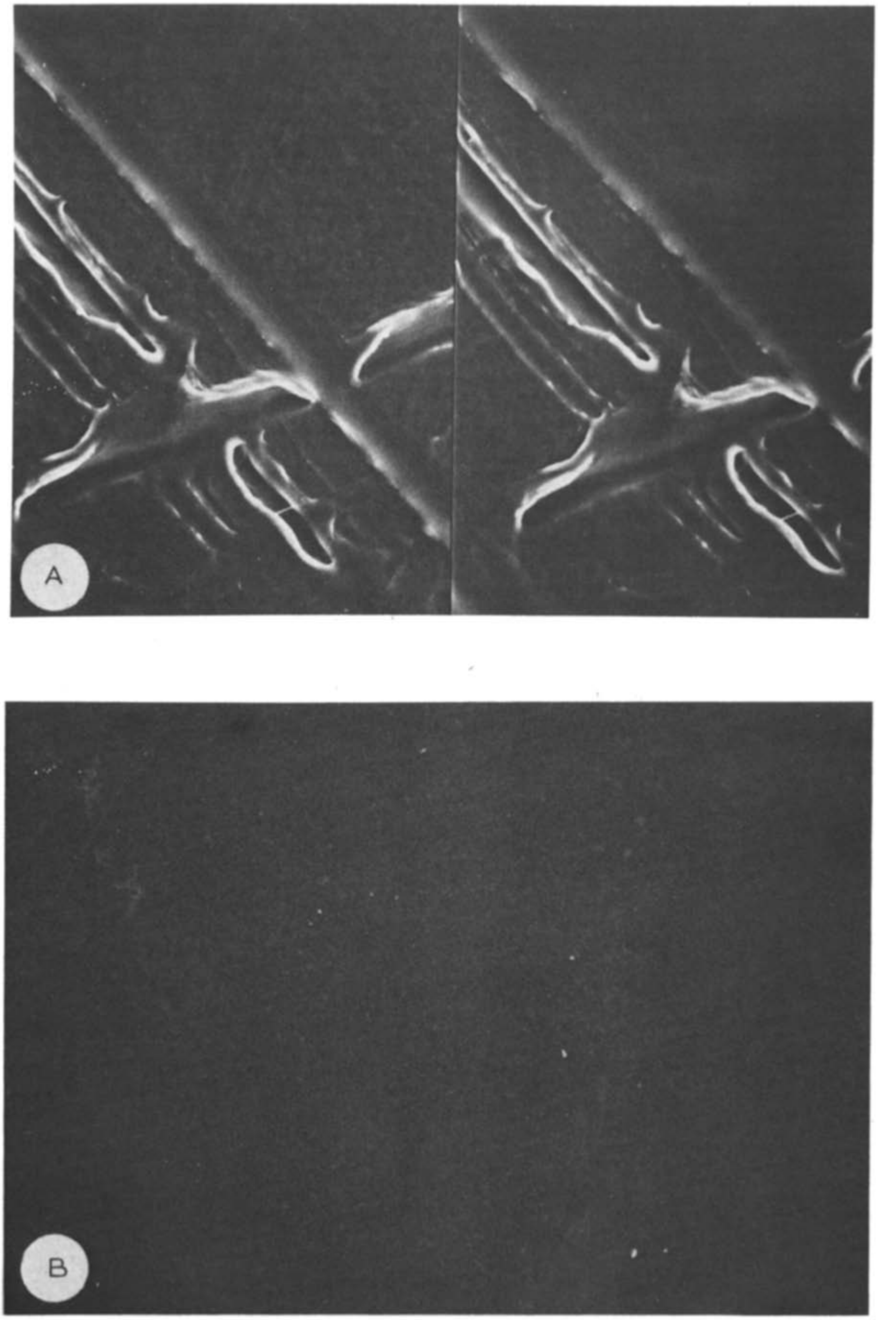

Fig. 2. Scanning electron micrographs of model surfaces. A: 'rough' PF (480×). 'Smooth' PF is characteristic of the right hand corner of 'Rough' PF. B: 'smooth' PMMA (2040×). C: 'rough' PMMA (2040×). D: 'smooth' PTFE (440×). E: 'rough' PTFE (500×).

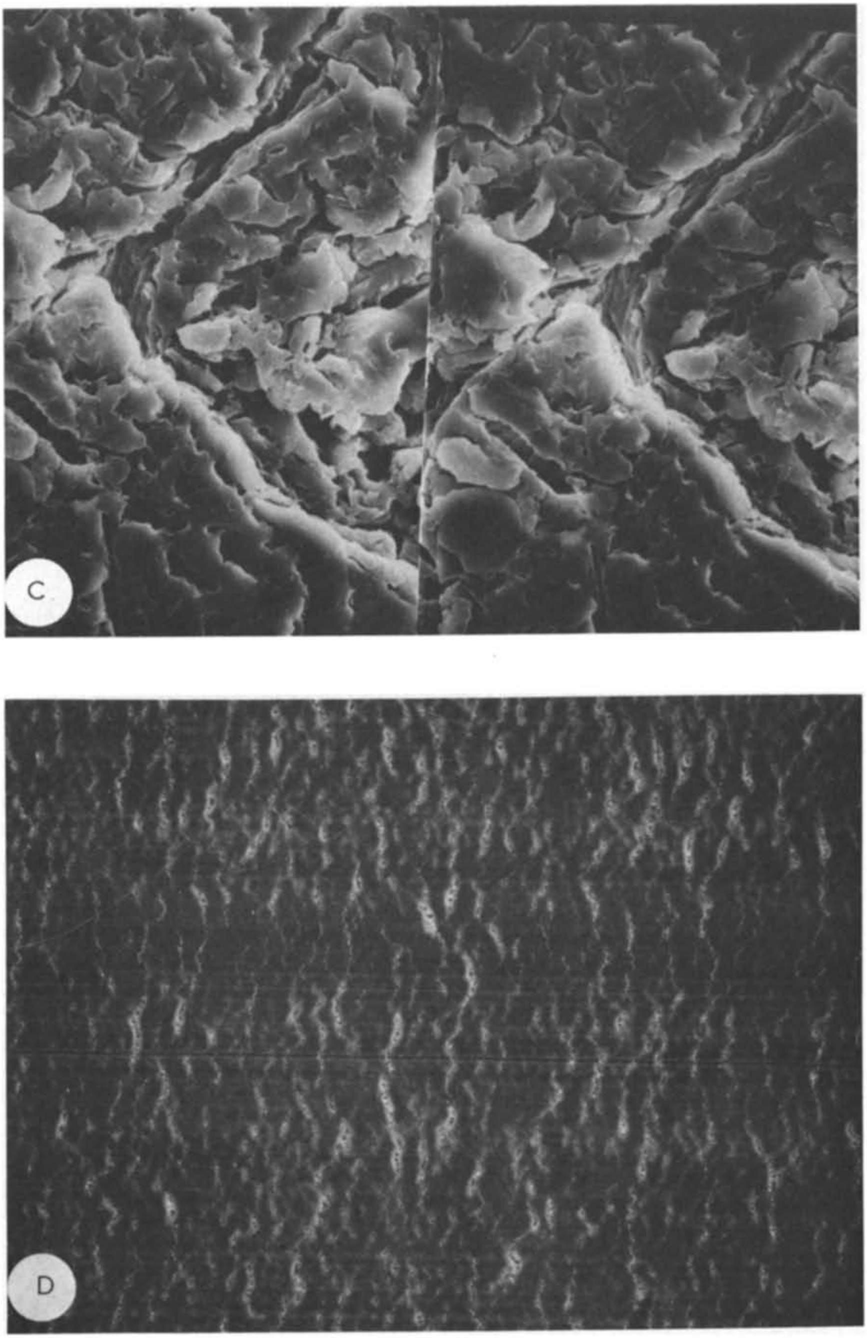

Fig. 2. continued.

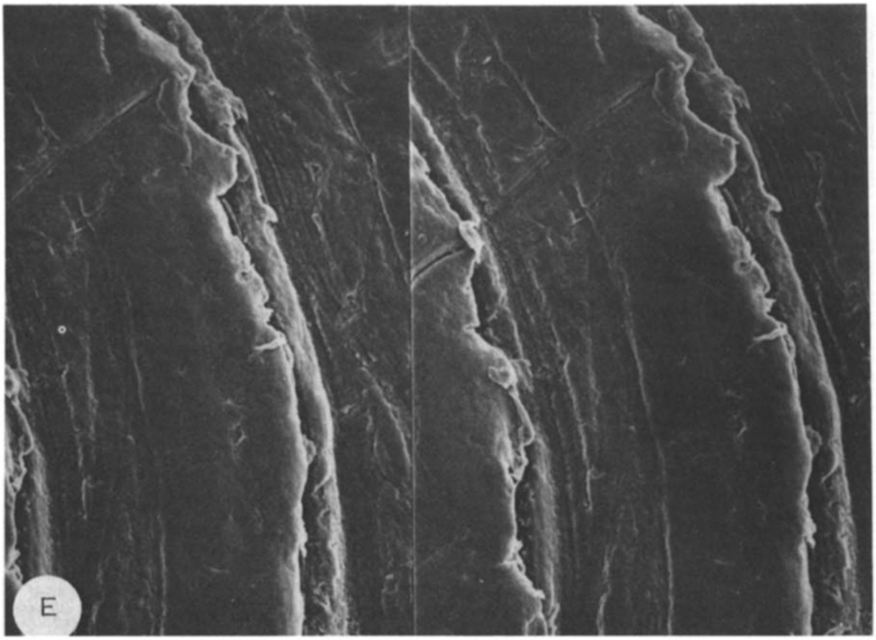

Fig. 2. continued.

well-defined surface energy made into samples differing primarily in their degree of roughness (PF, PMMA and PTFE) and comparing them with some typically poor wetting pharmaceutical materials, prepared as compressed disks.

The two liquids used in this study were triple-distilled water and ethylene glycol [10]. The surface tensions of these liquids at 25 °C, measured with a Wilhelmy plate apparatus [11], were in good agreement with literature values (Zografi and Yalkowsky, 1974). In the case of the compressed disks, a saturated aqueous solution of the particular drug was used to prevent dissolution of the solid.

Contact angle measurement

A chamber consisting of an air-tight plexiglass box of inner dimensions 15 × 15 × 15 cm, was built to allow control of the environment surrounding a drop during contact angle measurement. Several beakers filled with test liquid were placed inside the chamber to maintain a saturated atmosphere to prevent evaporation. The temperature inside the chamber near the drop was maintained at 25 ± 0.2°C by circulating water through copper tubing. Details of the apparatus are presented elsewhere (Johnson, 1982).

A known volume of test liquid was either added or removed using a syringe assembly [12] fitted with an Agla micrometer head and holder [13]. Advancing and

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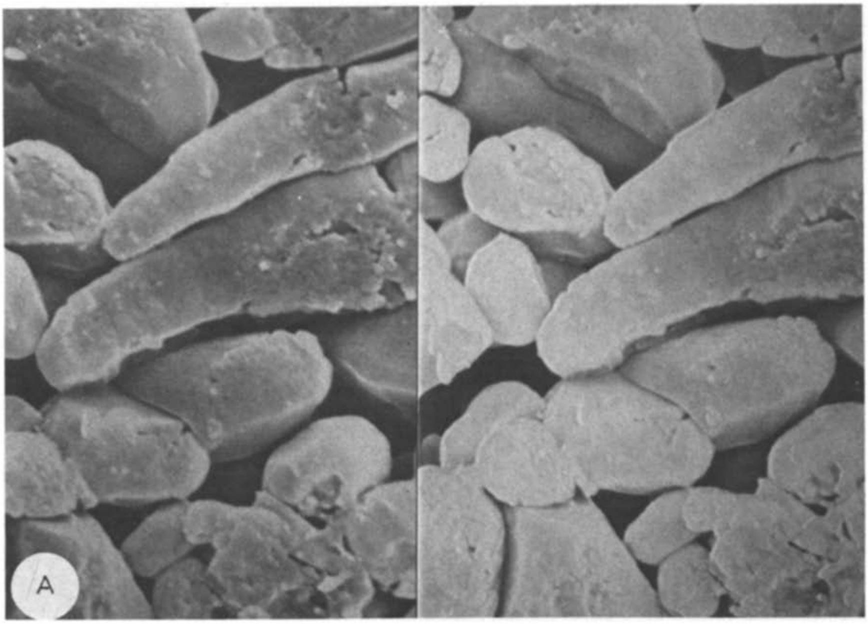
[10] Ethylene Glycol, Aldrich Chemical Company, Milwaukee, WI.

[11] Roller-Smith Precision Balance, Federal Pacific Electric Company, Newark, NJ.

[12] Hamilton Company, Reno, NV.

[13] Burroughs Wellcome and Company, London, U.K.



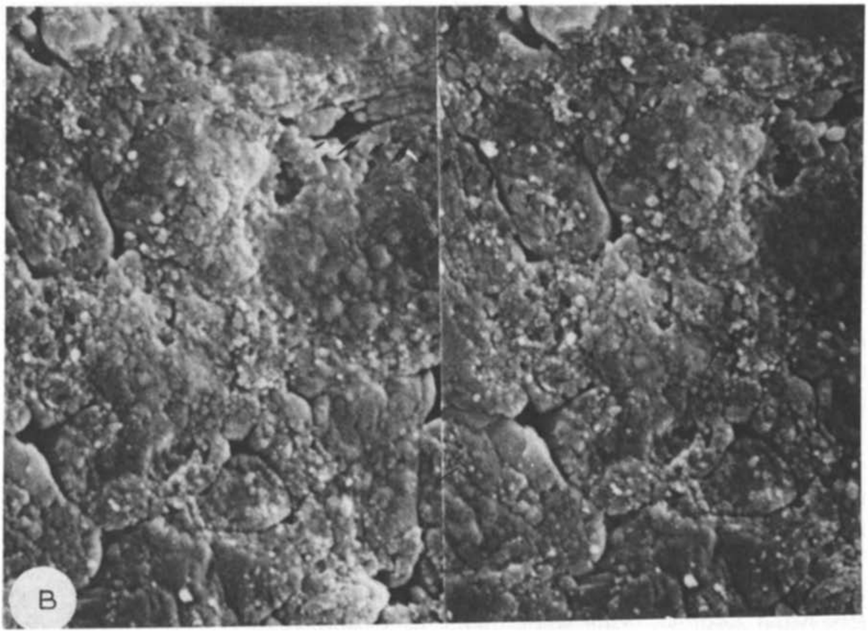


Fig. 3. Scanning electron micrographs of compressed disks. A: griseofulvin at 7,000 PSI (11,750×). B: griseofulvin at 25,000 PSI (11,500×). C: Indomethacin (9750×). D: Hydrocortisone (9750×).

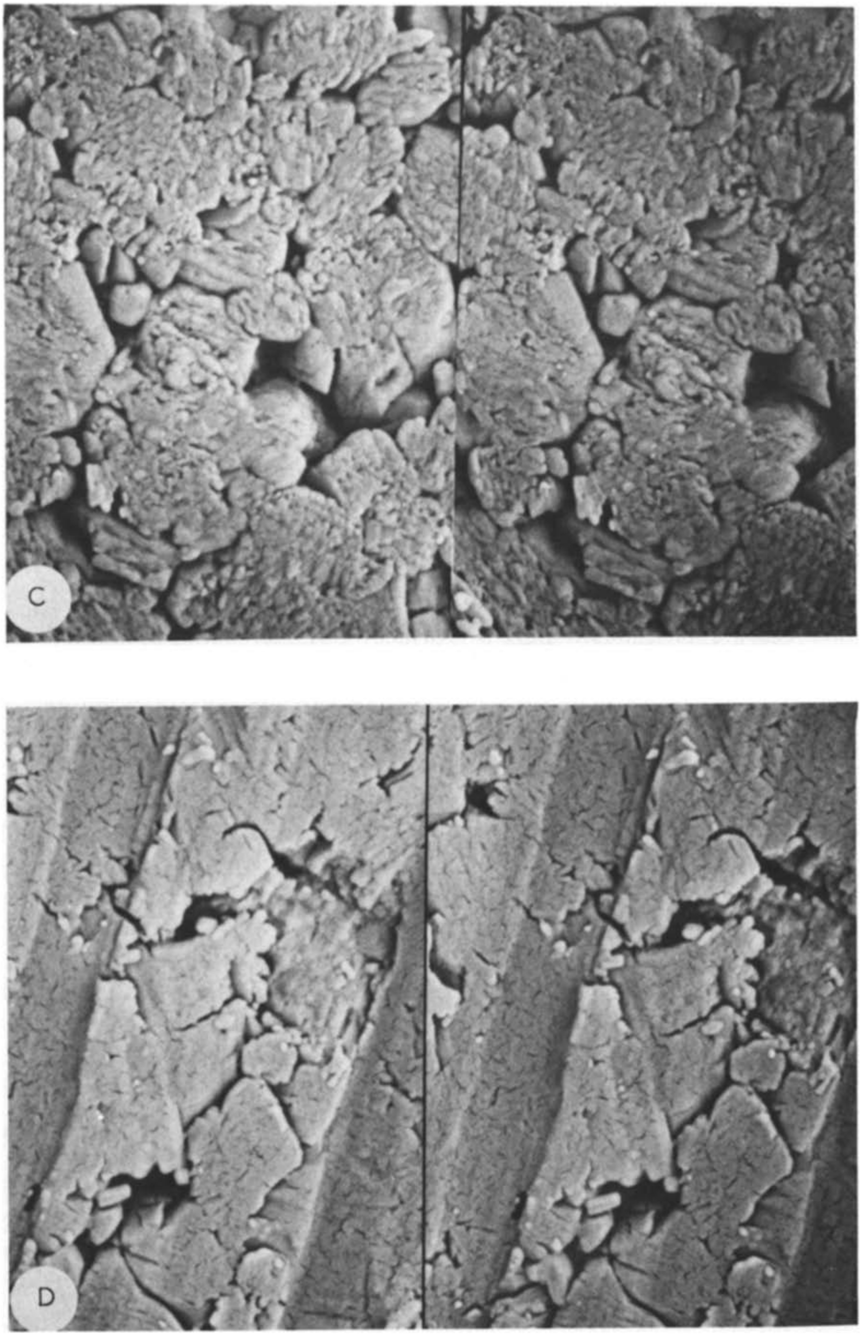


Fig. 3. continued.

receding angles on the same drop were measured in one of two ways. In method A the syringe needle was placed close to the surface and the drop was slowly applied. The needle remained in contact with the drop so that any desired amount of liquid could be removed or added. Method B, adapted from the work of Oliver et al. (1980), consisted of delivering the liquid from below the sample through a 1 mm hole. To do this the apparatus was designed so that the hole extended down through the support base upon which the sample sits. A 20-gauge Teflon tube [14] needle with luer hub attached to the micrometer syringe provided the means of continually delivering or removing an accurate volume of liquid.

The sessile drop, sitting on a solid, was viewed through a glass window using a goniometer-telescope [15]. Contact angles were read directly to the nearest 0.1° from each side of the drop. One minute was usually sufficient time for equilibration when using water and ethylene glycol. Several readings were made on the same drop and an average taken. The final contact angles reported represent the average of such values obtained with different solid samples. They generally had a standard deviation of 1–2°.

Results

Preliminary studies on ‘smooth’ paraffin surfaces were carried out to evaluate the apparatus and the two methods of delivering or removing liquid, and no significant differences in contact angles were observed. Also as part of the evaluation process, contact angles of water on all solid surfaces were measured as a function of drop volume. The procedure involved placing a drop on the surface and measuring the advancing angle after increments of liquid were added, using method A. At a certain point the drop volume was decreased to volumes at which advancing angles had previously been measured. In this way it was possible to observe hysteresis for drops of equal volume, one in an advancing mode and the other in a receding mode. Selected comparisons using method B gave results in very good agreement with method A, so method A was the method used unless otherwise indicated.

Comparison of results obtained with the various smooth solid samples in Table 1 leads to a number of interesting observations. (1) Some hysteresis still exists, as might be expected for a chemically heterogeneous surface (Johnson and Dettre, 1964b). (2) As expected if chemical heterogeneity was a factor, hysteresis is greatest for the more polar PMMA sample than for PF or PTFE. (3) Values of θ_A and θ_R appear relatively independent of drop volume for any one solid sample. For ‘rough’ surfaces it appears that: (1) hysteresis is much greater than for ‘smooth’ surfaces; (2) the hysteresis appears to be greater for smaller drop volumes; (3) hysteresis appears to become constant with decreasing volume in the case of PF and PTFE, but not for PMMA [16]; and (4) the changes in hysteresis in all cases appear to primarily reflect

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[14] Hamilton Company, Reno, NV.

[15] Gaertner Scientific Corporation, Chicago, IL.

[16] For the ‘rough’ PMMA sample a constant value of 20° for the contact angle with water was reached with further decrease in the drop volume.

TABLE 1

ADVANCING AND RECEDING CONTACT ANGLES AS A FUNCTION OF WATER DROP VOLUME

Paraffin (Smooth)			PMMA (Smooth)			PTFE (Smooth)		
Volume (μl)	θ_A	θ_R	Volume (μl)	θ_A	θ_R	Volume (μl)	θ_A	θ_R
20	108°	96°	17	77°	50°	26	114°	99°
30	108°	96°	34	75°	49°	34	114°	101°
40	108°	98°	51	77°	54°	43	118°	104°
50	108°	–	77	76°	–	51	118°	111°
						60	119°	–

Paraffin (Rough)			PMMA (Rough)			PTFE (Rough)		
Volume (μl)	θ_A	θ_R	Volume (μl)	θ_A	θ_r	Volume (μl)	θ_A	θ_R
34	111°	77°	34	82°	27°	34	119°	65°
51	114°	78°	51	84°	47°	43	118°	68°
68	113°	86°	68	85°	61°	51	120°	71°
85	111°	101°	85	84°	73°	68	118°	83°
102	112°	–	102	84°	–	85	119°	95°
						102	118°	–

TABLE 2

EQUILIBRIUM ADVANCING AND RECEDING CONTACT ANGLES AT 25°

Solid/Liquid	Contact Angles						References
	Smooth		Rough		Literature[a]		
	θ_A	θ_R	θ_A	θ_R	θ_A	θ_R	
PF/water	108°	96°	110°	77°	110°	99°	Bartell and Shepard, 1953
PTFE/water	118°	97°	118°	63°	117°	96°	Good and Koo, 1979
PMMA/water	76°	52°	85°	20°	74°	51°	Dann, 1970
PF/ethylene glycol	82°	73°	84°	60°	83°	–	Dann, 1970
PTFE/ethylene glycol	93°	79°	95°	45°	92°	79°	Good and Koo, 1979
PMMA/ethylene glycol	54°	38°	51°	~0°	52°	–	Dann, 1970

[a] Literature values appear to have been obtained with a degree of 'smoothness' comparable to 'smooth' samples in this study.

changes in the receding angle since changing drop volume does not seem to significantly affect the advancing angle.

Table 2 presents equilibrium advancing and receding angles determined to be independent of volume for the various surfaces. Again, it is clear that the advancing angles for PF and PTFE are not greatly affected by the change from a 'smooth' to a 'rough' surface, but that receding angles are greatly affected by roughness. A small effect on advancing angle apparently due to roughness is seen with PMMA, but again the effect on receding angle is much greater. It is also possible that the smooth and rough PMMA surfaces exhibit some difference in the chemical nature of their surface groups which could give rise to a small change in the intrinsic contact angle.

In order to further analyze the factors influencing receding angles on these rough surfaces, a number of more detailed experiments were carried out. Using method A it was possible to increase or decrease the drop volume in small increments, such that the volume was known, and to measure both the contact angle and drop dimensions; i.e. the width of the drop base in contact with the solid for each volume. Results typical of all surfaces studied are shown in Table 3. Note that starting with a 26 μl drop and going up to 43 μl in an advancing mode produces reasonably constant contact angles and the expected increase in drop base dimension needed to maintain the constant contact angle with increasing volume. When the drop volume is reduced, hence the drop is put into a receding mode, different behavior is observed depending on the volume of drop remaining. From 43 μl to about 9 μl the contact angle decreases, but the width of the drop base does not change. Hence the contact angle decreases to accommodate the changing volume of liquid. This lack of

TABLE 3

ADVANCING AND RECEDING CONTACT ANGLES FOR ETHYLENE GLYCOL ON ROUGH PTFE AT 25° AT VARIOUS DROP VOLUMES

Drop volume (μl)	Contact angle	Drop base (mm)
26	91°	5.0
34	95°	5.5
43	93°	6.3
34	83°	6.5
31	78°	6.4
26	72°	6.4
22	68°	6.6
17	61°	6.3
14	57°	6.5
9	51°	6.3
5	49°	5.8
4	47°	5.4
2	47°	5.4
9	51°	5.3
26	54°	5.4
43	88°	5.5
60	95°	6.2

base width change with changing volume has been referred to as 'hinging' since the angle changes without movement of the drop base (Oliver et al., 1980). Fig. 4 schematically represents what is occurring during the 'hinging' process, as compared to the point where the static receding angle has been reached.

In Table 3 it can be seen that further reduction of the drop volume below 9 μl leads to a relatively constant receding angle of about 47° and the movement of the drop base to a smaller width. This is taken as the true receding angle for the sample. Reintroduction of liquid up to the original volume of 43 μl produces hinging and an accompanying increase in contact angle to a value which is close to the original advancing angle. Further increases in volume produce the static value of θ_A and the expected drop width increase. Thus, as long as the drop volume is such that static advancing and receding angles cannot be assumed, artificial angles will appear due to the phenomenon of hinging. Comparison of the different systems varying in surface energy and roughness, in Table 2 with both water and ethylene glycol, clearly indicates that the greater the roughness the greater the tendency to hinge and produce large values of hysteresis. Throughout these studies no effect due to time or the method used was observed.

To further confirm this observation, drops of water on various solids were allowed to evaporate slowly from a solid surface while receding contact angles and base widths were measured. As seen in Table 4 for water evaporating from the 'rough' PTFE surface some hinging occurs as in Fig. 4A from 102 μl to about 27 μl, at which point the static value of θ_R is reached. At subsequent time periods the drop continues to evaporate with its base receding and its θ_R remaining constant as shown in Fig. 4B. As a point of comparison, note in Table 5 that all of the compressed disks with advancing contact angles in the range of 60–73° exhibited a 0° receding angle. Griseofulvin compressed to the two pressures gave essentially the same

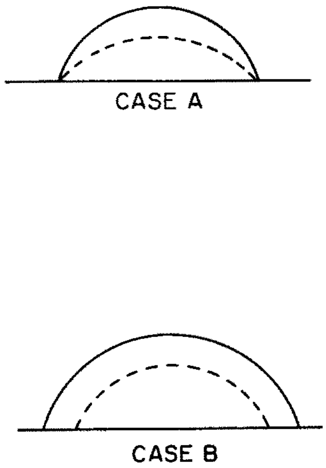

Fig. 4. Receding contact angle behavior. Drop profile changes from solid line to dashed line when the drop volume decreases. Case A: hinging. Case B: equilibrium values of θ_A and θ_R have been attained.

advancing contact angle, despite some change in roughness due to compressional force.

Discussion

The results of this study have a number of important implications for the evaluation of wetting in pharmaceutical systems. In all of the systems studied a significant contact angle hysteresis occurs primarily because of roughness effects on the receding angle, θ_R. This great sensitivity of the receding angle is important since it can lead to zero contact angles if the equilibrium advancing angle, θ_A, is about 70° or less, as is the case for most drugs (Zografi and Tam, 1976). That this effect is primarily a function of roughness is seen in Table 6, where $\Delta\theta_R$, the change in receding contact angle from smooth to rough surfaces is shown to be relatively independent of the liquid being used. The fact that advancing contact angles are not as greatly affected by roughness as the receding angle for the types of systems used in this study, including griseofulvin compressed to different pressures, indicates that

TABLE 4

RECEDING CONTACT ANGLE WITH EVAPORATION OF A WATER DROP ON ROUGH PTFE AT 25°

Volume (μl)	Contact angle	Drop base (mm)
102	113°	7.0
91	110°	6.9
78	102°	6.7
71	95°	6.7
64	88°	6.8
49	80°	6.6
44	71°	6.8
35	64°	6.6
27	61°	6.0
22	60°	5.6
17	58°	5.3
11	58°	4.4

TABLE 5

CONTACT ANGLES[1] ON COMPRESSED DISKS OF VARIOUS DRUGS

	θ_A	θ_R
Hydrocortisone	60°	~ 0°
Indomethacin	73°	~ 0°
Griseofulvin	65°	~ 0°

[1] Liquids were saturated solutions of each drug

advancing angles can be used as a reasonable estimate of the equilibrium intrinsic angle. On the other hand, the receding angle should not be used to imply anything about the surface energetics of a drug or excipient. It can be used, however, as a useful indication of degree of surface roughness. Another important conclusion to draw from these studies is that considerable error in contact angle measurement can inadvertently occur if liquid drops are allowed to evaporate to an extent where 'hinging' occurs due to geometrical factors.

Considering the complex and random nature of the roughness patterns seen in Figs. 2 and 3, it is interesting to note that in all cases drops placed on such surfaces appeared to spread out and recede quite symmetrically. This indicates that significant spreading into radial channels does not occur and that the concentric groove model is a reasonable model for liquid wetting in such cases. Indeed, the 'stick-jump' behavior, reflective of a concentric groove model (Huh and Mason, 1977), was observed in all cases, and advancing and receding angles changed in the directions predicted. This would not be so for θ_R, for example, if one assumed that Eqn. 5 (Cassie-Baxter equation) was applicable, since in that case the increase in roughness would be expected to increase θ_R, rather than decrease it (Dettre and Johnson, 1964). Along these lines, Carli and Colombo (1982) recently measured the effect of porosity of magnesium stearate and Eudragit GL tablets on advancing contact angles and demonstrated small increases with increasing porosity; the changes were of the same magnitude observed in this study for PF and PTFE. This was interpreted by Carli and Colombo (1982) in terms of Eqn. 5. A further test of this model by measuring receding angles as a function of porosity, however, would have been helpful in more clearly determining the appropriate model to use.

Finally, with regard to receding angles, there appears to be one other interesting pharmaceutical implication of this study. If we assume that the polymer film coating process involves wetting and spreading of coating solution on the tablet surface, and if coalescence of drops has not yet taken place, evaporation of solvent can occur either from a drop which is receding or one which is stationary, depending on the receding contact angle. From the observation made in this study with the compressed disks, most likely such drops would exhibit zero contact angle, θ_R, and thus maintain good coverage of the surface as evaporation occurred. This, in turn, should promote a greater tendency for better polymer film adhesion. Thus, a rough tablet surface could serve to facilitate good adhesion in this manner.

TABLE 6

CHANGE IN RECEDING ANGLES, θ_R, DUE TO ROUGHNESS

Solid	$\Delta\theta_R$	
	Water	Ethylene glycol
Paraffin	19°	13°
PTFE	34°	34°
PMMA	43°	~ 38° [a]

[a] Receding angle on rough PMMA with ethylene glycol was ~ 0°.

Conclusions

(1) For the relatively non-polar solids used in this study, roughness of the type encountered in pharmaceutical systems produces significant contact angle hysteresis by affecting the receding angle much more than the advancing angle.

(2) With compacted systems where the advancing contact angle is in the range of 60–70°, receding angles can be reduced to zero degrees at moderate levels of roughness.

(3) The effects of roughness on randomly rough compressed disks appear to be qualitatively consistent with predictions of the concentric groove model.

(4) Measurement of advancing contact angles on highly compressed disks are most likely reasonable estimates of the intrinsic contact angle. No conclusions concerning intrinsic wettability however can be drawn from the measurement of receding contact angles.

Acknowledgements

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