

THE SPHERICAL AGGLOMERATION OF AQUEOUS MINERAL
SUSPENSIONS BY AN IMMISCIBLE LIQUID

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by
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"TO THE MEMORY OF MY MOTHER"

ABSTRACT

An investigation has been made of the spherical agglomeration of an aqueous suspension of alkyl sulphate coated alumina by a second immiscible liquid. Alumina particles ranging in size from 86 to less than 10 μm were used. Various non-polar liquids were employed but the system most extensively investigated was alumina/water/iso-octane. The conditions for good agglomeration have been determined and the effect of the main variables on agglomerate size, composition and strength studied. The physico-chemical conditions required for good agglomeration were determined. The selective agglomeration of alumina from an ilmenite-alumina mixture was also investigated.

Agglomeration of alumina occurred at sodium dodecyl sulphate concentration corresponding to contact angle between alumina, water and oil of 90° and over. The adsorption density of S.D.S. on alumina was greater when the oil was present than when it was absent.

Larger agglomerates were formed by increasing the rotational speed and by decreasing the amount of suspending liquid. Agglomeration of alumina occurred within a narrow range of bridging liquid volumes. The rate of agglomerate growth was determined primarily by the bridging liquid content. Differences in agglomerate growth characteristics were observed between the coarse and fine alumina particles. The amount of oil required to agglomerate different alumina size fractions was proportional to the agglomerate pore volume. The fractional filling of the agglomerate pore volume by oil varied with particle size, being smaller with the finer material.

Stronger agglomerates were obtained by decreasing the particle size or by increasing the spread of the alumina size fractions. The agglomerate strength was also affected by the oil content.

Alumina was selectively agglomerated and separated from alumina-ilmenite mixtures using S.D.S. to modify the alumina surface.

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CHAPTER 1
INTRODUCTION

INTRODUCTION

1.1 Treatment of slimes in mineral processing

The slimes fraction of an ore can be defined as that material too fine for efficient treatment by the process under consideration. Thus slimes in a gravity concentration process might be less than say 50 μm in size, whereas those in flotation can be less than 10 μm . Furthermore, the slime size is not just dependent on the type of process, but also depends on the mineral mixture to be separated. This is especially true of flotation where sulphide ores down to about 1 μm can be treated, but fluorite ores have to be deslimed at about 20 μm prior to flotation.

In the past the mineral industry has not been too seriously hindered by slimes. Where water and space were available the slimes were simply dumped in settling lagoons or some convenient river. The situation is, however, rapidly changing, because of environmental pollution considerations and also the loss of valuable material in the slimes is no longer economically justified. New processes are being sought to treat not only the slimes produced during the liberation of valuable minerals, but also to treat those deposits where the mineral grains are very fine e.g. less than 2 μm as in the case of kaolin deposits.

Of the mineral separation techniques in common use, flotation treats the finest particles. Even in this process, however, slimes cause many problems. The optimum particle size range for flotation is about 10 to 100 μm , but below this size the flotation rate decreases and the minerals

are not recovered in a reasonable time.¹ Hydrodynamic considerations show that the reduction in flotation rate with particle size is related to the decreased probability of bubble-particle collisions^{2,3}. Some authors^{4,5} further suggest that very fine particles might never collide with a bubble either because they will be swept away in the streamlines or because of the presence of diffusiophoretic forces. Slimes also consume large amounts of collector, become coated on coarser particles⁶ and are entrained in the froth⁷. All of these factors are discussed in detail by Klassen and Mokrousov⁸.

Most of the processes suggested for the selective treatment of slimes are based on exploiting differences in the surface chemical properties of minerals. Such processes as 'piggy back'⁹ and column flotation¹⁰, two-liquid flotation¹¹, two-liquid extraction¹², selective flocculation¹³ and spherical agglomeration process are being considered. These processes have recently been reviewed^{14,15} and their future usage considered.

1.2 Use of oil in mineral separation

The use of an oil phase for the concentration or extraction of fine particles dates back to the late 19th century¹⁶. At this time oil was used not only as a collector for sulphide minerals¹⁷, but also as a bouyancy medium for the concentration of hydrophobic minerals. The dispersion of oil in water is energetically more favourable than that of air in water. Furthermore, the interfacial area generated is greater and the drop size smaller than that obtained with air in water dispersions. Two-liquid systems therefore, have the advantage of a high probability of particle-drop collisions and also of a large interfacial area for particle attachment.

The techniques that use oil can be divided into three groups according to the amount of oil used. These groups are:

- i) Emulsion flotation¹⁸
- ii) Oil spherical agglomeration
- iii) Two-liquid flotation or extraction

In emulsion flotation up to 2 Kg/tonne of ore, of a non-polar oil is added to improve the distribution of a fatty acid collector and to increase the hydrophobicity of the collector coated particles. Examples include the flotation of manganese¹⁹ and ilmenite ores²⁰.

The two-liquid flotation process involves the addition of a non-polar oil (up to 30% of the total volume) to a collector conditioned mineral pulp. The oleophilic particles concentrate at the oil/water interface and the mineral laden oil drops rise to the top to form a separate layer. Separation of the oil-rich layer from the aqueous phase is readily achieved either by draining off the aqueous phase or alternatively allowing the organic-rich phase to overflow into a launder. Application of the process to the treatment of tin ores^{21,22}, kaolins²³, hematite^{24,25} and fluorite-barite slimes²⁶ in the presence of the collectors usually employed in the flotation of these minerals has shown that selective mineral separations can be made. The two liquid flotation process depends on the formation of a contact angle between the mineral, water and oil and the larger the angle the greater the work of adhesion of the oil to the solid. A contact angle is obtained because of the adsorption of collector at the mineral/water interface. Just recently Stratton-Crawley¹² has shown that in the presence of a suitable surfactant contact angles approaching 180° are possible. Under these conditions complete extraction of the particles into the oil occurs and a process analogous to the solvent extraction of metal ions

is achieved. The spherical agglomeration process uses less oil than the two liquid flotation process and it is considered in more detail in the next section.

1.3 Spherical agglomeration of minerals in liquid suspensions

The spherical agglomeration process, described by Farnand, Smith and Puddington²⁷, provides another way of upgrading and recovering finely divided solids suspended in a liquid. In this process the fine solids are agglomerated and separated from the liquid phase by the use of a small amount of a second liquid. This second liquid is immiscible with or very sparingly soluble in the suspending medium, and furthermore, it preferentially wets the relevant solid particles. Subsequent agitation of the suspension causes the solid to become coated (partially or totally) with the second liquid. Collisions between similarly coated particles result in the particles sticking together because of the formation of liquid bridges, and for this reason the second liquid is usually called a "bridging liquid". With the aid of a suitable tumbling action, compact and approximately spherical agglomerates ranging in diameter up to 2 cm or more can be formed. Water is normally used as the suspending medium, while the bridging liquid is usually non-polar. The process works efficiently however with the roles of the organic and aqueous phases reversed.

The form and strength of the agglomerated product is very dependent on the amount of bridging liquid added, the degree and type of agitation, and on size, size distribution, and surface conditioning of the relevant particles. With relatively large amounts of bridging liquid, two immiscible liquid phases are formed and the particles either concentrate at the liquid-liquid interface as in

the two-liquid flotation process^{11,28}, or are transferred into the carrier phase²⁹. Addition of too little bridging liquid results in the formation of microagglomerates or flocs, which are quite weak and difficult to separate by mechanical means. The type and degree of agitation applied to the suspension influence significantly the size and size distribution of the agglomerates produced, and Sirianni and co-workers³⁰ have reviewed experience gained with various types of mixing equipment. The type of agitation is important because it must not only distribute the bridging liquid uniformly, but also promote interparticle collisions and agglomerate growth. Another aspect which is of considerable importance is the relative wettability of the suspended solids. This can be controlled by the addition of conditioning agents. Selectivity in the treatment of an aqueous mineral mixture with a non-polar oil bridging liquid is achieved by conditioning the ground ore with a collector which will render the surface of one of the minerals oleophilic. A small amount of oil is then added and conditioning continued either in a ball mill, high speed blender, grease kettle, shaker, inclined pan or drum agglomerator, or in a rolling tube³⁰ until the oleophilic particles become sufficiently agglomerated. They are then removed from the aqueous pulp by screening or sedimentation. Collectors, activators and depressants can be employed in this process in a similar way to their use in flotation^{31,32}.

The possible uses of the spherical agglomeration process are as follows:

- i) the removal of fine particles from liquids or alternatively the removal of liquids dispersed in other liquids.

ii) The selective separation and concentration of minerals and

iii) The breaking of oil in water or water in oil emulsions. Finely ground particulate material is added to pick up the emulsified phase and form spherical agglomerate~~s~~.

The spherical agglomeration process was first described and named in 1960 by Puddington and co-workers³³, who described the agglomeration of barium sulphate suspended in benzene and other organic liquids, by the addition of small amounts of water. This was not, however, the first reference to the fact that coagulation of dispersed solids can occur if a second immiscible liquid is added³⁴. Kruyt and Van Selmas in 1943^{35,36} observed that glass beads suspended in halogenated hydrocarbons were agglomerated by the addition of small amounts of water.

Reviews of the spherical agglomeration process have been made by Puddington et al^{37,27} and Capes³⁸. Farnand²⁷ *et al.* gave examples of this technique and showed that graphite, zinc sulphide and calcium carbonate could be selectively removed from a mixture in aqueous suspension by addition of small amounts of oil. Sutherland^{39,40} studied the agglomeration of aqueous suspensions of graphite in a rotating drum, and tried to determine the effect of some of the operating variables such as drum load, speed of rotation, and suspension and bridging liquid concentrations. His experimental data ~~were~~ however, based on only one size fraction and therefore his proposed mechanism of agglomerate growth is not generally applicable. The results indicated that at least two mechanisms were involved ; the first involving the formation of small agglomerates from the finely suspended graphite and the second, the coalescence of these agglomerates to form larger spheres. The diameter of the spheres produced in the first stage appeared

to be dependent on the amount of bridging liquid available, whereas for the second stage the limit seemed to be fixed by the ability of the larger agglomerates to resist breakage. The rates at which these mechanisms, particularly the latter one, occurred were affected by operating conditions such as solids concentration and turbulence level. An artificially prepared mixture of graphite and calcium carbonate was selectively agglomerated with satisfactory results. Capes and Sutherland⁴¹ gave a more detailed analysis of the spherical agglomeration process and in their experiments water was a bridging liquid and the solid was various grades of sand. Bridging liquid requirements were correlated with the voids between the highly compacted sand particles. The final size reached by an agglomerate was considered to result from a balance between the destructive and the cohesive forces acting on the sand sphere.

Spherical agglomeration has been applied on the laboratory and pilot plant scales to treatment of mineral mixtures containing tin^{42,43}, iron and apatite^{44,45}, gold⁴⁶, germanium⁴⁷, ilmenite⁴⁸, barite⁴⁹, silica⁵⁰, and coal⁵¹⁻⁵⁷. In these works it was found that as the agglomerates grew they became more selective towards the hydrophobic mineral. Hydrophobic mineral particles forced less hydrophobic particles out of the agglomerate in competition to contact the organic bridging liquid. These observations suggest that more than one stage should be employed in a selective agglomeration process, and this point was also made by Meadus and Puddington⁴⁹ who treated the tailings from a lead-zinc mine to produce a high grade barite. Four-stage flotation of the barite had produced a grade of 95% but at a yield of only 25% of the available barite. In comparison a two stage agglomeration process yielded the same grade of barite at a recovery of over 80%.

The application of spherical agglomeration to the removal of a small amount of an organic liquid from suspension has been demonstrated by Sparks⁵⁸ in the continuous separation of bitumen from high clay tar sand. Recoveries of 95% and higher were obtained, and this is a promising technique for oil recovery from tar sand, which represents a considerable potential oil reserve.

Another application of this method which is receiving much interest is the beneficiation of fine coal with the following objectives; a) recovery of the carbonaceous material, b) rejection of the ash constituents, c) displacement of the water associated with the coal and d) disposal of the rejected tailing. In the work reported by Meadus et al⁵¹ the fractionation of coking coals was studied. The effect on the final product of using different bridging liquids such as hexane, cyclohexane, benzene, asphalt or coal tar distillates, and of grinding time, gangue depressants and modes of agitation, was discussed. The ash and sulphur contents of the beneficiated coal were found to be at very low levels, for example coal (-37 μm) containing 20% ash and 0.5% sulphur, gave agglomerates with 4.6% ash and 0.47% sulphur while recovery of the carbonaceous constituents was estimated to be not less than 95%. Generally coal slurries containing as much as 30 to 50% ash yielded agglomerates with less than 10% ash, while the recovery of the carbonaceous matter was always greater than 90% and often over 95%. Furthermore, use of the oil spherical agglomeration process for the cleaning and recovery of fine coals improved their thermal values because the water associated with coal from previous separations was displaced by the organic phase and excluded. Recently Nicol et al^{56,57} made an experimental study of the process parameters controlling the selective agglomeration of two raw coal slurries having mean particle sizes 0.35 mm and 0.25 mm.

They found that prior emulsification of the bridging liquid improved the process kinetics particularly with high viscosity oils, but that the grade of product and the other equilibrium properties of the system were not significantly affected. The claim that the use of emulsions reduces the oil requirements for agglomeration⁵⁹ was not confirmed by the results of their work. Data on agglomerate growth were also obtained but are of little general use because the basic properties of the agglomerated particles were not considered. Thus, the effect on agglomerate size of particle size and concentration can only be applied in their own system. The Shell pelletizing separator⁶⁰ is an example of this process carried out on an industrial scale. Its main function is to remove $-5\text{ }\mu\text{m}$ coal from an aqueous dilute suspension. Agglomerates 3 - 5 mm in diameter are formed.

Hematite flotation concentrates have been agglomerated from aqueous suspension to produce pellets for blast furnace feed using an horizontally rotated drum and coal tar as bridging liquid⁶¹. Conventional pelletization to form green pellets is difficult without prior removal of the fatty acid surface coating. The simultaneous performance of agglomeration and mineral separation make the process more advantageous than the conventional pelletizing technique. It was shown that the agglomeration efficiency of the hematite becomes a maximum when the surface of particles is covered by a complete monomolecular film of oleate. The finding that the size distribution of the agglomerates is not affected by the number of drum revolutions, and that the agglomerate size decreases as the drum speed and feed load in drum increase are questionable. It was concluded that the agglomeration efficiency is improved, that the size of agglomerates is increased, and that they become more spherical by using coal together with coal tar as bridging liquid.

Spherical agglomeration is also applicable to the removal of precipitated CaSO_4 formed during phosphoric acid production⁶². The fresh precipitate of CaSO_4 is very fine and difficult to separate by settling or filtration. The fine suspended particles can, however, be separated as densified bodies by agitating the slurry with a petroleum sulphate type surfactant and a light hydrocarbon liquid. Recently Szczypa and coworkers⁶³ reported the spherical agglomeration of flocculated sediments of wastes after sulphur flotation, containing highly dispersed CaCO_3 particles as the main mineral component. Agglomeration was obtained by transferring the initially flocculated waste (Maynofloc - 351 used as flocculant) into rotary motion. Homogeneous agglomerates were obtained 4.8 mm diameter containing 45-55% moisture, and having increased mechanical resistance which enabled them to be separated readily on a large mesh sieve.

Although the agglomeration process has been applied on the laboratory and pilot plant scales, little is known about the optimum conditions required, the fundamental principles controlling the agglomerate growth and the physico-chemical aspects involved. Furthermore, no systematic work has been carried out on the factors which affect agglomerate size, rate of agglomerate formation and the product properties, when an inclined agglomerator is used. The kinetics of spherical agglomeration in high speed blenders have, however, been studied in more detail. Recently Kawashima and Capes^{64,65} investigated the kinetics in a stirred vessel using silica sand, glass and calcium powders dispersed in carbon tetrachloride and agglomerated with aqueous chloride solution. Most of the parameters which influence the kinetics and agglomerate size were considered, and it was found that all the data could be represented by a first-order kinetics equation. Differences in behaviour between coarse and fine particles

were observed with regard to bridging liquid requirements without considering the possible mechanisms responsible for agglomerate formation. Even more recently the same authors⁶⁶ investigated the kinetics of spherical agglomeration of a binary mixture composed of sand (76, 89 or 106 μm) and CaCO_3 (3.8 μm) in liquid suspension at high agitation rates. The rate constant of agglomeration achieved a maximum value at the composition of the mixture corresponding to the closest binary packing in which fine particles just filled the interstices between coarse particles, and when the fine particles just covered the surface of the coarse particles. It was concluded that preferential coalescence between fine and coarse particles, and also random coalescence were operative.

It can be concluded that although the spherical agglomeration process has not yet been adopted as a large scale industrial process, it has shown considerable potential in a number of fields. At present the high prices of petroleum products make the process attractive mainly for more valuable ores. An important economic consideration in the application of the spherical agglomeration process is the recovery or subsequent use of the bridging liquid. If it is volatile, recovery and re-use may be preferable but a more attractive alternative is its use as a fuel or reactant in a later step of the process. In this case, the intimate contact obtained between the solid and the bridging liquid will be of considerable value. Capes, Smith and Puddington⁵³, and Mular and Puddington⁶⁷, made an economic assessment of the application of the process in coal preparation and in iron ore treatment respectively. It was shown that this method is technologically feasible, and its profitability is governed primarily by the value which can be assigned to the feed, and the cost and amount of oil used. A wide acceptance of the process, for example in the preparation of fine coal has been prevented in the past due to :

- i) high cost of oil,
- ii) the low market price of coal fines,
- iii) the mechanical difficulties which are in some cases associated with the separation of the agglomerated product,
- and iv) the high energy requirement necessary to cause phase separation⁶⁸.

CHAPTER 2
THEORETICAL CONSIDERATIONS

2

THEORETICAL CONSIDERATIONS

2.1 Basic thermodynamic considerations for a two liquid-solid system2.1.1 Wetting

The spherical agglomeration process is based on the preferential wetting of the solid by one of the two liquids present. It is, therefore, dependent on the contact angles between the three phases and on the solid-liquid and liquid-liquid interfacial tensions. The interfacial tension of the two solid-liquid interfaces will be dependent on the nature of the solid and liquids, and whether or not the solid surface has been modified by the presence of a surfactant layer.

In a solid/liquid/vapour system (Fig. 2.1a) bubble attachment to the solid surface is described by Young's equation⁶⁹ which for ideal equilibrium conditions becomes:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad (2.1)$$

where γ_{SV} , γ_{SL} and γ_{LV} are the interfacial tensions of the solid/vapour, solid/liquid and liquid/vapour interfaces; and θ is the contact angle measured through the aqueous phase respectively. For a finite value of the contact angle it follows that the following condition must be fulfilled

$$\gamma_{SV} - \gamma_{SL} < \gamma_{LV} \quad (2.2)$$

The work of adhesion of a liquid to a solid (W_{SL}) is defined by the Dupré equation

$$W_{SL} = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \quad (2.3)$$

and the combination of equation (2.3) and (2.1) relates the contact angle to the surface tension of the liquid i.e.

$$W_{SL} = \gamma_{LV} (1 + \cos\theta) \quad (2.4)$$

For a two liquid-solid system (Fig. 2.1b) where the liquids are water (w) and a non-polar oil (o), the Young's equation becomes:

$$\gamma_{So} - \gamma_{Sw} = \gamma_{ow} \cos\theta \quad (2.5)$$

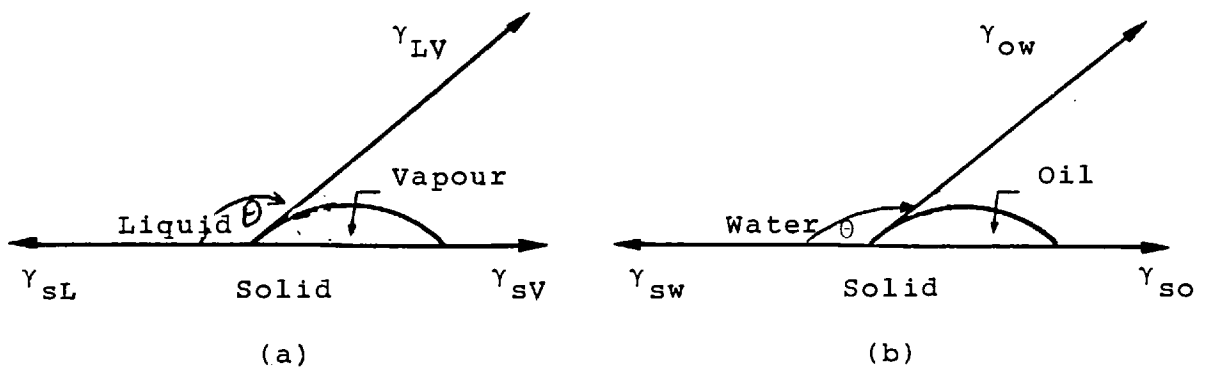


Fig. 2.1: Contact angle vector diagrams for Young's equation

The works of adhesion of the water (W_{ws}) and the oil (W_{os}) to the solid are given by:

$$W_{ws} = \gamma_w + \gamma_s - \gamma_{ws} \quad (2.6)$$

$$\text{and } W_{os} = \gamma_o + \gamma_s - \gamma_{os} \quad (2.7)$$

where γ_w , γ_s and γ_o are the surface tensions of the water, solid and oil respectively.

Unfortunately these equations cannot be combined with Young's expression to give the works of adhesion in useful measurable terms. Combination of equations (2.7) and (2.6) in the following way gives the condition for the displacement of one liquid from the solid surface by the other:

$$W_{os} - W_{ws} = \gamma_o - \gamma_w - (\gamma_{os} - \gamma_{sw}) \quad (2.8)$$

which on substituting from equation (2.5) becomes:

$$W_{os} - W_{ws} = \gamma_o - \gamma_w - \gamma_{ow} \cos \theta \quad (2.9)$$

This shows that the difference in work of adhesion of the two liquids to the solid is dependent on the difference in surface tensions of the two liquids, the liquid-liquid interface tension and the contact angle. All these quantities are measurable. Equation (2.9) gives the condition for θ to be obtuse ($>90^\circ$) which will correspond to the oil advancing over the solid i.e.

$\gamma_{ow} \cos \theta$ must be negative

and

$$W_{ws} - \gamma_w < W_{os} - \gamma_o \quad (2.10)$$

The difference of the work of adhesion and surface tension is often referred to as the adhesion tension of the liquid on the solid^{70,71}. Reference to equation (2.4) shows that the adhesion tension of the water (A_{ws}) and oil (A_{os}) to the solid are also equal to $\gamma_w \cos \theta_w$ and

$\gamma_o \cos \theta_w$ respectively, where θ_w and θ_o are the contact angles measured in the presence of the relevant liquid and its vapour. For preferential wetting of the solid by the oil it follows therefore that

$$A_{os} > A_{ws}$$

and

$$\gamma_s - \gamma_{so} > \gamma_s - \gamma_{ws}$$

or

$$\gamma_{os} < \gamma_{ws} \quad (2.11)$$

The latter is also readily obtained from Young's equation. For complete displacement of the water by the oil (i.e. $\theta \rightarrow 180^\circ$), from equation (2.9)

$$W_{os} \gg W_{ws} + \gamma_o - \gamma_w + \gamma_{ow} \quad (2.12)$$

or, alternatively, for complete displacement of the oil (i.e. $\theta \rightarrow 0^\circ$)

$$W_{os} \ll W_{ws} + \gamma_o - \gamma_w - \gamma_{ow} \quad (2.13)$$

Strictly speaking, allowances should be made in the above equations for the decrease in surface energies caused by the adsorption at the solid/water interface of the organic phase and vice versa. This can be done by including terms referred to as "equilibrium spreading pressures" or "film pressures" (π). The film pressure at the oil/solid interface, saturated with water is defined as the difference between the oil/solid interfacial tensions obtained before and after water has been adsorbed at the surface.

$$\pi_{os,w} = \gamma_{os} - \gamma_{os,w} \quad (2.14)$$

These terms have been omitted from the above treatment for the sake of simplicity and also because their inclusion would not significantly alter the conclusion. This point is also argued by Melrose⁷² who has shown that in two liquid systems the film pressure can be neglected.

The above analysis suggests that in the oil spherical agglomeration process the migration of a solid particle from the aqueous phase to the oil phase is governed by the relative values of the interfacial tensions and contact angle. The conditions for spherical agglomeration or concentration of the particles at the oil/water interface and their dependence on interfacial tensions and contact angle, are readily visualised in Fig. 2.2, as reported by Shergold⁷³.

2.1.2 Laplace equation

The configuration of a two-liquid interface is described by the equation of Laplace⁷⁴, which relates the difference in hydrostatic pressure across the interface to the local mean curvature (J) and surface tension (γ_{ow}) of the interface. If the interface is assumed to take the form of an arc of a circle then the capillary pressure for hydrostatic equilibrium is given by the well known equation

$$P_c = P_w - P_o = \gamma_{ow} J = \gamma_{ow} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \cos\theta \quad (2.15)$$

where P_c is the capillary pressure,

$J = \frac{1}{R_1} + \frac{1}{R_2}$ is the mean curvature of the interface,

R_1, R_2 are the two normal radii of curvature contained by the two mutually perpendicular phases, and $\theta = 180 - \theta_{sow}$.

The radii of curvature R_1 and R_2 are vector quantities and hence have direction as well as magnitude. To be con-

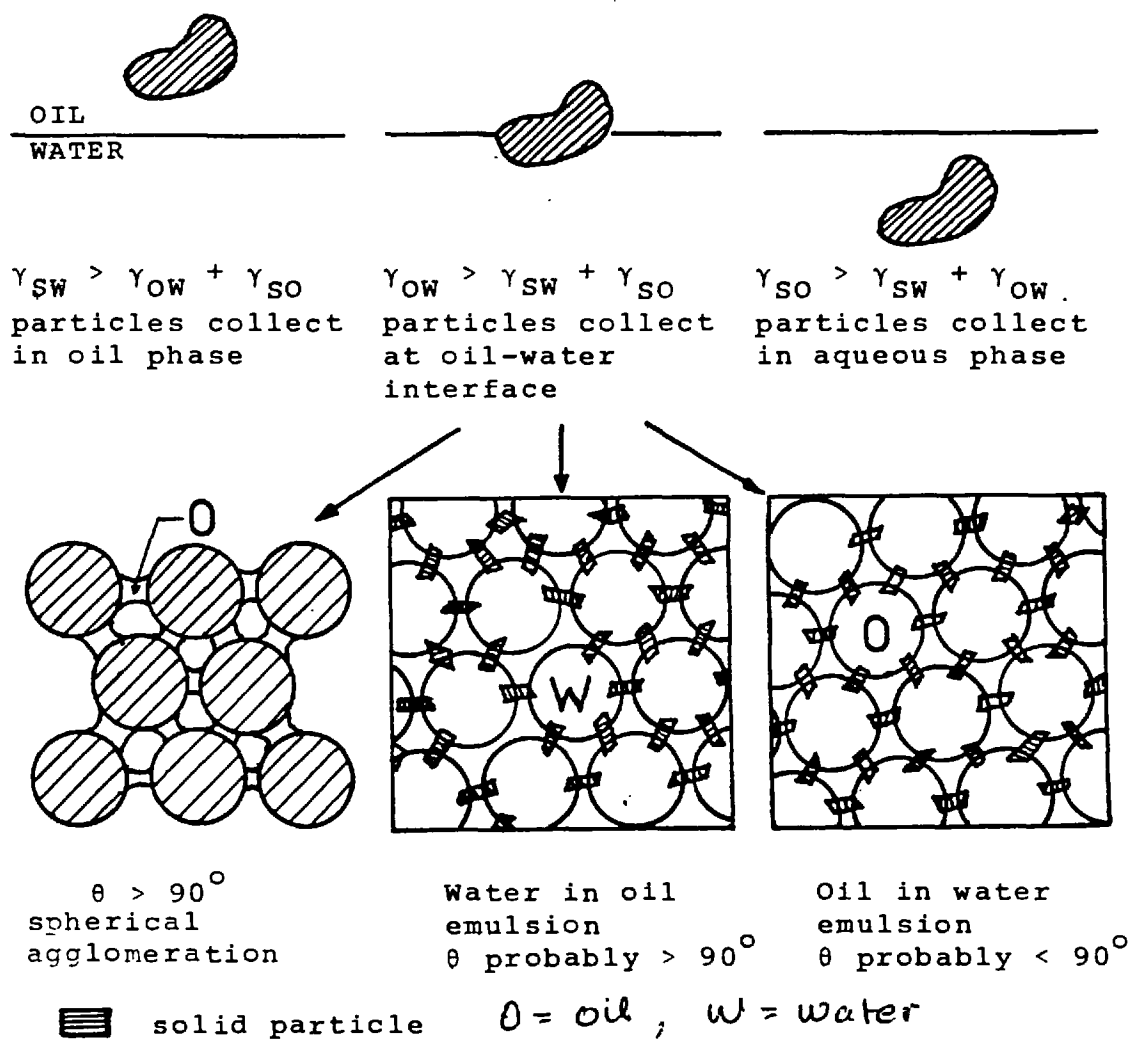


Fig. 2.2: The dependence of the concentration of mineral particles at the oil/water interface on the interfacial energies and contact angle

sistent with later calculations of P_c the centre of rotation of a radius of curvature is given a negative sign if it lies on the side of the interface occupied by the fluid which preferentially wets the solid. It should be remembered that the contact angle (θ_{sow}) of the oil on solid surface is measured through the aqueous phase.

The size of pores in an agglomerate is sufficiently small for the oil/water interfaces to be described as having a constant mean curvature. In the case where a capillary is small enough and has a circular cross-section of radius R , the meniscus represents a portion of a sphere, $R_1 = R_2 = R$ and $P_c = 2\gamma/R$. It is obvious, however, that if there is a finite contact angle (θ_{sow}) $P_c = 2\gamma\cos\theta/R$. For a meniscus rising in a capillary, the walls of which taper outwards at an angle of ψ to the horizontal, the Laplace equation assumes the form $P_c = 2\gamma\cos(\theta + \psi)/R$, where R is the radius of the capillary. In general the shape of a meniscus is of interest in many theoretical and practical problems, particularly in cases where the forces exerted by the meniscus have to be determined. The Laplace equation will present serious difficulties however when relatively complex solid surface configurations are involved. Many authors^{75,76} have studied meniscus properties and given formulae to describe possible configurations. Melrose⁷⁷ considered the Gaussian curvature configuration and found that such a surface, when expressed in Cartesian form, is given by the following expression

$$r(1 + q^2) - 2pqs + t(1 + p^2) = J \{1 + p^2 + q^2\}^{3/2} \quad (2.18)$$

where

$$p = \frac{\delta z}{\delta x}, \quad q = \frac{\delta z}{\delta y}, \quad r = \frac{\delta^2 z}{\delta x^2}, \quad s = \frac{\delta^2 z}{\delta x \delta y}, \quad t = \frac{\delta^2 z}{\delta y^2}$$

Thus the general case corresponds to the non-linear second order partial differential equation of the elliptic type.

2.2 Strength of agglomerates

2.2.1 Effect of oil volume and solid wettability

The possible distribution of the organic phase (bridging liquid) within the pores of an agglomerate is shown in Fig. 2.3 by analogy with the formation of agglomerates from solid particles and a single liquid (pelletizing). The bridging liquid can be present in different amounts to give agglomerates in the pendular, funicular, capillary or saturated state. In the present work aggregates formed in the spherical agglomeration process will be termed "agglomerates" and those formed in green pelletization as "pellets" or "granules".

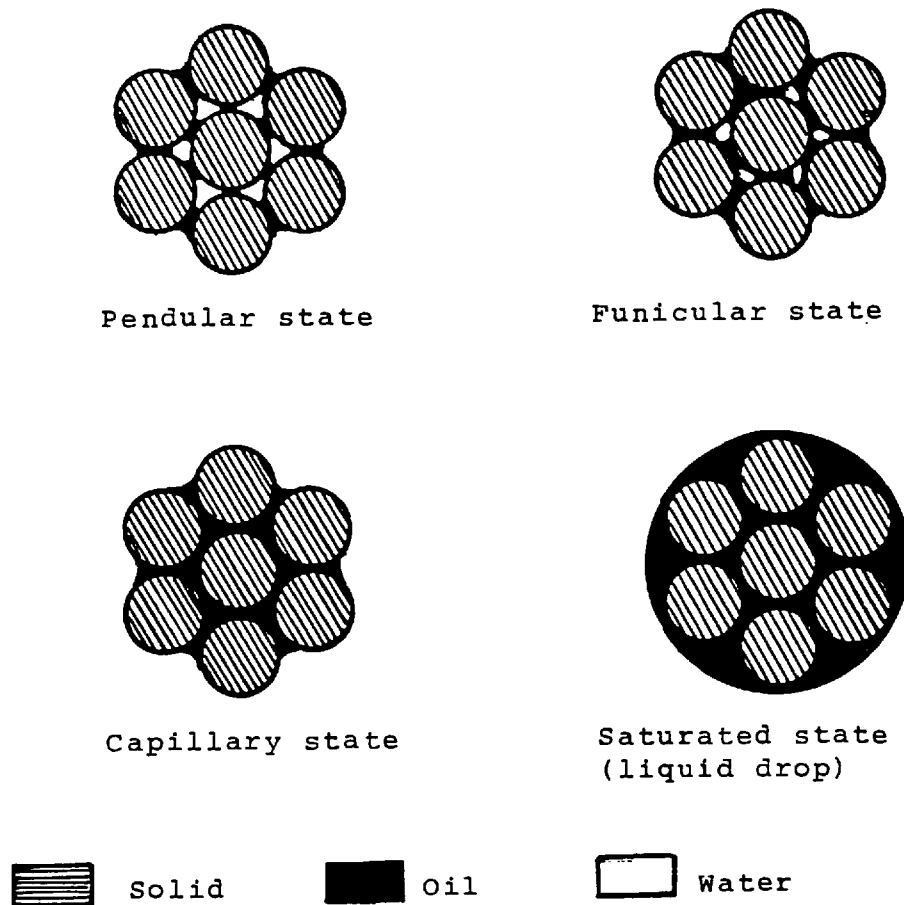


Fig. 2.3: Bridging liquid distribution in agglomerates

Pendular state. The organic phase occurs as discrete double concave lens shaped rings around grain-to-grain contacts, and if it completely wets the solid it will additionally coat the remainder of the particles with a very thin film. This state gives rise to a flocculated product with an open structure, which is brittle and easily broken down.

Funicular state. Addition of further bridging liquid to the pendular rings causes them to grow and merge to form a continuous network of the organic phase. The particles are drawn closer together by capillary forces resulting in the formation of spherical agglomerates.

Capillary state. When the agglomerate pores are completely filled with the second liquid the capillary state is reached. Here the cohesion forces which result from the interfacial tension between the two liquids have their maximum value, and agglomerates show plastic flow properties and can be deformed without being fractured.

Saturated state. When even more of the organic liquid is added, the product changes to soft paste, the solids being effectively totally enclosed in a large drop of bridging liquid. This state is, however, of much less importance.

Newitt and Conway-Jones⁷⁸ based their work on the studies of Haines^{79,80} and Fisher⁸¹ in the field of soil mechanics and investigated the theory of granule formation in an air-water-solid system. They proposed expressions to calculate the granule strength in the pendular, funicular and capillary states, and gave experimental evidence to support the validity of their theoretical considerations. Rumpf^{82,83} carried out experiments in which the tensile strengths of granules were determined by a practical

technique. The results were in close agreement with the theoretical values for the pendular state, but were always low for the capillary state due to possible air inclusions. His work also suggested a correlation between the tensile strength and the compressive strength of green granules, and he found that the ratio of compressive strength/tensile strength was 0.5 to 0.7.

Summarised in Table 2.1 are expressions proposed by many authors to describe the strength of agglomerates in the field of pelletization,⁸⁶ soil mechanics, etc. The validity of those equations is based on a number of assumptions, i.e. regular systems of spherical packing, circular or constant meridian curve of the curvature of the liquid air interface, and zero contact angle.

Although these assumptions often serve to give a good qualitative description of the systems involved, the results obtained are very difficult to correlate with real systems. The theoretical tensile strengths of agglomerates of monosized particles proposed by Rumpf⁸² equation A4, Table 2.1, will be accurate only if the following assumptions are valid:

- i) The solid particles are spheres
- ii) The liquid bridges are on the average randomly distributed across the section and over all directions in space
- iii) The effective bonding forces are distributed about a mean value which can be used to represent each one
- iv) Granule cross-sections are homogeneous and possess equal strength across their whole areas.

Table 2.1: Expressions to determine strength of pellets due to capillary and interfacial tension forces at various bridging liquid contents

Pendular State	Funicular State	Capillary State
(A ₁) $F_p = 2\pi r\gamma \left[1 + \tan\frac{\phi}{2} \right]$ (81)	(B ₁) $\sigma_{zf} = S P_c$ (78)	(C ₁) $\sigma_{zc} = P_c = \frac{\gamma}{m}$ (82)
(A ₂) $F_p = \frac{2\pi r\gamma(1 - 2\tan\frac{\phi}{2})}{1 + \tan\frac{\phi}{2}}$ (79)	(B ₂) $\sigma_{zf} = \frac{\sigma_{zp} + (S - S_p)(\sigma_{zc} - \sigma_{zp})}{1 - S_p}$ (82)	(C ₂) $\sigma_{zc} = P_c = X' \frac{\gamma}{r}$ (78)
(A ₃) $F_p = \pi R_2^2 \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$ (84)		(C ₃) $\sigma_{zc} = P_c = X \frac{1 - \epsilon}{\epsilon} \cdot \frac{\gamma}{r}$ (78)
(A ₄) $\sigma_{zp} = \frac{9}{8} \frac{(1 - \epsilon)}{nd^2} K.H$ (82)		
(A ₅) $\sigma_{zp} = cf \left(H, \frac{1}{d^3} \right)$ (85)		
(A ₆) $\sigma_{zp} = f. (1 - \epsilon) K \frac{H^*}{d}$ (87)		

Key to formulae: F_p = tensile force at an individual bridge (N), r = radius of a spherical particle (m), γ = interfacial tension at the liquid bridge interface (N/m), $1/R_1 + 1/R_2$ = mean curvature of oil/water interface, d = particle diameter (m), ϕ = semi-angle subtended by wetted meniscus (rad.), σ_{zp} = tensile strength of a pendular pellet (N/m²), K = mean coordination number, H = mean particle force (N), ϵ = porosity of pellet, f = factor dependent on shape of particle, σ_{zf} = tensile strength of a funicular pellet (N/m²), σ_{zc} = tensile strength of a capillary pellet, S = fraction of pore volume filled by bridging liquid in funicular state, S_p = fraction of pore volume filled by bridging liquid in pendular state, P_c = average capillary pressure, m = mean hydraulic radius of the pores (m), X, X' = dimensionless factors depending upon the type of packing.

In the spherical agglomeration process the approximate strength of the agglomerates formed can be determined by the equations given in Table 2.1 provided that the solid is completely wetted by the bridging liquid and all the other assumptions made in the derivation of these equations are met. To express the forces responsible for the strength of an agglomerate in terms of ϕ , which is a measure of the oil volume in contact with two spherical particles, it is necessary to consider the forces acting to hold two adjacent particles together, Fig. 2.4.

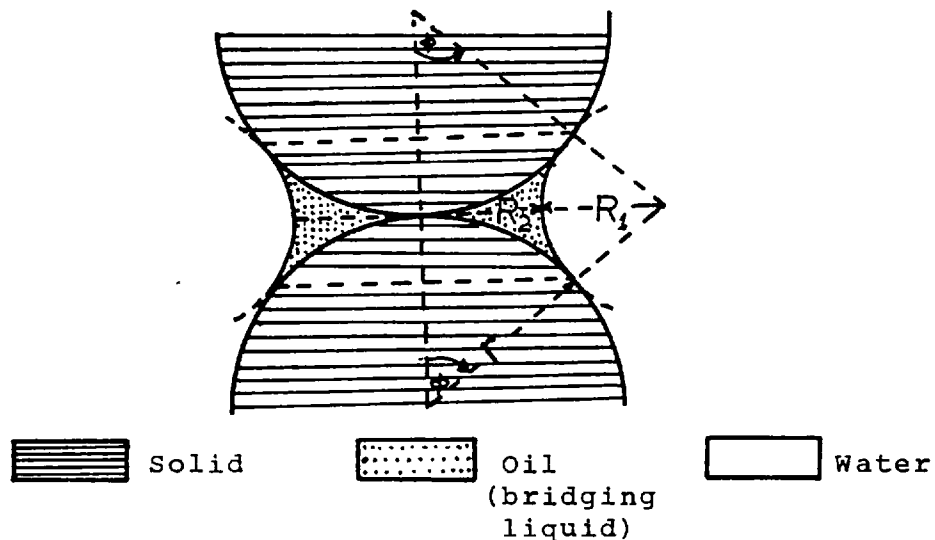


Fig. 2.4: Section through two spherical particles in contact showing lens of bridging liquid at a point of contact

Assuming that the oil/water interface is an arc of a circle of radius R , the main forces acting on the two particles are as follows:

- i) The tension exerted by the oil/water interface. If R_2 is the radius of the neck of the bridging liquid connecting the two spheres, the force which

results is given by

$$F_1 = 2\pi R_2 \gamma_{ow} \quad (2.17)$$

ii) The force which arises because the hydrostatic pressure in the oil is lower than that in the aqueous phase. This force described by the Laplace equation depends on the curvature of the meniscus

$$P_c = P_w - P_o = \pi R_2^2 \gamma_{ow} \left(\frac{1}{R_1} - \frac{1}{R_2} \right) \quad (2.18)$$

Thus the total tensile force due to pendular liquid bridge is the sum of (2.17) and (2.18) given by

$$F_p = 2\pi R_2 \gamma_{ow} + \pi R_2^2 \gamma_{ow} \left(\frac{1}{R_1} - \frac{1}{R_2} \right) = \pi R_2 \gamma_{ow} \frac{R_1 + R_2}{R_1}$$

From the geometry of the Figure 2.4

$$R_1 + R_2 = r \tan \phi, \quad R_1 = r(\sec \phi - 1), \quad R_2 = r(1 + \tan \phi - \sec \phi)$$

Hence

$$F_p = \frac{2\pi r \gamma_{ow}}{1 + \tan \frac{\phi}{2}} \quad (2.19)$$

According to this expression F_p increases as the volume of oil composing the pendular bridge decreases. This can be explained by the fact that the radius of curvature R_1 of the oil/water interface decreases faster than R_2 and sets up an increasingly high pressure deficiency in the oil phase. Another feature of equation (2.19) is that high values for the strength at a single contact are attained only with large particles. However, the strength of an agglomerate depends upon the number of particle to particle bonds per unit of cross-sectional area, and this in turn depends on the sizes of particles present and the manner in which they are packed. To

obtain, therefore, the strength per unit area the force F_p must be divided by the area projected by each particle on the relevant plane, i.e. $F_p/4r^2$, (N/m^2) for open packing and $F_p/r^2\sqrt{2}$ for close packing. For regular packing of spheres the oil menisci remain isolated when $\phi \leq 30^\circ$ in the case of close packing and when $\phi \leq 45^\circ$ for open packing.

Mason and Clark⁸⁸ designed a special apparatus for the measurement of the forces exerted on two spheres when the liquid bridges consisted of a di-n-butylphosphate/liquid paraffin mixture suspended in water. The maximum observed forces agreed with the theoretical calculations of Fisher⁸¹, except that for small liquid bridges the maximum force appeared to diverge from that given by theory. This is to be expected however, since the perimeter of contact between oil and sphere is small, and any discontinuity of the surface could give a higher percentage error than would a similar discontinuity in a larger bridge.

Considering agglomerates in the capillary state, the interfacial forces exist only at their surfaces and it is these which give rise to bonding forces. According to the theory discussed above, the strength increases as oil is progressively removed, until a value is reached when the aqueous phase begins to penetrate the agglomerate pore space. It has been shown⁸² that the contribution of surface tension forces to granule strength is negligible when compared with capillary pressure. The equations given under the capillary state column in Table 2.1 can be used to determine the strength of agglomerates. For non-uniformly sized particles, the hydraulic mean diameter introduced in Rumpf's formula (Table 2.1, C_1) can be estimated by assuming that the pore space between the particles can be regarded as equivalent to a bundle of

parallel capillaries with a common equivalent radius (m_e)
It can readily be shown that⁸⁹

$$m_e = 2 \left(\frac{\epsilon}{1 - \epsilon} \right) \frac{1}{\rho_s S_w} \quad (2.20)$$

where ρ_s is the density of the particles and S_w the weight specific surface area of the powder. Newitt's formula (Table 2.1, C_3) gives the maximum resultant force for randomly packed particles of irregular shape but approximately uniform size.

Alternatively, predictions of the range of agglomerate strengths for the capillary state can be made by taking the two extreme values of the cross sectional area of the pores at the outer agglomerate layer. The pressure produced by a meniscus situated at either position can be calculated. The pore radius (m_i) for uniformly sized particles is related to particle size as follows⁸⁴:

m_1 , maximum = r and m_2 , minimum = $(\sqrt{2} - 1)r$ for open packing,

m_1 , maximum = $0.288r$ and m_2 , minimum = $0.155r$ for close packing, where r is the radius of the spherical particles.

Substituting these values in the equation $P_c = \frac{2\gamma_{ow}}{m_i}$ the cohesive force limits can be found.

Calculations indicated⁷⁸ that in the capillary state the values of cohesive stress of agglomerates are 3 to 4 times those obtained for the cohesive stress in the pendular state.

In the funicular state the strength is intermediate in magnitude between the capillary and pendular states. Larger quantities of bridging liquid produce higher forces and give rise to a greater mobility of the particles.

Barlow⁹⁰ has reviewed the various particle-particle bonding mechanisms for conventional granulation systems. All the above equations make explicit the dependence of agglomerate strength on interfacial tensions, porosity and particle size.

It was pointed out in section 2.1.1 that in the spherical agglomeration process the contact angle is usually between 90 and 180°. The degree of wettability of the solid surface affects the strength of agglomerates. For a constant value of ϕ , which has been defined above as the distance in units of arc between the point where the spheres touch (Fig. 2.4) and the point where the oil/water interface meets the sphere, both the mean curvature of the interface and the volume of bridging liquid associated with unit volume of particle change as a function of contact angle. Table 2.2 presents the effect of contact angle on radius of curvature ($\frac{2}{J'} = \frac{1}{R_1} + \frac{1}{R_2}$) and the volumes of liquid bridges (v) after Kruyer⁹¹.

Table 2.2 : Effect of contact angle on radius of curvature of the oil/water interface and volume of liquid bridges

Contact angle θ_{sow} (°)	$\phi = 30^\circ$		$\phi = 15^\circ$	
	J'/r	$v/2\pi r^3 \times 10^{-3}$	J'/r	$v/2\pi r^3 \times 10^{-3}$
140	3.790	14.26	0.1525	1.01
150	1.162	13.19	0.1168	0.97
160	0.710	12.05	0.0973	0.92

Clearly the strength of an agglomerate decreases as the oleophobicity decreases.

A few authors^{91,92,93} have studied the effect on the forces between particles of various curvature configurations for a range of contact angles. The volume and the surface area of the liquid which forms the bridges between particles is of interest in various engineering applications⁹⁴ and particularly in petroleum reservoir engineering^{95,96}. Equations for calculating these variables have been presented by a number of authors^{97,98}.

In the pendular state the maximum attractive force between two spherical particles making contact was calculated in the presence of a contact angle⁹⁹ from

$$F_{\max} = 2\pi r \gamma \sin \phi \cdot \sin(\phi + \theta) + \Delta P \pi r^2 \sin^2 \phi \quad (2.21)$$

In the capillary state, to obtain the strength of an agglomerate when a finite contact angle exists, the interfacial tension (γ_{ow}) in the equations given in Table 2.1, must be multiplied by $\cos \theta$. For example, Rumpf's equation (Table 2.1, C_1) for this state becomes

$$\sigma_{zc} \approx P_c = \frac{\gamma_{ow} \cos \theta}{m} \quad (2.22)$$

The analysis above has shown that the packing characteristics of solid particles are very important in determining agglomerate strength. It must be stressed that no comprehensive relationship between variables describing a packing arrangement of comminuted irregular particles has so far been possible, although the coordination number has received much attention in the field of particle packing^{100,101}

2.2.2 Surface forces between solid particles

Finely divided particles in liquid suspension are subjected to attractive and repulsive forces and summation of these forces determines whether or not coagulation occurs. The repulsive forces originate from the well

known fact that solid particles suspended in water acquire a net surface charge because of the dissociation of surface ionogenic groups or the preferential adsorption of ions. Counter-ions in the vicinity of the solid/liquid interface maintain electrical neutrality and give rise to the well established electrical double layer.. When two liked-charged particles come together the double layers overlap and repulsion between the particles occurs.

The attractive force between the particles is the Van der Waals force which results from the fluctuating atomic dipole - induced dipole (London) - force universally present in matter. Although this force is weak for pairs of atoms, it is substantially additive for all the atoms in colloidal particles and the net particle-particle interaction is significant.

The calculation of the total interaction energy between the particles and the component energies can be carried out using the theory independently established by Verwey and Overbeek, and Derjaguin and Landau, and known as the D.L.V.O. theory. More simply the interaction can be considered in the form of a potential energy-distance diagram consisting of two parts (a) an attraction due to Van der Waals - London potential and b) a contribution derived from the repulsion of the electrical double layer Fig. 2.5.

When V_A and V_R are summed a potential energy barrier exists which prevents coagulation. An increase in double layer repulsion increases the size of the energy barrier and vice versa. Stable colloidal suspensions are, therefore characterized by a large energy barrier. Complete removal of the barrier is not essential for coagulation because it is quite possible that the particles will have sufficient kinetic energy to overcome the barrier. Under these conditions the effective charge on the particles is significant but small

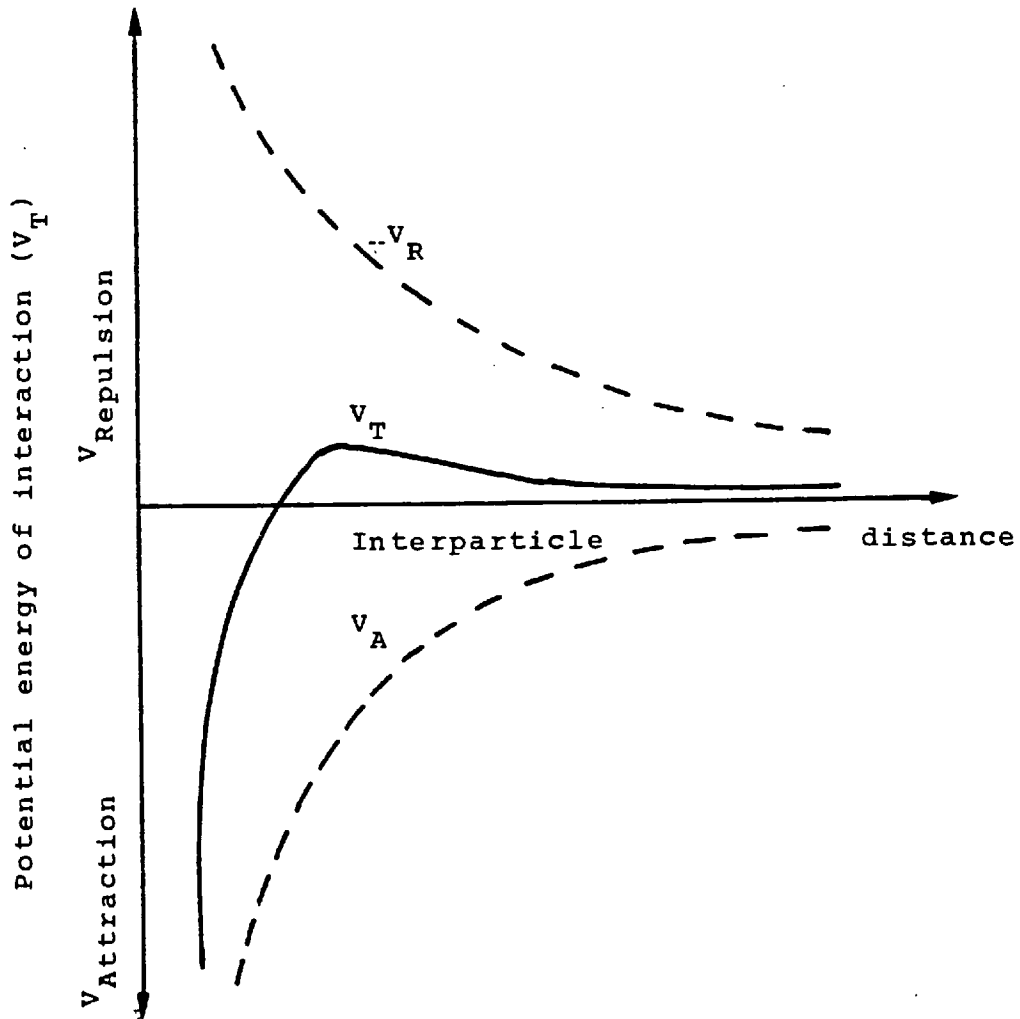


Fig. 2.5 Potential energy-distance diagram

Some other forces influence the particle interactions a) Solvation of surfaces which results in repulsive forces between the particles, and b) hydrophobic association which comes into effect when a particle collision results in direct contact between hydrophobic particles. Possible evidence

for the latter type of interaction is the observation that when ionic surfactants are used to "discharge" certain colloidal dispersions of opposite sign, the maximum rate of coagulation is not found exactly at the zero point of charge but when an appreciable excess of surfactant has been adsorbed. There is no way of quantifying this force at present.

In the spherical agglomeration process the Van der Waals force will be confined to very small areas around the points of contact. The presence of adsorbed liquid films effectively increases the proximity between particles in an agglomerate and may therefore increase the significance of particle attraction due to these forces. Furthermore, if platy minerals characterised by high surface perfection are closely packed and in parallel orientation, then the Van der Waals forces can also reach appreciable values. Meissner et al.^{102,103} found that very fine particles of zinc oxide (up to 1.3 μm) agitated in air were spontaneously agglomerated and they attributed this to the action of Van der Waals forces. Turner and Balasubramanian¹⁰⁴ estimated the magnitude of the contribution to the agglomerate strength of Van der Waals, electrical forces, and forces due to adsorbed layers and concluded that the contribution of each was fairly small. They also reviewed the various equations proposed for these types of forces.

2.2.3 Other forces

In the agglomeration of magnetic particles it has been found that magnetic attraction has a significant effect on agglomerate strength¹⁰⁵. Calculation of this effect is, however, difficult. When the component particles are irregular geometrical interlocking can take place giving rise to increased agglomerate strength.

The strength of agglomerates which have been subjected to heating, drying etc., may be increased by the formation of solid bridges. Solid bridges are promoted by sintering, chemical reactions, melting, crystallization of dissolved material and hardening of a bonding agent at the points of contact between the particles.

Finally, the contribution of mechanical forces applied to the suspension is confined to bringing the individual particles, clusters or agglomerates within the agglomerate charge into contact with one another. The forces discussed can then bring about agglomerate growth.

2.3 Objectives of the present work

The aims of this investigation were as follows:

1. To determine the optimum conditions required to spherically agglomerate various minerals when they were present in both the monomineralic state and in a mineral mixture. Emphasis was placed on determining the optimum particle size and size distribution, and the minimum size for spherical agglomeration. Factors affecting agglomerate growth were considered.

2. To determine the relationship between the optimum conditions and the physico-chemical processes involved in a selected system. This included a study of the three interfaces involved, namely the oil/water, solid/water and solid/oil interfaces in the presence of surfactant.

3. To determine the consistency and other properties of the agglomerates.

and

4. To consider various mechanisms of the agglomerate growth.

CHAPTER 3

STUDY OF THE FACTORS AFFECTING THE SIZE AND
SIZE DISTRIBUTION OF AGGLOMERATES, AND
PERCENT SOLID AGGLOMERATED

3. STUDY OF THE FACTORS AFFECTING THE SIZE AND SIZE DISTRIBUTION OF AGGLOMERATES, AND PERCENT SOLID AGGLOMERATED

3.1 Materials

Ground fused alumina (alpha), obtained from Universal Abrasives Ltd., Stafford, was used as the solid. Prior to use, the alumina size fractions were washed in 10% HCl, rinsed well with double distilled water, and then dried at a temperature of 135°C. This procedure was adopted to remove any soda adhering to the alumina particles. Alumina was used because it has a high zero point of charge (zpc pH 6.7 - 9.4) and therefore, over a wide pH range has a positive surface charge. This means that strong electrolyte anionic surfactants can be used to modify the surface properties of the alumina in acid media and the problems associated with weak electrolytes are avoided. Furthermore the surface chemistry of the alumina / water interface, both in the absence and presence of strong electrolyte type anionic surfactants, is reasonably well documented. A semi-quantitative XRF scan analysis showed that the alumina was at least 99% pure and that there was trace amounts of Si, S, Cl, K, Ca, Fe, Sn, Ba and Ga.

Sodium dodecyl sulphate (S.D.S.), a "chemically pure" reagent (from B. Newton Maine Ltd), was used as the anionic surfactant. This reagent has the structural formula $C_{12}H_{25}SO_4Na$ and because of its strong electrolyte properties it is not extracted into a non-polar organic liquid.

The organic phase was initially 2,2,4 - trimethylpentane (iso-octane) of GPR grade, which was passed through an activated alumina column to remove traces of surface active material. It was established that the iso-octane did not produce agglomeration in the absence of added S.D.S. In later tests, short and long chained paraffins were used as

the organic liquid.

All aqueous solutions were prepared with high purity double distilled water. Adjustments of pH were made with solutions of Analar HCl and NaOH. All other chemicals were of Analar grade.

3.2 Physical properties of the alumina.

Spherical agglomeration tests were conducted on various alumina size fractions ranging from about 86 μm to less than 10 μm . Some of these fractions were closely sized, whereas others covered a much broader size range. The physical properties of the various alumina grades used throughout this work are summarised in Table 3.1. The -86 + 27 μm alumina fraction was supplied by Universal Abrasives Ltd., and all the relatively coarse fractions i.e. -63 + 53, -53 + 45 and -45 + 27 μm alumina were prepared from this fraction by sieving. Finer particle sizes were obtained by grinding 100g from the -86+27 μm material in an agate vibratory mill for 1 hour. An agate mill was used for the grinding because of the ease with which impurities could be removed from the grinding surface by the use of chromic-sulphuric acid cleaner solution. The ground product (-53 μm) was divided into more closely sized fractions (ie -53+30, -53+20, -20+10, -10 μm) by the beaker decantation method. The sediment was dispersed three times to minimise the amount of incorrectly sized material in each fraction. A detailed size analysis of each fraction was obtained with a Coulter Counter.

The true density of the alumina was determined at a temperature of 25°C by means of a pycnometer following the procedure given in British Standard 3482, 1974. The value obtained, 3.90 g/cm³, is slightly lower than the value 3.97 g/cm³

Table 3.1.: Properties of the alumina grades used.

Particle Size μm	Specific surface area m^2/g	Fractional voidage	
		loosely poured	Vibrated
+86 + 27	0.085	0.56	0.440
-63 + 53	0.071	0.58	0.440
-53 + 45	0.094	0.59	0.452
-45 + 27	0.110	0.61	0.471
-53 + 30	0.250	0.49	0.380
-53 + 20	0.46	0.53	0.370
-20 + 10	0.50	0.66	0.435
-53	2.2	0.67	0.410
-10	3.7	0.75	0.545

quoted in the literature ¹⁰⁶ for alumina. The bulk densities of the different alumina size fractions were calculated from the weight of dry solid required to fill a 25 ml measuring cylinder with hand tapping following the recommendations described by Roller ¹⁰⁷. The results obtained are also summarised in Table (3.1) where it can be seen that the voidage of close packed size fractions were influenced to a small extent by the particle size and size distribution. Wide size fraction solids were compacted closer than narrowly sized ones with approximately equal average particle diameters. This can be explained by the filling of the interstices between large particles by much smaller particles ¹⁰⁸. The size fractions containing a substantial amount of very fine particles ($\sim 10 \mu\text{m}$) had the highest fractional voidage.

The size distributions of some of the alumina fractions employed are shown in Figures 3.1 and 3.2. The alumina fractions were analysed using a "Model Z_B Industrial" Coulter Counter. Some modification of the standard procedure was, however, found necessary. The agitation system was replaced by a robust agitator operated with compressed air, entrainment of air bubbles in the sample was prevented by means of baffles. The settling of particles at the bottom of the orifice tube was avoided by flushing the inside of the tube periodically using a three way tap. All other operations including the reduction of data were carried out as recommended by Coulter Electronics Ltd. The results showed that there was usually up to 10% of the material finer than the nominal minimum size of the fractions. In some cases however a higher proportion of fines was present, for example in the fraction $-20 + 10 \mu\text{m}$ alumina where about 19% by weight of the sediment was finer than

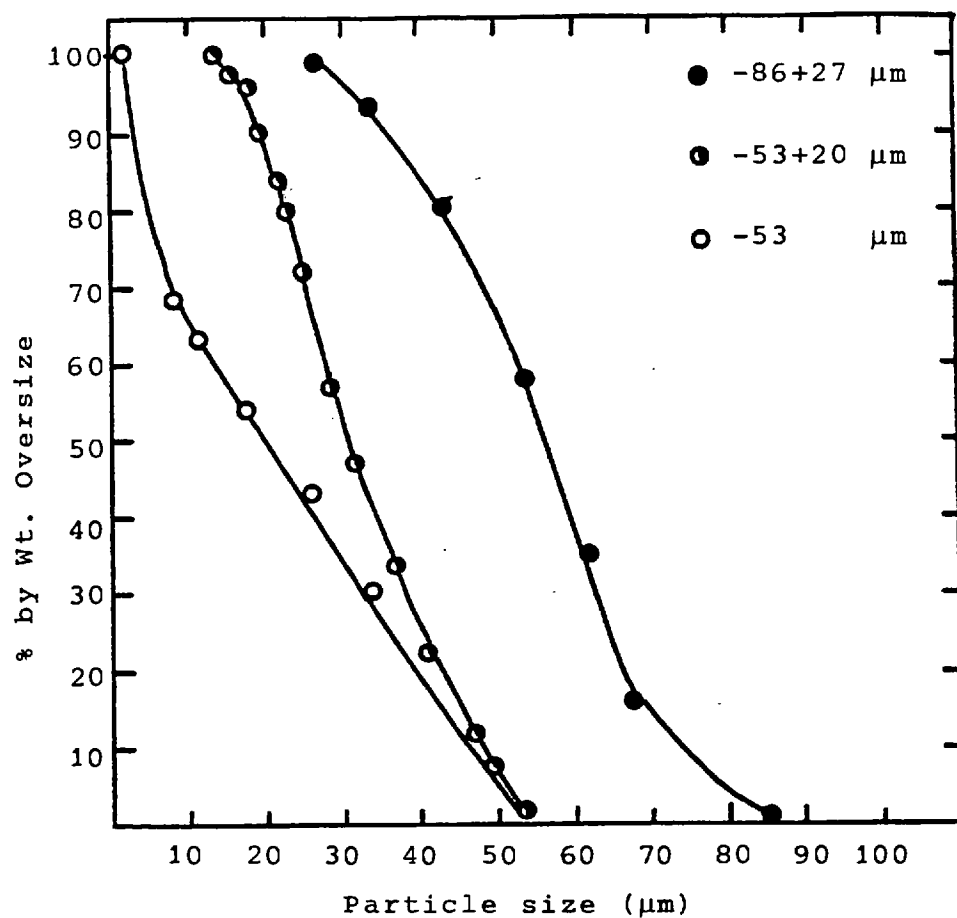


Fig. 3.1: Particle size analysis for wide size fractions of alumina determined by Coulter Counter

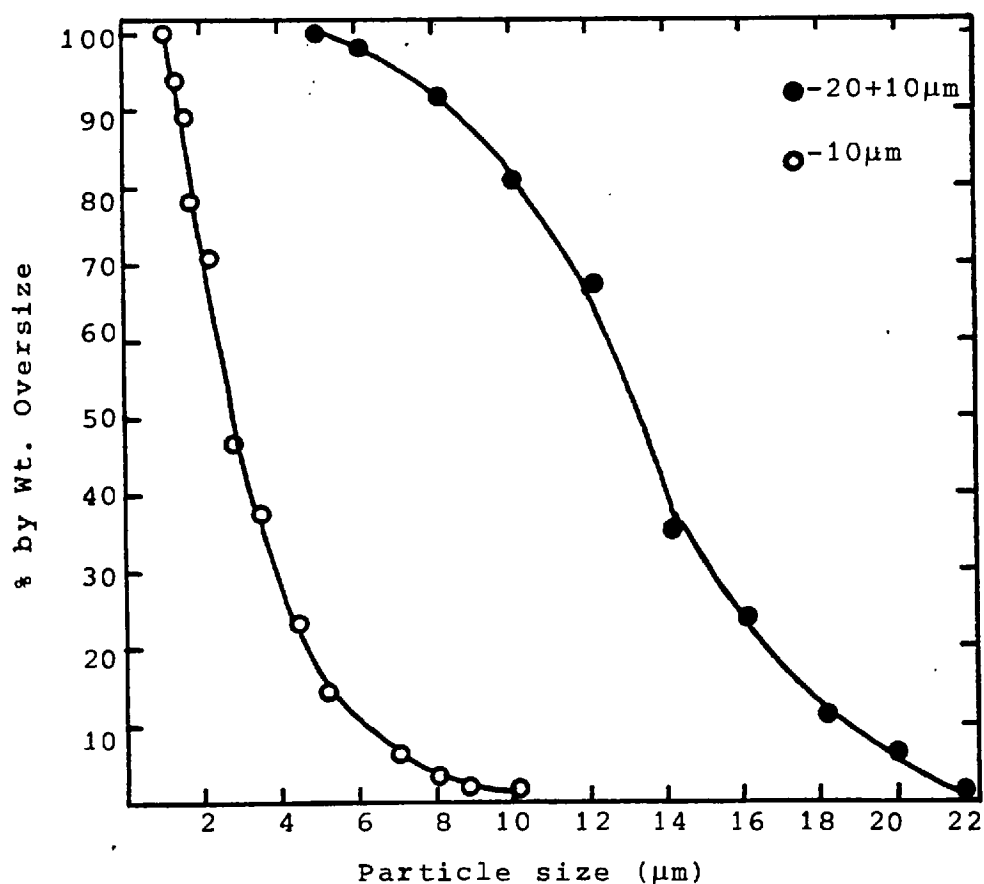


Fig. 3.2: Particle size analysis for narrow size fractions of alumina determined by Coulter Counter

10.2 μm . It was not ascertained what the minimum size of -53 and -10 μm alumina was, since this method is not accurate at particle sizes finer than 1 μm . *The Coulter Counter determines volume diameter.*

The surface area of the various alumina fractions presented in the Table 3.1 was measured by the Monosorb surface area analyser manufactured by the Quantachrome Corporation.

3.3 Properties of the bridging liquids.

The bridging liquids used are summarised in Table 3.2 with some of their physical properties which were determined at $25^{\circ}\text{C} \pm 0.1$. Mixtures of pure heptane and hexadecane were also used to obtain bridging liquids of different viscosities. A calibration curve of viscosity against hexadecane content (Fig. 3.3) was made and then the required viscosity obtained by interpolation. Viscosities were determined with an Ostwald viscometer¹⁰⁹ with a flow time between 1 and 10 min. Before each run the viscometer was thoroughly cleaned with warm chromic acid and it was then clamped accurately vertical in a glass-sided water bath whose temperature was controlled by a thermostat to $\pm 0.1^{\circ}\text{C}$. Each measurement was replicated four times. Density determinations were carried out using density bottles, making all the necessary corrections.

The various bridging liquids used in this work can be considered to be essentially insoluble in water and vice-versa, although some slight solubilization occurs. In the literature the solubilities in water of various hydrocarbons are cited (Table 3.2) and a relationship between the logarithm of the solubility and the molar volume of hydrocarbon has been proposed¹¹⁰. Lindenberg¹¹¹ stated that if the logarithms of the solubilities of the hydrocarbons are

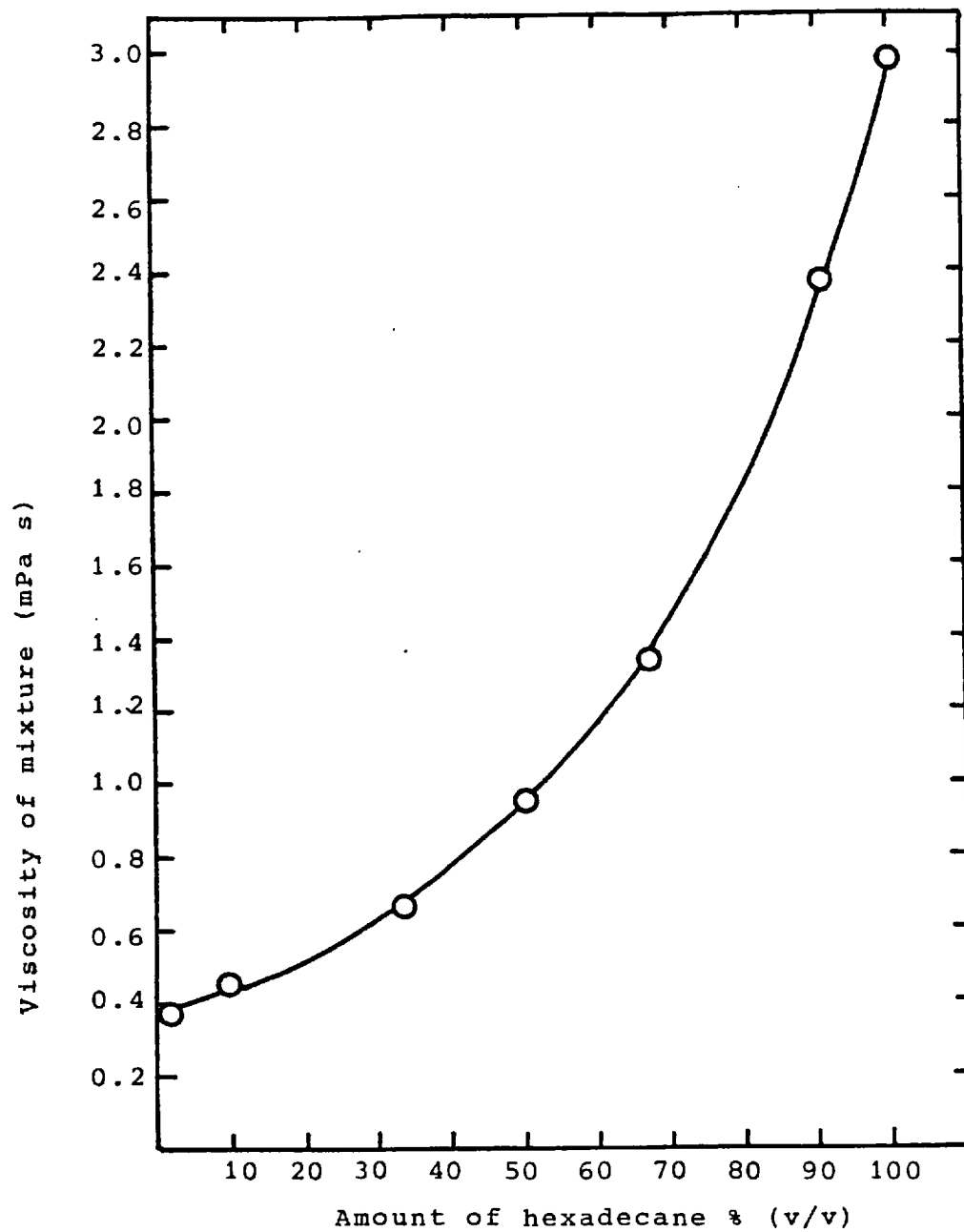


Fig. 3.3: The viscosity of hexadecane/heptane mixture as a function of the amount of hexadecane in the mixture

Table 3.2.

Bridging liquids.

Type of oil	Structural formula	Grade	Supplier	Viscosity mPas	Density (g.cm ⁻³)	Solubility in water. g oil per 10 ⁶ g water
2,2,4-trimethyl- pentane (Iso-octane)	$(\text{CH}_3)_3\text{C} \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3)_2$	pure, 99.5%	B.D.H.	0.481	0.691	2.44 (110)
n-heptane	$\text{CH}_3(\text{CH}_2)_5\text{CH}_3$	puriss 99.0%	Koch-light	0.391	0.681	2.93 "
n-Octane	$\text{CH}_3(\text{CH}_2)_6\text{CH}_3$	puriss 99.0%	Koch-high	0.511	0.698	0.66 "
n-Decane	$\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	puriss 99.0%	Koch-light	0.842	0.725	-
n-tetradecane	$\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$	puriss 99.0%	Koch-light	2.06	0.762	-
n-hexadecane	$\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$	puriss 99.0%	Koch-light	2.99	0.770	-
Benzene	C_6H_6	Analar	B.D.H.	0.608	0.878	1780 "

plotted against their molar volumes, a straight line is obtained for the saturated and aromatic hydrocarbons. McAuliffe¹¹⁰ found however, that the aromatic hydrocarbons have considerably higher solubilities for a given molar volume than the saturated ones, due to the higher vapour pressure of branched-chain hydrocarbons. Hydrocarbon solubilities in aqueous surfactant solutions below the critical micelle concentration (C.M.C) have been shown to be equal to their water solubilities.¹¹²

3.4 Description of agglomerator.

Agglomeration was carried out in a 600 ml beaker (8.8 cm in diameter and 12 cm in depth) which could be rotated at various constant speeds and with its axis of rotation at angles between 0° and 90° to the horizontal. The apparatus was similar to conventional pan and drum agglomerators, except that the size enlargement process took place under a blanket of liquid rather than in air. The vessel was also deeper than conventional equipment to accomodate the liquid suspension. Preliminary tests revealed that small baffles were required in the beaker to provide the required turbulence, and also to key the suspension to the beaker walls to give a good rolling action. Four corrugations about 3mm high and 4cm long running from the bottom were pressed into the sides of the beaker spaced at 90° intervals. The problem of exactly reproducing the agglomerator was overcome by making a graphite mould, which fitted into a plain 600 ml beaker, and which had four shaped hobs cut into it to allow the heated beaker to be formed into the required patterns. The agglomerator described above was fitted to a turntable connected via a gear box to a DC shunt motor, which had a maximum speed of 300 rpm. Turntable speed was measured by a tachogenerator

attached to the driving turntable spindle. The tachogenerator characteristics was 10 volts per 1000 revolutions. A sectional view and a picture of the experimental apparatus are shown in fig. 3.4 and plate 3.1. respectively.

Prior to using this agglomerator the effect of different designs was investigated. Tests were initially conducted with $-86 + 27 \mu\text{m}$ alumina in a beaker, and agitation was provided by a centrally located flat turbine impellor at 700 rpm, situated at a constant distance from the base of the beaker. During this testwork it was noticed that the impellor damaged the larger agglomerates at certain speeds. The agglomerates formed were relatively small at speeds where good mixing occurred, and it was therefore concluded that more gentle agitation was required. Baffles of various shapes and sizes were cemented in the beaker at 90° intervals. It was found that large baffles caused the break up of the initially formed agglomerates, and that small baffles produced a mixture of agglomerates and flocs. Generally it was found that more bridging liquid was required to achieve 100% agglomeration with baffles than without. Cement material or the baffles themselves adsorbed a portion of the added oil so that the oil available was not enough for sufficient interparticle bridges. The shape of corrugations pressed into the beaker also affected the agglomeration, but in this case the agglomerates were not broken as agglomerate growth proceeded. With corrugations there was no tendency for the material to collect at the joint between the baffle and beaker. Accumulation of material had an adverse effect on the agglomeration in baffled containers. Other types of agglomerator, such as rolling tubes were also studied, but it was found that the most reproducible results were obtained from the agglomerator previously described.

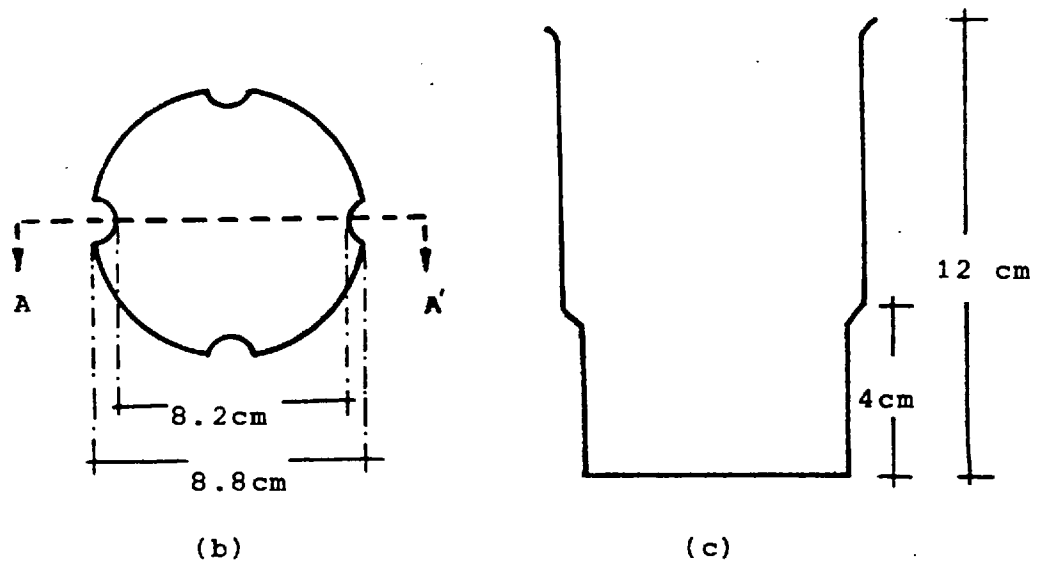
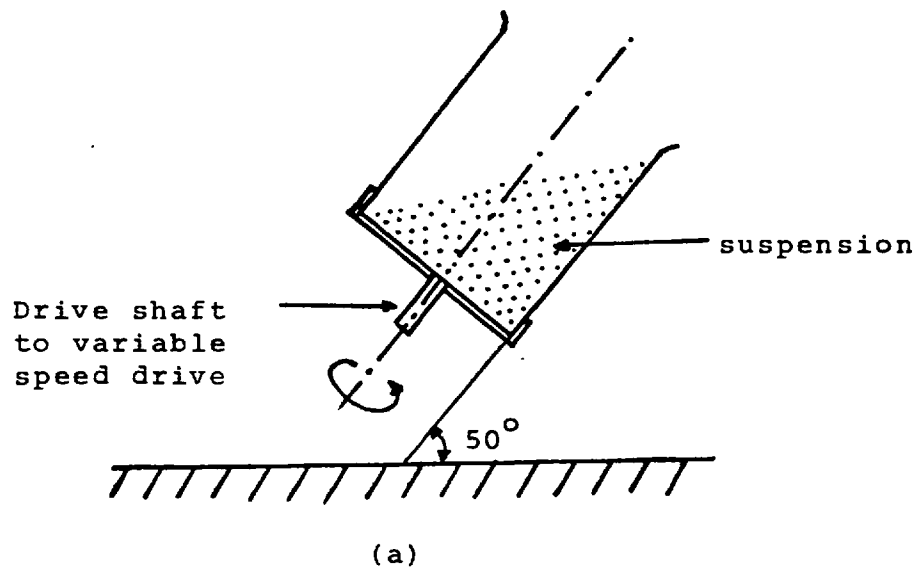
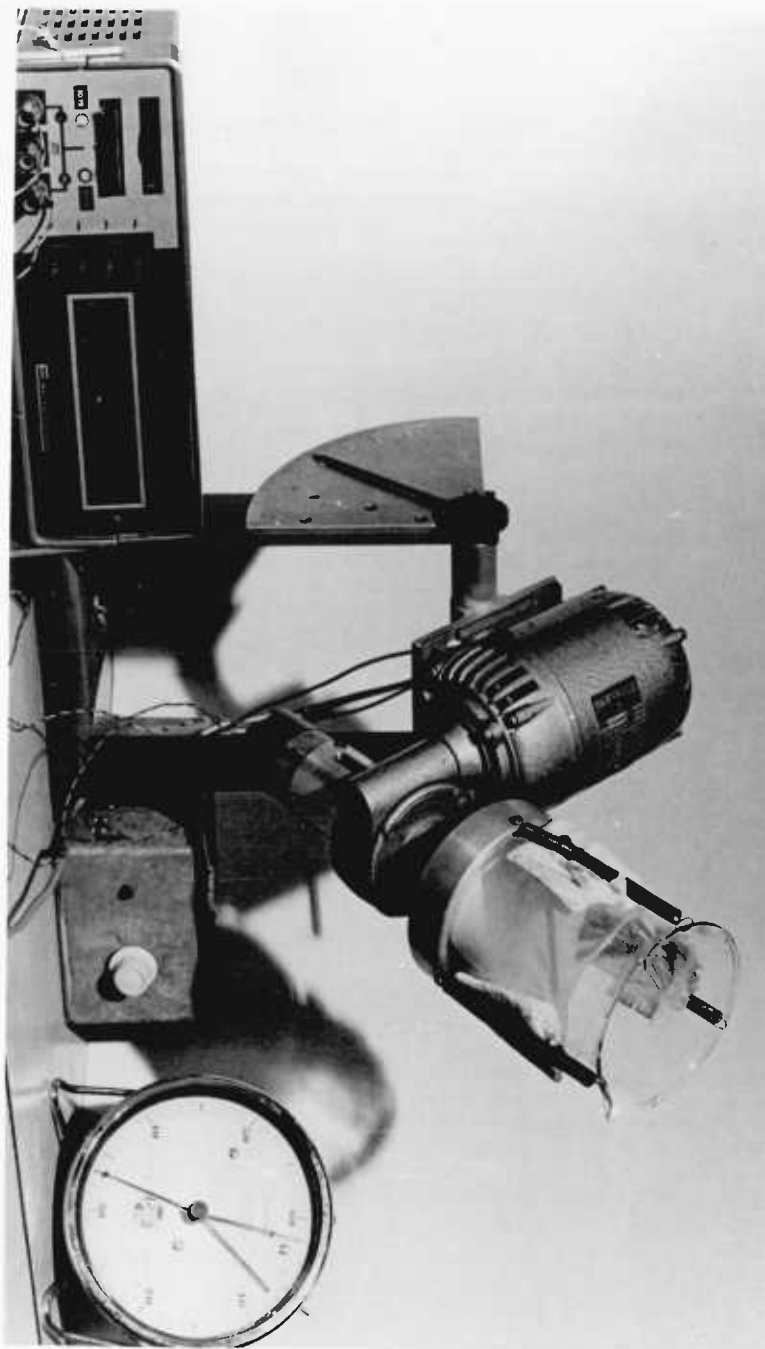


Fig.3.4: Diagram of agglomeration apparatus

- a) inclined agglomerator
- b) cross-section at the base of the agglomerator beaker
- c) elevated section AA'

Plate 3.1: Apparatus for agglomeration tests



3.5 Agglomeration procedure.

For simplicity it was decided to carry out all experiments batchwise and to accept the limitations this imposed with regard to the applicability of the results to continuous systems.

A standardised procedure for making agglomerates has been used throughout this study unless it is stated otherwise. In this, 200ml of S.D.S. solution at a known concentration was added to 40 g of alumina already in the agglomerator, and the pH was adjusted with HCl. After the alumina had been conditioned for 10 min at the required speed, a measured quantity of the bridging liquid was introduced drop-wise from a small pipette, and the agglomeration time was measured from the commencement of the oil addition. The open top of the agglomerator was then covered with a polythene sheet held by an elastic band to minimise loss of oil by evaporation. The resulting mixture was agitated, and after the desired interval had elapsed, the agglomerator was stopped and its contents were wet screened on a 420 μm mesh in a shallow bowl. Care was taken during the gentle screening operation to ensure that the agglomerates remained submerged in the supernatant solution until all the fines had passed through the screen.

3.6 Assessment of agglomerates produced.

The following measurements were made to assess the agglomerates produced during each experiment.

- (i) The degree of agglomeration was determined as the percentage of solids retained on the 420 μm sieve.

- (ii) The size distribution of the agglomerates was determined photographically. The agglomerates were spread out in a monolayer on a glass plate with a scale and two reference spheres to give the magnification and a photograph taken. The diameters were determined using a transparent overlay printed with a range of circles, having successively increasing diameters, which covered the agglomerate size range produced in each test.
- (iii) The number mean agglomerate diameter $\bar{D}$ was calculated for each size distribution using

$$\bar{D} = \frac{\sum N_i D_i}{\sum N_i} \quad (3.1)$$

where D_i = arithmetic mean value of the i th size interval

and N_i = number of agglomerates in the i th size interval

In the case of an irregularly shaped agglomerate, the mean of its two principal dimensions was taken as its diameter. $\bar{D}$ has been used throughout to characterise the size of the agglomerates from each experiment. Bridging liquid additions have been specified on a volume of dry solid basis, that is

$$\text{Oil addition \%} = \frac{\text{Volume of bridging liquid}}{\text{True volume of solid}} \times 100 \quad (3.2)$$

This enables a direct comparison to be made between results for different agglomerating materials.

3.7 Important variables in the oil spherical agglomeration process.

The variables in the spherical agglomeration process can be divided into two categories. Those which are external to the system include the design of the agglomerator, its speed of rotation and the angle of inclination. The internal variables can be considered to include surfactant concentration, pH, solid concentration, particle size, and the amount of bridging liquid and its properties. Internal variables relate to the nature of the charge in the agglomerator, while the external variables define the type and degree of the agitation to which a given charge is subjected.

3.8 Range of variables after preliminary tests.

Preliminary testwork was conducted to establish the levels of the parameters at which a high degree of agglomeration was obtained combined with the formation of large agglomerates. In all subsequent testwork all the variables except the one whose effect on agglomeration was being studied, were kept at the levels shown in Table 3.3.

Table 3.3 Values of the various variables after preliminary tests.

VARIABLE	VALUE
Speed of rotation	70 $\pm$ 2 rpm
Angle of inclination	50°
Conditioning time	10 min
Agglomeration time	30 min
Volume of aqueous phase	200 ml
Weight of solids	40g
S.D.S. concentration	7.5×10^{-4} M
pH (end of conditioning time)	3.5 $\pm$ 0.1
Bridging liquid addition	73.2%

The $-86 + 27 \mu\text{m}$ alumina was used exclusively in preliminary studies, and also for most of the experimental program except that concerned with the investigation of the effects of particle size, agglomeration time and oil volume.

The reproducibility of results in a number of different beakers, all made using the special graphite mould, was tested. The standard deviation of nine similar tests in one beaker was found to be 0.75 and that for one test in each five similar beakers was 0.72. Comparison of these values using the F-test based on 8 degrees of freedom, showed that the difference was significant only at the 0.05 level.

3.9 RESULTS

3.9.1 Effect of speed of rotation and angle of inclination

The influence of speed of rotation, on the percentage of particles agglomerated, and on the size of the agglomerates, was investigated using the conditions summarised in Table 3.3 (Section 3.8). Fig. 3.5 shows that 100% agglomeration was achieved at speeds greater than 35 r.p.m. At lower speed the turbulence was insufficient to distribute the oil, and most of it remained on the surface of the suspending liquid . An upper speed limit was imposed because a critical value was reached when the alumina was held almost continuously against the walls of the beaker by centrifugal force. Growth of large agglomerates was brought about by increasing the speed above the minimum necessary for agglomeration. This was because the rolling action improved at higher speeds, and because particles, clusters and agglomerates only adhered together when they collided with sufficient momentum.

In Fig. 3.6 it can be seen that increasing the agglomerator speed to 100 r.p.m. markedly increased the mean diameter of the agglomerates as a function of agglomeration time, and that the same effect was not achieved by increasing the agglomeration time to give a similar number of revolutions. This demonstrates the importance of the momentum with which collisions took place. These findings are broadly in agreement with results obtained from pelletization studies⁷⁸. Since satisfactory sphericity and agglomerate size were obtained at speeds between 50 and 90 r.p.m., it was decided to select 70 r.p.m. for all further testwork.

In experiments to investigate the influence of the angle of inclination, it was found that 100% agglomeration resulted for angles to the horizontal of less than 65° ,

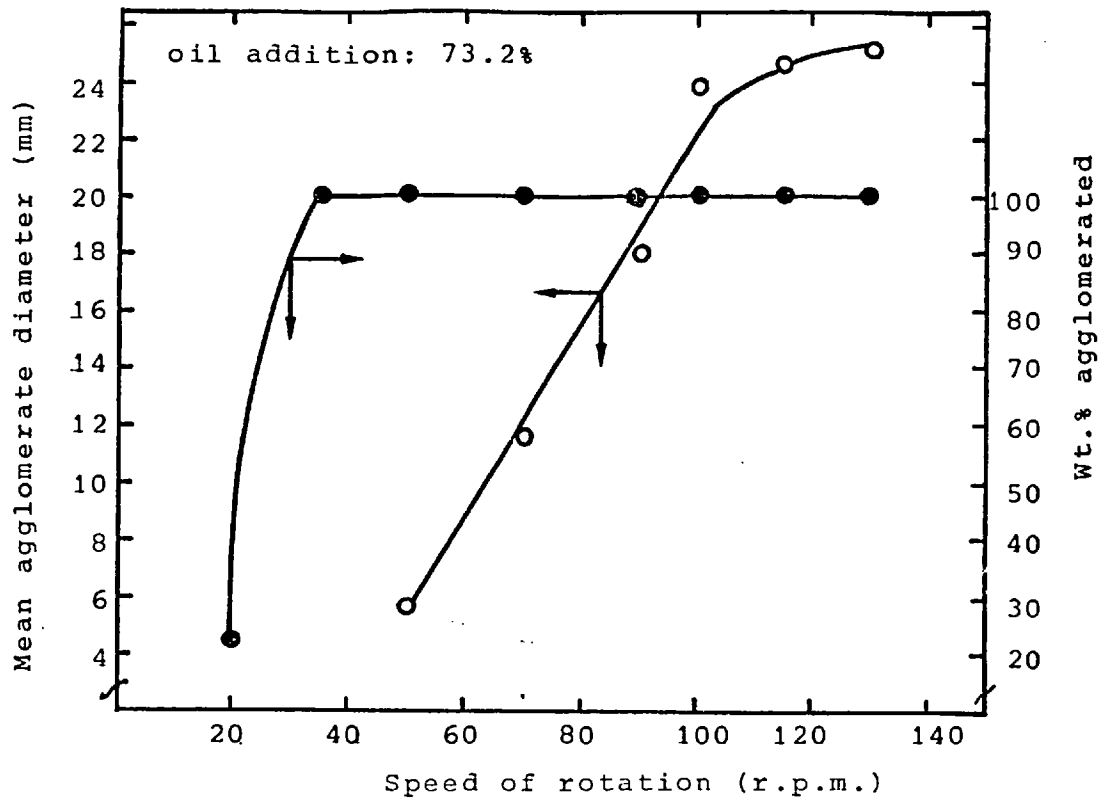


Fig.3.5: The effect of speed of rotation on degree of agglomeration and agglomerate size.

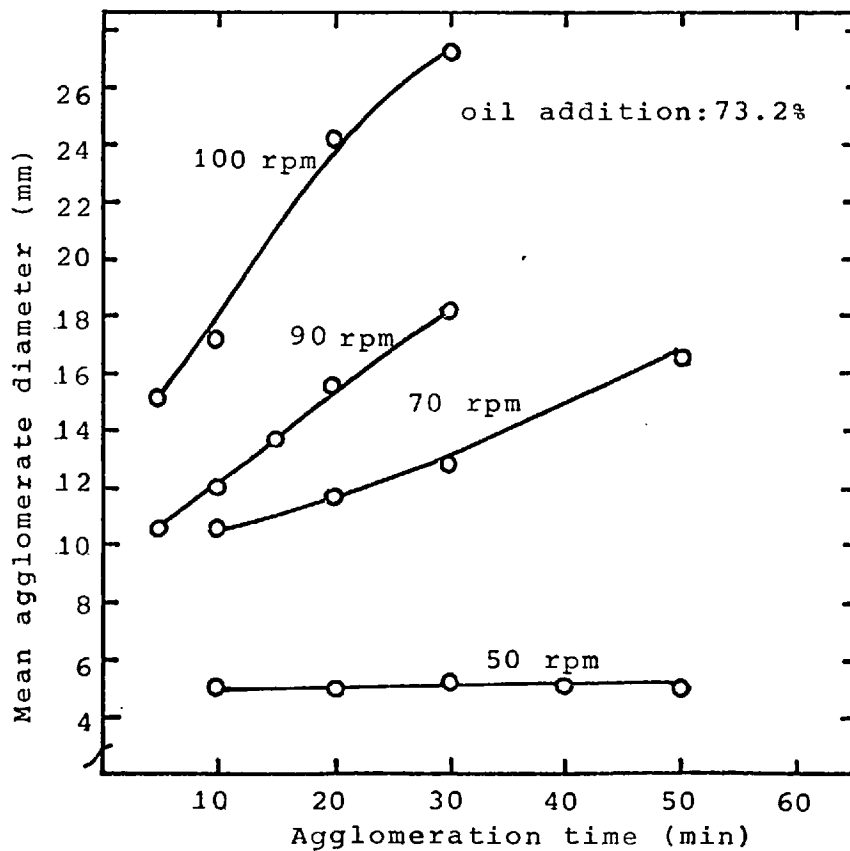


Fig. 3.6: Variation of agglomerate growth with agglomeration time for different speeds of rotation

while maximum agglomerate sizes were obtained at angles below 55° . Agglomerate size was not significantly dependent on inclination angle between 30° and 55° and therefore an angle of 50° was used in all further testwork.

3.9.2 Effect of pulp density and quantity of suspension

Fig. 3.7 shows the percent alumina agglomerated and the mean agglomerate size for various weights of solids in 200 ml of aqueous phase. In all these tests the amount of S.D.S. present was kept constant at 3.75×10^{-6} moles per g alumina. At pulp densities below 10%, both the percentage of alumina agglomerated and the mean size of the agglomerates decreased markedly. This was because most of the agglomerates rolled on the beaker surfaces without tumbling and colliding. It was observed, however, that large agglomerates could be produced with complete recovery of the alumina by increasing the speed of rotation from the standard 70 r.p.m. to 90 r.p.m. even with a pulp density of only 7.5% solids. As the pulp density was increased above 10%, at the standard speed, larger agglomerates were produced more quickly because the higher concentration of solids increased both the frequency of particle collisions and the cascading action in the agglomerator.

Similar effects were observed when the weight of solids was kept constant, and the volume of the aqueous phase progressively reduced. Aqueous phase volumes of 250, 200, 150 and 100 cm³ yielded mean agglomerate diameters of 8.7, 10.3, 11.1 and 15.3 mm respectively, with 100% agglomeration, for a constant 40 g of solids. In addition to the factors mentioned above, these observations can be attributed to the more effective distribution of the bridging liquid as the volume of the aqueous phase decreased.

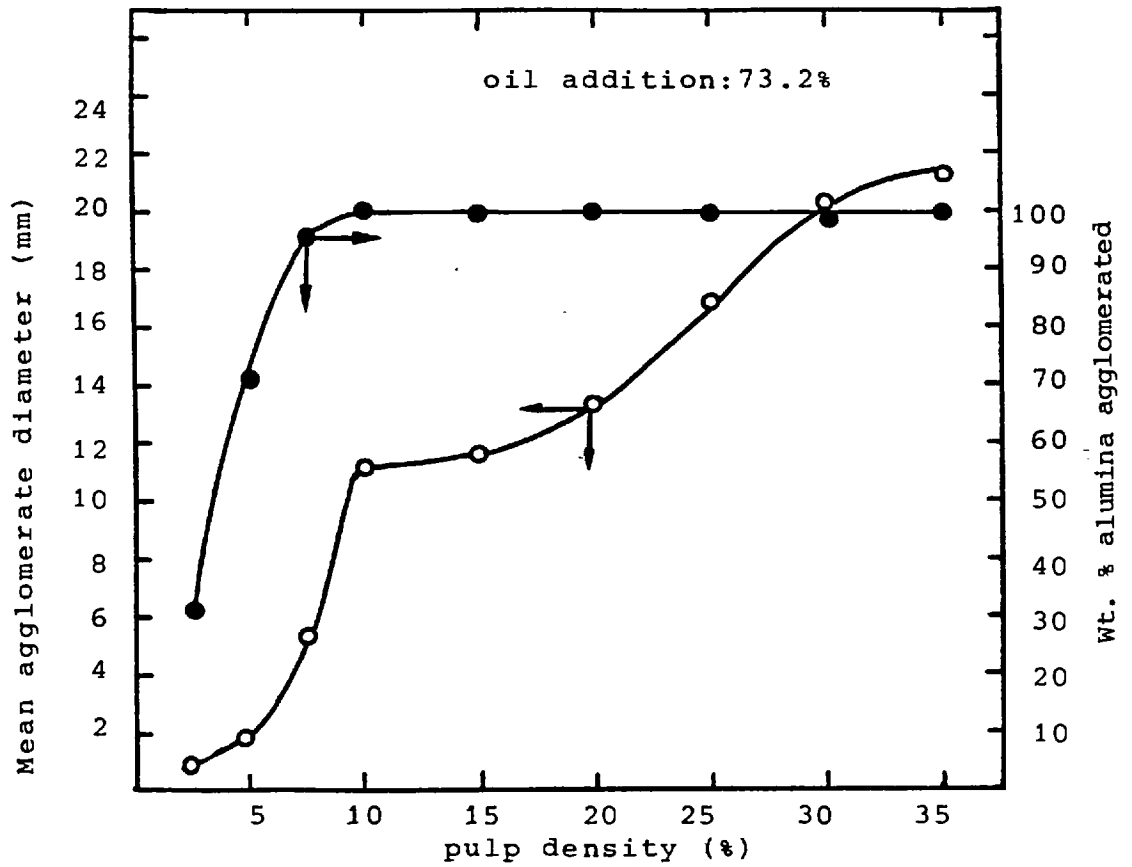


Fig.3.7: Influence of pulp density on degree of agglomeration and agglomerate size.

3.9.3 Effect of S.D.S. concentration

The effect of S.D.S. concentration on the agglomeration of alumina and the size of agglomerates is shown in Fig.

3.8. Complete agglomeration was obtained for initial S.D.S. concentrations greater than 2.5×10^{-4} M, but as the concentration was reduced below this, the percentage agglomerated dropped quickly to zero and only flocs were formed. After the addition of oil, separation of the alumina was slow in solution containing less than 5×10^{-4} M of S.D.S., but above this, separation occurred in less than one minute, and was still rapid up to the highest S.D.S. concentration tested which was 10^{-2} M. At surfactant concentrations exceeding 10^{-3} M, the aqueous phase always remained cloudy due to the presence of emulsified oil droplets.

The mean size of the agglomerates increased with increasing S.D.S. concentrations up to 10^{-3} M, but for higher concentrations it decreased, the size distribution became much narrower, and the agglomerates were weaker. At lower S.D.S. concentration down to 2.5×10^{-4} M, loose aggregates were formed immediately and they grew by coalescence into a more widely sized product.

When the oil addition was reduced from the standard level of 73.2% found in the preliminary experiments to 63.4% of iso-octane, satisfactory agglomeration was achieved only for S.D.S. concentrations between 5×10^{-4} and 1×10^{-3} M, in which agglomerates without significant difference in size were produced. At S.D.S. concentrations above 1×10^{-3} M the total alumina changed to spherical agglomerates at one stage, but they broke-up as the agglomerate growth process proceeded.

As a result of the tests at oil addition of 73.2% an S.D.S. concentration of 7.5×10^{-4} M was chosen for investigation of other variables.

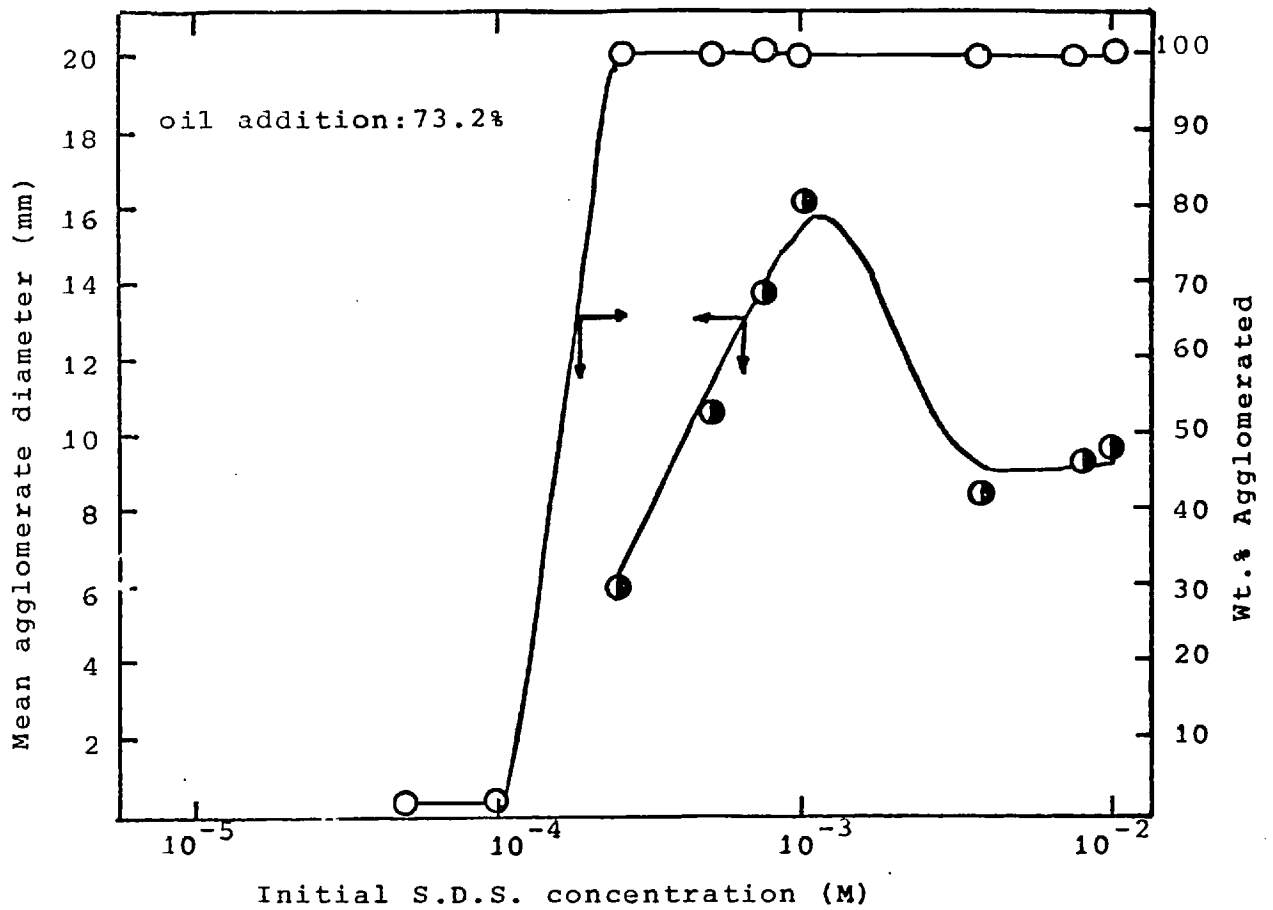


Fig.3.8: The effect of S.D.S. concentration on degree of agglomeration and agglomerate size. .

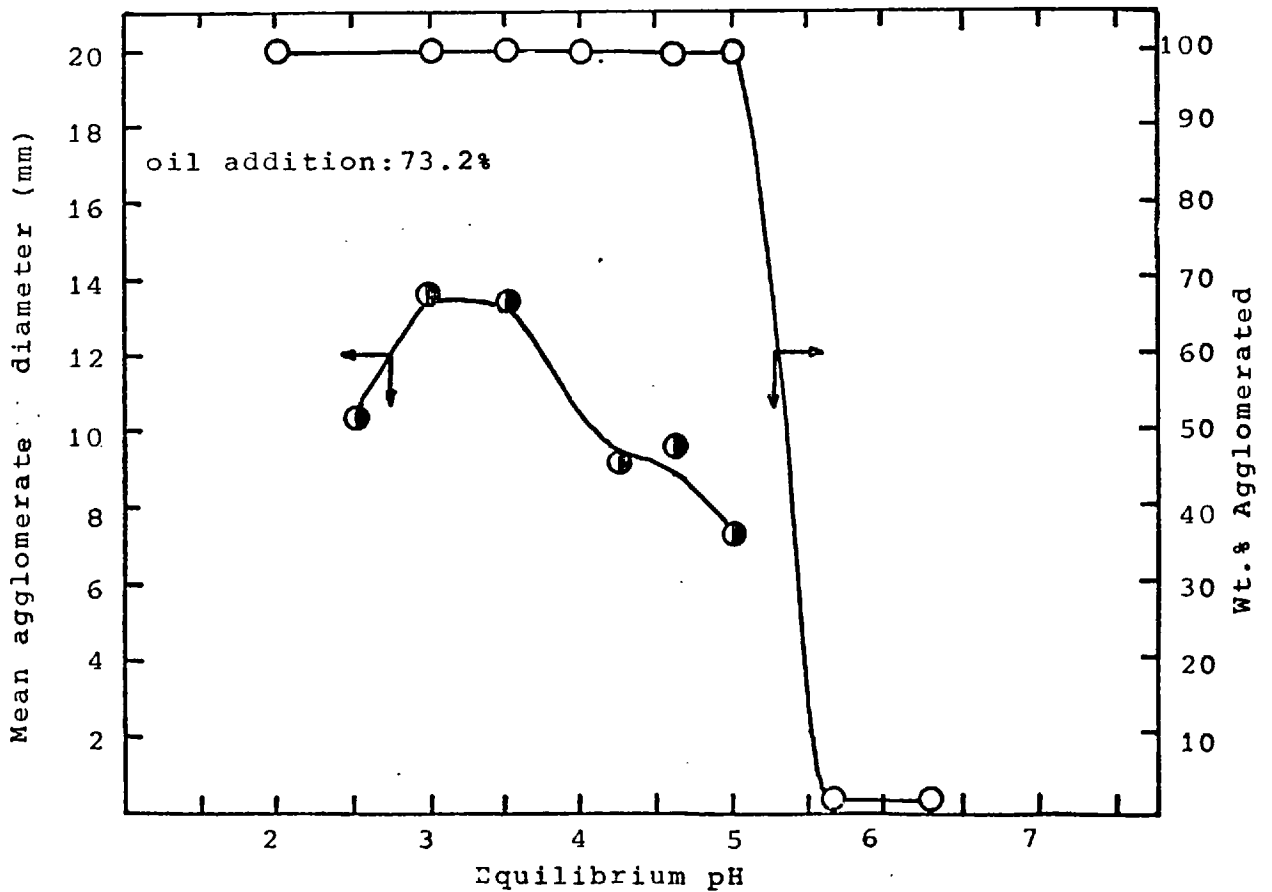


Fig.3.9: Effect of pH on degree of agglomeration and agglomerate size.

3.9.4 Effect of pH

The effect of pH on the percent alumina agglomerated and on agglomerate size is shown in Fig. 3.9. No agglomeration took place above pH 5.6, but it was excellent at pH values below 5. The largest agglomerates were formed between ^{pH} 3.0 and 3.5 and they were sufficiently strong for ordinary handling and reasonably spherical. A small delay in alumina agglomeration was observed at pH values above 4.5, while below this value aggregation occurred very quickly (less than one minute) after the oil had been added. The pH value of 3.5 was selected for further testwork.

It has been reported by many authors¹¹³⁻¹¹⁵ that in the alumina/alkyl sulphate system adsorption increases as the pH decreases below the zero point of charge and the results obtained in the present work are consistent with this.

3.9.5 Effect of bridging liquid volume

The effect of different iso-octane additions on the agglomeration of -86+27 μm alumina is presented in Fig. 3.10 where the average agglomerate diameter and percent agglomerated are plotted as a function of oil volume. The range of oil volumes studied was between 34.2% and 78.1%. It was difficult to measure the response of the agglomeration process at very low oil additions (<48.8%) and under these conditions the following observations were made. Initially flocs were formed which after about 5 minutes tumbling began to change slowly to agglomerates and then grew by picking up the unagglomerated material. At longer agglomeration times all the alumina was agglomerated and further growth occurred as a result of crushing and redistribution of the fragments among the surviving agglomerates. Eventually, when the agglomerates approached a size between 10 and 12 μm the breakage of the agglomerates was greater than the

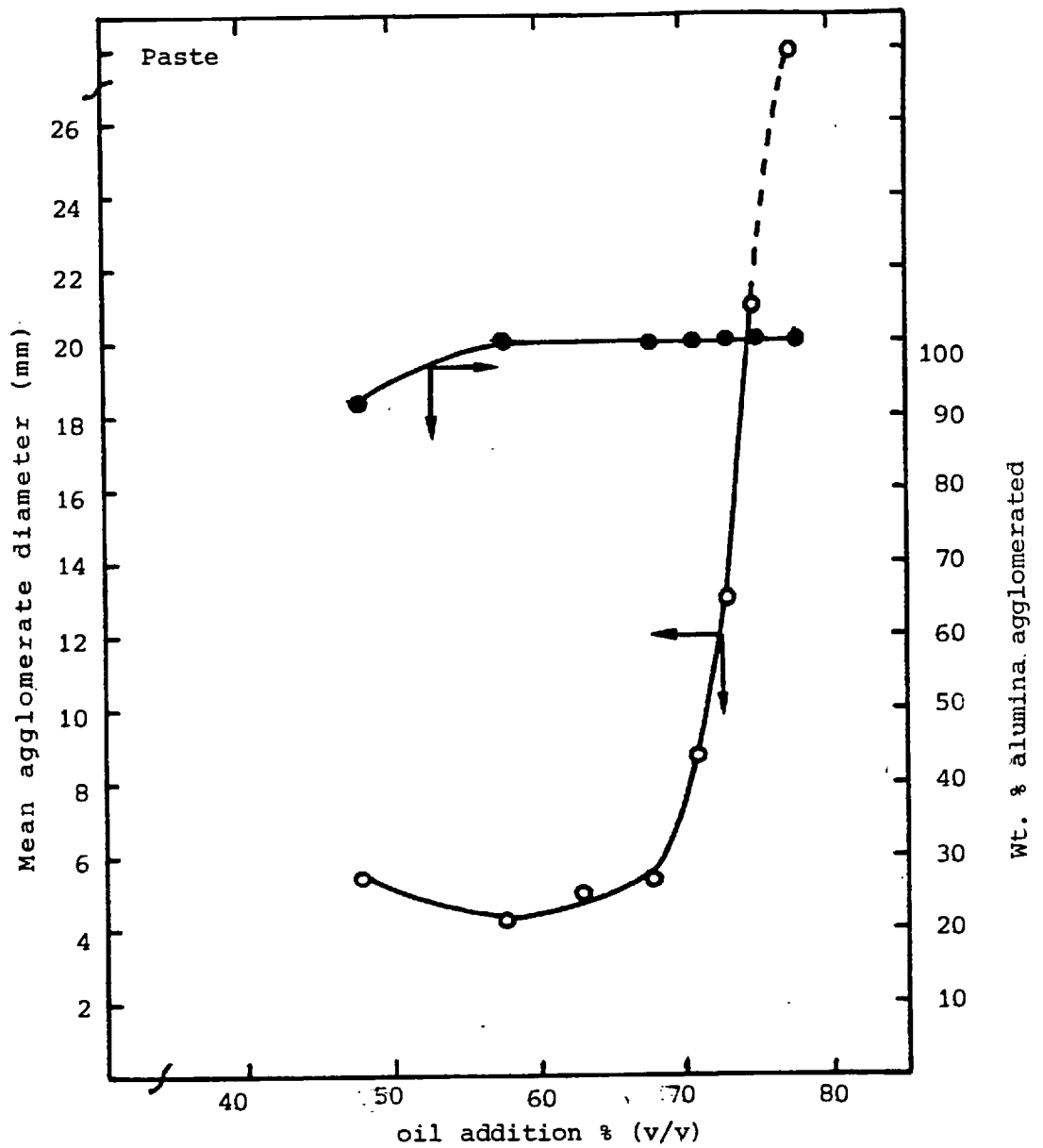


Fig: 3.10: The effect of oil volume on degree of agglomeration and agglomerate size

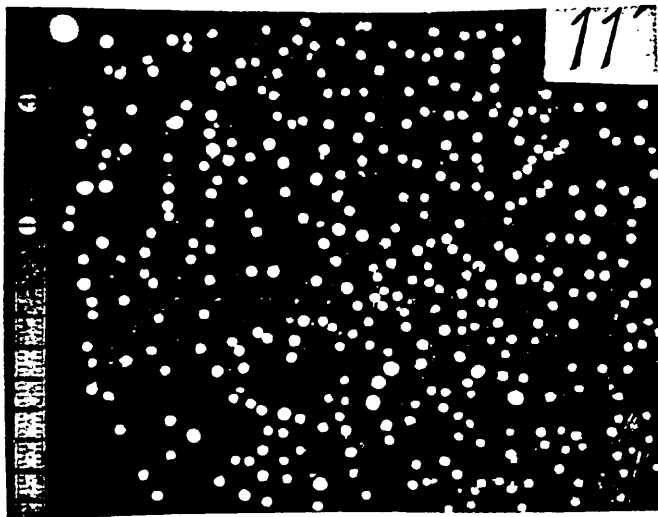
formation rate and a mixture of fragments resulted. Sometimes very large and weak agglomerates, which collapsed during the screening stage were formed. It would appear that in this region of bridging liquid addition there was insufficient oil to form the required minimum interparticle bridges necessary for agglomerate strength.

Iso-octane additions between 48.8% and 68.3% gave compact spherical agglomerates ranging in size from 4.0 up to 6.1 mm, possessing a high degree of sphericity. An increase in oil addition above 68.3% produced a sharp increase in agglomerate diameter with a small change in the bridging liquid concentration. When the bridging liquid additions exceeded 73.2%, either very large irregularly shaped agglomerates were produced or the particles formed into a soft paste, which did not tumble but slid as a coherent mass. If the paste was periodically broken up the mixture began tumbling again and eventually very large non-spherical agglomerates resulted (20 mm or more in size) and these were very soft and tended to deform under their own weight on standing. The successive photographs shown in plate 3.2 illustrate the agglomerates produced at various bridging liquid concentrations.

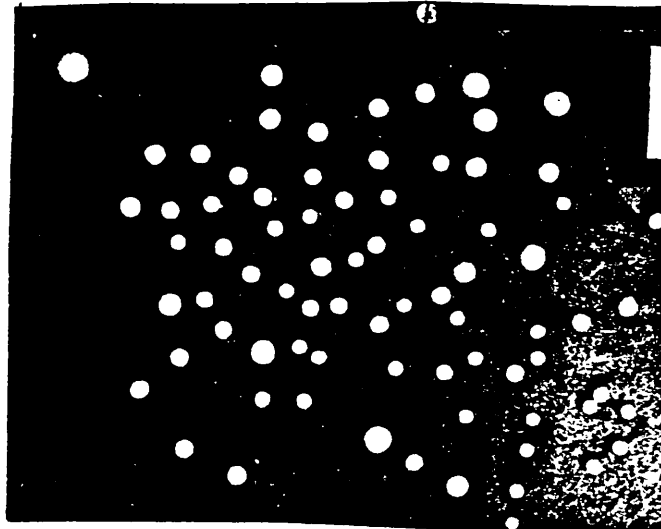
These results clearly show that there is a minimum and a maximum amount of bridging liquid required to form good agglomerates. Too little liquid produced incomplete agglomeration and too much resulted in the formation of a paste. The mean agglomerate diameter was dependent to a very large extent on the amount of oil added and this is also true in conventional pelletization processes¹¹⁶⁻¹¹⁸.

3.9.6 Effect of bridging liquid viscosity

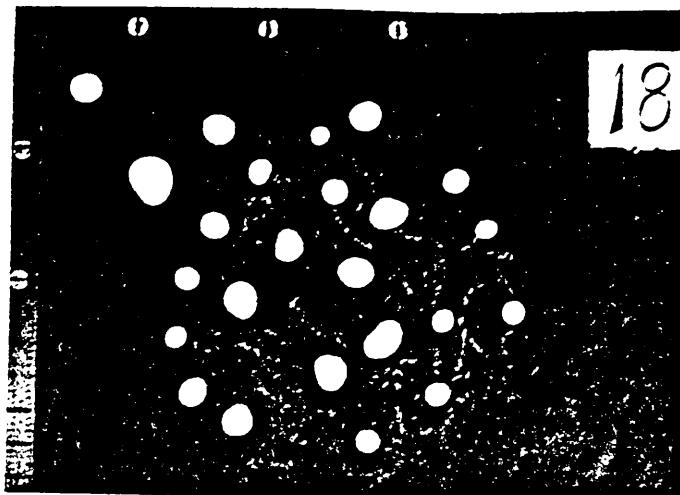
Agglomeration tests were carried out with the paraffins summarised in Table 3.2 together with benzene to investigate



Oil addition 68.3%



Oil addition 70.7%



Oil addition 72.4%



Oil addition 75.7%

divided paste

Plate 3.2. Agglomerate form of $-86+27\ \mu\text{m}$ alumina at various iso-octane additions

the effect of viscosity on agglomerate growth. The results obtained are presented in Fig. 3.11 and they show that all the bridging liquids had a similar effect on the agglomerate diameter except that the amount of oil required to form the same size of agglomerate increased with a decrease in viscosity, except with benzene. The curve obtained with hexadecane (viscosity = 2.99 mPa s) was almost coincident with that obtained when tetradecane was used (viscosity = 2.06 mPa s). This is probably attributable to the poor distribution of the more viscous oil in the allotted agglomeration time. In all cases good agglomeration was only achieved over a narrow range of bridging liquid volumes.

To determine whether the observed results with the different hydrocarbon liquids were attributable to viscosity changes and not to variations in density, solubility and interfacial tension, a series of tests was conducted with a bridging liquid composed of different proportions of hexadecane and heptane. With such a mixture a wide range of viscosities was obtained at almost constant interfacial tension and density. The difference in densities was less than 0.1 g/cm³. The results obtained are summarised in Fig. 3.12, where the average agglomerate size produced by the pure hydrocarbons is compared to that obtained with the hexadecane/heptane mixtures. The oil volume was maintained at 68.3% throughout this series of experiments. With both types of bridging liquid the agglomerate diameter increased with viscosity but larger agglomerates were formed with the pure hydrocarbons. Fig. 3.12 shows also that slightly larger agglomerates were obtained with tetradecane (2.06 mPa s) than with hexadecane (2.99 mPa s). This implies that there is an optimum viscosity for the agglomeration and that above this value the agglomerate size decreases due to poor distribution of the more viscous oil over the particle surfaces. No attempt was made to investigate the effect of very viscous liquids.

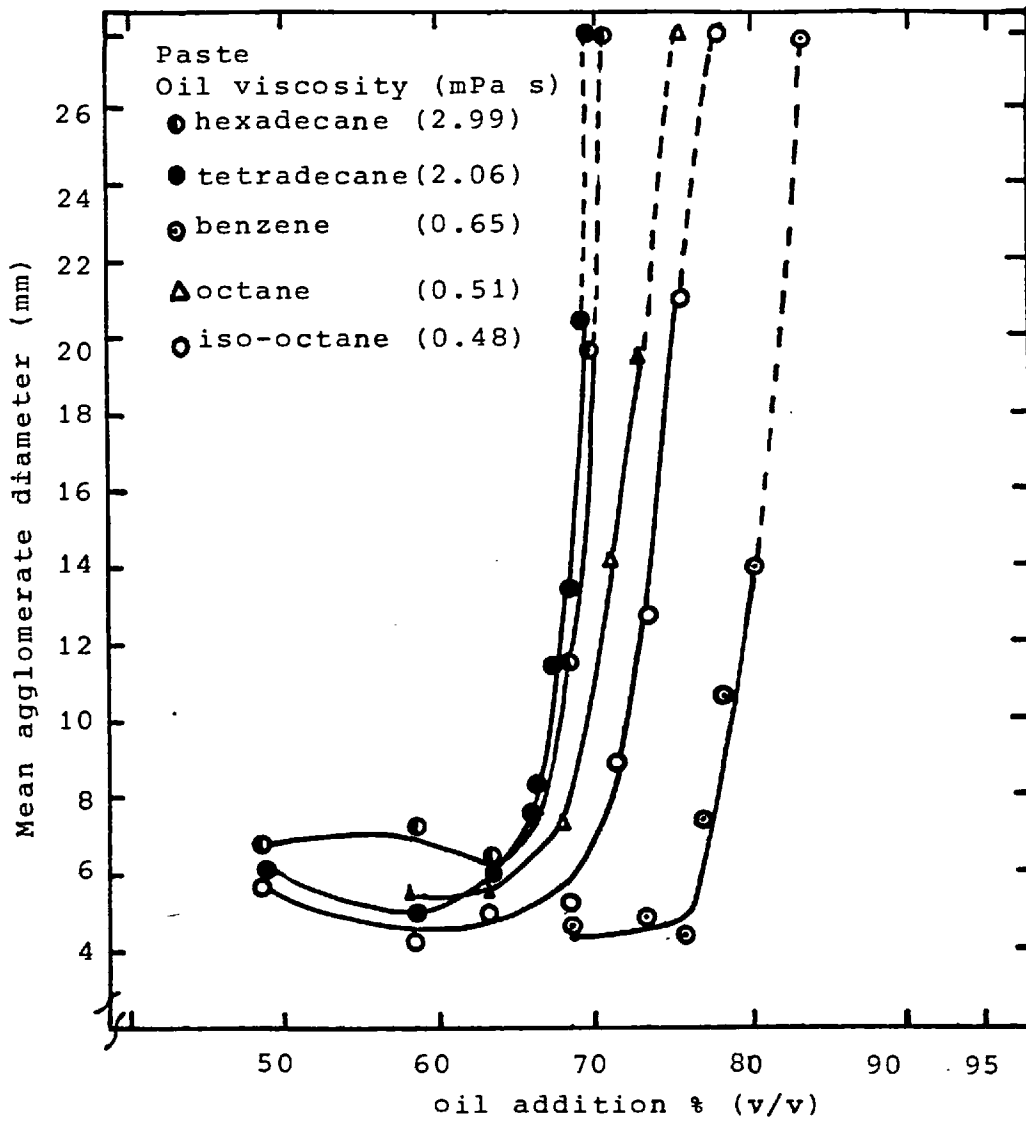


Fig. 3.11: Mean agglomerate diameter as a function of oil volume at different viscosities

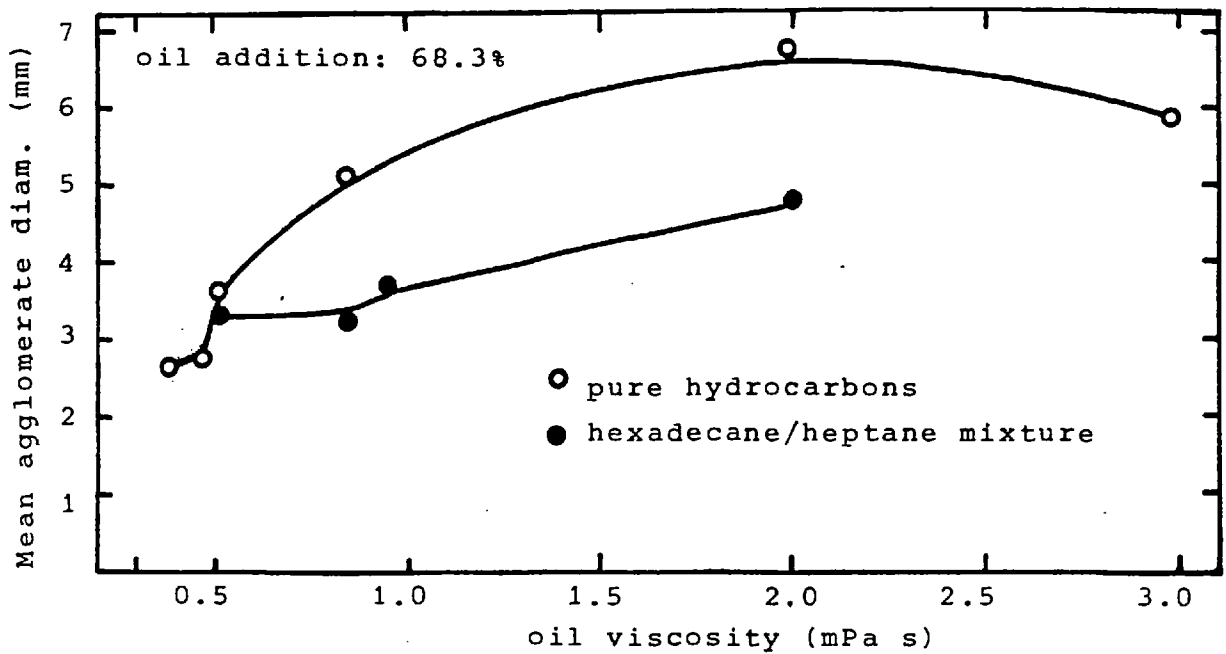


Fig. 3.12: The effect of oil viscosity on agglomerate size

The results obtained with the hexadecane/heptane mixtures and pure hydrocarbons show that agglomerate diameter increases with bridging liquid viscosity and that in the latter case the effect is complicated by changes in interfacial tension, density and affinity for the hydrophobic alumina surface.

3.9.7 Effect of particle size and size distribution of alumina

3.9.7.1 Agglomeration of relatively coarse size fractions

Several size fractions of alumina were agglomerated with different volumes of iso-octane using the conditions previously established. Measurements of the agglomerate diameters gave the results shown in Fig. 3.13. In all cases 100% agglomeration was obtained. The effect of oil volume on the agglomeration of each size fraction was similar, and good agglomerates were only formed over a narrow bridging liquid volume range. Furthermore, a rapid increase in agglomerate diameter occurred when the oil volume exceeded a value dependent on the particle size. At high oil volumes pastes were formed and at oil additions below those shown in Fig. 3.13 a mixture of flocs and small agglomerates were obtained.

The amount of bridging liquid required to agglomerate narrowly sized fractions increased with a decrease in mean particle size and this is demonstrated by the results obtained with the -63+53, -53+45 and -45+27 μm size fractions. This trend was not, however, continued and the -20+10 μm fraction required much less oil than the coarser fractions. Furthermore, the -53+20 μm fraction required far less oil than the -53+45 μm fraction. The latter can partly be explained by the fact that in wide size fractions the interstices between the large particles will be partially filled by small particles. The position of the curve for

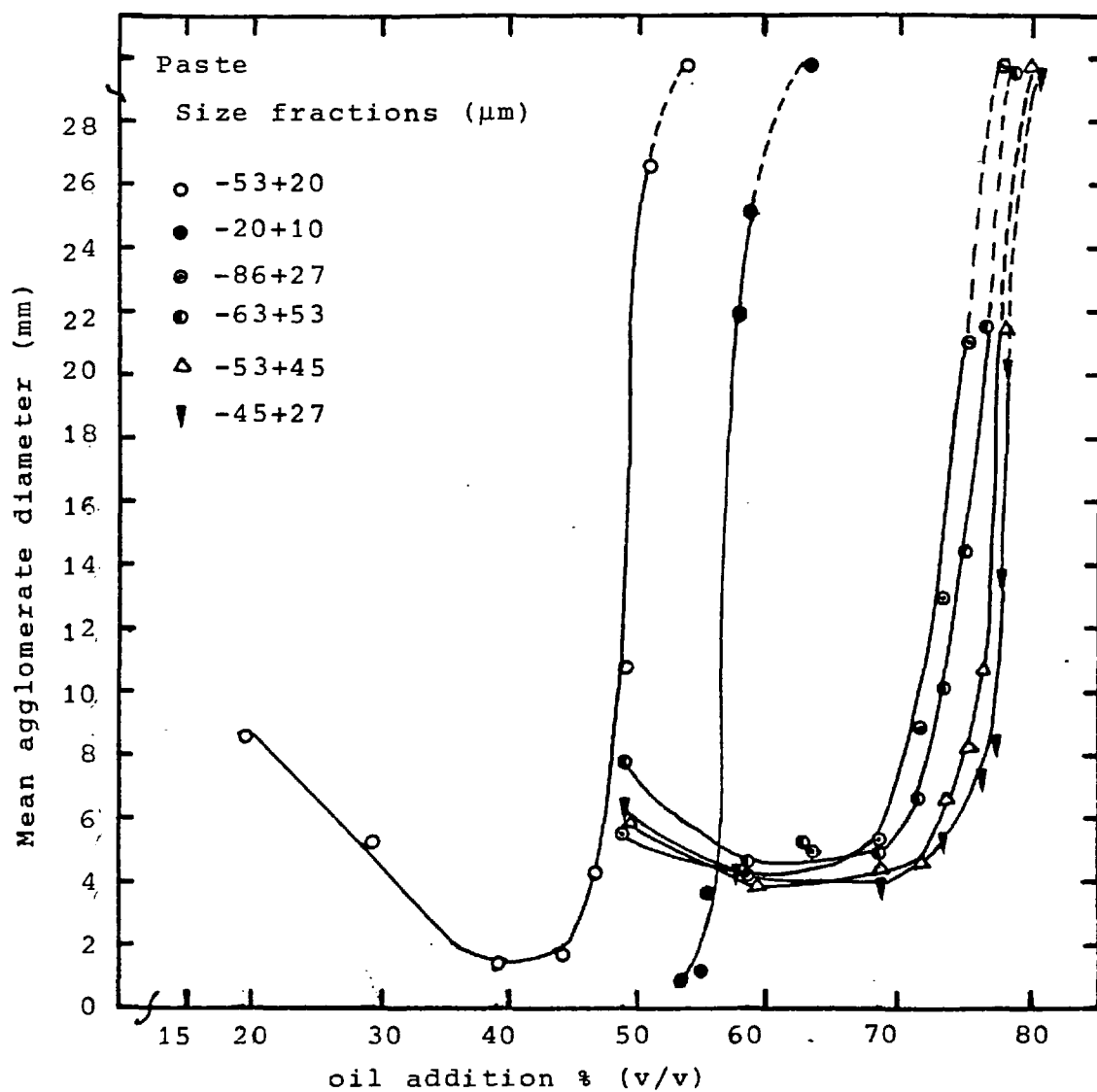


Fig. 3.13: Mean agglomerate diameter as a function of oil volume for various size fractions

the -86+27 μm alumina relative to that of -45+27 μm fraction can be explained in a similar way.

In general those size fractions containing material finer than 27 μm did not agglomerate well. The agglomerates were of variable size and somewhat irregular, especially in the region where the size was very sensitive to the bridging liquid volume. Furthermore there was an induction period before coalescence and agglomeration occurred. The amount of bridging liquid required was, however, less than that required for coarser fractions.

An estimation of the maximum amount of oil required for the capillary state can be obtained from the pore volume of the feed material. Comparison of this volume with the maximum amount of bridging liquid that can be tolerated before a paste forms (hereafter referred to as the "paste volume") shows that for most size fractions there is a good correlation between the bridging liquid requirements and the porosity of the different size fractions. This comparison is shown in Table 3.4.

Table 3.4: Comparison of the porosity of the alumina size fractions with the paste volume

Particle size range (μm)	Porosity of feed alumina after vibration (%)	Maximum oil volume required % ml/cm ³ alumina	
		Calculated	Experimental (paste volume)
-86+27	44.0	78.5	75.1
-63+53	44.0	78.5	76.6
-53+45	45.2	84.8	78.0
-45+27	47.1	88.8	79.5
-53+20	37.0	58.5	48.8
-20+10	43.5	77.0	55.6

These values show quite clearly that as the porosity of the particle size fraction increases so does the amount of bridging liquid required. It would therefore appear that porosity is far more important than particle size in determining the agglomerate size obtained at a given bridging liquid volume.

At coarse sizes there was a reasonably good correlation between the pore space and the paste volume.

However, at finer sizes (-53+20, -20+10 μm) the oil volume was significantly less than expected. This suggests that either fine particles pack differently in an agglomerate to coarse particles or that some water accompanies the fine particles.

3.9.7.2 Agglomeration of very fine sizes of alumina

Fine alumina i.e. -53, -10 μm and -5 μm fractions could not be agglomerated in the inclined agglomerator within an agglomeration time of 30 minutes and a wide range of S.D.S. concentration, bridging liquid volume and ionic strength. Agglomerates were only formed by increasing the initial S.D.S. concentration to approximately 2.5×10^{-3} M and after an agglomeration time of about two hours. This effect, demonstrated in Fig. 3.14 suggests that under the standard conditions used the alumina was not sufficiently hydrophobic and that an insufficient number of particle-particle collisions occurred. Further tests showed that by adding the bridging liquid stagewise agglomeration of the fine fractions improved. This effect was demonstrated with the -10 μm fraction. The agglomerates produced were quite strong and they had the appearance of coalesced smaller agglomerates. Some of the features of these agglomerates are shown in Plate 3.3. On adding all the oil at one stage the coarsest particles agglomerated and formed a paste which did not tumble. The removal of these particles from the pulp reduced turbulence and hence collisions between the remaining particles and oil.

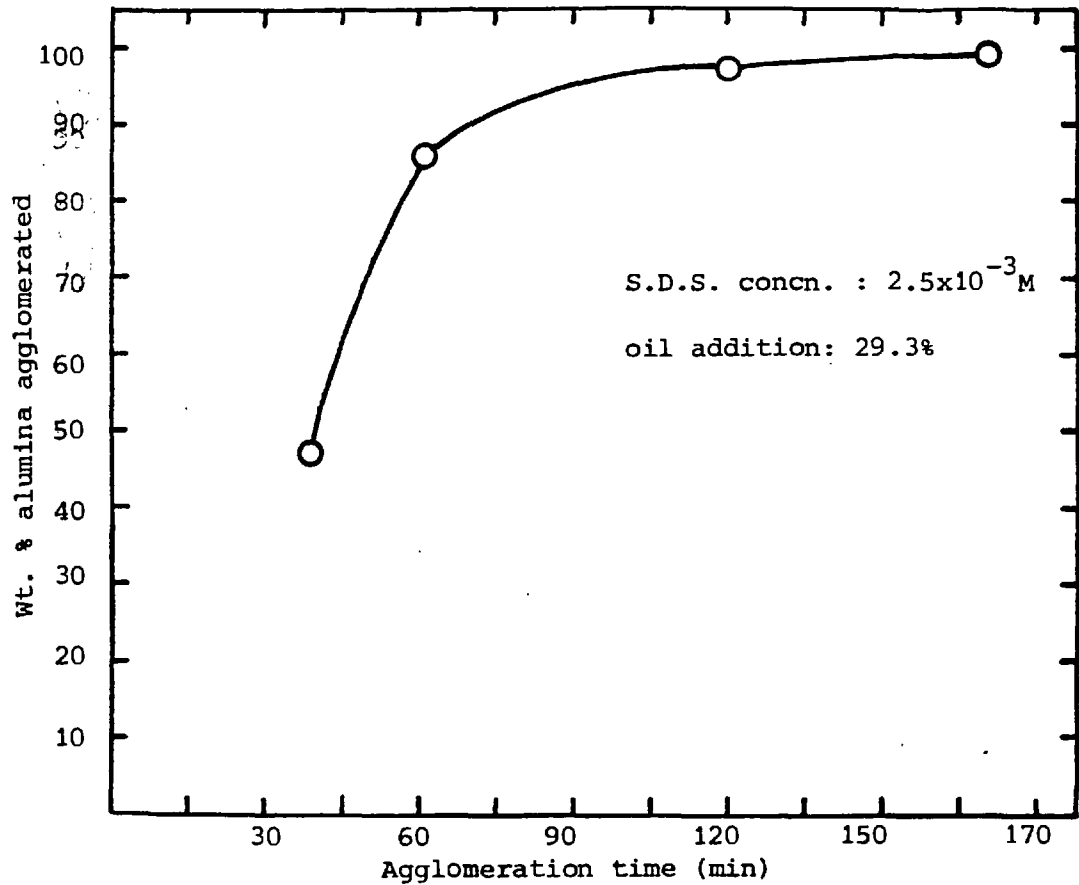


Fig. 3.14 The effect of agglomeration time on the agglomeration of fine alumina ($-53\ \mu\text{m}$) in the inclined agglomerator

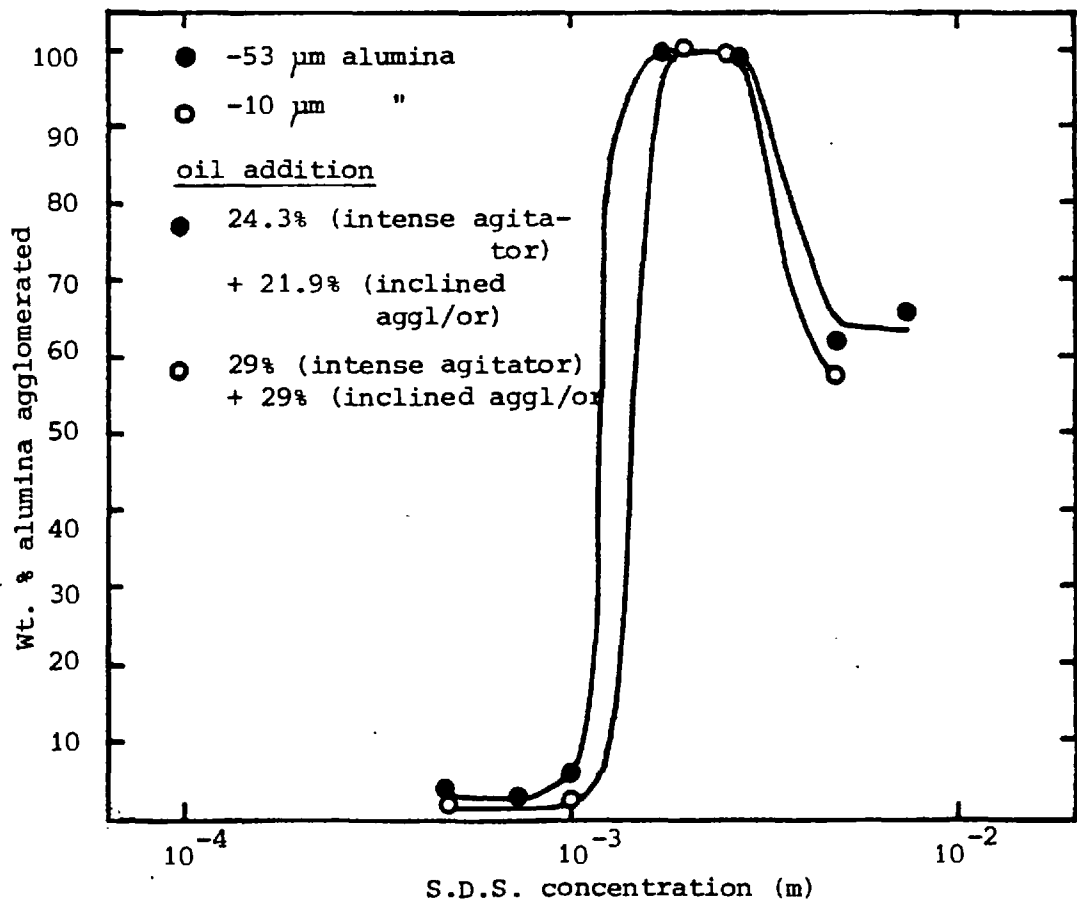


Fig. 3.15. The effect of S.D.S. concentration on percent alumina agglomerated

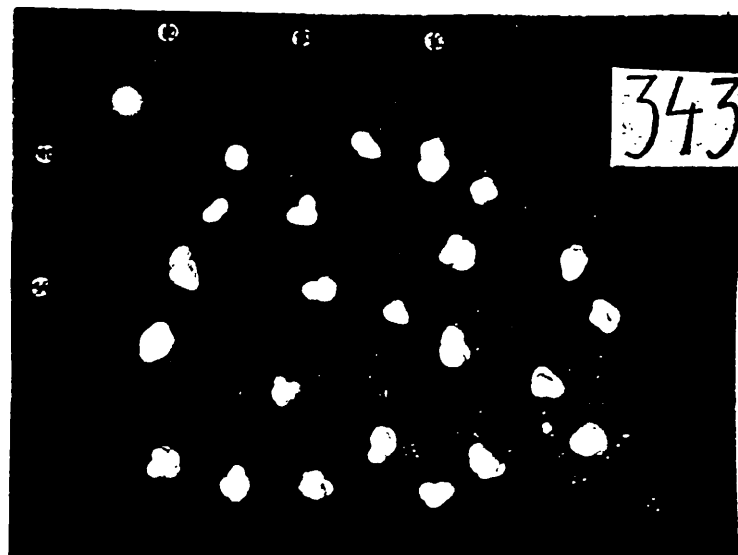
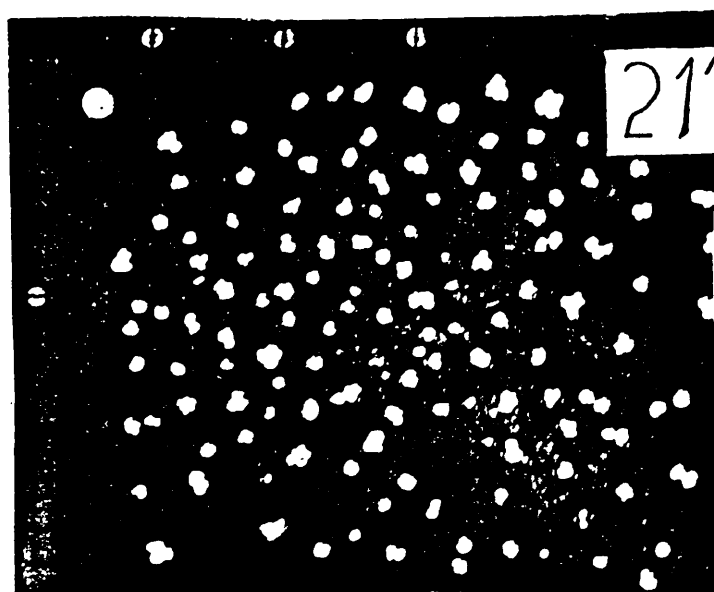
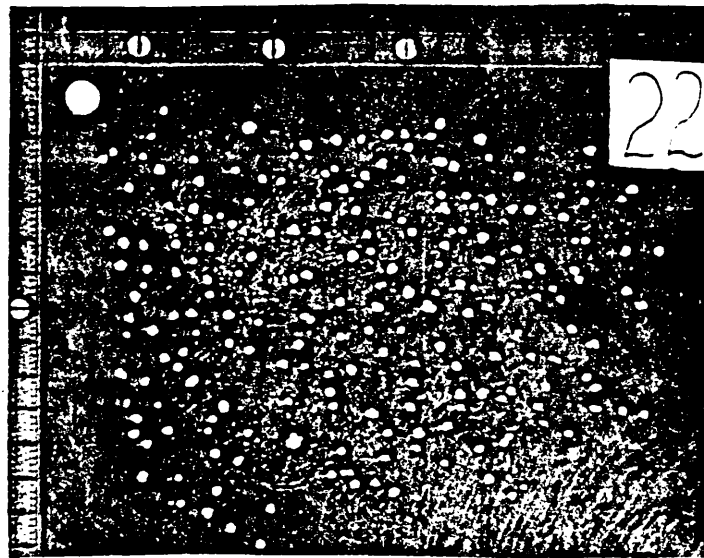


Plate 3.3. Agglomerate form of $-53\ \mu\text{m}$ alumina with stagewise oil additions in the inclined agglomerator

To increase the rate of collision between the alumina particles, the suspensions were preconditioned in a 600 ml beaker with a centrally located impellor (with two inclined 45° blades, 1 x 2 cm) rotating at 1075 r.p.m. and situated 0.8 cm from the beaker bottom. The alumina was first conditioned with S.D.S. for 10 minutes, iso-octane added and then conditioning continued for a further 10 minutes. At the end of this period small agglomerates and flocs were observed and these were enlarged when the beaker plus contents was transferred to the inclined agglomerator and a further small amount of iso-octane added. The agglomeration time in the inclined agglomerator was set at 30 minutes.

The concentration of S.D.S. was critical both when a preconditioning stage was used and also with the inclined agglomerator on its own. Maximum agglomeration of -10 μm and -53 μm fractions was obtained only over a narrow range of S.D.S. concentrations (Fig. 3.15).

The effect of bridging liquid volume on the agglomerate size and the percent alumina agglomerated in the presence of 2.5×10^{-3} M S.D.S. is shown in Fig. 3.15. The amount of iso-octane added in the preconditioning stage was 24.4% and 29.3% for the -53 and -10 μm fractions respectively. The maximum total oil volume added (preconditioning stage and inclined agglomerator) was 47.5% for -53 μm alumina and 51.3% for the -10 μm size fraction, and above these values a paste was formed in both cases. These values, therefore, correspond to the paste volume. Comparison of Fig. 3.16 and Fig. 3.13 shows that less oil was required to agglomerate the very fine alumina than the coarse alumina.

With very fine alumina, however, the porosity values obtained in a vibrated dry system do not fit into the sequence exhibited by the coarser material ($>-45+27 \mu\text{m}$)

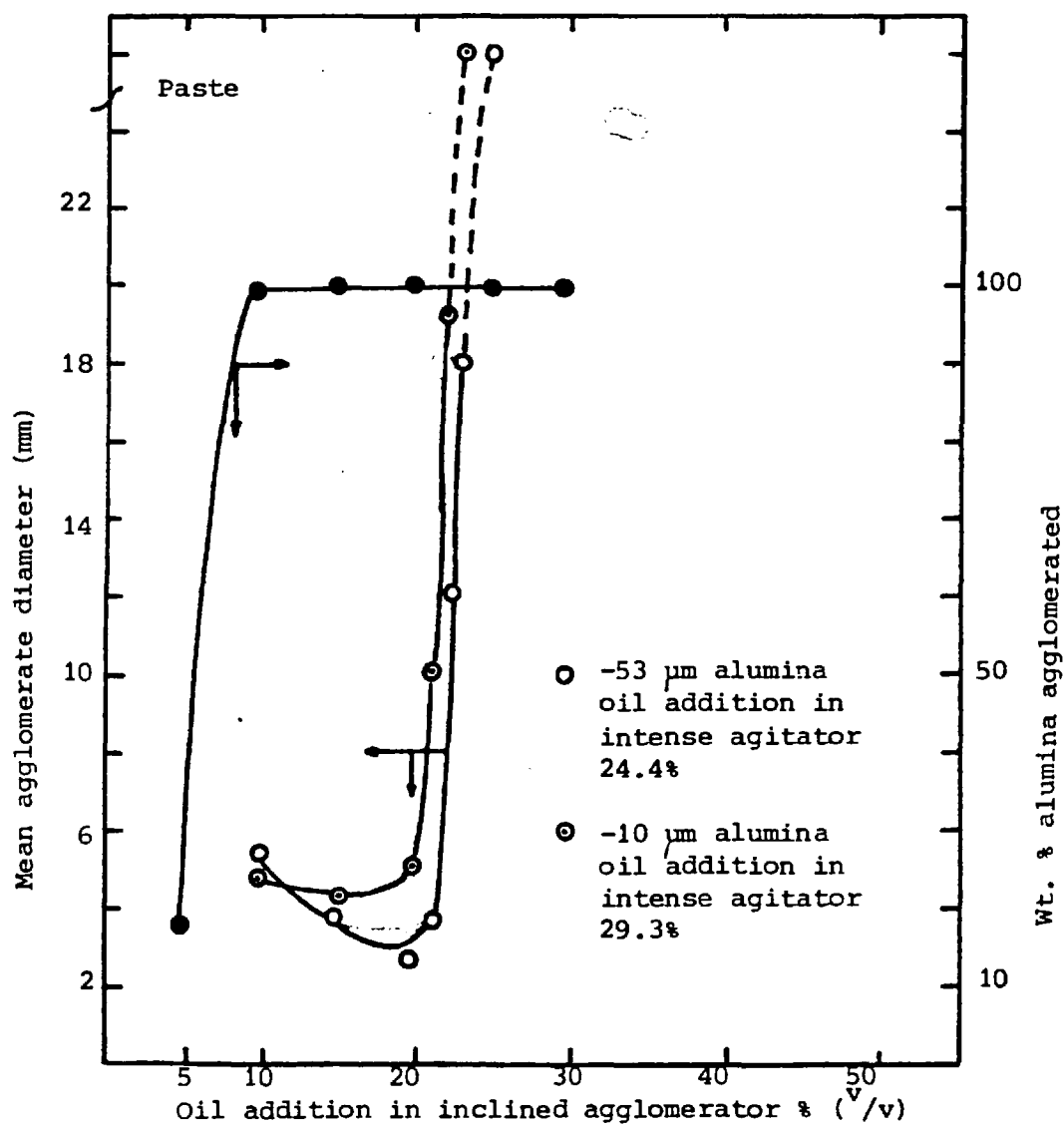


Fig. 3.16 The effect of oil volume on amount of alumina agglomerated and agglomerate size.

when it was agglomerated in the inclined agglomerator. It can be seen from Table 3.5 that these fine fractions required much less oil than that estimated from their pore volumes in the dry packed state. The significant difference between the calculated and experimental maximum oil volumes found with the very fine alumina may be explained as in the case of the $-53+20\ \mu\text{m}$ fraction. in terms of different packing characteristics or association of water with the agglomerates made from the fine alumina.

Table 3.5: The correlation between porosity of feed alumina and maximum volume of bridging liquid required

Particle size (μm)	Porosity of feed alumina after vibration (%)	Maximum oil required % ml/cm ³ alumina	
		Calculated	Experimental (paste volume)
-53	41.0	69.3	~45.8
-10	54.5	117.1	~50.7

The agglomerates formed by preconditioning followed by conditioning in the inclined agglomerator showed good sphericity at the lower oil additions, but at higher values larger agglomerates were formed with a wide spread of sizes and their shapes were irregular. Adding all the oil to the preconditioning stage produced much smaller agglomerates.

3.9.8 Variation of agglomerate growth as a function of time at various oil additions - Characteristics of agglomerate size distributions

A series of experiments was designed to investigate the growth of agglomerates composed of different particle sizes as a function of agglomeration time and quantity of bridging liquid.

In Fig. 3.17 the growth of agglomerates of -86+27 μm alumina is shown for bridging liquid volumes in the range 48.8 to 75.1%. Frequency distributions were determined at agglomeration times greater than 10 minutes, because in the earlier stages, depending on the oil volume added, the agglomerates were either uncompacted and non-spherical or there were unagglomerated voluminous flocs present. Within 60 seconds of adding the bridging liquid the alumina particles began to aggregate, the nature of the aggregates being dependent on the volume of the bridging liquid. Flocs were formed at low oil additions, large loose aggregates at high oil contents, and a mixture of small aggregates and flocs at intermediate additions. The tumbling action of the agglomerator squeezed the aggregates together so that their internal pore space was reduced and almost completely filled with bridging liquid. At bridging liquid additions between 58.5% and 68.3% no further growth of the agglomerates occurred after the initial 10 minutes. Increasing the volume of oil increased the rate of agglomerate growth and at volumes greater than 68.3% the agglomerates grew with time and either reached a constant equilibrium size or formed a paste. At bridging liquid volumes below 58.3% some growth of the agglomerates did occur after the initial stage of their formation but the growth mechanism appeared to be different. Visual observation suggested that growth was by coalescence of agglomerates at bridging volumes above 68.3%, while at the low oil addition of 48.8% it occurred by crushing and the layering of the fragments around surviving agglomerates. Similar results were obtained with tetradecane and hexadecane except that the corresponding oil volume addition ranges were slightly different. The results obtained with the relatively coarse size fractions i.e. -63+53, -53+45, and -45+27 μm were also similar to those obtained with the -86+27 μm fraction. Various stages in the growth of agglomerates are illustrated in plate 3.4.

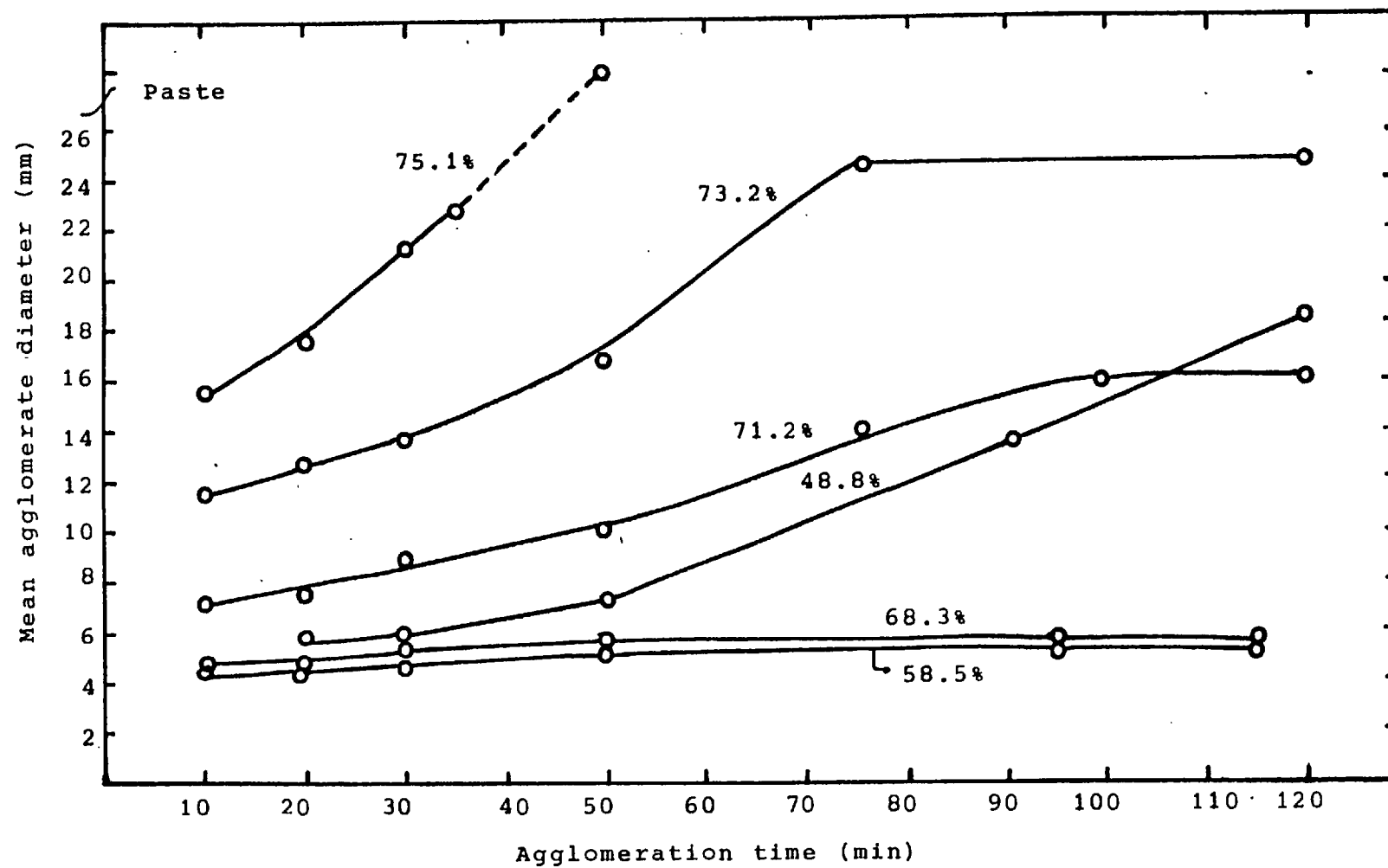
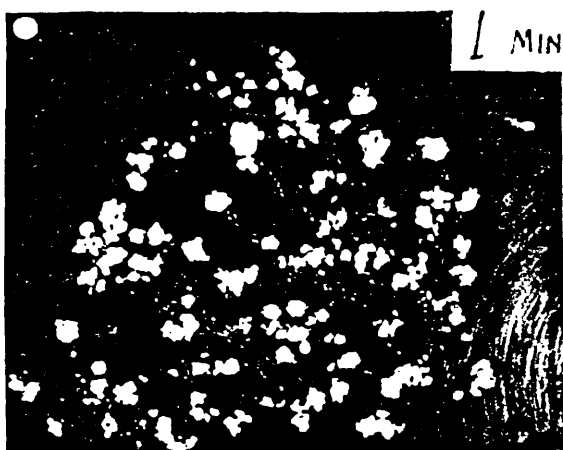
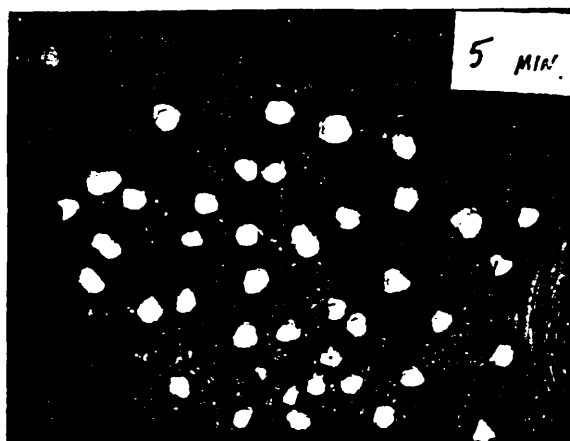


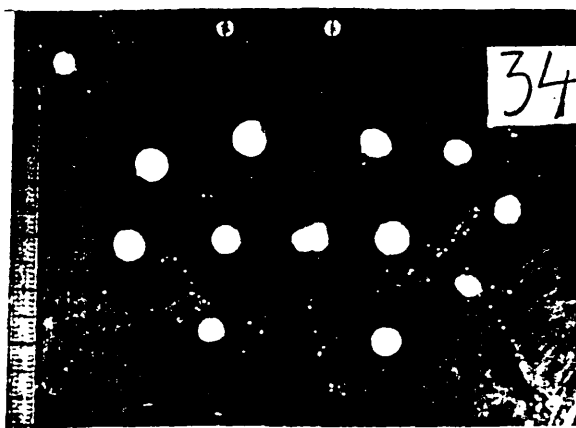
Fig. 3.17: Agglomeration of $-86+27\ \mu\text{m}$ alumina with different levels of iso-octane



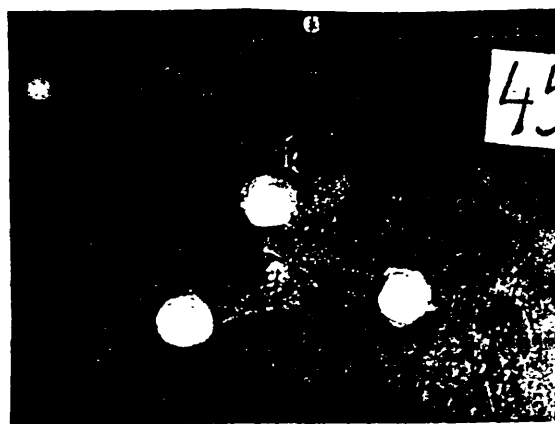
Oil addition: 75%
Agglomeration time: 1 min



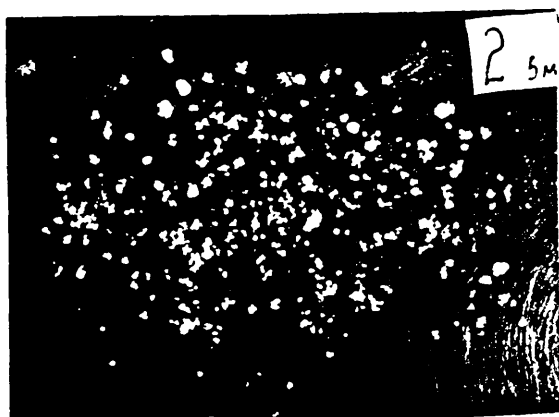
Oil addition: 75%
Agglomeration time: 5 min



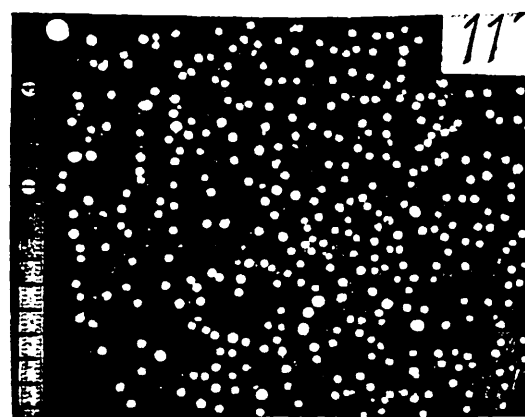
Oil addition: 75%
Agglomeration time: 10 min



Oil addition: 75%
Agglomeration time: 30 min



Oil addition: 68.3%
Agglomeration time: 5 min



Oil addition: 68.3%
Agglomeration time: 30 min

Plate 3.4. Successive photographs illustrating the agglomerate growth as a function of time for -86+27 μ m alumina with different iso-octane additions

In Fig. 3.18 the growth of agglomerates of -53+20 μm alumina is shown as a function of time. Comparison of Fig. 3.18 with Fig. 3.17 shows that as in the case of the coarser alumina fractions there was a bridging liquid volume at which very little growth occurred after an initial induction period of about 10 to 15 minutes. At lower oil additions the agglomeration rate also increased as the oil volume decreased, but agglomerates were only formed after about 20 minutes, and after 30 minutes perfect and narrowly sized ($\bar{D} \pm 1 \text{ mm}$) spherical agglomerates were achieved. Chipping and abrasion between the agglomerates decreased their size slightly at longer agglomeration times.

The comparison of the agglomeration behaviour of -53+20 μm and -86+27 μm size fractions shows that the agglomerates formed during the initial stages ($\leq 10 \text{ min}$) were considerably smaller with the finer size fractions than with the coarser material. With the -53+20 μm alumina the slow enlargement process in the early stages was followed by rapid coalescence of the small spherical agglomerates at oil additions of 48.8% and 50.7%. The rapid increase of agglomerate size and the shape of the spheres (clusters of smaller agglomerate units) during this secondary agglomeration are seen in the sequence of photographs in plate 3.5.

The induction period of the finer particles necessary for agglomerate formation and growth increased longer as the amount of bridging liquid decreased. Similar observations were made with the -20+10, -53 and the -10 μm size fractions, except that different oil levels were required to produce the same agglomerate growth. With the -53+20 and -20+10 μm size fractions and using the standardized procedure the alumina particles began to separate as agglomerated species after about 3 to 5 min. and up to 10 minutes respectively after the oil phase had been added.

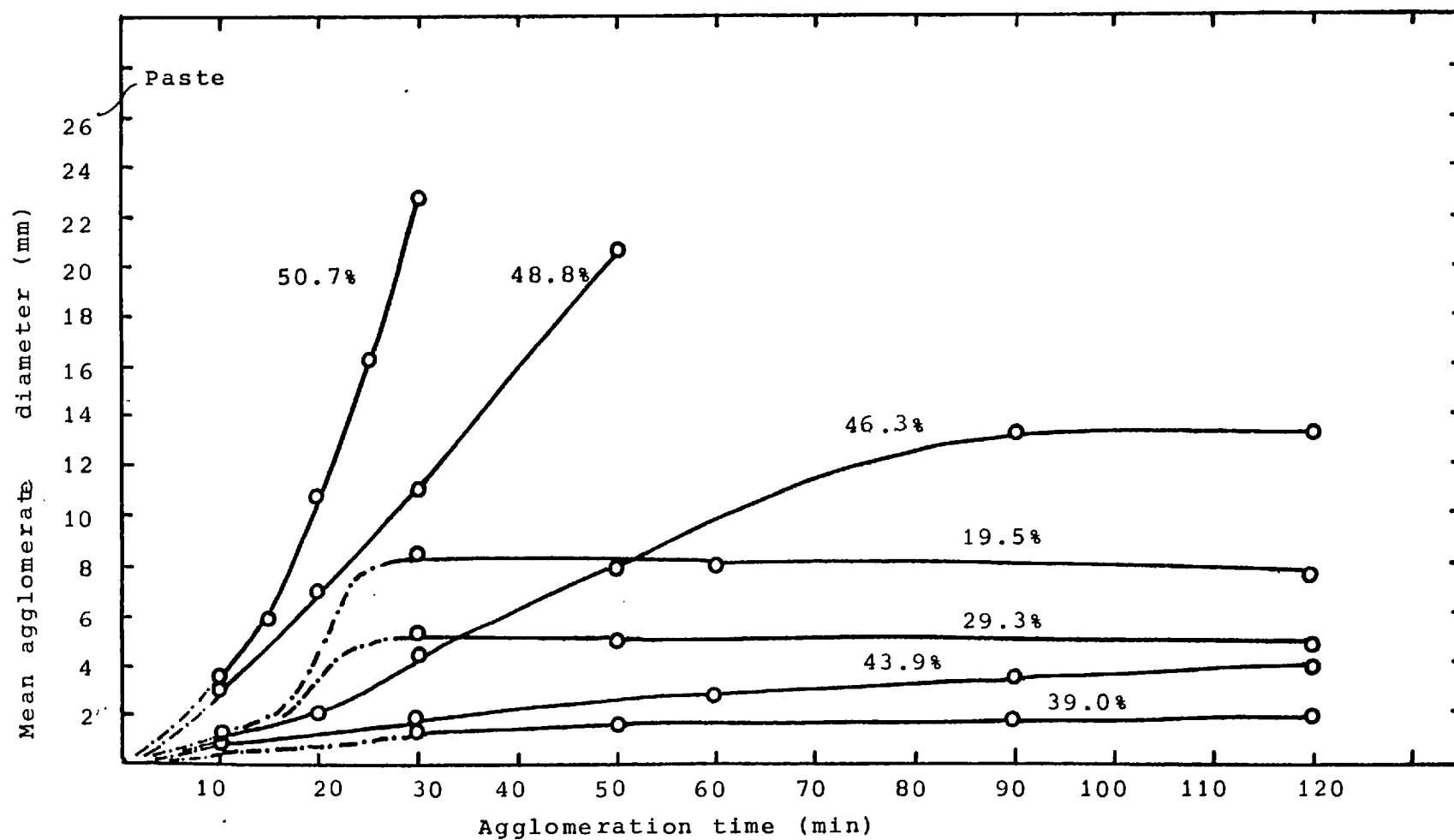


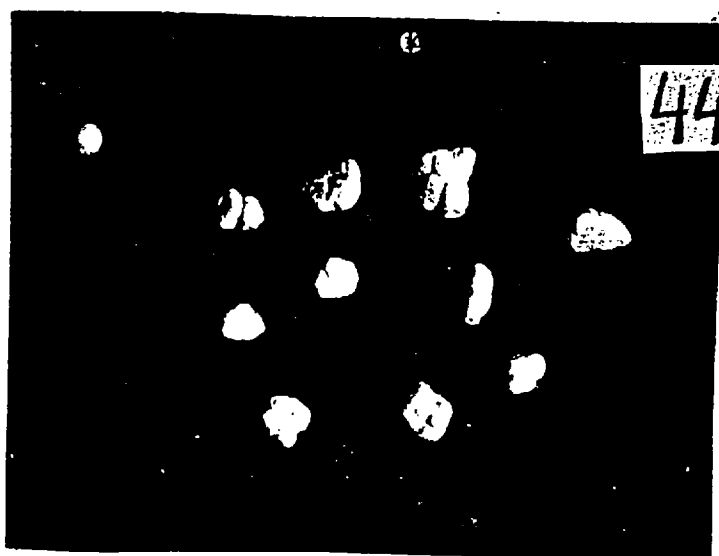
Fig. 3.18: Agglomeration of $-53+20\ \mu\text{m}$ alumina with different levels of iso-octane



Oil addition: 49.2%
Agglomeration time
15 min



Oil addition: 49.2%
Agglomeration time
20 min



Oil addition: 49.2%
Agglomeration time
30 min

Plate 3.5. Various stages in agglomerate growth as a function of time for $-53+20\ \mu\text{m}$ alumina with an iso-octane addition of 49.2%

The cumulative size distributions of the agglomerates composed of -86+27 μm alumina at different agglomeration times and bridging liquid volumes are shown in Figs. 19 - 22. These results show that the agglomerates grew mostly at the expense of the disappearance of the small ones. Coalescence of large agglomerates was also observed. At a given oil addition the spread of the agglomerate size distribution was not very sensitive to agglomeration time. The position of the distribution curves at a given time was however, dependent on the bridging liquid volume with the curves at high volumes showing coarser agglomerate sizes. In most of the oil concentration range the diameter of the largest agglomerates was 1.5-2.0 times the diameter of the smallest with the exception of the very low oil additions (48.8%) where the agglomerate diameters were within ± 1 mm of the average agglomerate size.

In Figs. 23 and 24 the results from Figs. 19 and 20 are replotted in dimensionless form¹¹⁸; the number of agglomerates with a diameter equal to or greater than a specified diameter is plotted against the ratio of this diameter to the mean agglomerate diameter. The size distributions obtained after different times at a given bridging liquid volume gave coincident curves when presented in this way. A major portion of these curves would be described by a straight line except for the upper and lower ends, where deviations from the linear relationship occur. It is also indicated in these figures that in most experiments the middle 90% (by number) of the agglomerates had diameters between 0.8 - 0.9 and 1.3 - 1.4 times the average agglomerate diameter.

The effect of oil volume on the agglomerate size distribution with -86+27 μm alumina is presented in Table 3.6, which shows that the spread of agglomerate sizes decreased as the oil volume was reduced. With a higher viscosity oil, (tetradecane),

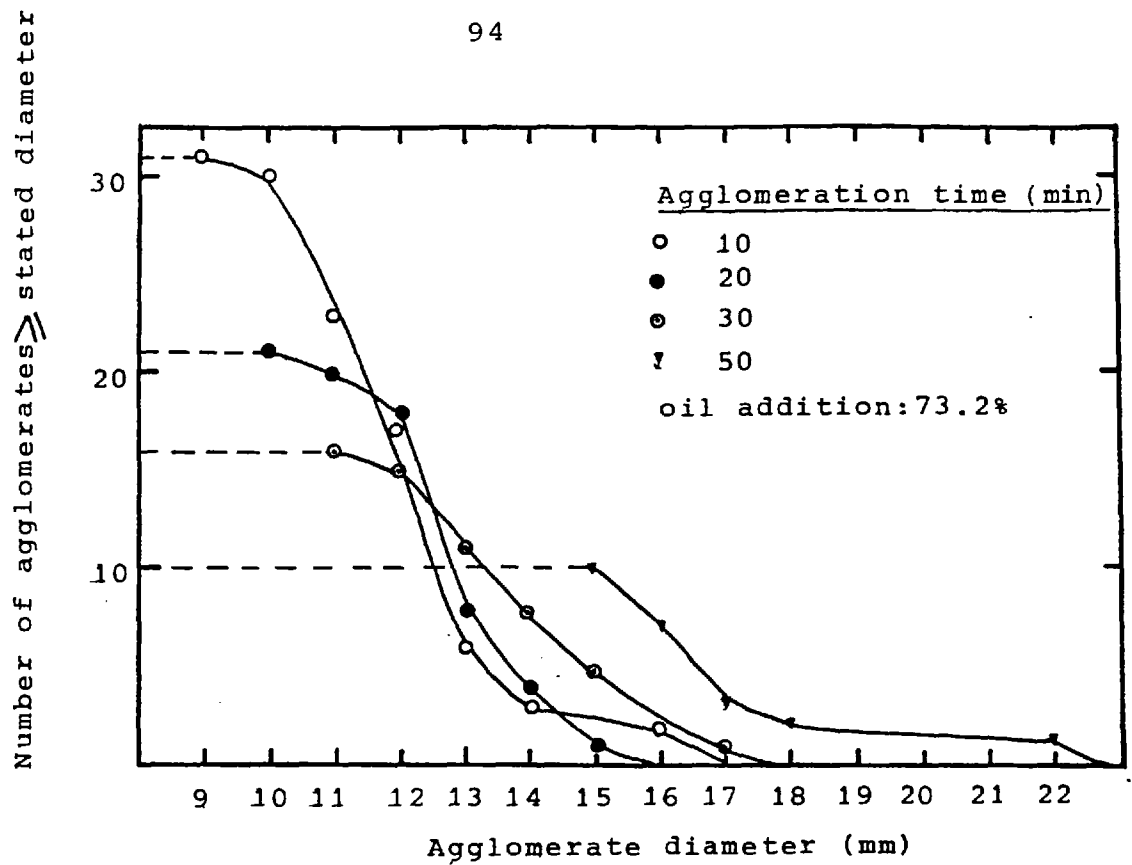


Fig.3.19: The effect of agglomeration time on agglomerate size distribution with -86+27 μ m alumina. Oil addition=73.2%.

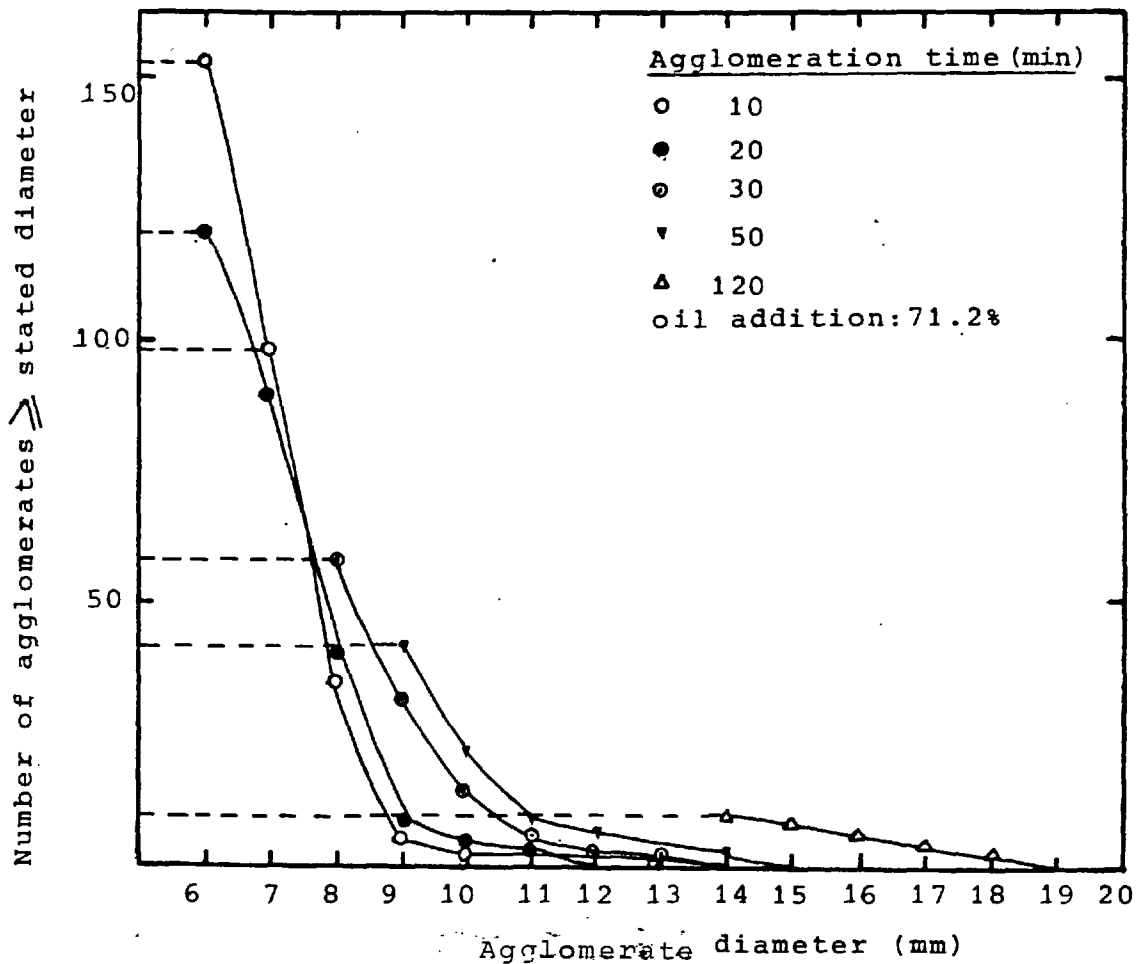


Fig. 3.20: The effect of agglomeration time on agglomerate size distribution with -86+27 μ m alumina. Oil addition=71.2%

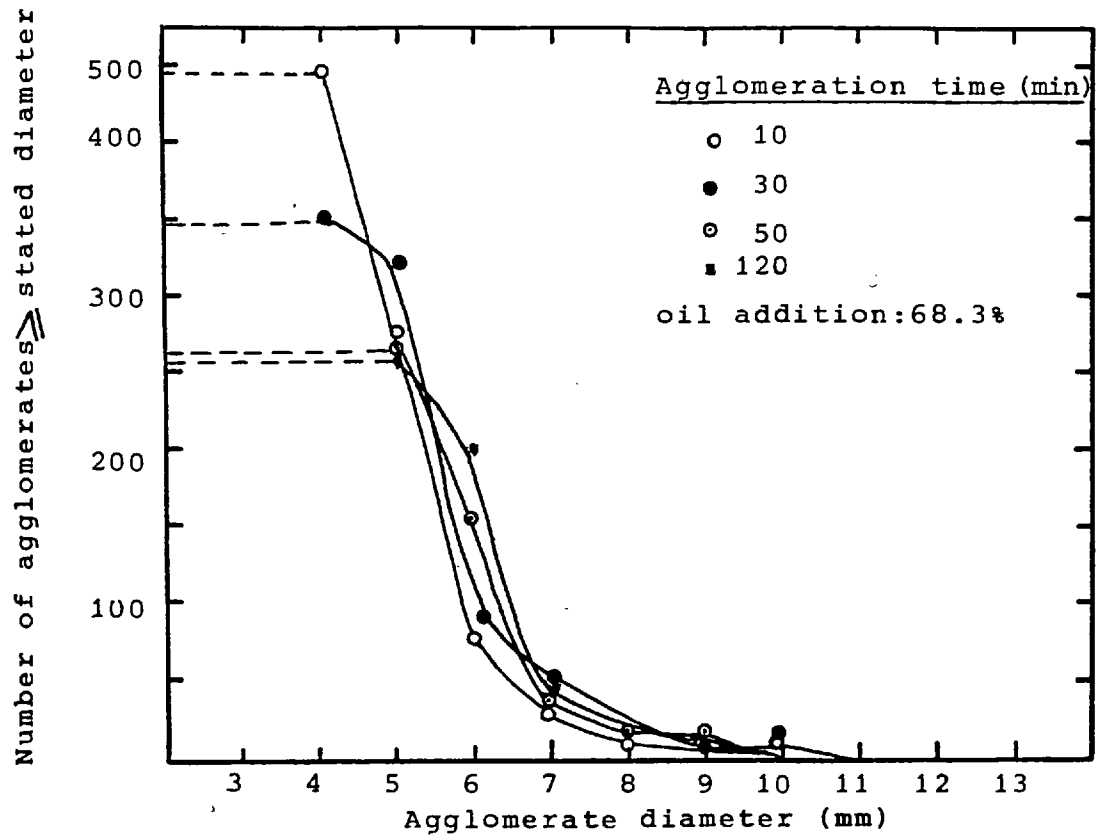


Fig.3.21: The effect of agglomeration time on agglomerate size distribution with -86+27 μ m alumina. Oil addition = 68.3%

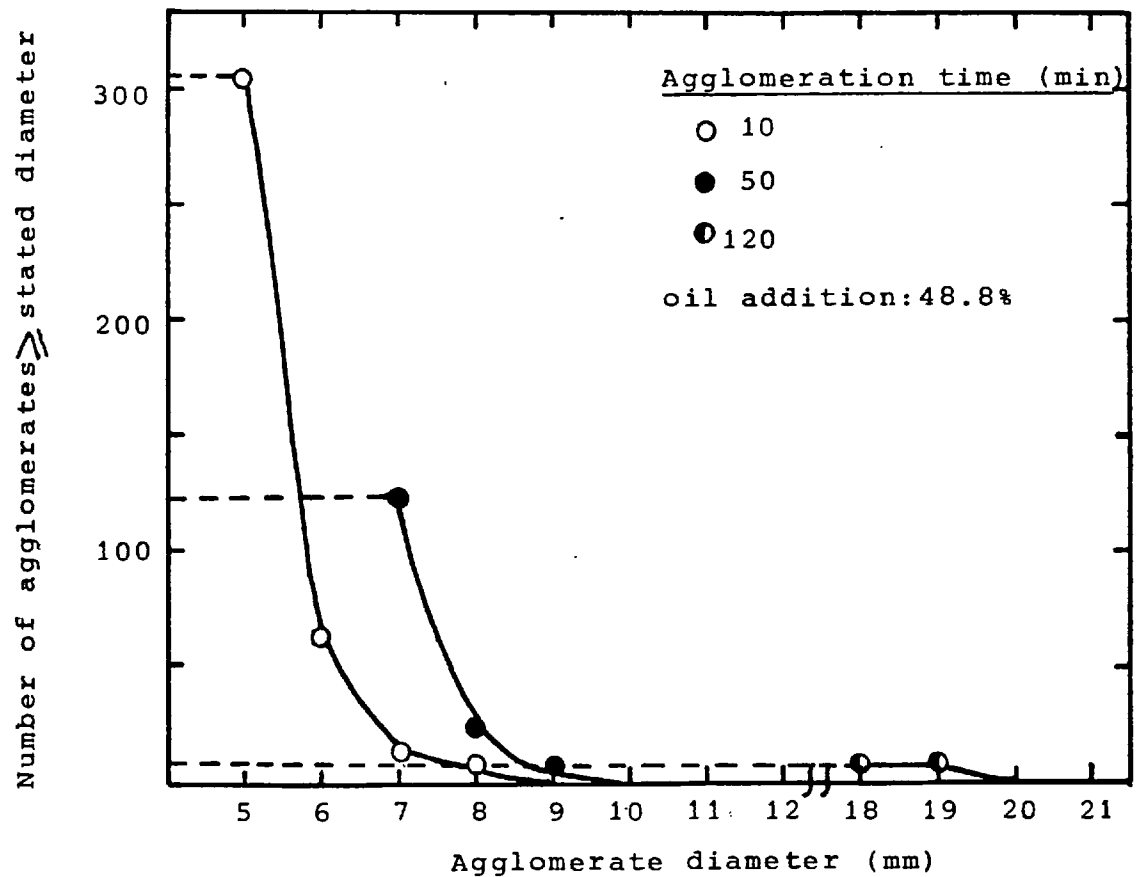


Fig. 3.22: The effect of agglomeration time on agglomerate size distribution with -86+27 μ m alumina. Oil addition = 48.8%

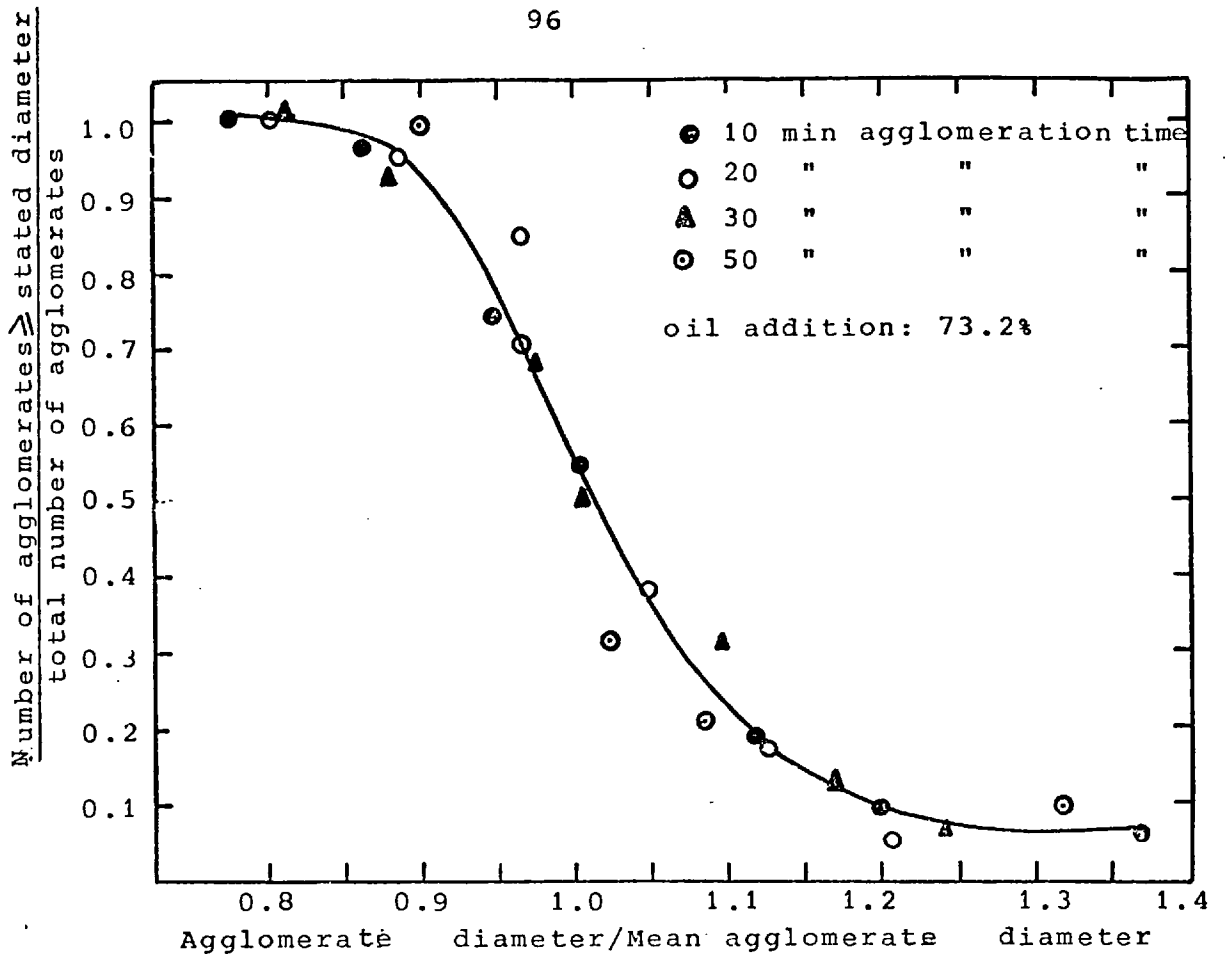


Fig. 3.23: Results from Fig. 3.19 replotted in dimensionless form

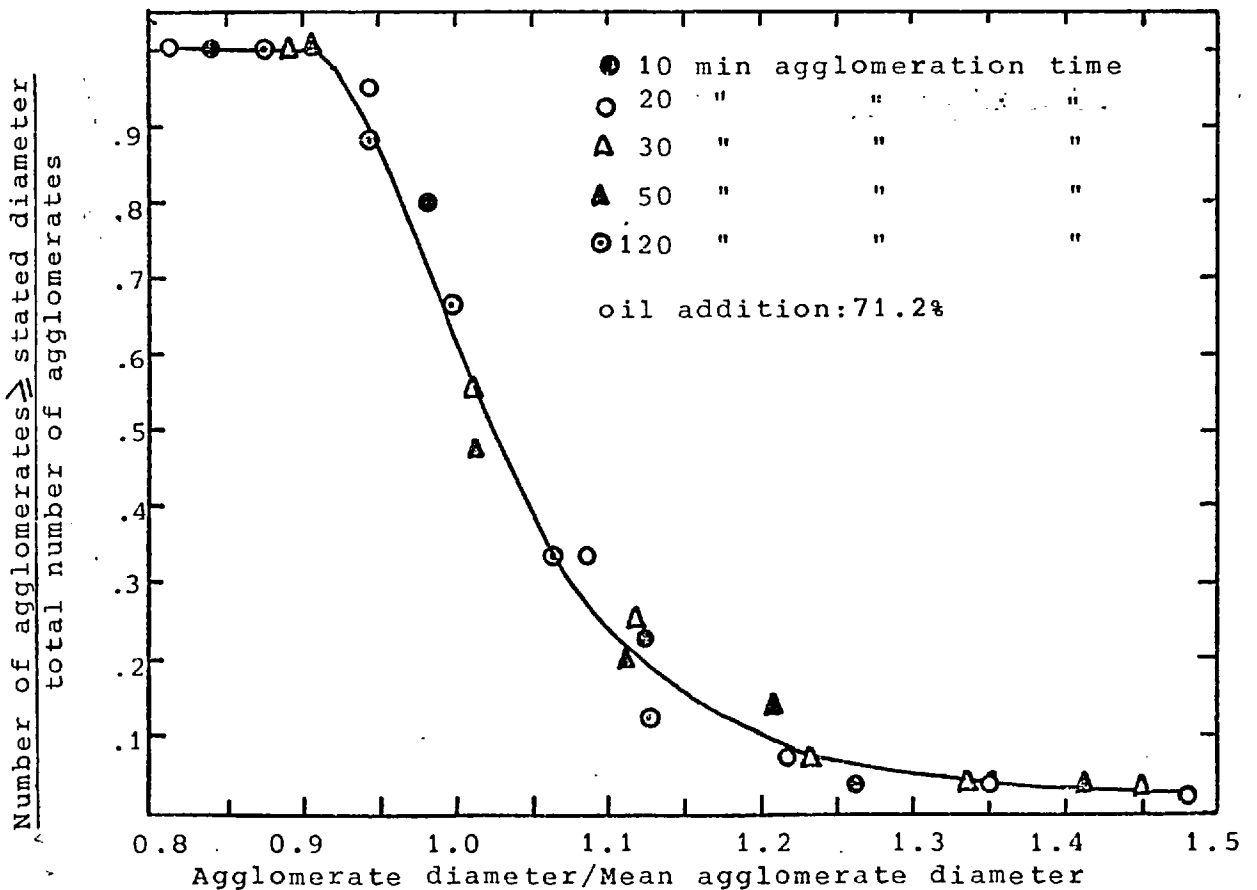


Fig. 3.24: Results from Fig. 3.20 replotted in dimensionless form

(see Table 3.7) the agglomerates covered a slightly wider size range

Table 3.6: Effect of oil volume on characteristics of agglomerate size distribution for -86+27 μm alumina/iso-octane system

Agglomeration time: 30 minutes

Oil addition ml/cm ³ alumina (%)	Mean agglomerate diameter (mm)	Standard deviation	Variance
73.2	13.6	1.6	2.7
71.2	8.9	1.1	1.2
68.3	5.4	0.9	0.8
58.5	4.1	0.7	0.5
48.8	5.6	0.7	0.5

Table 3.7: Effect of oil volume on characteristics of agglomerate size distribution for -86+27 μm alumina/tetradecane system

Agglomeration time: 30 minutes

Oil addition ml/cm ³ alumina (%)	Mean agglomerate diameter (mm)	Standard deviation	Variance
68.3	11.5	1.7	2.9
65.8	8.2	1.8	3.3
63.4	5.9	1.5	2.4
58.5	4.8	0.9	0.9
48.8	5.9	0.7	0.5

Tables 3.8 and 3.9 show the characteristics of agglomerate size distribution for -53+20 μm alumina at various oil additions and different agglomeration times at an oil addition of 46.3%. It can be seen from Table 3.8 that the spread of agglomerate size increased considerably especially at oil additions at which large agglomerates (>5 mm) were produced by rapid coalescence. Table 3.9 shows that the agglomerate size range became wider as a function of agglomeration time in cases where the initially formed small agglomerates grew to larger ones.

Table 3.8: Effect of oil volume on characteristics of agglomerate size distribution for -53+20 μm alumina/iso-octane system

Agglomeration time: 30 minutes

Oil addition ml/cm ³ alumina (%)	Mean agglomerate diameter (mm)	Standard deviation	Variance
50.7	22.9	9.9	99.4
48.8	10.9	3.0	9.2
46.3	4.3	0.9	0.8
43.9	1.7	0.8	0.6
39.0	1.6	0.9	0.9
29.3	5.3	0.8	0.6
19.5	8.1	0.5	0.3

Experiments with the above fine size fractions i.e. -20+10, -53, and -10 μm alumina confirmed that the spread in agglomerate size was higher with the fine fractions rather than with coarse ones at oil volumes where large agglomerates were formed. In this region the sphericity of the agglomerates made of the fine size fractions was poor and an elongation ratio of approximately 1.2 was measured.

Table 3.9: Effect of agglomeration time on characteristics
of agglomerate size distribution for -53+20 μm
alumina/iso-octane system

Oil addition: 46.3%

Agglomeration time (min)	Mean agglomerate diameter (mm)	Standard deviation	Variance
20	1.9	1.1	1.2
30	4.3	0.9	0.8
50	7.9	1.3	1.8
120	13.2	1.5	2.4

3.10

SUMMARY

Spherical agglomeration of alumina in aqueous suspension can be obtained with a non-polar bridging liquid by modifying the surface of the alumina with an anionic surfactant such as sodium dodecyl sulphate. The degree of agglomeration and the agglomerate size is dependent on the surfactant concentration and pH. Too little surfactant produces an alumina surface that is not sufficiently hydrophobic to form agglomerates and too much results in emulsification of the bridging liquid and the formation of small agglomerates.

The agglomerate size is dependent on a balance between the degree of agitation required to produce a high number of particle-particle collisions and that which will cause agglomerate destruction. Gentle agitation produces a steady growth of agglomerates and under conditions of high shear stress the agglomerates are small¹¹⁹.

The volume of bridging liquid has a marked effect on agglomerate size and provided that the volume is above a certain value the size increases with volume until a paste is formed. Below a certain bridging liquid volume the agglomerates made from coarse alumina fractions appear to grow by a different mechanism. The increase in agglomerate size with bridging liquid volume is not surprising because more liquid will be available for bridging and filling the inter-particle interstices. Unlike other authors^{120,118} however a linear dependence of average agglomerate size on bridging liquid volume was not found. The packing characteristics of the agglomerating material *are of great* importance in determining the amount of bridging liquid required for satisfactory agglomeration¹²¹.

CHAPTER 4

SELECTIVITY OF THE SPHERICAL AGGLOMERATION PROCESS

4. SELECTIVITY OF THE SPHERICAL AGGLOMERATION PROCESS

4.1 Details of the experiments

Experiments have been carried out with the object of showing whether spherical agglomeration can be applied to selectively separate one mineral from a multicomponent mixture. Synthetic mixtures of alumina and ilmenite using S.D.S. as the collector and iso-octane as the bridging liquid were employed for these studies. Although these minerals are not encountered as a natural mixture, they form a useful model system since both are oxides with high z.p.c. values. Attempts to separate them have been made without the addition of activators and depressants in a region where both minerals were positively charged. In preliminary work it was established that the ilmenite used did not agglomerate when the variables were changed within reasonable limits. Experiments were therefore made with the objective of selectively agglomerating and separating alumina from aqueous suspensions consisting of mixtures of alumina and ilmenite particles.

Large lumps of very high grade ilmenite ore provided by Titania A/S, Norway, were crushed and then ground in an agate vibratory mill. A number of size fractions were prepared from this material by dry screening and sedimentation techniques. The ilmenite size fractions used in the selective agglomeration tests included -75 + 45, -53+45, -45+30 and -45 μm material. The size distributions of the widely sized materials, i.e. -75+45 and -45 μm were determined by Cyclosizer and are shown in Table 4.1.

A semiquantitative XRF scan analysis showed that the ilmenite was of high purity. Table 4.2 gives the minor and trace elements present in the sample. Although the formula for ilmenite is normally given as FeTiO_3 , it is more

Table 4.1 Size analysis of the widely sized ilmenite grades.

Nominal size fraction μm	Particle size range Stokes diam. (ds), μm	Wt % in range
- 75+45	-75+63	28.4
	-63+53	31.0
	-53+45	18.7
	-45	<u>21.9</u>
		100.0
- 45	-45+20	30.4
	-30+21.5	12.2
	21.5+15	12.2
	-15+10	10.6
	-10+7.5	6.2
	-7.5	<u>28.4</u>
		100.0

Table 4.2 XRF analysis of ilmenite sample

Major	Intermediate	Minor	Traces
>5%	(0.5 -5) %	(0.5-0.05) %	<0.05%
Ti Fe		Mg	Cl
		Si	Cr
		Ca	K
		Cr	Ni
		Mn	Cu
			Zn

fully expressed as (Fe,Mg,Mn). TiO_3 , and therefore in addition to titanium and iron, ilmenite may contain a certain amount of magnesium and manganese.

It was found that when the pulverised ilmenite powder was attacked with hot concentrated HCl an insoluble residue always remained, and this comprised 4.5% by weight of the ilmenite ore. A sample of this residue analysed by X-R diffraction did not indicate the presence of $FeTiO_3$ or TiO_2 , and probably a complex silicate compound was the main source of the undissolved material.

Mixtures of alumina and ilmenite in various proportions constituting a total weight of 40g were conditioned in 200ml S.D.S. solution at a constant concentration ($pH = 3.5 \pm 0.1$) for 10 min and then the bridging liquid was added. The amount of bridging liquid employed was 2% less than that found to be the "paste volume" for each size fraction in the testwork with the alumina/iso-octane/S.D.S. solution system. The oil addition, specified as a percentage of the dry volume of the alumina particles, was kept constant as the mixture composition was varied. In each experiment the mixture was conditioned in the presence of iso-octane for 30 min and the agglomerated product was then separated by screening ($+ 420 \mu m$) and washed carefully with water to remove the ilmenite particles that were not incorporated in the agglomerates. The agglomerate size distribution was determined using the method previously described for alumina. The amounts of alumina in the products obtained at the end of each agglomeration time were determined by treating the product with boiling concentrated HCl. The insoluble alumina was collected in a filter and then weighed, and these weights were corrected to allow for the undissolved part of the ilmenite ore. The percent alumina agglomerated, grade of product, and mean agglomerate diameter was determined for each run and the selectivity of the agglomer-

ation process was assessed.

4.2 . Preliminary work

The zero point of charge of ilmenite was measured by the solid titration method ¹²² at 20°C with -45 µm material. It was found that after 12 hours of agitation the zero point of charge occurred at pH = 9.1 ± 0.1, and that the ilmenite surface was therefore, positively charged below this pH. This is close to the value of 9.5 measured by Parkins ¹²³ on ilmenite from the same source. A considerable amount of testwork was undertaken to investigate the response of ilmenite to agglomeration in the S.D.S. solution/iso-octane system. The variables studied included ilmenite particle size, S.D.S. concentration between 10⁻⁶ and 2 x 10⁻³ M, pH, iso-octane additions between 10% and 150% of the alumina volume and agglomeration time. In all cases the added bridging liquid floated in the surface of the suspension at the end of agitation, indicating that no appreciable wetting of the ilmenite by iso-octane occurred. Similar results were obtained with decane and tetradecane.

Although no agglomeration of the ilmenite was obtained it was clear from two-liquid flotation tests that the S.D.S. adsorbed at the ilmenite/water interface. Complete concentration of -45µm ilmenite was obtained at the iso-octane/water interface at pH values below 7 and at S.D.S. concentrations in the 10⁻⁵ to 10⁻³ M range. In alkaline media the amount of ilmenite concentrated at the interface decreased and at pH 11 only half of that added was concentrated there. The procedure used in these tests was similar to that described by Shergold and Mellgren ²⁵. These results clearly show that S.D.S. was adsorbed by the ilmenite to give a hydrophobic surface but that the surface was not hydrophobic enough for good agglomeration. It was therefore possible to selectively agglomerate the alumina.

4.3

RESULTS

4.3.1 Effect of bridging liquid volume and particle size on selectivity.

The effect on selectivity of different iso-octane additions was investigated using a synthetic mixture composed of equal parts by weight of -86 + 27 μm alumina and -45 μm ilmenite at an initial S.D.S. concentration of $7.5 \times 10^{-4} \text{ M}$. Fig. 4.1 shows that the percentage of the alumina agglomerated was always above 95% and that the maximum ilmenite content of the agglomerates was 2%. The results suggest that the volume of iso-octane added had no significant effect on the grade of the agglomerates while its influence on agglomerate size was similar to that observed for alumina alone. Also the amount of oil needed to form a soft paste was approximately that which would have been required had alumina only been present. This indicates that ilmenite particles entrapped in the alumina agglomerates did not significantly disturb the packing characteristics of the -86 + 27 μm alumina. The product formed had a high degree of sphericity and especially at the lower oil additions showed a narrow size distribution ($\bar{D} \pm 1 \text{ mm}$).

Fig. 4.2 illustrates the selectivity obtained as a function of the weight percent of alumina in the feed. For these experiments mixtures were prepared with -86 + 27 μm alumina and -75 + 45 μm ilmenite, and a constant oil addition of 73.2% was used. It can be seen that a very high degree of agglomeration (98%) was achieved when the mixture contained 37% by weight alumina and this remained constant as the alumina content of the mixture was increased, but it dropped to only 18% when the mixture contained 25% alumina. This decrease can probably be explained in terms of the decreasing probability of collisions between oil drops and

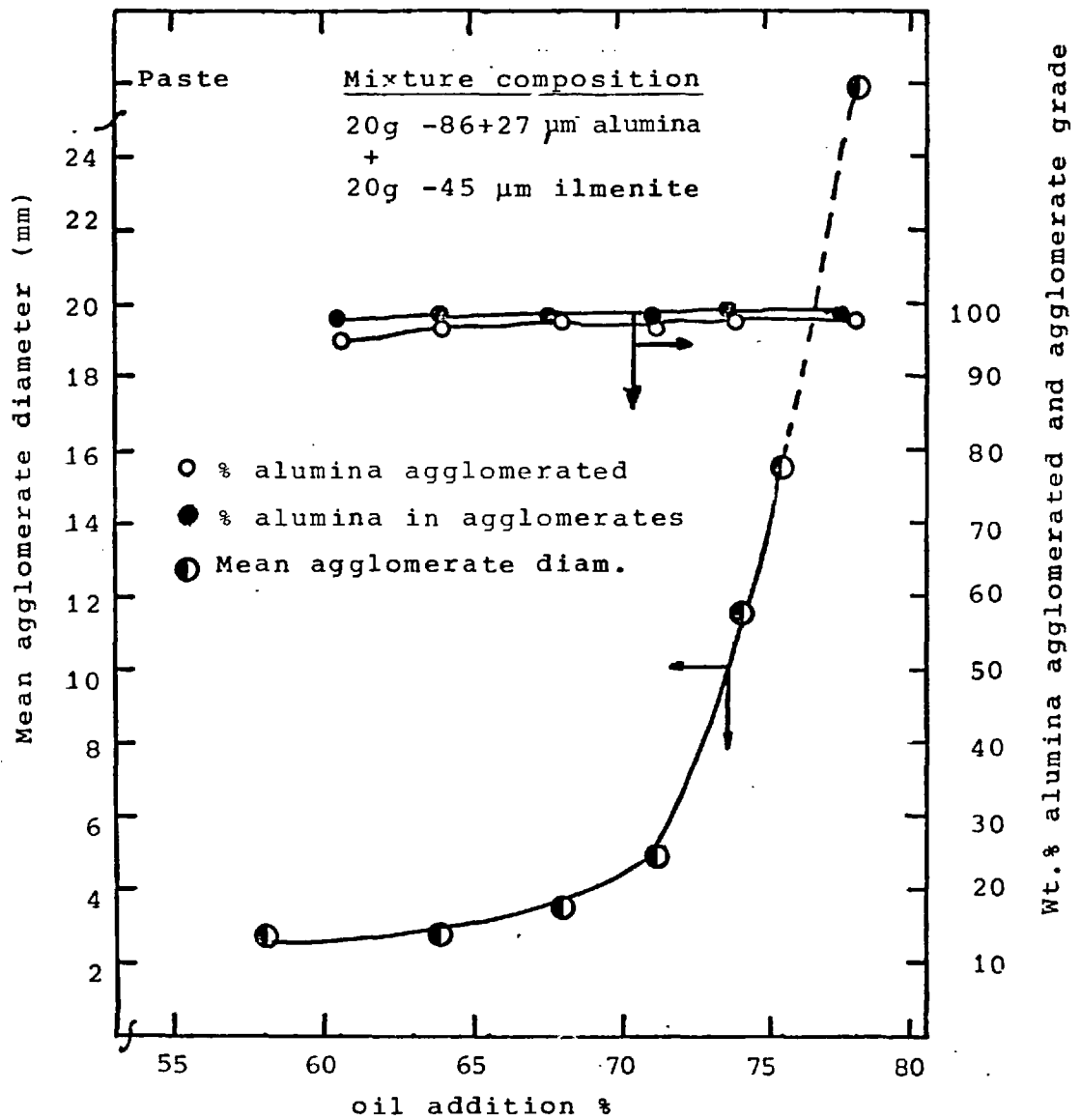


Fig. 4.1: Effect of oil addition on percent alumina agglomerated and agglomerate size

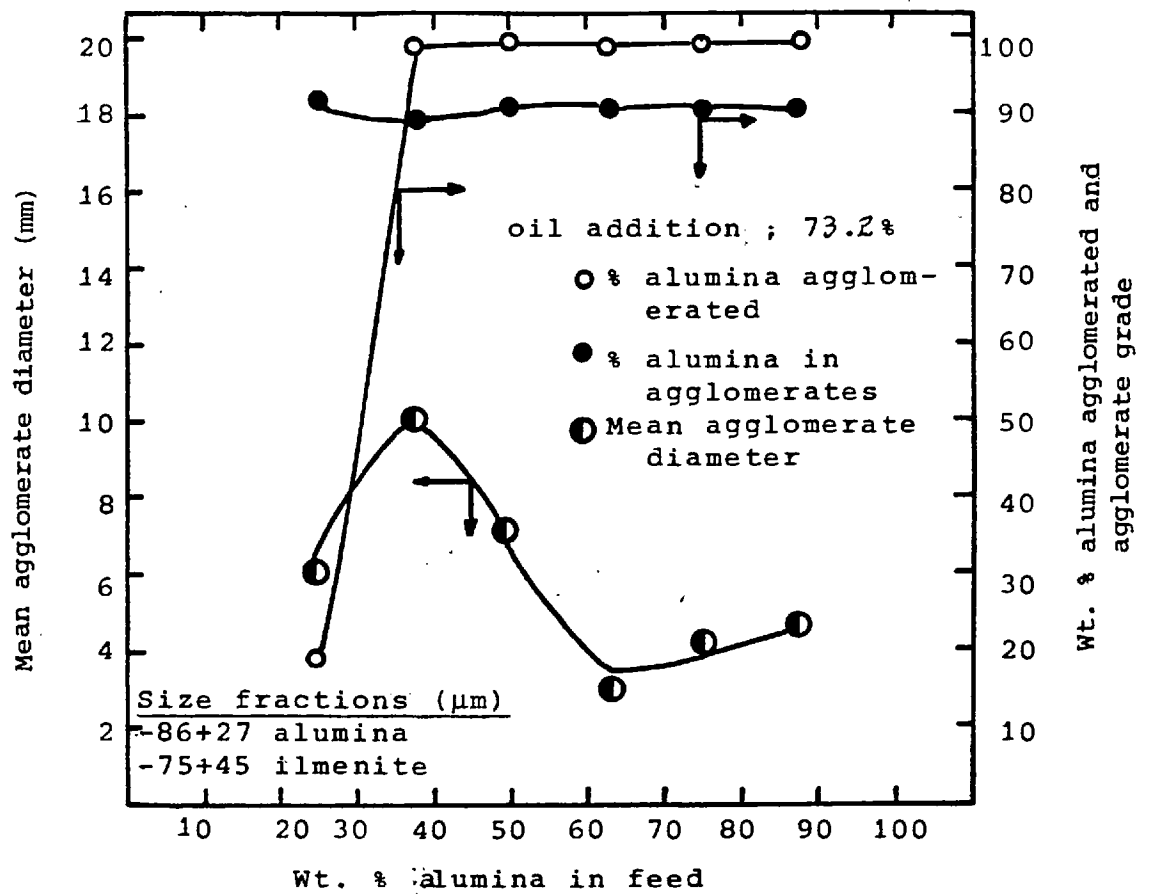


Fig. 4.2: Effect of alumina/ilmenite mixture composition on percent alumina agglomerated and agglomerate size

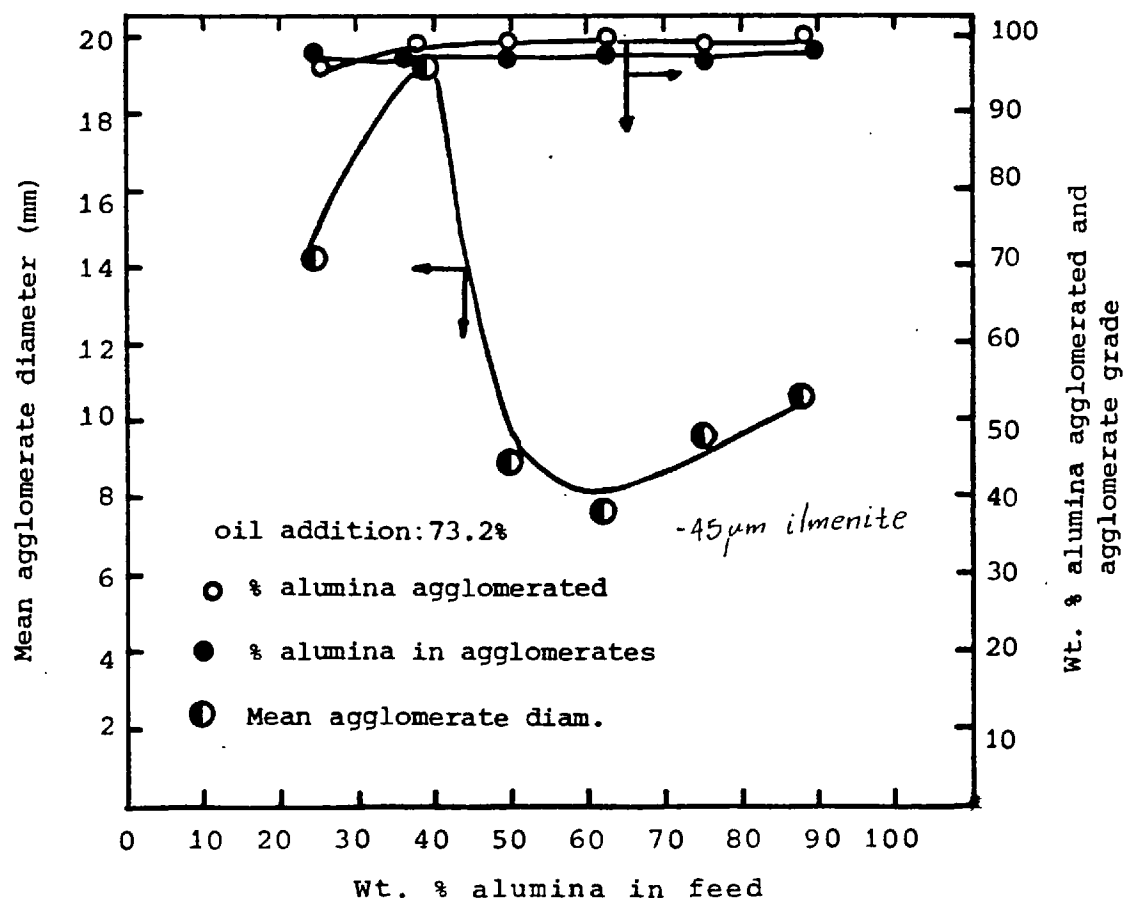


Fig. 4.3: Effect of alumina/ilmenite mixture composition on percent alumina agglomerated and agglomerate size.

alumina particles and also between oil coated alumina particles, and it was found that increasing the speed of rotation to 90 rpm the percent alumina agglomerated was 99% instead of the 18% obtained with the standard 70 rpm. The ilmenite content of the agglomerates stayed at approximately 10% for each of the mixture compositions tested. An improvement in the grade of product was made by replacing the ilmenite size fraction by $-45\mu\text{m}$ material. Fig. 4.3 shows that the grade of the product increased from 90 to between 98 and 99% without a corresponding deterioration in the alumina agglomeration. The relation between agglomerate size and mixture composition was of a similar type in both sets of experiments, but the agglomerates were about twice the size in the experiments using $-45\mu\text{m}$ ilmenite. In both cases agglomerate size showed a peak at 37.5% alumina in the feed and a minimum at 62.5%.

Selective agglomeration tests were carried out with different mixture compositions and a range of particle sizes while maintaining the system variables ^{at} values which had already been used for alumina alone. In almost all cases degrees of alumina agglomeration and the alumina content in the agglomerates were between 90 and 99%. But generally the percent alumina agglomerated was poor when feed compositions containing less than 25% of alumina by weight were employed using a speed of 70 rpm. It was also observed that the agglomerate size curve exhibited a peak at a certain value of the mixture composition which depended on the alumina particle size fraction used. In Table 4.3 the recoveries and grades of product are summarised for various particle size mixtures made up using equal weights of alumina and ilmenite.

Table 4.3. Percent alumina agglomerated and agglomerate grade with different particle sizes of alumina and ilmenite.

Weight of alumina = 20g

Weight of ilmenite = 20g

Particle size range (μm)		Percent alumina agglomerated (%)	Percent alumina in agglomerates (%)
Alumina	Ilmenite		
- 86+27	- 75+45	98.5	91
- 53+45	- 53+45	96.0	89
- 53+30	- 53+30	93.5	97.8
- 53 +	- 45	96.5	97.2

+ Pretreatment stage with the high speed agitator used.

4.4

DISCUSSION

The higher grade of agglomerates obtained when a fixed size fraction of alumina mixed with a fine rather than a coarse ilmenite size fraction was treated may be attributed to two main causes.

- i) The rejection of fine particles trapped between the highly porous aggregates formed initially will be easier because the fine ilmenite will more readily find its way through the compacting and rearranging particles.

and

- ii) A coarse particle has a higher probability of being trapped during agglomerate growth because it is more likely than a fine particle to be centrifuged into the region containing partially formed agglomerates.

The larger agglomerates produced with mixtures containing fine ilmenite rather than relatively coarse material (Figs. 4.2 and 4.3) may be connected with the porosity values of the agglomerates. A fine ilmenite size fraction can be expected to contribute to the reduction of the agglomerate pore space without disturbing its packing characteristics. This is supported by the finding that smaller agglomerates were produced in the $-86+27\ \mu\text{m}$ alumina/ $75+45\ \mu\text{m}$ ilmenite system than those which resulted when only $-86+27\ \mu\text{m}$ alumina was used. However, whether or not the peak in agglomerate size is connected with minimum agglomerate porosity has not been definitely established and in these experiments it was not possible to hold constant all of the variables controlling agglomerate growth. Those which were not constant included the equilibrium surfactant concentration, the interfacial

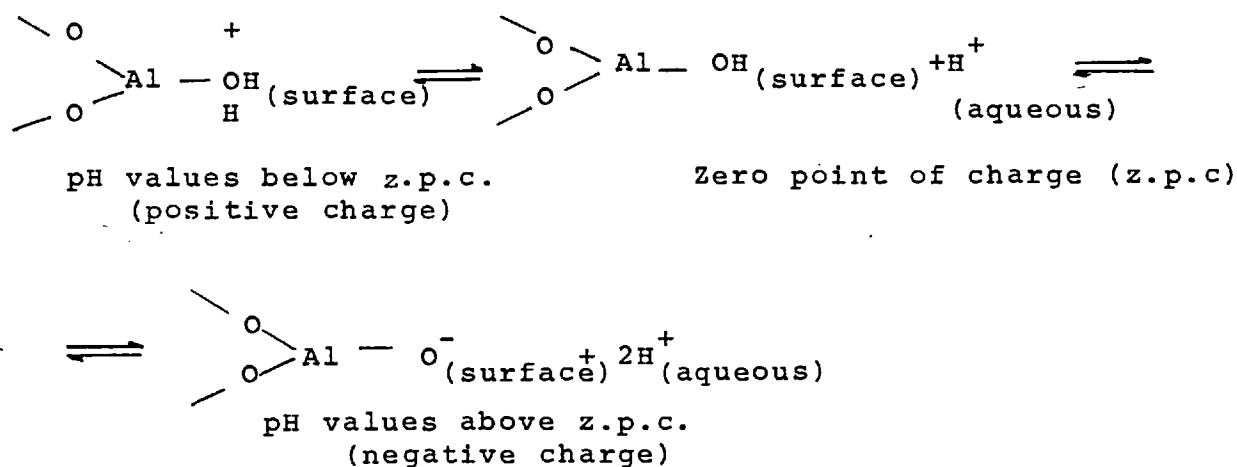
tension between the two liquids and the turbulence in the suspension. To ascertain the effect of the former two factors a study of S.D.S. adsorption on ilmenite and alumina would be required so that an approximately constant equilibrium surfactant concentration could be maintained when changes in the mixture composition were made.

CHAPTER 5
PHYSICO-CHEMICAL ASPECTS

5. PHYSICO-CHEMICAL ASPECTS

5.1 Theory.5.1.1 The alumina/water interface.

When alumina particles are immersed in water the surface acquires a charge because of the dissociation of ionic sites in the surface or the preferential adsorption of ions. Many authors^{124,125} have shown that OH^- and H^+ ions are potential determining for alumina and that the surface charge is dependent on the pH. It is not possible, however, to distinguish between the adsorption of H^+ or OH^- ions or the dissociation of these ions from surface sites¹²⁶. One way of representing the charging mechanism



Alumina hydrates in the presence of water and this step may be visualised as an attempt by the exposed surface atoms to complete their coordination shell of nearest neighbours. Morimoto and Nagao¹²⁷ have found that alumina hydrates on the surface only as far as 7.3 OH groups per $100 \text{ \AA}^2$ when exposed to saturated water vapour. Whether the surface hydroxyl groups ionize as acids or bases will be dependent on the extent to which they are polarized by

the co-ordinating aluminium ions. In comparing the polarization of the hydroxyl groups in $\text{Al}(\text{OH})_3$, and AlO.OH the ratio of electrostatic bond strength is $3/2$ suggesting that the polarization should be ^{more} pronounced in AlO.OH than in $\text{Al}(\text{OH})_3$ ¹²⁵. An alternative charging mechanism proposed by Parks and DeBruyn ¹²⁶ for simple oxide minerals involves the adsorption of charged hydroxo complexes of the form $\text{M}(\text{OH})_4^{z-4}$ (z is the valency of metal). Since the concentration in solution of these complexes is pH controlled electrokinetic measurements do not permit distinction between the two different mechanisms. Parks and De Bruyn ¹²⁶ also suggested that the zero point of charge of the solid coincides with the minimum solubility of the solid and showed this to be true for Fe_2O_3 .

When the adsorption of H^+ ions is equal to the adsorption of OH^- ions the alumina is said to be at the zero point of charge (z.p.c). ¹²⁸. The pH of the zpc is determined by potentiometric titrations. At the zpc the surface charge may not in fact be zero because of the adsorption of other non-potential determining ions. When the surface charge is zero because of the adsorption of ions from all sources the alumina is at the pH of the iso-electric point (i.e.p). This value is found by electrokinetic methods.

If an equation analogous to the Nernst expression is applied to the alumina/water interface the surface potential (ψ_o) can be related to the activity of the potential determining ions by the equation

$$\psi_o = \frac{KT}{Ze} \ln \left(\frac{a}{a_o} \right) \quad (5.1)$$

where K = the Boltzman's constant

- T = the absolute temperature
 z = the valence of potential determining ion
 e = the electronic charge
 a = the activity of the potential determining ion
 a_o = the activity of the potential determining ion at the z.p.c.

In aqueous solution the charge on a solid surface is counter balanced by an equal and opposite charge present in the surrounding solution, giving rise to the well known electrical double layer (fig. 5.1). The electrical double layer in the aqueous phase is divided into two parts, namely the Stern layer and the Gouy or diffuse layer. The plane separating these two layers is termed the Stern plane and it represents the position of closest approach of hydrated counter ions to the solid surface. Electrical neutrality is maintained at all times because the sum of the charges in the Stern layer and diffuse layer is equal and opposite to the surface charge. In the absence of specific adsorption effects the potential decreases rapidly (Fig. 5.1,a) at first and then more slowly as the distance from the surface increases. Adsorption of counter ions in the diffuse layer is given by the Gouy-Chapman relationship for a symmetrical electrolyte which is

$$\sigma_d = \sqrt{\frac{2 RT \epsilon}{\pi}} \cdot C \cdot \sinh \frac{z.F.\psi_d}{2 RT} \quad (5.2)$$

- where σ_d = charge in the diffuse double layer
 ϵ = dielectric constant of medium
 R = gas constant

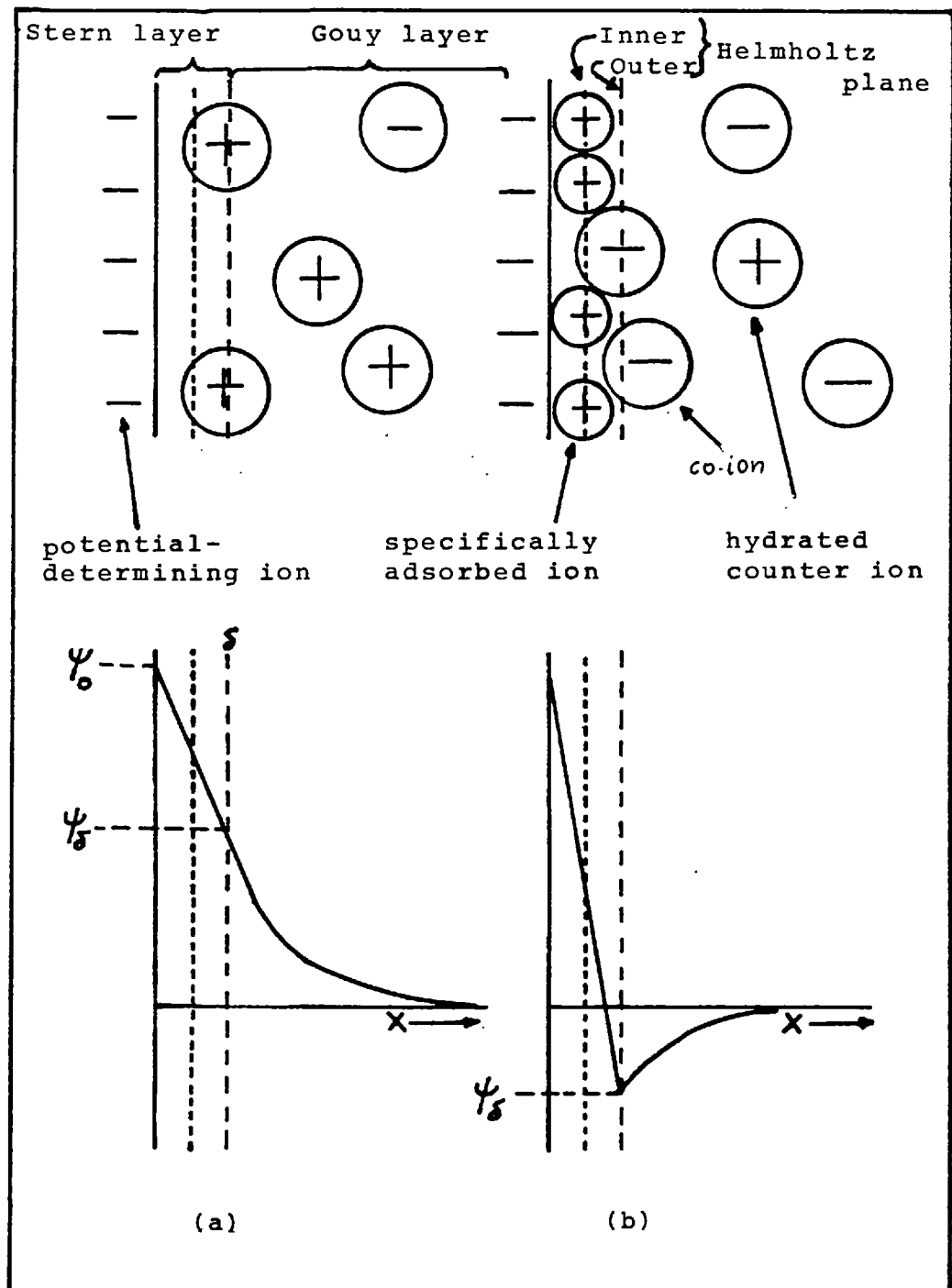


Fig. 5.1: Stern-Graham model of the solid/water interface
 (a) in the absence and (b) in the presence
 of specific adsorption

C = the concentration of ions in the bulk solution

F = Faraday constant

T = absolute temperature

Shown also in the potential diagram is the zeta potential, this is important because it is the only potential that can be experimentally determined by electrokinetic methods. When an electric field is applied to a suspension of particles they migrate to the electrode bearing the opposite sign. In doing so they take part of the double layer enclosed between the solid surface and a plane of shear which is generally considered to be situated just outside the Stern plane. The potential at the shear plane is termed the zeta potential. Generally the zeta potential can be substituted for the Stern potential in the various double layer equations without incurring any large errors. Davies and Rideal¹²⁹ have summarised studies on the numerical relationship between the zeta potential and the surface potential at the oil/water interface and the micelle/water interface. Recently Wnek and Davies¹³⁰ predicted the zeta potential of alumina by postulating a surface reaction mechanism whose equilibrium constants depend on surface potential.

5.1.2 The alumina/water interface in the presence of S.D.S.

Indifferent electrolytes, like NaCl, decrease the zeta potential of alumina to zero at high ionic strength because the double layer becomes compressed. Alkyl sulphate anions can, however, act not only as counter ions i.e. when the surface is positively charged at pH values below the zpc., but also by specific adsorption. When the latter occurs the zeta potential decreases rapidly to zero

and changes sign over a relatively narrow S.D.S. concentration range. The adsorption of alkyl sulphates at the alumina/water interface is consistent with the generally accepted theory of the adsorption of long-chain electrolytes by oxides¹³¹⁻¹³⁴.

At low adsorption densities the surfactant ions are adsorbed by Coulombic attraction for the oppositely charged surface. Ion exchange with counter ions in the diffuse part of the double layer occurs and as a result the zeta potential does not change. As the adsorption increases adsorption in the Stern layer occurs and the mechanism of adsorption becomes one of hydrophobic association between the hydrocarbon chains. The entry of charged species into the Stern layer produces a marked dependence of the zeta potential on the surfactant concentration. Gaudin and Fuerstenau¹³⁵ have compared the formation of hydrophobic associations at the solid/water interface with micellization in bulk solution. The concentration at which associations began was termed the critical hemimicelle concentration.

Based on the Stern-Grahame treatment of the double layer, adsorption of counter ions at the plane δ is given by the equation

$$\Gamma_{\delta} = 2 r C \exp (-\Delta G_{\text{ads}}^{\circ} / RT) \quad (5.3)$$

where Γ_{δ} = the adsorption density (moles/m²)
 r = the effective radius of the adsorbed ion (m)
 C = the bulk density of ions (moles/m³)
 $\Delta G_{\text{ads}}^{\circ}$ = the standard free energy of adsorption

The free energy of adsorption of S.D.S. is composed of

$$\Delta G_{\text{ads}}^{\circ} = \Delta G_{\text{elect}}^{\circ} + \Delta G_{\text{CH}_2}^{\circ} \quad (5.4)$$

$$= ze\psi_s + n\phi_{\text{CH}_2} \quad (5.5)$$

where $\Delta G_{\text{elect.}}$ = the electrostatic contribution to the free energy resulting from Coulombic interaction with the surface charge in the double layer.

ΔG_{CH_2} = the hydrophobic bonding contribution resulting in the association of the hydrocarbon chains of adsorbed collector ions at the interface.

n = the average number of associating CH_2 groups per hydrocarbon chain

ϕ_{CH_2} = the cohesive energy per mole of CH_2 groups removed from water upon association

A value of $-1RT$ has been evaluated for ϕ_{CH_2} from electrokinetic and flotation determinations^{136,137} which is in agreement with values obtained from solubility data^{138,139} and micelle formation in bulk solution.

5.1.3. Objectives.

In the spherical agglomeration of alumina sodium dodecyl sulphate plays a dual role; firstly it adsorbs at the alumina/water interface and controls the hydrophobicity of the solid particles, and secondly it adsorbs at the oil/water interface and determines the interfacial tension which affects the agglomerate strength. In view of the importance of these effects a study was undertaken of the physico-chemical factors that control the spherical agglomeration.

process. Studies on the related properties of interfacial tension, adsorption density, contact angles and zeta potential were made to determine the conditions necessary for the agglomeration of alumina by an oil as bridging liquid in the presence of SDS.

5.2. Experimental.

5.2.1 Materials

The coarse grained alumina ($-86 + 27 \mu\text{m}$) was used for the adsorption tests and the $-10 \mu\text{m}$ alumina for electrokinetic measurements. The physical properties of these fractions are summarised in Table 3.1. The $-10 \mu\text{m}$ powder was fused in a Vernevil flame-fusion furnace at a temperature of 2300°C to form a suitable pellet for contact angle measurements. This specimen was polished using successively finer diamond powders (down to $1 \mu\text{m}$) on a clean "Selvyt" cloth. Microscopic examination of the polished alumina surface under reflected light showed that the surface was quite smooth. Attempts to prepare specimens for contact angle studies by sintering compressed tablets of $-10 \mu\text{m}$ alumina at 1200°C resulted in very porous discs which were unsuitable for the wettability tests.

Doubly distilled water containing very low levels of surfactant impurity (as evidenced by bubble persistence tests) was used throughout. All the experiments were carried out at room temperature ($20-25^{\circ}\text{C}$).

5.2.2. Adsorption studies.

Adsorption measurements were made by determining the residual S.D.S. concentration in the agglomeration tests. Preliminary tests showed that equilibrium was rapidly established and that the residual concentrations assumed a constant value within 10 min. In some tests the bridging liquid was omitted and under these conditions the alumina suspension was agitated for 15 min. The reversibility of the adsorption was studied by varying the solid to water

ratio. At the end of the conditioning period, samples (50ml) of the supernatant solution were taken and centrifuged to separate the solid and oil droplets from the aqueous phase. After checking the final pH of the aqueous phase the S.D.S concentration was determined. The adsorption density was deduced from the difference between the initial and residual S.D.S. concentrations.

The method of S.D.S. determination was similar to that suggested by Gregory¹⁴⁰ for the analysis of anionic surface active agents. The S.D.S. solutions were reacted with a copper triethylenetetramine complex in an alkaline medium of monoethanolamine and the complex was extracted into an isobutanol-cyclohexane mixture. Addition of diethylammonium diethyldithiocarbamate to the extracted complex produced a colour which was determined spectrophotometrically in a Unicam SP500 double beam spectrophotometer at 435 mμ.

Blank determinations were made with each batch of S.D.S. analysis.

5.2.3. Contact angle studies.

The contact angle between the solid water, and bridging liquid phases gives an indication of the wettability of the solid by the two liquids and influences the shape of the bridging liquid meniscus between two particles. The value of the measured contact angle depends, however, on whether the relevant liquid phase is receding or advancing over the solid surface. Contact angle hysteresis can be attributed to two causes. Surface roughness has a significant effect on hysteresis and has been theoretically investigated by Huh and Mason¹⁴¹. Most current methods of measurement of contact angle do not permit accurate measurement of

hysteresis since the liquid phase in the neighbourhood of the three-phase contact line is subjected to uncontrolled vibration during measurement ¹⁴². Although the contact angle may be given by Young's equation, sub-microscopic surface roughness produces an apparent contact angle which is different from both the advancing and receding contact angle. In Wenzel's equation ¹⁴³.

$$\cos \theta' = r \cos \theta \quad 5.6$$

The equilibrium contact angle θ is connected with the observed value through a roughness factor r , which is always greater than 1 except for an ideally smooth surface when it is equal to 1. Although equation (5.6) is widely accepted, it is not considered reliable by many authors ¹⁴⁴. The other cause of hysteresis is that suggested by Cassie ¹⁴⁵ where the solid/water interface is different after the recession of the bridging liquid from the same interface which has not been previously covered by bridging liquid. Gaudin ¹⁴⁶ has shown in the air/water/solid system that if the bubble is laterally displaced there should be a rearrangement of the adsorbed species and this is not a spontaneous process, the receding and advancing angles are, therefore, different. The hysteresis of contact angle in the system organic liquid/water/rutile also has been investigated by the same author and coworkers ^{147,148}.

The relationship between the contact angle and adsorption of surfactant of the solid/water interface is not straightforward. Some authors ^{149,150} have argued that in the air/water/solid system there is a direct relationship between hydrophobicity and adsorption. Other authors ¹⁵¹, however, have shown that no such

relationship exists but that the contact angle reflects the orientation of the adsorbed surfactant species¹⁵². Shergold and Mellgren²⁵ have shown that in the hematite/iso-octane/water system in the presence of S.D.S., the contact angles are controlled by the orientation of the adsorbed species and whether or not the adsorption density falls within the ion exchange or hydrophobic bonding region of the adsorption isotherm.

Contact angles were measured with a captive drop apparatus. The polished alumina was added to various concentrations of S.D.S. in a silica spectrophotometer cell, which was placed on the modified stage of a Beck 6000 microscope, mounted horizontally. Illumination was provided by a lamp fitted with a focussing lens and rigidly fixed to the base of the microscope. The objective was a 25mm lens and the eye piece a Vickers "Dick-Wright slotted ocular" with a magnification of about 10X, which was capable of reading angles to $\pm 0.1^\circ$. Oil drops were formed at the tip of an "Agla" micrometer syringe. The micrometer syringe was fixed to a platform which was capable of movement in both a horizontal and a vertical plane by means of two "Research instruments" micro-manipulators mounted in the respective planes. This device enabled the oil drop to be brought into contact with any desired area on the surface of the polished sample. Contact angles were measured at the oil/water/alumina line of contact by lining up the cross-wires.

The procedure adopted throughout these tests was as follows. Mixtures of 40 ml S.D.S. solution and 10 ml oil were equilibrated by shaking in a conical flask at a known pH. The resulting emulsions were centrifuged and the phases separated. After measuring the final pH of the aqueous phase the alumina specimen was conditioned in 20 ml for approximately 15 min. and then

transferred quickly to the sample cell which contained a small amount of the original equilibrated surfactant solution. This procedure minimised dilution effects. An oil drop of fixed volume, formed on the tip of the "Agla" micrometer syringe dipping in the aqueous phase was brought gently into contact with the alumina surface and after it had advanced to an equilibrium position the volume of the drop was increased by a known amount. The angle between the three phases was measured through the aqueous phase after 5 min. equilibration, and this angle was called the "final advancing angle". The oil drop was then returned to its original volume, and the 'receding angle' was measured after a further 5 minutes. It was found that at large values of the contact angle a "sessile drop" was formed by pulling the micrometer syringe away from the alumina surface. When the contact angle was larger than 100° with iso-octane the formation of the sessile drop occurred spontaneously when the oil drop contacted the alumina surface. Under these conditions the contact angles of the sessile drop were measured after 5 minutes equilibrium. In all cases the contact angles on both the left and right sides of the oil drop were measured and then an average of the two values taken. Under a given set of conditions the contact angles were measured at three different points on the polished surface and the average determined. The polished alumina was cleaned before and after each contact angle measurement by repeated rinsing with distilled water followed by immersion in warm H_2O_2 (28.9% H_2O_2) - 100 volumes. Concentrated aqueous NH_3 was then added to give approximately 1 part NH_3 to 10 parts H_2O_2 . After the foaming had subsided the alumina was rinsed with distilled water and stored under water. This procedure gave hydrophilic surface provided that the alumina was not permitted to contact air. All other cleaning procedures including chromic-sulphuric acid, nitric acid-alcohol and UV radiation treatment^{154,155} failed to give zero contact angles against air.

5.2.4. Electrokinetic Studies.

Electrokinetic measurements were made to determine the iso-electric point of alumina and the magnitude of the zeta potential in the presence of S.D.S. Measurements were made using the microelectrophoresis method and zeta potentials were calculated from the mobility data by the Helmholtz-Smoluchowski equation. According to this equation

$$u = \frac{\epsilon \chi \zeta}{\eta} \quad (5.7)$$

where u = velocity of electrophoresis (ms^{-1})
 ϵ = dielectric constant of suspending medium
 χ = field strength gradient (Vm^{-1})
 η = viscosity of the dispersion medium (Ns m^{-2})
 and ζ = zeta potential (V).

This equation must be corrected in most cases for retardation, relaxation and other effects that are present in electrophoresis. Henry¹⁵⁶ has shown that the above equation must be multiplied by a factor f_H , the retardation factor, which is a function of a/r , where a is the particle radius and r is the double layer thickness. For spherical particles, f_H varies from $2/3$ to 1 . This correction factor is valid only for $\zeta \leq 25\text{mV}$. The relaxation effect arises from the fact that when a particle suspension is subjected to an electric field the outer part of the double layer moves in a direction opposite to that of the particle, thus deforming the original symmetry of the double layer. By electric conduction and diffusion the double layer tends to restore its symmetry but a short time known as the "relaxation time" is necessary before this can happen. Calculation

of the relaxation correction is a difficult mathematical and theoretical problem, and a satisfactory solution has not been reached. Overbeck's calculation¹⁵⁷ indicates that the relaxation effect may be small in the case of 1-1 electrolytes for all values of a/r ; for values of a/r greater than 10^2 both the retardation and relaxation corrections are small. When a/r is in the range 0.1 to 100 and multivalent electrolytes are involved, both correction factors may be large. All these effects have been reported extensively in literature¹⁵⁸⁻¹⁶⁰.

The electrophoretic mobility of $\sim 10 \mu\text{m}$ alumina particles was determined using a Rank Bros. particle microelectrophoresis apparatus (MK.II). Dilute suspensions of the alumina powder were prepared under various conditions and allowed to equilibrate for 15 hours and the final pH was measured. Aliquots of these suspensions were added to the electrophoresis cell and the mobility of the particles at the stationary levels¹⁶¹ under a given voltage determined. In each determination the velocities of at least 10 particles were measured travelling in one direction and then the same number in reverse. The electrophoretic mobility (u) was evaluated from the particle velocity (v) and the conductivity of the suspension (k) by the following expression

$$u = \frac{v \cdot k \cdot A}{I} \quad (5.8)$$

where A = cross-sectional of the cell and
 I = current

Equation (5.8) can be rewritten as

$$u = \frac{vL}{V} \quad (\text{m}^2 \text{s}^{-1} \text{V}^{-1}) \quad (5.9)$$

where V = applied voltage
 L = effective inter-electrode distance = R.K.A.
 and R = resistance across cell.

The effective inter-electrode distance for the cell in these determinations was 8.73 cm.

Values of zeta potentials were obtained from the electrophoretic mobility by the use of equation (5.7) which at 25°C becomes

$$\zeta = 12.83 \cdot u \cdot 10^5 \quad (5.10)$$

where ζ is measured in V.

Approximate values for the position of the zpc were obtained using the methods of Berube and DeBruyn¹⁶², and Parks and DeBruyn¹²⁶. In the first method lg samples of -10 μ m alumina were added to 50 ml volumes of distilled water at pH values near the expected zpc. The direction and change of pH with time was noted. When no further change occurred the pH was considered to be at or close to the zpc. The technique is reasonably rapid but is only accurate if there are no other H^+ or OH^- consuming reactions taking place. The second technique involved titrating sodium hydroxide against a suspension of alumina in a known concentration of HCl. By comparing the curve with that obtained in the absence of alumina the net abstraction of H^+ and OH^- was calculated. This technique suffers from the same disadvantage as the first but a check on whether or not other reactions are taking place can be made by titrating at different ionic strengths.

5.2.5. Surface/Interfacial tension studies.

The interfacial tensions between the various oils and S.D.S. solutions were determined with the objective of calculating the adsorption of S.D.S. at the oil/water interface. The values were also used to estimate the capillary forces present in the agglomerates.

Interfacial tension measurements were made using the drop-volume method of Gaddum¹⁶³ with the correction of Harkins and Brown¹⁶⁴. Drops of the aqueous phase were formed in the organic phase at the end of the glass capillary attached to an "Agla" micrometer syringe. The volume of the drop was slowly increased until it became detached together with its small satellite drop¹⁶⁵. The interfacial tension was calculated from the formula

$$\gamma = \frac{F.V.\Delta\rho.g}{R} \quad (5.11)$$

where V = volume of drop

$\Delta\rho$ = density difference for the two liquids

R = capillary radius

g = gravity constant

F = Harkins and Brown correction factor.

The diameter of the glass capillary was 0.589 ± 0.001 cm as determined by travelling microscope. Measurements were made at a temperature of $25.0 \pm 0.1^\circ\text{C}$.

Prior to determining the interfacial tension of a given oil/S.D.S. solution the two phases were mutually saturated by shaking. After separating the phases using a centrifuge some of the oil was added to a portion of

the aqueous phase contained in a glass vessel so that two layers were formed. The syringe was filled from the remaining aqueous phase and then placed vertically so that the tip of the capillary penetrated into the organic phase. Care was taken to ensure that the glass capillary was hydrophilic and that no small oil drops entered the capillary. The volume of each drop was increased rapidly to about 90% of its detachment value and then the drop was allowed to age for 5 min. Detachment of the drop was then obtained by slowly increasing the volume during a 1 min period. The volume of 5 drops was determined at each different set of conditions and an average volume obtained. The same method was used to measure the surface tensions of the various liquids studied.

5.3.

RESULTS

5.3.1. Adsorption Studies.

The adsorption isotherm of S.D.S. at the alumina/water interface both in the presence and absence of iso-octane is shown in fig. 5.2. The shape of the isotherm in the absence of iso-octane is sigmoidal and this is consistent with the adsorption of monofunctional surfactant species followed by moderate molecular interactions¹⁶⁶. Adsorption densities corresponding to a close-packed vertically oriented monolayer of sulphate ions (about 6×10^{-6} moles m^{-2} assuming each head group occupies $25 \text{ \AA}^2$ ¹⁶⁷) were not obtained because the technique was inaccurate at high surfactant concentrations. The adsorption was reversible over the S.D.S. concentration range studied. Good agglomeration corresponded to adsorption densities greater than 0.1 and 0.30 of the vertically oriented monolayer coverage in the absence and presence of iso-octane respectively.

During agglomeration the abstraction of S.D.S. from solution was higher than that obtained in the absence of iso-octane. This increase cannot be attributed solely to the adsorption of S.D.S. at the oil/water interface in the agglomerates because the amount of water they entrained was small (see Chapter 6.2.2.). The results suggest, therefore, that the adsorption density of S.D.S. at the alumina/oil interface was greater than that at the alumina/water interface. A number of authors^{168,169} have applied the Young's and Gibbs' equations to the solid/liquid/vapour system and reached the conclusion that in flotation systems contact angles can only be established if the adsorption at the solid/gas interface is greater than that

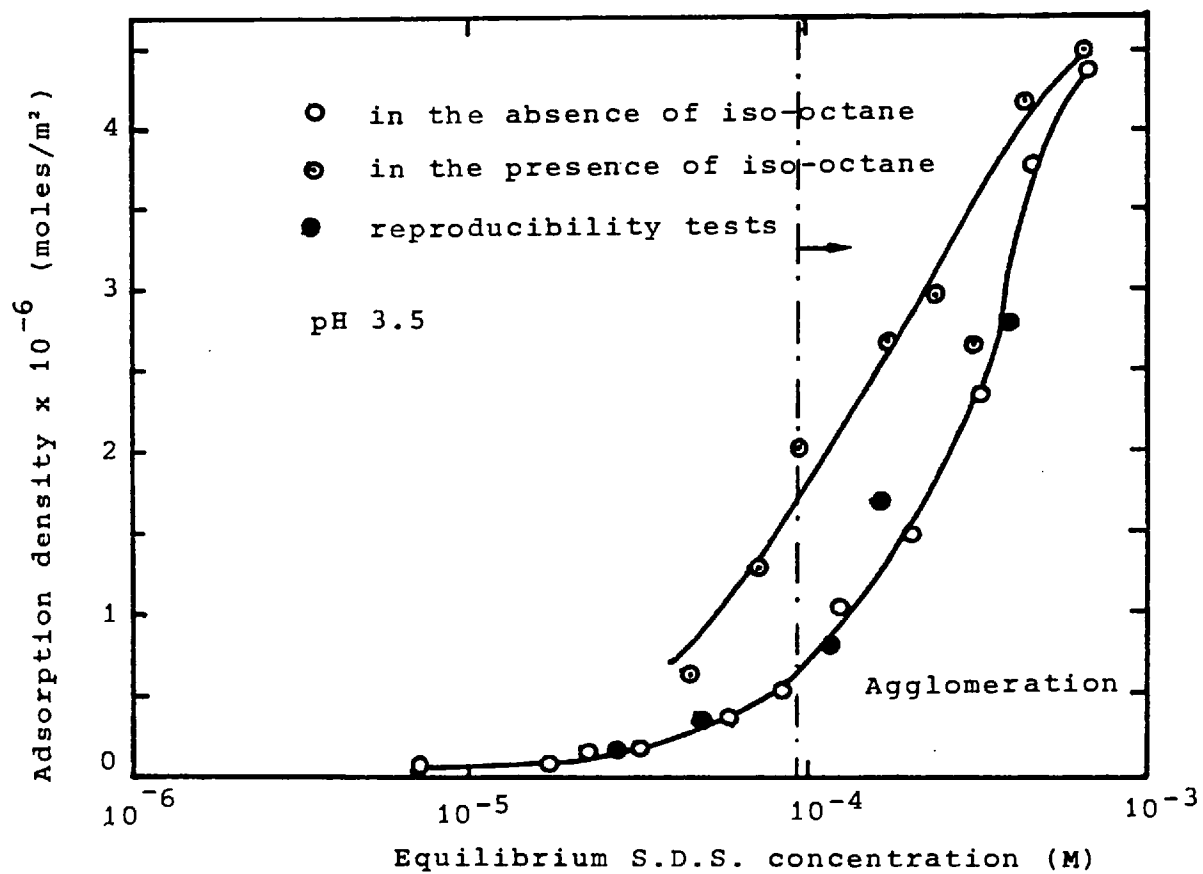


Fig. 5.2: Adsorption isotherm of S.D.S. on alumina in the presence and absence of iso-octane

at the solid/water interface. Despite a number of attempts 170,171 to experimentally prove this, completely unambiguous results have not been obtained. Similar theories have also been proposed for the formation of a contact angle between two liquids and a solid.

5.3.2. Contact angle studies.

In Fig. 5.3 the effect of S.D.S. concentration on the contact angles of iso-octane on alumina at pH 3.5 ± 0.1 is given. The final advancing angles (θ_A) were smaller than the receding angles (θ_R). At surfactant concentrations above 5×10^{-4} M sessile drops were formed and it is these angles (θ_s) that are represented in Fig. 5.3 and are combined with the receding angles at low surfactant concentrations. Comparison of these results with the adsorption and agglomeration data shows that all the alumina was agglomerated if the receding contact angles were close to or greater than 90° and that an increase in adsorption density was accompanied by an increase in contact angle. When oil was removed from a sessile drop the diameter of the drop remained approximately constant and greater contact angles than these given in Fig. 5.3. were measured. The final receding angle exceeded 165° . These observations suggest that the initially formed sessile drops do not represent an equilibrium situation and that the very high contact angles obtained by removing oil from them was caused by the existence of an oil film on the alumina surface. At high surfactant concentrations some definite time period was required before actual contact was established. This time period increased with increasing surfactant concentration and for 7.5×10^{-3} M and 10^{-2} M aqueous S.D.S. concentration induction periods of 2 and 3-4 minutes were required respectively.

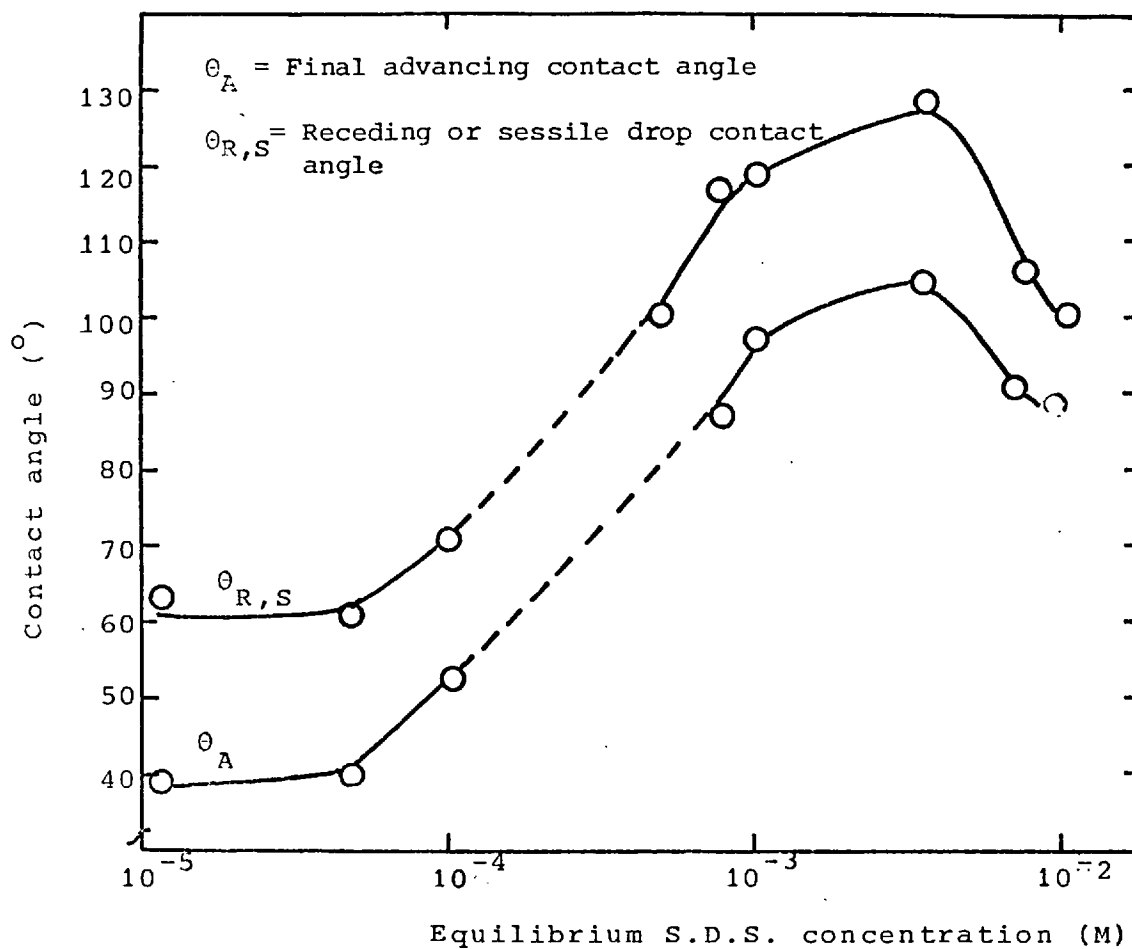


Fig.5.3: Effect of S.D.S. concentration on contact angles at pH 3.5 ± 0.1

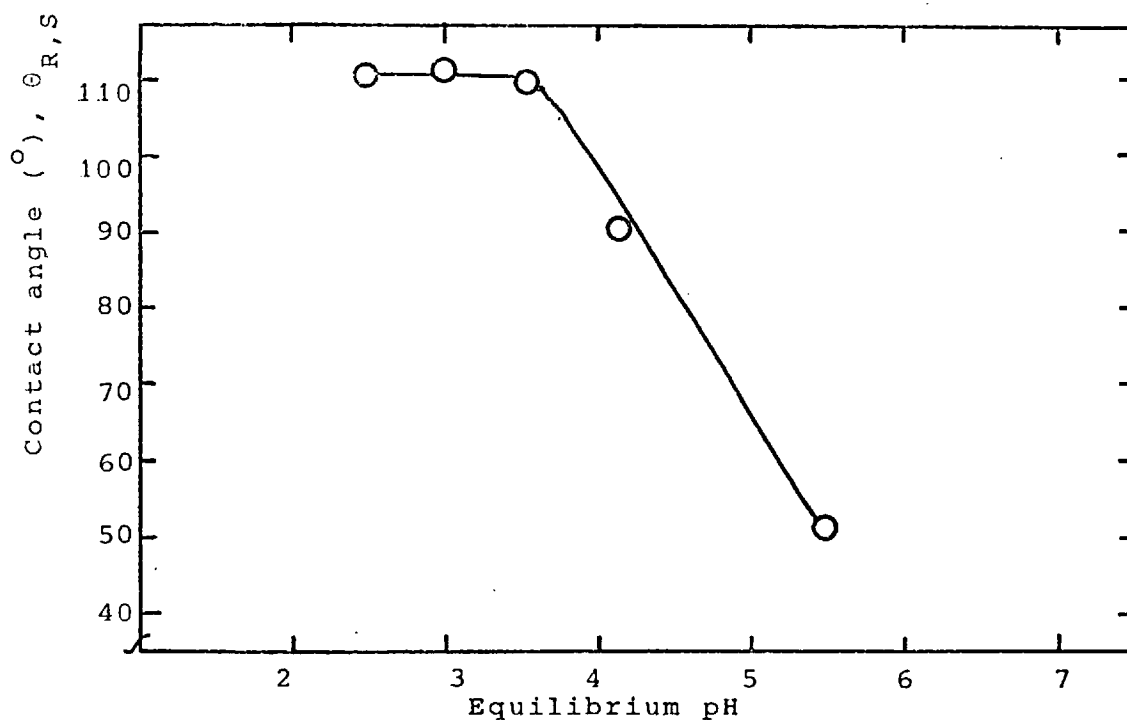


Fig. 5.4: Effect of pH on contact angles of Iso-octane on alumina at S.D.S. concentration 5×10^{-4} M.

At high S.D.S. concentrations the contact angle decreased. Whether this is attributable to the onset of micellization or the formation of an adsorbed bilayer with the polar groups pointing into the aqueous phase is difficult to assess because of the absence of reliable adsorption data. Some authors¹⁷² suggest that for oil/water/solid systems the contact angles remain unchanged at the onset of bilayer formation or micellization because the outer adsorbed layer is solubilised by the oil. In these cases a considerable induction period is often a prerequisite for contact¹⁷³. Other authors^{12,18}, however, disagree and have shown that the contact angle decreases to zero.

The contact angle decreased as the pH increased and this is demonstrated in Fig. 5.4. At pH values below 4.5 and at an S.D.S. concentration of 5×10^{-4} M sessile drops were obtained. The dependency of the contact angle on the pH is consistent with the adsorption of dodecyl sulphate ions by Coulombic attraction. As the pH decreases from to the positive surface charge will increase and so, therefore, will the adsorption.

The contact angles obtained between the various oils used in this study and the alumina and water phases at an S.D.S. concentration of 5×10^{-4} M and pH 3.5 ± 0.1 are shown in Table 5.1. This S.D.S. concentration was selected because it corresponded to the equilibrium concentration in most of the agglomeration tests.

With the exception of the most viscous oils the receding angles were close to or greater than 90° and the sessile drop angles were somewhat larger. The value of the latter is not too significant because it is doubtful that equilibrium was attained. As the volume of the sessile

Table 5.1. Contact angle of the various oils used on alumina.

Type of oil	$\theta_A (+5^\circ)$ ($^\circ$)	$\theta_R (+5^\circ)$ ($^\circ$)	Sessile (+10 $^\circ$) ($^\circ$)
hexadecane	55	66	120
tetradecane	56	67	115
Decane	73	93	117
Octane	60	85	120
heptane	58	85	120
benzene	89	96	126

drop was reduced the angle tended to 180 $^\circ$.

5.3.3. Electrokinetic Studies.

The iso-electric point of alumina occurred at pH 7.8 $\pm$ 0.2 as shown by the zeta potential results presented in Fig. 5.5. This value is low compared to many values quoted in the literature^{174,175}, but is similar to that obtained by Homes¹⁷⁶ for flame fused synthetic sapphire.

The potentiometric titrations showed that the z.p.c. of the alumina was pH 7.1 using KCl at different concentrations. This value was confirmed by the simple method of Berube and DeBruyn¹⁶². Specific adsorption of small amounts of cationic impurity is the most likely reason for the difference between the i.e.p. and the z.p.c. values.

The zeta potential results obtained in the presence of S.D.S (Fig. 5.6) are consistent with the adsorption of long chain alkyl sulphate ions by Coulombic attraction to the positive alumina surface followed by hydrophobic bonding interaction at higher

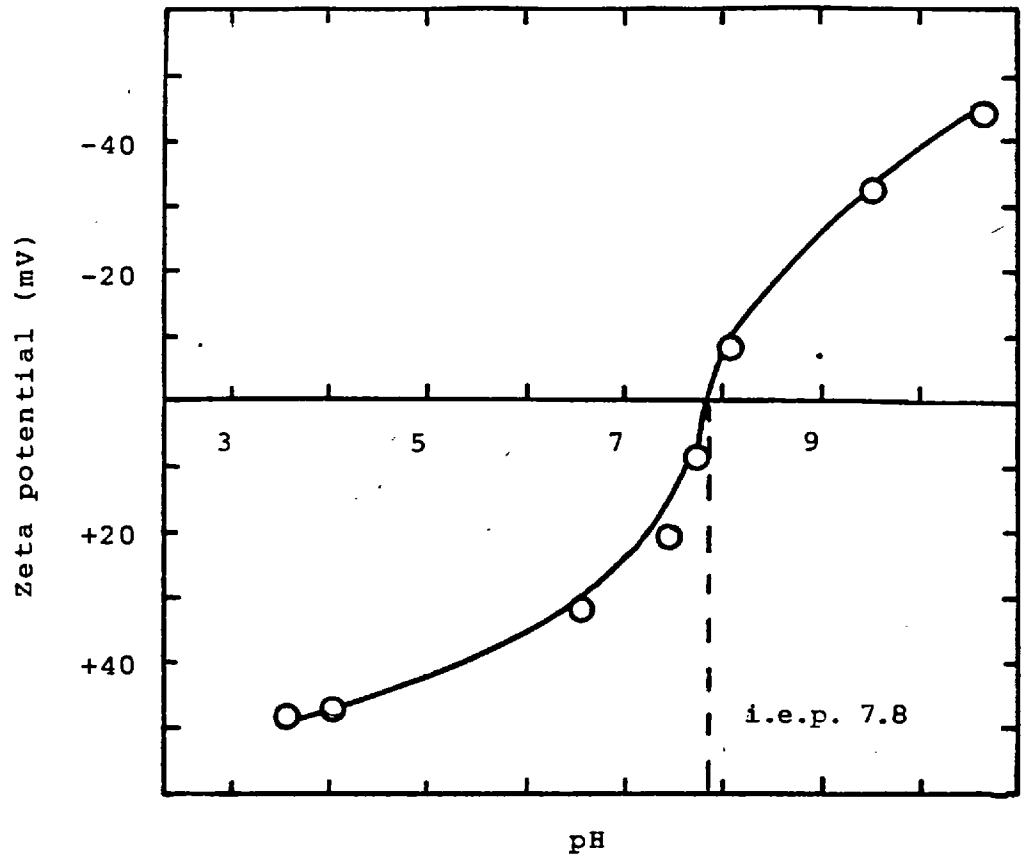


Fig. 5.5: Zeta potential of alumina as a function of pH

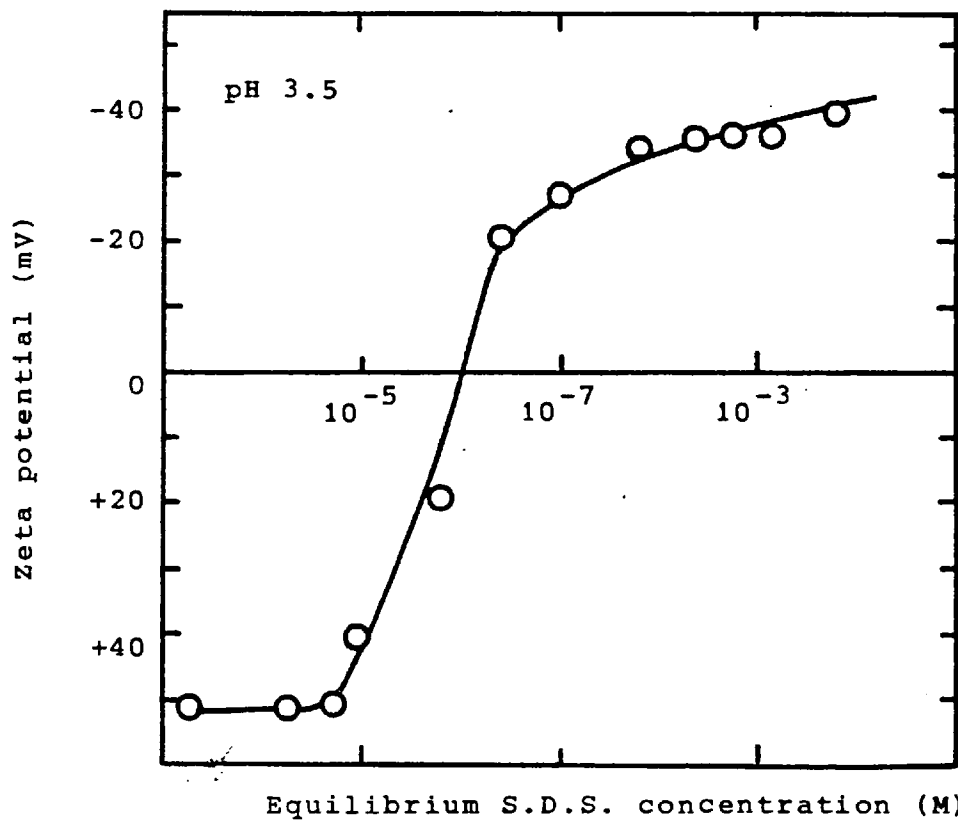


Fig. 5.6: Zeta potential of alumina as a function of S.D.S. concentration at pH 3.5 ± 0.1

adsorption densities. At low S.D.S. concentrations the zeta potential was independent of concentration, but at concentrations above $7.5 \times 10^{-6} \text{ M}$, at pH 3.5, an increase in S.D.S. concentration decreased the positive zeta potential and made it negative. In the S.D.S. concentration range 10^{-5} to 10^{-4} M the zeta potential changed markedly with concentration, but above 10^{-4} M the rate of change was much smaller. The abrupt change in zeta potential at an S.D.S. concentration of $7.5 \times 10^{-6} \text{ M}$ has been attributed to the onset of hydrophobic associations in the Stern layer. Thus the critical hemimicelle concentration (C_{HMC}) for S.D.S. at pH 3.5 was about $7.5 \times 10^{-6} \text{ M}$.

Comparison of the adsorption isotherm (Fig. 5.2) with the zeta potential data (Fig. 5.6) shows that the rapid increase in adsorption occurred after the surface sites had been neutralized, and that in the region where the adsorption showed the largest increase the zeta potential changed less markedly with S.D.S. concentration. Whether or not this is a real effect is difficult to assess because the alumina used in the electrokinetic studies was ground very much finer than that used in the adsorption determinations. It is possible that the former had a more reactive surface than the latter so that the electrokinetic results were displaced to lower S.D.S. equilibrium concentrations. However, Stratton-Crawley (12) recently obtained similar adsorption and zeta potential results in rutile of the same particle size. If both alumina samples have the same surface characteristics then the results indicate that adsorption in the Stern layer and consequently a change in zeta potential is not necessarily accompanied by an overall increase in the adsorption in the double layer. Fuerstenau and other authors^{134,11} suggested that the inflexion point in the adsorption density - equilibrium

surfactant concentration isotherm at

low surfactant concentration, corresponds to the initiation of hemimicellization. The results of the present work and other studies ¹⁷⁷ showed that the onset of hemimicellization occurs at surfactant concentration below the beginning of the abrupt increase in adsorption density.

5.3.4. Surface/Interfacial tension studies.

The interfacial tension between iso-octane and water after one passage ^{of the iso-octane} through an activated alumina column was 48.32 mNm^{-1} . This value is lower than the value of 49.69 mNm^{-1} recorded in literature ¹⁷⁸. Further purification steps including passing the iso-octane twice through the alumina column and storing the water over activated carbon increased the value to 49.35 mNm^{-1} .

A plot of the iso-octane interfacial tension as a function of S.D.S. concentration at $\text{pH } 3.5 \pm 0.1$ is given in Fig. 5.7. The interfacial tension decreased regularly with increasing concentration of surfactant until the C.M.C. was reached where it became constant. Similar results were obtained at other pH values above pH 3.0 but at lower values slightly lower interfacial tensions were obtained. Cockbain ¹⁷⁹ attributed this pH effect to hydrolysis of the alkyl sulphate ion.

The C.M.C. determined from the interfacial tension data was approximately $8 \times 10^{-3} \text{ M}$ and this compares well with literature values ¹⁸⁰ and also that obtained by conductivity measurements of S.D.S. solutions. In the latter case there was a slight difference between the values obtained in the presence and absence of iso-octane - the value in the presence of iso-octane being the lowest.

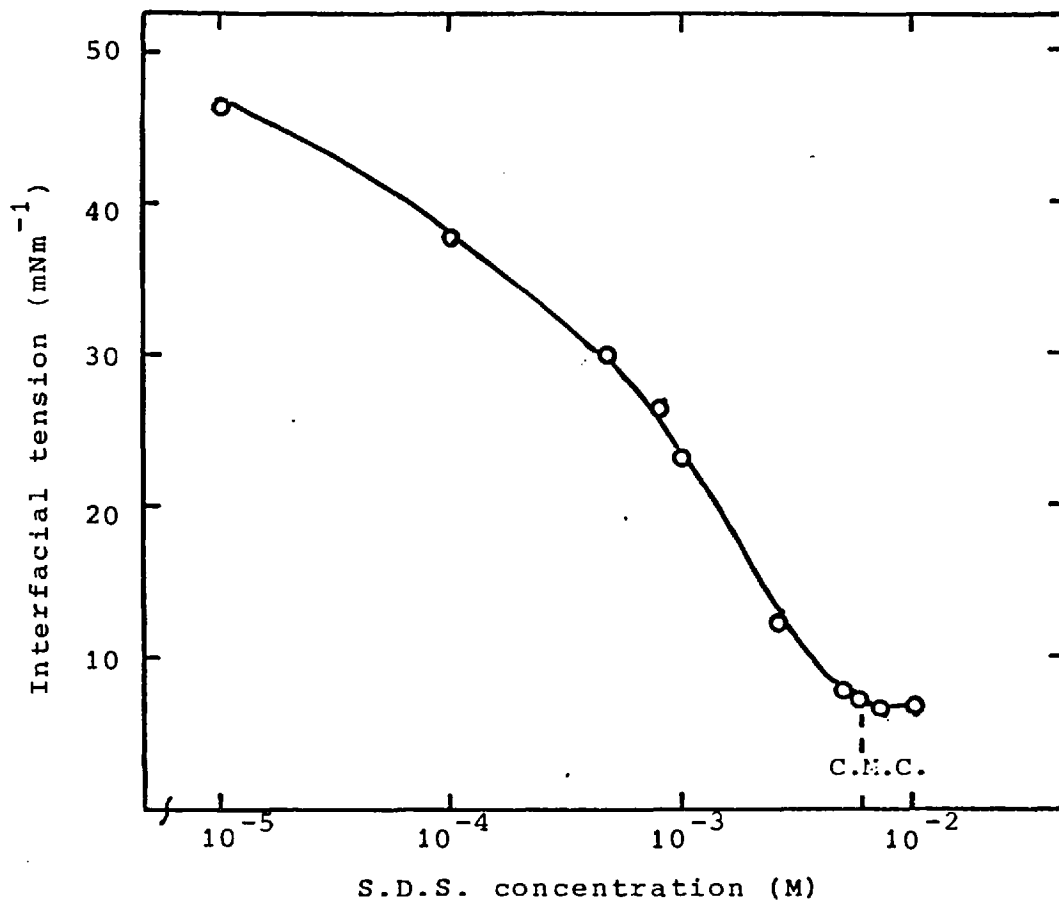


Fig. 5.7: Interfacial tension between iso-octane and water as a function of S.D.S. concentration at pH = 3.5±0.1

Solubilization of the oil in the micelle has been suggested ¹⁸⁰ as a possible reason for this observation.

The interfacial tensions between various oils and water were determined at an S.D.S. concentration of $5 \times 10^{-4} \text{ M}$ and the results obtained are summarised in Table 5.2.

Table 5.2. Surface and interfacial tension of the various oils used.

Type of oil	Surface tension (mNm^{-1})	Interfacial tension against (mNm^{-1})	
		pure water	S.D.S. $5 \times 10^{-4} \text{ M}$
iso-octane	18.87	48.32	30.50
heptane	20.25	49.31	30.95
Octane	20.50	49.80	31.0
tetradecane	25.27	51.21	30.8
hexadecane	26.50	52.70	32.15
Benzene	27.50	33.90	17.3

The adsorption of dodecyl sulphate ions at the oil/water interface can be determined from the Gibbs adsorption isotherm in the form

$$-d\gamma = 2RT \Gamma d \ln C \quad (5.12)$$

where Γ is the surface excess of the long chain electrolyte in moles per m^2 and C is the molar concentration (moles/m^3) This form of the equation is considered to be valid provided that the solution does not contain any excess inorganic electrolyte ^{179,181}. In the presence of excess univalent-univalent electrolyte the equation becomes ¹⁸²

$$-d\gamma = \Gamma RT d \ln C \quad (5.13)$$

The interfacial tensions in this investigation were determined in the absence of excess inorganic electrolyte and equation 5.12 was therefore used to ^{give the} results shown in Table 5.3. Also presented is the adsorption density at the alumina/water interface at the same equilibrium concentration.

Table 5.3. Adsorption density of S.D.S. on iso-octane/water interface and on alumina/water interface. PH = 3.5 ± 0.1

S.D.S. concentration (M).	Adsorption density x 10 ⁶ moles/m ²	
	O/W	S/W
5 x 10 ⁻⁵	0.74	0.24
1 x 10 ⁻⁴	1.00	0.44
2.5 x 10 ⁻⁴	1.05	1.75
7.5 x 10 ⁻⁴	2.04	3.79
1 x 10 ⁻³	2.26	4.42

If it is assumed that at the high S.D.S. concentrations the oil/water interface was saturated with dodecyl sulphate ions then the area per adsorbed ion would be about 74 Å². This value is somewhat higher than the 50 - 60 Å² 183,11 usually associated with a close packed monolayer, but this can be attributed to the fact that the concentration was much lower than the C.M.C. and that the interface was not truly saturated.

It is not possible to determine the total adsorption of S.D.S. at the various interfaces because the area of the oil/water interface is unknown. However, some authors 169,170 using Gibbsian thermodynamics have related the adsorption at the various interfaces with the interfacial tension

and contact angles. The equation obtained is

$$\Gamma_{SO} = \Gamma_{SW} + \Gamma_{OW} \cos \theta + \frac{\gamma_{OW} \sin \theta}{RT} \cdot \frac{d\theta}{d \ln C} \quad (5.14)$$

where Γ is the adsorption density of the surface active agent at the corresponding interface.

C is the molar concentration of the surfactant in the solution

R is the gas constant

The other variables have their usual significance.

Application of equation 5.14 to the results given in Figs. 5.2, 5.3 and 5.7 and in table 5.3 gives S.D.S. adsorption densities at the alumina/oil interface corresponding to about three monolayers thick. This is not in agreement with the measured adsorption density.

5.4 DISCUSSION - COMPARISON WITH AGGLOMERATION RESULTS

The studies on the physicochemical factors involved in the spherical agglomeration process confirm that S.D.S. can be used to modify the contact angle between alumina, water and a non-polar oil so that agglomeration occurs. The S.D.S. is adsorbed at the alumina/water interface under conditions where it can act as a counter ion in the electrical double layer surrounding the alumina particles. This corresponds to pH values below the zero point of charge. The electrokinetic, adsorption and contact angle results were consistent with those obtained by other authors and suggest that the dodecyl sulphate ions were first adsorbed by an ion exchange and then by hydrophobic associations. Spherical agglomeration was obtained under those conditions where the S.D.S. was strongly adsorbed at the alumina/water interface.

The hydrophobicity of the alumina increased with an increase in S.D.S. concentration and S.D.S. adsorption density. This is consistent with the agglomeration results where both increases in the amount agglomerated and the agglomerate size were obtained (Fig. 3.8). An increase in contact angle should increase the capillary forces and the work of adhesion between the particles and the oil. These in turn should produce stronger agglomerates.

When the contact angle between the solid, water and bridging liquid is zero the bridging liquid will only exist between two particles as a separate drop and no adhesion between the drop and the surface will be obtained. As the contact angle increases the capillary pressure will be such that water will tend to rise up the pores between the two solid particles and displace the oil. This tendency

will decrease as the contact angle increases and become zero at an angle of 90° . Above 90° the oil will displace water from the pores and eventually the gap between the particles will be filled with oil. Under these conditions good agglomerates should be obtained because the pores will be filled and oil will spread over the particles so that collisions will result in more bridges. The contact angle results confirm that good agglomeration was only obtained if the receding or sessile drop contact angle was near or greater than 90° .

At oil additions where growth occurred with a significant rate, larger agglomerates were obtained as the S.D.S. increased up to a certain level. This may be attributed to the fact that at the agglomerate surface the bridging liquid was withdrawn to a greater depth in the interstices between the particles as the contact angle increased, and therefore, more oil was available to fill the internal pore space. In addition, the slow displacement of the aqueous phase by the oil occurring at small contact angles may also ^{be the} reason for the reduced agglomerate size obtained at low S.D.S. concentrations. When the S.D.S. concentration became higher than 10^{-3} M the agglomerate size decreased because in this region the alumina hydrophobicity decreased and oil loss due to emulsification occurred. Further more, the interfacial tension of the oil/S.D.S. solution was considerable low at S.D.S. concentrations approaching the C.M.C. The effect of pH on agglomeration can be explained in similar way.

The agglomeration tests showed that good agglomerates can form even under conditions where the interfacial tension between water and bridging liquid is low. Low interfacial tensions should produce weak agglomerates. In pelletization of completely hydrophilic and closely sized sand it was found¹¹⁸ that the ratio of surface tension of the bridging liquid to mean particle diameter must be greater than

4600 dynes/cm² to allow the mixture to be granulated. In the present work values of this ratio as low as 1250 dynes/cm² gave good agglomeration.

The agglomeration tests showed that agglomerate growth occurred if the bridging liquid volume was above a certain critical value. At low bridging liquid volumes even though the alumina was wetted by the bridging liquid good agglomerates would not be formed because there would be insufficient oil to fill the pores between the particles.

CHAPTER 6
AGGLOMERATE PROPERTIES

6. AGGLOMERATE PROPERTIES

6.1 General and Experimental detail

6.1.1 Packing characteristics of agglomerates

It was shown in Chapter 3 that to make agglomerates with a satisfactory shape and strength, the pore space should be almost completely filled with bridging liquid. It is, therefore, important to determine the packing characteristics of powders with differing sizes and size distributions under the conditions in which agglomerates are formed, since they will exert an important influence on oil requirements for successful agglomeration. Further, the manner in which the particles pack together will affect the ease with which the suspending liquid can be displaced by the bridging liquid, and will therefore affect the kinetics of the agglomeration process.

Agglomerate porosity is defined as the ratio between the pore volume of an agglomerate and its total volume expressed as a percentage, and it can be calculated according to the formula

$$P = \frac{V - m/\rho}{V} \times 100 \quad (6.1)$$

where P is the porosity, V is the agglomerate volume, m is the dry weight of the agglomerate and ρ is the true density of the particles.

Pore volumes were measured by carefully transferring the agglomerates produced without loss of liquid to a cylinder containing a known volume of the liquid in which the agglomerates were formed. A graduated glass tube was connected to the top of the cylinder, so that volumes could be measured to an accuracy of ± 0.5 ml. The exact volume corresponding

to the scale of the cylinder /glass tube system was found by calibration. After the agglomerates had been placed in the measuring cylinder, the liquid level was raised by adding more of the same suspending liquid from a burette until it rose into the graduated tube. The volume of the agglomerates was then calculated from knowledge of the total amount of liquid used. The agglomerates were next dried so that they were free from oil and water, and then weighed and their porosity calculated using equation (6.1).

Porosity values for ten determinations using agglomerates produced under the same conditions gave a standard deviation of 3 - 4 % at the 0.95 level of confidence. The effects of oil volume, agglomeration time, oil viscosity and particle size and size distribution on the compactness of the agglomerates were investigated.

6.12 Bridging and suspending liquid associated with agglomerates

Following the addition of an immiscible liquid to an aqueous suspension of particles agglomerates are gradually formed and water, which wets the alumina less than the bridging liquid, is slowly displaced from the growing agglomerates. Capillary, gravity and impressed external pressure forces help the bridging liquid to replace most of the water during the compaction process. Water in some of the pores is occasionally bypassed, and due to a mechanism similar to that illustrated in Fig. 6.1, there will always be a residual water content in the agglomerates. The quantity of water remaining in an agglomerate is determined by the wettability characteristics of the solid particles, the sizes and distributions of the pores within agglomerates, the viscosities of the two liquids and the interfacial tension between the oil and water^{184, 185}.

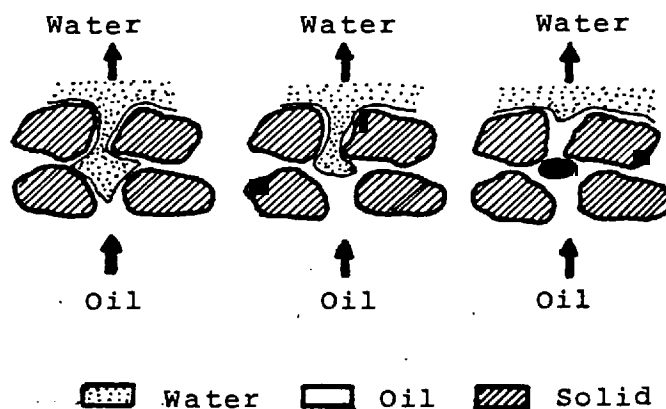


Fig. 6.1: Water displacement by oil in an imbibition process. The particles are oil wetted.

A series of experiments was designed to determine the amounts of oil and water associated with agglomerates as a function of particle size, size distribution and type of oil. A Dean and Starke moisture determination apparatus was employed with toluene as the liquid medium. The apparatus consisted of a spherical flask (250 ml), a condenser and a graduated receiver. The agglomerates, after they had been weighed, were placed in the flask containing 100 to 150 ml toluene and the whole mixture was strongly heated until no more water was collected in the graduated tube. The aqueous phase which separated into the lower part of the graduated receiver, was allowed to stand for at least an hour before its volume was read and during this time any dispersed oil droplets separated out. Knowing the wet and dry weights of the agglomerates, and also the water content, the amount of oil associated with the agglomerates was calculated by subtraction. From these results and the agglomerate porosity it was possible to determine the percentage of the agglomerate pore space occupied by oil, water and also by air.

3.13 Strength of agglomerates

Many tests have been devised to assess agglomerate strength. They fall into three categories namely, tensile tests, compressive tests, and friability tests¹⁸⁶. The strength of agglomerates cannot however, normally be defined sufficiently by one single characteristic parameter. The relationship between strength parameters depends to a large extent on the bonding mechanism (pendular, funicular, capillary) within the agglomerates, and therefore any such relationship cannot be applied to agglomerates in which the various bonding mechanisms are present at the same time.

Tensile strength is defined as the unidirectional maximum tensile force per unit cross-sectional area in a plane within the agglomerate at right angles to the direction of the applied tensile force when locally constant and purely tensile stress prevails in the fracture cross-section of the material, regarded as a continuum¹⁸⁷. This complex definition foreshadows the difficulties of measuring tensile strength. All the methods reported^{82, 87} are very difficult to apply to the relatively weak agglomerates produced in the oil spherical agglomeration process, because specially shaped specimens cut from the bulk material of the agglomerate are required. The importance of friability and fall tests is to assess the ability of the agglomerates to withstand handling. In practice the most commonly used test is the compression test which involves measuring the force required to crush an agglomerate. This test was selected for the present work, because in practice agglomerates usually have to withstand compressive forces during processing rather than tensile ones. Unfortunately little fundamental information can be gained from a compressive test as the mode of fracture of the agglomerate is complex and the measured strength cannot be correlated with the theoretical values calculated from the forces involved at individual bridges.

Experimental difficulties are experienced in measuring the crushing strength of small agglomerates less than 2 mm in diameter, and most commercially available instruments cannot measure very low compression strength with sufficient accuracy. Furthermore, it has been established that the rate at which the load is applied affects measured strength values, and it was, therefore, necessary to apply the load at a controlled and reproducible rate. Several instruments have been reported^{188, 189, 200}, but none of them appeared to be suitable for the present work.

An existing testing machine was modified to make it suitable for determining the strength of spherical agglomerates in either air or under liquids. The machine, which is shown in Fig. 6.2, was fitted with a motor and drive unit F to raise or lower the ram E at a constant velocity of 5.48 mm/s. A coarse adjustment handle H was provided for positioning the ram before starting the motor. A balance, reading to 0.1 g, measured the failure load and was placed on top of the moving ram so that the balance pan could be used as the lower crushing face. To allow tests to be carried out under liquids, the upper fixed crushing face A was extended by fitting to it a brass disc B 25 mm in diameter mounted on a slender stem 50 mm long and with a diameter of 1.5 mm. The cross-sectional area of this stem was sufficiently small to cause only a negligible displacement of liquid as it moved downward during a crushing test.

Each agglomerate to be tested was placed in turn in a flat dish on the balance pan. If required, sufficient of the liquid in which the agglomerate had been formed was poured into the dish to completely cover both the agglomerate and the brass disc. The zero reading was taken and the drive motor started. During a test the balance reading was observed continuously until it paused, remained stationary for a short time, and then began to fall rapidly. The maximum reading

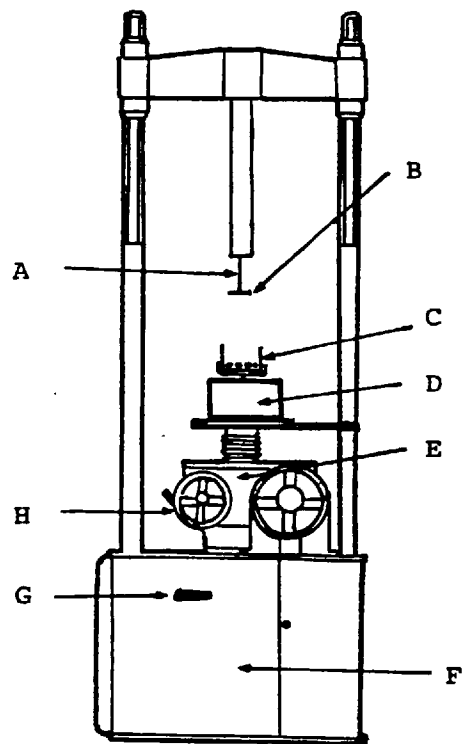


Fig.6.2: Compressive strength testing machine
where A = thin stem, B = circular disc,
C = flat bottomed bowl, D = electrical
balance, E = ram, F = drive unit,
G = motor switch, H = coarse adjustment
handle

obtained was taken, and after subtraction of the zero, assumed to give the breaking load of the agglomerate. In the case of relatively strong agglomerates formed from very fine material, and also for agglomerates previously dried and then tested in air, a more brittle type of fracture occurred with the balance reading falling back quickly to zero after reaching its maximum value. For these agglomerates the reading could only be estimated to ± 2 g.

The strengths of agglomerates ranging in weight usually from about 0.2 to 3.5 g were measured in air and under the aqueous liquid in which they had been formed. In the latter measurements the effect of the interfacial tension acting on the stalk supporting the top crushing plate was considered negligible. Each agglomerate was dried and weighed after the determination of its strength and a plot of failure load against agglomerate weight obtained. Agglomerate size was not used because it was very difficult to measure the agglomerate diameter without taking the agglomerate out of the solution and also in some cases the agglomerates were not spherical.

6.2 RESULTS

6.2.1 Agglomerate porosity measurements

The variation of the porosity of agglomerates made from -86+27 μm alumina as a function of agglomeration time, oil volume, and type of oil was measured. The results obtained with iso-octane are given in Table 6.1.

Table 6.1: Agglomerate porosity as a function of agglomeration time of -86+27 μm alumina iso-octane system

Oil addition ml/cm ³ alumina (%)	Porosity values (%)				
	Agglomeration time (min)				
	10	20	30	50	120
75.1	-	-	44.5	-	-
73.2	47.50	46.0	44.0	43	43
71.2	47.50	47.0	45.5	43	43
68.3	-	-	46.0	-	-
63.4	-	-	46.0	-	-
58.5	-	-	46.0	-	-
48.8	-	-	46.5	-	-

Caution must be exercised in the interpretation of these results in view of the accuracy of the experimental measurements, but slightly lower porosities appear to have been achieved at the higher oil contents. This is probably because with more oil the agglomerates became more malleable and less brittle, and therefore, adjusted so that the particles packed a little closer together.

Table 6.1 shows that the porosity reached a minimum value 50 minutes from the start of the agglomeration process. A number of tests were therefore conducted to determine whether the speed of rotation would affect the minimum value and the time taken to achieve it. Increasing the speed from 60 to 110

r.p.m. did not affect the agglomerate porosity after 30 minutes, by which time the value was $43.5\% \pm 1$. However, after an agglomeration time of only 10 minutes, the product made at 70 r.p.m. showed a porosity about 2% higher than that obtained at 110 r.p.m.

Porosity measurements carried out on the agglomerates produced using bridging liquids having a higher viscosity than iso-octane i.e. tetradecane and hexadecane, gave values of approximately 46.0% after 30 minutes. Thus the differences in oil requirements found between iso-octane and higher viscosity oils cannot be explained in terms of changes in the compaction characteristics of the agglomerates. The reduction in agglomerate porosity as a function of time obtained with tetradecane as bridging liquid is shown in the table below.

Table 6.2: Variation of agglomerate porosity with agglomeration time

Bridging liquid: tetradecane (2.06 mPa s), oil addition: 63.4%, size fraction -86+27 μm alumina

Agglomeration time (min)	Agglomerate porosity (%)
10	47.5
20	47.0
30	46.5
50	45.5
120	43.0

The porosity values of agglomerates formed from the various size fractions of alumina were determined for the iso-octane additions that produced the largest spherical agglomerates during a period of 30 minutes. The results summarised in Table 6.3 indicate that the degree of compaction of the particles in an agglomerate was approximately the same as that produced by high-frequency vibration in a dry system for the

relatively coarse material (-86+27, -63+53, -53+45, -45+27 μm), but considerably lower in the case of finer material (-53+20, -20+10, -53, -10 μm). It is evident that agglomerates made with the fine material compacted more tightly than those made with the coarser fractions. It can be concluded therefore that the fine alumina particles underwent reduction in their dry porosity because of rearrangement of the particles under the influence of the liquid medium. As expected, size fractions with broader distributions resulted in more closely packed agglomerates.

Table 6.3: Values of porosity for various grades of alumina with iso-octane as bridging liquid

Agglomeration time: 30 minutes

Particle size range (μm)	Oil addition ml/cm ³ alumina (%)	Porosity values (%)	
		feed material vibrated	agglomerate
-86+27	73.2	44.0	44.0
-63+53	76.1	45.0	44.0
-53+45	78.0	45.3	46.0
-45+27	77.5	47.1	45.0
-53+20	48.8	37.0	34.9
-20+10	50.0	43.5	37.5
-53	46.4	41.0	35.9
-10	50	54.5	41.0

6.2.2 Analysis of pore space of agglomerates

The amount of bridging liquid associated with the agglomerates was determined for a range of oil additions under conditions in which complete agglomeration was achieved. The results obtained with iso-octane, tetradecane and hexadecane are given in Table 6.4. The average of four experiments carried out under similar conditions was taken in these determinations.

Table 6.4: Oil and water associated with agglomerates at
varying oil additions for -86+27 μ m alumina/
iso-octane system

Agglomeration time: 30 minutes

Oil addition ml/cm ³ alumina (%)	Oil content ml/cm ³ alumina (%)	Water content ml/cm ³ alumina (%)
<u>Iso-octane</u>		
75.1	68.9	9.6
73.2	66.8	8.8
71.2	64.9	10.7
68.3	62.0	17.0
65.8	57.0	19.5
58.5	52.0	24.7
48.8	41.0	-
<u>Tetradecane</u>		
73.2	72.2	7.1
68.3	68.2	9.9
65.8	65.0	11.7
63.4	63.4	13.2
58.5	57.8	20.3
48.8	48.0	-
<u>Hexadecane</u>		
73.2	71.6	9.5
68.3	66.8	10.2
65.8	65.0	10.4
63.4	63.4	12.7
58.5	58.0	15.0
48.8	48.0	-

These results indicate that about 10% of the iso-octane (b.p. 99.23°C) originally added to the alumina suspension was lost by evaporation and adhesion to the agglomerator walls. The oils with relatively low volatilities however, (tetradecane

and hexadecane with b.p. 253.7 and 287°C respectively) showed only very small losses during the agglomeration process. Small losses were also obtained with decane and octane. Oil loss due to dissolution is not expected with the above oils (Table 3.3).

The amount of water associated with the agglomerates is also presented in Fig. 6.3 as a function of oil addition. The water contents measured in this series of experiments included both water trapped within agglomerates and also that retained on their surfaces when they were removed from the suspending liquid. It was not possible to determine the proportion of the total water content which remained on the surface, but this must have been small when high oil additions were used, since under these conditions only a few agglomerates or a paste were produced with a relatively low surface area. For lower oil additions it was therefore only possible to calculate the fraction of the pore spaces filled with oil and not that filled with a mixture of oil and water.

The displacement of water from the agglomerates increased with an increase in the amount of bridging liquid but with iso-octane there was a minimum water content and that occurred at a bridging liquid volume approximately 2% less than the "paste volume" (Fig. 3.10). Both with tetradecane and hexadecane, however, it was observed that at high bridging liquid additions where a paste formed (Fig. 3.11) the water content decreased further. The water content of the agglomerates formed with the high viscosity oils was lower than that obtained with iso-octane.

The filling of the pore spaces of agglomerates made with different alumina size fractions and employing iso-octane as bridging liquid, was investigated under the conditions described in Chapter 3. In Table 6.5 the approximate amount of oil associated with the largest agglomerates is presented.

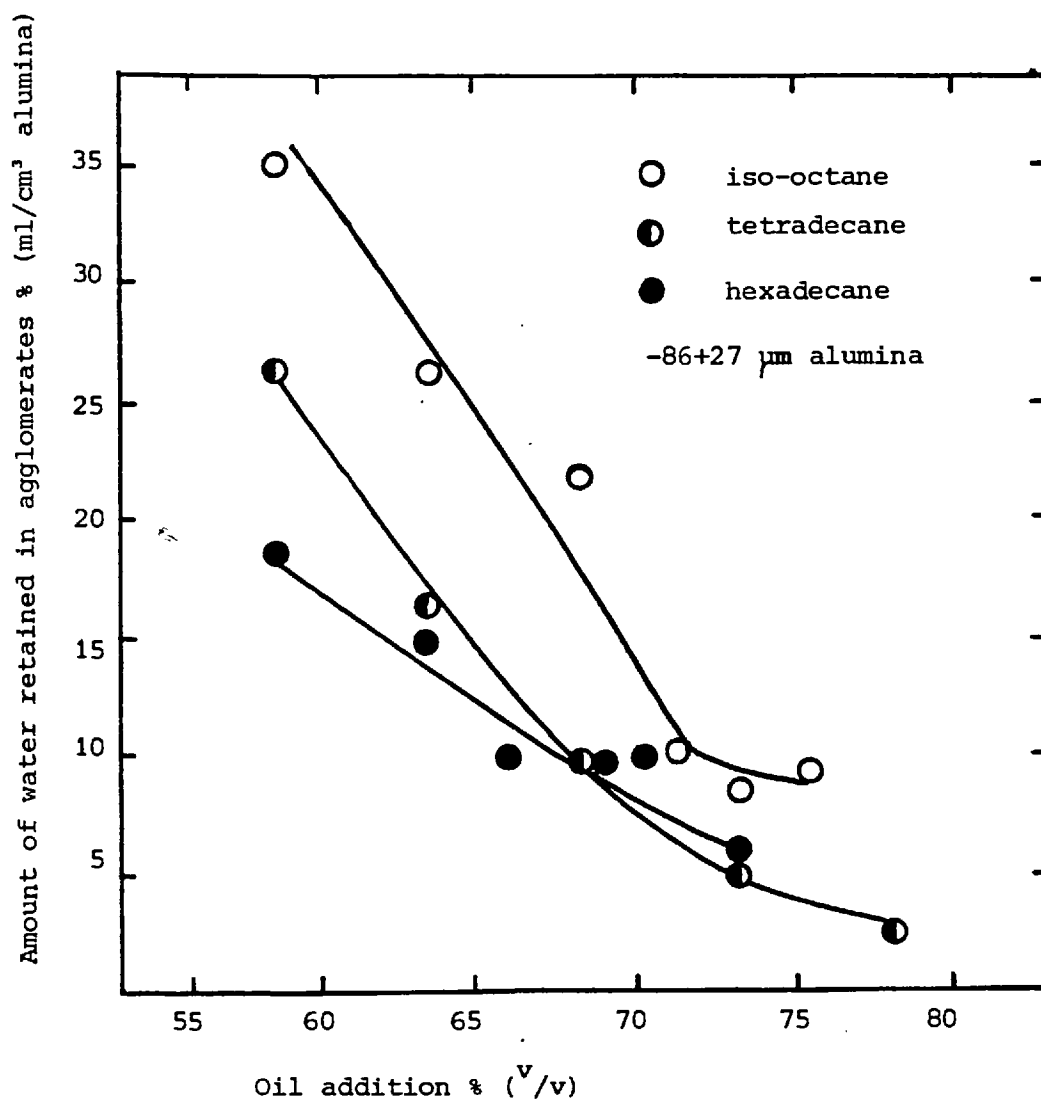


Fig. 6.3. Amount of oil retained in agglomerates as a function of oil volume.

Table 6.5: Water and iso-octane contents of agglomerates made using different particle size fractions and iso-octane as bridging liquid

Agglomeration time: 30 minutes

Particle size range (μm)	Oil addition ml/cm ³ alumina (%)	Oil content ml/cm ³ alumina (%)	Water content ml/cm ³ alumina (%)
-86+27	75.1	68.97	9.6
-63+53	76.1	69.26	11.1
-53+45	78.1	71.7	9.7
-45+27	80.0	73.1	8.7
-53+20	50.7	44.8	11.1
-20+10	56.1	47.8	13.1
+ -53	46.3	28.3	19.5
+ -10	51.0	41.4	27.0

+ Preconditioning by intense agitation was used for these size fractions.

The data show that the amount of water trapped in agglomerates formed from the fine grained alumina was greater than that associated with coarse fractions. With -53 and -10 μm alumina the oil content of the agglomerates was significantly less than that added initially. Oil losses during the preconditioning stage were the main reason for this difference.

6.2.3 The relationship between the bridging liquid content and the agglomerate packing characteristics

Measurements of the porosity of agglomerates and of the contents of the pore spaces enable the bridging liquid requirements to be specified for the formation and growth of agglomerates. The fractional filling of the pores in agglomerates made from -86+27 μm alumina, using iso-octane as bridging liquid were calculated from the data in Table 6.1 and 6.4, and the values obtained are given in Table 6.6.

Table 6.6: The agglomerate pore contents for various iso-octane additions using -86+27 μm alumina

Oil addition ml/cm ³ alumina (%)	Fractional filling of the pore volume		
	by oil based on oil addition (%)	by oil	by oil + water
		based on measured volume (%)	(%)
75.1	93.5	85.5	97.5
73.2	91.5	83.5	94.5
71.2	86.0	78.0	-
68.3	82.0	74.5	-
65.8	76.5	69.5	-
58.5	71.0	62.5	-
48.8	53.0	48.5	-

The third column in Table 6.6 shows that between 48 and 85% of the agglomerate porosity was filled with bridging liquid for oil addition which resulted in the successful formation of agglomerates using -86+27 μm material. The remaining space must have been occupied by entrapped water and air. The fractional agglomerate pore space occupied by oil plus water is given only for two oil additions where only a few agglomerates resulted and the water that remained on their surfaces was therefore negligible compared to that existing within the agglomerates. These results suggest that the air content did not exceed 6% of the pore volume. Reference to Fig. 3.17 where the rate of agglomerate growth is presented as a function of time for various oil additions shows that a substantial rate of agglomerate growth occurred only when the bridging liquid associated with the agglomerates occupied more than about 75% of the pore spaces. Another interesting observation from comparing Table 6.6 and Figure 3.17 is that the amount of bridging liquid required to form agglomerates was always less than that required to fill the whole volume of the pores and this deficit was inversely related to agglomerate size.

The results obtained with tetradecane (Table 6.2 and 6.4) were used to calculate the fractional filling of the pores by oil, water and air for -86+27 μm material, and the values obtained are given in Table 6.7. Hexadecane gave similar results.

Table 6.7: The agglomerate pore contents for various tetradecane additions using -86+27 μm alumina

Oil addition ml/cm ³ alumina (%)	Fractional filling of the pore volume		
	by oil based on oil addition (%)	by oil	by oil + water
		based on measured volume	
		(%)	(%)
70.2	87.3	85.5	94.5
68.3	84.5	83.0	95.0
65.8	79.4	78.5	-
63.4	76.5	75.5	-
58.5	70.6	69.5	-
48.8	58.8	57.5	-

The data given in Table 6.7 show that there was no detectable change in the fraction of the pore spaces filled by the bridging liquid after an agglomeration time of 30 minutes when the oil viscosity was increased from 0.481 mPa s (iso octane) to 2.06 mPa s (tetradecane). When the viscosity increased from 2.06 mPa s to 2.99 mPa s (hexadecane), however, the poorer distribution of the oil phase slightly influenced the agglomerate size (Fig. 3.11) but the amount of oil present in the agglomerates after 30 minutes was unchanged.

The bridging liquid content of agglomerates formed from the various size fractions is given in Table 6.8 as a percentage of the pore space occupied. The amount of oil bridging liquid added corresponded to just below the "paste volume" for the coarse fractions and that required to give maximum size

agglomerates with the finer fractions. For the -53+20 μm fraction a range of bridging liquid concentrations was investigated.

Table 6.8: The agglomerate pore contents for various alumina size fractions with iso-octane as bridging liquid

Agglomeration time: 30 minutes

Particle size range (μm)	Oil addition ml/cm ³ alumina (%)	Fractional filling of the pore volume		
		by oil based on oil addition (%)	by oil	by oil + water
			based on measured volume (%)	(%)
-63+53	76.1	95.0	83.5	96.0
-53+45	78.1	93.0	84.0	95.0
-45+27	80.0	95.0	85.5	94.0
-53+20	50.7	94.5	83.5	100.5
	48.8	91.0	72.5	93.0
	46.3	86.0	68.5	98.0
	43.9	78.0	63.0	-
	39.0	69.0	57.0	-
	29.0	48.0	44.0	-
	19.50	32.0	28.0	-
-20+10	56.1	95.8	79.0	102.0
-53	46.3	83.3	50.0	85.0
-10	51.0	72.0	58.5	96.0

The agglomeration characteristics of the -86+27 μm material compared with -53+20 μm alumina indicate that although in both cases the agglomerate growth continued at a significant rate (Figs. 3.17 and 3.18) when the oil content occupied more than 75% of the agglomerate pores, the finer size fraction was satisfactorily agglomerated at a fractional filling as low as 28%. With the coarser fraction the agglomerates broke down

if their associated oil content was reduced below about 45%. Another interesting feature of the above measurements is that the upper oil content for the extremely fine material ($-53, -10 \mu\text{m}$) was approximately half that necessary to saturate the pore volume of the agglomerates.

6.2.4 Compressive strength of agglomerates

The relative strength of agglomerates formed from each size fraction was measured at varying iso-octane additions. Fig. 6.4 shows graphically the failure load of a number of agglomerates made from $-86+27 \mu\text{m}$ alumina plotted against their dry weight. The agglomerates tested were formed by using iso-octane additions of 68.3 and 73.2%. The compressive strength appeared to be dependent upon agglomerate size, and consequently upon the agglomerate weight which has been adopted as a basis for comparison in all subsequent plots. For each oil addition, a linear relationship was assumed to exist between failure load and agglomerate weight, and the method of least squares was, therefore, used to fit the best straight line to each set of crushing strength measurements. Figure 6.4 shows that the failure load increased with agglomerate weight. Although a larger increase in strength with increase in agglomerate weight was found with the higher oil addition, comparison of the crushing strengths obtained with the two oil additions is not really possible, since the values overlap only in a very small region, and differences are not considered significant.

The effect of the oil volume associated with the agglomerates on the compressive strength was found to be marked at very low oil additions using $-53+20 \mu\text{m}$ alumina. Figure 6.5 shows clearly that stronger agglomerates resulted with an iso-octane addition of 29.3 than those obtained with 19.5% although larger agglomerates were produced with the lower oil addition. These additions produced agglomerates with oil contents in the lower region of the funicular state as was explained previously. (Table 6.8, see also section 2.2.1).

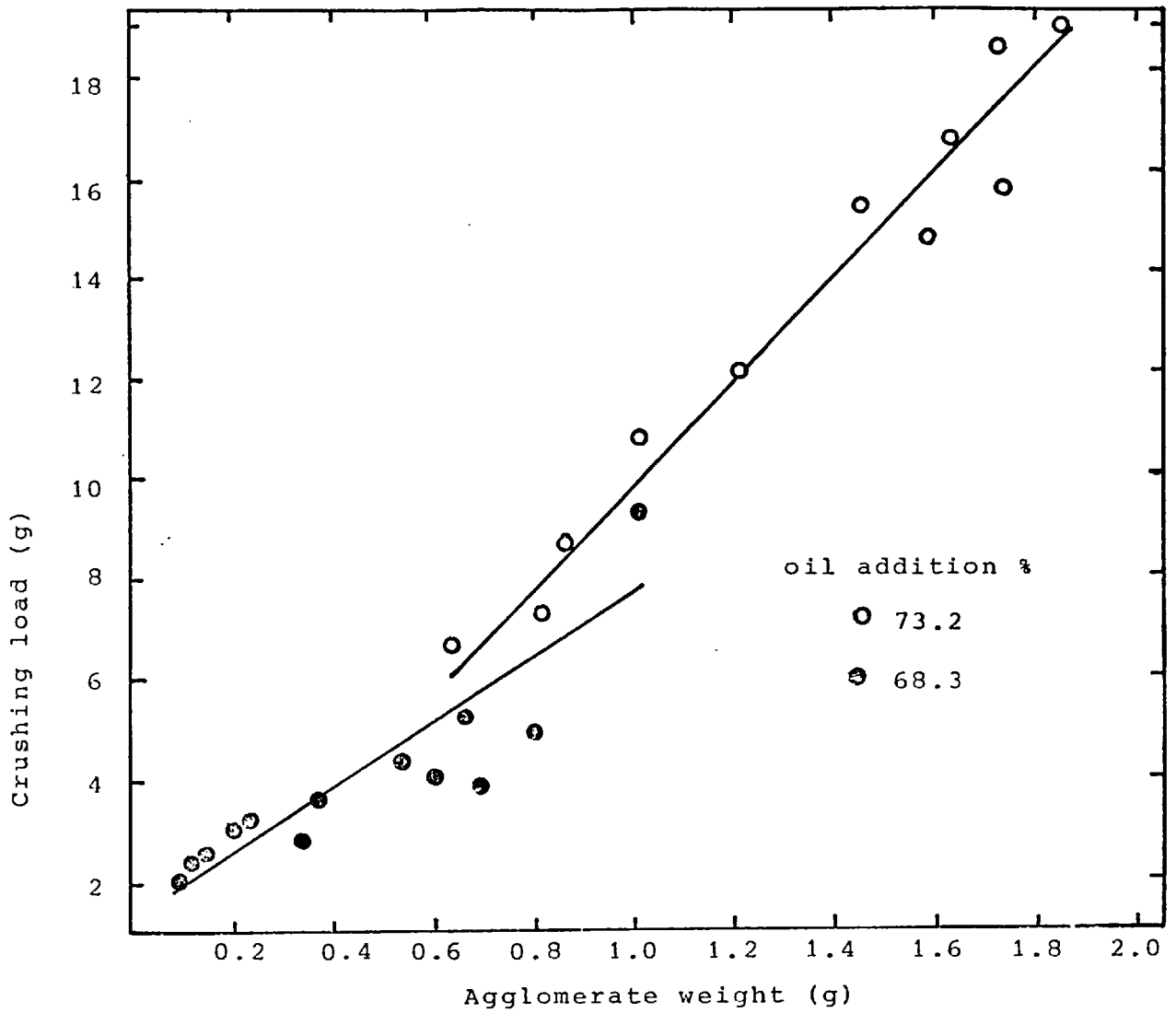


Fig. 6.4: Crushing load as a function of agglomerate weight for -86 +27 μm alumina/iso-octane system.

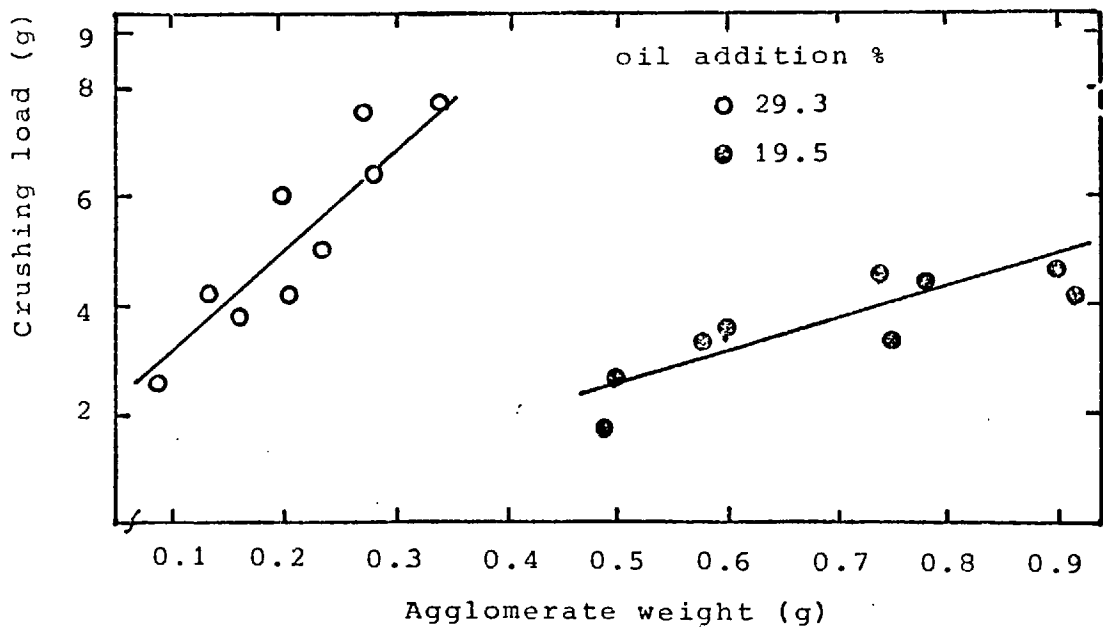


Fig. 6.5: Crushing load as a function of agglomerate weight for -53 +20 μm alumina/iso-octane system.

A more detailed investigation of the effect of oil volume on strength was made with $-45+27\ \mu\text{m}$ alumina throughout the oil concentration range where distinct spherical agglomerates were produced. Figure 6.6 demonstrates the high dependence of compressive strength upon agglomerate size at oil additions between 77% and 48.5%. At lower bridging liquid volumes (e.g. 39%) the failure load was not very dependent on the agglomerate weight. This corresponds to the region where a different growth mechanism was operative. The average strength of agglomerates of a given weight generally increased slightly with oil addition in agreement with theoretical predictions^{78, 201}. The reverse of this tendency observed in a few cases (e.g. intersection of curves 2 and 3) must be attributed to the fact that the resistance to stress shown by an agglomerate made from particles of a fixed size depends not only on the quantity and intrinsic strength of the bridging liquid, but also on its distribution within the pore volume. The manner in which the amount of bridging liquid influences this distribution is very difficult to determine quantitatively. It is possible that individual agglomerates produced under the same conditions may have a different fractional filling of their pore space from the measured average value.

The effect of both particle size and size distribution of alumina, was determined by measuring the crushing load of similar size agglomerates formed from various size fractions. The iso-octane addition was varied to obtain agglomerates of the required size. In each case products covering a wide agglomerate weight range were made to permit reliable comparisons of their strength characteristics. This was not found possible for alumina fractions finer than $30\ \mu\text{m}$ where compressive strengths were measured on agglomerates weighing less than 1 g, because the large agglomerates were somewhat irregular in shape. The results obtained for seven different size fractions are plotted in Figs. 6.7 and 6.8 on log-log scales. The absolute values and the scatter of the crushing strength measurements are

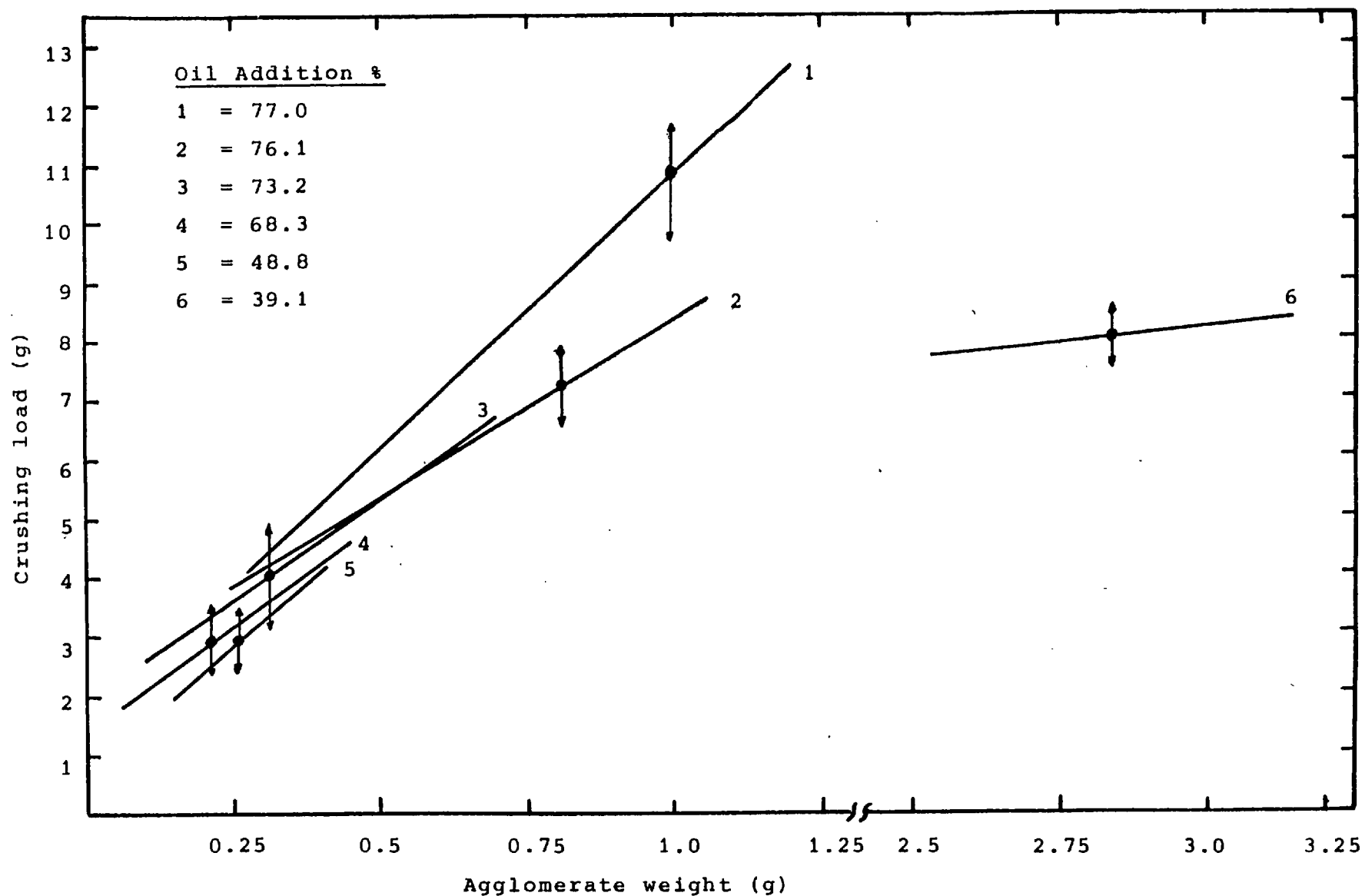


Fig. 6.6: Crushing load as a function of agglomerate weight for $-45+27\ \mu\text{m}$ alumina/iso-octane system at different bridging liquid additions

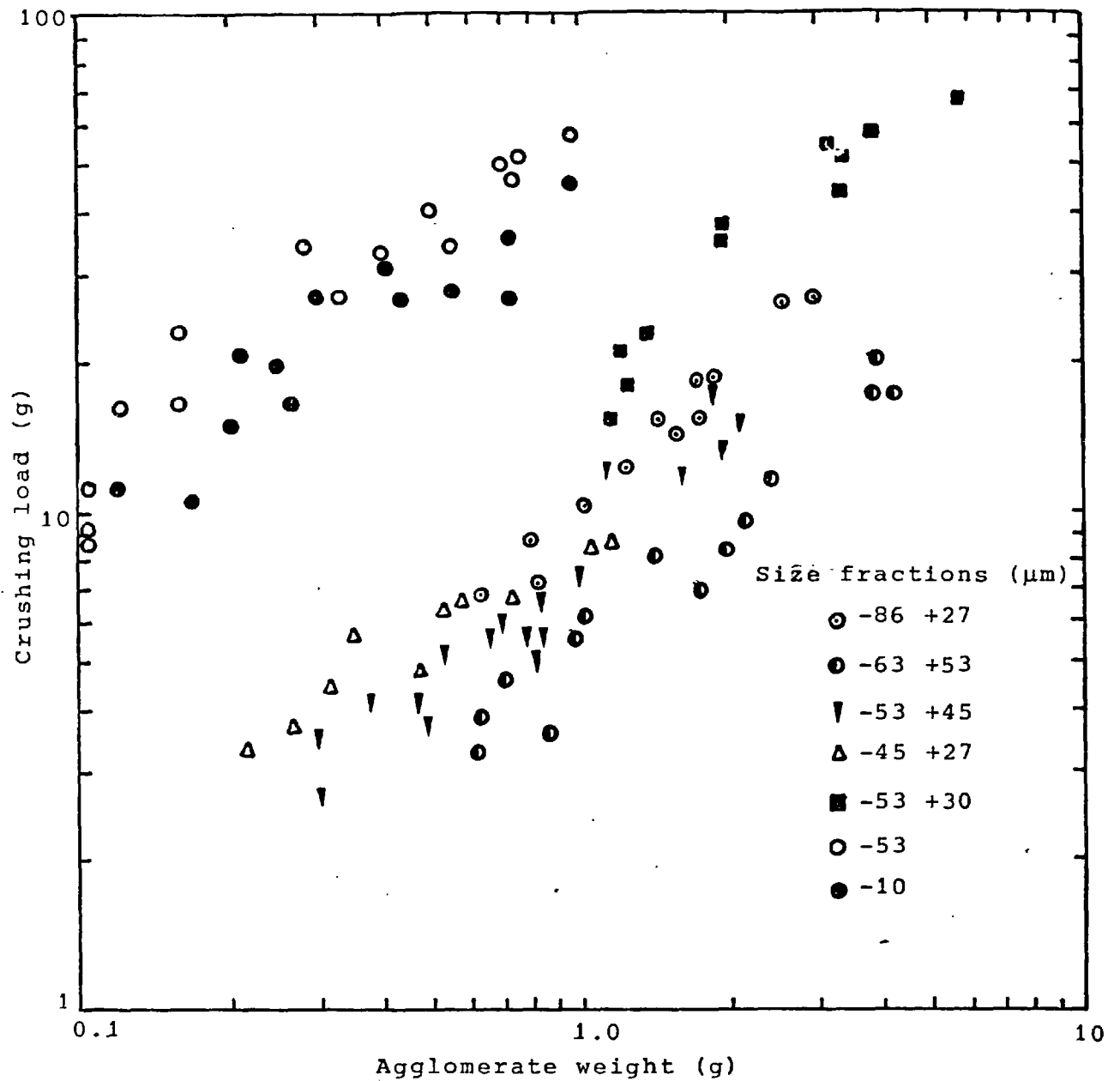


Fig. 6.7: Crushing load as a function of agglomerate weight for different size fractions using iso-octane as bridging liquid.

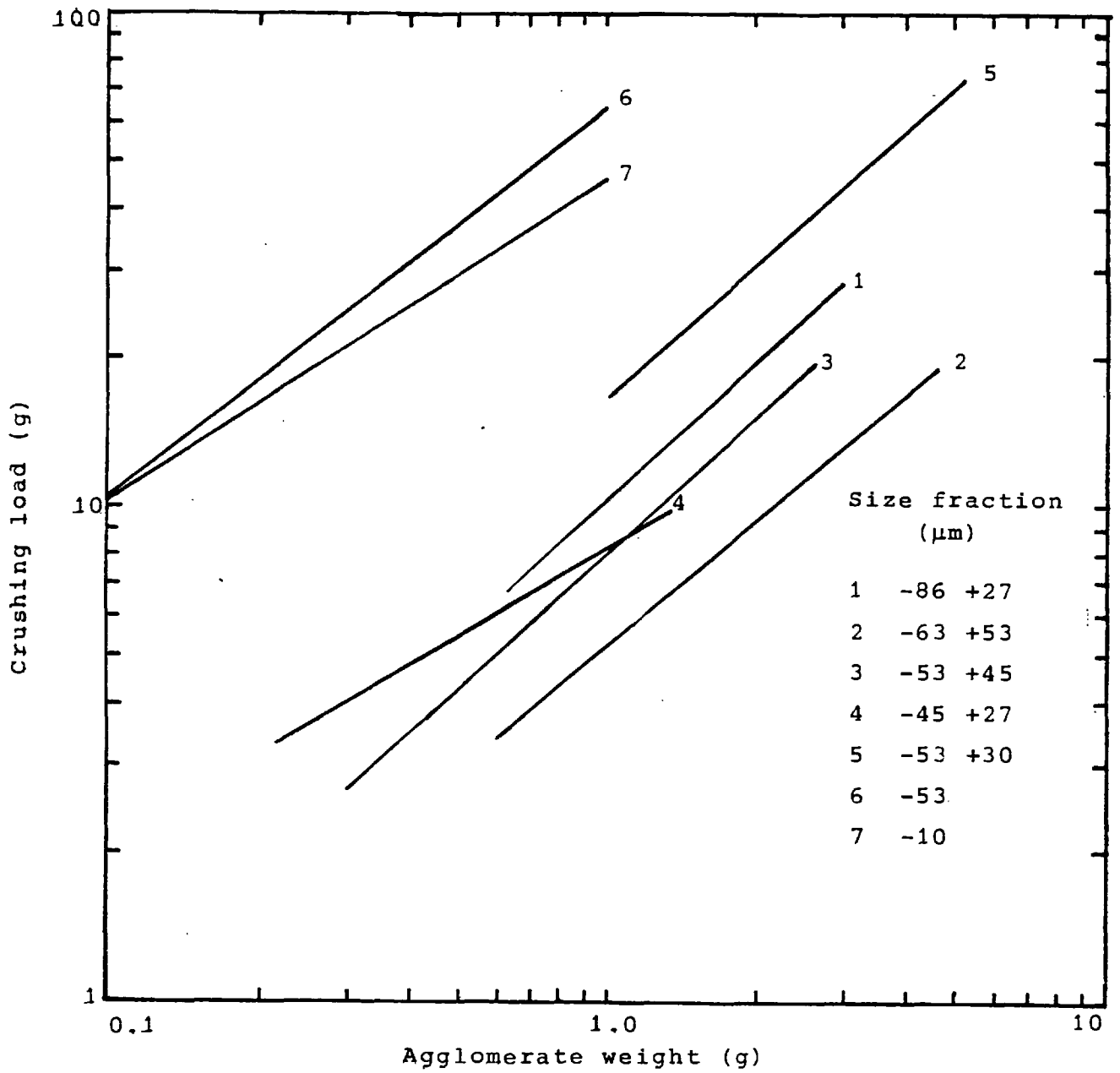


Fig. 6.8: The results of agglomerate strength of different size fractions given in Fig. 6.7 approximated by straight lines.

illustrated in Fig. 6.7 while in Fig. 6.8 all the data are approximated to straight lines to facilitate comparisons. Apparently the initial particle size and size distribution have an effect on the mechanical properties of agglomerates. Generally, stronger agglomerates were produced by decreasing the particle size, or by increasing the width of the size distribution of fractions with the same mean particle size. The fact that stronger agglomerates were made when the alumina particle size became smaller simply reflects the increasing number of particles and hence the number of liquid bridges per unit volume, and also the larger capillary pressure.

For agglomerates of similar properties and composed of narrowly sized materials a correlation appears to exist between the particle surface area and the strength. This is no longer true when the strength of agglomerates formed from a wide particle size distribution is compared with that of agglomerates from a narrow distribution for example -53 and -10 μm alumina. The reason for this can be attributed to the following factors which are not apparent when only the crushing load-agglomerate weight graphs are considered.

- i) The packing factor $(1 - \epsilon)/\epsilon$ was ignored in the determinations; an improved packing factor would compensate for a decrease in specific surface as explained in section 2.2.1.
- ii) The very large particles in a size distribution should have no effect on agglomerate strength provided that coarse particles do not disturb the packing of the fines surrounding them⁸².
- iii) Differences in the degree of sphericity of agglomerates, observed particularly with the fine material, imply that a shape factor should be incorporated.

The above factors may explain why, for example, the -53 μm alumina produced agglomerates having a higher strength than did the -10 μm materials in spite of the specific area and the reciprocal of the average particle size being smaller in the case of the -53 μm material. In addition, it was found that different amounts of aqueous phase and air were trapped in agglomerates made from powders composed of different particle sizes. It was not possible to assess the effect of this, since no agglomerates were found completely free from water, but on theoretical grounds it appears likely that a water free agglomerate would be slightly stronger. The possibility that the oil distribution is not homogeneous which was discussed in relation to strength of the agglomerates formed from -45+27 μm alumina with different oil additions may also explain the agglomerate strength results for different particle sizes. However, compressive strength determinations can only give some qualitative trends, rather than quantitative information because it is not possible to produce agglomerates in which only the property being studied is varied, particularly when starting from particles with different size distributions.

If it is assumed that agglomerate strength can be related to weight by a straight line on a log-log basis as in Fig. 6.8, then an equation of the following form must be satisfied.

$$L = K_1 W^{n_1} \quad (6.2)$$

where L is the crushing load (g)

W is the agglomerate weight (g)

and K_1 , n_1 are parameters which will vary according to the agglomerating conditions and the material agglomerated.

The parameter n_1 is represented by the slope of the lines in Fig. 6.8 and it can be seen that n_1 depends on the size distribution of the material forming the agglomerates, and

values between 0.3 and 1.0 were obtained. Similarly K_1 , which shows the position of the line on the graph, also depends on the size distribution. Apparently the oil volume affects the values of these parameters.

The influence of oil viscosity on the compressive strength of the product was investigated using $-86+27\ \mu\text{m}$ alumina, and iso-octane, decane, tetradecane, hexadecane and hexadecane/heptane mixtures. Initially, as in the previous experiments, strength measurements were made with the agglomerates immersed in the liquid in which they were formed. Agglomerates of approximately equal size and with approximately equal fractions of their pore spaces filled with oil, gave compressive strengths with a maximum scatter of $\pm 3\ \text{g}$ independently of oil viscosity. In Fig. 6.9, some of the results obtained with three oils of different viscosities are presented. No conclusion can be attached to the effect of viscosity up to $2.99\ \text{mPa s}$, since the differences noticed were not systematic and could have been caused by other effects such as differences in oil distribution etc. It should be noted that when benzene was used as bridging liquid, the compressive strength was always less than $7\ \text{g}$ for agglomerates with weights up to $2\ \text{g}$. This was not unexpected, since of the oils used, benzene has the lowest interfacial tension. (Table 5.2).

When compressive strengths were measured in air, higher values were found. Agglomerates produced from $-86+27\ \mu\text{m}$ alumina, using tetradecane as bridging liquid, were tested in both air and under liquid, and as can be seen in Fig. 6.10 the results indicate that the strength in air was approximately twice that under water. This increase in agglomerate strength might be explained in terms of changes in some of the factors associated with the capillary forces, such as contact angle and curvature of the interfaces. However, the interfacial tension did not contribute positively to this increase except in the case of benzene which has a higher surface tension against air than against $5 \times 10^{-4}\ \text{M}$ SDS solution (Table 5.2). The

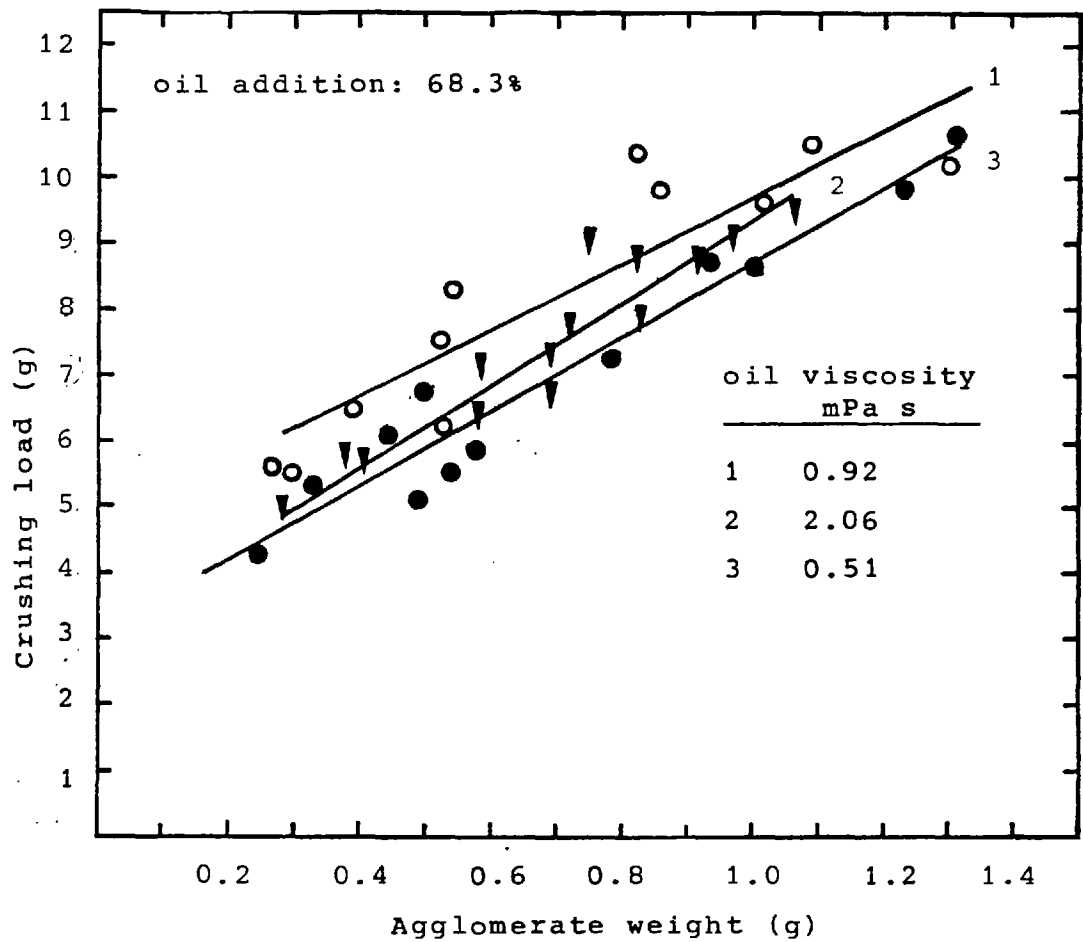


Fig. 6.9: Crushing load as a function of agglomerate weight for -86+27 μm alumina at different bridging liquid viscosities

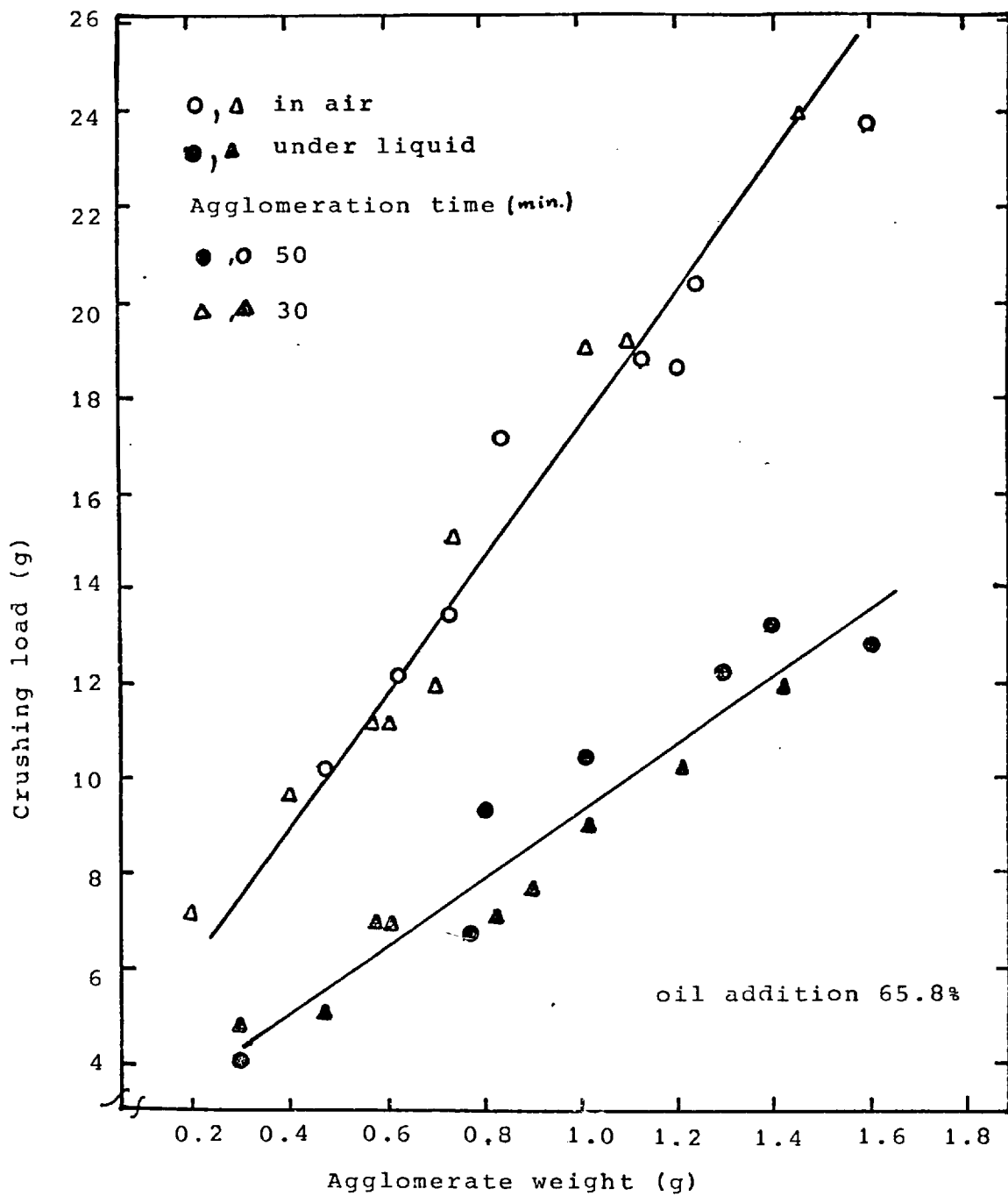


Fig. 6.10: Crushing load-agglomerate weight relation for -86 +27 μm alumina/tetradecane system.

compressive strength of agglomerates where iso-octane was used as bridging liquid was initially higher in air than under liquid, but it decreased with time of exposure to air. In air it is expected that with volatile oils the curvature of the bridging liquid surface will be increased initially due to evaporation, and hence a high pressure deficiency will be set up within the liquid. Further evaporation will lead to a reduction in strength as air enters the agglomerate pores. This is in agreement with the theory in which capillary forces are said to be proportional to the fractional filling of pore space by the bridging liquid.

Agglomerates formed from the coarse size fractions ($\geq -45+27\mu\text{m}$) with iso-octane, collapsed under their own weight in an air environment after being left for a few hours at room temperature, presumably because the increasing pressure deficiency was not sufficient to counter the loss of oil, and the cohesive stress, therefore, dropped to zero. Similar agglomerate strength and bridging liquid content relations have also been observed by other workers²⁰². The finer size fractions ($\leq -53+20\mu\text{m}$) gave agglomerates which exhibited some degree of strength even though almost completely free from oil, but the agglomerates formed by the very fine alumina (-53 and $-10\mu\text{m}$) had a considerable compressive strength when all the oil had evaporated. Fig. 6.11 shows the strength of agglomerates for $-53\mu\text{m}$ alumina when under liquid and in an air environment after various periods at room temperature ($\sim 20^\circ\text{C}$). A sharp increase in the strength was noticed in air and this reached its maximum value after many hours. Similar results were obtained with $-10\mu\text{m}$ alumina. In both cases crushing loads as high as 300 g were measured, although the agglomerates tested were less than 0.5 g in dry weight.

Figs. 6.10 and 6.12 show that there was no observable increase in agglomerate strength for agglomeration times greater than 30 min using $-86+27\mu\text{m}$ alumina and two different tetradecane additions, i.e. 65.8% and 63.4%. This was true whether the agglomerates were tested in air or under liquid, but weaker agglomerates resulted when the mixture conditioning was only

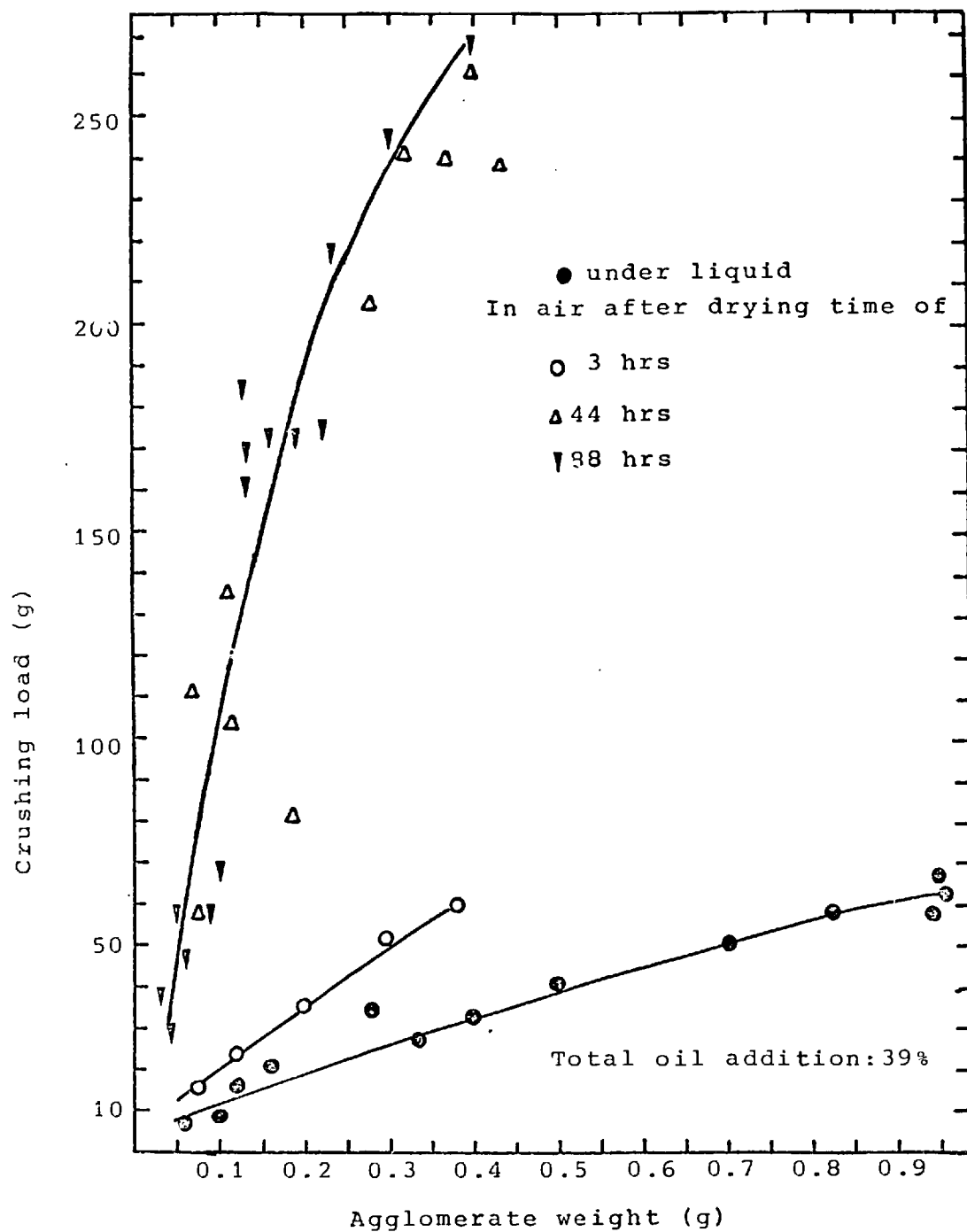


Fig. 6.11: Crushing load as a function of agglomerate weight for $-53\mu\text{m}$ alumina/iso-octane system.

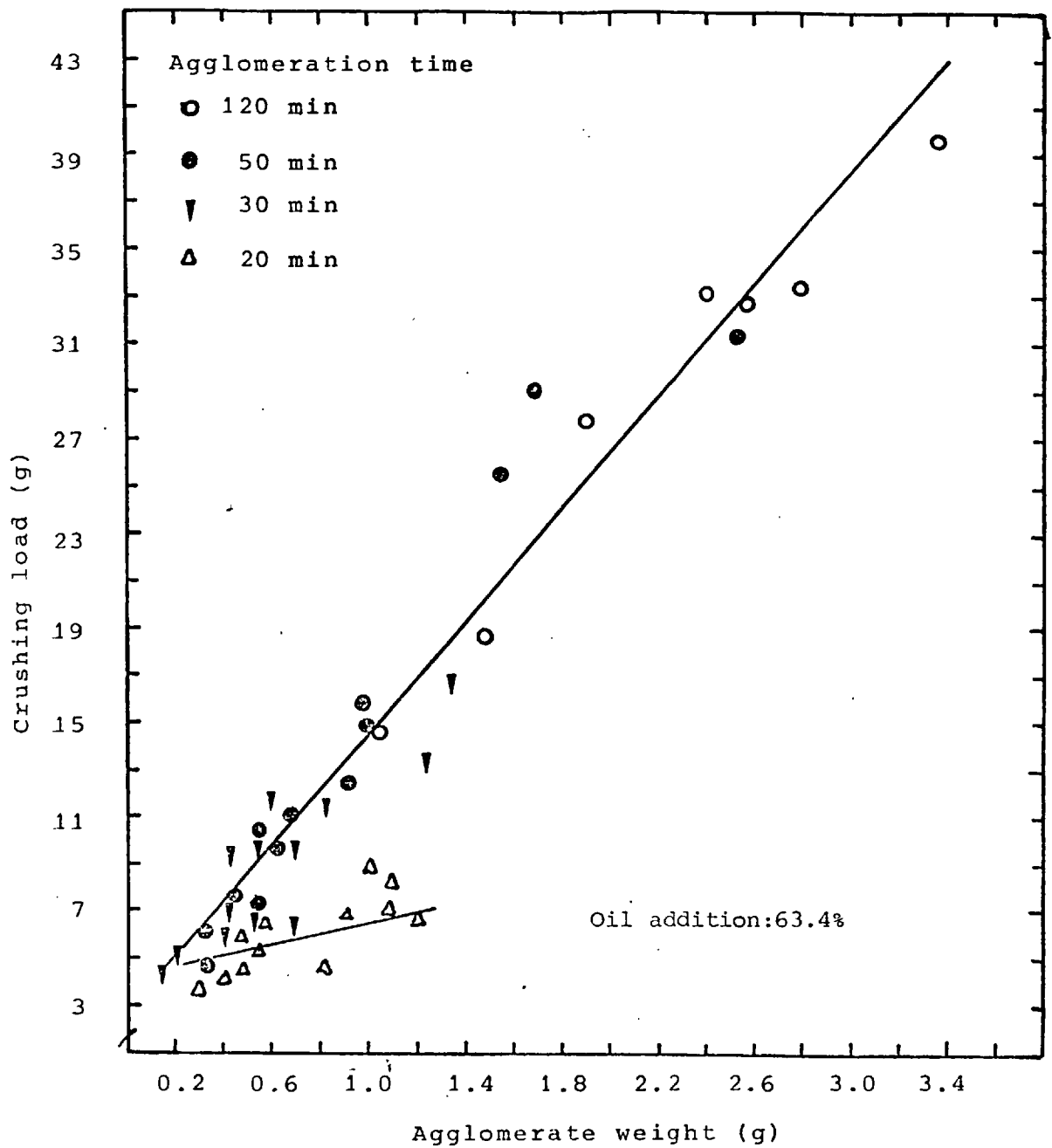


Fig. 6.12: Crushing load as a function of agglomerate weight for $-86 + 27 \mu\text{m}$ alumina/tetradecane system at different agglomeration times. The agglomerate strength was measured in air.

20 minutes. Similar observations were made when the effect of agglomeration time was investigated with $-45+27\ \mu\text{m}$ alumina at an iso-octane addition of 73% in which the strength measurements were carried out under the suspending liquid. These results indicate that compaction of agglomerates does not continue for long periods, thus agreeing with the porosity measurements.

It was observed that agglomerates tested under liquid fractured by splitting along a meridian into two approximately hemispherical sections, causing a tensile failure across a disc-shaped section, Fig. 6.13. The crack, which probably originated inside the agglomerate, appeared firstly at a point between the poles and the equator, but rapidly spread across the whole agglomerate. With increase in oil content the agglomerates deformed more easily and those made from fine alumina and tested in air after the oil had evaporated were brittle and broke into a number of pieces.

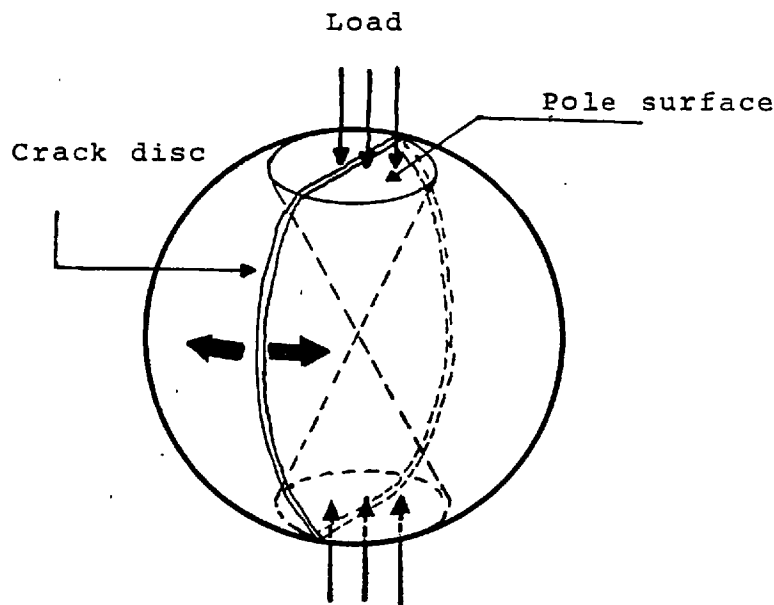


Fig.6.13: Schematic representation of agglomerate at fracture

6.3 DISCUSSION

6.3.1 Packing characteristics - Contents of agglomerate pore spaces

Table 6.3 shows that the agglomeration process can give rise to closer packing than a dry vibrated bed especially with relatively fine particles ($\leq 45+27 \mu\text{m}$). This is attributed to the following.

- i) The bridging liquid improves the degree of compaction by providing capillary forces between the particles and by lubricating the passage of particles past one another.
- ii) The compacting force is applied to small aggregates of particles, so that attenuation due to interparticle friction is very much reduced.
- iii) During agglomeration the forces act on the particles from random directions, while in vibration they act mainly in one direction only.

Fig. 6.3 and Table 6.4 show that less water is associated with agglomerates when they are made using an oil with a high viscosity. If it is assumed there were no significant differences in the wettability characteristics, the reasons for this could include.

- i) The agglomerates obtained at a given oil addition were larger when a higher viscosity oil was used and they, therefore, had smaller surface areas per unit mass. Consequently the amount of water adhering to their surfaces would have been less.

- ii) Use of a higher viscosity oil improved the efficiency with which water was displaced because of the slower flow of the liquid through the agglomerate pores.

The amount of water associated with agglomerates was also found to be affected by the size and size distribution of the agglomerating material. Table 6.5 shows that more water was trapped with the finer material and assuming the wettability characteristics of the various alumina grades were similar this can be explained as follows

- i) For agglomerates of a given size the pore size decreases as the particle size decreases. Consequently greater capillary forces will be developed with the fine material and therefore larger amounts of water will be sucked into the agglomerates.
- ii) The bridging liquid in the outermost layer of the agglomerates will be withdrawn from the agglomerate surface to a depth λ (Fig. 6.14) into the interstices between the particles. The withdrawal parameter λ increases as the particle size decreases due to the larger capillary forces and together with the increased number of particle interstices this leads to an increased amount of water being retained on the surfaces of agglomerates.
- iii) The fine particles were in a coagulated form at the S.D.S. concentrations employed and the structure of the flocs probably allowed a significant amount of water to be enclosed by the bridging liquid.

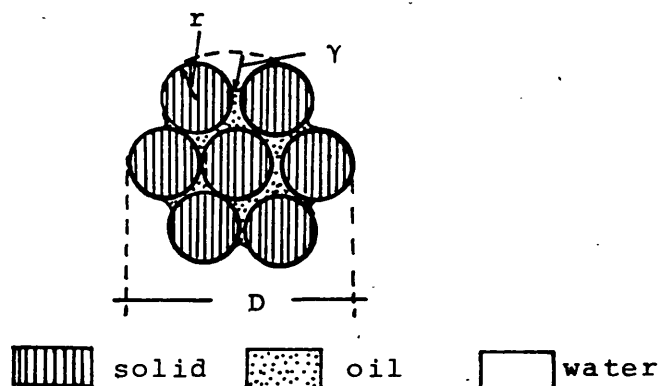


Fig. 6.14: Ideal cross-section of an agglomerate

D = agglomerate diameter

r = particle radius

λ = withdrawal parameter

Porosity and wettability measurements showed no significant differences when either a hydrocarbon or iso-octane was used. The apparently higher oil requirement when a low viscosity oil was employed may have been because not all of the oil added was incorporated into agglomerates. Table 6.4 shows that with iso-octane as bridging liquid about 7% (specified on dry solid volume) of the oil added was either lost by evaporation or perhaps coated onto the agglomerator walls. The "paste volume" for the most volatile iso-octane (75%) is similar to that obtained with the more viscous oils (68 - 70%) when allowance is made for iso-octane loss. Even more benzene than iso-octane was required probably because as can be seen from Table 3.2 there was a further loss in this case due to its dissolution in water equal to an oil addition of 4%.

In general the bridging liquid required to occupy the pore volume of an agglomerate made from fine material is less than that needed in the case of coarser particles even for the same agglomerate porosity. This is explained by reference to Fig. 6.14 where it can be seen that less bridging liquid is needed to achieve the capillary state when there are more particle interstices and withdrawal parameter values are higher. Agglomerates usually changed to a paste when the oil content exceeded 80 to 85% of the agglomerate pore volume (Table 6.8). This level^{was} reduced to between 50 and 60% for the alumina fractions containing substantial amounts of $-10\text{ }\mu\text{m}$ material and the high water content trapped with this material may also explain the low fractional filling of pores by the oil phase. However, if the water in an agglomerate is completely surrounded by bridging liquid the agglomerate will behave as though the pores were occupied solely by the oil. This is true for those agglomerates in which the internally incorporated water does not significantly influence the agglomerate strength.

The lower limit of bridging liquid required for the formation of agglomerates varied with particle size. Coarse particles gave good agglomerates when the bridging liquid occupied at least 45 - 48% of the agglomerate pore space. With finer particles this limit reduced considerably and for example the $-53+20\text{ }\mu\text{m}$ alumina was satisfactorily agglomerated with a fractional filling of the pore volume down to 28%.

Work in related fields has led to similar results. A study of granulation⁷⁸ showed that granules were formed at a significant rate only when the bridging liquid filled more than about 90% of the voids between highly compacted sand particles. Capes and Danckwerts¹¹⁸ found that in most cases between 85 and 93% of the voids in granules

from a damp sand were filled with liquid. In addition in a work⁴¹ involving the agglomeration of sand suspended in an organic phase with water as bridging liquid it was shown that spherical agglomerates were formed when the bridging liquid occupied between $44\% \pm 2\%$ and $81\% \pm 4\%$ of the void space. In this work particle size fractions were in the range $-150 + 10 \mu\text{m}$. Butensky and Hyman²⁰³ obtained an upper value of 89% for all the material they used except the finest fraction ($-44+20 \mu\text{m}$) where only 74% of the granule void space was filled with bridging liquid. The same authors, and also Sherington⁸⁶ proposed a model to relate the size of granules to the amount of bridging liquid for granulation in a rotating drum. The basis of their system is shown in Fig. 6.14. They assumed that the agglomerate surface is free from bridging liquid at equilibrium, because otherwise additional particles would be attached to the agglomerates making them larger. Their model has been developed to describe systems composed of monosized spherical particles whose packing characteristics can be predicted. The equation suggested by Sherington is

$$y = k(1 - 3 \lambda b) \quad 6.3$$

where y = the ratio of liquid to solid volume

k = the ratio of void to solid volume
in the granule

b = the ratio of particle to granule
diameter

λ = the withdrawal parameter

Application of their model to spherical agglomeration of comminuted particles leads to erroneous results for several reasons. The parameter λ is difficult to determine for irregularly shaped material, and the model was developed only for monosized particles. A certain amount

of the suspending medium is trapped in the agglomerates and this is controlled by a number of complex variables and is difficult to predict. Furthermore, the results obtained by Butensky et al²⁰³ fit the model under conditions at which the amount of liquid was not sufficient to produce granule growth after the initial stages.

6.3.2. Agglomerate strength.

The compressive strength results clearly show the dependence of agglomerate strength on particle size and size distribution, porosity and oil content. The failure load was found to be correlated only approximately with agglomerate weight by equation (6.2) and the parameters K_1 and n_1 were constant only for a given set of agglomerating conditions. In studies of the compressive strength of pellets, it is common practise to normalize the data for different sizes by dividing individual loads at failure by the square of the pellet diameter instead of dividing by weight as in the present work. The general form of the proposed equation relating crushing load to agglomerate diameter is given by ²⁰⁴.

$$L = K_2 D^{n_2} \quad (6.4)$$

Similar to K_1 in equation (6.2), K_2 is a measure of the intrinsic strength of the liquid bridges between the particles. Equation (6.4) can be applied to agglomerates produced by the present process, but the index n_2 will take different values for different sets of conditions. Newitt and Conway-Jones⁷⁸ and Capes and Sutherland⁴¹ fitted their results by putting n_2 equal to 2 implying that strength is proportional to agglomerate square diameter. It has been demonstrated by Capes²⁰⁴, using a simple geometric model, that the parameter n_2 would be expected to be equal to 2 if there is a uniform bond distribution, and any value between 1 and 2 is possible for the various bonding mechanisms. Consequently pellets in the capillary state normally have a value of n_2 close to 2, since the liquid bridges form a continuous network and are distributed uniformly across the whole pellet cross-sectional area. The fact that pellets are never filled completely with bridging liquid indicates that

in practise n_2 would be expected to take values below 2. Greaves and English²⁰⁵, considering the data of Ulrich and Han²⁰⁶, have normalized the strength of pellets with different diameters by assuming $n_2=2$, but if this assumption is not made, and the data are fitted by the least square procedure, it becomes evident that n_2 is not equal to 2 for both green and dry agglomerates²⁰⁷. It was also shown that Cahn and Karpinki's²⁰⁰ results, treated on the basis of $n_2=2$, gave a general decrease in mean compressive strength with increasing pellet size²⁰⁷. Linkson and coworkers²⁰⁸ related breaking load and diameter of green pellets and found that an index greater than 2 was obtained for material which grew by a coalescence mechanism, while an index less than 1 was obtained for materials which grew by crushing and layering. Variability in the value of exponent n_2 in other dry pellet systems has also been reported.

It can be concluded that the compressive strength of agglomerates is not necessarily proportional to their weights or to the squares of their diameters, and since one of these assumptions has commonly been made, this has led in some cases to erroneous interpretation of experimental data.

If the agglomerate strength theory developed in Chapter 2 is valid, then the mechanical strength of an agglomerate must be directly related to the cohesive forces set up during its formation. Considering as an example agglomerates made from a wide size fraction e.g. $-86+27\text{ }\mu\text{m}$, their probable strength has been calculated using the theoretical expressions given in Table 2.1. For agglomerates in the funicular state,

$$F_f = S \cdot P_c \quad (6.5)$$

where

F_f = cohesive strength in the funicular state

s = fractional filling of agglomerate pore space
by bridging liquid

and P_c = average capillary pressure or the suction developed
in the pure liquid.

If the measured strength of an agglomerate is proportional to the capillary forces, a factor K' may be defined such that $K_2 = K' F_f$, where K_2 is the specific strength defined as the load required to crush an agglomerate having a cross-sectional area of 1 cm^2 , and F_f depends on the mechanism of agglomerate failure. Approximate calculations suggest that a value of 0.7 can be assumed for the factor K' . Thus the strength of an agglomerate can be calculated using the expression (Table 2.1, B_1, C_3).

$$K_2 = K' \times 4.0 \times \frac{1-\epsilon}{\epsilon} \times \frac{\gamma_{ow} \cos \theta}{r} \times s \text{ (g/cm}^2\text{)} \quad (6.6)$$

To apply this equation to agglomerates made with $-86+27 \mu\text{m}$ alumina the following values were assumed.

r = mean number (r_N) or weight (r_W) radius of particles
($r_N = 23 \times 10^{-4} \text{ cm}$, $r_W = 28 \times 10^{-4} \text{ cm}$), $\theta = 180-110 = 70^\circ$,
 $\gamma = 30 \text{ mNm}^{-1}$, $\epsilon = 0.44$, $s = 80\%$ (arbitrary but of the
right order).

$$\therefore K_2 = \frac{0.7 \times 4.0 \times \frac{1-0.44}{0.44} \times \frac{30 \cos 70}{981} \times 0.80}{23 \times 10^{-4}} = 13 \text{ g/cm}^2$$

The theoretical specific strength based on the mean weight radius of particles was calculated to be $K_2 = 10.6 \text{ g/cm}^2$. The data given in Fig. 6.4 show that the strength of an agglomerate having a cross-sectional area of one square centimeter, which corresponded to a weight of 1.64 g was

16.2 $\pm$ 2g; the weight of an agglomerate having unit cross-sectional area was calculated using the bulk densities of the agglomerates given in section 6.2.1. It can be seen that the experimental value is in reasonable agreement with that predicted using equation 6.10.

A comparison between the experimental strengths of agglomerates and those predicted from theory is presented in Table 6.9 for the different size fractions used in this work.

Table 6.9 : Comparison between theoretical and experimental agglomerate strength.

Particle size range (μm)	fractional filling of the agglomerate pore volume of oil (%)	Specific strength (g/cm^2)		
		theoretical based on		Experimental
		r_N	r_W	
-86 + 27	80	13	10.5	16.4
-63 + 53	80	9.9	9.4	8.0
-53 + 45	80	12	11	12.5
-45 + 27	80	14.9	14	15
-53 + 20	40	17.2	14	34.8
	26	11.2	9.1	10.8
-53	40	-	42	110 $\pm$ 10
-10	50	-	149	70 $\pm$ 10

The mean number particle radius reflects the number of liquid bridges in an agglomerate more accurately and it therefore gives a better prediction of agglomerate strength, but it was not possible to determine this radius for the -53 and the -10 μm alumina because of background noise interference at particle sizes below 2 μm during size analyses of these materials with a Coulter Counter.

Table 6.9 shows quite good agreement between theoretical and experimental agglomerate strengths for the relatively coarse size fractions ($\geq -45+27 \mu\text{m}$).

Calculations with $-53+20\mu\text{m}$ alumina are referred to oil additions shown in fig. 6.5, for which agglomerates weighing less than 1 g were obtained. The experimental specific strength corresponding to an agglomerate weight of 1.9 g was found by extending the appropriate straight lines up to this weight (fig. 6.5), and probably accounts for the poor agreement with the theoretical values. With the very fine alumina ($-53, -10 \mu\text{m}$) the experimentally determined strengths were very different from those predicted by theory. The fractional fillings used with these aluminas are of the right order, since it has been shown in table 6.8 that they change to paste at values above approximately 50% and 58% respectively. Some probable reasons for the disagreements between the theoretically and experimentally determined strength values for the very fine alumina might be (a) the large amount of aqueous phase found to be trapped in the pores, (b) the use of r_w in the calculations instead of r_N , and (c) the assumption that the failure load-agglomerate weight relationship given in figs. 6.7 and 6.8 can be extended to agglomerates having a cross-sectional area of one square centimeter (1.87 and 1.73 g dry agglomerate weight respectively). Additionally the model on which equation 6.10 is based was developed for irregularly shaped particles but of uniform size, and some of the fractions used in the present work contained fairly wide distributions of sizes.

The fact that agglomerates made from material which did not contain particles less than $10 \mu\text{m}$ exhibited negligible compressive strength when all of the bridging liquid had been removed, helps to establish the validity of the capillary theory, which predicts maximum strength when the particles

are compacted to minimum porosity and the agglomerates contain just enough liquid to saturate the agglomerate pore space. When the particles are dry the capillary forces disappear and hence if they provide the only bonding mechanism, the dry strength will be negligible.

In the presence of significant amounts of $-10\ \mu\text{m}$ particles (mean surface radius of particles was found to be in the colloidal region for these fractions), the capillary theory is no longer applicable, since it was found that the dry strength, far from being negligible, was many times the strength in the presence of oil. There is no evidence that Van der Waals forces or other surface forces make an appreciable contribution. Rumpf⁸² has calculated the approximate tensile strength due to Van der Waal's forces as

$$\sigma_z = \frac{4.15 \times 10^{-20}}{\ell^2 r} \quad (\text{kg/cm}^2) \quad (6.7)$$

where ℓ is the shortest distance between the surface of two spheres (cm) and r is the radius of the particle spheres (cm). Apart from surface forces the only remaining bonding mechanisms are those due to interlocking or frictional forces and possibly those resulting from hardening of colloidal particles which act as a mortar or glue when agglomerates dry. In these cases the zeta potential plays a role in determining the proximity of the very fine particles. Stone²⁰⁹ found that the higher the negative zeta potential of the bentonite which he used as an additive, the higher was the strength of the corresponding pellet.

In the conventional pelletization process most workers report that when normal balling techniques are employed, and additives are not used, the compressive strength of dried

pellets is lower than that of the original green pellets²¹⁰. However when binders are used the reverse may be true^{206, 211}. In the present work it has been established that for the very fine particle size fractions even without the use of an additive the dry strength of agglomerates is much higher than their strength in the presence of oil.

Comparing the strength of spheres produced by the oil spherical agglomeration process and by a green pelletization process, it is apparent that for similar sized particles stronger agglomerates are formed by the latter process due primarily to the high surface tension of water which is normally used as bridging liquid. However, the compaction achieved in pelletization is normally no better than that obtained in the present work. The strength of green pellets can however be improved by the use of various additives as has been shown by Ball and coworkers²¹² who investigated their role in the various stages of the pelletizing process.

CHAPTER 7
MECHANISM OF AGGLOMERATE GROWTH

7.

MECHANISM OF AGGLOMERATE GROWTH.

7.1 Coalescence and Crushing.

The results obtained in this work show that spherical agglomerates, similar to pellets, can grow by two different mechanisms. In the first, two or more agglomerates collide and coalesce and in the second, agglomerates grow by picking up the fragments resulting from collisions between other agglomerates. These mechanisms are commonly referred to as growth by coalescence and by crushing and layering respectively. Transition from one growth mechanism to the other occurs depending on the conditions in the agglomeration system.

The characteristics of the growth process were different depending on whether the powder was fine or relatively coarse. This may be due to differences in the strengths of the agglomerates since those made from finer materials tended to be the strongest. Agglomeration of $-86+27\ \mu\text{m}$ alumina will be discussed first and the behaviour of this material will be regarded as typical of coarse size fractions.

When bridging liquid was added to a suspension of coarse alumina whose surface had previously been rendered hydrophobic, highly porous flocs or perhaps larger aggregates were formed by coalescence in the first minute. The oil first spread over the surface of the liquid, but as particles of alumina contacted the oil layer they became coated and adhered together. The sizes of the aggregates formed depended mainly upon the amount of oil added. Plates 3.4 show some quite large aggregates which resulted from fairly high oil additions, and also the flocs produced when insufficient oil was present to form a large number of

interparticle liquid bridges. The irregular networks of particles were held together by pendular bonds, but the tumbling action inside the agglomerator assisted by capillary forces, converted these to stable agglomerates within a few revolutions provided that sufficient oil was present.

The tumbling motion tended to break up the weak flocs and aggregates in the initial stages and so agglomerates could not grow until they had been compacted sufficiently to give stronger funicular type bonding. When growth started a further but relatively small agglomerate growth began. At this stage a further but relatively small degree of compaction took place and if the oil content was greater than about 75% by volume of that required to completely fill the pore spaces, then oil was squeezed on to the surface as rearrangement of the particles took place. Consequently, the surface layers behaved plastically and were therefore fairly easily deformed, thus permitting growth to occur by further coalescence fig. 3.17. The form of the plot showing the size distribution of the agglomerates as a function of time (fig. 3.19) changed at this point as the total number of agglomerates decreased under high bridging liquid concentrations.

In the agglomerate growth region some agglomerates were irregular in shape and showed quite clearly where two or more had united and furthermore they took some time to be kneaded into a spherical shape because they tended to roll preferentially on their major axes. The growth process occurred more rapidly at high oil contents, and decreased as the size of the agglomerates increased. Plates 3.4 illustrate how growth took place at quite large agglomerate sizes.

The suggestion that agglomerate growth took place mainly by coalescence is supported by the observation that the rate of growth decreased at longer agglomeration times, since it would be expected that a crushing and layering type of mechanism would result in continued steady growth. However, other less important mechanisms probably contributed to agglomerate growth in the later stages. In addition to a small amount of crushing and layering, it is believed that abrasion occurred and resulted in the transfer of small groups of particles from one agglomerate to another. The main result of the secondary effects was to improve the sphericity of the agglomerates and eliminate a few of the smaller ones.

At low oil additions ($\leq 48.8\%$), weaker agglomerates were formed with the result that in the later stages at least, growth occurred mainly by crushing and layering. Once the initial stages of formation and compaction into spherical agglomerates had taken place, growth became quite fast (figs. 3.17 and 3.22) and continued at a high rate. This can be attributed to the weakness of the agglomerates in collisions because of the paucity of oil. Whenever the agglomerator was stopped, fragments were seen which were available to combine with other agglomerates.

As a check, some experiments were carried out using an addition of 58.5% of iso-octane but leaving the agglomerator uncovered to allow progressive removal of the oil by evaporation. The results showed that a considerable increase in agglomerate diameter occurred after 20 to 30 minutes and that the oil content of the agglomerates had fallen below the 48.8% level. Prolonged agglomeration times under these conditions resulted in products consisting only of fragments, but similar experiments in which the agglomerator was covered led eventually to stable agglomerates whose

diameters remained constant (fig. 3.17).

The relatively coarse size fractions of alumina tended therefore to give a product consisting of almost perfect spherical shapes at the low oil additions. This was because growth by coalescence ceased in the later stages. Also in the absence of an excess of oil at the surfaces, the outer layers no longer behaved plastically and any irregularities were ground away.

When relatively fine particle size fractions were agglomerated, crushing and layering did not take place at any stage, even for low oil additions. Fig. 6.5 shows that for oil additions of only 19.5 and 29.3% with $-53+20\ \mu\text{m}$ alumina the agglomerates were quite strong, and they were therefore able to withstand the effects of collisions without breaking. The growth curves fig. 3.18 levelled off because of the lack of excess oil at the surfaces, and this occurred quite early in the process at low oil additions. Plate 3.5 clearly shows growth by coalescence in the case of the $-53+20\ \mu\text{m}$ alumina fraction.

A detailed analysis of agglomerate growth by either coalescence or crushing and layering in a batch system is desirable because it is the first stage in the development of a mathematical model of the system. The analysis of many particulate systems is based on representing the agglomerate size distribution function in terms of reduced size and time variables, and then obtaining a solution of the kinetic equation in which only the reduced size variable appears. The reduced size distribution function is said to be "self preserving" if it depends only on the reduced size e.g. D/D_m - agglomerate diameter/mean agglomerate diameter - and not on time. Sastry²¹³ has investigated size distribution of pellets during their growth by isolating the coalescence

mode of growth in green pelletization. He developed a theoretical model representing the collision - coalescence rate as a multiple of two functions; one dependent on the size of the coalescing pellet and the other dependent on the material characteristics and operating conditions prevailing during the balling process. He tested his model with experimental data obtained from the formation of taconite pellets and found that the pellets possessed a remarkable self-preserving size distribution truly independent of the conditions under which they were made. Kapur^{214, 215} studied the kinetics of granulation by non-random coalescence and crushing and layering separately. He also showed that both mechanisms resulted in size distributions which eventually become self-preserving,²¹⁶ in terms of an appropriate dimensionless granule size. His theoretical results were in reasonable agreement with experimental data. In the present work the agglomerate size distribution also showed an invariant behaviour as a function of time (see chapter 3) but no detailed analysis was undertaken to examine the effect of the other variables involved in the system.

7.2. Comparison of the spherical agglomeration process with pelletization.

The oil spherical agglomeration process is closely related to size enlargement by pelletization in which pre-wetted material is placed in a rotating drum or pan, or on a vibrating surface where it is formed into approximately spherical balls. Wet pelletization has been extensively investigated by a considerable number of authors and its technological and theoretical aspects in the field of iron ore pelletizing have been reviewed by Ball and coworkers⁸⁹ and Madigan²¹⁷. The fundamental principles and the kinetics of the process are however still not fully understood²¹⁸.

To compare oil spherical agglomeration with pelletization a distinction must be made between batch and continuous operation and also between fine and coarse powders. In batch pelletization systems most workers agree that the initial stages of pellet growth occur by a coalescence mechanism and this is in agreement with observations made in the present agglomeration work. The mechanism involved in the later stages is, however, a source of controversy. According to Newitt and Conway-Jones⁷⁸ who studied three grades of approximately uniformly sized silica sand, and two mixed grades consisting of wide size distributions below 50 μm the only mechanism responsible for granule growth was considered to be coalescence, although they performed no specific experiments to verify this. Kapur and Fuerstenau^{117,219}, demonstrated the existence of three regimes during pellet formation and growth and called these the nucleation, transition and ball growth regimes. They used a comminuted limestone which was all finer than 200 μm and 25% finer than 12 μm . They showed that coalescence was the primary growth mode in the nuclei region, and that this mechanism continued to operate in the transition region and perhaps beyond in the region of ball growth as well²²⁰. Similar conclusions were reached by Sastry and Fuerstenau²²¹ who pelletized an iron ore and used tracer experiments to support their results. Capes and Danckwerts^{118,222} studied granulation of damp, closely sized sand between 165 μm and 49 μm with different results. They found that beyond a certain pellet size coalescence was supplanted by crushing and layering. They postulated as a result of tracer studies, that the smallest granule is crushed by intergranule collisions and that the resulting fragments are picked up by the surviving granules. A linear relationship was shown to exist between the initial diameters of the granules and their diameters after a finite amount of growth. They first thought that self-

preserving growth is characteristic of granules growing by ^{the} crushing and layering mechanism only. The results obtained in ^{the} present work and by other authors, already mentioned, showed that the self-preserving distribution of the agglomerates neither supports nor disproves either mechanism. Capes²²³, pelletizing silica sand (90%, by weight, $-104 + 43 \mu\text{m}$) and using a low water addition of 0.27 ml per g of sand stated that there is an upper critical limit on the pellet diameter for growth by coalescence which he postulated would be affected by among other factors, the water content and plasticity of the pellets. At the water content he used the limit was found to be 1-2 mm and this was verified by tracer studies. Linkson and coworkers²⁰⁸, suggested that whether or not coalescence is the predominant mechanism in the later stages of growth depends on the particle size of the pelletizing material. They found that with $-50 \mu\text{m}$ sand no crushing of existing pellets occurred, but material with an average diameter of $163 \mu\text{m}$ exhibited both mechanisms, i.e. initially coalescence and at later stages crushing and layering. Linkson's results are similar to those found in the present work.

The disagreements in growth mechanisms postulated by the different authors can be attributed to different materials and bridging liquid levels. Agglomeration processes are in general very complex and it is unwise to assume that the growth mechanism found for one material necessarily applies to another under different conditions.

In a continuous system in which feed material is added continuously to a tumbling load of pellets, it has been found that regardless of the powder size, the feed is able to form stronger bonds with the charge of established pellets than with other fine particles. This is no doubt related

to the capillary force existing between the fine material and the large pellets, which would be expected to be considerably greater than that between two particles of the fine material. In contrast with batch operation in continuous operations, the layering process of growth maintains a constant total number of pellets and results in an equal increase in the diameter of all the pellets over a given time period²²⁴. The possibility of the pellets breaking in this system is considerably lower than in a batch process presumably due to the cushioning effect of the incoming feed material.

No work has so far been reported on the growth mechanism in a batch oil spherical agglomeration process, apart from fine coal, which would enable comparisons to be made with the results from the present work. It can be concluded, however, that the proposed mechanisms of agglomerate growth in the alumina/oil/SDS solution system are similar to those observed in pelletization studies if the differences in particle properties and bridging liquid content etc., used by different workers are taken into consideration.

CHAPTER 8
SUMMARY AND CONCLUSIONS

8. SUMMARY AND CONCLUSIONS

An investigation has been made of the agglomeration of an aqueous suspension of alkyl sulphate coated alumina by a second immiscible liquid. The conditions for good agglomeration have been determined and the effect of the main variables on agglomerate size, composition and strength studied. The variables investigated included particle size and pulp density, bridging liquid volume, type and viscosity, agitation rate, pH and sodium dodecyl sulphate concentration. A corrugated 600 ml glass beaker gently rotated with its axis inclined to the horizontal was used as the agglomerator.

An attempt was made to determine the physico-chemical conditions required for good agglomeration. Measurements were made of, the adsorption of S.D.S. at the alumina/water and bridging liquid/water interfaces, and the wettability of alumina at different S.D.S. concentrations. The effect of S.D.S. adsorption on the zeta potential of alumina was also determined.

Agglomeration tests were conducted on ilmenite-alumina mixtures to determine whether or not spherical agglomeration was selective. The variables investigated included composition of the mixture and particle size distribution.

From the results of these studies the following conclusions can be made.

1. Aqueous suspensions of alumina can be agglomerated by alkanes provided that the alumina surface is modified by the adsorption of sodium dodecyl sulphate. The amount of alumina agglomerated and the agglomerate size are at a maximum at pH

values below the alumina z.p.c. where the dodecyl sulphate ions can adsorb by Coulombic attraction followed by hydrophobic bonding at high adsorption densities. The agglomerate size increases with dodecyl sulphate concentration but at concentrations approaching the cmc of the surfactant it decreases again.

2. Agglomeration is obtained at S.D.S. concentrations corresponding to receding contact angle and sessile angle between alumina, water and bridging liquid of 90° and over. Under these conditions the adsorption density of S.D.S. at the alumina/water interface is well below that required to form a close packed vertically oriented monolayer. The presence of a high negative zeta potential on the alumina particles does not prevent the formation of agglomerates.

3. The abstraction of S.D.S. from an aqueous alumina suspension is greater when the bridging liquid is present than when it is absent. Furthermore the increase cannot be attributed to adsorption at the bridging liquid/water interface. Greater adsorption at the alumina/bridging liquid interface than, at the alumina/water interface is therefore suggested.

4. Good agglomerates can form under conditions where the interfacial tension between water and the bridging liquid is low.

5. The degree of agitation in the agglomerator affects agglomerate size. Large agglomerates are formed by increasing the rotational speed (within limits) and by decreasing the amount of suspending liquid. The reasons are increased particle-particle collisions and better distribution of the

bridging liquid.

6. Spherical agglomerates of alumina are only formed within a narrow range of bridging liquid volumes. With low bridging liquid additions a bulky flocculated mass is formed and at high additions a paste is produced. The amount of oil required to agglomerate different alumina size fractions is proportional to the porosity of the feed and the pore volume of the agglomerates. With relatively coarse fractions ($\geq 45+27 \mu\text{m}$) the agglomerate pores contain between about 50 and 85% bridging liquid but this fractional filling of the agglomerate pore space is reduced with fine particles and for example $-53+20 \mu\text{m}$ alumina gives good agglomerates for pore fillings between 28% and 83%. At the finer sizes (-53 and $-10 \mu\text{m}$) pastes are formed if the pore volume contains more than 50 and 58% bridging liquid respectively. In agglomerates made from coarse alumina the particle packing is similar to that obtained if the feed is vibrated in a dry bed, but with the fine fractions a greater degree of particle rearrangement occurs during the formation of agglomerates and porosities are lower than in a vibrated system.

7. Very fine alumina ($-10 \mu\text{m}$) is agglomerated most conveniently by preconditioning at high shear rates with part of the bridging liquid volume. The small agglomerates are then enlarged by adding them to the agglomerator with the rest of the bridging liquid volume.

8. Agglomerates of a particular alumina particle size always contain some quantity of air and water irrespective of the conditions of their formation. The water content, however, varies with particle size.

9. The rate of agglomerate growth is determined primarily by the bridging liquid content, and comparatively small changes in oil contents considerably alter the rate of growth. It appears that there is an oil content below which the rate of growth due to agglomerate coalescence is negligible. Differences in agglomerate growth characteristics are observed between the fine and coarse alumina particles. The most significant of these is the existence with the fine particles of an induction period of slow growth which is followed by a period of rapid agglomerate growth especially at high oil contents. Also the fine size fractions have the ability to agglomerate satisfactorily at lower fractional filling of the pore space by oil. The induction period becomes longer as the amount of bridging liquid is decreased. With all size fractions the kinetics of agglomerate growth are highly sensitive to the content of bridging liquid.
10. The sphericity and spread in agglomerate size distribution increases inversely with particle size but depends directly on the oil content. The agglomerate size distributions obtained after different times but at a fixed addition of bridging liquid give coincident curves when plotted in a dimensionless form.
11. Although the agglomerate size vs. oil addition relation is similar with bridging liquids having different properties (viscosity, density, volatility, solubility in water) the oil requirements to achieve a certain agglomerate size are not the same. Less water is trapped within agglomerates as the viscosity of the oil is increased up to 2.99 mPa s.

12. Stronger agglomerates are produced by decreasing the particle size or by increasing the spread of the alumina size distribution in agreement with other work on pelletization and with theoretical considerations. Generally stronger agglomerates are also obtained at higher oil contents up to a certain level. The strength of agglomerates made from alumina size fractions which do not contain particles less than 10 μm can be predicted by the capillary forces theory.

13. When bridging liquid is first added to a suspension, highly porous, loosely held flocs, or large aggregates of alumina particles are formed by coalescence, and the tumbling action assisted by capillary forces converts these configurations to stable agglomerates. In cases where subsequent growth occurs there are two basic mechanisms contributing to the growth of the small agglomerates which are formed initially. These mechanisms are first coalescence, and second crushing and layering. Growth may take place due to one or both of these mechanisms, combined possibly with certain secondary processes. Crushing and layering dominates only in cases where weak agglomerates are formed.

14. Alumina can be selectively agglomerated and separated from mixtures of alumina and ilmenite using sodium dodecyl sulphate to modify the alumina surface. High recoveries and product grades are obtained at different mixture compositions and particle sizes even for very fine sizes. The mean size is affected by both particle size of the two minerals and mixture composition.

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