International Journal of Pharmaceutics, 79 (1992) 47–60

IJP 02626

Movement of liquids through powder beds

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(Received 2 June 1991)
(Accepted 20 August 1991)

Key words: Capillary pressure; Lactose; Microcrystalline cellulose; Particle size; Pore size; Powder bed; Pressure membrane; Saturation (liquid; irreducible)

Summary

The movement of hydrophilic fluids into and out of beds of two grades of lactose, microcrystalline cellulose (MCC) and mixtures of the two materials has been assessed by a pressure membrane technique. While water was an appropriate fluid to use with MCC, because of its solvent properties, it proved unsuitable for use with lactose and the binary mixtures with MCC. In these cases, a 50:50% mixture of ethanol and water proved acceptable. The method clearly illustrated the differences in the movement of fluid in the two grades of lactose, which differed in particle size, and between lactose and MCC. These differences could be quantified in terms of limiting saturation pressures, irreducible saturation and 'apparent' pore distributions. The MCC introduces absorptive and adsorptive influences into the binary mixtures with lactose which are absent or minimal in the lactose systems. Such effects are undoubtedly involved in ensuring that these binary mixtures can be used to produce spherical granules by extrusion/spheronisation whereas the process is not successful for lactose alone.

Introduction

The preparation of spherical particles by extrusion/spheronisation requires a mass with specific rheological characteristics. An essential feature of this rheology is the presence of water in association with the powdered ingredients. The mobility or, rather, limited mobility of this water, as the material is forced through apertures during extrusion or subjected to centrifugal force during spheronisation, is fundamental to the process. Loss of water or movement to different parts of the system will change the rheological characteristics. This is illustrated by the work of Fielden et al. (1989) where the influence of particle size on extrusion rheology was demonstrated. These changes must be associated with the movement of fluid in the bed. It is therefore important to measure this movement if an understanding of formulation and process variables is to be quantified.

Theory

The flow of liquids through a porous medium is governed by the same principles that apply to

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fluid confined in various types of containers. However, the fluid flowing through a porous medium will experience additional effects due to the proximity of the solid interface to practically all the molecules of the fluid. The interactions which are produced have been described by Scheidegger (1974) under four main headings.

(1) *Adsorption*

Van der Waals forces of attraction cause adsorption of the fluid at the solid interface. The extent of the interaction depends on the nature of the adsorbent and adsorbate, the surface area of the adsorbate and temperature and pressure. The net effect is that a finite number of molecules are always present at the surface of the adsorbent.

(2) *Capillary condensation*

The influence of the walls of the pores may cause some of the fluid to condense to form another phase. This second phase lines the walls of the pores as a static film of variable thickness. If the film emerges to form menisci the phenomenon is known as capillary condensation.

(3) *Displacement associated with wetting*

Depending on the contact angle between two fluids, one will wet the solid more preferentially than the other. Therefore, one fluid (the preferentially wetting one) will penetrate into a porous medium against a less wetting one. The relative wettability is a consequence of the presence of capillary forces.

(4) *Capillary forces*

Capillary forces act at the interface between two immiscible liquids when one liquid is displacing the other in a porous medium. Under circumstances in which the displacing fluid is a gas, capillary forces dominate. Three saturation regimes are possible; they are described for an ideal porous medium, consisting of spheres according to Versluys (1927), as

(i) Complete saturation

The porous medium is completely saturated with the liquid phase.

(ii) Pendular regime

The porous medium has the lowest possible saturation with the liquid occurring in the form of pendular bridges throughout. Since the pendular bodies do not touch each other, there is no possibility of liquid flow in this regime.

(iii) Funicular regime

The porous medium exhibits an intermediate saturation stage with both phases. If the pendular bodies of the pendular regime expand through the addition of fluid, they eventually become so large that they both touch each other and merge. The result is a continuous network of the fluid phase across the porous medium, allowing flow to occur along what must be very tortuous (funicular) paths.

Water is retained in porous materials mainly as a result of the adsorption and capillary effects. In the previous example, water in the funicular saturation regime is retained by capillary effects resulting from surface tension. Moisture retention is strongly influenced by the matrix suction and the pore size distribution. In the pendular regime the adsorption effect dominates. This is particularly critical in less porous materials such as clays where water retention may be influenced by electric double layers and the presence of exchangeable cations. However, it is difficult to separate these two mechanisms since the adsorbed films may be in contact with capillary water held in wedges. The complexity of this double effect is such that it is now more usual to consider the combined effect of adsorption and capillary potential, and this has been called the 'matrix potential' (Hillel, 1971).

If the gas pressure above the porous matrix is raised above atmospheric pressure, gas will enter the pores. This displacement will be opposed by the surface tension of the liquid. The combined effect of all these forces is such that, at a consistent applied pressure, a pressure differential exists between the gas and the liquid, and an equilibrium is established in which no further movement of liquid occurs. This pressure (P) is called the capillary pressure (P_c) and is a function of the saturation (S) of the porous bed:

$$P_c = P_c(S) = P(\text{liquid}) - P(\text{gas})$$

The existence of capillary pressure may be explained by considering the porous medium as consisting of an assembly of capillaries, and by describing the surface tension and pressures developed by the curvature of a liquid meniscus (Hillel, 1971; Kirkham and Powers, 1972).

Capillary curvature and capillarity

In a single capillary, the liquid meniscus curves upwards due to its surface tension and attraction of the liquid molecules to the capillary walls. This causes the pressure just beneath the meniscus to drop below atmospheric pressure. Young and Laplace derived an expression for the pressure (P) developed under a general curved surface using a free energy model, where

$$P = \tau(1/R_1 + 1/R_2) \tag{1}$$

where R_1 and R_2 are the principal radii of curvature and τ is the surface tension of the liquid. In circular capillaries of radius r cm, the meniscus is assumed to be hemispherical so that

$$R_1 = R_2 = r/\cos \Phi \tag{2}$$

where Φ is the contact angle of the liquid. If it is assumed that the liquid makes zero contact angle with the capillary wall, then Eqn 1 reduces to

$$P = -2\tau/r \tag{3}$$

The pressure deficit below the meniscus causes the atmospheric pressure on the water outside a capillary to force water into the tube to a height h_t. Capillary rise ceases when the negative pressure is balanced by the pressure (P_w) created by the hydrostatic head. This pressure is given by

$$P_w = -h_t \pi r^2 g\rho/\pi r^2 = -h_t g\rho \tag{4}$$

where g is the acceleration of gravity and ρ is the density of water. The negative signs in Eqns 3 and 4 arise from the convention that measurements made from the liquid surface to the atmosphere are negative, hence, h_t and R are negative. At equilibrium a balance between the forces P and P_w is maintained, therefore, the left-hand side of Eqn 3 may be equated to the right-hand side of Eqn 4 so that the negative pressure P may be written as

$$P = -h_t g\rho \tag{5}$$

The negative pressure under the meniscus is described as a tension (T) so that

$$T = h_t g\rho \tag{6}$$

In discussing water movement in soil, the tension T under a water film is often expressed in terms of an equivalent hydraulic head, which is the height h_t of water standing in a capillary tube corresponding to a given pressure. Justification of the use of h_t is seen from Eqn 6 where the tension corresponds to h_t cm of water. However, the pF scale (after Crooney and Coleman, 1954) is more commonly employed. This is the logarithm of the equivalent hydraulic head of water in cm, and thereby the use of very large values of equivalent hydraulic head is avoided. The applied pressure in terms of pF is then plotted as a function of the saturation of the porous bed.

The tension under a meniscus may also be related to the radius of a circular capillary. At equilibrium the upward force due to surface tension in Eqn 3 is balanced by the pressure of the hydraulic head of water in Eqn 4. Therefore

$$2\tau/r = h_t g\rho \text{ or } h_t = 2\tau/rg\rho \tag{7}$$

Carman (1941) devised a more general expression which could be applied to capillaries of non-uniform cross-section. For such capillaries, Eqns 1 and 4 may be equated, giving

$$-h_t = \tau(1/R_1 + 1/R_2)g\rho \tag{8}$$

The various expressions for $(1/R_1 + 1/R_2)$, for cross-sections of different shapes, were replaced by a single quantity. This was justified by rediscussing capillary rise from a more simplistic viewpoint, i.e. as representing an equilibrium between an upward force due to surface tension acting over a perimeter, and a downward force due to gravity acting over the area of the cross-section, so that

$$\tau \times \text{perimeter} = h_t g\rho \times \text{area}$$

and Eqn 8 becomes

$$h_t = \tau/g\rho m \tag{9}$$

where m represents the ratio of the area to the perimeter, and its reciprocal replaces the term for the total curvature of the meniscus, i.e.

$$(1/R_1 + 1/R_2) = 1/m \tag{10}$$

If Eqns 7 and 9 are compared, it can be seen that $2m$ is the radius of a circular capillary with the same ratio of perimeter to area as the given non-circular capillary, and is known as the mean hydraulic radius.

Using Eqn 9 in this way, individual pF values may be converted into mean hydraulic radii, which suggests the possibility of determining the pore size distribution curve for a given bed structure.

Procedures

A review of the methods available in determining the relationship between the capillary or matrix potential of the powder bed and its moisture content has been given by Crooney et al. (1952). The method used in this work is based on the pressure membrane technique described by Richards (1941), and is illustrated diagrammatically in Fig. 1. The method involves increasing the equilibrium pressures at various degrees of saturation of the porous bed during a displacement process. Fig. 2 is included to illustrate the principles on which the apparatus operates. The capillary tubes in the illustration represent the pores of various diameter in a porous matrix which is partly saturated with liquid. The tubes are attached to a porous membrane which is in contact with the liquid phase at atmospheric pressure. Pressure may be introduced into the chamber containing the capillaries. The figure is drawn for the case of initially atmospheric pressure. If a pressure equal to h_{t_1} cm of water is now applied, the column h_{t_1} will drain to the top level of the membrane. If the pressure is increased to h_{t_2} cm, column h_{t_2} will similarly drain, and if h_{t_3} cm is applied all three capillaries will drain. It has been found that in order to drain a pore P in the semi-permeable membrane, much higher pressures are required, e.g. approx. 100 kPa for a 0.15 μm membrane. This concept of capillary drainage may be related to the emptying of the pores in a

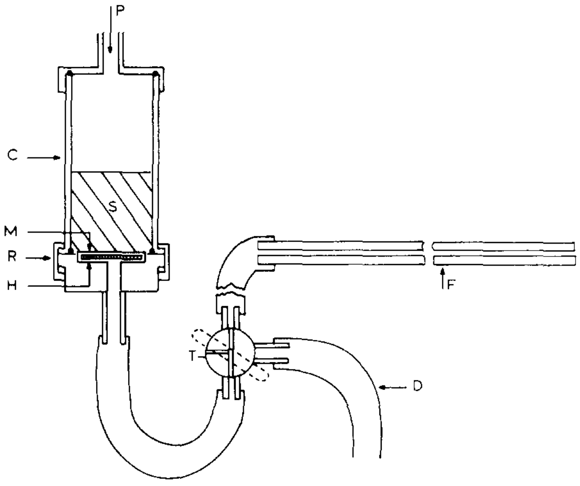

Fig. 1. Diagrammatic representation of the pressure membrane apparatus. C, pressure chamber; D, drain tube; F, capillary tube; H, filter holder; M, membrane filter; P, applied pressure; R, locking collar; S, sample; T, three-way tap.

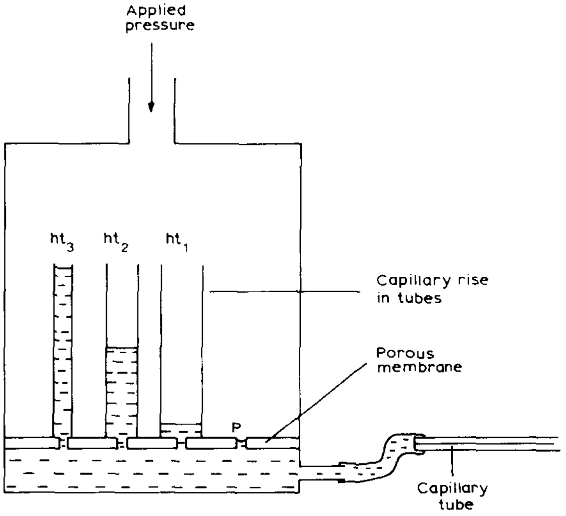

Fig. 2. Diagram illustrating the operation of the pressure membrane apparatus.

porous medium by Eqn 9 which indicates that the radius of the pores is inversely proportional to the capillary or matrix potential, ($h_t \propto 1/m$).

The actual changes occurring in the apparatus may now be described. When the gas pressure surrounding the wet powder bed is increased, the liquid in the sample suffers an increase in pressure. The face of the sample is in contact with liquid at atmospheric pressure through the membrane and, consequently, liquid will pass through the membrane. This process continues until the liquid in the sample is at atmospheric pressure. When the pressure in the chamber is released, the chamber returns to atmospheric pressure, and the pressure of the liquid in the sample now falls to a value which is less than atmospheric by an amount equal to the gas pressure previously applied. A suction is therefore present in the sample immediately on release of the pressure. Therefore, re-absorption of the free liquid from the reservoir will occur. The amount of liquid removed at various pressures may be measured and the relationship between suction potential and moisture content can be estimated for the material in the drying state.

The process may then be reversed by lowering the pressure in stages and measuring the volume of liquid being sucked back, and the moisture content relationship can be found for wetting conditions. The hysteresis between advancing and receding contact angles explains why the capillary pressure also exhibits the effects of hysteresis.

Materials and Methods

Materials

The powder samples were two grades of 'coarse' and 'fine' lactose BP (Dairy Crest U.K.) and microcrystalline cellulose (Avicel PH101, FMC Corp.) as used previously (Fielden et al., 1989). The fluids used were: absolute alcohol diluted to 50% with distilled water and saturated with lactose, which was filtered; and distilled water. The liquids were degassed under a vacuum prior to use. The surface tension of the ethanol solvent was determined by a du Nouy ring tensiometer, and the density by a density bottle (BS 733). The values were 31.37 kN m^{-1} and 0.936 kg m^{-3}, respectively. The surface tensions and density values for pure water were found to be 72.8 kN m^{-1} and 1.002 kg m^{-3}, respectively.

The pressure membrane apparatus

The apparatus consisted of a stainless-steel pressure chamber (Sartorius SM 16223) fitting in three sections (Fig. 1). Tubing connected the top section to a nitrogen cylinder which provided the source of gas pressure. Fine control of the gas pressure was achieved by fitting a regulator valve (Norgren 0–60 psi [lb/inch^2]) calibrated in units of 1 psi distal to the cylinder valve (BOC nitrogen M.15-NG). An air-tight seal was maintained between the three sections by soft rubber washers. A 0.2 μm membrane (Nucleopore) was mounted at the base of the cylinder on a filter support. The base of the pressure chamber was connected via a three-way tap by PVC tubing to a calibrated capillary tube (0.0189 ml per cm) of approx. 60 cm length. This was positioned horizontally at the same level as the membrane and a metre rule was placed above this so that the amount of liquid leaving or entering the sample when the pressure was changed could be observed. This allowed the moisture content of the sample to be calculated without removing the latter from the apparatus.

Method

The integrity of the filter was tested prior to its use, as any leakage would invalidate the results. The pressure chamber was half filled with the liquid being used in the experiment. A small pressure was applied to the chamber and the liquid was allowed to flow from the pressure chamber until a continuous length existed from the filter to a suitable position in the capillary tube. Excess fluid was drained as waste. The pressure on the filter was then increased to 68.9 kPa m^{-2} and applied for 5 min. A constant meniscus position in the capillary indicated that the filter was satisfactory. Leaking filters were recognised by the flow of liquid along the tube at a slow constant rate.

A slurry of powder and liquid was prepared in a beaker and transferred to the pressure chamber. The quantity of powder used was standardised (typically 5 g), and a minimum amount of fluid added, so that the slurry was just pourable. The gas above the sample was 'humidified' by placing a sponge, dampened with the same liquid, at the top of the pressure chamber. This minimised evaporation of solvent from the sample and the risk of precipitating lactose from the saturated solution.

The system was allowed to drain into the capillary and reached equilibrium as judged by a constant position of the meniscus in the tube (typically 30 min was allowed). The position was adjusted to the start of the capillary tube by means of the three-way tap. The relationship between the volume of liquid extracted as a function of time was obtained by applying known pressure to the chamber and observing the position of the meniscus in the flow tube at timed intervals, until a constant position was reached. In practice, 60 min was allowed for the equilibrium to be established. The pressure was then released and similarly the movement of the meniscus in the opposite direction was noted, as the liquid was being sucked back into the sample. When the capillary remained stationary the damp mass of powder was weighed and dried to constant weight, in order to establish its liquid content. This value was adjusted to allow for the mass of residual solid adhering to the pressure chamber and membrane after removal of the sample, and for the mass of lactose which precipitated from the liquid on drying.

The percentage saturation (expressed as volume of liquid per 100 g of solid) of the sample, as a function of pressure, was determined by repeating the procedure with a series of increasing pressures from 2.4 to 68.9 kPa m^{-2}. The meniscus advanced at each pressure increment and gradually became stationary, or proceeded very slowly as equilibrium at that pressure was reached. When the meniscus was stationary (or if its movement was less than 0.5 cm min^{-1}), the position was noted and the pressure was increased to the next value. When the maximum pressure was reached, the process was reversed by decreasing the pressure stepwise to atmospheric pressure. The liquid content at each pressure was calculated from the volume of liquid pushed out and the final liquid content of the sample.

Results and Discussion

The influence of the liquid phase on fluid movement

A problem was immediately encountered in the selection of a liquid phase that was compatible for all three solids. Water was satisfactory for use with microcrystalline cellulose, but in experiments with lactose a saturated solution of lactose (17% w/w) would have to be used to prevent any effects due to the dissolution of the powder bed. For such a system the volume of liquid extracted at a given pressure for the lactose/water system is low, and continually rises at a slow rate. Therefore, the saturated lactose solution is unsatisfactory for use as the liquid phase, because the moisture content of the powder bed is too slow to reach equilibrium. This was attributed to a combination of the effects that a concentrated lactose solution has on altering the surface tension, wettability, and viscous properties of pure water, thereby altering the mobility of the liquid through a powder mass.

A liquid phase was required that had physical properties similar to those of water, but in which lactose was sparingly soluble. Various organic solvents were tested. Some were found to be compatible with lactose, but none gave entirely satisfactory results with microcrystalline cellulose. In general, the solvents were found to move more freely than water through the microcrystalline cellulose in particular, which meant that either an equilibrium liquid content was never reached (e.g. dilute propylene glycol, glycerol, ethanol) or drainage was so thorough that application of the lowest pressure caused complete removal of the liquid phase (e.g. dodecane, toluene). However, a compromise was accepted and the liquid chosen was ethanol diluted to 50% with a saturated aqueous solution of lactose. Fig. 3 compares the effect of this liquid phase with water on the relationship between the volume of liquid extracted as a function of time for microcrystalline cellulose.

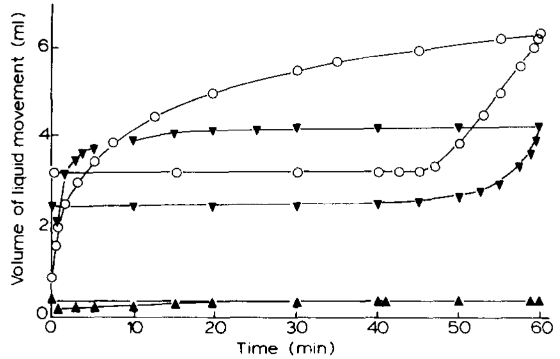

Fig. 3. Volume of liquid movement as a function of time at 17.3 kPa m^{-2} for various powder-liquid systems. (▲) Fine lactose-water; (▼) MCC-water; (○) MCC-50% ethanol.

The water flow curve shows a high initial rate of drainage (from 0 to 5 min) which then levels off to a very slow rate, and after 30 min, the powder bed has usually equilibrated at that pressure. Similarly, in the reabsorption phase, water is initially rapidly sucked in during the first 5 min, before reaching an equilibrium value. These characteristics are modified by the ethanol solvent. Greater mobility of the solvent through microcrystalline cellulose is demonstrated by the removal of a larger volume from the powder bed. After the initially high drainage rate, the rate declines and becomes constant at 0.15 ml min^{-1}. This is maintained from 30 to 60 min (the duration of the experiment). As a result, relatively more solvent is reabsorbed when the pressure is released, namely, 3.21 ml of ethanol compared with 1.80 ml of water. It follows then that the equilibrium liquid content of the microcrystalline cellulose will be lower with ethanol than with water, the respective values being 120.0 and 169.6% for those experimental conditions. The greater mobility of ethanol over water through porous beds has also been reported by Parker (1921), who commented that it was caused by preferential wetting of the former solvent for the substrate. This property was used as a technique for displacing water from soil beds. The difference in behaviour of the two solvents, however, must be attributed to differences between their physical properties, e.g. surface tension, viscosity, density and possible interactions with the microcrystalline cellulose-liquid interface. Therefore, results between the three powder samples may only be compared if the same liquid phase is used. Fig. 4a shows the effect of pressure on the volume of liquid extracted with time for microcrystalline cellulose and two grades of lactose.

For application of the same gas pressure the volume of liquid removed and the magnitude of the hysteresis loop for microcrystalline cellulose are far greater than for both grades of lactose, and similar curves are produced at both pressures. The lactose samples may be distinguished by the coarse grade having a larger hysteresis loop at low pressure (17.3 kPa m^{-2}) which does not differ significantly from the loop obtained at the higher pressure (55.1 kPa m^{-2}). In contrast, at 17.3 kPa m^{-2} (Fig. 4a), the fine lactose releases less fluid from the powder bed, and has a negligible hysteresis effect when the pressure is released. Different results are obtained when the experiment is repeated at a higher pressure. At

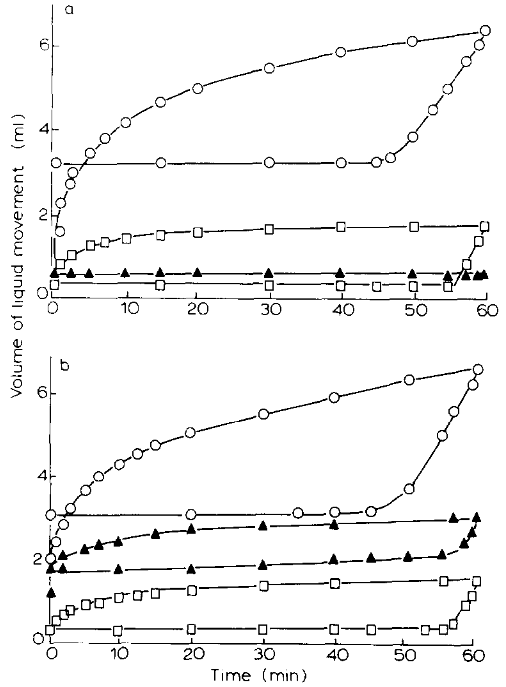

Fig. 4. Volume of liquid movement (50% ethanol liquid phase) as a function of time at various pressures. (□) Coarse lactose; (▲) fine lactose; (○) microcrystalline cellulose. (a) Pressure, 17.3 kPa m^{-2}; (b) pressure, 55.1 kPa m^{-2}.

55.1 kPa m^{-2} (Fig. 4b), a large volume of fluid is removed from the fine lactose matrix and an appreciable quantity is reabsorbed when the pressure is released. The different behaviour at both pressures may be explained as follows. The particles in the fine lactose bed are tightly packed and contain very few large pores. Therefore, at low pressure, when only these pores are emptied, a small quantity of fluid is removed and the powder bed reaches equilibrium saturation rapidly. Consequently, when the pressure is released, reabsorption is marginal since the pressurised bed had decreased its liquid content by a correspondingly small volume. Application of a higher pressure (Fig. 4b), however, enables some of the small pores to empty, therefore a greater volume of fluid is removed. These small capillaries have a higher suction potential and hence a larger volume of liquid is reabsorbed when the pressure is released. This explains why saturation of the powder bed decreases markedly from 30 to 17% when the higher pressure is applied.

Conversely, the coarse lactose consists mainly of large pores which have a low suction; therefore, lower pressures are required to remove liquid from the powder bed, and higher pressures do not appreciably increase the drainage. Hence, the saturations of the powder beds at 17.3 and 55.1 kPa m^{-2} are very similar, namely 10 and 17%, respectively.

The difference in the pore size distribution of the two grades of lactose causes a variation in the reabsorption mechanism of the wet powder bed (Fig. 4) when the pressure is released. The reabsorption rate in the coarse lactose is initially high (0.029 ml min^{-1}) then declines steeply and stops within 10 min when equilibrium is established. In contrast, the initial reabsorption rate for fine lactose is high (0.031 min^{-1}), but then continues at a slower rate (0.0008 ml min^{-1}), and is sustained for at least 60 min (the duration of the experiment). This is further evidence of the smaller dimensions of the pore space in the matrix composed of fine lactose. Residual reabsorption is caused by the suction potential of the small capillaries in the bed and takes longer to

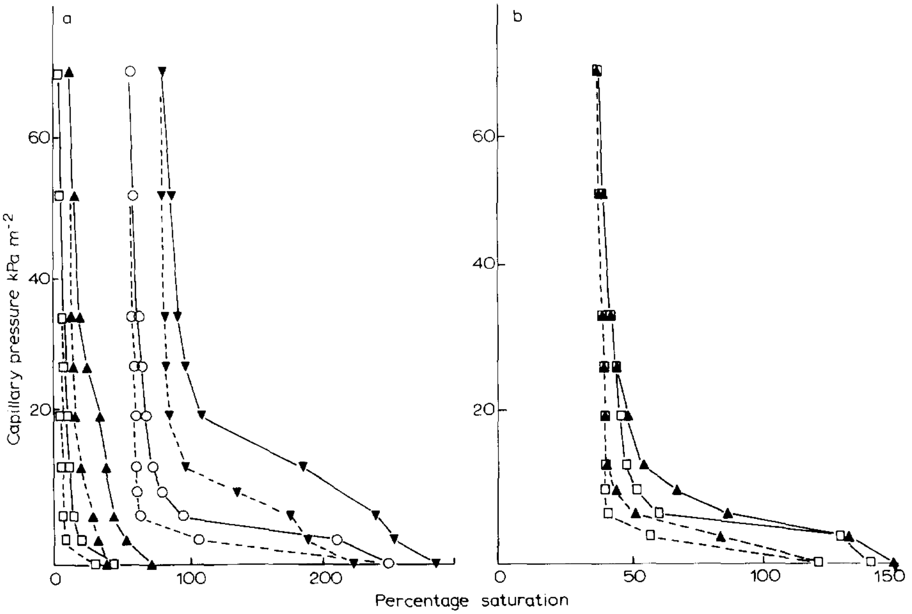

Fig. 5. Capillary presssure as a function of saturation for various powder systems. (a) Microcrystalline cellulose in water (▼) and in (○) 50% ethanol; coarse (□) and fine (▲) lactose in 50% ethanol. (b) Lactose and microcrystalline cellulose mixtures in 50% ethanol. (———) Drying curve; (— — —) wetting curve.

complete. Washburn (1921) suggested that this may be due to increased resistance to flow which is inherent to fine capillaries.

The above findings are emphasised in more detail in the curves relating the matrix potential to the saturation of the porous bed (Fig. 5). The following characteristics are displayed by each sample:

(i) As the pressure increases along the drying curves, more liquid is drained out of the powder beds and the slope becomes progressively steeper, until it is vertical. At low suction values the relatively larger pores which cannot retain liquid against the applied pressure will drain out. Recalling the capillary expression, Eqn 3 ($P = -2\tau/r$), a gradual increase in pressure results in the emptying of absorbed liquid from progressively smaller pores. Thus, at high pressures only the narrowest pores, which have the greatest suction potential, retain the liquid phase. Similarly, high capillary pressures are associated with reducing the thickness of hydration envelopes covering the solid particles, as previously described. Therefore, at high pressures liquid retention is increasingly due to adsorption effects and is strongly influenced by the texture and specific surface of the sample.

(ii) Saturation of the samples reaches a limiting value at high suction pressures where the wetting and drying curves merge. This implies a pendular saturation regime. The two important factors determining retention of the remaining fluid are adsorption effects and hydraulic isolation.

Hydraulic isolation is highly dependent on the geometry of the solid and the solid-liquid interface. The effect has been studied by Morrow (1970), who introduced the phrase 'irreducible saturation', which refers to the liquid that remains in a porous bed, regardless of any further increase in applied pressure. The model in Fig. 6 can be used to describe more realistically the mechanism of liquid retention in pores. Here the emptying of two slightly larger diameter vertical pores (at low pressure) will result in the hydraulic isolation of the liquid in the horizontal connecting capillary. Fig. 6 relates this to the drainage of a saturated powder bed under an applied pressure, where the pressures and 1/pore sizes are of the order $P_1 < P_2 < P_2 < P_4$. Thus, the pressure required to empty the pores (i.e. the entry pressure) is related to the pore size. P_1 therefore will be the first to drain. This causes hydraulic isolation of P_2 which will therefore be unable to drain at pressure P_2. When pressure P_3 is reached area P_3 canot empty because it is surrounded by P_4, an area with high entry pressure. Area P_3 will, therefore, not be emptied until pressure P_4 is reached when both P_3 and P_4 empty. In this model P_2 remains hydraulically isolated and is therefore responsible for irreducible saturation.

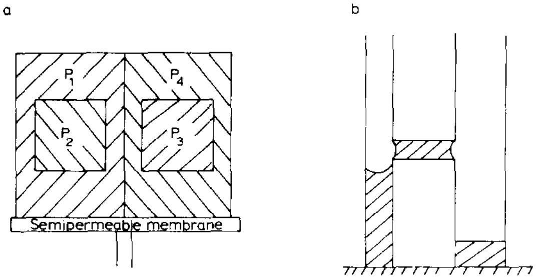

Fig. 6. Simple pore models representing capillary retention in porous media. (a) A heterogeneous porous mass with entry pressures $P_1 < P_2 < P_3 < P_4$. (b) Tube network model for a porous bed.

(iii) In general, the relationship between saturation and capillary pressure is not unique. There is a difference in the saturation value depending on whether the measurement is made in the desorption (drying) or sorption (wetting) phase. It can be seen in Fig. 4a that each sample is drier, at a given pressure, when that pressure is approached in the wetting condition than in the case of the drying condition. This hysteresis effect has been attributed to several causes (Hillel, 1971; Kirkham and Powers, 1972).

(a) The geometric non-uniformity of the individual pores, which are generally irregularly shaped voids interconnected by smaller passages: This results in the 'ink-bottle' effect, illustrated in Fig. 7, which considers a hypothetical pore of a relatively wide void of radius R bounded by narrow channels of radius r. If initially saturated (Fig. 7a), this pore will drain abruptly at the moment when the pressure exceeds P_r, where $P_r = 2\tau/r$. For this pore to re-wet, however, the

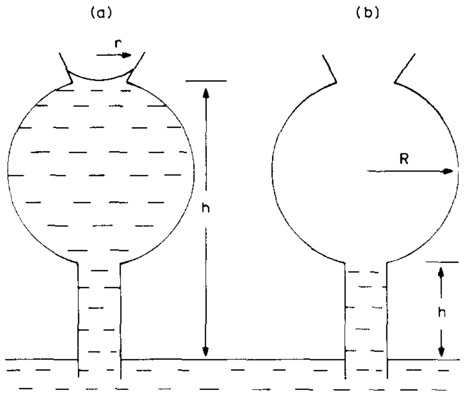

Fig. 7. 'Ink-bottle' effect determines equilibrium height of water in a variable-width pore: (a) in capillary drainage; (b) in capillary rise.

suction must decrease to below P_R, where $P_R = 2\tau/R$, whereupon the pore abruptly fills. Since $R > r$ it follows that $P_r > P_R$ and the pore re-fills at a lower pressure in the sorption phase. Therefore, desorption depends on the narrow radii of the interconnection channels, whereas sorption is governed by the maximum diameter of the large pores. These discontinuous spurts of liquid, called 'Haines jumps', are more readily observed in coarse powder beds (Haines, 1930). Other causes of the hysteresis effect include the following.

(b) The contact angle effect, by which the contact angle is greater and hence the radius of curvature is greater, in an advancing (wetting) meniscus than in the case of a receding one. A given water content will tend, therefore, to exhibit greater suction in desorption than in sorption. Contact angle hysteresis can arise because of surface roughness, the presence and distribution of adsorbed impurities on the solid surface, and the mechanism by which liquid molecules adsorb or desorb when the interface is displaced.

(c) Entrapped air within the matrix can further decrease the water content of a newly wetted porous bed. Failure to attain true equilibrium can accentuate the hysteresis effect. Distortion of the results due to entrapped air was avoided by degassing the liquid phase prior to use.

Comparison of coarse and fine grades of lactose

Hysteresis curves The hysteresis curves for the coarse and fine grades of lactose are very different (Fig. 4a). The hysteresis effect for the coarse lactose is more prominent at low pressures, whereas the fine lactose exhibits the effect over a wider pressure range. In addition, the equilibrium saturation at all pressures is lower in the coarse lactose. As a result, the fine lactose is distinguishable from the coarse by having a larger area of hysteresis and being displaced to the right.

Desorption curves The desorption curve for the coarse lactose shows that liquid is removed much more readily, i.e. at lower pressures. This confirms the presence of a greater proportion of large diameter pores. The limiting pressure, the pressure above which little change in saturation occurs, is approx. 6.86 kPa m^{-2} and corresponds to a saturation of 12%. The low limiting pressure implies that the coarse lactose has very few small diameter pores. In contrast, the desorption curve for fine lactose is less steep and shows that higher pressures are required to remove its liquid phase. The limiting pressure (29.4 kPa m^{-2}) and corresponding saturation (25%) are much higher than for coarse lactose. Therefore, this sample has a higher proportion of smaller diameter pores.

Irreducible saturation The causes of fluid retention at high pressures in the region where the desorption and sorption curves merge have already been discussed. The irreducible saturation of the fine lactose is approximately twice that of coarse lactose, the values being 16.6 and 7.9% respectively. The results are consistent with the work of Morrow (1970). Using an experimental model of a homogeneous porous medium (made of regular glass micro-beads), the magnitude of the irreducible saturation was shown to be independent of particle size and fluid variables such as density, interfacial tension, viscosity or wettability, but was a function of the pore space in the matrix. Further work with mixtures of bead sizes to simulate a heterogeneous porous bed showed that irreducible saturation could be varied. This led to the conclusion that the dominating influence was the heterogeneity of the pore structure. The fine grade lactose, which has a wider size distribution than the coarse lactose, would therefore be expected to have a greater value of irreducible saturation.

Sorption curves As the pressure is decreased along the sorption curves, very little change in percentage saturation is observed in both lactose samples until the pressure becomes low. The fine lactose begins to reabsorb liquid at a higher pressure, 19.6 kPa m^{-2}, compared to the coarse lactose which reabsorbs at 29.4 kPa m^{-2}. This is a further indication of the presence of smaller diameter capillaries in the fine lactose, which have a higher suction potential. These capillaries are evidently absent from the coarse lactose matrix and therefore reabsorption takes place at low pressures, consistent with the filling of large diameter pores.

Capillary pressure-saturation for microcrystalline cellulose

The microcrystalline cellulose-ethanol and microcrystalline cellulose-water curves stand quite apart from the lactose curves, suggesting that this material has very different fluid retaining properties (Fig. 4a). The desorption curve with ethanol shows a larger reduction in saturation from 250 to 75%, when the pressure is increased from zero to the limiting pressure of 9.8 kPa m^{-2}. This implies that the microcrystalline cellulose matrix has a greater proportion of pores that are larger in diameter than those in coarse lactose. This enables the matrix to retain a much higher degree of saturation at lower pressures. However, the powder bed must also contain a larger proportion of smaller diameter pores, as application of higher pressures can force the removal of even more liquid.

The irreducible saturation of microcrystalline cellulose is about 60% with ethanol, which is approx. 5-times that of the lactose samples. Thus, at higher pressures, microcrystalline cellulose is capable of retaining a much higher degree of saturation. Therefore, the hydraulic isolation and adsorption effects discussed previously are more predominant and play a more important role in the retention of fluids in microcrystalline cellulose powder beds than in lactose. This indicates a much stronger physical interaction of the liquid phase with microcrystalline cellulose than lactose, and the interaction is more pronounced when the liquid phase is water.

When the liquid phase added to microcrystalline cellulose is changed from ethanol to water, the area of hysteresis is increased and the curve is displaced to the right. However, the two curves describe removal of water from essentially the same pores. Therefore, the differences must be attributed to differences between the physical properties of the liquid phases, and the extent of interaction with the microcrystalline cellulose-liquid interface. In changing the solvent from ethanol to water, the limiting pressure for microcrystalline cellulose is increased from 9.8 to 19.0 kPa m^{-2}. However, the reduction in saturation of the powder bed in going from zero to equilibrium pressure is very similar for the two solvents, i.e. 170 and 180% for water and ethanol, respectively. This is evidence that the same diameter pores are being emptied, but that a higher pressure is required to achieve this when water is the liquid phase, due to the physical properties of water. In contrast, the irreducible saturation for the two liquid phases differs, and is 60% with ethanol and 90% with water. This disagrees with the above-mentioned results of Morrow (1970), which stated that fluid properties did not significantly influence the magnitude of irreducible saturation. However, this hypothesis was derived from work on glass bead models which adsorb a negligible volume of liquid phase, and therefore irreducible saturation, due to adsorption effects, was ignored. Previous work on the thermal analysis of the materials (Fielden et al., 1988) has indicated that microcrystalline cellulose interacts strongly with water, forming hydrogen bonds, and adsorbing more than one layer of molecules. If it is assumed that the extent of hydraulic isolation in the microcrystalline cellulose-water, and microcrystalline cellulose-ethanol systems is the same, the higher irreducible saturation observed with the former suggests that water interacts more strongly than ethanol with the microcrystalline cellulose surface.

Behaviour of binary mixtures of microcrystalline cellulose and lactose

Microcrystalline cellulose was mixed in equal proportions with one of the lactose samples and the pore size distribution of the binary mixture

TABLE 1

Values of the irreducible saturation [a] and saturation at zero pressure [a] for various powder systems with the ethanol liquid phase

Powder system	Saturation at zero pressure (%)	Irreducible saturation (%)	Limiting pressure (kPa m^{-2})
Fine lactose	31.8	7.9	22.1
Microcrystalline cellulose: fine lactose (5:5)	118.6	41.3	13.7
Coarse lactose	37.4	16.6	3.4
Microcrystalline cellulose: coarse lactose (5:5)	120.5	40.4	13.7

[a] Volume of ethanol (ml) per 100 g of solid.

was assessed. The aim was to imitate the mixture of microcrystalline cellulose-lactose (5:5) that is used in extrusion-spheronisation, and to investigate the movement of fluid through this matrix. The results are shown in Fig. 4b using ethanol as the liquid phase. The curves for both binary mixtures are displaced to the right of those corresponding to lactose alone. The magnitude of the change in fluid-retention properties is best indicated by comparing the irreducible saturations and saturations at zero pressure (obtained along the sorption curves) for the single and binary mixtures (Table 1). Increases of about 85% in the saturation at zero pressure and 30% in the irreducible saturation are seen in the binary mixtures compared to the single powder samples. The microcrystalline cellulose introduces absorptive properties and adsorptive influences into the binary mixture which are absent or minimal in the lactose matrices. Therefore, a binary mixture has greater fluid-retention properties than a lactose powder bed. However, the properties of the mixture containing coarse lactose are modified to a noticeably lesser extent, although the curve has the same tendency to be displaced to the left of the mixture containing fine lactose that is seen in the single powder bed. The displacement is more pronounced at low capillary pressures, where the microcrystalline cellulose-coarse lactose has a lower saturation at a given pressure than the mixture containing fine lactose. This indicates that the former has a noticeably larger proportion of wide diameter pores. This mixture is therefore more porous and results in an increased mobility of the liquid phase. This is also the reason for the observation of a lower limiting pressure for the mixture containing coarse lactose (Table 1). The limiting pressure value of the fine lactose is decreased by 8.3 kPa m^{-2} in the binary mixture because this mixture has a greater proportion of larger diameter pores. However, an increase of 3.3 kPa m^{-2} is seen with the coarse lactose binary mixture, due to the presence of small diameter pores, which must be absent in the single powder bed. The binary mixtures show similar behaviour at higher pressures above 19.6 kPa m^{-2}, in contrast to the corresponding curves for the singular powder bed, which are distinguishable at all pressures below the maximum. Therefore, the properties of microcrystalline cellulose (adsorption and absorption) are dominant over those of lactose in binary mixtures at higher pressures.

Pore size distribution curves

The dimensions of the pore space for the microcrystalline cellulose and lactose samples are illustrated by presenting results of the percentage saturation as a function of the derived value of the hydraulic radius from Eqn 9. Results for single powders are shown in Fig. 8a and for mixtures of microcrystalline cellulose-lactose in Fig. 8b.

The curves show hysteresis which differs for the drainage and imbibing stages. The causes of this have been previously discussed. However, it should be noted that the capillary model of a porous bed on which Eqn 9 is based is a gross oversimplification of the system. Possible alternative pore models were reviewed by Van Brakel (1975) but none were found that could satisfactorily describe an actual system. The major drawback was indicated to be the lack of knowledge about the forms of the menisci that might be present in a porous bed, and the error caused by

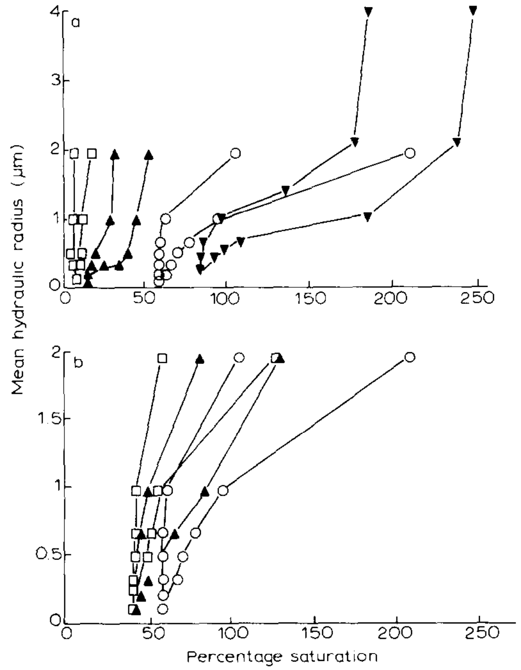

Fig. 8. Mean hydraulic radius as a function of saturation for (a) lactose and microcrystalline cellulose; (b) binary mixtures of lactose and microcrystalline cellulose. (a) 50% Ethanol liquid phase: (□) coarse lactose; (▲) fine lactose; (○) microcrystalline cellulose; water liquid phase: (▼) microcrystalline cellulose. (b) (□) Coarse lactose-microcrystalline cellulose, (△) fine lactose-microcrystalline cellulose, (○) microcrystalline cellulose.

assuming zero contact angle at the solid-liquid interface. Thus, it should not be expected that the calculated values of the pore size give the actual pore size distribution. Hence, the pore size distribution curves give, at best, a qualitative indication of the nature of the pore spaces involved.

Fig. 8 shows the relative dimensions of the capillaries as the powder bed is being drained. As previously stated, increasingly smaller diameter capillaries are being emptied/filled as the suction pressure increases/decreases. The hysteresis effect for all the samples results in relatively larger diameter pores filling in the sorption stage than have been emptied during desorption. This result is expected from the 'ink-bottle' effect described above.

Although the above plots are difficult to interpret, they do, nevertheless, permit differentiation between the coarse and fine grades of lactose and the effects of solvent change on microcrystalline cellulose. It is also possible to distinguish between the binary mixtures of microcrystalline cellulose containing the coarse and fine lactose grades (Fig. 8b), confirming the previous observation that the former has the larger pore size distribution. Carman's equation (1941), $h_t = \tau/mg\rho$, has been applied to characterise the pore structure of pharmaceutical tablets, by measuring the rate of water penetration into the tablet (Ganderton, 1969). In agreement with the present results, it was also found that a more coarse pore network arose when granules of increasing size were used to prepare the tablet.

Conclusions

The technique of monitoring the movement of fluid out of, and into, a powder bed enables the relationship between the saturation of the bed to be measured as a function of time and applied pressure. This may be used to characterise the powder bed structure and differentiate between powders of different mean particle size, e.g. lactose, or powders with different properties such as microcrystalline cellulose. The simplest method of distinguishing between the samples is to determine the removal of fluid as a function of time, at a constant applied pressure. From this the equilibrium liquid content and extent of hysteresis may be used as parameters for comparison. However, there are disadvantages: firstly, the procedure should be repeated, using at least two varying pressures, to ensure that the results are correctly interpreted; secondly, results are prone to errors, since they are highly dependent on accurate sampling and the structure of the powder bed. Therefore, it is preferable to measure the movement of liquid as a function of pressure. There are several advantages:

(i) Only one sample of the powder is required to derive the above curve, therefore errors due to sampling are eliminated.

(ii) The characteristics of the powder bed are determined for a wide range of pressures, allowing a more extensive comparison to be made between the different materials.

(iii) An indication is obtained of the relative pore sizes of the materials being studied.

The shortcomings of the apparent 'pore size distribution' curves have already been discussed, and they may be of limited use in distinguishing between samples. In view of this, it seems preferable to characterise the various systems by the capillary pressure-percentage curves. A useful parameter derived from this relationship is the irreducible saturation. The magnitude of this value may indicate the extent of solid-liquid interaction, permitting differentiation between materials that can adsorb a liquid phase (microcrystalline cellulose) and those which do not (lactose).

Through the pressure membrane technique, improved understanding is possible of the physical characteristics which make microcrystalline cellulose an essential ingredient in extrusion formulations. Results from a study of differential thermal analysis of microcrystalline cellulose-water showed that the microcrystalline cellulose adsorbs 0.856 mol (15.41 ml) water per 100 g solid (Fielden et al., 1988). The level of irreducible saturation for this system is 84.6 ml per 100 g solid. Taking the difference between these values, it is concluded that the level of hydraulic isolation in the microcrystalline cellulose-water system is 69.2 ml water per 100 g solid. Thus, microcrystalline cellulose is able to trap a large volume of liquid within its substrate and retain it despite the application of high pressures. In this way the movement of water through the plastic mass is controlled during processing. This might be one of the most important qualities that is required, making microcrystalline cellulose a necessary ingredient for extrusion-spheronisation. Such formulations generally have high moisture contents and inclusion of microcrystalline cellulose may obviate separation of the liquid phase, as the material is being pressurised during extrusion and spheronisation.

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