

THIN FILM DRAINAGE AND
BUBBLE/PARTICLE ATTACHMENT
IN FROTH FLOTATION

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by

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Thesis Submitted to the University
of South Australia for
the Degree of Doctor of Philosophy in
Applied Science in Chemical Technology

February 1994

ABSTRACT

Three stages of bubble/particle interaction can be identified, all of which must occur successfully for flotation to take place. These stages consist of bubble/particle collision, followed by attachment and establishment of a stable bubble/particle aggregate. When a particle approaches a bubble the intervening thin liquid film must drain and rupture for attachment to take place. Experiments were conducted in which the influence of the degree of hydrophobicity of the solid surface and the effect of the background electrolyte concentration on the drainage rate of thin aqueous films trapped between a quartz plate and a fast approaching air bubble were examined.

The drainage rate was measured using laser interferometry to determine the film thickness as the air/aqueous solution interface approached the quartz/aqueous solution interface. When a bubble was rapidly bulged against a solid surface, a dimple formed such that the thickness at the boundary ring of the intervening liquid film was much smaller than it was at the film centre. At hydrophilic quartz plates the film drained to give a film of uniform thickness, whereas films formed at hydrophobic quartz plates drained only until they ruptured spontaneously, resulting in air/quartz contact.

The thin film drainage rate at hydrophilic surfaces was found to be influenced by changes in the ionic strength of the aqueous solution at surprisingly long distances, with differences in the drainage rates first becoming apparent when the film thickness at the boundary ring was approximately $1\mu\text{m}$. Similarly, the boundary ring film thickness was around $1\mu\text{m}$ when differences in the drainage rate were first observed with increasing hydrophobicity of the quartz plate.

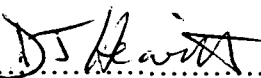
These results suggest that a hydrophobic force exists between an air bubble and a solid surface of weak to moderate hydrophobicity and is similar in magnitude to the electrical double layer force in dilute electrolyte solutions of $10^{-3}\text{mole dm}^{-3}$ in concentration. Furthermore, the range over which these forces operate appears to be considerably longer in a dynamic situation when one of the interfaces is deformable than is the case when equilibrium is attained.

Single bubble/particle attachment experiments were performed in a modified Hallimond tube where particles (in the size range 5 to $80\mu\text{m}$) were collected by single bubbles (in the size range 0.75 to 2mm) produced relatively slowly and in a single stream. The number of particles floated per bubble was found to increase with increasing particle hydrophobicity. By comparison between the number of floated particles and the

theoretical number of collisions the efficiency of attachment was determined. The attachment efficiency was found to decrease with increasing particle size. Larger bubbles were less efficient. The ionic strength of the solution in which the particles were suspended had little effect on the attachment efficiency of strongly hydrophobic particles. However, increased electrolyte concentration did improve the attachment efficiency of the less strongly hydrophobic particles. This effect increased with decreasing hydrophobicity. Induction time calculations showed that there is a minimum in the range of particle diameters from 30 to 40 μm , shifting to slightly lower particle sizes for smaller bubbles. These results allow a qualitative interpretation of the relative contributions of thin film drainage effects and bubble spreading kinetics.

The measured attachment efficiencies were used in combination with valid collision and stability models to calculate fast flotation rate constants from first principles for several particle sizes and three different contact angles. A satisfactory comparison with rate constants extracted from previous 'batch' flotation data was made. The experimental observations made studying the influence of the particle size and hydrophobicity, bubble size and the ionic strength, on the attachment efficiency has significant flotation process engineering implications. Consequently it is expected that development of more accurate models of the flotation process will continue.

This is to certify that this thesis contains no material which has been accepted for the award of any other degree or diploma and that, to the best of the candidate's knowledge and belief, this thesis contains no material previously published or written by another person, except when due reference is made in the text of the thesis.

A handwritten signature in black ink, appearing to read 'DJ Hewitt', is written over a horizontal dotted line.

David J Hewitt

ACKNOWLEDGEMENTS

I would like to acknowledge my supervisor, Professor John Ralston whose drive and enthusiasm was always an inspiration. I am grateful for both the general assistance of Dr. Daniel Fornasiero and, more particularly, with the theoretical model calculations.

Financial support from the Australian Research Council is gratefully acknowledged.

Dr. Len Fisher's supervision of the thin film experiments is gratefully acknowledged as well as his time and effort in making my time at University College London productive and enjoyable.

I would like to thank the staff of the School of Chemical Technology who not only helped me from time to time, but also provided assistance in sounding out various experimental ideas. The glass-blowing skills of Mr. Chris Smith also proved to be invaluable in this respect.

For the love of Marianne I can never say enough. I am also grateful for the support of Marianne's mother and my father.

Memoriam

This thesis is dedicated to the memory of my mother who died (26/5/91) during the course of my study.

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Glossary of Key Terms

α is the angle for the transition of the spherically deformed part of the bubble surface to the part which is unperturbed

γ is the surface tension

γ_{LG} is the surface tension of the liquid/gas interface

γ_{SG} is the surface tension of the solid/gas interface

γ_{SL} is the surface tension of the solid/liquid interface

γ_s is the Young-Laplace pressure

ς is the curvature of the interface

ϕ is the fraction of the particle total

η is the bulk viscosity

η_a is the apparent viscosity measured

φ is the stream function of the fluid flow around the bubble

φ_c is the grazing trajectory of the fluid flow at the bubble surface

ψ_{qw} is the surface potential at the quartz-water interface

ψ_{aw} is the surface potential at the air-water interface

κ^{-1} is the Debye length

λ is the wavelength

μ_i is the chemical potential of species i

$\pi(h)$ is the disjoining pressure corresponding to film thickness, h

π_{el} is the disjoining pressure due to electrical double layer forces

π_{st} is the disjoining pressure due to steric or structural forces

π_{vdw} is the disjoining pressure due to van der Waals forces

θ is the equilibrium contact angle

θ_c is the critical contact angle

θ_m maximum angle of contact

θ_n is the collision angle

ρ_p is the density of the particle

ρ_f is the density of the fluid

$\Delta\rho$ is the difference between the densities of the particle and the fluid

τ_c is the the contact time

τ_{ind} is the induction time

τ_{ffd} is the thin film drainage time

τ_{plc} is the time of movement of the three phase line of contact

$v_{p\theta}$ is the tangential component of the particle velocity

u_b is the velocity of the bubble

u_p is the velocity of the particle

v_r is the velocity of the particle relative to the bubble
 ξ_0 is the surface vorticity (the tangential velocity gradient at the bubble surface)
 v_{Re} is the velocity of film thinning according to Reynolds theory
 v_t is the total velocity of film thinning
 A_{ij} is the Hamaker constant for bodies of material i and j at short distances in a vacuum
 A_{sp} is the specific surface area per gram of solid
 C is the particle concentration (per unit volume)
 C_0 is the particle concentration at time $t = 0$
 d_b is the bubble diameter
 d_p is the particle diameter
 $d_{max,g}$ is the gravitational maximum particle size which can be floated
 $d_{max,v}$ is the kinetic maximum particle size which can be floated
 $d_{min,k}$ is the minimum particle size which can be floated
 E_A is the efficiency of bubble/particle attachment
 E_{Coll} is the efficiency of bubble/particle collection
 E_C is the efficiency of bubble/particle collision,
 E_{det} is the energy of detachment
 E_G is the gravitational effect on the collision efficiency
 E_{Ic} is the interception effect on the collision efficiency
 E_{Id} is the ideal collision efficiency
 E_{In} is the inertial effect on the collision efficiency
 E_S is the efficiency of stability of the bubble/particle aggregate
 F is the force driving the film thinning
 G is the gas volumetric flow rate
 g is the acceleration due to gravity
 h is the film thickness
 h_0 is the thickness in the centre of the film
 h_b thickness at the barrier ring of the film
 k is the Boltzmann constant,
 k_f is the "fast" rate constant of flotation
 k_s is the "slow" rate constant of flotation
 N_b is the number of bubbles per unit volume
 n is the number of ions per unit volume θ is the fraction of all colliding particles that collide between the front stagnation point and angle θ_n
 n_i is the number of moles of species i
 n_0 is the refractive index of the air bubble
 n_1 is the refractive index of the aqueous film
 n_2 is the refractive index of the quartz plate

P is the pressure

P_b is the pressure within the bubble

R is the fraction of particles recovered

R_b is the radius of the bubble

R_p is the radius of the particle

r_f is the film radius

S is the entropy

St is the Stokes Number

T is the absolute temperature

V is the volume of the film

V_r is the reference volume of height h through which the bubbles rise

W_{SG} is the work done to separate liquid water from the solid surface and replace it by an adsorbed water layer in equilibrium with saturated water vapour

ze is the charge on the electrolyte ions

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CHAPTER 1. INTRODUCTION

The aim of this study is to investigate the elementary processes which must occur for froth flotation to take place. Froth flotation is a heterocoagulation process, which allows for the separation of particles of different hydrophobicities. Froth flotation is commonly used for the beneficiation of a wide variety of ores, coal oil shale, tar sand and industrial waste and is therefore of considerable economic importance.

As a separation process, froth flotation has been around for over 100 years, yet still research continues on the intricacies of the process. In essence, froth flotation involves bubbling air through a slurry of particles and removing the more hydrophobic particles to a froth layer at the top of a flotation cell, where the froth can be collected along with the floated particles. A mineral ore is mined and then crushed to a particle size which is typically less than $100\mu\text{m}$, followed by the addition of chemicals known as collectors to an aqueous slurry of the particles. The role of the collector is to selectively adsorb on to the desired mineral rendering it hydrophobic, while other particles in the slurry remain hydrophilic or, at least, of lesser hydrophobicity. When air is bubbled through the slurry in a flotation cell, hydrophobic particles become attached to the air bubbles and rise to the froth layer on the surface of the suspension. Frothers are added to the float cell to maintain the froth layer until the froth is separated from the slurry, taking with it the floated mineral particles.

In flotation practice, mineral selectivity is achieved by the use of various reagents such as the collectors and frothers already mentioned. Other chemicals act as depressants, activators and modifiers, all of which affect the recovery of the particles. In this study a fundamental understanding is sought of the interaction between the particle and the air bubble, so a model system is required in which the parameters considered to be significant can be controlled. Considering only the interaction of an air bubble with a hydrophobic particle, certain elementary microprocesses have been identified which must occur for flotation to take place.

These elementary processes can be divided into three steps as follows: a) collision of the particle with the bubble, with the formation of an intervening thin liquid film; b) drainage of the thin film to the point of rupture, followed by recession of the three phase line of contact, giving rise to an area of contact between the particle and the bubble leading to; c) formation of a stable bubble/particle aggregate.

The efficiency of particle collection, E_{Coll} , can be described in terms of the efficiency with which these elementary processes take place giving:

$$E_{\text{Coll}} = E_C E_A E_S$$

where E_C is the efficiency of bubble/particle collision, E_A is the efficiency of bubble/particle attachment, and E_S is the efficiency of stability of the bubble/particle aggregate.

Considerable work has been carried out developing models which describe the efficiency of collision between mineral particles and bubbles. The efficiency of formation of stable bubble/particle aggregates has also been investigated although some arguments still exist. The efficiency of attachment is less well understood. Several models have been used to predict the contact time between a bubble and a particle; the contact time being the time period during which the particle is in a region of "close approach" to the bubble. The induction time is the time required for bubble/particle contact to form after the particle has moved into the region of close approach to the bubble (i.e. the particle has "collided" with the bubble). Previous work has shown that if the induction time is less than the contact time, then the particle will become attached to the bubble.

Collision between a solid particle and an air bubble leads to the formation of an intervening thin liquid film. The time for this thin film of liquid to drain, rupture, and form a stable area of contact is the induction time. A definitive model allowing prediction of the induction time for a bubble/particle system has yet to be described. The most significant parameters in determining the induction time are the hydrophobicity of the particle and the ionic strength of the medium in which the particles are suspended.

Questions arise concerning the stability of the thin liquid film as well as the effect of hydrophobicity and ionic strength on the drainage of the thin film, particularly the distance at which these effects become significant. From a hydrodynamic basis, models have been proposed predicting the contact time between a particle and a bubble, with the two most important parameters in these models being the diameters of the particle and bubble (and their velocity which, however, is a function of their diameter).

The impact of the degree of hydrophobicity of the particle on the attachment efficiency and the bubble and particle size dependence on the overall collection efficiency still require elucidation. To study the influence of these parameters, particularly on the efficiency of attachment, a model system must be used which allows strict control of variables likely to affect the particle collection efficiency of the bubbles and which also permits certain parameters to be varied in a controlled manner.

The work reported here deals with experiments conducted using a model system, in two separate aspects of the fundamentals of the bubble/particle attachment process. The first section probes the effect of surface hydrophobicity and ionic strength of the background electrolyte solution, on drainage and rupture of thin aqueous films when a bubble is forced against a quartz plate. In the second part, experiments on particle collection by a single stream of bubbles and the resulting attachment efficiency of the particles by the bubbles are discussed.

In the thin film drainage experiments a quartz plate was used. Methylation was performed using trimethylchlorosilane (TMCS), allowing the hydrophilic/hydrophobic nature of the plate to be varied in a controlled manner. An air bubble was bulged against the plate and the rate of drainage of the thin liquid film formed between the bubble and the plate was studied using laser interferometry. To more closely model the situation which occurs in flotation when a bubble collides with a particle, both being in motion, the thin film drainage rate was measured by rapidly expanding the air bubble against the plate.

Variations in the thin film drainage rate with changes in surface hydrophobicity of the plate and/or changes in the ionic strength of the background electrolyte solution, allowed the effect of the hydrophobic and electrical double layer forces on the drainage rate to be observed. The effect of these "surface forces" was of particular interest as it has already been established that it is indeed these very forces which control the stability and thickness of thin liquid films on surfaces. Models have been developed to describe the rate of drainage of thin films and, in most cases, they have been based on hydrodynamics with little consideration of the effects of surface forces, for the latter are thought not to extend far into the solution. There is also little experimental data to test the theoretical models, including the effect of surface hydrophobicity and ionic strength, particularly with the deformable surface.

From the viewpoint of flotation, a good description of the rate of drainage of the thin aqueous film should permit a better understanding of the sub-processes which must occur during the induction time. The ultimate goal is to adequately model the flotation process. Bubble/particle interactions experiments were conducted in order to obtain measurements of the efficiency of particle collection by bubbles under well-controlled conditions. The number of particles collected per bubble was compared with the maximum number of collisions which could have occurred as calculated using recent models taken from the literature, permitting the attachment efficiency to be determined. These measurements were made for three bubble sizes, for three different size fractions of particles and for a range of hydrophobicities. The attachment efficiency was also determined as a function of the ionic strength of the background electrolyte solution.

Calculation of the sliding times for the various bubble/particle combinations involved, again using recent models from the literature, allowed derivation of the induction times corresponding to each value of the attachment efficiency. The induction time has been discussed in terms of the contributions of the thin film drainage time and the time for movement of the three phase line of contact across the particle surface.

Finally, the overall collection efficiencies (E_{Coll}) were calculated. These values of E_{Coll} were used to determine values of the 'fast' rate constant for the conditions under which the experiments reported by Crawford and Ralston (1988) were performed. General agreement between the rate constant results from the two independent sets of experiments was considered as validation of both the models and the approach taken in the interpretation of the results obtained in this study.

CHAPTER 2. THIN FILM DRAINAGE - LITERATURE REVIEW

When a hydrophobic mineral particle approaches an air bubble in a flotation cell, the two interfaces (viz. the air/liquid interface and the solid/liquid interface) are separated initially by a thin aqueous film. The liquid film must drain until the film is thin enough to rupture. If the drainage rate is slow the film will not reach the point of rupture, the particle will not become attached to the air bubble and flotation will not take place. A study of the thin film drainage rate and the factors which affect it are therefore of interest due to their importance in understanding the process of bubble/particle attachment and hence flotation.

When an air bubble approaches a finite solid surface in a liquid, an area of "contact" (or interaction) may be identified, as indicated in Figure 2.1. Liquid will flow out of the film because of the pressure difference between the film and the bulk liquid.

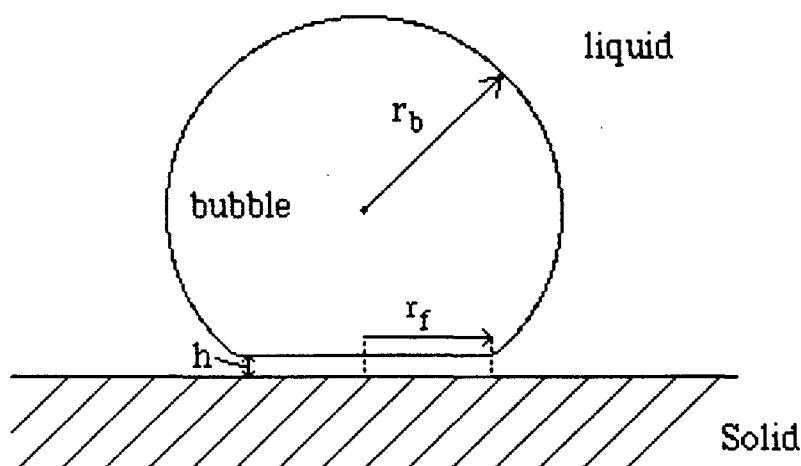


Figure 2.1 Formation of a wetting film between a bubble and a solid plate.

2.1 Disjoining Pressure

The concept of the disjoining pressure arose from the classical experiments of Derjaguin and Kussakov (1939) who observed that when an air bubble is pressed against a hydrophilic glass plate immersed in water, the intervening liquid drains, to leave a uniform equilibrium film. The film behaves as though there were an excessive pressure acting normal to the film opposing further reductions in film thickness. This

excess pressure, referred to by Derjaguin as the disjoining pressure, represents the difference between the pressure within the bubble and that in the bulk liquid adjacent to the solid surface. If the film radius is considerably smaller than the bubble radius, the pressure inside the bubble will change only slightly when it is pressed against the solid. The pressure in the film will be same as the pressure in the bubble so essentially the disjoining pressure is the difference between the pressure in the film and the bulk liquid.

For the water film between an air bubble and a solid surface, a small reversible change in the internal energy (dU) is given by (Hunter, 1987a):

$$dU = TdS - PdV + \sum \mu_i dn_i \quad 2.1$$

where T is the absolute temperature, S is the entropy, μ_i is the chemical potential of species i , n_i is the number of moles of species i , P is the pressure, and V is the volume of the intervening film.

The temperature and the pressure are constants for all elements of the interface and S , n and U are extensive variables. It is possible to say that the whole interface will have a volume V obtained by summing the elemental volumes (dV) and thus, the chemical potential of species i in the interface will be obtained by summing the dn_i . Similarly $S = \sum dS$ and $U = \sum dU$, so that the internal energy of the interface is given by:

$$U = TS + \sum \mu_i n_i - PV \quad 2.2$$

Differentiating equation 2.2 gives

$$dU = TdS + SdT + \sum \mu_i dn_i + \sum d\mu_i n_i - PdV - VdP \quad 2.3$$

Subtraction of equation 2.1 from equation 2.3 yields:

$$SdT - VdP + \sum d\mu_i n_i = 0 \quad 2.4$$

For pure water, the Gibbs free energy of the system is given by:

$$\sum d\mu_i n_i = n_{H_2O} d\mu_{H_2O} \quad 2.5$$

At constant temperature and combining equations 2.4 and 2.5, gives:

$$dP = \frac{n_{H_2O}}{\bar{V}} d\mu_{H_2O} \quad 2.6$$

(Note that $\frac{V}{n_{H_2O}}$ is the molar volume of pure water $\bar{V}$)

Equation 2.6 indicates that a change in the chemical potential of water may cause a change in interface pressure and the absolute value of dP is the disjoining pressure, so that the disjoining pressure is given by:

$$\pi = \frac{d\mu_{H_2O}}{\bar{V}} \quad 2.7$$

Thus π results from the difference in chemical potential of water in the bulk and in the film. The chemical potential of water, μ_{H_2O} , is not necessarily constant across the interface, but is rather a function of the distance, h , from the surface. Noting that $n_{H_2O}\mu_{H_2O}$ is the Gibbs free energy, G , gives:

$$\pi(h) = -\left(\frac{\partial G(h)}{\partial h}\right)_{T,P} \quad 2.8$$

which indicates that the disjoining pressure $\pi(h)$ is defined as the derivative of the specific excess Gibbs free energy of the film with respect to the film thickness h . Thus, when $\pi(h) > 0$, the liquid film is stable and resists thinning. If $\pi(h) = 0$, the layer is unstable with no resistance to thinning, while if $\pi(h) < 0$, attraction exists and thinning occurs with spontaneous rupturing of the film.

The disjoining pressure consists of contributions from essentially three sources, i.e. electrical double layer forces, van der Waals forces and steric or structural forces: these contributions are considered to be additive (Derjaguin and Churaev, 1976) hence:

$$\pi(h) = \pi_{vdw} + \pi_{el} + \pi_{st} \quad 2.9$$

As mentioned earlier, the disjoining pressure is given by:

$$\pi(h) = P_b - P_l \quad 2.10$$

where P_b is the pressure within the bubble and P_l is the pressure in the bulk liquid adjacent to the solid surface.

$P_b - P_l$ is equal to $2\gamma/r_b$ where γ is the surface tension of the liquid and r_b is the radius of the bubble. This provides a very useful method for the investigation of small disjoining pressures at solid/liquid/gas interfaces.

The components which contribute to the overall disjoining pressure can be considered individually and, by summation of the components the total disjoining pressure can be determined. This process leads to the validation of the DLVO theory (Derjaguin and Landau, 1940 and Verwey and Overbeek, 1948) where, by describing the interaction of two interfaces (the solid/liquid and the liquid/air interfaces) in terms of the van der Waals and electrical double layer forces, not only the stability of the thin liquid film was rationalised but also the equilibrium thickness of the wetting layer.

2.1.1 van der Waals Component

Molecular forces between atoms, ions and molecules, known collectively as van der Waals forces, occur due to interactions between ions, permanent dipoles, induced dipoles and fluctuating elementary charges in neutral molecules. The so-called microscopic theory attributed to Hamaker (1937) involved the summation of the interaction between the individual pairs of molecules. Following this concept interactions involving various geometries have been considered, with the van der Waals disjoining pressure for two large plane-parallel plates separated by a distance h given by (Schulze, 1984):

$$\pi_{vdw} = \frac{-A_{ij}}{6\pi h^3} \quad 2.11$$

where A_{ij} is the Hamaker constant for bodies of material i and j at short distances in a vacuum.

A more rigorous treatment was developed by Lifshitz (see Visser, 1972), using the macroscopic approach in which the interacting phases are considered as being of a fluctuating, continuous nature with interaction occurring through a continuous medium. The Lifshitz treatment makes allowance for the effect of the dielectric permeability of the medium on the propagation of the attraction forces, but suffers from the disadvantage that it requires a knowledge of the dielectric properties of the medium over a wide range of frequencies. For asymmetrical cases such as the air/aqueous solution/quartz configuration (where $n_{air} < n_{aq\ sol'n} < n_{quartz}$), the Hamaker constant is negative which means that the van der Waals force is repulsive (Visser, 1972).

2.1.2 Electrostatic Component

When two interfaces, such as a quartz/aqueous solution interface and an aqueous solution/air interface, approach each other, their associated ion double layers overlap one another. In the region of overlap the ion concentration is higher than the bulk phase, giving rise to osmotic pressure and electrostatic interaction forces. These forces are dependent on the electrical potential at the interface and the ionic strength of the background electrolyte solution. These forces have been studied extensively and are described in considerable detail in colloid chemistry textbooks (e.g. Hunter, 1989).

A number of different equations for the electrostatic component of the disjoining pressure can be derived, depending upon the geometry and the the magnitude of the surface potentials involved and considering the interfaces to be planar surfaces separated by a univalent electrolyte the electrostatic component is given by the following expression developed by Hogg, Healy and Fuerstenau (1966):

$$\pi_{el} = \frac{4e^2n}{kT} \left(\frac{-\left(\psi_{qw}^2 + \psi_{aw}^2\right) + \psi_{qw}\psi_{aw}(\exp(\kappa h) + \exp(-\kappa h))}{(\exp(\kappa h) + \exp(-\kappa h))^2} \right) \quad 2.12$$

where n is the number of ions per unit volume in the aqueous film, k is the Boltzmann constant, ze is the charge on the electrolyte ions, T is the absolute temperature, ψ_{qw} and ψ_{aw} are the surface potentials at the quartz-water and air-water interfaces respectively and κ^{-1} is the Debye length and is given by: $\kappa^{-1} = \left(\frac{\epsilon kT}{2nz^2e^2} \right)^{1/2}$ in which ϵ is the permittivity (Shaw, 1980). This expression is valid for all κh , but only for $\psi < 25\text{mV}$. Alternatively, Verwey and Overbeek (1948) derived the following equation for the disjoining pressure between two plane-parallel surfaces of dissimilar surface potential :-

$$\pi_{el} = \left(64nkT \tanh\left(\frac{ze\psi_{qw}}{4kT}\right) \tanh\left(\frac{ze\psi_{aw}}{4kT}\right) \right) e^{-\kappa h} \quad 2.13$$

Although no assumptions have been made regarding the magnitude of the surface potentials, this equation is only valid for $\kappa h \gg 1$. When calculating π_{el} , it has generally been common, but not necessarily correct, practice to use experimental zeta potential values in place of surface potentials, particularly for cases of low ionic strength; i.e. $I < 10^{-3}\text{mole dm}^{-3}$ (Lyklema, 1977).

2.1.3 Structural Component

Structural forces may arise from the interaction of structurally modified liquid layers which exist at the interface (Derjaguin and Churaev, 1974). It is well recognised that hydrophilic solids are strongly hydrated and the water molecules at the surface have a well ordered structure. So, upon interaction of a quartz/water interface and air/water interface, a certain amount of energy is required to disrupt the ordered water structure (i.e. an increase in entropy).

Measurements of the adsorption of water vapour on quartz made by Pashley and Kitchener (1979) have shown that the radius of action of structural forces can substantially increase (several times) with increasing hydrophilicity of the solid substrate. Marcelja and Radic (1976) proposed that the decay of the structural forces in pure water could be approximated by an exponential dependence such as:

$$\pi_s(h) = K \exp(-h/l) \quad 2.14$$

The value of the constant K was related to the ordering state of the dipole moments of the liquid and the value of constant l to the corresponding correlation length. A further correction allows separation of the part of the boundary layer immediately adjoining and more strongly bound to hydrophilic surfaces and whose state is less sensitive to changes in the electrolyte concentration as suggested by Pashley (1982):

$$\pi_s(h) = K \exp(-h/l) + K_0 \exp(-h/l_0) \quad 2.15$$

with the parameters K_0 and l_0 relating to the inner part of the boundary layer. Churaev and Derjaguin (1985) pointed out that there were no grounds available for distinguishing Pashley's hydration forces from the general definition of structural forces, including all of the changes in the structure of water under the influence of the solid surface. Churaev and Derjaguin compared theoretical calculations and experimental results with the inclusion of structural forces in the disjoining pressure calculations and set $K > 0$ for hydrophilic surfaces and $K < 0$ for some hydrophobic surfaces.

Derjaguin and Churaev (1989) recognised in their review of the current state of the theory of surface forces that the development of the theory of structural forces is very much in its infancy.

2.1.4 Variations in Disjoining Pressure with Film Thickness

Examination of the disjoining pressure as a function of film thickness permits the prediction of film stability. In Figure 2.2, curve i) illustrates the behaviour expected for a water film held between a hydrophilic surface and an air bubble and since $\pi(h)$ is positive everywhere the film will be stable at all thicknesses (Ralston, 1983).

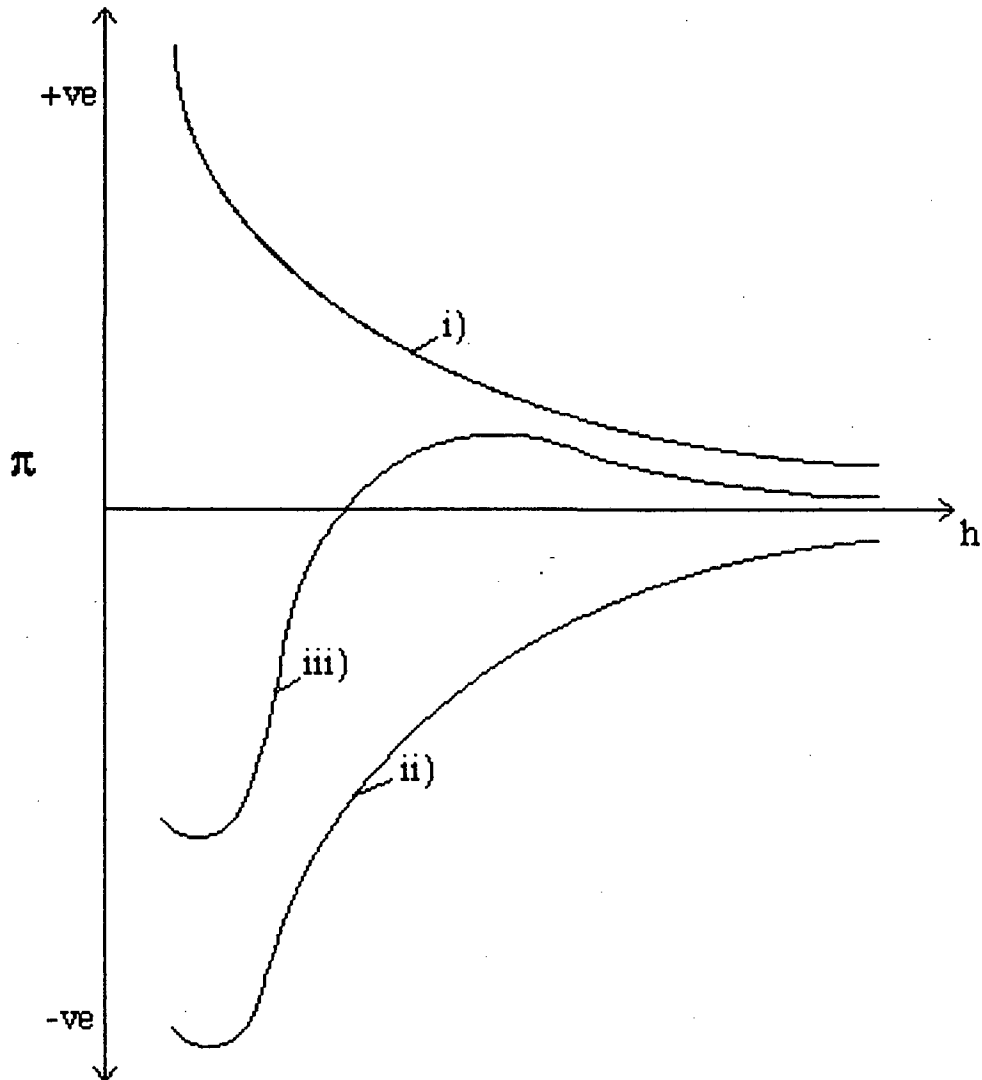


Figure 2.2 Variation of the disjoining pressure with film thickness for the case of an air bubble approaching a solid surface of varying hydrophobicity (curve i) - hydrophilic surface; ii) strongly hydrophobic surface; iii) moderately hydrophobic surface).

In the case of a water film between an extremely hydrophobic solid and an air bubble, represented by curve ii), $\pi(h)$ is negative, so the film is completely unstable and will rupture spontaneously. In the case of surfaces which are moderately hydrophobic π will vary as illustrated by curve iii), giving rise to the possibility of a relatively thick metastable film (about the thickness of the double layer, κ^{-1}). This film may become unstable and thin further, and finally rupture as was the case for a more strongly hydrophobic surface.

2.2 Thickness of Wetting Films

The thickness of equilibrium wetting films has been determined experimentally by a considerable number of workers, who have used the disjoining pressure concept to conveniently explain the observations made. For example, Read and Kitchener (1967) determined the thickness of wetting films left when a liquid drains from a smooth silica plate. An air bubble was trapped, and a polished vitreous silica disc was raised slowly towards the air bubble under scrupulously cleaned conditions. The thickness of the thin liquid film was determined by examining the series of Newton's rings produced by interference of the monochromatic light used to illuminate the film.

Read and Kitchener (1969) further examined the variation in equilibrium film thickness with electrolyte concentration on silica surfaces and showed that for $h > 20\text{nm}$ the most important contribution to the disjoining pressure arose from the electrical double layer repulsive forces. Stable films of uniform thickness were observed, the thickness being of the correct order of magnitude as predicted by DLVO theory with decreasing thickness with increasing electrolyte concentration consistent with the theory.

Experiments similar to those of Read and Kitchener have been reported by Schulze and Cichos (1972) in which a very small air bubble was pressed against a quartz plate with the film thickness determined using an interferometric technique. For pH values ranging from 5 to 10, little change in the film thickness was observed, while at pH=2 close to the point of zero charge for quartz, the film thickness remained constant at approximately 10nm irrespective of the strength of the KCl solution being used in the experiments. The results (at neutral pH) of Schulze and Cichos are summarised in Table 2.1.

KCl (mole dm ⁻³)	Zeta Potential/ quartz/solution (mV)	Zeta Potential/ air/solution (mV)	Measured Film Thickness (nm)
10 ⁻⁵	-87	-34	52
10 ⁻⁴	-87	-34	52
10 ⁻³	-70	-34	41
10 ⁻²	-34	-34	19
10 ⁻¹	-20	-34	11

Table 2.1 Variation in the thickness of wetting films on quartz (Schulze and Cichos, 1972), together with zeta potential data for the quartz/solution and air/solution interfaces.

The rapid coalescence of gas bubbles with hydrophobic surfaces in water has been observed for many years (e.g. Evans, 1954). The formation of metastable flat aqueous films on hydrophobic silica surfaces (Blake and Kitchener, 1972) as well as the rupture of aqueous dimpled films on silica surfaces in the presence of surfactants (Aronson and Princen, 1975) have also been studied.

Blake and Kitchener (1972) determined wetting film thicknesses on optically polished vitreous silica plates. Clean plates were completely wetted, whereas with methylated silica non-zero contact angles were observed. The film thickness measurements for these two types of surfaces however, showed very little difference in behaviour, provided the films were formed slowly. In earlier work (Laskowski and Kitchener, 1969) it had been established that the zeta potential of a quartz interface was essentially unaffected by the methylation process.

Blake and Kitchener concluded that the formation of metastable films on hydrophobic surfaces was due to long-range electrical double layer repulsion and the ultimate rupture of the metastable flat films was due to other forces of distinctly shorter range which became effective during local thinning caused by mechanical or thermal fluctuations. They suggested that the removal of silanol groups by methylation leaves a hydrophobic surface because there exists, at the junction of the non-polar groups with the water phase, a boundary plane across which there are fewer hydrogen bonds per unit area than across any plane in bulk water.

The adsorption of water vapour on smooth crystalline quartz was studied by Pashley and Kitchener (1979). They varied the relative vapour pressure and determined the film thickness using ellipsometry. Films of 150nm thickness were observed in saturated water vapour, although the film thickness decreased markedly with the slightest amount of contamination.

Films of aqueous KCl solutions on the surface of quartz were investigated by Zorin et al (1991). The films were formed by pressing down a spherical meniscus from a cylindrical capillary onto a planar surface. In these experiments, with KCl solutions of concentrations of 10^{-2} – 10^{-3} mole dm^{-3} , the β -films stabilised by the π_{el} component of the disjoining pressure were observed to break down to a thin α -film (stabilised by the π_{vdw} component) in the course of a few tens of seconds. When these films rupture a finite contact angle is measured in contact with thin α -films.

Zorin et al (1991) also reported thicknesses of wetting films formed at different capillary pressures. The value of ψ_{qw} was taken from experimental data and the value of ψ_{aw} was chosen to best fit the experimental film thickness. For KCl concentrations of 10^{-4} – 10^{-3} mole dm^{-3} the best agreement was found for a value of $\psi_{aw} = -45\text{mV}$ which is in agreement with data obtained by Exerowa (1969).

The zeta potential at the air/solution interface had been shown to have a negative sign in work reported some time ago (i.e. Alty, 1924). Subsequent observations (e.g. Schulze and Cichos, 1972; Huddleston and Smith, 1976; Collins et al, 1978) have also shown that the zeta potential of air bubbles is negative, and the most commonly used values are those of Schulze and Cichos, mentioned earlier.

Derjaguin and Churaev (1987) measured the contact angle for aqueous KCl solutions on modified quartz. They used the well-known Frumkin-Derjaguin theory of wetting to relate the equilibrium contact angle to the isotherm of the disjoining pressure of the wetting film and, as shown by Derjaguin and Churaev, the relationship is given by:

$$\cos \theta = 1 + (1/\gamma) \left(\int_{h_0}^{\infty} \pi(h) dh + \pi_0 h_0 \right) \quad 2.16$$

where θ is the equilibrium contact angle, h_0 is the thickness of the wetting film in equilibrium with the bulk liquid, π_0 is the disjoining pressure corresponding to that film thickness, and $\pi(h)$ is the isotherm of the disjoining pressure. Derjaguin and Churaev found good agreement between measured contact angles and calculated angles using

values of ζ_{aw} which they had reported earlier (Churaev and Derjaguin, 1985) and ranged from -55mV for $10^{-5}\text{mole dm}^{-3}$ KCl up to 0mV in $10^{-1}\text{mole dm}^{-3}$ KCl.

Li and Somasundran (1991) reported values for the zeta potential of nitrogen bubbles measured using a Lazer Zeta Meter. Values for ζ_{aw} were given as a function of pH for 10^{-1} , 10^{-2} and $10^{-5}\text{mole dm}^{-3}$ NaCl and pH6 for example, varied from -75mV in $10^{-5}\text{mole dm}^{-3}$ NaCl up to approximately -20mV in $10^{-1}\text{mole dm}^{-3}$ NaCl.

A review of wetting films was presented by Churaev and Zorin (1992) in which β -films are described on the basis of long-range electrical double layer forces and α -films are considered to be controlled by the action of structural forces. Interference methods were used by Zorin et al (1992) to determine the thickness of wetting films of aqueous solutions of NaCl on silica and the experimental data were in good agreement with predictions according to theory based on electrostatic forces acting between film surfaces with unequal potentials.

2.3 Drainage of Thin Films

Of considerable interest is the rate of drainage of thin films to either form stable thin films, or, in the case of unstable films, drain to the point of rupture. As a first approximation Reynolds' theory of hydrodynamic lubrication can be used to describe the rate of liquid flow which occurs for a thin liquid film which is formed between two parallel rigid discs. Reynolds (1886) proposed:

$$F = \frac{3n^2\eta\pi}{2h^3} r_f^4 \frac{dh}{dt} \quad 2.17$$

where h is the film thickness, η is the bulk viscosity, F is the force driving the film thinning, n is the number of immobile surfaces and r_f is the film radius. This theory is based on a simplification of the Navier-Stokes equations of continuum hydrodynamics.

Scheludko and Platikanov (1961) showed that, since pressure is related to force by the following equation:

$$P = \frac{F}{\pi r_f^2} \quad 2.18$$

where, in the case of a bubble pressed against a solid plane, P is the pressure causing the film thinning, then substitution for F in equation 2.17 gives:

$$\frac{dh}{dt} = -\frac{2h^3P}{3n^2\eta r_f^2} \quad 2.19$$

which leads to:

$$\frac{d(1/h^2)}{dt} = \frac{16P}{3n^2\eta r_f^2} \quad 2.20$$

Where the bubble surface is extendable, $n=1$ and:

$$\frac{1}{h^2} - \frac{1}{h_o^2} = \frac{16P}{3\eta r_f^2} (t - t_o) \quad 2.21$$

For a draining film, $P = \frac{2\gamma}{r_b} - \pi$, giving:

$$\frac{1}{h^2} - \frac{1}{h_o^2} = \text{constant} \left(\frac{2\gamma}{r_b} - \pi \right) (t - t_o) \quad 2.22$$

The Reynolds theory gives a satisfactory description of the drainage of non-polar liquids between molecularly smooth mica surfaces, down to film thicknesses of 50nm or so, as shown by Chan and Horn (1985). In the case where one of the interfaces can be deformed, the situation is not as simple. It was first noted by Derjaguin and Kussakov (1939), but also by other workers since, that when a bubble approaches a solid surface, the bubble dimples and acquires a reverse curvature so that the central lens of liquid is entrapped by a thinner barrier ring.

A hydrodynamic theory for the profile and evolution of the dimple was developed by Frankel and Mysels (1962). This theory takes into consideration only the capillary pressure but neglects the disjoining pressure which arises at low film thicknesses. Frankel and Mysels introduced a radial pressure gradient given by $\left(-\gamma \frac{d^3z}{dr^3} \right)$ and they derived equations for the film thickness at the centre, h_o :

$$h_o = \left(\frac{0.0096 n^2 \eta r_f^6}{\gamma r_b t} \right)^{\frac{1}{4}} \quad 2.23$$

and for the thickness at the barrier ring, h_b :

$$h_b = \left(\frac{0.0090 n^2 \eta r_f^2 r_b}{\gamma t} \right)^{\frac{1}{2}} \quad 2.24$$

Combining the equations 2.23 and 2.24 gives an expression for h_b/h_o :

$$\frac{h_b}{h_o} = 3.066 \frac{r_b}{r_f^2} h \quad 2.25$$

which indicates that the dimple should become relatively more pronounced as the film thins. In order to provide an experimental check for the Frankel and Mysels theory for the shape of the dimple, Platikanov (1964) carried out measurements on macroscopic circular thinning liquid films on solid substrates. Platikanov determined the shape of the dimple by photographing the interference pattern produced by the films in reflected monochromatic light. For films of $10^{-1} \text{ mole dm}^{-3}$ KCl on glass, Platikanov observed drainage rates which were in approximate agreement with Frankel and Mysels theory, however the dimple became less pronounced with time, contrary to the theoretical prediction.

Hartland and Robinson (1977) proposed a model for the dimpled draining film in which the dimple profile is modelled as two parabolas joined at the point of inflexion. Expressions for the drainage rate at the centre and barrier ring derived using this model become algebraically identical with the Frankel and Mysels equations for films of small radius. The Hartland and Robinson model allowed the complete profile of the dimple to be generated with the drainage rate at the centre and barrier ring respectively given by:

$$h_o = 0.117 \left(\frac{2\pi n^2 \eta r_f^6}{\gamma r_b t} \right)^{\frac{1}{4}} \quad 2.26$$

and

$$h_b = 0.370 \left(\frac{n^2 \eta r_f^2 r_b}{2\pi \gamma t} \right)^{\frac{1}{2}} \quad 2.27$$

Hartland and Robinson used a photographic method to determine the thickness of a film of either nitromethane or aqueous glycerol between silicone oil and a horizontal stainless steel plate. They found that film thicknesses predicted by these equations were approximately 10% higher than their experimental values at the centre and 40% lower at the barrier ring.

The process of thinning of a film between a deformable bubble and a solid was considered by Dimitrov and Ivanov (1978). They interpreted the available experimental results and demonstrated theoretically that when the interfaces are a short distance from each other the film can be assumed to be practically plane-parallel, and thus deduced an expression for the film thickness as a function of time coincident in form with the Reynolds equation, i.e.:

$$h_o = \left(\frac{\eta r_f^2 r_b}{\gamma t} \right)^{\frac{1}{2}} \quad 2.28$$

According to Dimitrov and Ivanov the difference between the result predicted by the model was within the uncertainty level in the experimental values, particularly during the later stages of drainage with small film thicknesses and small bubble radii.

Analytical solutions were obtained for the velocity of thinning by Jain and Ivanov (1980) in their model of the dimple profile, based on the premise that all of the energy dissipation takes place at the barrier ring; they derived the following equation for the film thickness at that point:

$$h_b = 0.433 \left(\frac{\eta r_f^2 r_b}{\gamma t} \right)^{\frac{1}{2}} \quad 2.29$$

This model suggests that the presence of a dimple increases the velocity of thinning as compared to a film without a dimple (i.e. the Reynolds case of plane-parallel interfaces). The applicability of Reynolds to the case of an air bubble approaching a solid surface was questioned since the air/liquid interface is deformable and not plane-parallel. This is particularly significant in the initial or middle stages of the film's

evolution when the deformation of the film surface and therefore the deviation from Reynolds theory are at their maximum.

Hartland (1969) numerically calculated the alteration of the film's profile as a function of time. A differential equation was developed to describe the variation in the shape of the film with time. The effect, on the deformable air/liquid interface, of the pressure gradient due to radial viscous flow was considered, with the variation of symmetrical experimental profiles occurring between that predicted by assuming that the bubble interface is immobile or fully mobile. Hartland tested his model by studying the gravity approach of golden syrup containing potassium iodide, through sextol phthalate towards a stainless steel plate. The observation was made that the film's deformation at the centre diminished as it thinned, but a ring of lesser thickness remained at the barrier ring.

2.3.1 The thinning of a thin aqueous film between a solid plane and an air bubble.

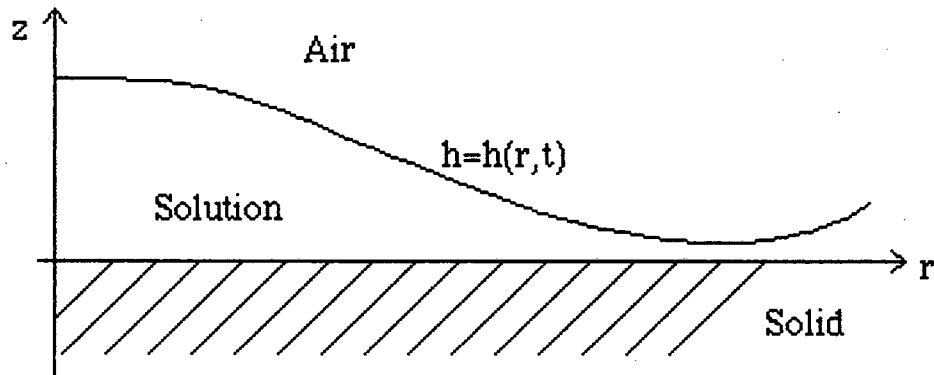


Figure 2.3 The profile of the dimple for an air bubble approaching a solid plane.

For an air bubble approaching a solid plane as shown in Figure 2.3, assuming radial symmetry about the z axis, then the film thickness $h=h(r,t)$ is a function only of radial position r and time t . If the film is very thin with respect to characteristic radii, derivatives of h with respect to r are much smaller than unity, velocities are purely radial and the pressure P in the film is a function of radius only (Buevich and Lipkina, 1978).

For slow thinning the inertia of the fluid is neglected. Setting to zero the forces acting on a small volume element relates P to shear stress Λ :

$$\frac{\partial \Lambda}{\partial z} = \frac{\partial P}{\partial r} \quad 2.30$$

For laminar flow the viscosity η of the film relates the velocity gradient to the shear stress:

$$\frac{\partial v}{\partial z} = \frac{\Lambda}{\eta} \quad 2.31$$

The film layer in contact with the solid is stationary and in the absence of surfactants the layer in contact with the air has a zero shear viscosity. This gives a parabolic velocity profile and the average (radial) velocity $\bar{v}(r)$ is given by:

$$\bar{v}(r) = -\frac{h^2}{3\eta} \frac{\partial P}{\partial r} \quad 2.32$$

The equation of continuity relates the rate of thinning to the average velocity to give:

$$\frac{\partial h}{\partial t} = -\bar{v} \frac{\partial h}{\partial r} - \bar{v} \frac{h}{r} - h \frac{\partial \bar{v}}{\partial r} \quad 2.33$$

whence:

$$\frac{\partial h}{\partial t} = \frac{h^2}{3\eta} \left(h \frac{\partial^2 P}{\partial r^2} + 3 \frac{\partial h}{\partial r} \frac{\partial P}{\partial r} + \frac{h}{r} \frac{\partial P}{\partial r} \right) \quad 2.34$$

One component of the pressure is the Young-Laplace pressure $\gamma\zeta$ where γ is the tension of the air-film interface and ζ is the curvature of that interface. With the approximation that $\frac{\partial h}{\partial r} \ll 1$, the curvature of this surface of revolution is:

$$\zeta = \frac{\partial^2 h}{\partial r^2} + \frac{1}{r} \frac{\partial h}{\partial r} \quad 2.35$$

The interaction of the two interfaces produces a force per unit area π , to give:

$$P = -\gamma\zeta - \pi \quad 2.36$$

Substitution into equation 2.36 for the local thinning rate gives an equation relating h , r and t , thus:

$$\begin{aligned} \frac{\partial h}{\partial t} = & -\frac{h^2\gamma}{3\eta} \left(h \frac{\partial^4 h}{\partial r^4} + \left(\frac{2h}{r} + 3 \frac{\partial h}{\partial r} \right) \frac{\partial^3 h}{\partial r^3} + \left(-\frac{h}{r^2} + \frac{3}{r} \frac{\partial h}{\partial r} \right) \frac{\partial^2 h}{\partial r^2} + \left(\frac{h}{r^3} - \frac{3}{r^2} \frac{\partial h}{\partial r} \right) \frac{\partial h}{\partial r} \right) \\ & - \frac{h^2}{3\eta} \left(h \frac{\partial^2 h}{\partial r^2} \frac{\partial \pi}{\partial h} + \left(\frac{\partial h}{\partial r} \right)^2 \left(h \frac{\partial^2 \pi}{\partial h^2} + 3 \frac{\partial \pi}{\partial h} \right) + \frac{h}{r} \frac{\partial h}{\partial r} \frac{\partial \pi}{\partial h} \right) \end{aligned} \quad 2.37$$

This equation, which has been presented without the physical derivation by Buevich and Lipkina (1978), cannot be solved analytically and numerical solutions of the general case are exceedingly awkward because of the high order derivatives. Specific cases can be solved but comparison with experiment is not always helpful because of the sensitive dependence on initial conditions.

Lin and Slattery (1982) developed a model similar to that just described for the thinning of a liquid film as a small drop or bubble approaching a solid plane, employing the same basic differential as described by Hartland (1969), although they refined this model by redefining the boundary conditions. Lin and Slattery compared their model with the experimental values of Platikanov using the experimental time $t=0.30$ seconds as the point at which the thinning rate was independent of position which they define as according to their model. After matching the dimple profile at these times, Lin and Slattery found good agreement for the dimple shape for other experimental times up to 100 seconds.

The effect of London-van der Waals forces were taken into account for the Lin and Slattery model by Chen and Slattery (1982) and the effect of electrical double layer forces were included by Chen (1984). Chen and Slattery included the disjoining pressure due to van der Waals forces where the extra force is given by:

$$\pi_{vdw} = -\frac{B}{hm} \quad 2.38$$

where B is equivalent to the Hamaker constant and m takes the values of 3 for $h < 12\text{nm}$ and 4 for $h > 40\text{nm}$. In taking into account electrostatic forces, Chen used the following equation to calculate this component of the disjoining pressure:

$$\pi_{el} = \left(64nkT \tanh\left(\frac{ze\psi_{qw}}{4kT}\right) \tanh\left(\frac{ze\psi_{aw}}{4kT}\right) \right) e^{-\kappa h} \quad 2.13$$

noting that it was valid only for $\kappa h > 1$. Chen compared the model with Platikanov's experimental results, using the streaming potential values for the zeta potential for the silica-aqueous KCl solution interface reported by Jones and Wood (see Chen, 1984) and Wiese et al (1971) and the values of Schulze and Cichos (1972) for the air-aqueous KCl solution interface to calculate π_{el} . The result of including π_{el} was to give good qualitative agreement with experimental results in that, for less concentrated KCl solutions thicker films were formed in shorter times.

2.3.2 Flow of Electrolyte in the Vicinity of an Interface

When considering the flow of electrolyte out of the thin film through the barrier ring of the dimple, the effect of the double layer which exists at the interfaces should be taken into account. This has been studied by observing flow of aqueous electrolyte solutions through capillaries of very small diameter (i.e. $< 10\mu\text{m}$) and the flow behaviour is clearly dependent on the concentration of electrolyte (e.g. Hildreth, 1970; Churaev et al, 1981; Levine et al, 1975).

The existence of the double layer manifests itself as an "apparent" increase in viscosity. The theory of these electroviscous effects, as they are referred to, are covered in detail in Hunter (1981). When an electrolyte flows through electrically charged capillaries under a pressure gradient, a streaming potential is established. This potential will produce a backflow of liquid by an electro-osmotic effect, and the result is a diminished flow in the forward direction.

The liquid appears to exhibit an enhanced viscosity if its' flow rate is compared with the flow in the absence of double layer effects, so that the effect can be expressed in terms of a ratio of η_a/η where η_a is the apparent viscosity measured and η is the viscosity of the bulk. Since this effect is a function of the electrical double layer strength there will be a dependence upon the zeta potential, ζ of the interface and the Debye thickness, κ^{-1} . The variation as a function of distance from the surface, given in terms of κh , is shown in Figure 2.4 using data for $\zeta = -125\text{mV}$ given in Hunter (1981). The initial steep rise (for very small κh) due to the extensive overlap of the interacting double layers. Measurement of the viscosity of thin liquid films between two solid surfaces of mica (Israelachvili, 1986) showed that the viscosity increase close to the surface are satisfactorily explained by double layer forces (i.e. the electroviscous effect).

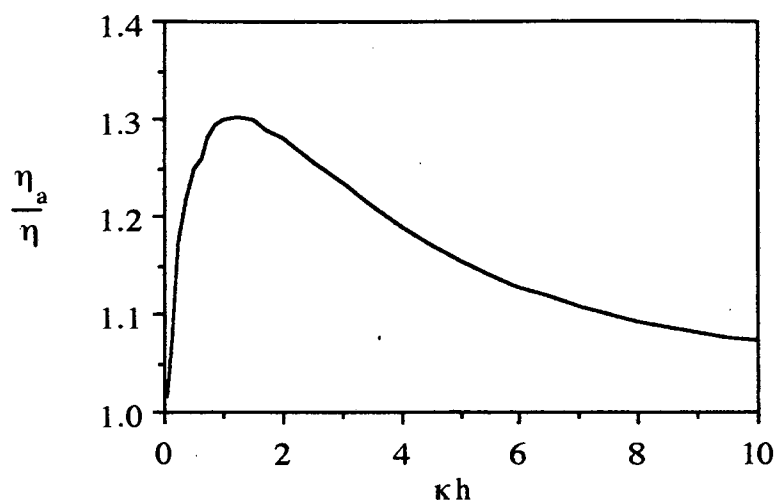


Figure 2.4 The ratio of the apparent viscosity to the bulk viscosity as a function of the distance from the surface for a zeta potential of -125mV .

Hough and Ottewill (1983) studied the effect of ionic strength on the measured viscosity in experiments using an optically polished glass surface and a smooth, deformable, spherical, rubber cap. They found that the apparent viscosity showed a marked increase with decreasing electrolyte concentration, much greater than that simply due to the presence of electrical double layer forces. Henniker (1952) reported that with a ceramic disk having an effective pore diameter $0.30\mu\text{m}$, the flow of water through it was increased by seven times by rendering the pores hydrophobic.

2.4 Experimental Investigations of Thin Film Drainage

Platikanov (1964) clearly showed evidence for the dimpled behaviour in observing the drainage rates of films of $10^{-1}\text{mole dm}^{-3}$ KCl and aniline as discussed above. Extensive experimental work has also been carried out on the influence of various interfacial parameters on the drainage rate for fluid/fluid interfaces.

The effect of the presence of surfactant in either the continuous or the dispersed phase has been investigated by Radoev et al (1974), Traykov and Ivanov (1977) and Ivanov (1980). The influence of interfacial tension gradients was examined (Lee and Hodgson (1968)), as well as changes in interfacial viscosities (Barber and Hartland (1976); Ivanov and Dimitrov (1974)). The role of flow in both the dispersed and the continuous phases has been investigated by Jeffreys and Hawksley (1965), Murdoch

and Leng (1971), Woods and Burrill (1972) and Jones and Wilson (1978). Mackay and Mason, (1963) Hartland (1967) and Lang and Wilke (1971) studied the drainage of pure films, whereas experiments involving the thinning of films with soluble surfactant in both phases have been reported by Traykov and Ivanov (1977) and Zapryanov et al (1983). According to Traykov and Ivanov the presence of surfactant in the dispersed phase has no influence on the rate of thinning.

Cain and Lee (1985) developed a method for studying the drainage and rupture of liquid films between two captive air bubbles. The film thickness was measured by means of an optical interference method with 0.8mm bubbles immersed in aqueous KCl solutions of varied strength. Films formed in 1.0 mole dm⁻³ KCl were found to drain more slowly and rupture at smaller thicknesses than for 0.5 mole dm⁻³ KCl and films could not be formed in 0.1 mole dm⁻³ KCl.

The Reynolds theory for the rate of film thinning is based on the assumptions of tangential immobility and plane-parallel configuration of film interfaces. For surfactant free systems with film radii larger than a certain small value (approximately 5x10⁻³cm), the draining films are neither immobile nor plane-parallel and departures from both plane-parallel configuration and Reynolds theory increase as the film radius increases. Ruckenstein and Sharma (1987) developed a theory to explain their experimental results for film drainage rates, which were orders of magnitude larger than Reynolds velocity.

The Ruckenstein and Sharma theory used the frequency of temporal oscillations and the propagation speeds of experimentally observed thickness non-homogeneities from the equations of motion. They proposed that the pumping of the fluid, generated by the thickness fluctuations, gives the dominant contribution to the velocity of film thinning. As noted earlier, Reynolds theory gives the following expression for the velocity of thinning:

$$v_{Re} = -\frac{dh}{dt} = \frac{2h^3P}{3n^2\eta r_f^2} \quad 2.19$$

A number of experimental studies (e.g. Radoev et al, 1983; Manev et al, 1984) have concluded that this expression does not always adequately describe the drainage rate of thin films with radii greater than 10⁻²cm. In the experimental study of Radoev et al (1983), deviations from a plane-parallel configuration were first observed with films with radii of 5x10⁻³cm, and the films became increasingly non-homogeneous in thickness as the film radius was increased further. These non-homogeneities owe their

origin probably to film thinning and the associated hydrodynamic instabilities (according to Ruckenstein and Sharma). The amplitude of these surface corrugations is dependent on film thickness, at least for films with surfaces which are tangentially immobile. Since the velocity of film thinning is dependent upon film thickness then fluctuations in the film thickness lead to changes in film drainage rate. Ruckenstein and Sharma developed a model to predict the enhancement of film drainage, considering the existence of these surface waves and the effect of the waves in pumping fluid out of the film. Thus the total velocity of thinning v_t is given by:

$$v_t = \frac{4.9h^2P}{\eta r_f} \frac{\epsilon_t}{\lambda} \gg v_{Re} \quad 2.39$$

where λ is the wavelength of the non-homogeneities (typically $5 \times 10^{-3} \text{cm}$) and ϵ is the amplitude of the thickness non-homogeneities, with ϵ given by:

$$2\epsilon = \epsilon_t = (797r_f^{0.25} - 209) \text{ \AA} \quad 2.40$$

where r_f is given in cm. The agreement between this model and experimental data (Radoev et al, 1983) was very good.

Recently Tambe and Sharma (1991) proposed a hydrodynamic model to describe the drainage rate between two liquid drops separated by an immiscible liquid, taking into account the effects of the visco-elastic nature of the interface, although they assumed a plane-parallel film in which the flow is Newtonian. They showed that the interfacial elasticity and the interfacial viscosity are significant in terms of their effect on the drainage rate.

2.5 Film Rupture

Experimentally it has been observed that thin liquid films often rupture at well-defined thicknesses (Scheludko, 1962). It has been suggested by Scheludko that the rupture of thin films is initiated by thermal fluctuations which lead to corrugation of the film surface. If, during a fluctuation, the change in the attractive force with a small change in distance exceeds the change in total repulsive force with a small change in distance, then rupture of the film will occur. These fluctuations can be considered as cylindrical micro-corrugations in the surface of a microscopically plane-parallel film, with the fluctuations having a wavelength, λ .

The rupturing distance of films can be calculated using an equation proposed by Vrij (1966):

$$h_{cr} = 0.268 \left(\frac{A^2 r_f^2}{f \gamma a} \right)^{1/2} \quad 2.41$$

where a is the capillary radius and f is some constant. By studying thin, free liquid films and applying sinusoidal wave oscillations Vrij and Overbeek (1968) deduced that there is a critical wavelength, λ_{cr} , and rupture occurs when $\lambda > \lambda_{cr}$ and $r_f > \lambda$. Ruckenstein and Jain (1974) obtained data for the rupture of films of a surfactant free system and applied a similar analysis. The characteristic time of growth of perturbations due to thermal or other fluctuations of the film was observed to increase with increasing film viscosity, decreasing film thickness and negative disjoining pressure (Dimitrov, 1982).

The stability of liquid films and the critical film thickness at which rupture took place was investigated Schulze and Birzer (1987) who found that their experimental data was best fitted by the following expression:

$$h_{cr} = b (\gamma_{LG} (1 - \cos \theta_A)^m) \text{ nm} \quad 2.42$$

where the parameters b and m were determined empirically and found typically to take the values: $33.9 < b < 42.4$ and $0.16 < m < 0.18$. They compared this to the expression derived by Radoev et al (1983) in which h_{cr} was given by:

$$h_{cr} = \left(\frac{9(3kT/\gamma\alpha^2)^{1/2}}{64v\gamma\eta(6\pi)^2} \right)^{1/5} A^{0.4} \quad 2.43$$

where $\alpha = \frac{dh}{d\epsilon}$ accounting for the conjugation of surface waves with amplitude ϵ and v is the mean wave velocity.

It was proposed (Sharma and Ruckenstein, 1987) that thermal perturbations superimposed on hydrodynamic waves also start to grow for very thin films due to dispersion interactions. They suggested that the growth rates of thermal perturbations are much larger than for the hydrodynamic surface waves and, as such, lead to film rupture and help to explain film rupture thicknesses measured experimentally which are much larger than the earlier theories predicted. Also, as Scheludko (1967) pointed out, the critical thickness of rupture is in fact a function of film radius.

CHAPTER 3. THIN FILM DRAINAGE - EXPERIMENTAL

The drainage rates of thin, aqueous films were studied using optical interferometry. The most common way of using an optical interferometer to measure thin film profiles is to illuminate the film with a parallel, monochromatic light beam so as to produce a set of interference fringes (Newton's rings if the film is axisymmetric) whose spacing and intensity give the profile (Platikanov, 1964). The disadvantage of this approach is that the accuracy of the intensity measurement, and hence the accuracy of the calculated film thickness, is limited.

More accurate thickness measurements can be made if the incident beam is focussed onto a small area of the draining film and the intensity of the reflected beam from this area is measured as a function of time (Fisher et al, 1980). This method was used to study the drainage rates of thin films formed between an air bubble and a solid surface.

3.1 Description of the Instrument

The optical interferometric instrument capable of accurate measurements of the thickness of thin liquid films was constructed by CSIRO, North Ryde, NSW. A description of the instrument in the configuration in which it was used in this study follows. The light source was a 2mW He-Ne laser, emitting light of wavelength 632.8nm, stabilised (Bennett et al, 1973) to ensure little or no variation in the laser intensity.

Figure 3.1 is a schematic representation of the instrument. As can be seen a more detailed diagram of the thin sample chamber (shown in Figure 3.2), a vertically polarised laser beam (L) is directed via a polarising beamsplitter (B) through an objective lens (O). After passing through windows (W1 and W2), the beam enters an air-filled teflon septum (S1), fed by a syringe (S2) via a silastic tube (T). The beam passes through a mica quarter wave plate (M), angled to prevent unwanted reflections and is focussed at the front face of an optically polished quartz prism (Q).

An air bubble (A), initially just out of contact with the quartz surface, is bulged rapidly by allowing a solenoid controlled plunger (P) to rapidly compress a section of the silastic tubing. The reflected laser beam again passes through the quarter wave plate, so becoming horizontally polarised and able to pass through the beamsplitter and enter a detecting photomultiplier.

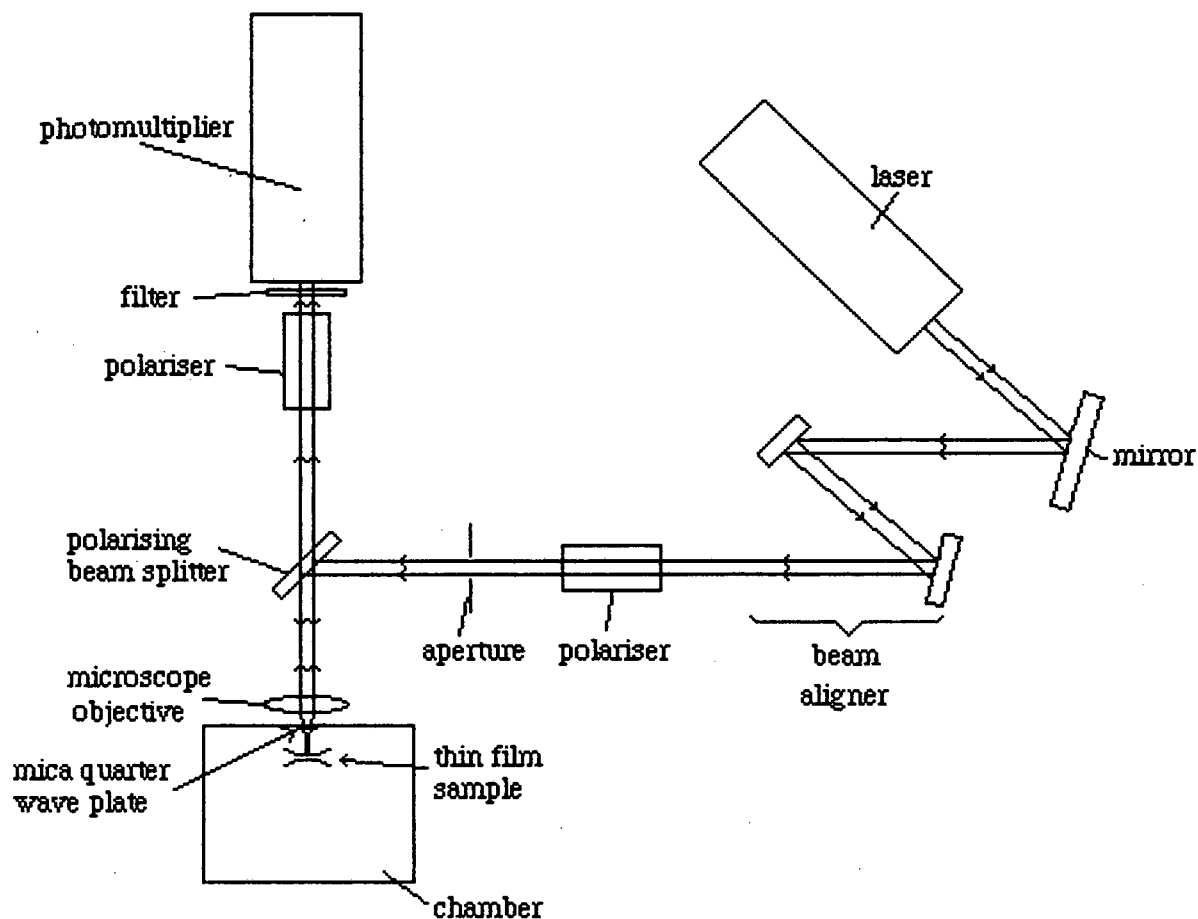


Figure 3.1 Schematic representation of the instrument.

This optical arrangement is such that normal incidence illumination can be used without problems of reflection from windows and other optical components. The quartz surfaces were optically polished (to 0.1 wavelengths) with the rear surface at 30° to the front so that light reflected from the rear surface was deflected from the light measurement system. The diameter of the focussed laser beam in the plane of the draining film is approximately $30\mu\text{m}$ and, with the beamsplitter and objective mounted on a micrometer driven carriage which could be moved laterally, the focussed beam was scanned across the draining film.

The method used to form the draining film between air bubble and quartz surface is considered in detail. An air bubble was first bulged from a hole in a teflon chamber, to an apical height of 0.58mm, giving a bubble of radius 1.16mm.

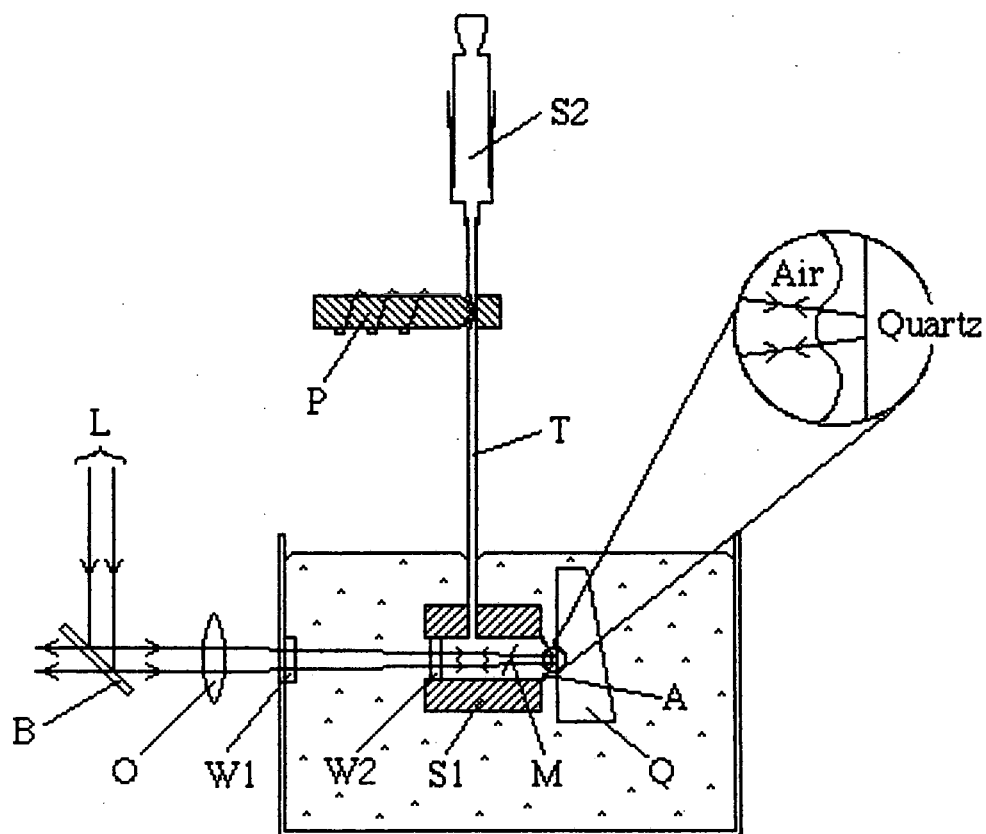


Figure 3.2 A schematic representation of the apparatus used to measure thin film drainage rates.

In addition to the axial optical system, the bubble was viewed side-on through a camera, and the apex of the bubble was placed close to the quartz surface by moving the quartz plate towards the bubble using the micrometer on the quartz holder.

After optical alignment to ensure that the quartz/water interface was at the focal plane of the objective lens and normal to the optical axis of the laser beam and that the reflected beams from the quartz/water and water/air interfaces were coincident with the optical axis, the experiment was initiated by activating a solenoid controlled plunger to rapidly compress a section of the silastic tubing of the air line supplying the bubble.

3.2 Data Analysis

When the aqueous film between the air bubble and quartz plate becomes thin, interference occurs between the two reflected light beams (from the air/water and water/quartz interfaces respectively). When the film thickness equals a multiple of half the wavelength of light the two waves interfere constructively and an interference fringe maximum is produced. Conversely, when the film thickness is a quarter of a wavelength different from the half wavelength multiple, then a minimum interference fringe will occur. By monitoring the interference fringes as a function of time, the rate at which the film thickness is changing (i.e. the thin film drainage rate) was determined.

The difference in film thickness between a fringe maximum and minimum is equal to $\lambda/4n$ (i.e. $632.8/4(1.333) = 118.7\text{nm}$) where n is the refractive index of the fluid in the thin film. For light reflected normally from a film of thickness h , and for an aqueous film of refractive index n_1 , formed between a quartz plate of refractive index n_2 and an air bubble of refractive index n_0 , then the reflectance is given by (Heaven, 1970):

$$R = \frac{\alpha^2 + \beta^2 + 2\alpha\beta \cos\delta}{1 + \alpha^2\beta^2 + 2\alpha\beta \cos\delta} \quad 3.1$$

$$\text{where } \alpha = \frac{(n_2 - n_1)}{(n_2 + n_1)}, \beta = \frac{(n_1 - n_0)}{(n_1 + n_0)} \text{ and } \delta = \frac{4\pi n_1 h}{\lambda}$$

As the film thins until it becomes plane parallel at which time the fringes reach their absolute intensities; for the air/water/quartz system (Heaven, 1970) the intensity of the maximum is given by:

$$R_{\max} = \left(\frac{n_2 - n_0}{n_2 + n_0} \right)^2 \quad 3.2$$

and the intensity of the minimum by:

$$R_{\min} = \left(\frac{n_1^2 - n_0 n_2}{n_1^2 + n_0 n_2} \right)^2 \quad 3.3$$

The time difference between successive maxima and minima corresponds to a change in the film thickness of 118nm. From the interference pattern recorded as a function of time the thickness of the draining film may be calculated and film drainage rates subsequently determined.

3.3 Materials

3.3.1 Clean Quartz Surfaces

Quartz plates were used in these experiments as these surfaces have been studied extensively and methods for cleaning the plates and rendering them hydrophobic were already readily available. Quartz was obtained from H.A. Groiss, Optical Precision Works, Wantirna South, Victoria, in the form of wedges cut from a bulk sample (G. Bottley Pty. Ltd., U.K.).

Perfectly clean quartz is known to be hydrophilic (Iler, 1979), so great care was taken to ensure extreme cleanliness of the quartz plates. Various methods of cleaning quartz surfaces have been studied (Pashley and Kitchener, 1979) and after consideration of the methods available the following procedure was followed to clean the plates used in this study. The plates were immersed in hot, concentrated nitric acid (Univar, AR grade) for several hours, followed by rinsing with copious amounts of fresh twice distilled water. This was followed by immersion in a hot, 30% Potassium Hydroxide (Univar, AR grade) solution for 1 to 2 minutes.

The "steam test" (Vig et al, 1975) was used to determine the cleanliness of the quartz surfaces. This involved holding a clean, cool, dry plate over hot, clean water. The appearance of uniform interference fringes on the quartz surface caused by even condensation of a wetting film of water, indicated that the surface was clean and had a low or zero degree contact angle. If trace amounts of hydrophobic contamination were present on the surface, the interference fringes were irregular or the water condensed in droplets.

Between experiments with hydrophilic plates, the plates were cleaned by soaking overnight in freshly prepared chromic acid, followed by rinsing with copious amounts of twice distilled water.

3.3.2 Preparation of Hydrophobic Surfaces

The well-established method of rendering quartz surfaces hydrophobic by controlled reaction with trimethylchlorosilane (TMCS) was used (Blake and Ralston, 1985). Hair (1977) and Chmielowiec and Morrow (1983) used infra-red spectroscopy to follow the reaction of TMCS with silica and concluded that trimethylsilane (TMS) groups become chemisorbed on the silica surface, producing a stable hydrophobic surface with tightly bound TMS groups (see Figure 3.3). Laskowski and Kitchener (1969) noted that the contact angle of such hydrophobic surfaces decreased with time if the surface was in contact with water. Drying overnight at 110°C re-established the original contact angle.

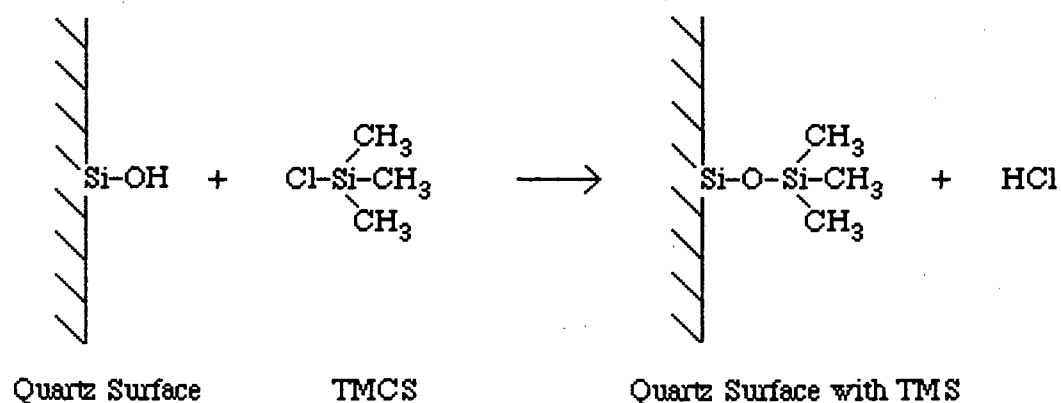


Figure 3.3 Reaction of TMCS with a silica surface to render the surface hydrophobic.

The method of controlled methylation of quartz surfaces described by Blake and Ralston (1985) was followed to produce plates of various degrees of hydrophobicity. Solutions of redistilled, dried TMCS (Aldrich) were prepared in redistilled, dried cyclohexane (BDH, AR grade). Freshly cleaned, dry quartz plates were immersed for various periods of time, in solutions of $2 \times 10^{-4} \text{ mole dm}^{-3}$, at room temperature, to produce plates which varied in their degree of hydrophobicity. The plates were rinsed with cyclohexane and dried overnight at 110°C before use.

The hydrophobicity of the plates was characterised by measuring the advancing and receding water contact angles using the captive bubble technique. The results of the contact angle measurements on the plates after particular times of exposure to TMCS solutions are shown in Table 3.1

Time in 2×10^{-4} mole dm^{-3} TMCS solution (min.)	Contact Angle $\pm 2^\circ$ (Advancing or Receding water)
1	8°
2	18°
5	42°
10	65°
60	88°

Table 3.1 Contact angles on quartz plates after exposure to TMCS (in cyclohexane) solutions for the times shown.

The captive bubble technique was used for measuring the water contact angle. The method involves pressing a bubble against a plate immersed in water, until contact just occurs. A photograph was taken of the bubble profile and the contact angle was measured directly from the print of the photograph, with a protractor, to an accuracy of $\pm 2^\circ$. The advancing water contact angle was obtained by withdrawing the bubble from the surface, although in practice this event occurred as a minor volume change (about 1%).

The advancing and receding contact angles were the same, within experimental error showing that the plates exhibited little or no contact angle hysteresis, indicating that the plates were both uniform in their surface coverage of TMS groups and very smooth. This behaviour is consistent with the results of experiments performed at the University of Melbourne (Trau et al, 1992) in which silica plates exposed to TMCS vapour showed no hysteresis. Only when the silica plates were exposed to relatively concentrated solutions of TMCS in hexane did the resultant hydrophobic plates exhibit contact angle hysteresis. The dilute TMCS solutions used in this study to render quartz plates hydrophobic appear to produce films similar to those obtained using TMCS vapour.

When measuring the contact angles, great care was taken to ensure proper equilibration and to prevent mechanical distortion. The syringe used to produce the bubble as well as the sample cell in which the measurements were made, were carefully cleaned to minimise any contamination of the quartz surface as it is well known that even very low levels of surface contamination will result in inaccurate contact angles.

3.3.3 Preparation of Salt Solutions

Sodium chloride solutions were prepared from analytical grade, recrystallised sodium chloride, which had been baked for 6 hours at 650°C to remove any organic impurities. The solutions were filtered through 0.2µm filters (Acrodisc, Gelman Sciences, UK) before use and the final salt concentration was calculated from the measured conductivity of the solution. Great care was taken to ensure that all parts of the apparatus which were in contact with the aqueous solutions were kept scrupulously clean.

3.4 Experimental Method

Reproducible results were only obtained if the initial conditions remained the same, so particular attention was paid to achieving the same distance of separation between the air bubble and quartz plate before the experiment was initiated. The plate/bubble separation distance and, subsequently, the radius of the draining film, were kept constant from one experiment to the next by using a spurious reflected beam, which always appeared near the apex of the bubble to set the plate at the same distance from the bubble before the bubble was expanded. The solenoid controlled plunger ensured that the silastic tubing was always compressed by the same amount. The early drainage rates (i.e. for times less than 5 seconds) for films between the air bubble and hydrophilic quartz plates were compared to check that reproducibility of the early drainage was indeed achieved.

Scanning across the draining film and recording the interference pattern as a function of the radial distance from the centre of the film permitted the shape of the film to be determined. The characteristic dimple shape noted by others previously was observed, that is the film thickness was found to decrease with increasing distance from the centre ($r = 0$) with a minimum thickness at the edge of the film or boundary ring ($r = 0.20\text{mm}$). For drainage at a hydrophilic surface the fringe orders (of the interference pattern) can be assigned by counting back since at equilibrium the fringe order is zero. Each experiment was performed in triplicate with a reproducibility of better than 2%. All experiments were performed at a pH of 5.8 ± 0.2 .

It was necessary to show that the fringe reached in the interference pattern when the aqueous film had drained to an equilibrium film thickness was indeed within the fringe of zeroth order (i.e. the first fringe to appear in the interference pattern). To clarify this point, the film in low ionic strength solution (ca $10^{-5}\text{mole dm}^{-3}$ NaCl) was allowed to

drain so that it attained an equilibrium film thickness. In a salt solution of this concentration the film thickness at equilibrium was approximately 120nm corresponding to the first minimum of the interference pattern (assuming the first fringe had been reached).

The ionic strength of the salt solution was increased in a number of steps until the concentration reached $10^{-2}\text{mole dm}^{-3}$. At each step the film was allowed to come to equilibrium and it was found that, as a progressively thinner film was formed, the interference pattern observed moved from what was assumed to be the first minimum towards the zeroth maximum and did not move through another maximum. This observation was taken to be confirmation that the first fringe had been reached. Film thicknesses could then be determined by "counting back".

CHAPTER 4. THIN FILM DRAINAGE - RESULTS AND DISCUSSION

Observation of the drainage pattern which evolves when the bubble is bulged against the quartz plate did not reveal any detectable asymmetry in the bubble shape although scanning across the draining film was made in the horizontal plane. In other words scanning the draining film on either side of the centre did not give detectably different drainage rates at the same radii with all other conditions held constant.

4.1 Changes in Film Radius

As discussed in the experimental section the distance of separation between the air bubble and the quartz surface before the bubble was bulged towards the plate had to be controlled precisely. Micrometers attached to the moving parts of the instrument permitted small, reproducible changes to be made to the separation distance. This resulted in small changes in the area of contact between the bubble and the plate, allowing small changes in the film radius to be studied. In Figure 4.1 the experimental drainage rate curves in doubly distilled water are shown for a series of experiments with increasing film radius at a hydrophilic quartz surface.

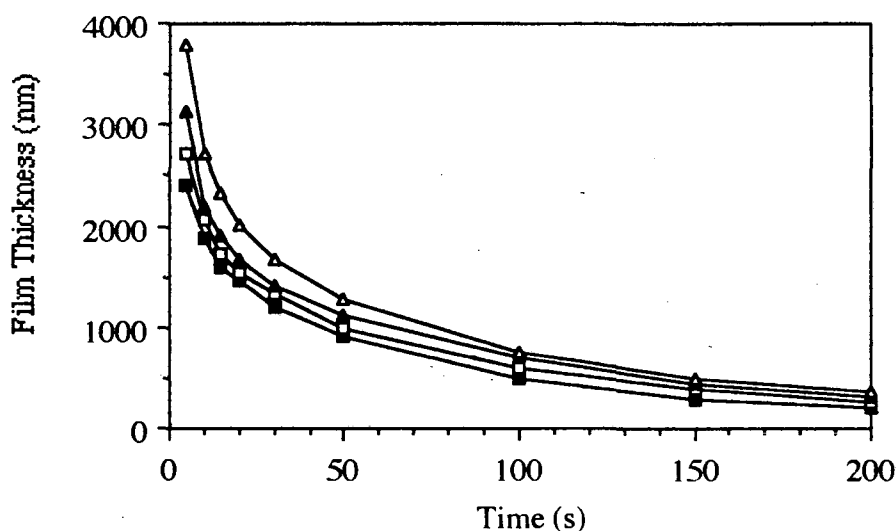


Figure 4.1 Drainage rates at the centre of films on hydrophilic quartz plates in conductivity water for various values of film radius (i.e. for film radius values of 0.22mm (■), 0.24mm (□), 0.26mm (▲) and 0.32mm (△).

4.1.1 Comparison with Other Theories

For the early drainage rates (for times less than 50 seconds) a plot of the inverse of the square of the film thickness against time results in a straight line (Figure 4.2). The gradient of this line increases with decreasing film radius, as expected both by either the Reynolds theory (equation 2.21) or that of Dimitrov and Ivanov (equation 2.28).

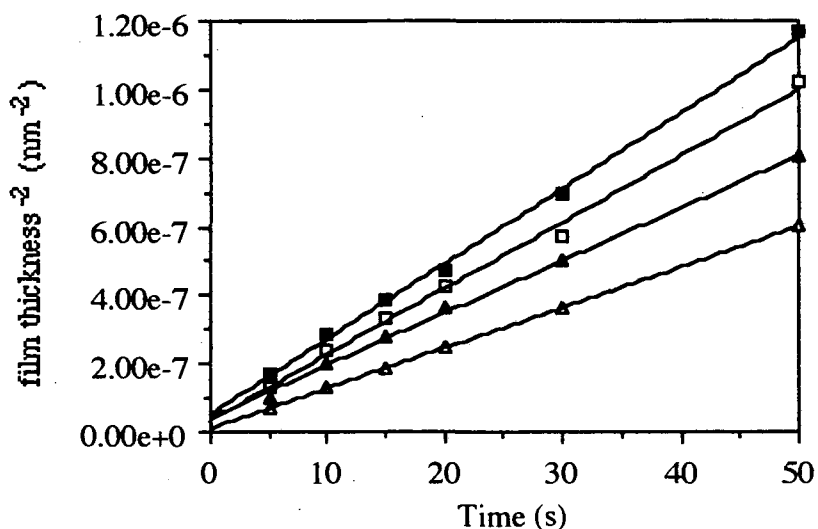


Figure 4.2 The inverse of the square of the film thickness versus time for film radius values of 0.22mm (■), 0.24mm (□), 0.26mm (▲) and 0.32mm (△) (i.e. for the same data as shown in Figure 4.1).

Film Radius (cm)	Experimental Slope ($\times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$)	Theoretical Slope 1 ($\times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$)	Theoretical Slope 2 ($\times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$)
0.022	2.19	1.38	1.30
0.024	1.93	1.16	1.09
0.026	1.53	0.99	0.93
0.032	1.18	0.65	0.61

Table 4.1 The experimental gradient derived from the plot of (film thickness)⁻² versus time (shown in Figure 4.2) is given for various film radii observed. Theoretical calculations of the gradient are shown for Reynolds theory (theoretical slope 1) and Dimitrov and Ivanov (theoretical Slope 2).

The following values were used in the theoretical calculations shown in Table 4.1: $\gamma = 72.8 \text{ mN/m}$, $\eta = 0.01 \text{ Poise}$ and $r_b = 0.116 \times 10^{-3} \text{ m}$. The two surfaces (i.e. air-water and quartz-water) clearly interact with one another at large distances of separation and exhibit “Reynolds-like” behaviour, but yield gradients which differ from theoretical predictions as can be seen in the Table. Clearly, the presence of the dimple at the deformable air/water interface significantly alters the drainage rate, and is not taken into account in hydrodynamic models which assume plane parallel interfaces.

4.2 Equilibrium Film Thicknesses

In the case of clean, hydrophilic quartz plates the thin film drainage rate slows down and eventually appears to stop (reaching a mechanical equilibrium at least). At this equilibrium point, the bubble surface flattens and the system may be described as an asymmetric film of two parallel plates (air and quartz), interacting through a thin liquid film. This phenomena has been noted extensively before (as discussed in section 2.2), although it was encouraging to observe that it occurred in the case of these experiments as well.

4.2.1 Disjoining Pressure Calculations

The DLVO theory may be used to interpret the equilibrium film thicknesses observed at the hydrophilic quartz surface by relating the pressure inside the bubble to the disjoining pressure which exists in the quartz-aqueous film-air configuration. When the Laplace pressure inside the bubble is exactly equal to the disjoining pressure at the interface, the aqueous film no longer drains and an equilibrium situation is reached. The Laplace pressure was calculated using the following equation:

$$P = \frac{2\gamma}{(r_b - r_f)} \quad 4.1$$

The film thickness at which equality occurs can be determined theoretically by calculating the disjoining pressure as a function of film thickness and the film thickness so determined may be compared with the experimental results determined as a function of salt concentration.

The disjoining pressure can be determined through calculation of the van der Waals (π_{vdw}) and electrostatic (π_{el}) components and for structural effects (π_s) as noted in

section 2.1. The van der Waals component was determined using equation 2.11 (given in chapter 2) and the value of the Hamaker constant has been given for this system as $-1.1 \times 10^{-20} \text{J}$ (Schulze, 1984).

The electrostatic component was calculated with equation 2.13 using the values determined by Jones and Wood (see Chen, 1984) and Wiese et al (1971) employing a streaming potential method for the zeta potential at the quartz-aqueous solution interface (values as shown in Table 4.2). The value used for the zeta potential at the air-aqueous solution interface was -34mV , determined by Schulze and Cichos (1972).

Ionic Strength (mole dm^{-3})	ψ_{qw} (mV)	ψ_{aw} (mV)	$1/\kappa$ (nm)
1×10^{-5}	-148	-34	96.2
2.5×10^{-4}	-130	-34	19.2
5×10^{-4}	-126	-34	13.6
1×10^{-3}	-122	-34	9.6

Table 4.2 Calculations of the disjoining pressure were made using the values shown for the zeta potential for the quartz/aqueous film interface (ψ_{qw}) and the air/aqueous film interface (ψ_{aw}). The Debye thickness of the electrical double layer (κ^{-1}) is given for a 1:1 electrolyte at 25°C .

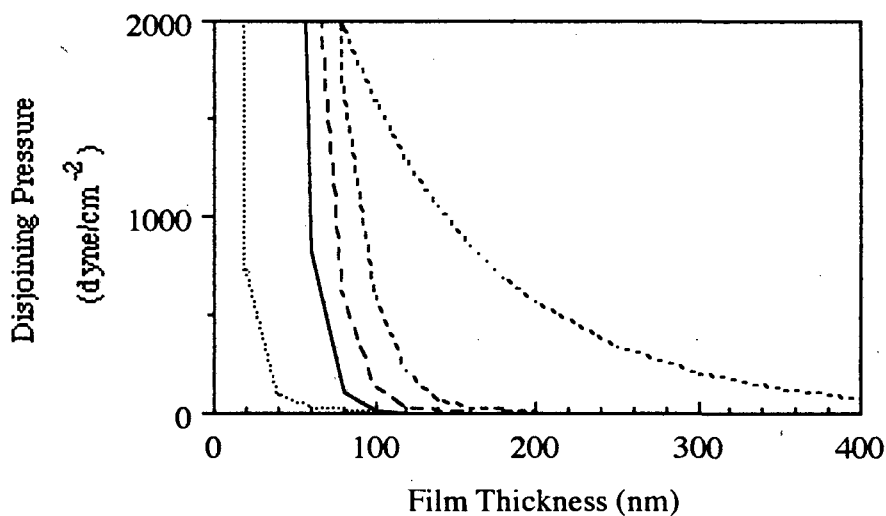


Figure 4.3 The disjoining pressure in wetting films on quartz. Shown are the van der Waals component (.....) and the electrostatic component calculated for ionic strength solutions of $10^{-3} \text{mole dm}^{-3}$ (—), $5 \times 10^{-4} \text{mole dm}^{-3}$ (---), $2.5 \times 10^{-4} \text{mole dm}^{-3}$ (....) and $10^{-5} \text{mole dm}^{-3}$ (.....).

The calculated disjoining pressures for the electrostatic component for the four ionic strength values shown in Table 4.2, and the van der Waals component are shown in Figure 4.3. It can be seen that both of these components are positive which results in a overall repulsive force between the two interfaces and, hence, a stable film, the thickness of which is dependent on the ionic strength of the salt solution. For aqueous films at hydrophilic surfaces the observation of stable films can be adequately described without considering the existence of a structural component of the disjoining pressure. This point will be discussed later, particularly in relation to drainage and rupture of films at hydrophobic quartz plates.

The film thickness at which the total disjoining pressure was equal to the Laplace pressure in the bubble was determined for the ionic strength of the solutions studied. Despite the approximations made in the calculations of the disjoining pressure, the agreement between calculated and experimental film thickness is good at low salt concentration, diverging at higher values (see Table 4.3).

4.2.2 Potential at the Air/water Interface

In Table 4.3, the results of back-calculating the surface potential at the air/aqueous solution interface are shown assuming that the experimental film thicknesses were correct and determining the corresponding values of the disjoining pressure.

Ionic Strength (mole dm ⁻³)	Experimental Film Thickness (nm)	Theoretical Film Thickness (nm)	ψ_{aw} (mV)
1×10^{-5}	118	93.2	-45.0
2.5×10^{-4}	63	79.6	-13.7
5×10^{-4}	36	65.6	-3.5
1×10^{-3}	26	52.9	-1.6

Table 4.3. Experimental and theoretical values determined for the equilibrium film thickness for the salt concentrations used in the investigation. Calculated values of ψ_{aw} are given assuming that the experimental film thicknesses are correct and using the values for ψ_{qw} given in Table 4.2.

The charging mechanism at either the air-water interface or air-aqueous solution interface remains unknown, although as mentioned in chapter 2 it has been observed experimentally that air bubbles suspended in water bear a negative charge. It is unclear how the zeta potential would be vary with salt concentration, however recent

work (Li and Somasundaran, 1991) has shown the usual trend in that the zeta potential at a particular pH value, decreases with increasing electrolyte concentration. Simple electrolytes such as KCl increase the surface tension of water and the Gibbs Equation shows that negative surface excess ion concentrations result, increasing in magnitude with increasing salt concentration. Cations such as H^+_{aq} are apparently located at a distance further away from the air/water interface than anions (e.g. OH^-_{aq}) thus the electrokinetic unit, that being the air bubble in water, bears a net negative charge. Assuming that the zeta potential decreases with increasing electrolyte concentration, the calculated values for ψ_{aw} shown in Table 4.3 are at least reasonable but require experimental confirmation.

4.3 Drainage at Hydrophilic Surfaces

Clean quartz plates have been used in the work reported to this point, providing hydrophilic surfaces upon which to observe the effect of changes in the film radius, and the thickness of the equilibrium films. In this section the profile of films formed at hydrophilic surfaces will be considered whilst hydrophobic surfaces are the subject of the following section.

4.3.1 Influence of Salt Concentration

Using clean quartz plates the drainage rates at hydrophilic surfaces were determined in sodium chloride solutions of varying concentration, permitting the effect of electrostatic forces on the thinning process to be studied. The drainage rates were also measured at regular intervals across the film and from these results the film profile could be determined. As an example, the film thickness versus time curves are shown in Figure 4.4 for changes in position across the film in $10^{-3} \text{ mole dm}^{-3}$ sodium chloride solution indicating the increase in drainage rate which occurs moving away from the centre of the thinning film.

4.3.2 Scans Across the Dimple

Drainage rates made across the film for the four salt concentrations used in this study ranging from $10^{-5} \text{ mole dm}^{-3}$ and $10^{-3} \text{ mole dm}^{-3}$ salt solutions are shown in Figures 4.5a and 4.5b. The drainage rate at the centre of the film decreases with increasing salt concentration whereas at the boundary ring the reverse is true.

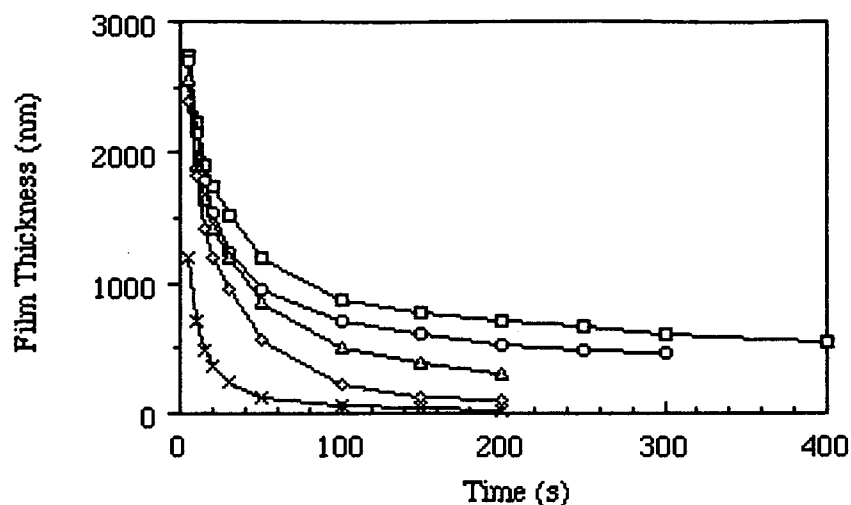


Figure 4.4 Film thickness versus time curves for films formed in 10^{-3} mole dm^{-3} salt solution at regular distances across the film; at the centre, $r = 0$ ($\square$), at $r = 0.05\text{mm}$ ($\circ$), $r = 0.10\text{mm}$ ($\triangle$), $r = 0.15\text{mm}$ ($\diamond$) and at the boundary ring $r = 0.20\text{mm}$ ($\times$).

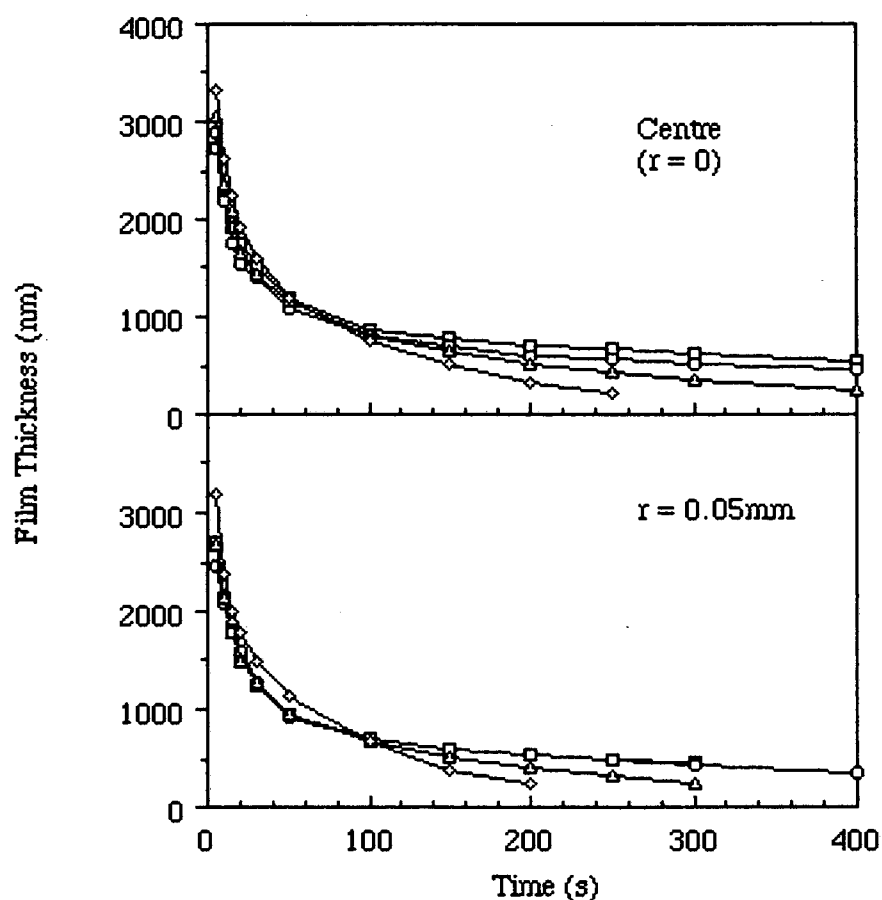


Figure 4.5a Drainage rates measured at the centre ($r = 0$) and at $r = 0.05\text{mm}$ from the centre for films at hydrophilic quartz plates for aqueous NaCl solutions of 10^{-3} mole dm^{-3} ($\square$), 5×10^{-4} mole dm^{-3} ($\circ$), 2.5×10^{-4} mole dm^{-3} ($\triangle$) and 10^{-5} mole dm^{-3} ($\diamond$).

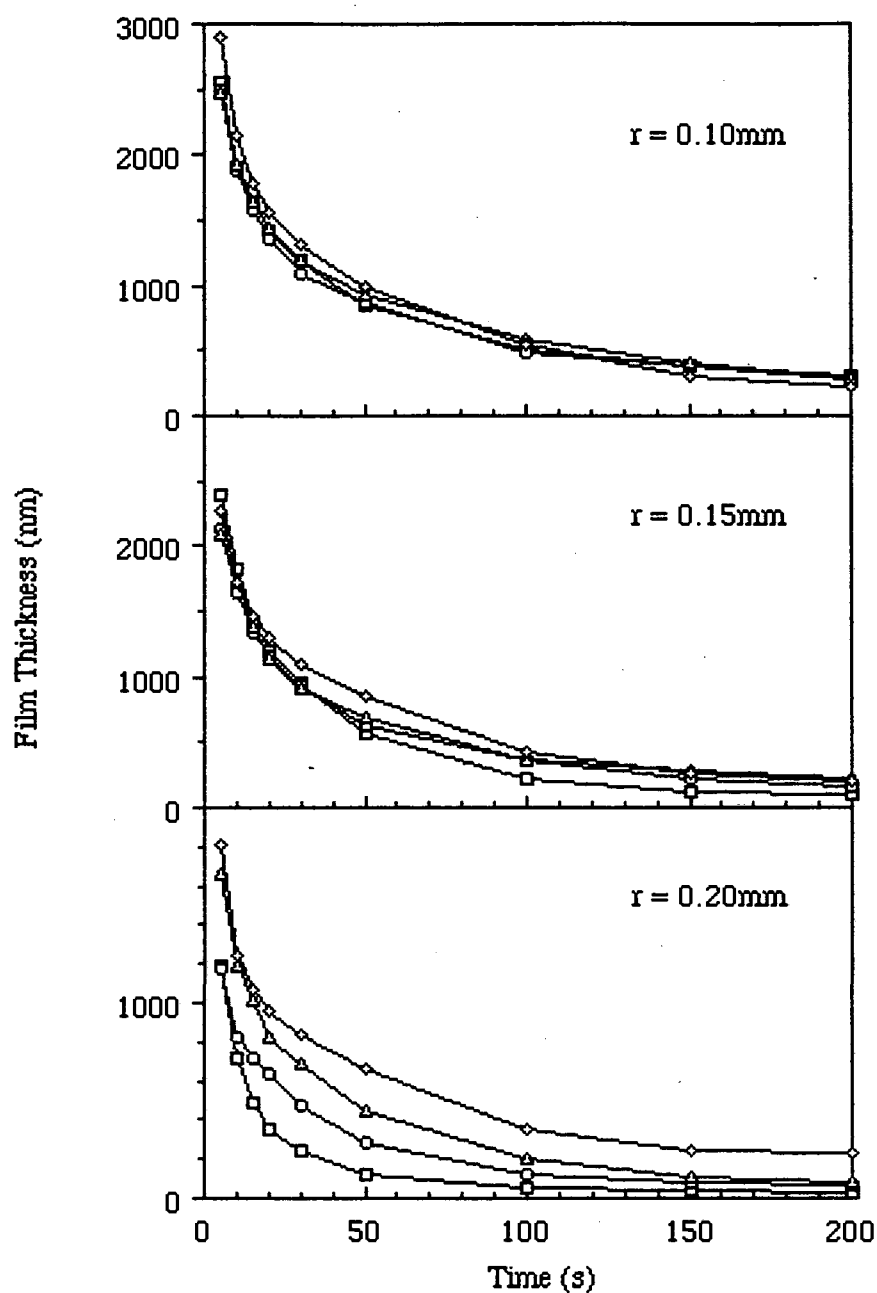


Figure 4.5b Drainage rates measured at the $r = 0.10\text{mm}$, $r = 0.15\text{mm}$ and at the boundary ring ($r = 0.20\text{mm}$) from the centre for films at hydrophilic quartz plates for aqueous sodium chloride solutions of $10^{-3}\text{ mole dm}^{-3}$ ($\square$), $5 \times 10^{-4}\text{ mole dm}^{-3}$ ($\circ$), $2.5 \times 10^{-4}\text{ mole dm}^{-3}$ ($\triangle$) and $10^{-5}\text{ mole dm}^{-3}$ ($\diamond$) concentration.

4.3.3 Comparison with Other Theories

As described in section 2.3 considerable work has been carried out modeling the drainage rates at the centre and the boundary ring of the dimple. Using the equations discussed in chapter two as well as values for the parameters already given earlier in this chapter, the film thickness was determined according to the models of Frankel and Mysels, 1962 (equations 2.23 and 2.24) and Hartland and Robinson, 1977 (equations 2.26 and 2.27).

In Figures 4.6a and 4.6b the results of the models are compared with the drainage rates observed for $10^{-3}\text{mole dm}^{-3}$ and $10^{-5}\text{mole dm}^{-3}$ sodium chloride solutions. These models predict t^{-n} dependence with $n = 0.25$ at the centre and $n = 0.5$ at the boundary ring, in disagreement with our findings.

The differential equation relating the film thickness to radial distance from the film centre and to time, shown in Chapter 2 (equation 3.37) took account of the effects of surface forces by incorporation of the disjoining pressure. This equation cannot be solved analytically and, due to the presence of the fourth order derivative, the film profile must be known with great accuracy, particularly at the boundary ring if any fit to experimental data is to be obtained.

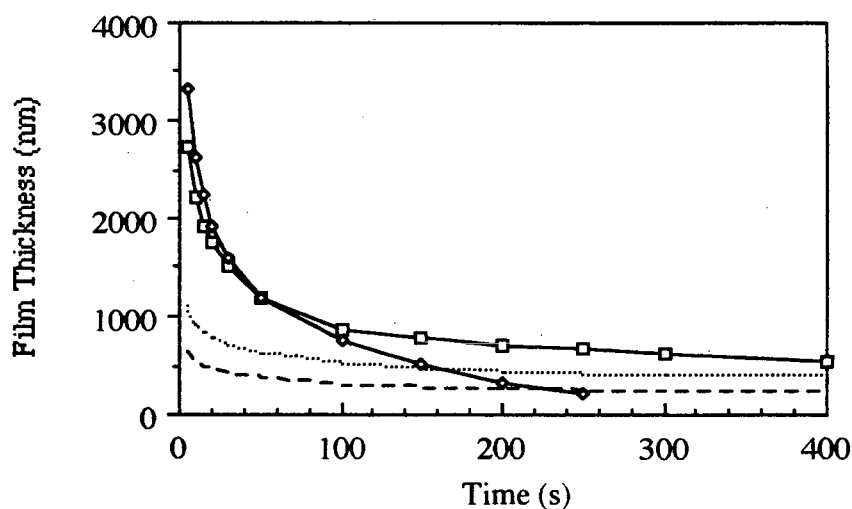


Figure 4.6a Drainage rates at the centre for films at hydrophilic quartz plates comparing the result in sodium chloride solutions of concentrations $10^{-3}\text{mole dm}^{-3}$ and $10^{-5}\text{mole dm}^{-3}$ ($\diamond$) with the theoretical models of Frankel and Mysels (.....) and Hartland and Robinson (---).

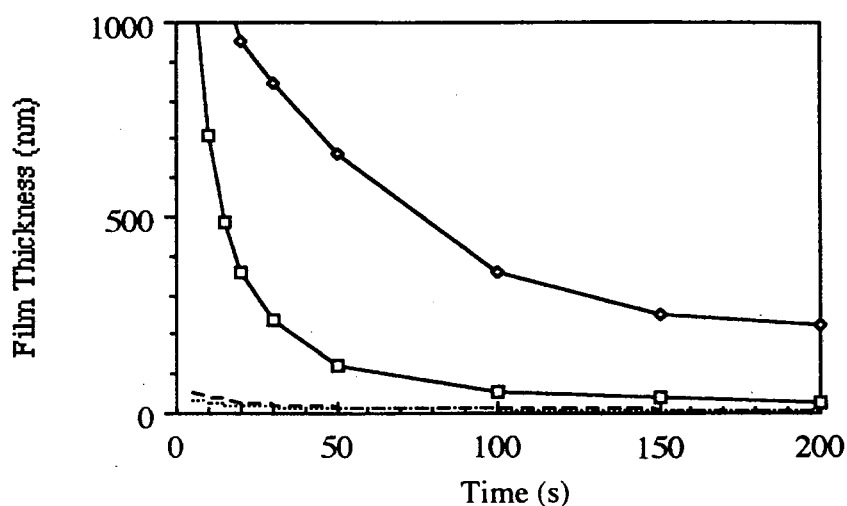


Figure 4.6b Drainage rates at the barrier ring for films at hydrophilic quartz plates comparing the result in sodium chloride solutions of concentrations $10^{-3} \text{ mole dm}^{-3}$ and $10^{-5} \text{ mole dm}^{-3}$ (◇) with the theoretical models of Frankel and Mysels (.....) and Hartland and Robinson (---).

The accuracy required to adequately fit the experimental data far exceeds that obtained in this work or any other published studies. Furthermore, it was found by Lin and Slattery (1982) that solutions to the hydrodynamic equations for film drainage, used to predict draining film profiles as a function of time, are very sensitive to the initial conditions. The results of experiments performed by Doubiez (1991) in which measurements were made of the drainage rate of thin liquid films formed between a free surface and an approaching air bubble showed that models based on the lubrication approximation failed to predict the initial stage of drainage.

4.3.4 Dimple Profiles

The influence of the concentration of electrolyte on the drainage rates observed in these experiments can be further illustrated by examining the profile of the dimple as it changes with time for each concentration of sodium chloride solution studied. Examples of the influence of the sodium chloride solution concentration on the dimple profile are shown in Figures 4.7a and 4.7b. These profiles indicate that the dimple becomes more pronounced as the salt concentration is increased and are the first reported observations of this effect (Hewitt et al, 1993).

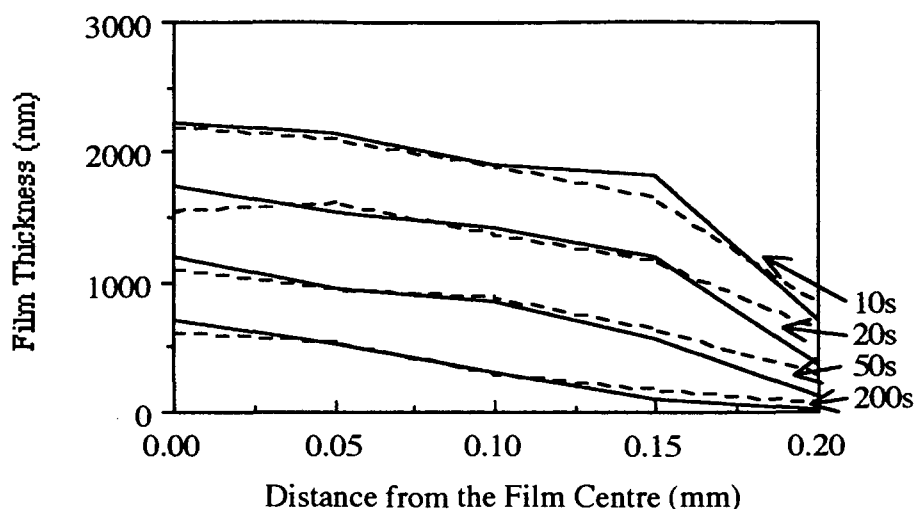


Figure 4.7a Profiles showing the film evolution at 10, 20, 50 and 200 seconds after the bubble was bulged against the quartz plate, in $10^{-3}\text{mole dm}^{-3}$ (—) and $5 \times 10^{-4}\text{mole dm}^{-3}$ (---) sodium chloride solutions.

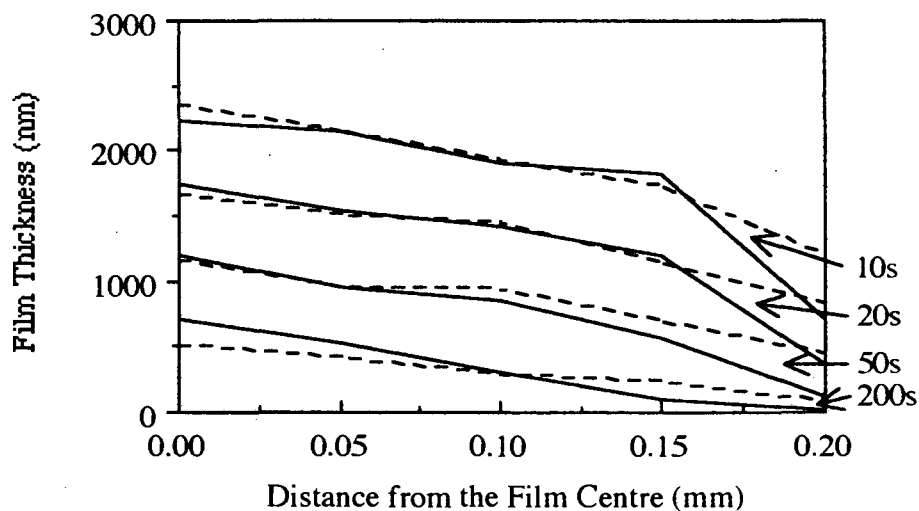


Figure 4.7b Profiles showing the film evolution at 10, 20, 50 and 200 seconds after the bubble was bulged against the quartz plate, in $10^{-3}\text{mole dm}^{-3}$ (—) and $2.5 \times 10^{-4}\text{mole dm}^{-3}$ (---) sodium chloride solutions.

From the results shown it is clear that the distances over which these equilibrium forces act are very much smaller than where the influence of salt concentration on drainage rate is detected. It is unlikely therefore, that the classic equilibrium surface forces approach is relevant to the dynamic case. Qualitatively, this effect can be

explained in terms of the decreased electrostatic repulsion with increasing salt concentration, allowing the film to drain more rapidly at the boundary ring. The drainage rate at the centre is then controlled by the rate at which the aqueous solution can pass through the boundary ring.

4.3.5 Dimple Volume

Changes in the dimple volume reflect the flow rate of electrolyte at the boundary ring so a determination of the rate of volume change as a function of the electrolyte concentration was considered to be informative. The dimple volume was calculated from the film profile and assuming that the dimple was axisymmetrical (see Appendix A). The results are shown in Figure 4.8 for the four electrolyte concentrations studied.

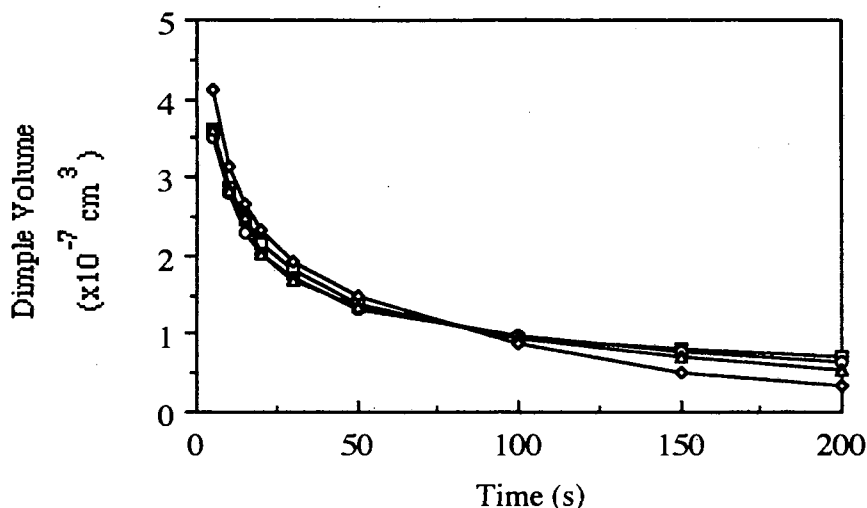


Figure 4.8 Dimple volume changes with time for films at hydrophilic quartz plates for sodium chloride solutions of 10^{-3} mole dm^{-3} (□), 5×10^{-4} mole dm^{-3} (○), 2.5×10^{-4} mole dm^{-3} (△) and 10^{-5} mole dm^{-3} (◇) concentration.

The derivative of the dimple volume with respect to time was derived and plotted against the film thickness at the boundary ring (see Figure 4.9) which gave somewhat inconclusive results. The dimple volume change does not appear to be purely a function the flow rate through the boundary ring, but also in this case shows a dependency on the electrolyte concentration.

The flow of electrolyte at the boundary ring could be compared to the flow through very fine bore capillaries as described in section 2.3.2. As a simple, qualitative

explanation of the observed results it is proposed that increasing salt concentration is manifested as an effective increase in capillary radius at the boundary ring as the double layer is compressed, leading to an increased drainage rate as liquid drains out from the centre of the dimple through the boundary ring. For simple capillary drainage, the flow rate varies at least with the fourth power of the capillary radius (Mulcahy, 1984). The reduced flow which occurs with decreasing electrolyte concentration has been measured and reported as an increase in the apparent viscosity. At film thicknesses at kh values of ten the apparent viscosity is approximately 10% higher than the bulk value which would give a reduced flow at the boundary ring with decreasing electrolyte concentration.

The theory developed for flow in fine capillaries has been developed to explain observations made with capillaries having rigid walls whereas the films involved in this study consisted of one rigid wall and a deformed air/aqueous solution interface. This could well be the key difference when comparing the films in this study with the existing theory.

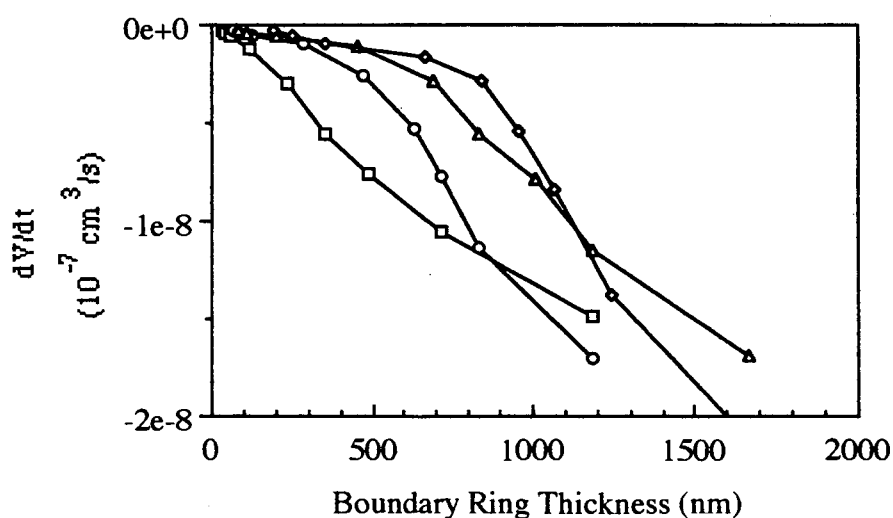


Figure 4.9 The rate of change of the dimple volume with respect to time plotted against the film thickness at the boundary ring for films at hydrophilic quartz plates for sodium chloride solutions of $10^{-3} \text{ mole dm}^{-3}$ ($\square$), $5 \times 10^{-4} \text{ mole dm}^{-3}$ ($\circ$), $2.5 \times 10^{-4} \text{ mole dm}^{-3}$ ($\triangle$) and $10^{-5} \text{ mole dm}^{-3}$ ($\diamond$) concentration.

4.4 Drainage at Hydrophobic Surfaces

Clean quartz plates were rendered hydrophobic as described in section 3.3.2 and thin film drainage rates were determined in exactly the same way as for hydrophilic plates. As described in the experimental method (section 3.4) clarification of the fringe order had to be established since equilibrium films were not observed with hydrophobic plates. The early drainage pattern (less than 5 seconds) at these hydrophobic plates was matched with that at hydrophilic plates and the fringe order was then assigned to the interference pattern. This method of assigning the fringe order was not thought to be unreasonable since, for these drainage times, the corresponding film thicknesses were at least equal to or greater $5\mu\text{m}$.

4.4.1 Hydrophobic Interaction

The effect of increasing hydrophobicity is shown in Figure 4.10 in which the drainage rates are shown for films formed in $10^{-5}\text{mole dm}^{-3}$ sodium chloride solutions. Attempts were made to measure the drainage rates at surfaces with higher hydrophobicity (e.g. $\theta_c = 65^\circ$) but the films ruptured very quickly, certainly too fast to allow the film to be scanned and the drainage at the boundary ring to be determined. Even with the hydrophobic plates, for which the results are shown in Figure 4.10, the film lifetime was sometimes quite short and the rupture time varied in a somewhat random manner.

4.4.2 Effect of Changes in Salt Concentration

The combined influence of changes in the aqueous salt solution concentration with increased hydrophobicity was only determined in the case of the slightly hydrophobic plate (i.e. $\theta_c = 8^\circ$) as with plates which were more hydrophobic the films ruptured too quickly to allow film drainage rates to be determined. The observed rates of film thinning at a slightly hydrophobic quartz plate are shown in Figure 4.11 and as was the case for hydrophilic plates, the drainage rate at the boundary ring increased for increasing sodium chloride solution concentration.

In Figure 4.12, comparison of the drainage rates of films at hydrophilic plates is given with those at plates of low hydrophobicity in sodium chloride solutions of concentrations $5 \times 10^{-4}\text{mole dm}^{-3}$, $2.5 \times 10^{-4}\text{mole dm}^{-3}$ and $10^{-5}\text{mole dm}^{-3}$. The effect of the slight degree of hydrophobicity of the plates in increasing the drainage rate at the boundary ring was consistent across the electrolyte concentration studied.

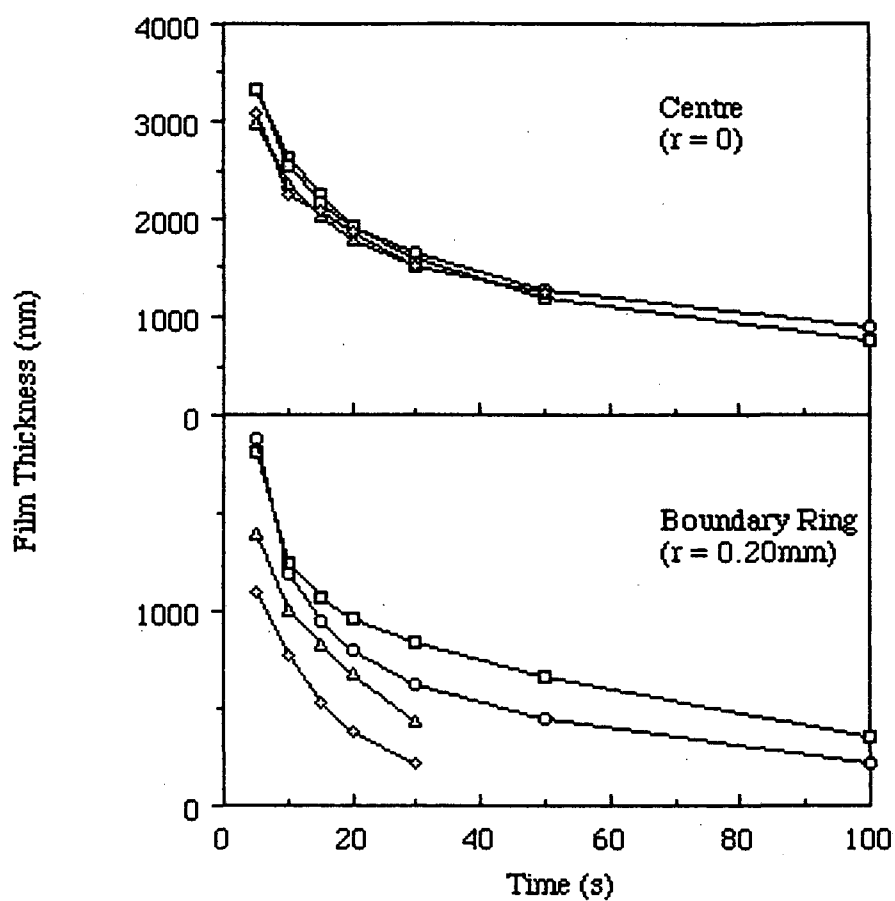


Figure 4.10 Drainage rates at the centre and the boundary ring for films at surfaces of different hydrophobicity in $10^{-5}\text{mole dm}^{-3}$ sodium chloride solutions. The hydrophobicity is indicated by the receding water contact angle θ_c as follows: $\theta_c = 0^\circ$ ($\square$), $\theta_c = 8^\circ$ ($\circ$), $\theta_c = 18^\circ$ ($\triangle$) and $\theta_c = 42^\circ$ ($\diamond$).

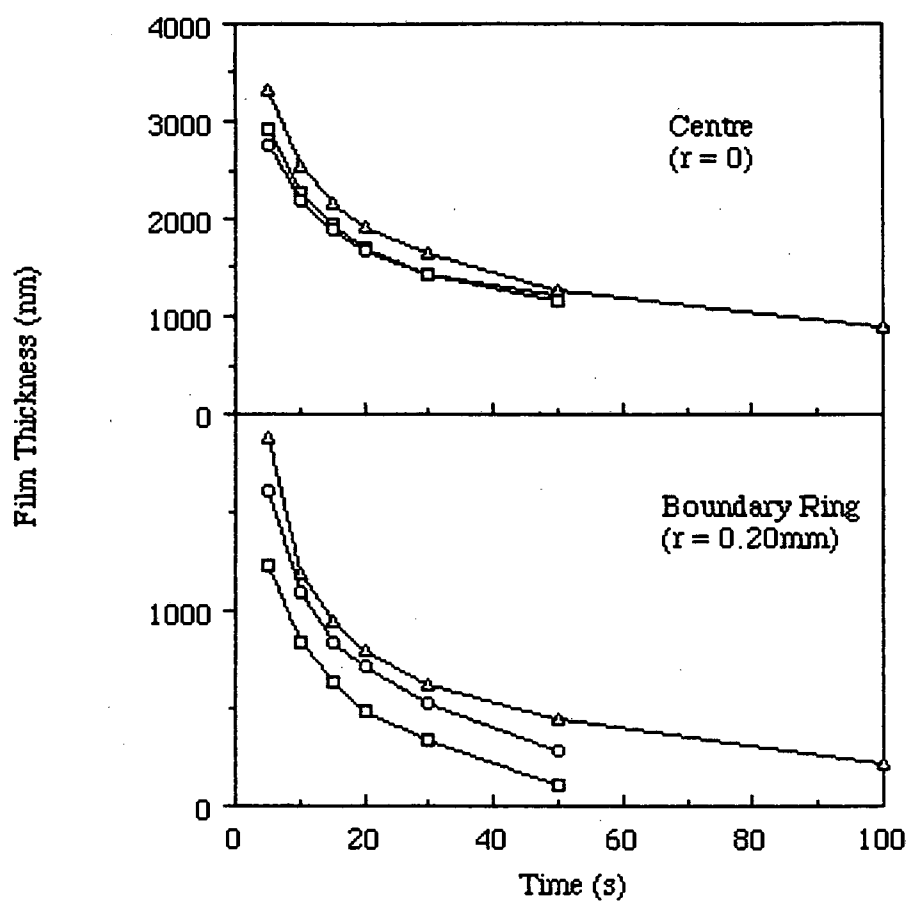


Figure 4.11 Drainage rates at the centre and the boundary ring for films at quartz of low hydrophobicity ($\theta_c = 8^\circ$) in $5 \times 10^{-4} \text{ mole dm}^{-3}$ (□), $2.5 \times 10^{-4} \text{ mole dm}^{-3}$ (○) and $10^{-5} \text{ mole dm}^{-3}$ (△) sodium chloride solutions.

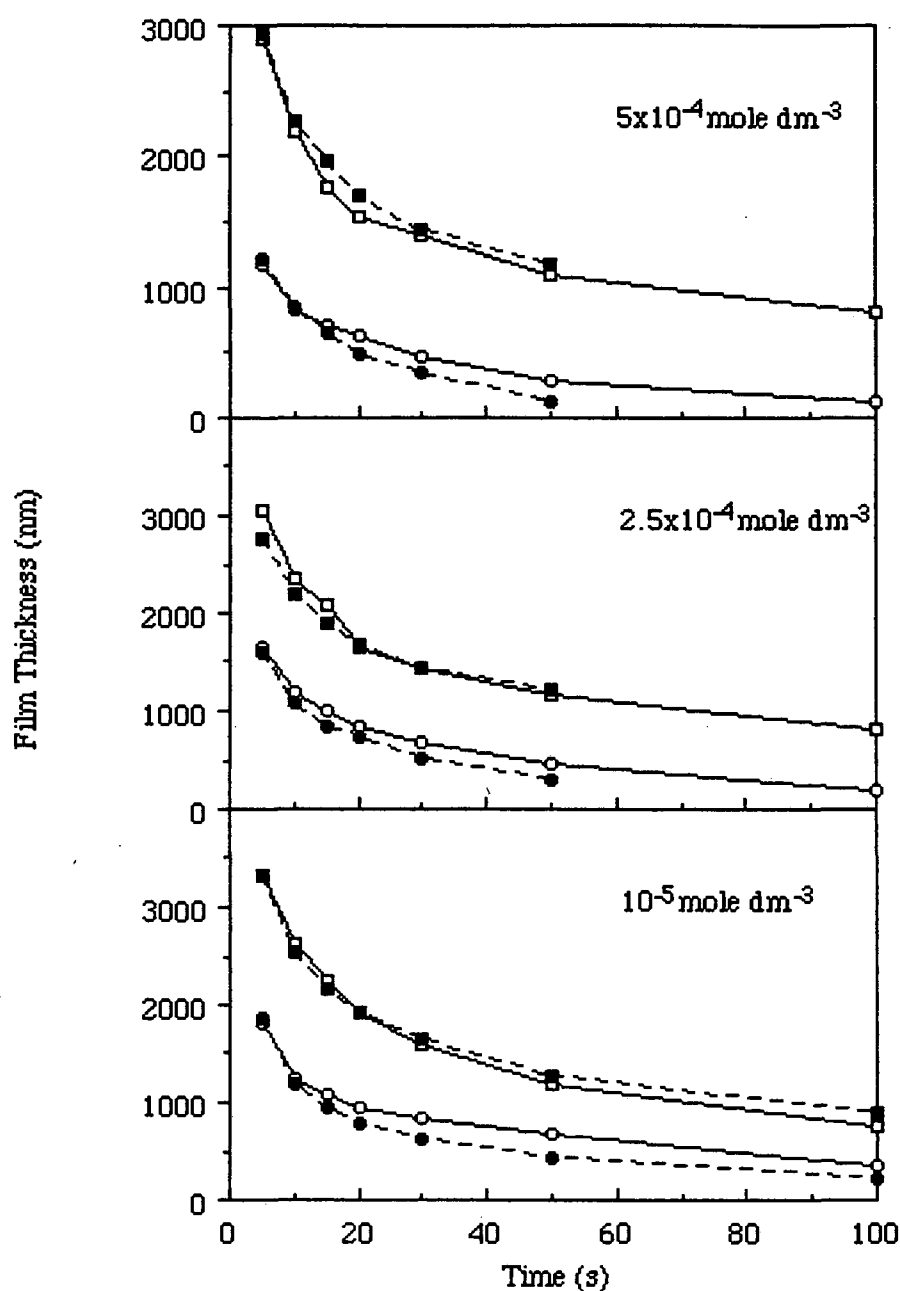


Figure 4.12 The drainage rates at the centre (squares) and at the boundary ring (circles) for hydrophilic (open symbols, solid lines) and slightly hydrophobic ($\theta_c = 8^\circ$; closed symbols, dashed lines) quartz plates are shown for sodium chloride solutions of concentrations as indicated.

4.4.3 Comparison with Previous Work

The metastable films on hydrophobic surfaces reported by Blake and Kitchener (1972) were certainly not seen in this study. This is not surprising really, since in Blake and Kitchener's work the films were formed by pressing a bubble against a plate extremely slowly while ensuring that there was absolutely no mechanical or thermal shocks whatsoever. Conversely, in this study a bubble was bulged against a plate very quickly so that liquid drained from the intervening film as fast as the hydrodynamic and surface forces would allow.

An indication of the magnitude and range of hydrophobic interactions should be forthcoming from experiments involving the interaction of an air bubble with a hydrophobic quartz surface. The observations in this study suggest that hydrophobic interactions are of the same magnitude as electrostatic forces, since the influence of both of these effects become apparent at similar distances in the dynamic case of an air bubble fast approaching a solid surface.

Experiments carried out by Israelachvili (Israelachvili and Adams, 1978) with the surface forces apparatus in which hydrophobised rigid mica surfaces were used showed that it was possible to directly measure the strength and range of the hydrophobic interaction. Further work at the Australian National University (numerous published papers could be quoted here but for example see Israelachvili and Pashley, 1982; Christenson, 1987) has shown that hydrophobic interactions are an order of magnitude stronger than the van der Waals-dispersion force, although the molecular mechanism underlying the observed hydrophobic attractive force is still not understood.

It has been suggested that there is a gradual change from a repulsive hydration force which occurs between hydrophilic surfaces, to an attractive hydration force with increasing surface hydrophobicity (Israelachvili, 1985). It is not clear then how changes in the concentration of electrolyte solution between hydrophobic surfaces would influence the observed hydrophobic interaction.

Christenson and Claesson (1988) reported the spontaneous formation of cavities between hydrophobic surfaces in water, which went some way in explaining the long range over which the attractive hydrophobic force operates. Rather than consider the attraction in terms of structural effects in the intervening film of water, Christenson

and Claesson proposed that the hydrophobic interaction is not a true equilibrium force, but originates from an imbalance of the kinetic and cohesive pressures in the water layer.

The attractive forces between hydrophobic surfaces may have an hydrodynamic origin (Ruckenstein and Churaev, 1991), with these long range forces being due to the instability of the planar interfaces between a hydrophobic surface and the water layer, caused by the incompatibility of the two. Fluctuations of the two water interfaces generated by the instability are apparently hydrodynamically correlated.

Essential to an understanding of the origin of these forces is a knowledge of their dependence on physical parameters such as salt concentration. Recently Xu and Yoon (1989, 1990) have published results of coagulation experiments conducted on aqueous suspensions of methylated silica. They found that for strongly hydrophobic solids the attractive hydrophobic interaction dominates the repulsive electrostatic force at 10^{-3} mole dm^{-3} electrolyte concentrations.

4.5 Conclusions

The experiments involving changes in the film radius clearly indicate that a hydrodynamic effect is significant in determining the overall drainage rate. It is also obvious that the formation of a dimple in the deformable air/water interface modifies the drainage rate at the centre of the film and leads to deviations from the theory for film thinning derived assuming two plane parallel interfaces.

4.5.1 Hydrophilic Surfaces

Reasonable agreement was obtained between experimental equilibrium film thicknesses (i.e. when drainage has ceased) and those calculated using the DLVO theory. A degree of uncertainty remains concerning the potential at the air/aqueous interface, however overall the sign and magnitude of this parameter appear to be a good representation of the result of the charging mechanism which is in operation.

The measurement of the drainage rates of thin aqueous films trapped between a hydrophilic, smooth quartz surface and a rapidly approaching air bubble as a function of salt concentration shows a surprisingly long range dependency. As the salt concentration was increased the drainage rate at the dimple centre decreased whereas it increased at the boundary ring resulting in a dimple which became more

pronounced. This influence of salt concentration on the profile of the dimple, observed here for the first time, began to take effect at distances of around $1\mu\text{m}$, considerably further than distances over which these forces were expected to have any effect. Qualitatively, the compression of the double layer would explain the trends in the observed changes in the drainage rates with variations in the ionic strength of the aqueous solution. However the distances at which the differences in drainage rates become apparent are an order of magnitude greater than could be predicted or explained using the static or equilibrium DLVO model.

Equilibrium electrostatic forces are known to decay over 10nm in $10^{-3}\text{mole dm}^{-3}$ 1:1 electrolyte solution and a considerably longer range in less concentrated solutions, and while adequately explaining the thickness of equilibrium films it is not clear at what distances differences should begin to become significant in the drainage rates of films in electrolyte solutions of different concentration. However, at distances greater than that over which electrostatic forces are known to extend at equilibrium the drainage rates of thin films formed in solutions of different salt concentrations must begin to differ.

The combination of the dynamic impact of these electrostatic forces and the hydrodynamics of the dimpled air/aqueous solution appears to result in the long range effect observed in this study. The effect of changes in the ionic strength of the electrolyte solution and hence the influence of electrostatic forces in the dynamic situation will be considered further when the results of the bubble/particle attachment experiments are discussed.

4.5.2 Hydrophobic Surfaces

The experiments on hydrophobic surfaces are more limited than hoped for due to the difficulties encountered with these surfaces, but the enhanced drainage rate results observed between an air bubble and partially methylated quartz plates indicate that the attractive force between hydrophobic surfaces is of the same order of magnitude (i.e. strength and range) as electrostatic forces present in (1:1) electrolyte solutions of 10^{-5} to $10^{-3}\text{mole dm}^{-3}$ concentration.

As in the case of the influence of electrostatic forces in films at hydrophilic surfaces, the strength and range of the hydrophobic force appears to be magnified in the dynamic situation observed in this study and there is no reason to suggest that the

hydrophobic force in an equilibrium situation, such as that studied by Blake and Kitchener (1972), is very much different to an equilibrium electrostatic force.

4.5.3 Experimental Strategy

Determining the exact fringe number when analysing the interference pattern obtained for a film draining at a strongly hydrophobic quartz plate presented a problem in the way the interference technique was used in this study. This problem could be overcome by the introduction of light of another wavelength although this would be difficult with the current apparatus and is a future experiment. The very short lifetimes of the films formed at strongly hydrophobic surfaces limited the usefulness of this present technique as there was not enough time to scan the draining film and establish the drainage rate at the boundary ring. That the films are indeed short-lived (e.g. Figure 4.10) is of some comfort to the flotation experiments, where bubble-particle attachment should be fast.

Nevertheless, these experiments do show conclusively that the drainage rate at the boundary ring regulates the drainage rate at the centre of the film. It was also obvious, while observing film rupture at hydrophobic surfaces, that once film rupture had occurred, the three phase line of contact move across the surface very quickly and an area of bubble/plate contact was established in less than one second even with only moderately hydrophobic quartz plates. This is in accord with the observations of Newcombe and Ralston (1994).

CHAPTER 5. BUBBLE/PARTICLE COLLECTION MECHANISMS - LITERATURE REVIEW

Without surface alteration most minerals of practical interest are not hydrophobic enough to be naturally floatable. It has been generally thought that flotation will only occur if a finite contact angle is established between the particle and the air bubble, although this has been questioned by Derjaguin and Dukhin (1981) for fine particles. This theory discusses the possibility of contactless flotation in the case of fine particles, although as yet there is no experimental proof of this phenomenon.

Flotation, however, is dependent on both kinetic and thermodynamic effects and the contact angle alone does not define the flotation rate. Even when thinning and rupture of the liquid film between a bubble and a particle is (energetically) feasible, the bubble and particle may move apart before the film thinning process has reached the point of rupture and, hence, attachment does not occur.

Flotation of a given particle to the froth level is the result of the successful occurrence of three bubble/particle events: collision, attachment and retention (or lack of detachment). The first is controlled by the hydrodynamic conditions, the second depends on a combination of surface forces and hydrodynamics, and the third is a balance between the kinetic energy of the bubble-particle aggregate and the force of detachment at the three phase line of contact. This review briefly examines the major developments which have led to our current understanding of these processes, paying particular attention to the role played by surface forces. Bubble/particle attachment processes are extensively reviewed in the next chapter.

5.1 Bubble/Particle Collection

The first quantitative attempts to describe the flotation rate in terms of bubble/particle interactions considered the probability of bubble/particle collision to be a fundamental parameter in determining the rate of flotation (Gaudin, 1932). In his landmark paper, Sutherland (1948) described the flotation rate in terms of the collection efficiency i.e the fraction of particles in a bubble's path which are collected by the bubble.

Particles larger than several microns in diameter will not be substantially affected by Brownian motion and will touch the bubble if the trajectory followed by the

particle, determined by hydrodynamics, comes within one particle radius of the bubble surface according to Sutherland. The "collection radius" of the bubble is given by $\sqrt{3rR}$ where r is the particle radius and R is the bubble radius. Assuming that the flow of liquid around a bubble could be calculated from potential flow theory (i.e. high Re_b), Sutherland predicted the removal rate of particles. This assumption of potential flow is valid only for high Reynolds numbers (i.e. $Re_b \gg 1$). The Sutherland theory, as a first approximation, gives an adequate description of bubble/particle collision, but completely overlooks the attachment and the aggregate stability efficiencies.

Derjaguin and Dukhin (1960/61) presented a detailed theory of flotation in which they considered that the approach of the mineral particle towards the bubble surface takes place in three stages, corresponding to movement through 3 zones, shown in Figure 5.1.

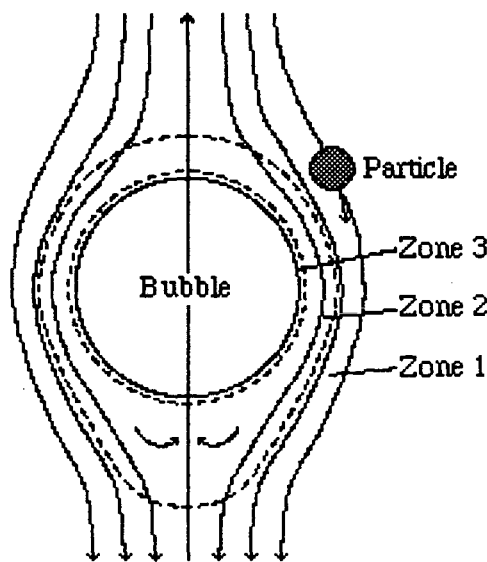


Figure 5.1 Zones in the fluid streamlines around the bubble surface according to Derjaguin and Dukhin (1960/61).

In zone 1, which is sufficiently far away from the bubble so as to be outside the range of molecular forces and diffusional processes, the particles move under the action of hydrodynamic forces.

Zone 2 is that region where the flow of liquid around the bubble gives rise to a tangential stream at the surface of the bubble which disturbs the equilibrium of adsorbed ions. The return of disturbed ions is controlled by a combination of diffusion rate and an electrophoretic force giving rise to a “diffusiophoretic force” which particles experience on entering this zone. These diffusiophoretic forces reflect the differing mobilities of the cations and anions, and result in strong electric fields in this zone.

Zone 3 is that region in which interparticle forces become important and can accelerate or retard the rate of thinning of the liquid film between the bubble and the particle. The Derjaguin and Dukhin approach is conceptually very useful and forms the basis of modern theories of flotation.

Flint and Howarth (1971) attempted to provide a complete analysis of the viscous effects in bubble/particle interaction. They circulated a stream of glycerol solution containing a suspension of glass beads past fixed nylon spheres. Flint and Howarth did not measure contact between spheres in their system, but measured the position of the glass beads relative to the fixed spheres as a function of time, thereby determining experimental trajectories. According to their analysis, particle behaviour may be characterised by two dimensionless parameters, namely a particle inertia parameter:

$$K = \frac{\rho_p d_p^2 v_r}{9 \eta d_b} \quad 5.1$$

and a particle gravity parameter:

$$G = \frac{\Delta \rho d_p^2 g}{18 \eta v_r} \quad 5.2$$

where d_p is the particle diameter, d_b is the bubble diameter, v_r is the velocity of the particle relative to the bubble, η is the viscosity of the fluid in which the bubble and particle are moving, g is the acceleration due to gravity, ρ is the density of the particle and $\Delta \rho$ is the difference in the densities of the particle and the fluid. Flint and Howarth deduced that a limiting value of the collision efficiency is given by:

$$E_c = \frac{G}{(1+G)} \quad 5.3$$

which holds for fine particles where $K < 0.1$ and particle inertial effects may be ignored.

The results of the flow experiments conducted by Flint and Howarth were compared with their theory, based on solving the relevant equations of motion and thus allowing predictions of the trajectories of the particles approaching a bubble to be made. Reasonable predictions were found for the interaction between a bubble rising through a dilute, stationary suspension of particles, up to the point of close approach with the bubble.

Reay and Ratcliffe (1973) considered particles less than $20\mu\text{m}$ and bubbles less than $100\mu\text{m}$ in diameter and found that by ignoring inertial forces, but taking into account gravitational forces, the efficiency of collision, E_C , given by:

$$E_C \propto \left(\frac{d_p}{d_b}\right)^n \quad 5.4$$

where n is dependent on the relative particle density, ρ_p/ρ_f , and has a value of 2.05 for $\rho_p/\rho_f = 2.5$.

Interceptional and gravitational collision efficiencies were presented by Weber and Paddock (1983), using numerical solutions to the complete Navier-Stokes equations. Expressions were derived relating both the gravitational and interceptional collision efficiencies to the Reynolds number of the air bubble and the particle/bubble diameter ratio. These equations have formed the basis of more recent models such as the model described by Schulze (1989) which is discussed at length in chapter 6.

Since the form of the fluid stream around the bubble is the main factor that affects the trajectory of particles in the collision process, it is essential to incorporate a realistic fluid flow pattern around the bubble in order to analyse the collision efficiency. The stream functions that describe the flow pattern around moving bubbles vary with the bubble Reynolds number, so Jiang and Holtham (1986) developed a model for the interception efficiency of collision using different stream functions. They based their calculations on Stokes' stream function which accurately described the fluid flow past a bubble at low Re_b without the need to include the inertial force. At higher Re_b Ossen's stream function in which the inertial term is considered, was used. As a result of using these stream functions the

model derived by Jiang and Holtham predicted an increase in collision efficiency with decreasing bubble size primarily due to the fluid flow pattern around the moving bubbles.

Fine particles are difficult to float because of the inability of these particles to deviate from the fluid streamlines around the bubble and hence collide with the bubble, manifesting itself in a low efficiency of collision. Improved recovery of fine particles can be achieved if the particles are provided with more inertia, which is the fundamental concept of the air-sparged hydrocyclone. In this flotation system fine particles obtain high inertia due to the centrifugal force field developed by the swirl motion of the slurry in the hydrocyclone (Miller and Van Camp, 1982). Alternatively, fine particles may be aggregated thereby increasing E_C and then floated (see Derjaguin et al, 1984).

In a most thorough, recent review of the hydrodynamics of bubble/particle collision Schulze (1989) described a model which allows calculation of the collision efficiency for the particles and bubbles of the diameters used in this study. In the development of the model, Schulze has shown where use has been made of the expressions derived in the models discussed earlier and consequently it was felt that this approach was the best available at the time that this study was undertaken. The complete model for the collision efficiency outlined by Schulze is described in detail in Chapter 6 and example calculations using this model are given in Appendix B. The results of these calculations provide the basis for the discussion and interpretation of the results obtained in this study (see Chapter 8).

5.2 Bubble/Particle Attachment

The efficiency of attachment is the fraction of the colliding particles which actually become attached to the bubble, that is, which leads to bubble/particle union occurs. The time that the particle spends in a region of close approach to the bubble is referred to as the contact time and this is considered to consist of either the time of collision (or impact) or the sliding time during which the particle slides around the bubble.

For attachment to occur the thin aqueous film which forms between the particle and the bubble must drain and rupture (thin film drainage time, τ_{fd}) and a stable three-phase line of contact must be formed (three phase line of contact spreading time, τ_{plc}). The time for these two events to occur is described as the induction time

(Sven-Nilsson, 1934). Only those particles that are in a region of close approach for a time greater than or equal to the induction time will actually form a stable bubble/particle contact. That is, the contact time τ_c must equal or exceed the induction time, τ_{ind} , thus:

$$\tau_c \geq \tau_{ind} = \tau_{fd} + \tau_{plc} \quad 5.5$$

The resultant attachment efficiency then is dependent on the interplay between the contact time and the induction time. Note that if there is a delay or significant sluggishness in the formation of the three phase contact line, bubble/particle attachment may not occur.

5.2.1 Contact Time

When the particle approaches the bubble two different types of interaction may occur. Collision may take place in which the bubble surface is deformed and the bubble rebounds (unless attachment takes place) or the particle may slide over the bubble surface as shown in Figure 5.2.

Which of the two interactions predominates in flotation depends upon a number of factors, but collision processes are more important with large particles and high relative velocities. Sliding times are therefore of more interest with smaller particles such as those used in this study particularly because they are considerably longer than collision times for these particles.

5.2.2 Collision Time Models

Evans (1954) developed a collision time model in which calculations were made using the equation of harmonic oscillation of the colliding particle normal to the deformed bubble surface. Scheludko (1976) modified the Evans model by correcting the equation of oscillation used, taking into account the additional co-oscillating mass of the meniscus adjacent to the particle. The corrected collision time model gave results 2 to 3 times greater than the Evans model, but was still too small to explain the experimental values.

Schulze et al (1989) have shown experimentally that measured collision times are substantially longer than the previous models predicted. A model was therefore developed which assumed non-linear oscillation, taking into account the particle

mass, the mass of liquid accelerated by the particle and the non-spherical deformation of the bubble surface upon contact with the particle. Calculations made using this model showed the collision time to be independent of bubble size and, for particle diameters of less than $80\mu\text{m}$, to be less than 0.5 milliseconds (shown in the next chapter in section 6.2.1).

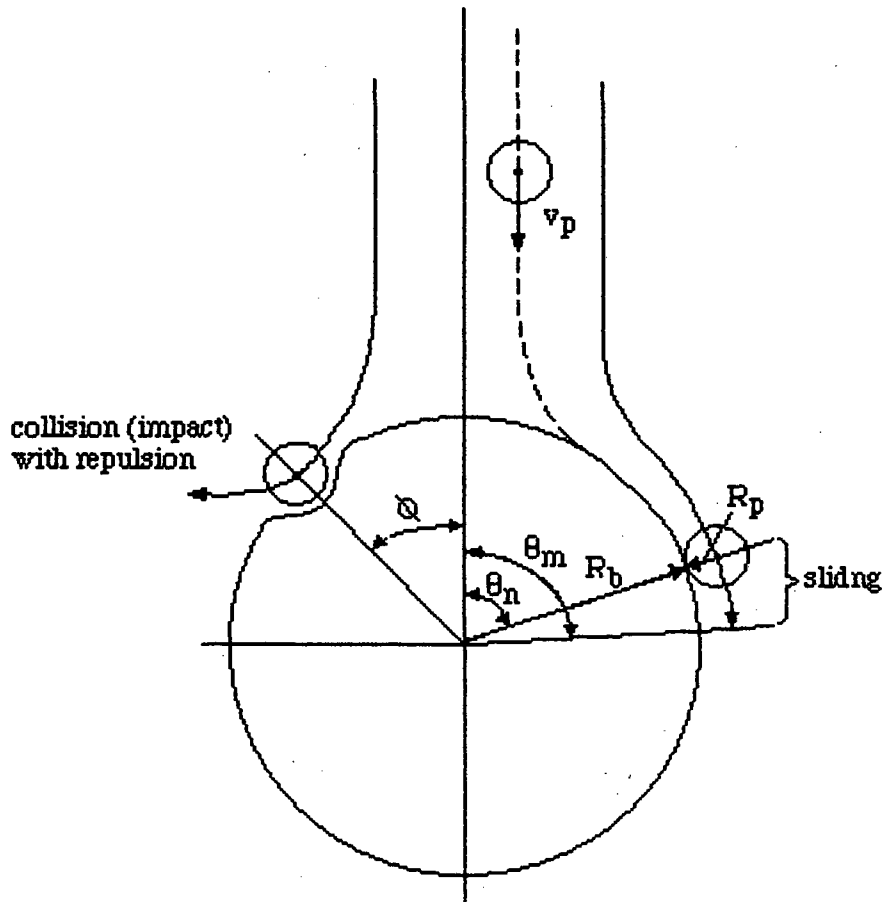


Figure 5.2 Schematic representation of collision and sliding interactions between the bubble and particle. The collision angle of a collision process (ϕ) and a sliding process (θ_n) are shown. Other parameters indicated are the bubble radius (R_b), particle radius (R_p), particle velocity (v_p) and the maximum angle of the sliding process (θ_m) before the radial component of the particle's velocity is negligible compared with its downward velocity.

5.2.3 Sliding Time

Sutherland (1948) considered that bubble/particle attachment could occur while the particle was sliding around the particle and therefore regarded the contact time as the sliding time (as shown in Figure 5.2). Potential fluid flow at the bubble surface was assumed by Sutherland in order to derive an analytical solution for the sliding time. It has since been pointed out by Dobby and Finch (1986) that potential flow is not relevant to flotation size bubbles and gives velocities which are too high, resulting in a model which fails to predict the important effects of particle size. A more appropriate model has been developed by Dobby and Finch. The Dobby and Finch model is based on the experimental data of Seeley (1975) for the liquid velocity distribution on the upper surface of the bubble. This model is described in detail in the next chapter as it is used to calculate the sliding times for the experiments conducted in this study.

Dobby and Finch fitted their model to the experimental results provided by the photographic data of Schulze and Gottschalk (1981). Schulze and Gottschalk reported sliding times as a function of angle of collision, and found only reasonable agreement with the potential flow model of Sutherland, after correcting an error in Sutherland's original model in which the sliding time was over-estimated by a factor of 2. The experimental results of Schulze and Gottschalk were then found to compare more favourably with the Dobby and Finch model.

The Dobby and Finch model suggests that the decrease in floatability observed with increasing particle size is due to a decrease in the attachment efficiency. Their model also suggests the the attachment efficiency for very small particles is very high but that preference for these particles is poor. This is due to the long sliding times for very small particles, so that even particles for which the induction time is long contact the bubble and float.

As noted by Yoon and Luttrell (1989), for a given bubble and particle size, the distance travelled by a particle along the surface of a bubble is a function of the angle of collision. Only when the angle of collision is smaller than some limiting angle will the particle have a sliding time longer than the induction time and attachment will occur. The value of the limiting angle will be dependent on the magnitude of the tangential velocity of the particle as it slides over the bubble surface. Jiang and Holtham (1988) demonstrated the existence of a maximum collision angle. By studying the flow of quartz particles past a bubble, they found

that, with increasing collector concentration (which rendered the particles more hydrophobic) the maximum collision angle for attachment increased.

5.2.4 Induction Time

Sutherland linked the removal rate of particles to the induction time and his calculations showed that the attachment efficiency is reflected in the induction times. Other researchers such as Philippoff (1952) and Evans (1954) studied induction time by carrying out experiments in which a bubble was pressed against a flat mineral surface. More recently there have been attempts to determine the induction time experimentally by measuring the particles of different species captured by an air bubble on the tip of a capillary tube that is forced against a bed of particles for a short period of time (Laskowski and Iskra, 1970 and Yoon and Luttrell, 1985).

Ye and Miller (1988) and Ye et al (1989) carried out such induction time experiments where the time that the bubble was pressed against the particle bed was varied, so that a distribution of the percent attachment versus controlled contact time was obtained. From this distribution, the time for which 50% of the particles had become attached to the bubble was determined and was arbitrarily taken to be the induction time. There was a good correlation observed in that a decrease in the induction time was associated with an increase in the contact angle and an increase in the floatability of the five coal types tested.

Ye and Miller (1989) compared calculated contact times based on sliding time models with their measured induction times and suggested that some of the coal samples studied should have floated although they were known not to float (i.e. for these samples the induction time was less than the calculated sliding time). From this, Ye and Miller concluded that the bubble/particle collision process was of greater significance than the sliding process, at least in systems involving coal particles.

In froth flotation systems involving sulphide minerals the particle size is typically in the range 10-100 μ m, whereas in the coal processing the size of the particles being dealt with is in the range of 100-500 μ m. This may account for the difference in the relative significance of the sliding and colliding processes although it is not that straightforward as the density of coal is considerably less than that of sulphide mineral particles.

In view of the short duration of bubble/particle contact, film thinning and rupture must occur very rapidly for flotation to be successful. In considering the film thickness at which rupture may occur, it is clear that sharp projections on the particle should facilitate the process. Experimental observations to date (particularly the work of Anfruns and Kitchener, 1977) have only allowed a qualitative assessment of the role of particle surface roughness and heterogeneity on the film thinning and film recession processes. Blake and Ralston (1985) also reported experiments in which the addition of urea enhanced the flotation rate of hydrophobic glass spheres but not of hydrophobic angular quartz particles thus providing further evidence for the importance of surface roughness in film drainage and rupture.

Clearly any analysis of the induction time which assumes a parallel-plane film misses the strong influence of film dimpling upon film drainage which has been observed in the earlier section of this work. Calculations made by Schulze (1989) using Reynolds theory for the film drainage rate resulted in induction times one to two orders of magnitude greater than the contact times observed experimentally. However, the use of Taylor's equation, applicable to particles with tips and edges, reduces film drainage times to the same order as collision times (Schulze et al, 1989). For broken particles the prospects of attachment during collision are much better than for smooth or spherical particles which discussed further when analysing the experimental results of Anfruns and Kitchener (1977), in section 5.5.

Li et al (1990) considered a more complete hydrodynamic theory for the thinning of a dimpled liquid film between a bubble and a solid particle and applied it to the rate of collection of particles by flotation. The profile of the gas/liquid interface across the dimple was described using the model developed by Lin and Slattery (1982), Chen and Slattery (1982) and Chen (1984) taking into account the influence of the disjoining pressure attributable to van der Waals and electrical double layer forces.

The effect of van der Waals forces was described in the model by a parameter which was related to the static contact angle. Li et al compared results of their model with the induction times determined experimentally on samples of coal, using the values for the contact angles also reported in the same work by Ye and Miller (1988). The agreement between the model and the experimental results was sufficient encouragement to further develop the model to predict flotation rates. As a result of this extension of their model, Li et al deduced that the attachment

efficiency was essentially independent of bubble size (for $r_b \gg r_p$), so that dependence of the flotation rate on the particle size (r_p) occurs primarily through the collision efficiency for small r_p and the flotation rate increases with r_p . For larger r_p , E_A decreases so that the flotation rate increases with the particle size more slowly. The absolute values of particle size at which the changes take effect depend on the density of the particles.

Crawford and Ralston (1988) used the Sutherland model to determine induction times from experimental flotation data and found that for a given particle size, the induction time decreases with increasing hydrophobicity. The induction time also, went through a minimum in particle diameter with constant particle hydrophobicity, reflecting the size of the most readily floated particle. Again, with constant hydrophobicity, the induction time was found to decrease with increasing ionic strength at constant particle hydrophobicity due to a reduction in the electrostatic repulsion between particles and particles.

The experimental methods used for determining induction times all suffer from the disadvantage that there is still insufficient understanding of the effect on the induction time of the process of bubble deformation and energy dissipation during bubble/particle collision. Also, not enough information exists concerning attractive forces between hydrophobic surfaces and their influence during bubble/particle interaction to allow description of how the thin film of liquid between a particle and a bubble drains and ruptures, as a particle slides or rolls around a bubble.

5.2.5 Attachment Efficiency

Yoon and Luttrell (1989) developed expressions relating the induction time to the attachment efficiency (or the probability of attachment using their terminology) depending on the flow conditions around the bubble, characterised by the Reynolds number. Three regions of flow conditions were identified, namely Stokes, intermediate and potential flow. Expressions for the attachment efficiency have been derived for these three different flow conditions. For Stokes flow conditions E_A is given by:

$$E_A = \sin^2 \left(2 \arctan \exp \left(\frac{-3 v_b t_{ind}}{2 r_b (r_b/r_p + 1)} \right) \right) \quad 5.6$$

For intermediate flow conditions the attachment efficiency is given by:

$$E_A = \sin^2 \left(2 \arctan \exp \left(\frac{-(45 + 8\text{Re}_b^{0.72}) v_b t_{\text{ind}}}{30 r_b (r_b/r_p + 1)} \right) \right) \quad 5.7$$

and for potential flow conditions by:

$$E_A = \sin^2 \left(2 \arctan \exp \left(\frac{-3 v_b t_{\text{ind}}}{2 (r_b + r_p)} \right) \right) \quad 5.8$$

These equations show that the value of the attachment efficiency is higher for smaller induction times for a given particle size. More interesting though is that according to this work, E_A increases with decreasing particle size for a given induction time. Also Yoon and Luttrell showed that E_A increases for decreasing bubble size for a given particle size across a range of induction times, down to bubble diameters of approximately $350\mu\text{m}$, below which E_A falls away dramatically.

Jiang (1991) developed an expression for E_A as a function of the adhesion angle, β_a (measuring the angle from the vertical axis through the centre of the bubble - see Figure 5.2) which is the critical collision angle above which attachment does not occur. It is clear that the adhesion angle should be a function of the size of the interacting bubble and particle as their sizes directly effect the velocity of the particle across the bubble surface which, in turn, influences the sliding time. Given that the induction time must be equal to or less then the sliding time for attachment to occur, the influence of changes in the sliding time on the probability of attachment becomes obvious. Jiang notes that to determine the specific particle size-adhesion angle function, more investigation is required to obtain experimental evidence to support this model.

5.3 Efficiency of Stability

Captured particles are attached to a bubble by the action of capillary forces along the contact perimeter and remain attached when the bubble rises to the froth layer, whereas entrained particles fall away when motion ceases. Floatability is dependent on whether the solid is hydrophobic or hydrophilic. However there is a limit to the size of the particle which may be floated by a bubble.

The coarse particle limit occurs when either the gravitational force on the particle is too great to be overcome by the buoyancy effect of the bubble, or the kinetic energy

of the bubble/particle aggregate is sufficient to cause detachment. Calculations based on the models developed by Scheludko et al (1976) and Schulze (1984) are shown in detail in Chapter 6. Scheludko balanced the gravitational force with the capillary force between the particle and the air bubble to obtain values for $d_{\min, g}$. Subsequently, Schulze considered the range of forces acting on the bubble/particle aggregate in determining the energy required to detach the particle from the bubble. When the particle is sufficiently large such that kinetic energy of the bubble/particle aggregate exceeds the detachment energy then the maximum particle diameter which will float can be calculated. Further details including the relevant equations are given in section 6.3.1.

Consideration of the fine particle limit in flotation and the attendant problem of bubble/particle attachment/detachment requires some discussion of the wetting film which is formed when a bubble collides with a particle. As the film thins there is an interaction between the solid/liquid interface and the gas/liquid interface, manifesting itself as the disjoining pressure. If a solid is hydrophobic the thin film of water between the bubble and particle is unstable, and such films spontaneously rupture.

The radial velocity of the particle (i.e. the speed of the particle towards the centre of the bubble) is important in determining the ability of the particle to move close enough to the bubble to cause the thin film to drain and rupture. Scheludko and his co-workers (1976) have emphasized the role of line tension in the formation of the bubble/particle aggregate, and have suggested that a limiting factor in the capture process may be the speed at which the 3-phase line of contact spreads across the surface of the solid.

Determination of the correct value to use for the line tension is still the subject of debate. The minimum size of particles which has been shown to float experimentally was used by Scheludko et al to calculate the line tension. More recently, work by Drelich and Miller (1992) has shown that the "pseudo-line tension" which includes the effects of surface imperfections, can be determined from examining the relationship between hydrophobicity of the particle and bubble size.

The critical bubble base radius, r_c , below which there is no effective attachment between the solid surface and the bubble can be estimated from the relationship of the bubble size with the particle hydrophobicity which is characterised by the

advancing water contact angle. This parameter decreases with decreasing bubble size, and the critical value of the contact radius between a bubble and methylated quartz decreases from $0.85\mu\text{m}$ for $\theta = 36^\circ$ to $0.01\mu\text{m}$ for $\theta = 72^\circ$ according to Drelich and Miller. Calculation of the fine particle limit of floatability based on the this work is shown in the next chapter (section 6.3.2).

5.4 The Flotation Rate

Considering the removal of particles in the batchwise flotation process, then the recovery at any point in time can be defined by $\left(\frac{C_0 - C}{C_0}\right)$ where C is the particle concentration (per unit volume) and C_0 is the particle concentration at time $t = 0$. The recovery as a function of time can then be described by the following rate equation (Ralston, 1983):

$$\frac{dR}{dt} = k(1 - R) \quad 5.9$$

where R is the fraction of particles recovered, and k , the rate constant, is given by:

$$k = \frac{3 G E_C E_A E_S h}{2 d_b V_r} \quad 5.10$$

where G is the gas volumetric flow rate and V_r is the reference volume of height h through which the bubbles rise. The value of k is normally determined experimentally from a graph of $\ln(1-R)$ versus time. For monodispersed particles of the same hydrophobicity, a linear plot is obtained and k is determined from the gradient. For polydisperse particle size systems (i.e. even for narrow size distributions) a two component fit is used and a fast and a slow rate constant (k_f and k_s respectively) are extracted.

A number of investigators have studied the relationship between the flotation rate constant, k , and the relative diameters of the particles and bubbles. Various analyses have produced different results, for example: $k \propto \frac{d_p}{d_b^3}$ (Sutherland, 1948)

and $k \propto \frac{d_p^2}{d_b^3}$ (Reay and Ratcliffe, 1973). The Sutherland theory, based on potential

flow, showed that the relationship between the recovery of particles, R , and the induction time is given by:

$$R = 1 - \exp \left(-t \left(\frac{3 \pi \phi n_b r_p u_r N_b}{\cosh^2 (3 u_r t_{ind} / 2 n_b)} \right) \right) \quad 5.11$$

where ϕ is the fraction of particles retained in the froth following bubble/particle attachment, u_r is the bubble/particle relative velocity and N_b is the number of bubbles per unit volume.

Flotation experiments (reviewed by Trahar, 1981) have found a dependence on particle size following the relationship $k \propto d_p^n$ where n varies between 1 and 2, showing marked differences between angular particles and smooth spheres. The flotation rate was increased significantly when the bubble size was decreased in experiments reported by Ahmed and Jameson, (1985) particularly in the case of the flotation of fine particles (i.e. $d_p < 20 \mu\text{m}$). Crawford and Ralston (1988) found, in flotation experiments with quartz particles which had been modified to give contact angles ranging from 50° to 88° , that within experimental error, $n = 1.0 \pm 0.1$ in the relationship $k \propto d_p^n$, linking the flotation rate constant to the particle size.

5.5 The Anfruns and Kitchener Experiments

Anfruns and Kitchener carried out experiments to determine the collision efficiency of single bubbles of various sizes in a vertical flow tube. Various size fractions of both angular quartz particles and smooth glass beads were methylated and the collection efficiency determined by introducing a single bubble into a 0.1 per cent suspension of each fraction. Bubbles ranging from 0.4mm up to 1.2 mm in diameter were studied. The efficiency of collection was calculated by taking the ratio of the number of particles captured by a bubble to the maximum number of particles with which the bubble could collide. This maximum number is the number of particles that lie geometrically in front of the bubble; i.e. the number of particles contained in a 'vertical cylinder' equal to the height of the particle suspension with a radius equal to the radius of the bubble plus the radius of the particle. Particles which lie at least a distance equal to their radius away from the bubble are not considered to be capable of colliding with the bubble. If it assumed that the suspension is homogeneous then as a particle moves out of the path of the bubble, it is replaced by another particle.

Anfruns and Kitchener concluded that the rate of collection of hydrophobic quartz particles agreed within experimental error with the calculated rate of collision, both in absolute terms as well as in the dependence on particle size and bubble size. They further concluded that the hydrodynamic theory (Flint and Howarth, 1971; Reay and Ratcliffe, 1973) was substantially correct and that the efficiency of capture was 100% for this system. With smooth glass beads (Ballotini), which had the same surface properties as the treated quartz, the efficiency of collection was considerably lower than with the quartz particles. They ascribed the difference to the effect of angularity (or particle roughness) causing the rupture of wetting films in the case of the quartz particles (by the surface roughness being of the same if not greater magnitude than the wetting film). The influence of long-range electrical double-layer forces on flotation was clearly demonstrated with the smooth glass beads, the flotation of which was increased by addition of KCl.

From this work Anfruns and Kitchener suggested that the double-layer repulsion between silica/water and air/water interfaces has the greatest opportunity to reveal itself during the slow, regular thinning expected for smooth, spherical particles. In a dynamic system and with angular particles, which rotate as they slide around the bubble, film rupture and hence particle capture can be guaranteed for strongly hydrophobic particles.

Anfruns and Kitchener based their calculation of the collision efficiency on a bubble Reynolds number of 40 (which strictly only applies for bubbles of diameter 0.6mm), as it was for this particular value of Re_b that they were able to use an approximate explicit equation for the stream function. For larger bubbles the Reynolds number was greater than 40, and when the model described by Schulze (1989, see Chapter 6) is applied to these experiments the theoretical collision efficiency is slightly increased. This means that the efficiency of capture of methylated quartz particles was not 100%, as concluded by Anfruns and Kitchener and that there was room for a potential increase in capture efficiency by carrying out the experiments in electrolyte (KCl) solutions of high concentration (viz. 1 mole dm^{-3}).

For this particular study the interpretation of the results should be tempered, taking into account the approximate nature of the calculation of the efficiency of collision. Nevertheless the experiments of Anfruns and Kitchener remain very significant, for they represent the first real attempt to determine the efficiency of collection of particles by single bubbles, albeit at a fixed hydrophobicity and bubble size.

5.6 The Crawford and Ralston Experiments

The experiments reported by Crawford and Ralston on angular quartz particles represent the only experiments to date where a flotation domain has been identified for particles of varying particle size and hydrophobicity. Flotation experiments were conducted in a modified Hallimond tube, and the flotation rate and recovery of quartz particles in very narrow size fractions were determined. The experiments were also carried out as a function of particle hydrophobicity, allowing threshold values expressed in terms of the static advancing water contact angle, above which flotation occurs, to be identified. A flotation domain was then established experimentally in terms of particle hydrophobicity across a wide particle size range for bubbles of known size and velocity. The bubble size distribution used in these experiments was constant with a number average diameter of 1.2 ± 0.7 mm and an average bubble density of $5 \times 10^6 \text{ m}^{-3}$. Also the pH was held constant at 5.7 ± 0.1 and $10^{-3} \text{ mole dm}^{-3} \text{ KNO}_3$ was used as the indifferent background electrolyte. In certain experiments the ionic strength was varied between 10^{-5} and $10^{-1} \text{ mole dm}^{-3} \text{ KNO}_3$.

The flotation domain established by Crawford and Ralston describes the region for which the stability efficiency equals unity as a function of particle size and hydrophobicity. The kinetic theory proposed by Schulze (1984) was found to predict satisfactorily the behaviour of medium to coarse particles, whereas there was only qualitative agreement between the experimental data and Scheludko's theory (Scheludko et al, 1976) of fine particle flotation. These two models are described fully in the following chapter (see section 6.3) when the efficiency of stability is discussed in terms of how it applies to the experiments conducted in this present study.

Crawford and Ralston used their experimental data to construct plots of $\ln(1-R)$ as a function of time, which permitted determination of the rate constants of the fast and slow floating components in the manner described by Trahar (1981). It was observed that the dependence of the fast rate constant on particle size was essentially linear for various degrees of particle hydrophobicity.

5.7 Contact Angle and Wetting

As has already been discussed, the hydrophilic/hydrophobic nature of the particle surface (i.e. the ability of water to wet the particle surface) is of considerable

importance in determining the floatability of a particle. A quantitative measure of the wettability of a solid is the contact angle.

Traditionally, when determining the usefulness of contact angles the occurrence of contact angle hysteresis, i.e. differences between the advancing contact angle and receding contact angles (Crawford et al, 1987) has normally been attributed to inhomogeneities on the surface. These may take the form of geometric (surface roughness) or energetic inhomogeneities (a heterogeneous surface in terms of chemical groups). For flotation the water receding contact angle would appear to be relevant, as the aqueous phase must retreat from the solid; in contact angle studies, the water advancing angle is generally a more reproducible quantity (Crawford et al, 1987).

Young's equation describes the general thermodynamic condition for three-phase contact between the particle, aqueous solution and the gas bubble where there is a finite contact angle at three phase boundary (see Figure 6.3).

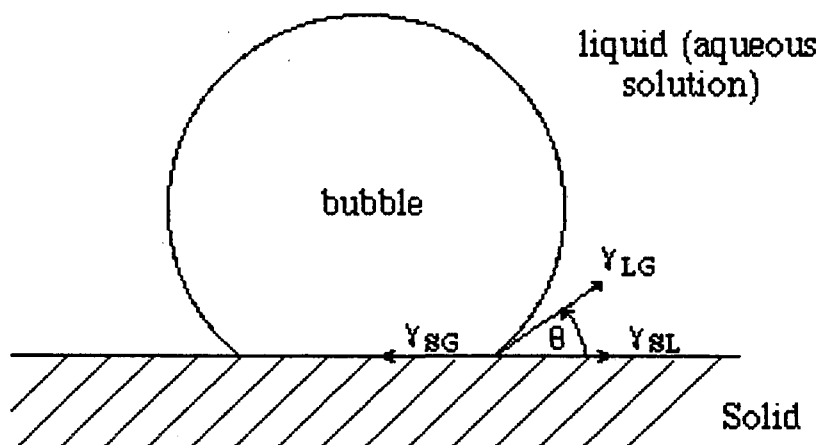


Figure 5.3 Bubble/solid contact showing a finite contact angle (θ) and the associated surface tensions.

Thus Young's equation, modified to take into account saturation of the gas phase with water vapour, gives:

$$\cos \theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} \quad 5.12$$

where θ is the contact angle, γ_{SG} , γ_{SL} and γ_{LG} are the solid/gas, solid/liquid and liquid/gas interfacial tensions (surface free energy per unit area) respectively.

The work W_{SG} , required to separate liquid water from the solid surface and replace it by an adsorbed water layer in equilibrium with saturated water vapour is given in the Dupre relationship:

$$W_{SG} = \gamma_{SG} + \gamma_{LG} - \gamma_{SL} \quad 5.13$$

In other words, wettability as it applies to flotation can be assessed in terms of the work of adhesion, W_{SG} which is defined as the work per unit area of the solid surface required to separate a solid/liquid interface into a solid/gas and liquid/gas interface. Combining equation 5.13 with Young's equation (5.12) gives:

$$W_{SG} = \gamma_{LG} (1 + \cos \theta) \quad 5.14$$

Therefore, for air to displace water so that a finite contact angle is obtained with an air bubble i.e.:

$$W_{SG} < 2\gamma_{LG} \quad 5.15$$

Thus a thermodynamic condition for flotation is that the work of adhesion of the water to the solid must be less than the work of cohesion of water and the work of adhesion shows a clear dependency on the contact angle (shown in equation 5.14).

The contact angle is certainly influenced by such factors as the degree of surface roughness and chemical heterogeneity. These parameters become most evident in their contribution towards contact angle hysteresis which occurs between advancing and receding contact angles (e.g. Crawford et al, 1987). The contact angle is also influenced by the concentration of the potential determining ions (pH for quartz) and the indifferent electrolyte concentration (Fokkink and Ralston, 1988). In this study the pH was constant and the experiments were carried out in relatively dilute, but known concentration electrolyte solutions so that these effects were standardised.

CHAPTER 6. BUBBLE/PARTICLE ATTACHMENT – MODELS OF PARTICLE COLLECTION

Following the previous chapter in which a number of different models were reviewed, the approach used to analyse the bubble/particle attachment results obtained in this study is now dealt with in detail.

6.1 Efficiency of Collision

To characterise a collision process between a particle and a bubble, the efficiency of collision, E_C is defined as the ratio of the actual number of bubble/particle collisions per unit time to the number of particles in the path of the bubble at a large distance (i.e. in a flow tube with a cross-sectional area equal to the projected area of the bubble - the particle trajectories are assumed to follow straight lines). To permit interpretation of the experimental results obtained in this study the model of the efficiency of collision according to Schulze (1989) was used. A review of this model now follows. The particle and bubble dimensions and a grazing streamline are shown in Figure 6.1.

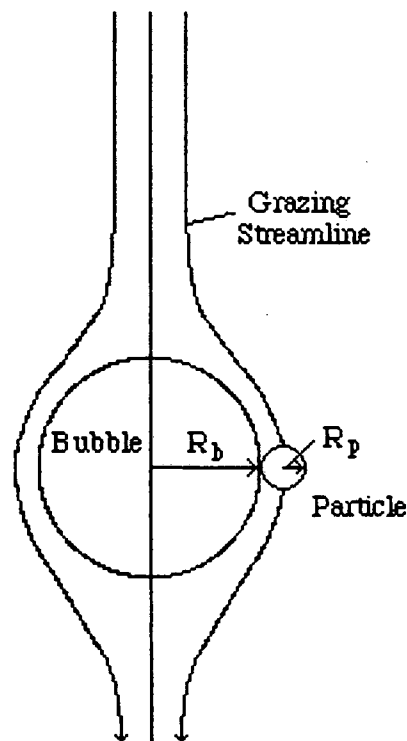


Figure 6.1 Schematic representation of bubble/particle interaction

The ideal collision efficiency, E_{Id} represents the maximum collision efficiency and is given by (Schulze, 1989):

$$E_{Id} = \left(1 + \frac{d_p}{d_b}\right)^2, \quad 1 \leq E_{Id} \leq 4 \text{ for } d_p \leq d_b \quad 6.1$$

In reality particle trajectories deviate from straight lines and various collision effects may be defined. The particles may follow the fluid streamlines around the bubble, without any change in direction, giving rise to the interception effect, E_{Ic} which results in a decrease in the number of collisions. Particle inertial forces result in an increased collision rate, given by the inertial effect, E_{In} . The sum of the particle mass and the fluid mass accelerated with it can be taken as the inert mass allowing the inertial force to be determined. The inertial effect is generally ignored for fine particles, such as those of diameter less than $20\mu\text{m}$ (Reay and Ratcliffe, 1973). The gravitational effect, E_G , also leads to a slightly increased number of collisions due to the settling velocity imposed on the particle due to gravity. There is however, a certain angle of approach above which no bubble/particle collision can occur (Weber and Paddock, 1983) referred to as θ_c , the critical angle, corresponding to the grazing trajectory shown in Figure 6.1.

Three broad regions of bubble/particle interaction, defined in terms of the particle size can be perceived: a) collisions of large particles and bubbles depend mainly on inertial effects, b) medium-sized particles collide with rising bubbles while settling, and c) small particles are carried along in the stream-lines and will not contact a bubble other than by diffusion across the stream-lines.

In the countercurrent flow regime of a single bubble, which exists in the bubble/particle attachment experiments performed in this study, the following effects are ignored: i) collision in the turbulent region behind the bubble, ii) collision caused by diffuse or turbulent particle motion, iii) particle retardation by a 'cloud' of bubbles, the spaces between which are smaller than the particles (i.e. the cloud effect). The collision process is considered to consist of a spherical bubble rising upwards, encountering spherical particles settling downwards at Stokesian settling velocities.

6.1.1 Interception Effect

This effect implies that the particle trajectories and the fluid streamlines around the bubble coincide (i.e. that the particles follow the fluid streamlines). The collision efficiency is then determined by the fluid streamlines (in the flow field of the bubble) which are characterised by the Reynolds number dependent stream function, φ . The trajectory along which the particle just touches the bubble is called the grazing trajectory and φ_c is the value of the stream function which is associated with the grazing trajectory. Here the particle is just touching the bubble at $\theta = \theta_c \leq \frac{\pi}{2}$ and $r_c = \frac{(d_p + d_b)}{2}$.

The critical angle, θ_c , is measured from the stagnation point at the front of the bubble, where the fluid streamlines "graze" the bubble. In any calculation of the collision efficiency, sliding time, collision time etc., whether or not the bubble surface is mobile or immobile is important. Depending on the degree of mobility, the normal and tangential components of fluid flow along the bubble change their values considerably, depending on the degree of retardation. Even in very pure, aqueous systems such as those encountered in this study, traces of surfactant cause bubble surfaces to be immobile. This was most certainly the case in the Anfruns and Kitchener experiments (Anfruns and Kitchener, 1977) Hence an immobile bubble surface is assumed in this study (see also section 6.1.4).

According to Schulze (1989) the following approximate equations can be used to describe the stream function of the grazing trajectory on a completely immobile bubble surface:

i) for $\left(\frac{d_p}{d_b}\right) \leq \left(\frac{1}{\xi_0}\right)$:

$$\varphi_c = \left(\frac{3}{4}\right) \left(\frac{d_p}{d_b}\right)^2 \left(1 + \frac{(3/16) Re_b}{1 + 0.249 Re_b^{0.56}}\right) \quad 6.2$$

where the surface vorticity (the tangential velocity gradient at the bubble surface) is given by:

$$\xi_0 = \left(\frac{3}{2}\right) \left(1 + \frac{(3/16) Re_b}{1 + 0.249 Re_b^{0.56}}\right) (1/\sin\theta_c) \quad 6.3$$

where Re_b is given by:

$$Re_b = \frac{v_b d_b \rho \Pi}{\eta} \quad 6.4$$

and $\theta_c = 78.1 - 7.37 \log Re_b$ (for $20 < Re_b < 400$) 6.4a

ii) for $\left(\frac{d_p}{d_b}\right) > \left(\frac{1}{\xi_o}\right)$:

$$\varphi_c = \exp \left(\ln \varphi (1/\xi_o) + \left(\frac{2.6328 - \ln \varphi (1/\xi_o)}{1.4569 - \ln (1/\xi_o)} \right) \left(\ln(d_p/d_b) - \ln(1/\xi_o) \right) \right) \quad 6.5$$

where φ is the value of φ_c for case i).

Having established the value of the grazing function, the collision efficiency based on the interception effect can be determined using the following equation:

$$E_{Ic} = \frac{2\varphi_c}{1 + v_s} \quad 6.6$$

where v_s is equal to v_p/v_b .

6.1.2 Inertial Effect

The following relationship describing the inertial effect has been derived by Plate (see Schulze, 1989) based on the data of Flint and Howarth (1971):

$$E_{In} = \left(\frac{1}{1 + v_s} \right) \left(1 + \frac{d_p}{d_b} \right)^2 \left(\frac{St}{St + a} \right)^b \quad 6.7$$

where $St = \frac{\rho_p d_p^2 v_b}{9 \eta d_b}$ (i.e. St is the Stokes Number) and the coefficients a and b ,

dependent on Re_b have been determined empirically and are shown in Table 6.1. The Stokes Number represents the ratio of inertial to drag forces and provides a measure of the tendency of a particle to follow the fluid flow. A small value of St indicates that a particle will follow the streamlines closely, while those particles having larger values of St will deviate from the fluid flow streamlines.

Re_b	>500	250-500	100-250	50-100	25-50
a	0.5	0.6	0.8	1.12	2.06
b	2.0	2.0	2.0	1.84	2.06

Table 6.1 Values of the coefficients a and b used in equation 6.7, determined empirically for the Reynolds number regimes as shown.

6.1.3 Gravitational Effect

The particle settling velocity due to gravity operating at large distances from the bubble does not change its value or direction. According to Weber and Paddock (1983), for particles approaching a bubble at angles greater than the critical angle, θ_c no collision can occur. For particles having a finite settling velocity the gravitational efficiency of collision is given by Weber and Paddock (1983):

$$E_G = \left(1 + \frac{d_p}{d_b}\right)^2 \left(\frac{v_s}{1 + v_s}\right) \sin^2 \theta_c \quad 6.8$$

where $v_s = v_p/v_b$ and θ_c is the critical angle (described in equation 6.4a).

6.1.4 Overall Collision Efficiency

The overall collision efficiency is determined from the individual collision efficiencies in the following manner:

$$E_C = E_{lc} + E_G + \left(1 - \frac{E_{lc}}{(1 + (d_p/d_b))^2}\right) E_{ln} \quad 6.9$$

Interceptional collision alone occurs for particles which follow the fluid streamlines exactly. Gravitational collision alone is hypothetical and would occur for particles having a finite settling velocity but zero size. In equation 6.9, additivity is presumed; i.e. a simple combination of E_{lc} , E_G and E_{ln} . This need not be the case (Derjaguin et al, 1984).

It is notable that the effect of the centrifugal force acting on a particle that moves along the bubble surface has been neglected. This force increases with increasing tangential component of the particle velocity, $v_{p\theta}$, and means that particles do not reach the bubble surface beyond a certain angle, θ_t . $v_{p\theta}$ is dependent on the degree of retardation of the bubble surface and leads to a reduction in the overall collision efficiency. The theoretical overall collision efficiency has been compared with experimental values (e.g. Anfruns and Kitchener, 1977) and the correlation observed has been considered to be very good, although the experimental values tend to be slightly higher than the model would predict (Schulze, 1989). This could be due to the negative effect of the centrifugal force for it is not considered in the model. Certainly work is required to further define the reduction on E_C of the centrifugal force. However the information to date theoretically is sparse and experimentally non-existent, so that its exact impact cannot be assessed. The agreement between equation 6.9 and experiment is sufficiently good for the calculation of E_C to be treated with confidence.

In Figure 6.2 the results of applying the model described by equation 6.9 to bubbles of varying size over the particle range of 1–100 μm are shown. The efficiency of collision is shown for bubbles diameters of 0.5, 1.0 and 2.0mm for which typical values for bubble velocity (i.e. 10, 15 and 25 cm/s respectively) were used (see Leja, 1982). Values for other parameters used in the model included: fluid density $1.0 \times 10^{-3} \text{ kg/m}^{-3}$, particle density $2.65 \times 10^{-3} \text{ kg/m}^{-3}$, fluid viscosity 0.01 Poise and fluid surface tension 72.8 mN/m. It is clear from this figure that the efficiency of collision increases with increasing particle diameter and decreasing bubble size. A sample calculation is given in the Appendix B.

In the collision efficiency model described it was assumed that the bubble surface was immobile, even though in the experiments to which the model was applied the bubble surface should have theoretically been free and mobile. However, it has been shown that this is a practical impossibility since even in the experimentally cleanest system possible, surface active agents are present in minute quantities and become concentrated at the bubble surface. As discussed by Anfruns and Kitchener (1977), a virgin bubble surface lasts only a few milliseconds before it becomes immobile due to Maragoni effects. It is interesting to note that according to Weber and Paddock (1983), calculations assuming a mobile bubble surface show the efficiency of collision due to the interception effect, E_{IC} , to be an order of magnitude greater than for an immobile surface.

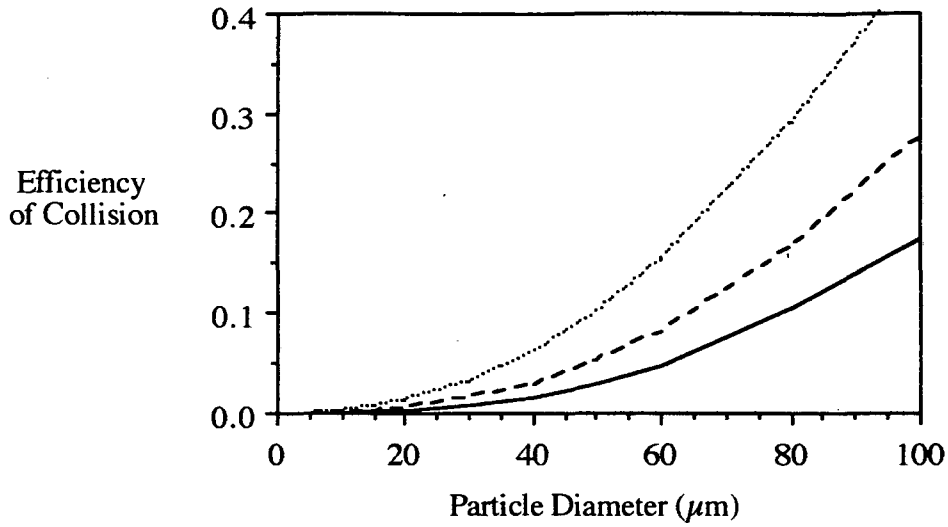


Figure 6.2 Efficiency of collision calculated using the model described in section 6.1, as a function of particle size for various bubble sizes; i.e. $d_b = 2\text{mm}$ (—), $d_b = 1\text{mm}$ (---) and $d_b = 0.5\text{mm}$ (.....).

6.2 Efficiency of Attachment

The aim of an attachment model is to predict the fraction of particle collisions which are successful and lead to bubble/particle attachment. Attachment will be successful for those particles which reside “near” (i.e. within a region of close approach) the bubble for sufficient time for the thin liquid film formed between the particle and the bubble to drain, rupture and for a stable three-phase line of contact (wetting perimeter) to form i.e. the fraction of collisions for which the contact time is equal to, or longer than the induction time.

6.2.1 Collision Time Calculation

Schulze et al (1989) assumed that the colliding particle underwent non-linear oscillation normal to the deformed bubble surface and subsequently derived the following equation for the collision time:

$$t_{\text{coll}} = \left(\pi^2 r_p^3 (\rho_p + 1.5\rho_{fl}) / 3\gamma \right)^{1/2} f \quad 6.10$$

In equation 6.10, f is a non-linear function dependent upon the particle size, surface tension and the angle (α) which is the angle for the transition of the spherically deformed part of the bubble surface to the part which is unperturbed. It characterises both the degree of deformation and also the radius of the thin liquid film which forms between the bubble surface and the colliding particle (see Figure 6.3).

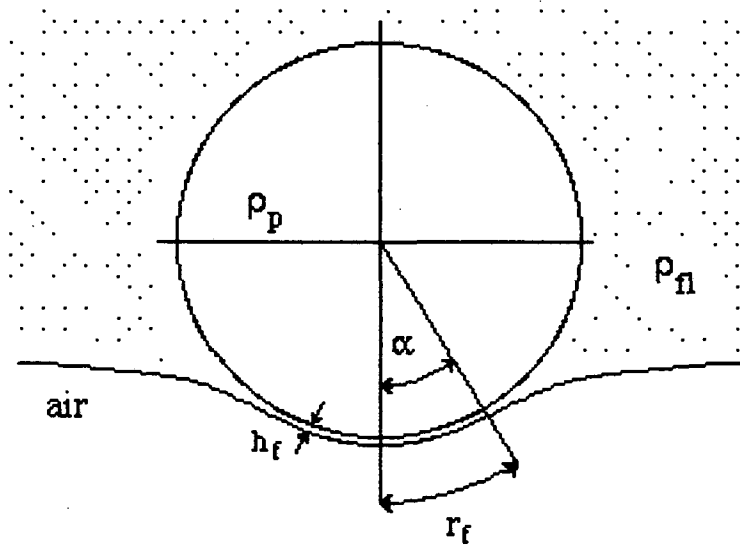


Figure 6.3 Deformation of the air/liquid interface by a colliding particle indicating the angle of deformation, α (ignoring any dimple formation for the sake of simplicity).

An approximate equation for the value of the function f is given by (Schulze et al (1989) equation 18a):

$$f = \left(\frac{\ln(3.494 \cdot 10^{-3} \gamma / \alpha^2 r_p^2 \rho_n)}{\left(\ln(2.119 \cdot 10^{-3} \gamma / \alpha^2 r_p^2 \rho_n) \right)^{1/2}} \right) \quad 6.11$$

It has been shown experimentally that the angle α is usually less than 25° , and the influence of α on f is minimal, so that f can be approximated by a function which varies only with particle size in a particular liquid. Using the Schulze et al model collision times can be calculated as a function of particle size as shown in Figure 6.4 (for a sample calculation see Appendix B).

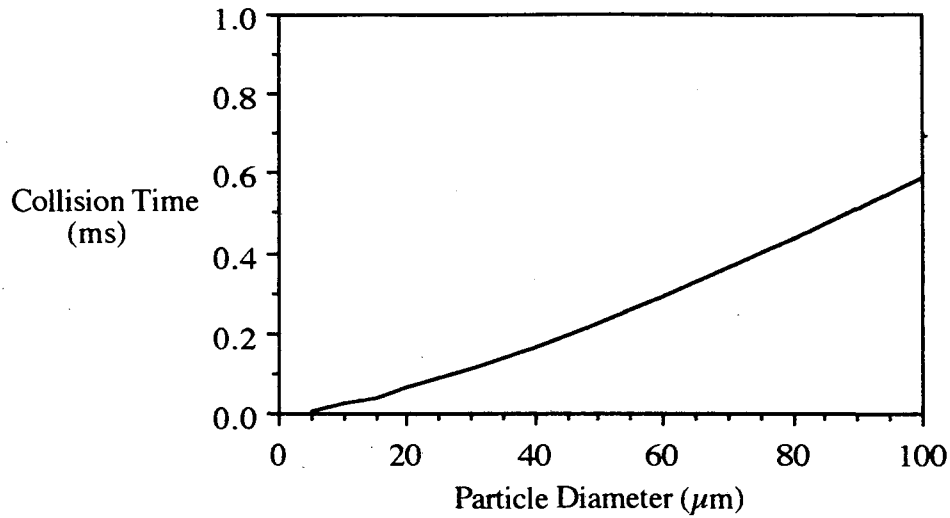


Figure 6.4 Collision time calculated using the Schulze et al (1989) model.

6.2.2 Sliding Time Calculation

The Sutherland approach was used to determine the sliding time, the time required for a particle to slide over the bubble surface under potential flow conditions giving (Sutherland 1948, equation 13):

$$t_{sl} = \frac{4 (r_b + r_p)}{v_r \left(2 + \left(\frac{r_b}{(r_b + r_p)} \right)^3 \right)} \ln \cot \left(\frac{\theta_n}{2} \right) \quad 6.12$$

where θ_n is the collision angle (recall Figure 5.2) and v_r is the bubble/particle relative velocity, equal to $v_p + v_b$ for a settling particle encountering a rising bubble.

Dobby and Finch (1986) pointed out that Sutherland's solution overestimates t_{sl} by a factor of 2. Results of the sliding time calculations using Sutherland's corrected equation are shown in Figure 6.5. The limited particle size effect for this model is clearly evident.

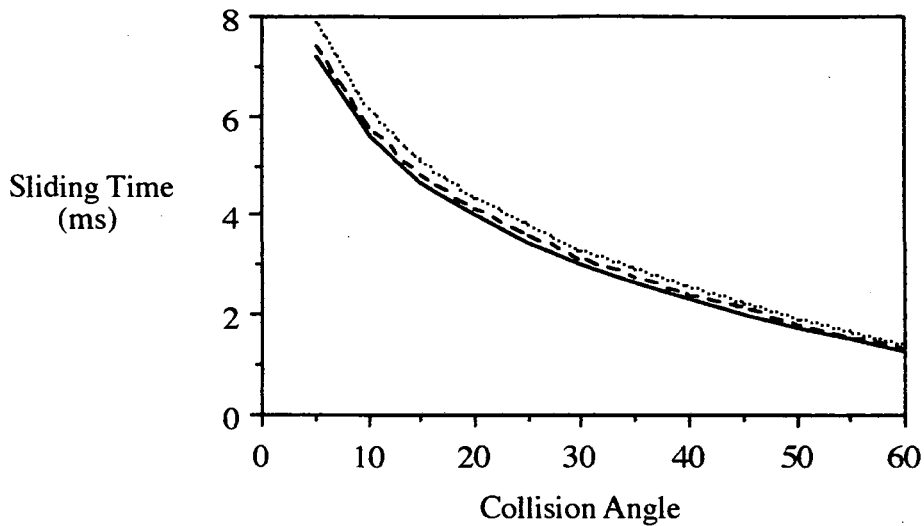


Figure 6.5 Sliding Times using Sutherland's model for bubble diameter of 1mm, and changes in particle size; viz. $d_p = 100\mu m$ (—), $d_p = 40\mu m$ (---) and $d_p = 20\mu m$ (.....).

The model proposed by Dobby and Finch (1986, 1987) is similar to that developed by Sutherland (1948) in which particle collection is considered to occur by particle collision followed by the particle sliding around the bubble. Dobby and Finch developed their model initially for the single bubble-single particle system, and then attempted to model the more practical case of a bubble swarm. The negative effect of centrifugal forces are not considered in either the Sutherland or Dobby and Finch models.

In the Dobby and Finch model it was important to test the assumption of potential flow ($Re_b \gg 1$) made in the Sutherland approach. This assumption was shown not to be applicable for the bubble size (circa 1-2mm bubble diameter) normally used in flotation. They showed that the tangential component of the fluid velocity at the bubble surface is much lower for bubbles of intermediate Reynolds number than for potential flow.

The tangential velocity on the bubble surface can be calculated from the surface vorticity, ξ_s (i.e. the tangential velocity gradient). Woo (1971) obtained data for ξ_s which had been derived from numerical solutions to the Navier-Stokes equations for $Re = 0.2$ to 400. The following correlations have been made for $0 < \theta_n < 90$:

$$\xi_s = a + b\theta_n + c\theta_n^2 + d\theta_n^3 \quad 6.13$$

The coefficients a to d (in equation 6.13) for $20 < Re < 400$ are given by:

$$\begin{aligned} a &= -0.01082 - 7.273 \times 10^{-4} Re + 1.735 \times 10^{-6} Re^2 - 2.046 \times 10^{-9} Re^3 \\ b &= 0.0745 + 3.013 \times 10^{-3} Re - 7.402 \times 10^{-6} Re^2 + 8.931 \times 10^{-9} Re^3 \\ c &= -4.276 \times 10^{-4} - 1.977 \times 10^{-5} Re + 5.194 \times 10^{-8} Re^2 - 6.520 \times 10^{-13} Re^3 \\ d &= -1.103 \times 10^{-6} - 1.032 \times 10^{-7} Re + 1.397 \times 10^{-10} Re^2 - 1.334 \times 10^{-13} Re^3 \end{aligned}$$

Experimental results for velocity distributions close to the surface of a rigid sphere have been obtained by Seeley et al (1975) for $Re_b = 290$ and $\theta_n = 45^\circ$. Dobby and Finch based their model on this data and derived equations for estimating the mean particle tangential velocity ($v_{p\theta}$) and then assumed that the factors obtained applied for other values of Re_b and θ_n . Two linear models were used to approximate the experimental data, resulting in the following equations for $v_{p\theta}$.

i) for $(d_p/d_b) \leq 0.03$

$$v_{p\theta} = (0.7\xi_s v_b d_p/d_b) + v_p \sin \theta_n \quad 6.14$$

and ii) for $(d_p/d_b) > 0.03$

$$v_{p\theta} = 0.7\xi_s v_b \left(\left(\frac{d_p - 0.03d_b}{d_p} \right) 0.06 + \left(\frac{9 \cdot 10^{-4} d_b}{d_p} \right) \right) + v_p \sin \theta_n \quad 6.15$$

The end of bubble/particle contact is referred to as the maximum angle of contact, θ_m , and is calculated by finding the angle at which the radial component of the particle settling velocity (directed toward the bubble surface) is equal to the radial component of the liquid velocity (directed away from the bubble surface). Dobby and Finch reported various values of θ_m , although Schulze (1989) assumed a value of 80° .

The time for the particle to travel from θ_n to θ_m (i.e. the sliding time) according to the Dobby and Finch model can now be calculated using the following equation:

$$t_{sl} = \left(\frac{\theta_m - \theta_n}{360} \right) \left(\frac{\pi(d_b + d_p)}{v_{p\theta}} \right) \quad 6.16$$

Sliding times determined using this model are shown in the Figure 6.6 as a function of particle size for a range of collision angles, and it is clear that for increasing collision angle, the sliding time decreases. For example If the collision angle is held constant at 15° or 35° say, the effect of changes in bubble size can be seen as in the Figure 6.7.

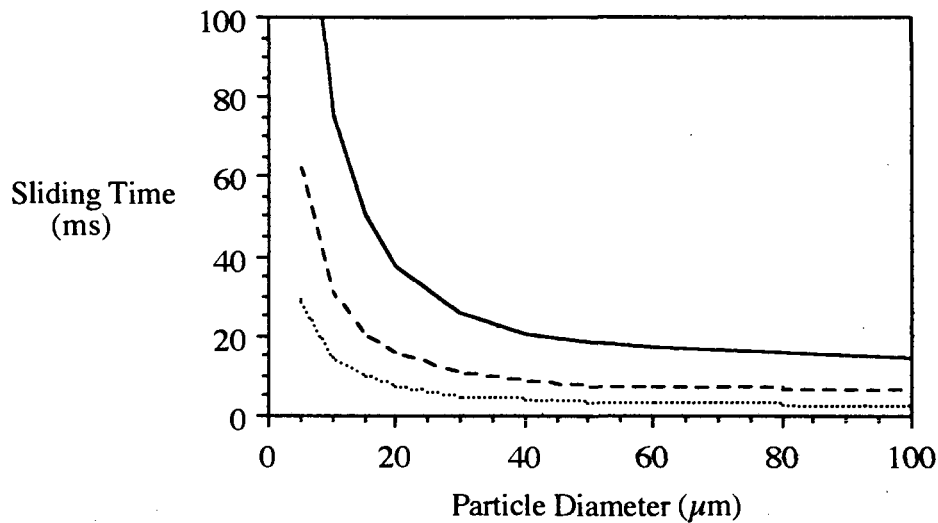


Figure 6.6 Sliding Times calculated using the Dobby and Finch model for a 1mm diameter bubble and collision angles of $\theta_n = 20^\circ$ (—), $\theta_n = 40^\circ$ (---) and $\theta_n = 60^\circ$ (.....).

It is interesting to note that large particles have longer sliding times for smaller bubbles compared with larger bubbles. This is more obvious when the sliding time is plotted as a function of collision angle, holding the particle size constant at 20, 40 and $100\mu\text{m}$, and observing the effect of changes in bubble size as in Figure 6.8. The relative positions for bubble diameters of 0.5, 1 and 2mm are reversed for 20 and $100\mu\text{m}$ particles, but bubble size does not influence the sliding time for $40\mu\text{m}$ particles.

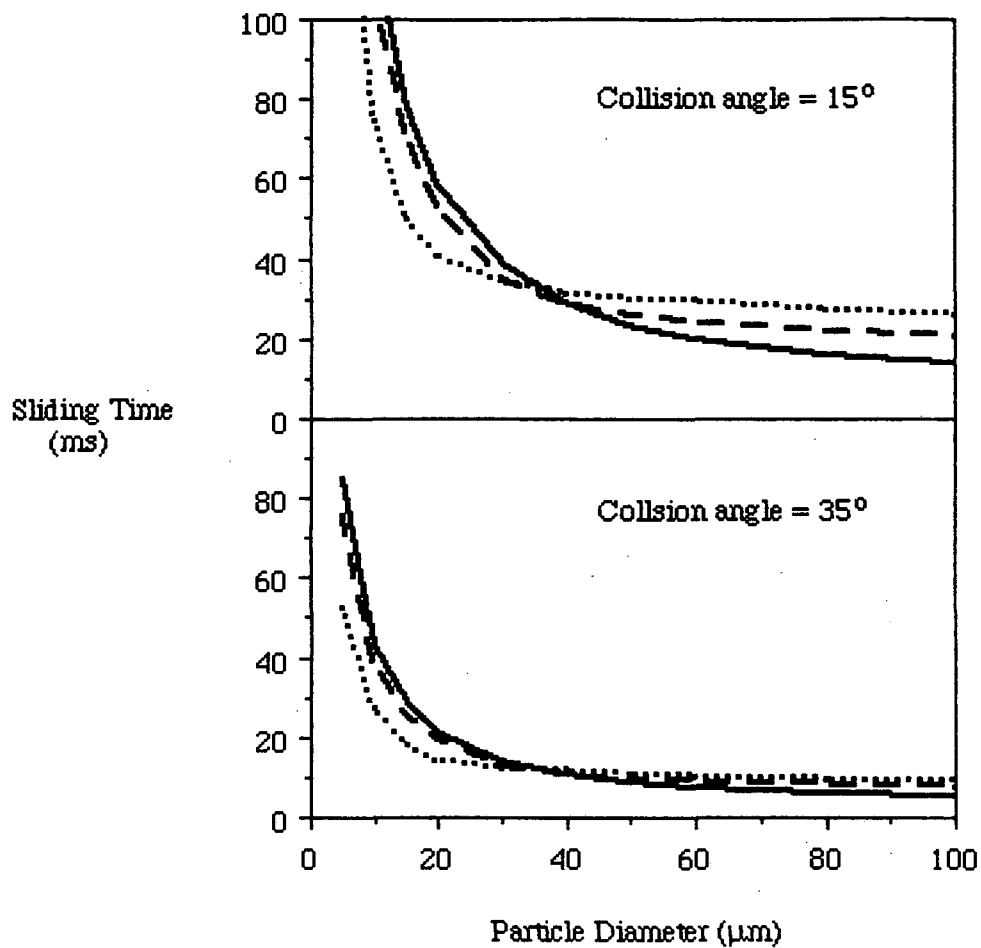


Figure 6.7 Sliding times (calculated using the Dobby and Finch model) for a collision angles of 15° and 35° showing the effect of changing the bubble size; i.e. $d_b = 2\text{mm}$ (—), $d_b = 1\text{mm}$ (---) and $d_b = 0.5\text{mm}$ (.....).

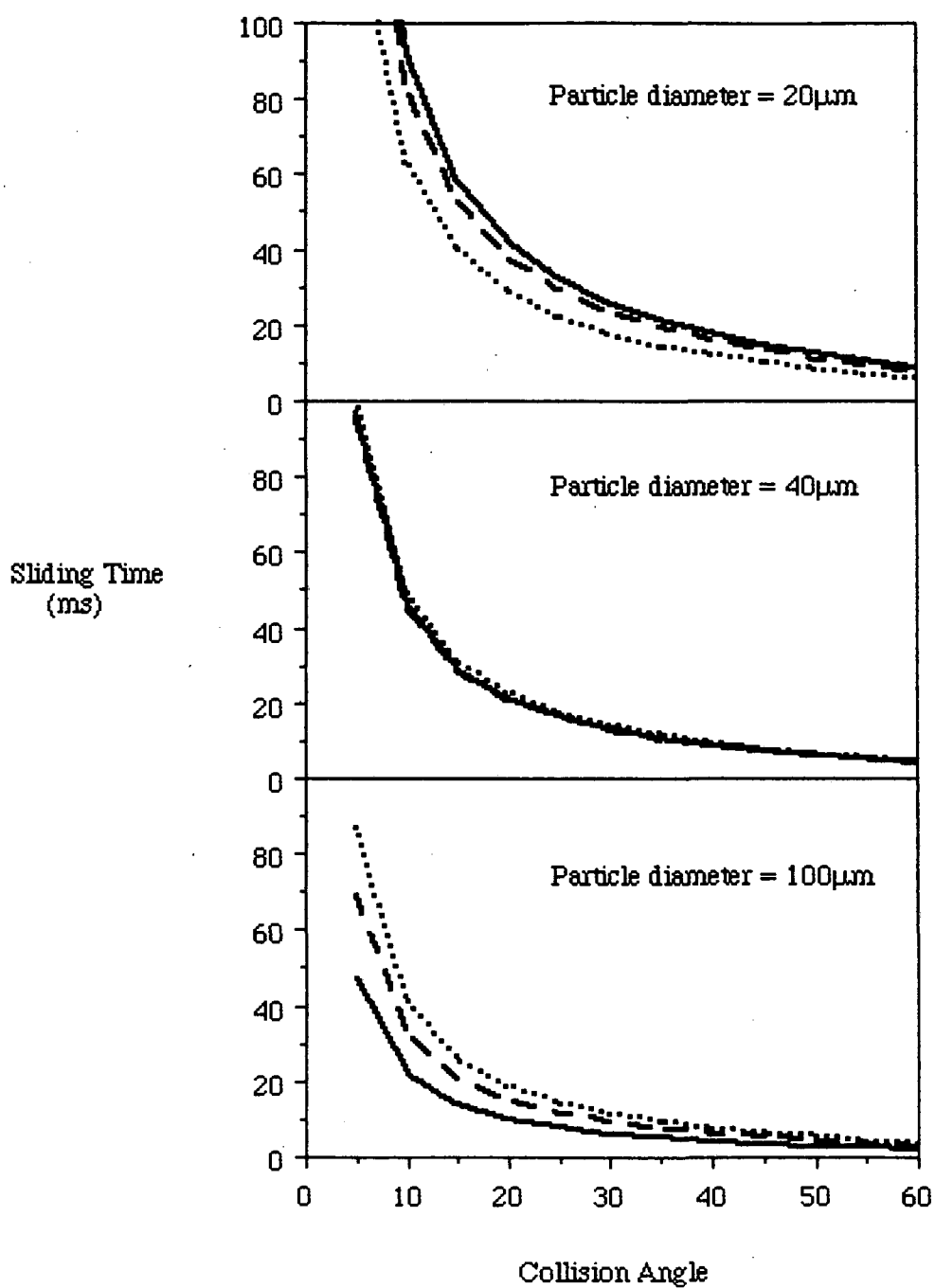


Figure 6.8 Sliding times (calculated using the Dobby and Finch model) for a particle diameters of $20\mu\text{m}$ (top), $40\mu\text{m}$ (middle) and $100\mu\text{m}$ (bottom) showing the effect of changing the bubble size; i.e. $d_b = 2\text{mm}$ (—), $d_b = 1\text{mm}$ (---) and $d_b = 0.5\text{mm}$ (.....).

6.2.3 Distribution of Collision Angles

To complete the model of attachment efficiency, knowledge of the distribution of collision angles is required, as this allows quantification of the likelihood of a sliding time of a particular duration. Dobby and Finch used, as an approximation, the following equation:

$$n_{\theta} = \frac{\sin^2 \theta_n}{\sin^2 \theta_c} \quad 6.17$$

where n_{θ} is the fraction of all colliding particles that collide between the front stagnation point and angle θ_n . It is now possible to plot the sliding time against the cumulative percent of collisions for various values of bubble size and particle diameter as illustrated in Figure 6.9 for bubbles of 1mm.

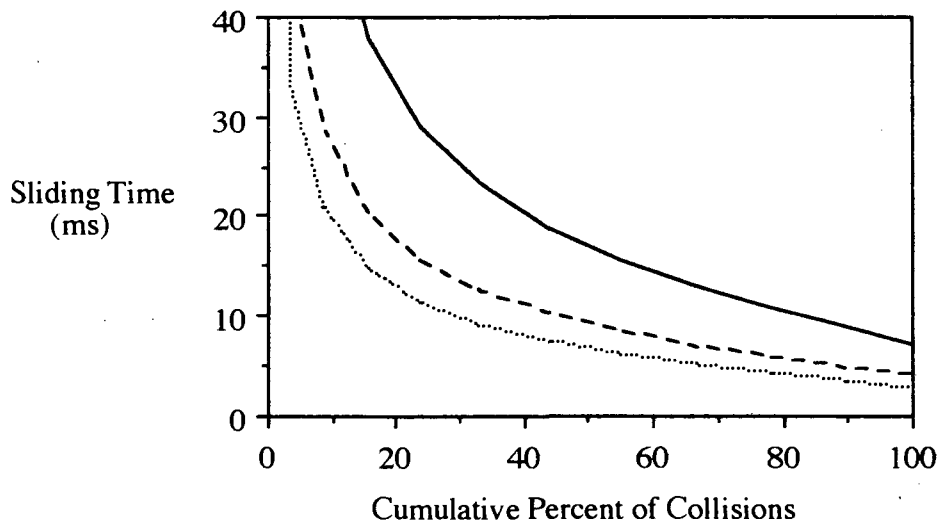


Figure 6.9 Sliding times (calculated using the Dobby and Finch model) for a bubble diameter of 1mm plotted against the cumulative percentage of bubble/particle collisions for various particle diameters; i.e. $d_p = 20 \mu m$ (—), $d_p = 40 \mu m$ (---) and $d_p = 100 \mu m$ (.....).

If the efficiency of attachment (E_A) is measured then the angle θ_n can be determined for which sufficient number of collisions would have long enough sliding times to give the particular attachment efficiency observed experimentally. In other words the cumulative percentage of collisions up to and including the value of θ_n should be equal to the efficiency of attachment for this represents that fraction of the total number of

collisions with long enough sliding times for bubble/particle attachment to have occurred. This can be written as follows:

$$\theta_n = \sin^{-1} (E_A \sin^2 \theta_c)^{1/2} \quad 6.18$$

For the value of θ_n determined from the experimental result, the sliding time can be back-calculated, and this value of t_{sl} is equal to t_{ind} for the particular system for which the efficiency of attachment was obtained. The induction time, then, is the determining factor giving rise to the E_A result obtained and may be found by using the model to derive the fraction of collisions for which t_{sl} is equal to or greater than t_{ind} and attachment occurred. Using the thin film drainage experiments described in the earlier chapters, it was hoped that a qualitative explanation could be developed for a fast moving bubble contacting a plate. Currently surface forces are not adequately dealt with in the present literature theories and the influence of bubble spreading kinetics has also been overlooked until very recently.

6.3 Efficiency of Stability

The third part of the efficiency of collection concerns the stability of the bubble/particle aggregate. The efficiency of stability, E_s , is discussed in terms of E_s equal to zero or one depending upon whether or not the bubble and the particle can form a stable aggregate, which results in defining limits of flotation, outside of which E_s is zero and the efficiency of collision and attachment are irrelevant. Specifying limits of flotation implies that there exists a flotation domain which can be determined for coarse particles and also fine particles, and these two cases will be considered in turn.

6.3.1 Coarse Particle Limit

The flotation limit for coarse particles is the maximum particle size for which the adhesive force acting on the three-phase line of contact between the bubble and the particle is large enough to keep the aggregate intact. There is a gravitational limit to the size of the particle which a bubble can float, since heavier particles will fall off the bubble and, according to Scheludko et al (1976), this maximum particle size, $d_{max,g}$ is given by:

$$d_{max,g} = \left(\frac{3\gamma}{2\Delta\rho g} \right)^{1/2} \sin \left(\frac{\theta}{2} \right) \quad 6.19$$

where θ is the contact angle at the three-phase line of contact (see Figure 6.10).

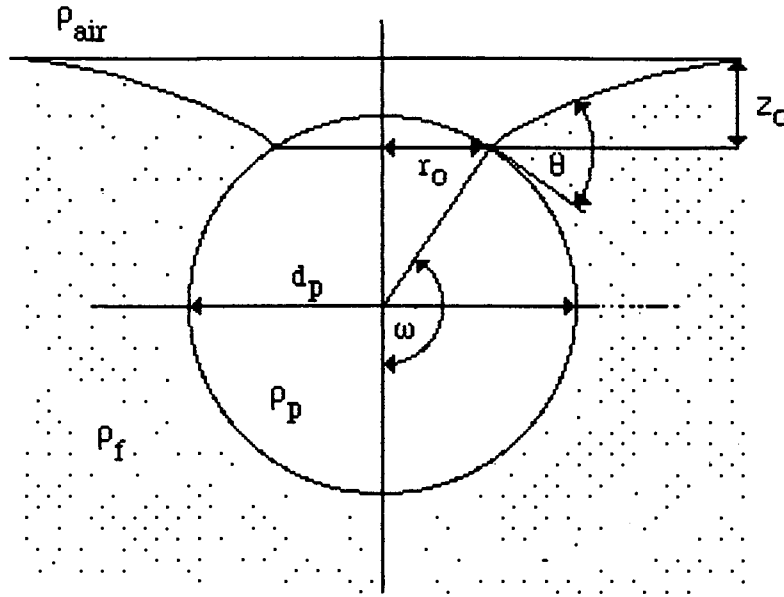


Figure 6.10 Schematic diagram of a particle at the bubble/liquid interface, indicating the contact angle, θ .

The gravitational limit, $d_{\max,g}$, is quite large (as can be observed in Figure 6.12). Of far more significance for particles less than circa $100\mu\text{m}$ is the kinetic limit. The kinetic limit, $d_{\max,v}$, occurs when the kinetic energy of the particle equals the detachment energy. The energy of detachment, E_{det} , corresponds to the work done in forcing a particle to move from its equilibrium position, h_e , at the liquid/vapour interface, to some critical point, h_c , where detachment occurs and the particle moves into the liquid phase. E_{det} is determined from the sum of the various forces involved and is given by:

$$E_{\text{det}} = \int_{h_e}^{h_c} \Sigma F dh (\omega) \quad 6.20$$

Schulze (1984, p. 183) considered the following forces to be important in determining E_{det} : i) the force of gravity, ii) the static buoyancy of the immersed part of the particle, iii) the hydrostatic pressure of the liquid column height z_0 on the contact area (see Figure 9) , iv) the capillary force at the three-phase line of contact acting in a vertical direction, v) additional detaching forces which are represented as the product of particle

mass and an acceleration b_m of the bubble/particle aggregate, vi) and the effect of the capillary pressure in the gas bubble acting on the contact area. The full expression for E_{det} is given by:

$$E_{det} = \int_{h_c(\omega)}^{h_c(\omega)} \left[\frac{2}{3} \pi R_p^3 \rho_f g \left\{ 1 - \frac{2\rho_p}{\rho_f} \cos^3 \omega + \frac{3h}{2R_p} \sin^2 \omega - \frac{3}{a^2 R_p^2} \sin \omega \sin(\omega + \theta) \right\} \right. \\ \left. - \pi (R_p \sin \omega)^2 \left\{ \frac{2\gamma}{R_b} - 2R_b r_f g \right\} \right] dh \quad 6.21$$

where R_p and R_b are the particle and bubble radii, ρ_f and ρ_p are the fluid and particle densities and a is the capillary or Laplace constant. Equation 6.21 may be solved numerically and values for E_{det} are presented in tabulated form by Schulze (1984).

The kinetic energy of the particle is given by:

$$KE = \frac{\pi}{12} d_p^3 \rho_p v_t^2 \quad 6.22$$

where v_t is the velocity of the particle and is taken equal to the bubble velocity when the particle is attached to the bubble.

In Figure 6.11, the detachment energy is plotted against the particle size and overlaid is the particle kinetic energy for various values of v_t . From this plot it is possible to determine $d_{max,v}$ as a function of contact angle for various values of v_t as shown in Figure 6.12. This approach, using a graphical method, allows determination of $d_{max,v}$ whereas if the kinetic energy (equation 6.22) is equated with the energy of detachment (equation 6.21) then $d_{max,v}$ is given by:

$$d_{max,v} = 2 \left(\frac{3}{2\pi \rho_p v_t^2} \int_{h_c(\omega)}^{h_c(\omega)} \left[\frac{2}{3} \pi R_p^3 \rho_f g \left\{ 1 - \frac{2\rho_p}{\rho_f} \cos^3 \omega + \frac{3h}{2R_p} \sin^2 \omega - \frac{3}{a^2 R_p^2} \sin \omega \sin(\omega + \theta) \right\} \right. \right. \\ \left. \left. - \pi (R_p \sin \omega)^2 \left\{ \frac{2\gamma}{R_b} - 2R_b r_f g \right\} \right] dh \right)^{1/3} \quad 6.23$$

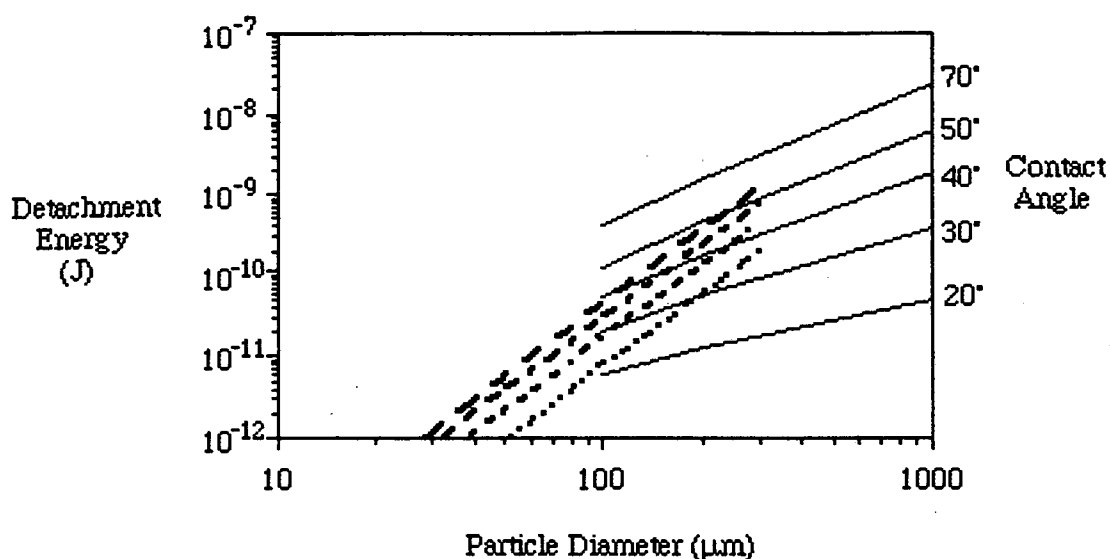


Figure 6.11 Detachment energy is indicated by the solid lines (equation 6.21) for the contact angles as indicated on the right hand axis; the particle kinetic energy (equation 6.22) as a function of v_t is displayed as broken lines; i.e. $v_t = 25\text{cm/s}$ (---), $v_t = 20\text{cm/s}$ (----), $v_t = 15\text{cm/s}$ (.....) and $v_t = 10\text{cm/s}$ (.....).

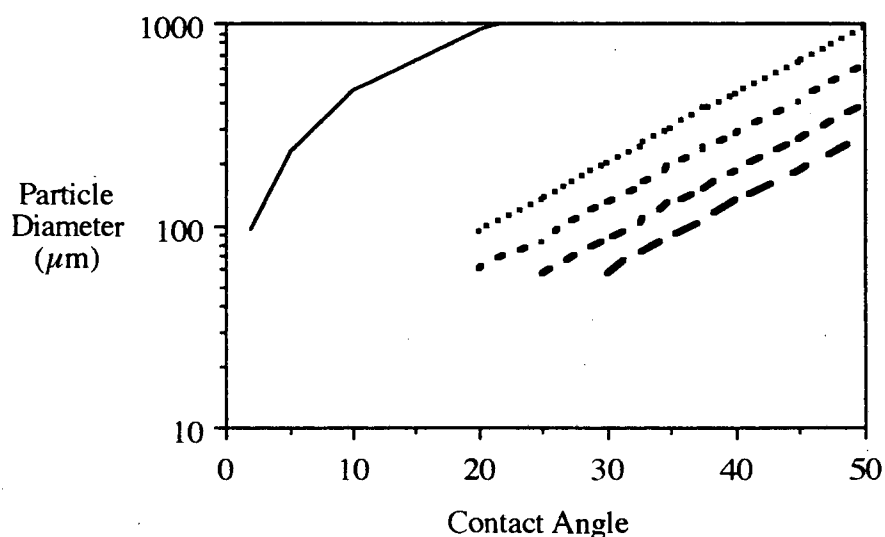


Figure 6.12 The maximum floatable particle size is shown as a function of contact angle for $d_{\max,g}$ (—, equation 6.19) and for $d_{\max,v}$ (broken lines, equation 6.23) for the values of v_t shown in Figure 6.11; i.e. $v_t = 25\text{cm/s}$ (---), $v_t = 20\text{cm/s}$ (----), $v_t = 15\text{cm/s}$ (.....) and $v_t = 10\text{cm/s}$ (.....).

6.3.2 Fine Particle Limit

There is a lower limit to the size of a particle which can form a stable bubble/particle aggregate. According to Scheludko et al (1976) there is a critical work of expansion of the three-phase line of contact required to form a stable bubble/particle contact, and when this is equated with the kinetic energy of the particle the following expression is obtained for the minimum particle diameter $d_{\min,\kappa}$ which can be floated:

$$d_{\min,\kappa} = \left(\frac{24 \kappa^2}{v_b^2 \Delta \rho \gamma_{LV} (1 - \cos \theta)} \right)^{1/3} \quad 6.24$$

where κ is the line tension, opposing expansion of the three-phase line of contact.

There is some uncertainty as to the correct value to use for the line tension but a value of $5.6 \times 10^{-10} \text{N}$ has been proposed and can be used to determine $d_{\min,\kappa}$. Experimental work does not support this value (Crawford and Ralston, 1988). An alternative approach has been recently developed by Drelich and Miller (1992) using the following equation derived from the earlier study of Scheludko et al (1976):

$$d_{\min,\kappa} = \left(\frac{24 r_c^2 \gamma_{LV} (1 - \cos \theta)}{\Delta \rho v_b^2} \right)^{1/3} \quad 6.25$$

where r_c is the critical base radius below which there is no effective attachment and is related to the line tension as follows:

$$\kappa = \gamma_{LV} (1 - \cos \theta) r_c \quad 6.26$$

The critical value of r_c can be estimated after extrapolation of a plot of $\cos \theta$ vs r^{-1} (or θ versus r to $\theta = 0$), which then allows $d_{\min,k}$ to be determined for various values of bubble rise velocity, as shown in Figure 6.13.

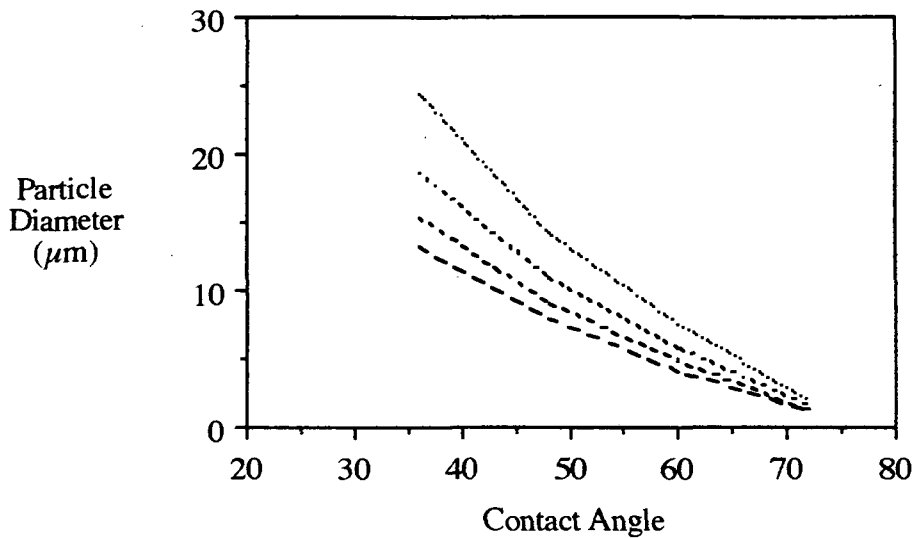


Figure 6.13 The minimum floatable particle size (equation 6.25) is shown as a function of contact angle for different values of v_t ; i.e. $v_t = 25\text{cm/s}$ (---), $v_t = 20\text{cm/s}$ (-.-.-), $v_t = 15\text{cm/s}$ (.....) and $v_t = 10\text{cm/s}$ (-----).

6.3.3 Flotation Domains

It can now be established that a flotation domain exists for which E_s is equal to one (i.e. bubble/particle aggregates are formed and are stable) and outside of which E_s equals zero. Flotation cannot occur outside this domain since the bubble/particle aggregates are not stable. Such a flotation domain is shown in Figure 6.14 for a bubble with an ascent velocity of 20cm/s.

Attempts to relate the theoretical limits to a practical flotation system have generally been unsuccessful, until the experimental work of Crawford and Ralston (1988) in which the flotation behaviour was studied using a model system of angular quartz particles with the particle size and contact angle being systematically varied. Previously, water soluble collectors had been used, causing variables such as surface tension, electrical double layer properties and kinetic aspects of collector adsorption to complicate the system being studied and making very difficult, if not impossible to compare experimental data with theoretical predictions.

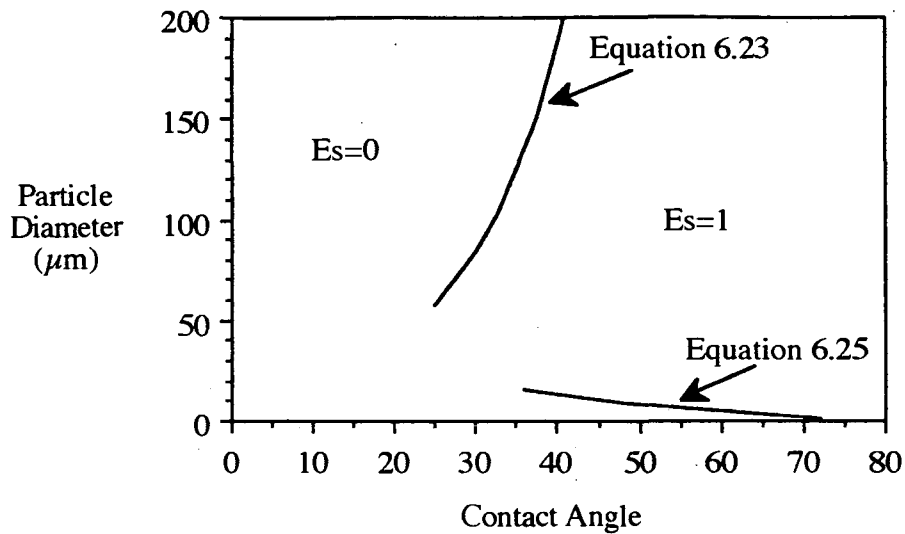


Figure 6.14 Particle diameter/particle contact angle regions (i.e. the flotation domain) are shown as indicated for which stable bubble/particle aggregates are possible ($E_s = 1$) and where they do not occur ($E_s = 0$) for, as an example, $v_t = 20\text{cm/s}$. Equation 6.23 gives the values for $d_{\max,v}$ and equation 6.25 allows the values of $d_{\min,\kappa}$ to be calculated. As can be seen the theoretical models do not yet completely 'dove-tail' together at the intermediate particle sizes (viz. $20\text{-}50\mu\text{m}$).

In the experiments of Crawford and Ralston, the hydrophobicity of the quartz particles was varied using trimethylchlorosilane, and these particles were classified into size fractions of narrow particle diameter limits. Batchwise flotation experiments were then conducted with these particles in a Hallimond tube under conditions of known bubble size, bubble density, pulp density, pH and ionic strength. The experimental results obtained from the study by Crawford and Ralston showed that there is a critical contact angle for each particle size fraction below which flotation does not occur.

The critical contact angles required for flotation for each particle size determined experimentally by Crawford and Ralston are shown in Figure 6.15. Both the advancing and receding critical contact angles are shown (squares and circles respectively), superimposed over the theoretical curves (solid lines) shown in Figure 6.14 for $v_t = 20\text{cm/s}$.

From Figure 6.15, it is clear and that the contact angle-particle size dependence shows a distinct minimum at a particle diameter of approximately $40\mu\text{m}$. There good agreement

between theory and the experimental data of Crawford and Ralston particularly for the larger particle sizes and the receding water contact angles. For small particles the results show that a larger contact angle is required for them to float which supports the model developed by Drelich and Miller. This agreement between the flotation limit for fine particles and the predictions of Drelich and Miller (equation 6.24) is very encouraging although Drelich and Miller gave data for very fine particles much smaller than those studied by Crawford and Ralston.

These results are used as the basis of determining whether the efficiency of stability is equal to one or zero in the discussion of the experimental results obtained in this study (see chapter 8).

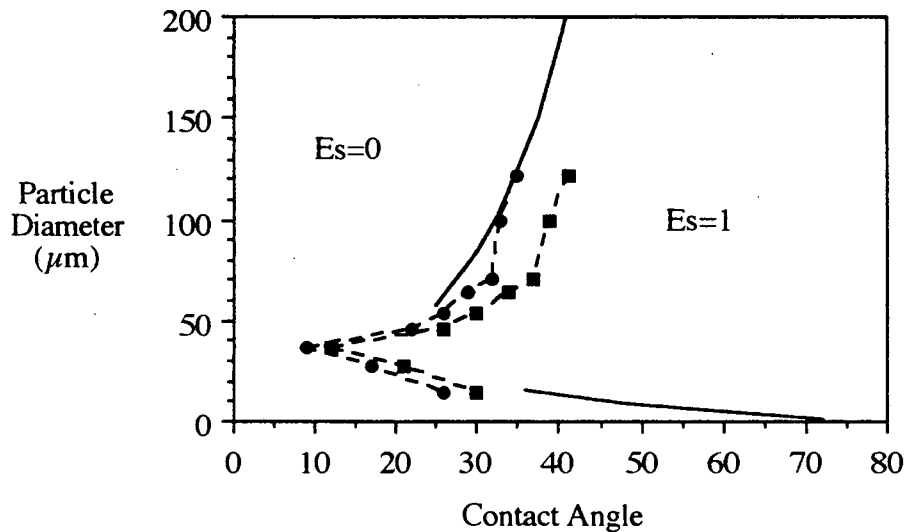


Figure 6.15 The experimental data of Crawford and Ralston indicating the advancing water contact angle (■) and the receding water contact angle (●) required for flotation to occur as a function of particle size. The solid lines are the results of the models discussed (equations 6.22 and 6.24) and shown in Figure 6.14 for $v_t = 20$ cm/s.

6.4 Conclusions

Experiments aimed at determining the attachment efficiency, E_A may therefore be performed by measuring the collection efficiency, E_{Coll} of particles of known size and hydrophobicity by bubbles of known size and velocity. Verification that the stability efficiency is unity can then be made, given that the experiments correspond to regions within the flotation domain described in the previous section. The collision efficiency can be calculated using the model discussed in section 6.1, allowing extraction of the value of E_A from the following equation:

$$E_{Coll} = E_C E_A E_S \quad 6.25$$

The bubble/particle attachment experiments reported in this study, as far as can be ascertained, represent the first determinations of the attachment efficiency for variations in particle size and hydrophobicity.

CHAPTER 7. BUBBLE/PARTICLE ATTACHMENT - EXPERIMENTAL

To obtain data on bubble/particle attachment, particles and bubbles must interact under stringently controlled conditions. The size and hydrophobicity of the particles as well as the bubble size and the concentration of electrolyte in the background aqueous solution were all varied in a systematic manner.

7.1 Preparation of Particle Fractions

Quartz particles, fractionated on the basis of their size, were further distinguished by variations in their hydrophobicity. The advancing water contact angle was determined in order to characterise the particle fractions of different hydrophobicity produced by partial methylation of the surface of the particles.

7.1.1 Particle Sizing

Optical grade high purity quartz (G. Bottley Pty. Ltd., London) was crushed and sieved into three particle size fractions. The particles were angular in appearance with rough surfaces. Narrow size distributions were obtained by successive beaker decantation. Particle size measurements were made using a HIAC Model PC-320 Particle Counter and a Malvern Model 2600C Particle Sizer.

The HIAC Particle Counter determines the particle size distribution by measuring the amount of light blockage, a function of the projected area of the particles. A very dilute suspension of the particles (less than 5,000 particles per cm^3) is pumped through a 90 μm channel placed between a light source and a sensor so that the attenuation of the light beam can be measured. The data obtained is based on a number distribution of the particle size which can be transformed to a distribution based on volume for comparison with other particle sizing techniques.

The Malvern 2600C Particle Sizer is based on laser light diffraction. In this instrument a He-Ne laser beam is directed through a stirred suspension of particles and the diffracted light is collected and focussed on to a detector placed in the focal plane of the lens. The detector consists of 16 concentric, semicircular photosensitive rings. The data from the detector is processed and a volume distribution of the closest fit to that data is produced. The results reported are given in terms of "equivalent spherical

diameters" strictly speaking, in no way taking into account the irregularities in the particle shape.

The two particle sizing techniques are based on different principles so, particularly for the angular (non-spherical) quartz particles used in this study, the actual particle size results are expected to exhibit some differences (Hewitt et al, 1991). The data obtained using the HIAC is based on a number distribution which will be dominated by the fine particles in the distribution. When the transformation of the number distribution is made to a distribution based on volume, errors in the count of the large particles (i.e. 60–80 μm) will be magnified compared with the error involved in the contribution of the fine particles (i.e. 5–10 μm) to the final volume distribution. A larger particle (say 80 μm) will contribute the same proportion to a volume distribution as 1000 8 μm particles, so if the count of these particles is made with an error of 1%, it can be seen that when the transformation from number to volume distribution is made this error will be more significant in the case of the larger particles. The Malvern instrument produces a result based on the volume distribution so that the contribution of the fine particles will be prone to larger errors, compared with the large particles, when transforming the distribution to one based on number.

7.1.2 Particle Contact Angle Measurements

Quartz particles were used in this study as they are well-characterised and readily rendered hydrophobic by exposure to TMCS by the reaction already described in section 3.3.2. Particles (10g) were stirred in $2 \times 10^{-4} \text{ mole dm}^{-3}$ solutions (100 cm^3) of TMCS in cyclohexane for short times depending on the degree of hydrophobicity desired, followed by collection in a crucible and rinsing with clean, dry cyclohexane. The particles were then dried overnight at 110°C and stored in a dessicator until they were required.

Characterisation of the degree of methylation of the surface of the particles was made by measuring the advancing water contact angle for these particles using the particulate contact angle apparatus developed in our laboratory (Diggins et al, 1990). The experimental apparatus used for the contact angle measurements is shown in Figure 7.1. It consists of a glass column, the lower end of which tapers to a narrow capillary (C) with an inside diameter of 0.38mm, effectively retaining the particles. At the top, the column is closed by a valve (A) either enabling the pressure build-up above the macroscopic meniscus to be monitored or permitting the over-pressure to be vented after equilibrium is reached.

Prior to a measurement, a small quantity of coarse particles was placed in the column to act as a porous plug. These prevented the particles under consideration either from falling through the capillary inlet or from blocking it. The column was filled with the particles, whilst gently tapping to ensure uniformity of packing. The column was then installed and the reservoir (D) filled with the liquid under study, ensuring that the valve at the top of the column was closed to the atmosphere. Once the reservoir has been filled the valve (A) was opened. Due to the special construction of the capillary at the lower end of the column, the liquid was automatically forced into the bed by the combined effects of a steadily increasing curvature of the liquid meniscus and the hydrostatic head. This ensures that the macroscopic meniscus in the particle bed was as flat as possible.

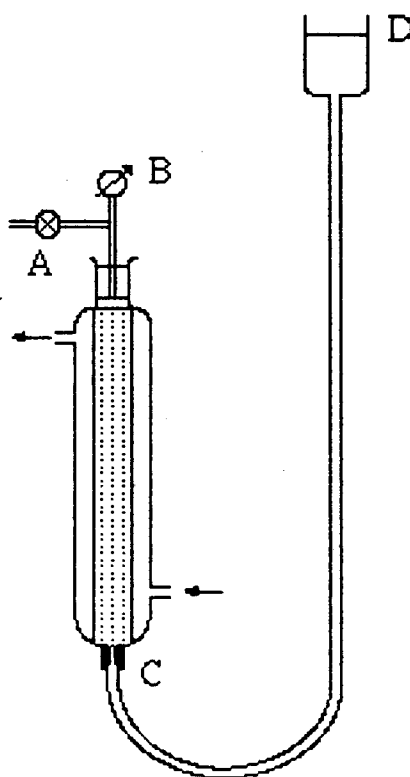


Figure 7.1 A schematic diagram of the apparatus used to determine the particulate contact angle.

After a brief time, valve (A) was closed and the liquid continued to rise in the bed until the capillary pressure, together with the hydrostatic head, was exactly compensated by

the over-pressure in the top part of the column. The pressure increase was recorded by a pressure transducer (B).

To determine the contact angle for the particles, it is necessary to use the Laplace-White equation (White, 1982) which is given by:

$$\Delta P = \frac{\gamma_{LV} \cos \theta \phi A_{sp}}{(1-\phi)} \quad 7.1$$

This expression contains three unknown variables, the volume fraction of the solid in the packed bed, ϕ , the specific surface area per gram of solid, A_{sp} , and the contact angle, θ . A perfectly wetting liquid (e.g. cyclohexane in the case of quartz) for which $\cos \theta$ is unity was used to determine the ΔP for a given particle size fraction. It has been shown that the volume fraction and the specific surface area are simply dependent on the particle size, are reproducible experimentally and are independent of the hydrophobicity of the particles. The value for ΔP obtained using cyclohexane can then be used for comparison with the experimental values found using water for particles of the same size fraction but of varying degrees of hydrophobicity.

When comparing the values obtained for ΔP using different liquids, account must be taken for the difference in their surface tension. When water is the liquid under consideration and with cyclohexane as the perfectly wetting liquid, the expression used was:

$$\cos \theta = \frac{\gamma_{\text{cyclohexane}} \Delta P_{\text{water}}}{\gamma_{\text{water}} \Delta P_{\text{cyclohexane}}} \quad 7.2$$

Having established the value of the over-pressure for cyclohexane, the contact angle for water as the wetting liquid could be calculated. This was used to verify that clean quartz was actually hydrophilic and did give a contact angle of zero, for the measurement of contact angle is particularly sensitive to surface contamination.

Contact angle measurements were made in triplicate and the average of these results was recorded with an error of $\pm 4^\circ$. This error figure represents the spread of the triplicate results rather than the accuracy of an individual measurement, which was more precise. The particles from the different size fractions were hydrophobised such that the contact angles of each fraction agreed within the limits of experimental error, and the reported contact angle was rounded off to the nearest five degrees.

The advancing water contact angle results determined were used basically to allow comparison between the relative hydrophobicity of the particles. It has been shown experimentally that advancing contact angles measured on quartz plates and particles methylated under the same conditions are in good agreement with each other (Crawford et al, 1987). In this study, it was found that by filtering the particles after flotation, washing with high purity water and drying at 110°C, the particles could be recovered and the initial advancing contact angle result could be obtained again within the limits of experimental error.

7.1.3 Preparation of Particle Suspensions

Particle suspensions were prepared immediately prior to being used in bubble/particle collection experiments, although the particles were taken from previously sized, surface modified and dried particle fractions stored in a dessicator. Firstly, suspensions of hydrophilic particles (i.e particles which had been scrupulously cleaned following the cleaning procedure used for the quartz plates in the thin film drainage experiments (see section 3.3.1), were prepared and used to determine entrainment values.

Particle suspensions using hydrophobic particles were then prepared and single bubble flotation experiments were carried out following the identical procedure used in the measurement of the entrainment values. The experimental procedure is described in detail later in this chapter. Particle suspensions of 0.1% by weight were used, and all suspensions were 'conditioned' for 10 minutes (i.e. stirred vigorously) before use. This conditioning stage was found to be particularly important for the suspensions of strongly hydrophobic particles since these particles were not wet well and were not dispersed into the aqueous suspension very quickly.

High-purity water used in the particle suspension preparation was taken directly from a milli-Q system consisting of one stage of reverse osmosis, two stages of ion exchange and two stages of activated carbon treatment followed by a final filtration step. The specific conductivity of the water was equal to, or less than $3 \times 10^{-5} \Omega^{-1} \text{ m}^{-1}$ and the pH was 5.8 ± 0.2 . The surface tension was 72.8 mN/m at 20°C and the bubble persistence time ('shake test') was not more than three seconds. The preparation of materials and all measurements were performed at room temperature (i.e. 20–25°C). Only recrystallised KCl of AR grade was used in the preparation of aqueous electrolyte solutions where these were used as the suspending liquid.

7.2 Air Bubbles

For these experiments single bubbles in the size range between 0.5 and 2mm were produced by restricting the gas flow through a fine needle with an inside diameter of 0.12mm. It has been shown that in water or very dilute aqueous solutions very small bubbles (less than 1mm in diameter) are spherical and rise with a steady rectilinear motion (Clift et al, 1978). Bubbles larger than 1mm are not spherical, but resemble flattened spheroids or ellipsoids and their vertical motion becomes irregular as a function of time.

Small bubbles are held in spherical form by surface tension, an effect which diminishes as the bubble radius increases and the inertia of the oncoming liquid tends to flatten the bubble against the restraining surface tension. The inertial effect is in turn influenced by the particular shape adopted by the bubble, so that there is a constant interaction between the shape, rise velocity and the local Laplace pressure.

7.2.1 Bubble Formation at Orificies

At very low flow rates and when the orifice is small, the bubble size at the time of detachment is determined by the balance between capillary force and buoyancy. If the diameter of the orifice is d_o then the capillary force holding the bubble is $\pi d_o \gamma$ and the buoyancy is equal to $\pi d_b^3 \Delta \rho g / 6$ (where $\Delta \rho$ is the density difference between air and water), assuming that the bubble is spherical. Thus, at the point of detachment the bubble size will be given by:

$$d_b = \left(\frac{6 d_o \gamma}{\Delta \rho g} \right)^{1/3} \quad 7.3$$

For a bubble detached from a needle with an inside diameter of between 0.12 and 0.25mm, this expression gives a bubble diameter ranging from 1.75mm to 2.23mm, as observed experimentally.

Bubble formation under constant flow, constant pressure conditions as well as the effect of liquid viscosity and liquid density on bubble size have been examined extensively (e.g. Kumar and Kuloor, 1970; Marmur and Rubin, 1976), however the orientation of the orifice and the influence of this on bubble size has not been studied to any great extent. Some early qualitative studies (e.g. Sullivan et al, 1964) have shown that as the orientation of the orifice changes the bubble size changes.

Changing the orientation of the needle was therefore used in this study to change the bubble size in a controlled manner. It was found that with the needle pointing vertically upwards, the bubble size was the largest so that at flow rates of four or five bubbles per second the bubble diameter was approximately 2mm as described by equation 7.3. As the orientation of the needle was changed through 180° (i.e. vertically downwards) the bubble size decreased. The three angles used for the orientation of the needles producing bubbles of three different sizes are described in further detail in the next section in which the strategy followed in the experiments is developed.

7.3 Experimental Method

A modified Hallimond tube was used to obtain data on the efficiency with which quartz particles become attached to a rising air bubble. The flotation cell used is shown in Figure 7.2. This diagram in fact incorporates two different cells which were used, one with the needle pointing vertically upwards and another with two alternative needle orientations. A 0.1% suspension of quartz particles was prepared and conditioned for ten minutes before being pumped through the flotation cell, after which the cell was isolated from the particle flow by shutting off both the inlet and outlet valves. The particles were then allowed to settle under tranquil conditions while bubbles were introduced, one at a time, via a needle at the bottom of the cell. All of the experiments were performed at a pH of 5.8 ± 0.2 .

A video camera was used to record the bubbles on tape so that the recording could be played back to permit the number of bubbles to be counted. Typically the bubble flow rate was between five and ten bubbles per second and an experiment would run for 30 to 40 seconds. The particles which became attached to the bubbles and floated were collected and the number of particles determined using the HIAC Particle Counter. In this way the number of particles collected per bubble could be determined. The experiments were performed in triplicate for each suspension and the average of the three results was taken. The number of particles which were floated was so small as to be insignificant compared with the number of particles per cm^3 in 0.1% suspensions.

Before use the flotation cell was scrupulously cleaned. The cleaning procedure involved soaking the cell in hot, concentrated nitric acid for 1-2 hours followed by washing with copious amounts of high-purity water. The cell was then dipped in a hot, 30% aqueous potassium hydroxide solution for 1 to 2 minutes, followed again by washing with copious amounts of high-purity water.

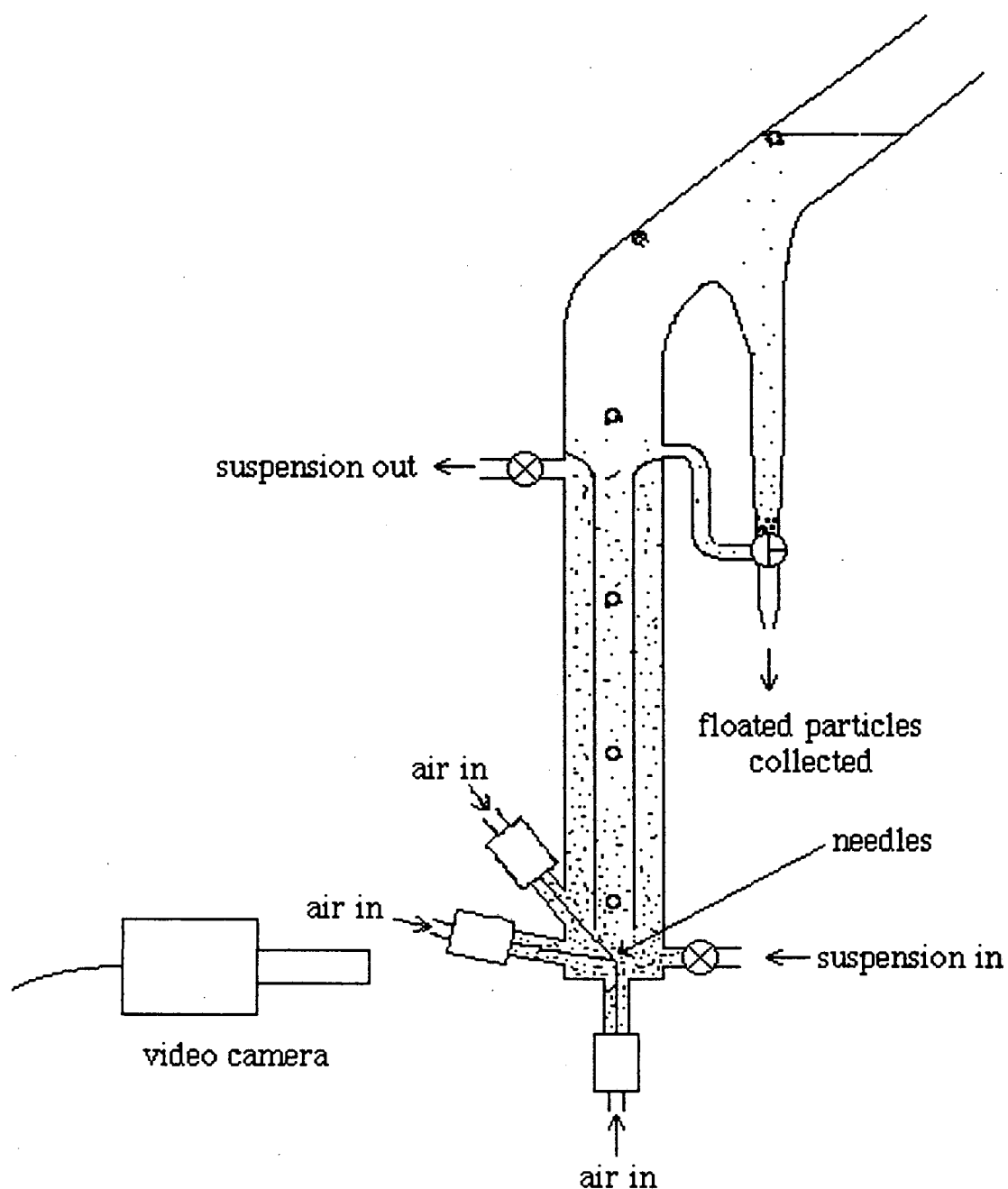


Figure 7.2 Schematic diagram of the float cell used in the bubble/particle attachment experiments indicating the three different orientations employed for the needle used for the introduction of the air bubbles into the cell.

Hydrophilic particles were used to obtain a measure of the number of particles collected by entrainment. Quartz particles which had been rendered hydrophobic were then used and the number of particles floated per bubble were determined, from which the entrainment value, obtained using the following procedure, was subtracted.

A 'blank' result was determined before every experimental measurement, by carrying out a HIAC particle count on milli-Q water to ensure that a low count was obtained (i.e. <10 particles per cm^3) indicating that the particle counter was clean before each particle count measurement. To ensure that the float cell was clean milli-Q water was pumped through the cell, and bubbles passed through to collect any particles present. Again a low particle count (i.e. <10 particles per cm^3) was required before continuing.

The entrainment value was then determined by passing bubbles through 0.1% suspension of hydrophilic particles. This was performed for each particle size fraction and, for all three bubble sizes used in this study, the number of particles 'collected' per bubble was less than 10 for particle diameters between 5 and $10\mu\text{m}$, less than 5 for particles between 10 and $20\mu\text{m}$, less than 2 particles between 20 and $30\mu\text{m}$, and less than one particle in each of the other three size ranges measured (i.e. $30\text{--}40\mu\text{m}$, $40\text{--}60\mu\text{m}$ and $60\text{--}80\mu\text{m}$).

The bubble size and rising velocity were measured using the video camera aligned horizontally to the bubble stream. A scale mounted adjacent to the float cell allowed the bubble diameter to be measured and the number of individual frames on the video tape recording of a rising bubble (corresponding to $1/25$ th of a second) were counted for a bubble to cover a known vertical distance. An average of ten bubbles was taken in obtaining both the average bubble diameter and also the bubble rise velocity and the results for these parameters reported in chapter 8 involved an error of $\pm 5\%$. The accuracy of the individual particle counts was relatively high and the repeatability of each count was better than $\pm 2\%$. The reproducibility of the number of particles collected per bubble was generally within $\pm 10\%$ or better (discussed further in section 8.2).

The straight section of the cell above the region filled with particles was incorporated in the cell design to reduce the entrainment of very fine particles. This section was filled with particle-free suspending liquid, which effectively 'washed' the fine particles from the bubble/particle aggregate, and was successful in minimising entrainment. It was thought that a downward flow of liquid in this section would further reduce entrainment, but this was found not to be necessary. Nevertheless, future work could involve introducing a variable flow of the 'washing' liquid, and investigating the effect on the stability of the bubble/particle aggregate (i.e. vary the value of E_S in a controlled manner).

CHAPTER 8. BUBBLE/PARTICLE ATTACHMENT - RESULTS AND DISCUSSION

Experiments were carried out using three different size fractions of quartz (i.e. 10-20 μm , 20-40 μm and 40-80 μm) and three bubble sizes (viz. bubbles of diameter 0.75, 1.2 and 2.0mm). For these combinations of particle and bubble size, experiments were conducted in which the degree of particle hydrophobicity and the concentration of the background electrolyte solution were varied.

8.1 Particle Size Fractions

For each of the three particle size fractions, the relative numbers of particular size particles present varied enormously. Particle suspensions of 0.1% were used and from the particle count results determined using the HIAC Particle Counter, the number of particles in each size range could be determined. In Figure 8.1, the percentage of the number distribution in six particle diameters covering the size range 5-80 μm for each of the three size fractions used, calculated from the HIAC count results, is shown.

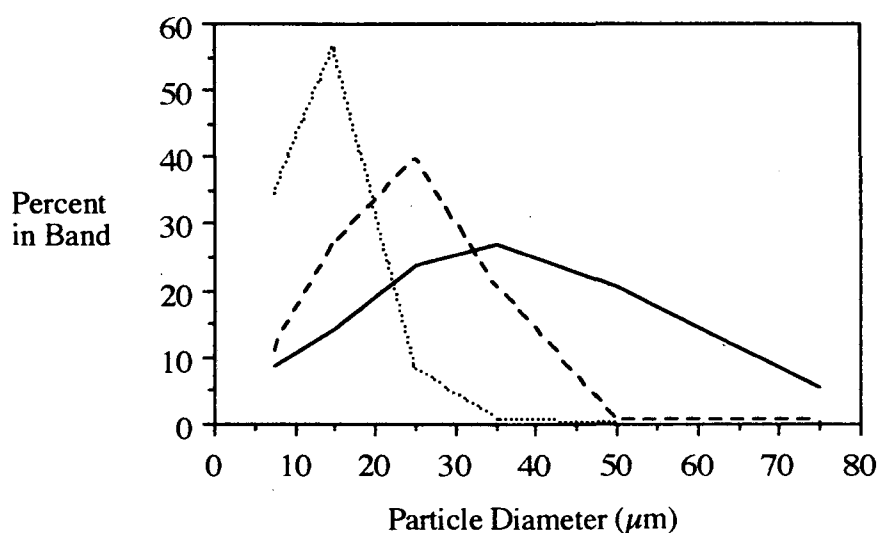


Figure 8.1 Particle size by number based on the HIAC results for three size fractions of quartz particles. Broadly speaking the size fractions can be identified by the following ranges: 10-20 μm (.....), 20-40 μm (---) and 40-80 μm (—).

The HIAC results can be transformed to give a particle size distribution based on volume (also equivalent to a weight distribution) and can be compared with the result obtained using the Malvern Particle Sizer. The Malvern result determined using the light diffraction technique is shown in Figure 8.2, as the percentage in 32 particle diameter intervals. Also shown in the Figure 8.2 is the HIAC result after transformation from a number distribution to a volume distribution. Based on these results, the three particle size fractions can be identified by the nominal range which they cover, giving fine (10-20 μm), medium (20-40 μm) and coarse (40-80 μm) fractions.

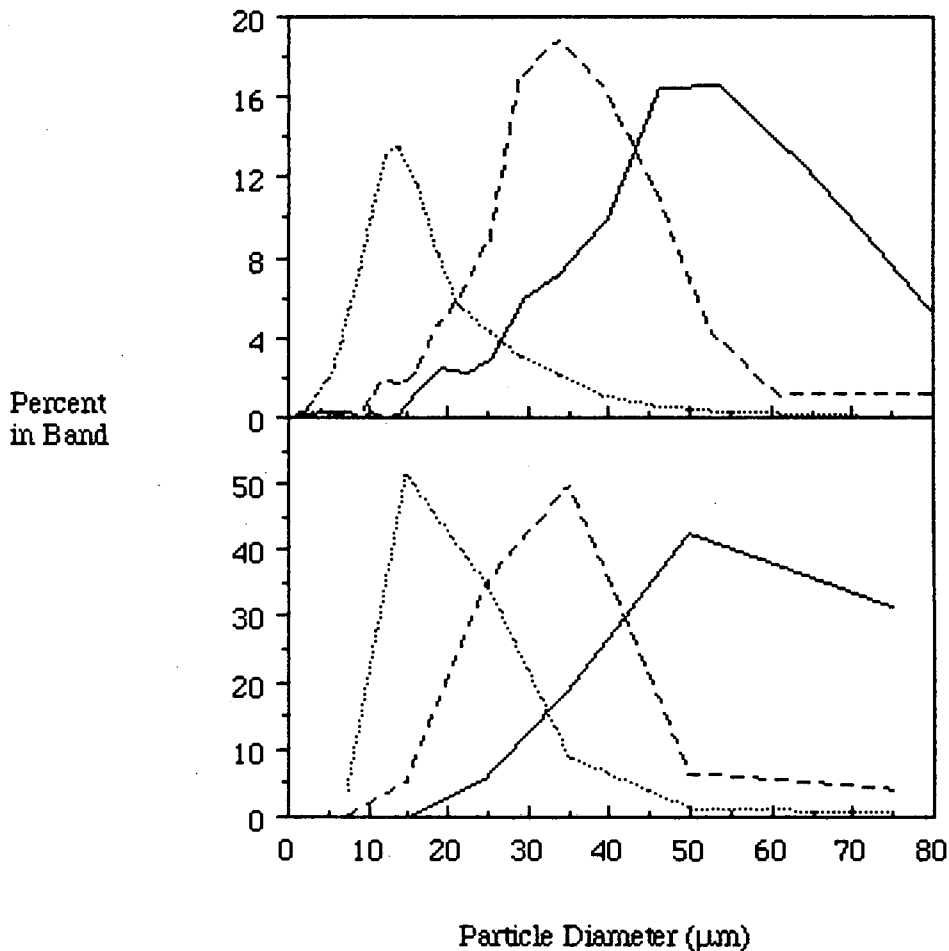


Figure 8.2 Particle size distributions by volume for the three particle size fractions prepared: fine (10-20 μm :.....); medium (20-40 μm :---); coarse (40-80 μm :—) fractions, determined using the Malvern Particle Sizer (top) and the HIAC Particle Counter (bottom).

The collision efficiencies calculated using the model described in section 6.1. are given in Table 8.1, for the bubble and particle diameters indicated (see Appendix B for sample calculation). Also shown in Table 8.1 is the volume of the path of the bubble through the suspension in the flotation cell, assuming that the bubble is spherical. Account is taken of the diameter of the particle, the centre of the particle must be at least a distance equal to the particle's radius away from the bubble's path so as not to interact with the bubble (see Appendix C).

<u>Particle Diameter</u> <u>Interval (μm)</u>	5-10	10-20	20-30	30-40	40-60	60-80
Ave. Diameter (μm)	7.5	15	25	35	50	70
<u>Collision Efficiency</u>						
$d_b = 0.75\text{mm}$ ($v_b = 10\text{ cm/s}$)	1.25×10^{-3}	4.66×10^{-3}	1.42×10^{-2}	2.75×10^{-2}	6.15×10^{-2}	1.35×10^{-1}
$d_b = 1.2\text{mm}$ ($v_b = 20\text{ cm/s}$)	7.65×10^{-4}	2.87×10^{-3}	9.48×10^{-3}	2.07×10^{-2}	4.86×10^{-2}	1.19×10^{-1}
$d_b = 2.0\text{mm}$ ($v_b = 25\text{ cm/s}$)	4.15×10^{-4}	1.75×10^{-3}	5.38×10^{-3}	1.19×10^{-2}	2.95×10^{-2}	7.71×10^{-2}
<u>Volume of Bubble</u> <u>Path (cm^3)</u>						
$d_b = 0.75\text{mm}$	0.108	0.110	0.113	0.116	0.121	0.127
$d_b = 1.2\text{mm}$	0.275	0.278	0.283	0.287	0.295	0.304
$d_b = 2.0\text{mm}$	0.712	0.718	0.725	0.732	0.743	0.757

Table 8.1 Collision efficiencies calculated using the model described in section 6.1 and the volume of the bubble's path through the flotation cell described in section 7.3 for the bubble (d_b) and particle diameters shown (example calculation shown in Appendix C).

<u>Particle Diameter Interval</u> (μm)	5-10	10-20	20-30	30-40	40-60	60-80
Ave. Diameter (μm)	7.5	15	25	35	50	70
<u>Fine Size Fraction</u> Particle Count/ cm^{-3}	68975	112075	16415	1505	70	10
<u>Collisions/bubble</u> $d_b = 0.75\text{mm}$	9.31	57.45	26.34	4.80	0.52	0.17
$d_b = 1.2\text{mm}$	14.49	89.42	44.04	8.94	1.00	0.36
$d_b = 2.0\text{mm}$	20.38	140.82	64.03	13.11	1.54	0.58
<u>Medium Fraction</u> Particle Count/ cm^{-3}	3751	9110	13403	6925	302	68
<u>Collisions/bubble</u> $d_b = 0.75\text{mm}$	0.51	4.67	21.50	22.09	2.25	1.17
$d_b = 1.2\text{mm}$	0.79	7.27	35.95	41.14	4.33	2.46
$d_b = 2.0\text{mm}$	1.10	11.45	52.27	60.32	6.62	3.97
<u>Coarse Fraction</u> Particle Count/ cm^{-3}	948	1592	2631	2981	2278	614
<u>Collisions/bubble</u> $d_b = 0.75\text{mm}$	0.13	0.82	4.22	9.51	16.95	10.56
$d_b = 1.2\text{mm}$	0.20	1.27	7.06	17.71	32.66	22.19
$d_b = 2.0\text{mm}$	0.28	2.00	10.26	25.97	49.93	35.84

Table 8.2 Particle Counts and Collisions per Bubble for each Particle Size Fraction.

The particle count result obtained using the HIAC, for 0.1% suspensions of each of the three particle size fractions was used to determine the number of bubble/particle collisions which would occur for a bubble of known diameter. The number of collisions was calculated for six size intervals for the three size fractions of particles, as shown in Table 8.2 and an example calculation is given in Appendix C. The number of possible particle collisions per bubble is equal to the number of particles in the bubble's path multiplied by the collision efficiency.

8.2 Experimental Results

Experiments were carried out to determine the number of particles attached per bubble, as a function of particle hydrophobicity for various values of bubble size and particle size. As described earlier, the hydrophobicity of the particles is indicated by the contact angle. For all of these experiments the particle diameter/contact angle conditions are such that the particles will form stable bubble/particle aggregates and $E_S = 1$ except in a couple of instances, as discussed in section 6.3.3. For example, the result shown previously in chapter 6 (Figure 6.15) is reproduced in Figure 8.3 to highlight the region where E_S equals 0, and the particles will not float.

Figure 8.3 shows the situation for $v_t = 20\text{cm/s}$, corresponding to $d_b = 1.2\text{mm}$. It is clear from this figure that particles of low hydrophobicity (i.e. $\theta=20^\circ$) with diameters in the range $25\text{--}40\mu\text{m}$ will float. This flotation domain for these particles will be shifted slightly down for larger bubbles, and to slightly higher particle diameters for smaller bubbles due to the relative velocities of these bubbles, as discussed in section 6.3. Particles of moderate hydrophobicity (i.e. $\theta\geq 50^\circ$) will float right across the particle size range as $E_S = 1$ except for the very fine particles (i.e. $<10\mu\text{m}$).

In some cases the maximum number of collisions expected per bubble was very low as shown in Table 8.2, and in these cases the number of particles floated per bubble was not sufficiently high to permit accurate, reproducible results to be obtained. It was observed that as a rule, in those particle/bubble interactions for which the maximum number of collisions was less than the entrainment value (given in section 7.3), the experimental error in the result was large compared with the actual number of particles collected per bubble. This was the situation for most of the results for particle less than $10\mu\text{m}$, and for the larger particles with the smallest bubble ($d_b = 0.75\text{mm}$).

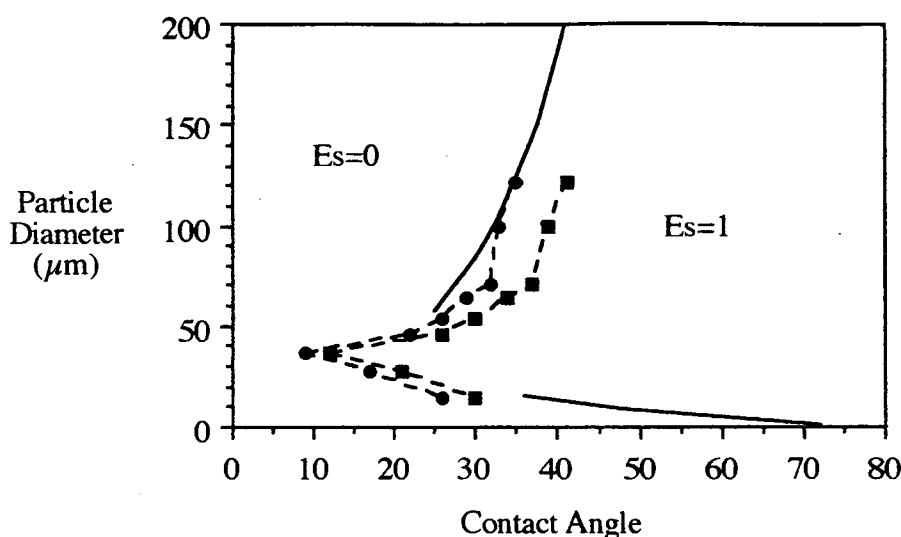


Figure 8.3 The flotation domain for $u_t = 20 \text{ cm/s}$ which corresponds to $d_b = 1.2 \text{ mm}$. Note that $E_S = 1$ for particles of low hydrophobicity (i.e. contact angle = 20°) in the particle diameter range $25\text{--}40 \mu\text{m}$.

In Figure 8.4 the results of the number of particles attached per bubble is shown for the coarse particle size fraction ($40\text{--}80 \mu\text{m}$) for three different bubble sizes, ranging from $0.75\text{--}2.0 \text{ mm}$. In all cases, the more hydrophobic particles ($\theta = 88^\circ$) became attached in greater numbers than did the particles of lesser degrees of hydrophobicity. Decreases in particle hydrophobicity (down to $\theta = 20^\circ$) were matched by a decrease in the number of attached particles.

In Figure 8.5 the results are shown in terms of variations in the particle diameter, holding the bubble diameter constant. In this Figure the number of particles attached per bubble are shown for the three particle size fractions and for a bubble size of 0.75 mm (as in Figure 8.4, the solid line is the number of collisions per bubble based on the collision efficiency calculation, and as such represents the result for $E_A = 1$ and $E_S = 1$).

The effect of ionic strength of the background electrolyte is demonstrated in Figure 8.6, for a bubble size of 0.75 mm and for the coarse particle size fraction ($40\text{--}80 \mu\text{m}$). The top part of the figure shows the results for experiments conducted in high purity water (i.e. water with specific conductivity less than $3 \times 10^{-5} \Omega^{-1} \text{ m}^{-1}$). These results can be compared with those obtained using an aqueous solution of $10^{-3} \text{ mole dm}^{-3}$ potassium chloride as the suspending electrolyte.

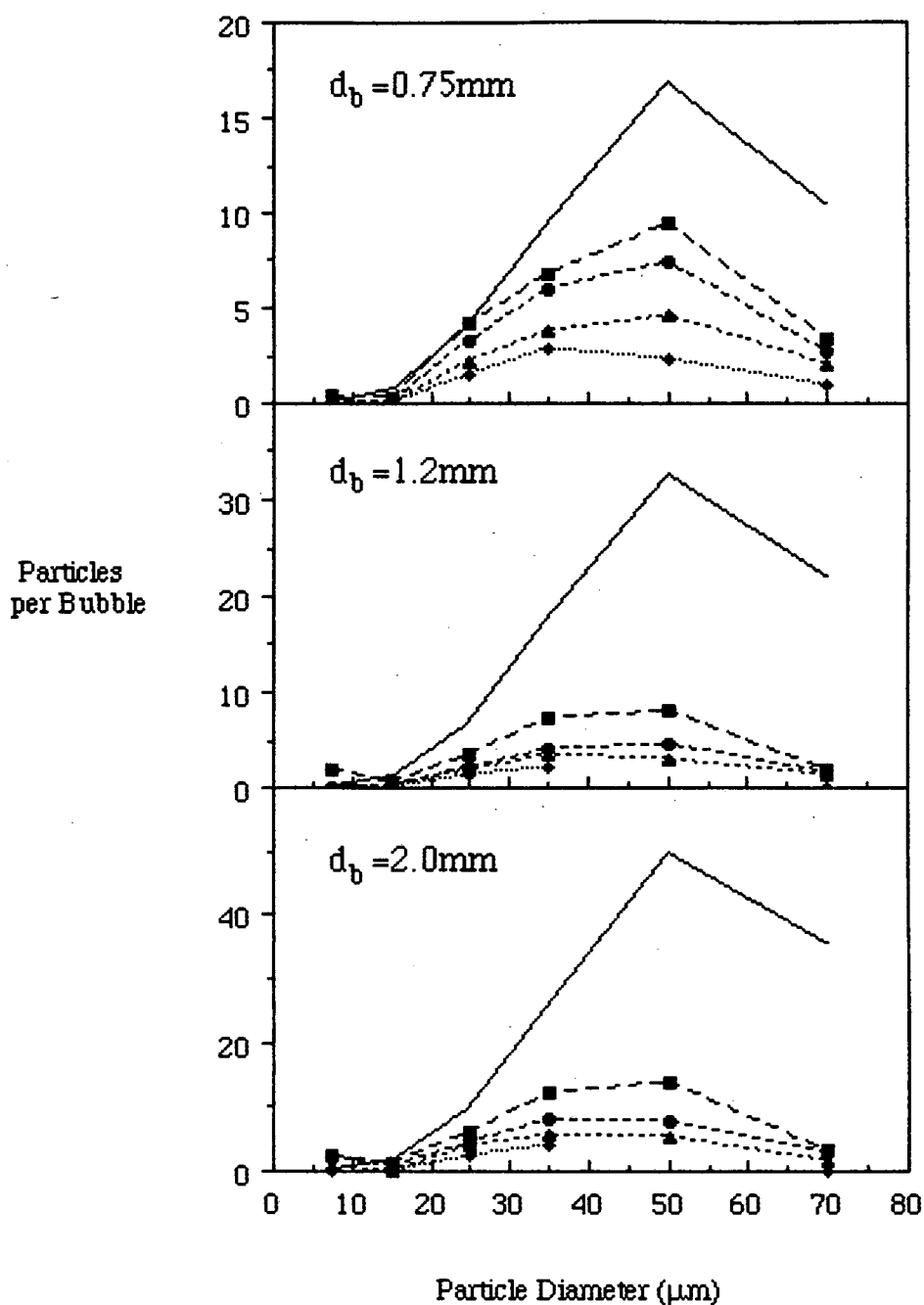


Figure 8.4 Particles collected per bubble, in water, for bubble diameters of 0.75mm (top), 1.2mm (middle) and 2.0mm (bottom) for coarse size fraction quartz particles of varying degrees of hydrophobicity; i.e. $\theta = 20^\circ$ (---◆---), $\theta = 50^\circ$ (---▲---), $\theta = 65^\circ$ (---●---) and $\theta = 88^\circ$ (---■---). The solid line represents the number of collisions per bubble based on the efficiency of collision calculation (i.e. assuming $E_A = 1$).

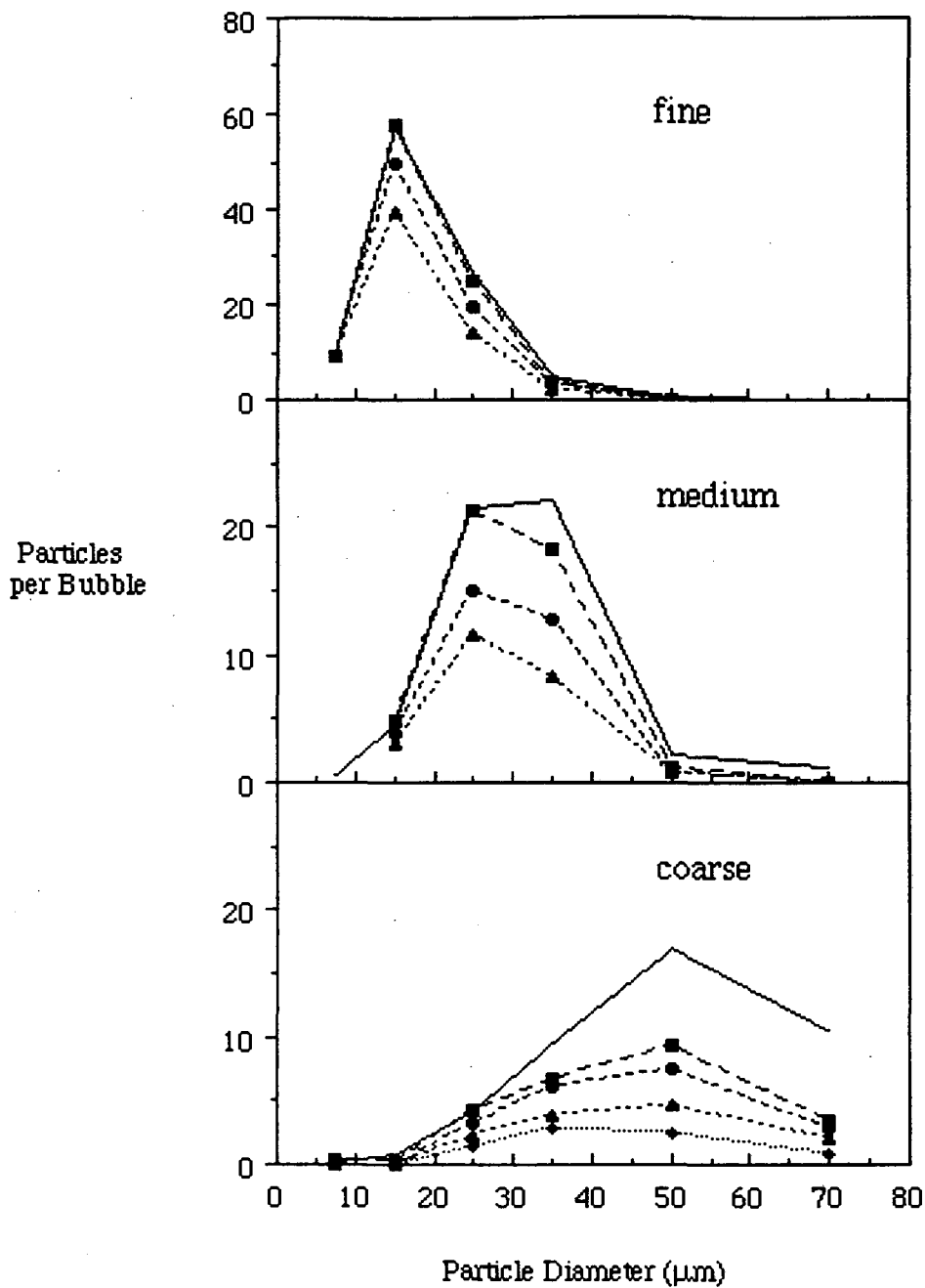


Figure 8.5 Particles collected per bubble, in water, for a bubble diameter of 0.75mm and quartz particles of fine (top), medium (middle) and coarse (bottom) size fractions and of varying degrees of hydrophobicity; i.e. $\theta = 20^\circ$ (---◆---), $\theta = 50^\circ$ (---▲---), $\theta = 65^\circ$ (---●---) and $\theta = 88^\circ$ (---■---). The solid line represents the number of collisions per bubble based on the efficiency of collision calculation (i.e. assuming $E_A = 1$).

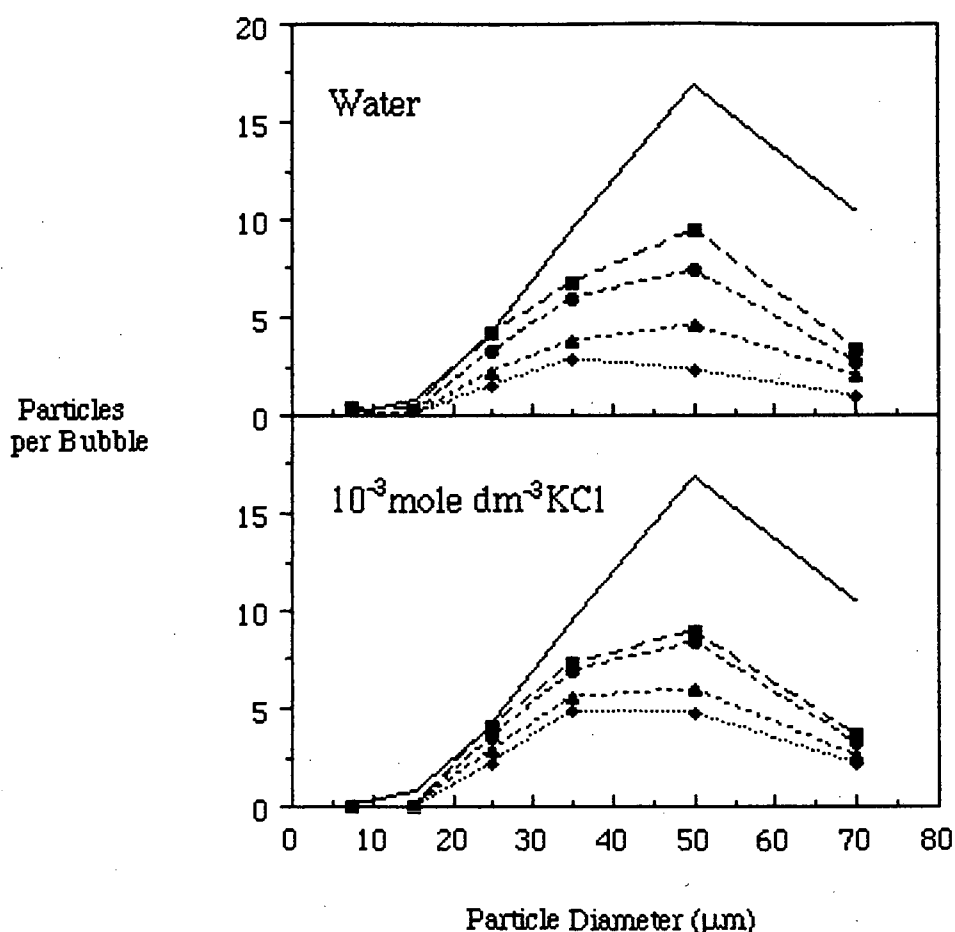


Figure 8.6 Particles collected per bubble in water (top) and 10^{-3} mole dm^{-3} KCl (bottom) for a bubble diameter of 0.75mm and coarse size fraction quartz particles of varying degrees of hydrophobicity; i.e. $\theta = 20^\circ$ (---◆---), $\theta = 50^\circ$ (---▲---), $\theta = 65^\circ$ (---●---) and $\theta = 88^\circ$ (---■---). The solid line represents the number of collisions per bubble based on the efficiency of collision calculation (i.e. assuming $E_A = 1$).

It should be noted that the effect of increasing the ionic strength of the background electrolyte does not drastically alter the number of attached particles in the case of the most hydrophobic particles ($\theta = 88^\circ$), but certainly the number of attached particles increases for particles with lower degrees of hydrophobicity. This point will be discussed further later in this chapter, and will become more evident when the attachment efficiency and the induction time are considered. The observation that electrolytes exert more effect the more hydrophilic the surfaces are is also observed for bacterial adhesion.

8.3 Attachment Efficiency

The attachment efficiency was determined by taking the ratio of the experimentally determined number of particles attached per bubble, to the number of particle collisions which can occur for each bubble, calculated using the collision efficiency model and assuming $E_A = 1$. In Figure 8.7, the attachment efficiency results are shown for the fine particle size fraction (10-20 μ m) for the three different bubble sizes and an example calculation is given in Appendix C.

The attachment efficiency was found to decrease with decreasing particle hydrophobicity and, broadly speaking, decreased with increasing particle size. This result is observed consistently, for all of the bubble sizes and particle size fractions studied, as further illustrated in Figure 8.8. In this Figure, a comparison is made between the results for moderately hydrophobic particles ($\theta = 50^\circ$) shown with dashed lines, and the results for strongly hydrophobic particles ($\theta = 88^\circ$) shown with solid lines.

The three size fractions gave essentially the same attachment efficiency for any particular bubble size and particle hydrophobicity, so the relative proportions of different size particles which were present at various levels in the three size fractions did not influence the attachment efficiency of the different size particles. In other words, the attachment efficiency of a particle was not changed by the presence of large numbers of particles of a similar size or of a different size.

The attachment efficiency of the small bubble is higher than for larger bubbles right across the particle size range studied as well for particles of a particular degree of hydrophobicity. Examination of the effect of indifferent background electrolyte should allow elucidation of the relative contributions of the parameters which effect the attachment efficiency.

The influence of the ionic strength of the background electrolyte on attachment efficiency can be seen in Figure 8.9, in which the difference between carrying out the experiments in high purity water and 10⁻³ mole dm⁻³ KCl is shown. The attachment efficiency was not altered markedly for strongly hydrophobic particles, but the effect of the ionic strength became more noticeable as the degree of hydrophobicity of the particle decreased. This effect was observed for all three bubble sizes studied and is illustrated in Figure 8.9 for $d_b = 0.75$ mm, and for $d_b = 1.2$ mm in Figure 8.10.

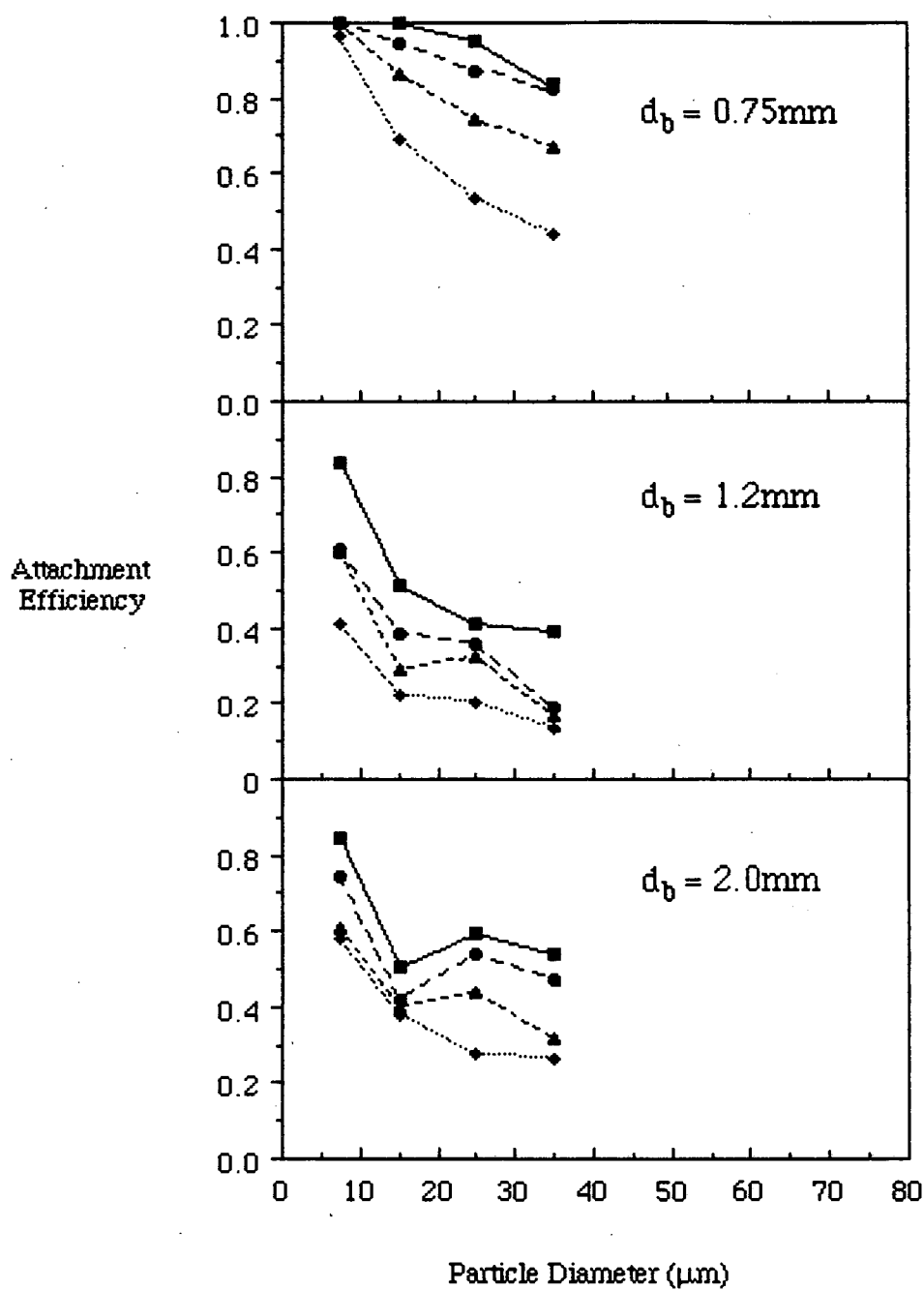


Figure 8.7 Efficiency of attachment for a bubble diameter of 0.75mm (top), 1.2mm (middle) and 2.0mm (bottom) and fine size fraction quartz particles of varying degrees of hydrophobicity; i.e $\theta = 50^\circ$ (---◆---), $\theta = 65^\circ$ (---▲---), $\theta = 75^\circ$ (-●-) and $\theta = 88^\circ$ (—■—).

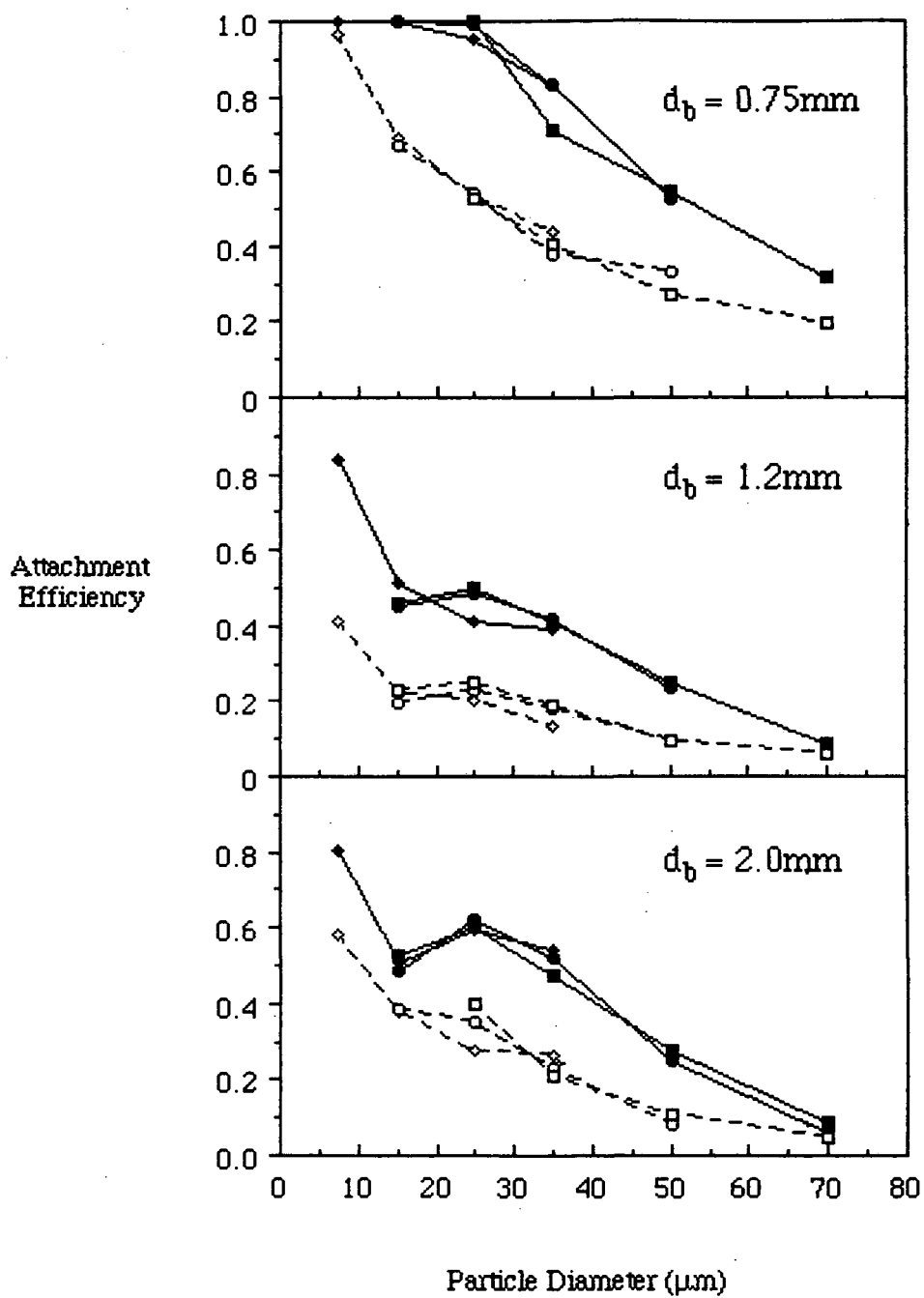


Figure 8.8 Efficiency of attachment indicating the differences for moderately hydrophobic, $\theta = 50^\circ$ (open symbols, dashed lines) and strongly hydrophobic, $\theta = 88^\circ$ (closed symbols, solid lines) particles for a bubble diameter of 0.75mm (top), 1.2mm (middle) and 2.0mm (bottom) and fine ($\diamond, \blacklozenge$), medium ($\circ, \bullet$) and coarse ($\square, \blacksquare$) size fraction quartz particles in water.

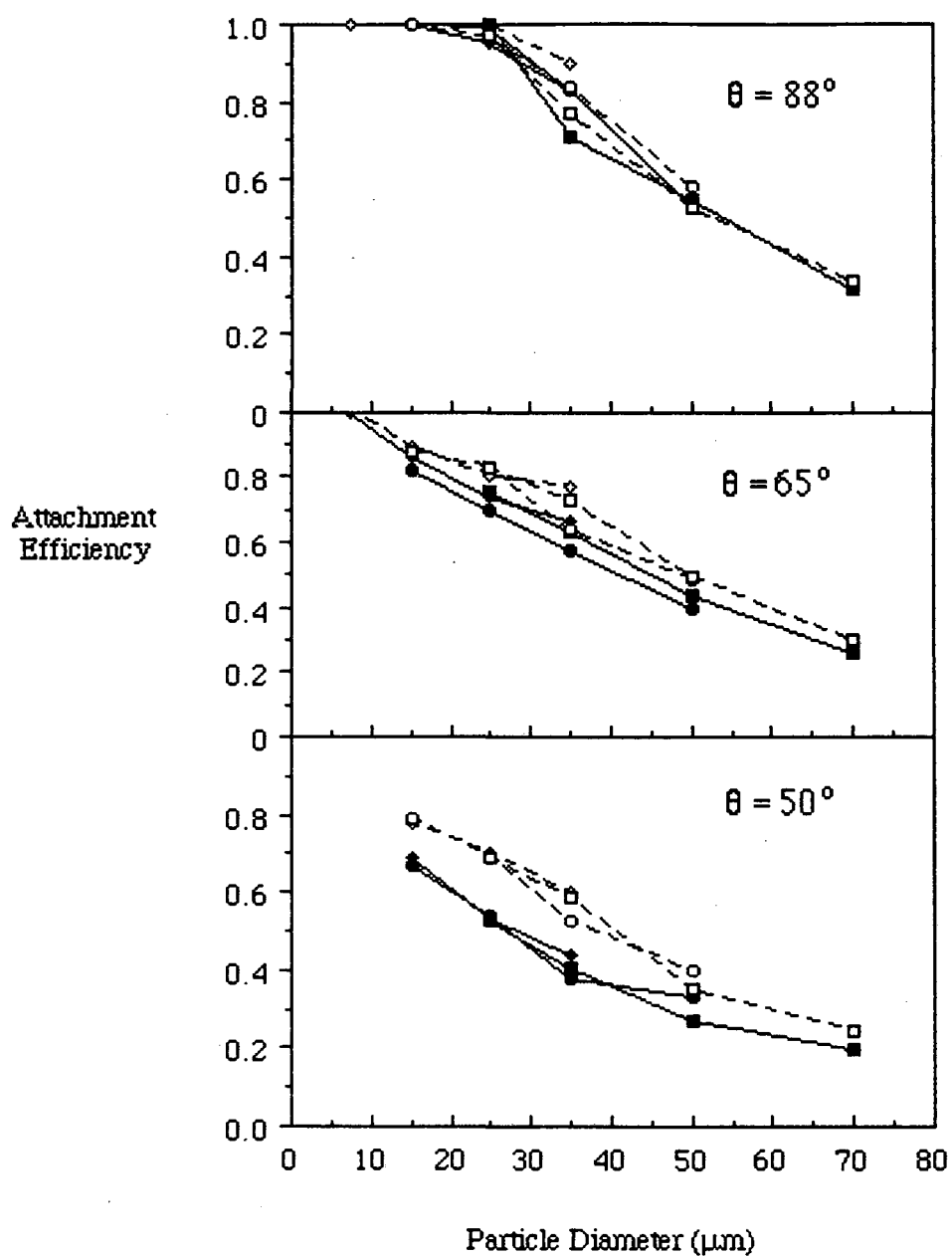


Figure 8.9 Efficiency of attachment indicating the differences for strongly hydrophobic and moderately hydrophobic particles (i.e. $\theta = 88^\circ$, $\theta = 65^\circ$ and $\theta = 50^\circ$; top, middle and bottom sets of graphs respectively) for a bubble diameter of 0.75mm and fine ($\blacklozenge$, $\diamond$), medium ($\bullet$, $\circ$) and coarse ($\blacksquare$, $\square$) size fractions in water (closed symbols, solid lines) and in $10^{-3}\text{ mole dm}^{-3}$ KCl (open symbols, dashed lines).

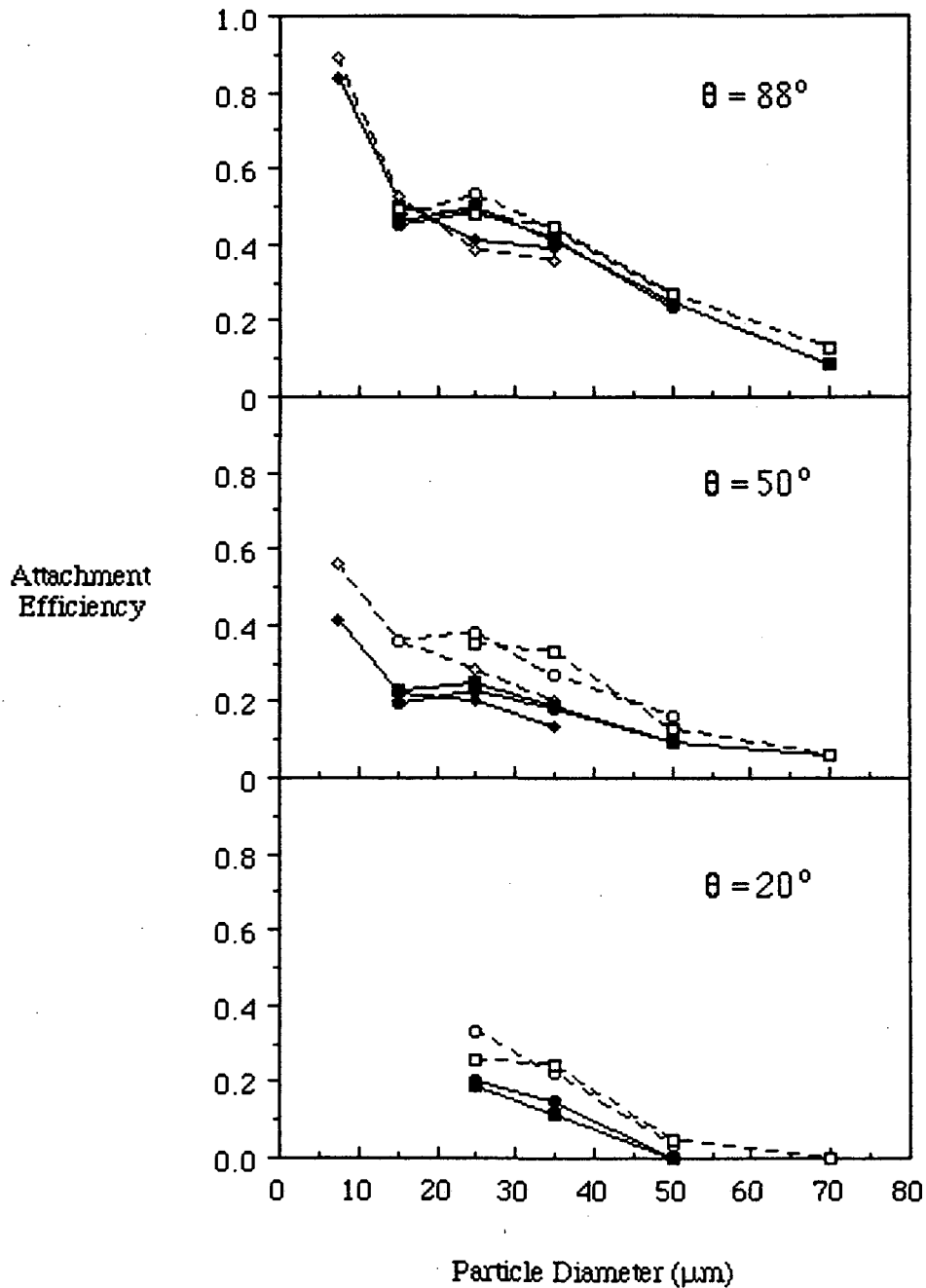


Figure 8.10 Efficiency of attachment indicating the differences for strongly hydrophobic, moderately hydrophobic and weakly hydrophobic particles (i.e. $\theta = 88^\circ$, $\theta = 50^\circ$ and $\theta = 20^\circ$; top, middle and bottom sets of graphs respectively) for a bubble diameter of 1.2mm and fine ($\blacklozenge, \diamond$), medium ($\bullet, \circ$) and coarse ($\blacksquare, \square$) size fractions in water (closed symbols, solid lines) and in $10^{-3} \text{ mole dm}^{-3}$ KCl (open symbols, dashed lines).

The consistency of the influence of ionic strength across the three bubble sizes is shown in Figure 8.11. In this figure, the attachment efficiencies are shown for the same series of particles, considering only differences between water and $10^{-3}\text{mole dm}^{-3}$ KCl with changes in bubble size.

In this figure, the attachment efficiencies are shown for the same series of particles, and considering only differences between water and $10^{-3}\text{mole dm}^{-3}$ KCl with changes in bubble size. There is an increase in the attachment efficiency for the particles of moderate hydrophobicity for all three bubble sizes, whereas the attachment efficiency of the strongly hydrophobic particles is essentially unchanged, particularly for the smallest bubble.

As the background electrolyte concentration is increased from $10^{-5}\text{mole dm}^{-3}$ KCl, through $10^{-3}\text{mole dm}^{-3}$ KCl, to $10^{-1}\text{mole dm}^{-3}$ KCl, the effect is to increase the attachment efficiency of the particles of lower degrees of hydrophobicity, particularly for the smaller particles in the coarse particle size fraction ($40\text{-}80\mu\text{m}$) with large bubbles of diameter of 2.0mm as shown in Figure 8.12.

The results obtained for experiments concerning the effect of the ionic strength indicate that it is only when the hydrophobicity is reduced that the influence of ionic strength becomes significant. This is consistent with the hypothesis that the hydrophobic force 'swamps' the electrostatic double layer force in the case of the strongly hydrophobic particles. If the hydrophobic component to the interaction energy between the bubble and the particle is reduced, then the contribution due to the overlapping electrical double layers associated with the approaching interfaces becomes significant.

In the experiments of Anfruns and Kitchener, little or no change in the floatability was observed with changes in the ionic strength of the background electrolyte for fully methylated quartz particles. They did observe a change for smooth glass spheres, but this was attributed to the change in surface roughness between these particles and the angular quartz particles.

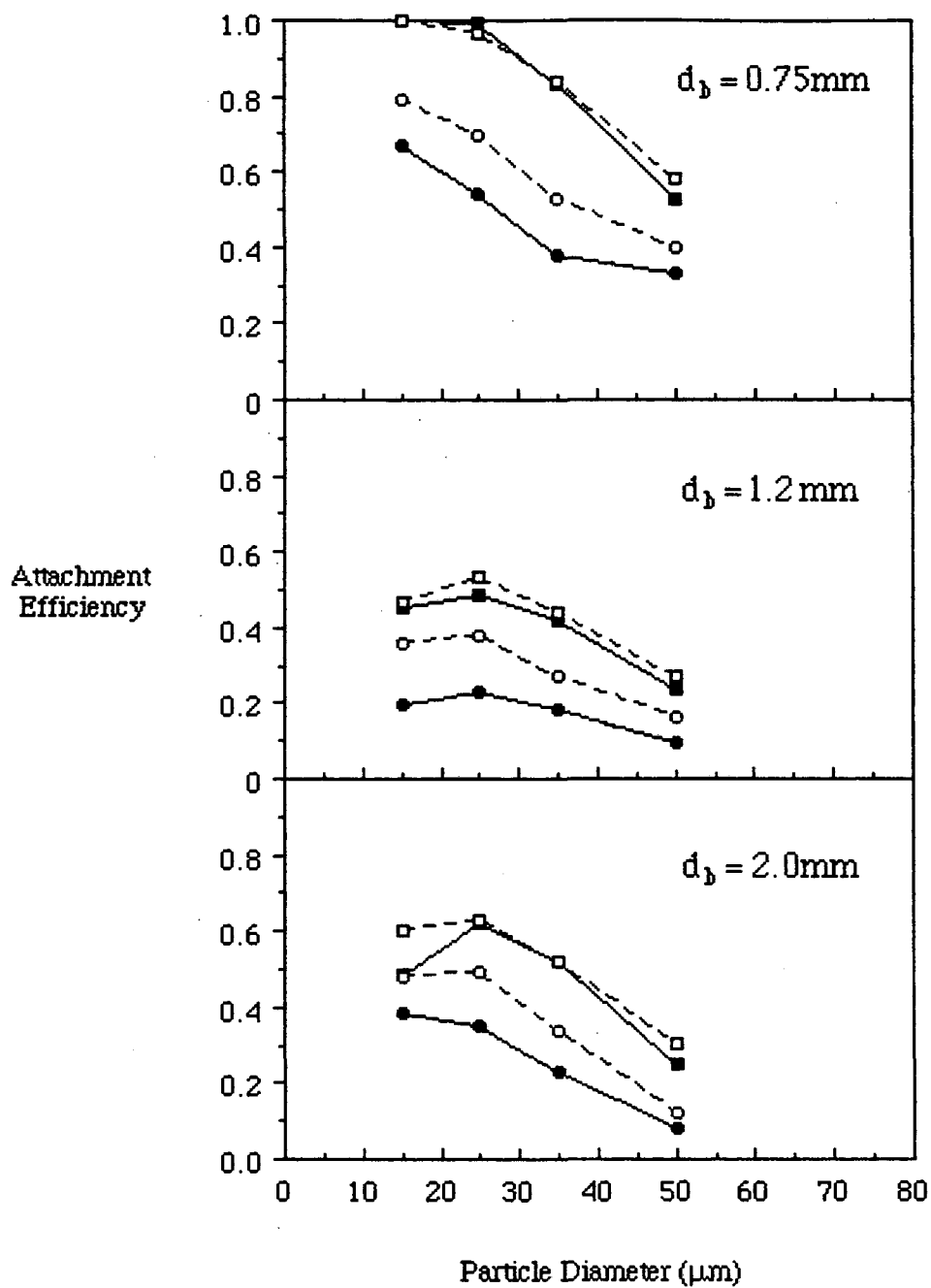


Figure 8.11 Attachment efficiency for strongly hydrophobic ($\theta = 88^\circ$ (■, □)) and moderately hydrophobic ($\theta = 50^\circ$ (●, ○)), medium size fraction particles with bubble diameters of 0.75mm (top), 1.2mm (middle) and 2.0mm (bottom), in water (closed symbols, solid lines) and in $10^{-3}\text{ mole dm}^{-3}\text{ KCl}$ (open symbols, dashed lines).

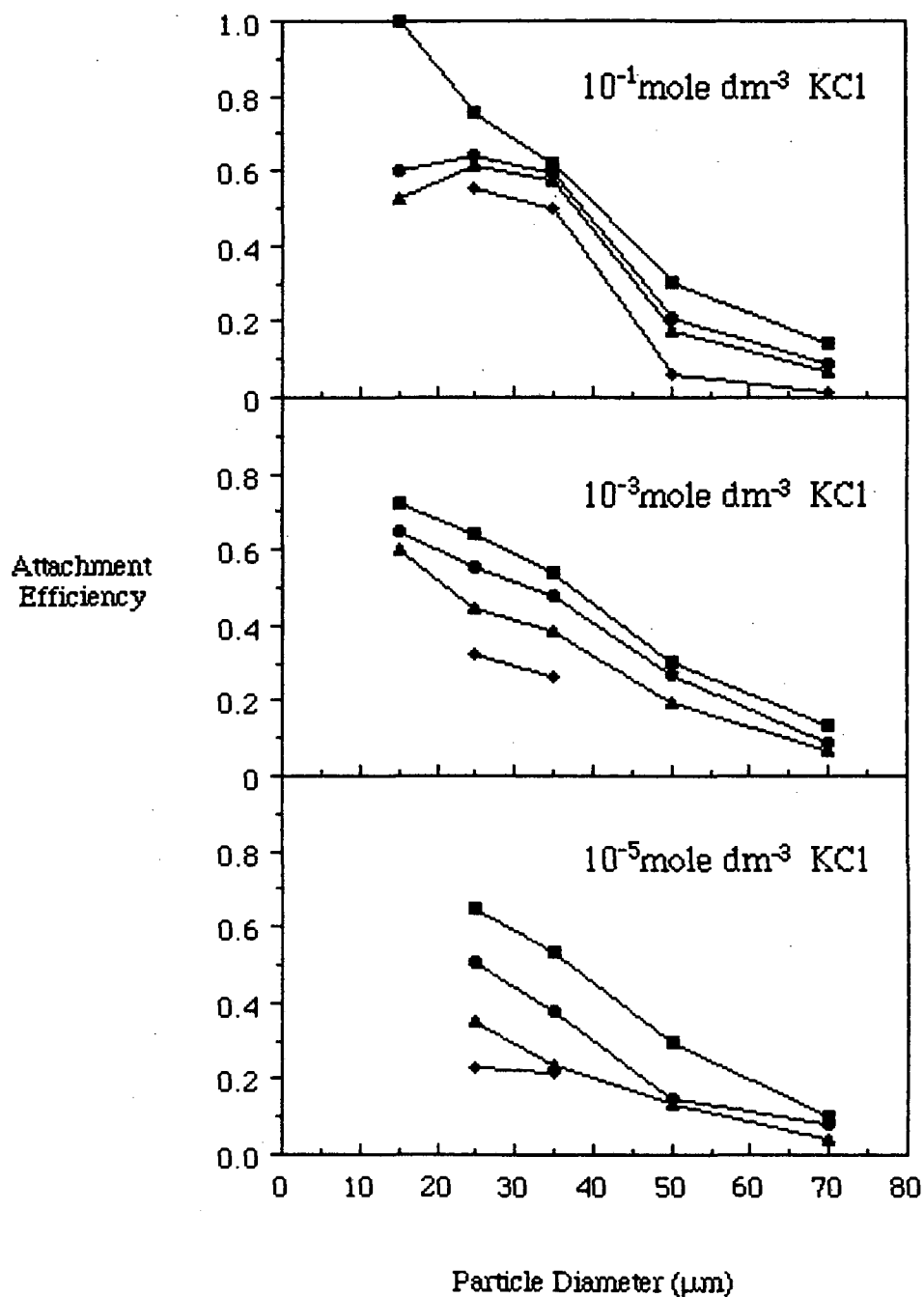


Figure 8.12 Attachment efficiency for particles of coarse size fraction and of various degrees of hydrophobicity (i.e. $\theta = 88^\circ$ (■), $\theta = 65^\circ$ (●), $\theta = 50^\circ$ (▲) and $\theta = 20^\circ$ (◆)), with bubbles of diameter 2.0mm, in $10^{-1} \text{ mole dm}^{-3}$ KCl (top), $10^{-3} \text{ mole dm}^{-3}$ KCl (middle) and $10^{-5} \text{ mole dm}^{-3}$ KCl (bottom).

The comparative strength of the hydrophobic interaction and the contribution of the electrical double layer forces was considered by Xu and Yoon (1989, 1990) after they had conducted a series of coagulation experiments on aqueous suspensions of methylated silica. In these experiments, the ionic strength of the background electrolyte was held constant, and the variation in the degree of coagulation was monitored as a function of the pH.

The pH range over which coagulation was found to occur was extended with increasing particle hydrophobicity since it was only at high pH that the magnitude of the zeta potential became large and hence the electrostatic repulsive force increased sufficiently to prevent coagulation. At neutral pH values the hydrophobic force was sufficient to overcome the electrical double layer force in the case of strongly hydrophobic particles. Xu and Yoon calculated that contributions due to dispersive van der Waals forces are relatively short range and not significant enough to explain the coagulation results obtained.

The experiments in this study also suggest that an attractive interaction occurs between approaching hydrophobic interfaces such as air bubbles and hydrophobic particles. In the case of strongly hydrophobic particles dispersed in aqueous solutions, the attractive hydrophobic force appears to be comparable to the electrical double layer forces which exists in dilute electrolyte solutions or high purity water, both in terms of their decay length and magnitude.

The attachment efficiency observed is a result of the interplay of film drainage and bubble spreading kinetics to the induction times. The latter is now calculated and can then be discussed in terms of the relative significance of the thin film drainage time and the time for expansion of the three phase line of contact between the particle/liquid/air bubble entity.

8.4 Induction Times

Induction times were calculated for the experimental attachment efficiencies. Using the model developed by Dobby and Finch, described in detail in chapter 6, the minimum sliding time corresponding to the observed attachment efficiency was determined and equated with the maximum induction time for that particular bubble/particle interaction.

For example, if a particle of $25\mu\text{m}$ has an attachment efficiency of 0.6 with a bubble of 0.75mm , then the minimum contact time (due to sliding) can be calculated for 60% of bubble/particle collisions for that bubble/particle size combination (i.e. calculation of the time for which 60% of the collisions have an equal or greater sliding time - see example calculation in Appendix C). The induction time for this bubble/particle interaction must then be equal to the calculated sliding time given that for these size bubbles and particles the collision time is relatively short and can be ignored.

The induction times for strongly hydrophobic particles ($\theta = 88^\circ$) show a minimum for particle of diameters of $30\text{--}40\mu\text{m}$, for bubbles of 1.2 and 2.0mm and for smaller bubbles ($d_b = 0.75\text{mm}$) this minimum occurs for particles of diameter $25\mu\text{m}$ (see Figure 8.13). For particles of moderate hydrophobicity ($\theta = 50^\circ$), these induction time minima occur although they are not as pronounced.

In all cases, as shown in Figure 8.13, the induction times increase markedly for particles with small diameters (i.e. $d_p < 10\mu\text{m}$). According to the Dobby and Finch sliding time model, fine particles have much longer sliding times than larger particles, so even though the attachment efficiency may be higher for fine particles, this is not due to these particles having shorter induction times compared with larger particles.

A further comparison of the induction time for particles with varying degrees of hydrophobicity interacting with bubbles of different sizes is also shown in Figure 8.14. The induction times for the small bubble ($d_b = 0.75\text{mm}$) are shorter than for the large bubbles for all particles, irrespective of the particle size and hydrophobicity.

Figure 8.15 shows that the induction time for the smallest bubble is less than for the larger bubbles for the fine particle fraction ($10\text{--}20\mu\text{m}$). In the case of the medium and coarse particle fractions (i.e. the $20\text{--}40\mu\text{m}$ and $40\text{--}80\mu\text{m}$ fractions respectively), the induction time for the small bubble is less than for the larger bubbles, although the difference becomes progressively less with increasing particle size.

As expected from the attachment efficiency results, the change in ionic strength between water and $10^{-3}\text{mole dm}^{-3}$ KCl caused a decrease in the induction time of the moderately hydrophobic particles without markedly effecting the strongly hydrophobic particles. As can be seen in Figures 8.16a and 8.16b, this effect was most clear cut with the small bubble while larger bubbles showed the same trend, albeit less obviously.

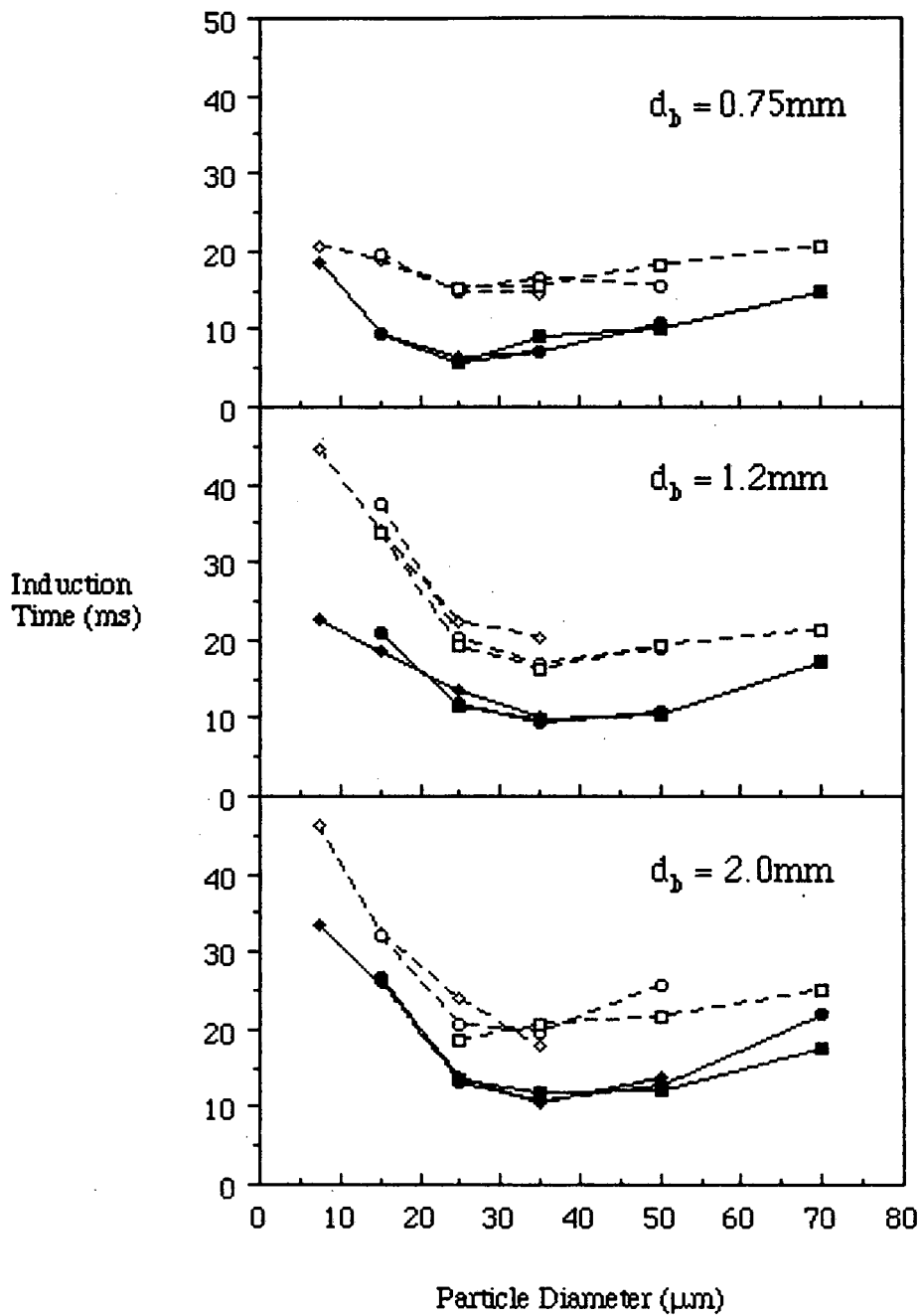


Figure 8.13 Induction times for strongly hydrophobic ($\theta = 88^\circ$) particles of fine (—◆—), medium (—●—) and coarse (—■—) size fractions and for moderately hydrophobic particles ($\theta = 50^\circ$) of the same size fractions (i.e. fine (---◇---), medium (---○---) and coarse (---□---) are shown for bubble diameters of 0.75mm (top), 1.2mm (middle) and 2.0mm (bottom) in water.

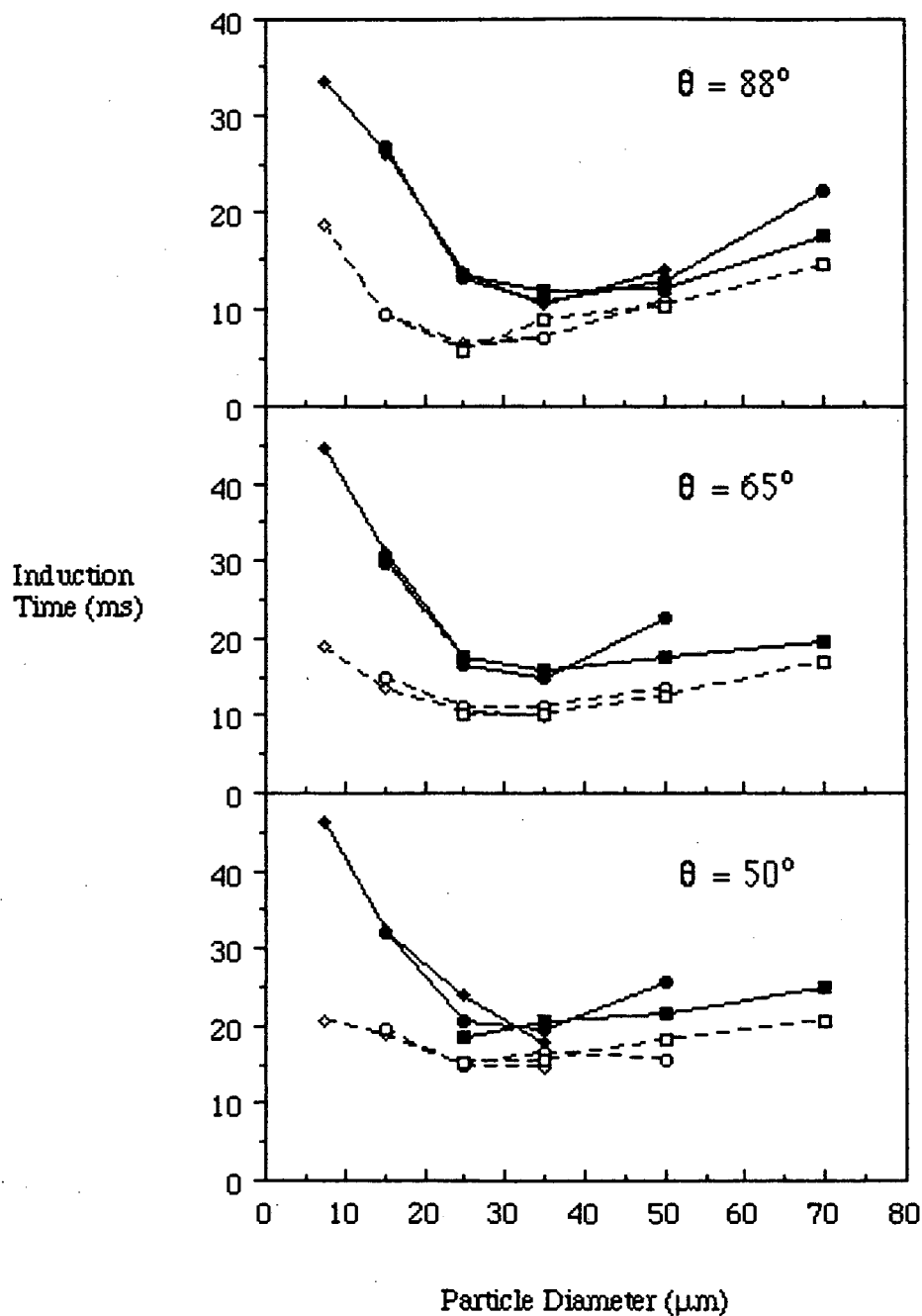


Figure 8.14 Induction times for strongly hydrophobic particles ($\theta = 88^\circ$; top) and moderately hydrophobic particles ($\theta = 65^\circ$ and $\theta = 50^\circ$; middle and bottom respectively) with bubbles of diameters 0.75mm (---) and 2.0mm (—) and for fine ($\diamond, \blacklozenge$), medium ($\circ, \bullet$) and coarse ($\square, \blacksquare$) size fraction particles in water.

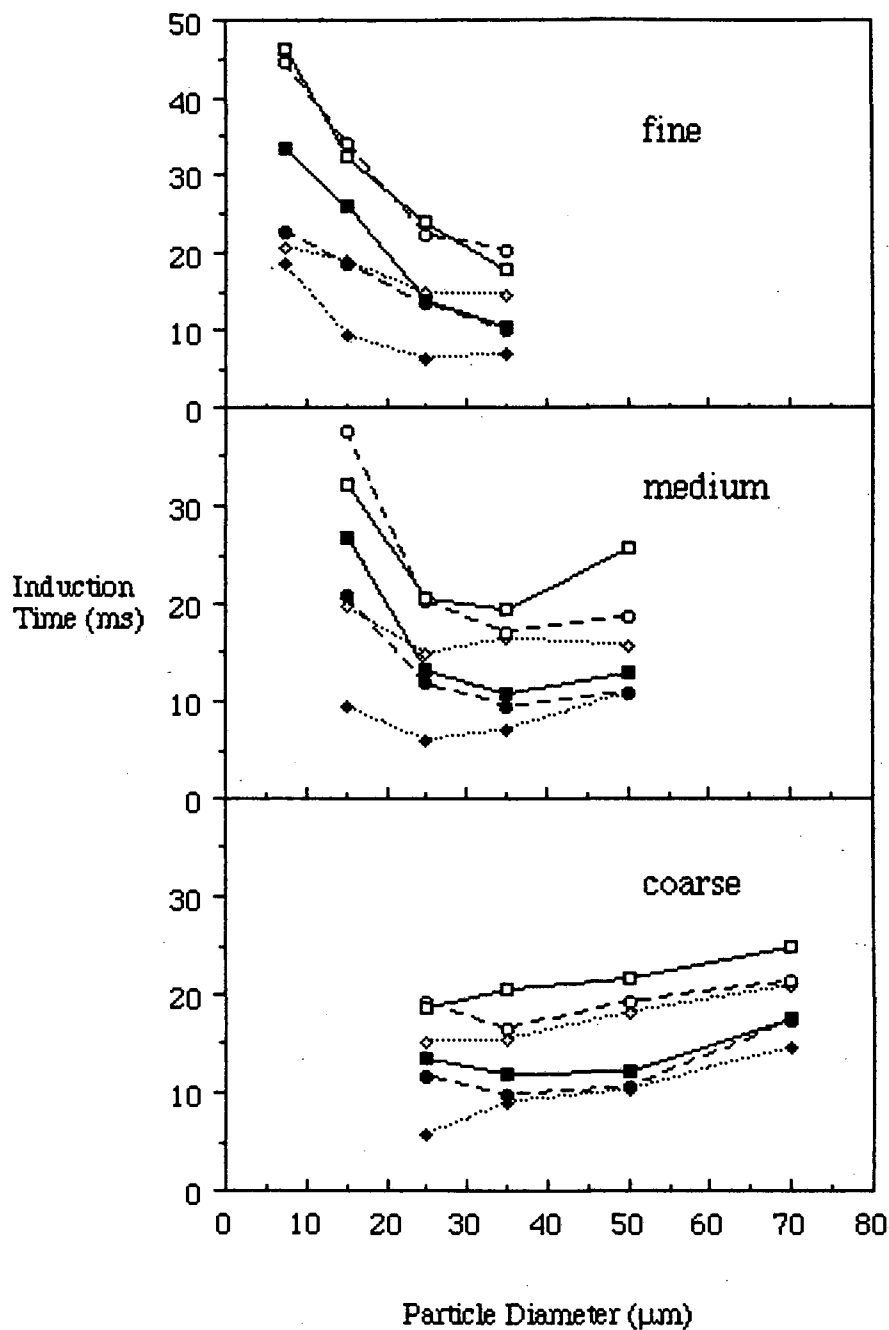


Figure 8.15 Induction times for strongly hydrophobic particles ($\theta = 88^\circ$) with bubbles of diameters 0.75mm (.....◆.....), 1.2mm (--●--) and 2.0mm (—■—) and for moderately hydrophobic particles ($\theta = 50^\circ$) with bubbles of the same diameters (i.e. 0.75mm (.....◇.....), 1.2mm (--○--) and 2.0mm (—□—)), for fine, medium and coarse size fraction particles in water.

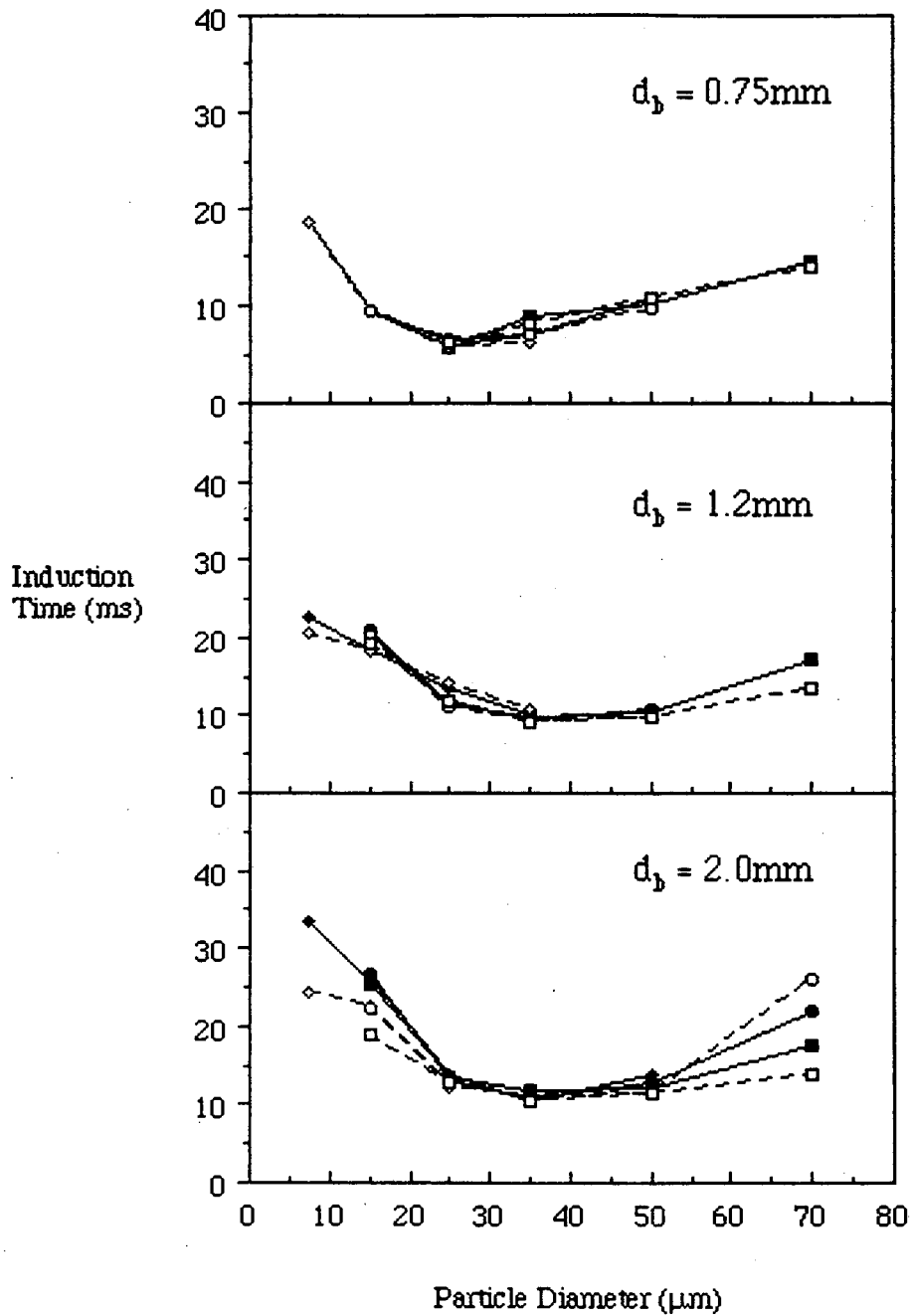


Figure 8.16a Induction times for strongly hydrophobic particles ($\theta = 88^\circ$) of fine (—◆—), medium (—●—) and coarse (—■—) size fractions in water compared with the same fine (---◇---) medium (---○---) and coarse (---□---) size fractions in $10^{-3}\text{mole dm}^{-3}$ KCl (---□---), for bubble diameters of 0.75mm (top), 1.2mm (middle) and 2.0mm (bottom). See Figure 8.16b for the same results for moderately hydrophobic particles (i.e. $\theta = 50^\circ$).

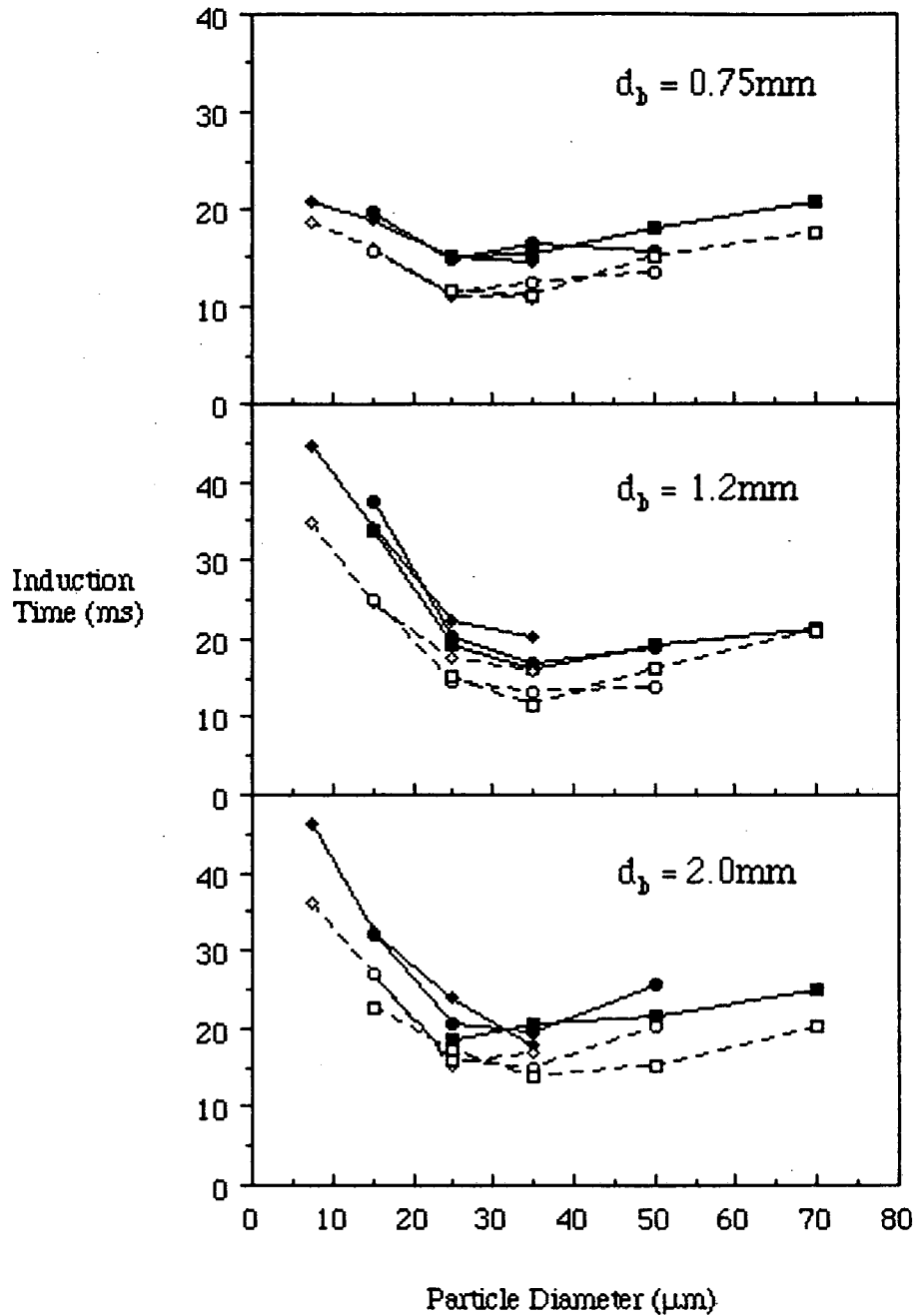


Figure 8.16b Induction times for moderately hydrophobic particles ($\theta = 50^\circ$) of fine (—◆—), medium (—●—) and coarse (—■—) size fractions in water compared with the same fine (---◇---) medium (---○---) and coarse (---□---) size fractions in $10^{-3}\text{ mole dm}^{-3}\text{ KCl}$ (---□---), for bubble diameters of 0.75mm (top), 1.2mm (middle) and 2.0mm (bottom). These results can be compared directly with the results for strongly hydrophobic particles ($\theta = 88^\circ$), shown in Figure 8.16a.

The two components of the induction time can now be considered and their relative contributions estimated. As described earlier in section 5.2, the induction time comprises the time for thin film drainage, τ_{tfd} and the time for expansion of the three phase line of contact across the particle surface, τ_{tplc} . It has been established experimentally that for hydrophobised quartz surfaces, τ_{tplc} is unaffected by variations in pH and ionic strength (Newcombe and Ralston, 1992) and therefore there is no significant influence of electrical double layer forces on this parameter. τ_{tplc} is only influenced by hydrophobicity, given by the contact angle and the structure of the hydrophobising organic layer. It also decreases with decreasing bubble size.

The decrease in the induction time with increasing hydrophobicity for fixed bubble size and ionic strength could be due to decreases in either τ_{tfd} or τ_{tplc} , as both of these parameters decrease with increasing hydrophobicity. It is also not obvious which parameter provides the major contribution in the particle size dependency observed with the induction time.

In those interactions in which both the bubble size and particle hydrophobicity were fixed, changes caused by variations in the ionic strength must be brought about by the influence of electrical double layer forces on the thin film drainage rate only. It was observed that, as the hydrophobicity decreased, the influence of the electrical double layer forces became more apparent, particularly for surfaces for which the advancing contact angle was less than 65° , in electrolyte (1:1) solutions of concentration $10^{-3} \text{ mole dm}^{-3}$. Hydrophilic surfaces represent an extreme where electrical double layer forces dominate, as the thin film drainage experiments showed, for the thickness of the equilibrium film was partly due to the existence of these forces (both electrostatic and van der Waals forces contribute) and varied accordingly with the electrolyte concentration. Thin film drainage experiments support the bubble/particle attachment studies. The force which exists between an air bubble and a solid surface of weak to moderate hydrophobicity is similar in magnitude to the electrical double layer force in dilute electrolyte solutions of concentrations up to $10^{-3} \text{ mole dm}^{-3}$.

As the bubble size was varied the induction time showed the same trend irrespective of the ionic strength; i.e. it decreased as the ionic strength increased. For a fixed bubble size the induction time increased with both decreasing hydrophobicity and ionic strength. The induction time for smaller bubbles was less than that for larger bubbles for constant particle size, hydrophobicity and ionic strength. The thin film drainage time for a bubble/particle interaction involving a small bubble is less than for a larger

bubble. The thin film drainage experiments showed that the drainage rate was faster for smaller film radius (see section 4.1) which is consistent with smaller bubbles interacting with particles such that the radius of the intervening, thin, liquid film is smaller than for large bubbles. Smaller bubbles, however, reach their equilibrium "wetting" radius more rapidly than do larger bubbles (Newcombe and Ralston, 1993) at the same hydrophobicity. Clearly both τ_{fd} and τ_{tpc} decrease with decreasing bubble size, at least over the bubble sizes studied (i.e. $0.5 \times 10^{-3} \text{m} < d_b < 2.5 \times 10^{-3} \text{m}$).

The minimum in the induction time versus particle size plots was observed to move to smaller particle diameters with decreasing bubble size so clearly the relative sizes of the particle and the bubble are important. There appear to be two mechanisms at work with changes in the particle size, with a change-over occurring at $d_p = 30\text{--}40 \mu\text{m}$, depending on the bubble size, but independent of the ionic strength. This is approximately consistent with the Crawford and Ralston (1988) observation of a minimum in the degree of hydrophobicity required for flotation occurring at a particle size of circa $40 \mu\text{m}$. This minimum will shift slightly depending upon the bubble size and ionic strength.

It has been shown that the following parameters, namely bubble size, particle size, the degree of hydrophobicity of the particle surface (quantified by the contact angle) and the ionic strength of the aqueous solution in which the bubble/particle interaction takes place all influence the thin film drainage time. However, the time for the movement of the three phase line of contact across the surface after rupture of the intervening thin film is influenced by all of these parameters except the ionic strength. It is this difference which can be used to differentiate the contributions of these two time components to the overall induction time.

Examining the effect of varying the bubble size at fixed hydrophobicity and ionic strength, shows clearly that the attachment efficiency of small bubbles is higher than for larger bubbles. Since a thin film of smaller radius drains more quickly and also a smaller bubble spreads more quickly both τ_{fd} and τ_{tpc} contribute to a lower induction time in the case of the smaller bubble and therefore a higher attachment efficiency. Similarly if the bubble size and the ionic strength are fixed and the degree of hydrophobicity of the particle is varied both components contribute to a lower induction time for the more hydrophobic particle. That is, the drainage time decreases for thin films at surfaces with increasing degrees of hydrophobicity and the τ_{tpc} also decreases for this change in the hydrophobicity, giving an overall result of a much higher attachment efficiency for the more hydrophobic particle.

Variations in the ionic strength at fixed bubble size and hydrophobicity of the particle showed that, particularly for moderate and low hydrophobicity, the attachment efficiency increased with increasing ionic strength. The related decrease in the induction time associated with this increased attachment efficiency could have only been due to a decrease in the thin film drainage time with increasing ionic strength, as the time for movement of the three phase line of contact is fixed.

8.5 Efficiency of Collection

As described in chapter 5 (section 5.4) the flotation rate constant is proportional to the overall collection efficiency for a given flow rate, where the collection efficiency is equal to the product of the efficiencies of collision, attachment and stability. The collection efficiency can be determined then, by multiplying the collision efficiency by the attachment efficiency, given that the stability efficiency is equal to one, as is the case in this investigation.

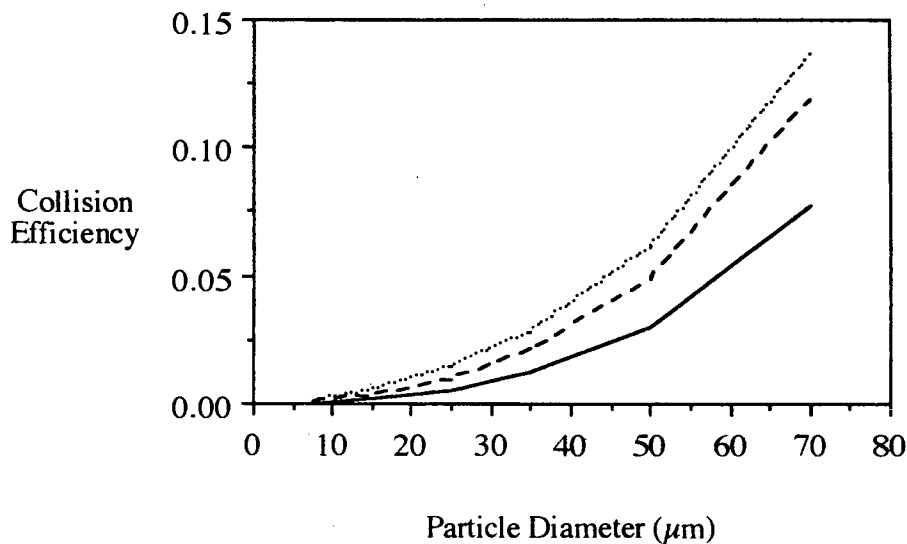


Figure 8.17 The calculated collision efficiency is shown for bubbles with diameters of 0.75mm (.....), 1.2mm (---) and 2.0mm (—).

The calculated collision efficiencies given in Table 8.1 are shown in Figure 8.17 for the three bubble sizes used in the experiments. (Note that in Figure 6.2 calculated collision efficiencies are shown for bubbles of diameters different to those used in this investigation and described in this chapter) The experimental attachment efficiencies

were then converted to efficiencies of collection using these calculated collision efficiencies (see Appendix C for an example calculation). Examples of efficiency of collection results obtained are given in Figures 8.18 and 8.19.

Figure 8.18 shows that the efficiency of collection increases with particle size except for the large particles with the larger bubble sizes. Clearly then, the fall in the attachment efficiency of the large particles is more than compensated for by the increase in the collision efficiency, except in the case of the large particles with the larger bubbles when the attachment efficiency decreases markedly. Similarly, as can be seen in Figure 8.19, the collection efficiency increases with increasing particle size, particularly in the case of the small bubble. In fact the 0.75mm diameter bubble is often two to four times more efficient at collecting particles of diameter $\geq 15\mu\text{m}$ than are the larger bubbles.

8.6 Rate Constants

As discussed in chapter 5 (section 5.6) Crawford and Ralston (1988) reported experimental rate constants for the flotation of methylated quartz particles. These rate constants were determined from graphs of $\ln(1-R)$ versus time, whence "fast" and "slow" rate constants were determined from a two component fit to the curves. Based on the analysis shown in section 5.4, the "fast" rate constant, k_f , which corresponds to the Crawford and Ralston study can be calculated for the collection efficiencies obtained here. A direct comparison can be made of those results (i.e. from the Crawford and Ralston study and this investigation) obtained under the same experimental conditions such as pH, ionic strength and where the particle size and hydrophobicity and the bubble size were approximately equal.

From chapter 5 the following equation for the rate constant, k was given:

$$k = \frac{3 G E_C E_A E_S h}{2 d_b V_r} \quad 5.9$$

The following values for the various parameters were given by Crawford and Ralston:

- G (the gas volumetric flow rate) = $60 \text{ cm}^3/\text{min} = 1 \text{ cm}^3/\text{s}$
- V_r (the reference volume) = 255 cm^3
- h (pulp height) = 33 cm .

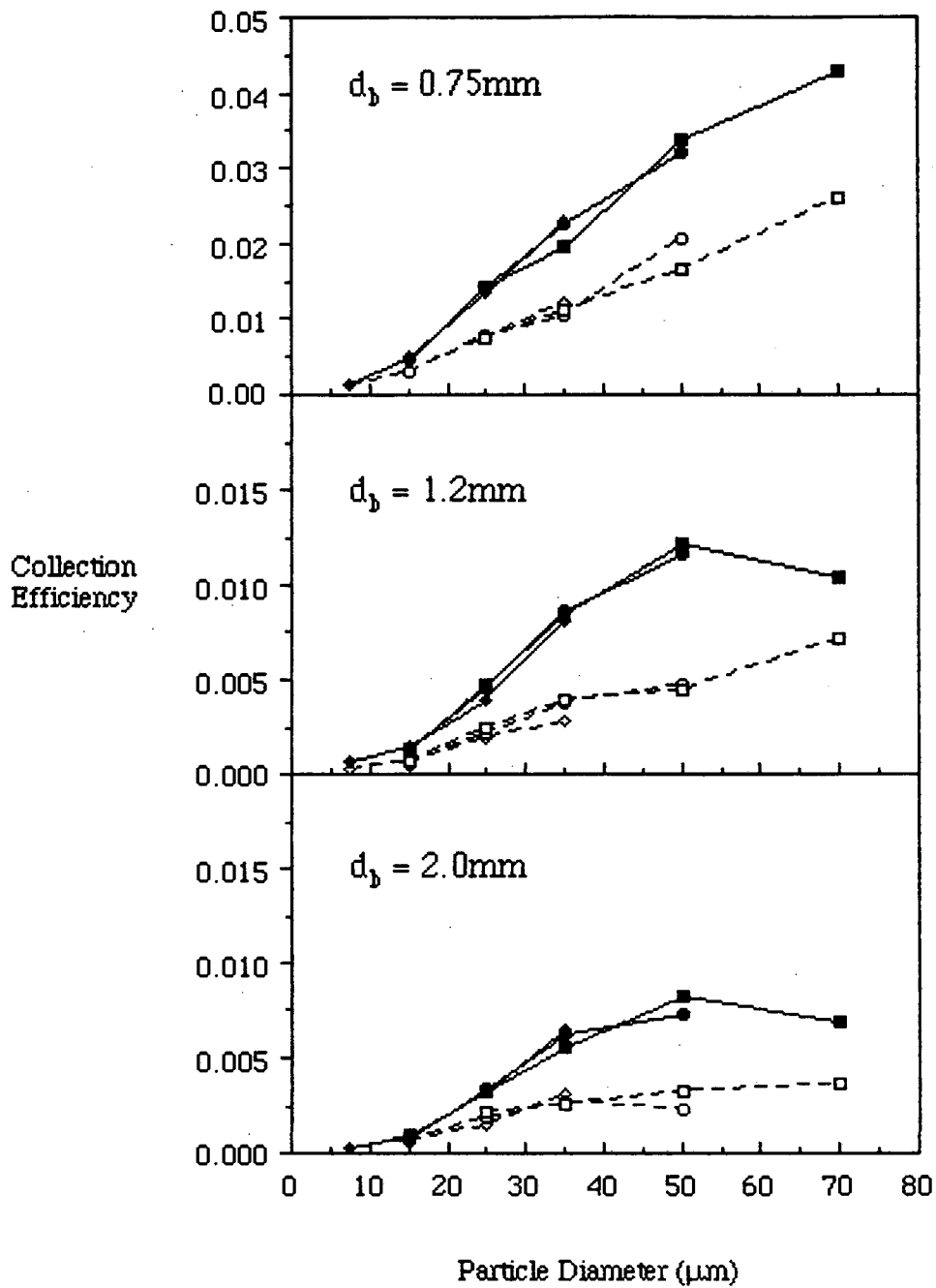


Figure 8.18 Collection efficiencies for strongly hydrophobic ($\theta = 88^\circ$) particles of fine (—◆—), medium (—●—) and coarse (—■—) size fractions and for moderately hydrophobic particles ($\theta = 50^\circ$) of the same size fractions (i.e. fine (---◇---), medium (---○---) and coarse (---□---)) are shown for bubble diameters of 0.75mm (top), 1.2mm (middle) and 2.0mm (bottom) in water.

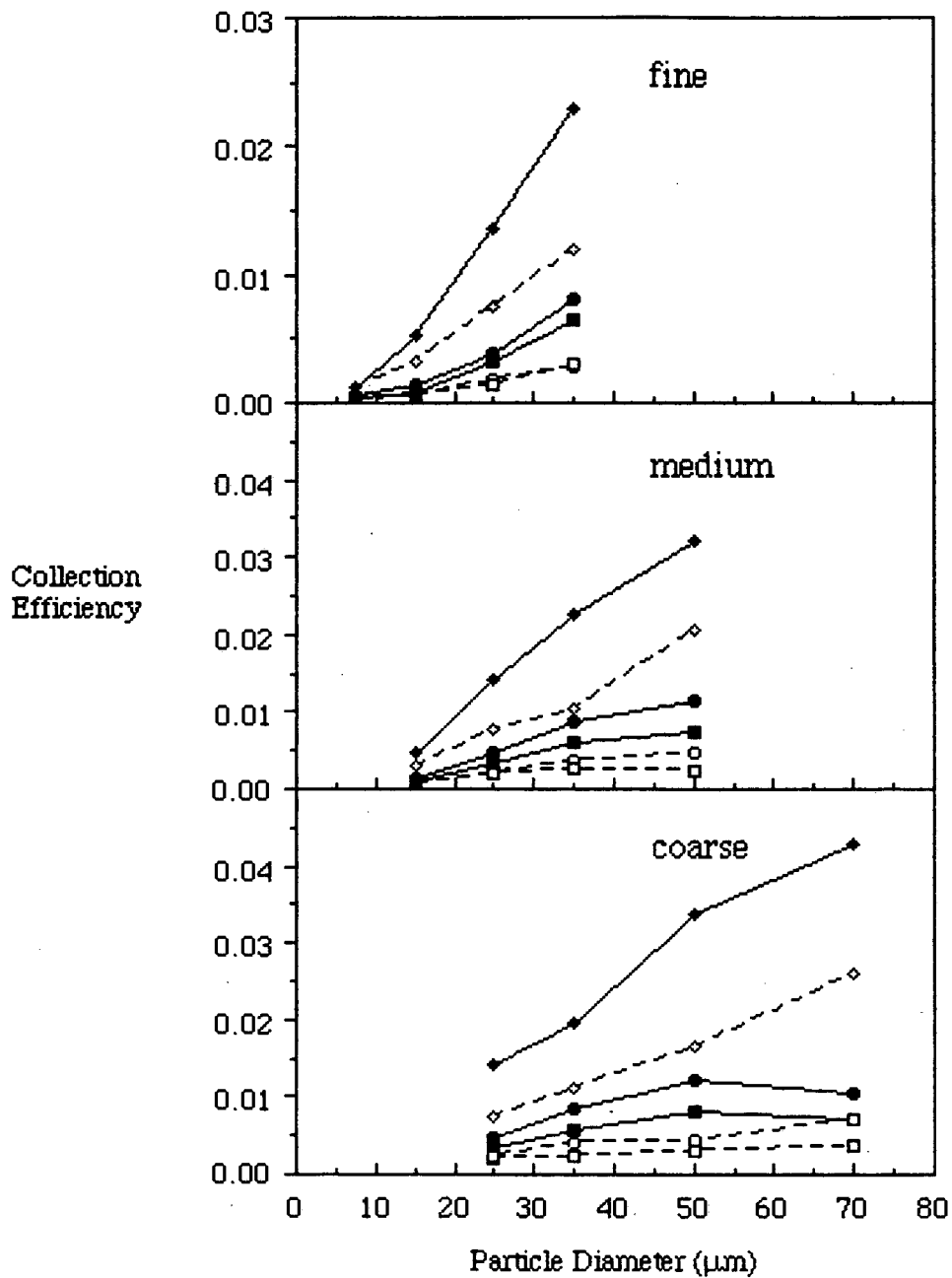


Figure 8.19 Collection efficiencies for strongly hydrophobic particles ($\theta = 88^\circ$) with bubbles of diameters 0.75mm (—◆—), 1.2mm (—●—) and 2.0mm (—■—) and for moderately hydrophobic particles ($\theta = 50^\circ$) with bubbles of the same diameters (i.e. 0.75mm (--◇--), 1.2mm (--○--) and 2.0mm (--□--)) and fine (top), medium (middle) and coarse (bottom) size fraction particles in water.

The rate constants corresponding to the Crawford and Ralston work can then be calculated from the collection efficiencies determined experimentally in this study as follows:

$$k = 97.059 E_{\text{Coll}} \quad 8.1$$

allowing direct comparison to be made between the rate constants determined in the two sets of experiments.

Examples of the rate constant results for corresponding values of particle size and hydrophobicity are given in Table 8.3 for experiments conducted in an ionic strength solution of $10^{-3} \text{ mole dm}^{-3}$ and pH 5.6 ± 0.2 for a bubble diameter of 1.2mm in both studies. Considering the completely different methods followed in determining the rate constant in each set of experiments, the agreement between the values obtained for the rate constants is remarkably good supporting the model adopted here.

Crawford and Ralston Rate Constants			Rate Constants from This Study		
Particle Size (μm)	Contact Angle (degrees)	Rate Constant (min^{-1})	Particle Size (μm)	Contact Angle (degrees)	Rate Constant (min^{-1})
15	88	0.4 ± 0.2	15	88	0.15 ± 0.02
	69	0.10 ± 0.06		65	0.12 ± 0.01
	56	0.07 ± 0.03		50	0.10 ± 0.01
46	88	0.9 ± 0.1	50	88	1.29 ± 0.13
	65	0.5 ± 0.1		65	0.69 ± 0.07
	46	0.22 ± 0.05		50	0.59 ± 0.06

Table 8.3 Fast rate constants reported by Crawford and Ralston compared with rate constants calculated from collection efficiency results obtained in this study. In both cases, methylated angular quartz particles were floated in $10^{-3} \text{ mole dm}^{-3}$ electrolyte solutions by bubbles of average diameter of 1.2mm. The results are shown for particle size/contact angle combinations from the two studies that are approximately equivalent. Note that for the values of the rate constants calculated from this study the error shown is derived from the errors in the collection efficiency data (see Appendix C).

8.7 Conclusions

Flotation experiments on the absolute rate of capture of angular, methylated quartz particles by bubbles were carried out as a function of ionic strength at fixed pH. The number of particles attached to a bubble and hence floated was determined for suspensions of quartz particles of various degrees of hydrophobicity for three size fractions.

Attachment efficiency decreases with decreasing hydrophobicity and increasing particle size. The high attachment efficiency of fine particles was observed for all three bubble sizes. The effect of the ionic strength on the attachment efficiency was not significant for strongly hydrophobic particles, but became progressively stronger as the degree of hydrophobicity decreased. This effect was observed for all three bubble sizes studied. This influence of the ionic strength on attachment efficiency complements the enhanced thin film drainage rates observed when a fast approaching air bubble impinges on a quartz surface of varying hydrophobicity as discussed in chapter 4. Increasing salt concentration resulted in a more rapidly thinning thin liquid film, due to an increased rate of drainage at the boundary ring.

The induction time calculations show clearly the existence of a minimum for particles of approximately 30-40 μm . Examining the effect of varying the bubble size at fixed hydrophobicity and ionic strength indicates that the induction time for small bubbles is higher than for larger bubbles. Since a thin film of smaller radius drains more quickly and also a smaller bubble spreads more quickly both τ_{ufd} and τ_{iplc} contribute to a lower induction time in the case of the smaller bubble. Similarly if the bubble size and the ionic strength are fixed and the degree of hydrophobicity of the particle is varied both components contribute to a lower induction time for the more hydrophobic particle. That is, the drainage time decreases for thin films at surfaces with increasing degrees of hydrophobicity and the τ_{iplc} also decrease for this change in the hydrophobicity. The decrease in the induction time which occurs with increasing ionic strength for fixed bubble size and fixed particle size and hydrophobicity was due to a decrease in the thin film drainage time only, as τ_{iplc} was unchanged in this case.

The efficiency of collection increases with particle size which implies that the efficiency of collision must increase at a faster rate than the efficiency of attachment decreases with increasing particle size. The one exception where the efficiency of collision did not increase with particle size was for large particles interacting with large bubbles. In this case, the attachment efficiency became very small so that the effect of the increase in the collision efficiency was negated.

The rate constants determined from this study and those reported by Crawford and Ralston were in good agreement given the quite different techniques used. The one area of slight discrepancy was for strongly hydrophobic ($\theta = 88^\circ$), small particles ($d_p = 15\mu\text{m}$) although the overall trend was consistent across the two studies. The rate constants decrease with decreasing hydrophobicity and are larger for the intermediate size particles than for the small particles.

CHAPTER 9. SUMMARY AND CONCLUSIONS

Flotation may be defined as a process whereby mineral and other particles are concentrated by selective adhesion to air-liquid interfaces. The process involves attachment of desired mineral particles to air bubbles and the removal of the mineral particle/bubble aggregate from the surface of the pulp as a mineral concentrate. The process of froth flotation is of considerable commercial significance so it is advantageous that a thorough knowledge of the sub-processes involved is obtained. It is to this end that this study is directed.

Direct observation of the behaviour of mineral particles and bubbles in an operating cell does not appear promising because of the complexity of the system. By making observations on model systems, it is expected that the fundamental processes and the parameters which affect them can be identified and useful models can then be used to describe and predict the outcome of the flotation process.

Three stages of bubble/particle interaction have been identified, all of which must occur successfully for flotation to take place. Initially the bubble and particle must collide, followed by attachment of the particle to the bubble after which the bubble/particle aggregate must remain stable while it rises to the froth layer. The collision process has been studied extensively and a reliable model describing the efficiency of collision has been developed. A flotation domain, in which the formation of a stable bubble/particle aggregate is possible, has been established experimentally and described theoretically.

The attachment process is less well understood. By considering the various sub-processes involved, in this study the significance of parameters affecting the process were elucidated. When a particle approaches a bubble the intervening thin liquid film must drain and rupture for attachment to take place. By examining the influence of the degree of hydrophobicity and the effect of the background electrolyte concentration in studies of the thin film drainage rate of thin aqueous films trapped between a quartz plate and a fast approaching air bubble, the events of drainage and rupture of thin films between the particle and a bubble were described.

The influence of parameters including the diameters of the bubbles and particles was observed in bubble/particle attachment experiments where variables such as particle hydrophobicity and the ionic strength of the background electrolyte solution were controlled. The thin film drainage and bubble/particle attachment experiments are separately summarised.

9.1 Thin Film Drainage Summary

The thin film drainage experiments were conducted under extremely clean conditions. The drainage rate was measured using interferometry to determine the film thickness as the air/aqueous solution interface approached the quartz/aqueous solution interface. A laser light beam was directed onto a bubble bulged against a quartz plate such that the beam reflected from the two approaching interfaces (i.e. the air/aqueous solution interface and the quartz/aqueous solution interface). The reflected beams interfered with each other and produced interference fringes which were used to determine the film thickness.

When a bubble was rapidly bulged against the quartz surface, a dimple formed such that the thickness at the boundary ring of the intervening liquid film was much smaller than it was at the film centre. At hydrophilic quartz plates the film then drained to give a film of uniform thickness, whereas films formed at hydrophobic quartz plates drained only until they ruptured spontaneously. This rupture was followed by movement of the three phase line of contact to establish an equilibrium, dewetted area of air/quartz contact (still with a monolayer of water vapour on the solid surface).

The dimple which forms in the thin film became more pronounced as the salt concentration was increased. The drainage rate at the centre of the dimple decreased with salt concentration, whereas it increased at the boundary ring. The influence of salt concentration on drainage rate was sensed at relatively large distances. The enhanced rate at the boundary ring may arise, to some extent, from mechanisms similar to those which dictate the flow rates of aqueous solutions through very fine capillaries. For the early stages of drainage (i.e. for times less than 50 seconds) the inverse of the square of the film thickness against time plot was linear. This was true for drainage at the centre of the dimple and at the boundary ring. Extant drainage rate theory and experiment cannot currently be fully rationalised.

Reasonable agreement was obtained between experimental equilibrium film thicknesses (i.e. when drainage has ceased) and those calculated using the DLVO theory. Compression of the double layer qualitatively explains the trends in the observed changes in the drainage rates with variations in the ionic strength of the aqueous solutions, however, the distances at which the differences in the drainage rates became apparent were an order of magnitude greater than could be predicted or explained using the static or equilibrium DLVO model. The deformable nature of the air/aqueous

solution interface and the ability of this interface to form a dimple, clearly deserves special consideration and it is this property which could eventually result in providing a quantitative explanation for the unusual observations made in these experiments.

9.2 Bubble/Particle Attachment Summary

Bubble/particle attachment experiments were conducted to further examine the interaction of bubbles with solids so as to determine the influence of the degree of hydrophobicity of the solid surface and the ionic strength of the background electrolyte, but in the more directly applicable (to flotation) situation where bubbles are interacting with particles. A modified Hallimond tube was used to collect particles floated by bubbles, where the latter were produced relatively slowly and in a single stream. The number of particles floated per bubble was found to increase with increasing particle hydrophobicity as expected. By comparison of the number of floated particles with the theoretical number of collisions the efficiency of attachment was determined.

The attachment efficiency was found to decrease with increasing particle size for all three bubble sizes. The attachment efficiency also decreased with increasing bubble size. Changes in the ionic strength did not influence the attachment efficiency of the strongly hydrophobic particles, although for moderately hydrophobic particles the efficiency of attachment increased with increasing ionic strength. Clearly the influence of the electrostatic forces which vary as a function of the ionic strength was more significant for the moderately hydrophobic particles than for the more strongly hydrophobic particles. The increase in the attachment efficiency seen in these experiments complements the observations made in the thin film drainage experiments in which the drainage rate at the boundary ring increased with increasing ionic strength.

Calculations identified the existence of a minimum in the induction time as a function of particle size occurring at approximately 30-40 μm . Examining the effect of either varying the bubble size or varying the degree of hydrophobicity, at fixed ionic strength indicated that the induction time for small bubbles was lower than for larger bubbles. Since a thin film of smaller radius drains more quickly and also a smaller bubble spreads more quickly both τ_{fd} and τ_{plc} contribute to a lower induction time in the case of the smaller bubble. Similarly, for increasing hydrophobicity both components contribute to a lower induction time for the more hydrophobic particle. That is, the drainage time decreased for thin films at surfaces with increased degrees of hydrophobicity and the τ_{plc} also decreased for this change in the hydrophobicity. The decrease in the induction time which occurred with increased ionic strength for fixed

bubble size and fixed particle size and hydrophobicity was due to a decrease in the thin film drainage time only, as τ_{tpc} was unchanged in this case.

For increasing particle size, the attachment efficiency decreased whereas the collision efficiency increased at a faster rate, so that (given that $E_S = 1$) the overall collection efficiency showed a general increase with particle size. The one exception to this general observation was for the interaction of large bubbles with large particles. The calculated 'fast' rate constants showed the same trend with particle size as the collection efficiency.

9.3 Conclusions

In this study the important sub-processes governing bubble/particle capture have been studied in detail. The fast approaching bubble/plate experiments revealed, for the first time, the influence of the ionic strength, hydrophobicity and bubble size on thin film drainage. Although it has not been possible to extract the hydrophobic force directly, the geometry of the bubble profile has been identified as a function of salt concentration. These experiments also showed that under dynamic conditions electrostatic double layer and attractive forces between hydrophobic surfaces are sensed at large distances.

In the bubble/particle interaction experiments the attachment efficiencies were determined for the first time, as a function of bubble size, particle size, hydrophobicity and ionic strength. Although it is not possible at present to give exact quantitative results for the contributions of thin film drainage time (τ_{fd}) and time of movement of the three phase line of contact (τ_{tpc}) to the induction time (τ_{ind}) it is possible to qualitatively state whether one or both contribute.

Flotation rate constants were calculated using literature models for several particle sizes and three different contact angles, using the measured attachment efficiencies in combination with valid collision and stability models. A satisfactory comparison with rate constants extracted from previous 'batch' flotation data was made. The compilation of attachment efficiencies as a function of particle size, bubble size, ionic strength and contact angle provides a useful reference source for future flotation rate constant predictions. As a result of these findings there are significant flotation process engineering applications, i.e. it may be possible to construct far more reliable models of the flotation process in practice.

APPENDIX A

Dimple Volume

Figure 1 shows a representation of the dimple cross-section, where the 'height' of the dimple is given by $f(r)$; that is as a function of the radial distance r . The dimple is assumed to be axisymmetrical whereby the dimple sweeps through 2π radians (i.e. a full circle) about the z -axis, with a radius r_0 .

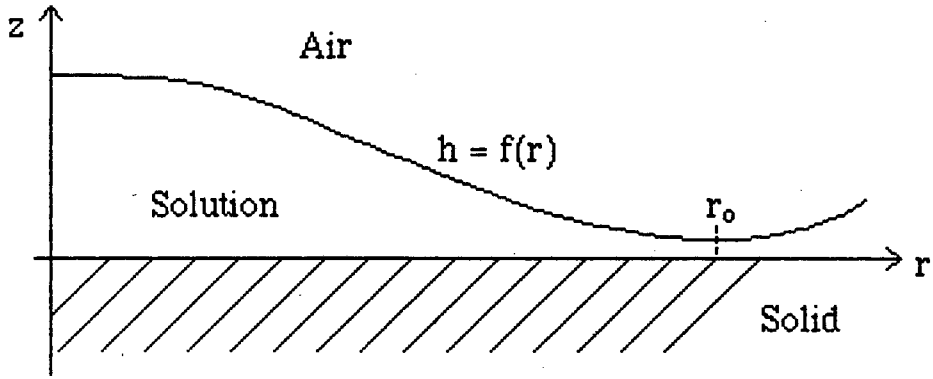


Figure 1. Schematic representation of the 'dimpled' thin liquid film trapped between the fast approaching air bubble and a solid quartz plate.

The dimple volume (V) is given by:

$$V = \int_0^{r_0} 2\pi r f(r) dr \quad A1$$

It has been shown (Fisher et al, 1992) that an empirical fit of the dimple profile $f(r)$ can be approximated satisfactorily by a polynomial of the type:

$$f(r) = ar^6 + br^2 + c \quad A2$$

Substitution for $f(r)$ in equation A1 gives the following equation for the volume of the dimple:

$$V = 2\pi \int_0^{r_0} [ar^7 + br^3 + cr] dr \quad A3$$

Giving:

$$V = 2\pi \left(\frac{ar^8}{8} + \frac{br^4}{4} + \frac{cr^2}{2} \right)_0^{r_0} \quad A4$$

Example Dimple Volume Calculation

For $10^{-3} \text{ mole dm}^{-3}$ NaCl and at time = 5 seconds:

Fitting a polynomial of the type given in equation A2 gives the following values for the variables:

$$a = -7.8085 \times 10^4$$

$$b = 7.496 \times 10^{-2}$$

$$c = 2.730 \times 10^{-4}$$

Substitution for these variables in equation A4 with $r_0 = 0.02 \text{ cm}$ gives:

$$\begin{aligned} V &= 2\pi \left(\frac{(-7.8085 \times 10^4)(0.02)^8}{8} + \frac{(7.496 \times 10^{-2})(0.02)^4}{4} \right. \\ &\quad \left. + \frac{(2.730 \times 10^{-4})(0.02)^2}{2} \right) \\ &= 3.6033 \times 10^{-7} \text{ cm}^3 \end{aligned}$$

APPENDIX B

Sample calculation of collision efficiency, collision time and sliding times (Schulze, 1989) for bubble diameter of 0.75mm and particle diameter of 15 μ m.

Collision Efficiency

$$\text{Given: } d_b = 0.75 \text{ mm} = 0.075 \text{ cm}$$

$$d_p = 15 \mu\text{m} = 1.5 \times 10^{-3} \text{ cm}$$

$$v_b = 10 \text{ cm/s}$$

$$\rho_f = 1.00 \text{ g/cm}^3$$

$$\rho_p = 2.65 \text{ g/cm}^3$$

$$\eta = 1 \text{ centipoise} = 0.01 \text{ g/cm s}$$

$$v_p = \left(\frac{d_p^2 (\rho_p - \rho_f) g}{18 \eta} \right) = 0.0202 \text{ cm/s}$$

$$\gamma = 72.8 \text{ dyne/cm}$$

$$g = 9.81 \times 10^2 \text{ cm/s}^2$$

$$Re_b = \frac{v_b d_b \rho_f}{\eta} = 75 \quad (\text{Eq. 6.4})$$

$$\frac{d_p}{d_b} = 0.02$$

$$v_s = \frac{v_p}{v_b} = 0.00202$$

Interception Effect (E_{Ic})

$$\theta_c = 78.1 - 7.37 \log Re_b = 64.28 \quad (\text{Eq. 6.4a})$$

$$\begin{aligned} \xi_o &= \left(\frac{3}{2} \right) \left(1 + \frac{(3/16) Re_b}{1 + 0.249 Re_b^{0.56}} \right) (1/\sin \theta_c) \quad (\text{Eq. 6.3}) \\ &= 7.836 \end{aligned}$$

$$\left(\frac{1}{\xi_o} \right) = 0.128 ; \left(\frac{d_p}{d_b} \right) \leq \left(\frac{1}{\xi_o} \right) \text{ hence:}$$

$$\begin{aligned}\varphi_c &= \left(\frac{3}{4}\right) \left(\frac{d_p}{d_b}\right)^2 \left(1 + \frac{(3/16) Re_b}{1 + 0.249 Re_b^{0.56}}\right) \\ &= 1.412 \times 10^{-3}\end{aligned}\quad (\text{Eq. 6.2})$$

$$E_{lc} = \frac{2\varphi_c}{1 + v_s} = 2.82 \times 10^{-3} \quad (\text{Eq. 6.6})$$

Inertial Effect (E_{In})

From Table 6.1 $a = 1.12$ and $b = 1.84$ and

$$\begin{aligned}St &= \frac{\rho_p d_p^2 v_b}{9 \eta d_b} = 8.83 \times 10^{-3} \\ E_{In} &= \left(\frac{1}{1 + v_s}\right) \left(1 + \frac{d_p}{d_b}\right)^2 \left(\frac{St}{St + a}\right)^b \\ &= 1.38 \times 10^{-4}\end{aligned}\quad (\text{Eq. 6.7})$$

Gravitational Effect (E_G)

$$\begin{aligned}E_G &= \left(1 + \frac{d_p}{d_b}\right)^2 \left(\frac{v_s}{1 + v_s}\right) \sin^2 \theta_c \\ &= 1.71 \times 10^{-3}\end{aligned}\quad (\text{Eq. 6.8})$$

Overall Collision Efficiency

$$\begin{aligned}E_C &= E_{lc} + E_G + \left(1 - \frac{E_{lc}}{(1 + (d_p/d_b))^2}\right) E_{In} \\ &= 4.66 \times 10^{-3}\end{aligned}\quad (\text{Eq. 6.9})$$

Collision Time

$$t_{\text{coll}} = \left(\pi^2 r_p^3 (\rho_p + 1.5\rho_f)/3\gamma \right)^{1/2} f \quad (\text{Eq. 6.10})$$

From Schulze, 1989: $f = 4.79$, giving:

$$t_{\text{coll}} = 0.043 \text{ ms}$$

Sliding Time (Dobby and Finch)

For $\theta_n = 20^\circ$ and 40° , and $\theta_m = 80^\circ$

$$\xi_s = a + b\theta_n + c\theta_n^2 + d\theta_n^3 \quad (\text{Eq. 6.13})$$

$$= 4.47 \text{ for } \theta_n = 20^\circ \text{ and } 7.30 \text{ for } \theta_n = 40^\circ$$

where the coefficients a to d for $20 < \text{Re} < 400$ are given by:

$$\begin{aligned} a &= -0.01082 - 7.273 \times 10^{-4} \text{Re} + 1.735 \times 10^{-6} \text{Re}^2 - 2.046 \times 10^{-9} \text{Re}^3 \\ &= -0.0565 \end{aligned}$$

$$\begin{aligned} b &= 0.0745 + 3.013 \times 10^{-3} \text{Re} - 7.402 \times 10^{-6} \text{Re}^2 + 8.931 \times 10^{-9} \text{Re}^3 \\ &= 0.2627 \end{aligned}$$

$$\begin{aligned} c &= -4.276 \times 10^{-4} - 1.977 \times 10^{-5} \text{Re} + 5.194 \times 10^{-8} \text{Re}^2 - 6.520 \times 10^{-13} \text{Re}^3 \\ &= -1.618 \times 10^{-3} \end{aligned}$$

$$\begin{aligned} d &= -1.103 \times 10^{-6} - 1.032 \times 10^{-7} \text{Re} + 1.397 \times 10^{-10} \text{Re}^2 - 1.334 \times 10^{-13} \text{Re}^3 \\ &= -8.114 \times 10^{-6} \end{aligned}$$

$$(d_p/d_b) < 0.03 \text{ hence}$$

$$v_{p\theta} = (0.7\xi_s v_b d_p/d_b) + v_p \sin \theta_n \quad (\text{Eq. 6.14})$$

$$= 0.633 \text{ cm/s for } \theta_n = 20^\circ \text{ and } 1.035 \text{ cm/s for } \theta_n = 40^\circ$$

$$t_{\text{sl}} = \left(\frac{\theta_m - \theta_n}{360} \right) \left(\frac{\pi(d_b + d_p)}{v_{p\theta}} \right) \quad (\text{Eq. 6.16})$$

$$= 63.3 \text{ ms for } \theta_n = 20^\circ \text{ and } 25.8 \text{ ms for } \theta_n = 40^\circ$$

APPENDIX C

Maximum Number of Collision per Bubble

Using the example in Appendix B, the maximum number of collision possible per bubble is given by:

$$N_{\max} = V_f N_p E_C \quad C1$$

where V_f is the Volume through which the bubble flows and,
 N_p is the Number of Particles per unit volume.

For bubble diameter of 0.75mm and particle diameter of $15\mu\text{m}$ with a pulp height of 22.5cm then:

$$\begin{aligned} \text{Given: } d_b &= 0.75 \text{ mm} = 0.075 \text{ cm} \\ d_p &= 15 \mu\text{m} = 1.5 \times 10^{-3} \text{ cm} \\ h &= 24.0 \text{ cm} \end{aligned}$$

$$\begin{aligned} \text{Then: } V_f &= \pi/4 (d_b + d_p)^2 h \\ &= \pi/4 (0.075 + 1.5 \times 10^{-3})^2 (24.0) \\ &= 0.110 \text{ cm}^3 \quad (\text{see Table 8.1}) \end{aligned} \quad C2$$

The HIAC Particle Counter was used to obtain N_b for the 0.1% suspension giving, for $d_p = 15\mu\text{m}$:

Particle size Fraction: i) Fine, $N_b = 112075$; ii) Medium, $N_b = 9110$;
iii) Coarse, $N_b = 1592$

Substitution in Equation C1 gives the following maximum collisions per bubble (see Table 8.2):

$$\begin{aligned} \text{i) Fine Particle size Fraction: } N_{\max} &= (0.110) (112075) (4.66 \times 10^{-3}) \\ &= 57.45 \text{ collisions per bubble} \\ \text{i) Medium Particle size Fraction: } N_{\max} &= (0.110) (9110) (4.66 \times 10^{-3}) \\ &= 4.67 \text{ collisions per bubble} \\ \text{i) Coarse Particle size Fraction: } N_{\max} &= (0.110) (1592) (4.66 \times 10^{-3}) \\ &= 0.82 \text{ collisions per bubble} \end{aligned}$$

Attachment Efficiency

The maximum number of collisions per bubble represents the case for $E_A = 1$, so that the number of particles collected per bubble as a fraction of $N_{\max}$ gives the value of E_A for that experiment. For example:

For the fine size fraction and moderately hydrophobic particles ($\theta = 50^\circ$) in water, the number of particle collected per bubble was $N_C = 39.4 \pm 10\%$, therefore:

$$E_A = \frac{39.4 (\pm 10\%)}{57.45}$$
$$= 0.686 \pm 0.07$$

Induction Time

To calculate the induction times sliding times was determined for all possible collision angles. The fraction of possible collisions which were successful must equal the attachment efficiency, so that from the distribution of sliding angles the maximum sliding angle (θ_n) corresponding to the experimental value of E_A was determined using equation 6.18, i.e.:

$$\theta_n = \sin^{-1} (E_A \sin^2 \theta_c)^{1/2} \quad (\text{Eq. 6.18})$$

For $E_A = 0.686$ and θ_c (from appendix B) = 64.28° then: $\theta_n = 48.3^\circ$.

The sliding time was calculated using the Dobby and Finch model as shown in Appendix B which gives:

For this example $\theta_n = 48.3$ then:

$$\xi_s = a + b\theta_n + c\theta_n^2 + d\theta_n^3 \quad (\text{Eq. 6.13})$$

and substitution for a, b, c and d using the values given in Appendix B gives:

$$\begin{aligned} \xi_s &= (-0.0565) + (0.2627)48.3 + (-1.618 \times 10^{-3})48.3^2 \\ &\quad + (-8.114 \times 10^{-6})48.3^3 \\ &= 7.943 \end{aligned}$$

$(d_p/d_b) = 0.02 < 0.03$ hence:

$$v_{p\theta} = (0.7 \xi_s v_b d_p/d_b) + v_p \sin \theta_n \quad (\text{Eq. 6.14})$$

$$= (0.7 (7.943) (10) (0.02)) + (0.0202) \sin(48.3)$$

$$= 1.127 \text{ cm/s for } \theta_n = 48.3^\circ$$

The sliding time is given by:

$$t_{sl} = \left(\frac{\theta_m - \theta_n}{360} \right) \left(\frac{\pi(d_b + d_p)}{v_{p\theta}} \right) \quad (\text{Eq. 6.16})$$

$$= \left(\frac{80 - 48.3}{360} \right) \left(\frac{\pi(0.075 + 1.5 \times 10^{-3})}{1.127} \right)$$

$$= 18.78 \times 10^{-3} \text{ s}$$

Thus, for a collision angle $\theta_n = 48.3^\circ$, $t_{sl} = 18.78$ milliseconds. This sliding time represents the maximum time required for the attachment process to be complete to yield the particular attachment efficiency result obtained and, therefore, is equal to the induction time.

Collection Efficiency

The collection efficiency is given by equation 6.25:

$$E_{Coll} = E_C E_A E_S \quad (\text{Eq. 6.25})$$

So for $E_C = 4.66 \times 10^{-3}$, $E_A = 0.686$ and $E_S = 1$, then:

$$E_{Coll} = (4.66 \times 10^{-3}) (0.686 \pm 10\%) (1)$$

$$= 3.20 \pm 0.32 \times 10^{-3} \text{ (see Figure 8.18)}$$

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